Authors Responses to Reviewers

We appreciate the helpful comments made by reviewers.

Below, we indicate in detail the revisions made to the manuscript.

Text form the original is shown in blue.

Changes in the revised manuscript are shown in red.

Referee #1

Comments to Author

General Evaluation

This manuscript entitled "Long-range atmospheric transport of volatile monocarboxylic acids with Asian dust over high mountain snow site, central Japan" by T. Mochizuki et al. describes analytical results of monocarboxylic acids together with inorganic ions etc. in snowpack samples collected from a snow pit in Japan. The authors insist that Asian dusts can uptake volatile monocarboxylic acids during long-range transport and the dusts coated with organic acids act as effective ice nuclei to cause snowfalls. There have been only few reports which discuss the atmospheric uptake of organic compounds to Asian dust particles. Thus, the topic of this paper is interesting and also needs to be investigated from the view of the climate science. Hence, this manuscript is recommended for publication in Atmospheric Chemistry and Physics, although needs several modifications.

Specific Comments

1) P.2, L23: "IN" has already been defined in the line 6.

Response:

We have removed the entire description of IN following the comments provided by reviewer 2.

2) p.3, L.30: "The sample was concentrated down to 10 ml using a rotary evaporator under vacuum at 50 °C"; p.4, L.4: "... and then dried using a rotary evaporator under vacuum, followed by blown-down with pure nitrogen gas"

The authors should describe how long it usually takes to reduce the water volume via each process. Such information would help readers who will try this method.

Response:

We did not measure how long it takes to reduce the sample water volume via rotary evaporator under vacuum. We have modified the following descriptions in the manuscript.

The sentence "The sample was concentrated down to 10 ml using a rotary evaporator under vacuum at 50 °C." has been revised to "The sample was concentrated down to 10 ml using a rotary evaporator under vacuum (20 mmHg) at 50 °C." (Page 3, Lines 27-28).

The sentence "The pH of the sample was checked to be 8.5–9.0 and then dried using a rotary evaporator under vacuum, followed by blown-down with pure nitrogen gas." has been revised to "The pH of the sample was checked to be 8.5–9.0 and then dried using a rotary evaporator under vacuum (20 mmHg), followed by blown-down with pure nitrogen gas for 30 seconds. The former process general requires 15-20 min." (Page 3, Line 32 – Page 4, Line 2).

3) p.5, L24: "We found that differences in the concentrations of each monocarboxylic acids between sample #4 and sample #4' are within the analytical uncertainties."
How large was the analytical uncertainty? The QA/QC for all the analytical methods should be mentioned in the paper.

Response:

Based on the comment, we modified the following sentences.

The sentence "Analytical errors using authentic standards were within 12%." has been revised to "Analytical errors in the GC/FID analysis using authentic standards were within 2%. Relative standard deviations based on triplicate analysis of real samples were within 12%." (Page 4, Lines 19-20).

The sentence "We found that differences in the concentrations of each monocarboxylic acids between sample #4 and sample #4' are within the analytical uncertainties." has been revised to "We found that differences in the concentrations of each monocarboxylic acids between sample #4 and sample #4' are comparable to the relative standard deviations." (Page 5, Lines 24-25).

4) p.7, L.5: "… the ratios of Mg/Ca at the Murodo-Daira site …"
Are the ratios based on the mass concentration or the molar concentration? Should be clearly described.

Response:

Based on the comment, we modified the following sentences.

The sentence "In addition, the ratios of Mg/Ca at the Murodo-Daira site in 2009 and 2011 are 0.08 and 0.12, respectively." has been changed to "In addition, the mass concentration ratios of Mg/Ca at the Murodo-Daira site in 2009 and 2011 are 0.08 and 0.12, respectively." (Page 7, Lines 5-6).

5) P.7, L.10: "To investigate the effect of Asian dust on LMW monocarboxylic acids, we plotted major LMW monocarboxylic acids (i.e., formic plus acetic acids) against nss-Ca^{2+} using all the data points (Fig. 4)."

