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Water-soluble dicarboxylic acids in the tropospheric aerosols collected over East Asia and western North Pacific by ACE-Asia/C-130 aircraft

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Abstract

Tropospheric aerosols were collected during C-130 aircraft campaign over the East Asia/Pacific region in April to May 2001 and were analyzed for low molecular weight dicarboxylic acids. Homologous series of C₂-C₅ dicarboxylic acids were detected, for the first time, in the polluted troposphere in the Asian region using aircraft. Oxalic acid (C₂) was found to be the most abundant species followed by malonic (C₃) or succinic (C₄) acid. Total concentrations of C₂-C₅ diacids (44-870 ngm⁻³, av. 310 ngm⁻³) are similar to those reported in urban Tokyo near the ground level. Concentrations of oxalic acid showed a positive correlation ($r^2 = 0.70$) with total organic carbon (TOC), although other diacids showed weaker positive correlation. These results suggest that water-soluble dicarboxylic acids and TOC were emitted from similar sources on the ground in the Asian continent and/or produced by the photochemical oxidation of anthropogenic organic compounds in the atmosphere. The diacid-carbons were found to comprise 0.2 to 3.3 % (average, 1.8 %) of TOC. Water-soluble dicarboxylic acids may play an important role in controlling the chemical and physical properties of organic aerosols in the polluted troposphere over the East Asia and western Pacific.

1. Introduction

Low molecular weight (LMW) dicarboxylic acids such as oxalic, malonic and succinic acids have been reported in the aerosols from the continental and marine atmosphere [Grosjean et al., 1978; Norton et al., 1983; Satsumabayashi et al., 1990; Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Wang et al., 2002; Mochida et al., 2003a]. These carboxylic acids are now recognized as ubiquitous organic components in the tropospheric aerosols. Because they are important water-soluble constituents, it has been suggested that organic aerosols enriched with dicarboxylic acids may alter the hygroscopic properties of atmospheric particles and play an important role in the cloud formation process by acting as cloud condensation nuclei [Saxena et al., 1995]. Dicarboxylic acids can be directly emitted from combustion sources such as motor exhausts [Kawamura and Kaplan, 1987] and biomass burning [Narukawa et al., 1999; Oros and Simoneit, 2001]. Further, LMW diacids are produced in the atmosphere by the photochemical oxidation of volatile and semi-volatile organic compounds of both anthropogenic and natural origin [Grosjean and Friedlander, 1980; Kawamura et al., 1996]. However, their sources and formation mechanisms are still poorly understood.

Most of the previous studies of dicarboxylic acids have been conducted at ground level using continental and remote island sites as well as research ships. Aircrafts have rarely been used for studies of dicarboxylic acids in tropospheric aerosols. The few aircraft observations that have been conducted in the free troposphere over the arctic region [Talbot et al., 1992] and the western North Pacific [Narukawa et al., 2003] reported oxalic acid and other diacid species. Their concentrations were generally much lower than those reported in the Arctic and North Pacific at ground level [Kawamura et al., 1996; Kawamura and Sakaguchi, 1999]. However, Ruellan et al. [1999] reported very high concentrations of oxalic acid (1170 ngm^{-3}) in plumes from biomass burning over central Africa. Although other dicarboxylic acid species were not measured, this study suggested that concentrations of diacids in the middle and upper troposphere could be significantly enhanced by strong convection.

Asia is one of the most important source regions for anthropogenic aerosols and their precursors as well as mineral dust from arid regions [Duce et al., 1980, 1991; Huebert et al., 2003]. Steadily increasing emissions of inorganic and organic pollutants from Southeast Asia have focused attention on both air quality and the radiative forcing of Earth climate in the Asian Pacific region. In April and May 2001, an intensive international collaborative study was conducted over the East Asian and Northwestern Pacific region using aircraft (the NCAR/NSF C-130), ships (NOAA *R/V Ron Brown* and JAMSTEC *R/V Mirai*) and coastal and remote island sites (for more information see <http://saga.pmel.noaa.gov/aceasia/index.html>). During the ACE-Asia campaign (Asian Pacific Regional Aerosol Characterization Experiment), atmospheric aerosols were studied over the western rim of the Pacific Ocean including the East China Sea, Japan Sea, Korean Peninsula, and Japanese Islands.

