**Biogeosciences
Discussions**

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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We greatly appreciate the extensive effort that Ulo Niinemets has spent in thoroughly reviewing our manuscript. The very helpful comments have greatly improved our manuscript. Our responses to each of the 24 comments and the changes made to the manuscript are provided below.

Comment 1

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.

Response 1

We now include a brief discussion on the importance of stomatal control over biosphere-atmosphere FA and AA exchange fluxes:

Line 378: "In addition, one potentially important control over biosphere-atmosphere exchange of FA and AA that is currently not considered is the role of canopy conductance which may have a seasonal pattern in the Amazon (Vourlitis et al., 2008, Sommer et al., 2002). Unlike isoprene whose emission rates have been shown to be insensitive to changes in stomatal conductance due to the counterbalancing effect of isoprene buildup in the intercellular air spaces following stomatal closure (Fall et al., 1992), physicochemical simulations suggest that stomatal behavior may influence FA and AA exchange rates (Niinemets et al., 2003). Due to the high water solubility of these compounds, gas-phase concentrations within plants do not significantly increase upon decreased stomatal conductance due to their preferential partitioning into the aqueous phase (Niinemets et al., 2003). However, this model does not include biological consumption within plants which may limit the potential for large pools of FA and AA to accumulate in plants upon stomatal closure. However, as has been experimentally demonstrated for acetaldehyde (Jardine et al., 2008), stomatal conductance may only influence the FA and AA exchange velocities (slope of flux versus concentration curve) and not the compensation points (x-intercept of flux versus concentration curve) which are primarily determined by the relative rates of biochemical production

and consumption processes. Nonetheless, the lack of available experimental data on the relationship between stomatal conductance and FA and AA exchange rates and compensation points, these ideas remain speculative. This highlights the need for a focused study on the plant physiological and environmental factors that influence the bidirectional exchange of FA and AA between plants and the atmosphere."

Comment 2

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.

Response 2

The glass structure at Biosphere 2 efficiently attenuates all of the UVB radiation and UVA wavelengths between 320 and 385 nm needed to drive photooxidation of isoprene and monoterpenes. Therefore, we assume that FA and AA production from gas-phase photooxidation of biogenic isoprenoids is negligible. Evidence for the lack of oxidants (OH and O3) needed to drive significant atmospheric oxidation of isoprene inside the tropical rainforest mesocosm at Biosphere 2 has been reported. When transparent Teflon gas sample bags were filled with ambient air from the mesocosm, exposed to the sun inside the mesocosm, and analyzed for isoprene concentrations over the course of the day, no change was observed despite strong diurnal changes in environmental conditions and ambient isoprene concentrations (Pegoraro et al., 2005). Therefore, we assume that ambient concentrations of FA and AA reflect plant emissions. We now include two supplementary figures S1 and S2 showing methanol emissions from two tropical species together with FA and AA emissions. In addition, we include additional examples of ambient concentrations and branch fluxes inside the Biosphere 2 rainforest mesocosm in relationship with ambient and branch enclosure air temperature (Figures S3-S6, supporting information). We note that we only studied FA and AA emissions from 8 tropical plant species in the Biosphere 2 rainforest mesocosm out of 91 species currently present. Differences in FA/AA ratios between branch and mesocosm scales are expected since ambient air measurements integrate emissions from all vegetation in the mesocosm while branch measurements isolate one particular species.

Line 278: "As has previously been observed from other plants (Harley et al., 2007, Huve et al., 2007), we observed strong methanol branch emission bursts from several tropical species in the morning following stomatal opening in accord with liquid phase accumulation at night followed by morning release (Figs. S1 and S2, supporting information). In some cases, (e.g. H. rosa-sinensis, Fig. S1), methanol emissions were dominated by the morning burst while in others (e.g. S. campanulata, Fig S2), large methanol emissions occurred both in the morning and during mid-day when PAR was elevated. In contrast with methanol, FA and AA did not show morning bursts suggest-

