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Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition

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Abstract

Atmospheric particles were collected for one year (2001-2002) at a site Gosan on Jeju Island, South Korea. The samples were analyzed for water-soluble dicarboxylic acids and related compounds using a capillary GC and GC/MS. Total carbon and nitrogen contents, as well as their stable isotopic ratios, were also determined using elemental analyzer (EA) and EA/IR/MS, respectively. Elemental and isotopic analyses were also performed after the HCl vapor treatment of aerosol samples. The results demonstrate that calcium carbonate of dust origin was not a significant component, except for a few dust event samples. Carbonates most likely reacted with acidic species (such as H_2SO_4, HNO_3 and organic acids) in the atmosphere during a long-range transport, and did not contribute to the total aerosol carbon, except for few strong dust episodes that occurred in spring. This study also demonstrates that nitrate and ammonium largely contribute to aerosol nitrogen and organic nitrogen is minor component in the Asian aerosols. Acidic aerosols enriched with sulfate likely adsorb NH_3 gas that is emitted from soils in Asia whereas mineral dust particles containing carbonate may adsorb HNO_3 and volatile organic acids.

Homologous series of dicarboxylic acids (C_2-C_{12}) including unsaturated structures as well as ketocarboxylic acids (C_2-C_9) were detected in the aerosol samples with oxalic (C_2) acid being the most abundant species followed by malonic (C_3) or succinic (C_4) acids. Total concentrations of diacids (130-2070 ng m^{-3}) are one or two orders of magnitude greater than those reported for remote marine aerosols in the North Pacific, but are equivalent to those reported for urban aerosols. Very high concentrations of dusts (up to 880 μg m^{-3}) and water-soluble dicarboxylic acids were often observed in early spring. However, their correlation ($r=0.27$) is not strong throughout the campaign. Although both mineral dusts and diacids are derived from the Asian continent, they originate from different sources and source regions. Diacids are probably emitted from urban sources in East Asia and produced by secondary photochemical oxidation of their precursors, whereas dusts are derived from the arid interior regions. This study provides evidence for photochemical production of water-soluble organic acids in East Asia and the western North Pacific rim.

1. Introduction

Organic acids are ubiquitous in the atmosphere (e.g., Kawamura and Kaplan, 1991), natural waters (e.g., Thurman, 1985) and sediments (e.g., Lewan and Fisher, 1994). Due to the carboxyl groups, they play an important role in geochemical processes on the earth surface in several ways. For example, small organic acids such as formic, acetic, and oxalic acids dissolve calcium carbonate and other minerals resulting in a secondary porosity in sedimentary rocks (Surdam et al., 1984). This process contributes to the migration of oils that are produced from geopolymers such as kerogen (e.g., Tissot and Welte, 1984). Although the sources and formation mechanisms are still not well understood, microbial oxidation of organic matter and thermal degradation of geopolymers (kerogen and humic acids) are important sources of organic acids (Kharaka et al., 1983; Kawamura et al., 1986; Kawamura and Kaplan, 1987; Lewan and Fisher, 1994). Small organic acids are abundantly present in oil formation waters (Kharaka et al., 1983). Organic acids also form organo-metal complexes in the sedimentary and aquatic environments. This process accelerates the dissolution of trace metals in sediments and particles in the natural waters. The formation of the metal complexes has an impact on the geochemical behaviors of metals in river and ocean waters as well as sediments, controlling their distribution and transport on the earth surface.

Organic acids are also present in the atmosphere as gases, adsorbed on particles as well as dissolved in rainwaters and on snow crystals (Grosjean et al., 1978; Dawson et al., 1980; Keene et al., 1983; Kawamura and Kaplan, 1985; Kawamura et al., 1985a,b; Kawamura and Kaplan, 1991; Nolte et al., 1997). Mono- and di-carboxylic acids have been reported in continental aerosols (Grosjean et al., 1978; Norton et al., 1983; Kawamura and Kaplan, 1986; Satsumabayashi et al., 1990; Kawamura et al., 2000; Wang et al., 2002), marine aerosols (Kawamura and Usukura, 1993; Barboukas et al., 2000; Kawamura and Sakaguchi, 2001, Mochida et al., 2003a) and aerosols from polar regions (Li and Winchester, 1993; Kawamura et al., 1996a,b; Narukawa et al., 2002). Because they are very water soluble, their presence in the aerosols alters the chemical and physical properties of atmospheric aerosols (Saxena et al., 1995). In general, atmospheric particles act as cloud condensation nuclei (CCN) and contribute to the formation of cloud droplets (e.g., Yu, 2000). In these processes, organic acids serve as an agent to enhance hygroscopic properties of the particles and play an important role in the cloud processes. This effect is important, as the water-soluble properties of organic aerosols indirectly control solar radiation out at the earth's atmosphere, thus cooling the earth surface (IPCC 2001). On a regional scale, such as the Asian Pacific region, aerosols produced by anthropogenic activity could reduce the effect of global warming caused by greenhouse gas on a global scale (Huebert et al., 2003).

Nitrogen is also important atmospheric composition and is abundantly present in aerosols and rain (e.g., Yeatman et al., 2001; Mace et al., 2002). For example, total nitrogen contents in urban aerosols from Tokyo are relatively high comprising 2-15 % (av. 5 %) of aerosol mass (Kawamura et al., 1995). The weight ratios of total nitrogen to total carbon in the aerosols are on average 4.8 (range, 2.1-10.9). Occasionally, aerosol nitrogen is about a half of the carbon content. Although nitrate and ammonium ions have been most extensively studied in aerosols, their relationship to total aerosol nitrogen has not been studied. Further, stable carbon and nitrogen isotopic ratios of aerosols have not extensively been studied (Chesselet et al., 1981; Cachier et al., 1986; Narukawa et al., 1999; Yeatman et al., 2001; Martinelli et al., 2002; Turekian et al., 2003). However, they could provide additional information on the source and source region of aerosols and their transformation processes in the atmosphere.

In this study, we conducted an organic geochemical study on the atmospheric particles collected at a site in Gosan on Jeju Island off Korea Peninsula. Particular attention has been paid to atmospheric chemical studies in East Asia because anthropogenic emissions of gas and aerosols in this region are significant on a global scale due to the growing industrial activity (Huebert et al., 2003). Further, arid inland areas (such as Gobi and Takla Makan deserts) are important source regions in spring for long-range atmospheric transport of mineral dusts over the Pacific (e.g., Duce et al., 1980; Uematsu et al., 1983; Mori et al., 2002) and contribute to the sediments in the deep ocean floor (e.g., Blank et al., 1985). The Gosan site has been used as a "super site" of ground stations during an intensive period of the ACE-Asia (Asian Pacific Regional Aerosol Characterization Experiment) campaign (Huebert et al., 2003). Jeju Island is located in the pathway of atmospheric transport of the aerosol particles from the Asian continent to the Pacific. Here, we report on one year measured data of water-soluble organic compounds (dicarboxylic acids, ketoacids and dicarbonyls) and total carbon and nitrogen contents as well as their stable isotopic ratios. We also report on the chemical characterization of major ions and total carbon and nitrogen as well as their stable isotopic composition, and discuss the contribution of soil dust to the aerosols and their transformation processes in the atmosphere during a long-range transport.

2. Experimental

Aerosol sampling (totally 107 samples) was conducted at Gosan site on Jeju Island (33°29'N, E126°16'E) as part of ACE-Asia campaign from April 2001 to March 2002 on a daily or few days basis. The island (126.08 – 126.58°E, 33.06-126.58°N, area: 1,847 km^2) is located at the boundary of the Yellow Sea and the East China Sea, and is surrounded by mainland China, Korea Peninsula, and Kyushu Island, Japan (Fig. 1). The Gosan site is located on a cliff (elevation: 71 m above sea level) on the western edge of the island facing the Asian continent and is isolated from residential areas. The population of the island is 552,000, but major residential areas are located entirely on the northeast side of the island. Dominant winds are westerlies in winter to spring whereas winds from the Pacific (from the south) occur in summer. Aerosol particles were collected on pre-combusted (450°C, 3 hours) quartz fiber filters (Pallflex 2500QAT-UP, 20 cm x 25 cm) using a high-volume air sampler (Kimoto AS-810). The sampler was installed on top of a tower (15 m above the ground) during April 2001. After May 2001, the sampler was moved to the rooftop of a trailer, at a height of ca. 3 m above ground. Before and after the sampling, filters were stored in a clean glass jar (150 ml) with a Teflon-lined cap. The filter samples were stored at –20°C in a dark room prior to analysis. Several field blanks were taken at the site by attaching the filter to the sampler for few seconds without sucking air. Aerosol mass concentrations were obtained by weighing the quartz filter before and after the aerosol sampling.

Totally, 48 aerosol filter samples were used for the analysis of water-soluble diacids and related compounds using the method described in Kawamura and Ikushima (1993) and Kawamura (1993) with some modification. Briefly, aliquots of the filters were extracted with pure water (5 ml x 3), followed by the extraction with ethyl acetate (5 ml x 3). The latter solvent was used to extract fatty acids and other lipids. The extracts were combined and concentrated using a rotary evaporator under a vacuum and then dried using a nitrogen blow-down system under atmospheric pressure. The concentrated extracts were reacted with 14 % BF_3/n-butanol in a pear-shaped flask (25 ml) to derivatize carboxyl groups to butyl esters and carbonyl group to dibutoxy acetals. The derivatives were extracted and then analyzed with a HP 6890 gas chromatograph (GC) installed 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 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.

Identification of the diacid butyl esters was conducted by comparing the GC retention times with those of authentic standards. Mass spectra of the organic compounds were also obtained with a GC/MS (ThermoQuest, Trace MS) using a similar GC condition. Duplicate analyses of several filter samples showed that the analytical errors for major diacids were within 10 %. Spiked experiments using authentic standards (oxalic, malonic, succinic and adipic acids) into quartz filter showed that recoveries were 77 % for oxalic acid and better than 86 % for other diacids. Recoveries of glyoxylic acid, pyruvic acid, and methylglyoxal were 88 %, 72 %, and 47 %, respectively (Kawamura and Yasui, in preparation). The procedural blanks showed that contamination levels of the diacids during the analysis were less than 5 % of the sample. The data reported here are corrected for the procedural blanks, but not for recoveries.

For the total carbon (TC) and nitrogen (TN) analyses, aerosol filter samples (n=107) were cut in small disk (area, 3.14 cm^2) and analyzed using an elemental analyzer (EA) (Carlo Erba, NA 1500). Stable carbon and nitrogen isotopic analyses were also conducted using the same EA interfaced to isotope ratio mass spectrometer (IRMS) (ThermoQuest, Delta Plus) by the method described in Narukawa et al. (1999). The samples were analyzed in duplicate and averaged concentrations and isotopic ratios are reported here after the blank correction. Reproducibility of TC and TN measurements was within 2 %. Analytical errors in the carbon and nitrogen isotope ratios were within 0.2 and 0.3 ‰, respectively. In order to remove carbonate carbon from the aerosol TC, other filter cuts were treated with HCl vapor as follows. Each filter cut was placed in a 50 ml glass vial and was exposed to HCl vapor overnight in a glass (10 liter) desiccator. Excess HCl was removed from the sample with NaOH and P_2O_5 in a desiccator. The HCl-treated filters were analyzed for TC and TN as well as their isotopic ratios as described above. We found a loss of TN content during the HCl treatment due to the evaporative removal of nitrate (as HNO_3) from the filter sample.

Aliquots of filter samples (0.78-3.14 cm^2) were also analyzed for major anions and cations using ion chromatography (Dionex, DX-500) by the method described in Narukawa et al. (2002). Duplicate analyses of the aerosol samples showed the analytical errors to be within 20 %.

3. Results and Discussion

3.1. Total aerosol mass concentrations

Throughout one-year observation of aerosols at Jeju Island, we found enhanced concentrations of total aerosol mass in spring, as shown in Fig. 2a. Total aerosol masses were generally around 100 μg m^{-3} or less, but they significantly increased in spring to more than 400 μg m^{-3}. Especially, we observed the concentration of more than 800 μg m^{-3} in 2002 March. Very high dust concentrations (up to 640 μg m^{-3}) were also recorded in Sapporo, Hokkaido, Japan (Kawamura et al., 2002). Higher concentrations observed in spring are associated with strong westerly winds and uplift of mineral dusts from main land China and Mongolia. In fact, very high aerosol mass concentrations (1,000 to 10,000 μgm^{-3}) have been reported in spring near the source regions of the interior Asian continent (Mori et al., 2002). These values obtained in the coastal Southeast China Sea off Korea Peninsula are much higher than those reported in Tokyo (54-314 μg m^{-3}, av. 108 μg m^{-3}, Kawamura and Ikushima, 1993) and those observed at Chichi-jima Island in the western North Pacific (11-292 μg m^{-3}, av. 53 μg m^{-3}, Kawamura et al., 2003a). These results suggest that most of the peaks are involved with the outflow of Asian dusts from arid regions in Mongolia and Takla Makan deserts (Duce et al., 1980; Uematsu et al., 1983).

