Authors' response document following the review process of the manuscript:

Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season

Please find below the author's response to the questions of the two anonymous referees who commented our maunscript, accompagnied by the marked-up manuscript.

Author's reply to anonymous referee #1

Reply for the revision process of the manuscript untitled "Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season" published on ACPD.

First of all, we would like to thank the referee for her/his comments and suggestions which contribute to improve the quality of this manuscript. We answered all general and specific comments point-by-point as thoroughly as possible and adapted the manuscript accordingly.

Technical comments consisted of spelling mistakes and minor phrase structure, so they did not request a detailed author's reply. Consequently, we did not include them in this document. They will of course be taken into full consideration during the manuscript revision, and the text will be corrected accordingly.

The reply document is formatted as follows:

Comment n°X where X is a number is the comment number;

PX LY corresponds to the line Y in the page X; Sec. X corresponds to the section X;

Referee comment;

Author's reply;

Author's changes in the manuscript. Original text and revised text are detailed.

Page and line indexes after each comment number, in the author's reply and after the mention "original text" refer to the discussion manuscript published in ACPD.

Page and line indexes after the mention "revised text" refer to the revised marked-up manuscript.

References used to answer the referee comments were listed in "Author's reply references". As all these references were present in the discussion paper, no additional reference will be included in the revised paper following the referee #1 comments.

General comment

The focus of this paper is to investigate BVOC exchange on a maize field via comprehensive in situ measurements so as to examine previous results and BVOC emission models. The major conclusions from the authors were that BVOC exchange fluxes in the maize field was lower considerably than those measured in other crops. As a result, a BVOC emission model created from standard emission factors seemed to overestimate BVOC emission fluxes and hence such the model should treat BVOC emissions case by case in different crops field. The authors further recommended to incorporate their SEF obtained from this field study in BVOC emission modeling. The evidence from their field study was strong and their arguments in the presentation were also reasonable. I recommend acceptance for publication in ACP after clarifying following questions.

The authors are very grateful to the referee for her/his positive comment. We adapted the manuscript following her/his questions and suggestions to make it clearer.

Specific comments

Comment n°1 (P3 Sec. 2.1.2; P5 Sec. 2.3)

I would suggest authors to give the expression of BVOC flux equation which should be the product of measured concentration and 'vertical velocity'. I would assume that '3D sonic anemometer' measures turbulent fluctuations of vertical wind, not vertical wind itself?

The 3D sonic anemometer measures the wind velocity at high frequency in 3 non parallel directions. So it gives measurements of the vertical wind speed component at high frequency; those measurements are also called instantaneous vertical wind speed w. w is then separated into two terms:

$$w = \overline{w} + w'$$

Where $\overline{w}$ corresponds to the mean vertical component of the wind speed, computed by averaging w over each half-hour, and w' corresponds to the fluctuations of the vertical wind speed component around this mean.

As this is well-known information, we will not detail this expression. However, to make the text clearer, we will explicitely write that the BVOC fluxes were calculated from the covariance between the BVOC concentration and the vertical component of the wind speed, both being measured at high frequency.

Original text (P3 L13-14): *The BVOC fluxes were computed every half-hour from high frequency vertical wind speed and BVOC concentration measurements using the disjunct eddy covariance by mass scanning (DEC-MS) technique.*

Revised text (P3 L14-15): *The BVOC fluxes were computed every half-hour using the disjunct eddy covariance by mass scanning (DEC-MS) technique, i.e. from the covariance between the vertical component of the wind speed and the BVOC mixing ratio, both variables being measured at high frequency.*

Comment n°2 (P11 L16)

Given the huge differences in normalized BVOC exchange rates among studies, we conclude [...] by normalizing T and PPFD'. Can BVOC exchange rate be normalized by solar zenith?

We used PPFD for normalisation as this is done by other authors measuring in the field (e.g. Park et al., 2014). But indeed, standard conditions defined by the up-scaling models are rather defined for particular solar zenith angle and PPFD transmission ratio (Guenther et al., 2006). We prefer to keep PPFD as the normalizing factor because we think that use of solar angle may bring uncertainties. Indeed, in Graus et al., 2013 and Das et al., 2003 articles, we did not find information about the solar angle and the PPFD transmission ratio. And we did not find enough information in those articles to estimate these values with accuracy. Consequently, we prefer keeping the normalisation by PPFD, since it is based on data given by the authors themselves, in order to rely on known values when comparing data.

Comment n°3 (P6 L9)

'According to a lower u_* threshold'. What is 'lower u_* threshold'?

The friction velocity, represented by the symbol "u_*", provides insights about the importance of turbulent processes on the site. Flux data measured by the eddy covariance technique are only valid when tracers are carried from the atmosphere to the ecosystem through turbulent exchange processes. Consequently, flux data are not representative anymore of the actual exchange between the ecosystem and the atmosphere when the turbulence is not important enough. Practically, we use u_* measurements to determine whether the turbulence is sufficient so that fluxes measured by the eddy covariance technique are valid. The value of u_* above which the turbulence is sufficient is then called the 'lower u_* threshold'.

Following your question, we will clarify in the section about friction velocity that flux data which were measured at u_* values below a certain threshold must theorically be discarded for non-soluble compounds.

Original text (P6 L9-10): *It should be noted that we did not filter BVOC fluxes according to a lower u_* threshold or to stationarity. Indeed, u_* can actually control soluble BVOC fluxes (*Aubinet et al., 2012*;Laffineur et al., 2012).*

Revised text (P6 L10-13): *It should be noted that we did not filter BVOC fluxes below a certain u_* threshold or according to stationarity. Theoretically, for non-soluble compounds, when measuring fluxes by the EC technique, flux data which were measured at u_* values below a certain threshold must be discarded (Aubinet et al., 2012). However, we did not apply this specific filtering criterion because u_* can actually control soluble BVOC fluxes (Aubinet et al., 2012;Laffineur et al., 2012).*

Comment n°4 (P10 L14 and P11)

'The methanol and acetaldehyde fluxes measured at our site were of the same order of magnitude for bare soil as for fully developed vegetation '; 'the soil was an important BVOC source and sink'. What is net flux of BVOC over bare soil?

The second sentence is not present in P11. We guess you refered to P13 L9? Using the eddy covariance technique, what we actually measure is the net flux between the ecosystem and the atmosphere. But we observed that for some compounds like methanol, most net fluxes were positive when the soil was bare. This means that for most data, there were net methanol emissions from the ecosystem to the atmosphere. From this we concluded that there were methanol sources in the ecosystem. On the opposite, for other compounds, such as acetic acid, most net fluxes were negative when the soil was bare, meaning that for most data there were net acetic acid uptakes from the atmosphere to the ecosystem. Then we concluded that there were acetic acid sinks in the ecosystem.

When we wrote 'the soil was an important BVOC source and sink', we intended to indicate that the soil was a source for some BVOC compounds while it was a sink for other BVOC compounds. The use of the terms "source" and "sink" without mentioning that they refered to different compounds was however probably confusing. In order to avoid any further confusion, we will complete this sentence.

Orignal text (P13 L9): *the soil was an important BVOC source and sink*.

Revised text (P14 L25-26): *the soil was an important methanol and acetaldehyde source, and an important acetic acid sink*.

References to author's reply to referee #1

Aubinet, M., Vesala, T. and Papale, D.: Eddy covariance a practical guide to measurement and data analysis, Springer, Dordrecht; New York., 2012.

Das, M., Kang, D., Aneja, V. P., Lonneman, W., Cook, D. R. and Wesely, M. L.: Measurements of hydrocarbon air-surface exchange rates over maize, Atmos. Environ., 37(16), 2269–2277, 2003.

Graus, M., Eller, A. S. D., Fall, R., Yuan, B., Qian, Y., Westra, P., de Gouw, J. and Warneke, C.: Biosphere-atmosphere exchange of volatile organic compounds over C4 biofuel crops, Atmos. Environ., 66, 161–168, 2013.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I. and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6(11), 3181–3210, doi:10.1029/2003GL017336; Adams, J., Constable, J., Guenther, A., Zimmerman, P., An estimate of natural volatile organic compound emissions from vegetation since the last glacial maximum (2001) Chemosphere- Global Change Science, 3, pp. 73-91; (1998) Global Change Scenarios of the 21st Century. Results from the IMAGE 2.1 Model, p. 296. , Alcamo, J., Leemans R., and Kreileman, E. (Eds.):

Pergamon & Elseviers Science, London; Alessio, G.A., De Lillis, M., Fanelli, M., Pinelli, P., Loreto, F., Direct a, 2006.

Laffineur, Q., Aubinet, M., Schoon, N., Amelynck, C., Müller, J. F., Dewulf, J., Van Langenhove, H., Steppe, K. and Heinesch, B.: Abiotic and biotic control of methanol exchanges in a temperate mixed forest, Atmos. Chem. Phys., 12(1), 577–590, doi:10.1016/j.ijms.2004.08.012, 2012.

Park, J. H., Fares, S., Weber, R. and Goldstein, A. H.: Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux-gradient similarity methods, Atmos. Chem. Phys., 14(1), 231–244, doi:10.5194/acp-9-5505-2009, 2014.

Author's reply to anonymous referee #2

Reply for the revision process of the manuscript untitled "Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season" published on ACPD.

First of all, we would like to thank the referee for her/his comments and suggestions which contribute to improve the quality of this manuscript. We answered all general and specific comments point-by-point as thoroughly as possible and adapted the manuscript accordingly.

Technical comments which consisted of spelling mistakes or minor phrase structure were not included in this document, as they did not request a detailed author's reply. They will of course be taken into full consideration during the manuscript revision, and the text will be corrected accordingly. Technical comments which requested some author's reply were discussed after specific comments.

The reply document is formatted as follows:

Comment n°X where X is a number is the comment number;

PX LY corresponds to the line Y in the page X; Sec. X corresponds to the section X;

Referee comment;

Author's reply;

Author's changes in the manuscript. Original text and revised text are detailed.

Page and line indexes after each comment number, in the author's reply and after the mention "original text" refer to the discussion manuscript published in ACPD.

Page and line indexes after the mention "revised text" refer to the revised marked-up manuscript.

References used to answer the referee comments were listed in "Author's reply references". As these references were present in the discussion paper or were not added in the revised texts, no additional reference will be included in the revised paper following the referee #2 comments.

General comment

This study reports new measurements of BVOC fluxes over a maize field in Belgium using eddy covariance. The authors are the first (to their knowledge) to observe a full growing season, and also the first to measure at a European site, making this data set a valuable addition to the extremely limited database of BVOC flux observations in maize fields. Compared to past cropland studies, including two American-based maize studies, they observed similar BVOC composition – methanol (dominant), acetic acid, acetone, acetaldehyde, terpenes – but concentrations were significantly lower in the present study. The emission factors prescribed for crops, as used in BVOC emission models, were higher than those estimated from the field measurements in this study. From these results, the authors conclude that BVOC exchanges from maize vary regionally around the world, and that emission factors in models should account for this variability. The emission factors estimated in this study are recommended as representative of C4 crops in north-western Europe. With data for the full growing season, the authors were able to quantify the relative contributions of soil and plant to BVOC fluxes, finding that the soil (bare soil in particular) contributed about as much as vegetation. This study, appropriate for ACP, makes a substantial contribution to the sorely limited observational record of BVOC fluxes in the ever-growing maize landscape. The purpose and goal is well articulated with strong motivating support. The methods are complete and clearly described. The conclusions drawn from the results follow logically, though may be overstated given still limited data and large uncertainties. Overall, the manuscript is well-written and merits publication in ACP provided the following comments are considered.

The authors are very grateful to the referee for her/his positive comment. We adapted the manuscript following her/his questions and suggestions to make it clearer, and we moderated some conclusions following her/his comments.

Specific comments

Comment n°1 (P2 L13 to P2 L 17)

What is the relative contribution from crops relative to other biogenic VOC sources (e.g., forests)? Any estimates on maize specifically? Though corn covers a large landscape, are emission rates large enough to significantly contribute to the global VOC budget?

Crops are considered by up-scaling models (Guenther et al., 2012) as smaller BVOC emitters than forests for terpenes, but as equal OVOC emitters.

At our knowledge, the only BVOC exchanges rates estimates available for maize come from Graus et al., 2013, Das et al., 2003 and this study. Das et al., 2003 concluded that maize is a major BVOC source and could significantly contribute to the air quality in regions where it is widely cropped, whereas Graus et al., 2013 concluded that maize contribution to air quality was small. On our site, we observed that maize was a small BVOC exchanger in comparison with other crops and grasses, thereby suggesting a negligible contribution of maize to air quality through BVOC exchanges.

However, to our opinion, evaluating the actual corn influence on the global BVOC budget remains currently very uncertain. First, there have been few studies dedicated to that crop and the observed BVOC exchanges rates strongly differed among studies. Second, there are strong differences in maize phenology and in maize growing season length among world regions. Consequently, the BVOC maize budget over its growing season may vary strongly among world regions. Therefore, before being able to answer the question, more long-term measurements studies focusing on maize should be conducted in different parts of the world to estimate the BVOC budget estimation in each region.

Comment n°2 (P2 L13 to P2 L19)

What did Das et al. and Graus et al. find? (i.e., the baseline knowledge going into this study)

Das et al., 2003 found high methanol and acetone emissions from maize and suggested that maize could play a great role in atmospheric chemistry in regions where maize is abundantly cropped, like the Corn Belt in USA.

Graus et al., 2013 identified some compounds emitted or taken up by the maize, and estimated the maize emission rate per liter of produced bio-ethanol. They concluded that maize did not play a great role in the atmospheric chemistry. The BVOC exchange rates they observed were lower than those observed by Das et al., 2003; they suggested a potential leaf age effect on emissions to explain those differences.

We did not mention all these findings in the "Introduction" section of the manuscript because we discussed them in the "Result and discussion" parts. Following your question, though, we will introduce them in the "Introduction" section in order to provide insights about the "baseline knowledge" to the reader.

Original text (P2 L13 to P2 L19): *So far as we know, only two BVOC measurement studies have dealt with maize (Das et al., 2003; Graus et al., 2013) […] In addition, both maize studies were conducted over only a few days and under poorly contrasted weather conditions, and were thus unable to evaluate the relative effects of climate and phenology on BVOC exchanges. Knowledge about BVOC exchanges from maize therefore remains very limited.*

Revised text (P2 L13 to P2 L24): *So far as we know, only two BVOC measurement studies have dealt with maize (Das et al., 2003; Graus et al., 2013) […] Graus et al., 2013 determined the BVOC exchange composition of maize leaves, and estimated the maize BVOC budget by up-scaling and extrapolating the BVOC fluxes they*

measured to the whole growing season. Das et al., 2003 found large methanol and acetone emissions from maize and suggested that that crop could play an important role in the atmospheric chemistry in regions where it is widely present, e.g. the Corn Belt zone in USA.

