Anonymous Referee #1

Finco et al. (2018) present a novel dataset of ozone and NOx fluxes at multiple levels from a month-long field campaign at a forest in Italy. The authors find that NO plays an important role on the observed ozone fluxes; ozone and NO reaction dominates the observed ozone flux near the canopy floor and determines the differences in observed ozone fluxes at higher levels in the canopy. The authors find that about half the ozone flux during the day actually occurs to the middle of the canopy, which is very interesting; it's typically considered that most of the ozone is deposited to the upper third of the canopy. At night, reaction of ozone and NO close to the ground dominates the ozone flux. The weakness of the paper is that there is quite a lot of data presented (thirteen figures) but the direction of the manuscript and the significance of the authors' findings are not always clear. I would encourage the authors to better guide the reader and contextualize their findings, clearly articulating how their study advances current understanding.
One way of better guiding the reader would be to hone the paper's objectives and including some overarching statements at the beginning of each section and move some of the figures to supplementary material.
After substantial revisions, I think this paper should be published in ACP.

RESPONSE
We thank the reviewer for the careful revision and his/her suggestions to improve this manuscript. We have clarified the aims of the paper in order to better guide the reader as requested. For this sake the Introduction has been revised, enhanced and reshaped.
Some of the Figures and Tables have been moved to the Supplementary material, and the Discussion has been refined to make it more focused on the paper topics.

General comments.

In the introduction, the authors motivate their work with ozone damage to ecosystems. But they do not introduce stomata, non-stomatal deposition pathways, or that air chemistry can impact observed fluxes. In the abstract, the authors mention that NOx can lead to ozone production, but in the introduction the authors mostly discuss ozone destruction by NO. Spelling out the connections and expanding their introduction would help readers follow along and see the value of the authors' approach.

RESPONSE
Ok, the introduction has been improved and expanded according to the reviewer's suggestion by listing all the deposition pathways including stomatal deposition.
The connections between different parts are now improved.

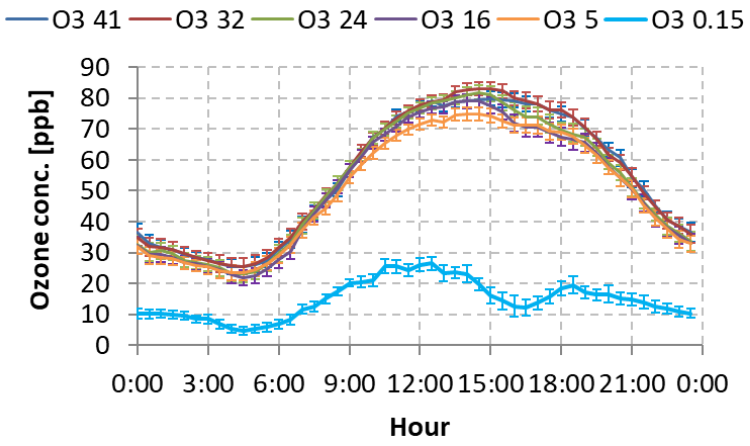
One of the authors' stated objectives is "to test the capacity of existing deposition mod-

els to predict intra-canopy dynamics involving ozone reactions with NOx and VOCs".
But I do not see any analysis in the paper addressing this objective.

RESPONSE
The reviewer is right. We realized that this objective was improperly inserted among the objectives of this paper.
We think that data from this field campaign could be used to test the O3 deposition predicting capacity of some of the existing deposition models, particularly on the intra-canopy dynamics of O3 and NOx.
We are aware that a new model named ESX is under development as a follow up of the ECLAIRE project and that data presented in this paper will be used to calibrate and validate it. Our sentence was meant to be referred to this follow up.
Thus, the text has been modified as follows:
The detailed dataset of this campaign will also allow future tests on the capacity of existing deposition models to correctly predict ozone deposition dynamics on forest ecosystems, and particularly intra-canopy dynamics involving ozone reactions with NOx.

Why aren't there confidence intervals on the figures with averages?

RESPONSE
We have already posted two comments in the discussion about this referee's remark. In our humble opinion we think that in many figures of our manuscript, because of the presence of five lines (or more) in the figures, the use of error bars could be misleading for the reader because error bars are overlapping and could hide the diurnal course of the plotted parameters.
For example, please refer to the following graph reporting the diel course of [O3] at six levels. The error bars hide the course of the ozone concentrations at the different heights when the lines are close. For example, it is nearly impossible to understand the course of the ozone concentrations at 41 m.



However, we agree with the reviewer that the explication of the uncertainties of the means is of primary importance. So, we would suggest to report the range of the variation of the standard error for each curve (from the minimum to the maximum values observed in the 24h) in the text of the figure captions, without losing statistical robustness and the possibility to clearly appreciate the diel courses.
The following Figure reports and example of how we cope with this issue throughout the manuscript.

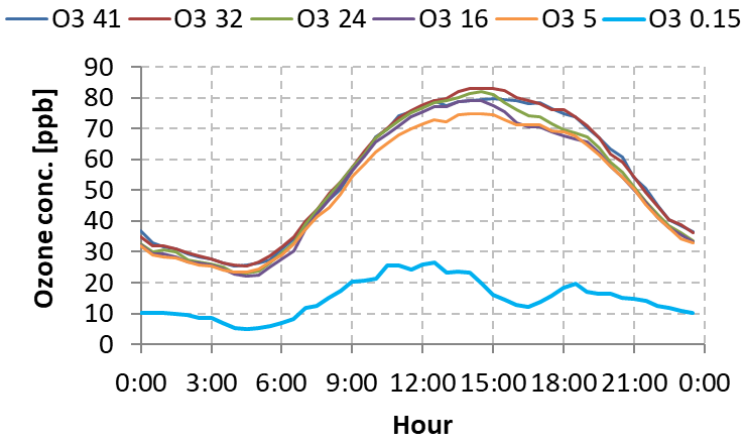


Figure 1 - Average diel courses of ozone concentrations at the six levels (41 m, 32 m, 24 m, 16 m, 5 m and 0.15 m). The maximum and the minimum standard error of the half-hourly means were respectively 3.0 and 1.7 ppb for 41 m, 3.0 and 1.8 ppb for 32 m, 3.4 and 1.9 ppb for 24 m, 3.4 and 1.8 ppb for 16 m, 2.9 and 1.7 ppb for 5 m, and 3.4 and 1.0 ppb for 0.15 m.

The current contents of the discussion seem like they would better fit in the results, as there is a lot of new data analysis.

RESPONSE
We understand the point of view of the reviewer. However, while the data analysis reported in the Results are merely descriptive and represent the groundwork for the following Discussion, the new data analyses shown in the Discussion are functional to support the interpretations of the Results. Moreover, the data analyses in the Discussion summarize several different results and help us to draw the Conclusions.
In our opinion, moving part of the Discussion in the Results would also implicate many cross-references to other results that could be still unexplained in that part of the manuscript.

There are many figures, and relatively little text. My feeling is that many of the figures could be moved to supplementary material.

RESPONSE
OK, we have moved to supplementary material some figures which are not essential for the interpretation of the behavior of the gas exchange at the forest (Table 1, Figure 1a, 1b, 1d, 1e, Figure 7, Figure 8b) and figures, like the cospectra ones (Figure 11a, 11b, 11c, 11d), which were used only for excluding some tangential hypotheses.
We have tried to keep in the manuscript only the most relevant figures.

It would be helpful to the reader if the authors were more generous in referencing their figures. For example, on page 11, lines 16-24 there is no reference to any figures.

RESPONSE
Ok, thank you. Some additional references to the figures have been added in the text, as suggested.

The authors should check their in-line references for commas after the author name or "et al." and whether their use of commas or semi-colons between references is consistent (and ACP policy as to whether there is a difference between in-line references used with "e.g." vs. not).

RESPONSE
Ok, corrected.

In general, I would recommend that the authors do not use words that express a value-judgement, like "extremely", "remarkable", "peculiarity".

RESPONSE
Ok. These adjectives have been removed throughout the manuscript.

Line-by-line comments.
Abstract.
Generally readers are not going to know what "in the framework of the European FP7 project ECLAIRE" means.

RESPONSE
The reference to the ECLAIRE project has been deleted from the abstract and moved to the acknowledgements.

Instead of saying “A partition of the ozone fluxes will be shown to identify the most relevant sinks” the authors should say report their most important finding in their abstract.

RESPONSE
Ok, thanks. The abstract has been modified accordingly to this suggestion.

Page 2, Line 4: “had” should be “has”

RESPONSE
Thank you for reporting it to us. However, in the revised version of the Introduction the whole sentence has been removed.

Page 2, Line 30-31: It’s not clear to me why this is relevant

RESPONSE
In the revised version of the Introduction this sentence has been slightly modified and it was meant to underline that this paper is part of a group of companion papers which present different aspects of the same joint monitoring campaign performed under the ECLAIRE project. Since other reviewers asked for information about the interaction of O3 with VOCs, this sentence is simply functional to direct them to the papers which explain that in details.

Page 3, Line 4: What is a “climax” ecosystem?

RESPONSE
A climax ecosystem is an ecosystem at its maximum development stage (mature). At this stage the ecosystem is at a steady state from an energetic and ecological point of view.
We have added a short description of it in brackets in the text.

Page 3, Lines 8 & 12: Here and in the remainder of the paper, I find it difficult to distinguish between the terms “dominant” and “dominated”. Are there other ways the author could describe them?

RESPONSE
These are typical ecological terms. The dominant tree layer is composed by the higher trees of the ecosystem, while the dominated layer is made up of the lower trees and the understorey.
However, following the reviewer’s suggestion, in order to help the reader unfamiliar with these ecological terms we adopted other more common terms to describe them.

Page 3, Line 13: Atmospheric chemists may not know what nemoral means.

RESPONSE
Nemoral is the scientific way to refer to the understorey. However, following the reviewer's suggestion, we have changed this term in the text with the more common term understorey.

Page 3, Line 24: How do the authors calculate the fetch size?

RESPONSE
We intended for fetch the maximum upwind distance from the tower, where surface was homogeneous in composition and micrometeorological behavior. We calculated it as the distance between the tower and the edge of the forest in each direction.
Following the reviewer's remark, in order to clarify, we have decided to substitute the term "fetch" with "distance from the edge of the forest".

Page 3, Line 30: Will the authors please use "instrument models" or "instrument types" here instead of "model"?

RESPONSE
OK, thanks. Corrected in the text

Page 3, Line 31: 10 m away from the tower in the vertical? Or in the horizontal?

RESPONSE
In horizontal direction. A sentence has been added in the text to clarify the direction.

Page 4, Lines 4-10: Are COFA, ROFI, FROM, and GFAS acronyms? If so, it would be helpful to spell out what they stand for.

RESPONSE
COFA, ROFI and FROM are acronyms; we have now specified their meaning in the text.
GFAS instead is the name of a spin-off German company created to develop the instrument which was called with the same name of the company. However, this company is no longer running.

Page 4, Line 19: Why how the data are stored (i.e., in hourly files) relevant?

RESPONSE
Ok, we agree that how the data were collected and stored is not particularly relevant but it was mentioned in order to provide a complete information.

Page 4, Line 26-27: I'm not sure that I understand. Why is the chamber only measured for six minutes? What do the authors use the measurement of the reference chamber for?

RESPONSE
The reference chamber acted as a blank, and it was necessary for the correct flux calculation in the measuring chambers. Please note that after each measuring chamber was sampled, a measurement in the reference chamber was also performed.
For each measuring chamber we had 6 minutes of sampling and 6 minutes of measurement in the reference chamber. Using 5 measuring chambers, the overall cycle lasted exactly 60 minutes (6min x 5 + 6min x 5).
We have inserted a reference to the Bütterbach-Bahl paper where this system is well described and to which the reader could refer for further details.

Page 5, Line 8: I don't think model should be abbreviated, here and elsewhere

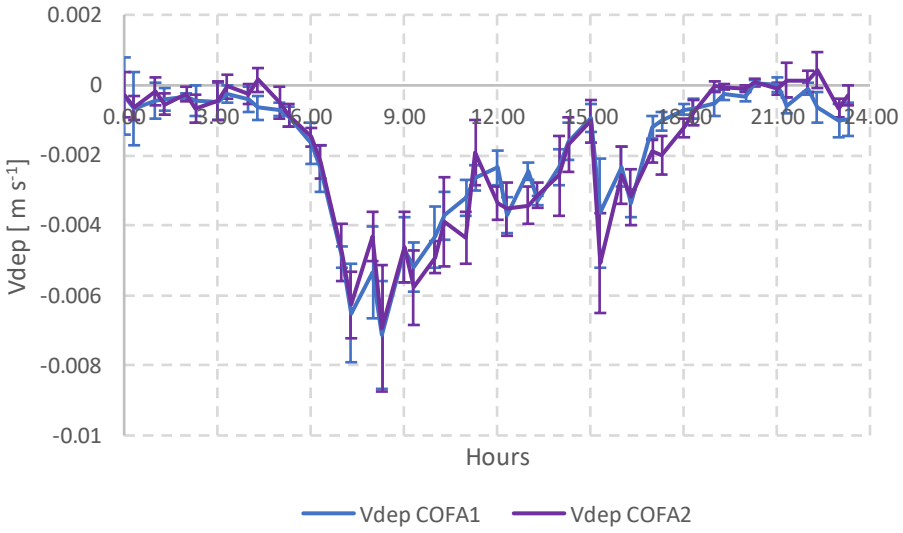
RESPONSE
Ok thanks, corrected in the text

Page 5, Line 22-24: The authors should check the consistency of their abbreviations. For example, Campbell Scientific is abbreviated in one sentence but in the next sentence it is not.

RESPONSE
Ok thanks, corrected in the text

Page 6, Line 7-9: What was the result of the inter-comparison between the two COFAs?

RESPONSE
The two instruments were two clones, so we did not expect any particular difference between their measurements. In any case, we decided to run the two COFAs in parallel for 5 days (the typical duration of a coumarin-47 target) in the month following the end of the field campaign.
The figure below shows the average diel course of the deposition velocity measured with the two instruments in the inter-comparison period. A good agreement between the two instruments can be appreciated.



Page 6, Line 10: Are the authors examining the relative standard deviation for a given half-hour?

RESPONSE
Yes, we have considered the standard deviation of each half-hour of the deposition velocity of each of the three instruments.

Page 6, Line 11: Why is systematic in parenthesis?

RESPONSE
Ok, thank you. This was an oversight. Parenthesis have been removed.

Page 6, Line 22: I don't think including this sentence is necessary.

RESPONSE
OK, thank you. The sentence has been removed.

Page 7, Line 9: "were" should be "was"

RESPONSE
Ok, thank you. Corrected.

Page 7, Line 10: What does “semi-hourly” mean?

RESPONSE
It means half an hour: the text was corrected accordingly.

Page 7, Line 13: “k” should be “K” in kinematic

RESPONSE
Ok, thank you. Corrected.

Page 7, Line 26: Is V0 the initial voltage?

RESPONSE
No, V_o is an estimation of the voltage at zero ozone concentration. The text has been corrected to explain this concept.

Page 7, Line 32: The “C” of “C_O3” is missing

RESPONSE
Ok, thanks. Corrected in the text.

Page 7, Line 33: “let” should be “allow”

RESPONSE
Ok, thanks. Corrected in the text

Page 8, Line 17: What is “it” here?

RESPONSE
“It” was meant to indicate ozone. The text has been slightly corrected.

Page 8, Line 7-19: What is the timescale that the authors correct for storage over?

RESPONSE
The timescale used to correct for storage over was every half an hour. We have added this information in the text.

Page 8, Line 24: There is a “the” missing from between “cooled” and “air”

RESPONSE
Ok, thank you, corrected in the text.

Page 8, Line 28: Is this local time? If so, it would be more straightforward to refer to it as local time.

RESPONSE
Yes, it is local time. The text has been modified accordingly.

Page 8, Line 29: Do the authors mean the respective lower and higher levels by “other ones”?

RESPONSE
Yes, that’s the correct meaning. The text was slightly modified in order to clarify.

Page 8, Line 29-30: I think the authors mean that only two significant rainfalls occurred during the campaign and they happened at the end of the campaign

RESPONSE
Yes. The text has been modified accordingly to the reviewer’s suggestion.

Page 11, Line 10: Why is this remarkable?

RESPONSE
The good agreement between ozone fluxes and LE fluxes (water fluxes) indicates an important role of the stomatal activity in the ozone removal process, and for this reason it should be remarked, even though this topic was not furtherly discussed in the manuscript because it is beyond the aim of this work. The water flux in closed canopies is used as an indicator of the stomatal activity. High LE fluxes = high stomatal aperture.
Anyway, we have removed this adjective and we have slightly modified this sentence in order to be more clear.

Page 11, Line 11: Why would ozone fluxes and LE fluxes be correlated?

RESPONSE

The latent heat flux (water flux) can be considered as an indicator of the stomatal activity in closed canopy. The higher water fluxes the higher stomatal opening. Consequently, higher stomatal opening lead to higher ozone uptake by stomata. Is thus not surprising that LE and ozone fluxes are correlated above a physiologically active vegetation.
Please refer also to the response above.

Page 12, Line 1: There is a rogue "g);" in this line that needs to be deleted

RESPONSE
Ok, thanks. Deleted from the text.

Page 12, Lines 7-8: But there weren't necessarily decreases in emission, there were just decreases in the observed flux (perhaps one could call this the effective emission?)

RESPONSE
We did not completely get the point raised by the reviewer, sorry.
Speaking of soil NO we have used the terms "emissions" and "fluxes" as synonymous because at the soil level NO is always emitted in our ecosystem.
In any case, we have followed the reviewer suggestion by substituting the term "emissions" with "observed fluxes" in the text when appropriated.

Page 12, Lines 9-10: Instead of "followed nearly symmetrical" I would say they were close to inversely proportional

RESPONSE
Yes, the reviewer is right, the term symmetrical should be intended as reflection symmetry. The text has been corrected as suggested, thanks.

Page 12, Lines 11-12: Do the authors mean that the simultaneous minimums?

RESPONSE
No, we mean that the NO fluxes and NO2 fluxes had a simultaneous minimum and maximum, respectively, in the afternoon. The sentence has been modified in order to clarify this.

Page 12, Lines 14-16: The authors should refer to the figures that they are concluding this from. Will the authors please be more explicit about what they mean by "in relation to" here? Why is NO deposition most apparent at this time?

RESPONSE

We have now inserted references to the Figures to support our explanation.
The NO deposition peak above the canopy in the morning can be deduced in Figure 10e (now Figure 9e), black line. The NO deposition peak in the morning can also be deduced from Figure 10b (now Figure 9b) where a small NO gradient can be appreciated and a minimum of the NO concentrations at canopy level can be observed.
This deposition peak is likely related to NO consumption at the top-canopy level early in the morning.
"Why is it most apparent at this time?". We do not exactly know why. However, one possible explanation could be linked to the stomatal uptake of NO2 (which is more soluble in the sub-stomatal cavities water than NO, Teklemariam et al., 2006) by the upper canopy leaves, and this occurs in the early morning when stomata re-open. This NO2 sink would lead to a shift of chemical equilibrium towards an enhancement of the reaction between O3 and NO, thus resulting in the observed O3 deposition peak.
The term "In relation to" was intended as "correlated to". We have modified this term and all the sentence in order to clarify what we mean.

