Atmospheric Environment 62 (2012) 272–280

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

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[a,*], Kohei Matsumoto[a], Eri Tachibana[a], Kazuma Aoki[b]

[a] Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[b] Department of Earth Science, Faculty of Science, Toyama University, Gofuku, Toyama 930-8555, Japan

HIGHLIGHTS

- ► We determined C_1–C_{10} monocarboxylic acids in High Mountain snow in Japan.
- ► C_1 or C_2 was dominant acid followed by C_3 and then C_4.
- ► Benzoic acid was abundant in snow with dust layer.
- ► Formic acid may react with Asian dust during atmospheric transport.

ARTICLE INFO

Article history:
Received 4 April 2012
Received in revised form
1 August 2012
Accepted 6 August 2012

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^{-1}-snow, av. 34.8 ng g^{-1}) or formic acid (2.6–48.1 ng g^{-1}, 27.7 ng g^{-1}), followed by propionic acid (0.6–5.2 ng g^{-1}, 2.8 ng g^{-1}). 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}, 1.4 ng g^{-1}) 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}, 1.5 ng g^{-1}) were more abundant in the granular and dusty snow. Total monocarboxylic acids (16–130 ng g^{-1}, 74 ng g^{-1}) were found to account for 1–6% of DOC (270–1500 ng g^{-1}, 630 ng g^{-1}) 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, 2001). Formic and acetic acids have also

---

[*] Corresponding author.
E-mail address: kawamura@lowtem.hokudai.ac.jp (K. Kawamura).

1352-2310/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2012.08.018

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, 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 $\sim$1200 and $\sim$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. Fig. 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 snowfield 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 α, p-dibromoacetophenone (0.1 M, 50 μl) were added to the flask as well as dicyclohexyl-18-crown-6 (0.01 M, 50 μl) 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-bromophenacyl 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