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Aircraft measurement of dicarboxylic acids in the free tropospheric aerosols over the western to central North Pacific

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ABSTRACT

Aircraft observation of aerosols was conducted in February 2000, for spatial and vertical distributions of dicarboxylic acids in the free troposphere over the western to central North Pacific. Oxalic, malonic, adipic and azelaic acids were detected in the aerosol samples as the major species. Concentrations of these diacids decreased exponentially with an increase in altitude. They were higher in the western North Pacific (130°E) and decrease eastward. Local flights conducted over Naha (Okinawa), Iwo-jima and Saipan showed that diacid concentrations decreased from the lower to upper troposphere. In the atmosphere over Saipan, where the air is not strongly affected from polluted East Asia, diacid concentrations were almost below the detection limit. Vertical profiles of diacids over Naha and Iwo-jima would be typical over the western North Pacific during winter, suggesting that diacids were significantly injected to the free troposphere from East Asia. Backward air mass trajectories also suggested that the diacids in the free troposphere over the North Pacific are strongly affected by the outflow from East Asia. Diacids, which were produced by both primary emission and secondary photochemical processes in polluted air of East Asia, could alter the physico-chemical properties of aerosols in the free troposphere over the western North Pacific.

1. Introduction

Previous field measurements suggest that sulfate and organic compounds are both important components of aerosols that act as cloud condensation nuclei (CCN) (Novakov and Penner, 1993; Rivera-Carpio et al., 1996; Matsumoto et al., 1997; Hegg and Kaufman, 1998). Based on a modeling study, Kerminen (2001) reported that organics are more important than sulfate in initiating the growth of the fine particles that can be activated to form cloud droplets. Low molecular weight dicarboxylic acids are one of the most abundant water soluble organic compound classes identified in the atmospheric aerosols (Sempéré and Kawamura, 1994), and may significantly contribute to CCN due to the hydrophilic properties (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Limbeck and Puxbaum, 2000). Liu et al. (1996) reported that CCN numbers were highly correlated with the concentrations of particles >0.01 μm diameter and oxalate at the surface observation. Further, the soluble organics contribute more to the aerosol volume than the aerosol mass because of lower density, thus organics may be more important in determining the direct radiative properties of aerosols (Li et al. 1996).

Dicarboxylic acids are now recognized as ubiquitous aerosol constituents in the urban (Grosjean

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et al., 1978; Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994; Souza et al., 1999; Tran et al., 2000), suburban (Norton et al., 1983; Yokouchi and Ambe, 1986; Satsumabayashi et al., 1990; Limbeck et al., 2001), and marine atmosphere (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999), as well as polar regions from the Arctic (Li and Winchester, 1993; Kawamura et al., 1995; Kerminen et al., 1999; Narukawa et al., 2002) and the Antarctic (Kawamura et al., 1996). These diacids are directly emitted to the atmosphere by fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999) and have been reported to be the oxidation products of aromatic hydrocarbons and alkanes by the laboratory studies (Hatakeyama et al., 1987; Behnke et al., 1999; Kleindienst et al., 1999; Edney et al., 2000; Kalberer et al., 2000). A number of observations on diacids in aerosols were conducted at the surface level. However, the spatial and vertical distributions of diacids in aerosols in the free troposphere have rarely been studied (Talbot et al., 1992; Ruellan et al., 1999).

Aerosol particles originating from East Asia have received great interest in the fields of atmospheric chemistry and physics over the western North Pacific. This ocean is located on the leeward of East Asia, in which large industrial cities are present, and from which a heavily polluted air mass flows over the ocean. Matsumoto et al. (l998) and Mochida et al. (2003) reported that oxalic acid in marine aerosols over the western North Pacific is influenced by continental anthropogenic activity during winter. Thus, dicarboxylic acids in the free troposphere over the North Pacific might affect the physico-chemical properties of aerosols by adsorption on pre-existing particles. In February 2000 aircraft observation of atmospheric aerosols and gases was carried out in the free troposphere over the western to central North Pacific as a PACE-7 (Pacific Atmospheric Chemistry Experiment) project. The purpose of this study is to clarify the spatial and vertical distributions of dicarboxylic acids in the free tropospheric aerosols over the North Pacific along the Asian continent.

