

Authors' Response to Co-Editor

After the revision, I need to say that overall integrity was reduced. I will reconsider after major revisions.

Response:

We appreciate the critical but helpful comments. Please find our point-to-point responses as below.

1. Two major flaws: First, monoacids will not react with O₃. Second, the new sentence in Abstract that "concentrations of LMW monoacids did not correlate with nss-SO₄²⁻ and NO₃⁻, indicating that LMW monoacids are derived from the local sources" has a logical flaw. The fact indicates that they are not likely from urban sources, and never indicate about the local sources.

Response:

We confirmed that gaseous LMW monoacids will not react with O₃.

Following the comment, the sentence was modified as below.

"Concentrations of LMW monoacids did not show correlations with anthropogenic tracers such as nss-SO₄²⁻ and NO₃⁻, indicating that anthropogenic contribution is not important." Please see page 1, lines 17–18.

2. Uta et al. (2012) was cited many times in text as important source of information for this manuscript, but it did not appear in the reference list.

Response:

We made a mistake in the author name.

We have replaced "Uta et al., 2012" by "Effimert et al., 2012".

We also added the following papers in the reference section.

Kawamura, K. and Gagosian, R. B.: Implication of ω-oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty acids, *Nature*, 325, 330-332, 1987.

Tsai, Y. I. and Kuo, S. C.: Contributions of low molecular weight carboxylic acids to aerosols and wet deposition in a natural subtropical broad-leaved forest environment, *Atmos. Environ.*, 81, 270-279, 2013.

3. It was good to include soil analysis, but the sampling was made at a different site, for which no justification was provided. Detection of high concentrations of lactic acid, C₁ and C₂ monoacids in soil supported the idea that they originate from soil or bacterial processes, but the fact that gaseous lactic acid did not show positive correlation with C₁-C₆ monoacids (page 5, lines 11-12) did not support the idea. Further, the authors claim first that branched chain monoacids including iC₄ (and iC₅, isopentanoic acid) are known as common metabolites of bacteria (page 5, line 3) and regarded them as a tracer from that emission sector. But they did not show up in high concentrations from soil analysis, denying their assumption. Overall my impression is that the soil analysis introduced more puzzle. Analysis of soil from the same site as atmospheric measurements were made is important.

Response:

Following the comment, we modified the corresponding sentences and added few sentences in the revised manuscript, as follows.

"Although we did not collect a forest soil sample from Sapporo during the air-sampling period, we collected a surrogate soil sample (surface ~3 cm) from a broad-leaf forest at Chubu University campus in central Japan on October 31, 2018. The soil sample was analyzed for LMW monoacids after water extraction employing the analytical protocol described in the experimental section. LMW normal (C₁–C₁₀), branched (iC₄) and hydroxyl monoacids were detected in the soil sample (Kunwar et al., unpublished data, 2018). We found high abundances of formic (7400 ng g_{wet soil}⁻¹) and acetic (4260 ng

$\text{g}_{\text{wet soil}}^{-1}$) acids in the soil sample, which were significantly higher than the rest of monoacids ($\sim 1800 \text{ ng g}_{\text{wet soil}}^{-1}$). Interestingly, hydroxyacids such as glycolic ($1680 \text{ ng g}_{\text{wet soil}}^{-1}$) and lactic ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$) acids were abundantly detected in the soil samples together with isobutyric acid ($77 \text{ ng g}_{\text{wet soil}}^{-1}$) (Kunwar et al., unpublished data, 2018). These preliminary results suggest that monoacids in the forest atmosphere are in part derived from forest soil via microbial decomposition of plant debris and subsequent emission to the air.

However, it is not easy to evaluate the quantitative contribution of monoacids from the forest floor. It is likely that molecular composition of LMW monoacids in soil may depend on a variety of parameters including types of microorganisms in soil, soil organic matter and exudation from plant roots. On the other hand, we consider that photo-oxidation of biogenic VOCs such as isoprene and monoterpenes is an important source of formic and acetic acids in the atmosphere (Paulot et al., 2011).” Please see page 5, lines 5–19.