Air mass trajectory analyses demonstrated that air masses in winter and spring mostly came from the west (Asia). In contrast, southerly winds often came from the Pacific Ocean in the summer time. We also observed very high concentrations of Ca in aerosol samples with a high mass. The correlation coefficient between aerosol mass and Ca concentration is high ($r = 0.90$) for all samples, as seen in Fig. 3a, although the highest correlations were found to occur at specific times in the year. For example, correlation was very strong for the 2001 spring ($r = 0.997$, April 12-20, see Fig. 3b) and the winter season ($r = 0.98$; October 2002 to March 2003) whereas it was very weak ($r = 0.02$) for the summer season (June to September, 2002). Dusts are mostly derived from Asian continent in winter to spring and marine contributions are in general not important for the aerosol samples studied over Jeju Island ($r = 0.51$ for both the aerosol concentrations and Na).

3.2. TC contents and stable carbon isotopic ratios

Table 1 summarizes the results of total carbon (TC) and nitrogen (TN) measurements of the aerosol samples as well as stable carbon and nitrogen isotopic composition and major ions. Total carbon contents ranged from 1.3 μg m^{-3} to 22.9 μg m^{-3} with an average of 6.5 μg m^{-3}. These values are much lower than those observed in urban areas such as Tokyo (10.2-44.1 μg m^{-3}, av. 22.3 μg m^{-3}, Kawamura and Ikushima, 1993) and Beijing (24-85 μg m^{-3}, av. 49 μg m^{-3}, Sekine et al., 1992). However, they are much higher than those reported for the remote marine atmosphere in the Pacific (e.g., Chichi-jima, 0.11-1.9 μg m^{-3}, av. 0.63 μg m^{-3}, Kawamura et al., 2003a). These results suggest that Jeju Island located in the western Pacific rim is heavily influenced from the Asian continent, where both emission of mineral dusts and organic pollutants are significant. TC/aerosol mass ratios for the Jeju samples (1.2-13.7 %, av. 6.6 %, see Table 1) are lower than those obtained from year-round observation in Beijing (9.2-23 %, av. 17 %, Sekine et al., 1991) and Tokyo (9.2-38 %, av. 21 %, Kawamura and Ikushima, 1993). However, they are much higher than those (0.2-5.4 %, av. 1.8 %, Kawamura et al., 2003a) obtained in Chichi-jima in the western North Pacific (see Fig. 1 for the map).

Fig. 4a presents seasonal changes in the TC contents in the aerosol samples collected over Jeju Island without and with HCl treatment. Highest TC values were measured in spring and autumn and less frequently in winter, whereas lowest values were measured in summer. Total organic carbon (TOC) that is defined as TC obtained after HCl treatment of aerosols shows seasonal changes similar to TC (Fig. 4a). The values of TOC are sometimes significantly lower than those of TC. The results indicated that up to 30 % of total carbon were removed from the aerosols by the treatment with HCl vapor. However, the highest removal rates were limited to some samples collected in March, May, October and November. Summer and winter samples did not show a significant decline of TC after the HCl treatment except for one sample (KOS43, July 9-16, 2001). The removed carbon may have existed as carbonate and/or volatile organic forms as discussed later.

Fig. 4b presents carbon isotope ratios for TC (without HCl treatment) and TOC (with HCl treatment). δ^{13}C values of TC ranged from –15.5 ‰ to –26.6 ‰ whereas those of TOC ranged from –17.9 ‰ to –23.5 ‰. Interestingly, δ^{13}C values of TC for the spring samples indicated heavier isotopic ratios more than –20 ‰ and the rest of the samples showed a range of –23 ‰ to –25 ‰. Such heavier isotopic ratios (> -20 ‰) have not generally been reported in the previous study on marine aerosol samples (e.g., Chesellet et al., 1981; Cashier et al., 1986; Turekian et al., 2003), aerosols affected by forest fires (Narukawa et al., 1999) and aerosols from Amazon (Martinelli et al., 2002) . The heavy isotope ratios may be associated with the presence of carbonate carbon derived from desert dusts, which generally contain calcium carbonate whose δ^{13}C values are close to zero (Craig, 1953). In fact, yellow sand (Kosa) samples collected from the loess layer (1.8-2.5 m from the surface) in Gunsu Province of China (Nishikawa et al., 2000) showed that 1.44 -1.69 % of the dusts were present as inorganic carbon (corresponding to 62-93 % of total carbon, see Table 2).

We analyzed the desert dust samples (yellow sand samples) for carbon and nitrogen isotopic composition with and without HCl treatment (Table 2). Using isotopic mass balance equations as below, carbon isotopic ratios of removed carbon from the Chinese loess samples ($\delta^{13}C_{\text{Removed C}}$) were calculated to be –0.3 ‰ to –1.3 ‰ (Table 2), suggesting that removed carbon was present as carbonate.

$$TC = TOC + \text{Removed Carbon (mostly carbonate such as } CaCO_3\text{) by HCl treatment}$$

$$f_{TOC} + f_{Removed\ C} = 1$$

$$f_{TOC} = TOC/TC, \quad f_{Removed\ C} = (TC - TOC)/TC$$

$$\delta^{13}C_{TC} = f_{TOC} \times \delta^{13}C_{TOC} + f_{Removed\ C} \times \delta^{13}C_{Removed\ C}$$

In the equations above, f_{TOC} and $f_{Removed\ C}$ refer to a fraction of TOC and removed C in total carbon (TC), respectively. These results suggest that Asian aerosols transported from arid regions should contain abundant carbonate carbon when aerosol sampling was conducted during strong dust events.

Using the same mass balance equations, we calculated stable carbon isotopic ratios for the removed carbon from the aerosols by HCl treatment. The results of aerosol samples showed $\delta^{13}C$ ratios for the removed carbon ranging from –35 ‰ to +3 ‰ with an average of -22 ‰ and median of -24 ‰. Fig. 5 describes the seasonal variation of the amounts of removed carbon from the aerosol samples as well as their $\delta^{13}C$. The $\delta^{13}C$ data are presented for the samples whose removal rates are > 5% because of the low accuracy for the samples with the lower removal rates. These data demonstrate that, except for a few samples collected in spring, major portion of the removed carbon by HCl treatment are not carbonate, rather they are largely composed of organic carbon. Low molecular weight organic acids are likely candidates for removed organic carbon. Sakugawa and Kaplan (1995) reported carbon isotopic ratios for formic acid (-28 ‰ to -31 ‰, mean: -30 ‰) and acetic acid (-18 ‰ to -21 ‰, mean: -20.5 ‰) in Los Angeles atmosphere. More recently, Glasius et al. (2001) reported $\delta^{13}C$ values of formic plus acetic acids in the atmosphere of Europe to be -23 ‰ to –31 ‰.

These organic acids are abundantly present in the urban atmosphere (e.g., Kawamura et al., 2000), thus it is reasonable to consider that volatile organic acids (present as salts in aerosols) are removed by HCl vapor treatment. Although they are mostly present as gases, a small portion of the acids (less than 20%) in the atmosphere may be strongly adsorbed on aerosol particles as well (Kawamura et al., 1985b). Thus, formate and acetate that are originally present as particles can be removed from the aerosols by evaporation on exposure to HCl vapor. Some dicarboxylic acids such as oxalic acid could also be removed from aerosols by exposure to HCl. We measured the carbon isotopic ratios of oxalic acid in the selected aerosol samples and found their carbon isotopic values to be in a range from -17.6 ‰ to -21.9 ‰ (Kawamura et al., 2002, unpublished results). Turekian et al. (2003) reported the δ^{13}C values of oxalate in the Bermuda aerosols to be around -21 ‰.

In contrast, several spring samples showed significantly heavier isotopic values around 0 ‰ for the removed carbon by HCl treatment (Fig. 5). This suggests that a major portion of the removed carbon is not organic. They are rather derived from carbonates originated from desert dusts, which may be long-range transported through the atmosphere from arid regions in Asia. The aerosol samples whose δ^{13}C values for the removed carbon are isotopically heavy (> -5 ‰), were all collected during strong dust events (dust concentrations ≥ 270 μg m^{-3}). Some other samples that were collected in spring showed carbon isotopic ratios between –10 ‰ and –20 ‰. These results indicate that mineral dusts containing carbonate are transported over the western Pacific rim without total dissolution by acidic components such as sulfuric acid. However, such a transport is limited to the spring season when strong dust events generally occur. We believe that carbonates uplifted in the air most likely adsorb acidic gas and particles such as nitric acid, sulfuric acid, and possibly organic acids. Then, they react with carbonates in the aerosols to release CO_2 to the air during a long-range transport over the Asian continent. The precursor gases (SO_2, NO_x and volatile organic compounds) of the acidic species are emitted from industrial locations and converted to inorganic and organic acids in the atmosphere. These acids are generally in sufficient concentration to quantitatively remove aerosol carbonates within the atmosphere of East Asia, except during strong dust events, when the atmospheric titration by the acids is insufficient.

3.3. TN contents and nitrogen isotopic ratios

Fig. 6a presents a seasonal change in the total N (TN) contents and those after the

HCl treatment of aerosol samples. By the HCl vapor treatment, 7-70 % (av. 40 %) of nitrogen was removed. Removed nitrogen is present as nitrate. This is supported by the positive correlation (r = 0.92) obtained between NO_3^- and removed N with the slope close to unity and intercept of nearly zero (see Fig. 7a). Nitrate was found to account on average for 41 % (median: 40 %, range: 4-90 %) of the TN in the Asian aerosols. In contrast, ammonium nitrogen comprises on average 50 % of TN (median: 51 %, range: 7-90 %) in the aerosols. Interestingly, a strong correlation was obtained between NH_4 measured by IC and total N (hereafter defined as remained N) measured by EA after the HCl vapor treatment (see Fig. 7b). Further, NO_3 plus NH_4 nitrogen correlate well with TN contents, as seen in Fig. 7c. These results demonstrate that nitrate and ammonium ions account for a significant portion of TN, indicating that organic nitrogen is less important fraction in the Asian aerosols. Asian aerosols enriched with acidic species may significantly adsorb NH_3 that is released from soils. NH_3 also react with acidic gases (HNO_3, H_2SO_4, RCOOH) to result in a small particle, which will be further incorporated to pre-existing aerosols.

Fig. 6b presents seasonal changes in the $\delta^{15}N$ for the aerosol TN and remained N (after HCl treatment). The nitrogen isotopic ratios for the bulk aerosols ranged from –3.7 ‰ to 12.4 ‰ with an average of 4.2 ‰ whereas those after HCl treatment ranged from –5.4 ‰ to 21.9 ‰ with an average of 6.6 ‰ (Table 1). It was found that $\delta^{15}N$ of aerosols collected in spring and summer generally shift to heavier values on HCl treatment (Fig. 6b) and vice versa for winter samples. The results of spring and summer samples suggest that removed nitrogen (mostly as HNO_3) should have relatively lighter values. Negative $\delta^{15}N$ values (e.g., -12 ± 9 ‰) were reported for aerosol NO_3^- in the coastal sites of UK (Yeatman et al., 2001). Using the similar isotopic mass balance equation for carbon isotopic ratios, $\delta^{15}N$ values were calculated for the removed N as follows.

TN = Remained N + Removed Nitrogen (mostly HNO_3) by HCl treatment

$f_{\mathrm{Remained\ N}} + f_{\mathrm{Removed\ N}} = 1$

$f_{\mathrm{Remained\ N}}$ = Remained N/TN, $f_{\mathrm{Removed\ N}}$ = (TN - Remained N)/TN

$$\delta^{15}N_{\text{Remained N}} = f_{\text{Remained N}} \times \delta^{13}C_{\text{Remained N}} + f_{\text{Removed N}} \times \delta^{15}N_{\text{Removed N}}$$

Fig. 8 presents a seasonal variation of $\delta^{15}N$ values for the removed N (mostly as HNO_3) together with the amount of removed N. In general the $\delta^{15}N$ values are lower in summer (-1.7 ‰ for the average of May to September samples) than in winter (+4.6 ‰ for the average of November to February samples), although very light $\delta^{15}N$ values were obtained for some spring sample.

