

## Authors' Responses to reviewers

We appreciate the helpful comments made by reviewers.

Following the two reviewer's comments, we have removed Figure 7. Figure numbers were reorganized.

We have changed the configuration of section 3 (Results).

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

### Reviewer 1:

*Manuscript describes the results from the measurements of low molecular weight acids in the forest air in Japan. These acids have effects on atmospheric chemistry, acidity and clouds, but their sources and concentrations in the air are poorly known. Even with very limited data set, study gives new knowledge on these poorly known compounds.*

*However, major improvements on interpreting the results is needed.*

*Major comments:*

*Comment 1: It would be very interesting to see how big fraction of the particulate mass these acids comprise. Could you add some information on particle mass?*

### Response:

Thanks for the comment. Unfortunately, we did not measure the aerosol mass. However, we confirmed the presence of a relationship between particle-phase fractions ( $F_p$ ) and mass concentrations of total LMW monoacids in particle phase, except for C<sub>3</sub>, C<sub>9</sub>, and C<sub>10</sub> monoacids. We have added the following sentences in the revised manuscript.

" $F_p$  of LMW monoacids showed positive correlations with mass concentrations of total LMW monoacids in particle phase ( $r^2 = 0.24\text{--}0.46$ ), except for C<sub>3</sub>, C<sub>9</sub>, and C<sub>10</sub>. Although we did not measure the aerosol mass, gaseous LMW monoacids in the forest atmosphere may be adsorbed on the existing particles." Please see page 6, lines 29-31.

*Comment 2: More discussion on other possible sources are needed. For example production in the air in gas phase may be very important and also transport from anthropogenic or other sources.*

### Response:

We have checked backward air mass trajectories at a level of 300 m. We have added the following sentences in experimental and result sections.

"We calculated seven-day air mass back trajectories at a height of 300 m above sea level using the Meteorological Data Explorer (METEX) provided by the National Institute for Environmental Studies (<http://db.cger.nies.go.jp/metex/index.html>)." Please see page 3, lines 31-33.

"This forest site is located a few kilometers south of Sapporo city. The dominant wind direction

was from east and south throughout the sampling period. We compared the concentrations of individual monoacids together with  $\text{nss-SO}_4^{2-}$ : an anthropogenic aerosol tracer 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 a correlation with  $\text{nss-SO}_4^{2-}$  ( $r^2 < 0.14$ ). The majority of sampling air was not affected by urban area. In addition, Figure 5 shows seven-day air mass back trajectories (300 m a.s.l.) for the study period from 28 June to 8 July at the sampling site. Most of the air masses passed through the Pacific Ocean during the measurement period, except for 28 June. This result may suggest that the air masses arriving at the forest site are not affected by the outflows from East Asia and far East of Russia.” Please see page 4, lines 19-26.

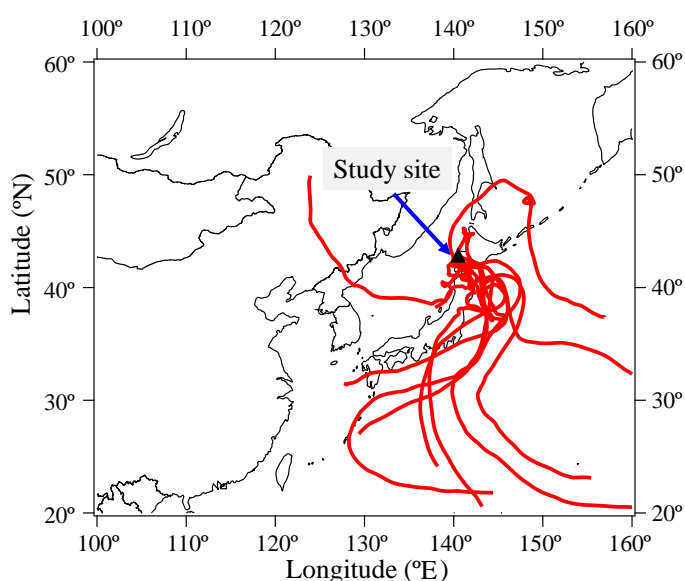


Figure 5. Seven-day air mass back trajectories at a height of 300 m a.s.l. during the sampling period.

*Comment 3: Please discuss also on lifetime of these compounds and background levels. For example for acetic acid lifetime in the air is around two week while for decanoic acid only few hours.*

**Response:**

Based on the suggestion, we have added the following sentences in the revised manuscript.

