# *Interactive comment on* "Ecosystem-scale compensation points of formic and acetic acid in the central Amazon" *by* K. Jardine et al.

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Overall, this is a very skilled and an interesting study that makes several important points. Understanding ecosystem controls on organic acid emissions and deposition is highly relevant and this study makes a nice contribution towards understanding these controls. There are a few minor aspects that could be improved as detailed below. However, there is a major omission that needs to be addressed. Specifically, the study ignores the theory of the role of stomata on the emission and uptake of water-soluble volatiles. Compounds with a low Henry's law constant such as formic and acetic acid can be stored in leaf liquid phase and this can exert a major control on the emission kinetics. The theory of stomatal control of VOC emission, including formic and acetic acid, has been developed by Niinemets and Reichstein (Niinemets and Reichstein,

2003a; Niinemets and Reichstein, 2003b). I would not mention this here, but it is pertinent given the reported data. Authors say that the emissions of formic and acetic acid peaked together with light and temperature in mid-day, but this is not correct for branch emissions. In fact, branch emissions peaked BEFORE the maximum light and temperature values (Fig. 1 lower panel). This is consistent with the emissions of these highly water-soluble compounds from leaf liquid phase during stomatal opening. a certain equilibrium concentration of these compounds is built up during the time when stomata are closed at night, and during stomatal opening this storage pool is emptied. The situation is very similar as with methanol (Harley et al., 2007; Hüve et al., 2007). On the other hand, the ambient air concentrations of formic and acetic acids peak together with light and temperature, or the emission peaks occur AFTER the maxima in light and temperature (Fig. 1 upper panel). Authors do not discuss this discrepancy in the MS, but this difference between the temporal kinetics of ambient air concentration and emission time courses is important with major mechanical implications. Given that the emission time courses are partly driven by stomata, while the ambient concentrations are apparently not, this discrepancy actually suggests that ambient concentrations in this Biosphere II experiment maybe do not reflect the emissions of acids only. In fact, the ambient concentrations of these compounds can be partly driven by oxidation of other emitted plant volatiles such as isoprene and monoterpenes, emissions of which peak at mid-day, followed by peaking atmospheric reactivity in this semi-closed system. Differences in the ratio of FA/AA between individual branches and ambient air further support this suggestion.

The other issue that might deserve mentioning is that the Henry's law constant and thus, the compensation point of the organic dissociatable compounds such as organic acids or bases will depend on the pH of the leaf liquid phase. As pH of cell walls may rapidly change, and also vary with leaf water status, it might be important to point out. In addition, pH on leaf surface will depend on the microbial activity of leaf surface that is particularly relevant in understories of tropical forests. The pH dependence of the compensation point is currently routinely used, e.g. to simulate bidirectional

exchange of ammonia (Farquhar et al., 1979; Nemitz et al., 2000; Schjoerring et al., 1998). Given that ammonia and these organic acids behave very similarly from the modeling point of view, I do not honestly see the value of the statement that "this is the first" (p9298,L27). Based on solid physico-chemical principles, there is no doubt that there is a compensation point for the organic acids, and it is surprising that this is still not included in models in a generalized manner.

p9296, L4-5. This is an important point.

p9286,L11. Formic and acetic acid are actually among the most "non-volatile" plant compounds, i.e., partition preferably to liquid phase.

p9286,L16-17 vs. L11-12. When there are no stronger acids in precipitation, these organic acids will have quite a large potential to partition to particle phase. On the other hand, the presence of any stronger acid in the precipitation, e.g. during the "burning season" will importantly alter the bidirectional exchange of organic acids between vegetation and atmosphere, as it will effectively reduce the dissociation of organic acids, thereby increasing their volatility. This statement will require revision based on the dependence of the Henry's law constant on pH.

p9288,L5-8. "branches" reads awkward. Why not "plant leaves"?

p9288,L12. Solubilization as well, depending on pH. Plants have a huge capacity to store these organic acids.

p9290. how long was the line?

p9291,L1. better use other symbol for the slope. m stands for meter

p9291,L7. Why not zero air for calibration?

P9291, L24-26. You said that the ecosystem is dominated by legumes and palms, and only one legume species is studied and no palms. This makes it real hard to scale up to ecosystem level on the basis of these data, i.e., we cannot be very conclusive

C3494

as regards to the differences in acid ratios obtained from enclosure study and from ambient measurements.

p9292, L1-4. So altogether 4 lines? Also, I guess the lines were measured subsequently, so "continuously" is not appropriate here. This section altogethe is hard to understand and needs revision.

p9292, L23/P9293, L1-3. What was the overall canopy height? What about the above-canopy measurements?

p9293, L9. 8-10 m is real shade

p9296 and elsewhere in the text. When used in unit, nmol not nmole

p9297. better strengthen these arguments with what we know about the emission controls of water-soluble compounds, as well as mention the role of pH.

p9298, L13-18. Somehow not logically linked with the preceding text. Seems to need revision.

p9299,L2. I disagree with "an". As outlined above, the compensation point will depend on stomatal openness, and on temperature and pH effects on the Henry's law constant of these acids.

p9299, L6-8. This is overtly simplified as the dynamics will be driven by stomata, secondary oxidation of highly reactive plant VOCs, distribution of dry and wet surfaces in the ecosystem etc. A single compensation point is an illusion.

Fig. 1, lower panel. The unit is awkward. In recent Biogeosciences paper, we have argued that one should normally not use powers of ten in units (Niinemets et al., 2011). What is the unit then, pmol or micromol, and why do you multiply only the first number?

Fig. 3. What can importantly alter these gradients is the variation in surface wetness along the canopy. Normally leaf surface is on average drier in the upper canopy.

C3495

Fig. 4, What is the standard error of the estimate of the compensation point? It is unlikely that the estimates are statistically different. In fact, the theory predicts a lower compensation point for acetic acid due to lower Henry's law constant.

Farquhar, G.D., Wetselaar, R., and Firth, P.M. (1979) Ammonia volatilization from senescing leaves of maize. Science, 203, 1257-1258. Harley, P., Greenberg, J., Niinemets, Ü., and Guenther, A. (2007) Environmental controls over methanol emission from leaves. Biogeosciences, 4, 1083-1099. Hüve, K., Christ, M.M., Kleist, E., Uerlings, R., Niinemets, Ü., Walter, A., and Wildt, J. (2007) Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata. Journal of Experimental Botany, 58, 1783-1793. Nemitz, E., Sutton, M.A., Gut, A., San José, R., Husted, S., and Schjoerring, J.K. (2000) Sources and sinks of ammonia within an oilseed rape canopy. Agricultural and Forest Meteorology, 105, 385-404. Niinemets, Ü., Kuhn, U., Harley, P.C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovici, L., Geron, C., Guenther, A.B., Kesselmeier, J., Lerdau, M.T., Monson, R.K., and Peñuelas, J. (2011) Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols. Biogeosciences, 8, 2209-2246. Niinemets, Ü., and Reichstein, M. (2003a) Controls on the emission of plant volatiles through stomata: a sensitivity analysis. Journal of Geophysical Research - Atmospheres, 108, 4211, doi:4210.1029/2002JD002626. Niinemets, Ü., and Reichstein, M. (2003b) Controls on the emission of plant volatiles through stomata: sensitivity or insensitivity of the emission rates to stomatal closure explained. Journal of Geophysical Research - Atmospheres, 108, 4208, doi:4210.1029/2002JD002620. Schjoerring, J.K., Husted, S., and Mattsson, M. (1998) Physiological parameters controlling plant-atmosphere ammonia exchange. Atmospheric Environment, 32, 491-498.

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C3496