Atmospheric Research 185 (2017) 158–168

Contents lists available at ScienceDirect

Atmospheric Research

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

Spatio-temporal distributions of dicarboxylic acids, ω-oxocarboxylic acids, pyruvic acid, α-dicarbonyls and fatty acids in the marine aerosols from the North and South Pacific

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ARTICLE INFO

Article history:
Received 5 April 2016
Received in revised form 12 October 2016
Accepted 26 October 2016
Available online 28 October 2016

Keywords:
Aerosols
Spatio-temporal distributions
Dicarboxylic acids
Oxalic acid
Glyoxylic acid

ABSTRACT

Aerosol samples (TSP) were collected during a cruise in the North (3°05′N–34°02′N) and South (6°59′S–25°46′S) Pacific to investigate the spatio-temporal distributions of water-soluble dicarboxylic acids and related compounds. The molecular distributions of diacids were characterized by the predominance of oxalic (C_2) acid followed by malonic (C_3) and then succinic (C_4) acid. However, we found a predominance of C_4 over C_3 in the aerosol sample that was collected in the western North Pacific Rim with a heavy influence from continental air masses. Atmospheric abundances of short chain diacids (C_2–C_4) are 2–3 times higher in the North Pacific than in the South Pacific. During the cruise, abundances of C_2 in the western North Pacific are 5 times higher than those in the rest of the samples collected. Moreover, the aerosol samples collected in the western North Pacific demonstrated that glyoxylic (ωC_2) acid and methylglyoxal (MeGly) were dominant together with C_2. We found a strong correlation between C_2 and ωC_2 ($r = 0.87$) and C_2 and MeGly ($r = 0.97$) in the western North Pacific aerosols but the correlations are significantly weak in the samples from the central North Pacific and Southern Ocean. Diacids were found to account for 1.6 to 14% of organic carbon with higher values in the western North Pacific. These results, together with 7-day backward air mass trajectories, indicate that ωC_2 and MeGly are both originated from the photochemical oxidation of continent-derived organic precursors including isoprene, which can serve as precursors for the production of C_2 during long-range atmospheric transport.

1. Introduction

Atmospheric aerosols are composed of various organic compounds, which can significantly contribute to the aerosol mass loading and alter the chemical and physical properties (Mochida et al., 2003; Legrand et al., 2007). Marine-derived primary organic aerosols (POA) are produced by bubble bursting and wave breaking processes that are driven by the wind actions over the surface ocean (Rinaldi et al., 2010). On the other hand, marine secondary organic aerosols (SOAs) are essentially produced by the atmospheric reactions of anthropogenic and biogenic volatile organic compounds (BVOCs) with oxidants such as ozone (O_3), nitrogen oxides (NO_x) and OH radicals (Claeys et al., 2004, 2007; Jaoui et al., 2005). However, the fate of marine organic aerosols is highly uncertain (Miyazaki et al., 2014). Organic matter in primary marine organic aerosols may act as an important precursor/source and sink for OH radicals, leading to their degradation and production of low molecular weight (LMW) dicarboxylic acids (Zhou et al., 2008). LMW dicarboxylic acids have potential influences on the physical properties of organic particles thus play an important role in the hygroscopic growth of particles (Prenni et al., 2003) and the activation of cloud condensation nuclei (Liss and Lovelock, 2007; Booth et al., 2009).

Both of the primary and secondary sources of LMW dicarboxylic acids and related compounds are well documented in literatures (e.g., Kawamura and Bikkina, 2016). Water-soluble dicarboxylic acids may also be produced from photochemical and aqueous phase oxidation of biogenic unsaturated fatty acids and volatile organic compounds (VOCs) such as isoprene emitted from the ocean surface (Bikkina et al., 2014; Sempéré and Kawamura, 2003) coupled with gas-to-particle conversion (Zhang et al., 2010). As illustrated in Fig. 1, in-cloud processing of isoprene is an important contributor to SOA production in the marine atmosphere, which can alter the global distribution of hygroscopic organic aerosol.

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http://dx.doi.org/10.1016/j.atmosres.2016.10.022
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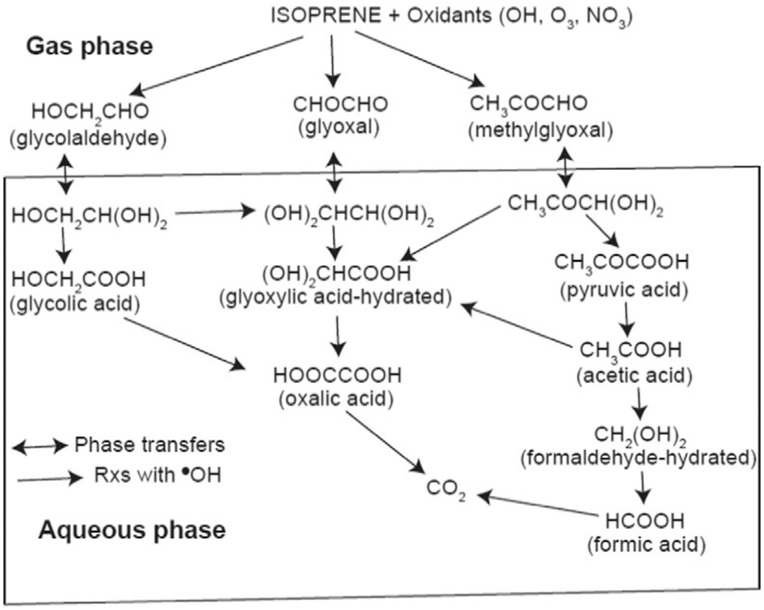

Fig. 1. In-cloud isoprene chemistry for the formation of major diacids: glyoxylic acid, pyruvic acid, and oxalic acid (modified from Lim et al., 2005).

