

## Response to the reviewer comments

text written in blue = corrections made/planned at the time of submitting the response letter

text written in red = corrections made to the manuscript together with the submission to BG

Referee #1:

General comments:

The paper is well written and is the first to show the use of the eddy covariance technique for CO flux measurements. It is interesting to see a CO flux dataset with a high temporal resolution over 9 months, which is novel. Quite some studies have shown a diurnal CO cycle before but, as they say, this study is the first one to study the change in diurnal cycle over several months. The paper gives a good overview of how CO fluxes can be predicted or modeled by showing correlation matrices for many different variables, and by showing how the correlation matrices are changing over the season. This is for example very useful information for climate and carbon transport models and therefore a valuable dataset.

However, the interpretation of the dataset is at some points weak. With the Eddy Co-variance measurements, they try to answer process level based questions, which their dataset is not fully suitable for. For example, the measured EC CO fluxes are a net result (sum) of several processes (uptake by soil, production by soil, production by dead organic matter and production by living plants) and each of these uptake and emission processes have their own dependencies on environmental variables. While not being able to separate these sources (and their mechanisms and dependencies), still process level based questions are tried to be answered by use of best fitting correlation matrices, and by use of several assumptions (for example the assumption of stable soil CO uptake). When the paper wants to focus on process level based questions, this approach and its considerations and restrictions should be discussed in more detail. Also some other parts of the dataset interpretation and dataset explanation need some more work. Furthermore, by discussing the limitations of the interpretation part, they can determine interesting (process level) research topics/setups for future CO flux studies, thereby contributing ideas for future CO flux studies.

In general, I would consider this a nice dataset which should be published. However, as said, the interpretation of this dataset is at some points weak and needs to be worked on. The points which should be revised or rewritten are more elaborately described in the 'specific comments' section.

We want to thank the reviewer for these constructive and important comments. We have now addressed the general concern of how to interpret the results with the current data set. We have added more discussion about challenges in separating the different processes of CO exchange, and restrictions of this study setup in addressing process level issues. We have also estimated the effect of temperature dependency of the CO uptake, as requested, and we have carefully edited the text so that we do not over interpret the results related to CO forming processes. Furthermore, we moved part of the process level discussion to the end of the paper to suggest ideas for future research topics on CO exchange. **In addition to the specific comments below, we have extensively modified the discussion, and part of the introduction to better introduce the processes involved in CO exchange, discuss the interpretation of the results, and also to compare the results from this study to other published work. These changes are marked in red, as everywhere in the manuscript.**

Specific comments:

The terms photodegradation, thermal degradation and abiotic degradation are not always used with care. With the EC method it is hard to separate different uptake and emission processes. Based on correlation coefficients, they conclude that radiation is the main driving factor of CO emission. This conclusion cannot be made based on their data. Radiation has many indirect effects such as on temperature, biological activity, etc. From their data it is hard to conclude whether direct photodegradation, or indirect effects of radiation (such as indirect photodegradation (fragmentation of organic matter) or thermal degradation) are the main cause of the CO production. In some places in the paper, this is well acknowledged (page 11, line 4-8). In other places this is neglected and the statistical correlation to radiation is given as a proof for direct photodegradation being the main cause. The difference between direct and indirect photodegradation should be explained, and conclusions on this subject should be formulated more carefully.

Thank you for taking this topic up. Indeed, we agree that we have not been consistent with the use of the terms photodegradation, thermal degradation and abiotic degradation. We have now used more space to explain these different mechanisms, including direct and indirect photodegradation (see e.g. Page 2, lines 20-29, Page 3, lines 1-3). We also aim at not overstating process level drivers of CO fluxes as our data does not allow us to conclude this (see e.g. Page 13, lines 21-28, Page 14, lines 10-13). We have now carefully gone through the text and modified it so that we do not make too strong statements or process level conclusions based on our results.

They make an important (risky) assumption by saying that biological soil CO uptake is constant, based on the paper of Conrad & Seiler (1985). However, other CO flux studies have observed the typical biological temperature response wherein biological activity increases with temperature (for example: Ingersoll 1973, Whalen & Reeburgh (2001), others). Also, especially in cold ecosystems, a small temperature change usually influences biological rates significantly. The assumed stable soil CO uptake assumption in this ecosystem seems unlikely. With the current dataset, this assumption cannot be validated or falsified. So, the authors should reconsider this assumption and think of the consequences if there is a typical temperature response, for example as found by Whalen & Reeburgh (2001), with a Q10 of 2.0. How would this influence their main conclusions? Either this possibility should be discussed, or the 'stable production' assumption should be removed from their manuscript.

We agree that the use of an assumption of a stable soil CO uptake was too simplistic, and as reported by e.g. Ingersoll (1973) and Whalen and Reeburgh (2001) not correct. Assuming a temperature response of Q10 of 1.8 for the CO uptake reported by Whalen & Reeburgh (2001), we estimated the daytime CO uptake from the night-time net CO fluxes and soil temperatures. We used soil temperature at 2.5 cm depth in the calculation as we considered that this is closest to the location where microbial CO consumption takes place. Hence, we assumed that the night-time CO fluxes (near constant negative fluxes) result from microbial CO consumption, which has a temperature response. The resulting daytime CO uptake estimated for each measurement period (Summer, Early Summer, Mid-Summer, Late Summer, Autumn, Late Autumn) allowed us to estimate the gross CO production during daytime, which is the difference between net daytime net CO flux and calculated daytime CO uptake. These results are now reported in two tables: Table 1. The mean, median and 25-75<sup>th</sup> percentiles of the net CO fluxes, net daytime CO fluxes and net night-time CO fluxes for each measurement period. Table 2. The gross daytime CO emission (gross FCO), difference between daytime and night-time soil temperatures, daytime CO uptake (using Q10 of 1.8), and gross daytime CO emission (gross FCO (Q10, 1.8)).

Based on these calculations, we find that the daytime CO uptake is almost twice as high as the night-time CO uptake. This is further reflected in significantly higher gross daytime CO emissions. In Page 13, lines 5-13) we have added discussion on the diurnal variation in CO uptake as well as the effect of this to the gross CO emissions, which is now largely overcome by the high CO uptake.

Concerning possible biological CO production mechanisms, they hypothesize that CO emissions are not driven by microbial activity. While it is likely that the observed CO emissions are not driven by microbial activity, the used argumentation might be misleading: they base it on the poor correlation between FCO and FN<sub>2</sub>O, and the poor correlation between FCO and RESP. However, FCO is a net flux (sum) of uptake and production, while RESP and FN<sub>2</sub>O are solely production fluxes. This makes the validity of the correlation questionable. Also, in case the CO production is caused by biological as well as by abiotic sources, would this not result in the same poor correlation between FCO and FN<sub>2</sub>O? With the current dataset, it is difficult to determine whether biological fluxes are present, but saying that the poor correlation indicates the absence of biological sources might be misleading. In previous studies, what are the magnitudes of the reported biological fluxes? In this ecosystem, would they have the same magnitude? Are they also expected in autumn when vegetation is less active/dormant/etc? If the authors believe that biological fluxes play a (small) role, it would be good to spend some sentences on the assumed mechanisms and maybe indicate the magnitude of the observed biological fluxes in other studies as a comparison.

We agree with the reviewer that the used argumentation in explaining the CO production mechanisms was not sufficient. We also agree that the poor correlation between daytime FCO and FN<sub>2</sub>O, or FCO and RESP does not prove that the CO emissions are not driven by microbial activity. We have modified this chapter to include discussion on the reasons why we do not expect the CO formation to be of microbial origin (Conrad and Seiler, 1980), and to give a better understanding of the abiotic and biotic CO production mechanisms. We also discuss the connections between FCO and FN<sub>2</sub>O as we found significant negative correlation between night-time FCO and FN<sub>2</sub>O, indicating involvement of N<sub>2</sub>O forming microbes in the CO uptake (see later our answer focusing on FN<sub>2</sub>O, and manuscript at page 15, lines 8-18). We also added more discussion on the current understanding of biological CO production, however, as there is very little information available on this topic, we stated also that biological CO formation and its importance is currently still poorly understood.

In the discussion (page 11, line 21-25), they use the high C to N ratio to confirm their theory that photodegradation is the main cause. However, this argument is not explained. Why does a high C to N ratio confirm the hypothesis?

After going through the text in the manuscript and reconsidering the reviewer suggestions, we do understand how naïve it was to suggest photodegradation as the main process leading to CO emissions. We understand that abiotic CO formation is a result of both photodegradation and thermal degradation, which cannot be fully separated in field experiments due to e.g. indirect effects radiation. Currently, there are studies supporting for higher contribution of photodegradation to the CO formation (e.g. Lee et al., 2012), but also studies suggesting thermal degradation as the dominant CO forming process (e.g. van Asperen et al., 2015). Related to the C to N ratio of the plant material, a meta-analysis shows that CO formation via photodegradation increases with C to N ratio of the plant material (King et al., 2012). Also, as the plant material in our measurement site has a high C to N ratio, and as this dry plant material was well exposed to radiation in the spring, we expect that the conditions were suitable for CO formation via photodegradation. However, this does not confirm that photodegradation was the dominant process at our site, nor does it exclude thermal degradation to take place.

We have now carefully gone through the text, including this paragraph, to discuss more generally the combined effect of photodegradation and thermal degradation. Instead of searching for one specific process, we consider that it is more important to discuss the combined effect of abiotic processes (photodegradation and thermal degradation).

The comparison to other variables (NEE; heat and energy flux) is stated as a goal in the last paragraph of the introduction, but it is not well explained what is expected. Also, in general the comparison is held very small, especially for the N<sub>2</sub>O fluxes. The results are only shown in a table but not discussed, and the N<sub>2</sub>O fluxes are hardly mentioned in the Discussion and forgotten in the Conclusion. For the N<sub>2</sub>O results, the reader is referred to another paper. If the authors think that the N<sub>2</sub>O story is an important part, since they state their interest in the introduction, they should show some N<sub>2</sub>O results, interpret these results, and spend some text on why they expect a correlation. Does a N<sub>2</sub>O figure maybe fit in Figure 1? Or, if they prefer to refer to the other paper, please then describe the N<sub>2</sub>O fluxes (magnitude and diurnal variation) briefly in this paper.

We appreciate this concern. We have added text to clarify why we would expect correlations between FCO and other measured variables. With some of them (heat flux, radiation, energy flux) it is clear based on process understanding and previous studies stating that CO emissions are driven by radiation and temperature, however, with some of the measured scalars (e.g. NEE, RESP) we did not know what to expect as there is very limited information available on the links between them and FCO. **Based on understanding of biological CO formation, a negative correlation between FCO and NEE would indicate involvement of a biological component in the CO production. Indeed, the FCO and NEE correlated negatively ( $r=-0.469$ ) during early summer (days 146-160), which gives support to the CO formation from living and actively photosynthesizing plants. With respect to FN<sub>2</sub>O and FCO, 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<sub>2</sub>O production/uptake in the soil. Nitrifiers are among a diverse microbial community oxidizing CO in soils (Jones and Morita, 1983; King and Weber, 2007). Hence 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 FN<sub>2</sub>O and FCO. In fact, we found significant negative correlations between FN<sub>2</sub>O and FCO during night-time 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 a marked role of nitrifiers in CO consumption at the reed canary grass site, however, we cannot confirm this as no microbial community structure analysis was conducted.**

Jones, R.D., Morita, R.Y.: Carbon monoxide oxidation by chemolithotrophic ammonium oxidisers. *Can. J. Microbiol.* 29, 1545-1551, 1983.