ing that they do not accumulate at night, possibly due to rapid consumption by primary metabolism (e.g. AA activation to acetyl-CoA and FA conversion to tetrahydrofolic acid) and/or their sources are strongly light and temperature dependent (e.g. dependent on photosynthesis, glycolysis, photorespiration, etc.). In general, we found that branch fluxes and ambient concentrations of FA and AA tracked air temperature well (see Fig. 1 and supplementary Figs. S1-6). In order to prevent cold stress at night, air handlers often turned on to warm the air when the ambient temperatures dropped below to 20 °C. In response, FA and AA ambient concentrations slightly increased (see Fig. 1 and supplementary Figs. S1-6). In addition, maximum ambient air temperatures and FA and AA ambient concentrations often occurred 1-2 hours after maximum PAR (see Fig. 1 and supplementary Figs. S1-5). Moreover, because some branch enclosures were located on the west side of the mesocosm which receives sunlight later than the east side, enclosure air temperatures increased in the morning before direct sunlight was received by the branches (Fig. 1, supplementary Fig. S6, S5). In these branches, FA and AA emissions significantly increased with temperature prior to the strong rise in PAR. These observations suggest that de-novo biosynthesis and emissions of FA and AA are not completely dependent upon photosynthesis. However, the importance of light is implied from ambient air observations during the winter where ambient air temperatures at night approached those during the day (due to heating at night by the air handlers) yet ambient FA and AA concentrations were greatly stimulated during the day relative to the night (supplementary Fig. S3). In addition, FA and AA emissions from a single species (mango: M. indica), appeared to track PAR better than air temperature (supplementary Fig. S3)."

Comment 3

The other issue that might deserve mentioning is that the Henry's law constant and thus, the compensation point of the organic dissociable 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).

Response 3

Line 419: "In addition, a pH dependence of the ecosystem compensation point may be expected since changes in pH will influence the relative abundance of protonated versus ionized organic acids in aqueous solutions, thereby changing their volatility, water solubility, and reactivity to further metabolism. The pH within plant cells may rapidly change and vary with environmental conditions such as light, temperature, and leaf water status. Among other factors, the pH on leaf surfaces will depend on the pH of precipitation and microbial activity that is particularly important in understories of tropical forests. The pH dependence of the compensation point is currently used to simulate bidirectional exchange of ammonia (Farquhar et al., 1979, Nemitz et al., 2000, Schjoerring et al., 1998)."

Comment 4

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.

Response 4

Despite some similarities with ammonia, to our knowledge a compensation point model has not been developed to describe the biosphere atmosphere exchange of FA and AA. Nonetheless, it is always important to obtain experimental evidence for model predictions and it cannot be assumed that the processes that are observed at the branch

scale will occur at the ecosystem scale. Our study is the first clear study showing that plant canopies can be a net source of FA and AA to the atmosphere and the first ecosystem-scale evidence that biosphere-atmosphere exchange of FA and AA are determined by ambient concentrations and an ecosystem scale compensation point.

Comment 5

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

Response 5

Yes.

Comment 6

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

Response 6

FA and AA are both highly volatile and water soluble. We now highlight the high water solubility of FA and AA below. Line 66: " FA and AA are highly water soluble (low Henry's law constant $< 1 \times 10-2$ Pa m3 mol), and therefore partition preferably to the liquid phase (Niinemets et al., 2003) where they may significantly contribute to the hygroscopicity of cloud condensation nuclei particles and therefore impact precipitation processes (Yu, 2000)."

Comment 7

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.

Response 7

Line 75: "However, the presence of strong acids like nitric acid in precipitation derived from biomass burning during the dry season may limit the partitioning of weak acids like FA and AA into precipitation."

Comment 8

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

Response 8

Line 116. "branches" replaced with "plant leaves".

Comment 9

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

Response 9

Unlike methanol, we do not have evidence that large pools of FA and AA are stored in plants but instead suggest that FA and AA are rapidly metabolized. We adjust this statement to reflect the fact that water solubility alone cannot explain the high deposition velocities observed for many oxidized volatile organic compounds. Line 119: "Recent observations suggest that the deposition of many oxidized volatile organic compounds from the atmosphere to plant canopies can occur with significantly higher deposition velocities than expected from solubility alone (Karl et al., 2010). Active metabolic consumption of oxidized volatile organic compounds (VOCs) by plants can lead to efficient uptake thereby sustaining a large concentration gradient between the atmosphere and the intercellular air spaces; a process that does not occur in simple dry deposition schemes. Like other reactive compounds like ozone, many reactive oxidized VOCs like FA and AA that are intermediates in metabolic pathways may be lost

almost immediately upon entering a leaf through stomata."

Comment 10

p9290. how long was the line?