However, both studies were conducted over only a few days and under poorly contrasted weather conditions. Consequently, they were unable to evaluate the relative effects of climate and phenology on BVOC exchanges, so that the current estimated maize BVOC budget is uncertain. Knowledge about BVOC exchanges from maize therefore remains very limited.

Comment n°3 (P2 L25)

Define "standard"

Standard conditions refer to the standard conditions defined by up-scaling models. More particularly, we relied on the standard conditions described in Guenther et al., 2006. This will be explicitely mentioned in the revised manuscript.

Original text (P2 L25): *What quantity of BVOCs is exchanged in a maize field under standard environmental conditions?*

Revised text (P2 L30-32): *What quantity of BVOCs is exchanged in a maize field under the standard environmental conditions (standard conditions correspond to the environmental conditions defined for the MEGAN up-scaling model in Guenther et al., 2006)?*

Comment n°4 (P3 L26)

Replace "a few" with a numeric range, if possible.

This will be done in the revised manuscript version.

Original text (P3 L26): *In order to prevent water vapour condensation in the main sampling line, […], the sampling line was thermally insulated and heated a few degrees above ambient temperature.*

Revised text (P3 L28): *In order to prevent water vapour condensation in the main sampling line, […], the sampling line was thermally insulated and heated on average 2.6°C above the ambient temperature.*

Comment n°5 (P7 L3)

Combine with previous paragraph.

This will be done in the revised manuscript version.

Comment n°6 (P8 L26 and P8 L28)

What are "normal" (L26) and "natural" (L28) weather conditions for this area?

Normal conditions are defined by the Royal Meteorological Institute of Belgium. They correspond to averaged conditions observed at the meteorological station of Uccle (Belgium) over a period of 30 years (1981-2010). The "normal" mean temperature in Belgium is 3.6°C, 10.1°C, 17.5°C and 10.9°C while the "normal" precipitation is 220.5 mm, 187.8 mm, 224.4 mm and 219.9 mm for winter, spring, summer and fall, respectively (*Résumé climatologique de l'année 2012* published on the RMI website: http://www.meteo.be/meteo/view/fr/10275209-2012.html). These conditions will be mentioned in the revised manuscript.

By the term "natural conditions", we mean environmental conditions that occur under real field conditions, in contrast to lab conditions or cuvette conditions. We will replace this term by "real" to be less confusing.

Note that, following the comments n°12 and 13, the text in the Sec. 3.2 was modified and the section was moved after the Sec 3.5.

Original text (P8 L26): *The weather conditions during the study were among normal for the time and place (Royal Meteorological Institute, Belgium).*

Revised text (P14 L5-9): *The weather conditions during the study were normal for the time and place (normal conditions are defined by the Belgian Royal Meteorological Institute by averaging records taken in Uccle, Belgium over the period 1981-2010. It corresponds to 3.6°C, 10.1°C, 17.5°C and 10.9°C and to 220.5 mm, 187.8 mm, 224.4 mm and 219.9 mm cumulated precipitation in winter, spring, summer and fall, respectively).*

Original text (P8 L28): *The maize field grown at LTO was thus well representative of the fields of maize grown under natural weather conditions […]*

Revised text (P14 L10): *The maize field grown at LTO was thus well representative of the fields of maize grown under real conditions […]*

Comment n°7 P9 L22

Do plants take up monoterpenes? Are they not primarily emitted? Perhaps downward flux doesn't necessarily signify uptake in this case?

Plants are mostly known to emit monoterpenes, but it has been demonstrated that some nonemitting plant species were also able to take up terpenes (Noe et al., 2008). Furthermore, significant monoterpenes deposition has also been observed at ecosystem-scale on mountain grassland (Bamberger et al., 2011). As a result, the occurrence of monoterpenes uptakes on our site is not something aberrant.

Then, we did not evaluate whether maize actually consumed these monoterpenes, or if there were other monoterpenes sinks in our ecosystem. This is the reason why we mentioned "monoterpenes uptakes" but never told about "plant monoterpenes uptakes" in the discussion manuscript.

However, in order to avoid any further confusion, we will specify that the uptakes were observed between the atmosphere and the field and not between the atmosphere and the maize itself.

Orginal text (P9 L22): *Significant emissions were found for both compounds during all stages, apart from R2, during which uptake of monoterpenes was observed instead.*

Revised text (P10 L1-2): *Significant emissions were found for both compounds during all stages, apart from R2, during which the monoterpenes have been taken up by the maize field ecosystem.*

Comment n°8 (P9 L23 to P9 L26)

Consider revising these paragraph breaks.

We suggest moving the L25 to L26 at the end of the Sec. 3.3.

Orginal text (P9 L25 to P9 L26): *Small but significant benzene and toluene uptake was observed for all phenological stages. Each compound contributed up to7% to the total BVOC exchange.*

Besides, each investigated BVOC showed different seasonal dynamics, indicating that the sources, sinks strength and/or exchange mechanisms differed for each compound.

The BVOC exchange composition observed at LTO matched those observed on diverse croplands and grasslands fairly well […] In addition, our observations disagree with the hypothesis proposed by White et al. (2009) that maize could be an important toluene source.

Revised text (P10 L3 to P10 L18): *Small but significant benzene and toluene uptake was observed for all phenological stages. Each compound contributed up to 7% to the total BVOC exchange.*

The BVOC exchange composition observed at LTO matched those observed on diverse croplands and grasslands fairly well […] In addition, our observations disagree with the hypothesis proposed by White et al. (2009) that maize could be an important toluene source.

Lastly, each investigated BVOC showed different seasonal dynamics. This indicates that the sources, sinks strength and/or exchange mechanisms differed for each compound.

Comment n°9 (P9 L27 to P10 L4)

These lines seem to belong in Sec 3.5.1.

The lines P9 L27 to P10 L4 intend to compare the BVOC composition between studies in a qualitative way (this is: what was emitted? What was taken up? Which were the major compounds? Did the maize field exchange the same compounds as other grassland and cropland...).

In contrast, the Sec 3.5.1. intends to compare the BVOC between studies in a quantitative way (this is: is the BVOC exchange rate similar to other studies ?).

We prefer keeping both discussions separated because they lead to different conclusions: qualitatively, the BVOC composition found at LTO is similar to other studies, but quantitatively, the exchanges rates were lower.

However, to clarify this distinction, we will indicate the terms “quantitative” and “qualitative” in the text or section title when relevant.

Original text (P9 L1): *BVOCs exchanged at LTO*

Revised text (P9 L11): *BVOCs exchange composition at LTO and qualitative comparison with other crops*

Original text (P9 L27): *The BVOC exchange composition observed at LTO matched those observed on diverse croplands and grasslands fairly well.*

Revised text (P10 L7): *Qualitatively, the BVOC exchange composition observed at LTO matched those observed on diverse croplands and grasslands fairly well.*

Original text (P10 L27): *Comparison of BVOCs exchanged at LTO with other maize BVOC studies*

Revised text (P11 L10): *Quantitative comparison of BVOCs exchange rates at LTO with other maize BVOC studies*

Original text (P11 L22): *Comparison of BVOCs exchanged at LTO with other crops*

Revised text (P12 L3): *Quantitative comparison of BVOCs exchange rates at LTO with other crops*

Comment n°10 (P11 L1 to P11 L2)

The maize field area seems relatively small (155 x 255 m, Pg 3, L4) and makes me wonder about the possibility of advection bringing in low-VOC air, thus resulting in lower VOC than other studies. Are the field sites of Das et al. and Graus et al. much larger and thus less influenced by outside air? Any correlations with wind direction that suggest advective influences? How does the flux footprint at the measurement heights on P3 L17-18 compare with size of the field (185 x 255 m) on P3 L4? Of course, if there is an advective signal, this puts into the question the validity of the horizontal homogeneity assumption and challenges whether this is representative of north-western Europe or "ecosystem-scale."

First of all, we apologize having misprinted the field dimension. The actual maize field is approx. 398*255 m (10.1 ha) instead of 185*255 m. The coordinates of the maize field used in all calculations were correct, though, therefore not jeopardizing the outputs of this manuscript. The field dimension will be corrected in the revised manuscript.

When talking about "lower VOC", we did not understand whether you were refering to lower VOC concentration or to lower VOC fluxes. As lower ambient VOC concentration would have resulted in higher VOC emissions from our site in comparison with other maize studies, accordingly to Niinemets et al., 2014, whereas the opposite trend was observed, we assumed that you were refering here to the possibility of underestimated VOC fluxes caused by advection processes.

Then, we are quite confident that the low measured BVOC fluxes did not result from a methodological bias induced by advective processes.

First, for footprint calculations, the variations of the displacement height (estimated as 2/3 of the maize height, the latest being estimated on a daily basis, Sec. 2.1.3) and of the mast height over the maize growing season were taken in account. Consequently, changes in footprint due to mast elevation and maize growth were taken in account. It resulted that when the maize was high (stages R1 and R2), only 7% of the data had a maize field contribution lower than 90%. This suggests that most of the time, BVOC fluxes that were measured were actually well representative of the maize field.

Second, we did not observe any influence of the wind direction that could have indicated advective processes for any compound, neither for concentration nor for flux.

Thirdly, the site is known to be poorly affected by advection processes as it is almost flat (slope of 1.2%) and located on a plateau at a large scale (no hill or mountain near the site).

Lastly, the data used to compare our exchanges with those of the other maize studies were selected to represent exchanges under warm and light conditions. Under such conditions, the turbulence is well developped, so the advective processes should be minor and thereby cannot explain the lower exchanges observed on our site in comparison with other studies.

Original text (P3 L4): *The study was carried out on a silage maize (Zea mays L., varieties Prosil and Rocket) field about 185 x 255 m […]*

Revised text (P3 L4): *The study was carried out on a silage maize (Zea mays L., varieties Prosil and Rocket) field about 398 x 255 m […]*

Comment n°11 (P12 L27)

What are the "default values" and what are they based on?

A "default" value of 2.0 µg g^{-1}DW h^{-1} was assigned for all OVOC when there is no available emission factor for a compound and for a plant species (Karl et al., 2009). This value was taken from the "default" value assigned in the NatAir database (Steinbrecher et al., 2009) when there is not enough data available to determine experimentally an emission factor. Steinbrecher et al., 2009 indicated that they based their OVOC values on Seco et al., 2007, which reported OVOC fluxes measurements from trees ranging from 0.2 to 4.8 µg $g^{-1}h^{-1}$, and on the emission factors used in the MEGAN database (Guenther et al., 2006).

Following your question, we will specify that the "default" values are values based on the emission factors determined from other ecosystems instead of actual OVOC fluxes measurements. Note that, following the comments n°12 and 13, the text was moved after the Sec 3.5.

Original text (P12 L27): *Karl et al. (2009) noticed, however, that the SEFs given for croplands are default values because of the lack of information for those ecosystems.*

Revised text (P13 L32): *Karl et al. (2009) mentioned, however, that, because of the lack of information for those ecosystems, the SEFs for croplands are default values, i.e. values assigned by databases and up-scaling models from SEF observed on other ecosystems.*

Comment n°12 (P13 L1 to P13 L2) and

Comment n°13 (P13 L24) – answered together with Comment n°12

Are you comfortable advising modelers to use these SEFs given all the uncertainties? Given the limited data, and the large discrepancies with the two studies cited here, I feel more data is needed to validate the SEFs found here before they are deemed a reliable representation of C4 crops in NW Europe. Instead, you might advise modelers to be wary that current SEFs may be overestimates and advise them to include that potential caveat in their studies.

Again, are you confident enough in your SEFs to say they "should" be used to represent C4 crop PFT?

The best method would actually rely on a lot of BVOC data taken at similar (for repeatability) and various (for a global representativity) locations for the same plant species when assigning emission factors in up-scaling models. However, despite the huge efforts made by BVOC measurers from these last decades, there are still a lot of plant species for which few BVOC fluxes information is available. As a result, modelers have to assign emission factors relying on a few species.

Particularly, only two crop studies were considered by Stavrakou et al., 2011 when assigning methanol emission factors: Schade and Custer, 2004 and Warneke et al., 2002. The first one was done on bare soil, the other one focused on alfalfa during harvest, so when emissions should be much higher than the basal emissions, according to what has been observed on diverse crops and grasses studies. Consequently, to our opinion, the current methanol emission factors assigned for agricultural ecosystems are not representative of the actual methanol emissions from croplands, and even less for C4 crops.

On the one hand, we are confident that maize can be used alone to represent the whole C4 crops PFT in NW Europe, because it represents 99% of the total C4 crop cultivated area in that region (percentage determined by comparing the harvested surface of diverse C4 crop species, data taken from FAOSTATS for the year 2015). This may be not true for other regions where other C4 crop species are also abondant, but we did not conclude about the other regions in this manuscript.

On the other hand, we are aware that the values we propose come from one site only and need thus to be cross-validated by other studies performed on sites similar to LTO, particularly when considering the variability in BVOC exchanges rates among studies. However, as specified in the Sec. 3.1, the maize field was grown at LTO for production purposes, so the common management practices for this region were used, and the weather conditions recorded on our site were among normal conditions for Belgium. As a result, we argue that the maize field grown at LTO behaved as a common maize field grown in this region, so that the measured BVOC exchanges rates should be representative of a maize field grown under normal weather conditions in the NW region. Then, in a study performed in controlled lab conditions and focusing on maize of the same variety as the one cropped at LTO (Mozaffar et al., 2016, submitted to AE), the methanol exchange rates were of the same range as the methanol exchange rates observed in this study, thereby validating somehow the exchanges rates we proposed. Thirdly, very pragmatically, these values are currently the only ones available for maize in NW Europe. We argue thus that they should be more representative of the actual BVOC exchanges rates from maize in this region than the "default" values assigned from other crops or other ecosystems, even if their extrapolability has not been validated yet. This is why we advised the use of our factors for the C4 crop PFT in the NW region, by clearly mentioning that our results were not extrapolable to other regions or global scale.

