| | |
|---|---|
| Title | Low molecular weight (C1-C10) monocarboxylic acids, dissolved organic carbon and major inorganic ions in alpine snow pit sequence from a high mountain site, central Japan |
| Author(s) | Kawamura, Kimitaka; Matsumoto, Kohei; Tachibana, Eri; Aoki, Kazuma |
| Citation | Atmospheric Environment, 62, 272-280<br>https://doi.org/10.1016/j.atmosenv.2012.08.018 |
| Issue Date | 2012-12 |
| Doc URL | http://hdl.handle.net/2115/51066 |
| Type | article (author version) |
| File Information | AE62_272-280.pdf |

Submitted to Atmos. Environ. April 4, 2012, revised July 6 2012, July 31 2012

# Low molecular weight ($C_1$-$C_{10}$) monocarboxylic acids, dissolved organic carbon and major inorganic ions in alpine snow pit sequence from a high mountain site, central Japan

Kimitaka Kawamura[1,*], Kohei Matsumoto[1], Eri Tachibana[1], and Kazuma Aoki[2]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[2]Department of Earth Science, Faculty of Science, Toyama University, Gofuku, Toyama 930-8555, Japan
*Corresponding author

Keywords: formic acid, acetic acid, propionic acid, lactic acid, glycolic acid, high mountain snowpack, sulfate, calcium, Asian dust

## Abstract

Snowpack samples were collected from a snow pit sequence (6 m in depth) at the Murodo-Daira site near the summit of Mt. Tateyama, central Japan, an outflow region of Asian dusts. The snow samples were analyzed for a homologous series of low molecular weight normal ($C_1$-$C_{10}$) and branched ($iC_4$-$iC_6$) monocarboxylic acids as well as aromatic (benzoic) and hydroxy (glycolic and lactic) acids, together with major inorganic ions and dissolved organic carbon (DOC). The molecular distributions of organic acids were characterized by a predominance of acetic (range 7.8-76.4 ng/g-snow, av. 34.8 ng/g) or formic acid (2.6-48.1 ng/g, 27.7 ng/g), followed by propionic acid (0.6-5.2 ng/g, 2.8 ng/g). Concentrations of normal organic acids generally decreased with an increase in carbon chain length, although nonanoic acid ($C_9$) showed a maximum in the range of $C_5$-$C_{10}$. Higher concentrations were found in the snowpack samples containing dust layer. Benzoic acid (0.18-4.1 ng/g, 1.4 ng/g) showed positive correlation with nitrate (r=0.70), sulfate (0.67), $Na^+$ (0.78), $Ca^{2+}$ (0.86) and $Mg^+$ (0.75), suggesting that this aromatic acid is involved with anthropogenic sources and Asian dusts. Higher concentrations of $Ca^{2+}$ and $SO_4^{2-}$ were found in the dusty snow samples. We found a weak positive correlation (r=0.43) between formic acid and $Ca^{2+}$, suggesting that gaseous formic acid may react with Asian dusts in the atmosphere during long-range transport. However, acetic acid did not show any positive correlations with major inorganic ions. Hydroxyacids (0.03-5.7 ng/g, 1.5 ng/g) were more abundant in the granular and dusty snow. Total monocarboxylic acids (16-130 ng/g, 74 ng/g) were found to account for 1-6% of DOC (270-1500 ng/g, 630 ng/g) in the snow samples.

## 1. Introduction

Recently, formic or acetic acid is considered as the most abundant organic gas species in the troposphere (Paulot et al., 2011). Preunkert et al. (2007) reported that concentrations of gaseous formic and acetic acids are twice higher than nitric acid and an order of magnitude higher than $SO_2$ in the Alpine site on molar basis. Homologous series of low molecular weight monocarboxylic acids ($C_1$-$C_{10}$) were first measured in rain and fog samples in Californian urban sites using a capillary gas chromatography (GC) employing p-bromophenacyl esters (Kawamura and Kaplan, 1984; Kawamura et al., 1985). Their molecular distributions are characterized by the predominance of formic or acetic acid, followed by propionic acid. Extensive measurements of organic acids in rain and snow samples were conducted in Los Angeles and its vicinity (Kawamura et al., 1996; Kawamura et al., 2001). Formic and acetic acids have also been reported in snow samples using an ion chromatography (IC) (Dibb and Arsenault, 2002), although IC has rarely detected longer-chain monocarboxylic acids $\geq C_3$ due to its lower sensitivity. $C_1$ and $C_2$ acids are also present in ice samples from Greenland (Osada and Langway, 1993; Legrand and de Angelis, 1996) and East Antarctic plateau (de Angelis et al., 2012) as well as snow samples from high mountain site in Japan (Osada et al., 2000). These monocarboxylic acids are mostly present as gases in the urban atmosphere (Kawamura et al., 1985) and a high mountain Alpine site (Preunkert et al., 2007).

Concentrations of monocarboxylic acids in the urban rainwater from Los Angeles are similar to or higher than those of dicarboxylic acids, whose molecular distributions are characterized by the predominance of oxalic acid (Kawamura et al., 1996) and whose aerosol concentrations are often recognized as the most abundant organic compound class (Kawamura and Yasui, 2005). Monocarboxylic acids ($C_1$-$C_{10}$) were found in motor exhausts and used engine oils (Kawamura et al., 1985; Kawamura et al., 2000). However, photochemical oxidations of various organic precursors from anthropogenic sources in the urban atmosphere are suggested as a major source of $C_1$-$C_{10}$ acids based on their diurnal daytime maxima and positive correlation to ambient temperature (Kawamura et al., 2000). Formic acid can also be produced in clouds by the oxidation of formaldehyde (Chameides and

Davis, 1983). Paulot et al. (2011) presented a budget of formic and acetic acids in the atmosphere with bottom-up estimate of ~1200 and ~1400 Gmol $yr^{-1}$ for formic and acetic acids on a global scale, respectively. They proposed that photochemical oxidation of biogenic volatile organic compounds, in particular isoprene, is an important source of formic and acetic acids. In contrast, Kuo et al. (2011) reported the presence of carboxylic acids including formic and acetic acids in pine leaves. Plant leaves are also important emission sources of atmospheric volatile organic acids (Gabriel et al., 1999). In fact, high abundances of formate and acetate were reported in rainwater from Amazon forest (Keene and Galloway, 1984). Paulot et al. (2011) reported that major sinks of volatile carboxylic acids are wet and dry deposition. In particular, snowflakes efficiently scavenge those organic acids from the upper atmosphere due to their large surface areas per weight.

Although organic acids have been studied in snow samples from North America and Europe (e.g., Kawamura et al., 2000; Legrand et al., 2003), there are no reports on homologous series of low molecular weight monocarboxylic acids in Asian region, in which anthropogenic emissions of organics are significant due to the enhanced economic growth in China (Huebert et al., 2003). The western rim of the North Pacific where Japanese Islands exist is located under the pathway of the atmospheric transport of pollutants from East Asia by westerly winds. Thus the atmospheric compositions of the marine atmosphere are significantly influenced by the Asian outflows. In this study, we collected snowpack samples from a pit sequence in the Murodo-Daira snowfield near the summit of Mt. Tateyama, central Japan, where very thick snow layers accumulate every winter to spring and disappear in late summer. The snowpack samples were analyzed for a series of monocarboxylic acids. Here, we report molecular distributions of monocarboxylic acids ($C_1$-$C_{10}$) including benzoic acid and hydroxyacids in the snow samples together with inorganic ions and dissolved organic carbon (DOC). The results will be discussed in terms of their sources and atmospheric transport from Asian Continent and the dust regions.

## 2. Samples and Methods

On 19 April 2008, snow pit hole (depth 6.6 m) was dug down to the ground at the

Murodo-Daira site (36.58°N, 137.60°E; elevation, 2450 m) near Mt.Tateyama (elevation, 3015 m), central Japan. Figure 1 shows a locality map of Mt. Tateyama with Japanese Island, Asian continent, the Sea of Japan and the Pacific Ocean. In the snow pit sequence, several dirty layers were recognized by eye observation. The snow samples with dust layers were later characterized by high concentrations of $Ca^{2+}$, suggesting a long-range atmospheric transport of Asian dusts over the Murodo-Daira snowfield. Seven snowpack samples (ca. 2-6 kg each) including dust layers were collected from the pit sequence and three surface snow samples were taken from the snow field near the pit site. They were placed in a pre-cleaned glass jar (8 L, Nos. 3 - 10) or Teflon bottles (6 L, Nos. 1 and 2) using a clean stainless steel scoop. Immediately after the sampling, mercuric chloride ($HgCl_2$) was added to the snow in a jar to avoid microbial degradation of organic compounds, which would be initiated when snow samples start to melt (Kawamura and Kaplan, 1990). Samples were sealed with a Teflon-lined screw cap, transported to Sapporo and stored in a dark refrigerator room at 4°C prior to analysis. Approximately 100 g of snow samples were also taken in a plastic bottle (200 ml) for inorganic ion analysis and stored at 4 °C without adding chemicals. Table 1 gives information of snowpack samples including sample depth and description of dust layers. The pit samples from 6.6 m sequence include various types of snow such as clean snow, dirty snow, snow with ice lens, granular snow and compacted snow.