King, G. M., and Weber, C. F.: Distribution, diversity and ecology of aerobic CO-oxidizing bacteria. *Nature Reviews, Microbiology*, 5, 107-118, 2007.

Moxley, J.M., and Smith, K.A.: Carbon monoxide production and emission by some Scottish soils. *Tellus*, 50B, 151-162, 1998.

Shurpali, N. J. et al. Neglecting diurnal variations leads to uncertainties in terrestrial nitrous oxide emissions. *Sci. Rep.* 6, 25739; doi: 10.1038/srep25739 (2016).

Looking at figure 2 and 3, they correctly conclude that not all CO fluxes can be initiated by radiation, since CO fluxes are already increasing when the sun is still down (in autumn), and they refer to the possibility of thermal degradation. With the assumption of stable soil CO uptake during the dark hours, and with the idea of thermal degradation being responsible for the increasing CO production during the morning hours in the dark, is it possible to (roughly) estimate how much thermal degradation is contributing to total CO fluxes? Can this be extrapolated to the day? And does this estimate change when there is no stable soil CO uptake assumed?

In order to estimate how much a temperature increase in the morning hours would contribute to the CO production via thermal degradation, we used a Q10-value of 2.1 (van Asperen et al., 2015) to estimate. At first we calculated the temperature differences at 2.5 cm depth in the soil between mid-night and morning hours just before the sunrise, when sun elevation angle became positive, during the six measurement periods. We found that the soil temperature decreased (0.1 to 1 °C) from mid-night to the morning hours. Similar trend was observed also in air temperature. This phenomena was consistent throughout the whole 7-month measurement campaign despite the fact that the time of sunrise changed markedly between the seasons (very short nights during the summer). The attached figure 1 illustrates the diurnal cycle in mean soil temperature for each of the six measurement periods together with sun elevation angle data. The graphs shows how the soil temperature still continues to decrease even after the sunset, when sun elev is above zero.

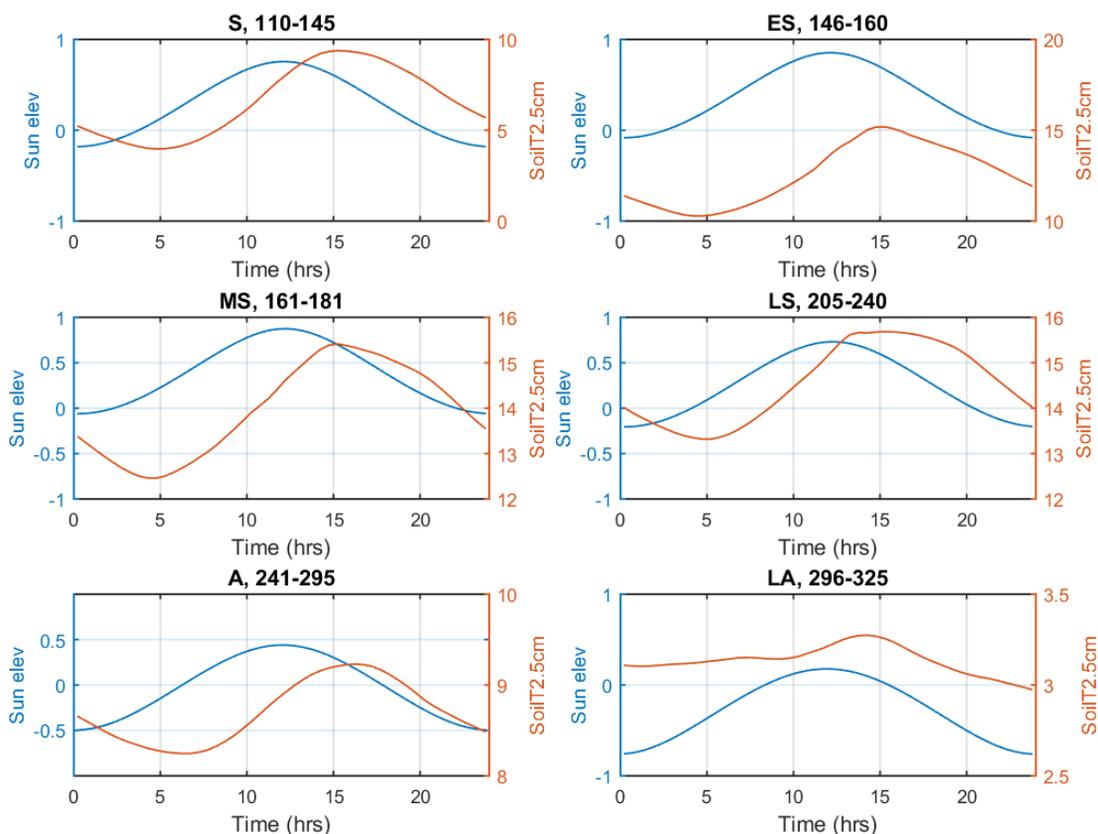


Figure 1. Mean sun elevation angle ( $h < 0$  night-time,  $h > 0$  daytime) and mean soil temperature at 2.5 cm depth at the reed canary grass crop over the six distinct measurement periods (S = Spring, ES = Early Summer, MS = Mid-Summer, LS = Late Summer, A = Autumn, LA = Late Autumn).

As a result, we do not expect temperature driven CO production via thermal degradation to take place in the early morning hours. As seen in the Fig. 2 and 3. and as stated by the referee, the CO fluxes are already increasing when the sun is still down. Hence, the increase in net CO fluxes during the morning hours indicates that CO production from an unspecified process increases, or CO uptake decreases during the morning hours, or that both of these take place. As explained above, we do not expect thermal degradation to be responsible for increased CO production, however, we can speculate that the CO uptake was affected by the decreasing temperature, as it was earlier estimated the CO uptake is temperature driven (see above, Q10 of 1.8). To conclude, based on this analysis, we cannot estimate the role of thermal degradation to the CO production at this site. **In Page 14, lines 1-16**, we have added discussion concerning this, and the challenges to separate thermal degradation from the CO production. We also added discussion on the possible effect of night-time temperature variation on CO uptake, partly explaining the increasing net CO flux during the early morning hours.

The sampling line material is made from PTFE, which is reported to be inert. However, was the whole sampling set up made of PTFE (from inlet to instrument)? Other materials are known to be possible strong CO emitters, and previous CO flux studies have found CO producing material in setups during blank tests (Schade 1999, van Asperen 2015). Has the setup been

tested for internal CO production and have blank tests been performed? If so, please mention this. If there is internal CO emission, it probably won't influence your results largely due to the large sampling flow, but if possible, it would be the best to quantify this.

All the sampling lines were made of PTFE, and due to the high flow rates in the sampling line, we did not expect internal CO production in the tubing, inlet or the whole measurement setup. We did not conduct material tests for the measurement setup we present in this paper, however, we have conducted extensive material tests with one of the analyzers (LGR-CW-QCL) and we have found that most of the common tube materials made of Teflon (FEP, PFA), or Nylon and Polyurethane release CO, and that this rate of release depends on temperature and radiation (unpublished data). We consider this is critically important in systems when a sample is accumulated within a system and when there is no constant flow through the system, such as static soil chambers. We added a sentence in the Materials & Methods (Page 6, lines 2-3) stating that PTFE tubing was found inert with respect to CO under constant-flow setup with the LGR-CW-QCL analyzer (unpublished data).

On Page 6, line 26-27, you estimate that the site is a net sink of CO for the 9 months, which is nicely shown in Table 1. Concerning that you seem to have a good idea of which environmental variables are important per time of the season, and that you are the first one to show a dataset with such high temporal resolution for 9 months, is it possible to give an estimate of the net CO fluxes for the other 3 months, so you can give an annual estimate? Such as done in Table 6 or 7, in the paper of Ingersoll (Soil's potential as a sink for atmospheric carbon monoxide, 1973). That would be an interesting addition.

We also think a full annual balance of FCO would be very interesting. Our measurements cover the snow-free period of little more than 7 months (not full 9 months as stated earlier). Based on our measurements, the FCO was rather constant during the autumn and late autumn, but very variable during the spring right after the snow melt when the measurements started. It is very probable that the FCO are minimal during the snow-cover period in December-February, as temperatures and radiation are low and we can expect rather small microbial CO consumption activity in the soil. However, for the spring period during the snow-melt in March-April, the assumption of small FCO 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 FCO from the measurement period probably underestimates the FCO during the early spring period. Nevertheless, we performed a back-of-envelope calculation assuming a mean FCO over the whole measurement campaign of  $-0.25 \text{ nmol m}^{-2} \text{ s}^{-1}$  to apply for the missing period of day 326 – day 109 (22 November 2011 - 18 April 2012). This results in an annual net cumulative FCO of  $-111 \text{ mg CO m}^{-2} \text{ yr}^{-1}$ . Based on only 7 months of measurements at one measurement site, and due to the lack of a process-based model for the CO exchange, we decided not to present the simple extrapolation of the annual FCO to grasslands in Finland. In Pages 12-13, lines 26- we have added our annual FCO estimates, and discussed their uncertainties.

Having done this exercise, it is easy to say that more high-resolution measurements are needed to cover the whole seasonal cycle in CO exchange, and to obtain a reliable estimate for annual CO balance from boreal ecosystems.

Technical corrections:

General:

- Please check your references, for example, Lee (2012) and Zahniser (2009) are missing in the reference list, but maybe there are more. - For many units in different places in the manuscript (ha<sup>-1</sup>, m<sup>-2</sup>), the 'superscript' is not used.  
- The hyphen is not used consistently throughout the manuscript - Different places in the manuscript: Please use the same term for G (ground heat flux or soil heat flux)  
Thank you for spotting these. We will go through them carefully.

Text:

- Page 2, line 2: of a strong greenhouse gas → of the strong greenhouse gas.  
Corrected.

- Page 2, line 12-17: quite some references are named in the different places in the manuscript, which are not named in this part. It might be nice if the references which are coming back in table 3, also come back here in the right place.  
We agree. We will check that all relevant references are added here.

- Page 2, line 18: Here is stated that CO emissions are thermal or UV-induced. However, it is not only by UV, also by visible radiation, as shown by Lee (2012). Lee (2012) is mentioned on page 9, line 21, but does not appear in reference list.  
Thank you for spotting this. We have added Lee (2012) to the reference list, and changed the sentence as follows: "...however, most often the CO production has been related to abiotic processes such as thermal or UV- or visible light-induced degradation of organic matter or plant material (references)" (Page 2, lines 17-19).