However, following the comment n°13, we realized that we did not discuss the extrapolability of our results clearly enough, so that we did not point out that additional studies should be performed in the NW region to validate it at a regional scale, given the large discrepencies in BVOC exchange rates among maize studies. Moreover, the discussion about the representativity of the maize field grown at LTO appeared at the beginning

of the Result and Discussion part (Sec 3.1), whereas the discussion about the use of SEFs measured at LTO by up-scaling models appears at the end of the Result and Discussion part (Sec 3.5). The link between both sections was thus probably not straightforward.

We will clarify this by moving the Sec. 3.1 after the Sec. 3.5. Then, in this section, we will discuss the extrapolability of our emission rates at a regional scale, their use in up-scaling models, and adapt the section "Conclusions" accordingly. The abstract being already more moderate than the "Conclusions" section, with the word "suggest" being employed instead of "advise" or "indicate", we did not modified it. Thirdly, following the comment n°13, we will specify everywhere that we restrict the extrapolability of our results to the C4 crops PFT in the NW European region and not to all agricultural lands or the global scale.We will also restructure some paragraphs of the "Conclusion" section (P13 L23 to P14 L3) in order to make it clearer and to avoid repetitions with the revised last section of the discussion. We will however pay attention to keep the original sense of the conclusion at the exception of the use of our SEFs by up-scaling models.

Original text (P8 L23 to P8 L30 and P12 L25 to P13 L2):
The maize variety grown at LTO was intended for silage (livestock feed) production purposes and the management practices commonly used in this region for this type of crop were thus applied. The weather conditions during the studynwere among normal for the time and place (Royal Meteorological Institute, Belgium). The BVOC composition, flux range and budget presented in this study are therefore representative of the fields of maize grown under natural weather conditions in the Hesbaye region of Belgium and, by extension, in north-western Europe, where maize is grown under similar pedo-climatic conditions (i.e., temperate maritime climate and silt or sandy-loamy soils) and for similar production purposes (i.e., farms with crops and livestock).

The SEF values used by up-scaling models rely on diverse BVOC flux measurement studies (see Guenther et al., 2012 and Lathière et al., 2006 for details). In particular, for Europe there is a comprehensive SEF inventory (Karl et al., 2009). Karl et al. (2009) noticed, however, that the SEFs given for croplands are default values because of the lack of information for those ecosystems. With regard to methanol, Stavrakou et al. (2011) used - only one SEF derived from alfalfa for all croplands, although this species accounts for only 1% of the cultivated area worldwide (FAOSTATS). In contrast, maize is the second most important crop and the most important C4 crop worldwide, accounting for 13 and 67% of the total cultivated area, respectively. In north-western Europe, it accounts for 12 and 99% of the total / C4 crop cultivated area, respectively. The C4 crop plant functional type considered by models can therefore be realistically equated with maize, especially in our region.
We would therefore advise modellers to use the SEFs reported in this study when estimating BVOC exchanges from C4 crops in north-western Europe.

Revised text (P13 L19 to P14 L18):

Implications for BVOC exchanges from croplands and use of SEFs measured at LTO by up-scaling models

Given the discrepancies between the SEF values used by the up-scaling models for the C4 crops and those measured on maize at LTO, one may wonder to which extent these differences could affect the estimations of cropland BVOC budget, and whether the SEF obtained in this study should be implemented in the models to represent (C4) croplands.

First, maize is the second most important crop and the most important C4 crop worldwide (FAOSTATS), accounting for 13 and 67% of the total cultivated area, respectively. Particularly, in north-western Europe, it accounts for 12 and 99% of the total / C4 crop cultivated area, respectively. This crop is thus of major importance when evaluating the importance of agricultural ecosystems. Particularly, the C4 crop plant functional type can be realistically equated with maize in NW Europe.

Then, despite the importance of maize in agricultural lands, SEF currently estimated for croplands (and also C4 croplands) do not rely on BVOC measurements performed on maize. For example, with regard to methanol, Stavrakou et al. (2011) used only one SEF derived from alfalfa for all croplands, although this species accounts for only 1% of the cultivated area worldwide (FAOSTATS). In particular, for Europe there is a comprehensive

SEF inventory (Karl et al., 2009). Karl et al. (2009) mentioned, however, that, because of the lack of information for croplands, the SEFs for those ecosystems are default values, i.e. values assigned by databases and up-scaling models from SEF observed on other ecosystems. Consequently, the SEF currently assigned for the C4 crop PFT are in fact not representative of the actual C4 crops SEF.

In this study, we provided SEF estimations from a maize field relying on measurements performed under real field conditions. The maize variety grown at LTO was intended for silage (livestock feed) production purposes and the management practices commonly used in this region for this type of crop were thus applied. In addition, the weather conditions during the study were normal for the time and place (normal conditions are defined by the Belgian Royal Meteorological Institute by averaging records taken in Uccle, Belgium over the period 1981-2010. It corresponds to 3.6°C, 10.1°C, 17.5°C and 10.9°C and to 220.5 mm, 187.8 mm, 224.4 mm and 219.9 mm cumulated precipitation in winter, spring, summer and fall, respectively). The maize field grown at LTO was thus reasonably representative of the fields of maize grown under real conditions in the Hesbaye region of Belgium and, by extension, in NW Europe, where maize is grown under similar pedo-climatic conditions (i.e., temperate maritime climate and silt or sandy-loamy soils) and for similar production purposes (i.e., farms with crops and livestock).

Therefore, in the absence of any robustly established SEF for C4 crop so far, we would suggest modelers to use the SEF determined at LTO for the C4 crop PFT instead of the current estimations. As the BVOC exchange rates measured on our site strongly differed from other maize studies performed on other sites, though, we also want to make them aware that SEF obtained in this study are likely not valid outside NW Europe and should therefore not be used in other world regions. We recommend additional BVOC measurement studies performed on maize fields located in other NW European sites to validate the spatial extent of the values proposed in this paper.

Original text (P13 L20 to P14 L14):
Our results showed, however, that the normalization of BVOC exchanges by T, PPFD and phenology was not enough to explain the huge difference in BVOC exchange rates among maize studies. This indicates that SEFs cannot be extrapolated to different world regions.

In this study, we proposed that our SEF values should be used for the C4 crop plant functional type. We also provided an estimation of the BVOC exchange budget of a maize field over a whole growing season. We argued that our values could be extrapolated to maize fields grown under similar agronomical and pedo-climatic conditions to those at LTO (i.e., in northwestern Europe).

With the SEF values observed at LTO being far lower than those currently used by models, especially for terpenes, and with maize being the second most important cultivated crop, our results showed a reduced importance of BVOC emissions from croplands in our region. This indicates that deforestation and afforestation should result in even larger terpenes emission changes than currently estimated, especially in areas where maize production is important.

Specific maize SEF and BVOC exchange budget values should be obtained for other important agronomic regions by conducting long-term BVOC measurement studies similar to this one and by using the maize varieties and management practices commonly used in these regions. BVOC exchange mechanisms between maize fields and the atmosphere also need to be better understood in order to identify the reasons for the huge differences in normalized BVOC exchange rates observed among maize studies and to discover if they behave according to up scaling model algorithms 5 beyond the standard conditions or to known OVOC exchange mechanisms (Niinemets et al., 2014). Given that each investigated compound had different exchange dynamics, mechanisms need to be evaluated separately for each compound, particularly for methanol on the LTO observations.

Finally, the BVOC exchange rates observed in this study were smaller than those observed in other crop studies in Europe, suggesting that maize is a small BVOC exchanger crop in this region. Few BVOC measurement studies have been conducted under natural conditions in Europe on cropland ecosystems, however, and even less if we confine the comparison to northwestern Europe. Future research should thus focus on other crops in order

to extend the comparison. In particular, BVOC exchanges should be measured for winter wheat because, in terms of cultivated area, it is the most important crop in our region (FAOSTATS).

Revised text (P15 L5 to P15 L20 and P15 L32 to P16 L10):
Our results showed that the normalization of BVOC exchanges by T, PPFD and phenology was not enough to explain the huge difference in BVOC exchange rates among maize studies in different parts of the world. Modelers should therefore be aware of the current large uncertainties in BVOC exchange rate for this crop.

However, given (i) the good representativity of the maize field grown at LTO in terms of management practices and of weather conditions typical of NW Europe, and (ii) the current absence of maize in SEF assignments for C4 crops by models, which contradicts with the major importance of that crop for that PFT, we would still suggest modelers using SEF values proposed in this paper for NW Europe. The lower SEF values observed on our site in comparison with those currently used by up-scaling models – in particular for terpenes- would then suggest an over-estimation of BVOC exchanges from C4 agricultural ecosystems in this region. This could result in larger terpenes emission changes than currently estimated when converting forested ecosystems to agricultural lands.

In contrast, the strong discrepancies in the BVOC exchange rates among studies performed in different world regions indicate that they are not extrapolable from one region to another. As a result, maize SEF and BVOC budget determined at LTO are likely not representative of other world regions (and by extension of the global scale) and should therefore be evaluated for each important agronomic region by conducting long-term BVOC measurement studies similar to this one and by using the maize varieties and management practices commonly used in these regions.

Besides, BVOC and specifically OVOC exchange mechanisms between maize fields and the atmosphere also need to be better understood in order to identify the reasons for the huge differences in normalized BVOC exchange rates observed among maize studies and to discover if they behave according to up-scaling model algorithms beyond the standard conditions (Niinemets et al., 2014). Given that each investigated compound had different exchange dynamics, mechanisms need to be evaluated separately for each compound, particularly for methanol which has been consistently shown as the compound dominating the exchanges.

Finally, future research should also focus on other crops in order to extend the comparison. For Europe, in particular, BVOC exchanges should be measured for winter wheat because, in terms of cultivated area, it is the most important crop in our region (FAOSTATS).

Comment n°14 (Sec 4 – Conclusions)

Can you draw any new conclusions about the evolution of BVOC fluxes from maize fields throughout the growing season now that you have this new data set that didn't exist before? For instance, can you comment on the variability throughout the season in Figure 1 and how the "plant phenology" dependence of modeled emissions (P12 L15) captures that variability?

We analyzed indeed the plant age effect on the methanol exchange from maize at leaf-scale and at ecosystem-scale. Results were however out of the scope of this article and were therefore not discussed. The outputs of the methanol exchange behavior along the maize growing season at leaf-scale have been very recently submitted (Mozaffar et al., 2016, submitted to AE); the ability of current BVOC up-scaling models to reproduce the methanol fluxes observed at LTO under non-standardized conditions will be detailed in a future paper.

Technical comments

Comment n°15 (P2 L15)

Spell out FAOSTATS

FAOSTATS = Food and Agriculture Organization of the United Nations Statistics Division.

Original text (P2 L15): *(FAOSTATS)*

Revised text (P2 L15): (Food and Agriculture Organization of the United Nations Statistics Division, FAOSTATS)

Comment n°16 (P8 L10)

Spell out BBCH, and define

BBCH is a German abbreviation that stands for Biologische Bundesanstalt, Bundessortenamt and CHemical industry (Meier 2001). It is a German scale used to identify the developmental stages of plant species. Those clarifications will be added at the first appearance of this abbreviation. Following them, the remark in P8 L 16-17 is not necessary anymore, it will thus be removed.

Original text (P8 L10): *G (germination – BBCH 00 to 14)*

Revised text (P8 L20-22): *G (germination – BBCH 00 to 14; BBCH stands for Biologische Bundesanstalt, Bundessortenamt and CHemical industry and is a decimal scale used to identify the developmental stages of plant species)*

Original text (P8 L16-17): *A detailed description of all the stages and their correspondence with BBCH codification (Meier, 2001), which is commonly used for crop phenological description, is given in Table 2.*

Revised text (P8 L27-28): *A detailed description of all the stages and their correspondence with BBCH codification (Meier, 2001) is given in Table 2.*

References to author's reply to referee #2

Bamberger, I., Hörtnagl, L., Ruuskanen, T. M., Schnitzhofer, R., Müller, M., Graus, M., Karl, T., Wohlfahrt, G. and Hansel, A.: Deposition fluxes of terpenes over grassland, J. Geophys. Res. D Atmos., 116(14), doi:10.1029/2010JD015457, 2011.

Das, M., Kang, D., Aneja, V. P., Lonneman, W., Cook, D. R. and Wesely, M. L.: Measurements of hydrocarbon air-surface exchange rates over maize, Atmos. Environ., 37(16), 2269–2277, 2003.

Graus, M., Eller, A. S. D., Fall, R., Yuan, B., Qian, Y., Westra, P., de Gouw, J. and Warneke, C.: Biosphere-atmosphere exchange of volatile organic compounds over C4 biofuel crops, Atmos. Environ., 66, 161–168, 2013.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I. and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6(11), 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471–1492, doi:10.5194/acp-11-8037-2011, 2012.

Karl, M., Guenther, A., Köble, R., Leip, A. and Seufert, G.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models, Biogeosciences, 6(6), 1059–1087, doi:10.1029/2003GL017000, 2009.

Niinemets, Ü., Fares, S., Harley, P. and Jardine, K. J.: Bidirectional exchange of biogenic volatiles with vegetation: emission sources, reactions, breakdown and deposition, Plant. Cell Environ., 37(8), 1790–1809, doi:10.1111/pce.12322, 2014.

Noe, S. M., Copolovici, L., Niinemets, Ü. and Vaino, E.: Foliar limonene uptake scales positively with leaf lipid content: “Non-emitting” species absorb and release monoterpenes, Plant Biol., 10(1), 129–137, 2008.

Schade, G. W. and Custer, T. G.: OVOC emissions from agricultural soil in northern Germany during the 2003 European heat wave, Atmos. Environ., 38(36), 6105–6114, doi:http://dx.doi.org/10.1016/j.atmosenv.2004.08.017, 2004.

Seco, R., Peñuelas, J. and Filella, I.: Short-chain oxygenated VOCs: Emission and uptake by plants and atmospheric sources, sinks, and concentrations, Atmos. Environ., 41(12), 2477–2499, 2007.

Stavrakou, T., Guenther, A., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P. F., Hurtmans, D., Karagulian, F., De MaziÃre, M., Vigouroux, C., Amelynck, C., Schoon, N., Laffineur, Q., Heinesch, B., Aubinet, M., Rinsland, C. and Müller, J. F.: First space-based derivation of the global atmospheric methanol emission fluxes, Atmos. Chem. Phys., 11(10), 4873–4898, doi:10.1029/2008GL033642, 2011.

Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R. and Curci, G.: Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries, Atmos. Environ., 43(7), 1380–1391, 2009.

Warneke, C., Luxembourg, S. L., De Gouw, J. A., Rinne, H. J. I., Guenther, A. B. and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, J. Geophys. Res. D Atmos., 107(7-8), 1–6, 2002.

Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season

A. Bachy[1], M. Aubinet[1], N. Schoon[2], C. Amelynck[2], B. Bodson[3], C. Moureaux[1], B. Heinesch[1]

[1] TERRA ~~Department BIOSE~~, Gembloux Agro-Bio-Tech, University of Liège, Gembloux, 5030, Belgium
[2] ~~Department Mass spectrometry~~, Royal Belgian Institute ~~of~~ for Space Aeronomy, Uccle, 1180, Belgium
[3] AGRO-BIO-CHEM ~~Department Agronomical Sciences~~, Gembloux Agro-Bio-Tech, University of Liège, Gembloux, 5030, Belgium

Correspondence to: B. Heinesch (bernard.heinesch@ulg.ac.be) and A. Bachy (aurelie.bachy@ulg.ac.be)

Abstract. Although maize is the second most important crop worldwide, and the most important C4 crop, no study on biogenic volatile organic compounds (BVOCs) has yet been conducted on this crop at ecosystem scale and over a whole growing season. This has led to large uncertainties in cropland BVOC emission estimations. This paper seeks to fill this gap by presenting, for the first time, BVOC fluxes measured in a maize field at ecosystem scale (using the disjunct eddy covariance by mass scanning technique) over a whole growing season in Belgium. The maize field emitted mainly methanol, although exchanges were bi-directional. The second most exchanged compound was acetic acid, which was taken up mainly in the growing season. Bi-directional exchanges of acetaldehyde, acetone and other oxygenated VOCs also occurred, whereas the terpenes, benzene and toluene exchanges were small, albeit significant. Surprisingly, BVOC exchanges were ~~as~~ of same order of magnitude on bare soil and on well developped vegetation, suggesting that soil is a major BVOC reservoir in agricultural ecosystems. Quantitatively, the maize BVOC emissions observed were lower than those reported in other maize, crops and grasses studies. The standard emission factors (SEFs) estimated in this study (231 ± 19 $\mu g m^{-2} h^{-1}$ for methanol, 8 ± 5 $\mu g m^{-2} h^{-1}$ for isoprene and 4 ± 6 $\mu g m^{-2} h^{-1}$ for monoterpenes) were also much lower than those currently used by models for C4 crops, particularly for terpenes. These results suggest that maize fields are small BVOC exchangers in north-western Europe, with a lower BVOC emission impact than that modelled for growing C4 crops ~~in this~~ in this part of the world. They also reveal the high variability in BVOC exchanges across world regions for maize and suggest that SEFs should be estimated for each region separately.

1 Introduction

In order to model future climate with high reliability, an in-depth understanding of all climate components and their interactions is necessary. Volatile organic compounds (VOCs) are among these components. Although VOCs constitute only a small fraction of the total air composition, their high reactivity has a significant ~~affect~~ effect on atmospheric chemistry and climate by affecting the methane lifetime in the atmosphere (Isaksen et al., 2009; Williams et al., 2013) and through the

Commentaire [A1]: Manuscript changes followed referee's comments and author's reply.
Each change refers to the author's reply documents as follows:

R X C n°Y stands for the Comment n°Y of the Referee X.

R X T stands for a technical comment (spelling mistake,…) of the referee X which was not discussed in the author's reply.

Commentaire [A2]: Update new structure name

Commentaire [A3]: Change according to comment of some co-authors.

Commentaire [A4]: Update new structure name

Commentaire [A5]: R2 T

Commentaire [A6]: R1 T
R2 T

Commentaire [A7]: R1 T
R2 T

Commentaire [A8]: R2 T

Commentaire [A9]: R2 T

formation of secondary organic aerosols (Sartelet et al., 2012; Ziemann and Atkinson, 2012) and tropospheric ozone (Fry et al., 2012; Isaksen et al., 2009; Sartelet et al., 2012; Tsimpidi et al., 2012). The understanding of VOC exchanges is therefore a research priority if better climate and air quality predictions are to be achieved (Lerdau and Slobodkin, 2002; Osborne et al., 2010).

There are numerous VOC sources (e.g., solvents, burning residues, micro-organisms). There is however a general consensus that most atmospheric VOCs originate from biogenic sources (hence the term biogenic VOCs, BVOCs), and particularly from plants (Fowler et al., 2009).

BVOC exchange composition and dependence on environmental factors are plant species-specific (Monson et al., 2013), and BVOC studies therefore need to broaden the range of investigated plants and ecosystems in order to estimate global BVOC exchanges with more accuracy (Lerdau and Slobodkin, 2002; Niinemets et al., 2014). This is currently not the case, however. Although forests have been the most widely studied ecosystem (see Niinemets et al., 2013 for a review), only a few BVOC studies have focused on croplands (Copeland et al., 2012; Crespo et al., 2013; Eller et al., 2011; Karl et al., 2005; Konig et al., 1995; Warneke et al., 2002). So far as we know, only two BVOC measurement studies have dealt with maize (Das et al., 2003; Graus et al., 2013), although it is the second most important crop in the world in terms of cultivated area (Food and Agriculture Organization of the United Nations Statistics Division, FAOSTATS), and in some regions is the dominant crop (e.g., the Corn Belt zone in the USA), and it could become even more important in meeting growing food needs (Hardacre et al., 2013) and enhancing biofuel production (Bellarby et al., 2010). Graus et al., 2013 determined the BVOC exchange composition of maize leaves, and estimated the maize BVOC budget by up-scaling and extrapolating the BVOC fluxes they measured to the whole growing season. Das et al., 2003 found large methanol and acetone emissions from maize and suggested that that crop could play an important role in the atmospheric chemistry in regions where it is widely present, e.g. the Corn Belt zone in USA.

However, both studies were conducted over only a few days and under poorly contrasted weather conditions. Consequently, they were unable to evaluate the relative effects of climate and phenology on BVOC exchanges, so that the current estimated maize BVOC budget is uncertain. Knowledge about BVOC exchanges from maize therefore remains very limited.

In order to fill this scientific gap, this study focused on BVOCs exchanged by maize, based on ecosystem-scale measurements performed over a whole growing season. So far as we know, it is the first study dealing with long-term BVOC measurements on maize. It sought to answer the following questions:

- Which BVOCs are exchanged in a maize field?
- How important is growing maize in terms of BVOC exchanges compared with other agricultural crops?
- What quantity of BVOCs is exchanged in a maize field under standard environmental conditions (standard conditions correspond to the environmental conditions defined for the MEGAN up-scaling model in Guenther et al., 2006)?

Commentaire [A10]: R2 T

Commentaire [A11]: R2 C n°15

Commentaire [A12]: R2 C n°2

Commentaire [A13]: R2 C n°3

2 Materials and Methods

2.1 Experimental set-up

2.1.1 Site and variety

The study was carried out on a silage maize (*Zea mays L.*, varieties Prosil and Rocket) field about 398~~185~~ x 255 m at the Lonzée Terrestrial Observatory (LTO) in Belgium (50°33'08" N, 4°44'42" E) from 17 May to 11 October 2012. The field is on a plateau with a small slope of 1.2%. There is more information about the LTO site in Moureaux et al. (2006).

The maize was sown on 17 May, emerged on 25 May and was harvested by 13 October 2012. Fertilizers were applied on 4 June 2012, and no measurements were taken between 30 May and 8 June 2012 in order to prevent fertilizer pollution of the instruments. During the study, the field was surrounded by sugar beet and there was a silo about 300 m north-west of the measurement mast. Subsequent analysis did not detect any significant influence of the surrounding crop or silo on the measured fluxes.

Commentaire [A14]: R2 C n°10

2.1.2 Flux measurements

The BVOC fluxes were computed every half-hour from high frequency vertical wind speed and BVOC concentration measurements using the disjunct eddy covariance by mass scanning (DEC-MS) technique, i.e. from the covariance between the vertical component of the wind speed and the BVOC mixing ratio, both variables being measured at high frequency. In this paper, fluxes are expressed per m² of soil and a positive flux indicates an emission from the ecosystem to the atmosphere.

Commentaire [A15]: R1 C n°1

The vertical wind velocity was measured at 20 Hz with a 3D sonic anemometer (Solent Research R3, Gill Instruments Lymington, UK) mounted on a 2.7 m-high mast. Due to maize growth and in order to have a reasonably aerodynamic measurement height, the anemometer was raised to 3.5 m high from 12 July 2012 to 17 August 2012 and to 3.9 m high from that date to harvest.

The BVOC concentrations were measured with a high sensitivity proton-transfer-reaction mass spectrometry (hs-PTR-MS) model (Ionicon Analytick GmbH, Innsbruck, Austria). Ambient air was continuously sampled close to the sonic anemometer through a main sampling line in perfluoroalkoxy alkanes (PFA) (Fluortechnik-Wolf, Esslingen-Berkheim, Germany), 18/20 m long (before and after 12 July 2012, respectively) and with an inner diameter of 6.4 mm and a flow rate ranging from 13 to 13.5 STP L min^{-1} (Standard Temperature and Pressure conditions corresponded to 273.15 K and 101.3. kPa). In order to prevent water vapour condensation in the main sampling line, which could dissolve some BVOC compounds, the sampling line was thermally insulated and heated on average 2.6°C~~a few~~ degrees above ambient temperature. A polytetrafluoroethylene (PTFE) filter (Pall, 47 mm diameter, 2 micron pore size) was installed 2/4 m (before and after 12 July 2012, respectively) downstream of the main sampling line inlet in order to keep the tube clean. Part of the air flow (0.1 STP L min^{-1}) was drawn into the hs-PTR-MS through a 1 m-long heated peek capillary with an inner diameter of 1 mm. The hs-PTR-MS and the sub-sampling line were installed in a temperature-controlled shelter (293 K) 15 m from the

Commentaire [A16]: R2 C n°4

measurement tower. Since no significant impact of the shelter on trace gas fluxes was identified, it was assumed that the distance between the shelter and measurement tower was enough to prevent wind distortion by the shelter from having a significant impact on wind conditions near the measurement tower.

2.1.3 Ancillary measurements

H_2O fluxes, friction velocity u_* and micro-meteorological variables were measured together with BVOC fluxes at a half-hourly scale. H_2O fluxes were measured using the conventional eddy covariance technique, with the same sonic anemometer as for BVOCs and a closed-path infrared gas analyzer (IRGA, Li-7000, LI-COR, Lincoln, NE, USA). u_* was measured with the sonic anemometer. Monitored meteorological variables relevant to this study were photosynthetic photon flux density (PPFD) (BF3, Delta_T Devices Ltd, Cambridge, UK) and air temperature (T) (RH T2, Delta_T Devices Ltd, Cambridge, UK). See Aubinet et al. (2009) for more information about the non-BVOC experimental set-up.~~There is more information about the non-BVOC experimental set-up in Aubinet et al. (2009).~~

Commentaire [A17]: R2 T

The phenological development of the maize was followed up through weekly site visits and from pictures taken every day with a phenological camera. Biomass and leaf area index (LAI) were measured on 7 and 4 dates, respectively, between the end of June and the harvest. The evolutions of the biomass and the LAI during the maize growing season were then evaluated by fitting a sigmoid function to the data. In addition, biomass and LAI were set at zero before maize emergence and set at their maximal value after 20 August 2012, in line with field observations.

2.2 PTR-MS operation

The hs-PTR-MS instrument was operated in the multiple ion detection mode. Thirteen different ion species, of which 11 were related to BVOCs (Table 1~~Table 1~~), were measured in a single measurement cycle. The dwell time for each ion species was 0.2 s and the total cycle time was 3.25 s.

The hs-PTR-MS was operated with a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V. The instrumental background was determined for 20 min every 4 h by switching the hs-PTR-MS inlet flow from ambient air to BVOC-free air, which was obtained by sending ambient air through a heated catalytic converter. Only the final 8 min were used for calculating the mean background values. The sensitivity of the instrument was calibrated every 2-3 days using a gravimetrically prepared mixture of BVOC gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA). The initial mixture, containing about 1 ppmv methanol, acetaldehyde and acetone and about 0.5 ppmv acetonitrile, isoprene, methyl vinyl ketone (MVK), methacrolein (MACR), methyl ethyl ketone (MEK), α-pinene and sabinene, with an accuracy of 5%, was used until 22 May 2012. From that date on, a second mixture containing about 1 ppmv methanol, acetaldehyde, MEK and cis-3-hexenol and about 0.5 ppmv acetonitrile, acetone, isoprene, MACR, MVK, benzene, toluene, m-xylene, α-pinene and sabinene, with an accuracy of 5%, was used instead. The compounds were further diluted (2-12 ppbv range) using a dynamic dilution system. Additionally, three calibrations as a function of relative humidity were performed during the study.

In this study, it was assumed that only acetone and acetic acid contributed to the m/z 59 and 61 ion signals, respectively. The calibration factor for acetic acid was estimated from the experimentally determined one for acetone by taking into account the fragmentation of the protonated molecules in the drift tube (Inomata and Tanimoto, 2010; Schwarz et al., 2009) and the ratio of the calculated collision rate constants (Su, 1994) and by assuming the same transmission efficiency for ions at m/z 59 and 61.

The m/z 69 signal (M69) is commonly associated to protonated isoprene in hs-PTR-MS BVOC studies, but it may also result from dissociative proton transfer to other BVOCs (Table 1~~Table 1~~). M69 emissions were observed on bare soil (Fig.1, the soil is bare during the stage G as explained in Table 2), but they did not significantly increase with T or PPFD (data not shown), indicating that they probably did not originate from isoprene sources during that period, as isoprene emissions are known to be strongly influenced by those driving parameters (Niinemets et al., 2013). However, when the crop developed, M69 emissions did increase with T and PPFD (data not shown) and could therefore, at least partly, be due to isoprene. Since our experimental set-up did not allow unambiguous identification of the compounds resulting in M69 fluxes, the calibration factor for isoprene was used in the M69 flux calculation. The M69 fluxes were therefore considered as an upper isoprene flux limit for all phenological stages apart from G.

The ion signal at m/z 83 was measured in order to represent green leaf volatiles (GLV, Table 1~~Table 1~~) and to evaluate the maize stress status. The observed exchanges were qualitative, however, and therefore this signal is not discussed in this paper.