Organic acids were measured by the method described in Kawamura and Kaplan (1984) and Kawamura et al. (1996). Approximately 150 ml of melted snow samples were transferred to a round glass flask (200 ml) and adjusted to pH 8.5-9.0 with 0.1 M KOH solution using a pH meter. The sample was concentrated down to ca. 0.5 ml using a rotary evaporator under vacuum at 60°C. The concentrates were passed through a Pasteur pipet column packed with cation exchange resin (DOWEX 50W-X4, 100-200 mesh, $K^+$ form) to derive all the organic acids to $RCOO^-K^+$ form (Kawamura and Kaplan, 1984). The eluents containing $RCOO^-K^+$ were placed in a 50 ml peer-shape flask and dried using a rotary evaporator under vacuum. Acetonitrile (4 ml) and $\alpha$, p-dibromoacetophenone (0.1 M, 50 $\mu$l) were added to the flask as well as dicyclohexyl-18-crown-6 (0.01 M, 50 $\mu$l) as a catalyst. The flask was sealed with a glass cap and clamp, sonicated in an ultrasonic bath and heated at

80°C for 2 h. During this procedure, monocarboxylic acids were derivatized to p-bromophynacyl esters. The reaction mixture was dried with a rotary evaporator and then transferred onto the $SiO_2$ column (Pasteur pipet). Excess reagent was eluted with 7 ml of n-hexane/dichloromethane (1:1) and then p-bromohenacyl esters were eluted with 2 ml of dichloromethane/methanol (95:5) into a glass vial (2 ml). The esters were dried under $N_2$ blow down and dissolved in n-hexane (50 or 100 μl).

Two micro liters of the n-hexane solution were injected to a capillary gas chromatograph (Agilent GC6890) installed with a split/splitless injector, fused silica capillary column (HP-5, 30 m × 0.2 mm i.d., film thickness 0.5 μm) and flame ionization detector. The ester fraction was also analyzed by GC/mass spectrometer (Thermo, Trace MS) with a similar GC column condition. The monocarboxylic acid esters were identified by comparing the GC retention times and mass spectra of authentic standards (Kawamura and Kaplan, 1984). Mass spectra of p-bromophenacyl esters of carboxylic acids were confirmed by a twin mass fragment peak (m/z 183 and 185) and twin molecular ion of p-bromophenacyl esters (e.g., m/z=242/244 for formic acid and m/z=256/258 for acetic acid), which are characteristic of $^{79}$Br (50.52%) and $^{81}$Br (49.48%) isotopes (Kawamura and Kaplan, 1984). p-Bromophenacyl esters of hydroxyacids (lactic and glycolic acids) were reacted with 99% N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) to derive OH group to TMS ether by heating at 70°C for 2 h in a sealed glass vial. The blank levels of the esters were less than 5 % of the minimum concentration of the real samples. The recoveries of monocarboxylic acids ($C_1$-$C_7$) spiked to Milli-Q water were better than 80 %. Analytical errors were within 15% for major organic acids. The concentrations reported here are all corrected for the laboratory blanks.

Major inorganic ions in snow samples were determined using a Metrohm ion chromatograph (model 761 compact IC) equipped with an AS-09 autosampler (Miyazaki et al., 2010). Anions were measured with a suppressor on a Shodex SI-90 4E column using an eluent mixture of 1.7 mM $NaHCO_3$ and 1.8 mM $Na_2CO_3$. Cations were determined on a Metrohm C2-150 column with 4 mM tartaric acid + 1 mM dipicolinic acid as an eluent. The overall uncertainty in the determination of ionic species is 4%. Although we did acidify the sample, the melt snow samples were already acidic (pH < 6), suggesting that major portion of Ca was dissolved in water and measured by IC.

Dissolved organic carbon (DOC) was determined using a Shimadzu TOC-5000 carbon analyzer after removing the particles in the melt water sample on a disk filter (Millex-GV, 0.22 µm, Millipore). Melt snow samples were first acidified with 1.2 M HCl. After purging dissolved inorganic carbon with ultra pure air, DOC was measured with a carbon analyzer. Blank values were subtracted from all standard and snow sample data. The analytical error of DOC measurements was 6%.

Six day back air mass trajectories were calculated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003; Rolph, 2003). The trajectories were calculated for air masses starting from the sampling site at 2000 and 3000 m height using the vertical velocity method and the reanalysis data (Aggarwal and Kawamura, 2008).

## 3. Results and Discussion

### *3.1. Inorganic Ions*

Concentrations of inorganic ions are presented in Table 2. $Ca^{2+}$, $Na^{+}$, and $NH_4^{+}$ were found as major cations, whose average concentrations are 635, 406, and 332 ng/g-snow, respectively. On the other hand, major anions were $SO_4^{2-}$, $NO_3^{-}$ and $Cl^{-}$, whose average concentrations were 1630, 1030 and 620 ng/g, respectively. Highest concentration of $Ca^{2+}$ was obtained in sample No. 6 (3360 ng/g) followed by No. 7 (908 ng/g), both of which are characterized by the presence of dust layer (Table 1). $Ca^{2+}$ is a major ionic species detected in Asian dust samples (Mori et al., 2002) and Chinese loess deposits (Nishikawa et al., 2000), which are the source of Asian dusts. Abundant $Ca^{2+}$ and $NH_4^{+}$ ions were detected in PM2.5 aerosol samples collected during spring, Asian dust season (Tsai and Chen, 2006). Hence, our snow sample Nos. 6 and 7 may be strongly influenced by atmospheric input of Asian dusts. In contrast, the highest concentrations of $NO_3^{-}$ (3590 ng/g) and $SO_4^{2-}$ (5480 ng/g) were obtained in sample Nos. 9 or 6, in both of which the presence of dust layer was recognized by eye observation (Table 1). Sample No. 9 is characterized by the highest concentration of $NH_4^+$ (1150 ng/g) (Table 2).

### *3.2. Dissolved Organic Carbon (DOC)*

DOC concentrations ranged from 268 ng/g to 1550 ng/g (av. 626 ng/g) (Table 3). Higher concentrations were found in snowpack samples such as Nos. 6 and 7, in which dust layer was recorded (Table 1). On the other hand, lower DOC values were found in relatively clean snow samples without dust layer (e.g., No. 4) and the sample with ice plate (No. 5). The DOC concentrations in the high mountain snow samples were found to be 25-150 times lower than those of California fog samples (Collett et al., 2008) and 33-193 times lower than those of cloud water samples (Decesari et al., 2005). They are also ca. 30 times lower than those of snow/sleet samples (20,000-23,000 ng/g) and several times lower than rainwater samples (1000-15,000 ng/g) from Tokyo (Sempéré and Kawamura, 1994). These comparisons show that the snow samples from the Mt. Tateyama region are not seriously contaminated as urban snow and rain samples although they are influenced from Asian Continent.

### *3.3. Organic acids*

In the surface snow and snow pit samples, homologous series of low molecular weight $C_1$-$C_{10}$ monocarboxylic acids were detected with a predominance of formic or acetic acid, followed by propionic ($C_3$) and then butyric ($C_4$) acids (Table 3). Although their concentrations decrease with an increase in the carbon chain lengths, $C_9$ acid is the most abundant followed by $C_6$ in the range of $C_5$-$C_{10}$. In addition to normal structures, branched chain ($iC_4$-$iC_5$), aromatic (benzoic) and hydroxy (lactic and glycolic) acids were also detected in the snow samples. Although propinoic ($C_3$) acid is generally the third most abundant normal monocarboxylic acid species in snow samples, lactic and benzoic acids became more abundant than $C_3$ in sample Nos. 3 and 6, respectively. Total concentrations of monocarboxylic acids ranged from 16 to 130 ng/g with an average of 74 ng/g. Interestingly, the highest concentration of formic acid was found in the sample No. 6, in which concentration of $Ca^{2+}$ was highest (Table 2). The concentrations of $C_1$ to $C_3$ monocarboxylic acids (11-123 ng/g, av. 65 ng/g) in the snowpack samples are comparable to or slightly higher than those (4.3-31.2 ng/g) reported in mountain snow samples from southern California

(Kawamura et al., 1996), but much higher than those (6-36 ng/g) reported in Greenland ice (Osada and Langway, 1993) and those (2-11 ng/g for $C_1$, 11-60 ng/g for $C_2$, and 0.7-2.4 ng/g for $C_3$) from Antarctic drift snow samples (Ohta et al., 1990). The mean concentrations in our samples ($C_1$: 27.7 µg/g, $C_2$: 34.8 µg/g) are significantly higher than those ($C_1$: 0.22-0.55 ng/g, $C_2$: 0.32-0.86 ng/g) reported in the ice cores from Antarctica (de Angelis et al., 2012).