- Page 2, line 22: Most of the reported CO flux measurements are either short-term field experiments from.... it seems that the author wants to make a point here that no CO measurements are made so far in this cropland boreal ecosystem, or are only made short-term. But neither of the point is clearly made. Is this the first measurement in this ecosystem? Or the first long term?  
We wanted to in the first place point out that this is the first long-term study reporting FCO from any ecosystem. We clarified this in the text.

And can there be an indication for which percentage of land use/Finland/boreal zone this ecosystem is representative for? (see paper Ingersoll, 1973, table 6,7)  
Despite of what we had written in the response letter of the BGD paper (that we would do the extrapolation according to Ingersoll (1974), we hesitated to continue in this direction. This is justified by the fact that we eventually had only 7 months of measurements instead of the 9 months reported in the BGD paper. Also, we consider that making such extrapolations from one measurement site in Finland, and from measurement which do not cover a full year, is too uncertain. Especially as we do not yet have a ready process-based model to gap-fill the missing data and make a reliable annual estimate of the site.

- Page 3, line 20: The footprint length is given, and the size of the field is given. I assume the author wants to implicate that the footprint is homogeneous in all directions, but this is not stated. Clarify for the reader.  
Page 4, line 15: We clarified that the footprint is homogenous in all directions.

- Page 3, line 20: A 6.3 ha field is introduced, is this the same field as meant in the rest of §2.1, before this sentence? Not clear formulated.  
Page 4, line 14: This sentence was rewritten to clarify that the study field was 6.3 ha in size.

- Page 4, line 16: No white space between '(see Fig.1c)' and 'Considering'.  
Corrected.

- Page 4, line 15-20: it is stated that in the majority of the measurements is representative for the RCG canopy. What happened to the minority of the data when it is not? Can this be mentioned?

We assumed homogeneous canopy in all directions i.e. the estimated footprint extent is applicable to all directions. We estimated that the upwind distance contributing 80% of flux under stable conditions ( $L = +10$  m), in case of low canopy, was 166 m. We use this as a very conservative estimate because low canopy existed only a short time period in the beginning of the campaign. For high canopy the respective distance was estimated to be 60 m. Therefore, considering minimum fetch in South direction 135 m, we concluded that fetch was sufficient under majority of observation conditions. No data rejection according to footprint estimation was done. We modified the sentence to be more clear.

- Page 4, line 25: Reference Zahniser is also missing.  
Corrected.

- Page 4, line 24-26: Unclear and incorrect sentences, please rephrase.

**Page 5, lines 16-21:** This sentence was clarified, and more information was given of the two analyzers used, the time periods they were used, and justification why data from one of them only was used when analyzing the seasonal and diurnal variability in the FCO. Reviewer #2 was also asking for more information on the instrument comparison. See more details of that in the response to Reviewer #2.

- Page 5, line 7: PTFE lines were used, which are under most conditions inert. However, other parts of the used material might not be. Has there been a blank measurement? If so, this should be mentioned.

We did not perform blank tests during this measurement campaign as we assumed that the PTFE lines were not a significant source of CO, and because potential CO emissions from the materials can be largely avoided in the high-flow setup. We acknowledge that many materials, including FEP, PFA and Nylon may emit large quantities of CO, especially in static systems with minimal flow speeds (unpublished data in laboratory experiments using the LGR-CW-QCL analyzer (model N2O/CO-23d, Los Gatos Research Inc.). However, in a laboratory experiment testing PTFE tubing at flow rates of 2.5 L/min, we did not find significant CO production in the tubing system (see **Page 6, lines 2-3**).

- Page 5, line 11: The measurement position of G and Tsoil etc is not named in the 'Material and Methods', although partly named later in the manuscript.

This information in addition to the information of how other supporting material was collected is now added in a new chapter (2.3 Supporting measurements) to the materials and methods section.

- Page 5, line 21: a verb is missing. Do you mean: LGR-CWQCL measurements were corrected for.....

We mean that the LGR-CW-QCL analyzer itself corrects for the water vapor effect (an inbuilt correction algorithm). This was clarified.

- Page 5, line 22: unclear sentence. Do you mean: the same applied to the AR-CWQCL measurements after software update in July 2011.

Yes, the same spectroscopic correction was applied to the AR-CW-QCL measurements after the software update. We clarified this part in the text.

- Page 6, line 15: while the length of periods were → while the lengths of the periods were.  
Corrected.

- Page 6, line 25: to the mid-June→ to mid-June.  
Corrected.

- Page 7, line 15: near constant CO uptake, is the value you found similar to other studies?  
We have added comparison of night-time CO fluxes measured in this study to those observed in other studies (Page 13, lines 21-26, see also Tables 4 and 5).

- Page 7, line 25-26: please mentioned '(days 110-145)' after 'during the spring'.  
Corrected.

- Page 8, line 1: Here the discussion suddenly jumps from CO to CO<sub>2</sub>, maybe introduce this a little clearer.

Page 10, line 7: We added introducing sentence to the start of the chapter stating that compared to the FCO, the net CO<sub>2</sub> exchange, expressed as net ecosystem exchange (NEE) was very small during the spring.

- Page 8, line 1: Have LAI and GAI been introduced before?  
Indeed, these variables were not introduced before. As also many other supporting measurements were not described earlier, we introduced a new chapter (2.3) describing "supporting measurements" and the methods used in measuring them.

- Page 8, line 1-5: N<sub>2</sub>O is not discussed at all here.  
Page 10, lines 12-16: We added a section describing the diurnal variation in N<sub>2</sub>O fluxes during the measurement period.

- Page 9, line 2-4: different type of ecosystems are compared here, but they lay in different climate zone. Does this comparison make sense then?  
Page 12, lines 12-25: We reconsidered this comparison and modified the text to explain similarities between measurement from the same ecosystem types, and on the other hand, similarities between measurements in the same climatic zone. The variation in CO fluxes seems to be so high, and continuous or long-term measurements so rare that it is difficult to see trends between different ecosystem types measured in the same climatic zone, or trends between different climatic zones with respect to CO fluxes from the same ecosystem type.

- Page 11, line 1: suggestion: we expect that radiation→ we expect that the effects of radiation.  
Corrected.

– Page 11, line 3: T soil at a depth of 2.5cm→ this should also be in materials and methods.  
We added a description in the materials and methods (section 2.3)

- Page 11, line 24: mean and stdev are mentioned, however, the mean value is missing.  
Maybe there was a printing error as in our version the mean was visible. Anyhow, this was checked to make sure that the numbers appear there.

- Page 11, line 26: the early summer emission→ the early summer CO emission.

Corrected.

Tables & Figures: In Table 3, a nice overview is given of previous CO studies. The fluxes which are reported here, are that daily averages? Several of these studies have also measured a daily cycle. Can the magnitude of these results be indicated? That might make the overview more complete.

Indeed, this information would be very valuable to the scientific community. However, we found that only very few studies report daytime and night-time CO fluxes, and that those reported fluxes may be based only on 24 hours' measurements (e.g. Zepp et al., 1997). For instance, Constant et al. (2008) measured CO fluxes by a flux gradient method over a grassland ecosystem for one year, but they do not specifically report night-time fluxes. With our knowledge, our study and the one by van Asperen et al. (2015) are the only studies available reporting daytime and night-time fluxes of CO. In page 13, lines 21-26, we have included these results in the discussion section, but not in the Table 3 (now renumbered as Table 4).

In Figure 4, NEE is mentioned. I assume this measured by the EC measurements of CO<sub>2</sub>? Maybe mention the trace gas in the caption, also in other places in the manuscript when mentioning NEE.

We added a description of the NEE (net ecosystem exchange of CO<sub>2</sub>) in the Figure 4 legend, and also in the text where NEE was mentioned (e.g. chapter 3.2 Diurnal variation).

## Response to the reviewer comments

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Referee #2:

### 1 General comments

The manuscript of Pihlatie et al. on carbon monoxide (CO) flux measurements above an agricultural bioenergy crop (reed canary grass) represents an important study on the biosphere-atmosphere exchange of CO. While previous studies mainly focused on short term measurements of CO fluxes, the authors present the first eddy covariance measurements of CO fluxes over an entire growing season, making it a unique study. Like this, the authors can investigate the dependency of the CO flux on different environmental parameters such as irradiation, temperature, crop cover, fertilization status, etc. Interestingly, the authors find that the reed canary grass ecosystem acted as a net source of CO at the beginning and a net sink during of the rest of the growing season.

Also, they measured a strong diurnal cycle, as opposed to other previous studies over cropland, with mostly net emission during daytime and net uptake during night. In their study the authors correlate the net CO flux with environmental parameters to obtain an understanding on the controlling processes. As the nature of CO exchange is complex with many possible sinks and sources that have been observed in previous studies, this is challenging. As a consequence, the conclusions made on the underlying processes can often only remain assumptions, and therefore, the study provides only limited new insight into processes of CO exchange. As stated by the authors, further process related studies are necessary for future research.

The authors use state of the art measurement techniques for the quantification of CO fluxes and the fluxes were analyzed according to standard quality control procedures. Furthermore, the manuscript is clearly structured and well written. Due to the unique data set, I suggest the manuscript to be published in BG, after the more specific comments below have been addressed.

We want to sincerely thank the reviewer for constructive comments that help to improve the quality of the manuscript. We have carefully addressed all the comments and responded to them as follows. We acknowledge the concern of risks in process-based interpretations of the results. We hope the corrections will satisfy these concerns and underline the future research needs and gaps in knowledge in this field of research. In addition to the specific comments below, we have extensively modified the discussion, and part of the introduction to better introduce the processes involved in CO exchange, and also compare the results from this study to other published work. These changes are marked in red, as everywhere in the manuscript.

### 2 Specific comments

P. 3, L. 16-20: At which day was the crop cultivated? For completeness, I suggest to add this information to this short description of the growing season.

Page 3, line 20: The crop cultivation date was added to the Materials and Methods section.

P. 4, L. 21-28: In this paragraph it is not clear that these are the same analyzers as used for the flux N<sub>2</sub>O intercomparison in Rannik et al. (2015). It would be good to state this in this

manuscript or move the above sentence “The comparison of four laser-based. . .” to the end of the paragraph.

**Page 4, line 28:** We modified this chapter so that it better states the same analyzers were used for the flux N<sub>2</sub>O intercomparison in Rannik et al. (2015). We also give more information of the data collection periods for the two analyzers used in this manuscript, and give reasoning why data from only one of them is used in correlation analysis of this paper. Please, see also our response to the comment concerning the results section at P. 6, L. 22. In response to this comment, we show the intercomparison of the two analyzers with respect to FCO, and we give this information shortly in the corrected manuscript.

P. 6, L. 4-7: Here it would be interesting to know, what the magnitude of the CO flux loss was, regarding the given response times of the EC systems. In context of the effect of the inlet lines, it would also be beneficial to mention their inner diameters in this section. According to Rannik et al. (2015) the reason for the larger response time of the system was caused by laminar flow due to a larger tubing diameter.

**Page 6, lines 23-24, and lines 26-28:** 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. We added the information of the inlet lines (inner diameter and lag time from tube flow).