Why did the authors use the log-log plot? Should be explained. In addition, p values for r^2 should be added. Why did the author use r^2 (coefficient of determination) instead of r (correlation coefficient)?

Response:

Instead of the log-log plot, we plotted Fig. 4 with a regular style. Fig. 4 shows a strong correlation between concentrations of formic plus acetic acids and nss-Ca^{2+}. The "r^2" has been changed to "r" in this manuscript. Based on the suggestion, we have modified Figure 4 with modified caption.

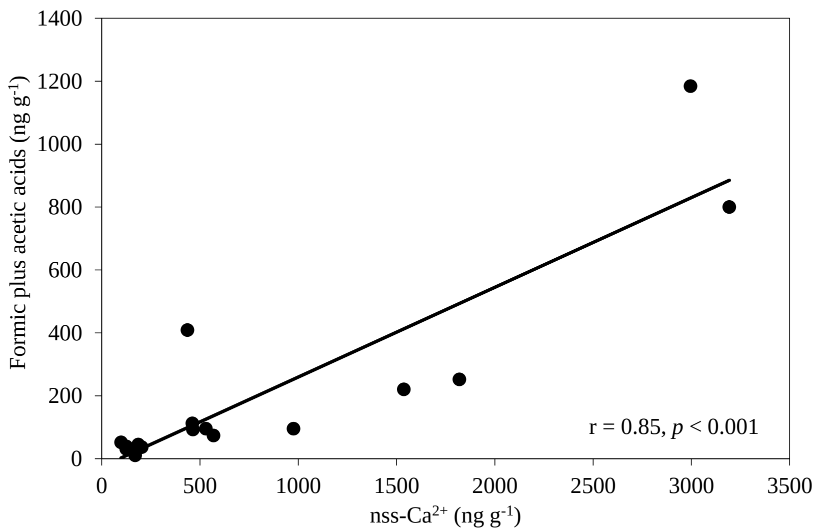

Figure 4: Linear regression plots between concentrations of formic plus acetic acids and nss-Ca^{2+} in Mt. Tateyama snow samples. (Page 19, Lines 6-7).

In addition, the sentence; "We found that formic plus acetic acids strongly correlate with nss-Ca^{2+} (r^2 = 0.73)." has been modified to "Concentrations of formic plus acetic acids were found to increase linearly with that of nss-Ca^{2+} (r = 0.85, $p < 0.001$)." (Page 7, Lines, 11-12).

6) P.7, L.26: "Figure 5 presents the relationship between formic plus acetic acids and pH of melt snow"
What function did the authors use? In addition, p values for r^2 should be described.

Response:

Based on the suggestion, the sentences; "We found that formic plus acetic acids positively correlated with pH (r^2 = 0.76). Their concentrations exponentially increased at pH range of > 6.0. Interestingly, concentrations of nss-Ca^{2+} positively correlate with pH (r^2 = 0.79) (Fig. 5)." have been changed to "Concentrations of formic plus acetic acids were found to increase exponentially with pH (r = 0.87, $p < 0.001$). Interestingly, concentrations of nss-Ca^{2+} were also found to increase exponentially with pH (r = 0.89, $p < 0.001$) (Fig. 5)." (Page 7, Lines 20-22).

We have modified the Y axis (left and right) and caption of Fig. 5 as follows.