“Concentrations of formic and acetic acids in gas phase were higher than those of  $\text{C}_3\text{-C}_{10}$  monoacids. The rate constants of gaseous formic, acetic, and propionic acids with OH radicals were 0.74, 1.2, and  $2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively (Dagaut et al., 1988). The rate constants of LMW monoacids may increase with an increase in carbon numbers of monoacids. Formic and acetic acids are more stable than  $\text{C}_3\text{-C}_{10}$  due to more hydrogen atoms in  $\text{C}_3\text{-C}_{10}$  acids to react with OH radicals, leading to lower concentrations of  $\text{C}_3\text{-C}_{10}$  monoacids in the atmosphere.” Please see page 4, lines 29-33.

“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 (C<sub>3</sub>-C<sub>6</sub> monoacids) (day:  $r^2 = 0.17-0.89$ , night:  $r^2 = 0.14-0.65$ ).” Please see page, 4 lines 36-39.

*Comment 4: Page 5, line 24-25: From only ambient air concentrations you cannot state that some are emitted from forest floor and soil microorganisms. Or do you have data on microorganisms? If so, please show it in manuscript. There are several different sources and sinks possibly affecting the concentration levels and for some compounds even background levels may be relatively high.*

**Response:**

We modified the sentences in the revised manuscript as follows.

“Branched chain monoacids including isobutylic acid are known as common metabolites of bacteria (e.g., *Bacteroides distasonis*) and fungi in soils (Uta et al., 2012 and references therein). LMW monoacids such as acetic and propionic acids can be produced by microbiological processes (Uta et al., 2012). In addition, exudation of organic acids is known to occur in vascular plants, mainly from roots (Curl, 1982). Shen et al. (1996) reported that formic, acetic, and propionic acids are contained in forest soil and rhizosphere soil. However, the possible contribution from the forest floor cannot be evaluated in the present study.” Please see page 4, line 42 - page 5, line 5.

*Comment 5: Page 5 and 6, lines 30 and 1-2: Even ambient air concentrations of monoterpenes, with clear temperature and light dependent emissions, do not most often show direct correlation with temperature since there are several processes affecting on ambient concentration levels in the air (e.g. mixing layer height, vertical wind, background levels and reactivity). Therefore I recommend you to remove this statement on contribution of soil being higher than forest canopy.*

**Response:**

Deleted as suggested.

*Comment 6: Page 6, lines 10-18: This paragraph is very unclear. It was not clear to me, when you discuss on gas phase and when particulate. I would expect that lots of formic and acetic acids are formed in the gas phase reactions of BVOCs and then these formed acids partition into particulate phase. Of course some additional could then be formed also in particles or their surfaces.*

**Response:**

We deleted the corresponding sentences and Figure 7 in the manuscript. Instead, we have added sentences in the revised manuscript. Please see our response to comment 7 as given

below.

*Comment 7: Page 6, line 23-24: BVOCs with double bonds do react in the air with  $O_3$  and  $NO_3$  also during the night. But after first reactions they have lost the double bonds and continue reactions with OH radicals, which are formed only during the day. Double bonds from BVOCs are lost well-before they form formic and acetic acid and therefore I expect that formic and acetic acids are formed in the reactions of other VOCs only during the day. I would expect that due to partitioning between gas and aerosol phase more is detected in particulate phase during colder the nights and then during the day when temperature increases they are evaporated. You should add discussion also on this.*

**Response:**

Thanks for the comment. We reorganized this section by deleting the sentence, “Formic and acetic acids are later-generation products of the oxidation of BVOCs (e.g., Ervens et al., 2008). BVOCs or their earlier-generation products may be continuously oxidized at night in the forest atmosphere.”

Instead, we have added few sentences as follows.

“Gas/particle partitioning of formic and acetic acids are discussed in section 4.2.” Please see page 5, line 26.

“Although  $F_p$  of LMW monoacids did not show a correlation with ambient temperature in nighttime ( $r^2 < 0.16$ ), except for propionic acid ( $r^2 = 0.31$ ), we found average  $F_p$  of LMW monoacids in nighttime were higher than those in daytime (Table 1).” Please see page, 5 line 42 - page, 6 line 2.