“Relatively high abundances of particulate lactic and isopentanoic acids were observed in the forest atmosphere (Table 1). A positive correlation was observed between lactic acid and isopentanoic acid in particle phase ($r^2 = 0.98$). Particulate lactic acid did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Effmert et al., 2012 and references therein). We confirmed that lactic acid is abundantly present in the forest soil from central Japan ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$), but isopentanoic acid is below the detection limit (Kunwar et al., unpublished data, 2018). Lactic acid is produced not only by bacteria (*lactobacillus*) (Cabredo et al., 2009) but also by the oxidation of isoprene with ozone (Nguyen et al., 2010). Microflora community in soil system may be different between the two sites; soil-sampling site in central Japan and air-sampling site in northern Japan. More in-depth studies are needed to better understand the emissions of normal, branched and hydroxyl monoacids from forest soil to the atmosphere and interaction between soil and the overlying atmosphere.” Please see page 5, lines 27–36.

4. *C₃-C₆ monoacids will also survive at least for a couple of days (against OH oxidation) and their mention "short-lived" (in section 4) is not supported. For which conclusion do the authors need these sentences (here and also those in page 4, lines 32-35)?*

Response:

We deleted a phrase of “short-lived” and the following sentences in revised manuscript.

“Concentrations of long-lived monoacids (formic and acetic acids) in gas phase showed positive correlation with short-lived monoacids (C₃-C₆).”

“The lifetimes of formic and acetic acids in gas phase are estimated to be 25 and 10 days, respectively (Paulot et al., 2011). These acids can be long range transported in the atmosphere. In gas phase, formic and acetic acids showed positive correlations with short-lived monoacids (C₃-C₆ monoacids) (day: $r^2 = 0.17-0.89$, night: $r^2 = 0.14-0.65$).”

We calculated the lifetimes of gaseous C₁-C₄ and iC₄ monoacids with OH radicals (OH radical concentration = $2.0 \times 10^6 \text{ molecule cm}^{-3}$) using the rate constants of gaseous C₁-C₄ and iC₄ monoacids (provided by NIST Chemical Kinetics Database). The lifetimes of these monoacids largely depend on the chain length, but these monoacids are relatively stable (> 2.8 days). Following the comment, the sentences were modified as below.

“To better understand molecular distributions of monoacids in gas phase (i.e., predominance of formic acid followed by acetic acid), we calculated the lifetimes of gaseous C₁-C₄ and iC₄ monoacids with OH radicals (OH radical concentration = $2.0 \times 10^6 \text{ molecule cm}^{-3}$) using the rate constants of gaseous C₁-C₄ and iC₄ monoacids (provided by NIST Chemical Kinetics Database). The lifetimes of gaseous formic, acetic, propionic, butyric and isobutyric acids with OH radicals are 12.9, 8.6, 4.8, 3.2 and 2.8 days.

These results showed that organic acids are relatively stable with longer lifetime for shorter-chain monoacids. This unique feature of lifetime can explain the predominance of formic acid due to the accumulation in gas phase and high concentrations of formic and acetic acids in the atmosphere.” Please see page 4, lines 29–35.

5. *Figure 7. Caption is wrong. No data on formic acid are shown.*

Response:

Corrected as below.

“Figure 7. Concentrations of acetic acid in particle phase as a function of those of nonanoic acid. The coefficient of determination shows that regression line is statistically significant ($p < 0.05$).”

I would suggest that the authors need to "clean up" their logic. After revision on individual point raised by the reviewers, clarity of discussion is lacking.

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 2' comment, we modified the corresponding sentences in the revised manuscript after the additional laboratory work on the analysis of forest soil samples for monoacids, as follows.

“Relatively high abundances of particulate lactic and isopentanoic acids were observed in the forest atmosphere (Table 1). A positive correlation was observed between lactic acid and isopentanoic acid in particle phase ($r^2 = 0.98$). Particulate lactic acid did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Effmert et al., 2012 and references therein). We confirmed that lactic acid is abundantly present in the forest soil from central Japan ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$), but isopentanoic acid is below the detection limit (Kunwar et al., unpublished data, 2018). Lactic acid is produced not only by bacteria (*lactobacillus*) (Cabredo et al., 2009) but also by the oxidation of isoprene with ozone (Nguyen et al., 2010). Microflora community in soil system may be different between the two sites; soil-sampling site in central Japan and air-sampling site in northern Japan. More in-depth studies are needed to better understand the emissions of normal, branched and hydroxyl monoacids from forest soil to the atmosphere and interaction between soil and the overlying atmosphere.” Please see page 5, lines 27–36.

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

“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 show correlations with anthropogenic tracers such as nss- SO_4^{2-} and NO_3^- , indicating that anthropogenic contribution is not important.” Please see page 1, lines 17–18.

In addition, we have added the following sentences in the revised manuscript.