It is of interest to note that very high concentrations of formic (1340 ng/g) and acetic (2400 ng/g) acids were reported in the snow sample from Murodo-Daira, Mt. Tateyama reion, when $Ca^{2+}$ content increased significantly (2200 ng/g) (Osada et al., 2000), although other monocarboxylic acids were not measured. In high-elevation Alpine glacier snow, high concentrations of $C_1$ and $C_2$ acids were reported when Saharan dusts were transported (Maupetit and Delmas, 1994). These studies, together with the results of our study, suggest that volatile organic acids in gaseous phase are adsorbed on the dust particles that are enriched with alkaline metals during long-range atmospheric transport and are scavenged with snowflakes to be deposited over the snowfields.

Highest concentration of total monocarboxylic acids (~130 ng/g) was found in sample No. 2 that is characterized by granular snow with slightly dusty color (Table 1), followed by sample No.1 (~98 ng/g) that is a fresh snow collected on the snowfield. On the other hand, the lowest concentration was found in sample No. 5 (~16 ng/g) followed by sample No.9 (~43 ng/g). Both samples are characterized by the presence of ice lens in the pit sequence although No. 9 sample is also characterized by the presence of dust (Table 1). Interestingly, sample No. 5 also showed very low concentrations of inorganic species (Table 2) as well as DOC (Table 3). This may suggest that, during the melting process of surface snow at the Murodo-Daira site when it was exposed to solar radiation and warmer temperature, water-soluble species may have selectively dissolved in the melt snow and moved down with melt water. Alternatively, loss of organic acids from the ice plate in sample No. 9 may be caused by microbial degradation of organic acids during melting process. Although organic acids could be decomposed in the melt snow sample like No. 9, most inorganic species are refractory to bacterial activity.

Benzoic acid is abundantly present in automobile exhausts and used engine oils

(Kawamura et al., 1985; Kawamura et al., 2000). This aromatic acid is also produced by photochemical oxidation of toluene in the atmosphere (Suh et al., 2003; Ho et al., 2010). The concentration of benzoic acid ranged from 0.18-4.1 ng/g with an average of 1.4 ng/g (Table 3). These values are slightly higher than those (0.7-0.9 ng/g) reported in mountain snow samples from southern California (Kawamura et al., 1996). The highest concentration of benzoic acid was observed in sample No.6 (4.13 ng/g), followed by sample No.7 (3.18 ng/g). Interestingly, both samples are characterized by the presence of dust layer (Table 1) and high concentrations of $Ca^{2+}$ (Table 2). The concentration of benzoic acid is relatively high in No.8 and No.9. Interestingly, both samples also show high concentrations of $Ca^{2+}$ (Table 2). These results suggest that Asian dusts, which are transported with organic pollutants over the Japanese Islands, significantly influenced the high mountain snow samples from the Murodo-Daira snowfield.

Concentrations of lactic and glycolic acids ranged from 0.02 to 4.16 ng/g and 0.004 to 1.54 ng/g, respectively. Lactic acid is relatively abundant in sample Nos. 3, 7, 8 and 10 whereas glycolic acid is abundant in sample Nos. 2 and 3. These hydroxyacids were for the first time detected in snow samples although they have been reported in rain and fog water samples (Avery et al., 2001; Pena et al., 2002; Raja et al., 2008) as well as in aerosols (Souza et al., 1999). The hydroxyacids are generally less abundant than $C_1$-$C_4$ acids in the snow and snow pit samples, however, lactic acid was found as the third most abundant monocarboxylic acid species following $C_1$ and $C_2$ acids in snow sample No. 3 and the forth in sample No. 7 (Table 3).

Contributions of total monocarboxylic acids to DOC in snow samples range from 1.0 to 5.9% with an average of 3.0% (Table 3). Highest value was obtained in snow sample No. 2 that is characterized by the presence of dust layer whereas lowest value was found in snow pit sample No. 5 in which ice plate was found. This result again suggests that low molecular weight organic acids may have been selectively removed either by vertical transport or microbial decomposition when snow melted.

### *3.4. Post-depositional changes of organic acids*

Because some ice layers were recognized in the snow pit sequence as stated above

(Table 1), it is very likely that the distributions of organic acids are modified during the snow melting processes including percolation of the melt water and re-freezing. During the re-freezing of melt water, organic as well as inorganic species may be excluded from the ice formed, lowering their concentrations in ice. In fact, their concentrations were much lower in the snow samples with ice layer, demonstrating that the low molecular weight (water-soluble) organic acids were moved down together with inorganic species, whose concentrations are also low (Table 2). Although we do not have an ambient temperature record at the snowfield site during the period from the winter to spring season, it is very likely that the temperature became above the freezing point during relatively warmer daytime period. Further, bacterial degradation and modification of organic compounds may be initiated in the melt snow. Thus, the concentrations of monocarboxylic acids may be underestimated in the snow samples with melt layers. However, the concentrations of monocarboxylic acids in a clean packed snow sample should better reflect the real distributions at the time of snowfall.

On the other hand, photochemical processes on the snow/air interface may cause a modification of the molecular distributions of low molecular weight carboxylic acids. However, photochemical behaviors of low molecular weight monocarboxylic acids in the air/snow interface are not well understood. This should be studied in future studies. Because formic and acetic acids are volatile, they can be emitted from the snow surface to the air during daytime under strong solar radiation. However, their evaporative losses should be minimal in the snow containing dust layers because alkaline metals form a complex with organic acids and stabilize them in snow. Reactive uptake of volatile organic acids on alkaline aerosols deposited on the snow surface may act as a sink of formic and acetic acids (de Angelis et al., 2012).

Although our snow pit samples retain the above-mentioned problems, the snow sequence data are still useful to understand the source and transport pathways of low molecular weight monocarboxylic acids in the high mountain site in central Japan.

### *3.5. Correlations among organic and inorganic species*

Major organic acids such as formic and acetic acids did not show any significant correlations with inorganic species. Because formic acid weakly correlated with $Ca^{2+}$ (r=0.43, n=10) and $Mg^+$ (r=0.37), this study suggests that gaseous formic acid may have reacted with these alkaline metals in aerosols. These metals are abundant in Asian dusts and are long-range transported in the atmosphere over Japanese Islands (Mori et al., 2003). The organic acid salts should have been scavenged by wet precipitation with snow. Because acetic acid did not show correlations with alkaline metal ions (e.g., $Ca^{2+}$, r=-0.2) or pollution tracers (e.g., $SO_4^{2-}$, r=-0.30), it is unlikely that $C_2$ acid is associated with primary sources such as dusts or polluted sources. Rather acetic acid is likely produced in the atmosphere by photochemical oxidation of various organic precursors (Kawamura et al., 2000; Paulot et al., 2011). Benzoic acid is the only organic species that shows a positive correlation with several inorganic species such as nitrate (r=0.70), sulfate (0.67), $Na^+$ (0.78), $Ca^{2+}$ (0.86) and $Mg^+$ (0.75). These positive correlations suggest that benzoic acid in the snow samples is most likely associated with polluted aerosols that are transported from Asian continent together with Asian dusts. This interpretation seems to be reasonable because benzoic acid is abundantly detected in automobile exhausts (Kawamura et al., 1985; Kawamura et al., 2000) and reported abundantly in the urban atmosphere (Kawamura et al., 2000; Ho et al., 2010) and urban rainwater samples (Kawamura et al., 1996).

Among the organic acid species detected, we found strong positive correlations. For example, propionic acid ($C_3$) showed positive correlations with $C_4$ (r=0.85), $C_6$ (0.72), $iC_4$ (085) and $iC_6$ (0.74) acids (Table 4). Butylic acid ($C_4$) also positively correlates with $C_6$ (r=0.87) and $iC_4$ (0.98) acids. Hexanoic acid ($C_6$) showed a strong correlation with $iC_4$ (r=0.93) and lactic (0.80) acids. These organic acids may be derived from similar sources or produced by similar photochemical processes. Interestingly, lactic and glycolic acids showed a strong correlation (r=0.81) in the snow samples. Because these hydroxyacids can be produced by microorganisms such as lactobacillus, yeasts, and acetic acid bacteria (e.g., Kataoka et al., 2001), the hydroxyacids detected in the snow samples may be derived from soil and/or ocean, where microorganisms are abundantly present.

