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Characteristics of formate and acetate concentrations in precipitation at Jeju Island, Korea

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ABSTRACT

$HCOO^-$ and CH_3COO^- concentrations were analyzed in precipitation samples collected at two sites on Jeju Island during 1997–2003: one at Mt. Halla and the other within Jeju City. The volume-weighted mean concentrations of $HCOO^-$ and CH_3COO^- were 1.28 and 0.89 μmol/L at Mt. Halla, and 2.06 and 1.15 μmol/L in Jeju City, respectively. Those ionic components showed low concentrations in summer compared to other seasons. In order to investigate major factors to affect the concentration variations of the organic acids in precipitation, the concentrations of the organic acids between growing and non-growing seasons of plants, the regression analyses and the ratios of HCOO−/CH3COO$^-$ were examined. As a result, it is considered that the concentrations of $HCOO^-$ and CH_3COO^- in precipitation might be influenced mainly by photochemical conversion of precursors emitted from terrestrial vegetation during active plant growing seasons, but by direct emission from the anthropogenic sources such as vehicles during non-growing seasons. The high concentrations of $HCOO^-$ and CH_3COO^- were mostly associated with northwesterly winds from the continental area, on the other hand, the low concentrations with the winds coming from the North Pacific. The contributions to precipitation acidity by HCOOH and CH_3COOH tended to increase during the plant growing seasons, remaining at a low 10% throughout most of the events, while increasing to 30–40% during occasional precipitation events.

1. Introduction

Generally the rain acidity tends to be influenced by sulfur oxides (SO_x) and nitrogen oxides (NO_x) emitted from industrial activities and vehicles. These oxides are then converted to acidic compounds via photochemical reactions with hydroxyl radical (HO·), hydrogen peroxide, and peroxy radicals (HOO, ROO) in the atmosphere. In addition, several organic acids and methanesulfonic acid (MSA) also partially contribute to the precipitation acidity. Although their extents are generally less than those by inorganic acids such as H_2SO_4 and HNO_3, their relative contributions tend to be increased in remote areas such as tropical forests (Galloway et al., 1982).

Formic acid (HCOOH) and acetic acid (CH_3COOH) were present in the atmosphere over 90% in mass in the gaseous form and less than 10% in the particulate phase and, particularly, about 80% of carboxylic acids in the particulate phase are in fine particles with diameters of less than 1.0 μm in a semiurban site in northeastern USA (Khwaja, 1995). In the eastern USA and Amazon Bay, only 10–20% of pyruvic acid ($CH_3COCOOH$) and 1–2% of formic acid occurred in the particle phases (Andreae et al., 1987). It was also reported that formic acid and acetic acid occurred principally in the gas phase (≥98%) at a site in eastern Virginia (Talbot and Beecher, 1988). In Southern California, 94% of the formic acid and 88% of the acetic acid in the atmosphere were present as gaseous species (Grosjean, 1989).

Organic acids in the atmosphere originate mainly from biogenic and anthropogenic sources. The direct emissions from vegetation growing processes are among typical biogenic