“As discussed in the next section, lifetimes of monoacids are relatively long (e.g., 12.9 days for formic acid), suggesting a long-range atmospheric transport of monoacids from other areas. The dominant wind direction was from east and south throughout the sampling period. We compared the concentrations of individual monoacids together with nss- SO_4^{2-} and NO_3^- : anthropogenic 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 any significant correlations with nss- SO_4^{2-} ($r^2 < 0.14$) and NO_3^- ($r^2 < 0.11$). The majority of sampled air was not influenced by urban air masses.” Please see page 4, lines 17–23.

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 9.

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 C_1 – C_6 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, we modified the corresponding sentences in the revised manuscript as below.

“Although we did not collect a forest soil sample from Sapporo during the air-sampling period, we collected a surrogate soil sample (surface ~3 cm) from a broad-leaf forest at Chubu University campus in central Japan on October 31, 2018. The soil sample was analyzed for LMW monoacids after water extraction employing the analytical protocol described in the experimental section. LMW normal (C_1 – C_{10}), branched (iC_4) and hydroxyl monoacids were detected in the soil sample (Kunwar et al., unpublished data, 2018). We found high abundances of formic ($7400 \text{ ng g}_{\text{wet soil}}^{-1}$) and acetic ($4260 \text{ ng g}_{\text{wet soil}}^{-1}$) acids in the soil sample, which were significantly higher than the rest of monoacids ($\sim 1800 \text{ ng g}_{\text{wet soil}}^{-1}$). Interestingly, hydroxyacids such as glycolic ($1680 \text{ ng g}_{\text{wet soil}}^{-1}$) and lactic ($1860 \text{ ng g}_{\text{wet soil}}^{-1}$) acids were abundantly detected in the soil samples together with isobutyric acid ($77 \text{ ng g}_{\text{wet soil}}^{-1}$) (Kunwar et al., unpublished data, 2018). These preliminary results suggest that monoacids in the forest atmosphere are in part derived from forest soil via microbial decomposition of plant debris and subsequent emission to the air.

However, it is not easy to evaluate the quantitative contribution of monoacids from the forest floor. It is likely that molecular composition of LMW monoacids in soil may depend on a variety of parameters including types of microorganisms in soil, soil organic matter and exudation from plant roots. On the other hand, we consider that photo-oxidation of biogenic VOCs such as isoprene and monoterpenes is an important source of formic and acetic acids in the atmosphere (Paulot et al., 2011).” Please see page 5, lines 5–19.

We have added the following sentence in abstract.

“The forest soil may be a source of gaseous C_1 – C_6 monoacids in the forest atmosphere.” Please see page 1, line 20.

In addition, the sentence was modified as below.

“Correlations of C_1 – C_6 monoacids with iC_4 suggest that forest floor is a source of gaseous C_1 – C_6 monoacids in the forest atmosphere.” Please see page 4, line 42 – page 5, line 1.

Comment 5. Page 5, line: You claim that ‘We suggest that major portion of C_1 – C_6 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.

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

In addition, we modified the corresponding sentences in the revised manuscript after the additional laboratory work on the analysis of forest soil samples for monoacids. Please see our response to comment 5.

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:

We modified the corresponding sentences in the revised manuscript. Please see our responses to comments 3 and 5.

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:

We calculated the lifetimes of gaseous C₁-C₄ and iC₄ monoacids with OH radicals (OH radical concentration = 2.0×10^6 molecule cm⁻³) using the rate constants of gaseous C₁-C₄ and iC₄ monoacids (provided by NIST Chemical Kinetics Database). The lifetimes of these monoacids largely depend on the chain length, but these monoacids are relatively stable (> 2.8 days). Following the comment, the sentences were modified as below.

“To better understand molecular distributions of monoacids in gas phase (i.e., predominance of formic acid followed by acetic acid), we calculated the lifetimes of gaseous C₁-C₄ and iC₄ monoacids with OH radicals (OH radical concentration = 2.0×10^6 molecule cm⁻³) using the rate constants of gaseous C₁-C₄ and iC₄ monoacids (provided by NIST Chemical Kinetics Database). The lifetimes of gaseous formic, acetic, propionic, butyric and isobutyric acids with OH radicals are 12.9, 8.6, 4.8, 3.2 and 2.8 days. These results showed that organic acids are relatively stable with longer lifetime for shorter-chain monoacids. This unique feature of lifetime can explain the predominance of formic acid due to the accumulation in gas phase and high concentrations of formic and acetic acids in the atmosphere.” Please see page 4, lines 29–35.