2. Sampling and chemical analysis

2.1. Sample collection

Aircraft observations were carried out from 13 to 21 February 2000 on board a research jet aircraft (Gulfstream-2) in the free troposphere between 2 and 10 km over the western to central North Pacific. Aircraft routes are shown in Fig. 1. Aerosol sampling was conducted between 15° and 60°N. Local flights were carried out for vertical profiles over Naha (Okinawa) (26.2°N, 127.7°E), Iwo-jima (24.8°N, 141.3°E) and Saipan (15.2°N, 145.7°E). Table 1 presents information on the filter samples collected. Averaged sampling time was about 100 min and averaged sampling volumes were about 20 m^3. The air volume was standardized to the ambient temperature/pressure at a ground level.

Sample air was introduced through an isokinetic intake (outer diameter 5.8 mm, inner diameter 5.4 mm) projecting into the airstream from the aircraft fuselage. The distance between the intake and aircraft fuselage was 200 mm. The outer and inner diameters of the intake increased linearly to 32 and 20 mm at a distance of

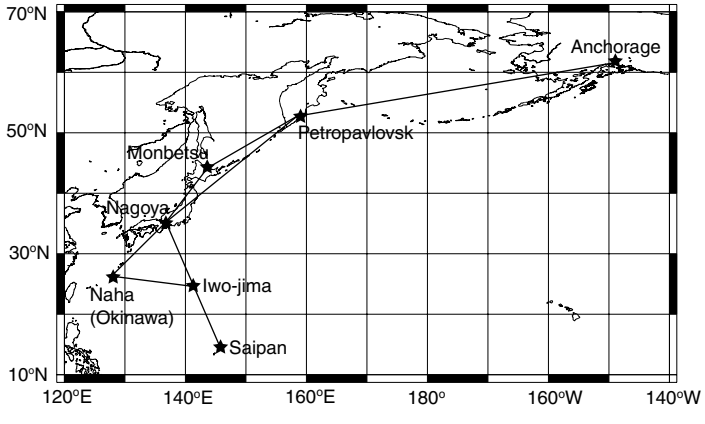

Fig. 1. Flight tracks of aircraft during PACE-7 campaign over the North Pacific.

Table 1. *Description of aerosol filter samples collected in the free troposphere during PACE-7 campaign over the North Pacific*

Sample no.	Date (yr/mo/d)	Location	Altitude (km)
1	2000/2/13	Nagoya–Naha	4.9
2	2000/2/13	Naha	8.1–11.1
3	2000/2/13	Naha	5.0
4	2000/2/13	Naha	2.0
5	2000/2/14	Naha–Iwo-jima	4.6
6	2000/2/14	Iwo-jima	8.1–11.1
7	2000/2/14	Iwo-jima	5.0
8	2000/2/14	Iwo-jima	2.0
9	2000/2/14	Iwo-jima–Nagoya	4.9
10	2000/2/17	Nagoya–Petropavlovsk	7.6
11	2000/2/17	Petropavlovsk–Anchorage	7.6
12[a]	2000/2/19	Anchorage–Petropavlovsk	10.7
13	2000/2/19	Petropavlovsk–Monbetu	10.7
14	2000/2/19	Monbetsu–Nagoya	4.9
15	2000/2/19	Nagoya–Saipan	4.6
16[a]	2000/2/20	Saipan	8.1–11.1
17	2000/2/20	Saipan	5.0
18	2000/2/20	Saipan	2.0
19	2000/2/21	Saipan–Nagoya	10.7

The aerosols samples (nos. 2–4, 6–8 and 16–18) were collected during a local flight at Naha, Iwo-jima and Saipan, respectively. Sample nos. 12 and 13 were collected in the lower stratosphere.

[a]The filter samples were not analyzed due to failure to cut the filter.

