Title	Photochemical production and loss of organic acids in high Arctic aerosols during long range transport and polar sunrise ozone depletion events
Author(s)	Kawamura, Kimitaka; Imai, Yoshie; Barrie, Leonard A.
Citation	Atmospheric Environment, 39(4), 599-614 https://doi.org/10.1016/j.atmosenv.2004.10.020
Issue Date	2005-02
Doc URL	https://hdl.handle.net/2115/10508
Type	journal article
File Information	KawamuraAE2005.pdf

Atmospheric Environment (in press, October 27, 2004)

Photochemical production and loss of organic acids in high Arctic aerosols during long range transport and polar sunrise ozone depletion events

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Keywords: Dicarboxylic acids, long-range transport, photochemical production, polar sunrise, vanadium, bromine,

Abstract

Unique daily measurements of water-soluble organics in fine (< 2 µm) and coarse (> 2 µm) aerosols were conducted at Alert in the Canadian Arctic in winter to spring of 1992. They yield insight into photochemical production and loss of organics during long-range transport and ozone depletion events following polar sunrise. Comprehensive analyses of α,ω-dicarboxylic acids (C_2-C_{12}), ω-oxocarboxylic acids (C_2-C_9) and α-dicarbonyls (C_2, C_3) as well as pyruvic acid and aromatic (phthalic) diacid were conducted using GC and GC/MS techniques. Oxalic (C_2) acid was generally the dominant diacid species in both fine and coarse fractions, followed by malonic (C_3) and succinic (C_4) acids. Concentrations of total diacids in the fine aerosol fraction (0.2-64 ngm^{-3}) were 5-60 times higher than those in the coarse fraction (0.01-3 ngm^{-3}). After polar sunrise in early March, the total concentration of fine aerosol diacids increased by a factor of 3 to 5 while the coarse mode did not change significantly. From dark winter to sunlit spring, temporal changes in correlations and ratios of these water-soluble organics to vanadium and sulfate measured simultaneously suggest that atmospheric diacids and related organic compounds are largely controlled by long-range atmospheric transport of polluted air during winter, but they are significantly affected by photochemical production. The latter can occur in sunlight either during transport to the Arctic or during photochemical events associated with surface ozone depletion and bromine chemistry near Alert in spring. Conversion of gaseous precursors to particulate matter via photochemical oxidation was intensified at polar sunrise, resulting in a peak in the ratio of total diacids to V. During ozone depletion events, complex patterns are indicated in photochemical production and loss depending on the diacid compound. Unsaturated (maleic and phthalic) diacids were inversely correlated with particulate Br whereas saturated diacids (C_2-C_4) positively correlated with particulate Br. These results suggest that Br chemistry associated with ozone depletion leads to degradation of unsaturated diacids and to the production of smaller saturated diacids.

1. Introduction

It has been pointed out many times that the lower Arctic troposphere during winter/spring is a unique chemical reactor. Considerable evidence shows changes in atmospheric composition after polar sunrise related to particles and gases that undergo photochemical-induced reactions. These reactions include (1) gas to particle conversion by the oxidation of sulfur dioxide to sulfate (Barrie and Hoff, 1985; Barrie et al., 1989), (2) conversion of marine-derived reactive bromine that is involved in the destruction of O_3 and associated production of particulate Br over the Arctic Ocean (Barrie et al., 1988; Bottenheim et al, 1990; McConnell et al., 1992; Li et al., 1994, Spicer et al 2002) and (3) oxidative degradation of non-methane hydrocarbons by Cl and Br atom attack (Jobson et al., 1994). During surface ozone depletion events in the Arctic at Alert, concentrations of NMHCs, alkyl nitrates, trichloro- and tetrachloro-ethylene and peroxides were found to decrease (Jobson et al., 1994; Yokouchi et al., 1994; Bottenheim et al., 2002a) whereas formaldehyde, acetone, and halogenated hydrocarbons ($CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$) are among the group whose concentrations were enhanced (de Serves, 1994; Yokouchi et al., 1994; Boudries et al., 2002; Guimbaud et al., 2002; Sunmer et al., 2002) as well as gaseous and particulate total Br (Barrie et al., 1994a; Spicer et al., 2002).

Other evidence for significant change after polar sunrise has been found in the water-soluble organic chemical composition. Based on one year of weekly samples of non-size-segregated aerosols at Alert, Kawamura et al. (1996a) reported a significant increase in the concentrations of small dicarboxylic acids (C_2-C_6), ω-oxocarboxylic acids (C_2-C_4) and α-dicarbonyls (C_2-C_3) after polar sunrise (March to April). More recently, using weekly size-segregated samples, Narukawa et al. (2003a) reported an anti-correlation between ozone and short-chain diacid concentrations after polar sunrise. Halogenated diacids were also detected in the Arctic aerosols possibly as a result of halogen chemistry (Narukawa et al., 2003b). Despite the ground breaking insights provided by these analyses, they are limited by the mismatch in averaging time of a week and processes such as ozone depletion that occur on time scales of hours to days. Thus, there is substantial potential in utilizing higher temporal resolution data to study the photochemical production and loss of diacids.

Here, we report three months of daily size segregated aerosol measurements of water-soluble diacids, ketoacids and α-dicarbonyls in aerosol samples collected on a daily basis during Polar Sunrise Experiment 1992 (PSE92) at Alert (viz. Barrie et al, 1994b). Temporal changes in atmospheric concentration and molecular composition of these organic species are compared with those of vanadium and sulfate measured simultaneously by Barrie et al (1994a, c). The influence on diacid abundance and chemical composition of long range atmospheric transport of polluted air masses, photochemical production and transformation and bromine chemistry associated with surface ozone depletion is explored.