- Teklemariam, T. A. and Sparks, J. P.: Leaf fluxes of NO and NO2 in four herbaceous plant species: The role of ascorbic acid, Atmos. Environ., 40, 2235-2244, 2006.
- Stella, P., Kortner, M., Ammann, C., Foken, T., Meixner, F. X., and Trebs, I.: Measurements of nitrogen oxides and ozone fluxes by eddy covariance at a meadow: evidence for an internal leaf resistance to NO2, Biogeosciences, 10, 5997-6017, 2013.

Page 12, Lines 22-25: Are the authors talking about the decreasing instrument footprint size at lower levels of the canopy? I think their logic needs to be spelled out a little more.

RESPONSE
Yes, the reviewer is right.
A possible explanation of these differences could lie in the different footprints of the eddy covariance measurements. The footprints of the measurements at 41 m, 32 m and 24 m were all falling inside the surface of the upper forest crown, even though 24 m level was just at top-canopy edge. The size of the footprint areas obviously decreased at decreasing measuring heights. However, in absence of any source or sink of the considered scalar, the horizontal homogeneity of the studied ecosystem ensures the validity of the constant flux hypothesis and thus the measurements referred to different footprints should be the same, i.e. fluxes with larger footprints (measurements at 41 m and 32 m) should be comparable to those with smaller footprints (measurements at 24 m).
The above sentences have been added in the discussion section to improve the explanation on the possible role of the horizontal homogeneity and different footprints.

Page 13, Line 12: The authors should be careful as to whether they refer to time as HH.MM or HH:MM, here and elsewhere

RESPONSE
Ok, thanks, corrected in the text. We have chosen the HH:MM notation.

Page 13, Lines 4-21: I find the discussion of the sensible heat fluxes interesting, but tangential. It would be helpful to the reader if the authors did not digress.

RESPONSE
Ok, following the reviewer's suggestion we have decided to remove this part of the discussion. As a consequence, also the Figure 12 was removed because it was meant to support this removed part.

Page 13, Lines 27-34 & Page 14, Lines 1-7: This text should be one paragraph, not three. Also, I would avoid using the word "fact"

RESPONSE
Ok, thank you, the text has been corrected accordingly to the reviewer's suggestions.

Page 14: Lines 1-3: I am not sure I am following this description well. It would be helpful if the authors more clearly spelled out their calculation. Perhaps pointing the readers to compare the grey dashed line and the red line would be helpful for readers.

RESPONSE
Thanks for this suggestion. This analysis is based on the hypothesis that the ozone fluxes measured at 24 m were greater because in the upper canopy (around 24 m) a chemical reaction between O3 and NO took place.
So, supposing a stoichiometric reaction between NO and O3 at the top of the canopy, by subtracting to the 24m O3 fluxes an amount of ozone equal to the NO converging at the top of canopy every half-hour, the part of the O3 flux not caused by this chemical sink is obtained. This is shown in the Figure 13 (now Figure 10) where the measured O3 flux at 24 m is represented as a green line and the resulting part of the O3 flux at 24 m not due to the NO sink is reported as a dark grey dashed line, being the NO fluxes converging from above and below canopy represented by the black and purple lines respectively.
The good agreement between the ozone fluxes at 32 m (Figure 13, red line) and the part of the O3 flux at 24 m not due to the NO sink (Figure 13, dark grey dashed line) suggests that the enhancement of the O3 fluxes observed at 24 m was related to the interactions of O3 with NO at the top canopy level.
We have modified the text following the reviewer's suggestions and indicated the correspondence between the subtracted quantities and the lines in the graph of Figure 13 (now Figure 10)

Page 14, Line 4: instead of "to this ozone sink", will the authors say something like "to

the observed ozone flux”?

RESPONSE
Yes, the referee is right, we have modified the text accordingly to the suggestion

Page 14, Lines 4-5: By “the contribution of the NO deposited from the atmosphere above”, are the authors talking about the contribution of NO transported into the forest to the observed ozone fluxes?

RESPONSE
Yes, we meant the deposition of NO transported into the forest from the atmosphere above, as measured at the 32 m level. The text has been changed accordingly.

Page 14, Line 6: What is the “top canopy enhancement of the ozone sink”?

RESPONSE
In this case we meant the fluxes at 24 m which were greater than the fluxes at the higher levels. Thanks for this remark, the text has been corrected to clarify the meaning of this sentence.

Page 14, Line 8: The “of that” is unnecessary

RESPONSE
Ok, thanks. Corrected in the text

Page 14, Lines 8-25: This should be one paragraph, not three

RESPONSE
Ok, thanks. Corrected in the text.

Page 14, Lines 33-34: Please clarify the last calculation - "the residual of the difference of ozone deposition at 5 m and the NO emitted from soil”.

RESPONSE
Thanks for the observation, we agree with the reviewer that this sentence was not completely clear. We meant that the ozone deposition to the forest floor was calculated as the stoichiometric difference between the ozone flux at 5 m and the NO flux emitted by soil, namely the amount of ozone which is not removed by chemical reaction with NO.
The text has been modified to clarify the calculation.

Also, do the authors perform this calculation on half-hourly data or on the campaign averages for a given hour?

RESPONSE
This calculation has been performed on the campaign averages for every given hour.

Page 15, Line 3: Specify that it's ecosystem removal relative to air chemistry removal

RESPONSE
Sorry, we are not sure having completely understood this point. Maybe it was not so clear we were addressing the ozone removal by the forest crown.
Roughly speaking, a forest ecosystem = canopy + soil + trunk space air.
In this sentence we were addressing to the canopy component of the ecosystem (excluding the soil and the trunk space air). For this sake we used the term "forest canopy" and not the term "ecosystem" in the first part of the sentence. Instead, in the second part of the phrase we mentioned the term ecosystem referring to all the components.
Following these definitions, the percentage of ozone removal by the forest canopy (upper and lower canopy layers) was nearly 80% of the total amount of ozone deposition measured at 32m. The remaining part (20%) was removed by understorey and soil surface (2%) and air chemistry (18%, reactions with NO).
We have slightly modified line 3 and specified the above percentages in the following text.

Page 15, Line 5: Isn't the depression in the ozone deposition to the dominated crown?

RESPONSE
The reviewer is right, and a midday depression in the ozone deposition can be appreciated also in the dominated crown (lower canopy layer).
However, since this observation is not necessary to the overall discussion we have decided to remove it.

Page 15, Line 14: Specify NO depletion of ozone

RESPONSE
OK, thanks. Corrected.

Page 15, Line 17: What do the authors mean by "stirred"?

RESPONSE
We meant that inside the chambers the air was perfectly mixed during the measurements.

Page 15, Line 19: Why is only a small amount of uptake of NO possible? What are the references for this?

RESPONSE
It is likely that NO2 is deposited but not NO, both due to the fact that the reaction time of NO with O3 is fast and that NO2 has a much higher solubility than NO. Teklemariam et al. (2006) reported that the concentration of NO in the leaf is always larger than 99% of that outside which means no deposition. They report that NO2 is more soluble in water and exhibits a faster hydrolysis rate compared to NO (Henry's law coefficient of NO2 is an order of magnitude higher than that of NO). In Stella et al., for instance, NO2 deposition was detected but no NO deposition was reported.

- Teklemariam, T. A. and Sparks, J. P.: Leaf fluxes of NO and NO2 in four herbaceous plant species: The role of ascorbic acid, Atmos. Environ., 40, 2235-2244, 2006.
- Stella, P., Kortner, M., Ammann, C., Foken, T., Meixner, F. X., and Trebs, I.: Measurements of nitrogen oxides and ozone fluxes by eddy covariance at a meadow: evidence for an internal leaf resistance to NO2, Biogeosciences, 10, 5997-6017, 2013.

The sentence has been slightly modified and these two references have been added.

Page 15, Line 20: What do the authors' findings mean for the canopy reduction factor for NOx?

RESPONSE
The canopy reduction factor (CRF) for NOx is the fraction of NO emitted by the soil that does not exit the plant canopy but is converted to NO2 and then taken up as NO2. Since we argue that all soil NO is transformed to NO2, we would need to estimate the NO2 deposition to the canopy and the NO2 flux above the canopy to correctly estimate that factor. In the absence of NO2 flux measurements, this can only be done by interpretation via a numerical model, which will be the focus of a follow-up paper.

Page 15, Line 27: Which studies are these values comparable to?

RESPONSE
The average maximum of the ozone fluxes was between 10 and 15 nmol m-2 s-1 like, for instance, in Gerosa et.al (2005, 2009a), in Fares et al. (2010) or in Finco et al. (2017). These references have been added to the text, even if usually we do not insert references in the Conclusions.

- Gerosa, G., Vitale, M., Finco, A., Manes, F., Ballarin Denti, A., and Cieslik, S.,: Ozone uptake by an evergreen Mediterranean forest (Quercus ilex) in Italy. Part I: micrometeorological flux measurements and flux partitioning, Atmos. Environ. 39, 3255-3266, 2005.
- Gerosa, G., Finco, A.,Mereu, S., Vitale, M., Manes, F., BallarinDenti, A.: Comparison of seasonal variations of ozone exposure and fluxes in a Mediterranean Holm oak forest between the exceptionally dry 2003 and the following year, Environ. Pollut. 157, 1737–1744, 2009a.
- Fares, S., F. Savi, A., Muller, J.B.A., Matteucci, G., Paoletti, E.: Simultaneous measurements of above and below canopy ozone fluxes help partitioning ozone deposition between its various sinks in a Mediterranean Oak Forest, Agr. Forest Meteorol. 198–199, 181–191, 2014.
- Finco, A., Marzuoli, R., Chiesa, M., & Gerosa, G. (2017). Ozone risk assessment for an Alpine larch forest in two vegetative seasons with different approaches: comparison of POD1 and AOT40. Environmental Science and Pollution Research, 24(34), 26238-26248.

General comments on figures and tables.
Table 1: What does the text in the parentheses mean?

RESPONSE
The text in the parentheses reports the manufacturer of the instrument and the country where it was made.
Pease note that in the revised version of the manuscript Table 1 was moved in the Supplementary material (Table S1).

What do these instruments measure?

RESPONSE
Apart from the first two columns (anemometers and ozone analysers, for which it should be clear what they measure), in the brackets after each instrument/probe we have added a synthetic information on which parameter they measure and an explanation of it was given in the caption.

What height is the nearby mast?

RESPONSE
The height of the nearby mast was 5 m as specified in the paragraph 2.3, however, we have added this information also in the caption which has been completely rewritten.

Figure 5: What are the distributions over?
All the days in the measurement campaign?

RESPONSE

Every average diel course is referred to the second part of the campaign, when, after the intercomparison period, the fast ozone analyzers were deployed at 32 m, 24 m and 16 m.
A sentence was added in the paragraph 2.7 to clarify that the averages are referred to the "profile" period.
In each diel course each point represents the average of all the measurements made in different days at the same half-hour. For instance, the point at 13:30 represents the average of all the measurements made in different days between 13:00 and 13:30.

What is z? What is L?

RESPONSE
z is the measuring height and L is the Obukhov length, this information has been added in the caption

What are the values of z/L used for each class?

RESPONSE
We used the following classification taken from Gerosa et al. 2017, which is an adaptation of the Table from Foken et al. (2008):

Stability classes	***L value***	**z/L for z=41 m**
Very stable	0 < *L* <=10	0 < *L* <=4.1
Stable	10 < *L* <=100'000	4.1 < *L* <=0.00041
Neutral	Abs(L) > 100'000	Abs(L) > 0.00041
Unstable	-100'000 <= *L* < -100	-0.00041 <= *L* < -0.41
Very unstable	-100 <= *L* < 0	-0.41 <= *L* < 0

This information has been added in the caption of Figure 4.

References:
- Gerosa G., Marzuoli R., Monteleone B., Chiesa M., Finco A., 2017. Vertical ozone gradients above forests. Comparison of different calculation options with direct ozone measurements above a mature forest and consequences for ozone risk assessment. FORESTS 8, 337.
- Foken, T.: Micrometeorology, Springer-Verlag, Berlin Heidelberg, Germany, 2008.

The height label is missing for plot e).

RESPONSE
Ok, thanks, the information has been added.

Figure 10d: Please indicate the green line is rainfall.

RESPONSE
Ok, added in the caption, thanks.

Also, is rainfall in the context of NO fluxes discussed?

RESPONSE
Yes, it is. The role of rainfalls and rain events in enhancing the NO soil emission was discussed in the context of the NO fluxes.

Are all figures averages over the entire campaign?
If so, please specify in the figure captions.

RESPONSE
Not exactly, all the average diel courses are referred to the second part of the campaign when the fast ozone analyzers were deployed along the tower at different heights. A sentence was added in section 2.7 to specify this information without repeating it in every caption.

Anonymous Referee #2

Interactive comment on “Characterisation of ozone deposition to a mixed oak-hornbeam forest. Flux measurements at 5 levels above and inside the canopy and their interactions with nitric oxide” by Angelo Finco et al.
Anonymous Referee #2
Received and published: 15 June 2018

Close examinations of the pathways controlling ozone deposition in the forest setting are important for understanding the oxidation chemistry in the forest, secondary organic aerosol formation, the boundary layer ozone budget, and, as mentioned in this manuscript, the impact of ozone on plant health. In this manuscript, the authors presented the ozone and NOx concentration gradient and flux data, and the associated meteorological parameters from the ECLAIRE campaign in 2012, as well as the initial data analyses, which would lead to a subsequent model analysis, as implied in the Introduction, that may generate model predictions of intra-canopy dynamics involving ozone reactions with NOx and VOC. As a result of the month-long summertime observations of ozone and NOx at multiple height within and above a forest canopy at the most polluted area in Europe, this dataset provides a valuable case study of ozone dynamics and related canopy scale processes, and biosphere-atmosphere exchange. However, as specified below, major revisions are recommended.

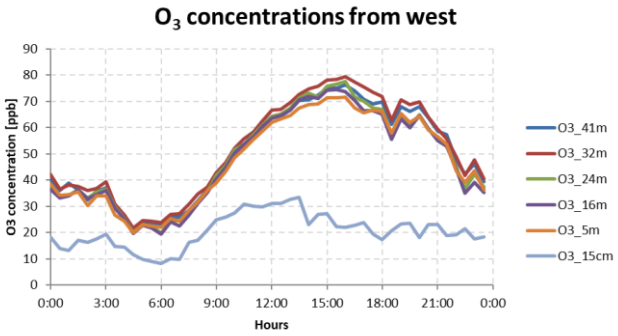
The authors performed a fairly detailed treatment of the meteorological data to obtain the ozone fluxes at the measurement heights. Results of the fluxes at multiple elevations throughout the canopy provide information on the sources and sinks, thus the processes that affect the trace gas species in the forest. Given the data being from a month-long campaign under different meteorological conditions, the analysis could be strengthened and the conclusions may be better supported and possibly modified with the following additional considerations.

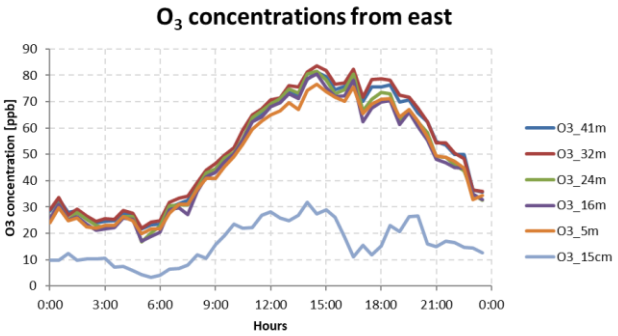
RESPONSE
We thank the reviewer for the careful revision and his/her suggestions to improve this manuscript.

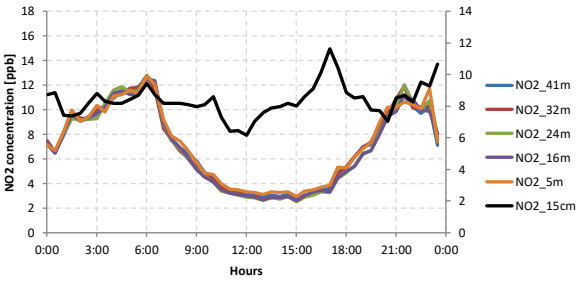
1) Above canopy influences from air transported to the surface layer above the canopy.
According to the data, about 50% of the wind is from either east or west with the rest from other directions. Are there any differences in the quantities measured that coincide with the wind direction differences? Are the possible influence of the different amount of the pollutants (ozone and NOx) transported to the site considered?

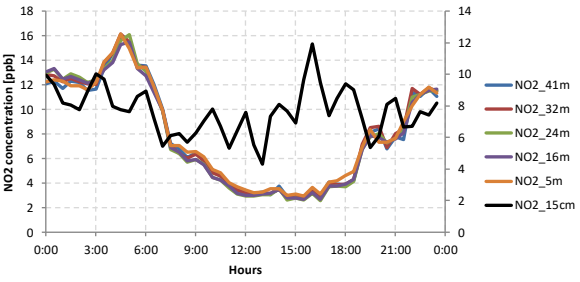
RESPONSE
Thanks for this suggestion. We have explored this possibility, but we did not find significant results that might explain, for instance, the greater ozone fluxes at 24 m. The behavior of the NOx and O3 concentrations was similar regardless of the wind provenance, so we have focused our attention on the in-canopy processes. For example, here below we report the average diel course of ozone and NOx concentrations above and below canopy when the wind was blowing from east (right graphs) or west (left graphs). Obviously there are some differences, but they are very weak and not relevant. For instance, O3 maximum was slightly higher when the wind was blowing from east, while NO was 1 ppb higher in the morning peak when the wind was blowing from west, and also the NO_2 peak was lower in the morning (-4

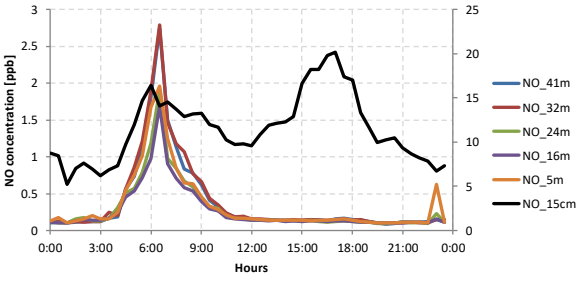
ppb). However, since the “vertical” behavior of the NOx concentrations was similar independently from the wind direction (NO concentrations had a minimum at the canopy level height while NO_2 concentrations were almost constant at all heights) we concluded that the peculiar behavior showed by the fluxes at 24 m was more linked to processes happening in the forest rather than to advection of pollutants from different directions.