45 mm from the inlet tip, respectively. The sample air was then introduced through the tube (inner diameter mm) into a manifold (60 mm in diameter and 290 mm in length) in the cabin of the aircraft. The aerosol particles were collected on a 90-mm Teflon filter (German Sciences, Zefluor pore size 1 μm) using a filter sampler made by the Meteorological Research Institute, Japan. The volumetric air flow-rate through the filter was 200 L min^{-1}. Part of the collected filter (25 mm diameter) was used for the analysis in this research. Particle loss between the inlet and filter sampler was examined using ambient aerosols in a similar air flow-rate as the aircraft observation. It was found that particles with radii larger than 1 μm have a particle loss $>$50%.

2.2. Chemical analysis

The analytical procedure for diacids was modified from Kawamura and Ikushima (1993). The aerosol filter was extracted with Milli Q water under ultrasonication for water-soluble organic compounds. The extracts were passed through a glass column (Pasteur pipet) packed with quartz wool to remove particles such as carbon black and filter debris. Less water-soluble organic compounds that include long-chain organic acids were extracted with ethyl acetate from the residue of the filter samples. Both extracts were combined and concentrated almost to dryness by a rotary evaporator under a vacuum. 14% Borontrifluoride in *n*-butanol (ca. 0.2 mL, Alltech Associates, Inc.) was added to dried extracts. The extracts and reagent were mixed under ultrasonication and then heated at 100 °C for 1 h to derive carboxylic acid *n*-butyl esters. The esters were extracted with 10 mL *n*-hexane after adding 10 mL Milli Q water and 0.2 mL acetonitrile, the latter makes the excess *n*-butanol transfer into the aqueous phase more effectively. The *n*-hexane layer was washed with pure water (10 mL $\times$ 4). The esters were dried by using a rotary evaporator and nitrogen blow-down system and then dissolved in 20 μL of *n*-hexane.

The *n*-butyl esters were determined with a capillary gas chromatograph (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (CP-Sil 5 CB, 60 m $\times$ 0.32 mm i.d. $\times$ 0.25 μm film thickness) and FID detector. The identification of the compounds was performed with a gas chromatograph/mass spectrometer (ThermoQuest, Trace GC2000 and Trace MS) equipped with an on-column injector and fused-silica capillary column (DB-5MS, 60 m $\times$ 0.32 mm i.d. $\times$ 0.25 μm film thickness) by using authentic standards. Recoveries of the authentic carboxylic acids were 70% for oxalic (C_2) acid and better than 90% for succinic (C_4) and adipic (C_6) acids. Procedural blanks showed a small peak of oxalic acid dibutyl ester in the GC chromatograms. However, their blank levels were almost constant and generally less than 10% of that for the aerosol samples. The concentrations of oxalic acid were corrected for the blanks. Detection limits for the used analytical method were about 0.1 ng m^{-3}.

3. Results and discussion

3.1. Molecular composition and concentrations of dicarboxylic acids

Molecular compositions of homologous dicarboxylic acids, including oxalic (C_2), malonic (C_3), adipic (C_6) and azelaic (C_9) acids, were detected for the first time in the aerosol samples from the free troposphere. Concentrations of succinic (C_4) and other diacids and ketoacids were below the detection limit

Table 2. *Concentrations (ng m^{-3}) of dicarboxylic acids in the free tropospheric aerosol samples collected during PACE-7 over the North Pacific*

	Lower (2–4 km) ($n = 3$)		Middle (4–7 km) ($n = 8$)		Upper (>7 km) ($n = 6$)	
Dicarboxylic acid	Range	Average	Range	Average	Range	Average
Oxalic (C_2)	<0.1–52.9	28.0	<0.1–14.3	6.4	<0.1–12.1	3.1
Malonic (C_3)	<0.1–11.9	6.4	<0.1–4.6	2.1	<0.1–1.3	0.7
Adipic (C_6)	<0.1–3.6	2.3	<0.1–2.1	0.9	<0.1–1.6	1.0
Azelaic (C_9)	<0.1–5.1	1.7	<0.1–1.3	0.5	<0.1–0.8	0.3

Table 3. *Comparison of mean concentrations (ng m^{-3}) of oxalic acid in the free tropospheric aerosols*

Location	Date	Oxalic acid	Reference
Arctic	July–August 1988	16[a], 19[b]	Talbot et al. (1992)
Central Africa	November–December 1996	1170[c]	Ruellan et al. (1999)
Austrian Alps	April–May 1997	150	Limbeck and Puxbaum (2000)
North Pacific	February 2000	13	This work