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 ($1.79E^{-12}$ cm³/molecule s), larger acids do not seem to be much short-lived when OH oxidation is solely considered.

Response:

Based on comment 3, we deleted a phrase of “short-lived” and the following sentences in revised manuscript.

“Concentrations of long-lived monoacids (formic and acetic acids) in gas phase showed positive correlation with short-lived monoacids (C₃-C₆).”

“The lifetimes of formic and acetic acids in gas phase are estimated to be 25 and 10 days, respectively (Paulot et al., 2011). These acids can be long range transported in the atmosphere. In gas phase, formic and acetic acids showed positive correlations with short-lived monoacids (C₃-C₆ monoacids) (day: $r^2 = 0.17-0.89$, night: $r^2 = 0.14-0.65$).”

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 (iC₄) and hydroxyl (glycolic and lactic) monoacids were detected in the soil sample. We modified the corresponding sentences and added the sentences in the revised manuscript.

“Although we did not collect a forest soil sample from Sapporo during the air-sampling period, we collected a surrogate soil sample (surface ~3 cm) from a broad-leaf forest at Chubu University campus in central Japan on October 31, 2018. The soil sample was analyzed for LMW monoacids after water extraction employing the analytical protocol described in the experimental section. LMW normal (C₁-

C₁₀), branched (iC₄) and hydroxyl monoacids were detected in the soil sample (Kunwar et al., unpublished data, 2018). We found high abundances of formic (7400 ng g_{wet soil}⁻¹) and acetic (4260 ng g_{wet soil}⁻¹) acids in the soil sample, which were significantly higher than the rest of monoacids (~1800 ng g_{wet soil}⁻¹). Interestingly, hydroxyacids such as glycolic (1680 ng g_{wet soil}⁻¹) and lactic (1860 ng g_{wet soil}⁻¹) acids were abundantly detected in the soil samples together with isobutyric acid (77 ng g_{wet soil}⁻¹) (Kunwar et al., unpublished data, 2018). These preliminary results suggest that monoacids in the forest atmosphere are in part derived from forest soil via microbial decomposition of plant debris and subsequent emission to the air.

However, it is not easy to calculate the quantitative contribution of monoacids from the forest floor. It is likely that molecular composition of LMW monoacids in soil may depend on a variety of parameters including types of microorganisms in soil, soil organic matter and exudation from plant roots. On the other hand, we consider that photo-oxidation of biogenic VOCs such as isoprene and monoterpenes is an important source of formic and acetic acids in the atmosphere (Paulot et al., 2011).” Please see page 5, lines 5–19.

“Relatively high abundances of particulate lactic and isopentanoic acids were observed in the forest atmosphere (Table 1). A positive correlation was observed between lactic acid and isopentanoic acid in particle phase ($r^2 = 0.98$). Particulate lactic acid did not show correlations with other LMW monoacids detected in particle phase ($r^2 < 0.17$). Isopentanoic acid can be produced by bacteria such as *Clostridium* spp. and *Bacteroides* spp. (Effmert et al., 2012 and references therein). We confirmed that lactic acid is abundantly present in the forest soil from central Japan (1860 ng g_{wet soil}⁻¹), but isopentanoic acid is below the detection limit (Kunwar et al., unpublished data, 2018). Lactic acid is produced not only by bacteria (*lactobacillus*) (Cabredo et al., 2009) but also by the oxidation of isoprene with ozone (Nguyen et al., 2010). Microflora community in soil system may be different between the two sites; soil-sampling site in central Japan and air-sampling site in northern Japan. More in-depth studies are needed to better understand the emissions of normal, branched and hydroxyl monoacids from forest soil to the atmosphere and interaction between soil and the overlying atmosphere.” Please see page 5, lines 27–36.

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

Response:

We deleted the following sentence in the revised manuscript.

“Formic and acetic acids are intermediate products in the oxidative degradation of various VOCs. They may be very stable intermediate products before the oxidation to CO₂.”

We have checked references. We made a mistake in the author name.

We have replaced “Uta et al., 2012” by “Effmert et al., 2012”.

We have added the following papers in the reference section.

Kawamura, K. and Gagosian, R. B.: Implication of ω -oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty acids, *Nature*, 325, 330-332, 1987.

Tsai, Y. I. and Kuo, S. C.: Contributions of low molecular weight carboxylic acids to aerosols and wet deposition in a natural subtropical broad-leaved forest environment, *Atmos. Environ.*, 81, 270-279, 2013.