In this study, we collected filter samples of organic aerosols in the East Asian region using the C-130 aircraft as part of the ACE-Asia program. The aerosol samples were analyzed for water-soluble organic acids using a capillary GC and GC/MS. Here, we present the distributions of dicarboxylic acids in the aerosol samples and discuss their transport from the ground sources to the upper troposphere as well as photochemical production and transformation in the marine boundary layer and free troposphere.

2. Experimental

Aerosol samples were collected during research flights RF05 to RF19 of the C-130 (see Figure 1 for the sampling area) between 8 April and 4 May, 2001. The altitudes of the flights during sample collection ranged from 40 m to 7000 m. Aerosol samples were collected on a pre-combusted (550°C) quartz filter (25 mm) with a cross section of 5.66 cm² and a flow rate of 9.3 liter/min (27 cm/sec) during C-130 aircraft campaign. Air was conveyed into the aircraft by a gradually-curved solid diffuser inlet. Aerosol samples were collected using a side channel of a Particle Concentrator Brigham Young University Organic Sampling System (PC-BOSS). Our PC-BOSS sampler was identical to that diagrammed in Eatough et al. [1999] and

Lewtas et al. [2001], except that we had only a single filter pack behind the denuder (see Figure 2).

A quartz filter that sampled undenuded air upstream of the sampler is referred to as the “sideall” filter (Figure 2). One sideall filter sample was collected during each flight. Total sideall sampling times and volumes were roughly 1.5-4 hours and 1.1-2.8 m³ (STP), respectively. Sample flow was measured using a thermal mass flowmeter (which measures mass of air flow per time) and integrated over the sample time to get the STP volume of the air sampled. This filter was used for the study of dicarboxylic acids and related compounds. Concurrent with each flight’s sideall sample, 3 to 5 sequential aerosol samples were collected using baked quartz filters (47 mm) in the main stream of the PC-BOSS sampler, in which a denuder removed volatile organic compounds [Lewtas et al., 2001]. The filter samples were analyzed for organic carbon (OC) and elemental carbons (EC) by a Sunset Lab’s thermal/optical analyzer [Bertram et al., 2003, to be submitted]. The averaged concentrations of OC were used as TOC in this study to compare with the concentrations of dicarboxylic acids.

Fifteen sideall filter samples were used in this study. Aliquots (typically, 1-2 cm²) of the filters were analyzed by the method described in Kawamura and Ikushima [1993] and Kawamura [1993] with some modification. Briefly, the samples were extracted with pure water (5 ml x 3) under ultrasonic agitation (3 min.), followed by the extraction with ethyl acetate (5 ml x 3). The latter solvent was used to recover fatty acids and other lipids. The extracts were combined and concentrated using a rotary evaporator under a vacuum and then further concentrated using a nitrogen blow-down system at atmospheric pressure. The concentrated extracts were reacted with 14% BF₃/n-butanol in a pear-shaped flask (25 ml) to derivatize carboxyl groups to butyl esters. The derivatives were extracted and then injected to a HP 6890 gas chromatograph (GC) with a split/splitless injector, fused silica capillary column (HP-5, 0.2 mm x 25 m x 0.52 μm film thickness), and a flame ionization detector. The GC column oven temperature was programmed from 50°C (2 min.) to 120°C at 30°C/min. and then to 320°C at 5°C/min. For the structural identification, mass spectra of the organic

compounds were obtained for two samples using ThermoQuest GC/MS (Trace MS) with a similar GC condition.

For the determination of the organic compounds, we used C₂-C₁₀ dicarboxylic acid dibutyl esters as external standards. The compound identification was based on the matching of GC retention times of standards and on mass spectra obtained by GC/MS. Laboratory blanks were run together with sample analyses. Although entire field blank filters were not available in this study, we used the edges of sample filter as a surrogate field blank, since the filter surface was not exposed to the sample air. These field blanks should mimic any contamination during sampling, transport and storage of the exposed sections. Since the filters were partially masked, the cross section for air sampling (5.66 cm²) was roughly one quarter of the whole filter area (ca. 20 cm²). The GC peak areas for major diacids in the field blanks were less than 10 % (oxalic acid) and 30 % (malonic acid) of the sample filters, except for the RF05 sample whose GC peak areas were quite small. The data presented here were corrected for both lab and field blanks by subtracting their GC peak areas from those of the samples.