[a]High Article (>60°N).
[b]Sub-Article (50–60°N).
[c]Harmattam layer.

or blank level. Oxalic acid was found to be the most abundant diacid, followed by malonic, adipic and azelaic acids in the free troposphere (Table 2). The mean concentration of oxalic acid in the lower troposphere (altitude 2–4 km) is about four times higher than in the middle troposphere (altitude 4–7 km), which is twice as high as than that in the upper troposphere (altitude >7 km). Malonic acid showed a trend similar to oxalic acid. The mean concentration of adipic acid in the lower free troposphere is three times higher than in the middle troposphere, whereas mean concentration of adipic acid in the middle troposphere was nearly equivalent to that of the upper troposphere. A similar trend was also found for azelaic acid. This study showed that the mean concentration of oxalic acid (13 ng m^{-3}) in the free troposphere over the North Pacific is comparable to those (16–19 ng m^{-3}) of the Arctic, but lower than those (1170 ng m^{-3}) from central Africa during the biomass burning season (Table 3).

3.2. *Vertical and spatial distributions of dicarboxylic acids in the free tropospheric aerosols over the North Pacific*

Figure 2 shows the vertical distributions of diacids in the free troposphere over the North Pacific. Vertical distributions of malonic, adipic and azelaic acids were reported for the first time in the free troposphere. Over Naha (13 February) and Iwo-jima (14 February), their concentrations showed a strong gradient from the lower to upper troposphere, although oxalic acid showed a relatively high concentration (12.1 ng m^{-3}) in the upper troposphere over Naha. In the region between Nagoya (35.2°N, 136.9°E) and Anchorage (61.2°N, 149.9°W) (see the points for 17 and 19 February in Fig. 2), concentrations of diacids in the middle and upper troposphere were almost equivalent, but lower than those over Naha and Iwo-jima (see the points for 13 and 14 February in Fig. 2). A relatively high concentration of adipic acid (1.6 ng m^{-3}) was obtained in the upper troposphere between Petropavlovsk (53.0°N, 158.7°E) and Monbetsu (44.3°N, 143.4°E) (see the point for 19 February in Fig. 2c). Over Saipan (20 February), oxalic and malonic acid concentrations were below the detection limit or blank level (the results are not shown in Fig. 2). Adipic and azelaic acids were detected in the middle troposphere over Saipan with concentrations similar to those in between Nagoya and Anchorage (17 and 19 February). In the upper troposphere between Saipan and Nagoya (21 February), malonic and adipic acids were detected at relatively high concentration levels, whereas oxalic and azelaic acids were below the detection limit. Roughly, diacid concentrations decreased exponentially with altitude, although high concentrations of diacids (e.g. adipic acid, Fig. 2c) were sporadically observed in the upper troposphere.

