

Authors' Response to Co-Editor and reviewers

We appreciate the helpful comments made by Co-Editor and reviewers.

Below, we indicate our point-to-point responses in blue.

Co-Editor:

Comments to the Author:

The two reviewer judged the revised manuscript. At least one reviewer still showed great concern about the scientific quality. Particularly the reviewer requests some more concrete evidence that lactic acid is produced by microorganisms, and to argue the possibility of other sources (e.g., photochemistry) more carefully. I find that revision is on the right track but would need to consider if the authors could address to these points.

My additional concern is on Figure 9. How to interpret the negative correlation with RH during nighttime? Better not to show regression lines when the correlation is not statistically significant? (also for other figures)

Response:

Based on the reviewer's comment, we modified the corresponding sentences in the revised manuscript after the additional lab work on the analysis of forest soil samples for monoacids.

"Gaseous lactic acid in daytime did not show positive correlations with C₁–C₆ monoacids ($r^2 < 0.004$), whereas lactic acid in nighttime show positive correlations with C₃–C₆ ($r^2 = 0.45$ – 0.65) although they were rather scattered. Particulate lactic acid also did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Formation processes of C₁–C₆ acids may be different from hydroxy monoacids." Please see page 5, lines, 11-14.

"In this study, relatively high concentrations of particulate lactic and isopentanoic acids were observed. Lactic acid is primary produced by Bacteria (*Lactobacillus*) (Cabredo et al., 2009) and from the plant tissues (Raja et al., 2008). Lactic acid can also be produced by the oxidation of isoprene with ozone in (Nguyen et al., 2010). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Uta et al., 2012 and references therein). A positive correlation was observed between lactic acid and isopentanoic acids in particle phase ($r^2 = 0.98$). We confirmed that lactic acid is abundantly present in forest soil ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$) but isopentanoic acid is not (unpublished data). Lactic and isopentanoic acids may be linked to the biosynthetic processes in the forest soil system as well." Please see page 5, lines 22-28.

Based on the suggestion, regression line was deleted when the correlation is not statistically significant (please see Figures 6, 7, 8, and 9). We have added the following sentence in figure captions (Figures 6, 7, 8, and 9).

The sentence “The coefficient of determination shows that regression line is statistically significant ($p < 0.05$).” Please see Figures 6, 7, and 8.

The sentence “The coefficient of determination shows that regression line is statistically significant ($p < 0.1$).” Please see Figure 9.

Reviewer 1

Authors gave sufficient answers to reviewer comments and improved their manuscript based on them. However, I still have some minor concerns listed below:

Comment 1. I would think that SO_4 is not good tracer for urban air, since general traffic is not usually emitting it. SO_4 is mainly emitted by ships and certain industry. Please, correct that. Could you use for example NO_x as an urban traffic tracer?

Response:

NO_3^- is good tracer for urban air. We have modified the sentences in the revised manuscript as follows.

“Concentrations of LMW monoacids did not correlate with $nss-SO_4^{2-}$ and NO_3^- that are used as anthropogenic tracers, indicating that LMW monoacids are derived from the local sources within the forest ecosystem.” Please see page 1, lines 16-18.

“We compared the concentrations of individual monoacids together with $nss-SO_4^{2-}$ and NO_3^- : anthropogenic aerosol tracers to evaluate the influence of anthropogenic air mass transport from urban area. We confirmed that individual monoacids in both gas and particle phases did not show correlation with $nss-SO_4^{2-}$ ($r^2 < 0.14$) and NO_3^- ($r^2 < 0.11$).” Please see page 4, lines 20-23.

“Concentrations of LMW monoacids in gas and particle phases did not correlate with $nss-SO_4^{2-}$ and NO_3^- (anthropogenic tracers).” Please see page 7, lines 2-3.

Comment 2. Page 4, line 13: Do you define somewhere, what is short-chain acids and what is long-chain?

Response:

Following the comment, the sentence was modified as below.

“Formic (C_1) and acetic (C_2) acids are largely present in gas phase.” Please see page 4, line 12.

Comment 3. Check the values in Table 1. At least night time values and F_p for Lactic acid cannot be correct.

Response:

Individual values of F_p were first calculated by each measurement data and then average values of F_p were calculated by individual values of F_p . Values of F_p (Table 1) are different from F_p calculated by average concentrations of gaseous and particulate monoacids.