P. 6, L. 8-10: As stated here, more data had to be removed during daytime than during night-time. However, especially at night-time flux data has to be often rejected due to insufficiently developed turbulence. For this, a flux quality criterion using e.g. integral turbulence characteristics as suggested by Foken and Wichura (1996) is often applied. Also a test on stationarity, which was not applied for the N<sub>2</sub>O fluxes in Rannik et al. (2015) for intercomparison reasons, might be important for CO.

We did not perform flux stationarity test. First, a range of tests was applied according to Vickers and Mahrt (1997), which ensure data screening for system malfunctioning as well as physical but unusual behavior, including the non-stationary conditions. Therefore we did not perform an additional test for stationarity according to Foken and Wichura (1996), and we relied on the tests performed. It is the choice of the researcher to choose the test, however, statistically different tests tend to identify the same occasions of measurements, whereas the result depends also on the threshold criteria applied. E.g. Rannik et al. (2003) analysed performance of different tests and concluded that flux tests based on relative errors such as the stationarity test by Foken and Wichura (1996) are not feasible when the fluxes are small and therefore the relative errors becomes large. Therefore, we chose to perform tests on single time series to ensure quality of measurements used in the analysis and not using the flux stationarity test because the CO fluxes are frequently small and respectively with large relative random errors. **This is discussed on Page 7, lines 2-5.**

Rannik, Ü., Aalto, P., Keronen, P., Vesala, T. and Kulmala, M., 2003. Interpretation of aerosol particle fluxes over a pine forest: Dry deposition and random errors. *J. Geophys Res.*, 108 (D17), pp. AAC 3-1—3-11. DOI: 10.1029/2003JD003542.

P. 6, L. 22: The results chapter presents the measured CO flux and its correlation with various environmental parameters. In addition, I find it important to also present the CO mixing ratios as they can influence the CO flux significantly. Especially, the amount of CO uptake might be largely dependent on the available atmospheric CO. To rule out the effect of changing atmospheric CO levels on the CO flux when interpreting the results, CO mixing ratios should then also be included in the correlation analysis.

We had the atmospheric CO mixing ratio data (MCO) in the original correlation analysis, however, as the correlations between daytime MCO and FCO were very poor ( $r < 0.2$ ), we did not include MCO in the table 2. Now we have added MCO in the revised version Table 3. In Page 12, lines 15: We also added a short discussion on the potential effect of MCO on CO uptake at our site, as suggested by the referee.

In the response letter published in BGD we discussed the correlation between CO flux and concentration obtained through averaging for certain time of day. Diurnal variation in environmental variables is natural due to variation in solar radiation and resulting boundary layer development processes. Also, the concentrations and fluxes have very different source areas. The fluxes represent the local source area whereas the concentrations with long atmospheric life time (such as CO) can be affected by very distant sources and modulated by diurnal cycle in atmospheric mixing. Therefore, correlation in diurnal variation between CO fluxes and concentrations does not necessarily stem from the causal relationship between these variables. Due to these reasons we have omitted the discussion from the revised manuscript.

P. 6, L. 22: As it was mentioned in the method section, two different instruments for the CO flux measurements were used. However, in the result section the data from both analyzers is only shown as the cumulative flux in Figure 1f. If two independent analyzer are used, I would expect a paragraph or statement on the comparability of both measurements. This would give a better insight into the associated flux errors and would be also be valuable information for the CO flux community. Looking at the cumulative flux estimates, there seems to be a good agreement between days 205-270, while after that both fluxes seem to differ. Also, it should be stated in the manuscript that the presented fluxes (despite the green cumulative curve) are from the AR-CWQCL instrument while the LGR-CWQCL instrument was only operated from day 205.

We agree that it would benefit the scientific community to show the intercomparison data of these two gas analyzers. For the period when both AR-CWQCL and LGR-CWQCL were measuring FCO, we made plots showing the FCO measured by LGR-CWQCL against the FCO measured by AR-CWQCL (Figure 1). Also, we plotted the time series of half-hourly mean FCO and the daily mean FCO from both analyzers (Figure 2). This comparison shows considerable agreement between the analyzers with a slope of 0.96 and correlation coefficient of 0.95. The comparison shows that LGR-CWQCL shows slightly (4%) smaller fluxes compared to AR-CWQCL. The difference between the analyzers, however, is very small, giving us confidence in the use of either of the analyzer in further analysis. In page 8, lines 18-23 we have added a chapter in the results section describing the intercomparison of the two analyzers, however, we think it is unnecessary to show a figure from this comparison.

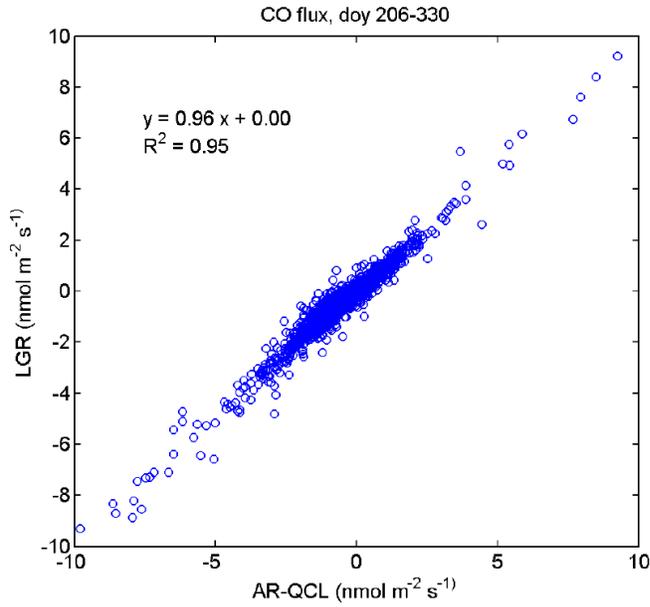


Figure 1. Comparison of FCO measured by LGR-CWQCL (LGR) against the FCO measured by AR-CWQCL (AR-QCL) over the period days 206-330 at the reed canary grass crop.

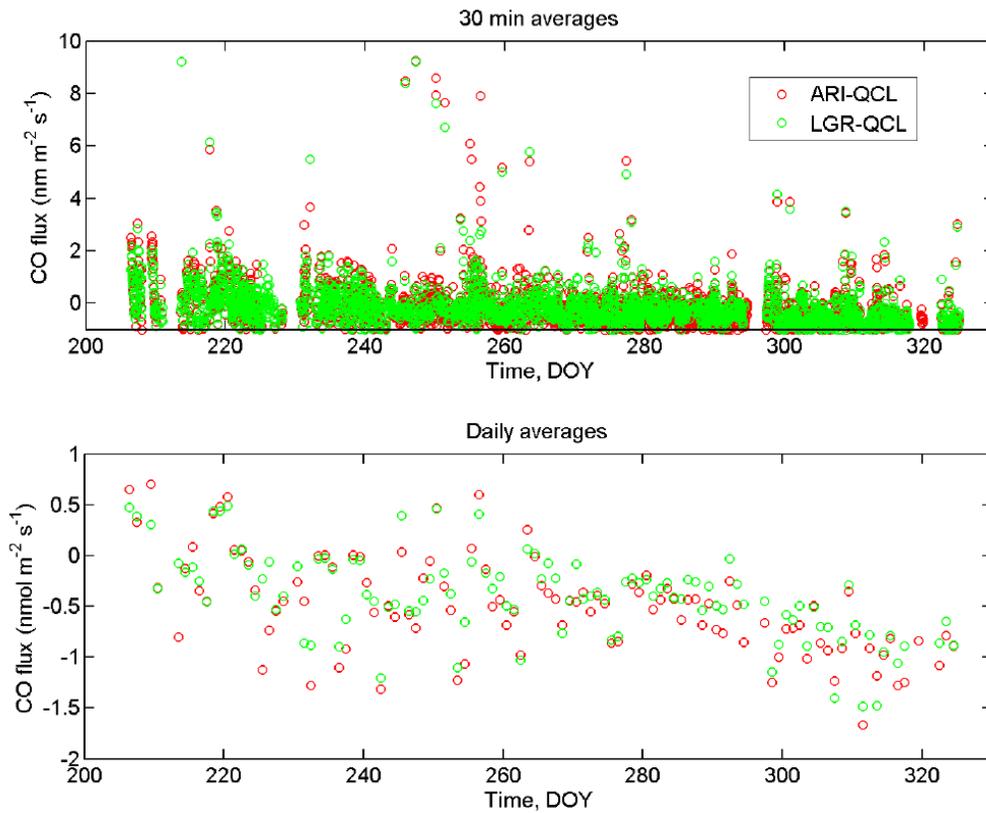


Figure 2. Half-hourly mean FCO and daily mean FCO measured by AR-CWQCL (ARI-QCL) and LGR-CWQCL (LGR-QCL) during the period of days 206-330.

P. 9, L. 11-13: To correct for this bias, a gap-filling method can be applied for the calculation of cumulative CO fluxes.

We used a simple statistical gap-filling method to test how this would affect the cumulative FCO over the whole measurement season (Figure 4). The gap-filling was performed by choosing randomly the unique missing values from within time-window  $\pm 5$  days, by differentiating days and nights (according to elevation of sun). This simple gap-filling was performed for days excluding those which had no single measurements available. Hence, the gap-filling method removes possible bias due to different fraction of missing during day- and night-time. However, it does not guarantee correct cumulative sum because days with no data were not gap-filled including the measurement break. We hesitated to gap-fill the periods when no data was available due to the relatively poor correlations between the measured variables and FCO, especially during summer period (days 181-205). **In page 11, lines 25-27 we mentioned that we tested this simple statistical gap-filling method, and that we decided not to present these results.**

The gap-filling exercise in Figure 4 shows that the emission period in the spring and in late summer is strengthened due to the even contribution of daytime and night-time data, which in this case includes a higher number of positive FCO. Similarly, the gap-filling leads to strengthened CO uptake in the autumn indicating that a higher number of night-time data was missing from that period. Overall, the cumulative curve of the original data and the gap-filled FCO result in very similar CO uptake rate after the 7-months of measurements. At this point, we hesitate to include the gap-filled data in the manuscript as it does not change the interpretation of the results. Still, we are happy to include the data if the reviewers/Editor see this as an informative and important part of the manuscript.