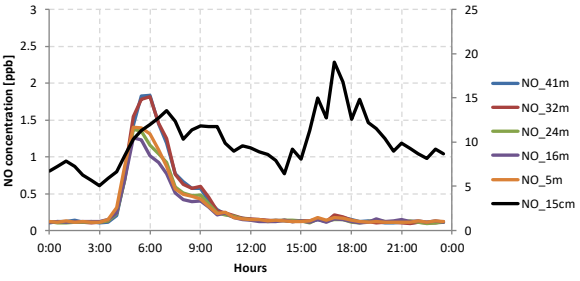












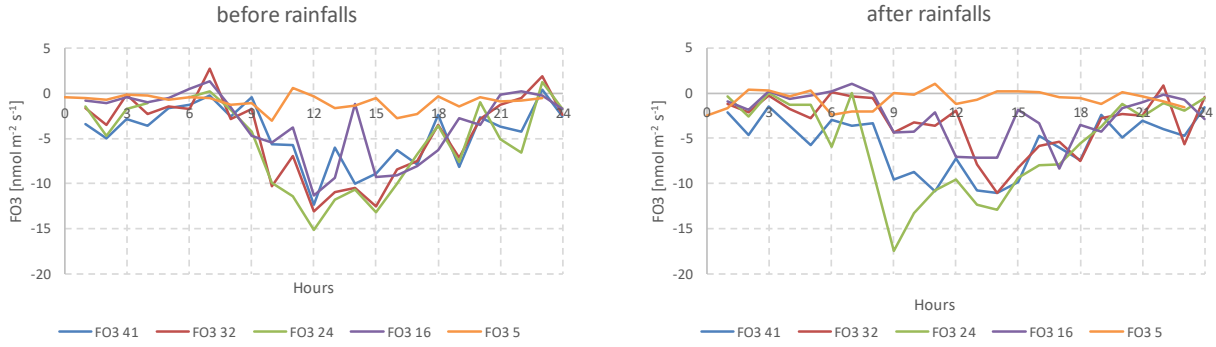
*note: right x-axis is referred to the NOx measurements at soil level (15 cm)

2) The fluxes under the stable/unstable conditions within the canopy. If I understand it correctly, in Figure 4, y-axis is the percent of the measurement time. If so, there were times the entire canopy was either stable or unstable throughout a 24-hour period. It would be informative to separately analyze the data under these two regimes, especially when considering the within the canopy stability in the context of the enhanced ozone deposition flux at 24 m.

RESPONSE
We are not sure we have understood the reviewer's point.
Figure 4 report the percentage of the times that at a given half-hour there was a stable/unstable atmosphere at a certain level during the measuring campaign.
That being said, from the morning to the late afternoon at 41 m, 32 m and 24 m there were nearly always unstable/very unstable conditions. At 41 m only 3.3% of the measurements were characterized by stable conditions between 8:00 and 18:00 (Figure 4a) and this percentage was only 4.1% at 32 m (Figure 4b) and 19.4% at 24 m in the same hours.
Stable conditions in the central hours of the day were more frequently observed only for the lower measuring points (16 m and 5 m), so in our opinion there were too few data to significantly compare for contrasting conditions of the atmospheric stability on the entire canopy and above, and to verify whether this influenced the ozone deposition flux at 24 m, sorry.

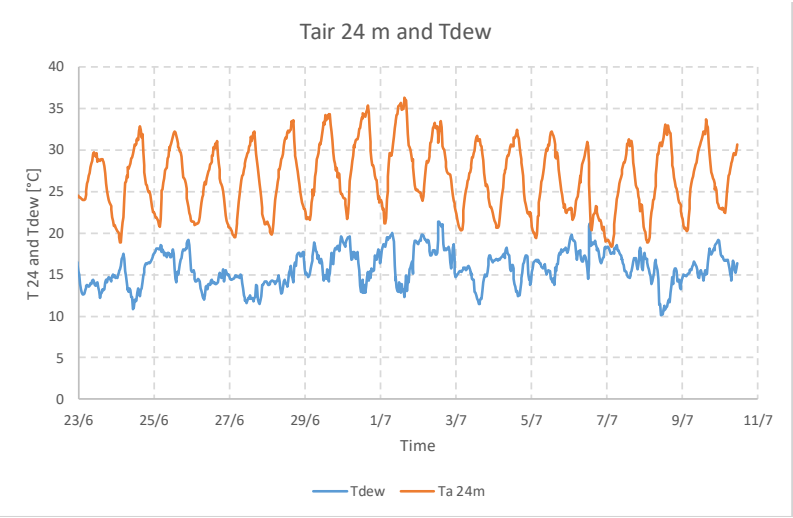
3) Dry and wet conditions. Apparently after the rainfall on July 6, the NO/NO2 fluxes increased dramatically. How did these changes affect the ozone deposition flux?

RESPONSE
Thanks for the comment and the suggestion. The peak of the ozone fluxes at 24 m increased by 70% after the rainfall in the morning hours, as reported in the Figure below, where the average diel course of the ozone fluxes of 3 days before rainfalls (from 4th to 6th July) and 3 days after (from 8th to 10th) are shown.
This is consistent with the hypothesis that the flux enhancement at 24 m is linked to the NO flux from the forest floor. Instead, the ozone fluxes at the other levels remained more or less unchanged, with the only exception of the flux at 32 m which was never greater than 5 nmol m^{-2} s^{-1} as absolute value from 9.00 to 12.00.
However, since only one rainfall event occurred during the field campaign, we have preferred not to include this analysis in the manuscript because of the questionable representativeness of our data with respect to this condition.



In addition, it is known surface wetness affect ozone deposition as well. It would be instructive if the dry/wet conditions can be contrasted in the data analysis.

RESPONSE
We have also considered the possible influence of surface wetness on the O3 flux deposition, but we have excluded a significant role of water/dew because the canopy was almost always dry as witnessed by the dew temperature which remained well below the air temperature, as it can be observed in the figure reported below.
Moreover, the relative humidity at canopy level (24 m) was almost never above 90% (less than 1% of the data), thus excluding the possibility of dew formation on leaves and branches.
Also in this case we have preferred not to include this analysis in the manuscript because of the questionable representativeness of our data with respect to this condition. Moreover, we would like to avoid to enlarge excessively the paper, which has been already considered too long.



The data analysis results, as stated in the manuscript now, would be more convincing if the above-mentioned aspects were considered. One of the main conclusions in the manuscript is that the enhanced ozone flux at the canopy top is due to the combined NO fluxes from above the canopy and the soil emission, thus an enhanced chemical sink of ozone. However, there are other factors such as stomatal uptake and photochemical reactions involving NOx, O3 and BVOCs, both processes obviously associated with sunrise, that affect the ozone flux. The net result could well be an increased flux. Are there data available from this campaign that would help the authors address these possibilities?

RESPONSE
We agree with the reviewer.
However, BVOC dynamics during this field campaign was already described in Schallart et al. (2016) and Acton et al. (2016). Preliminary results from Nemitz et al. (2013) showed a nearly negligible role of the BVOCs on the O3 deposition fluxes, since less than 3% of the deposited ozone was destroyed by reaction with BVOCs. As a consequence, we can exclude a significant role of BVOC emissions and have not included this topic in this manuscript.
Moreover, the role of the BVOCs and their interactions with ozone will be dealt in detail in another future paper more focused on the chemistry from a modelistic point of view.
Stomatal ozone flux partition was not presented in the paper because evapotranspiration fluxes were available only at the topmost level of the tower (41 m). Since we do not have evapotranspiration

measurements at 32 m, 24 m and 16 m we could not evaluate the stomatal contribution to the ozone fluxes at the different canopy layers with the usual stomatal flux partition procedure. Instead, we preferred to focus our manuscript on the attribution of the total ozone deposition to the different canopy layers. In our humble opinion, including a stomatal flux partition referred to the whole canopy along with the attribution of the total ozone fluxes to the different canopy layers (upper, lower canopy layers, understorey, forest floor), could have been confusing for the reader.
Moreover, the inclusion of a new section on stomatal fluxes would have made the manuscript longer, particularly because a long description of the partition methodology and calculation should have been added to the Material and methods.
However, more than one new papers dealing with the ozone stomatal fluxes at the same site are in preparation and will cover longer measuring periods, namely annual and pluriannual duration.

References:
- Schallhart, S., Rantala, P., Nemitz, E., Taipale, D., Tillmann, R., Mentel, T. F., Loubet, B., Gerosa, G., Finco, A., Rinne, J., and Ruuskanen, T. M.: Characterization of total ecosystem-scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest, Atmospheric Chemistry and Physics 16, 7171-7194, 2016.
- Nemitz E, Langford B., Di Marco C F, Coyle M., Braban C., Twigg, Gerosa G, Finco A , Valach A, Acton J , B. Loubet 4 , S. Schallart , R. Gasche , E. Diaz-Pines , S. Fares , J. Westerlund , Å. Hallquist , C. Gritsch , S. Zechmeister-Boltenstern and M.A. Sutton. Quantifying Chemical Interactions in a Forest Canopy – First Results from the ÉCLAIRE Campaign at Bosco Fontana, Po Valley, 2013.
- Acton, W. J. F., Schallhart, S., Langford, B., Valach, A., Rantala, P., Fares, S., Carriero, G., Tillmann, R., Tomlinson, S. J., Dragosits, U., Gianelle, D., Hewitt, C. N., and Nemitz, E.: Canopyscale flux measurements and bottom-up emission estimates of volatile organic compounds from a mixed oak and hornbeam forest in northern Italy, Atmos. Chem. Phys., 16, 7149–7170, 2016.

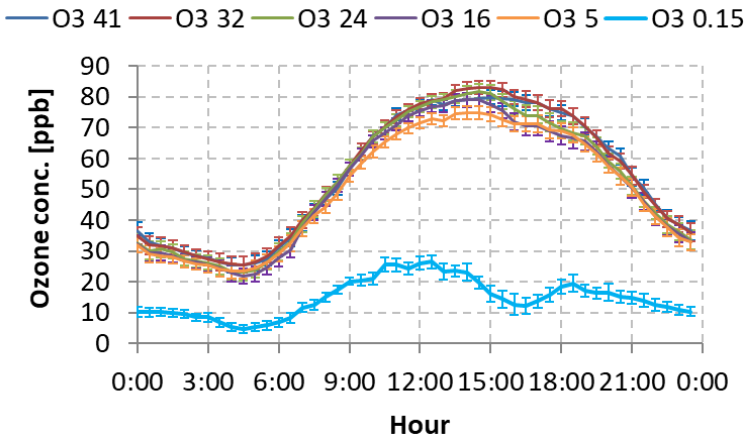
It would help the readers to better understand and assess the data if the authors could present the time series plots, including error bars when appropriate, of the measurement results.

RESPONSE
Sorry, we are not sure we have understood the reviewer's point.
We have already shown the time series plots of the most important variables like the ozone concentrations and fluxes, the NO and NO_2 fluxes, LE fluxes, air temperature at different levels and rain. However, the reviewer #1 requested to move many figures to the supplementary material because of the high number of Figures presented in the manuscript. Following his suggestion, we have preferred to move the above-mentioned Figures based on raw time-series to the supplementary material.
Regarding the error bars, maybe we misunderstood, but they do not apply to the raw time-series because every point there represents one measurement only.
Instead, for the diel courses where each point represents the average of many measurements, please refer to the following answer.

It is also important to show the standard deviation (if the mean values are used) or the interquartile range (if median values are used) in the average diurnal course plots including Figure 6.

RESPONSE

We have already posted two comments in the discussion about this referee's remark. In our humble opinion we think that in many figures of our manuscript, because of the presence of five lines (or more) in the figures, the use of error bars could be misleading for the reader because error bars are overlapping and could hide the diurnal course of the plotted parameters.
For example, please refer to the following graph reporting the diel course of [O3] at six levels. The error bars hide the course of the ozone concentrations at the different heights when the lines are close. For example, it is nearly impossible to understand the course of the ozone concentrations at 41 m.



However, we agree with the reviewer that the explication of the uncertainties of the means is of primary importance. So, we would suggest to report the range of the variation of the standard error for each curve (from the minimum to the maximum values observed in the 24h) in the text of the figure captions, without losing statistical robustness and the possibility to clearly appreciate the diel courses.
The following Figure reports and example of how we cope with this issue throughout the manuscript.

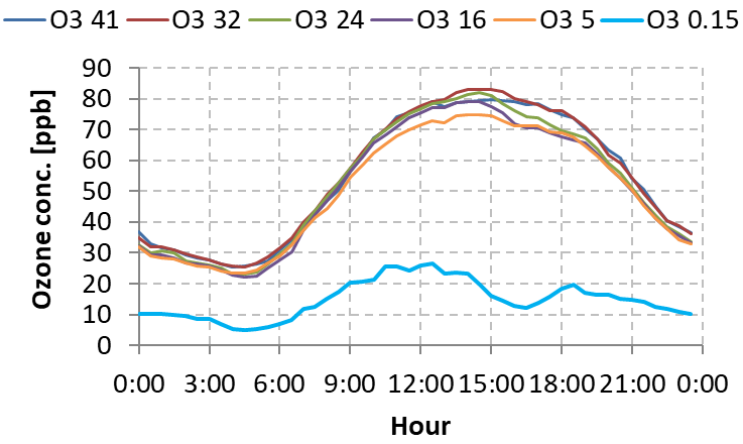


Figure 2 - Average diel courses of ozone concentrations at the six levels (41 m, 32 m, 24 m, 16 m, 5 m and 0.15 m). The maximum and the minimum standard error of the half-hourly means were respectively 3.0 and 1.7 ppb for 41 m, 3.0 and 1.8 ppb for 32 m, 3.4 and 1.9 ppb for 24 m, 3.4 and 1.8 ppb for 16 m, 2.9 and 1.7 ppb for 5 m, and 3.4 and 1.0 ppb for 0.15 m

In Table 1 where it is not indicated or obvious, please list the measurements next to the instruments listed, for example, HMP45 (temperature, humidity).

RESPONSE
Ok, thank you, Table 1 has been rearranged and now include all the requested data.
Pease note that in the revised version of the manuscript Table 1 is now available in the Supplementary material (Table S1).

I may have missed the point in Figure 8 but cannot readily see from which height are the plotted ozone mixing ratio results.

RESPONSE
Ok, the reviewer is right. We have added the measuring height of the ozone concentration data in the caption.
Pease note that in the revised version of the manuscript Figure 8a is now Figure 7 and Figure 8b has been moved to the supplementary material (Figure S3).

Also if possible, please unify the tick location and tick labels in plots 8a and 8b.

RESPONSE
Ok, thanks for the suggestion. Figure 8b has been moved to the supplementary material (Figure S3) and the time resolution of the x-axis was set like in Figure 8a.

I am not sure why the analysis of the enhanced O3 flux at 24 m is only for the morning (9:00-12:00). From the data, the enhancement, although decreasing after mid-day, lasts through 15:00. If, because of the scatter of the data, the fluxes were basically the same from 41 to 24 meters in the early afternoon, it needs to be shown and stated more clearly.

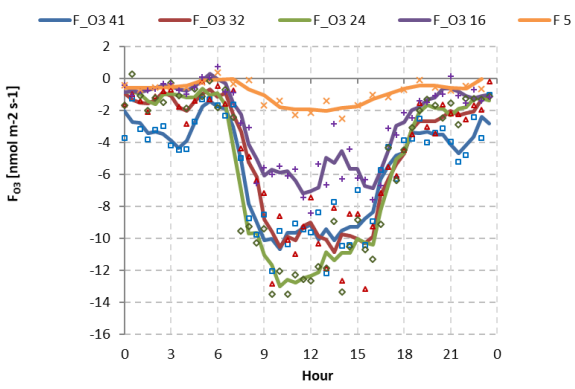
RESPONSE

The reviewer is right and we would like to thank him for this observation because he allowed us to realize that we made a mistake in assembling the final version of the manuscript.

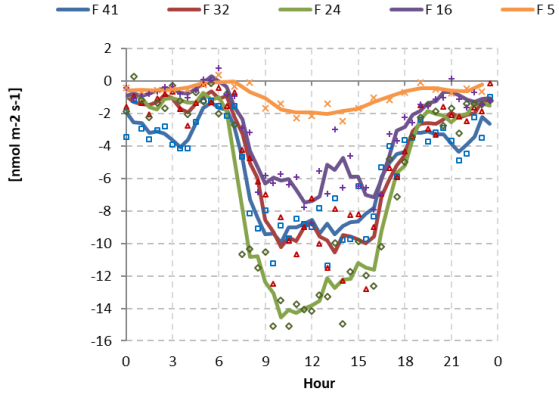
Unfortunately, a previous version of Figure 9 (now Figure 8) remained in the submitted document. This previous version reported the ozone fluxes calculated by applying an average Frequency Loss Correction (FLC) factor (one for each level) coming from a preliminary elaboration made with the ogive methodology (OG).

Instead, in the correct version of Figure 9, that we report below (9a, left graph), the fluxes were corrected for the high frequency flux losses by applying, half-hour by half-hour (for each level), the Experimental Transfer Function methodology (ETF) described by Aubinet et al. (2000, 2001, 2012).

9a – Correct version of Figure 9



9b – Previous (wrong) version of Figure 9



We abandoned the FLC initially calculated with the OG methodology because we realized that the ogive of the 24 m data (and only the 24 m ogive, not the others), beside showing the highest correction factor presented a relatively strange shape: the ozone ogive was not a monotonic increasing function but showed a relative maximum around 0.1 Hz and a following inflection between 0.1 and 1 Hz, as it can be observed in the following Figure. This feature could have resulted in an incorrect evaluation of the FLC factor.

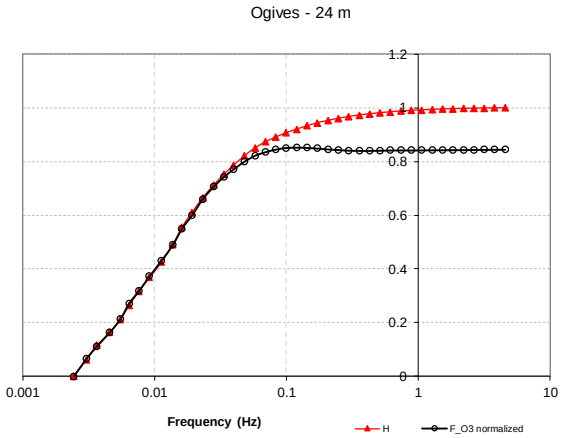


Figure - Normalized ogives of ozone and sensible heat fluxes for the measurements at 24 m.

The ETF methodology on the contrary, is less affected by subjective interpretations as it is more easily automatable and applicable to each half-hour sample. For this reason, it was preferred to the OG methodology.
The application of the ETF correction resulted in a lesser pronounced overestimation of the 24 m ozone fluxes than with the OG methodology (Figure 9a and 9b), but the ozone fluxes of the other levels resulted relatively unaffected by this change of methodology, as reported in the following Table (where the overall average of the FLC factors after the application of the two methodologies are indicated).