The present result shown in Fig. 8 is consistent with the seasonal trend of $\delta^{15}N$ of NO_3^- in aerosols (2-8 ‰) collected in Germany (Freyer, 1991), although our values for removed N are a little lighter. A similar seasonal trend of $\delta^{15}N$ values was reported for rainwater NO_3^-, although the values are much lower (-6 ‰ to +1 ‰) (Freyer, 1991). The heavier isotopic ratios in winter may be due to reater contribution from coal combustion, because NO_x emissions from coal-fired boilers provide heavier $\delta^{15}N$ values (+6 ‰ to +13 ‰) than the NO_x emissions (-13 ‰ to –2 ‰) from motor vehicle exhausts (Heaton, 1990). Alternatively, winter samples may have more contribution from soil organic nitrogen because their $\delta^{15}N$ values are heavier (-5 ‰ to +25 ‰) (Moor, 1974). Our analyses of Chinese loess samples showed $\delta^{15}N$ values of +2.5 ‰ to +2.7 ‰ (Table 2). However, high dust samples gave generally lighter isotopic values. For example, $\delta^{15}N$ values of removed N showed a negative correlation with non-sea salt Ca (r = 0.55 for January to March, 2002), which can be significantly contributed from desert dusts. Desert dusts contain alkaline salts of Ca, Na and Mg and the aerosols influenced by the dusts may adsorb more gaseous HNO_3. Freyer (1990) reported that $\delta^{15}N$ of gaseous HNO_3 from Germany give more negative values (-2.2 ‰ to –3.0 ‰) compared to those of aerosol NO_3^- (+3.0 ‰ to +6.2 ‰). Heavier nitrogen isotopic ratios were reported for aerosol nitrate in northern (+15 ± 3 ‰) and southern UK (+10 ± 3 ‰) (Yeatman et al., 2001). Very light $\delta^{15}N$ values obtained in spring (Fig. 8) are not available to explain at this moment.

As seen in Fig. 6b, isotopically negative (-5 ‰ to 0 ‰) values of $\delta^{15}N$ (remained N) were obtained for the aerosol samples collected in winter and, to a lesser extent, spring seasons. Such isotopically light values are unlikely caused by organic nitrogen whose $\delta^{15}N$ values are in general isotopically more positive (Peters and Kaplan, 1978; Minagawa et al., 1984). Rather, they may be affected by the occurrence of ammonium salts in aerosols since ammonium N still remain in the aerosol samples after HCl vapor treatment as stated above. Our results are consistent with the isotopically light δ^{15}N values (-11.8 ± 1.1 ‰) of ammonium ion, which have been obtained for rainwater samples over the agricultural area of San Joaquin Valley, California (K. K. Liu and I. R. Kaplan, 2003, personal communication). Ammonia should be abundantly emitted from agricultural areas in Asia and may be trapped by acidic aerosols enriched with sulfate of Asian industrial origin. Further, NH_3 may react with acidic gases (i.e., HNO_3, HCOOH, CH_3COOH, HOOC-COOH) in the air to result in the salts (i.e., NH_4NO_3, $HCOONH_4$, CH_3COONH_4, $(HN_4)_2C_2O_4$), which should coagulate and then associate with pre-existing particles. Although emission of ammonia in agricultural areas should be greater in summer when soil surface temperatures are elevated, the δ^{15}N values of the summer aerosols did not show isotopically light values (see Fig. 6b). This is due to the change in wind direction at Gosan site; southerly winds dominate and westerly winds are weakened in summer.

3.4. Distributions of water-soluble dicarboxylic acids, ketocarboxylic acids and dicarbonyls

We detected homologous series of both α,ω-dicarboxylic acids (C_2-C_{12}) and ω-oxocarboxylic acids (C_2-C_9) in the aerosol samples. Aromatic (phthalic) diacid and mid-chain keto dicarboxylic acids (kC_3, kC_7) were also detected as well as α-ketoacid (pyruvic acid) and α-dicarbonys (C_2-C_3). Fig. 9 displays representative chemical structures of dicarboxylic acids, ketoacids and dicarbonyls detected in the aerosol samples. Throughout the one-year observation, oxalic (C_2) acid was found to be the most abundant water-soluble organic species followed by malonic (C_3) acid and occasionally by succinic (C_4) acid. The predominance of the smallest (C_2) diacid has been reported for the aerosol and rainwater samples from the urban (Kawamura and Kaplan, 1986; Kawamura and Ikushima, 1993; Wang et al., 2002) and remote marine regions (Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Mochida et al., 2003a) as well as the arctic atmosphere (Kawamura et al., 1996a), although some Antarctic aerosol samples showed a predominance of succinic acid (Kawamura et al., 1996b). Relative abundances of longer-chain diacids generally decrease with an increase in their carbon numbers, except for azelaic acid (C_9) that is more abundant than suberic (C_8) acid. This diacid (C_9) is an oxidation product of biogenic unsaturated fatty acids containing double bond at the C9-position (Kawamura and Gagosian, 1997). It is important to note that phthalic acid (aromatic acid) is often the fourth most abundant diacid in the Gosan aerosol samples collected in winter, following succinic acid. This aromatic acid is directly emitted from combustion sources (Kawamura and Kaplan, 1986) and/or has been considered to generate in the atmosphere by photochemical oxidation of aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993).

Table 3 presents concentration ranges and average and median concentrations for dicarboxylic acids, ketocarboxylic acids and α-dicarbonys. Total concentrations of diacids ranged from 130 ng m^{-3} to 2070 ng m^{-3} with an average of 660 ng m^{-3} (Table 3). These values are higher than those (90-1370 ng m^{-3}, average: 480 ng m^{-3}) reported in urban Tokyo (Kawamura and Ikushima, 1993), but are equivalent to the upper range (300-2100 ng m^{-3}) reported in the urban atmosphere from China (Wang et al., 2002). Further, the diacid concentration levels at Gosan site are several times higher than those (6-550 ng m^{-3}, av. 140 ng m^{-3}) reported at Chichi-jima in the western Pacific (Mochida et al., 2003a), a remote island 1000 km south of Japan (see Fig. 1 for the map). Concentration maxima occur most frequently in spring (April-May), but isolated maxima also occur in October, January, and March (Fig. 10a). These results indicate that the East Asian region over the East China Sea is heavily polluted, because small diacids are directly emitted from combustion processing of fossil fuels and subsequent conversion to carboxylic acids and carbonyls in the atmosphere by the photochemical oxidation of anthropogenic organic precursors (Kawamura and Kaplan, 1986; Kawamura and Ikushima, 1993). Ketoacids (2-170 ng m^{-3}, av. 53 ng m^{-3}) and α-dicarbonyls (0.1-84 ng m^{-3}, av. 12 ng m^{-3}) were also detected in the aerosol samples in the Jeju aerosols. Their concentrations are equivalent to those found in Tokyo (Sempéré and Kawamura, 1994; Kawamura and Ikushima, unpublished results).

During the intensive period (April, 2001) of the ACE-Asia campaign, aerosol samples were also collected in the marine boundary layer over the East China Sea, the Japan Sea, and the western Pacific Ocean near the Japanese Islands using the NOAA research ship *R/V* Ron Brown and NCAR aircraft (C-130). Similar concentrations of dicarboxylic acids were reported in the marine aerosols collected by a ship in the East China Sea (360-1300 ng m^{-3}, av. 760 ng m^{-3}, Mochida et al., 2003b), although much higher concentrations (430-1900 ng m^{-3}, av. 1100 ng m^{-3}) were obtained over the Sea of Japan (Mochida et al., 2003b). The data on diacids (130-1350 ng m^{-3}, av. 672 ng m^{-3}) measured at Gosan in April 2001, are consistent with those obtained on the *R/V* Ron Brown, but are much higher than those obtained in open ocean sampling between Japan and Hawaii (290-660 ng m^{-3}, av. 490 ng m^{-3} for the west of the ordinate 140°E, and 31-620 ng m^{-3}, av. 180 ng m^{-3} for the east of 140°E; Mochida et al., 2003b). In contrast, aircraft measurements of diacids at the same locations, but at altitudes ranging from 40 m to 7000 m demonstrated that the diacid concentrations (44-870 ng m^{-3}, av. 310 ng m^{-3}; Kawamura et al., 2003c) are equivalent or several times lower than those obtained at Gosan, Jeju Island. These results demonstrate that the diacid concentrations near the ground surface at Gosan are much greater than those of upper troposphere in the Asian Pacific region and those of the western to central North Pacific.

3.5. Sources of dicarboxylic acids: correlations with NH_4, NO_3, nss-SO_4 and other inorganic species

Based on the studies on dicarboxylic acids in both urban and marine aerosols, it is generally accepted that small diacids in the marine aerosols near coastal regions are derived from direct emission through fossil fuel combustion and photochemical oxidation of the anthropogenic and biogenic organic precursors in the atmosphere (Kawamura and Kaplan, 1986; Satsumabayashi et al., 1990; Kawamura and Ikushima, 1993; Mochida et al., 2003b). Fig. 11 shows relationship of concentrations of total diacids with those of ionic species in aerosols. Total diacids positively correlate with NH_4 (n = 0.83), NO_3 (r = 0.86) and nss-SO_4 (n = 0.83) during one-year observation. Positive correlation (r = 0.83) was also found between total diacids and TN (mostly NH_4 and NO_3 ions). These good correlations support that sources and origin of diacids are involved with combustion sources associated with human activities because nitrate and sulfate are both produced by the atmospheric oxidation of NO_x and SO_2 that are released from combustion sources (Finlayson-Pitts and Pitts, 2000).

We found a very good correlation between the diacid concentrations and concentrations of nss-SO_4 and nitrate in the winter aerosol samples collected from mid November to mid March. As shown in Figs. 11e and 11f, the correlation coefficients are very high ($r = 0.99$). This supports that sources of diacids in winter aerosols are strongly connected with combustion sources in Asian countries. In contrast, there is no relationship between the diacids and Na ($r = 0.05$, See Fig.11d). Similar results were found for Ca ($r = 0.15$), nss-Ca (0.16), Mg (0.05), Cl (0.08) and methanesulfonic acid (MSA) (0.04). Ca, Mg and Cl are important components of seawater whereas MSA is produced in the marine atmosphere by the photochemical oxidation of dimethyl sulfide (DMS) of marine phytoplankton origin (Berresheim et al., 1995). However, diacids positively correlated with K ($r = 0.65$), which is of continental origin. These results suggest that dicarboxylic acids in the aerosols over Jeju Island are derived from continental sources in the Asian industrial areas and also from the photochemical oxidation of anthropogenic organic precursors. We feel that secondary photochemical production of diacids is more significant than the primary emission for the Juju aerosols over the coastal western Pacific.

3.6. Photochemical production and destruction of water-soluble dicarboxylic acids

As seen in Fig. 10b, total diacids accounted for 0.8% to 6.2 % of TC (av. 3.1 %, median 3.0 %) with a maximum in August. These values are consistent with those (1.1-4.9 %, av. 3.2 %) reported in the western Pacific at 35°N to 40°S (Sempéré and Kawamura, 2003). However, they are three times higher than those (0.18-1.8 %, av. 0.95%) obtained in Tokyo (Kawamura and Ikushima, 1993), although a summer time maximum was also found in Tokyo. Higher values for Jeju Island indicate that diacid carbon contributes more to the total aerosol carbon possibly due to higher emissions of organic precursor compounds in the source areas than in Tokyo and their subsequent conversion to dicarboxylic acids in the atmosphere.

Alternatively, aerosols collected at Gosan may have experienced atmospheric oxidative reactions more significantly than urban aerosol samples from Tokyo because Jeju Island is located far away from the major pollution sources in Asian and thus atmospheric residence time of the former aerosols is longer than the latter. Diacids may be effectively produced in the air over Asian continent and the East China Sea during a long-range transport. It is of interest to note that higher total diacid-C/TC ratios (1.1-15.8 %, average 8.8 %, median 8.4 %) have been reported for the marine aerosols collected in the western North to central Pacific including tropics (Kawamura and Sakaguchi, 1999).

Throughout the one-year observation, we found that oxalic (C_2) acid-carbon in TC in the Jeju aerosols increased from spring to summer and decreased toward winter (see Fig. 12a). Similar seasonal trend was obtained for malonic (C_3) acid (see Fig. 12b). These results indicate that small diacids are preferentially produced in the summer time, when solar radiation and ambient temperatures are more suitable for photochemical reaction. However, succinic and other C_5-C_7 diacids did not show an increase in the diacid-C/TC ratios toward summer. C_4-C_7 diacids may be oxidized to result in smaller diacids (Kawamura and Sakaguchi, 1999). In contrast, C_8 and C_9 diacids, as well as $C_{7,\ 4\text{-oxo}}$ diacid, do display a maximum in summer (see Figs. 12f, 12g). Because these long-chain diacids are produced by the oxidation of unsaturated fatty acids, their precursors (biogenic unsaturated fatty acids) are supplied in greater quantity from surface ocean water. This is consistent with the air mass trajectory analyses, which demonstrates that winds originate most often from the Pacific Ocean in summer whereas winds mostly blow from the continents during other seasons of the year. Hydroxysuccinic (malic) acid did not show a seasonal trend (Fig. 12h).