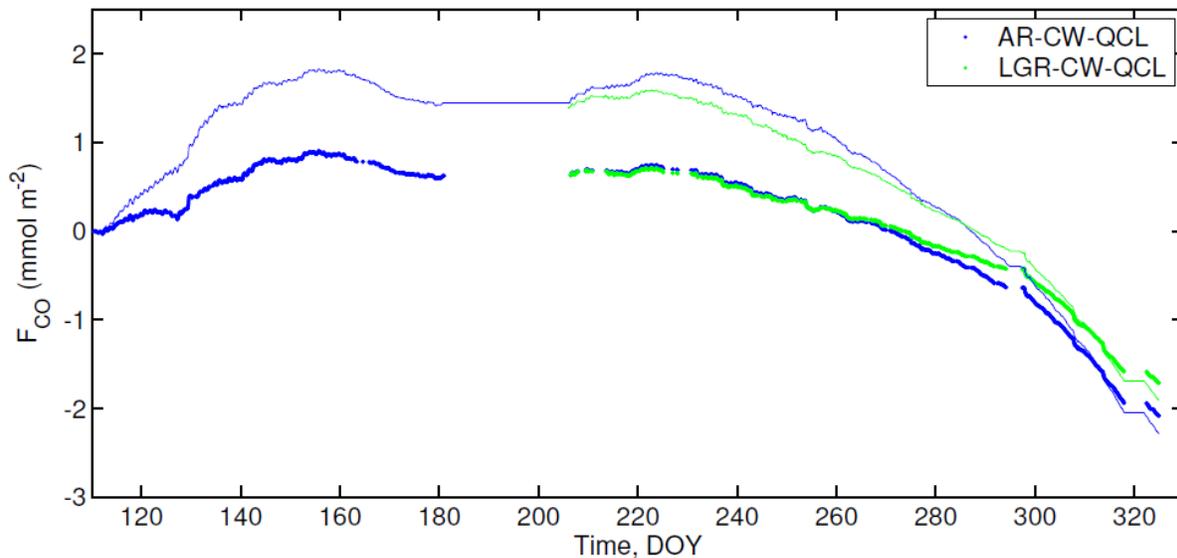


Figure 4. Cumulative FCO calculated from the measured data (bold lines) and gap-filled data (thin lines).

P. 7, L. 19-21: As stated, the concept of the gross FCO only holds if the CO uptake can be assumed to be constant over the entire diurnal cycle. However, especially turbulent transport and transport through the quasi-laminar boundary layer at the surface typically show distinct

diurnal cycles with maxima during daytime. Hence, I would expect the CO uptake to increase during the day, unless the CO uptake is limited mainly by soil microbial consumption or transport in soil (then, the CO flux would also mainly be independent from above surface CO-concentrations, which would change during day). Is there more evidence that can support the assumption of a constant CO uptake? The authors note that there is evidence from previous studies that the temperature effect on microbial consumption can be assumed to be small. In my opinion it should also be shown that the CO uptake is mainly limited by soil microbial consumption or transport in soil for the assumption of a constant CO uptake to be valid. Otherwise, the diurnal variation in the aerodynamic and the quasi-laminar boundary layer resistances would have to be taken into account. In general, the use of a bi-directional exchange model would be useful to address the issue of flux partitioning and importance of soil uptake, although I understand that this is challenging given the lack of detailed process studies on CO exchange and might be the scope of future research.

We agree that the use of the assumption of constant CO uptake may have been wrong. This was pointed out also by the referee #1, who suggested to use reported temperature dependencies of CO uptake from e.g. Whalen and Reeburgh (2001). As suggested, we used a Q10 value of 1.8 (Whalen and Reeburgh, 2001) to calculate the daytime CO uptake from the night-time CO fluxes over the six distinct measurement period. This allowed us to recalculate the gross CO emissions during daytime. Assuming this temperature dependency, the CO uptake was approximately 2 times higher during day than during night. As the net daytime FCO remained positive during the spring, early summer and late summer, we expect that also CO emissions must have increased during the day. **In a new table (Table 2), we report the soil temperature difference between day and night, which is used for calculating the temperature dependent CO uptake during daytime, and the consequent gross CO emissions.**

P. 8, L. 8-16: What was the applied definition for daytime and night-time periods? This is valuable information, as the correlation values are often largely dependent on the variation of the used parameters, which are typically larger during daytime. In this context, it might be also valuable to mention if the flux error had an impact on the weak correlations found during night-time.

Since random uncertainty of flux estimates is inherent property of the eddy covariance method, the correlations can be affected by these errors. Day- and night-time fluxes differed significantly in magnitude only during the first sub-period of the campaign, day 110-145, see Fig. 2, therefore we can expect that night-time correlation values were affected by the random flux errors more than the day-time values only during the first period. **In page 7, lines 14-15, we added the definition of daytime and night-time periods by stating that we used sun elevation angle ( $h < 0$  for night-time,  $h > 0$  for daytime) to separate between daytime and night-time data.**

P. 9, L. 11-13: To correct for this bias, a gap-filling method can be applied for the calculation of cumulative CO fluxes.

As explained above, we tested a use of gap-filling for missing data to estimate the effect of uneven data removal during daytime and night-time. This gap-filling indicates that the real FCO are more positive during the spring and summer compared to the actual quality screened data, which removes more data during daytime than during night-time. The cumulative gap-filled FCO curve (above) shows that both the emission period in the spring and the uptake period in the late summer and autumn may be more pronounced than that of the data without gap-filling. The resulting net cumulative FCO over the whole measurement period, however, seems to be very similar with or without gap-filling (see above). **Hence, we did not include gap-filled data in the manuscript. However, in Page 11, lines 25-27, we commented the use of gap-filling in order to justify not using it.**

P. 9, L. 14-15: As FCO describes the net CO flux, one should differentiate here more explicitly between the emission component and uptake component of the flux. Otherwise the reader may assume you are referring to the net emission/uptake.

Corrected.

### 3 Technical comments

P. 3, L. 4: Write “reed canary grass” instead of “read canary grass”. Correct also on P. 13, L. 9 and 19, L. 1.

Corrected.

P. 3, L. 13: Omit space after “27°” or introduce after all units (°, ‘, “). Use same degree sign as used in L. 15.

Corrected.

P. 3, L. 17: Use superscript for “-1” in “ha-1”.

Corrected.

P. 4, L. 10: Shouldn't it be “L=+-100 m” for the definition of the near-neutral range?

We used L = -100 m as the simulation case for neutral stratification. Since the absolute value of this L is much larger than the measurement height, the neutral stability assumption for this case is well justified.

P. 4, L. 16: Insert space before “Considering”.

Corrected.

P. 4, L. 26: Write “LGR-CWQCL” instead of “LGRCW-QCL” as in the rest of the manuscript.

Corrected. And in fact, **throughout the text**, we chose to use the abbreviation LGR-CW-QCL as in Rannik et al. (2015).

P. 6, L. 1: Do you intentionally differentiate between “co-variances” (here and L. 5) and “covariance”?

We did not intend to use “co-variances” but rather “covariance”. This is now corrected.

P. 6, L. 10: Write “daytime” instead of “day-time” as in the rest of the manuscript.

Correct also on P. 7, L. 15 and on P. 9, L. 24.

Corrected.

P. 6, L. 27: I suggest using “over the 9-month measurement period” instead of “in the end of the 9-month measurement period” as the used expression could be misleading otherwise.

Corrected.

P. 7, L. 17: Use superscript in units.

Corrected.

Figures 2-5: Instead of using the day of year numbers, I suggest to use the introduced classification of S, ES, MS . . . in the subplot titles (or use both, DOY + the classification). This makes it easier to compare with Figure 1 and descriptions in the text.

We modified the figures 2-5 to include the classification of S, ES, MS... + DOY (e.g. S, 110-145), similar to that presented in Tables 1 and 2.

#### 4 References

Foken, T. and Wichura, B.: Tools for quality assessment of surface-based flux measurements, *Agric. For. Meteorol.*, 78(1-2), 83–105, doi:10.1016/0168-1923(95)02248-1, 1996.

Rannik, Haapanala, S., Shurpali, N. J., Mammarella, I., Lind, S., Hyvönen, N., Peltola, O., Zahniser, M., Martikainen, P. J. and Vesala, T.: Intercomparison of fast response commercial gas analysers for nitrous oxide flux measurements under field conditions, *Biogeosciences*, 12(2), 415–432, doi:10.5194/bg-12-415-2015, 2015.

# 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. Emissions of CO have been reported from a wide range of soil-plant systems.

15 However, soils are generally considered as a sink of CO due to microbial oxidation processes. We measured CO fluxes by 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 CO<sub>2</sub>, N<sub>2</sub>O and heat fluxes as well as relevant meteorological, soil and plant variables in order to investigate factors driving the CO exchange.

20 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 July to November 2011. CO fluxes had a distinct diurnal pattern with a net CO uptake in the night and an 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 daytime CO fluxes and global radiation, net radiation, sensible heat flux, soil heat flux, relative humidity, N<sub>2</sub>O flux and net ecosystem exchange. The  
25 strong positive correlation between CO fluxes and radiation suggests towards abiotic CO production processes, whereas, the relationship of CO fluxes with net ecosystem exchange indicates towards biotic CO formation during crop growth. 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), which may lead to the production of the strong greenhouse gas ozone (O<sub>3</sub>). The reactions of CO and OH decrease the atmospheric capacity to oxidize atmospheric methane (CH<sub>4</sub>), 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 (N<sub>2</sub>O) (Myhre et al., 2013). Anthropogenic activities related to burning of fossil fuel and biomass (e.g. forest fires) and photochemical oxidation of CH<sub>4</sub> 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. In addition to CO consumption, production of CO has been found from a wide range of soils (Moxley and Smith, 1998; Gødde 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; Troxler 1972; Conrad and Seiler 1985b). Emissions of CO from water logged soils have often been attributed to anaerobic production of CH<sub>4</sub> (Funk et al., 1994; Varella et al., 2004); however, **most often the CO production has been related to abiotic processes such as thermal or 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). 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), while the separation between CO formation through thermal degradation and photodegradation, is challenging as indirect photodegradation can take place even in the absence of solar

radiation if adequate thermal energy is present (Lee et al., 2012). Photodegradation activity has also been proposed to facilitate microbial degradation through breaking down organic compounds making them easily available for microbial degradation (see King 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). The proposed processes, however, partly contradict each other as Wilks (1959) proposed that CO formation in green plants is linked to photodegradative activity involving the chlorophyll system, while Siegel et al. (1962) stated that while some oxygen is required, neither light nor chlorophyll are needed for CO is formation from seeds and growing plants. More recently, CO has been found to be formed e.g. —in stressed plants (He and He, 2014), in heme oxidation (Engel et al., 1972; Vreman et al., 2011) and aromatic amino acid degradation processes (Hino and Tauchi, 1987), and in lipid peroxidation reactions (Wolff and Bidlack, 1976).

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 & Crosby 2002; Lee et al., 2012). Reported CO flux rates in the field studies mostly range between -2 and 2 nmol m<sup>-2</sup> s<sup>-1</sup> with a tendency of higher CO uptake from natural and dry soils compared to managed or water-logged soils (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 & Hungria, 2002; Varella et al., 2004; Galbally et al., 2010). Also, there is a tendency of south to north gradient with higher CO emissions from tropical and Mediterranean ~~and tropical~~ 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; Kirchoff and Marinho, 1990) and in North American tundra (Gosink and Kelly 1979; 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 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<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), heat and energy as well as relevant soil, plant and meteorological variables. This allowed us to analyze the seasonality and diurnal variability in F<sub>CO</sub>, and to assess the driving variables of the F<sub>CO</sub>.