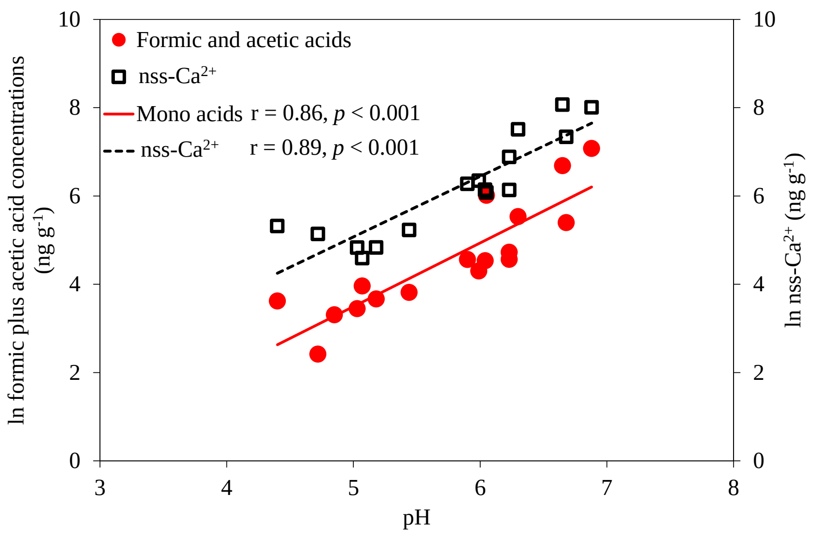

Figure 5: Correlation plots of natural logarithm of formic plus acetic acids and nss-Ca^{2+} in the snow pit samples against pH of the melt snow samples. (Page 20, Lines 1-3).

7) p.7, L.13: "The atmospheric transport of Asian dust over the Japanese Islands is a dominant factor to control the concentrations of nss-Ca^{2+} and formic and acetic acids in snow precipitations during winter to spring"
As the authors mentioned, it is reasonable that Asian dust is a dominant factor to

control the [nss-Ca^{2+}]. However, why is it also acceptable for the concentrations of formic and acetic acids?

Response:

We have modified the following descriptions in the manuscript.

The sentences; "The atmospheric transport of Asian dust over the Japanese Islands is a dominant factor to control the concentrations of nss-Ca^{2+} and formic and acetic acids in snow precipitations during winter to spring, when the Asian dust activity maximizes in North China." have been revised to "Asian dust particles may be a carrier of formic and acetic acids via acid/base reaction and forming carboxylate salts, when the Asian dust activity maximizes in North China." (Page 7, Lines 13-14).

8) p.7, L.21: "Average concentrations of formic and acetic acids and nss-Ca^{2+} in 2009 are higher than those in 2011. Total rainfall during December to February in Urumqi near the Taklamakan desert, China in 2009 (31 mm) was half of that in 2011 (60 mm), suggesting that soil moisture in 2009 should have been lower than that in 2011 and thus the soil surfaces in 2009 should have been more dried. The higher concentrations of organic acids and nss-Ca^{2+} in the 2009 snow pit samples should be caused by a strong influence of the Asian dust events in this year when the soil surfaces were more dried in the arid regions, although the detailed records of the Asian dust events in North China are not available."

This part seems too speculative. Does the water content on the dust surface really depend on the amount of rainfall? In addition, I wonder why the higher concentrations of the organic acids and Ca^{2+} should be caused by the more dried soil surfaces.

Response:

Our hypothesis was speculative. Based on the suggestion, we have modified the following sentences as follows.

The following sentences were deleted. "Total rainfall during December to February in Urumqi near the Taklamakan desert, China in 2009 (31 mm) was half of that in 2011 (60 mm) (Japan Meteorological Agency website: http://www.data.jma.go.jp/gmd/cpd/monitor/mainstn/obslist.php), suggesting that soil moisture in 2009 should have been lower than that in 2011 and thus the soil surfaces in 2009 should have been more dried. The higher concentrations of organic acids and nss-Ca^{2+} in the 2009 snow pit samples should be caused by a strong influence of the Asian dust events in this year when the soil surfaces were more dried in the arid regions, although the detailed records of the Asian dust events in North China are not available."

Instead we added the following sentences; "This may be related to a strong influence of the Asian dust events. However, the detailed records of the Asian dust events in North China are not available." (Page 7, Lines 16-18).

9) P.8., L.1: "The adsorption process of acidic components by aerosols may be different between gaseous organic acids and inorganic gases such as SO_2 and NO_x"
How different are they? Do the authors have any ideas?