A sharp drop of phthalic acid-C/TC ratios was found in early summer (Fig. 12i). The values decreased by 5 times from early April (ca. 0.1) to late July (ca. 0.02) and gradually increased toward winter (ca. 0.15). This seasonal variation is in contrast to the trend observed for oxalic and malonic acids. Phthalic acid is aromatic acid, which has been reported in diesel exhausts as the second most abundant diacid following oxalic acid (Kawamura et al., 1986) and been proposed to generate by photochemical oxidation of aromatic hydrocarbons (Kawamura and Ikushima, 1993). Because oceanic air mass reaches Jeju Island primarily in summer, contribution of phthalic acid from anthropogenic sources should be depressed whereas its contribution should be enhanced in winter, especially if polynuclear aromatic hydrocarbon-rich coal is used for heating fuel. However, photochemical degradation of phthalic acid may be responsible for the sharp drop of the diacid-C/TC ratios (Fig. 12i). The atmospheric degradation of phthalic acid should produce oxalic acid and some unsaturated diacids through ring-opening reaction. Interestingly, aliphatic unsaturated diacids (maleic, fumaric and methylmaleic acids) also show lower values of diacid-C/TC ratios in summer and higher values in winter (see Fig. 12j for maleic acid). These results suggest that dicarboxylic acids with unsaturated structure are more susceptible to atmospheric oxidation in summer and may serve as precursors of oxalic acid. Because there is no known anthropogenic source on Jeju Island, these unsaturated diacids are transported from the major cities in Asia to the western Pacific with oxidative production and degradation in the atmosphere.

4. Conclusion

We conducted one-year observation of atmospheric aerosols at Gosan site, Jeju Island in the East China Sea to better understand the source and behavior of water-soluble dicarboxylic acids. Aerosol samples were also studied for total carbon and nitrogen contents as well as their isotopic compositions and ionic compositions. Dicarboxylic acids were characterized by a predominance of oxalic acid followed by malonic acid. Concentrations of diacids varied significantly, but they were highest in spring and winter season and lower in summer. Diacids were found to positively correlate with nss-sulfate and nitrate throughout the year and with very high correlation coefficients during the winter season. Low molecular weight diacids accounted for up to 6 % of total aerosol carbon. Diacid-C/TC ratios were found to increase in summer mainly due to the photochemical production of small diacids and transformations of organic aerosols in the Asian Pacific region.

Some spring samples were found to contain carbonate carbon based on ^{13}C enrichment and high Ca content. However, most aerosol samples were found to contain only negligible amounts of carbonate. We conclude that, although mineral dusts are transported over Juju Island from desert areas of inland Asia, carbonates in the dusts have already reacted with inorganic acids (H_2SO_4, HNO_3) and possibly with organic acids during their long-range atmospheric transport. Measured stable carbon isotopic data demonstrate that Asian dust aerosols are subjected to serious alteration (titration) in the atmosphere. The amount of organic acids that were removed from the aerosols by the treatment with HCl vapor appears to account for a few percent to 20 % of organic carbon in the aerosols. Dicarboxylic acids that are produced by photochemical reactions may be absorbed on alkaline minerals of soil dust origin. Semi-volatile organic acids likely react with NH_3 to result in a formation of new particles, which coagulate and then associate with the pre-existing aerosols.

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Figure Captions

Fig. 1. A map of East Asia and the western North Pacific with Jeju Island (33°29’N, E126°16’E): a sampling location for Asian aerosols.

Fig. 2. Seasonal variation in the concentrations of (a) aerosol mass, (b) total carbon, and (c) total nitrogen in the marine aerosols collected in Jeju Island.

Fig. 3. Relationship between concentrations of total aerosol mass and non-sea salt Ca in the aerosols from Jeju Island.

Fig. 4. Seasonal changes in (a) the concentrations of total carbon (TC) and total organic carbon (TOC) and (b) stable carbon isotopic ratios for aerosols with and without HCl treatment.

Fig. 5. Seasonal variations in (a) amounts of removed carbon with HCl treatment and (b) δ^{13}C of the removed carbon.

Fig. 6. Seasonal changes in (a) total nitrogen (TN) contents and remained N with HCl vapor treatment and (b) nitrogen isotopic ratios of TN and remained N.

Fig. 7. Relationship for (a) nitrate (as N) and removed N with HCl treatment, (b) ammonium (as N) and remained N with HCl treatment, and (c) (nitrate + ammonium)-N and total N in the aerosol samples from Jeju Island. Nitrate and ammonium were measured by ion chromatography whereas TN and remained N were measured by EA. See the text for the methods.

Fig. 8. Seasonal changes in (a) removed nitrogen from aerosol samples by HCl treatment and (b) nitrogen isotopic ratios of removed nitrogen.

Fig. 9. Representative chemical structures of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls detected in the aerosol samples collected from Jeju Island.

Fig. 10. Seasonal changes in (a) concentrations of total diacids in the Asian aerosol samples and (b) relative abundance of total diacid-carbon in total aerosol carbon.

Fig. 11. Relationships between total diacid concentrations and concentrations of (a) NH_4, (b) NO_3, (c) nss-SO_4, (d) Na, (e) nss-SO_4 (f) NO_3 in the aerosol samples from Jeju Island. Plots 12a-12d are representative of all the data (one year) whereas plots 12e and 12f give only the data for limited period (November 15 to March 16).

Fig. 12. Seasonal changes in the relative abundances of (a) oxalic acid, (b) malonic acid, (c) succinic acid, (d) glutaric acid, (e) adipic acid, (f) azelaic acid, (g) 4-oxopimelic acid, (h) malic acid, (i) phthalic acid, and (j) maleic (hydroxysuccinic) acid in the total aerosol carbon (TC) in the aerosol samples form Jeju Island.

Table 1. Aerosol mass, total carbon (TC) and nitorgen (TN) contents, stable carbon and nitrogen isotopic composition, and major ions in the aerosol samples from East Asia.

Components	Minimum	Maximum	Average	Median
Bulk analyses				
Aerosol mass (μg m^{-3})	31	880	110	83
TC (μg m^{-3})	1.3	23	6.5	5.3
TOC (μg m^{-3})	1.1	17	5.9	4.9
Removed C (μgm^{-3})	-	6.3	0.58	0.20
Removed C (%)	-	31	6.3	4.2
TN (μg m^{-3})	0.58	16	3.1	2.6
Remaind N (μg m^{-3})	0.32	11	1.9	1.6
C/N weight ratio	0.81	8.3	2.4	2.1
TOC/Remaind N weight ratio	1.2	11	4.0	3.6
TC/Aerosol mass (%)	1.2	14	6.6	6.2
Isotope analyses (‰)				
δ^{13}C (TC)	-26.6	-15.5	-23.4	-23.4
δ^{13}C (TOC)	-26.9	-17.9	-23.5	-23.4
δ^{15}N (TN)	-3.7	12	4.2	3.8
δ^{15}N (Remained N)	-5.4	22	6.6	6.8
Ion analyses (μg m^{-3})				
Na	0.65	13	3.9	3.4
NH_4	0.15	13	2.1	1.5
K	0.11	2.4	0.62	0.48
Mg	0.10	2.0	0.60	0.49
Ca	0.06	13	1.4	0.7
Cl	0.14	24	5.2	3.4
NO_3	0.17	22	5.3	4.0
SO_4	2.4	29	9.0	7.5
MSA	0.00	0.13	0.02	0.00

TOC is defined as total carbon that remained with HCl vapor treatment of aerosol sample.
Remained N is defined as total nitrogen that remained in aerosols with HCl vapor tretment.

Table 2. Analytical results of standard yellow sand (Kosa) samples.

Compoments	CJ-1 (< 250 μm)	CJ-2 (< 100 μm)
Averaged particle size	38 μm	24 μm
Elemental comosition		
Total Carbon (TC)	1.76%	2.34%
Total Organic Carbon (TOC)	0.11%	0.90%
Inorganic Carbon (IC, CaCO3)	1.69%	1.44%
Total Nitrogen (TN)	0.03%	0.08%
C/N weight ratio	60	29
Isotopic composition		
δ^{13}C (TC)	-1.6 ‰	-9.8 ‰
δ^{13}C (TOC)	-21.5 ‰	-23.4 ‰
δ^{13}C (IC)	-0.3 ‰	-1.3 ‰
δ^{15}N (TN)	2.7 ‰	2.5 ‰

Table 3. Concentrations of low molecular weight dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the aerosol samples from East Asia.

Compounds	Concentrations (ng m^{-3})			
	Minimum	Maximum	Average	Median
Dicarboxylic acids				
Saturated straight-chain diacids				
Oxalic, C2	98	1550	473	373
Malonic, C3	10	175	67	57
Succinic, C4	8.3	153	52	41
Glutaric, C5	0.8	34	11	8.8
Adipic, C6	0.6	43	8.4	6.3
Pimeric, C7	0.2	9.3	2.6	2.0
Suberic, C8	0.0	9.6	2.6	2.1
Azelaic, C9	1.2	14	4.7	4.4
Sebacic, C10	0.0	4.7	1.1	0.9
Undecanedioic, C11	0.0	3.9	1.3	1.2
Dodecanedioic, C12	0.0	3.2	0.1	0.0
Branched-chain diacids				
Methylmalonic, iC4	0.0	4.2	1.1	1.0
2-Methylglutaric, iC6	0.0	4.0	1.0	0.8
Methylmaleic, mM	0.4	21	5.3	4.2
Unsaturated diacids				
Maleic, M	0.4	15	4.9	4.1
Fumaric, F	0.5	14	5.2	4.1
Phthalic, Ph	0.5	40	9.8	7.4
Keto or hydroxy diacids				
Oxomalonic, C3,oxo	0.0	9.6	1.9	1.4
4-Oxopimelic, C7,4oxo	0.0	13	4.5	3.6
Malic (hydroxysuccinic), hC4	0.0	9.7	3.0	2.6
Total diacids	130	2070	660	540
Ketocarboxylic acids				
α-Ketoacid				
Pyruvic, C3	0.6	54	13	9.1
ω-oxoacids				
Glyoxylic (2-oxoethanoic), ωC2	4.3	133	36	27
3-Oxopropanoic, ωC3	0.0	5.9	1.7	1.2
4-Oxobutanoic, ωC4	0.0	9.5	2.5	1.6
9-Oxononaoic, ωC9	0.0	4.0	1.4	1.3
Total ketoacids	2.1	172	53	45
Dicarbonyls				
Glyoxal, Gly, C2	0.0	3.9	0.5	0.3
Methylglyoxal, mGly, C3	0.7	83	11	8.1
Total dicarbonyls	0.08	84	12	8.5

Fig. 1 (Kawamura et al.)