Distributions of LMW diacids in remote marine aerosols are controlled by long-range transport of continental aerosols (Kundu et al., 2010; Fu et al., 2013a, b; Kawamura and Sakaguchi, 1999) and photochemical oxidation of BOVCs emitted from the ocean surface (Bikkina et al., 2014; Hoque et al., 2015).

Although several studies have been performed in a single hemispheric region over the Pacific, intra-hemispheric distributions of LMW diacids and related compounds have rarely been conducted during a single oceanic cruise (Sempéré and Kawamura, 2003). In the present study, remote marine aerosol samples were collected during a cruise of *M/V Bousei Maru* to cover the North and South Pacific during February to April 1994. This cruise is unique because of the dissimilarities of the hemispheres in terms of meteorology, wind patterns, and climate as well as biological productivity. For example, the coastal western North Pacific is highly influenced by polluted continental air masses transported from north China, Mongolia, Russia and Siberia. In contrast, the central North Pacific that is significantly influenced by the oceanic air masses (e.g., Bikkina et al., 2014) as it is far away from the pollution sources in the continents. The aerosol samples collected from the South Pacific can be influenced by the inward continental air masses from Papua-New Guinea, Southern Australia and New Zealand.

In this study, we conducted organic aerosol studies to characterize low molecular weight dicarboxylic acids, ω-oxoacids, pyruvic acids, α-dicarbonyls and fatty acids as well as organic carbon (OC), elemental carbon (EC) and water-soluble total nitrogen in the marine aerosol samples from the North and South Pacific. The objectives of the present study are to (1) characterize the molecular compositions of diacids and related polar compounds over the North and South Pacific Ocean, and (2) clarify the spatial distributions of water-soluble dicarboxylic acids and related compounds and their contributions to OC in the marine boundary layer of the North and South Pacific.

2. Methods

During the cruise of *T/V Bousei Maru* from 16 February to 1 April 1994, a total of 17 marine aerosol (TSP) samples were collected in the North Pacific (3°05′N–34°02′N, 144°52′E–173°49′W) and South Pacific (6°59′S–25°46′S, 154°28′E–173°55′W). A high volume air sampler was set up at the upper deck of the ship using pre-combusted (500 °C) quartz fiber filters (Pallflex-2500QAT-UP, 20 × 25 cm). The sampler was controlled by a wind sector (±60°) and wind speed ($\geq$5 m s^{-1}) system to avoid potential contamination from the ship exhausts (Kawamura and Sakaguchi, 1999). Sampling time was 48 to 72 h. Fig. 2 shows the cruise track. Total aerosol mass was determined by weighing the filter before and after the sample collection. Each filter was then stored individually in a pre-combusted clean glass jar with a Teflon-lined screw cap at −20 °C in darkness prior to analysis. Although the sample filters had been stored for a long time, degradation of organics on the filters should be insignificant under such a low temperature (Wang et al., 2006; Kawamura et al., 2010). Blank filters were exposed to the marine air in the sample shelter for a few seconds without pumping and then recovered into the glass jar (Sempéré and Kawamura, 2003).

Water-soluble diacids, ω-oxoacids, pyruvic acid, and α-dicarbonyls as well as fatty acids were determined using an improved method of Mochida et al. (2007) and Kawamura and Ikushima (1993). In brief, aliquots of filter samples were extracted with organic-free ultra pure water (5 ml × 3, >18 MΩ) under ultrasonic agitation for the isolation of diacids and other water-soluble organic compounds. The extracts were passed through a glass column (Pasteur pipet) packed with quartz wool for removing filter debris and particles. The extracts were adjusted to pH = 8.5–9.0 using a 0.05 M KOH solution and then concentrated to almost dryness using a rotary evaporator (~40 °C) under vacuum. After the dryness in N_2 blow down system, diacids, oxoacids, α-dicarbonyls and fatty acids in the concentrates were derivatized to butyl esters and dibutoxy acetals with 14% borontifluoride in *n*-butanol at 100 °C for 1 h.

The derivatives were extracted with *n*-hexane (~5 ml) after adding pure water (~5 ml). The hexane layer was concentrated to about 50 μl using a rotary evaporator, transferred to a glass vial (1.5 ml), consequently dried by N_2 blow down and dissolved in 100 μl of *n*-hexane. The derivatives (2 μl) were injected into a capillary gas chromatograph (GC) system (Agilent 6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25 m × 0.2 mm i.d., 0.5 μm film thickness) and flame ionization detector (FID). Identifications of esters and acetals were confirmed by comparing GC retention times and mass spectra with those of authentic standards. Mass spectral analysis was conducted with a GC/mass spectrometry system (Agilent MS) and quantification of compounds was performed by GC/FID. Fig. S1 shows a typical capillary gas chromatogram of the identified diacids in the aerosol sample (QFF 592) collected during the North-South Pacific cruise. Similar procedure was also performed for recovery and blank