	FLC applied	
level	Figure 9a (ETF corrected)*	Figure 9b (OG corrected)**
41 m	1.08239	1.01012
32 m	1.00912	0.98030
24 m	1.06197	1.18723
16 m	1.02083	1.06385
5 m	1.03198	1.03561

*The reported values for each level are the average of the FLC values calculated for each single half-hourly sample (i.e. each sample had its own correction factor).
** The reported values for each level are the single correction factors applied to all the half-hourly samples (i.e. the same factor was applied to all the half-hourly samples).

In order to demonstrate that it was just an oversight and a careless mistake we invite the reviewer to draw his attention on Figure 13 of the paper (now Figure 10) which was already based on the ozone fluxes ETF corrected.
By comparing the 24 m fluxes in Figure 13 with the 24 m fluxes of the Figure 9a (correct version) the reviewer can realize that the O3 fluxes at 24 m are the same (green lines), regardless of the different

averaging time (the time scale of the Figure 9a is half an hour - the time scale of eddy covariance fluxes - while the time scale of Figure 13 is one-hour - the time scale of the NO soil fluxes - and thus the eddy data were averaged on an hourly base).
We add here the Figure 13 of the manuscript for comparative purposes. As the reviewer can see, the peak values of the green lines in these two figures are the same (-13 nmol m-2 s-1) because Figure 13 was indeed made using the data of the 24m fluxes calculated with the ETF methodology.

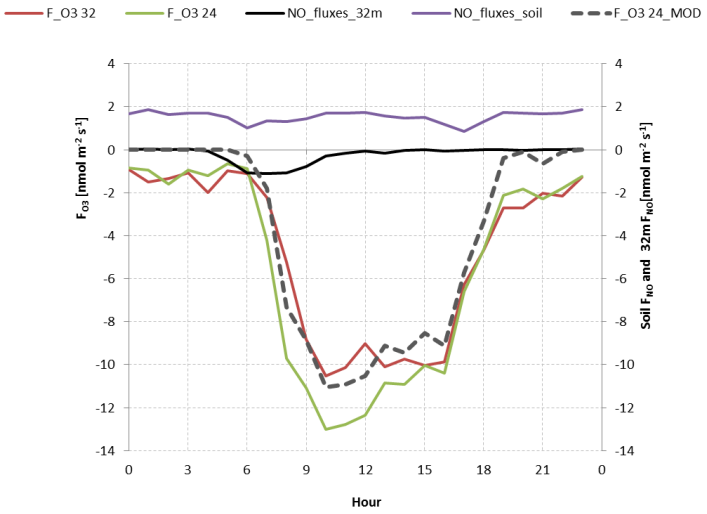


Figure 13 Average diel course of ozone fluxes at 32 m (red line), ozone fluxes at 24 m (green line), NO fluxes at 32 m (black line) soil NO fluxes (purple line) and modified ozone fluxes at 24 m (dashed grey line). This latter takes into account the role of the NO sink.

Now, considering the correct version of Figure 9 (Figure 9a), the reviewer can understand what we meant in the following sentence of the discussion:
"…Fluxes of ozone were similar at these two above-canopy heights, within the uncertainty of the measurement, but unlike for the fluxes of heat and momentum, measurements at 24 m showed a significantly larger ozone deposition than the two upper levels (32 m and 41 m) at certain times of the day. In the morning (9:00 to 12:00) 24 m ozone fluxes were on average nearly 3 nmol m-2 s-1 larger than above the canopy (Figure 9), while they were nearly equal on average from 13:00 to 18:00 (fluxes at 24 m were only 0.5 nmol m-2 s-1 larger)…"
Moreover, we would like to underline that the core of the discussion, i.e. the influence of the NO fluxes on 24 m fluxes, and the subsequent considerations were based on the analysis of the ETF correct data.
We thoroughly apologize for that.

References

- Aubinet, M., Grelle, A., Ibrom, A., Rannik, U., Moncrieff, J., Foken, T., Kowalski, A. S., Martin, P. H., Berbigier, P., Bernhofer, C., Clement, R., Elbers, J., Granier, A., Grunwald, T., Morgen- ¨ stern, K., Pilegaard, K., Rebmann, C., Snijders, W., Valentini, R., and Vesala, T.: Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology, Adv. Ecol. Res., 30, 113–175, 2000.
- Aubinet M, Chermanne B, Vandenhaute M, Longdoz B, Yernaux M, Laitat E (2001) Long term carbon dioxide exchange above a mixed forest in the Belgian Ardennes. Agric For Meteorol

108:293–315
- Aubinet M., Vesala T., Papale D. (eds): Eddy Covariance. A practical guide to measurement and data analysis. Springer, 438 pp, 2012.

The authors used Figure 12 to explain the effect of the thermal bubbles and why the greater sensible heat flux at 32 m than at 41 m. However, the data shown are from 13:00 on July 5th. It is not clear whether this is a special case or an example of a typical situation.

RESPONSE
Figure 12 was just an example of a typical situation which was observed quite often in the temperature raw data.
However, we agreed with the reviewer #1 that, even though interesting, this part of the discussion should be removed in order to avoid excessive digressions from the main topic (ozone and NOx interactions). As a consequence, Figure 12 and the discussion on the sensible heat fluxes at 32 and 41 m have been removed from the manuscript.

The manuscript could use some help with the English language usage and organization.
For example, Page 2, line 4, “Prompted by its phytotoxicity” –> Because of the phytotoxicity of ozone, . .

RESPONSE
Ok, thanks. This sentence has been rephrased.

Page 2, line 6, “. . ., 2013), thanks also to the. . ..” may be changed to, for example: . . ., 2013). Eddy covariance measurements were made possible thanks to the . . .

RESPONSE
Ok, thanks. Corrected in the text.

Page 2, line 16 – 18 and line 26-28, field campaign information was repeatedly given.

RESPONSE
Ok, thanks. The second sentence has been removed.
The Introduction has been improved and expanded according to the suggestions of the reviewer #1.

Characterisation of ozone deposition to a mixed oak-hornbeam forest. Flux measurements at 5 levels above and inside the canopy and their interactions with nitric oxide

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Abstract

A one-month field campaign of ozone flux measurements along a 5-levels vertical profile above, inside and below the canopy, was run in a broadleaved mature forest of the Po Valley, Northern Italy. The study aimed at characterizing ozone flux dynamics and their interactions with NO_x fluxes from the forest soil and the atmosphere above the canopy. The ozone fluxes measured at the levels above the canopy were in good agreement among them, thus confirming the validity of the constant flux hypothesis, while below canopy the ozone fluxes were lower than above. However, at the upper canopy edge (24 m) the ozone fluxes were surprisingly higher than above in the morning hours. This was attributed to an ozone sink with NO both emitted from soil and deposited from the atmosphere converging at the top of the canopy. Moreover, this mechanism was eased by the morning coupling between the forest and the atmosphere, while in the afternoon the 24 m fluxes became similar to those of the levels above as a consequence of the in-canopy stratification. Nearly 80% of the ozone deposited to the forest ecosystem was removed by the canopy: 33.3% by the upper canopy layer and 46.3% by the lower canopy layer. Only a minor part of ozone was removed by the understorey vegetation and the soil surface (2%), while the remaining 18.2% was consumed by chemical reaction with soil emitted NO. The collected data could be used to improve the ozone risk assessment for forests and to test the predicting capacity of ozone deposition models, with particular regard to the intra-canopy dynamics of ozone and NO_x.

1 Introduction

Ozone (O_3) had been widely documented as one of the most dangerous pollutant for plants (Wittig et al., 2009; Matyssek et al., 2012; Gerosa et al., 2015; Marzuoli et al., 2018), The deposition of O_3 on forest ecosystems has been extensively studied over the last 20 years with eddy covariance field campaigns (Padro, 1996; Cieslik, 1998; Lamaud et al., 2002; Mikkelsen et al., 2004; Gerosa et al., 2005, 2009a, 2009b; Launianen et al., 2013) which were made possible thanks also to the development of fast ozone analysers, functional for such measurements.

Measurements carried out in the 1990´s were usually short-term field campaigns, while more recently campaigns had extended the observation periods and therefore led to a better understanding of the processes controlling ozone deposition (Mikkelsen et al., 2004; Gerosa et al., 2005; Fowler et al., 2009; Rannik et al., 2012; Zona et al., 2014; Fares et al., 2010, 2012, 2014; Clifton et al., 2016, Finco et al., 2017).

These studies highlighted that an important deposition pathway is represented by the ozone uptake by trees, through leaves stomata. The ozone fraction entering the stomata strongly depends on the environmental and physiological factors which drive stomata opening (Jarvis, 1976; Emberson et al., 2000), starting from the soil water availability which is positively correlated to the stomatal ozone flux (Gerosa et al., 2009a; Büker et al., 2012)..

The other ozone deposition pathways are usually grouped as the non-stomatal deposition. The non-stomatal deposition includes many processes which have still to be understood in deep, such as: the thermal decomposition on dry surfaces (Cape, 2009), the deposition on wet surfaces (Fuentes et al., 1992; Altimir et al., 2004, 2006; Gerosa et al., 2009b), reactions stimulated by light (Coe et al., 1995; Fowler et al., 2001), chemical reactions with NO (Dorsey et al., 2004; Rummel et al., 2007; Pilegaard, 2001; Gerosa et al., 2009b), chemical reactions with biogenic, volatile organic compounds (BVOC) (Fares et al., 2010; Goldstein et al., 2004) or the deposition on soil (Stella et al., 2011).

In addition, the ozone deposition below the forest canopy is still unclear. Actually, very few studies have directly measured ozone fluxes below the canopy of the forest, for example, Launianen et al., (2013) and Fares et al., (2014) used these measurements to assess different deposition pathways and to validate ozone deposition models, while Dorsey et al., (2004) focused on the role of soil NO emission in the ozone flux dynamics.

There are still very few studies which reported ozone flux measurements at more than two levels along a vertical profile above and within a forest canopy (Dorsey et al., 2004; Foken et al., 2012), and none of these were made on a mature broadleaf forest according to our knowledge. On the contrary, measurements of vertical gradients of ozone concentration have already been quite investigated (Fontan et al. 1992; Keronen et al. 2003; Utiyama et al. 2003; Gerosa et al. 2005). However, from the latter studies a small to high variability of the ozone concentration inside the canopy emerged and there are still uncertainties on the drivers of these gradients. The major aims of this study were (i) to contribute to the understanding of the diel dynamics of ozone fluxes and ozone concentration gradients at five levels above and within a mature broadleaved forest canopy, (ii) to assess the amount of ozone deposited on the different forest layers (upper canopy, lower canopy, understorey, forest floor), (iii) to evaluate the role of the NO_x exchange on the ozone deposition, both at top canopy and at soil level. In addition, ozone

flux measurements at 5 levels allowed to test the validity of the vertical constant flux hypothesis for this gas in a forest ecosystem.

This work reports data from a joint field campaign which took place in 2012 in the framework of the European FP7 project ECLAIRE ("Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems") in the Po Valley (Italy), one of the most polluted areas in Europe. This campaign also included simultaneous flux measurements of volatile organic compounds, particles and ammonia which are reported elsewhere (Acton et al., 2016; Schallhart et al., 2016). The detailed dataset of this campaign will also allow future tests on the capacity of existing deposition models to correctly predict ozone deposition dynamics on forest ecosystems, and particularly intra-canopy dynamics involving ozone reactions with NO_x.

2 Material and methods

2.1 Site characteristics

Measurements were performed at the Bosco Fontana reserve (45°12'02"N, 10°44'44"E; elevation 25 m a.sl.) located in Marmirolo near Mantua, Italy. The measuring site is located just in the middle of the Po Valley, one of the most polluted areas of Europe, and it is represented by a mixed oak-hornbeam mature forest, a typical climax ecosystem for that area, (i.e. an ecosystem at its maximum stage of development). The forest forms part of a 233 ha nature reserve classified as a Site of Communitarian Importance and Special Protection Zone (IT20B0011) and it is part of the Long-Term Environmental Research (LTER) network.

The upper canopy (dominant tree layer) is composed of the higher trees such as hornbeam (*Carpinus betulus*, 40.45 % of the total surface of the reserve), oak (*Quercus robur*, 17.09 %), red oak (*Quercus rubra*, 9.65 %) and Turkey oak (*Quercus cerris*, 7.06 %) (Dalponte et al., 2007). Some species (*Acer campestre*, *Prunus avium*, *Fraxinus ornus and oxycarpa*, *Ulmus minor*, *and Alnus glutinosa* along the small streams) are present but they account for no more than 3% of the total surface.

The lower canopy (dominated tree layer) is represented by the lower trees and it is composed of hazel (*Corylus avellana*), elder (*Sambucus* spp), cornell (*Cornus mas*), hawthorn (*Crataegus oxyacantha and monogyna*) and chequers (*Sorbus torminalis*). A thick understorey mostly composed of butcher's broom (*Ruscus aculeatus*, L) is also present.

The average height of the canopy is 26 m and the average single-sided leaf area index (LAI), measured by a canopy structure meter (LAI2000), averaged 2.28 m^2 m^{-2}, with a maximum of 4.22 m^2 m^{-2}.

The soil is a Petrocalcic Palexeralf, loamy skeletal, mixed, mesic (Campanaro et al., 2007) according to the USDA classification. The soil depth is 1.5 m with petrocalcic hardened layer between 0.80 and 1 m below the ground; this layer was formed after the gradual deepening of the water table.

The climatic characteristics are typical of the Po Valley, with humid and hot summers (Longo, 2004). The mean annual temperature is 13.2°C (period 1840-1997, Bellumé et al., 1998) and July is the hottest month (24.6°C).

The most frequent wind directions are generally from E and NE, in particular in spring and summer.

2.2 Measuring infrastructure

A 40 m tall scaffold walk-up tower was built inside the natural reserve (45°11'52.27"N, 10°44'32.27"E), at a distance from the edge of the forest ranging between a minimum of 390 m in the S direction and a maximum of 1440 m in the NE direction.

The infrastructure was equipped with instrumentation for four different kinds of measurements: fluxes of energy and matter (O_3, NO_x, CO_2, H_2O) with the eddy covariance technique, soil flux of O_3 and NO_x with dynamic chambers, vertical profiles of gas concentrations (O_3, NO_x) and air temperature and humidity, and additional meteorological and agrometeorological measurements (solar radiation, rainfalls, soil temperature, soil heat fluxes and soil water content).

2.3 Eddy covariance measurements of matter and energy fluxes

Four sonic anemometers (see Table S1for instrument models) were placed on the tower at four different heights: 16 m, 24 m, 32 m and 41 m. A fifth one was installed at 5 m a.g.l. on a pole, 10 m away from the tower, in the west direction. At the top tower level an open path infrared gas analyser (Model 7500, LI-Cor, USA) was also installed to measure the concentrations of water vapour and carbon dioxide, and at each of the five sampling heights a fast ozone instrument was installed to measure ozone vertical fluxes.

All the fast ozone instruments (Table S1) were based on the reaction between ozone and a cumarine-47 target which has to be changed after some days because its sensitivity declines exponentially with time (Ermel et al., 2013). Three fast ozone instruments, two COFA (Chemiluminescent Ozone Fast Analyzer) and the ROFI (Rapid Ozone Flux Instrument), which broadly followed the design of the GFAS instrument developed by Güsten and Heinrich, (1996), were equipped with a relatively big fan (about 100 L min^{-1}) which resulted in a fast consumption of the coumarin target. The other two instruments, a prototype developed by the National Oceanic and Atmospheric Administration (NOAA, Fast Response Ozone Monitor, Bauer et al., (2000)) and the commercial Fast Ozone Sensor (FOS, Sextant, NZ), both utilized a small membrane pump (2.5 L min^{-1}) and thus had a lower consumption of the coumarin targets compared to the other instruments. For this reason, the coumarin targets were changed every 5 days for the COFA and the ROFI and every 10 days for the FROM and the FOS. In both cases the coumarin targets were pre-conditioned just before use by exposing them to a concentration of 100 ppb of ozone for two hours.

Above-canopy fluxes of nitric oxide (NO) were measured at 32 m by means of a CLD780TR fast analyzer (Ecophysics, CH) based on the chemiluminescence reaction between O_3 and NO. The air to be analyzed was drawn from 32 m through a 3/8 ID Teflon tube main line at 60 L min^{-1} to the analyzer placed at the bottom of the tower. The analyzer was sub-sampling at 3 L min^{-1} from the main sampling line. The CLD780TR was calibrated with an 80 ppb standard produced using a dilution system (LNI 6000x, S) and a standard NO cylinder (18 ppm), at the beginning of the experiment and then weekly.

All the fast instruments and the sonic anemometers were sampled at 20 Hz through a customized LabVIEW (National Instruments, IRL) program and data were collected and stored in hourly files.

2.4 Soil NO, NO_2 and O_3 flux measurements

Fluxes and concentrations of NO, NO_2 and O_3 at the soil-atmosphere interface were determined by use of a fully automated measuring system as described in detail elsewhere (Bütterbach-Bahl et al., 1997; Gasche and Papen, 1999; Rosenkranz et al., 2006; Wu et al., 2010). Briefly: five dynamic measurement chambers and one dynamic reference chamber were installed at the site. Dimensions of the chambers were: 0.5 m x 0.5 m x 0.15 m (length x width x height). In contrast to the measuring chambers, the reference chamber was sealed gastight against the soil surface using a plate made of Perspex. Time resolution for flux measurements was 1 hour. Every chamber was closed and measured for 6 minutes, and before every sampling of a measuring chamber the reference chamber was sampled, resulting in a measuring cycle of 60 minutes. During sampling, the air from the chambers was sucked at a constant rate of 50 L min^{-1} and transported via PTFE tubing (inner diameter: 10 mm, length 20 m) to the analyzers. NO and NO_2 concentrations were determined using a chemiluminescence detector CLD 770 AL equipped with a photolytic converter (Models CLD 770AL and PLC 760, Ecophysics, CH), and O_3 concentrations were determined using an UV ozone analyzer (model TE49C, Thermo Environmental Instruments, USA). Corrections for initial concentrations of NO, NO_2 and O_3 at the outlet of each chamber and calculation of fluxes of NO and NO_2 was performed according to Bütterbach-Bahl et al. (1997). Calibration of the chemiluminescence detector was performed weekly using 40 ppb NO in synthetic air produced by dilution of standard gas (4 ppm NO in N_2) with synthetic air (80% N_2, 20% O_2) using a multi gas calibrator (model 6100, Environics, USA). Efficiency of photolytic conversion of NO_2 to NO was determined at least weekly as described in detail by Bütterbach-Bahl et al. (1997).