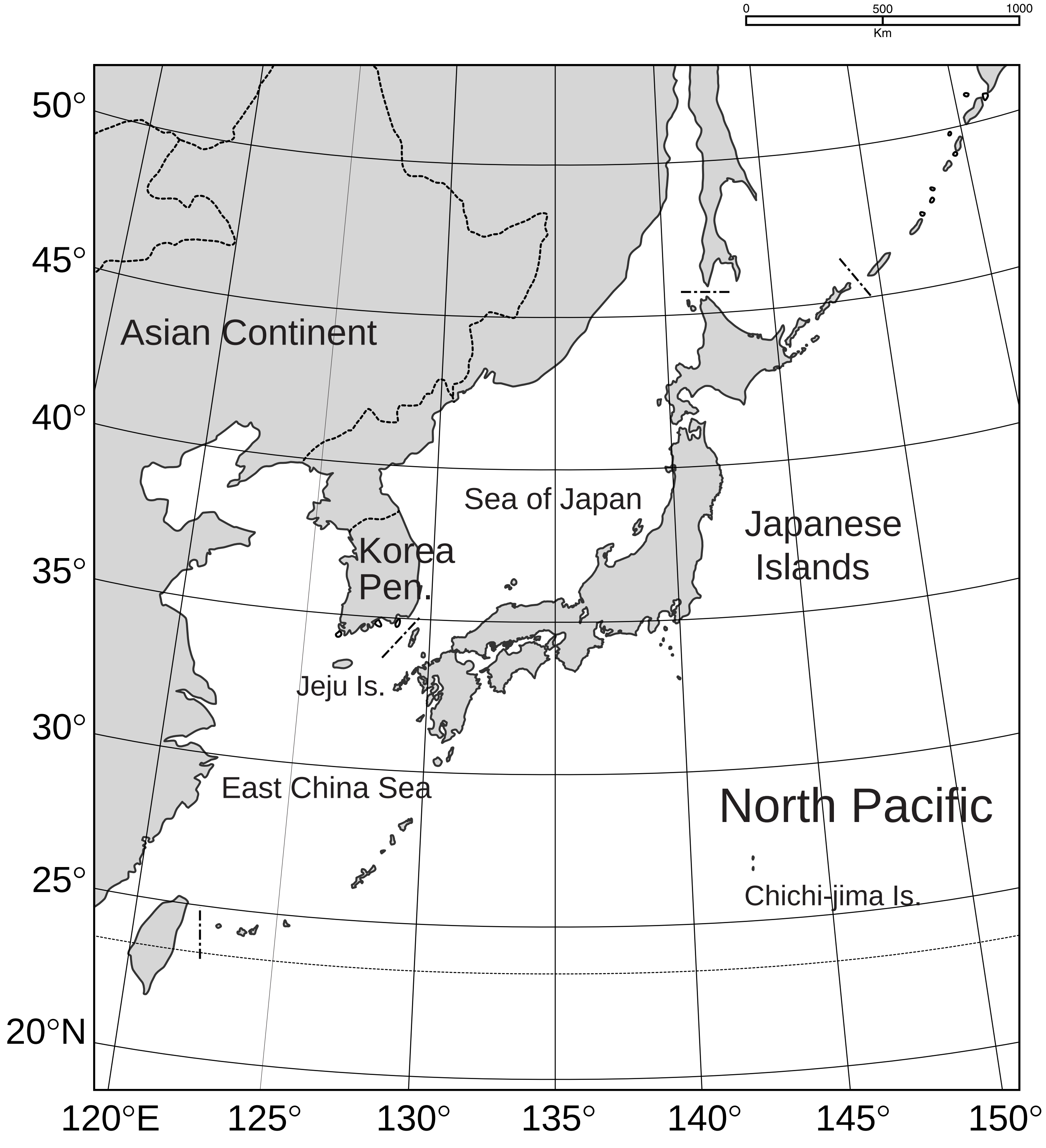
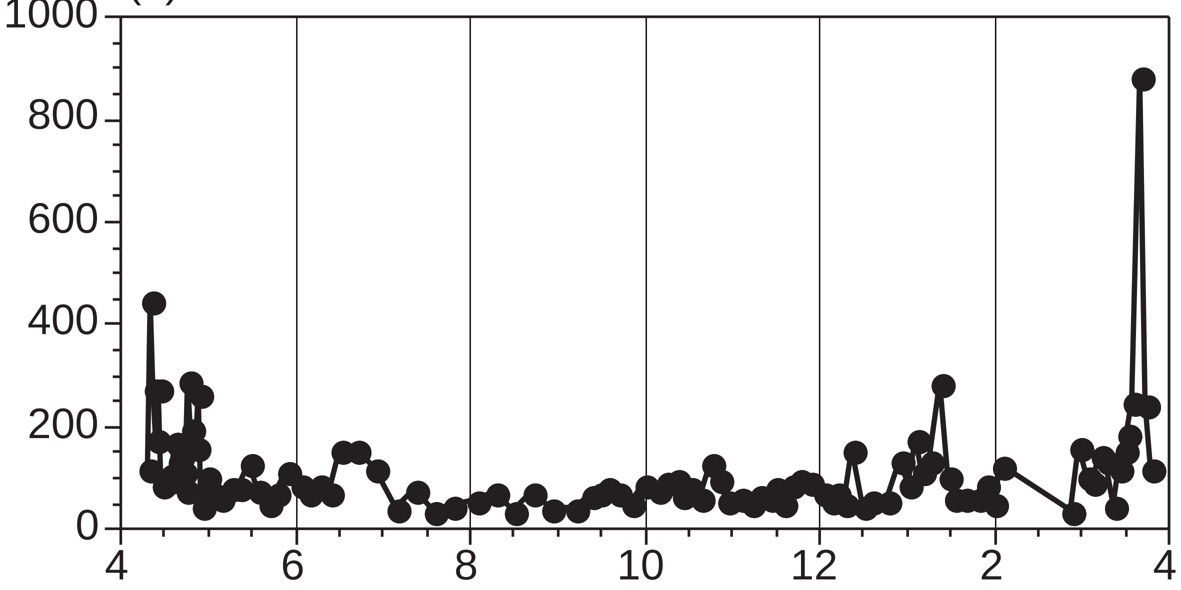
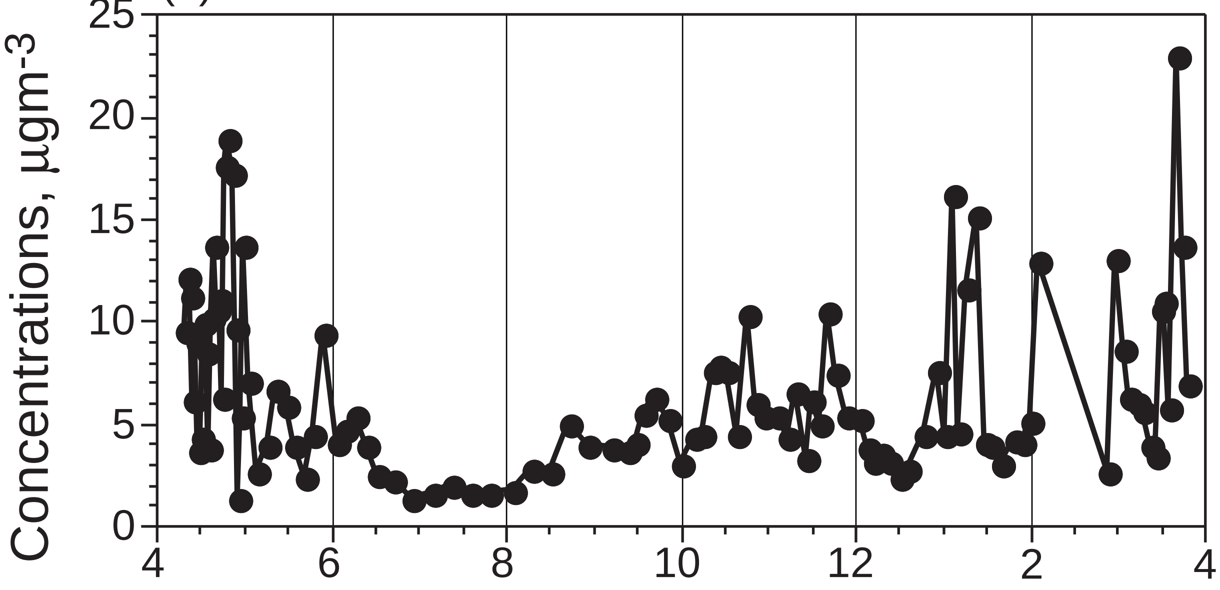


Fig.2 (Kawamura et al.)

(a) Aerosol Mass



(b) Total Carbon



(c) Total Nitrogen

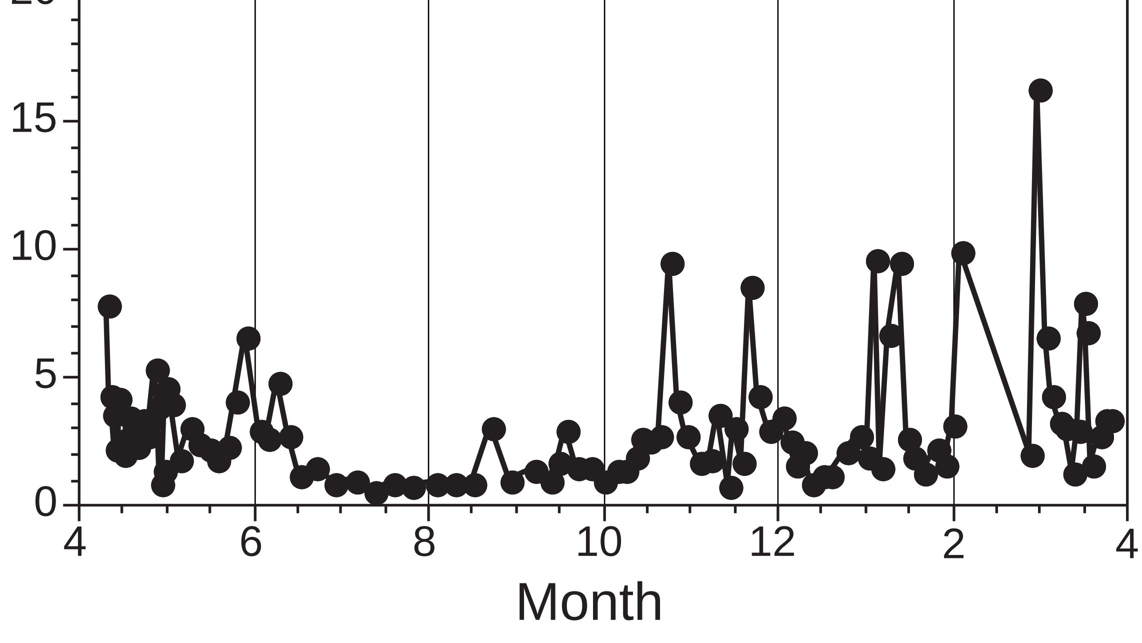
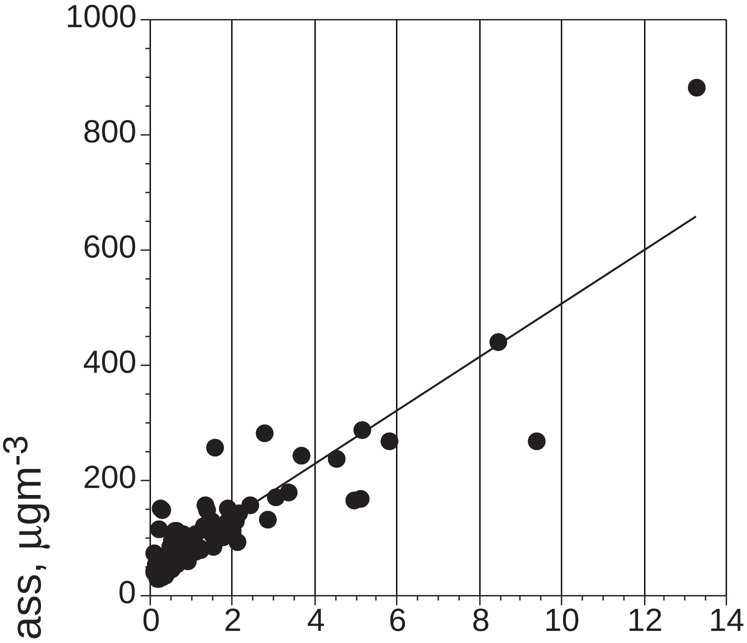


Fig. 3 (Kawamura et al.)

(a) April 2001 to March 2002 (R= 0.898)



(b) April 12-20, 2001 (R= 0.996)

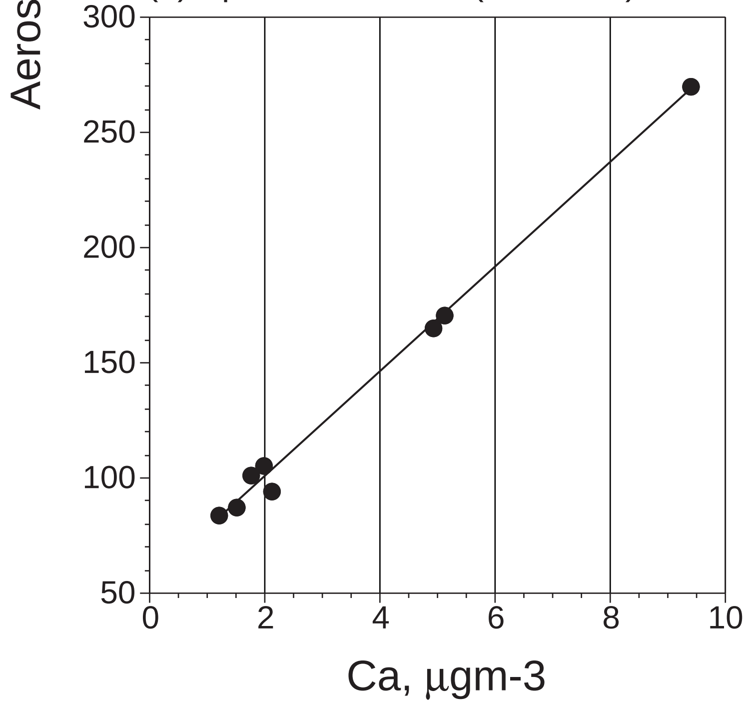
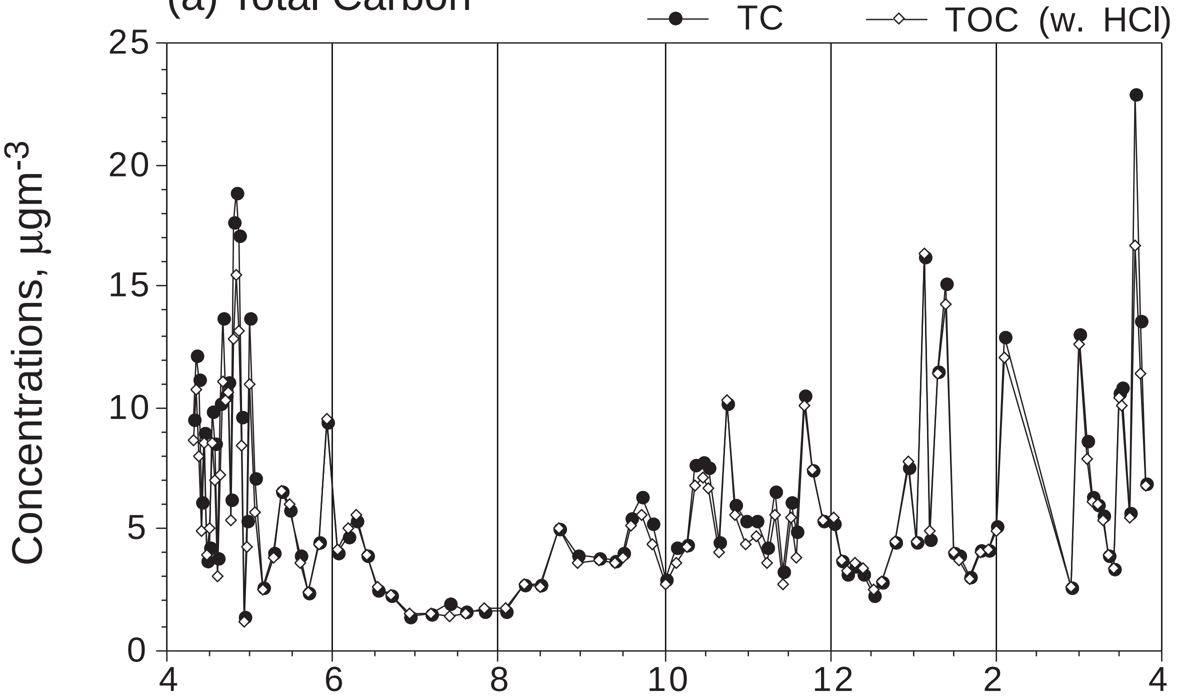


Fig. 4 (Kawamura et al.)