To test the recovery of diacids, we spiked authentic standards (mixture of C₂-C₅ diacids) to a quartz filter in duplicate and found that the recovery of oxalic acid was 81 % during the analytical procedure whereas those of malonic, glutaric and succinic acids were better than 90 %. Duplicate analyses of aerosol filter samples collected in Sapporo showed that analytical errors were within 10 % for major species such as oxalic, malonic and succinic acids [Umemoto et al., unpublished results, 2001]. The lower concentration values reported in this paper have higher uncertainties. Although some bi-functional carboxylic acids may exist in the gas phase, Mochida et al. [2003b] estimated that the relative abundance of gaseous oxalic acid is at most 30 % of the total (gas plus particulate) atmospheric concentrations in the marine boundary layer. Similar results have been reported for oxalate in the atmosphere of the Atlantic Ocean [Barboukas et al., 2000].

3. Results and Discussion

3.1. Molecular distributions of dicarboxylic acids

Although we detected C₂-C₁₁ diacids, C₂-C₄ ketoacids and C₁₂-C₂₄ fatty acids, we report here only C₂-C₅ saturated dicarboxylic acids and C₅ unsaturated (methylmaleic) acid because of the high blank levels relative to the samples (and thus high uncertainties) for the rest of the compounds. Table 1 presents concentration ranges of the C₂-C₅ diacids, with average and median concentrations. Oxalic acid (C₂, 26-650 ngm⁻³) was the most abundant diacid in all the samples studied. This single species accounted for 59-89 % (av. 76 %) of total diacid concentrations. Malonic (C₃) or succinic (C₄) acid was the second most abundant diacid species. The molecular characteristics of saturated aliphatic diacids are similar to those reported in the urban aerosols from Los Angeles [Kawamura and Kaplan, 1987], Tokyo [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994] and Nanjing, China [Wang et al., 2002].

Concentrations of total diacids ranged from 44 ngm⁻³ to 870 ngm⁻³ with an average of 310 ngm⁻³. The diacid concentration levels were similar to those (90-1370 ngm⁻³) of urban Tokyo aerosols collected at the ground level for this season [Kawamura and Ikushima, 1993], but are lower than the upper range (300-2100 ngm⁻³) from China [Wang et al., 2002].

Although diacids have been reported in the marine aerosols from the western North Pacific [Kawamura and Sakaguchi, 1999, Mochida et al, 2003a], their concentrations are roughly one order of magnitude lower than those reported in this study. Previous aircraft observation of oxalic and other diacid species in the free troposphere [Talbot et al., 1992; Narukawa et al., 2003] reported much lower concentrations than those in this study, except for the aircraft measurement of oxalate in biomass burning plumes [Ruellan et al., 1999]. In contrast, Mochida et al. [2003b] reported higher concentrations of LMW diacids (up to 1800 ngm⁻³) in surface marine aerosols over the Sea of Japan during the ACE-Asia campaign (10-11 April 2001). This value is >5 times higher than that (370 ngm⁻³) obtained by C-130 aircraft (average altitude of 2045 m) in Yellow Sea and East China Sea on the same date (11 April, 2001). Although the sampling locations were different, concentrations of diacids were higher near sea surface during a strong dust event.

3.2. Variation of dicarboxylic acids over the Asian/Pacific region

Figure 3 presents the variations of the concentrations of diacids in the Asian Pacific aerosols collected from April 8 to May 4, 2001. During the ACE-Asia campaign, high mineral dust events were observed on 10-12 and 24-27 April 2001 in many sites in East Asia. For example, very high concentrations of dust (up to $400 \mu\text{gm}^{-3}$ and $170 \mu\text{gm}^{-3}$, respectively) were recorded at Gosan site in Cheju Island [Kawamura et al., 2002]. During these two events, the diacid concentrations also increased, but they were not the highest in the sampling period (see Figure 3 for RF06/07 and RF13/14). The highest concentrations of diacids were obtained in the April 29 sample (RF15), which will be discussed later. This indicates that the source regions of diacids and their precursors are different from those of mineral dust, although both are located in the Asian continent. The latter is transported from the arid regions such as Gobi and Takla Makan deserts [Duce et al., 1980, 1991] whereas the former is associated with anthropogenic activities in the mega cities in Southeast Asia [Wang et al., 2002]. During ACE-Asia in Sapporo, Japan, we found that diacids and calcium are present in different sizes, with the former being enriched in fine particles and the latter in coarse particles [Kobayashi et al., unpublished results, 2002].