## 2 Materials and methods

### 5 2.1 Measurement site

The measurements were conducted on a mineral agricultural soil cultivated with a perennial reed canary grass (RCG, *Phalaris arundinaceae*, L. cv. Palaton) field located in Maaninka, Eastern Finland (63°9'48.69" N, 27°14'3.29" E). 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., 10 2012). The crop was cultivated in the beginning of June 2009. In 2011, the crop was fertilized in the beginning of the growing season (23 May) with an N-P-K-S fertilizer containing 76 kg N ha<sup>-1</sup> (NO<sub>3</sub>-N : NH<sub>4</sub>-N = 47:53). The crop from the previous season was kept at the site over the winter (Burvall, 1997), and was harvested on 28 of April (day 118) (Lind et al., 2016). The spring period (days 118-160) was characterized by fast crop growth with the crop height increasing from about 10 cm in mid-May to 1.7 m in late June, reaching the maximum height of 1.9 m in early July. The field was 6.3 ha in size 15 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.

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) 20 textural classification system. The soil pH varies from 5.4 to 6.1 within the ploughing layer from the surface to about 30 cm, and soil organic matter content between 3 and 11%. 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 25 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 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. 1c). Considering that prevailing wind direction during the measurement period was from SE and SSW directions, and the wind direction interval  $110-315^\circ$  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, 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 intercomparison of four laser-based fast-response gas analyzers to measure nitrous oxide ( $N_2O$ ) fluxes (Rannik et al., 2015).

The measurement height was 2.2 m until 30 June 2011 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 ( $50-110^\circ$  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 ( $T_{\text{air}}$ ) and relative humidity (RH) (model: HMP45C, Vaisala Inc.), precipitation ( $P_r$ ) (model: 52203, R.M. Young Company), global ( $R_{\text{glob}}$ ) and net radiation ( $R_{\text{net}}$ ) (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 ( $T_{\text{soil}}$ ) (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 ( $1 \times 1 \text{ m}^2$ ) and within each from three spots ( $8 \times 8 \text{ cm}^2$ ) 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 ( $L_s$ ). 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 = spring (S), days 146-160 = early summer (ES), days 161-181 = mid-summer (MS), days 205-240 = late summer

(LS), days 241-295 = autumn (A), and days 296-325 = 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 23 (IBM Corporation, United States).

10 To evaluate the gross CO flux rates (gross  $F_{CO}$ ), and the influence of temperature on CO uptake, we calculated the gross  $F_{CO}$  in two ways 1) by assuming an equivalent CO uptake during daytime as during 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). The gross  $F_{CO}$ , based on a constant CO uptake, was calculated by subtracting the night-time  $F_{CO}$  from the daytime  $F_{CO}$  for each six measurement periods (Table 2). The temperature dependent gross  $F_{CO}$  was calculated solving the  $R2$  in the equation

15 
$$Q_{10} = \frac{\left(\frac{R2}{R1}\right)^{10}}{(T2-T1)}$$

where  $Q_{10}$  is 1.8 (Whalen and Reeburgh, 2001),  $R1$  is the CO uptake rate during night-time ( $\text{nmol m}^{-2} \text{s}^{-1}$ ), 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, for each of the six measurement periods (Table 2).

### 3 Results

#### 20 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 161-322) (Fig. 1). Cumulative CO flux (cum  $F_{CO}$ ) curves show that the site was a net sink of CO over the 7-month measurement period. 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<sub>2</sub>O 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 was characterized by decreasing F<sub>CO</sub> and slowly dropping temperatures, decreasing radiation intensity, and decreasing photosynthesis activity of the crop (less negative NEE) (Fig. 1).

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<sub>CO</sub> agree reasonably well (Fig. 1f). A correlation scatter plot of the F<sub>CO</sub> from LGR-CW-QCL against F<sub>CO</sub> of AR-CW-QCL results on 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.

### 3.2 Diurnal variation

The F<sub>CO</sub> had a distinct diurnal pattern with a near constant CO 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 nmol m<sup>-2</sup> s<sup>-1</sup> (Fig. 2). The net F<sub>CO</sub> 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<sub>CO</sub> show a near constant uptake of CO over the whole measurement period (Fig. 2, Table 1.). The gross daytime CO emissions (gross F<sub>CO</sub>) were estimated in two ways: 1) assuming a constant CO uptake over daytime, and 2) accounting for temperature dependent CO uptake according to Whalen and Reeburgh (2001). The gross F<sub>CO</sub> 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 24). During mid-summer and autumn the daytime emissions were markedly smaller, and less than half of the emissions during the spring. The smallest gross F<sub>CO</sub> were measured in late autumn (Table 24). When the temperature

dependency in the CO uptake was taken into account, using a  $Q_{10}$  value of 1.8 (Whalen and Reeburgh, 2001), both the daytime CO uptake ( $F_{CO}$  uptake day( $Q_{10}$ , 1.8)), and the daytime emission- (gross  $F_{CO}$  day( $Q_{10}$ , 1.8)) were almost twice as high as the rates without the temperature correction (Table 2).

The diurnal  $F_{CO}$  over the six periods followed closely the daily pattern of  $R_{glob}$  (Fig. 3). However, 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 and 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 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  $N_2O$  emissions were on average 50% higher during the night than during the day (Shurpali et al., 2016).

### 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  $M_{CO}$ ,  $F_{N_2O}$  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  $F_{N_2O}$  ( $r=-0.336$ ,  $p<0.01$ ),  $H$  ( $r=0.315$ ,  $p<0.01$ ),- and  $LE$  ( $r=-0.241$ ,  $p<0.05$ ) in the spring and with  $M_{soil}$  ( $r=0.308$ ,  $p<0.01$ ) during early summer. A strong negative correlation was found

between  $F_{CO\_night}$  and  $F_{N_2O}$  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

- 5 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 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-
- 10 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.
- 15 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  $F_{CO}$  and its driving variables.
- 20 Cumulative CO fluxes (cum  $F_{CO}$ ) over the whole 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
- 25 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, 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 amount 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 were 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 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 overall 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 and with biweekly to monthly intervals, hence neglecting possible diurnal and seasonal variation in the fluxes (e.g. King, 2000; Varella et al., 2004; Galbally et al., 2010; van Asperen et al., 2015).

To calculate and annual CO balance of the RCG site, we used a mean  $F_{CO}$  over the whole measurement campaign of  $-0.25 \text{ nmol m}^{-2} \text{ s}^{-1}$  to apply for the missing period of day 326 – 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.

5 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-~~of~~ is suggested seems to be ~~clearly~~ a microbial process in the soil (Conrad &and Seiler, 1980), the production of CO has been  
10 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).

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  
15 (King, 2000; Whalen and Reeburgh, 2001). We did not find correlation between daytime or night-time CO concentration ( $M_{CO}$ ) and  $F_{CO}$ , indicating that  $M_{CO}$  is not limiting CO consumption at our site. In our site the daytime CO consumption, if existing, is overruled by a simultaneous CO production, creating the -strong diurnal pattern in the spring and early summer. Based on the temperature response of CO consumption using  $Q_{10}$  of 1.8 (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  
20 and 2). When this was taken into account in gross  $F_{CO}$  calculation, also daytime CO production -was markedly higher compared to the daytime CO production without the temperature corrected CO consumption. In 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, while night-time minimum chamber fluxes were  $-0.8 \text{ nmol m}^{-2} \text{ s}^{-1}$  and daytime maximum chamber fluxes were up to  $3 \text{ nmol m}^{-2} \text{ s}^{-1}$ , both measured over about one month period. Other reported diurnal CO fluxes are  
25 mostly over 24-hours only, and hence mainly demonstrate 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 drives 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, presence of oxygen, greater solar radiation exposure (no shading), and litter area to mass ratio (Tarr et al., 1995; King et al., 2012; Lee et al., 2012). Related to the C to N ratio of the plant material, a meta-analysis shows that CO formation via photodegradation increases with C to N ratio of the plant material (King et al., 2012). Also, as the plant material in our measurement site has a high C to N ratio (mean  $\pm$ stdev:  $66\pm 6.3$ ), 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 temperatures 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 Figures 2 and 3 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  $F_{CO}$  (data not shown). If also abiotic thermal degradation is temperature dependent as van Asperen et al. (2015) suggested, 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.

Based on understanding of biological CO formation, a negative correlation between  $F_{CO}$  and NEE would indicate involvement of a biological component in the CO production. Indeed, the  $F_{CO}$  and NEE correlated negatively ( $r=-0.469$ ) during early summer (days 146-160), which gives support to the CO formation from living and actively photosynthesizing plants. On the other hand, a poor correlations between  $F_{CO}$  and ecosystem respiration (RESP) throughout the measurement campaign indicates the microbial and plant respiratory activity does not play an important role in CO formation. At the RCG crop, the early summer CO emission period in May - June (days 146-160) coincides with the steepest slope in  $CO_2$  uptake

(more negative NEE), supporting the findings of 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. Similarly, we measured daytime CO emissions during July-August (days 205-240) when the crop had reached maximum height and was photosynthesizing actively, and when the dead plant litter on the ground was fully shaded from the sun by up to 1.9 m high crop and maximum LAI of 5.3 m<sup>2</sup> m<sup>-2</sup>. The fact that the CO emissions during the summer periods were lower than those during the spring are in line with the suggestion that the CO emissions from photodegradation generally decrease with increasing leaf area index (King et al., 2012), and that the CO photoproduction efficiency is lower for living plants compared to senescent or dead vegetation (Tarr et al., 1995; Erickson et al., 2015).

Although we cannot separate between biotic and abiotic CO formation at the bioenergy crop, our findings of daytime net CO emissions also during the peak LAI in July and maximum NEE, indicate that some CO may also be formed via plant physiological processes. In fact, CO has been found to be formed in living green plants under illumination and the presence of oxygen already in the 1950's (Wilks, 1959). Different abiotic stresses seem to induce CO production in plants (He and He, 2014) and biological CO formation has been observed via heme oxidation (Engel et al., 1972; Vreman et al., 2011), aromatic amino acid degradation (Hino and Tauchi, 1987), and lipid peroxidation reactions (Wolff and Bidlack, 1976). Carbon monoxide is also suggested to play an important role in cell-cell signalling (Ingi et al., 1996; He and He, 2014) and regulation of root growth (Xuan et al., 2007; Guo et al., 2008). The importance of these biological CO forming processes to the global CO budget is, however, still remain largely unknown (King and Crosby, 2002). An aspect demonstrating the lack of understanding in sink-source dynamics of CO, King and Crosby (2002) showed that plant roots are capable of producing CO, and that this CO source can be as high as the current global estimate of CO sink by soils.

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. Nitrifiers are among a diverse microbial community oxidizing CO in soils (Jones and Morita, 1983; King and Weber, 2007). Hence 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.