Response:

Our previous study showed a positive correlation between water soluble organic nitrogen (WSON) and nss-Ca^{2+} (Mochizuki et al., 2016). On the other hand, water soluble inorganic nitrogen (WSIN) (NH_4^+ plus NO_3^-) did not show a correlation with nss-Ca^{2+} (Mochizuki et al., 2016). We think that Asian dust is a factor to control the long-range transport of organic acids, WSON, WSIN, and inorganic ions including SO_4^{2-}, but the production process of salts, adsorption process on dust particles, and removal process in the atmosphere may be different. These phenomena do not make clear understanding in our study.

We have deleted the following sentences in the revised MS because they are too speculative.

"In contrast, SO_4^{2-} and NO_3^- did not show any correlation with pH (r < 0.10). These results may suggest that, during the atmospheric transport, dust particles do not efficiently uptake inorganic acids that are mostly present as particles. The adsorption process of acidic components by aerosols may be different between gaseous organic acids and inorganic gases such as SO_2 and NO_x, which are precursors of SO_4^{2-} and NO_3^-, respectively."

10) P.8, L.9: "Based on a good correlation between monocarboxylic acids and nss-Ca^{2+}, it is very likely that organic acids in aerosols exist in the form of salts such as $Ca(HCOO)_2$, $Ca(HCOO)(CH_3COO)$ and/or $Ca(CH_3COO)_2$"
Did the authors check the ion balance?

Response:

We calculated ion balance. The above-mentioned points were added in the revised MS.

"We calculated ion balance in the snow pit at the Murodo-Daira site near Mt. Tateyama. In this study, we could not use the data of chloride ion (Cl^-) because of the addition of $HgCl_2$ into snow samples. To calculate ion balance, we used equivalent ratio of Cl^- to Na^+ (1.26) obtained in the same snow pit in 2011 (Watanabe et al., 2012). Figure 6 shows total cations (Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) against total anions (F^-, MSA^-, NO_3^-, SO_4^{2-} and organic anions including normal (C_1-C_{10}), branched chain (iC_4-iC_6), aromatic (benzoic and toluic acid isomers), and hydroxyl (lactic and glycolic) monocarboxylic acids) (r = 0.95, p < 0.001). The slope (1.26) of more than unity indicates that excess cations exist in the snow pit at the Murodo-Daira site near Mt. Tateyama, although CO_3^- and HCO_3^-, and unidentified organic anions were not determined." (Please see Page 7, Lines 26-32).

We have added Figure 6 with the caption as below.

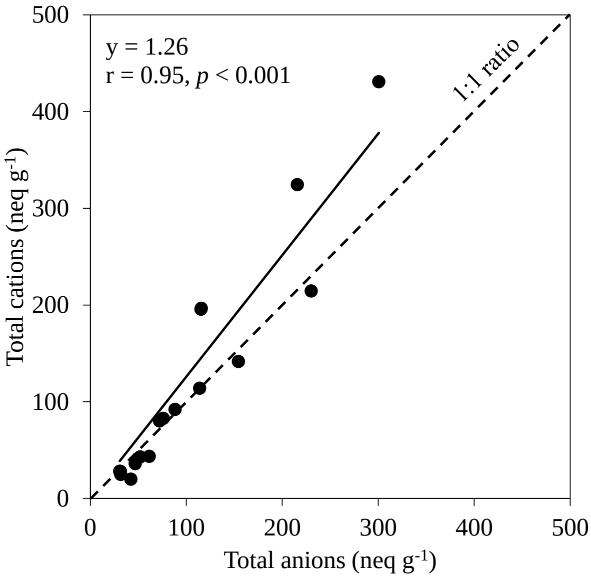

Figure 6: Linear regression plots between total cation equivalents (neq) and total anion equivalents (neq) in melt snow samples at the Murodo-Daira site near Mt. Tateyama. (Page 20, Lines 5-7).

11) P.8, L.15: "and thus organic acid salts can be long-range transported as particles in the atmosphere from the Asian Continent to the Japanese Islands without serious photochemical degradation"

How can the authors find "without serious photochemical degradation"?

Response:

We have added the following sentences in response to the above comment.