On 29 April, the ACE-Asia weather forecast team at Iwakuni predicted a strong outflow of polluted air masses from the Asian continent over the Yellow Sea and Sea of Japan. Hence, the research flight (RF 15) was designed to fly over the Yellow Sea, Korean Peninsula and Sea of Japan to collect these polluted aerosol samples (see Figure 4 for the flight track). As expected, the concentration levels of diacids, especially oxalic acid, were the highest in this sample. Furthermore, the color of the filter sample was the darkest and the concentration of OC was the highest among the samples studied. In general, the colors of filter samples were very light, either white or just slightly darkened. This suggested that the heavily polluted air masses were transported over the sampling areas on 29 April. It may be important to note that the highest level of oxalic acid (650 ngm^{-3}) in the Asian aerosols is about one half of the highest concentration (ca. 1200 ngm^{-3}) reported for the plume of biomass burning over central Africa [Ruellan et al., 1999].

Throughout the aircraft campaign, concentrations of diacids were higher the closer we were to the Asian continent. For example, during the flights RF06, 07, 13, 14, 15 and 18 over the Yellow Sea and Korean Peninsula, we obtained high concentrations of LMW diacids. These results seem to be consistent with the results of Narukawa et al. [2003], who reported a longitudinal decrease (from the west to the east) of oxalic and other diacids in the aerosols collected by aircraft in the free troposphere over the western North Pacific. However, the concentration levels in the present Asian aerosols are much higher than those (less than 100 ngm^{-3}) in February 2000 [Narukawa et al., 2003]. The difference in the diacid concentrations can be explained as follows. First, most of the aerosols studied by Narukawa et al. [2003] were collected in the free troposphere over the far east from the Asian continent (over the western North Pacific) whereas the samples studied here were collected in lower levels of the atmosphere including the marine boundary layers in the Asian Pacific region (over the Yellow Sea, East China Sea and Japan Sea). Second, the samples of Narukawa et al. [2003] were collected in February, two months earlier than the spring dust season. This study suggests that outflow of polluted air masses from the Asian continent is stronger in April than February.

3.3. Possible sources and formation processes of dicarboxylic acids

To better understand the sources and formation mechanisms of water-soluble organic acids, we conducted statistical analyses using the data sets of the aerosol samples ($n=15$). Table 2 shows correlation coefficients for the organic acids detected. A strong positive correlation ($r^2 > 0.75$) was obtained between saturated C_2 to C_5 diacids. Similar correlation has been reported for the diacid species in the marine aerosols collected from the western and central Pacific [Kawamura and Sakaguchi, 1999]. Kawamura and Sakaguchi [1999] proposed that the small diacids are mainly produced by atmospheric oxidation of anthropogenic hydrocarbons during long-range atmospheric transport of polluted air mass as well as transport of the compounds from the polluted regions. Mochida et al. [2003b] reported 4 years of observation on LMW diacids in the marine aerosols collected from the remote island, Chichi-Jima, in the western North Pacific. They combined the data sets of diacid

concentrations and the back air trajectory as well as emission inventory data (black carbon from fossil fuel burning). Based on the chemical and meteorological data analyses, they demonstrated that concentrations of C₂-C₇ diacids in the western North Pacific atmosphere are most likely controlled by the emissions of pollutants from anthropogenic sources in the Asian continent, followed by a long-range atmospheric transport and photochemical transformation.

Figure 5 presents a relationship ($r^2 = 0.70$) between the concentrations of oxalic acid and total organic carbon (TOC). The data is grouped into three categories by the concentrations of "OCvol," which is the fraction of aerosol OC that volatilized from the quartz filter and was collected by a backup carbon-impregnated glass fiber filter. The relationship between the oxalic acid concentrations and aerosol TOC was found, for the first time, in the tropospheric aerosol samples collected by aircraft. This result indicates that oxalic acid and TOC are from similar sources and source regions, and perhaps even formation processes. A similar positive correlation was found for other diacids, although the correlation coefficients with TOC ($r^2 = 0.27, 0.22, \text{ and } 0.32$ for C₃, C₄, and C₅, respectively) are lower than that ($r^2 = 0.70$) for C₂ diacid.