In our study, the fact that the strong correlations during the emission period between  $F_{CO}$  and global radiation, sensible heat flux and soil heat flux disappeared during the late summer and autumn indicates that the driving factors for CO exchange during the spring and early summer were different to those during the late-summer and autumn. We expect that when radiation as the driving factor for CO emissions decreased during late summer, soil CO consumption started to dominate, which is seen in the decreasing diurnal cycle in the  $F_{CO}$  and also in the strong correlation between  $F_{CO\_night}$  and  $F_{N_2O}$ . We also suggest that the source of CO may also have changed from the dead and senescent plant litter in the spring to the green living vegetation during mid-summer. Both of these have been identified as sources of CO via abiotic processes, however, the smaller emissions of CO from the living plants are explained by a lower production efficiency compared to senescent or dead vegetation (Erickson et al., 2015). Still the role of biological CO forming processes remain unresolved and call for further process-studies.

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 25-75<sup>th</sup> percentiles of the CO fluxes ( $F_{CO}$ ,  $\text{nmol m}^{-2} \text{s}^{-1}$ ) measured in a read canary grass (RCG) crop at Maaninka. Mean daytime (sun elevation,  
 2  $h_{\text{sun}} > 0$ ) and nighttime ( $h_{\text{sun}} < 0$ ) fluxes are calculated during six measurement periods (S = spring, ES = early summer, MS = mid-summer, LS = late summer, A = autumn, LA  
 3 = late autumn), and over the full measurement period from April to November 2011.

Period, days	$F_{CO\_day}$				$F_{CO\_night}$				net $F_{CO}$			
	mean	median	25 <sup>th</sup> -75 <sup>th</sup> percentile		mean	median	25 <sup>th</sup> -75 <sup>th</sup> percentile		mean	median	25 <sup>th</sup> -75 <sup>th</sup> 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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Table 2. Mean, median and 25-75<sup>th</sup> percentiles of the daytime gross CO fluxes (gross  $F_{CO}$ ,  $\text{nmol m}^{-2} \text{s}^{-1}$ ), temperature corrected daytime CO uptake (uptake  $F_{CO\_day}$ ) and  
 temperature corrected daytime gross CO fluxes (gross  $F_{CO\_day}$ ) calculated for the read canary grass (RCG) crop at Maaninka. The flux rates are calculated for six  
 measurement periods (S = 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. Soil temperature at 2.5 cm depth is used to correct for the temperature driven CO consumption using  $Q_{10}$ -value of 1.8 (Whalen and Reeburgh,  
 2001). Gross CO fluxes (gross  $F_{CO\_day}$ ) refer to the difference between daytime fluxes ( $F_{CO\_day}$ ) and nighttime fluxes ( $F_{CO\_night}$ ) presented in Table 1.

Period, DOY	gross $F_{CO\_day}$				$\Delta t_{\text{soil}}$	uptake $F_{CO\_day}(Q_{10}, 1.8)$				gross $F_{CO\_day}(Q_{10}, 1.8)$			
	mean	median	25 <sup>th</sup> -75 <sup>th</sup> percentile		$T_{\text{day}}-T_{\text{night}}$	mean	median	25 <sup>th</sup> -75 <sup>th</sup> percentile		mean	median	25 <sup>th</sup> -75 <sup>th</sup> 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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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 the field by chamber (transparent or dark), micrometeorological flux gradient or eddy covariance methods.

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

## Figure captions

5 Figure 1. (a) Daily mean air and soil temperatures, (b) global radiation sum ( $R_{\text{glob}}$ ), (c) daily precipitation sum (Pr) and soil water content (SWC), (d) weekly leaf area index (LAI) (blue) and green area index (GAI) (green), (e) net ecosystem exchange (NEE), and (f) cumulative CO fluxes (cum  $F_{\text{CO}}$ ; blue and green) and daytime mean CO fluxes ( $F_{\text{CO\_day}}$ ; red) over the 9-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 average CO fluxes ( $F_{\text{CO}}$ ,  $\text{nmol m}^{-2} \text{s}^{-1}$ ) from the reed canary grass crop from six distinct periods during the April to November 2011 measurement campaign. The vertical bars indicate  $\pm 1$  standard deviation of the fluxes.

15 Figure 3. Diurnal cycle of half-hour average global radiation ( $R_{\text{glob}}$ ,  $\text{W m}^{-2}$ ) the reed canary grass crop from six distinct periods during the April to November 2011 measurement campaign. The vertical bars indicate  $\pm 1$  standard deviation of the fluxes.

Figure 4. Diurnal cycle of half-hour average net ecosystem exchange (NEE,  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) from the reed canary grass crop from six distinct periods during the April to November 2011 measurement campaign. The vertical bars indicate  $\pm 1$  standard deviation of the fluxes.

20 Figure 5. Daytime half-hour average CO fluxes ( $F_{\text{CO}}$ ) against global radiation ( $R_{\text{glob}}$ ), sensible heat flux (H) and net ecosystem exchange (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  $\pm 1$  standard deviation are presented in black.

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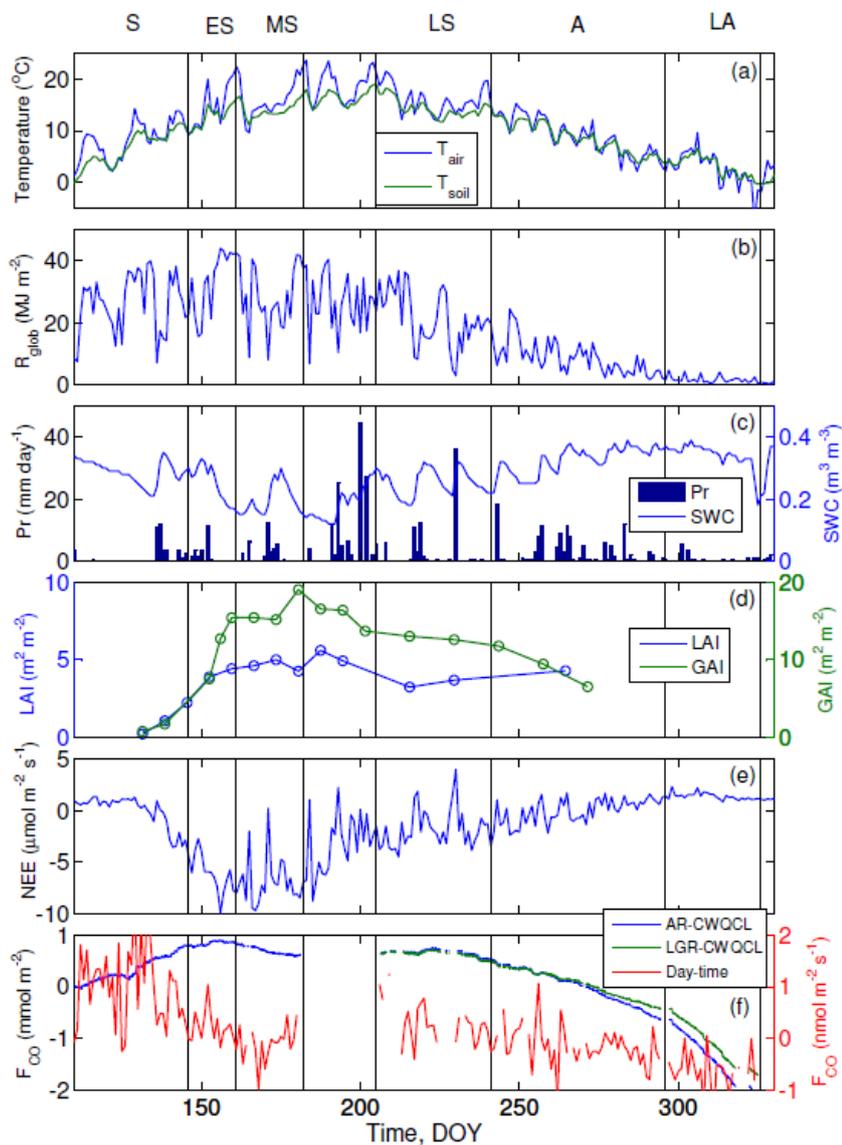


Figure 1. (a) Daily mean air and soil temperatures, (b) global radiation sum ( $R_{\text{glob}}$ ), (c) daily precipitation sum (Pr) and soil water content (SWC), (d) weekly leaf area index (LAI) (blue) and green area index (GAI) (green), (e) net ecosystem exchange (NEE), and (f) cumulative CO fluxes (cum  $F_{\text{CO}}$ ; blue and green) and daytime mean CO fluxes ( $F_{\text{CO, day}}$ ; red) over the 9-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.

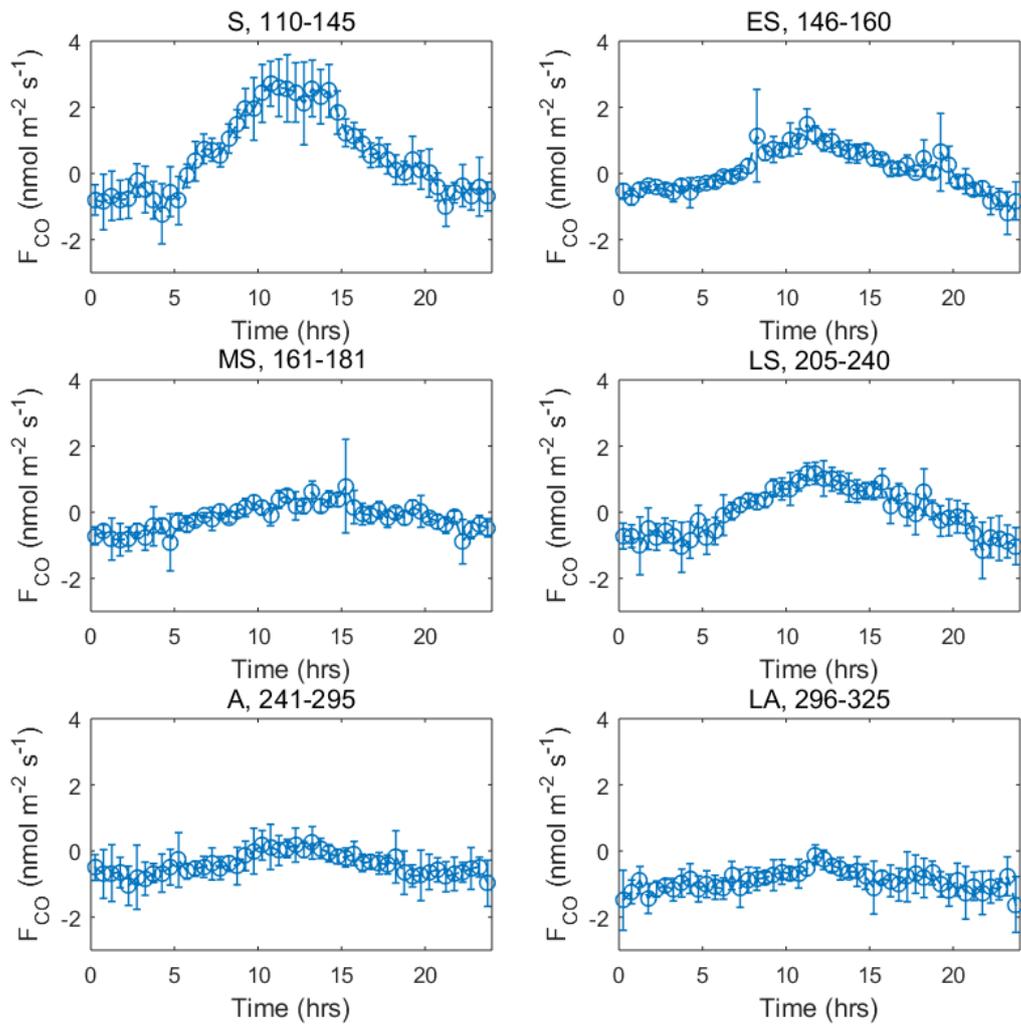


Figure 2. Diurnal cycle of half-hour average CO fluxes ( $F_{CO}$ , nmol m<sup>-2</sup> s<sup>-1</sup>) from the reed canary grass crop from six distinct periods during the April to November 2011 measurement campaign. The vertical bars indicate  $\pm 1$  standard deviation of the fluxes.