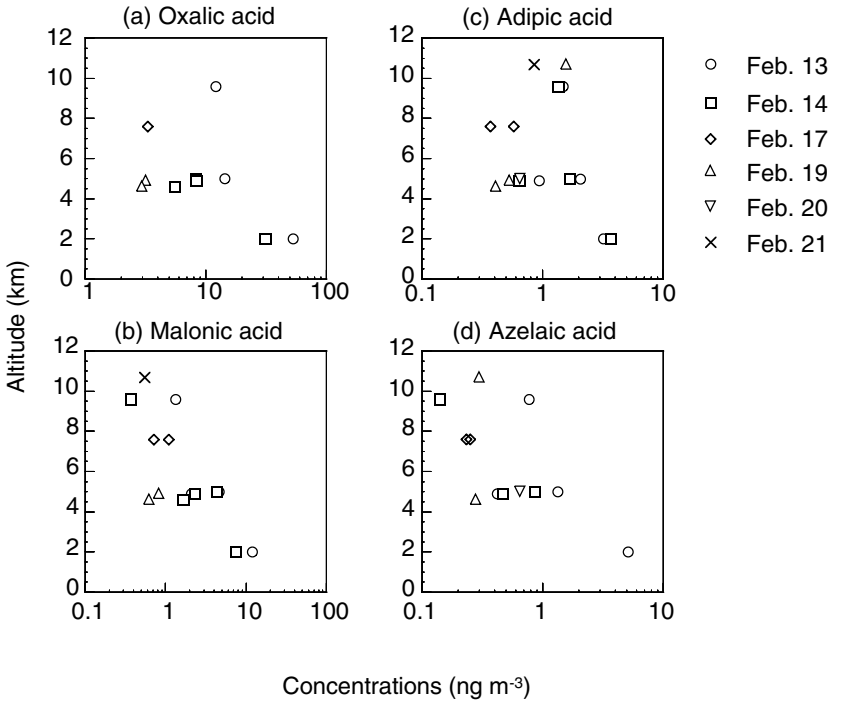

Fig. 2. Vertical distributions of the concentrations (ng m^{-3}) for (a) oxalic acid, (b) malonic acid, (c) adipic acid and (d) azelaic acid in the free troposphere over the North Pacific during PACE-7 campaign (February 2000). The concentrations were calculated using the standardized air volumes at the temperature/pressure at a ground level.

Figure 3 shows longitudinal distributions of diacids over the North Pacific. Concentrations of oxalic, malonic and azelaic acids were found to be high over the western North Pacific (around 130°E), where the air is strongly affected by outflow from East Asia. However, adipic acid showed sporadically higher concentrations (3.6 ng m^{-3}) in the lower free troposphere around 140°E. Concentrations of these diacids beyond 150°E were comparable to those around 180°E. These results imply that the diacids, which are produced by both primary emission and secondary photochemical processes, originated from East Asia and were transported to the free troposphere over the North Pacific. The emission of diacids and their precursors from East Asia into the free troposphere would affect the chemical composition of free tropospheric aerosols over the western North Pacific.

3.3. Vertical profiles of dicarboxylic acids over Naha (Okinawa) and Iwo-jima

Local flights were carried out over Naha (13 February), Iwo-jima (14 February) and Saipan (20 February). The diacids over Saipan were often below the detection limit. Figure 4 shows vertical profiles of the diacids with regression lines obtained by local flights over Naha and Iwo-jima, which lie to the leeward of East Asia. Concentrations of all the diacids decreased exponentially with altitude. From the regression lines, the height of the air mass collected can be expressed as a function of the diacid concentrations as follows:

$$z = a - b \log x,$$

where a and b are constant for each diacid, z is the height, and x is the concentration of a given diacid. From this equation, the concentration of the diacid can be expressed as a function of height:

$$x = 10^{a/b} \exp\left(-\frac{z}{b/\ln 10}\right).$$

When z is zero, x denotes a surface concentration of diacid. From the calculation using the above equation, the concentrations of the diacids in surface-level aerosols were obtained as 87 ng m^{-3} (oxalic acid), 28 ng m^{-3} (malonic acid), 4.1 ng m^{-3} (adipic acid)