In order to compare the water vapour fluxes obtained with the hs-PTR-MS and the IRGA, the hs-PTR-MS ion signal at m/z 39 (M39), a water vapour proxy, was post-calibrated using the mean half-hourly H_2O concentration measured by the IRGA (R^2=0.97), as described by Ammann et al. (2006).

2.3 BVOC flux computation

The general BVOC flux computation framework drew on the EUROFLUX methodology (Aubinet et al., 1999), which is designed for CO_2 flux measurements using the conventional EC technique. It was adapted for DEC-MS and low flux signal-to-noise ratio specificities when relevant. Means were computed using block averaging over 30 min periods and a 2D rotation was applied. The time lag between the wind and the concentration data streams was calculated using the technique recommended by Bamberger et al. (2010), Hörtnagl et al. (2010) and Taipale et al. (2010), whereby time lags and fluxes are determined by covariance maximisation, using the disjunct concentrations (so without imputation) to compute the cross-correlation curve and applying a smoothing function (a 3 s window size was chosen) to that curve prior to peak determination. The time lag mode found for methanol was 5.25 s, close to the M39 time lag mode (5.45 s) and to the theoretical time lag determined in situ by isopropylalcohol injection (5 ± 0.5 s). No mode was found for the other compounds investigated. A default value of 5.25 s was used when the maximal covariance was not found within the [2.75-7.75] s time window (between 49 and 78% of the data depending on the compound).

A frequency response correction accounting for low-pass filtering was applied on eddy flux data. The approach described by Moncrieff et al. (1997) was used, whereby each instrumental effect is modelled using a theoretical transfer function. The total transfer function was characterized by a half-power cut-off frequency of 0.4 Hz and was combined with the theoretical Kaimal co-spectrum, which is very close to the experimental sensible heat co-spectra (Kaimal and Finnigan, 1994), in order to determine a correction factor to apply to the fluxes. This factor ranged between 1 and 2, with a mean value of 1.29.

2.4 BVOC flux filtering

BVOC fluxes were discarded when the maize field contribution to the total flux footprint (Neftel et al., 2008) was below 70% (2% of the whole dataset), during hs-PTR-MS calibration and background measurement periods (22%), when the flux measurement system was stopped because of maintenance operations (1%), power failures (9%) or spraying events (6%), and when the fluxes were not computed because concentration or sonic anemometer data were not available (9%). This resulted in 3592 valid half-hourly flux data for each investigated compound (51% of the whole dataset).

It should be noted that we did not filter BVOC fluxes below a certain u_* threshold or according to stationarity. Theoretically, for non-soluble compounds, when measuring fluxes by the EC technique, flux data which were measured at u_* values below a certain threshold must be discarded (Aubinet et al., 2012). However, we did not apply this specific filtering criterion because u_* can actually control soluble BVOC fluxes (Aubinet et al., 2012; Laffineur et al., 2012). ~~It should be noted that we did not filter BVOC fluxes according to a lower u_* threshold or to stationarity. Indeed, u_* can actually control soluble BVOC fluxes (Aubinet, 2012; Laffineur et al., 2012).~~ Moreover we observed that u_* induced a higher flux random error, but not a systematic error. For all the investigated compounds, both daytime and nighttime fluxes presented a conical shape when plotted against u_* with the flux range increasing along with u_*.The flux detection limit (Sect. 2.5.2) was also positively well correlated with u_*, with R^2 ranging from 0.51 to 0.80, depending on the compound. In addition, the correlation between the H_2O fluxes measured with the IRGA and those measured with the hs-PTR-MS (M39) improved with decreasing u_*. Even if the random error increased with u_*, however, the mean exchanges of non-soluble compounds, evaluated by averaging fluxes per u_* class, did not significantly differ with u_*. This means that low u_* values did not create biased BVOC fluxes. Consequently, we did not apply a low u_* threshold to those fluxes.

The stationarity criteria designed for the conventional EC technique (Aubinet et al., 2012) and commonly used in BVOC flux studies were irrelevant for the BVOC fluxes measured at LTO. Stationarity filtering criteria calculated from M39 data (using the approach described by Foken and Wichura, 1996) did not remove the same data as those calculated from the IRGA H_2O data. In addition, for all the investigated BVOC compounds, both stationary and non-stationary data had similar diurnal dynamics and were correlated with the same environmental variables, suggesting that non-stationary data were not abnormal. Therefore, we did not apply that filtering criterion to the BVOC fluxes.

Commentaire [A18]: Reference corrected (also in references section)

Commentaire [A19]: R1 C n°3

2.5 BVOC flux error evaluation

2.5.1 Systematic error

The possible occurrence of a systematic error in the calculated BVOC fluxes was evaluated by (i) computing the flux distribution for each compound and (ii) comparing the H_2O turbulent fluxes computed from M39 with those computed from the IRGA data, following the approach used by Ammann et al. (2006).

The half-hourly flux distribution was quite symmetric around zero for each compound. No mirroring effect (Langford et al., 2015) was observed, indicating that the chosen time lag method did not create bias in the flux. Moreover, the M39 fluxes correlated well with the H_2O fluxes measured with the IRGA, even though the determination coefficient was lower (R^2=0.71) than the one reported by Ammann et al. (2006) (R^2=0.92). The regression slope did not significantly differ from 1, indicating that the H_2O fluxes calculated with the DEC-MS technique were not biased.

Consequently, we considered that the BVOC fluxes measured at LTO were not biased.

Commentaire [A20]: R2 C n°5

2.5.2 Random error

An individual 30-min flux random error was equated with its detection limit. The latter was computed as the standard deviation σ of the covariance function on a time lag window far from the theoretical time lag and therefore physically irrelevant, following the approach used by Spirig et al. (2005). Depending on the compound, 63 to 86% of the flux data were above the detection limit (moving to 15 and to 60% when 3σ was taken, as proposed by some authors). Langford et al. (2015) found that the root-mean-square (RMS) of the covariance function was a better estimator of flux random error than σ. When the RMS was compared with σ for fluxes measured in June 2012, however, we did not observe any significant differences (data not shown). The standard deviation method was therefore retained.

Although many BVOC fluxes were lying above their detection limit, flux data performed at the half-hourly scale were very scattered (except for methanol flux). Thus, in all analyses, fluxes were averaged over many observations during a specific period, typically the whole growing season or phenological stage.

2.6 BVOC budget computation

The BVOC budget was computed over the whole maize growing season for each compound separately, using the method recommended by Bamberger et al. (2014), with gaps smaller than or equal to 2 h (23% of the whole dataset) filled by linear interpolation, and gaps larger than 2 h (26%) filled using the mean diurnal variation (MDV) technique, with a 16-day window size centered on the missing data.

The budget error was evaluated by flux error propagation. The flux detection limit (1*σ) was used as the flux random error for measured fluxes. As gap-filled fluxes were determined from measured fluxes, the random error of each individual gap-filled flux was evaluated by propagating the error of the fluxes used to estimate that flux.

The error caused by the gap-filling technique itself was not quantified, but we argue that budgets reported in this paper are consistent for their order of magnitude. First, the gap-filling did not change the BVOC flux pattern. Then, when estimating flux data for gaps smaller than 2 h, the use of interpolation techniques other than linear resulted in flux values that were not significantly different from those obtained with linear interpolation. Thirdly, the MDV technique which was used to estimate fluxes in larger gaps has been shown to result in less error than other gap-filling techniques (Bamberger et al., 2014). In addition, most gaps lasted less than 1 day. 8 gaps exceeded 1 day; four of them lasted less than 2 days, and three of them lasted between 3 and 4 days. Only one gap lasted 10 days because of a spraying event. The uncertainty induced in the budget when estimating missing flux data for that gap was evaluated by filling all missing data either with the lowest or with the highest flux values measured within one month window size around the missing data. These extreme flux data induced a variation up to 257, 51, 39 and 53 $g_{BVOC}ha^{-1}$ in the methanol, acetaldehyde, acetone and acetic acid budgets, respectively. Although the budget was significantly modified (Table 5~~Table 5~~), its order of magnitude remained similar. Moreover, filling all missing data with extremely low or high flux is realistic only if weather conditions were particularly warm and dry or wet and cold when the gap occurred and if they remained constant during the whole gap duration, which was not the case at LTO. Indeed, a warm and dry period occurred during the first 5 days of the gap and was followed by a wetter and colder period during the 5 other days. Consequently, the BVOC budget that actually occurred during that period was certainly less extreme than the BVOC budget estimated by considering extreme flux values and therefore closer to the budget estimated using the MDV technique.

Commentaire [A21]: R2 T

3 Results and discussion

3.1 Maize phenological development

The maize growing season was divided into five distinct phenological periods: G (germination – BBCH 00 to 14; BBCH stands for Biologische Bundesanstalt, Bundessortenamt and CHemical industry and is a decimal scale used to identify the developmental stages of plant species); L (leaf unfolding – BBCH 14 to 16); S (stem elongation and leaf area development – BBCH 30 to 39); R1 (inflorescence development, flowering and grain emergence – BBCH 51 to 71); and R2 (grain maturation – BBCH 71 to 89). All the stages were determined by visual observations of the maize field, with the exception of the pivotal date between the stages R1 and R2, which was based on the difference in daily biomass growth because the visual observations were not good enough determine ~~where~~ when R1 ended and R2 began.

Commentaire [A22]: R2 C n°16

Commentaire [A23]: R1 T

A detailed description of all the stages and their correspondence with BBCH codification (Meier, 2001)~~, which is commonly used for crop phenological description.~~ is given in Table 2. Briefly, the ecosystem consisted of bare soil in stage G. The maize developed during the other stages, and so the ecosystem then included both soil and plants. Vegetative growth (i.e., leaves and stem) occurred during stages L and S. Reproductive growth (i.e., flowers and grains) occurred during stages R1 and R2. Vegetative growth was small (R1) to negligible (R2) during the reproductive growth period. It should be noted that,

Commentaire [A24]: R2 C n°16

as the maize variety grown at LTO is a 'stay green' variety, it was harvested before entering in senescence, and therefore the senescence phase was not included in the phenological description.

~~3.2 Representativity of BVOC exchanges measured at LTO~~

~~The maize variety grown at LTO was intended for silage (livestock feed) production purposes and the management practices commonly used in this region for this type of crop were thus applied. The weather conditions during the study were among normal for the time and place (Royal Meteorological Institute, Belgium).~~

~~The BVOC composition, flux range and budget presented in this study are therefore representative of the fields of maize grown under natural weather conditions in the Hesbaye region of Belgium and, by extension, in north-western Europe, where maize is grown under similar pedo-climatic conditions (i.e., temperate maritime climate and silt or sandy loamy soils) and for similar production purposes (i.e., farms with crops and livestock).~~

~~3.3~~3.2 ~~BVOCs exchanged at LTO~~BVOCs exchange composition at LTO and qualitative comparison with other crops

Throughout the study, methanol was the main compound exchanged (Fig.1), ranging from 31 to 76% of the total mean BVOC exchanges (Table 3, all percentages are given in mass basis). Methanol emissions were observed for all stages apart from L, which was characterized instead by uptakes resulting from wetter and colder conditions (data not shown).

Apart from methanol, other oxygenated VOCs (OVOCs; in this paper, this include methanol, acetic acid, acetaldehyde, acetone, MVK+MACR and MEK) were exchanged. The acetic acid, acetaldehyde, acetone, MVK+MACR and MEK contributions to the total BVOC exchange ranged from 0 to 22% during the phenological stages. Acetic acid, in particular, was the second most important compound exchanged over the growing season, contributing up to 16% of the total exchange for a single phenological period. It was taken up by the ecosystem throughout the growing season, apart from some days during stage R1 which were characterized by warm and dry conditions and during which small but significant acetic acid emissions were observed instead (Fig.2). Acetaldehyde and acetone fluxes were important during phenological stages, with contribution up to 22% for acetaldehyde and 7% for acetone, but their exchanges varied in magnitude and direction among the phenological stages, resulting in a small acetaldehyde uptake (5%) and a non-significant acetone exchange over the whole growing season. Small but significant MVK+MACR uptake occurred over the whole growing season, accounting for up to 4% of the total BVOC exchange. Uptake was more pronounced in stage R1, probably due to higher mixing ratios during that period (up to 1.2 ppbv as opposed to 0-0.4 ppvb for other stages), which favored dry deposition mechanisms (Niinemets et al., 2014; Tani et al., 2010). MEK was emitted from stages L to R1 and was taken up during the other stages. MEK exchanges were always significant, but never exceeded 5% of the total BVOC exchange.

Terpenes exchanges (in this paper, terpenes include monoterpenes and isoprene, the maximal exchange rate for the latter being estimated from M69 fluxes for all stages apart from G, Sect. 2.2) were 1 order of magnitude smaller than methanol exchanges and contributed up to 9% to the total BVOC exchange for a single compound. Significant emissions were found

Commentaire [A25]: Section moved at the end of Results and Discussion following R2 Cn°12

Commentaire [A26]: R2 Cn°9

for both compounds during all stages, apart from R2, during which the monoterpenes have been taken up by the maize field ecosystem~~uptake of monoterpenes was observed instead~~.

Small but significant benzene and toluene uptake was observed for all phenological stages. Each compound contributed up to 7% to the total BVOC exchange.

~~Besides, each investigated BVOC showed different seasonal dynamics, indicating that the sources, sinks strength and/or exchange mechanisms differed for each compound.~~

Qualitatively, t~~T~~he BVOC exchange composition observed at LTO matched those observed on diverse croplands and grasslands fairly well. The preponderance of methanol emissions over all other BVOCs has been reported in numerous cropland and grassland studies (Bamberger et al., 2010; Copeland et al., 2012; Crespo et al., 2013; Custer and Schade, 2007; Eller et al., 2011; Ruuskanen et al., 2011; Warneke et al., 2002), including maize studies (Das et al., 2003; Graus et al., 2013). Smaller (compared with methanol exchanges) but significant bi-directional exchanges of other OVOCs and terpenes were also reported in those studies.

The maize field at LTO was not an important monoterpene source, in contrast to the observation reported from an American maize field (Das et al., 2003). It was also a small toluene and benzene sink, whereas both compounds were found to be emitted by maize leaves in another study (Graus et al., 2013). In addition, our observations disagree with the hypothesis proposed by White et al. (2009) that maize could be an important toluene source.

~~Besides~~Lastly, each investigated BVOC showed different seasonal dynamics, indicating that the sources, sinks strength and/or exchange mechanisms differed for each compound.