Response 10

We now include the length of the heated gas sampling lines. Line 248: "The FA and AA gradient measurement scheme employed was based on that used in the AMAZE 2008 campaign (Karl et al., 2009) with six ambient air inlets at different tower heights (2, 11, 17, 24, 30, and 40 m) sequentially analyzed for VOCs (10 minutes at each inlet, one complete canopy profile per hour). The air sample tubing lengths were equal to the inlet heights plus an additional 4 m each to reach the detector in the instrument trailer directly adjacent to the tower."

Comment 11

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

Response 11

Line 199: It was not necessary to include a symbol for the slope (m) so it was removed.

Comment 12

p9291,L7. Why not zero air for calibration?

Response 12

We were not able to obtain ultra high purity zero air in Manaus, Brazil due to low availability and high cost and therefore calibrated under ultra high purity nitrogen rather than under air. Given that O_2^+ signals in the PTR-MS were < 4 % of H_3O^+ during measurements in air, we do not expect FA and AA calibration factors to show large differences in nitrogen versus air.

Comment 13

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 scaleup to ecosystem level on the basis of these data, i.e., we cannot be very conclusive as regards to the differences in acid ratios obtained from enclosure study and from ambient measurements.

Response 13

For practical reasons (large leaf sizes), we were unable to study FA and AA emissions from palms. However, it is not our intention to scale the branch emission data to the whole mesocosm scale but to show that emissions of organic acids from individual tropical species are enriched in FA relative to AA, which was also observed in ambient air at the whole mesocosm scale.

Comment 14

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

Response 14

We now include a revised version of this section. Line 224: "Three different air samples from the rainforest mesocosm were continuously pumped through heated (50 °C) Teflon (PFA, $\frac{1}{4}$ in. O.D. x 60 m) tubing into the adjacent laboratory for trace gas analysis and include zero air entering a single 5 L Teflon branch enclosure, branch enclosure air, and ambient mesocosm air at mid height (13 m). These gas samples as well as zero air inside the laboratory were sequentially analyzed for FA and AA concentrations by PTR-MS (each gas sample measured every hour)."

Comment 15

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

Response 15

We now include the average canopy height (30 m). The above canopy measurements were made at 40 m height.

Line 248: "The FA and AA gradient measurement scheme employed was based on that used in the AMAZE 2008 campaign (Karl et al., 2009) with six ambient air inlets extending throughout and above the 30 m tall canopy at 2, 11, 17, 24, 30, and 40 m tower heights. The six inlets were sequentially analyzed for FA and AA concentrations (10 minutes at each inlet, one complete canopy profile per hour)."

Comment 16

p9293, L9. 8-10 m is real shade

Response 16

Agreed

Comment 17

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

Response 17

All instances of nmole have been converted to nmol.

Comment 18

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.

Response 18

This section has now been updated to include a discussion on the possible effects of pH (see response to comment X) and stomatal conductance/water solubility (see response to comment Y).

Comment 19

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

Response 19

The text was reorganized with sentences logically linked with the preceding text.

Comment 20

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.

Response 20

While compensation points likely vary throughout the canopy for the reasons mentioned in the comment, the ecosystem compensation point, by definition, is a single value representative of the whole ecosystem.

Comment 21

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.

Response 21

We defined the ecosystem compensation point as the ambient concentration at which the concentration gradient between the top of the canopy (30 m) and above the canopy (40 m) is zero. As we describe in the manuscript; Line 398: "Furthermore, an ecosystem scale compensation point encloses exchange processes affected by multiple sinks and sources beyond vegetation including dissolving into surface water films within the canopy and at the surface, microbial processes, and within canopy gas phase photoox-

idation of VOCs."

Comment 22

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?

Response 22

To clarify this unit, we have removed the multiplier. This unit is nmol m-2 s-1 to be consistent with recent literature reports of FA and AA emission rates from plants (Seco et al., 2007).

Comment 23

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.

Response 23

We now mention this a possible contributing mechanism.

Line 348: "With leaf surfaces on average drier in the upper canopy, the increase in surface wetness within the canopy and at the surface likely contributes to FA and AA deposition there."

Comment 24

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.

Response 24

The compensation point is strongly influenced by both biological production and consumption processes in plants and therefore cannot be determined by water solubility

alone. We now include the standard deviation of the estimated ecosystem compensation points determined from error propagation of the standard deviation in linear fit coefficients (slope and y-intercept).

Line 56: Compensation points: 1.3 +/- 0.3 nmol mol-1: FA, and 2.1 +/- 0.4 nmol mol-1: AA Line 394: Compensation points: 1.3 +/- 0.3 nmol mol-1: FA, and 2.1 +/- 0.4 nmol mol-1: AA

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