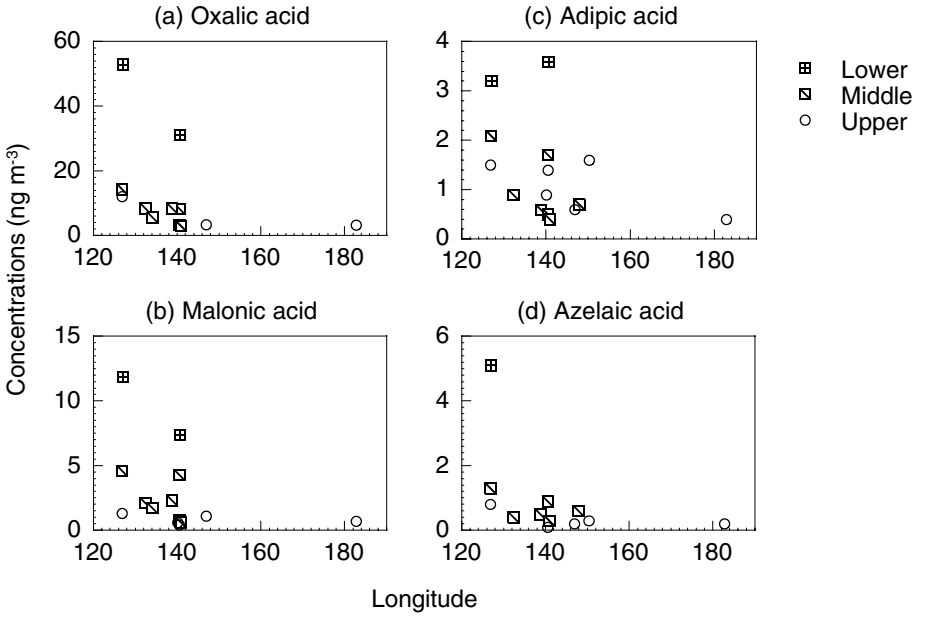

Fig. 3. Longitudinal distributions of the concentrations (ng m^{-3}) for (a) oxalic acid, (b) malonic acid, (c) adipic acid and (d) azelaic acid in the free troposphere over the North Pacific during PACE-7 campaign (February 2000).

and 16 ng m^{-3} (azelaic acid) (Table 4). Diacid concentrations at sea surface level in the western North Pacific, including the tropics, were measured in autumn to winter (Kawamura and Sakaguchi, 1999). These authors reported concentrations of oxalic acid (6.5–161 ng m^{-3}, av. 40 ng m^{-3}), malonic acid (1.3–54 ng m^{-3}, av. 11 ng m^{-3}), adipic acid (0.6–13 ng m^{-3}, av. 2.1 ng m^{-3}) and azelaic acid (0.17–4.0 ng m^{-3}, av. 0.57 ng m^{-3}). This study shows that the calculated concentrations of diacids in aerosols at sea surface level are consistent with the previous results based on shipboard observations. The vertical profiles of diacids obtained by local flights in this study might be typical of diacids in the aerosols over the western North Pacific under the influence of air pollution from East Asia in winter.

Jaenicke (1993) proposed that the aerosol mass concentration can be expressed as a function of height:

$$M(z) = M(0) \exp\left(-\frac{z}{H_p}\right)$$

where $M(0)$ is surface concentration and H_p is the scale height. Hence the scale height H_p is equal to $b/\ln 10$. H_p depends on each location and is equal to 0.9 km for the marine, 0.73 km for the remote continental, 2 km for the desert and 30 km for the polar aerosol types (Jaenicke, 1993). In this study, the scale heights were calculated to be 2.9 km (oxalic acid), 2.5 km (malonic acid), 7.8 km (adipic acid) and 2.2 km (azelaic acid) (Table 4). These scale heights are higher than 2 km, which was reported for desert (Jaenicke, 1993). These results may indicate a higher extent of air pollutants due to enhanced atmospheric convection and injection of diacids and their precursors from the ground level to the upper troposphere in East Asia.

3.4. *Source of dicarboxylic acids in the free tropospheric aerosols: air mass back trajectories*

To clarify the origin of the air mass with which the diacids and their precursors were transported, 5-d backward air mass trajectories (HYSPLIT results, Draxler and Hess, 1997; 1998) were computed. Figure 5 gives representative results over Naha (Okinawa), Iwo-jima and Saipan, where local flights were conducted. Over Naha and Iwo-jima, where diacids showed higher concentrations, the air masses at each altitude would be derived from East Asia (Figs. 5a and 5b), where the air is polluted by extensive human activity. On the other hand, concentrations of diacids over Saipan were very low or below the