~~3.4~~3.3 Role of soil in BVOC exchanges at LTO

The soil played an important role in the BVOC exchanges at LTO. Bare soil (stage G) showed emissions of methanol, acetaldehyde and acetone, and the strongest acetic acid uptake occurred during this stage.

It was reported by Schade and Custer (2004) that agricultural soils emit methanol and acetone under warm conditions. The maximal methanol (335 $\mu g m^{-2} h^{-1}$), acetone (136 $\mu g m^{-2} h^{-1}$) and acetaldehyde (102 $\mu g m^{-2} h^{-1}$) emissions recorded at our site in stage G were smaller than maximal emission values found by these authors (Table 4~~Table 4~~), but they were all within the range of the maximal emissions ~~reported~~ reported in the review of Peñuelas et al. (2014), i.e., 3-553 $\mu g m^{-2} h^{-1}$ for methanol, 4-806 $\mu g m^{-2} h^{-1}$ for acetone and 1.7-102 $\mu g m^{-2} h^{-1}$ for acetaldehyde.

Interestingly, however, the methanol and acetaldehyde fluxes measured at our site were of the same order of magnitude for bare soil as for fully developed vegetation (R1), both stages occurring under similar weather conditions, and the highest acetone emissions occurred during stage G. This means that soil BVOC exchanges were as important, if not more so, as plant BVOC exchanges at LTO. This observation goes against the current assumption that plant BVOC exchanges dominate soil BVOC exchanges (Peñuelas et al., 2014), at least for our ecosystem.

Commentaire [A27]: R2 Cn°7

Commentaire [A28]: Moved at the end of this section following R2 Cn°8

Commentaire [A29]: R2 Cn°9

Commentaire [A30]: R2 Cn°8

Commentaire [A31]: R2 T

It has been shown that maize leaves emit methanol, acetone and acetaldehyde (Graus et al., 2013). Moreover, significant methanol, acetone and acetaldehyde emissions have been measured in controlled chambers from maize leaves of the 'Prosil' variety (Mozzaffar, 2015 comm. pers), which is one of the two varieties grown at LTO. At ecosystem-scale, BVOC exchanged by maize should therefore increase along with plant development and associated biomass increases, and lead to higher methanol, acetone and acetaldehyde emissions during stage R1, compared with stage G, but this was not the case at LTO. We therefore conclude that, at least for those compounds, the soil source strength decreased during the maize growing season at LTO and thus reduced the importance of the soil in the total net measured BVOC exchange.

~~3.5~~3.4 Importance of maize as a BVOC exchanger compared with other crops

~~3.5.1~~3.4.1 ~~Comparison of BVOCs exchanged at LTO with other maize BVOC studies~~Quantitative comparison of BVOCs exchange rates at LTO with other maize BVOC studies

Commentaire [A32]: R2 Cn°9

So far as we know, there have been only two other BVOC studies focusing on maize. They were conducted in the United States of America over a few days and under particular weather conditions (Table 4~~Table 4~~).

We averaged the BVOC fluxes gathered at LTO under similar T, PPFD and phenological stages as the American studies in order to exclude as far as possible the phenological and meteorological effects on BVOC exchanges (Fig.2). The results showed that BVOC fluxes were much lower at LTO than in the two other maize studies, differing by a factor of 3 to 43 compared to Graus et al. (2013), depending on the compound, and by 2 orders of magnitude compared to Das et al. (2003).

The mean exchange reported by Graus et al. (2013), however, arose from leaf-scale measurements performed in controlled chambers. They were therefore affected by up-scaling issues and probably differed from the mean exchanges that would have been measured at their site at ecosystem scale and under natural environmental conditions. It is possible, therefore, that the discrepancies with our observations result from differences in experimental design.

In contrast, the BVOC flux study by Das et al., 2003 was conducted at ecosystem-scale under natural conditions. Their flux measurement technique (gradient) differed from the one we used (DEC-MS), but it has been shown in other BVOC flux measurement studies that both techniques lead to similar BVOC exchange magnitudes (Park et al., 2014; Karl et al., 2001). The two orders of magnitude difference in BVOC exchanges between their study and ours therefore reflects real and significant differences in BVOC exchanges between the two sites.

In this comparison, the BVOC exchanges have been normalized by T, PPFD and phenology. Other environmental conditions (e.g., humidity, soil type, soil fertility), as well as cultural regional practices (e.g., chosen maize variety, cultural management such as fertilizer use, irrigation), could, however, directly influence the BVOC exchange magnitude through constitutive or stress-induced pathways. They could also affect maize growth and phenology and therefore indirectly influence BVOC exchanges. Given the huge differences in normalized BVOC exchange rates among studies, we conclude that some of these other environmental conditions play a major role in the amount of BVOCs exchanged in a maize field, and therefore that BVOC exchange rates obtained for maize in one region cannot be extrapolated to another region simply by normalizing T and PPFD. We also conclude that the importance of maize fields in BVOC exchanges varies strongly among

regions of the world and therefore, in the next section, we will compare the BVOC exchanges measured at LTO only with those reported for other crops grown in Europe.

~~3.5.2~~3.4.2 ~~Comparison of BVOCs exchanged at LTO with other crops~~Quantitative comparison of BVOCs exchange rates at LTO with other crops

Commentaire [A33]: R2 Cn°9

The BVOCs exchanged at LTO were compared with diverse C4 and C3 crops and with mixed grassland species. Grasslands were included because their BVOC exchange composition is qualitatively similar to that of crop species (Bamberger et al., 2010; Crespo et al., 2013; Graus et al., 2013; Custer and Schade, 2007; Eller et al., 2011). It should be noted that, as this study focused on BVOC exchanged during the maize growing season, only BVOC exchanges reported for other crops during their growth period were taken in account, i.e., harvest-induced emissions were not considered for comparison.

In our opinion, a comparison of BVOC budgets is the best way to evaluate the relative importance of a crop in terms of BVOC exchanges, because the duration of growing seasons differs greatly from one crop to another (and also under different cultural conditions for the same crop). We reported in Table 5~~Table 5~~ the budget estimated for the maize field at LTO. The limited information on BVOC budgets that we found in the literature for other crops and grasses (also listed in Table 5~~Table 5~~), however, does not allow us to draw conclusions about the relative importance of maize in our region. The budgets reported by Crespo et al. (2013) and Graus et al. (2013) relate to different regions, in addition to which they were estimated from BVOC flux measurements conducted over a few days and under a narrow range of weather conditions, making them highly uncertain. The budget reported by Bamberger et al. (2014) includes grass-cutting events, whereas harvest-induced BVOC emissions were not considered at LTO.

We therefore compared the BVOC flux ranges and averages obtained at LTO with those of other European croplands and grasslands (Table 4~~Table 4~~). From the little information we found, we observed that for all investigated compounds the flux range observed at LTO was more than twice as low as that observed for *Miscanthus* (Copeland et al., 2012), another C4 crop. In addition, the methanol flux average measured at LTO was 9 times lower than that observed for a grassland (Bamberger et al., 2010). In contrast, the maximal methanol emission rate observed at the LTO site was twice as high as that reported for white clover (Custer and Schade, 2007). Maize field BVOC exchanges therefore seem to be smaller that those for other crops grown in Europe, but this result should be further confirmed by other BVOC exchanges studies performed on other crops in our region.

~~3.6~~3.5 BVOCs exchanged by a maize field under standard environmental conditions

Up-scaling models (Guenther et al., 2012 for MEGAN v2.1; Lathière et al., 2006 for ORCHIDEE) consider BVOC emissions from growing plants as a function of (i) an SEF that represents the mean emission of a particular plant functional type under standard environmental conditions, and (ii) a multiplicative factor depending on PPFD, T and plant phenology, which reflects the response in emissions to varying environmental conditions.

The SEF values used in current up-scaling models for C4 crops do not match those observed at the LTO site for any model or any compound (Table 6~~Table 6~~). In particular, the SEF values used for isoprene and monoterpenes were several orders of magnitude lower at LTO than those used by models. This difference was even greater for isoprene because the M69 signal was associated with isoprene for SEF computation at LTO, whereas it was probably not solely due to isoprene (Sect. 2.2). The SEF value measured at LTO for methanol was 2-4 times lower than that used by up-scaling models, while the SEF value measured for acetaldehyde was 0-11 times lower. The SEF values measured for acetone and acetic acid on our site were respectively 2 and 10 times lower than values used by MEGAN v2.1, and 2 and 5 times higher than values used by ORCHIDEE.

~~The SEF values used by up-scaling models rely on diverse BVOC flux measurement studies (see Guenther et al., 2012 and Lathière et al., 2006 for details). In particular, for Europe there is a comprehensive SEF inventory (Karl et al., 2009). Karl et al. (2009) noticed, however, that the SEFs given for croplands are default values because of the lack of information for those ecosystems. With regard to methanol, Stavrakou et al. (2011) used only one SEF derived from alfalfa for all croplands, although this species accounts for only 1% of the cultivated area worldwide (FAOSTATS). In contrast, maize is the second most important crop and the most important C4 crop worldwide, accounting for 13 and 67% of the total cultivated area, respectively. In north-western Europe, it accounts for 12 and 99% of the total / C4 crop cultivated area, respectively. The C4 crop plant functional type considered by models can therefore be realistically equated with maize, especially in our region. We would therefore advise modellers to use the SEFs reported in this study when estimating BVOC exchanges from C4 crops in north-western Europe~~.

3.6 Implications for BVOC exchanges from croplands and use of SEFs measured at LTO by up-scaling models

Given the discrepancies between the SEF values used by the up-scaling models for the C4 crops and those measured on maize at LTO, one may wonder to which extent these differences could affect the estimations of cropland BVOC budget, and whether the SEF obtained in this study should be implemented in the models to represent (C4) croplands.

First, maize is the second most important crop and the most important C4 crop worldwide (FAOSTATS), accounting for 13 and 67% of the total cultivated area, respectively. Particularly, in north-western Europe, it accounts for 12 and 99% of the total / C4 crop cultivated area, respectively. This crop is thus of major importance when evaluating the importance of agricultural ecosystems. Particularly, the C4 crop plant functional type can be realistically equated with maize in NW Europe.

Then, despite the importance of maize in agricultural lands, SEF currently estimated for croplands (and also C4 croplands) do not rely on BVOC measurements performed on maize. For example, with regard to methanol, Stavrakou et al. (2011) used only one SEF derived from alfalfa for all croplands, although this species accounts for only 1% of the cultivated area worldwide (FAOSTATS). In particular, for Europe there is a comprehensive SEF inventory (Karl et al., 2009). Karl et al. (2009) mentioned, however, that, because of the lack of information for croplands, the SEFs for those ecosystems are default

Commentaire [A34]: R2 T

Commentaire [A35]: Paragraph merged in the Sec 3.6 following R2 C n°12 and R2 Cn°13.

Commentaire [A36]: R2 Cn°12

Commentaire [A37]: Section (originally 3.1) moved following R2 C n°12, then merged with the previous paragraph and restructured according to this comment.

values, i.e. values assigned by databases and up-scaling models from SEF observed on other ecosystems. Consequently, the SEF currently assigned for the C4 crop PFT are in fact not representative of the actual C4 crops SEF.

In this study, we provided SEF estimations from a maize field relying on measurements performed under real field conditions. The maize variety grown at LTO was intended for silage (livestock feed) production purposes and the management practices commonly used in this region for this type of crop were thus applied. In addition, the weather conditions during the study were normal for the time and place (normal conditions are defined by the Belgian Royal Meteorological Institute by averaging records taken in Uccle, Belgium over the period 1981-2010. It corresponds to 3.6°C, 10.1°C, 17.5°C and 10.9°C and to 220.5 mm, 187.8 mm, 224.4 mm and 219.9 mm cumulated precipitation in winter, spring, summer and fall, respectively). The maize field grown at LTO was thus reasonably representative of the fields of maize grown under real conditions in the Hesbaye region of Belgium and, by extension, in NW Europe, where maize is grown under similar pedo-climatic conditions (i.e., temperate maritime climate and silt or sandy-loamy soils) and for similar production purposes (i.e., farms with crops and livestock).

Therefore, in the absence of any robustly established SEF for C4 crop so far, we would suggest modelers to use the SEF determined at LTO for the C4 crop PFT instead of the current estimations. As the BVOC exchange rates measured on our site strongly differed from other maize studies performed on other sites, though, we also want to make them aware that SEF obtained in this study are likely not valid outside NW Europe and should therefore not be used in other world regions. We also recommend additional BVOC measurement studies performed on maize fields located in other NW European sites to validate the spatial extent of the values proposed in this paper.

Commentaire [A38]: R2 Cn°11

Commentaire [A39]: R2 Cn°6

Commentaire [A40]: R2 C n°6

4 Conclusions

This work constitutes the first BVOC study performed in a maize field over a whole growing season. It showed that the maize field emitted mainly methanol. Smaller but significant bi-directional OVOC exchanges were also recorded, resulting in a net emission of methanol and MEK and in a net uptake of acetic acid, acetaldehyde and MVK+MACR during the maize growing season. Terpenes exchange (mostly emissions) and a small but significant benzene and toluene uptake were also observed. Exchanges occurred throughout the growing season and each compound had different dynamics.

The observations at LTO showed in particular that: (i) the soil was an important methanol and acetaldehyde source, and an important acetic acid sink~~the soil was an important BVOC source and sink~~; (ii) the BVOC exchanges were much lower than in other maize field studies, even when normalized by T, PPFD and phenology; (iii) they were also lower than those of other crops grown in Europe; and (iv) the estimated SEFs were much lower than those currently used by up-scaling models for the C4 crop plant functional type, of which maize is the main species.

Commentaire [A41]: R2 T

Commentaire [A42]: R1 C n°4

Soil BVOC exchanges were as important, if not more so, as plant BVOC exchanges when the soil was bare and they decreased when maize was grown. The contribution of soil exchanges was probably particularly important on our site because BVOC exchanged by maize at LTO were small compared with those reported for other crops and grasses.

Nevertheless, this work demonstrates that soil is a major actor in ecosystem-scale BVOC exchanges for some ecosystems. Future ecosystem-scale BVOC studies, particularly those investigating croplands, should therefore consider soil as a potential major BVOC reservoir. In addition, the BVOC exchange mechanisms between agricultural soils and the atmosphere need to be better understood in order to find out why these exchanges decrease during the maize growing season.

