

## ***Interactive comment on “Methanol exchange between grassland and the atmosphere” by A. Brunner et al.***

**A. Brunner et al.**

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We thank the referee for his very careful reading of the manuscript and the detailed comments. We agree with all technical comments and the suggestions concerning the text formulation, and we will modify the text accordingly. In the following we respond individually to the scientific comments and questions. Whenever the referee is cited, the text has been written inside quotation marks.

“P130, I12. From the information provided (tube diameter 3.5 mm, 4 lpm) I calculate a Reynolds number of 1600, which is more laminar than turbulent. This is an unfortunate choice, given the tube length of 30 m and the low measurement height, and it is therefore surprising that flux losses were as low as 25 to 55%.” “P131, I15. Why do the authors decide to repeat the same measurement value rather than match it up with the spot measurement of the associated vertical wind speed, using a dis-

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unct sampling protocol? I assume that this may be so that the authors can use spectral analysis techniques. However, this approach induces significant further flux loss which may also have contributed to the estimated losses of 25 to 55%.” The reviewer is correct with his comments, that the laminar tube flow and the repetition of the disjunct concentration measurements are not optimal concerning the high frequency damping. We have been aware of this fact. However, the quantitative effect of these two factors is smaller than estimated by the reviewer. In Ammann et al. (2006) we demonstrated, that the total damping effect is strongly dominated by sorption effects on the tube walls. Thus a turbulent tube flow and improved data treatment would have had practically no effect on the total damping (see also ACPD interactive comment [www.atmos-chem-phys-discuss.net/6/S3005/2006/](http://www.atmos-chem-phys-discuss.net/6/S3005/2006/) and [www.atmos-chem-phys-discuss.net/4/S2879/2004/](http://www.atmos-chem-phys-discuss.net/4/S2879/2004/) ). On the other hand, we preferred the non-disjunct eddy covariance calculation because of easier application (less noise) of spectral analysis and determination of the delay time by the maximum of the covariance function. We modified the method description in Sect. 2.3 to make these considerations more clear.

“P132, last sentence. I am not sure I understand this sentence.” We omitted the sentence.

“Section 2.3. I am surprised that the authors did not appear to have filtered the flux data according to fetch requirements, atmospheric stability and non-stationarity. Given the small extent of the fetch there are likely to be conditions at which most of the footprint is situated outside the field. It is clear that, since night-time fluxes are small, even large relative errors at night will not greatly influence the average flux. However, since the contribution of the field to the measured flux is presumably smallest when  $R_g$  is small, there may be a bias on the parameterisations. I therefore suggest, plotting less reliable fluxes in grey in Figs. 3 & 7 and excluding them from the plots used to derive parameterisations.” We performed a footprint analysis for the eddy covariance measurements. Because of the low measurement height (1.2 m above ground) and the main wind directions being mostly along the field axis, there were only few cases (c.

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5%) in which the footprint contribution of the study field was less than half. Most of the time, it was even more than 80%. Therefore, the application of a footprint criteria was not considered to be necessary. We added the information about the main wind direction and the low measurement height in Section 2.1. As pointed out by the referee, nighttime fluxes were generally small (despite the relatively large high-frequency damping correction) and mostly below the flux detection limit as quantified in Section 2.3. Thus the application of a common stationarity criteria (e.g. Foken and Wichura, 1996, AgForMet, 78, 83-105) would have resulted in the rejection of most nighttime data. This could more likely have resulted in a biased dataset, because only the significant but not representative larger nighttime fluxes (as e.g. displayed in Fig. 10) would have been retained. Additionally it has to be noted that the parameterisation was derived from ratios between methanol flux and water vapour flux selected for  $\text{FH}_2\text{O} > 4 \text{ mmol m}^{-2} \text{ s}^{-1}$ .

“P133, l15. Could the authors please specify whether this is single-sided or double-sided LAI.” The LAI shown here is a single-sided one. This information has been added to the methods.

“Fig. 4. It would be nice to see a polar plot of the concentration also. Is there evidence for contribution from nearby anthropogenic sources such as the near-by motorway?” We performed a polar plot analysis and found no significant effect. This is largely a consequence of the prevailing wind directions which are mostly along the field axis. This information was added to the site description.

“Fig.5. Have the authors tried to explain the residual of the regressions between  $F(\text{MeOH})$  and  $R_g$  (and  $F(\text{H}_2\text{O})$ ) with another meteorological variable. Could temperature explain some of the variability? Or is growth stage the main effect apart from  $R_g/F(\text{H}_2\text{O})$ ?” We performed linear regressions with more than one variable, e.g. including temperature and  $\text{FCO}_2$ . However, these calculations resulted in no significant improvement compared to the single parameter regressions. For the intensive field, the growth stage (LAI) indeed was the second important explaining parameter, as shown

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in section 4.3.