2.5 Vertical profile of O_3 and NO_x concentrations and air temperature and humidity

A computer driven system of Teflon tubes and solenoidal Teflon valves was used to characterize the vertical concentration profile of O_3 and NO_x above and within the canopy at 6 heights: 5 m, 8 m, 16 m, 24 m, 32 m and 41 m. The air samples drawn through 3/8 ID Teflon tubes (all of them 50 m long) from each level by a 30 L min^{-1} pump were sequentially sent to an UV ozone photometer (model 49C, Thermo Scientific, USA) and to a NO_x chemiluminescence analyser (model 42C, Thermo Environmental Instruments, USA) lodged in an air-conditioned container at the bottom of the tower. Both analyzers were sub-sampling at 2 L min^{-1} out of the 3/8 ID sampling lines.

All the tubes were insulated and continuously purged. Each level was sampled for 4 minutes after 1-minute wait to let the analyzers stabilize and then concentration data were recorded each half an hour with a customized LabVIEW program (National Instruments, USA).

The O_3 gradient analyzer was calibrated against a reference photometer before and after the field campaign and no significant deviation from the first calibration was observed. The NO_x analyzer was calibrated with the same procedure described above for the Ecophysics CLD780TR at the beginning of the experiment and then weekly.

Additional O_3 and NO_x concentrations at 0.15 m were also available from the soil chambers system previously described.

The ozone concentrations at 5 m, 16 m, 24 m, 32 m and 41 m were also used as absolute ozone reference for the fast ozone instruments all of which change sensitivity sufficiently fast to require constant calibration against a slow response absolute instrument.

Five temperature and relative humidity probes (model HMP45, Vaisala, Finland) were installed, at the higher tower levels (16 m, 24 m, 32 m and 41 m) and, additionally, at 11 m. All these probes were connected to a data logger (CR23x, Campbell Scientific, USA), sampled once per minute and stored as half an hour averages. Two additional temperature measuring points (PT100, Campbell Scientific, USA), were available at 1.5 m and 0.15 m a.g.l. and data were collected with the same personal computer used for the control of the dynamic chamber system.

2.6 Additional meteorological and agrometeorological measurements

On the top of the tower a net radiometer NR-lite (Kipp & Zonen, NL), a BF5 sunshine sensor for total and diffuse PAR (Delta-T Devices, UK), a PTB101B barometer (Vaisala, Finland) and a rain gauge (model 52202, Campbell Scientific, USA) were mounted.

Several soil probes were deployed in the soil 20 m from the bottom of the tower: four reflectometers for soil water content (model TDR 616, Campbell Scientific, USA), four soil heat flux plates (model HFP01SC, Hukseflux, NL) and four soil temperature probes (PT100, GMR Strumenti, I). All these sensors were connected to a data logger (CR13x, Campbell Scientific, USA), sampled once per minute and stored as half-hourly averages.

2.7 Measuring period

The measuring campaign began on 12th June and ended one month later, on 11th July 2012. From the 12th June to the 23rd June three fast ozone instruments (ROFI, FROM and one of the two COFA samplers) were all placed above the canopy at a height of 32 m in order to compare them and to characterize their performances ("Intercomparison period"). The COFA installed at the top of the tower started its measurements on 12th June and was not moved to level 32 m for the intercomparison because it was already compared with the second COFA before the campaign.

The intercomparison exercise allowed the agreement between the three instruments to be verified, and the average relative standard deviation was below 10%. Considering the intrinsic variation due to the different behaviour of individual coumarin targets no systematic correction was applied. The sextant analyzer, the one employed at 5 m, was calibrated after the field campaign against one of the two COFA. Also in this case, no significant deviation was observed and no corrections were applied.

On 24th June each fast ozone instrument was moved to a different level (Table S1) to begin the flux profile measurements which ended the 11th July ("Flux Profile period"). Every average diel course showed in the following sections is referred to this period.

The FOS installed at 5 m was checked after the field campaign by running it in parallel with the COFA previously used at 32 m in the intercomparison period.

2.8 Data processing

The flux measurement technique adopted here was the eddy covariance (Foken, 2008), which states that fluxes are equal to the covariance between the vertical wind component and the scalar of interest (Arya, 2001). An averaging period of 30 minutes was chosen for the calculation of the covariances.

Despiking. The data series were divided into 2 minutes sub-series and for each of them block average and standard deviation were calculated. Spikes were identified as the instantaneous data that exceeded the average of each sub-series for more than 3.5 times the standard deviation, as proposed by Vickers and Mahrt (1997). Spikes were removed from the series and the data were then gap-filled by a linear interpolation.

Rotations. Two axis rotations were applied to the instantaneous wind components to align u with the mean flow over the averaging period: the first rotation aligned the horizontal wind to the 30 minutes average u component (this rotation forces $\bar{v} = 0$), and the second one to rotate the xy plane in order to zero the 30 minutes average vertical component of the wind ($\overline{w} = 0$) (McMillen, 1988; Wilczak et al., 2001). These rotations corrected the little imperfections in the vertical alignment of the sonic anemometers and prepare the data for flux calculations. Samples with a second rotation (vertical tilt) angle greater than 15° were discarded.

Linear detrending. The fluctuations of each parameter (w', T', O_3') were calculated as the differences of each instantaneous value from the best linear fit (minimum square) of the considered time series in each half an hour data (Lee at al., 2004).

Time-lag determination. Ozone fluxes were calculated using a fixed time-lag between the vertical wind time series and the ozone concentration one. For each fast instrument the time lag which maximized the cross-covariance function between the vertical component of the wind and the ozone concentrations was identified and the more frequent lag was used in the calculations for every half an hour.

Elimination of the kinematic fluxes below the error threshold. The error threshold was quantified for each half-hourly data series by following the methodology proposed by Langford et al., (2015). The standard deviation of the auto-correlation function was calculated for each half-hourly data chunk, with lags ranging between 30 and 60 seconds from the characteristic time lag of each instrument. Kinematic fluxes lower than three times the standard deviation (relating to the 95th percentile) of were discarded.

Frequency loss correction.

The frequency loss correction factors for the different fast ozone analyzers were calculated using the experimental transfer function approach following the methodology proposed by Aubinet et al. (2000). This method considers the normalized cospectra for sensible heat as unaffected by frequency loss or, at most, affected by frequency loss which are negligible respect to those related to the other considered. The transfer function is calculated for every half-hour as the ratio between the normalized cospectra of ozone (in our case) and the normalized cospectra of sensible heat, then fitted with a Gaussian type function (Aubinet et al., 2001), and thus used to calculate a correction factor for each instrument. For further details, please refer to Aubinet et al. (2012).

Schotanus and WPL corrections. Fluxes of sensible heat (H), latent heat (LE) and trace gases were corrected for air density fluctuations. The formulation adopted for the correction of H was the one proposed by Schotanus et al., (1983) while the formulation used for LE and trace gases was the one proposed by Webb et al., (1980).

Calculation of fluxes in physical units. Fast ozone concentration data –acquired as voltages- and fast NO concentration data – acquired as counts per seconds- required additional processing to calculate quantitative fluxes in physical units. First, for all the fast ozone instruments the target zero V_0 (Muller et al., 2010) – i.e. the output voltage when ozone concentration is 0 ppb – was identified for each coumarin target employed. Then the ozone fluxes were calculated by the following equation (Muller et al., 2010):

$$F_{O3} = \frac{\overline{w'V'}}{\bar{V} - V_0} C_{O3} \quad (1)$$

where $\overline{w'V'}$ is the covariance between the vertical wind component and the raw output voltage of the fast ozone instrument, $\bar{V}$ is the average output voltage of the instrument in each half an hour, V_0 is the zero target, identified for the considered half an hour, and it represents an estimation of the voltage at zero ozone concentration, and C_{O3} is the ozone concentration measured by the reference ozone analyzer averaged over the same period. The data of the two hours following each target change were excluded in order to allow the target sensitivity to stabilize after the target installation.

Similarly, NO fluxes were calculated using the following equation:

$$F_{NO} = \frac{\overline{w'cps'}}{\overline{cps} - cps_0} S_{NO} \quad (2)$$

where $\overline{cps}$ (counts per seconds) is the NO raw data measurement averaged in each half an hour, and cps_0 and S_{NO} are the offset and the sensitivity of the analyser determined by calibration. Cps_0 ranged from 1000 to 2500 cps while S_{NO} ranged from 10000 to 12000 cps / (µmol m^{-3}).

Ozone storage. Ozone fluxes measured by eddy covariance were corrected for the ozone storage every half-hour. The ozone storage is the temporal variation of the vertical ozone profile below the measuring point located at the height z_m. It does not represent a true ozone removal or production process, but only a temporary accumulation of ozone in the air column below the measuring point or a temporary ozone release out of the same air column. For a non-reactive tracer, the proof of it is that the storage integrated over a whole day is null. The calculation of the ozone storage is necessary for a proper determination of the ozone deposition processes.

The correction of the ozone fluxes for the storage was made by means of the following equation (Rummel et al., 2007):

$$F_{StorO_3} = F_{O_3} + \frac{\partial}{\partial t} \int_0^{z_m} O_3(z) dz \quad (3)$$

where F_{StorO_3} are the ozone fluxes corrected by storage, F_{O_3} are the measured ozone fluxes obtained with the Eq. (1), and the second term on the right represents the ozone storage term. For a reactive tracer like ozone some of the stored gas may be destroyed by reaction with NO and potentially with VOCs before being re-released to the air space above, and thus, Eq. (3)

must be considered an approximation. A fully resolving 1D chemistry and exchange model would be required to quantify the effect of chemistry on the storage term more fully.

Stationarity check. Finally, the stationarity of each half-hour sample was verified following the methodology of Foken and Wichura (1996) and the non-stationary data were discarded.

3 Results

3.1 Microclimate

Significant rainfalls had cooled the air before the beginning of the field campaign so that, air temperature increased significantly in the first days and after that remained stable (Figure S1a). The average temperature at the top of the tower was 25.9 °C, while the lowest average temperature (23.1 °C) was recorded at 0.15 m. The maximum temperature during the whole period was 36.2 °C which was observed at the top of the canopy (24 m).

On average the temperature minimum was observed during night around 3:00 (solar local time, always the same hereafter) (Figure 1b) for the levels from 11 m to 24 m and one hour later for all the other levels, with values ranging from 19 °C to 21 °C. Two significant rainfall events occurred in the final part of the campaign accounting for a total of 108 mm of rain, but these did not affect significantly the air temperature (Figure 1a). In general, most of the days were sunny (only three days were partially cloudy) and humid, with nighttime peaks of relative humidity up to 80% and diurnal minima around 40%. Specific humidity q ranged, on average, between 10 and 13 g_{H_2O}/kg_{air} (Figure 1a). Below canopy levels (≤ 16 m) showed higher q than the above canopy levels early in the morning, around 6:00, and from 13:00 to 21:00, while the top-crown level (24 m) showed the lowest q values from 4:00 to 16:00. Specific humidity showed close agreement amongst the above canopy levels, with slightly higher values at 41 m.

The wind blew mostly from the East or West, with about 50% of the data in these directions (Figure 1c), whilst the N and S directions accounted for 12% of the data and the intermediate directions accounted for less than 20% of the data. The diurnal wind intensity at 41 and 32 m was on average around 2 and 1.5 m s^{-1} respectively (Figure S1d), and the wind intensity was slightly greater during night than during daytime, with nearly 1 m s^{-1} more at 41 m and 0.5 m s^{-1} at 32 m. The three lower levels showed very low intensity, below 0.5 m s^{-1}, with only a minor increase during the day.

The friction velocity (u^*) at the two upper levels above the canopy showed a very similar behaviour (Figure 1b) but u_* was slightly higher at 32 m (+6%). Diel maxima of u_* were about 0.5 m s^{-1} occurring between 9:00 and 13:00, after which they suddenly decrease of nearly 20% and then gradually decreased. The minimum (0.13 m s^{-1}) was observed around 20:00, after that a quite irregular behaviour during the night was observed with values between 0.2 and 0.3 m s^{-1}. The in-canopy measurements of friction velocity at the lowest three levels were significantly lower than the above canopy ones: 24 m and 5 m measurements were less than 50% of the two upper levels and 16 m measurements were around 70% less than above canopy levels. The diurnal maxima at noon were 0.25 m s^{-1} at 24 m, 0.18 m s^{-1} at 16 m and 0.26 m s^{-1} at 5 m and during the night the

friction velocity showed a flatter trend with values below around 0.1 m s^{-1} at 5 m and around 0.05 m s^{-1} for the two others levels.

3.2 Profiles of temperature, heat fluxes and atmospheric stability

Following sunrise, early in the morning, the heating of the top part of the canopy developed a thermal inversion in the forest with the ceiling at the top of the canopy (level 24 m) and the base at ground level (Figure 2a).

Above the canopy temperature gradients were strongly super-adiabatic from 4:00 to 17:00, however it should be noted that heat transfer increased significantly only when friction velocity increased.

During the morning, the gradual heating of the canopy extended to the upper canopy layer, reaching its maximum value at noon. As a consequence, the inversion ceiling was lowered to the bottom part of the tree crowns (16 m). But already from 2 pm the air layers in the middle of the trunk space started to cool and the inversion ceiling gradually reached the top of the canopy. By 6 pm the top of the canopy had cooled sufficiently for and the above-canopy atmosphere to become stable, which then attenuated overnight, without ever disappearing (Figure 2b).

The presence of an inside canopy thermal inversion is confirmed also by the measured sensible heat fluxes (Figure 3). Above the canopy the heat fluxes were strongly upward during the day. However, the sensible heat fluxes at 32 m were about 20% larger than those at 41 m.

In the upper part of the crown (24 m), sensible heat fluxes were less than half the above canopy ones in the central part of the day. On the contrary, the heat fluxes at 16 m and 5 m were almost always zero or negative (directed downwards). In relation to the strengthening of the thermal inversion in the afternoon, it is worth noting that the downward heat fluxes peaked at 2 PM at 5 m, two hours later at 16 m and four hours later at 24 m.

However, the forest released most of the energy as latent heat with a peak around 300 W m^{-2} at midday and with very small nighttime values.

Above the canopy the atmosphere was nearly always unstable during the day, while below canopy it was mostly stable, as shown in Figure 4. At the top canopy level (24 m) the most frequent condition in the central hours of the day was strong instability because of the canopy heating due to the radiation. Remarkably, stable conditions at this level strengthened from 3 pm to 7 pm just during the inversion.

Inside the canopy (16 m) the atmosphere was mainly stable or very stable. In particular, from 14:00 to 19:00 the inside canopy air was almost always very stable, as it happened for a shorter period in the morning from 6:00 to 8:00. During the night the atmosphere was mainly stable or very stable above canopy, while at 24 m and 16 m some nocturnal instability was observed, this latter might be due to numerical artifacts because the sensible heat fluxes were close to zero. A similar explanation can be used also for the stability class distribution at 5 m, for which some instability was observed. In any case, stable condition was the most frequent situation observed at that level.

3.3 Ozone concentrations profiles

Ozone concentrations above the canopy (41 m and 32 m) showed the typical bell-shaped diurnal pattern, with a maximum around 80 ppb at 14:00 and minimum around 25 ppb at 4:00 (Figure 5). The concentrations decreased slightly throughout the canopy (-9% between 32 m and 5 m), while there was a significant reduction near the ground (-72% between 32 m and 0.15 m). At ground level, average ozone concentrations never exceeded 27 ppb. It is worth noticing the second (relative) minimum observed at 16:00 at the lowest level; this minimum is in agreement with a slight reduction in the ozone concentrations observed in the upper levels inside the canopy (from 5 m to 24 m). These features can be better observed considering the vertical variations in Figure 6a and Figure 6b. During the night the in-canopy gradient of ozone was negligible, but from early morning a negative gradient rapidly developed and remained almost constant (around 0.2 ppb m^{-1}) during the daylight hours, except in the afternoon. The slope of this gradient increased in the afternoon: at 16:00 from 8 m to 32 m (around 0.5 ppb m^{-1}) and at 18:00 but only from 24 m to 32 m (around 0.8 ppb m^{-1}). Another peculiarity emerged from 13:00 to 15:30, when the ozone concentration just above the canopy (32 m) was on average higher (by 2.0 to 3.8 ppb) than above (41 m); moreover, in the same period, also the 24 m ozone concentration was higher than the one measured at 41 m (from 1.2 to 2.5 ppb).

3.4 Ozone fluxes profile

Ozone fluxes were corrected for the storage in the air layers below each measuring point. The magnitude of these corrections was not negligible and they were higher in the morning and in the evening (Figure S2) when the air layers in the trunk space are respectively refilling and emptying of ozone. Considering the whole 41m height air column, the greatest storage correction was nearly +5 nmol m^{-2} s^{-1} in the morning, while in the evening it was about -4 nmol m^{-2} s^{-1}, the integrated value over the day was null.

Ozone fluxes showed a regular behaviour with almost always negative values except for some positive peaks during night or during the transition between night and day, in particular in the lowest levels (Figure 7). The largest deposition flux was observed on 25th June at the 24 m with 46 nmol m^{-2} s^{-1} level in agreement with a peak of evapotranspiration (Figure S3). The following two days were nearly 50% lower and LE fluxes too. In general, ozone fluxes and LE fluxes seem to be correlated but there were some exceptions for instance on 3rd and 4th July. The smallest fluxes were observed on 6th July during the rainfall events, after which the ozone fluxes showed an increase (7th July) even if ozone concentrations were lower, corresponding to an increase of soil water content and evapotranspiration fluxes.

The diel average course of ozone fluxes (Figure 8) showed at all the levels the typical behaviour with low nighttime values and the greatest deposition in the central hours of the day.

Ozone fluxes measured above the canopy (41 m and 32 m) showed very good agreement, nearly overlapped during the day (Figure 8). Both increased very rapidly in the morning and then stayed almost constant (between 8 and 10 nmol m^{-2} s^{-1}) from 9:00 to 16:00, when they started to decrease. At 24 m, fluxes were not constant in the central part of the day and they were on average 40% greater than the above canopy levels with average peaks around 15 nmol m^{-2} s^{-1} (Figure 8). From 9:00 to 16:00,

air layers above canopy including the top of the crown (from 24 m to the top of the tower), seemed decoupled from the air below: the above layers were in superadiabatic conditions with intense air mixing (Figure 4a and 4b) while the below canopy experienced a thermal inversion which gradually expands towards the top of the canopy and even above after 16:00 (Figure 2b).

Greater fluxes at 24 m might be caused by the location of these measurements which are just in the transient region between well mixed superadiabatic air and the below canopy thermal inversion.

3.5 NO and NO_2 fluxes and concentrations

NO and NO_2 concentrations along the tower profile (excluding near ground measurements at 0.15 m) were relatively low with a maximum early in the morning respectively around 2 ppb for NO and around 14 ppb for NO_2. Both NO and NO_2 concentrations did not show great differences along the vertical profile (Figure 9a and Figure 9b). The greatest differences between the bottom and top level were only around 1 ppb, for both compounds, very early in the morning, between 4:00 and 9:00.