(a) Total Carbon



(b) Stable Carbon Isotopic Ratio

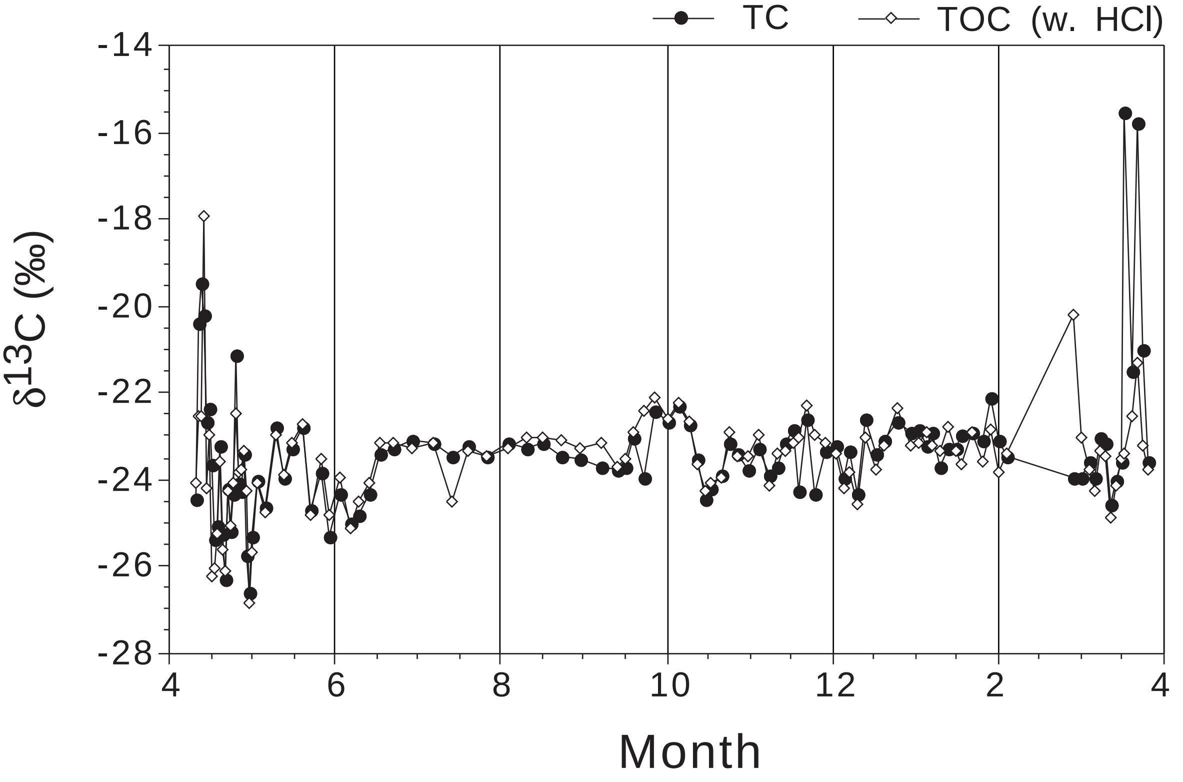
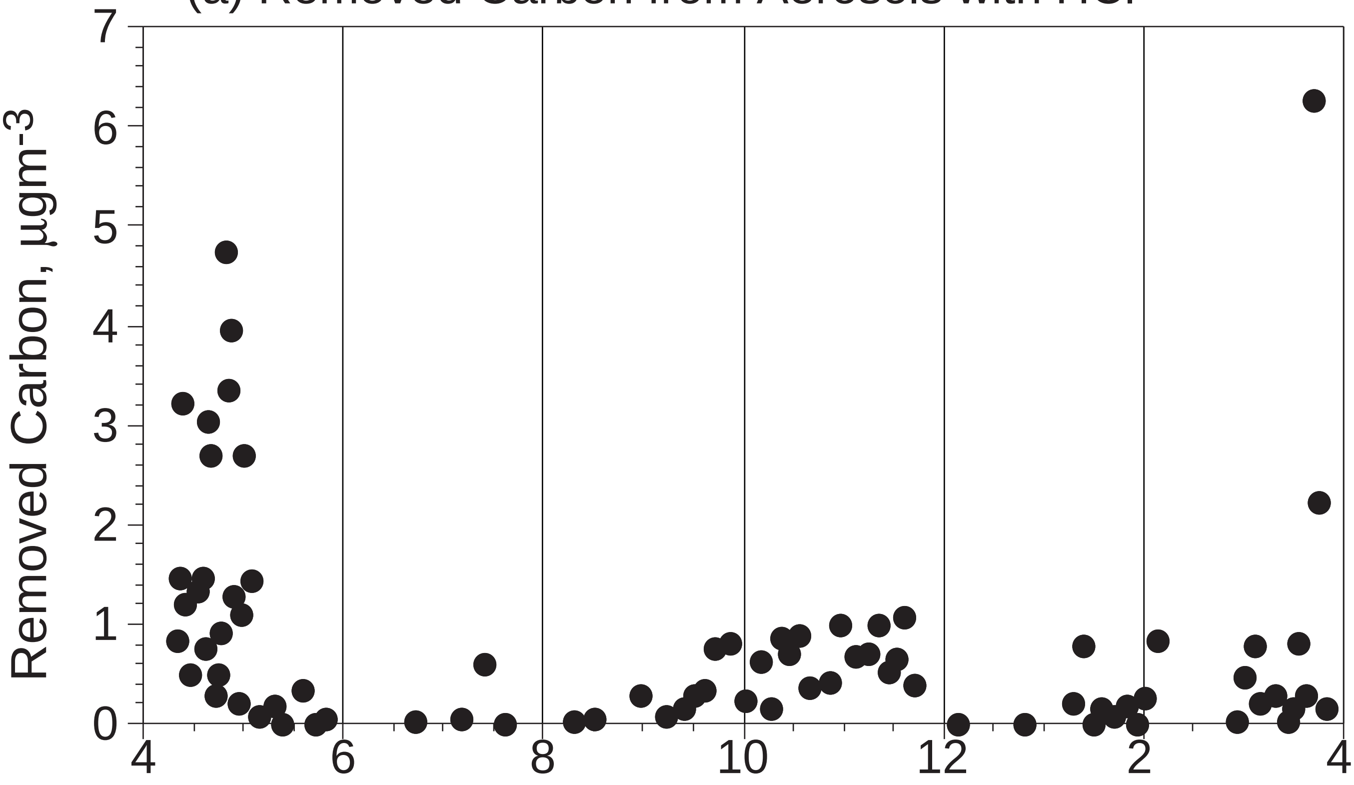


Fig. 5 (Kawamura et al.)

(a) Removed Carbon from Aerosols with HCl



(b) δ13C of removed C (removal rate > 0.05)

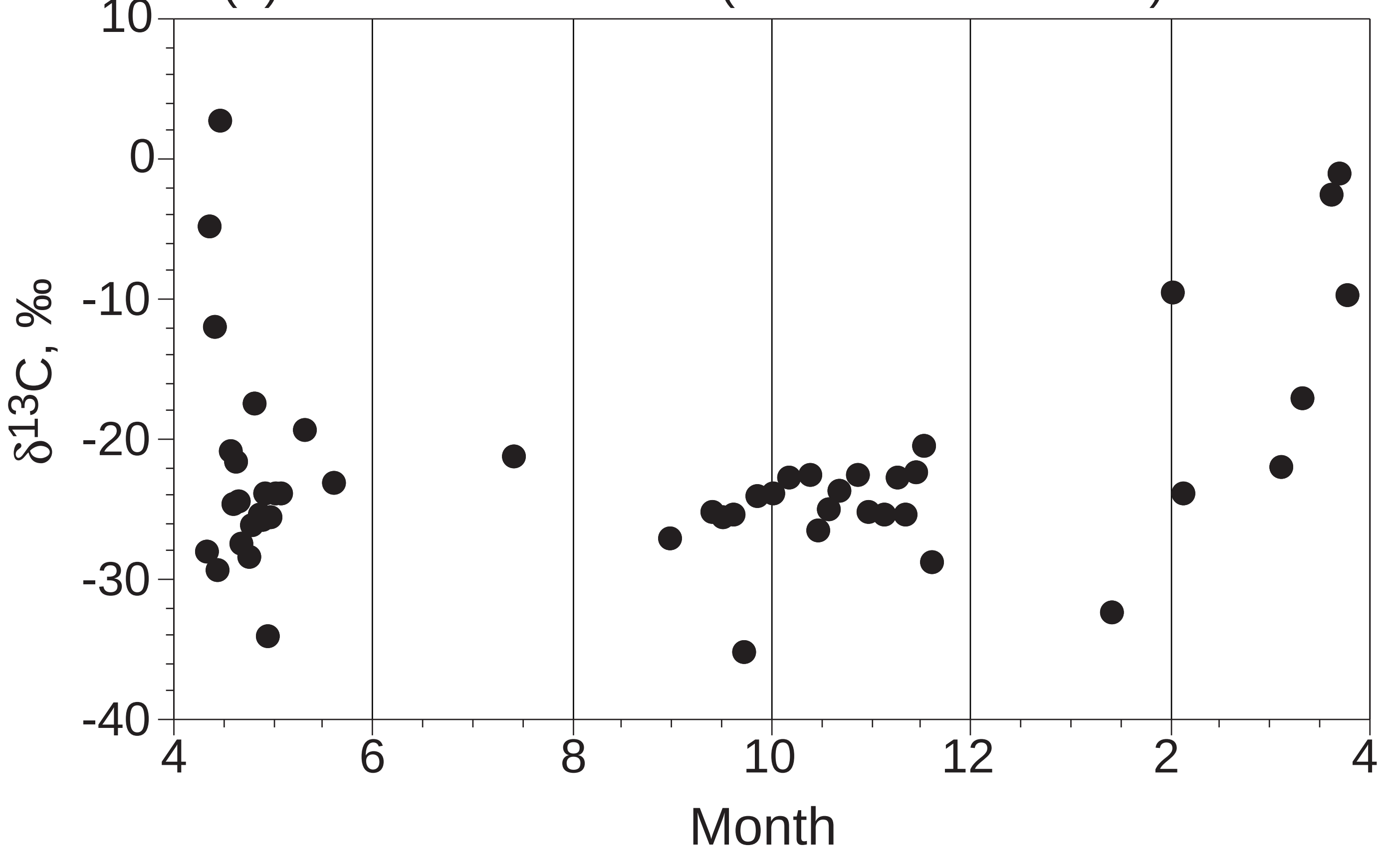
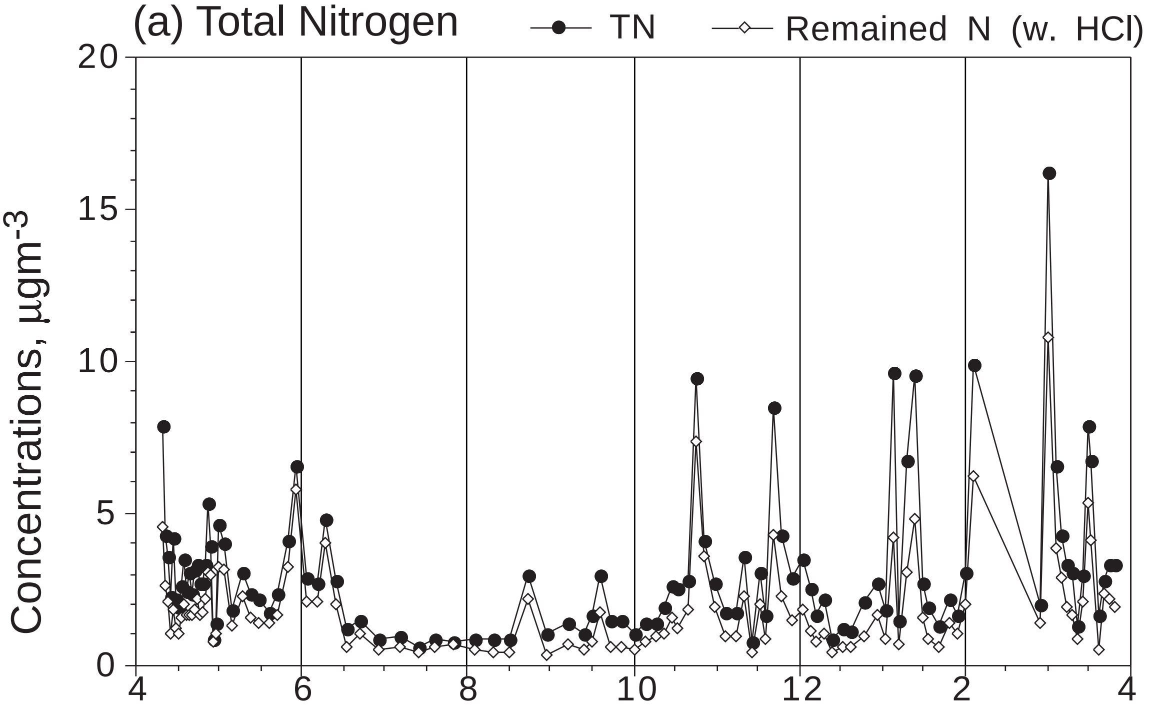
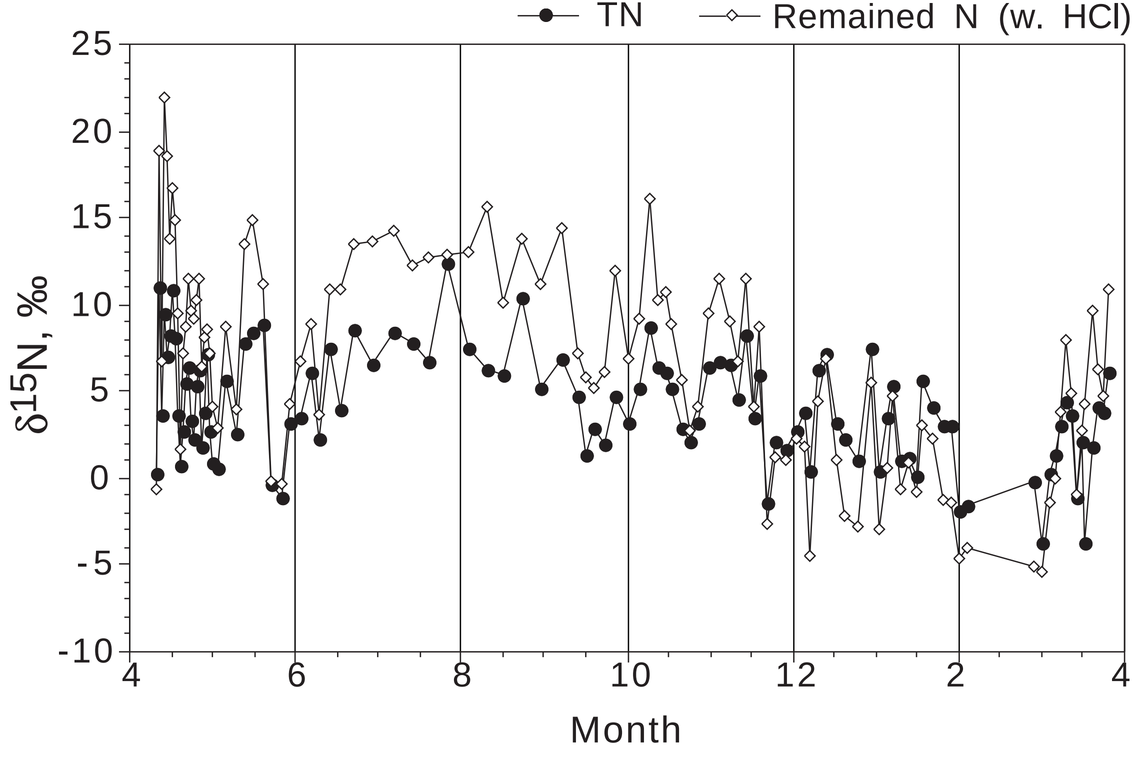