Total diacid-carbons were found to account for 0.24-3.3 % (av. 1.8 %) of TOC in the Asian aerosols. The variation in the values may indicate a different degree of photochemical alteration of organic aerosols, or it may be uncertainty due to the small sample volumes we could collect from the aircraft. The upper range of the airborne sample values for diacids are higher than those (0.2-1.8 %, av. 0.95 %) reported in the urban Tokyo aerosols collected at ground level [Kawamura and Ikushima, 1993], but lower than those (2.8-7.9 %) reported in China [Wang et al., 2002]. However, the present values are much lower than those (up to 18 %) reported in the remote marine aerosols from the central Pacific Ocean, in which photochemical aging of organic aerosols produces more highly oxidized compounds [Kawamura and Sakaguchi, 1999]. These comparisons suggest that the tropospheric Asian aerosols collected by aircraft are already aged to a certain degree, but should be further altered to result in the higher proportions of water-soluble organic acids in the organic aerosols during long-range transport.

4. Conclusions

Oxalic, and to a lesser extent, malonic and succinic acids were, for the first time, detected (up to 650 ngm^{-3} for oxalic acid) in the tropospheric aerosols collected by aircraft over the polluted East Asia/North Pacific region. Total dicarboxylic acids (C_2 to C_5) were found to account for 0.2-3.3 % (av. 1.8 %) of total organic carbon (TOC) contents in the aerosols. Concentrations of diacids positively correlated to TOC, with oxalic acid showing best correlation coefficient ($r^2 = 0.70$). The water-soluble organic acids either directly emitted from the ground sources and/or photochemically produced in the polluted troposphere over the Asian Pacific are important species in controlling the chemical and physical properties of atmospheric particles.

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Figure Captions

Figure 1. Sampling areas of C-130 aircraft campaign over the Asian Pacific region. Bold lines indicate the flight tracks of the aircraft during the sample collection of aerosol filters used in this study. The flight started at Iwakuni Base (indicated as star) generally at 9 am and ended at 5 pm. The aircraft usually flew in the dust plumes and/or polluted air masses during aerosol sampling with the altitudes ranging from ca. 40 m to ca. 7000 m in height. Prevailing winds were from the west to east or northeast during sampling periods.

Figure 2. Schematic diagram of PC-BOSS sampler used for the ACE-Asia C-130 campaign. Sideall quartz filter was used in this study. TMF means a thermal mass flowmeter. CIG means carbon impregnated glass fiber filter, which was used to collect any OC that may have volatilized from the quartz filter. This measures what might otherwise have been a negative artifact.

Figure 3. Variation of the concentrations of dicarboxylic acids in the aerosol samples collected in the Asian/Pacific region during C-130 research flights (RF05 to RF19) in 2001. For abbreviations, see Table 1.

Figure 4. C-130 flight track for RF15 (29 November 2001). The narrow blue lines mean a whole track during the flight. Bold red lines indicate the tracks during sampling period for the aerosol filter used in this study. The narrow black line indicates the 2D flight track on the ground level.

Figure 5. Relationship between concentrations of oxalic acid (C_2) and total organic carbon (TOC) contents in the Asian/Pacific aerosols collected by C-130 aircraft. TOC data were from Bertram et al. [2003, to be submitted]. TOC was calculated by averaging the values for 3 to 5 quartz filter samples collected by PC-BOSS sampler during the same flight.

Two points (RF05 and RF16) indicated by opened square were not included in the calculation of correlation coefficient due to a potential loss of aerosol carbon from the quartz filter used. OCvol is defined as a fraction of organic carbon that volatilized on the quartz filter during the passage of the air through the filter [Bertram et al., 2003, to be submitted]. When these two points are included, the correlation coefficient is lower ($r^2 = 0.52$). For OCvol, also see the section 3.3. (second paragraph) in the text.