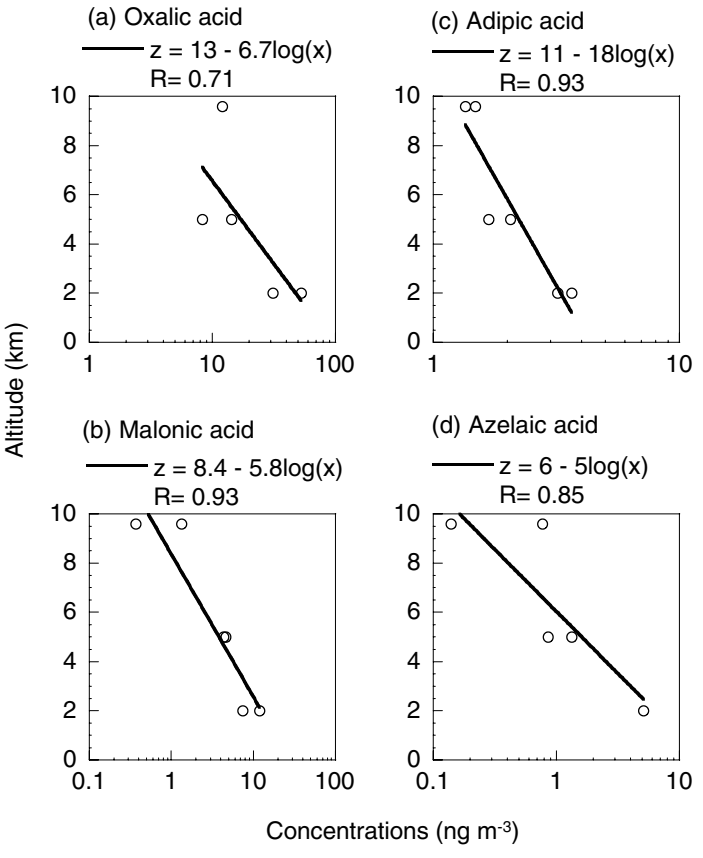

Fig. 4. Vertical profiles of the concentrations (ng m^{-3}) for (a) oxalic acid, (b) malonic acid, (c) adipic acid and (d) azelaic acid in the aerosols collected in a single day by a local flight (Naha and Iwo-jima) during PACE-7 campaign (February 2000). The data for Saipan are not plotted here because most diacids were below the detection limit. Regression lines were drawn by a least-squares fit.

detection limit when the air masses in the lower troposphere originated from the east, i.e. the central Pacific (Fig. 5c). In contrast, when the air masses in the middle and upper troposphere originated from Southeast Asia, adipic and azelaic acids were detected, although the concentrations were low. This study demonstrates that the air masses in the lower, middle and upper troposphere over Saipan are clearly different in origin than those over Naha and Iwo-jima.

These trajectory analyses suggest that diacids in the free tropospheric aerosols over the western North Pacific originate from East Asia and not from the open ocean, and that the relatively high concentrations of diacids over 130–150°E are strongly attributed to East Asia. Diacids that are present in aerosol particles may contribute to CCN and alter the physico-chemical properties of aerosols in the free troposphere over the western North Pacific. These diacids and their precursors are supplied from the ground level in East Asia to the upper troposphere by the enhanced convection.

Table 4. *Estimated surface concentrations of diacids and scale heights of diacid vertical profiles for the free tropospheric aerosols collected over Naha (Okinawa) and Iwo-jima in the western North Pacific*

Compound	Concentration (ng m^{-3})	Scale height, H_p (km)
Oxalic acid	87	2.9
Malonic acid	28	2.5
Adipic acid	4.1	7.8
Azelaic acid	16	2.2