Maize is cultivated in many regions of the world and is the main species of the C4 crop plant functional type. Our results showed ~~, however,~~ that the normalization of BVOC exchanges by T, PPFD and phenology was not enough to explain the huge difference in BVOC exchange rates among maize studies in different parts of the world. Modelers should therefore be aware of the current large uncertainties in BVOC exchange rate for this crop.

However, given (i) the good representativity of the maize field grown at LTO in terms of management practices and of weather conditions typical of NW Europe, and (ii) the current absence of maize in SEF assignments for C4 crops by models, which contradicts with the major importance of that crop for that PFT, we would still suggest modelers using SEF values proposed in this paper for NW Europe. The lower SEF values observed on our site in comparison with those currently used by up-scaling models – in particular for terpenes- would then suggest an over-estimation of BVOC exchanges from C4 agricultural ecosystems in this region. This could result in larger terpenes emission changes than currently estimated when converting forested ecosystems to agricultural lands.

In contrast, the strong discrepancies in the BVOC exchange rates among studies performed in different world regions indicate that they are not extrapolable from one region to another. As a result, maize SEF and BVOC budget determined at LTO are likely not representative of other world regions (and by extension of the global scale) and should therefore be evaluated for each important agronomic region by conducting long-term BVOC measurement studies similar to this one and by using the maize varieties and management practices commonly used in these regions. ~~This indicates that SEFs cannot be extrapolated to different world regions.~~

~~In this study, we proposed that our SEF values should be used for the C4 crop plant functional type. We also provided an estimation of the BVOC exchange budget of a maize field over a whole growing season. We argued that our values could be extrapolated to maize fields grown under similar agronomical and pedo-climatic conditions to those at LTO (i.e., in north-western Europe).~~

~~With the SEF values observed at LTO being far lower than those currently used by models, especially for terpenes, and with maize being the second most important cultivated crop, our results showed a reduced importance of BVOC emissions from croplands in our region. This indicates that deforestation and afforestation should result in even larger terpenes emission changes than currently estimated, especially in areas where maize production is important.~~

~~Specific maize SEF and BVOC exchange budget values should be obtained for other important agronomic regions by conducting long-term BVOC measurement studies similar to this one and by using the maize varieties and management practices commonly used in these regions.~~ Besides, BVOC and specifically OVOC exchange mechanisms between maize fields and the atmosphere also need to be better understood in order to identify the reasons for the huge differences in normalized BVOC exchange rates observed among maize studies and to discover if they behave according to up-scaling

model algorithms beyond the standard conditions ~~or to known OVOC exchange mechanisms~~ (Niinemets et al., 2014). Given that each investigated compound had different exchange dynamics, mechanisms need to be evaluated separately for each compound, particularly for methanol which has been consistently shown as the compound dominating the exchanges~~on the LTO observations~~.

Finally, ~~the BVOC exchange rates observed in this study were smaller than those observed in other crop studies in Europe, suggesting that maize is a small BVOC exchanger crop in this region. Few BVOC measurement studies have been conducted under natural conditions in Europe on cropland ecosystems, however, and even less if we confine the comparison to north-western Europe. F~~future research should ~~thus~~ also focus on other crops in order to extend the comparison. For Europe, ~~I~~in particular, BVOC exchanges should be measured for winter wheat because, in terms of cultivated area, it is the most important crop in our region (FAOSTATS).

Commentaire [A43]: Modification following the restructuration and the discussion in Sec 3.6, see R2 C n°12-13

Acknowledgements

The authors wish to thank Frédéric Wilmus, Henri Chopin and Alain Debacq for BVOC set-up installation and station monitoring, the farmer Mr. Van Eyck, the Lonzée-ICOS team for site follow-up and measurement of environmental parameters, and FNRS for its financial support (A2/5-MCF/DM-1.A.362.13F-FC 95918).

Commentaire [A44]: Correction following FNRS comment

References

Ammann, C., Brunner, A., Spirig, C. and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmos. Chem. Phys., 6(12), 4643–4651, doi:10.1029/2004JD004738, 2006.

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., Grünwald, T., Morgenstern, 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, 1999.

Aubinet, M., Moureaux, C., Bodson, B., Dufranne, D., Heinesch, B., Suleau, M., Vancutsem, F. and Vilret, A.: Carbon sequestration by a crop over a 4-year sugar beet/winter wheat/seed potato/winter wheat rotation cycle, Agric. For. Meteorol., 149(3-4), 407–418, 2009.

Aubinet, M., Vesala, T. and Papale, D.: Eddy covariance a practical guide to measurement and data analysis, Springer, Dordrecht; New York., 2012.

Bamberger, I., Hörtnagl, L., Schnitzhofer, R., Graus, M., Ruuskanen, T. M., Müller, M., Dunkl, J., Wohlfahrt, G. and Hansel, A.: BVOC fluxes above mountain grassland, Biogeosciences, 7(5), 1413–1424, doi:10.1029/1999jd900144, 2010.

Bamberger, I., Hörtnagl, L., Walser, M., Hansel, A. and Wohlfahrt, G.: Gap-filling strategies for annual VOC flux data sets, Biogeosciences, 11(8), 2429–2442, doi:10.5194/bg-11-2429-2014 10.5194/bg-7-1413-2010, 2014.

Bellarby, J., Wattenbach, M., Tuck, G., Glendining, M. J. and Smith, P.: The potential distribution of bioenergy crops in the UK under present and future climate, Biomass and Bioenergy, 34(12), 1935–1945, 2010.

Copeland, N., Cape, J. N. and Heal, M. R.: Volatile organic compound emissions from Miscanthus and short rotation coppice willow bioenergy crops, Atmos. Environ., 60, 327–335, 2012.

Crespo, E., Graus, M., Gilman, J. B., Lerner, B. M., Fall, R., Harren, F. J. M. and Warneke, C.: Volatile organic compound emissions from elephant grass and bamboo cultivars used as potential bioethanol crop, Atmos. Environ., 65, 61–68, 2013.

Custer, T. and Schade, G.: Methanol and acetaldehyde fluxes over ryegrass, Tellus, Ser. B Chem. Phys. Meteorol., 59(4), 673–684, 2007.

Das, M., Kang, D., Aneja, V. P., Lonneman, W., Cook, D. R. and Wesely, M. L.: Measurements of hydrocarbon air-surface exchange rates over maize, Atmos. Environ., 37(16), 2269–2277, 2003.

Eller, A. S. D., Sekimoto, K., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Monson, R. K., Graus, M., Crespo, E., Warneke, C. and Fall, R.: Volatile organic compound emissions from switchgrass cultivars used as biofuel crops, Atmos. Environ., 45(19), 3333–3337, 2011.

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

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Horváth, L., Loreto, F., Niinemets, U., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N. and Erisman, J. W.: Atmospheric composition change: Ecosystems-Atmosphere interactions, Atmos. Environ., 43(33), 5193–5267, 2009.

Fry, M. M., Naik, V., West, J. J., Schwarzkopf, M. D., Fiore, A. M., Collins, W. J., Dentener, F. J., Shindell, D. T., Atherton, C., Bergmann, D., Duncan, B. N., Hess, P., MacKenzie, I. A., Marmer, E., Schultz, M. G., Szopa, S., Wild, O. and Zeng, G.: The influence of ozone precursor emissions from four world regions on tropospheric composition and radiative climate forcing, J. Geophys. Res. Atmos., 117(D7), D07306, doi:10.1029/2011JD017134, 2012.

Graus, M., Eller, A. S. D., Fall, R., Yuan, B., Qian, Y., Westra, P., de Gouw, J. and Warneke, C.: Biosphere-atmosphere exchange of volatile organic compounds over C4 biofuel crops, Atmos. Environ., 66, 161–168, 2013.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471–1492, doi:10.5194/acp-11-8037-2011, 2012.

Hardacre, C. J., Palmer, P. I., Baumanns, K., Rounsevell, M. and Murray-Rust, D.: Probabilistic estimation of future emissions of isoprene and surface oxidant chemistry associated with land-use change in response to growing food needs, Atmos. Chem. Phys., 13(11), 5451–5472, doi:10.5194/acp-13-5451-2013, 2013.

Hörtnagl, L., Clement, R., Graus, M., Hammerle, A., Hansel, A. and Wohlfahrt, G.: Dealing with disjunct concentration measurements in eddy covariance applications: A comparison of available approaches, Atmos. Environ., 44(16), 2024–2032, 2010.

Inomata, S. and Tanimoto, H.: A Quantitative Examination of the Detection Sensitivities of Proton-Transfer Reaction Mass Spectrometry for Gaseous 2Propanol and Acetic Acid, Bull. Chem. Soc. Jpn., 83(8), 900–904, doi:10.1246/bcsj.20100043, 2010.

Isaksen, I. S. A., Granier, C., Myhre, G., Berntsen, T. K., Dalsøren, S. B., Gauss, M., Klimont, Z., Benestad, R., Bousquet, P., Collins, W., Cox, T., Eyring, V., Fowler, D., Fuzzi, S., Jöckel, P., Laj, P., Lohmann, U., Maione, M., Monks, P., Prevot, A. S. H., Raes, F., Richter, A., Rognerud, B., Schulz, M., Shindell, D., Stevenson, D. S., Storelvmo, T., Wang, W. C., van Weele, M., Wild, M. and Wuebbles, D.: Atmospheric composition change: Climate-Chemistry interactions, Atmos. Environ., 43(33), 5138–5192, 2009.

Kaimal, J. C. and Finnigan, J. J.: Atmospheric boundary layer flows: their structure and measurement., 1994.

Karl, M., Guenther, A., Köble, R., Leip, A. and Seufert, G.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models, Biogeosciences, 6(6), 1059–1087, doi:10.1029/2003GL017000, 2009.

Karl, T., Guenther, A., Lindinger, C., Jordan, A., Fall, R. and Lindinger, W.: Eddy covariance measurements of oxygenated volatile organic compound fluxes from crop harvesting using a redesigned proton-transfer-reaction mass spectrometer, J. Geophys. Res. Atmos., 106(D20), 24157–24167, doi:10.1029/2000jd000112, 2001.

Karl, T., Harren, F., Warneke, C., de Gouw, J., Grayless, C. and Fall, R.: Senescing grass crops as regional sources of reactive volatile organic compounds, J. Geophys. Res. Atmos., 110(D15), D15302, doi:10.1029/2005JD005777, 2005.

Konig, G., Brunda, M., Puxbaum, H., Hewitt, C. N., Duckham, S. C. and Rudolph, J.: Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species, Atmos. Environ., 29(8), 861–874, 1995.

Langford, B., Acton, W., Ammann, C., Valach, A. and Nemitz, E.: Eddy-covariance data with low signal-to-noise ratio: time-lag determination, uncertainties and limit of detection, Atmos. Meas. Tech. Discuss., 8(3), 2913–2955, doi:10.5194/amtd-8-2913-2015, 2015.

Lathière, J., Hauglustaine, D. A., Friend, A. D., De Noblet-Ducoudré, N., Viovy, N. and Folberth, G. A.: Impact of climate variability and land use changes on global biogenic volatile organic compound emissions, Atmos. Chem. Phys., 6(8), 2129–2146, doi:10.1029/2000JD000225, 2006.

Lerdau, M. and Slobodkin, L.: Trace gas emissions and species-dependent ecosystem services, Trends Ecol. Evol., 17(7), 309–312, doi:http://dx.doi.org/10.1016/S0169-5347(02)02535-1, 2002.

Meier, U.: Growth stages of mono-and dicotyledonous plants, BBCH Monograph, 2nd ed., Federal Biological Research Centre for Agriculture and Forestry., 2001.

Moncrieff, J. B., Massheder, J. M., De Bruin, H., Elbers, J., Friborg, T., Heusinkveld, B., Kabat, P., Scott, S., Soegaard, H. and Verhoef, A.: A system to measure surface fluxes of momentum, sensible heat, water vapour and carbon dioxide, J. Hydrol., 188-189(1-4), 589–611, 1997.

Monson, R. K., Jones, R. T., Rosenstiel, T. N. and Schnitzler, J. P.: Why only some plants emit isoprene, Plant, Cell Environ., 36(3), 503–516, 2013.

Moureaux, C., Debacq, A., Bodson, B., Heinesch, B. and Aubinet, M.: Annual net ecosystem carbon exchange by a sugar beet crop, Agric. For. Meteorol., 139(1-2), 25–39, 2006.

Neftel, A., Spirig, C. and Ammann, C.: Application and test of a simple tool for operational footprint evaluations, Environ. Pollut., 152(3), 644–652, 2008.

Niinemets, Ü., Monson, R. K. and SpringerLink: Biology, Controls and Models of Tree Volatile Organic Compound Emissions, Springer Netherlands : Imprint: Springer, Dordrecht., 2013.

Niinemets, Ü., Fares, S., Harley, P. and Jardine, K. J.: Bidirectional exchange of biogenic volatiles with vegetation: emission sources, reactions, breakdown and deposition, Plant. Cell Environ., 37(8), 1790–1809, doi:10.1111/pce.12322, 2014.

Osborne, B., Saunders, M., Walmsley, D., Jones, M. and Smith, P.: Key questions and uncertainties associated with the assessment of the cropland greenhouse gas balance, Agric. Ecosyst. Environ., 139(3), 293–301, 2010.

Park, J. H., Fares, S., Weber, R. and Goldstein, A. H.: Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux-gradient similarity methods, Atmos. Chem. Phys., 14(1), 231–244, doi:10.5194/acp-9-5505-2009, 2014.

Peñuelas, J., Asensio, D., Tholl, D., Wenke, K., Rosenkranz, M., Piechulla, B. and Schnitzler, J. P.: Biogenic volatile emissions from the soil, Plant, Cell Environ., 37(8), 1866–1891, 2014.

Ruuskanen, T. M., Müller, M., Schnitzhofer, R., Karl, T., Graus, M., Bamberger, I., Hörtnagl, L., Brilli, F., Wohlfahrt, G. and Hansel, A.: Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, Atmos. Chem. Phys., 11(2), 611–625, doi:10.5194/acp-9-5155-2009, 2011.

Sartelet, K. N., Couvidat, F., Seigneur, C. and Roustan, Y.: Impact of biogenic emissions on air quality over Europe and North America, Atmos. Environ., 53, 131–141, doi:10.1080/10473289.2011.603999, 2012.

Schade, G. W. and Custer, T. G.: OVOC emissions from agricultural soil in northern Germany during the 2003 European heat wave, Atmos. Environ., 38(36), 6105–6114, doi:http://dx.doi.org/10.1016/j.atmosenv.2004.08.017, 2004.