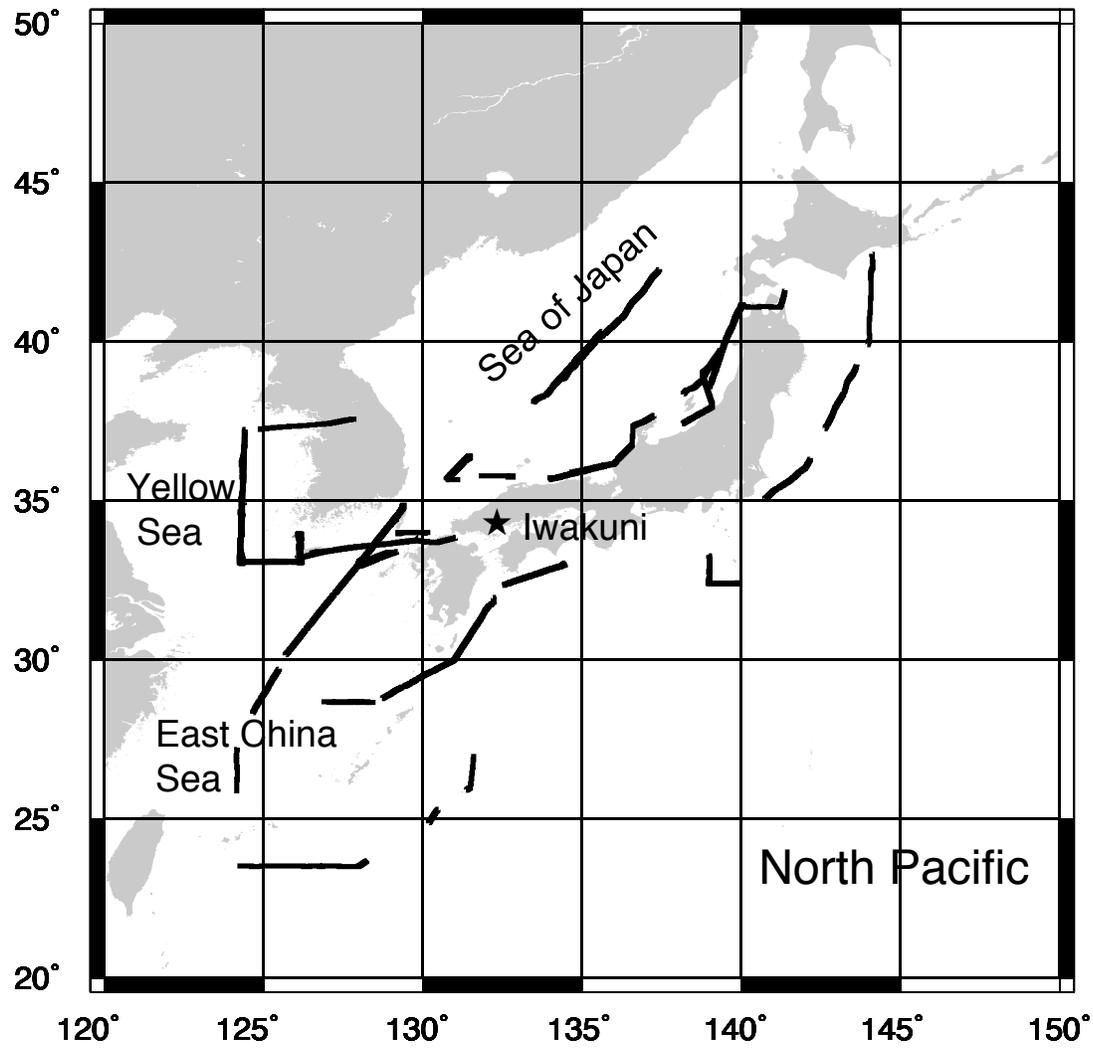
Table 1. Concentrations of dicarboxylic acids detected in the aerosol samples (n=15) collected by C-130 aircraft over East Asia, April to May 2001.