“Normalisation by LAI. As with other parameters such as canopy resistances, one would not necessarily expect the emission to scale linearly with LAI, for example because of shading effects. In addition,  $F(\text{H}_2\text{O})$  will already, to some extent, include some of the LAI dependence, while  $R_g$  does not. While the authors first assess the fluxes after normalisation through dividing by LAI, they later decide to implement LAI in a different functional relationship (Eq. 3). This introduces some inconsistency into the argument. It would be much more straight-forward to plot either the ratio  $F(\text{MeOH})/F(\text{H}_2\text{O})$  or, preferably,  $F(\text{MeOH})/R_g$  against LAI to derive the functional relationship on LAI.” We followed this suggestion and added a plot of  $F(\text{MeOH})/F(\text{H}_2\text{O})$  versus LAI (figure 11). See also comment to referee #3.

“ $R_g$  vs  $F(\text{MeOH})$ . In my opinion,  $R_g$  would be the preferable scaler as it is (a) more readily available, e.g. when predicting MeOH fluxes in models, (b) is a more basic parameter and (c)  $F(\text{H}_2\text{O})$  also depends on soil water. The question depends to some extent on what is driving the MeOH flux. Does  $F(\text{MeOH})$  respond primarily to stomatal conductance or is it associated with the water flux itself. Obviously, the water flux does not just depend on stomatal conductance, but also e.g. on surface temperature. The authors could make an attempt to estimate stomatal conductance from  $F(\text{H}_2\text{O})$  during dry periods in an attempt to learn more about the process of MeOH emission.” We do not consider our chosen parameterisation based on  $F(\text{H}_2\text{O})$  as the optimum choice for general use at other sites or for modelling purposes. In the present study we showed that  $R_g$  and  $F(\text{H}_2\text{O})$  correlated similarly well with the methanol flux. However, as illustrated in Fig. 10, the water vapour flux showed a better correlation during some nighttime cases and was chosen for this reason for the present evaluation.

“2P138, l8. How homogeneous is the plant species composition of the extensive field. Could heterogeneity have contributed to the smaller correlation coefficient?” The extensive field is largely composed of twelve different species, including graminoids, forbs and legumes. We observed an inhomogeneity in the distribution of some species which

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may indeed contribute to the smaller correlation coefficient.

“P140, I9. Why would the emission of a more soluble compound be more closely controlled by stomatal conductance? Intuitively I would have assumed the opposite? Also, the statement “The magnitude of daytime emissions also depends on the rate of methanol production within the leaves.” needs to be backed up by references or evidence.” The effect of stomatal conductance on soluble compounds is discussed in detail by Niinemets and Reichstein (2003a,b) and by Niinemets et al. (2004), as referenced in the manuscript. It is mainly based on the concept that the liquid phase in the leaf may serve as a buffer pool for the compound allowing a decoupling between the production and the emission. In this way the emission is mainly dependent on the stomatal conductance and not only on factors controlling the production. We also rephrased the text so that the statement about the influence of methanol production is now clearly related to references.

“P141, I14. Is this slower release consistent with the dynamic model?” Due to its relative complexity, we did not yet apply a dynamic model. But we will try to answer this question in our future work.

“the authors should make sure that the font of the symbols in the text matches those of the equations. For example,  $c(t)$  in line 23 on page 131 is non-cursive, while in Eq. (1) it is cursive. Cursive symbols may be preferable?” We changed the font of all symbols to cursive in the text as well as in the equations.

“P127, I12: specify more clearly “removal processes for methanol from the atmosphere are oxidation ...” The oxidation of methanol is described in detail by Monod et al. 2000, which will be properly cited in the revised manuscript.

“P129, I2. I believe, the site is now also a Supersite of the new NitroEurope programme, which could be mentioned for completeness.” We added this information in section 2.1.

“Eq. (4). The authors need to define  $y_0 = 0.00962$  or they need to state the units in

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which  $F(\text{MeOH})$  and  $F(\text{H}_2\text{O})$  should enter Eq. (4).” The units which enter the Eq. 4 are  $\text{nmol m}^{-2} \text{s}^{-1}$  for  $F\text{MeOH}$  and  $\text{mmol m}^{-2} \text{s}^{-1}$  for  $F\text{H}_2\text{O}$ , respectively. We added this information in section 4.3.

“Fig. 11. The symbol of  $F(\text{MeOH})_{\text{cal}}$  is invisible in my copy of the figure legend.” We changed the colour of  $F\text{MeOH}$  in Fig. 11 (new Fig. 12 a) for better visibility.

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Interactive comment on Biogeosciences Discuss., 4, 125, 2007.

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