Comment 4. Page 5, lines 6 and 7: You claim that ‘We suggest that gaseous C_1-C_6 monoacids are

emitted from the forest floor where soil microorganisms and plant roots contribute to the emissions of gaseous C₁-C₆ monoacids'. Based on you data you cannot make this strong conclusion. They can also be produced for example from the reactions of BVOCs.

Response:

Following the comment, the sentence was modified as below.

“Although we detected formic, acetic, propionic, and isobutylic acids in forest soil (Kunwar et al., unpublished data, 2018), a quantitative contribution from the forest floor cannot be evaluated in the present study. On the other hand, photo-oxidation of BVOCs such as isoprene and monoterpenes are major sources of formic and acetic acids in the atmosphere (Paulot et al., 2011). Our results suggest that forest floor may be a source of gaseous C₁-C₆ monoacids to the atmosphere.” Please see page 5, lines 7-10.

We have added the following sentence in abstract.

“Forest soil may be a source of gaseous C₁-C₆ monoacids in the forest atmosphere.” Please see page 1, lines 19-20.

Comment 5. Page 5, line: You claim that ‘We suggest that major portion of C₁-C₆ acids were emitted within the forest floor’. How do you know that it is not from isoprene oxidation or oxidation of some other VOCs? Do not make this strong conclusion.

Response:

Based on comment 4, we have modified the sentences in the revised manuscript. Please see our response to comment 4.

Reviewer 2

General comments:

I do understand that the authors cannot provide evidence for the emission of organic acids from the forest soil in this study. Under such circumstances, I expect the authors to provide strong convincing supporting data (for example, soil analysis data, laboratory bacterial experiment etc.) to strengthen the authors' claim. This is especially important when the authors propose a new source of marker compounds. In this revised manuscript the authors failed to do so, and they only provided a small number of biology related references to suggest microorganisms as a source of these acids in the atmosphere. Based on the comments during the discussion phase, and this comments that are substantiated below, I am not able to recommend this manuscript for publication in ACP.

Comment 1: Abstract

(Revised) Page 1 line 18: Is lactic acid really produced by microorganisms? Do the authors have concrete evidence for this? Correlation does not imply causation.

Response:

Following the comment, we deleted the following sentence in abstract and conclusion.

The sentence: "Isopentanoic acid in particle phase showed a positive correlation with lactic acid ($r^2 = 0.98$), which is produced by soil microbes."

We have added the following sentence in abstract.

"Forest soil may be a source of gaseous C₁–C₆ monoacids to the atmosphere." Please see page 1, lines 19-20.

In addition, we modified the corresponding sentences in the revised manuscript.

"Gaseous lactic acid in daytime did not show positive correlations with C₁–C₆ monoacids ($r^2 < 0.004$), whereas lactic acid in nighttime show positive correlations with C₃–C₆ ($r^2 = 0.45$ – 0.65) although they were rather scattered. Particulate lactic acid also did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Formation processes of C₁–C₆ acids may be different from hydroxy monoacids." Please see page 5, lines 11-14.

"In this study, relatively high concentrations of particulate lactic and isopentanoic acids were observed. Lactic acid is primary produced by Bacteria (*Lactobacillus*) (Cabredo et al., 2009) and from the plant tissues (Raja et al., 2008). Lactic acid can also be produced by the oxidation of isoprene with ozone in (Nguyen et al., 2010). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Uta et al., 2012 and references therein). A positive

correlation was observed between lactic acid and isopentanoic acids in particle phase ($r^2 = 0.98$). We confirmed that lactic acid is abundantly present in forest soil ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$) but isopentanoic acid is not (unpublished data). Lactic and isopentanoic acids may be linked to the biosynthetic processes in the forest soil system as well.” Please see page 5, lines 22-28.

Discussion

Comment 2: (Revised) Page 4 lines 33: This sentence does not make sense. Do the authors mean that OH oxidation is the sole reason for their different concentrations in the atmosphere?

Response:

Following the comment, the sentence was modified as below.