At soil level (0.15 m) the behaviour was completely different for both compounds. NO was always greater than the above levels (from 5 m to 41 m) with two peaks (Figure 9b): the first one at 6:00 around 15 ppb and the second one in the afternoon around 17:00 (nearly 20 ppb). NO_2 at soil level was relatively constant ranging from 7 to 12 ppb; even in this case two peaks were observed: at 6:00 (10 ppb) and around 17 (11 ppb).

NO and NO_2 fluxes at ground level were almost always mono-directional with NO emitted from soil and NO_2 deposited to the ground (Figure 9c). A significant change in the emission rate of NO and in the deposition of NO_2 was observed after the rainfalls happened between 6th and 7th July (Figure 9d).

The average diel course of soil fluxes showed an almost constant emission of NO with two decreases: the first one around 6:00 and the second one at 17:00. These two decreases of the observed fluxes were strictly linked with the stratification of the air above ground: an increase in the concentrations in a stratified environment led to a reduction of the concentration gradient between soil/litter and the atmosphere thus reducing the emission in turn. The average diel course of NO_2 deposition were nearly inversely proportional to the behaviour of the NO soil fluxes with a pronounced reduction of the deposition early in the morning and a less intense one in the afternoon. In the afternoon, the nearly simultaneous minimum of soil NO fluxes and maximum of NO_2 deposition (Figure 9e) indicates a gas phase titration with an ozone reduction by NO (Figure 5).

At the top canopy the net exchange of NO with the above atmosphere was very small except in the morning (Figure 9e), when the deposition peak between 6:00 and 11:00 reached -15 µg N m^{-2} s^{-1}. This NO deposition (Figure 9e) is correlated to the development of a small NO gradient above the canopy (Figure 9b) after the NO_2 photolysis. The NO gradient and fluxes became negligible (Figure 9b and Figure 9e) when NO_2 concentrations reached a minimum (Figure 9a) determined by the photolytic equilibrium of NO_x.

4 Discussion

Whilst turbulence and heat fluxes inside tree canopies had been studied more extensively, only few studies had attempted to partition ozone fluxes by means of flux measurements at different in-canopy heights (Dorsey et al., 2004; Launiainen et al., 2013).

The evaluation of flux profiles relies on the constant flux hypothesis, one of the most fundamental theories of micrometeorology (Arya, 1989). In the case of the Bosco Fontana measurements, one would expect that the fluxes measured at 41 m and at 32 m should be almost equal and then the deposition flux should decrease, in absolute terms, at the lower levels due the presence of different in-canopy sinks for momentum and ozone (stomata and surfaces of the leaves, branches and stems), and sinks and sources for heat. Consistent with this expectation, measured fluxes of heat and momentum were significantly reduced within the canopy. This may be due to differences in the flux footprint, coupled with heterogeneity in the canopy (Dalponte et al., 2007; Acton et al., 2016), but it does not appear to be dependent on wind direction. Because the 32 m measurements were made lower within the surface roughness layer, it is possible that fluxes were locally somewhat enhanced. Fluxes of ozone were similar at these two above-canopy heights, within the uncertainty of the measurement, but unlike for the fluxes of heat and momentum, measurements at 24 m showed a significantly larger ozone deposition than the two upper levels (32 m and 41 m) at certain times of the day. In the morning (9:00 to 12:00) 24 m ozone fluxes were on average nearly 3 nmol m^{-2} s^{-1} larger than above the canopy (Figure 8), while they were nearly equal on average from 13:00 to 18:00 (fluxes at 24 m were only 0.5 nmol m^{-2} s^{-1} larger).

A possible explanation of these differences could lie in the different footprints of the eddy covariance measurements. The footprints of the measurements at 41 m, 32 m and 24 m were all falling inside the surface of the upper forest canopy, even though the 24 m level was just at the top canopy edge. The size of the footprint areas obviously decreased at decreasing measuring heights. However, in absence of any source or sink of the considered scalar, the horizontal homogeneity of the studied ecosystem ensures the validity of the constant flux hypothesis and thus the measurements referred to different footprints should be the same, i.e. fluxes with larger footprints (measurements at 41 m and 32 m) should be comparable to those with smaller footprints (measurements at 24 m). In order to investigate alternative reasons for the enhancement of the ozone fluxes at 24 m a spectral analysis was performed to compare the normalized cospectra of the ozone fluxes at the different levels, and the role of the NO-realated ozone chemical sink was analysed.

Figure S4 shows the average normalized cospectra of the vertical component of wind and ozone for the measurements performed when the morning ozone enhancement at 24 m occurred (11:00) and when the 24 m ozone fluxes were comparable with the upper ones (15:00).

The cospectra analysis did not provide an obvious explanation for the enhancement of the fluxes observed at 24 m in the morning. Apart from the ozone cospectra at 16 m which had a very irregular behaviour, the other three cospectra did not show any particular difference which could explain the higher ozone fluxes at 24 m. The observed decrease of the ozone cospectra

at 24 m and 16m for frequency above 0.1 Hz is consistent with the notion that within the canopy the mean eddy-size is dictated by the canopy height.

The analysis of the NO related chemical sink instead, revealed a possible role of the convergence of two NO fluxes at the top of the canopy on the enhancement of the O3 fluxes at 24 m, i.e. the NO deposition flux from the air above the forest and the soil NO emission flux uprising from the forest floor. This can be argued by considering the differences between the O_3 fluxes measured at 24 m and those measured at 32 m (a level where the constant flux hypothesis is confirmed). The sum of these differences from 6:00 to 12:00 in the morning gives a value of 59.4 μmol O_3 m^{-2}, which is almost equal to the sum of the NO converging to the top of the crown both from above and below the canopy in the same hours (54 μmol NO m^{-2}).

Supposing a stoichiometric reaction between NO and O_3 at the top of the canopy, by subtracting to the 24m O3 fluxes an amount of ozone equal to the NO converging at the top of canopy every half-hour, the part of the O_3 flux not caused by this chemical sink is obtained. This is shown in the Figure 10 where the measured O_3 flux at 24 m is represented as a green line and the resulting part of the O_3 flux at 24 m not due to the NO sink is reported as a dark grey dashed line, being the NO fluxes converging from above and below canopy represented by the black and purple lines respectively.

The good agreement between the ozone fluxes at 32 m (Figure 10, red line) and the part of the O_3 flux at 24 m not due to the NO sink (Figure 10, dark grey dashed line) suggests that the enhancement of the O_3 fluxes observed at 24 m was related to the interactions of O_3 with NO at the top canopy level. The contribution of the NO emitted by soil to the observed ozone flux was relatively constant and greater than the contribution of the NO transported into the forest from the atmosphere above, because this latter was very low in the afternoon and relatively high only in the morning (Figure 9e). This observation is supported by the increased ozone fluxes at 24 m which were observed mostly in the morning and nearly ceased in the afternoon.

A possible explanation could be found in the forest-atmosphere decoupling during the afternoon compared to the forest-atmosphere coupling observed in the morning. In fact, the increase of the NO concentrations at soil level (0.15 m, Figure 9b) after midday, followed by the decrease of O_3 concentrations at the same level (Figure 5), suggests an air stratification inside the canopy and its decoupling from the above canopy air, as also found by Rummel et al., (2002) and Foken (2008). On the contrary the decrease of the soil level NO concentration (Figure 9b) from 6:00 to 12:00 in the morning suggests a relatively well-mixed canopy which is better coupled with the atmosphere above. This condition allowed also ozone and NO from the above canopy air to penetrate more easily into the canopy (see Figure 6b and the morning peak of Figure 9b). The afternoon stratification is also supported by the stability classes reported in Figure 4c and Figure 4d which were almost always stable or very stable both at 16 m and at 24 m from 15:00 to 18:00. In addition, the thermal inversion layer within the canopy increased its thickness during the afternoon (Figure 2b) rising form the 16 m observed around 12:00 to the 24 m observed from 14:00 to 16:00. Again, the morning coupling and the afternoon decoupling is supported by the diurnal course of the specific humidity observed below canopy (Figure 1a). In the morning the almost constant amount of water vapour above and below canopy (a part from the top-canopy 24 m level where there was an unidentified process removing water vapour) reveals an efficient mixing of the air while in the afternoon the increase of the specific humidity from the three lower levels, due to soil evaporation and understorey transpiration, reveals an air stratification below canopy and a forest decoupling from the above atmosphere.

The availability of ozone flux measurements at different heights within and above the canopy allowed a partition of the ozone fluxes among the different ecosystem layers: upper and lower crown, understorey and soil. To do that we have assumed the ozone flux measured at 32 m as a total deposition flux, then we calculated the NO sink as the sum of NO deposited from the top and emitted from soil assuming a stoichiometric reaction between NO and O_3. The ozone taken up by the upper canopy layer was identified as the difference between the ozone fluxes measured at 32 m and those measured at 16 m (ignoring the apparently enhanced values at 24 m), while the ozone taken up by the lower canopy layer was obtained as the difference between the ozone fluxes measured at 16 m and 5 m. Finally, the deposition to the forest floor (soil and the understorey vegetation) was calculated as the difference between the ozone flux at 5 m and the NO flux emitted by soil, namely the amount of ozone which is not removed by chemical reaction with NO.

The result of this exercise is shown in Figure 11, where it can be observed that the upper canopy layer of the forest removed about 1/3 of the total deposited ozone while the lower canopy layer of the forest removed the main part of the ozone (46.5%). The canopy removed nearly 80% of the ozone deposited to the forest ecosystem, but it is worth noticing that this amount includes both stomatal and non-stomatal uptake.

Only a minor part of O_3 was removed by the understorey vegetation or deposited to the soil (2.0%) while an important role was played by the NO sink, mainly due to soil emissions, which accounted for the 18.2% of the total ozone deposition.

This latter result is in general agreement with the observations of Dorsey et al., (2004) who found that in a Douglas fir plantation between 7% and 14% of the ozone deposition in the daylight hours could be attributed to the reaction with the soil emitted NO, while this fraction increased up to 41% during the night. Similarly, Pilegaard (2001) found that the NO sink accounted for a 25% of the ozone deposition in a Norway spruce forest, with an increase of this fraction up to 31% during the night.

Nearly all the nighttime ozone deposition at Bosco Fontana can be attributed to the NO depletion of ozone, which resulted the responsible process for the observed ozone deposition at night. The fact that NO reaction accounts for 100% of the nocturnal O_3 deposition would imply that other non-stomatal sinks are negligible during that time. It cannot have completely ruled out, however, that our stirred soil flux chambers could somewhat overestimate the nocturnal soil NO emission, due to the enhanced amount of mixing in the flux chamber compared with the true forest floor during calm nights. Similarly, the analysis assumes that the only sink of NO is reaction with O_3. A small amount of uptake of NO by vegetation is possible even if unlikely as shown by Teklemariam et al., (2006) and Stella et al. (2013). Overall this ecosystem did not behave as a net NO emitter because the whole NO produced at soil level is consumed within the canopy, but as a weak NO sink because of the small amount of NO received from the atmosphere in the first hours of the morning (Figure 9d). This differs from the observation of Dorsey et al. (2004) who estimated that nearly 60% of the NO emitted from the soil of a Douglas Fir forest escaped the trunk space to react aloft.

5 Conclusions

Ozone flux measurements were run along a vertical profile with five measuring points above, inside and below the canopy. The ozone flux measurements of the levels above the canopy were in good agreement between them and comparable with values reported for other forest types (Amthor et al., 1994; Gerosa et al., 2005, 2009a; Fares et al., 2014; Finco et al., 2017), since no measurements on oak-hornbeam forests were found in the literature. Ozone fluxes at 16 m and 5 m were lower than above the canopy, while at the top canopy edge (24 m) fluxes were surprisingly higher than above in the morning hours. The main cause of this enhancement has been attributed to an ozone sink due to a reaction with NO both emitted from soil and deposited from the atmosphere above the canopy. The morning enhancement of the ozone fluxes at 24 m was eased by the coupling between the forest and the atmosphere, while in the afternoon the decoupling and the in-canopy stratification led to 24 m fluxes comparable to those above the canopy.

Most of the ozone, nearly 80%, was removed by the forest canopy: in particular, the upper canopy layer removed 33.3% of the ozone deposited and the lower canopy layer 46.3%. Only a minor part of ozone was deposited on the soil and the understorey (2%), while the remaining part (18.2%) was removed by a chemical reaction with NO emitted by the soil. These findings might be useful to improve the ozone risk assessment for mature forests.

Finally, the complex diel dynamics of ozone and NOx observed at Bosco Fontana represent a challenge for modelists. The collected data will be available for the parameterization and the fine tuning of process models aimed at correctly reproducing the intra-canopy dynamics of ozone and NO_x

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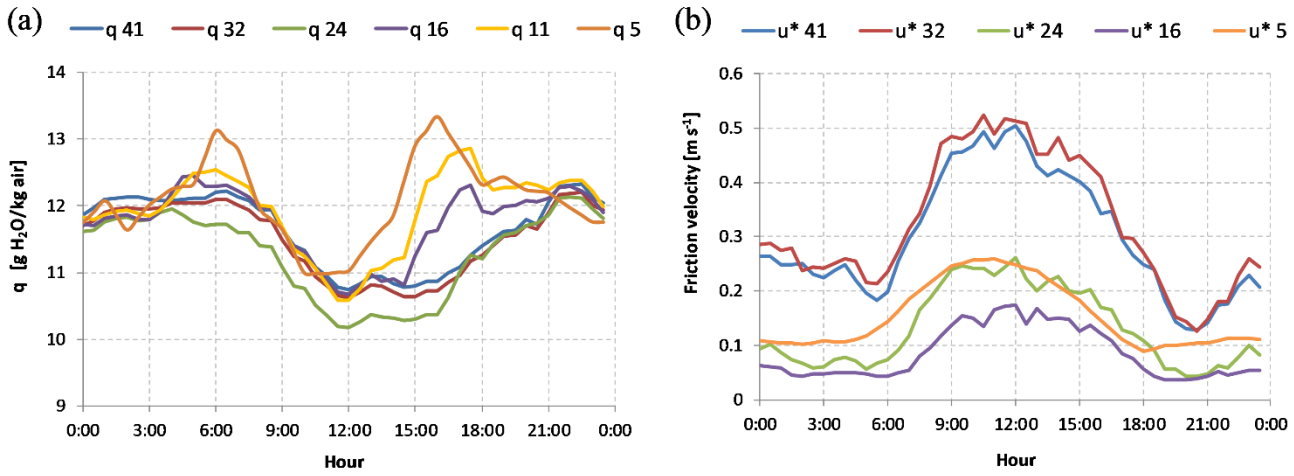

Figure 1 – (a) Average diel course of specific humidity at the five levels; (b) Average diel course of friction velocity at the five heights. For both figures the numbers in the curves label of the legend represent the measurement height (in meters). For figure (a) the maximum and the minimum standard error of the half-hourly means were respectively 0.45 g and 0.24 g H_2O/kg air for 41 m, 0.45 g and 0.25 g for 32 m, 0.49 and 0.24g H_2O/kg air for 24 m, 0.49 and 0.24 g H_2O/kg air for 16 m, 0.52 and 0.25g H_2O/kg air for 5 m. For figure (b) The maximum and the minimum standard error of the half-hourly means were respectively 0.05 and 0.02 m s^{-1} for 41 m, 0.06 and 0.03 m s^{-1} for 32 m, 0.03 and 0.01 m s^{-1} for 24 m, 0.02 and 0.01 m s^{-1} for 16 m, 0.02 and 0.01 m s^{-1} for 5 m.

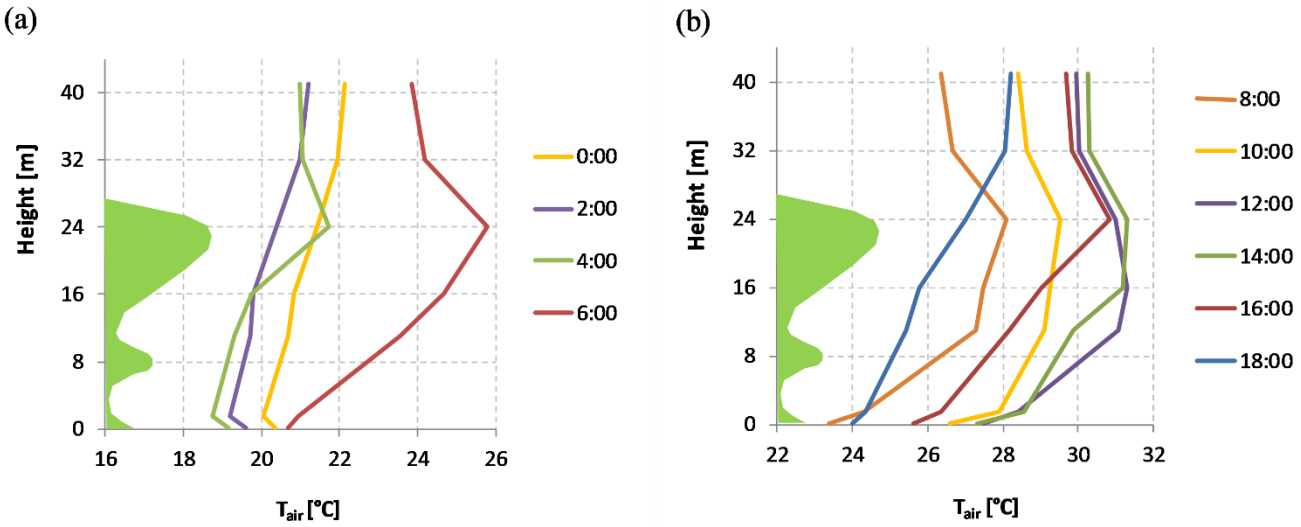

Figure 2 - Diurnal evolution of vertical profile of air temperature. (a) from 0:00 to 6:00 AM; (b) from 8:00 to 18:00. The green shaded area represents the vertical distribution of vegetation. The maximum and the minimum standard error of the half-hourly means were respectively, 0.35 and 0.32 °C for 0:00, 0.38 and 0.36 °C for 2:00, 0.40 and 0.37 °C for 4:00, 0.42 and 0.35 °C for 6:00, 0.35 and 0.31 °C for 8:00, 0.39 and 0.33 °C for 10:00 m, 0.40 and 0.33 °C for 12:00, 0.70 and 0.62 °C for 14:00, 0.73 and 0.52 °C for 16:00, 0.54 and 0.40 °C for 18:00.