Fig. 6 (Kawamura et al.)

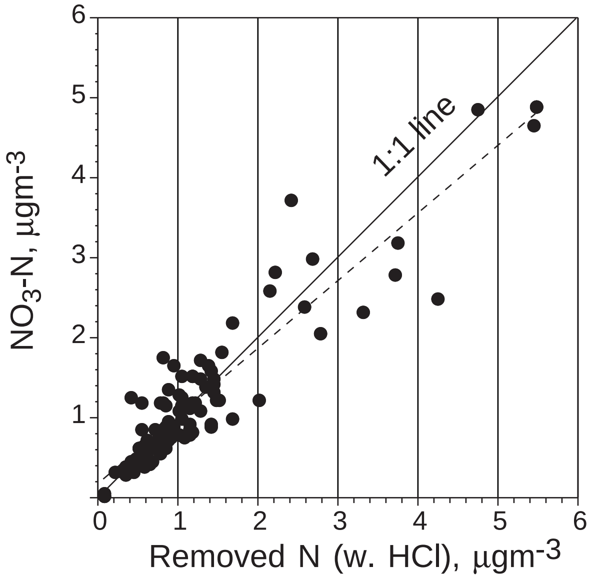
(a) Total Nitrogen

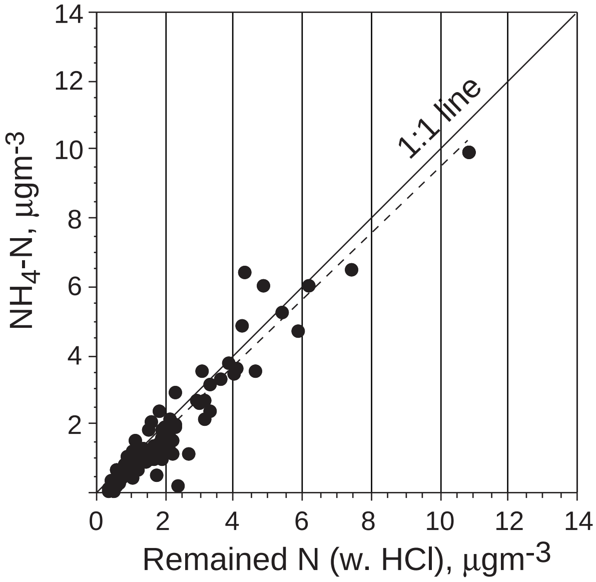


(b) Nirogen Isotope Ratios



new Fig. 7 (Kawamura et al.)


(a) Nitrate N (R = 0.93)


(b) Ammnonium N (R = 0.96)

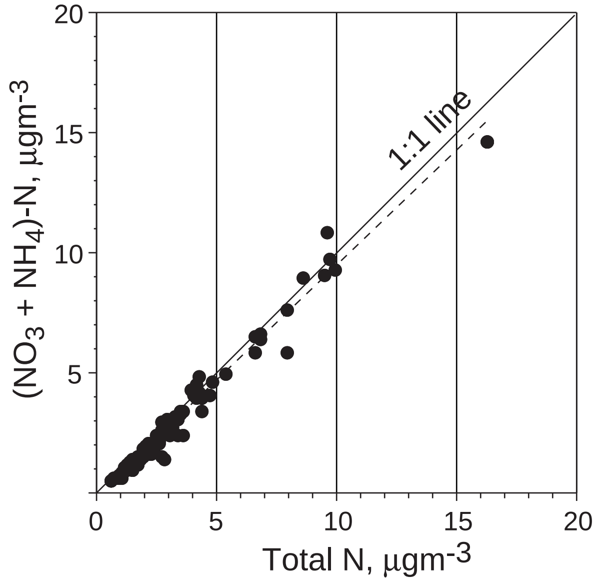
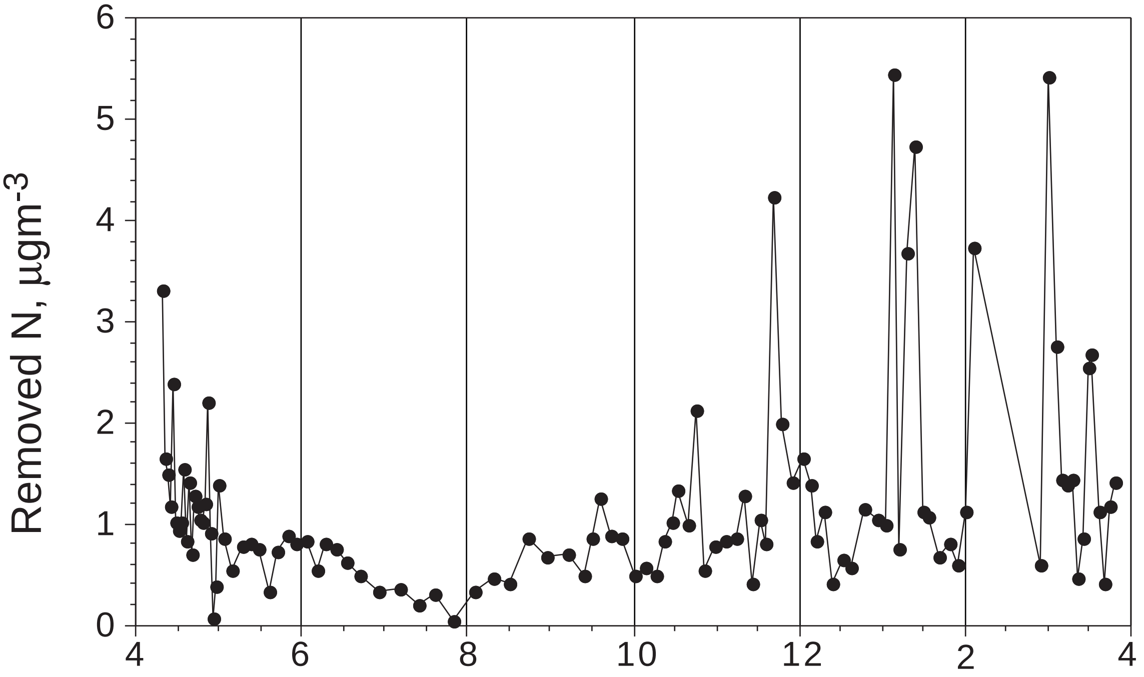

(c) Ammonium + nitrate N (R = 0.99)

Fig. 8 (Kawamura et al.)

(a) Removed Nitrogen



(b) $\delta^{15}N$ of Removed Nirogen

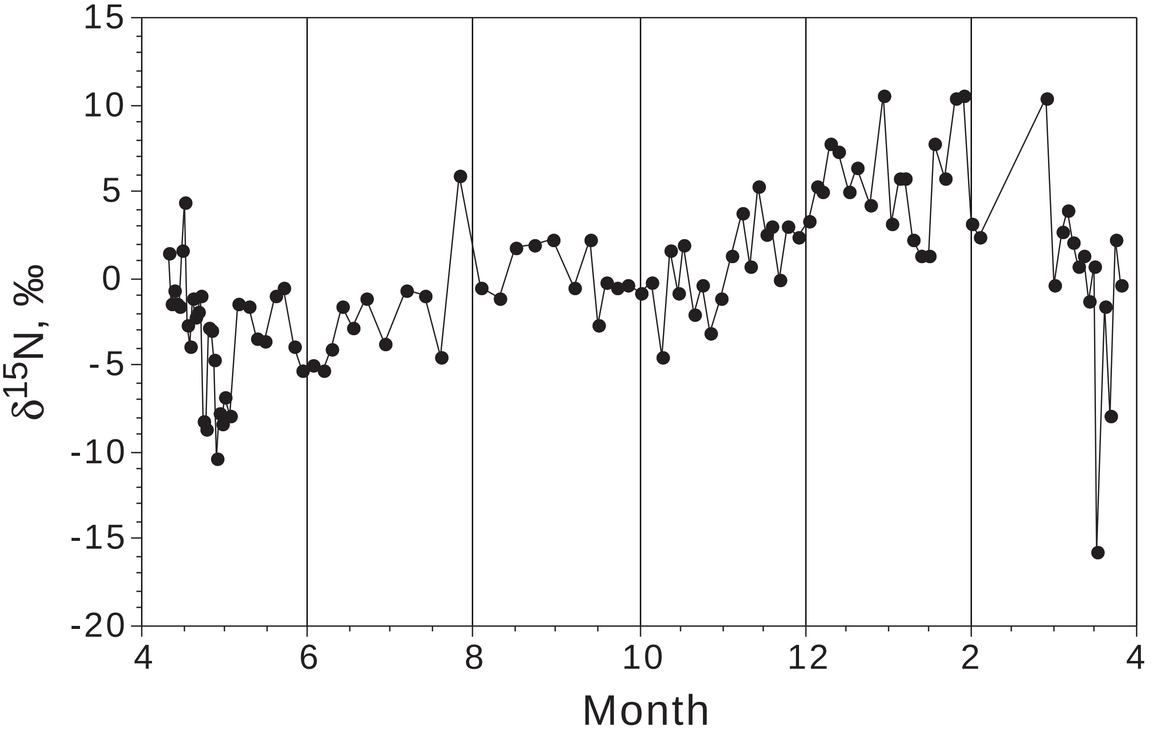
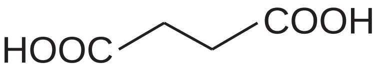


Fig. 9 (Kawamura et al.)