In contrast, strong positive correlations (r=0.72 to 0.96) were obtained for most combinations of major ions. In particular, $NO_3^-$ v.s. $SO_4^{2-}$ show a strong correlation (r=0.964), followed by $Cl^-$ v.s. $NO_3^-$ (0.96), $Na^+$ v.s. $SO_4^{2-}$ (0.96), $Cl^-$ v.s. $NH_4^+$ (0.93), $NO_3^-$ v.s. $NH_4^+$

(0.93) and $NH_4^+$ v.s. $SO_4^{2-}$ (0.83). The strong correlation between $NO_3^-$ and $NH_4^+$ suggests the formation of $NH_4NO_3$ in aerosols. The slope is close the unity on molar basis, suggesting that this formation likely occurs in the atmosphere. Similarly, correlation between $NH_4^+$ and $SO_4^{2-}$ suggests the formation of $(NH_4)_2SO_4$ or $(NH_4)HSO_4$ in the atmosphere during the transport. Weaker correlations were found for $Ca^{2+}$ v.s. $Cl^-$ (r=0.54), $Ca^{2+}$ v.s. $NO_3^-$ (0.54), $Ca^{2+}$ v.s. $NH_4^+$ (0.37), and $Mg^{2+}$ v.s. $NH_4^+$ (0.59). The major ions that showed strong correlations each other are abundant in either Asian dusts or polluted aerosols (e.g., Mori et al., 2002), suggesting that the snow samples from Murodo-Daira snow field are influenced by long-range atmospheric transport of Asian dusts as well as polluted aerosols. The good correlations between cations and anions suggest possible gaseous and/or heterogeneous reactions between various chemical species in the atmosphere, e.g., $CaCO_3$ and $HNO_3$, $H_2SO_4$ and $NH_3$, HCl and $NH_3$.

### *3.6. Possible sources of low molecular weight monocarboxylic acids including lactic and glycolic acids*

Branched-chain volatile fatty acids are known to be produced by anaerobic bacteria (e.g., Allison, 1978). Thus, *iso* $C_4$-$C_6$ acids may be involved with bacterial activity in either ocean surfaces or atmospheric particles. Interestingly, we found a good correlation (r=0.85, n=10) between *iso* monocarboxoylic acids ($iC_4$-$iC_6$) and methanesulfonic acid (MSA). Because MSA is a photochemically produced by the oxidation of dimethyl sulfide (DMS) that is mainly emitted from marine biological activity (Hatakeyama et al., 1985), these organic acids may be of marine biological origin. As *iso* $C_4$ acid showed strong correlations with $C_3$, $C_4$ and $C_6$ acids (Table 4), these monocarboxylic acids may be associated with bacterial activity. Although there is no significant correlation between aliphatic monocarboxylic acids and DOC, we found fairly strong relation between aromatic acid and DOC (r=0.91, n=10). Because benzoic acid is of combustion origin (Kawamura et al., 1985), significant fraction of DOC may be derived from anthropogenic sources such as fossil fuel combustion via long-range atmospheric transport from Asian Continent.

Because $C_8$ and $C_9$ monoacids can be produced by photochemical oxidation of unsaturated fatty acids such as oleic acid in the atmosphere (Kawamura and Gagosian, 1987), these compounds may be involved with atmospheric oxidation of particulate unsaturated fatty acids that are emitted from either terrestrial plants or marine phytoplankton. However, correlation between $C_8$-$C_9$ acids and MSA is rather weak (r=0.33-0.51), suggesting that $C_8$ and $C_9$ acids are associated with unsaturated fatty acids of terrestrial plant origin. Chameides and Davis (1983) proposed aqueous-phase formation of formic acid in clouds. In contrast, Stavrakou et al. (2012) recently proposed, based on satellite observation, a large source of formic acid from boreal and tropical forests via photochemical oxidation of biogenic non-methane hydrocarbons (terpenoids). Formic acid did not show any significant relation with organic or inorganic species.

Although lactic and glycolic acids showed a strong correlation as stated above, we could not find any significant relation between these hydroxyacids and inorganic ions. No correlation of hydroxyacids against dust components suggests that lactic and glycolic acids are not involved with soil dusts. Rather, they are associated with microbial activities in the ocean and/or aerosols, and/or photochemical production in the atmosphere. Microbial production is very likely because some microorganisms produce lactic and glycolic acids (Kataoka et al., 2001). Glycolic acid is also abundantly present in sugar cane and some other plants (Lehninger, 1975). Raja et al. (2008) reported high abundance of lactic acid in fogwater samples from Baton Rouge and considered as a major contributor to organic carbon. They suggested that lactic acid is emitted from plant tissues in the air surrounded by agricultural farmland near the Baton Rouge sampling site. Avery et al. (2001) reported lactic acid in rain samples with higher concentrations in daytime than nighttime. Peña et al. (2002) found that rainwater concentrations of lactic acid are higher in growing season. Souza et al. (1999) detected glycolic acid in atmospheric aerosols from urban site in Brazil and suggested that glycolic acid is emitted from biogenic sources.

Alternatively, Yang et al. (2008) suggested that hydroxyacids are formed by the photooxidation through the Russell mechanism (Russell, 1957). Warneck (2003) proposed that glycolic acid is an intermediate in the photochemical production of oxalic acid from ethene in marine cloud. Considering these reports, we can postulate that the sources of lactic and glycolic acids in the snowpack samples are of biological and/or photochemical origin. In addition, lactic acid bacteria (lactobacillus) exist in the air and lactobacillus composed of ca. 21% of total bacteria (Cabredo et al., 2009). Moreover, lactobacillus commonly exists in soil layers (e.g., Huysman and Verstraete, 1993). Thus, the hydroxyacids are likely derived from lactobacillus that are emitted from soils and grown in the atmospheric particles during long-range transport, and are deposited over snowfield with fresh snow.

### *3.7. Backward trajectory analysis for snow dust layer*

In order to understand the source regions of the dusts found in snow samples, backward trajectory analyses were carried out. Figure 2 presents the air mass trajectories calculated for January 11, February 11, March 3, and April 15, 2008, when the snow precipitation corresponding to sample Nos. 9, 7, 6 and 2 accumulated at the Murodo-Daira snow field site. Due to a lidar measurement at Imizu, Toyama Prefecture (http://www-lidar.nies.go.jp/Toyama/), dust episode was suggested for the snow sample No.6, which is characterized by high concentration of $Ca^{2+}$ (Table 2). All the air mass trajectories show that the air masses passed over north China and Mongolia and mega cities such as Beijing in north China. The air parcels were delivered over central Japan and the dust particles may have been fallen on the Murodo-Daira snowfield site either by dry deposition or wet scavenging with snow.

During winter to spring seasons, westerly winds dominate over East Asia and thus it is very likely that Asian dusts and pollutants emitted from China are long-range transported to the downwind regions including Japanese Islands where high mountains including Mt. Tateyama are located. During large Asian dust events (April 14-16, 2008), which were also recorded by a lidar measurement at Imizu, Toyama Prefecture (http://www-lidar.nies.go.jp/Toyama/), we found that source regions of air masses are in Eurasia including North China and Mongolia (Figure 2d).

## 4. Summary and Conclusions

A homologous series of low molecular weight ($C_1$-$C_{10}$) monocarboxylic acids, including branched-chain ($iC_4$-$iC_6$), benzoic and hydroxy (glycolic and lactic) acids, were determined in snowpack samples collected at snow pit sequence from Mt. Tateyama region, central Japan. Their molecular distributions were characterized by a predominance of acetic or formic acid, followed by propionic acid. Although concentrations of the organic acids generally decreased with an increase in carbon chain length, nonanoic acid ($C_9$) that is produced by photochemical oxidation of unsaturated fatty acids was a dominant species in the range of $C_5$-$C_{10}$. Major organic acids did not show a positive relation to inorganic ions, however, we found a weak correlation between formic acid and $Ca^{2+}$, suggesting that gaseous formic acid react with Asian dusts during long-range transport in the atmosphere. Benzoic acid showed strong positive correlations with nitrate, sulfate, $Na^+$, $Ca^{2+}$ and $Mg^+$, suggesting that this aromatic acid is involved with anthropogenic sources and Asian dusts. Major inorganic ions showed positive correlations each other; e.g., $NO_3^-$ v.s. $SO_4^{2-}$ (r=0.96), $Cl^-$ v.s. $NO_3^-$ (0.96), $Na^+$ v.s. $SO_4^{2-}$ (0.96), $Cl^-$ v.s. $NH_4^+$ (0.93), and $NO_3^-$ v.s. $NH_4^+$ (0.93), $NH_4^+$ v.s. $SO_4^{2-}$ (0.83). Highest concentrations of $Ca^{2+}$ and $Mg^+$ were obtained in the snowpack sample in which dust layer was observed. These results suggests that inorganic ions are co-varied each other due to the similar sources such as pollutions and dusts. No significant correlations of organic acids with inorganic ions suggest that low molecular weight monocarboxylic acids may be derived from various sources including fossil fuel combustion, photochemical oxidation of volatile organic compounds, plant emissions and bacterial activities.

