

Interactive comment on “Acetaldehyde exchange above a managed temperate mountain grassland” by L. Hörtnagl et al.

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Received and published: 9 February 2014

Answer to Reviewer #1

We thank Reviewer #1 for his/her comments and suggestions. In the following we carefully address his/her remarks and give an overview of revised sections in the manuscript.

Comment #1: “The focus of the work is on statistical analysis of longer-term data, but given the real-time nature of the PTR-MS, the authors should present an analysis of real-time diurnal flux measurements of acetaldehyde from a representative week (undisturbed and disturbed) and evaluate how environmental conditions influence them. Instead the authors immediately jump into long-term data analysis without

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first analyzing some representative diurnal and weekly patterns.”

Answer: On a half-hourly time scale, the random flux error of the vDEC method is relatively high (ca. 30%, Bamberger et al., 2010), making it difficult to reliably analyze exchange patterns and draw defensible conclusions. In order to reveal mechanisms involved in the control of acetaldehyde fluxes we tried to minimize the random error and focused our analysis on daily average values (which reduces the random error to <5%). Half-hourly flux values for 3 days before and 6 days after the cutting of the meadow are shown in Figure 4. Earlier studies at the same site have shown half-hourly acetaldehyde fluxes in relation to environmental variables. Namely, Bamberger et al. (2010) investigated time series of acetaldehyde and other VOC fluxes in relation to global radiation, temperature, latent heat flux and carbon dioxide before, during and after the cutting over the meadow of this study. Brillì et al. (2012) discussed BVOC exchange dynamics and compared them to leaf-level laboratory measurements.

Comment #2:” It appears that the flux of acetaldehyde is small to negligible for many periods except for the cutting of the grass. Thus, how quantitatively important is the cutting of the grass to the overall annual acetaldehyde emission? How important are these emissions to the regional acetaldehyde budget?”

Answer: The cutting of the grass is of great importance for the seasonal/annual acetaldehyde budget of the meadow. When days with management influence were excluded from the analysis, the grassland acted as a source of acetaldehyde only during one year, while it was a sink during all other years. Numbers detailing the amount of carbon associated with management events are already given in section 3.2. However, emission numbers for 2009 and 2011 also include the effect of manure spreading. In a revised version of the manuscript we therefore expanded section 3.2 and give additional information about the effect of manure spreading on resulting acetaldehyde carbon emissions. On p. 26131, line 14, the text now reads: “2009 and 2011 were similar: in both years all three cuts and the spreading of the manure were captured by the acetaldehyde measurements, resulting in 12 days influenced by anthropogenic actions

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that resulted in a total emission of 17.7 (2009) and 17.9 (2011) mg C m⁻², whereby emissions as a direct result of manure spreading accounted for 1.6 and 0.9 mg C m⁻², respectively." With this additional information, the cutting effect can be related to the observed overall acetaldehyde fluxes in all years. Our measurements do not include acetaldehyde exchange over the forest on the surrounding slopes of the valley or any anthropogenic emissions, a reliable estimate of the regional acetaldehyde budget is therefore not possible (and also beyond the scope of the present paper).

Comment #3: "Given the overall low fluxes of acetaldehyde, what is the limit of detection of the virtual disjunct eddy covariance system?"

Answer: The flux detection limit was calculated according to Karl et al. (2002b) and amounted to ca. 0.1 nmol m⁻² s⁻¹. We included this information in section 2.4 of a revised version of the manuscript.

Comment #4: "What other m/z values were measured every cycle and how long did one cycle take?"

Answer: The duration of each measurement cycle is specified in the 'PTR-MS setup' section. We added a sentence specifying the m/z ratios measured for each year to the section: "The mass to charge ratios measured for each year were m/z 33 (methanol), m/z 45 (acetaldehyde), m/z 59 (e.g. acetone, propanal), m/z 137 (sum of monoterpenes) and some additional m/z ratios to quantify the main fragment of monoterpenes and the primary ions."

Comment #5: "It is clear that the authors have collected data from a number of other m/z values to acquire additional data on other compounds, but unfortunately, this has compromised the quality of the acetaldehyde data. Instead, the authors should focus their PTR-MS on m/z 45 with 10 Hz true eddy covariance data."

Answer: A PTR-TOF was available for a period of approximately three months from June to August 2009, but not for the full four years of VOC measurements. The reviewer

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suggestion is thus not compatible with the main objectives of the paper to analyze the seasonal and inter-annual variability in the acetaldehyde exchange. During the time period of concurrent flux measurements, the low-resolution PTR-MS fluxes compared well to the high-resolution PTR-TOF fluxes (new Figure S1). This is in agreement with Hörtnagl et al. (2010), who showed that the vDEC method yields unbiased flux estimates but is characterized by a larger random uncertainty compared to the true EC method.