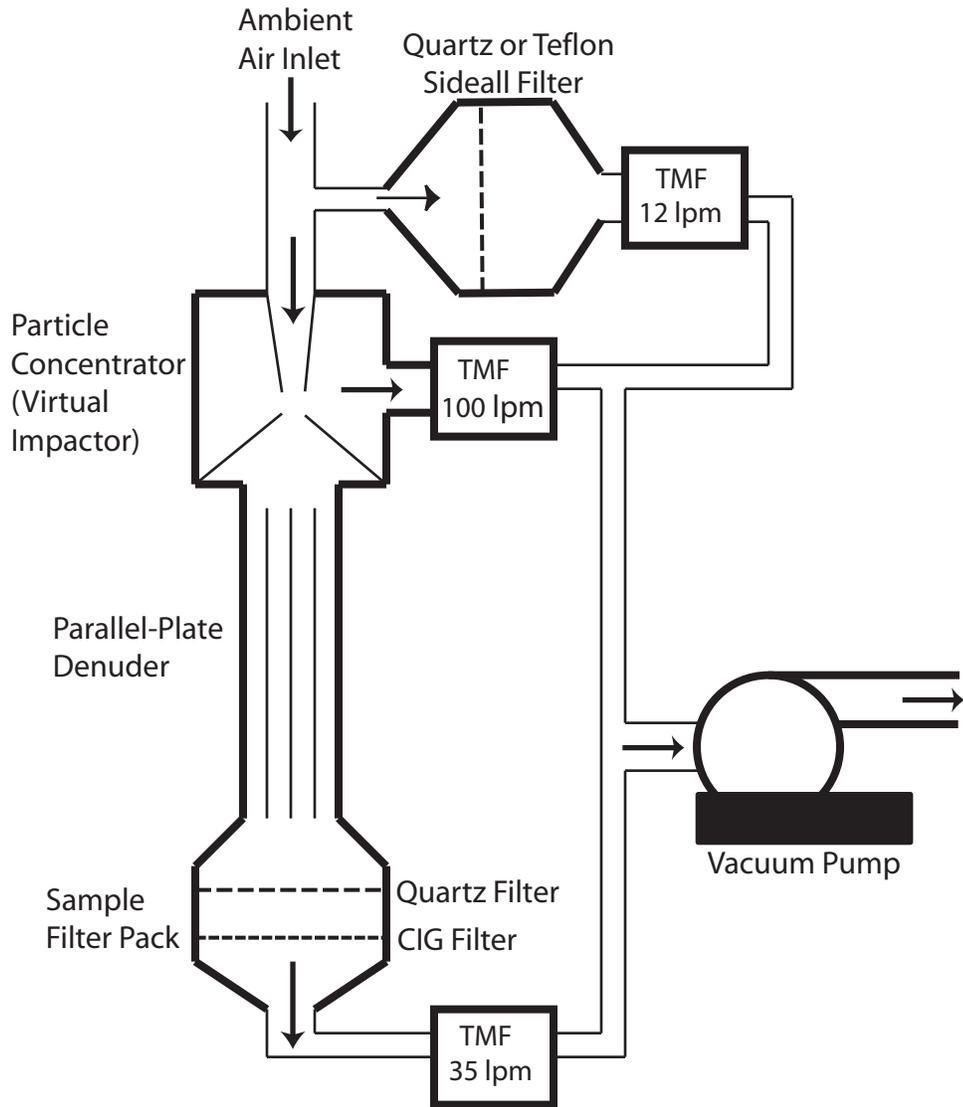
Dicarboxylic acids	Formula	abbrev.	No of samples above DL	Concentrations (ng m ⁻³)			
				Min	Max	Average	Median
Oxalic	HOOC-COOH	C ₂	15	26.1	656	239	214
Malonic	HOOC-CH ₂ -COOH	C ₃	15	2.7	87	40	36
Succinic	HOOC-(CH ₂) ₂ -COOH	C ₄	12	BDL	96	21	17
Glutaric	HOOC-(CH ₂) ₃ -COOH	C ₅	12	BDL	26	7.5	5.4
Methylmaleic	HOOC-CH=C(CH ₃)-COOH	mM	13	BDL	15	4	3

BDL: below detection limit (DL), DL are ca. 0.1 to 7 ng m⁻³ depending on species.

Table 2. Correlation coefficients (r²) among dicarboxylic acids in the Asian/Pacific aerosols collected by C-130 aircraft in 2001 April 8 to May 4.

Diacids	C ₂	C ₃	C ₄	C ₅
C ₂	1.00			
C ₃	0.75	1.00		
C ₄	0.87	0.92	1.00	
C ₅	0.95	0.82	0.96	1.00





ACE-Asia C-130 PC-BOSS Sampler