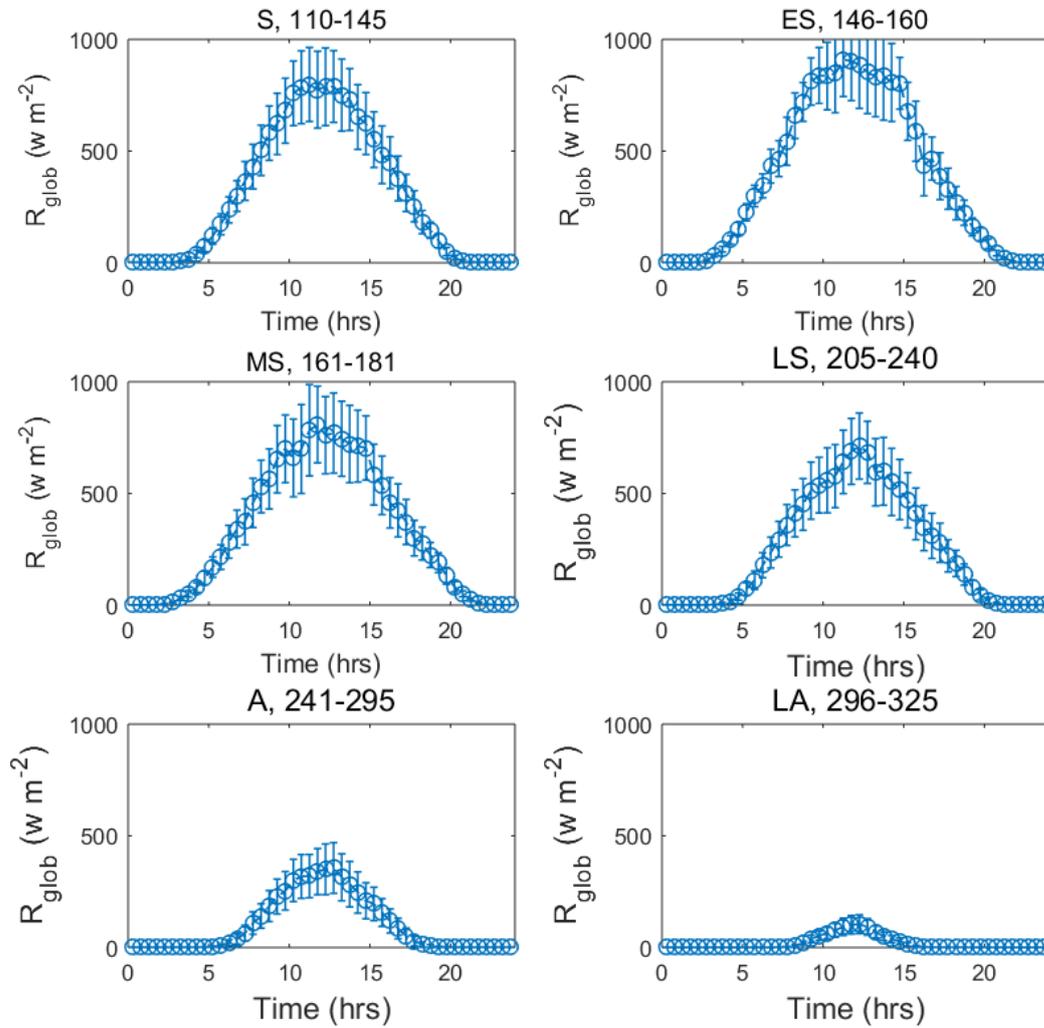


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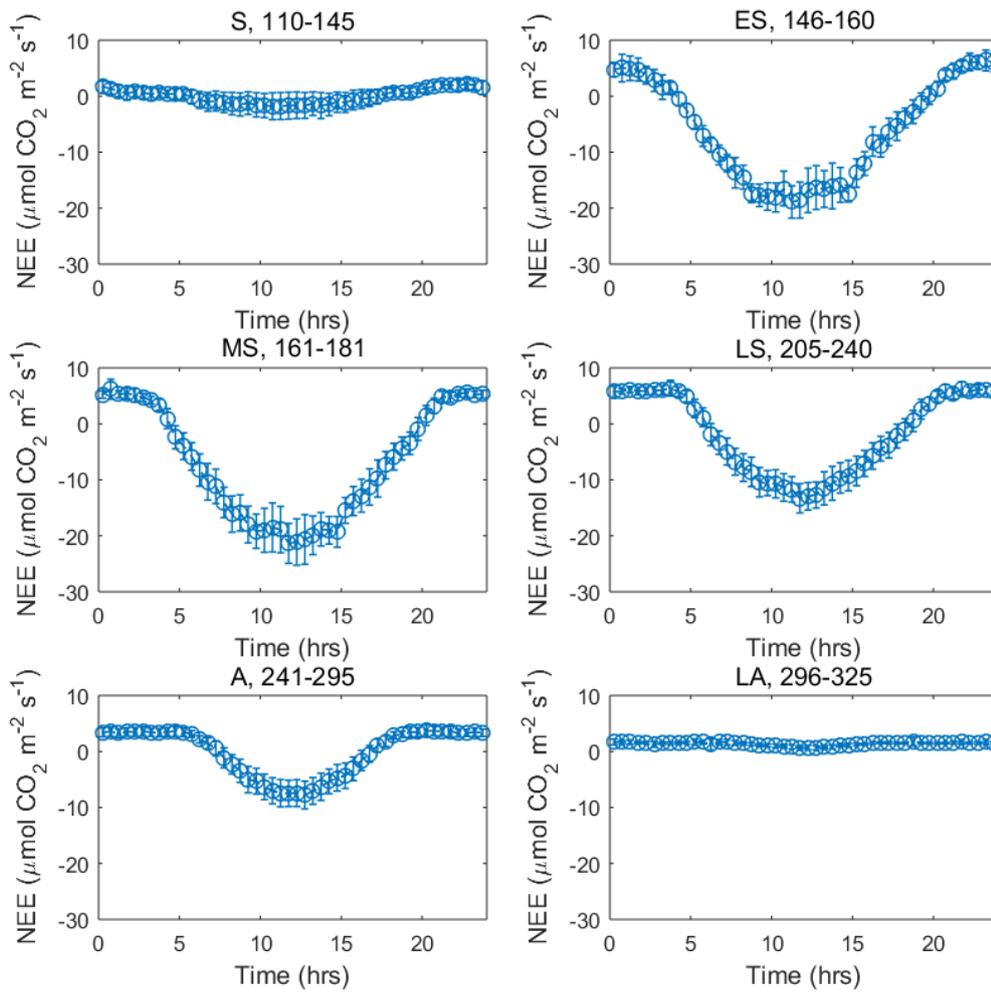


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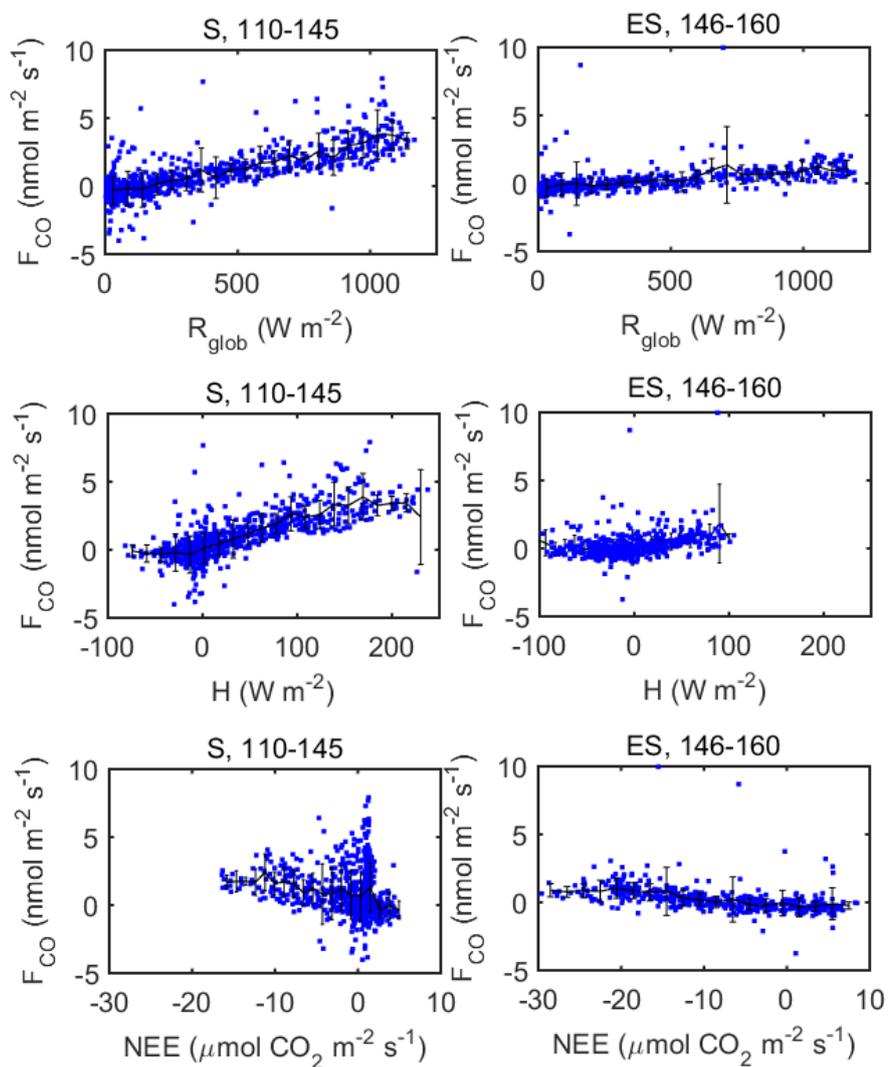


Figure 5. Daytime half-hour average CO fluxes ( $F_{CO}$ ) against global radiation ( $R_{glob}$ ), sensible heat flux ( $H$ ) and net ecosystem exchange ( $NEE$ ) measured over two emission periods ([Spring, days 110-145](#), [Early Summer, days 146-160](#)) at the reed canary grass crop in Maaninka.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