"In addition, the lifetimes of formic and acetic acids with OH radical are estimated to be 25 days and 10 days, respectively, at -13 °C assuming the OH concentration of 1.0×10^6 molecules cm^{-3} (Paulot et al., 2011). This timescale is much longer than that of atmospheric transport time of air mass from the Asian Continent to Mt. Tateyama." (Page 8, Lines 11-14).

12) P.8., L.29: "Therefore, benzoic acid can be used as an anthropogenic tracer."
Why can benzoic acid be used as an anthropogenic tracer? It is unclear which is the specific reason why the benzoic acid can be used as the tracer.

Response:

We are sorry for the unclear description. We modified following sentences in the revised MS.

The following sentences were deleted; "Benzoic acid is directly emitted from fossil fuel combustion (Kawamura et al., 1985) and also produced in the atmosphere by photo-oxidation of aromatic hydrocarbons such as toluene (Ho et al., 2015). Benzoic acid positively correlates with nss-Ca^{2+} (r^2 = 0.81). In addition, the average benzoic acid/nss-Ca^{2+} ratio obtained for the Murodo-Daira snowpit samples (0.0029) is 3-4 orders of magnitude higher than those obtained from the Kosa reference materials such as CJ-1 (0.0000024), CJ-2 (0.0000033) and Gobi (0.0000078). Benzoic acid may be also adsorbed on the pre-existing particles via atmospheric titration of alkaline dust particles derived from the Asian Continent. The air mass trajectories arriving at the Murodo-Daira site have passed over North China where many industrial regions and mega-cities (e.g., Beijing) are located (Fig. 3). Therefore, benzoic acid can be used as an anthropogenic tracer."

Instead, we added the following sentences in the revised MS; "Benzoic acid is directly emitted from fossil fuel combustion (Kawamura et al., 1985) and also produced in the atmosphere by photo-oxidation of aromatic hydrocarbons such as toluene (Forstner et al., 1997), which are derived from human activities. Benzoic acid positively correlates with nss-Ca^{2+} ($r = 0.90$, $p < 0.001$) (Fig. 7a). In addition, the average benzoic acid/nss-Ca^{2+} ratio obtained for the Murodo-Daira snow pit samples (0.0029) is 3-4 orders of magnitude higher than those obtained from the Kosa reference materials such as CJ-1 (0.0000024), CJ-2 (0.0000033) and Gobi (0.0000078). Benzoic acid may also be adsorbed on the pre-existing particles via atmospheric titration of alkaline dust particles derived from the Asian Continent. The air mass trajectories arriving at the Murodo-Daira site have passed over North China where many industrial regions and mega-cities (e.g., Beijing) are located (Fig. 3)." (Please see Page 8, Lines 23-30).

We have deleted the following reference to the references section.

Ho, K. F., Huang, R. -J., Kawamura, K., Tachibana, E., Lee, S. C., Ho, S. S. H., Zhu, T., and Tian, L. W.: Dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, fatty acids and benzoic acid in PM2.5 aerosol collected during CAREBeijing-2007: an effect of traffic restriction on air quality, Atmos. Chem. Phys., 15, 3111–3123, 2015.

13) P.8, L.31: "Formic plus acetic acids showed a strong positive correlation with benzoic acid (r^2 = 0.81)"

Which function did you use for the correlation analysis? The scatter plot should be displayed. (Also for the other correlation analysis results.)

Response:

Based on the suggestion, we have added Figure 7 with the caption as below.

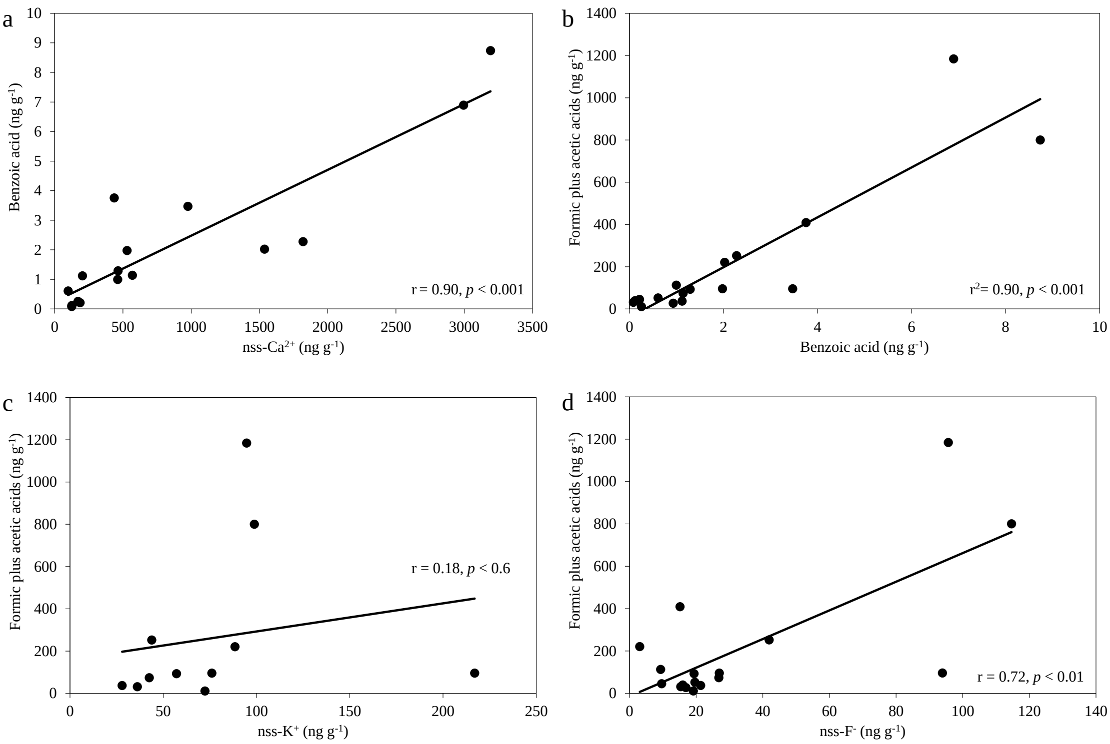

Figure 7: Linear regression plots between (a) concentrations of benzoic acid and nss-Ca^{2+}, (b) formic plus acetic acids and benzoic acid, (c) formic plus acetic acids and nss-K^{+}, and (d) formic plus acetic acids and nss-F^{-} in Mt. Tateyama snow samples. (Page 21, Lines 1-4).

We have modified the following sentences.

The sentence "Benzoic acid positively correlates with nss-Ca^{2+} ($r^2 = 0.81$)." has been revised to "Benzoic acid positively correlated with nss-Ca^{2+} ($r = 0.90$, $p < 0.001$). (Fig. 7a)." (Page 8, Line 25).

The phrase; "Formic plus acetic acids showed a strong positive correlation with benzoic acid ($r^2 = 0.81$), …" has been changed to "Formic plus acetic acids showed a strong positive correlation with benzoic acid ($r = 0.90$, $p < 0.001$) (Fig. 7b), …" (Page 8, Line 31).

The sentences; "In contrast, nss-K^+, a tracer of biomass burning (Zhu et al., 2015), and nss-F^-, a tracer of coal-burning (Wang et al., 2005), did not show a positive correlation with formic plus acetic acids ($r^2 < 0.03$), indicating that biomass and coal …" have been modified to "In contrast, nss-K^+, a tracer of biomass burning (Zhu et al., 2015) did not show a positive correlation with formic plus acetic acids ($r = 0.18$, $p < 0.6$) (Fig. 7c). nss-F^-, a tracer of coal-burning (Wang et al., 2005) shows a positive correlation with formic plus acetic acids ($r = 0.72$, $p < 0.01$) (Fig. 7d), however, they were rather scattered. Biomass and coal …" (Page 8, Line 32 – Page 9, Line 2).

Based on the suggestion, we have added Figure 8.

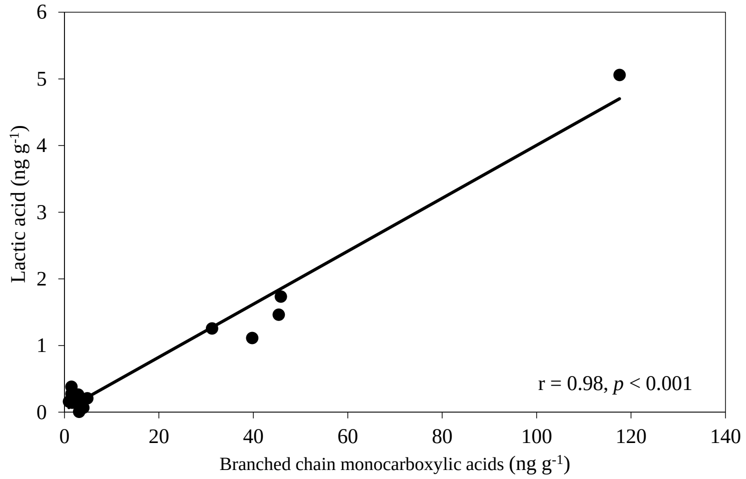

Figure 8: Linear regression plots between concentrations of branched chain (iC_4-iC_6) monocarboxylic acids and lactic acid in Mt. Tateyama snow samples. (Page 21, Lines 6-8).

We have modified the following sentence.

The sentence; "We found a strong positive correlation between branched chain (iC_4-iC_6) acids and lactic acid ($r^2 = 0.97$)." has been revised to "We found a strong positive correlation between branched chain (iC_4-iC_6) acids and lactic acid ($r = 0.98$, $p < 0.001$) (Fig. 8)." (Page 9, Lines 19-20).

Based on the suggestion, we have added Figure 9.

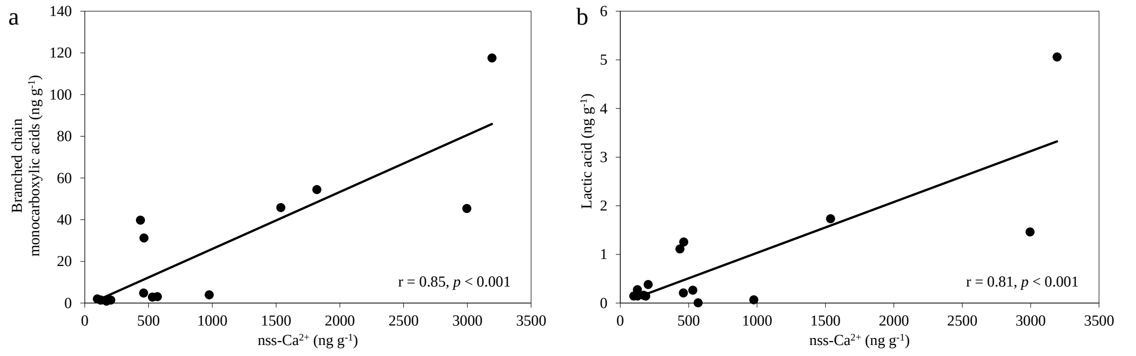

Figure 9: Linear regression plots between (a) concentrations of branched chain (iC_4-iC_6) monocarboxylic acids and nss-Ca^{2+} and (b) lactic acid and nss-Ca^{2+} in Mt. Tateyama snow samples. (Page 22, Lines 1-3).

We have modified the following sentence.

The sentence "Branched chain (iC_4-iC_6) acids and lactic acid showed a positive correlation with nss-Ca^{2+} ($r^2 = 0.72$)." has been revised to "Branched chain (iC_4-iC_6) acids ($r = 0.85$, $p < 0.001$) (Fig. 9a) and lactic acid ($r = 0.81$, $p < 0.001$) (Fig. 9b) showed a positive correlation with nss-Ca^{2+}." (Page 9, Lines 22-23).

In addition, we have modified the following sentences.

The sentence "We found a strong correlation (r^2=0.73) between formic plus acetic acids and non-sea-salt Ca^{2+} that is a proxy of Asian dust." has been revised to "We found a strong correlation ($r = 0.85$, $p < 0.001$) between formic plus acetic acids and non-sea-salt Ca^{2+} that is a proxy of Asian dust." (Page 1, Lines 15-16).

The phrase "Formic plus acetic acids also showed a positive correlation (r^2=0.81) with benzoic acid …" has been revised to "Formic plus acetic acids also showed a positive correlation ($r = 0.90$, $p < 0.001$) with benzoic acid …" (Page 1, Lines 18-19).

The sentence "Entrainment of organic acids by dusts is supported by a good correlation (r^2=0.76) between formic plus acetic acids and pH of melt snow samples." has been revised to "Entrainment of organic acids by dusts is supported by a good correlation (r = 0.86, $p < 0.001$) between formic plus acetic acids and pH of melt snow samples." (Page 1, Lines 24-25).

The sentences "We found that abundances of formic and acetic acids largely depend on non-sea-salt Ca^{2+} ($r^2 = 0.73$). These acids positively correlated with benzoic acid ($r^2 = 0.81$) that is primarily produced by fossil fuel combustion and secondary photochemical oxidation of anthropogenic toluene, indicating that monocarboxylic acids were mainly of anthropogenic and photochemical origin. Formic plus acetic acids exponentially correlated with pH ($r^2 = 0.76$) (pH = 4.7-6.9)." have been revised to "We found that abundances of formic and acetic acids largely depend on non-sea-salt Ca^{2+} (r = 0.85, $p < 0.001$). These acids positively correlated with benzoic acid (r = 0.90, $p < 0.001$) that is primarily produced by fossil fuel combustion and secondary photochemical oxidation of anthropogenic toluene and other aromatic hydrocarbons, indicating that monocarboxylic acids were mainly of anthropogenic and photochemical origin. Formic plus acetic acids exponentially correlated with pH (r = 0.86, $p < 0.001$) (pH = 4.7-6.9)." (Page 10, Lines 3-7).

14) p.10, L.14: I think the authors have incorrectly used "loss" instead of "loess".

Response:

Corrected to "loess". (Page 10, Line 12).

In addition, we have modified the following sentences.

The sentence "Details of analytical procedure were described previously (Kawamura et al., 2012)." has been revised to "Details of analytical procedure were described previously except for the pH adjustment with KOH solution (Kawamura et al., 2012)." (Page 4, Lines 16-17).

The sentence "They are adsorbed on the pre-existing particles via atmospheric titration with alkaline Kosa particles during the long-range atmospheric transport over the Japanese Islands." has been revised to "They are adsorbed on the pre-existing alkaline Kosa particles via atmospheric titration during the long-range atmospheric transport over the Japanese Islands." (Page 9, Lines 4-5).

The phrase "Total MCA-C/DOC ratio (av. 21%) in 2009 is significantly higher than those reported in rainwater from Los Angeles …" has been revised to "Total MCA-C/DOC ratio (av. 21%) in 2009 is significantly higher than those reported in rainwater samples from Los Angeles …" (Page 9, Lines 8-9).

The phrase "… suggesting that entrainment of organic acids in snow flakes is significant during the atmospheric transport from China to Japan." has been revised to "… suggesting that entrainment of organic acids in alkaline dusts and snow flakes is significant during the atmospheric transport from China to Japan." (Page 9, Lines 12-13).

We have added the following papers to the reference section.

Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: Molecular composition, Environ. Sci. Technol. 31, 1345-1358, 1997.

Watanabe, K., Nishimoto, D., Ishita, S., Eda, N., Uehara, Y., Takahashi, G., Kunori, N., Kawakami, T., Shimada, W., Aoki, K., and Kawada, K.: Formaldehyde and hydrogen peroxide concentrations in the snow cover at Murododaira, Mt. Tateyama Japan, Bull. Glaciol. Res., 30, 33-40, 2012.