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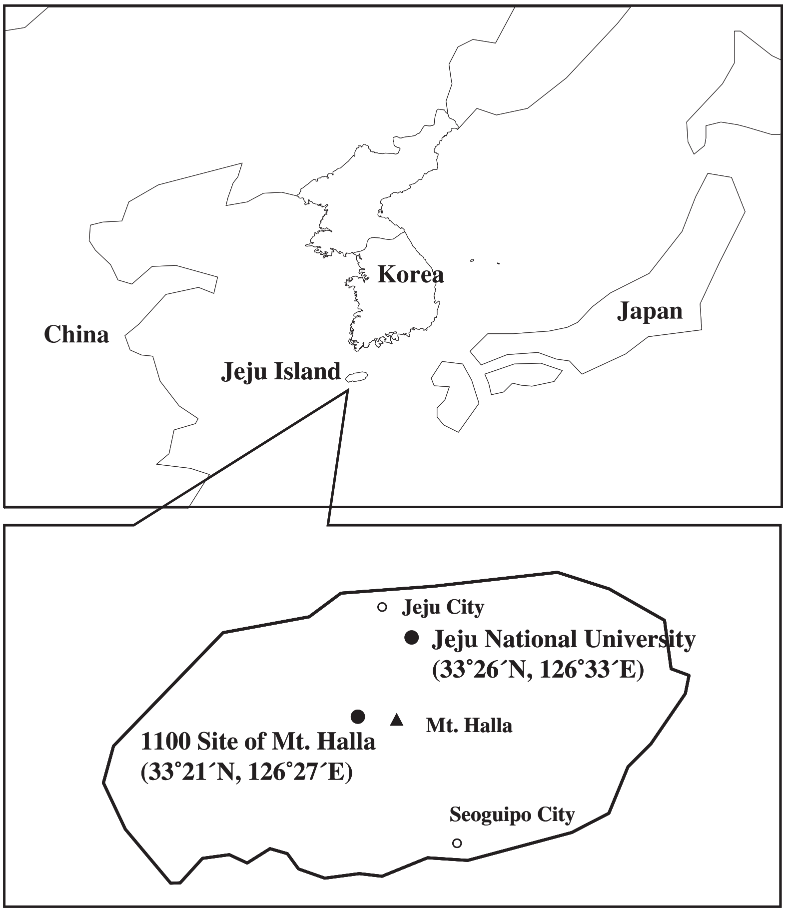

Fig. 1. Location of two sampling sites.

sources, whereas anthropogenic sources include vehicle emissions as well as the combustion of wood and agricultural debris (Chebbi and Carlier, 1996; Khare et al., 1997). In addition, organic acids can be formed indirectly via photo-oxidation reactions of precursors such as isoprene (C_5H_8), ethene (C_2H_4), and propene (C_3H_6), commonly emitted from woods, biological activities within the ocean, and combustion of fossil fuels (Likens et al., 1987; Keene and Galloway, 1988; Galloway and Keene, 1989).

The $CH_3COOH(g)$ and $HCOOH(g)$ concentrations and their ratios in the atmosphere vary according to the emission sources as well as their production paths. Commonly the concentrations of organic acids emitted directly from vegetation and formed secondarily in the atmosphere increase during the spring and summer plant growing seasons, as do those from marine sources (Keene and Galloway, 1988; Galloway and Keene, 1989; Pena et al., 2002; Avery et al., 2001, 2006). The concentration ratios of $CH_3COOH(g)/HCOOH(g)$ were about 2–10 from biomass burning (Talbot and Beecher, 1988). The ratio lies in the range of 1.8–2.4 for the vehicle emissions that are typical of most anthropogenic sources, and more or less in the range 2.1–2.5 when organic acids are emitted directly from plants. However, when isoprene is actively emitted and/or photo-oxidation occurs, the concentration ratio can decrease down below unity (Sanhueza et al., 1992; Chebbi and Carlier, 1996; Legrand and Angelis, 1996; Granby et al., 1997; Kesselmeier et al., 1998).

Table 1
Instrumental detection limit (IDL) and coefficient of variation (CV) for ion chromatography analysis.

Species	F^-	$HCOO^-$	CH_3COO^-	$CH_3SO_3^-$	NH_4^+	Na^+
IDL(μg/L)	1.4	0.7	0.9	1.7	11.9	6.2
CV(%)	0.9	0.4	0.6	1.1	6.1	3.1
Species	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-
IDL(μg/L)	14.1	5.3	10.3	8.1	9.8	4.4
CV(%)	5.1	6.5	3.6	2.2	2.7	2.0

Prior to this study, little research had been undertaken examining organic acids in precipitation in Korea and their acidification contribution. In this study, trace amounts of $HCOO^-$ and CH_3COO^- as well as major ionic components have been analyzed in precipitation at Jeju Island, which is a clean air area in Korea, between 1997 and 2003. This investigation reveals not only the concentration characteristics of the $HCOO^-$ and CH_3COO^- but also their emission sources and contribution to precipitation acidity in Jeju area.