“Formic and acetic acids are stable, leading to higher concentrations of formic and acetic acids in the atmosphere. In addition, we measured LMW monoacids in soil sample (surface ~3 cm) collected at a broad-leaf forest from Chubu University campus in Central Japan on October 31, 2018. LMW normal (C_1 – C_4 , C_7 – C_{10}), branched chain (i C_4), and hydroxyl (lactic and glycolic) monoacids were detected. Concentrations of formic ($7400 \text{ ng g}_{\text{wet soil}}^{-1}$) and acetic ($4260 \text{ ng g}_{\text{wet soil}}^{-1}$) acids were significantly higher than that of other detected monoacids ($\sim 1800 \text{ ng g}_{\text{wet soil}}^{-1}$) (Kunwar et al., unpublished data, 2018). Major portion of monoacids in the forest atmosphere is similar to that in forest soil sample, suggesting forest soil is a source of LMW monoacids as well.” Please see page 4, lines 35-41.

Comment 3: (Revised) Page 4 line 30: These OH rate constants aren't typically accepted values for these compounds. Please refer to NIST Kinetic Database for the list of more widely accepted gas phase OH rate constants of these compounds.

Response:

Following the comment, the sentences were modified as below.

“The rate constants of gaseous formic, acetic, propionic, butyric, and isobutyric acids with OH radicals are 0.45, 0.67, 1.20, 1.79, and $2.06 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (provided by NIST Chemical Kinetics Database). The rate constants of LMW monoacids with oxidant (OH radicals and ozone) may increase with an increase in carbon numbers of monoacids.” Please see page 4, lines 32-35.

Comment 4: (Revised) Page 4 line 39: What do you mean by short lived mono acid? What are the lifetimes of C3-C6 acids? From the gas phase OH rate constant of butyric acid ($1.79E^{-12} \text{ cm}^3/\text{molecule s}$), larger acids do not seem to be much short-lived when OH oxidation is solely considered.

Response:

The lifetimes of monocarboxylic acids (more large acids) may depend on not only OH radical oxidation but also O₃ oxidation. The lifetimes of monoacids (> C₅ monoacids) have not been reported. Based on comments 2 and 3, we have modified the sentences in the revised manuscript. Please see our responses to comments 2 and 3.

Comment 5: (Revised) Page 5 lines 1-7: A small number of references to related microbial activities and plant physiology aren't enough to claim a source of marker compounds in atmospheric samples, especially when environmental variables and biological activities can play significant roles in the emissions and transformations of precursor compounds. The authors may not have not taken soil samples during the campaign, but they can always go back later to get some samples, try to understand soil bacteria, or analyze extractable soil organics.

Response:

As suggested, we measured LMW monoacids in soil sample (surface ~3 cm) collected at a broad-leaf forest from Chubu University in Central Japan on October 31, 2018. LMW normal (C₁–C₄, C₇–C₁₀), branched chain (iC₄), and hydroxyl (lactic and glycolic) monoacids were detected in the soil sample. We modified the corresponding sentences and added the sentences in the revised manuscript.

“In addition, we measured LMW monoacids in soil sample (surface ~3 cm) collected at a broad-leaf forest from Chubu University campus in Central Japan on October 31, 2018. LMW normal (C₁–C₄, C₇–C₁₀), branched chain (iC₄), and hydroxyl (lactic and glycolic) monoacids were detected. Concentrations of formic (7400 ng g_{wet soil}⁻¹) and acetic (4260 ng g_{wet soil}⁻¹) acids were significantly higher than that of other detected monoacids (~ 1800 ng g_{wet soil}⁻¹) (Kunwar et al., unpublished data, 2018). Major portion of monoacids in the forest atmosphere is similar to that in forest soil sample, suggesting forest soil is a source of LMW monoacids as well.” Please see page 4, lines 36-41.

“Although we detected formic, acetic, propionic, and isobutylic acids in forest soil (unpublished data), a quantitative contribution from the forest floor cannot be evaluated in the present study.” Please see page 5, lines 7-8.

“We confirmed that lactic acid is abundantly present in forest soil (1860 ng g_{wet soil}⁻¹) but isopentanoic acid is not (unpublished data).” Please see page 5, lines 26-27.

Comment 6: (Revised) Page 5 lines 24: “somewhat end products” does not makes sense. It is either “end product” or “intermediate”.

Response:

Corrected as suggested. Please see page 5, line 41.

Reference added.

Raja, S., Raghunathan, R., Yu, X. Y., Lee, T., Chen, J., Kommalapati, R. R., Murugesan, K., Shen, X., Qingzhong, Y., Valsaraj, K. T., and Collett Jr., J. L.: Fog chemistry in the Texas-Louisiana Gulf Coast corridor, *Atmos. Environ.*, 42, 2048-2061, 2008.