Comment #6: "Another technical issue not addressed well by the authors is the actual measurement of acetaldehyde by PTR-MS. Did the authors obtain quantitative confirmation (e.g. by GC) of the ambient concentration measurements of acetaldehyde by PTR-MS? If not, how do the authors rule out the influence air pollutants and their fragments on m/z 45? What about the CO₂ interference on m/z45? This needs to be discussed in much greater detail. Can the authors quantify the influence of CO₂ on PTR-MS signals at m/z 45? CO₂ contributes significantly to this signal although the flux direction may be opposite to acetaldehyde. For example, photosynthesis would draw down CO₂, giving the appearance of an acetaldehyde uptake flux. While the sensitivity of the PTR-MS to CO₂ at m/z 45 may be low, its concentrations are many orders of magnitude higher than acetaldehyde. To provide more convincing information that CO₂ does not impact the results for acetaldehyde, the authors should present a figure showing a PTR-MS m/z 45 calibration to acetaldehyde and to CO₂ spanning the range of ambient concentrations observed. Moreover, if the PTR-TOFMS data is to be used in comparison to rule out the influence of CO₂, this data needs to be presented. However, no information whatsoever is provided for the PTR-TOFMS measurements."

Answer: Unfortunately we didn't have the opportunity to have a GC for the quantitative confirmation of acetaldehyde on m/z 45. However, a PTR-TOF instrument was installed in addition to the conventional PTR-MS at the field site for a period of approximately three months from June to August 2009. While the PTR-MS provides only nominal mass information, the PTR-TOF provides exact mass information and at m/z 45 and

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we identified a small peak which was assigned to CO₂ and a considerably higher one assigned to acetaldehyde. Flux values calculated for the mass of CO₂ were about one order of magnitude lower and showed no distinct diurnal or seasonal pattern, but just noise around zero. Additionally, a comparison of acetaldehyde fluxes measured by PTR-TOF versus acetaldehyde (m/z 45) fluxes measured by PTR-MS showed an excellent agreement (new Figure S1). This makes us confident that we have a negligible contribution of CO₂ on m/z 45 for the PTR-MS instrument. We are not aware of other air pollutants or their fragments contributing to the concentration signal on the exact mass of acetaldehyde (as measured by PTR-TOF).

Comment #7: "Moreover, why has the calibration factor for acetaldehyde varied so much over the four years (15/20/13/13)? Can the authors be sure of actual annual differences given this large variability in sensitivity? How did the sensitivity change over the course of one year? More importantly, why is the sensitivity for acetaldehyde an order of magnitude lower than typically observed in other systems (13-20 cps/ppbv versus 100-500 cps/ppbv)? Thus, given an ambient concentration of 1.0 ppbv acetaldehyde, did the authors really only measure 13-20 counts per second? What was the background of acetaldehyde on this m/z? Typically, background signals are higher than this. Although it is certain that acetaldehyde was present in the air and contributed to m/z 45, these issues need to be addressed before it can be concluded that the authors in fact measured acetaldehyde quantitatively."

Answer: Due to organizational reasons we performed measurements 2008, 2009 and 2011/2012 with three different PTR-MS instruments. Each of the different instruments had its own typical sensitivity range. Note that sensitivity and background values are not given in cps but in normalized counts per second (normalized to 1 million primary ions and 2.2 mbar drift tube pressure). Sensitivities in cps are based on the typical number of primary ions and drift tube pressure roughly estimated to be at least a factor of 5-7 higher for the years 2009, 2011 and 2012. The PTR-MS which was used in 2008 was indeed less sensitive. This was one reason why it was exchanged as soon