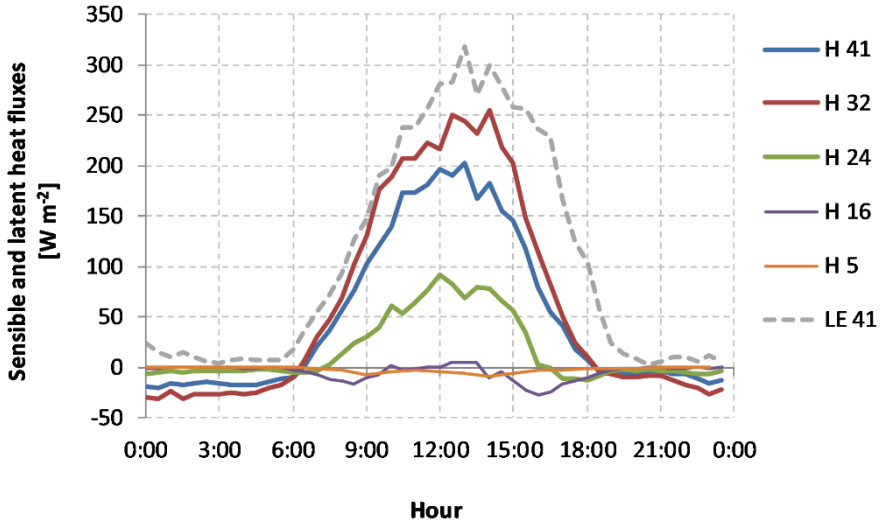

Figure 3 - Average diel course of sensible heat fluxes at the five levels (41 m, 32 m, 24 m, 16 m and 5 m, thick lines) and latent heat flux measured at 41 m (dashed line). The maximum and the minimum standard error of the half-hourly means for sensible heat fluxes were respectively 20.3 and 1.1 W m^{-2} for 41 m, 27.1 and 2.0 W m^{-2} for 32 m, 9.2 and 1.0 W m^{-2} for 24 m, 4.3 and 0.3 W m^{-2} for 16 m, 3.7 and 0.4 W m^{-2} for 5 m, 28.7 and 1.4 W m^{-2} for latent heat fluxes at 41 m.

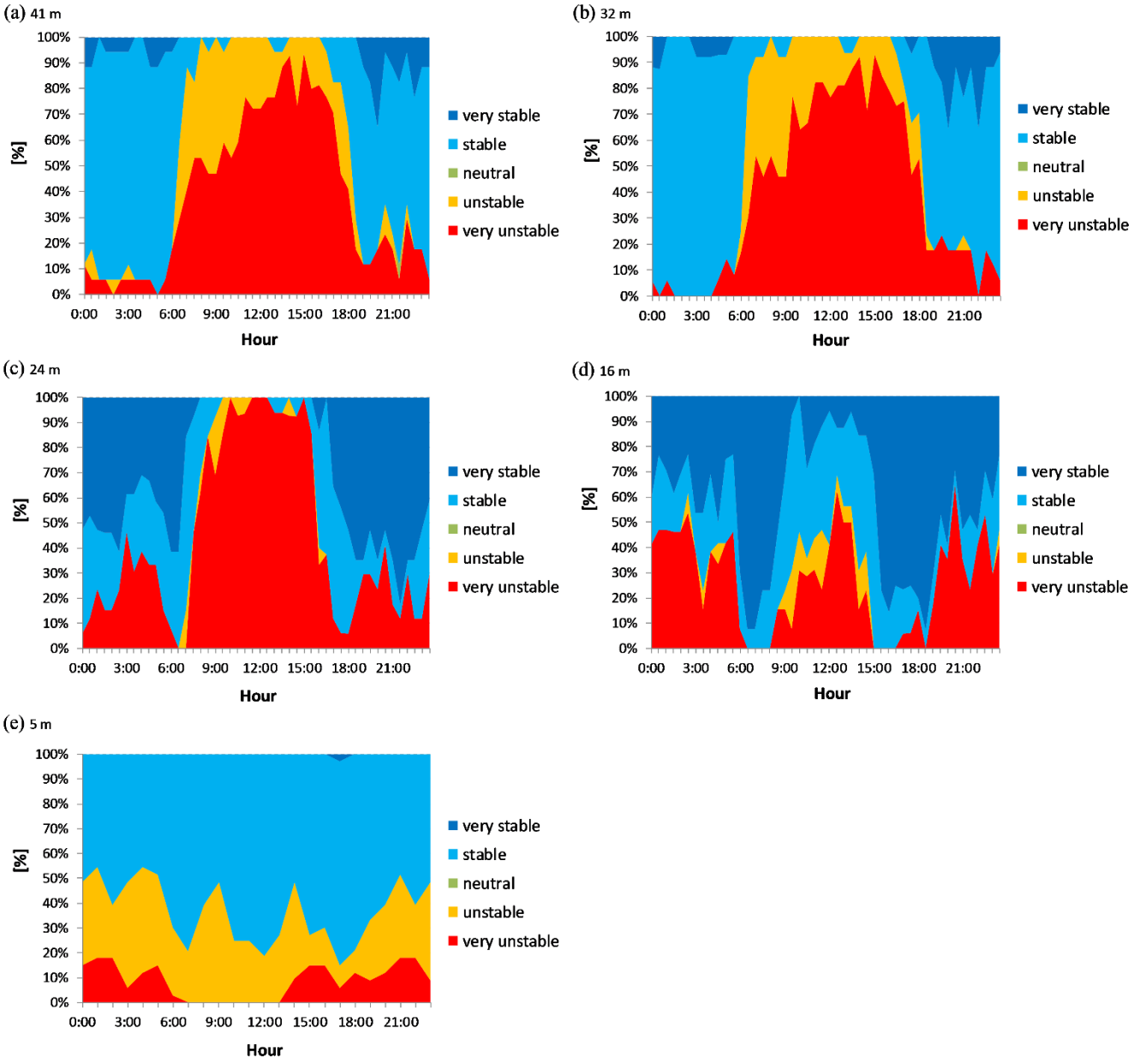

Figure 4 - Stability class distributions in the different hours of the day expressed as function of z/L for the different levels: (a) 41 m, (b) 32 m, (c) 24 m and (d) 16 m (e) 5 m. z is the measuring height while L is the Obhukov length. The stability classes were classified as follows according to Gerosa et al. (2017): very stable: $0<L\leq10$; stable: $10<L\leq100'000$; neutral: $abs(L)>100'000$; unstable: $-100'000\leq L<100$; very unstable: $-100\leq L<0$.

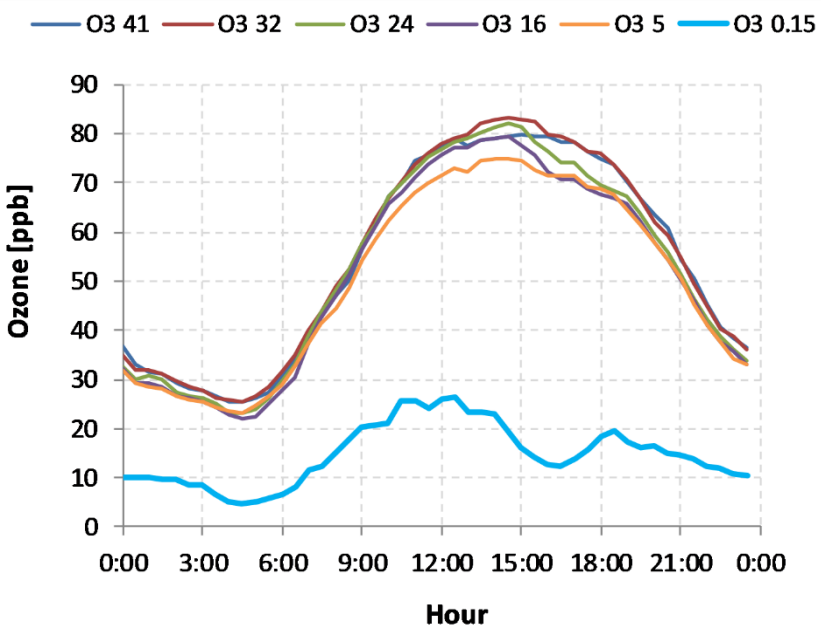

Figure 5 - Average diel courses of ozone concentrations at six levels (41 m, 32 m, 24 m, 16 m, 5 m and 0.15 m). The maximum and the minimum standard error of the half-hourly means were respectively 3.0 and 1.7 ppb for 41 m, 3.0 ppb 1.8 ppb for 32 m, 3.4 and 1.9 ppb for 24 m, 3.4 and ppb 1.8 for 16 m, 2.9 and 1.7 ppb for 5 m, 3.4 ppb and 1.0 ppb for 0.15 m.

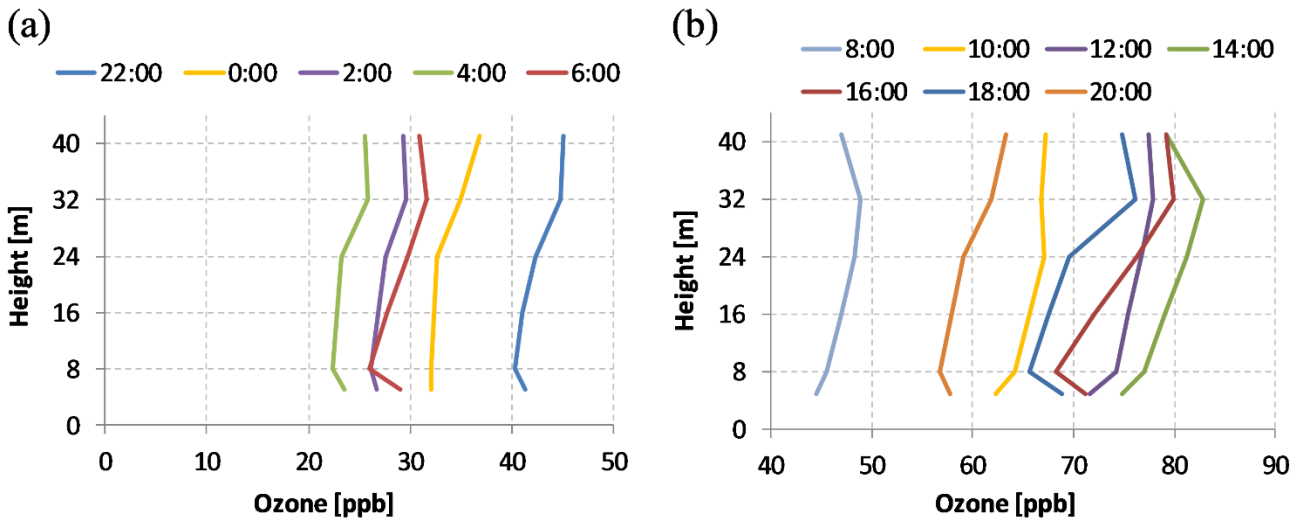

Figure 6 - Diurnal evolution of ozone concentration profiles: (a) from 22:00 to 6:00; (b) from 8:00 to 20:00. The time of the day to which measurements are referred is indicated in each figure label. The 0.15 m level has not been included here for a better visualization (ozone concentration at this level was around 10 ppb in (a) and below 25 ppb in (b)). The maximum and the minimum standard error of the half-hourly means were respectively 2.9 and 2.5 ppb for 0:00, 2.3 and 2.0 ppb for 2:00, 2.7 and 2.5 ppb for 4:00, 2.9 and 2.5 ppb for 6:00, 2.3 and 2.0 ppb for 8:00, 2.1 and 1.9 ppb for 10:00, 1.9 and 1.7 ppb for 12:00, 2.4 and 1.9 ppb for 14:00, 2.7 and 2.2 ppb for 16:00, 2.9 and 2.4 ppb for 18:00, 2.6 and 2.1 ppb for 20:00, 2.5 ppb and 1.9 ppb for 22:00.

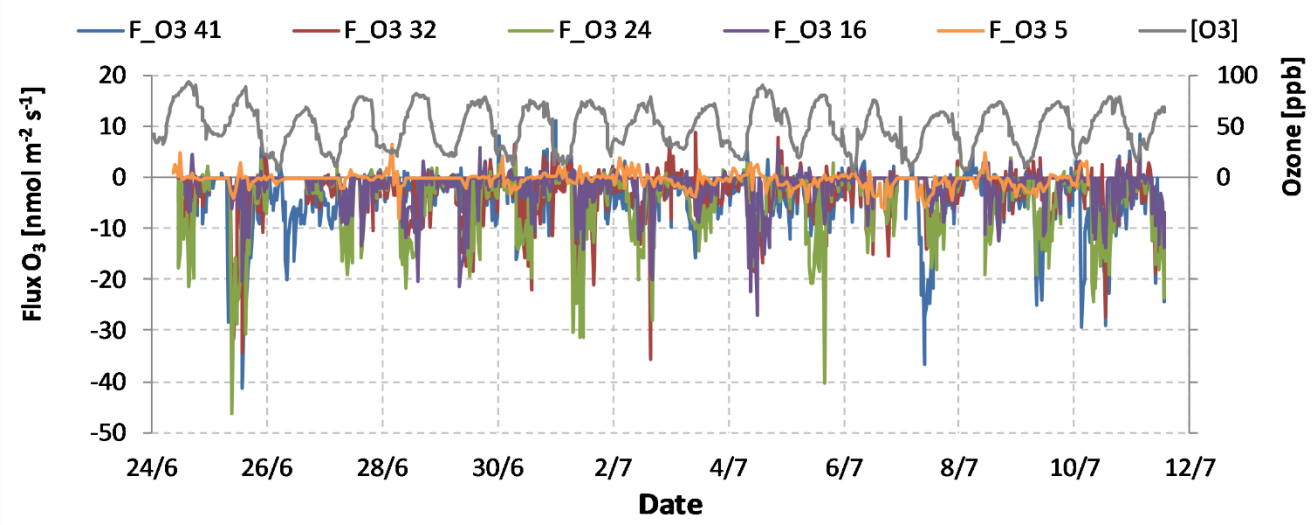

Figure 7 - Ozone fluxes at the five levels (41 m, 32 m, 24 m, 16 m and 5 m) and ozone concentration at 41 m during the "Flux Profile period".

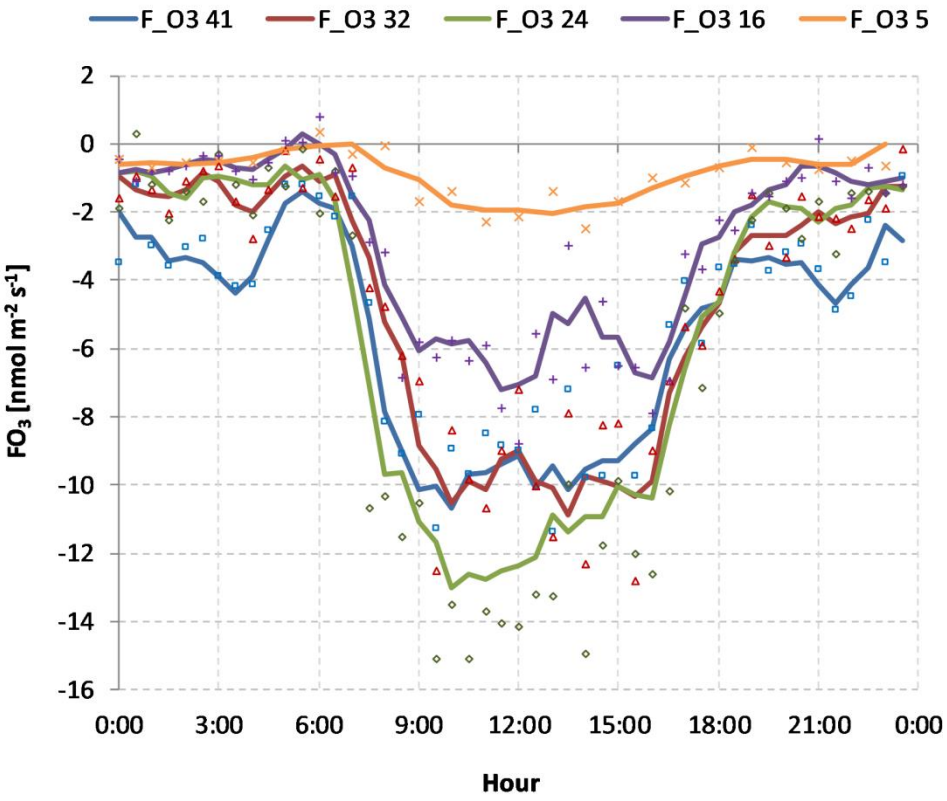

Figure 8 - Average diel courses of ozone fluxes during the "Flux Profile period" at the five levels (41 m, 32 m, 24 m, 16 m and 5 m). Dots represent half-hourly averages while lines are one hour and half running means centered on each half-hour. The maximum and the minimum standard error of the half-hourly means of O_3 fluxes were respectively 2.9 and 0.7 nmol m^{-2} s^{-1} for 41 m, 2.6 and 0.4 nmol m^{-2} s^{-1} for 32 m, 2.7 and 0.2 nmol m^{-2} s^{-1} for 24 m, 2.1 and 0.2 nmol m^{-2} s^{-1} for 16 m, 0.7 and 0.1 nmol m^{-2} s^{-1} for 5 m.

