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Discussions



# *Interactive comment on* "Environmental controls over methanol emission from leaves" *by* P. Harley et al.

**P. Harley et al.**

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Referee #1 raises the question of whether using zero air in all these measurements rather than air containing typical ambient concentrations of methanol may have biased the results. This is a question that I've grappled with from time to time and welcome any comments from the community. The referee suggests that this is unlikely to be a critical issue, but I think it requires close examination. It has been clearly shown that a variety of low molecular weight oxygenated VOC (e.g., formaldehyde, acetaldehyde, various organic acids) exhibit bi-directional fluxes defined by a compensation point. By definition, when ambient concentrations exceed the compensation point, leaf uptake occurs, and vice versa. This is simply a reflection of the fact that the flux obeys Fick's law, and is proportional to both the concentration difference between the leaf intercellular air space and the ambient air outside the leaf boundary layer and to stomatal



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conductance, with the direction of the flux determined by the concentration gradient. In principle, therefore, any VOC can exhibit bi-directional fluxes. In order for uptake to occur, however, significant physico-chemical (e.g., solubility) or chemical sinks must be present in the leaf to reduce the internal gas phase concentration to levels below those in the surrounding atmosphere. Surprisingly, no one to my knowledge has examined compensation point behavior for methanol, and it may be that the source strength of methanol production greatly exceeds any potential internal sinks (for example, methanol going into solution or oxidation of methanol to formaldehyde) such that emission predominates and the compensation point is quite high. However, at low temperatures and perhaps at low light, methanol production appears to decrease dramatically, and sinks may remain sufficiently high to lower the compensation point and allow methanol uptake, particularly if ambient concentrations are high. Certainly at the canopy scale, methanol deposition, particularly at night, has been observed, although the extent to which this represents leaf uptake is unclear. That methanol exhibits bi-directional fluxes is a relatively easy hypothesis to test, and I plan to do so at the earliest opportunity.

Referee #1 notes the fact that correlations between methanol emissions and transpiration are generally more robust than between emissions and stomatal conductance. He suggests the possibility that the flux of methanol may not represent only the gas phase flux which is modeled using the Niinemets-Reichstein Model but also a contribution of methanol dissolved in the transpiration stream. I considered this possibility and attempted to incorporate the methanol dissolved in the transpiration stream into my model calculations. The effect appeared to be negligible, making virtually no difference in model behavior. Although I can't rule out the possibility that methanol carried along in the transpiration stream (including methanol produced elsewhere in the plant) contributes to the flux, I concluded that the strong linear correlation between emissions and transpiration was largely fortuitous. Transpiration is proportional to stomatal conductance at constant temperature, but incorporates the effects of leaf temperature through changes in saturation vapor pressure. Methanol emissions, under certain conditions,



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are also proportional to stomatal conductance, incorporating effects of temperature through methanol production. Fortuitous or not, however, the strong correlation may prove useful in modeling emissions at the canopy scale, for instance, if similar correlations are apparent.

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Interactive comment on Biogeosciences Discuss., 4, 2593, 2007.



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