“We found that  $F_p$  of formic and acetic acids increase with increasing RH ( $C_1$ :  $r^2 = 0.30$ ,  $C_2$ :  $r^2 = 0.55$ ) (Figure 9), whereas other LMW monoacids did not show a correlation with RH ( $r^2 < 0.20$ ), except for butyric acid ( $r^2 = 0.55$ ) in daytime. Although  $F_p$  of LMW monoacids did not show correlation with RH in nighttime ( $r^2 < 0.15$ ), we found that average  $F_p$  of LMW monoacids in nighttime were higher than those in daytime (Table 1). Al-Hosney et al. (2005) and Prince et al. (2008) reported that the uptake of formic and acetic acids by  $CaCO_3$  can be enhanced by higher RH ( $C_1$ : RH > 62%,  $C_2$ : RH > 53%). In addition, liquid water contents (LWC) of aerosols were estimated using ISORROPIA-II model (Fountoukis and Nenes, 2007) with the data of inorganic ions and meteorological parameters. The aerosol LWC ranged from 1.4 to 14.6  $\mu g\ m^{-3}$  (av. 6.4  $\mu g\ m^{-3}$ ). Although  $F_p$  of LMW monoacids did not show strong correlations with LWC ( $r^2 < 0.24$ ), strong positive correlations were found between RH and aerosol LWC in daytime ( $r^2 = 0.47$ ) and in nighttime ( $r^2 = 0.74$ ). Higher RH may enhance the partitioning of gaseous formic and acetic acids to aerosol phase as a result of the condensation of water vapour on aerosol particles. Our results suggest that higher temperature depresses a

transfer of gaseous formic and acetic acids to aerosol phase and higher RH enhances the partitioning of gaseous formic and acetic acids to aerosol phase in the forest atmosphere.” Please see page 6, lines 5-17.

We have added new Figure 9 as below.

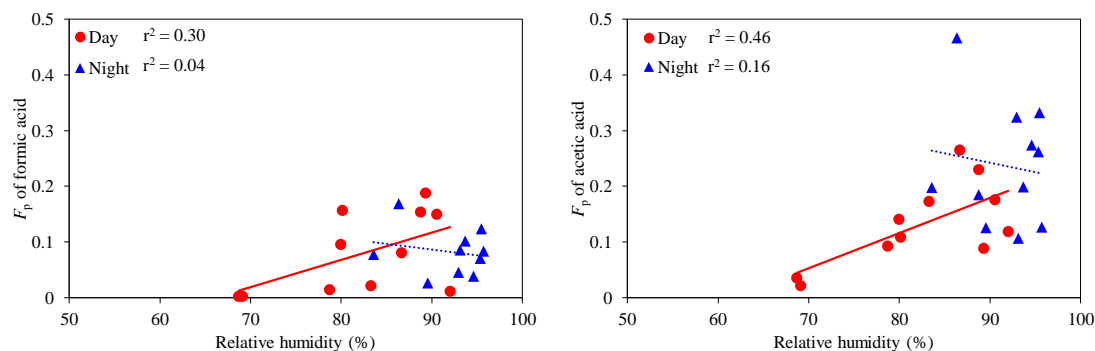


Figure 9. Particle-phase fractions ( $F_p$ ) of formic and acetic acids against relative humidity.

*Comment 8: Page 7, line 4-8: If lactic acid is more polar and more water soluble it will partition more to the particulate phase. Discuss also on this possibility.*

**Response:**

Thanks for the comment. Based on the comment, we added the following sentences.

“Although lactic acid is highly water-soluble,  $F_p$  of lactic acid did not show a clear correlation with relative humidity. High relative humidity (average: 87%) may be involved with the large  $F_p$  of lactic acid.” Please see page 6, lines, 21-22.

We deleted the following sentence; “These results suggest that particulate lactic and isopentanoic acids may be derived from primary sources in forest ecosystem via microbial activity.”

*Comment 9: Page 7, line 13. Effect of temperature applies also during nighttime.*

**Response:**

Based on comment 7, we already added the sentence in the revised manuscript. Please see our response to comment 7.

*Comment 10: More discussion on also sinks and lifetimes and effect of local chemistry is needed.*

**Response:**

Based on comment 3, we have added and modified the sentences in the revised manuscript. Please see our response to comment 3.

*Comment 11: Page 8, line 29. Add references on branched chain monoacids being an indicator*

*of soil microorganism processed.*

**Response:**

We have added a reference in the revised manuscript as below.

“Branched chain monoacids can be used as an indicator of soil microorganism processes (Uta et al., 2012 and references therein).” Please see page 7, lines 1-2.

*Comment 12: Page 8, line 30: Based on the data, it cannot be stated that microorganisms are source of these acids. They can as well be produced in the local reactions of other emitted compounds.*

**Response:**

Following the comment, the sentence was modified as below.

“Many kinds of LMW monoacids are exuded by plant roots (Curl, 1982) and derived from soil microorganism (Uta et al., 2012). We suggest that forest floor is another important source of gaseous LMW monoacids.” Please see page 7, lines 2-4.

*Comment 13: Page 8, line 32: Do you have any data on microbial activity? If not, remove this statement.*

**Response:**

Deleted as suggested.

