Interactive comment on “Seasonal and diurnal variation in CO fluxes from an agricultural bioenergy crop” by M. Pihlatie et al.

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Received and published: 25 May 2016

Response to the reviewer comments Dear Dr. Ivonne Trebs, and two reviewers,

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 Covariance 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.
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. We also aim at not overstating process level drivers of CO fluxes as our data does not allow us to conclude this. 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 in situ 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 nighttime net CO fluxes and air 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 CO flux and daytime CO uptake. These results are now reported in two tables: Table 1. The mean, median and 25-75th percentiles of the net CO fluxes, net daytime CO fluxes and net night-time CO fluxes for each measurement period. Table 2. The daytime and night-time air temperatures, daytime CO uptake (using Q10 of 1.8), and gross daytime CO emission.

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. 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 mis-
leading: they base it on the poor correlation between FCO and FN2O, and the poor correlation between FCO and RESP. However, FCO is a net in Cux (sum) of uptake and production, while RESP and FN2O are solely production in Cuxes. 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 FN2O? With the current dataset, it is difficult to determine whether biological in Cuxes 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 in Cuxes? 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 in Cuxes 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 in Cuxes 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 FCO and FN2O, 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 FOC and FN2O, and FCO and RESP, and possible reasons why we did not find significant correlations. We also added more discussion on the current understanding of biological CO production, the seasonality in biological CO fluxes, and whether biological CO production could significantly contribute to CO fluxes in our agricultural ecosystem.

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 naive 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 in Cux) 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 N2O in Cuxes. The results are only shown in a table but not discussed, and the N2O in Cuxes are hardly mentioned in the Discussion and forgotten in the Conclusion. For the N2O results, the reader is referred to another paper. If the authors think that the N2O story is an important part, since they state their interest in the introduction, they should show some N2O results, interpret these results, and spend some text on why they expect a correlation. Does a N2O in Agure maybe in At in Figure 1? Or, if they prefer to refer to the other paper, please then describe the N2O in Cuxes (magnitude and diurnal
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 positive correlation between FCO and NEE would indicate involvement of a biological component in the FCO, hinting towards biological CO production. With respect to FN2O, we would not expect a strong relationship with FCO measured in the field due to the difficulties in separating between overlapping abiotic CO production, microbial CO uptake (Conrad and Seiler, 1980; Moxley and Smith 1998), and microbial N2O 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 high nitrification activity may be reflected in higher CO oxidation in the soil. However, in the field, this is difficult to distinguish as the CO uptake and emission processes take place simultaneously and may cancel each other out. In our study site, no microbial community structure analysis was conducted, however, denitrification was suggested as the dominant N2O forming process especially during high-flux period in the spring and early summer (Shurpali et al., 2016). During the background flux period (days 206-280) the N2O fluxes are small due to low N availability indicating also low nitrification and denitrification activities. In order to distinguish between nitrifier driven CO consumption, microbial community analysis should have been conducted parallel to laboratory studies focusing on CO uptake in controlled conditions. Based on this, we did not want to add a new figure of FN2O, and we considered Figure 1 to be already very tight and have no space for additional scalars. We added more description of the FN2O dynamics, and referred to the recently accepted paper reporting the diurnal variability in FN2O (Shurpali et al., 2016).

Looking at Figure 2 and 3, they correctly conclude that not all CO in fluxes can be initiated by radiation, since CO in 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 in 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 A°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.

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The graphs show how the soil temperature still continues to decrease even after the sunset, when sun elev is above zero.

See pdf-file: 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. 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 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 wont influence your results largely due to the large sampling Cow, 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 analyzer (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 5) 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 nmol m\(^{-2}\) 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 mg CO m\(^{-2}\) yr\(^{-1}\). When we further extrapolated this to the grassland area in Finland (in total 14891 km\(^{2}\) (Eurostat, statistics, http://ec.europa.eu/eurostat/statistics-explained/index.php/File:Land_cover,_2012_LUCAS2012.png), we obtained a CO sink of -1649 tons CO yr\(^{-1}\). This estimate is slightly less but similar in magnitude as that produced by the model by Potter et al. (1996) for tundra, boreal and temperate zone soils, which we consider more realistic than the estimate by Ingersoll (1974), which is based on data from laboratory experiments with above ambient CO concentrations. We have added our annual FCO estimates, discussed their uncertainties and compared them to literature values in the discussion part of the manuscript.

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\(^{-1}\), m\(^{-2}\)) 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 ñ Cux or soil heat ñ Çux) Thank you for spotting these. We will go through them carefully.


- 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, line18: 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 also we elaborated a little more that also visible radiation may induce CO emissions.

- Page 2, line 22: Most of the reported CO ñ Çux measurements are either short-term ñ Åeld 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 ñ Årst measurement in this ecosystem? Or the ñ Årst 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/Finnland/boreal zone this ecosystem is representative for? (see paper Ingersoll, 1973, table 6,7) We have added information that the site can be classified as a grassland and as follows, FCO can be estimated for the grassland area of Finland. We also added information concerning the cultivation area of RCG crops as comparison to the area of grasslands generally. Based on the mean annual FCO estimated for our RCG crop, we estimated the FCO for grasslands in Finland as was done in Ingersoll 1974.

- Page 3, line 20: The footprint length is given, and the size of the ñ Åeld 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. We clarified that the footprint is homogenous in all directions.
A 6.3 ha area is introduced, is this the same area as meant in the rest of §2.1, before this sentence? Not clear formulated. 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. 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.

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 is now added 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 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 CO2, maybe introduce this a little clearer. We added introducing sentence to the start of the chapter
stating that compared to the FCO, the net CO2 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 “meteorological, soil and crop variables” and the methods used in measuring them.

- Page 8, line 1-5: N2O is not discussed at all here. We added a section describing the diurnal variation in N2O 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? 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

ï‘ñÇuxes 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. We modified the Table 3 to include information of daytime and night-time CO fluxes whenever this information was available.

In Figure 4, NEE is mentioned. I assume this measured by the EC measurements of CO2? 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 CO2) in the Figure 4 legend, and also in the text where NEE was mentioned (e.g. chapter 3.2 Diurnal variation).

Please also note the supplement to this comment: