



Long-range atmospheric transport of volatile monocarboxylic acids with Asian dust over a high mountain snow site, central Japan

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Abstract. To understand the long-range transport of monocarboxylic acids from the Asian continent to the Japanese islands, we collected snowpack samples from a pit sequence (depth ca. 6 m) at the Murodo-Daira snowfield near the summit of Mt. Tateyama, central Japan, in 2009 and 2011. Snow samples ($n = 16$) were analyzed for normal (C_1 – C_{10}), branched chain (iC_4 – iC_6), aromatic (benzoic and toluic acid isomers), and hydroxyl (glycolic and lactic) monocarboxylic acids, together with inorganic ions and dissolved organic carbon (DOC). Acetic acid (C_2) was found to be a dominant species (average 125 ng g^{-1}), followed by formic acid (C_1) (85.7 ng g^{-1}) and isopentanoic acid (iC_5) (20.0 ng g^{-1}). We found a strong correlation ($r = 0.88$) between formic plus acetic acids and non-sea-salt Ca^{2+} that is a proxy of Asian dust. Contributions of total monocarboxylic acids to DOC in 2009 ($21.2 \pm 11.6\%$) were higher than that in 2011 ($3.75 \pm 2.62\%$), being consistent with higher intensity of Asian dust in 2009 than in 2011. Formic plus acetic acids also showed a positive correlation ($r = 0.90$) with benzoic acid that is a tracer of automobile exhaust, indicating that monocarboxylic acids and their precursors are largely emitted from anthropogenic sources in China and/or secondarily produced in the atmosphere by photochemical processing. In addition, the ratio of formic plus acetic acids to $nss-Ca^{2+}$ (0.27) was significantly higher than those (0.00036 – 0.0018) obtained for reference dust materials of Chinese loess deposits from the Tengger and Gobi deserts. This result suggests that volatile and semi-volatile organic acids are adsorbed on the alkaline dust particles during long-range atmo-

spheric transport. Entrainment of organic acids by dusts is supported by a good correlation ($r = 0.87$) between formic plus acetic acids and pH of melt snow samples. Our study suggests that Asian alkaline dusts may be a carrier of volatile monocarboxylic acids.

1 Introduction

Low molecular weight (LMW) monocarboxylic acids such as formic ($HCOOH$) and acetic (CH_3COOH) acids are present in the atmosphere as major gaseous and particulate organic components (e.g., Kawamura and Kaplan, 1984; Kawamura et al., 2000; Paulot et al., 2011). Gaseous and particulate formic and acetic acids have been reported in urban (Kawamura et al., 2000), forest (Andreae et al., 1988), high mountain (Preunkert et al., 2007), marine (Miyazaki et al., 2014), and Arctic samples (Legrand et al., 2004). Salts of organic acids in aerosols are water-soluble and thus influence the radiation budget of the earth's atmosphere by acting as cloud condensation nuclei (CCN) (Kanakidou et al., 2005). In addition, LMW monocarboxylic acids have been detected in wet deposition such as rain, cloud and fog water, and snow samples (Maupetit and Delmas, 1994; Keene et al., 1995; Kawamura et al., 1996, 2012). Thus, organic acids are scavenged by wet deposition from the upper troposphere. It is also important to note that organic acids largely contribute to total acidity of rainwaters (Kawamura et al., 1996; Keene et al., 1983).

Formic and acetic acids have a variety of sources such as primary emission from motor exhausts (Kawamura et al., 2000) and vegetation (Kesselmeier et al., 1998), and secondary formation via the oxidation of anthropogenic and biogenic precursors such as toluene (laboratory data in Kawamura et al. (2000) reported that photochemical oxidations of various organic precursors are more important as a source of monocarboxylic acids in the troposphere. On the other hand, microorganisms are known to produce branched chain (iC_4 and iC_5) monocarboxylic acids (Allison, 1978).

The Japanese islands are located in the western North Pacific Rim, which is influenced by the Asian outflow of dusts and air pollutants. Asian dust (Kosa) events in the desert areas of North China promote the delivery of air pollutants with dust particles to the western North Pacific by westerly winds (e.g., Iwasaka et al., 1983). LMW monocarboxylic acids have been detected in alpine snow samples collected near the summit of Mt. Tateyama (Kawamura et al., 2012). They reported higher concentrations of monocarboxylic acids in snow pit samples with dust layers, suggesting that monocarboxylic acids may be associated with Asian dust during long-range atmospheric transport.

During the winter monsoon season, the Japanese high mountains facing the Sea of Japan are known to have heavy snowfall, which is associated with a significant evaporation of water vapors from the warm Tsushima Current in the Sea of Japan under a strong westerly wind condition. Alpine mountain snow sequences would provide useful information on the chemical states of Asian dust deposited over the snowfield, in which atmospheric organic acids are well preserved in snow layers (Osada et al., 2004).

In the present study, we collected snowpack samples from a pit sequence in the Murodo-Daira snowfield (ca. 6 m in depth) near the summit of Mt. Tateyama, central Japan, in April of 2009 and 2011. To better understand the sources of monocarboxylic acid and their long-range transport by Asian dust over the Japanese islands, 16 snowpack samples were analyzed for monocarboxylic acids, inorganic ions, and dissolved organic carbon (DOC) as well as reference dust materials of Chinese loess deposit samples collected from the Tengger and Gobi deserts. We discuss the contributions of LMW monocarboxylic acids to DOC as well as the association of monocarboxylic acids with alkaline dust particles during long-range atmospheric transport. Relations between monocarboxylic acids and pH values of the snowmelt water will also be discussed in terms of atmospheric titration of alkaline dust particles by acidic species, including organic acids during atmospheric transport.

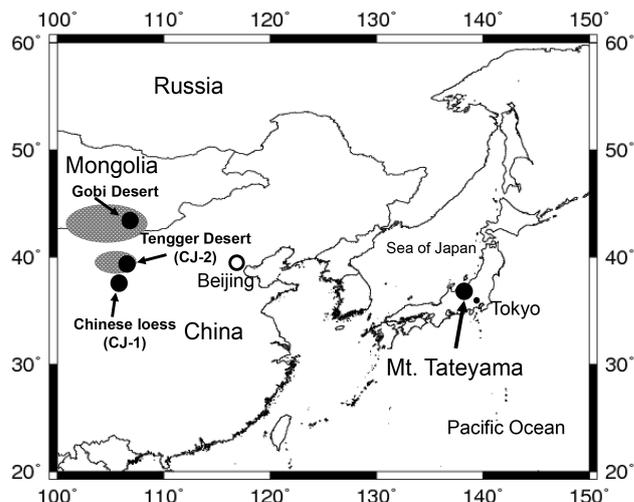


Figure 1. Location of the snowpack sampling site (Murodo-Daira) near Mt. Tateyama, central Japan. Sites are also shown for the loess deposit reference samples, which were collected from the Tengger and Gobi deserts in China and Mongolia (Nishikawa et al., 2000, 2013).

2 Material and methods

2.1 Sample collection

The details on the snow collection and sample storage methods were described in Kawamura et al. (2012) and Mochizuki et al. (2016). Snowpack samples were collected at the Murodo-Daira site (36.58° N, 137.36° E; elevation 2450 m) near Mt. Tateyama (elevation 3015 m), central Japan (Fig. 1). A snow pit hole (depth, ca. 6 m) was dug down to the ground. Table 1 provides descriptions of snow samples collected from the snow pit sequence, in which several brown-colored dirty layers were recognized by visual observation. Five snowpack samples including three dirty layers were collected from the pit sequence on 18 April 2009. Eleven snowpack samples including four dirty layers were collected from the pit sequence on 17 April 2011. In order to evaluate the consistent distributions of snow samples within the same snow horizon with dirty layers, another snowpack sample (no. 4') was collected at ca. 1 m away from the location of sample no. 4. Because the thickness of dirty layers in the snow pit sequence is ca. 10 cm or more, brown-colored particles are deposited together with snowflakes during snow precipitation rather than dry deposition.

The snow samples were placed in a pre-cleaned glass jar (8 L) using a clean stainless steel scoop. To avoid microbial degradation of organic compounds, mercuric chloride ($HgCl_2$) was added to the glass jar prior to collecting the snow sample. The sample jars were sealed with a Teflon-lined screw cap and transported to the laboratory in Sapporo within 4 days by a commercial refrigerated transport service, which kept the samples in darkness at ca. 5 °C and

Table 1. Descriptions of snowpack samples collected from a pit at Murodo-Daira near Mt. Tateyama, Japan, in 2009 and 2011. Snowpack sample no. 4' was collected from different snow pit sequences parallel to sample no. 4'. Bold letters represent dust layers.

Year	Sample ID	Snow depth (cm)	Description
2008–2009	No. 1	325–335	Weak dust layer Asian dust events were observed on 2 February 2009 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 2	410–420	Clean snow layer
	No. 3	425–435	Dusty snow layer Asian dust events were observed on 1 January 2009 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 4	520–530	Dusty snow layer Asian dust events were observed on 10 December 2008 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 4'	520–530	Dusty snow layer
	No. 5	530–540	Granular snow
2010–2011	No. 6	115–125	Granular snow with ice plate
	No. 7	169–178	Dusty and granular snow Asian dust events were observed on 22–24 February 2011 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 8	290–300	Compacted snow layer
	No. 9	390–400	Compacted snow layer
	No. 10	400–410	Dusty and compacted snow Asian dust events were observed on 31 December 2010 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 11	430–440	Compacted snow layer
	No. 12	460–466	Dusty and compacted snow Asian dust events were observed on 25–26 December 2010 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 13	507–527	Compacted snow with ice plate
	No. 14	542–548	Dusty and compacted snow Asian dust events were observed on 6 December 2010 by a lidar over Toyama. Air masses are derived from the Taklamakan and Gobi deserts.
	No. 15	590–605	Granular and compacted snow
	No. 16	630–635	Granular snow

constant humidity. The samples were stored in a dark refrigerator room at 4 °C prior to analysis.

We also analyzed the reference dust materials (Kosa) including Chinese loess deposits from the Tengger (CJ-1, < 250 µm and CJ-2, < 100 µm) and Gobi deserts (Gobi, < 10 µm). The reference materials were purchased from the National Institute for Environmental Studies, for the measurements of LMW monocarboxylic acids, inorganic ions, and DOC. Reference dust samples (0.1 g) were extracted with ultra-pure water by the methods as described below. The detailed information of reference samples is reported elsewhere (Nishikawa et al., 2000, 2013).

2.2 Chemical analysis

Monocarboxylic acids were determined as p-bromophenacyl esters using the capillary gas chromatography (GC) and GC-mass spectrometry (GC-MS) methods (Kawamura and Kaplan, 1984); 150 mL of melted snow samples were transferred to a pear-shaped glass flask (300 mL). To avoid the evaporative loss of volatile monocarboxylic acids from samples during analytical procedure, pH was adjusted to 8.5–9.0 by adding several drops of 0.05 M KOH solution to form organic acid salts (e.g., CH₃COO⁻K⁺). The sample was concentrated down to 10 mL using a rotary evaporator under vacuum (20 mm Hg) at 50 °C. The concentrates were fil-

tered through quartz wool packed in a Pasteur pipette. The filtrates were concentrated down to 0.5 mL. To convert all organic acids to $\text{RCOO}^- \text{K}^+$ form, the concentrates were passed through a glass column (Pasteur pipette) packed with cation exchange resin (DOWEX 50W-X4, 100–200 meshes, K^+ form). Organic acids were eluted with pure water and transferred in a 25 mL pear-shaped flask. The pH of the sample was checked to be 8.5–9.0 and then dried using a rotary evaporator under vacuum (20 mm Hg), followed by blow-down with pure nitrogen gas for 30 s. The former process generally requires 15–20 min.

Acetonitrile (4 mL) was added to the dried sample, and $\text{RCOO}^- \text{K}^+$ salts were reacted with α , p-dibromoacetophenone (0.1 M, 50 μL) as a derivatization reagent and dicyclohexyl-18-crown-6 (0.01 M, 50 μL) as a catalyst to derive p-bromophenacyl esters at 80 °C for 2 h. The reaction mixture was dried using a rotary evaporator under vacuum at 30 °C. The derived esters were dissolved in 0.5 mL of n-hexane/dichloromethane (2 : 1) mixture and then purified on a silica gel column (Pasteur pipette). Excess reagent was eluted with n-hexane/dichloromethane (2 : 1) mixture (7 mL) and then p-bromophenacyl esters were eluted with dichloromethane/methanol (95 : 5) mixture (2 mL) into a glass vial (2 mL). The esters were dried by blow-down using pure nitrogen gas and then dissolved in n-hexane (100 μL). In addition, the esters of hydroxyacids (lactic and glycolic acids) were reacted with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) with 1 % trimethylsilyl chloride and 10 μL of pyridine to derive trimethylsilyl (TMS) ethers for the hydroxyl (OH) group at 70 °C for 3 h.

p-Bromophenacyl esters and their TMS ethers were determined using a capillary gas chromatograph (HP GC6890, Hewlett-Packard, USA) equipped with a flame ionization detector. The esters were separated using a fused silica capillary column (HP-5, 30 m \times 0.2 mm i.d., film thickness 0.5 μm). The derivatives were also analyzed by GC-MS (Agilent GC7890A and 5975C MSD, Agilent, USA). The compounds were identified by comparing GC retention time and mass spectra of authentic standards. Details of analytical procedure were described previously (Kawamura et al., 2012), except for the pH adjustment with KOH solution. We tested the recoveries of authentic monocarboxylic acid standards (C_1 – C_{10} , iC₄–iC₆, benzoic, toluic, lactic, and glycolic acids) that were spiked into ultra-pure water. The results showed that the recoveries of organic acids were better than 80 %. Analytical errors in the GC/FID analysis using authentic standards were within 2 %. Total relative standard deviations based on triplicate analysis of real samples were within 12 %. Detection limits of organic acids were estimated to be 0.001–0.004 ng g^{-1} .

To measure inorganic ions, samples were passed through a membrane disk filter (0.22 μm , Millipore Millex-GV, Merck, USA) and the filtrates were injected into an ion chromatograph (Model 761 compact IC, Metrohm, Switzerland) equipped with an AS-09 autosampler (Kawamura et al.,

2012). Anion analysis was conducted using a Shodex SI-90 4E column and a 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3 solution as eluent. Cation analysis was conducted using a C2-150 column and a 4.0 mM tartaric acid + 1.0 mM dipicolinic acid solution as eluent. The total analytical precision is 4 % (Miyazaki et al., 2010).

After removing the particles in the samples on a disk filter (0.22 μm , Millipore Millex-GV, Merck, USA), DOC was determined using a total organic carbon (TOC) analyzer (Model TOC-Vcsh, Shimadzu) (Miyazaki et al., 2011).

2.3 Non-sea-salt ions

Concentrations of non-sea-salt ionic species X ($M_{\text{nss-x}}$) were estimated by the following equation:

$$M_{\text{nss-x}} = M_x - (X/\text{Na})_{\text{sw}} M_{\text{Na}},$$

where M_x and M_{Na} are the concentrations of X and of Na, respectively. $(X/\text{Na})_{\text{sw}}$ means the mass ratio of species X to Na in seawater (Duce et al., 1983). The ratios are 0.25 (SO_4^{2-}), 0.037 (K^+), 0.038 (Ca^{2+}), and 0.12 (Mg^{2+}) (Berg and Winchester, 1978). The ratio of F^- is 0.000146 (Yang et al., 2009).

2.4 Lidar observation and back trajectory analysis

We detected Asian dust events by the lidar observation (data are provided by the National Institute for Environmental Studies) over Imizu (36.70° N, 137.10° E), ca. 40 km northwest of Mt. Tateyama, Toyama Prefecture, Japan, during December to March in each year. The observation wavelength of the laser is 532 nm. Details of the extinction coefficient of dust particles were given in Shimizu et al. (2004). One example of a lidar image is presented in Fig. 2. Dense dust layers were recorded at the upper layers (3–4 km) over Imizu on 10 December 2008, whose dust event should be recorded in the snow pit sequences collected in 2009 (possibly corresponds to no. 4; see Table 1). This dust event was also recognized by the lidar observations at Niigata, Sendai, and Tsukuba in Japan. We estimated that Asian dust events observed on 10 December, 1 January, and 2 February during 2008–2009 and 6, 25–26 and 31 December, and 22–24 February during 2010–2011 correspond to sample ID nos. 4, 3, 1, no. 14, 12, 10, and 7, respectively (Table 1).

To investigate the source of air masses during the snow season (November to April), 7-day backward air mass trajectories were calculated at a level of 3000 m a.s.l. using an online program, Meteorological Data Explorer (METEX), which was developed by the National Institute for Environmental Studies (NIES), Japan. Meteorological data were obtained from the National Centers for Environmental Prediction (NCEP) Reanalysis data. Figure 3 shows the back air mass trajectories corresponding to selected dust layers (Table 1). The heights of air masses over the Asian continent and the Sea of Japan ranged from 2500 to 6000 m.

Table 2. Concentrations (ng g^{-1}) of monocarboxylic acids in snowpack samples collected from a snow pit sequence at Murodo-Daira near Mt. Tateyama, Japan, in 2009 and 2011 and reference dust materials. Bold letters represent dust layers.

Acid species	Snow sample ID (2009)										Snow sample ID (2011)										Reference dust materials		
	No.1	No.2	No.3	No.4	No.4'	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15	No.16	CJ-1	CJ-2	Gobi			
Aliphatic acids																							
Formic, C ₁	476	137	344	99.4	112	41.8	2.21	21.3	8.05	6.38	34.4	16.1	62.0	5.41	55.4	15.1	19.7	2420	3940	4402			
Acetic, C ₂	708	273	456	121	140	51.2	9.01	52.6	31.0	25.1	61.5	36.4	50.8	21.9	40.1	22.2	25.6	1435	18540	11170			
Propionic, C ₃	66.9	14.2	37.1	5.48	6.57	2.66	1.64	8.57	3.21	2.28	8.52	6.04	7.30	3.71	4.78	3.95	1.77	95	770	98			
Isobutyric, iC ₄	5.09	2.37	3.17	0.90	1.08	0.51	0.36	1.03	0.11	0.10	1.35	0.80	1.15	0.56	0.79	0.69	0.35	n.d.	n.d.	17			
Butyric, C ₄	10.0	4.21	7.20	1.31	1.64	0.85	0.60	1.12	0.39	0.32	2.60	1.52	1.76	1.20	1.46	1.31	0.35	39	319	44			
Isopentanoic, iC ₅	40.3	37.4	114	44.9	53.4	30.6	0.55	2.02	1.34	1.37	2.56	1.22	3.66	1.75	2.03	0.68	1.33	3	581	271			
Pentanoic, C ₅	2.55	1.51	2.41	0.92	1.12	0.48	0.33	0.71	0.09	0.08	1.04	0.44	0.58	0.47	0.57	0.52	0.17	15	204	25			
Isohexanoic, iC ₆	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.03	0.04	0.01	n.d.	0.08	0.01	0.03	0.02	0.06	0.09	n.d.	n.d.	n.d.	n.d.			
Hexanoic, C ₆	4.03	3.70	4.38	4.23	5.19	1.46	0.76	0.93	0.09	0.04	1.59	0.50	0.83	0.60	1.37	0.74	0.58	5	227	39			
Heptanoic, C ₇	2.01	1.03	2.09	0.61	0.73	0.74	0.03	0.41	0.11	0.08	1.39	0.11	0.49	0.25	0.29	0.37	0.13	3	82	0			
Octanoic, C ₈	1.04	0.25	1.38	1.03	1.26	0.55	0.16	0.15	0.02	0.01	0.46	0.11	0.09	0.15	0.23	0.19	0.07	4	125	14			
Nonanoic, C ₉	6.47	7.23	5.50	3.66	4.78	3.61	1.12	1.38	0.14	0.04	1.62	0.73	0.88	1.08	1.09	0.79	0.66	47	1400	3255			
Decanoic, C ₁₀	3.57	0.38	2.68	2.40	2.88	1.40	0.14	0.36	0.05	0.38	0.69	0.32	0.32	0.31	0.45	0.42	0.25	n.d.	n.d.	n.d.			
Sub-total	1330	481	981	286	331	136	16.9	90.6	44.7	36.1	117.8	64.3	129.9	37.4	108.6	50.4	51.0	4066	26190	19340			
Aromatic acids																							
Benzoic, Benz	6.89	3.75	8.74	2.02	2.28	1.29	0.25	1.14	0.12	0.08	3.47	0.61	1.00	0.93	1.98	1.12	0.21	26	62	68			
o-toluic	n.d.	n.d.	0.04	0.07	0.06	n.d.	n.d.	0.01	n.d.	n.d.	0.02	n.d.	n.d.	0.01	0.01	0.01	n.d.	n.d.	n.d.	n.d.			
m-toluic	0.44	0.71	0.50	0.33	0.37	0.30	0.03	0.08	n.d.	n.d.	0.05	n.d.	0.04	0.02	0.02	0.02	n.d.	n.d.	n.d.	n.d.			
p-toluic	0.09	0.06	0.11	n.d.	0.03	0.03	0.01	0.02	0.00	n.d.	0.07	0.01	0.03	0.02	0.03	0.02	0.01	n.d.	n.d.	n.d.			
Sub-total	7.42	4.53	9.39	2.42	2.74	1.62	0.29	1.25	0.12	0.08	3.61	0.62	1.06	0.97	2.04	1.16	0.22	26	62	68			
Hydroxyacids																							
Lactic, Lac	1.46	1.11	5.06	1.73	1.89	1.26	0.16	0.01	0.15	0.28	0.07	0.15	0.21	0.21	0.27	0.38	0.14	192	2124	1215			
Glycolic, Glyco	0.08	0.19	0.70	0.28	0.33	0.16	0.04	0.01	0.15	0.19	0.05	0.12	0.21	0.31	0.30	0.32	0.20	112	1020	385			
Sub-total	1.55	1.30	5.76	2.02	2.22	1.42	0.20	0.02	0.30	0.47	0.12	0.26	0.42	0.52	0.56	0.70	0.34	304	3144	1600			
DOC	1360	508	2380	865	936	469	507	904	544	381	1580	723	427	743	704	2110	576	73000	403000	267000			
Total MA-C/DOC (%)	35.6	36.7	15.8	13.1	14.1	12.1	1.5	3.9	3.2	3.7	2.9	3.5	10.8	2.1	5.4	1.0	3.2	2.0	2.9	3.3			

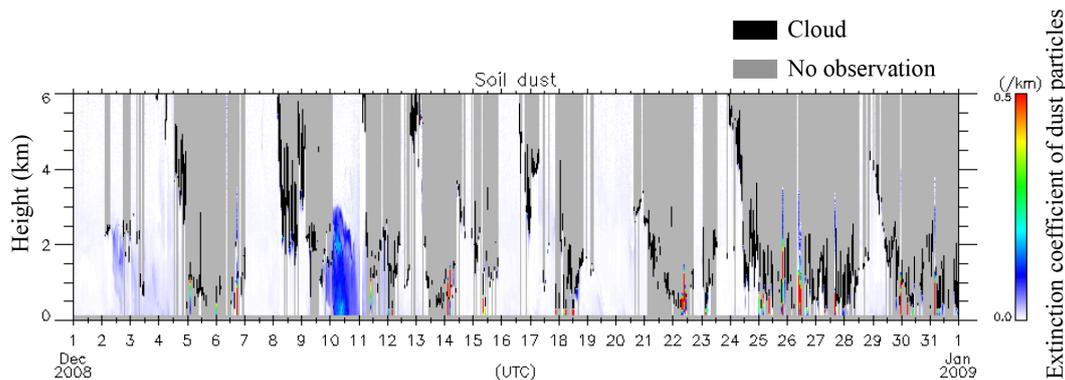


Figure 2. Example of lidar measurements of dusts obtained at Imizu, Toyama (ca. 40 km northwest of Mt. Tateyama) during 1–31 December 2008. The color scale indicates the extinction coefficient of dust particles based on lidar measurements. Black line represents clouds and gray shade above the black lines represents no data.

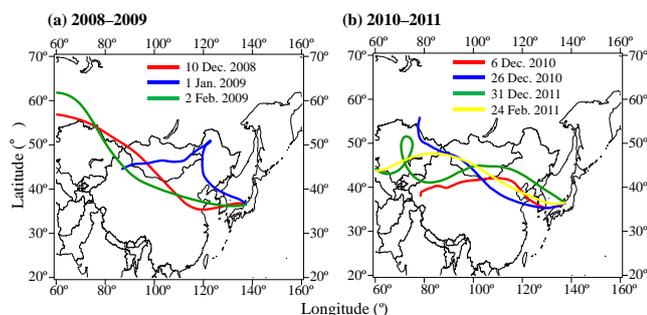


Figure 3. Seven-day airmass back trajectories at a level of 3000 m a.s.l. over the Murodo-Daira site in (a) 2008–2009 and (b) 2010–2011. Color lines show the trajectories associated with dust layers as observed by a lidar.

3 Results

3.1 Tateyama snow pit samples

Homologous series of low molecular weight normal aliphatic (C_1 – C_{10}), branched chain (iC_4 – iC_6), hydroxy (lactic and glycolic), and aromatic (benzoic acid and *o*-, *m*-, and *p*-toluic acid isomers) monocarboxylic acids were detected in the snow pit samples (Table 2). We found that differences in the concentrations of each monocarboxylic acid between sample nos. 4 and 4' are comparable to the total relative standard deviations based on triplicate analysis of real samples. Thus, we consider that each horizontal layer in the snow pit site is homogenous and that each snow sample is representative of the snowfall events over the Murodo site.

Acetic acid (C_2) was found to be the dominant species (2009: 51.2–708 $ng\ g^{-1}$; 2011: 9.01–61.5 $ng\ g^{-1}$), followed by formic acid (C_1) (2009: 41.8–476 $ng\ g^{-1}$; 2011: 2.21–62.0 $ng\ g^{-1}$). Concentrations of C_3 – C_{10} acids were 1–2 orders of magnitude lower than C_2 . In contrast, iC_5 acid (2009: 30.6–114 $ng\ g^{-1}$; 2011: 0.55–3.66 $ng\ g^{-1}$) was detected as

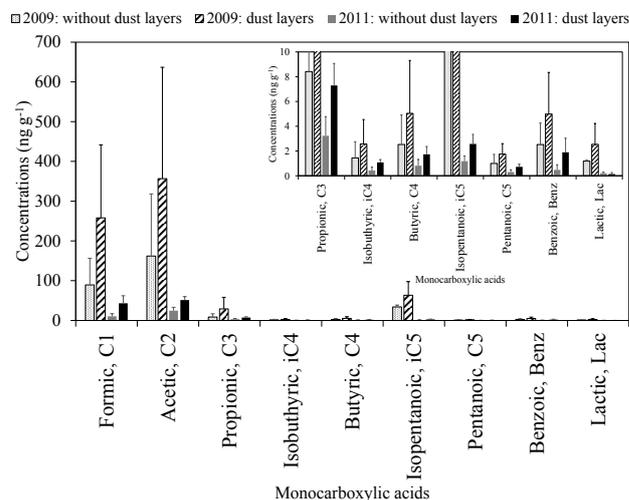


Figure 4. Concentrations of selected low molecular weight monocarboxylic acids in Mt. Tateyama snow samples.

the most abundant branched chain acid. Lactic and glycolic acids were also detected as hydroxyacids in the snow pit samples. Concentrations of lactic and glycolic acids are 1 and 2 orders of magnitude lower than those of major monocarboxylic acids (C_1 and C_2), respectively. The concentration of benzoic acid ranged from 0.08 to 8.74 $ng\ g^{-1}$. Total concentrations of toluic acid isomers were found to be significantly lower (average 0.07 $ng\ g^{-1}$) than that of benzoic acid (2.11 $ng\ g^{-1}$). Average concentrations of total monocarboxylic acids in the dust layers (2009: 739 $ng\ g^{-1}$; 2011: 114 $ng\ g^{-1}$) were greater than those without dust layers (2009: 313 $ng\ g^{-1}$; 2011: 43 $ng\ g^{-1}$) (Fig. 4). Concentrations of DOC ranged from 469 to 2380 $ng\ g^{-1}$ in 2009 and 381 to 2110 $ng\ g^{-1}$ in 2011 (Table 2). The highest concentration of DOC (2380 $ng\ g^{-1}$) was found in sample no. 3, in which a dust layer was observed.

Table 3. Concentrations (ng g^{-1}) of major ions and pH in snowpack samples collected from a snow pit sequence at Murodo-Daira near Mt. Tateyama, Japan, in 2009 and 2011 and reference dust materials. Bold letters represent dust layers.

Inorganic species	Snow sample ID (2009)										Snow sample ID (2011)										Reference dust materials		
	No.1	No.2	No.3	No.4	No.4'	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15	No.16	CJ-1	CJ-2	Gobi			
Anion																							
F ⁻	96	15	115	3	42	20	19	27	16	15	94	20	10	17	27	21	10	374 000	148 000	43 600			
MSA ⁻	1080	62	1250	204	172	83	83	62	64	75	128	93	51	129	117	66	74	665 000	224 000	215 000			
NO ₃ ⁻	534	130	458	316	224	150	791	1340	208	114	2020	88	104	428	1120	843	174	126 000	1 376 000	138 000			
SO ₄ ²⁻	1250	430	1460	728	536	364	845	1360	439	315	3010	310	260	549	1330	1070	282	2 493 000	24 038 000	1 853 000			
Total	2960	637	3280	1250	974	617	1740	2790	727	520	5250	511	424	1120	2600	2000	540	3 659 000	25 806 000	2 251 000			
nss-F ⁻	96	15	115	3	42	19	19	27	16	15	94	20	9	17	27	21	10	374 000	148 000	43 400			
nss-SO ₄ ²⁻	434	112	155	325	120	98	756	903	293	220	2440	215	n.d.	453	1040	967	192	2 008 000	23 010 000	1 592 000			
Cation																							
Na ⁺	3240	1270	5210	1610	1660	1060	356	1840	586	380	2310	380	1420	385	1160	417	362	1 942 000	4 111 000	1 047 000			
NH ₄ ⁺	111	41	200	268	243	78	235	291	54	36	842	47	34	56	517	190	41	336 000	1 460 000	18 700			
K ⁺	215	16	292	148	105	96	86	111	n.d.	50	302	n.d.	40	n.d.	119	43	n.d.	943 000	4 614 000	2 148 000			
Ca ²⁺	3120	485	3390	1600	1890	505	184	639	148	140	1060	113	515	n.d.	574	220	200	10 798 000	18 877 000	8 864 000			
Mg ²⁺	190	6	195	334	152	24	35	127	n.d.	13	78	n.d.	19	n.d.	35	33	n.d.	1 869 000	1 045 000	754 000			
Total	6880	1817	9290	3960	4050	1760	896	3010	787	619	4590	540	2020	442	2410	903	602	15 908 000	30 107 000	12 831 000			
nss-K ⁺	95	n.d.	99	88	44	57	72	43	n.d.	36	217	n.d.	n.d.	n.d.	76	28	n.d.	871 000	4 462 000	2 110 000			
nss-Ca ²⁺	3000	436	3190	1540	1820	464	170	569	125	125	976	99	462	n.d.	530	204	186	10 725 000	18 721 000	8 824 000			
nss-Mg ²⁺	n.d.	n.d.	n.d.	140	152	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1 636 000	552 000	628 000			
pH	6.9	6.1	6.7	6.7	6.3	6.0	4.7	6.0	5.2	5.0	6.2	5.1	6.2	4.9	5.9	4.4	5.4	–	–	–			

We detected cations (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , and NH_4^+) and anions (F^- , NO_3^- , SO_4^{2-} , and MSA^-) in snow pit samples collected in both 2009 and 2011 from the Murodo-Daira site near Mt. Tateyama (Table 3). Concentrations of nss-Ca^{2+} , nss-Mg^{2+} , nss-K^+ , nss-F^- , and nss-SO_4^{2-} were calculated as shown in Table 3. NO_3^- and nss-SO_4^{2-} are two major anions. The highest concentrations of NO_3^- (2020 ng g^{-1}) and nss-SO_4^{2-} (2440 ng g^{-1}) were obtained in sample no. 10, in which a dust layer was observed. On the other hand, Na^+ and nss-Ca^{2+} are two major cations. Higher concentrations of Na^+ and nss-Ca^{2+} were found in sample nos. 1 (Na^+ : 3240 ng g^{-1} ; nss-Ca^{2+} : 3000 ng g^{-1}) and 3 (Na^+ : 5210 ng g^{-1} ; nss-Ca^{2+} : 3190 ng g^{-1}), both of which showed the presence of a dust layer. The pH of melt snow samples ranged from 4.4 to 6.9 (Table 3). Higher pH was found in sample nos. 1, 3, and 4 ($\text{pH} = 6.7\text{--}6.9$), in which dust layers were observed.

Average concentrations of C_1 ($202 \pm 170 \text{ ng g}^{-1}$), C_2 ($292 \pm 249 \text{ ng g}^{-1}$), and iC_5 ($53.5 \pm 30.8 \text{ ng g}^{-1}$) in 2009 are 1 order of magnitude higher than those in 2011 (C_1 : $22.4 \pm 20.1 \text{ ng g}^{-1}$; C_2 : $34.2 \pm 15.8 \text{ ng g}^{-1}$; iC_5 : $1.69 \pm 0.88 \text{ ng g}^{-1}$). Similar trends were found for the average concentrations of minor monocarboxylic acids ($\text{C}_3\text{--}\text{C}_{10}$, iC_4 , and iC_6) in the snow pit samples in 2009 and 2011. The average concentration of DOC in 2009 ($1090 \pm 712 \text{ ng g}^{-1}$) is slightly higher than that in 2011 ($836 \pm 534 \text{ ng g}^{-1}$). The contribution of total monocarboxylic acids to DOC (total MCA-C / DOC) in 2009 ($21.2 \pm 11.6 \%$) is 6 times higher than that in 2011 ($3.75 \pm 2.62 \%$).

Average concentrations of NO_3^- ($657 \pm 633 \text{ ng g}^{-1}$) and nss-SO_4^{2-} ($748 \pm 682 \text{ ng g}^{-1}$) in 2011 are 2–3 times higher than those in 2009 (NO_3^- : $302 \pm 166 \text{ ng g}^{-1}$; nss-SO_4^{2-} : $207 \pm 139 \text{ ng g}^{-1}$). In contrast, average concentrations of nss-Ca^{2+} in 2009 ($1740 \pm 1190 \text{ ng g}^{-1}$) are 5 times higher than those in 2011 ($345 \pm 285 \text{ ng g}^{-1}$).

3.2 Reference dust materials

We detected LMW monocarboxylic acids, inorganic ions, and DOC in the water extracts from three reference dust materials (CJ-1, CJ-2, and Gobi) (Tables 2 and 3). Concentrations of total LMW monocarboxylic acids in the reference dusts were 4370 ng g^{-1} (CJ-1), $29\,390 \text{ ng g}^{-1}$ (CJ-2), and $21\,010 \text{ ng g}^{-1}$ (Gobi). The dominant LMW monocarboxylic acids were formic and acetic acids. Concentrations of DOC were $73\,000 \text{ ng g}^{-1}$ (CJ-1), $403\,000 \text{ ng g}^{-1}$ (CJ-2), and $267\,000 \text{ ng g}^{-1}$ (Gobi). Total MCA-C/DOC ratios in reference dust materials were 2.0% (CJ-1), 2.9% (CJ-2), and 3.3% (Gobi). Concentrations of nss-Ca^{2+} in the reference dust materials were $10\,700 \mu\text{g g}^{-1}$ (CJ-1), $18\,700 \mu\text{g g}^{-1}$ (CJ-2), and $8820 \mu\text{g g}^{-1}$ (Gobi).

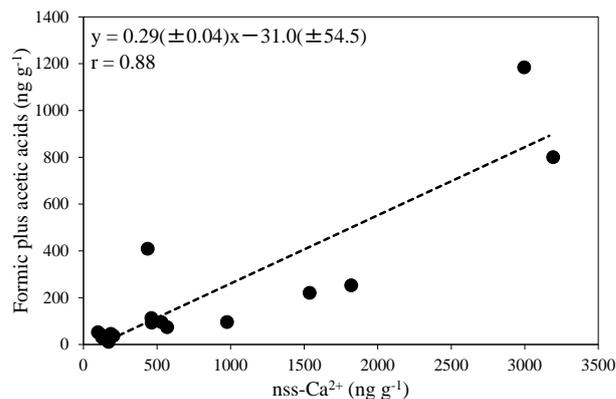


Figure 5. Scatter plot of concentrations of formic plus acetic acids vs. nss-Ca^{2+} in Mt. Tateyama snow samples. The dotted line represents the Deming linear regression.

4 Discussion

4.1 Influence of Asian dust

High concentrations of nss-Ca^{2+} were obtained in the dust layers of both 2009 and 2011. Ca^{2+} is known as a major metal ion to be transported from arid regions in North Asia with Asian dust (Mori et al., 2002; Tsai and Chen, 2006). In this study, contributions of nss-Ca^{2+} to Ca^{2+} in 2009 and 2011 are 95 and 91%, respectively. 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. These values are comparable to those in reference dust materials such as CJ-1 (0.17), CJ-2 (0.06), and Gobi (0.09). Therefore, nss-Ca^{2+} can be used as an indicator of mineral dust. High abundances of nss-Ca^{2+} in snowpack samples indicate that a strong outflow of dust particles from the Asian continent was involved with a heavy snow precipitation.

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. 5). Concentrations of formic plus acetic acids were found to increase linearly with that of nss-Ca^{2+} ($r = 0.88$). The air mass trajectories have passed over the Asian continent including North China and Mongolia (Fig. 3). Asian dust particles may be a carrier of formic and acetic acids via acid–base interaction, forming carboxylate salts, when the Asian dust activity maximizes in North China. The pathways of long-range transport and sources of formic and acetic acids will be discussed in the following Sects. 4.2 and 4.3.

Average concentrations of formic and acetic acids and nss-Ca^{2+} in 2009 are higher than those in 2011. This may be related to a strong influence of the Asian dust events, although the detailed records of the Asian dust events in North China are not available at this moment.

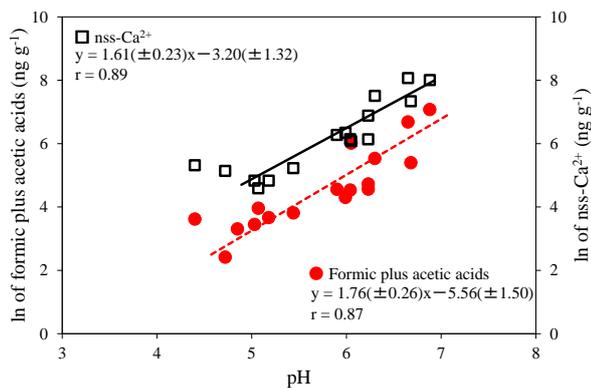


Figure 6. Scatter plots of the natural logarithm of formic plus acetic acids and pH, and natural the logarithm of nss-Ca²⁺ and pH. The solid and dotted lines represent the Deming linear regression.

4.2 Long-range transport of formic and acetic acids and aerosol acidity/alkalinity

Figure 5 presents the relationship between formic plus acetic acids and the pH of melt snow. Concentrations of formic plus acetic acids were found to increase exponentially with pH ($r = 0.87$). Interestingly, concentrations of nss-Ca²⁺ were also found to increase exponentially with pH ($r = 0.89$) (Fig. 6). Because LMW monocarboxylic acids have high vapor pressure (Saxena and Hildeman, 1996), they should be largely present as gases in the atmosphere (e.g., Kawamura et al., 1985; Liu et al., 2012). During long-range atmospheric transport, alkaline dust particles may be subjected to atmospheric titration by gaseous monocarboxylic acids.

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 a chloride ion (Cl⁻) because of the addition of HgCl₂ into snow samples as bactericide. To calculate ion balance, we used equivalent ratios of Cl⁻ to Na⁺ (1.26) obtained in the same snow pit in 2011 (Watanabe et al., 2012). Figure 7 shows total cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) against total anions (F⁻, MSA⁻, NO₃⁻, SO₄²⁻, and organic anions including normal (C₁-C₁₀), branched chain (iC₄-iC₆), aromatic (benzoic and toluic acid isomers), and hydroxyl (lactic and glycolic) monocarboxylic acids) ($r = 0.95$). 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 CO₃⁻ and HCO₃⁻, and unidentified organic anions were not taken into consideration.

We calculated the ratios of formic plus acetic acids / nss-Ca²⁺ for the Murodo-Daira snow pit samples and compared the ratios of formic plus acetic acids / nss-Ca²⁺ in the reference materials such as CJ-1, CJ-2, and Gobi. We found that formic plus acetic acids / nss-Ca²⁺ ratios for the Murodo-Daira snow pit samples (ave. 0.27) are significantly higher than those from CJ-1 (0.00036), CJ-2 (0.0012), and Gobi (0.0018) reference samples collected from the arid areas of

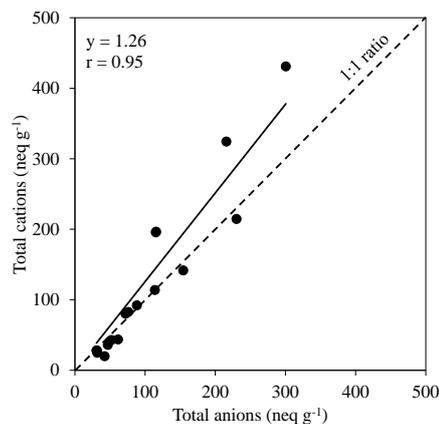


Figure 7. Linear regression plots between total cation equivalents (neq) and total anion equivalents (neq) in melt snow samples at the Murodo-Daira site near Mt. Tateyama.

North China. These results indicate that alkaline dust particles can adsorb gaseous MCAs in the atmosphere and largely control the long-range transport of LMW monocarboxylic acids from the Asian continent to the western North Pacific Rim. Based on a good correlation between monocarboxylic acids and nss-Ca²⁺, it is very likely that organic acids in aerosols exist in the form of salts such as Ca(HCOO)₂, Ca(HCOO)(CH₃COO), and/or Ca(CH₃COO)₂.

Prince et al. (2008) reported that gas-phase acetic acid is adsorbed on the surface of calcite (CaCO₃), a major mineral of dust particles. Acetic acid can form calcium acetate in the atmosphere (Alexander et al., 2015). Vapor pressures of those organic anions are significantly lower than those of free monocarboxylic acids. In addition, the lifetimes of formic and acetic acids with OH radicals are estimated to be 25 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 the atmospheric transport time of air mass from the Asian continent to Mt. Tateyama. Therefore, the acidity/alkalinity of an aerosol surface is an important factor in controlling the uptake of gaseous organic acids, and thus organic acid salts can be long-range transported as particles in the atmosphere from the Asian continent to the Japanese islands. Zhang et al. (2012) reported that pH of wet deposition for the last 2 decades showed a slight increase in the southeastern Tibetan Plateau, China, due to the presence of Ca²⁺ that is derived from Asian dust. We suggest that long-range atmospheric transport of LMW monocarboxylic acids associated with Asian dust over the Japanese islands would be changed in the future due to the changes in the emission of Asian dusts from the Asian continent that are associated with global warming and changes in land use (Zhang et al., 2003; Song et al., 2016).

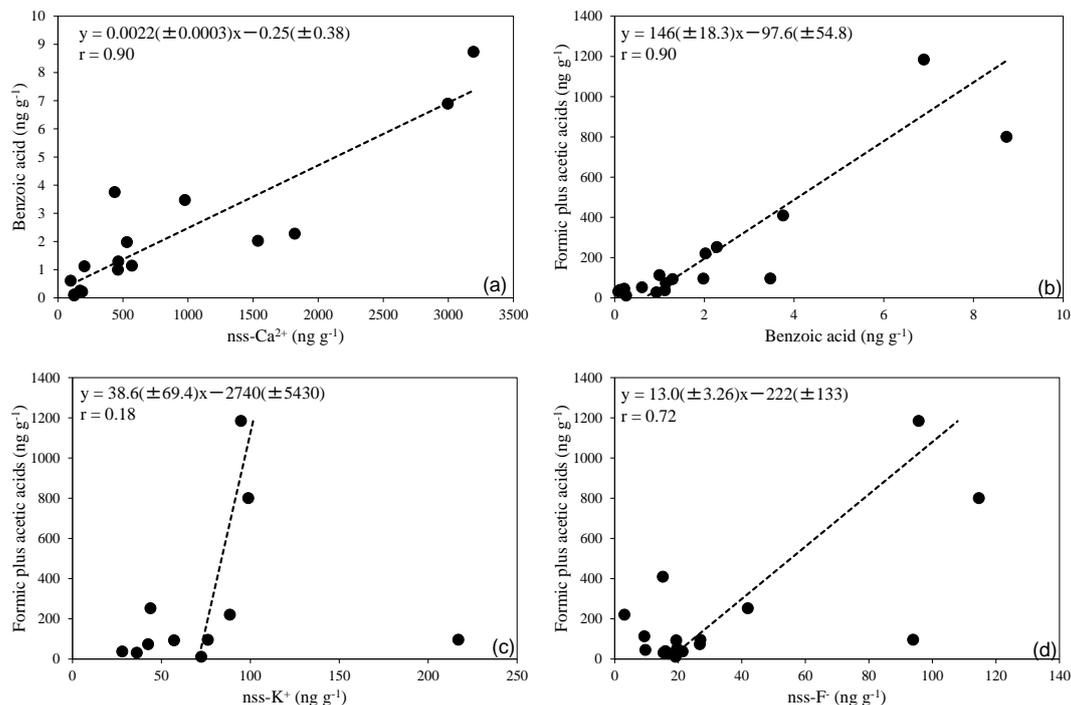


Figure 8. Scatter plots of (a) concentrations of benzoic acid vs. nss-Ca²⁺, (b) formic plus acetic acids vs. benzoic acid, (c) formic plus acetic acids vs. nss-K⁺, and (d) formic plus acetic acids vs. nss-F⁻ in Mt. Tateyama snow samples. The dotted line represents the Deming linear regression.

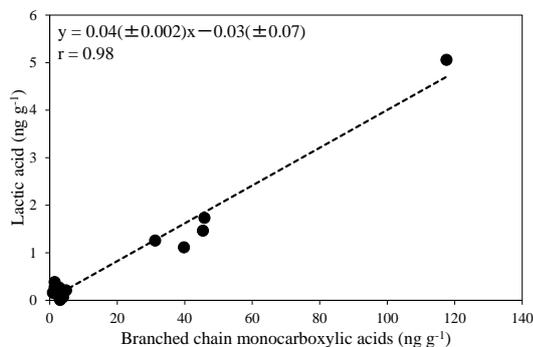


Figure 9. Scatter plot of concentrations of branched chain (iC₄–iC₆) monocarboxylic acids vs. lactic acid in Mt. Tateyama snow samples. The dotted line represents the Deming linear regression.

4.3 Major contributions of anthropogenic monocarboxylic acids

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 correlated with nss-Ca²⁺ ($r = 0.90$) (Fig. 8a). In addition, the average benzoic acid / nss-Ca²⁺ 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).