## Acknowledgements

This study was in part supported by the Japan Society for the Promotion of Science (Grant-in-Aid No. 1920405) and by the Environment Research and Technology Development Fund (B-0903) from the Ministry of the Environment, Japan. We thank N. Sugimoto of the National Institute of Environmental Studies for the supply of the lidar observation results in Toyama. We acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport model and READYwebsite (http://www.arl.noaa.gov/ready.php) used in this publication. We also thank Y. Yamamoto and N. Kanda for the help of trajectory analysis and Y. Miyazaki for the support of ion analyses.

References

Aggarwal, S.G., Kawamura, K., 2008. Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport. J Geophys Res-Atmos 113, doi:10.1029/2007jd009365.

Allison, M.J., 1978. Production of branched-chain volatile fatty-acids by certain anaerobic bacteria. Applied and Environmental Microbiology 35, 872-877.

Avery, G.B., Willey, J.D., Kieber, R.J., 2001. Diurnal variations in major rainwater components at a coastal site in North Carolina. Atmos Environ 35, 3927-3933.

Cabredo, S., Parra, A., Saenz, C., Anzano, J., 2009. Bioaerosols chemometric characterization by laser-induced fluorescence: Air sample analysis. Talanta 77, 1837-1842.

Chameides, W.L., Davis, D.D., 1983. Aqueous-phase source of formic-acid in clouds. Nature 304, 427-429.

Collett, J.L., Herckes, P., Youngster, S., Lee, T., 2008. Processing of atmospheric organic matter by California radiation fogs. Atmospheric Research 87, 232-241.

de Angelis, M., Traversi, R., Udisti, R., 2012. Long-term trends of mono-carboxylic acids in Antarctica: comparison of changes in sources and transport processes at the two EPICA deep drilling sites. Tellus B 64, 17331.

Decesari, S., Facchini, M.C., Fuzzi, S., McFiggans, G.B., Coe, H., Bower, K.N., 2005. The water-soluble organic component of size-segregated aerosol, cloud water and wet depositions from Jeju Island during ACE-Asia. Atmos Environ 39, 211-222.

Dibb, J.E., Arsenault, M., 2002. Shouldn't snowpacks be sources of monocarboxylic acids? Atmos Environ 36, 2513-2522.

Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.

Gabriel, R., Schafer, L., Gerlach, C., Rausch, T., Kesselmeier, J., 1999. Factors controlling the emissions of volatile organic acids from leaves of Quercus ilex L. (Holm oak). Atmos Environ 33, 1347-1355.

Hatakeyama, S., Izumi, K., Akimoto, H., 1985. Yield of SO2 and formation of aerosol in the photo-oxidation of DMS under atmospheric conditions. Atmos Environ 19, 135-141.

Ho, K.F., Lee, S.C., Ho, S.S.H., Kawamura, K., Tachibana, E., Cheng, Y., Zhu, T., 2010. Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006). J Geophys Res-Atmos 115, doi:10.1029/2009jd013304.

Huebert, B.J., Bates, T., Russell, P.B., Shi, G.Y., Kim, Y.J., Kawamura, K., Carmichael, G., Nakajima, T., 2003. An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts. J. Geophys. Res., [Atmos] 108, doi:10.1029/2003JD003550.

Huysman, F., Verstraete, W., 1993. Water-facilitated transport of bacteria in unsaturated soil columns - Influence of cell-surface hydrophobicity and soil properties. Soil Biology & Biochemistry 25, 83-90.

Kataoka, M., Sasaki, M., Hidalgo, A.R.G.D., Nakano, M., Shimizu, S., 2001. Glycolic acid production using ethylene glycol-oxidizing microorganisms. Bioscience Biotechnology and Biochemistry 65, 2265-2270.

Kawamura, K., Kaplan, I.R., 1984. Capillary gas-chromatography determination of volatile organic-acids in rain and fog samples. Analytical Chemistry 56, 1616-1620.

Kawamura, K., Ng, L.L., Kaplan, I.R., 1985. Determination of organic-acids (C1-C10) in the atmosphere, motor exhausts, and engine oils. Environ Sci Technol 19, 1082-1086.

Kawamura, K., Gagosian, R.B., 1987. Implications of $\omega$-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. Nature 325, 330-332.

Kawamura, K., Kaplan, I.R., 1990. Stabilities of Carboxylic-Acids and Phenols in Los-Angeles Rainwaters during Storage. Water Res 24, 1419-1423.

Kawamura, K., Steinberg, S., Kaplan, I.R., 1996. Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern California wet precipitations: Comparison of urban and nonurban samples and compositional changes during scavenging. Atmos. Environ. 30, 1035-1052.

Kawamura, K., Steinberg, S., Kaplan, I.R., 2000. Homologous series of $C_1$-$C_{10}$ monocarboxylic acids and $C_1$-$C_6$ carbonyls in Los Angeles air and motor vehicle exhausts. Atmos. Environ. 34, 4175-4191.

Kawamura, K., Steinberg, S., Ng, L., Kaplan, I.R., 2001. Wet deposition of low molecular weight mono- and di-carboxylic acids, aldehydes and inorganic species in Los Angeles. Atmos Environ 35, 3917-3926.

Kawamura, K., Yasui, O., 2005. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. Atmos. Environ. 39, 1945-1960.

Keene, W.C., Galloway, J.N., 1984. Organic acidity in precipitation of North-America. Atmos Environ 18, 2491-2497.

Kuo, S.C., Tsai, Y.I., Tsai, C.H., Hsieh, L.Y., 2011. Carboxylic acids in PM(2.5) over Pinus morrisonicola forest and related photoreaction mechanisms identified via Raman spectroscopy. Atmos Environ 45, 6741-6750.

Legrand, M., de Angelis, M., 1996. Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone. J Geophys Res-Atmos 101, 4129-4145.

Legrand, M., Preunkert, S., Wagenbach, D., Cachier, H., Puxbaum, H., 2003. A historical record of formate and acetate from a high-elevation Alpine glacier: Implications for their natural versus anthropogenic budgets at the European scale. J Geophys Res-Atmos 108, doi:10.1029/2003jd003594.

Lehninger, A.L., 1975. *Biochemistry, Second Edition*, Worth Publishers, Inc, New York.

Maupetit, F., Delmas, R.J., 1994. Carboxylic-acids in high-elevation Alpine glacier snow. J Geophys Res-Atmos 99, 16491-16500.

Miyazaki, Y., Kawamura, K., Sawano, M., 2010. Size distributions and chemical characterization of water-soluble organic aerosols over the western North Pacific in summer. J Geophys Res-Atmos 115, doi:10.1029/2010jd014439.

Mori, I., Nishikawa, M., Quan, H., Morita, M., 2002. Estimation of the concentration and chemical composition of kosa aerosols at their origin. Atmos Environ 36, 4569-4575.

Mori, I., Nishikawa, M., Tanimura, T., Quan, H., 2003. Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport. Atmos Environ 37, 4253-4263.

Nishikawa, M., Hao, Q., Morita, M., 2000. Preparation and evaluation of certified reference materials from Asian mineral dust. Global Environ. Res. 4, 103-113.

Ohta, K., Nishio, F., Osada, K., 1990. Organic components of Antarctic snow and ice, Part 1. Volatile fatty acids in snow drift. Proc. NIPR Symp. Polar Meterol. Glaciol. 3, 36-42.

Osada, K., Langway, C.C., 1993. Background levels of formate and other ions in ice cores from inland Greenland. Geophys Res Lett 20, 2647-2650.

Osada, K., Kido, M., Iida, H., Yabuki, H., Kohshima, S., Kawada, K., Nakawo, M., 2000. Chemical stratigraphy of water soluble constituents in spring snow cover at Murododaira, Tateyama Mts., Japan. Seppyo 62, 3-14.

Paulot, F., Wunch, D., Crounse, J.D., Toon, G.C., Millet, D.B., DeCarlo, P.F., Vigouroux, C., Deutscher, N.M., Abad, G.G., Notholt, J., Warneke, T., Hannigan, J.W., Warneke, C., de Gouw, J.A., Dunlea, E.J., De Maziere, M., Griffith, D.W.T., Bernath, P., Jimenez, J.L., Wennberg, P.O., 2011. Importance of secondary sources in the atmospheric budgets of formic and acetic acids. Atmos Chem Phys 11, 1989-2013.

Pena, R.M., Garcia, S., Herrero, C., Losada, M., Vazquez, A., Lucas, T., 2002. Organic acids and aldehydes in rainwater in a northwest region of Spain. Atmos Environ 36, 5277-5288.