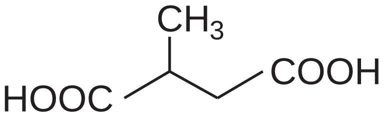
$HOOC-COOH$

(a) Oxalic acid (C2)

(b) Malonic acid (C3)



(c) Succinic acid (C4)

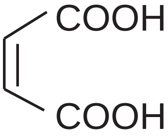


(d) Methylsuccinic acid (iC5)

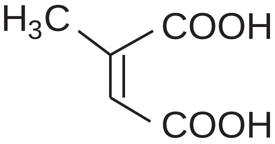
(e) Glutaric acid (C5)

(f) Adipic acid (C6)

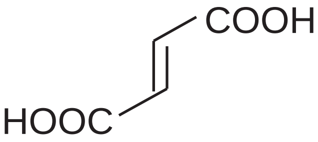
(g) Azelaic acid (C9)



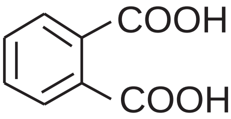
(h) Maleic acid (M)



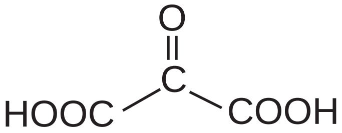
(i) Methylmaleic acid (mM)



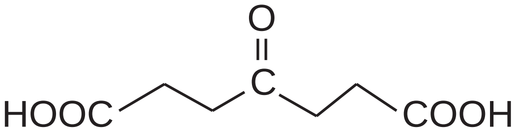
(j) Fumaric acid (F)



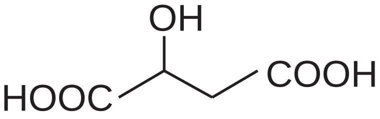
(k) Phthalic acid (Ph)



(l) Ketomalonic acid (kC3)



(m) 4-Ketopimelic acid (kC7)

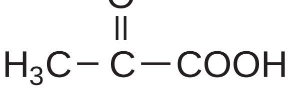


(n) Malic acid (hC4)

$HOC-COOH$

(o) Glyoxylic acid (ωC2)

(p) 4-Oxobutanoic acid (ωC4)

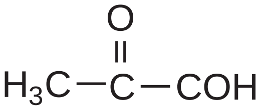


$H_3C-\overset{\overset{O}{\|}}{C}-COOH$

(q) Pyruvic acid (Pyr)

$HOC-COH$

(r) Glyoxal (Gly)

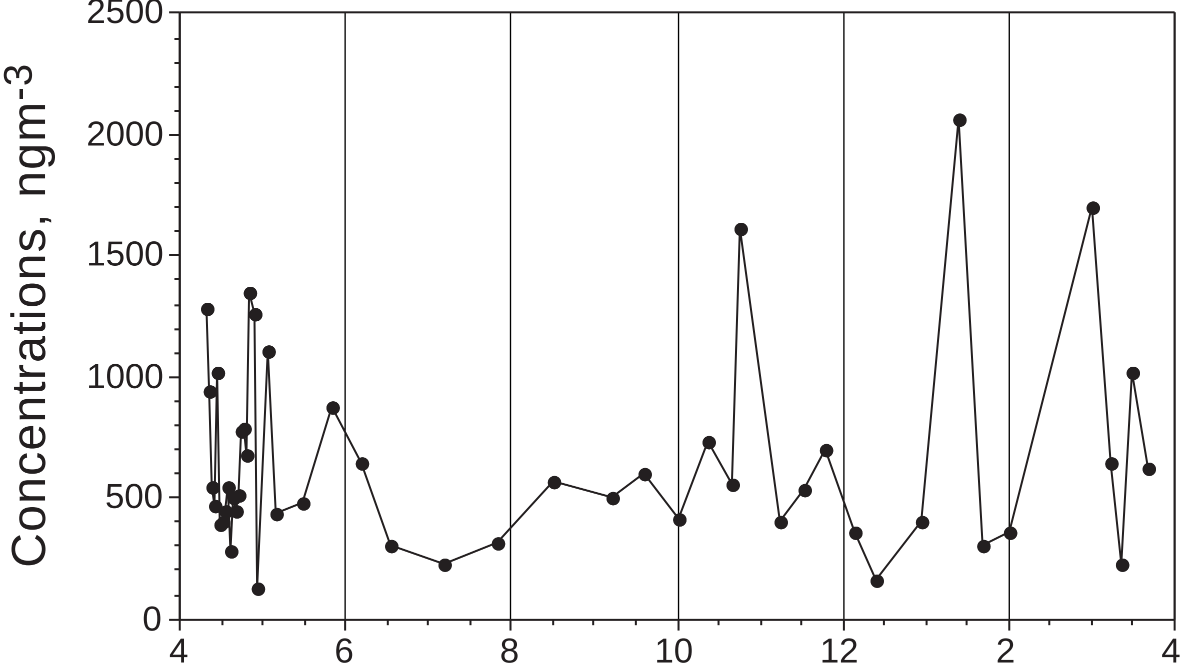


$H_3C-\overset{\overset{O}{\|}}{C}-COH$

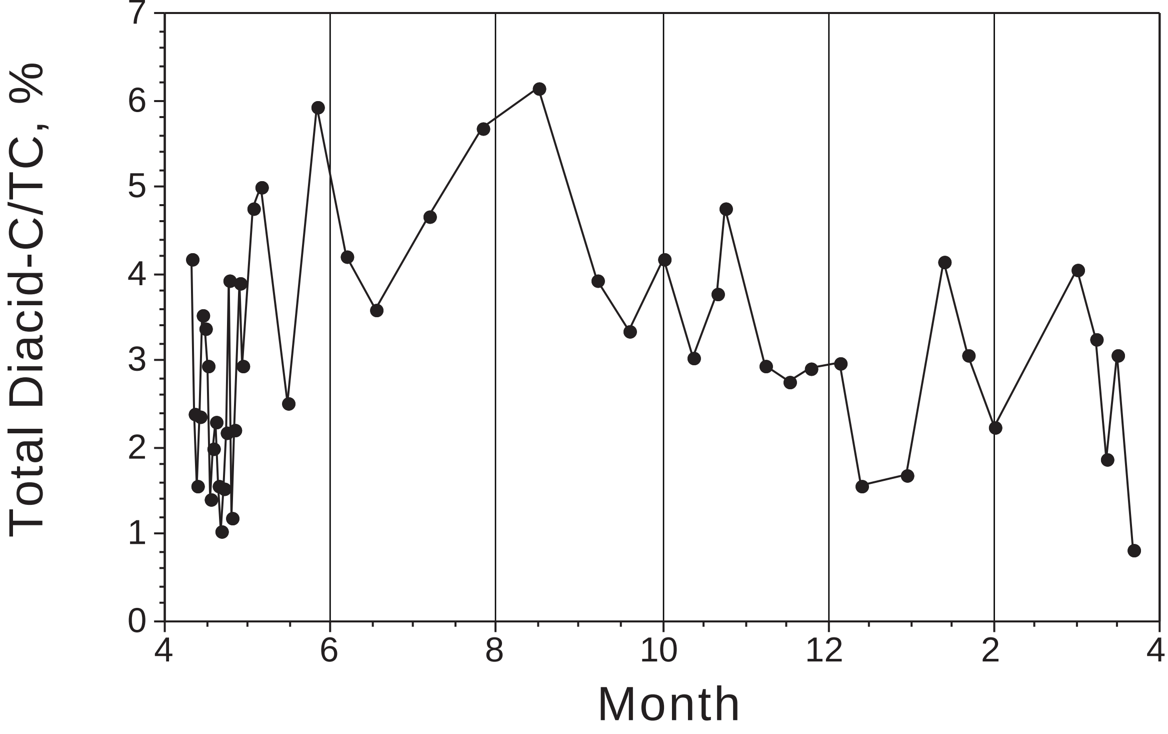
(s) Methylglyoxal (mGly)

new Fig. 10 (Kawamura et al.)

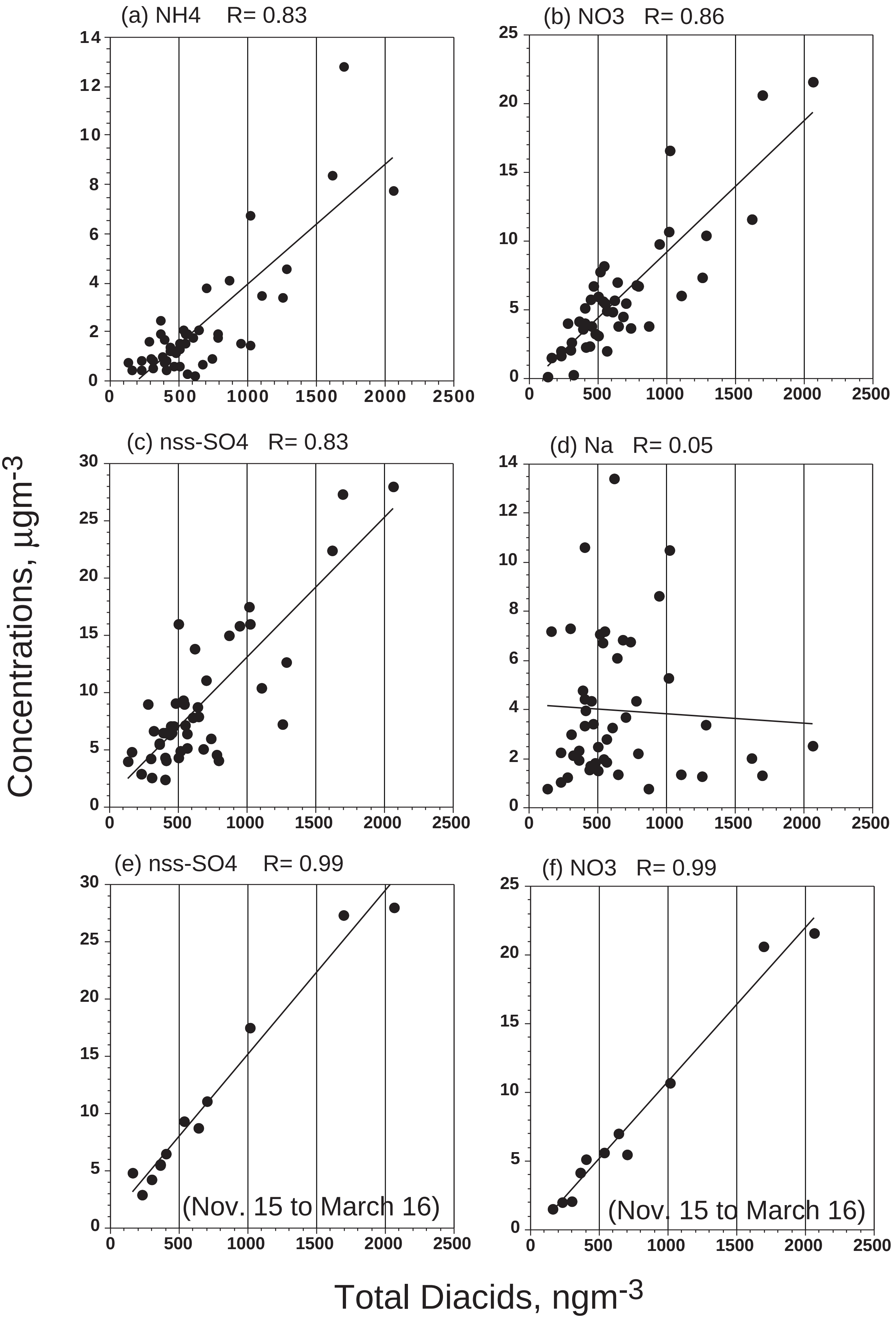
(a) Total Diacids



(b) % of Total Diacids in TC



new Fig. 11 (Kawamura et al.)



new Fig. 12 (Kawamura et al.)