Schwarz, K., Filipiak, W. and Amann, A.: Determining concentration patterns of volatile compounds in exhaled breath by PTR-MS, J. Breath Res., 3(2), 2009.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A. and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 5(2), 465–481, 2005.

Stavrakou, T., Guenther, A., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P. F., Hurtmans, D., Karagulian, F., De MaziÃre, M., Vigouroux, C., Amelynck, C., Schoon, N., Laffineur, Q., Heinesch, B., Aubinet, M., Rinsland, C. and Müller, J. F.: First space-based derivation of the global atmospheric methanol emission fluxes, Atmos. Chem. Phys., 11(10), 4873–4898, doi:10.1029/2008GL033642, 2011.

Su, T.: Parametrization of kinetic energy dependences of ion–polar molecule collision rate constants by trajectory calculations, J. Chem. Phys., 100(6), 4703, doi:doi:http://dx.doi.org/10.1063/1.466255, 1994.

Taipale, R., Ruuskanen, T. M. and Rinne, J.: Lag time determination in DEC measurements with PTR-MS, Atmos. Meas. Tech., 3(4), 853–862, doi:10.5194/bg-6-1655-2009, 2010.

Tani, A., Tobe, S. and Shimizu, S.: Uptake of methacrolein and methyl vinyl ketone by tree saplings and implications for forest atmosphere, Environ. Sci. Technol., 44(18), 7096–7101, 2010.

Tsimpidi, A. P., Trail, M., Hu, Y., Nenes, A. and Russell, A. G.: Modeling an air pollution episode in northwestern United States: Identifying the effect of nitrogen oxide and volatile organic compound emission changes on air pollutants formation using direct sensitivity analysis, J. Air Waste Manag. Assoc., 62(10), 1150–1165, 2012.

Warneke, C., Luxembourg, S. L., De Gouw, J. A., Rinne, H. J. I., Guenther, A. B. and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, J. Geophys. Res. D Atmos., 107(7-8), 1–6, 2002.

White, M. L., Russo, R. S., Zhou, Y., Ambrose, J. L., Haase, K., Frinak, E. K., Varner, R. K., Wingenter, O. W., Mao, H., Talbot, R. and Sive, B. C.: Are biogenic emissions a significant source of summertime atmospheric toluene in the rural Northeastern United States?, Atmos. Chem. Phys., 9(1), 81–92, doi:10.1029/2004JD005623, 2009.

Williams, J. E., van Velthoven, P. F. J. and Brenninkmeijer, C. A. M.: Quantifying the uncertainty in simulating global tropospheric composition due to the variability in global emission estimates of Biogenic Volatile Organic Compounds, Atmos. Chem. Phys., 13(5), 2857–2891, doi:10.5194/acp-13-2857-2013, 2013.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41(19), 6582–6605, 2012.

Tables

Table 1 m/z ratio of ion species measured at LTO and their potentially contributing compounds.

m/z	Ion species	Potentially contributing compounds
21	$H_3{}^{18}O^+$	3rd isotope of the 1st proton hydrate
33	CH_5O^+	Methanol
39	$H_5{}^{16}O^{18}O^+$	3rd isotope of the 2nd proton hydrate
45	$C_2H_5O^+$	Acetaldehyde (ACD)
59	$C_3H_7O^+$	Acetone, propanal
61	$C_2H_5O_2{}^+$	Acetic acid
69	$C_5H_9{}^+$	Isoprene, methyl butenols, pentenols, methyl butanal
71	$C_4H_7O^+$	Methyl vinyl ketone (MVK), methacrolein (MACR), pentanol
73	$C_4H_9O^+$	Methyl ethyl ketone (MEK)
79	$C_6H_7{}^+$	Benzene
83	$C_6H_{11}{}^+$	Hexenols, hexenyl acetates, hexanal
93	$C_7H_9{}^+$	Toluene
137	$C_{10}H_{17}{}^+$	Monoterpenes (MT)

Table 2 Maize phenological development. BBCH codification refers to Meier (2001). Both biomass and LAI refer to the beginning of a stage.

	Stage	Date			BBCH			Biomass [gm^{-2}]	LAI [m^2m^{-2}]	Description of maize development
Vegetative growth	G (germination)	14 May	-	4 June	00	-	14	0	0.00	From sowing to 4-leaf stage Emergence on 25 May Considered as bare soil throughout the stage due to small biomass and biomass growth
	L (leaf unfolding)	5 June	-	26 June	14	-	16[a]	49	0.01	From 4-leaf to 6-leaf stage Progressive canopy closure
	S (leaf area development and stem elongation)	27 June	-	5 August	30	-	39	152	0.10	From 6-leaf stage to panicle emergence Important increase in leaf area, maize height and biomass
Reproductive growth	R1 (inflorescence and fruit development)	6 August	-	29 August	51	-	71 (73)[b]	806	4.30	From panicle emergence to fruit maturation Stamen appearance by 10 August (BBCH 61) Max. LAI reached by 20 August (5.06 m^2m^{-2}) Important biomass increase
	R2 (fruit maturation)	29 August	-	12 October	71 (73)[b]	-	89[c]	1539 2019.2[d]	5.06	From fruit maturation to harvest Intermediate biomass increase

[a]stages 17 to 19 did not occur

[b]Estimation: Fruit visible at the end of the stage, but exact grain maturity not identifiable

[c]stages 97 and 99 did not occur

[d]harvest

Table 3 BVOC composition per phenological stage. Each percentage corresponds to the ratio of the absolute mean flux of a particular compound during a phenological stage to the sum of the absolute mean fluxes of all investigated compounds during that stage.

	G	L	S	R1	R2	Whole season
Methanol	55%	56%	76%	66%	31%	66%
Acetaldehyde	8%	11%	5%	8%	22%	5%
Acetone	7%	6%	0%	2%	5%	0%
Acetic acid	15%	11%	4%	7%	16%	12%
M69	9%	4%	6%	6%	3%	7%
MVK+MACR	0%	3%	3%	4%	4%	4%
MEK	2%	5%	2%	1%	3%	1%
Monoterpenes	1%	1%	2%	2%	5%	1%
Benzene	1%	3%	0%	1%	4%	2%
Toluene	2%	0%	1%	3%	7%	2%

Table 4 OVOC exchanges by diverse crops and grass species.

Flux [µgm^{-2}h^{-1}]		Avg ± SE	Min-Max						
Ecosystem	C4 crops					Grasses			Soil
Species	Maize				Miscanthus	White clover	Mixed grasses		Cambisoil
Methanol	27 ± 0.8	-342 - 708	3450 ± 1456[a]	821 ± 59[b]	-2000 - 3000	-213 - 320	131 - 1073	288[c]	0 - 533
Acetaldehyde	-2 ± 0.3	-179 - 155		159 ± 54 [b]	-1000 - 1000				
Acetone	-0.1 ± 0.2	-198 - 265	425 ± 223[a]	125 ± 10 [b]	-2000 - 2000				-48 - 242
Acetic acid	-5 ± 0.2	-347 - 206		380 ± 57 [b]	-1000 - 500		-41 - -35		
Author(s)	This study		Das et al. (2003)	Graus et al. (2013)	Copeland et al. (2012)	Custer and Schade (2007)	Ruuskanen et al. (2011)	Bamberger et al. (2010)	Schade and Custer (2004)
Location	Belgium		North Carolina	Colorado (USA)	United Kingdom	Germany	Austria	Austria	Germany
Meas. scale	Ecosystem		Ecosystem	Leaf	Ecosystem	Ecosystem	Ecosystem	Ecosystem	Ecosystem
Meas. technique	DEC-MS		Gradient	In situ cuvette	DEC-MS	DEC-MS	EC	DEC-MS	DEC-MS
BVOC conc. Instrument	PTR-MS		GC-MS	PTR-MS	PTR-MS	PTR-MS	PTR-MS-TOF	PTR-MS	PTR-MS
Meas. Duration [days]	148		4	2	30	40	2	155	5
Temperature range [°C]	4-29		24-27	30_c		15-30	1-29	16[c]	20-40

[a] midday fluxes
[b] fluxes up-scaled with an LAI of 6m^{2}m^{-2} (Graus et al., 2013)
[c] avg. growing season only

Table 5 BVOC budget estimated for maize at LTO and on diverse crops over a whole growing season.

[$g_{BVOC}ha^{-1}$] Crop	Methanol	Acetaldehyde	Acetone	Acetic acid	Author
Maize	960 ± 29	-70 ± 9	-1 ± 8	-181 ± 8	This study
	5521[a]	1075[a]	838[a]	2251[a]	Graus et al. (2013)
Elephant grass	20000	30000	37000		Crespo et al. (2013)
Miscanthus	3780[b]	680[b]	1180[b]	3580[b]	Graus et al. (2013)
Grassland	22171[c]	101[c]	200[c]		Bamberger et al. (2014)

[a] Original data in $g_{BVOC}L_{ethanol}^{-1}$. Converted with an ethanol yield of 0.38 $L_{ethanol}kg_{grain}^{-1}$, a grain:residue ratio equal to 1:1, and a biomass yield of 9.59Mgha^{-1}, as used by Graus et al. (2013).

[b] Original data in $g_{BVOC}L_{ethanol}^{-1}$. Converted with an ethanol yield of 0.4 $L_{ethanol}kg_{leaves}^{-1}$ and a leaf biomass of 5Mgha^{-1}, as used by Graus et al. (2013).

[c] Annual budget. Average of 2009 and 2011 budgets for methanol, 2009 budget only for other compounds. Original data in mg C $m^{-2}yr^{-1}$, converted with the molar mass of each individual compound.

Notice that budgets reported for grassland include both growing periods and cutting events.

Table 6 SEF recorded at LTO under standard environmental conditions and used in up-scaling models for C4 agricultural crops.

	This study						MEGAN v2.1[d]	ORCHIDEE[c]
	[µg m_{soil}^{-2} h^{-1}][a]			[µg g_{dw}^{-1} h^{-1}][b]			[µg m_{soil}^{-2} h^{-1}]	[µg g_{dw}^{-1} h^{-1}]
Isoprene	8[f]	±	5	0.058[f]	±	0.038	200	8.500
Monoterpenes	4	±	6	0.030	±	0.040	2	0.227
Methanol	231	±	19	1.642	±	0.137	500[d]/800[e]	2.667
Acetone	46	±	8	0.324	±	0.057	80	0.113
Acetaldehyde	7	±	9	0.046	±	0.065	80	0.046
Acetic acid	8	±	9	0.055	±	0.072	80	0.013

[a] Standard environmental conditions chosen to match MEGAN v2.1 standard environmental conditions (Guenther et al., 2012): 28°C ≤ T° ≤ 32°C; PPFD ≥ 1000 µmol$m^{-2}s^{-1}$; 4.38 m^2m^{-2} ≤ LAI ≤ 5.04 m^2m^{-2}.

[b] Specific leaf weight used for the conversion from msoil-2 to gdw-1: 29.0 $g_{DW,leaf}$ m_{leaf}^{-2}(meas. performed on a mature maize leaf of variety Prosil, Mozzaffar et al., 2015, pers. comm.). LAI used for conversion : 4.85 m^2m^{-2}

[c] Lathière et al. (2006.). SEF are here given in $\mu g_{Compound}$ instead of μg_C

[d] Guenther et al. (2012)

[e] Stavrakou et al. (2011)

[f] Derived from M69 flux

Figures

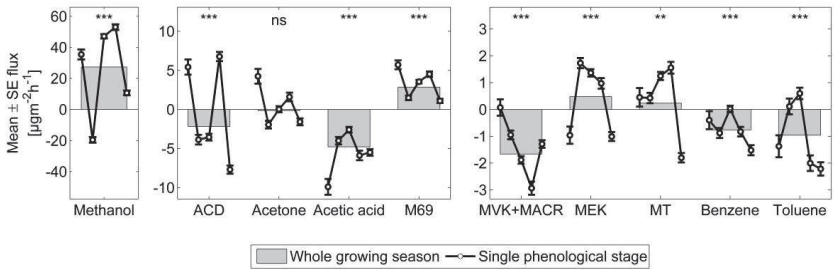

Figure 1 BVOC exchanges over the growing season. Phenological stages, from left to right: G, L, S, R1 and R2. Stars indicate the significance level of flux averages over the whole growing season. See Table 1~~Table 1~~ for compound abbreviations and Table 2 for phenological stage description. Note the varying scales used for the y axes.

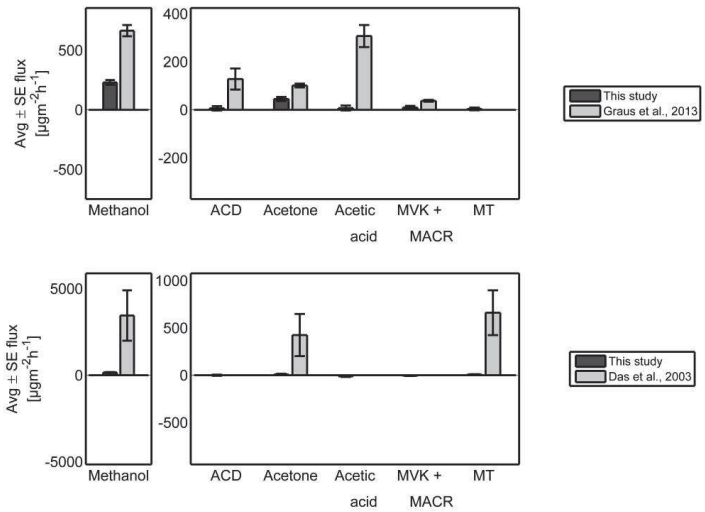

Figure 2 Comparison of BVOC exchanges at LTO with other maize studies. For comparison with Graus et al. (2013): R1 stage, 28°C ≤ T° ≤ 32°C; PPFD ≥ 1000 µmolm^{-2}s^{-1}. BVOC exchanges reported by Graus et al. (2013) were up-scaled with LAI measured at LTO during the R1 stage (4.86 m^{2}m^{-2}). For comparison with Das et al. (2003): L and S stages, 24°C ≤ T° ≤ 28°C, fluxes taken from 10:30 to 13:30 UTC in order to capture midday fluxes. See Table 1~~Table 1~~ for compound abbreviations and Table 4~~Table 4~~ for maize studies description. Note the varying scales for the y axes.