Preunkert, S., Legrand, M., Jourdain, B., Dombrowski-Etchevers, I., 2007. Acidic gases (HCOOH, CH(3)COOH, HNO(3), HCl, and SO(2)) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe. J Geophys Res-Atmos 112, doi:10.1029/2006jd008225.

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

Rolph, G.D., 2003. Real-time Environmental Applications and Display sYstem (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD

Russell, G.A., 1957. Deuterium-isotope effects in the autoxidation of aralkyl hydrocarbons -

Mechanism of the interaction of peroxy radicals. Journal of the American Chemical Society 79, 3871-3877.

Sempéré, R., Kawamura, K., 1994. Comparative distributions of dicarboxylic-acids and related polar compounds in snow rain and aerosols from urban atmosphere. Atmos Environ 28, 449-459.

Souza, S.R., Vasconcellos, P.C., Carvalho, L.R.F., 1999. Low molecular weight carboxylic acids in an urban atmosphere: Winter measurements in Sao Paulo City, Brazil. Atmos Environ 33, 2563-2574.

Stavrakou, T., Muller, J.F., Peeters, J., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P.F., Hurtmans, D., De Maziere, M., Vigouroux, C., Deutscher, N.M., Griffith, D.W.T., Jones, N., Paton-Walsh, C., 2012. Satellite evidence for a large source of formic acid from boreal and tropical forests. Nature Geoscience 5, 26-30.

Suh, I., Zhang, R.Y., Molina, L.T., Molina, M.J., 2003. Oxidation mechanism of aromatic peroxy and bicyclic radicals from OH-toluene reactions. Journal of the American Chemical Society 125, 12655-12665.

Tsai, Y.I., Chen, C.L., 2006. Characterization of Asian dust storm and non-Asian dust storm PM2.5 aerosol in southern Taiwan. Atmos Environ 40, 4734-4750.

Warneck, P., 2003. In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere. Atmos Environ 37, 2423-2427.

Yang, L.M., Ray, M.B., Yu, L.E., 2008. Photooxidation of dicarboxylic acids- Part II: Kinetics, intermediates and field observations. Atmos Environ 42, 868-880.

## Figure Captions

Figure 1. Locality map of snowpack sampling site (Murodo-Daira) near Mt. Tateyama, central Japan.

Figure 2. 6-days backward air mass trajectories for (a) 11 January (corresponding to snow sample No. 9), (b) 11 February (No. 7), (c) 3 March 2008 (No.6) and (d) 15 April (No. 2) from Mt. Tateyama region, Japan (sampling site of snow).

Figure 1

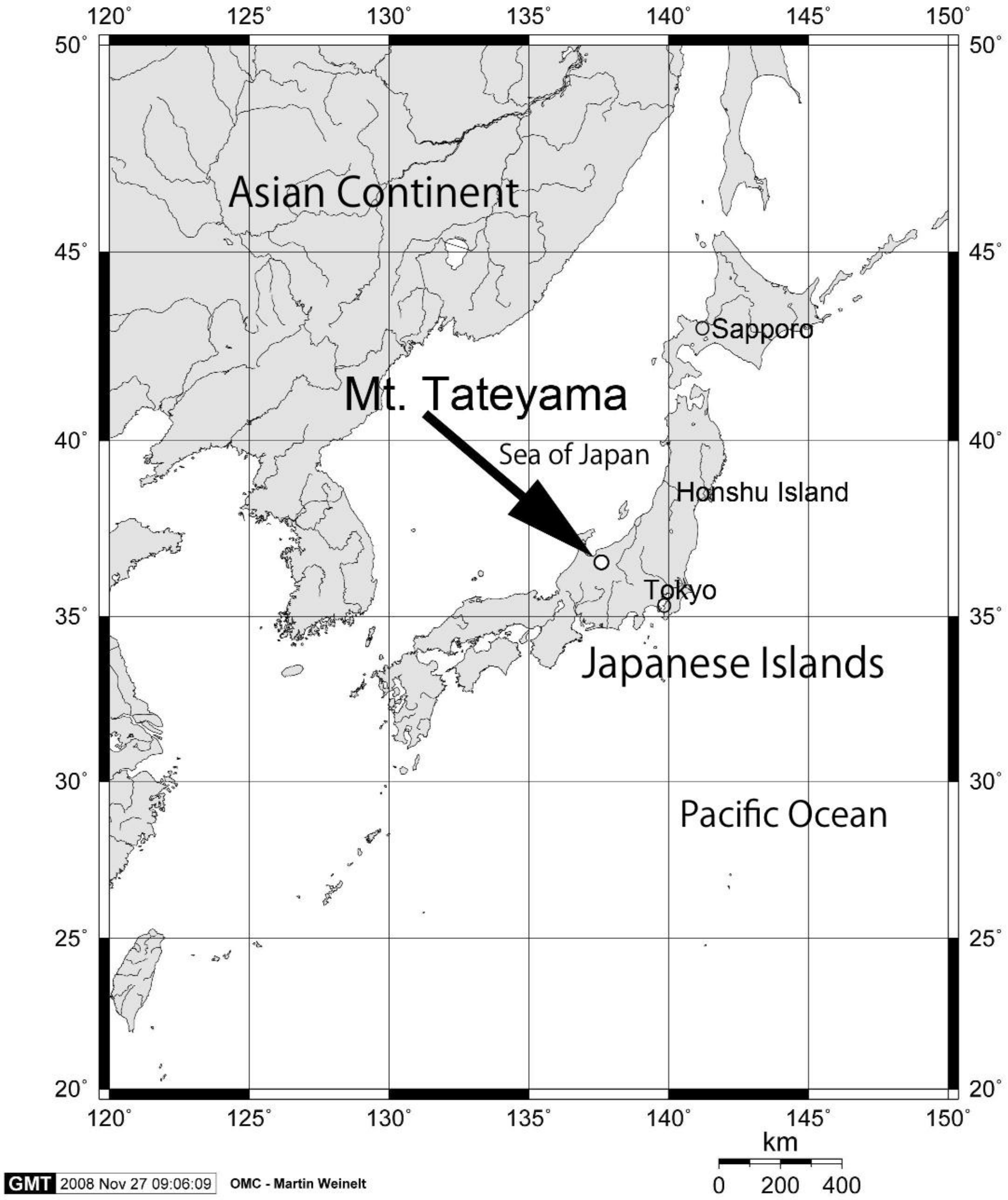
Asian Continent
Sapporo
Mt. Tateyama
Sea of Japan
Honshu Island
Tokyo
Japanese Islands
Pacific Ocean
120° 125° 130° 135° 140° 145° 150°
50° 45° 40° 35° 30° 25° 20°
km
0 200 400
GMT 2008 Nov 27 09:06:09
OMC - Martin Weinelt