Formic plus acetic acids showed a strong positive correlation with benzoic acid ($r = 0.90$) (Fig. 8b), indicating that they are derived from anthropogenic sources in the Asian continent. In contrast, nss-K⁺, a tracer of biomass burning (Zhu et al., 2015), did not show a positive correlation with formic plus acetic acids ($r = 0.18$) (Fig. 8c). nss-F⁻, a tracer of coal burning (Wang et al., 2005), shows a positive correlation with formic plus acetic acids ($r = 0.72$) (Fig. 8d); however, they were rather scattered. Biomass and coal burning is not a major source of monocarboxylic acids in the snow pit samples collected from the Murodo-Daira site near Mt. Tateyama. We consider that formic and acetic acids are both derived from anthropogenic and photochemical processes in the atmosphere of North China. They are adsorbed on the pre-existing alkaline Kosa particles via the atmospheric titration during a long-range atmospheric transport over the Japanese islands.

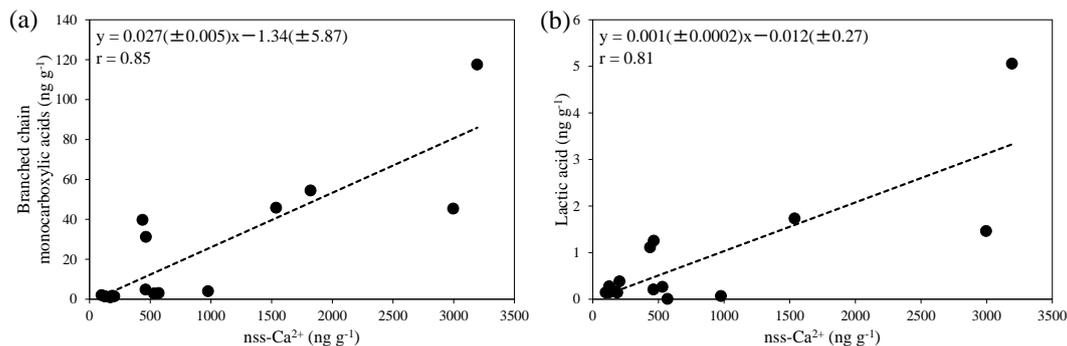


Figure 10. Scatter plots of (a) concentrations of branched chain (iC_4 – iC_6) monocarboxylic acids vs. $nss-Ca^{2+}$ and (b) lactic acid vs. $nss-Ca^{2+}$ in Mt. Tateyama snow samples. The dotted line represents the Deming linear regression.

The mean concentrations of formic and acetic acids in our samples in 2009 are higher than those reported in mountain snow samples from southern California (Kawamura et al., 1996), Tateyama (Kawamura et al., 2012) and the southern French Alps (Maupetit and Delmas, 1994), and ice core samples from Antarctica (de Angelis et al., 2012). The total MCA-C / DOC ratio (av. 21 %) in 2009 is significantly higher than those reported in rainwater samples from Los Angeles (4.4 %) (Kawamura et al., 2001), Shenzhen, China (2.3 %) (Huang et al., 2010), and reference dust materials (CJ-1: 2.0 %; CJ-2: 2.9 %; and Gobi: 3.3 %). These results indicate that water-soluble LMW monocarboxylic acids in the snow pit samples near Mt. Tateyama constitute a significant fraction of water-soluble organic carbon, suggesting that entrainment of organic acids in alkaline dusts and snowflakes is significant during the atmospheric transport from China to Japan.

4.4 Minor contributions of biogenic monocarboxylic acids

Branched chain (iC_4 – iC_6) monocarboxylic acids are produced by bacterial activity of *Bacteroides ruminicola*, *Megasphaera elsdenii*, and *Streptomyces avermitilis* (e.g., Allison, 1978; Hafner et al., 1991). It is of interest to note that iC_5 has not been reported in motor exhaust (Kawamura et al., 2000) and urban rainwater (Kawamura et al., 1996). Bacteria (*Lactobacillus*) and plant tissues are known to produce lactic acid (Cabredo et al., 2009; Baker and El Saifi, 1953). *Lactobacillus* mainly exists in soil (Huysman and Verstraete, 1993). We found a strong positive correlation between branched chain (iC_4 – iC_6) acids and lactic acid ($r = 0.98$) (Fig. 9). This strong correlation suggests that these organic acids are closely linked in the biosynthetic processes associated with bacterial activity in soils.

Branched chain (iC_4 – iC_6) acids ($r = 0.85$) (Fig. 10a) and lactic acid ($r = 0.81$) (Fig. 10b) showed a positive correlation with $nss-Ca^{2+}$. Maki et al. (2011, 2014) reported that bacterial communities are present in the layers of snow pit

sequences at Murodo-Daira near the summit of Mt. Tateyama and are considered to be associated with Asian dust events. Bacterial species responsible for branched monocarboxylic and lactic acids have not been reported in the Tateyama snow samples at this time. However, our results suggest that branched chain monocarboxylic acids may be produced by bacterial process in soils of the Asian continent and transported over the Japanese islands with Asian dust. The contribution of biogenic monocarboxylic acids is much lower than anthropogenic monocarboxylic acids.

5 Summary and conclusions

Low molecular weight normal (C_1 – C_{10}), branched chain (iC_4 – iC_6), hydroxyl (lactic and glycolic), and aromatic (benzoic and toluic isomers) monocarboxylic acids were detected in the snow pit samples collected from Murodo-Daira snowfield near the summit of Mt. Tateyama, central Japan. Acetic acid was detected as the dominant species (125 ng g^{-1}), followed by formic acid (85.7 ng g^{-1}) and isopentanoic acid (20.0 ng g^{-1}). Enhanced concentrations of monocarboxylic acids and $nss-Ca^{2+}$ were obtained in the snow pit samples with dust layers. We found that abundances of formic and acetic acids largely depend on non-sea-salt Ca^{2+} ($r = 0.88$). These acids positively correlated with benzoic acid ($r = 0.90$) 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 ($r = 0.87$) ($\text{pH} = 4.7$ – 6.9). Alkaline dust particles may be subjected to atmospheric titration by gaseous monocarboxylic acids.

In addition, we analyzed reference dust materials including Chinese loess samples from the Tengger and Gobi deserts for the measurements of LMW monocarboxylic acids and inorganic ions. The ratio of total monocarboxylic acid / $nss-Ca^{2+}$ at the Murodo-Daira snow pit samples (0.27) was found to be significantly (2 to 3 orders of magnitude) higher

than those of Chinese loess reference samples (0.00036–0.0018). These comparisons suggest that gas-phase monocarboxylic acids are easily adsorbed on the surface of pre-existing dust particles derived from the Asian continent to result in organic acid salts. Our study demonstrates that Asian dust is a key factor in promoting a long-range atmospheric transport of LMW monocarboxylic acids emitted and produced over North China to the western North Pacific Rim under a strong influence of the East Asian winter Monsoon. By forming the organic acid salts, LMW monocarboxylic acids can be more stabilized against the photochemical decomposition during long-range atmospheric transport.

6 Data availability

The data of this paper are available upon request to K. Kawamura (kkawamura@isc.chubu.ac.jp) or T. Mochizuki (tmochizuki@u-shizuoka-ken.ac.jp).

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