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Comment

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

**Anonymous Referee #1**

Received and published: 16 December 2013

The paper presented by Hörtnagl et al. presents an impressive four year data set of ambient acetaldehyde concentrations and vertical flux measurements at a managed grassland site in Austria. The authors show interesting data reflecting the well known, but poorly characterized bi-directional exchange behavior of acetaldehyde between that atmosphere and a vegetated ecosystem. However, a number of technical issues masked by the focus on long-term analysis need to be addressed before publication in ACP should be considered.

Specific comments 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 influ-

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ence them. Instead the authors immediately jump into long-term data analysis without first analyzing some representative diurnal and weekly patterns.

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? Given the overall low fluxes of acetaldehyde, what is the limit of detection of the virtual disjunct eddy covariance system? What other  $m/z$  values were measured every cycle and how long did one cycle take. 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.

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 CO<sub>2</sub> interference on  $m/z$  45? This needs to be discussed in much greater detail. Can the authors quantify the influence of CO<sub>2</sub> on PTR-MS signals at  $m/z$  45? CO<sub>2</sub> contributes significantly to this signal although the flux direction may be opposite to acetaldehyde. For example, photosynthesis would draw down CO<sub>2</sub>, giving the appearance of an acetaldehyde uptake flux. While the sensitivity of the PTR-MS to CO<sub>2</sub> at  $m/z$  45 may be low, its concentrations are many orders of magnitude higher than acetaldehyde. To provide more convincing information that CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>, this data needs to be presented. However, no information whatsoever is provided for the PTR-TOFMS measurements. Moreover,

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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.

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

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.

Acetaldehyde is not strictly biogenic as numerous anthropogenic sources are known. Thus the authors should reduce the acronym to VOC or OVOC.

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 dehydroge-

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nase bypass).

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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26117, 2013.

ACPD

13, C10028–C10031,  
2013

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