Figure 2

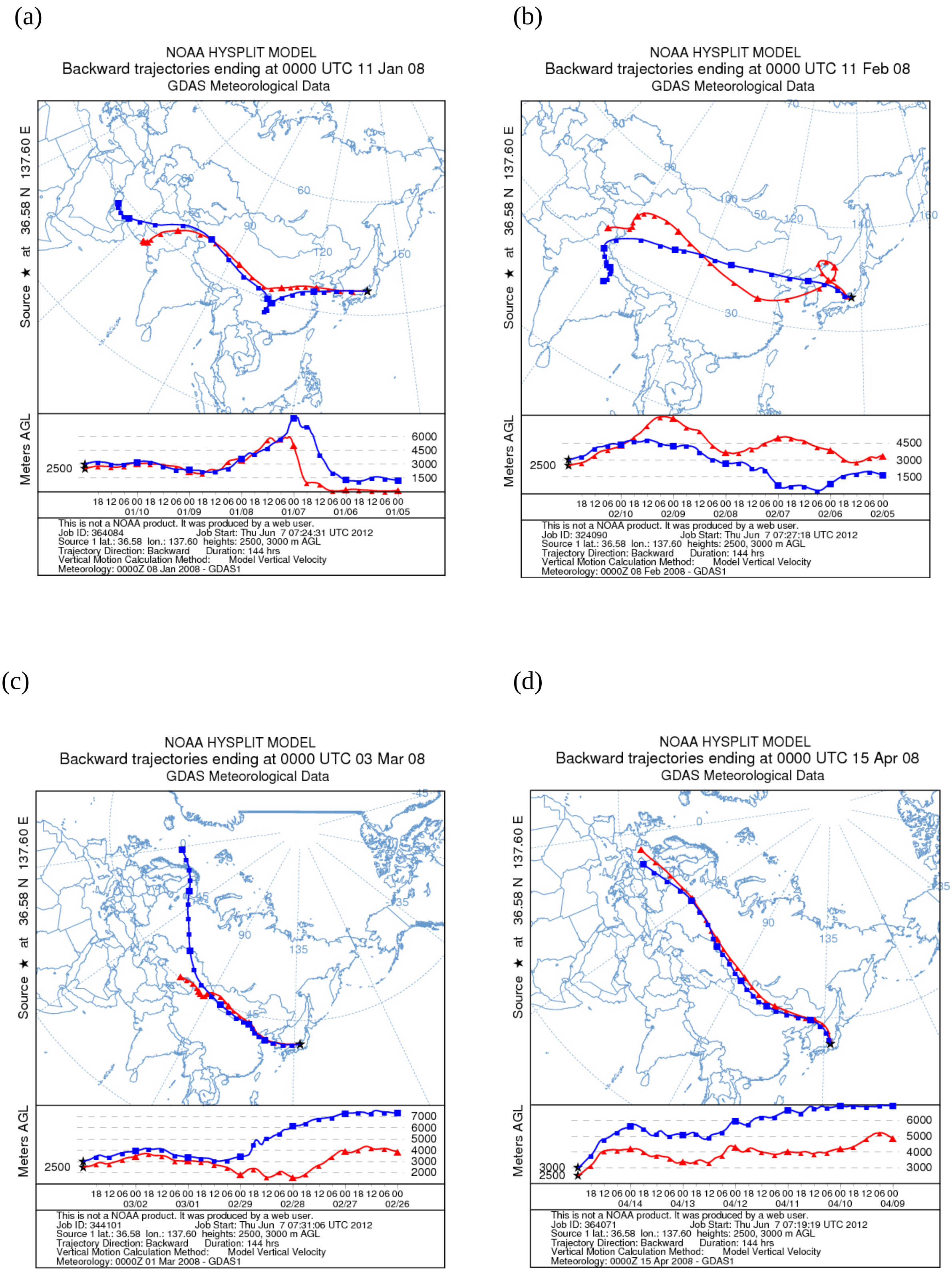
(a)
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 11 Jan 08
GDAS Meteorological Data
Source ★ at 36.58 N 137.60 E
Meters AGL
2500
6000
4500
3000
1500
18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00
01/10 01/09 01/08 01/07 01/06 01/05
This is not a NOAA product. It was produced by a web user.
Job ID: 364084 Job Start: Thu Jun 7 07:24:31 UTC 2012
Source 1 lat.: 36.58 lon.: 137.60 heights: 2500, 3000 m AGL
Trajectory Direction: Backward Duration: 144 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 08 Jan 2008 - GDAS1
(b)
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 11 Feb 08
GDAS Meteorological Data
Source ★ at 36.58 N 137.60 E
Meters AGL
2500
4500
3000
1500
18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00
02/10 02/09 02/08 02/07 02/06 02/05
This is not a NOAA product. It was produced by a web user.
Job ID: 324090 Job Start: Thu Jun 7 07:27:18 UTC 2012
Source 1 lat.: 36.58 lon.: 137.60 heights: 2500, 3000 m AGL
Trajectory Direction: Backward Duration: 144 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 08 Feb 2008 - GDAS1
(c)
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 03 Mar 08
GDAS Meteorological Data
Source ★ at 36.58 N 137.60 E
Meters AGL
2500
7000
6000
5000
4000
3000
2000
18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00
03/02 03/01 02/29 02/28 02/27 02/26
This is not a NOAA product. It was produced by a web user.
Job ID: 344101 Job Start: Thu Jun 7 07:31:06 UTC 2012
Source 1 lat.: 36.58 lon.: 137.60 heights: 2500, 3000 m AGL
Trajectory Direction: Backward Duration: 144 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 01 Mar 2008 - GDAS1
(d)
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 15 Apr 08
GDAS Meteorological Data
Source ★ at 36.58 N 137.60 E
Meters AGL
3000
2500
6000
5000
4000
3000
18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00
04/14 04/13 04/12 04/11 04/10 04/09
This is not a NOAA product. It was produced by a web user.
Job ID: 364071 Job Start: Thu Jun 7 07:19:19 UTC 2012
Source 1 lat.: 36.58 lon.: 137.60 heights: 2500, 3000 m AGL
Trajectory Direction: Backward Duration: 144 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 15 Apr 2008 - GDAS1

Table 1. Descriptions of surface snow samples (Nos. 1-3) collected around a pit site and snowpack samples (Nos. 4-10) collected from a pit (6.6 m in depth) at Murodo-Daira, Mt. Tateyama, Japan.

| Sample ID | Depth (m) from the surface | Description |
|---|---|---|
| No. 1 | Surface | Fresh snow (collected at 10:15) |
| No. 2 | Surface | Dusty and granular snow (fresh snow seemed not accumulated due to a strong wind around the site). Dusts may be deposited over the snowfield during Asian dust events that were observed on April 14-16, 2008 by a lidar over Toyama. |
| No. 3 | Surface | Granular snow (obtained at 15:15). Surface snow melted due to the warmer temperature and stronger radiation in the afternoon and granular snow was collected. |
| No. 4 | 0.1-0.2 | Clean snow layer |
| No. 5 | 0.5 | Snow with ice plate (ca. 2 cm thickness). Only ice layer was collected. |
| No. 6 | 0.90-1.1 | Dusty snow layer. Asian dust event on March 3, 2008 may the source of dirty layer due to a lidar observation in Toyama. |
| No. 7 | 1.2-1.3 | Weak dust layer possibly deposited on February 11, 2008. |
| No. 8 | 3.5-3.6 | Clean snow layer |
| No. 9 | 3.7-3.8 | Snow with ice plate and dusts. Dusts may have deposited on January 11, 2008. |
| No. 10 | 6.4-6.5 | Snow accumulated at the end of October, 2007 |

Sampling was conducted from 10:15 to 15:15 on April 19, 2008. Surface snow samples were collected near the pit site, but the locations were not exactly same.

Table 2. Concentrations (ng/g-snow) of major ions in surface snow and pit snowpack samples collected at Murodo-Daira in Mt. Tateyama, Japan.

| Major inorganic ions | Snow sample ID | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | No.1 | No.2 | No.3 | No.4 | No.5 | No.6 | No.7 | No.8 | No.9 | No.10 |
| *Anions* | | | | | | | | | | |
| $F^-$ | BDL | 4 | 7 | 6 | 6 | 49 | 24 | 7 | 20 | 3 |
| $MSA^-$ | 11 | 1 | 3 | 23 | 2 | 2 | 94 | 107 | 52 | 0 |
| $Cl^-$ | 199 | 42 | 212 | 474 | 167 | 1,490 | 874 | 26 | 2,240 | 458 |
| $NO_2^-$ | 44 | 59 | 58 | 19 | 13 | 18 | 18 | 96 | 33 | 63 |
| $Br^-$ | BDL | BDL | BDL | BDL | BDL | 4 | 3 | BDL | 7 | 1 |
| $NO_3^-$ | 126 | 159 | 158 | 243 | 162 | 3,030 | 2,190 | 135 | 3,590 | 489 |
| $SO_4^{2-}$ | 271 | 364 | 408 | 358 | 156 | 5,480 | 2,010 | 467 | 5,480 | 1,270 |
| Total | 652 | 629 | 845 | 1,123 | 506 | 10,100 | 5,210 | 837 | 11,400 | 2,280 |
| $nssSO_4^{2-}$ | 270 | 361 | 402 | 324 | 144 | 5,010 | 1,870 | 463 | 5,190 | 1,190 |
| *Cations* | | | | | | | | | | |
| $Na^+$ | 7 | 11 | 24 | 133 | 46 | 1,850 | 538 | 16 | 1,120 | 316 |
| $NH_4^+$ | 19 | 156 | 168 | 255 | 99 | 526 | 726 | 62 | 1,150 | 159 |
| $K^+$ | BDL | BDL | BDL | BDL | BDL | 174 | 109 | BDL | 160 | 90 |
| $Ca^{2+}$ | BDL | 72 | 99 | 43 | 40 | 3,360 | 908 | BDL | 401 | 154 |
| $Mg^{2+}$ | BDL | 34 | 81 | 24 | BDL | 427 | 105 | 2 | 197 | 46 |
| Total | 26 | 273 | 373 | 455 | 185 | 6,337 | 2,386 | 80 | 3,028 | 764 |

BDL: Below Detection Limit. Detection limits are ca. 0.5 ng/g-snow for anions and ca. 1.0 ng/g-snow for cations.