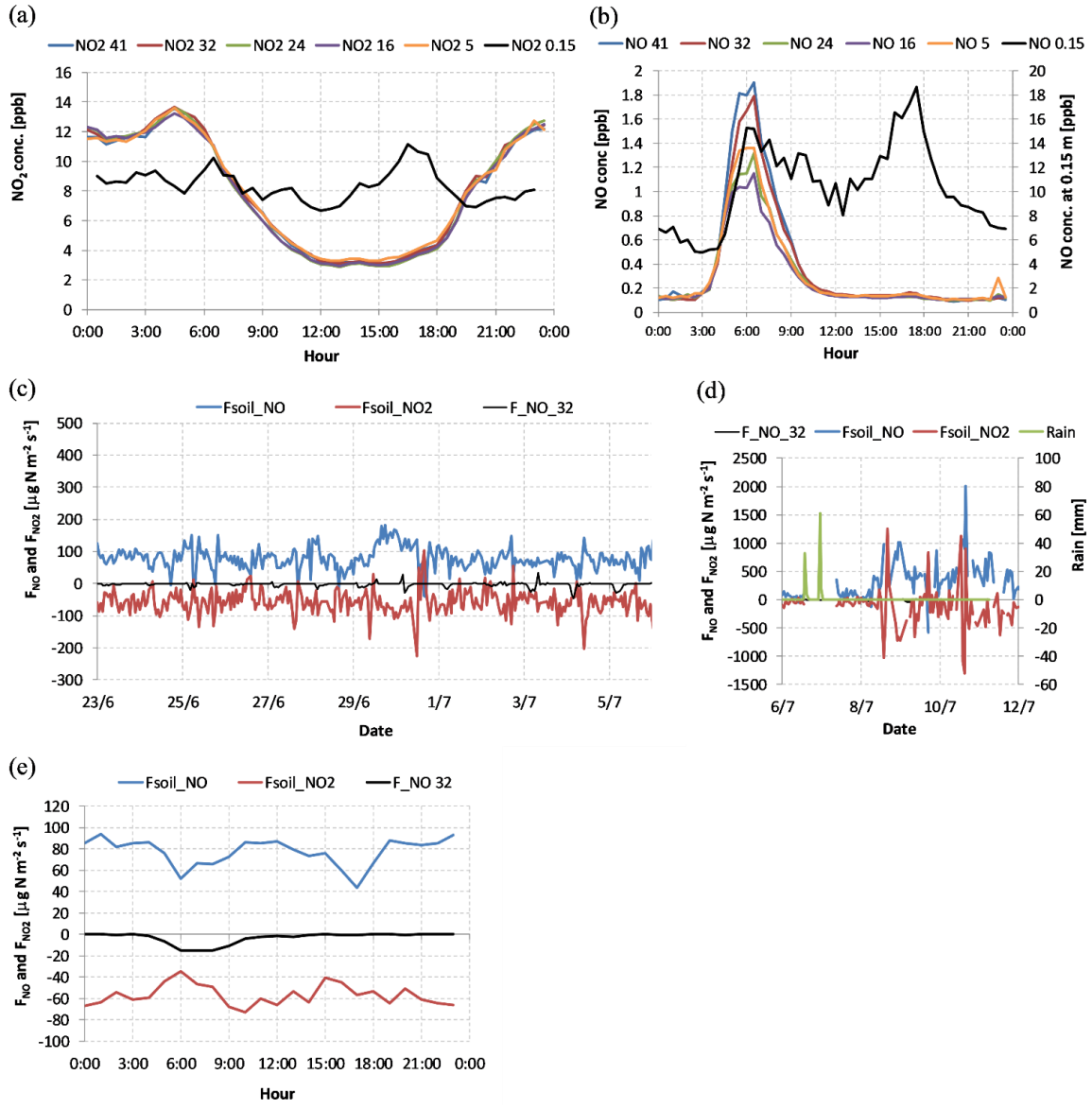

Figure 9 - NO and NO_2 concentrations and fluxes during the "Flux Profile period". (a) Average diel course of NO concentrations at the five levels (41 m, 32 m, 24 m, 16 m and 5 m); (b) Average diel course of NO_2 concentrations; c) Soil NO and NO_2 fluxes and NO fluxes at 32 m before rainfalls events; (d) Soil NO and NO_2 fluxes and NO fluxes at 32 m after rainfall events (green line); (e) Average diel course of soil NO and NO_2 fluxes and of NO fluxes at 32 m. Please, note the different scale between (c) and (d). For figure (a), the maximum and the minimum standard error of the half-hourly means of NO_2 were respectively 1.74 and 0.14 ppb for 41 m, 1.71 and 0.12 ppb for 32 m, 1.71 and 0.12 ppb for 24 m, 1.55 and 0.15 ppb for 16 m, 1.55 and 0.17 ppb for 5 m, 2.12 and 0.57 ppb for 0.15 m. For figure (b), the maximum and the minimum standard error of the half-hourly means of NO were respectively 0.45 and 0.006 ppb for 41 m, 0.41 and 0.003 ppb for 32 m, 0.41 and 0.004 ppb for 24 m, 0.34 and 0.004 ppb for 16 m, 0.34 and 0.004 ppb for 5 m, 3.11 and 0.65 ppb for 0.15 m. For figure (e) the maximum and the minimum standard error of the half-hourly means were respectively 11.0 and 3.6 µg N m^{-2} s^{-1} for F_NO soil, 16.2 and 4.2 µg N m^{-2} s^{-1} for F_NO_2 soil, 4.3 and 0.1 µg N m^{-2} s^{-1} for F_NO 32.

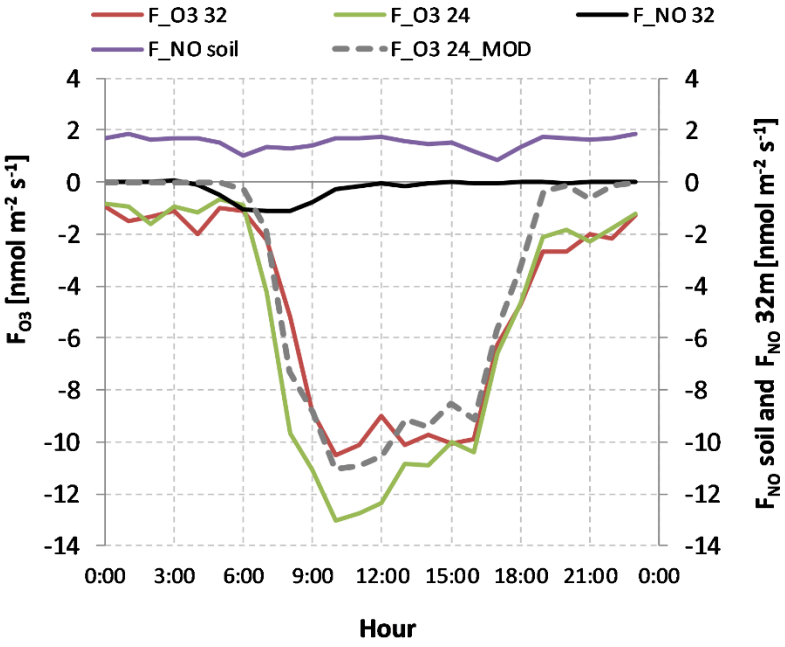

Figure 10 - Average diel course of ozone fluxes at 32 m (red line), ozone fluxes at 24 m (green line), NO fluxes at 32 m (black line) soil NO fluxes (purple line) and modified ozone fluxes at 24 m (dashed grey line). This latter takes into account the role of the NO sink.

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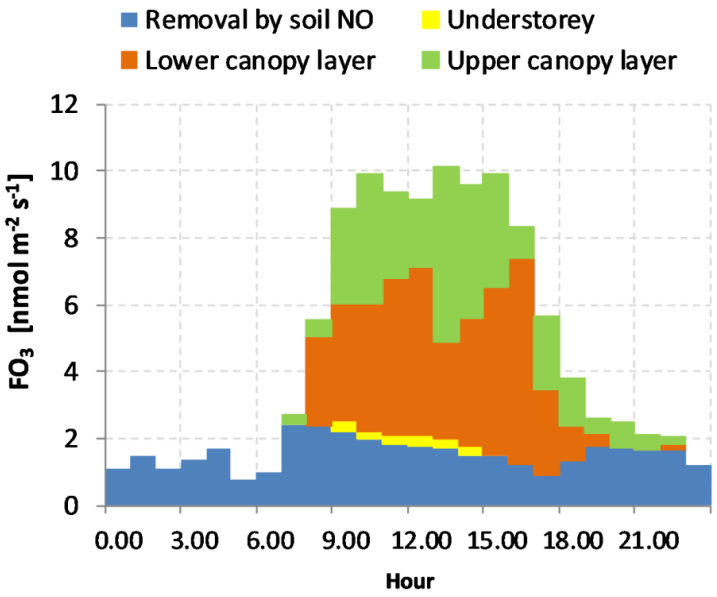

Figure 11 - Average diel course of the ozone removal by the different forest layers and by the NO emitted from the forest floor.

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Supplementary material

Table S1 - Instruments installed at each level of the tower and on the mast at 5 m a.g.l. In brackets are indicated the variable measured by each instrument and the manufacturer. (T is air temperature, RH is relative humidity, NR is net radiation, P is pressure, Rain is precipitation, SWC is soil water content, SHF is soil heat flux). The Soil dynamic chamber system is described in the methodological part.

Level / Height (m)	Ultrasonic anemometer	Fast ozone analyzer	Other fast analyzer	Slow sensors	
41	USA1 (*Metek, D*)	COFA (*Ecometrics, I*)	LI-COR 7500 (CO_2, H_2O, *Li-Cor, USA*)	HMP45	(T, RH, *Vaisala, FIN*)
				NR-lite	(NR, *Kipp & Zonen, NL*)
				BF5	(PAR,*Delta-T Devices, UK*)
				PTB101B	(P, *Vaisala, FIN*)
				Rain gauge 52202	(Rain, *Campbell Scientific, USA*)
32	HS50 (*Gill, UK*)	ROFI (*CEH, UK*)	CLD780TR (NO, *Ecophysics, CH*)	HMP45	(T, RH, *Vaisala, FIN*)
24	Windmaster PRO (*Gill, UK*)	FROM (*NOAA, USA*)	-	HMP45	(T, RH, *Vaisala, FIN*)
16	Windmaster PRO (*Gill, UK*)	COFA (*Ecometrics, I*)	-	HMP45	(T, RH, *Vaisala, FIN*)
11	-	-	-	HMP45	(T, RH, *Vaisala, FIN*)
5	R2 (*Gill, UK*)	FOS (*Sextant, NZ*)	LI-COR 7500 (CO_2, *Li-Cor, USA*)	-	
1.5	-	-	-	PT100	(T, *Campbell Scientific, USA*)
0.15	-	-	-	PT100	(T, *Campbell Scientific, USA*)
Soil	-	-	-	TDR mod 616	(SWC, *Campbell Scientific, USA*)
				HFP01SC	(SHF, *Hukseflux, NL*)
				PT100	(T, *GMR Strumenti, I*)
				Soil dynamic chamber system (*IMK-IFU, D*)	

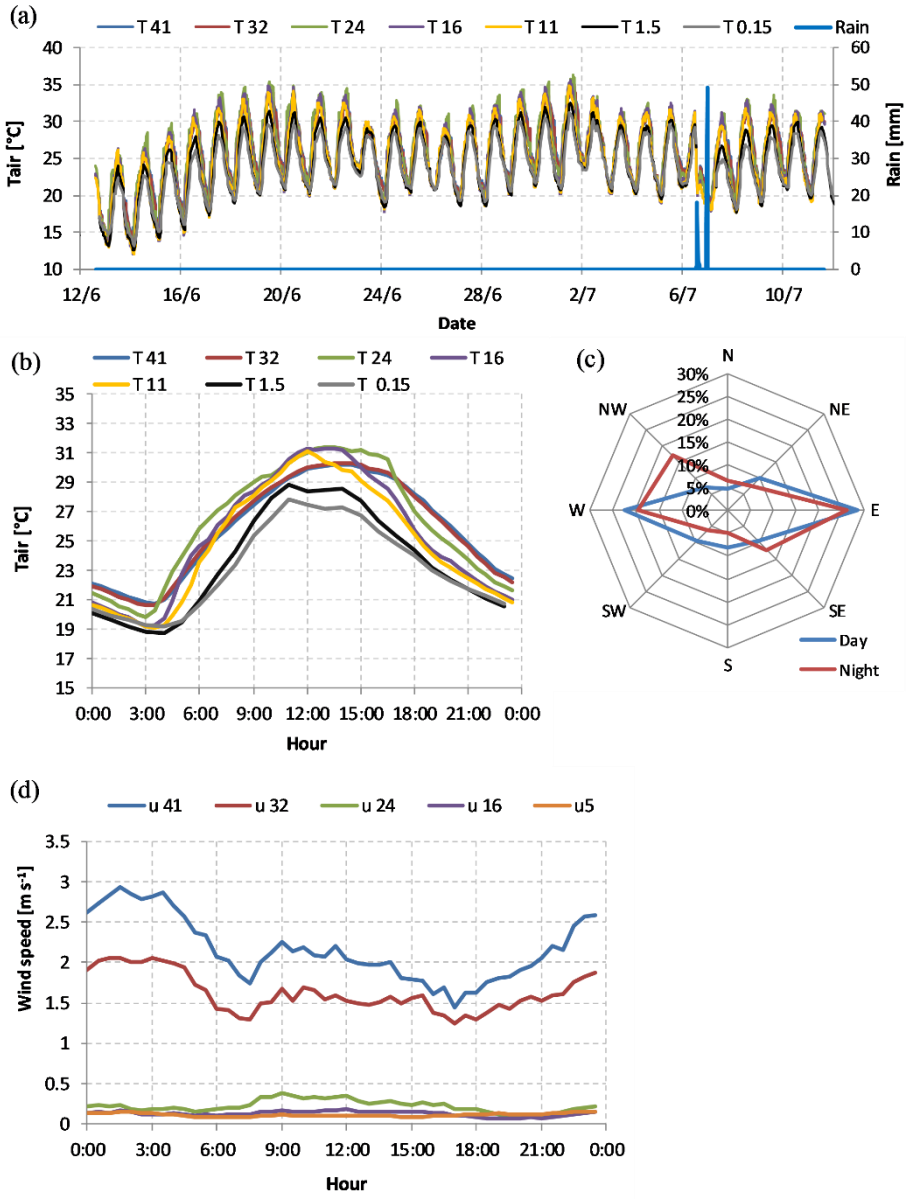

Figure S1 – (a) Rainfall amounts and temperature evolution at the seven heights. Blue lines are rainfalls. (b) Average diel course of air temperature at the seven heights. (c) Wind rose based on 41 m data, the radial axis unit indicates the percentage of the data in each direction, the blue line diurnal data, the red line nighttime data. (d) Average diel course of wind intensity at the five heights. For figures a), b), d) and e) the numbers in the curves label of the legend represent the measurement height (in meters). For figure b) The maximum and the minimum standard error of the half-hourly means were respectively 0.65 and 0.32 °C for 41 m, 0.66 and 0.33 °C for 32 m, 0.73 and 0.33 for 24 m, 0.71 and 0.31 °C for 16 m, 0.68 and 0.30 °C for 11 m, 1.10 and 0.65 °C for 1.5 m, 1.11 and 0.66 °C for 0.15 m. For figure (d) The maximum and the minimum standard error of the half-hourly means were respectively 0.32 and 0.12 m s^{-1} for 41 m, 0.28 and 0.08 m s^{-1} for 32 m, 0.05 and 0.01 m s^{-1} for 24 m, 0.02 and m s^{-1} 0.01 for 16 m, 1.11 and 0.03 m s^{-1} for 5 m.

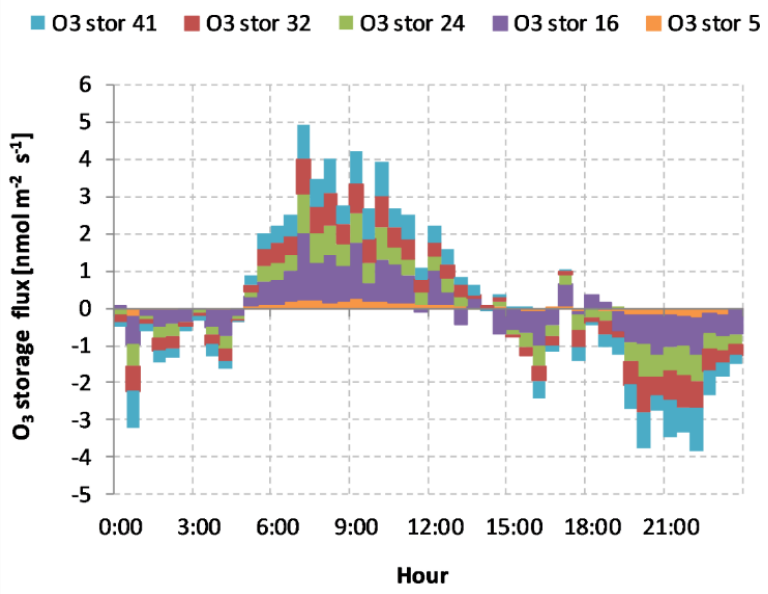

Figure S2 - Mean diel evolution of the ozone storage flux (the storage term of the Eq. 3). The contribution of the air column between adjacent flux measurement levels is indicated with a different color.

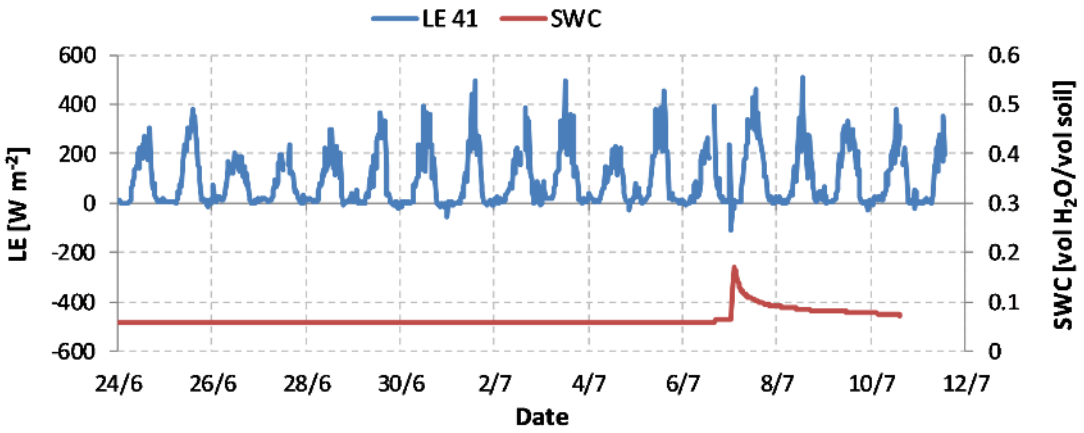

Figure S3 - Latent heat fluxes measured at the top of the tower (LE 41) and soil water content (SWC) expressed as volumetric ratio between water and soil.

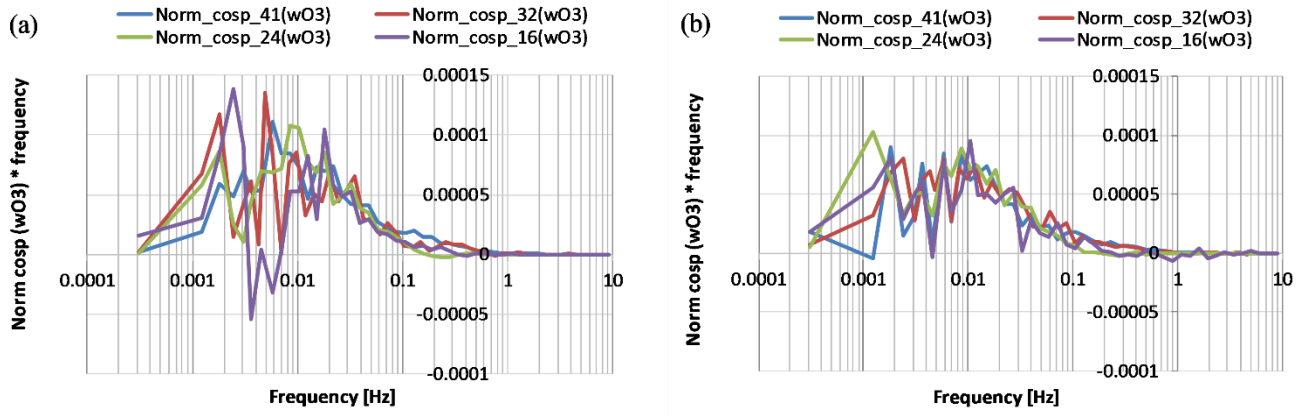

Figure S4 - Average normalized cospectra of the vertical component of the wind and ozone at 11:00 (a) and at 15:00 (b).