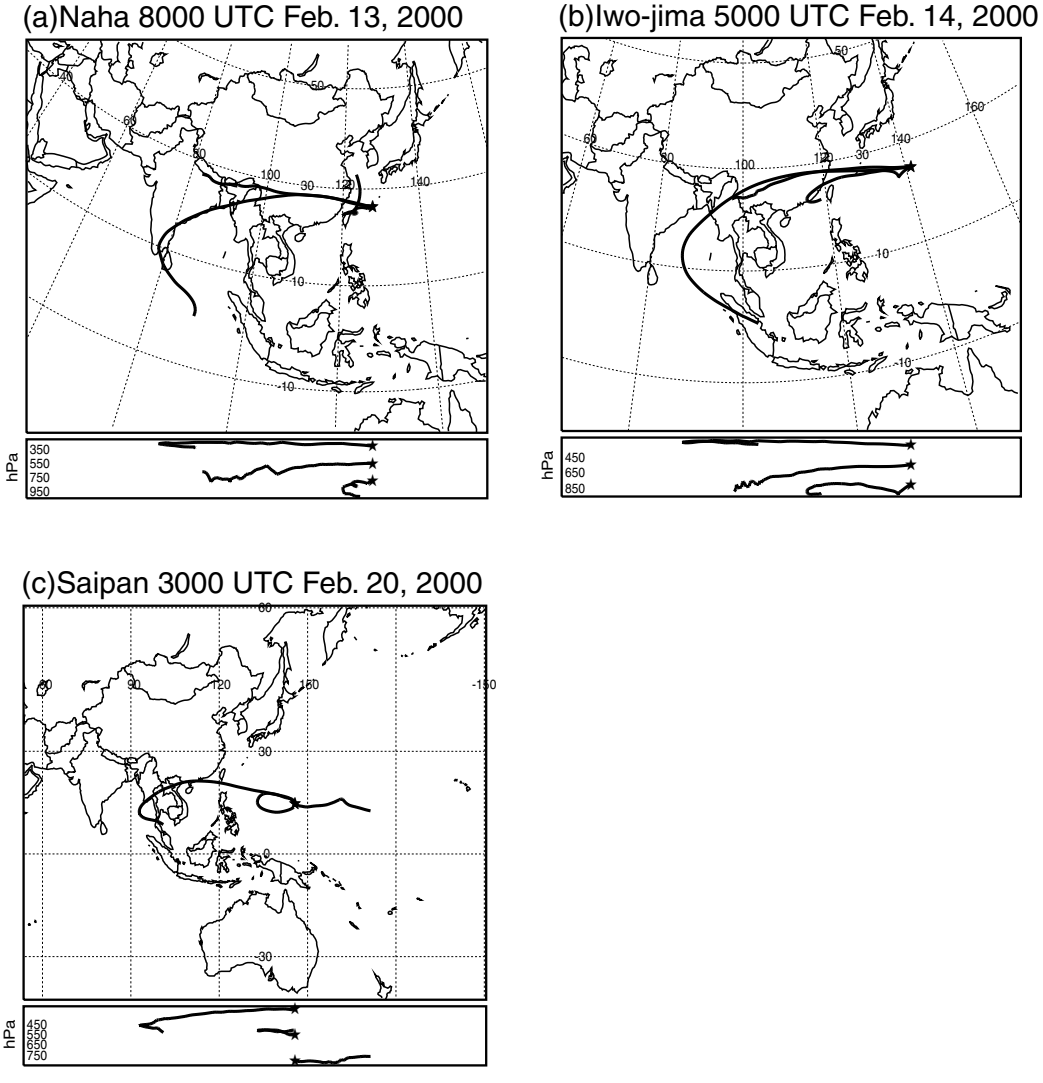

Fig. 5. Five-day backward trajectories for (a) Naha (26.2°N, 127.7°E), (b) Iwo-jima (24.8°N, 141.3°E) and (c) Saipan (15.2°N, 145.7°E). The calculation was started at three heights: 2, 5 and 9.6 km above ground level. FNL meteorological data were used and the program was taken from the NOAA web server.

4. Summary and conclusion

1. Oxalic (C_2), malonic (C_3), adipic (C_6) and azelaic (C_9) acids were detected in the free tropospheric aerosols over the North Pacific. Malonic, adipic and azelaic acids have, for the first time, been reported in the free troposphere.

2. Diacid concentrations decreased exponentially with increasing altitude in the free troposphere, although relatively high concentrations of diacids were sporadically obtained.

3. Concentrations of diacids in the free troposphere over the North Pacific were found to be high around 130°E and decreased toward the east. Their concentrations around 150°E were comparable to those over the central North Pacific (180°E). These results imply that diacids, which are produced by both primary emission and secondary photochemical

processes, originate from East Asia, are lifted up into the free troposphere and are transported eastward.

4. Local flights over Naha and Iwo-jima showed a clear vertical profile of diacid concentrations, with a strong gradient from the lower to upper troposphere. Concentrations of diacids at the surface level, estimated from the regression lines obtained, were found to be consistent with previously reported values from shipboard observations. These vertical profiles suggest that diacids and their precursors were strongly injected into the free troposphere over the western North Pacific by high-reaching atmospheric convection in East Asia.

5. This study, together with backward air mass trajectories, suggests that the concentrations of diacids in the free tropospheric aerosols over the western North Pacific are strongly controlled by the outflows from East Asia.

5. Acknowledgements

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