Table 3. Concentrations (ng/g-snow) of monocarboxylic acids and DOC in snow samples collected at Murodo-Daira site in Mt. Tateyama, Japan.

| Compound class | Acid species | Snow sample ID | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | No.1 | No.2 | No.3 | No.4 | No.5 | No.6 | No.7 | No.8 | No.9 | No.10 |
| Aliphatic acids | Formic, C1 | 15.9 | 48.1 | 37.3 | 31.2 | 2.6 | 48.1 | 25.8 | 36.6 | 12.5 | 19.0 |
| | Acetic, C2 | 76.4 | 73.0 | 25.2 | 23.6 | 7.8 | 26.2 | 27.9 | 33.6 | 20.9 | 33.2 |
| | Propionic, C3 | 1.40 | 2.44 | 2.01 | 1.28 | 0.59 | 2.98 | 5.23 | 5.15 | 2.79 | 4.29 |
| | Isobutyric, iC4 | 0.37 | 0.68 | 0.75 | 0.52 | 0.28 | 0.49 | 1.34 | 1.01 | 0.55 | 0.71 |
| | Butyric, C4 | 0.37 | 1.37 | 1.14 | 0.65 | 0.20 | 0.76 | 2.18 | 1.73 | 0.75 | 1.09 |
| | Isopentanoic, iC5 | 0.60 | 0.34 | 0.35 | 1.22 | 0.11 | 0.16 | 1.47 | 2.32 | 0.09 | 0.68 |
| | Pentanoic,C5 | 0.07 | 0.21 | 0.56 | 0.14 | 0.05 | 0.82 | 0.44 | 0.32 | 0.30 | 0.27 |
| | Isohexanoic, iC6 | 0.01 | n.d. | n.d. | n.d. | n.d. | 0.08 | 0.15 | 0.06 | 0.05 | 0.02 |
| | Hexanoic, C6 | 0.28 | 0.68 | 1.44 | 0.43 | 0.54 | 0.65 | 2.15 | 1.32 | 0.65 | 0.91 |
| | Heptanoic, C7 | 0.17 | 0.41 | 0.61 | 0.14 | 0.62 | 0.71 | 0.66 | 0.71 | 0.35 | 0.30 |
| | Octanoic, C8 | 0.14 | n.d. | n.d. | 0.22 | 0.76 | 0.96 | 0.67 | 0.94 | 0.54 | 0.24 |
| | Nonanoic, C9 | 0.31 | 0.92 | 1.30 | 0.39 | 1.34 | 1.30 | 0.70 | 2.61 | 1.02 | 1.66 |
| | Decanoic, C10 | 0.26 | 0.47 | 0.30 | 0.23 | 0.26 | 0.53 | 0.17 | 0.54 | 0.36 | 0.14 |
| sub total | | 96.3 | 128.6 | 71.0 | 60.0 | 15.2 | 83.7 | 68.9 | 86.9 | 40.9 | 62.5 |
| Aromatic acid | Benzoic | 1.16 | 0.18 | 0.18 | 0.65 | 0.56 | 4.13 | 3.18 | 1.65 | 1.39 | 0.75 |
| Hydroxyacids | Lactic | 0.11 | 0.48 | 4.16 | 0.14 | 0.02 | 0.51 | 2.47 | 1.65 | 0.66 | 1.63 |
| | Glycolic | 0.04 | 0.46 | 1.54 | 0.07 | n.d. | 0.09 | 0.21 | 0.13 | 0.13 | 0.18 |
| sub total | | 0.15 | 0.94 | 5.7 | 0.21 | 0.02 | 0.60 | 2.68 | 1.78 | 0.79 | 1.81 |
| Total | | 97.6 | 129.7 | 76.8 | 60.9 | 15.7 | 88.5 | 74.7 | 90.3 | 43.0 | 65.1 |
| | | | | | | | | | | | |
| DOC | | 828 | 477 | 297 | 295 | 268 | 1545 | 878 | 729 | 506 | 434 |
| Total organic acid-C/DOC (%) | | 2.42 | 5.93 | 5.6 | 4.62 | 1.04 | 1.26 | 1.7 | 2.56 | 1.7 | 3.05 |

n.d.: not detected. Detection limit: ca. 0.005 ng/g-snow.

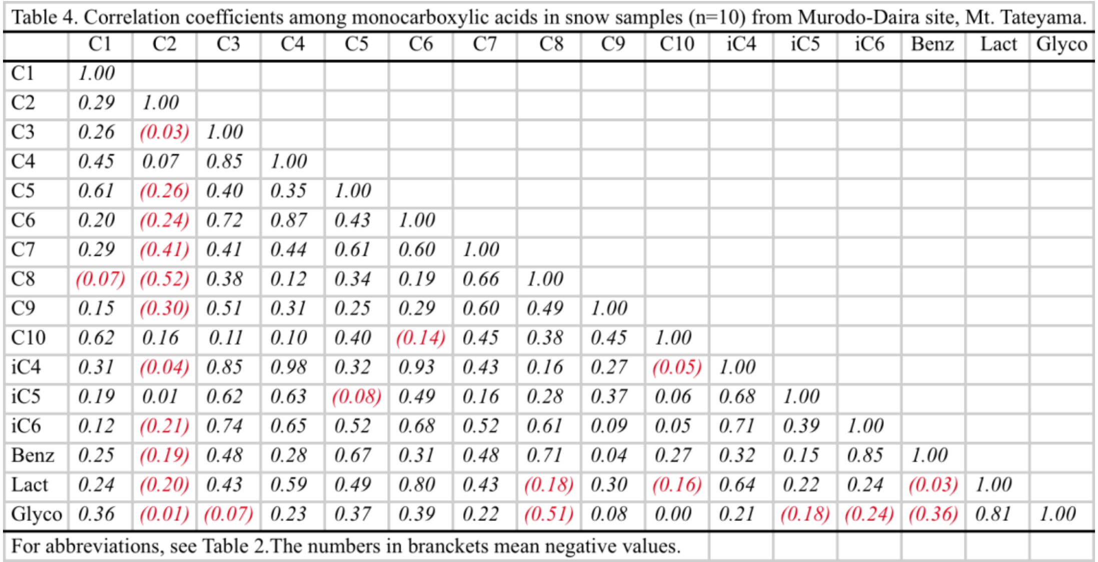

Table 4. Correlation coefficients among monocarboxylic acids in snow samples (n=10) from Murodo-Daira site, Mt. Tateyama.

| | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 | C10 | iC4 | iC5 | iC6 | Benz | Lact | Glyco |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C1 | 1.00 | | | | | | | | | | | | | | | |
| C2 | 0.29 | 1.00 | | | | | | | | | | | | | | |
| C3 | 0.26 | (0.03) | 1.00 | | | | | | | | | | | | | |
| C4 | 0.45 | 0.07 | 0.85 | 1.00 | | | | | | | | | | | | |
| C5 | 0.61 | (0.26) | 0.40 | 0.35 | 1.00 | | | | | | | | | | | |
| C6 | 0.20 | (0.24) | 0.72 | 0.87 | 0.43 | 1.00 | | | | | | | | | | |
| C7 | 0.29 | (0.41) | 0.41 | 0.44 | 0.61 | 0.60 | 1.00 | | | | | | | | | |
| C8 | (0.07) | (0.52) | 0.38 | 0.12 | 0.34 | 0.19 | 0.66 | 1.00 | | | | | | | | |
| C9 | 0.15 | (0.30) | 0.51 | 0.31 | 0.25 | 0.29 | 0.60 | 0.49 | 1.00 | | | | | | | |
| C10 | 0.62 | 0.16 | 0.11 | 0.10 | 0.40 | (0.14) | 0.45 | 0.38 | 0.45 | 1.00 | | | | | | |
| iC4 | 0.31 | (0.04) | 0.85 | 0.98 | 0.32 | 0.93 | 0.43 | 0.16 | 0.27 | (0.05) | 1.00 | | | | | |
| iC5 | 0.19 | 0.01 | 0.62 | 0.63 | (0.08) | 0.49 | 0.16 | 0.28 | 0.37 | 0.06 | 0.68 | 1.00 | | | | |
| iC6 | 0.12 | (0.21) | 0.74 | 0.65 | 0.52 | 0.68 | 0.52 | 0.61 | 0.09 | 0.05 | 0.71 | 0.39 | 1.00 | | | |
| Benz | 0.25 | (0.19) | 0.48 | 0.28 | 0.67 | 0.31 | 0.48 | 0.71 | 0.04 | 0.27 | 0.32 | 0.15 | 0.85 | 1.00 | | |
| Lact | 0.24 | (0.20) | 0.43 | 0.59 | 0.49 | 0.80 | 0.43 | (0.18) | 0.30 | (0.16) | 0.64 | 0.22 | 0.24 | (0.03) | 1.00 | |
| Glyco | 0.36 | (0.01) | (0.07) | 0.23 | 0.37 | 0.39 | 0.22 | (0.51) | 0.08 | 0.00 | 0.21 | (0.18) | (0.24) | (0.36) | 0.81 | 1.00 |

For abbreviations, see Table 2.The numbers in branckets mean negative values.