*Comment 14: Page 9, line 3: Based on the data shown here, this cannot be stated. Maybe they give some indication that soil could be a source, but it cannot be stated.*

**Response:**

We deleted the following sentences; “Forest floor including soil microorganisms contributes to the emissions of gaseous and particulate LMW monoacids. Our results may be useful to improve the understanding of organic aerosol formation in the forest.”

*Comment 15: Even with low concentrations C4-C10 acids can be very important and have higher local effect and higher emissions/sources that you would think by their concentrations. This is because their reactivity and lifetimes in the air are much shorter. Especially for these acids data on ambient concentrations and sources are very limited. Please, add more discussion also on these acids.*

**Response:**

Please see our response to comment 3.

*Comment 16: Could you add a table on the comparison with other studies?*

**Response:**

Based on the reviewer 2’ comment 15, we deleted section 4.3.

*Minor comments:*

*Comment 17: Language should be checked by some native speaker.*

**Response:**

We improved English as best as we could.

*Comment 18: Page 4 lines 15-18. Frist you tell that isopentanoic acid is most dominant in particles and then nonanoic acid. Please, correct these sentences.*

**Response:**

We deleted the following sentence; “Nonanoic acid (C<sub>9</sub>) is the dominant species (1.5–25 ng m<sup>-3</sup>, mean: 11 ng m<sup>-3</sup>) in particle phase, except for formic and acetic acids (Figure 3).”

*Comment 19: Page 4 line 25. What temporal trend? Please explain more clearly.*

**Response:**

We are sorry for the unclearness. We have rephrased the sentences as below.

“Day-to-day variations in monoacids detected did not show a clear diurnal trend.” Please see page 4, lines 4-5.

*Comment 20: Fig. 4. It is very hard to deviate between the days. Could you add for example some dashed lines between the days?*

**Response:**

We modified Figure 4 as follows. Please see the revised figure.

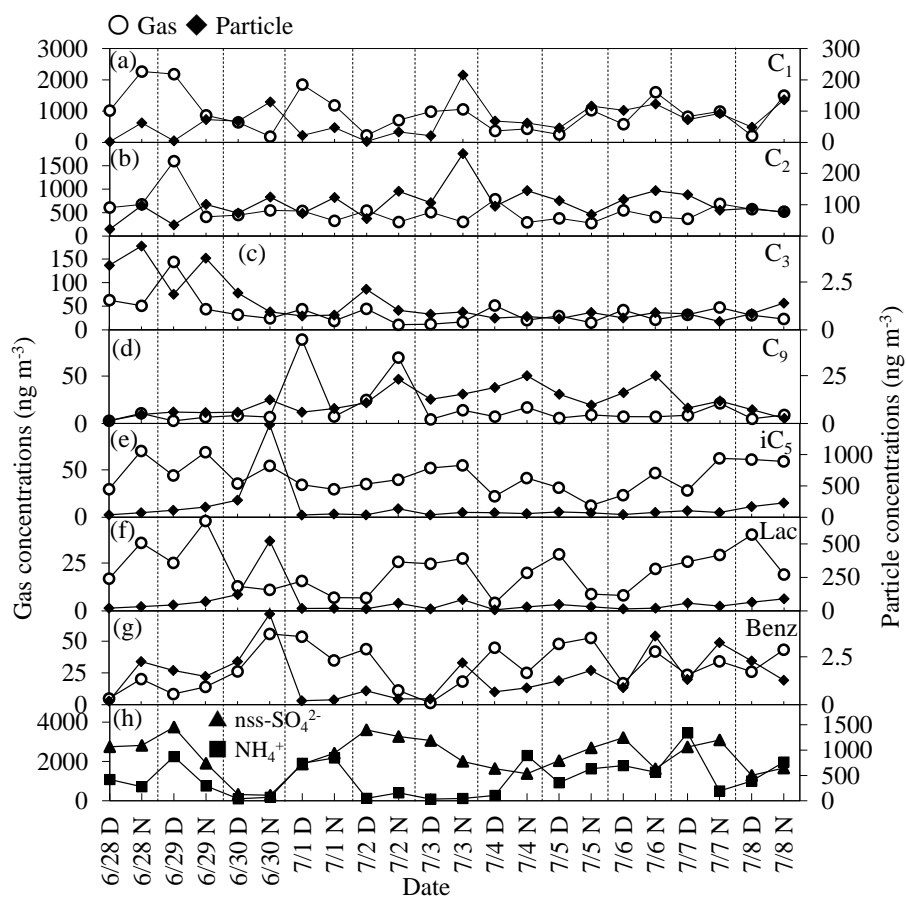


Figure 4. Diurnal variations in the concentrations of major monocarboxylic acids in gas (open circle) and particle (solid diamond) phases and inorganic ions (nss-SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>). Day: D, Night: N.



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