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as another PTR-MS was available (August 2008). As a consequence of the use of different instruments, the normalized sensitivities showed the observed variability. Additionally, we saw an annual variability, when values varied between 12 ncps/ppbv and 14ncps/ppbv e.g in 2011. The annual variability was mainly associated with the use of different secondary electron multipliers (which had to be changed at least 3 times for one year of measurements). To minimize uncertainties arising from the annual variability we calibrated the instrument every second day from 2009 on and interpolated sensitivities between adjacent measurements where applicable. Except of the exchange of the SEM, the differences between two subsequent calibrations were usually between 0.1 and 0.3 ncps/ppbv. The limit of detection for acetaldehyde concentrations was calculated for every calibration and was typically around 0.1 ppbv except for 2008 when it was higher. The background on m/z 45 was usually below 5 ncps and, except for some periods in 2008, which were removed by the QA/QC procedure, always lower than the measurement signal. As described in the Section 'Quality control' we applied a quality control on our data filtering out half hourly data with (a) the measured background signal of acetaldehyde being higher than its ambient concentration (averaged over half an hour) and (b) the background drift being greater than the sum of the standard deviations of the two adjacent background measurements before and after the flux averaging period. To clarify certain things we added some information in the section 'PTR-MS setup': p.26125, line 10: "(as well as directly before and after each maintenance, e.g. exchange of the ion source)" p.26125, line 14: ", normalized to 1 million primary ions and 2.2 mbar drift tube pressure" p.26125, line 14: "The limit of detection (at 1 s dwell time) was calculated during each calibration and was typically around 0.1 ppbv except for 2008, when it was around a factor of five higher." p.26125, line 20: "For a period of approximately three months from June to August 2009..." p.26125, line 24: "As shown in the supplementary information"..."(Figure S1)"

Comment #8: "Abstract: "The cutting of the meadow resulted in huge acetaldehyde emission bursts on the day of harvesting or one day later." Please provide the emission rates.

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Answer: Done as suggested. The sentence was reworded to “The cutting of the meadow resulted in huge acetaldehyde emission bursts of up to 16.5 nmol m⁻² s⁻¹ on the day of harvesting or one day later.”

Comment #9: “During undisturbed conditions, both uptake and emission fluxes were recorded.” At the same time?”

Answer: The sentence means to emphasize the bidirectional nature of acetaldehyde fluxes during undisturbed conditions and was reworded for clarity as: “During undisturbed conditions both periods with net uptake and net emissions of acetaldehyde were observed.”

Comment #10: “Introduction: “The emission or uptake of biogenic VOCs (BVOCs) by plants has many underlying causes, most of which are yet not fully understood.” I disagree with this comment as there are a large number of studies on the underlying BVOC metabolic processes. These should be described and cited.”

Answer: For many VOCs, our knowledge in terms of production and consumption in plants is still limited, e.g. acetaldehyde, while we have a better understanding of other compounds, e.g. isoprene and methanol. Therefore, we reworded the sentence to reflect a more general view: page 26119, line1: “While the processes underlying the exchange of some VOCs have been studied extensively (e.g. isoprene), knowledge for many other VOCs is still limited.” In addition, we included more information about metabolic processes as part of our answer to Comment #13 (see below).

Comment #11: “Acetaldehyde is not strictly biogenic as numerous anthropogenic sources are known. Thus the authors should reduce the acronym to VOC or OVOC.”

Answer: Done as suggested. In a revised version of the manuscript, we instead use the terms “biogenic VOC” or “biogenic OVOC” instead of “BVOC” or “BOVOC” when specifically addressing biogenic causes, and use the more general “VOC” and “OVOC” in other cases.

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Comment #12: “There are a number of studies clearly showing stomatal control over acetaldehyde exchange and the authors should cite them. It is also clear that acetaldehyde is a product of lipid oxidation reactions and this should also be included. In addition, the authors need to include recent studies that demonstrate an active generation of acetaldehyde directly in leaves from pyruvate through a fermentation like process in leaves (i.e. as a part of the so called pyruvate dehydrogenase bypass).”

Answer: We agree and included the following information in a revised version of the manuscript: p. 26120, line 18: “Jardine et al. (2008) reported that stomatal conductance controls acetaldehyde exchange rates but does not affect internal acetaldehyde concentrations due to continuous production and consumption processes.” Regarding stomatal control, the study by Loreto et al. (2006) is discussed in the manuscript. We also added citations to publications regarding the pyruvate dehydrogenase bypass pathway: p. 26120, line 3: “Karl et al. (2002a) attributed emission bursts after light-dark transitions to a “pyruvate overflow” mechanism in which acetaldehyde is formed directly in leaves through the decarboxylation of pyruvate as part of the pyruvate dehydrogenase bypass pathway. Findings by Jardine et al. (2012) were consistent with this explanation.”

Comment #13: “Figures in general are very difficult to read, especially the axis labels. Please reconsider which figures add the most to this paper. The text in Figure 1 is extremely difficult to read. Figure 7 is extremely small and impossible to read.”

Answer: For a revised version of the manuscript, axis labels were adjusted and font sizes increased where possible. The page orientation for Atmospheric Chemistry and Physics Discussions publications is ‘landscape’ by default, in contrast to publications in Atmospheric Chemistry and Physics (‘portrait’). The ‘landscape’ orientation in combination with the figure captions hampers the readability and visual appearance of vertical format figures like Figure 1 and Figure 7.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C12056/2014/acpd-13-C12056-2014-supplement.pdf>

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