2. Samples and Methods

Daily aerosol sampling was conducted from 22 January to 20 April 1992 at the high volume sampler site 500 m from the special studies laboratory (82.5°N; 62.3°W) at Alert which, in turn, was 5 km away from the nearest pollution source (a diesel generator). A high-volume virtual impactor sampler (designed by V. Marple) was used with Whatmann 41 filters to collect fine (aerodynamic diameter <2 μm) and coarse (aerodynamic diameter >2 μm) particles. Filters were changed generally at 1200 LST (1700 UT) every day. Total air volumes were roughly 1800 m^3 at standard conditions of 1 atm and 0°C. The surface air temperature during sample collection ranged from -40 °C in February to -19.5 °C in April.

An aliquot of the filters was used to analyze for water-soluble diacids, ketoacids and dicarbonyls using the procedure reported in previous studies (Kawamura and Ikushima, 1993; Kawamura et al., 1996a). Briefly, filter aliquots (1/4 for coarse and 3/8 for fine filters) were extracted with pure water. The water-soluble fraction was concentrated with a rotary evaporator in vacuum and then in a nitrogen stream. The concentrates were reacted with 14 % BF_3/n-butanol at 100 °C for 30 min. to derive carboxyl groups to butyl esters and aldehyde groups to dibutoxy acetals (Kawamura, 1993). The butyl esters and other derivatives were extracted with n-hexane and determined using a gas chromatography (GC) (Hewlett Packard, HP6890) equipped with a split/splitless injector, fused-silica capillary column (HP-5, 25 m x 0.2 mm i.d. x 0.52 μm film thickness). The identification of the compounds was performed by a comparison of GC retention times with those of authentic standards (derivatives of C_2-C_{11} diacids, glyoxylic acid, C_4 ω-oxoacid, pyruvic acid, glyoxal and methylglyoxal). The identification was also confirmed with a GC/MS (ThermoQuest, Voyager) under similar GC conditions.

Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 79 % for oxalic acid, 83 % for malonic acid, and better than 92 % for succinic and adipic acids. Recoveries of glyoxylic acid and pyruvic acid were 88 % and 72 %, respectively (Kawamura and Yasui, 2004). Duplicate analyses of few filter samples showed an analytical precision to be less than 10 % for major organic species. Field blank filters that were collected roughly every seven days showed some peaks of oxalic and phthalic acids. However, their concentration levels were less than 10 % (oxalic acid) and 24 % (phthalic acid) of filter samples. The concentrations reported in this paper are corrected for the field blanks, but not for the recoveries.

Major cations and anions, halogens (Cl, Br, I) and trace metals (Al, Mn, V, As, Sb, Zn) were analyzed in the filter samples using ion chromatography and instrumental neutron activation analysis (Barrie et al., 1994a,c).

3. Results and Discussion

3.1. Molecular composition and concentration changes of diacids, ketoacids, and α-dicarbonyls

Homologous dicarboxylic acids (C_2-C_{12}), ketocarboxylic acids (C_2-C_9) and α-dicarbonyls (C_2-C_3) were detected in the fine and coarse aerosols. Fig. 1 shows averaged molecular distributions of water-soluble organic species in fine and coarse aerosols collected from the Arctic for winter (January 26 to February 10) and ozone depletion period in spring (April 13-22). Saturated aliphatic diacids are the most abundant compound class, with oxalic acid dominant throughout the period except in early March when C_6 diacid prevailed. Branched chain structures (iC_4, iC_5) were also detected as well as unsaturated dicarboxylic acids such as maleic, fumaric, methylmaleic acids and aromatic (phthalic) acid. Dicarboxylic acids with additional functional group were also detected, including hydroxysuccinic (malic), oxomalonic (kC_3) and 4-oxopimelic (kC_7) acids. Among ketocarboxylic acids, glyoxylic acid (ωC_2) is the most abundant. Its concentrations are equivalent to 20 to 78 % of oxalic acid in fine aerosols. Other ketoacids detected include ω-oxocarboxylic acids (C_3-C_9) and pyruvic acid, although they are minor species. Glyoxal and methylglyoxal were also detected.

Table 1 lists organic compounds detected with the average and range of daily concentration for the fine and coarse modes for diacids, ketoacids, and dicarbonyls. The average concentration in fine (< 2 μm) aerosols was 64, 15 and 2.4 ng m^{-3} and in coarse (2 > μm) aerosols 3.5, 0.35 and 0.11 ng m^{-3}, respectively. For all compounds, more than 90 % are present in the fine aerosol fraction(< 2 μm). These results are consistent with a previous study at Alert using weekly samples in which more than 80 % of diacids were present in fine particles of diameter <1 μm (Narukawa et al., 2003a). The concentration of total dicarboxylic acids (fine plus coarse) was within the range reported in the previous studies at Alert in 1987-1988 (Kawamura et al., 1996a) and 1997 (Narukawa et al., 2003a). However, concentrations of unsaturated diacids (M, F, mM, Ph), keto and hydroxy diacids (kC_3, kC_7, hC_4), ketoacids (Pyr, ωC_2, ωC_3, ωC_4) and dicarbonyls in the daily samples are 2-4 times higher than those of weekly samples (Kawamura et al., 1996a). This may indicate that during longer sampling period (one week) some organic species are lost either by evaporation or degradation.

3.2. Winter-to-spring changes in the concentrations of individual organic species

During the course of PSE92, concentrations of total diacids in the fine aerosol fraction increased in the middle of March and stayed high in April (Fig. 2a). Similar trends were also observed for pyruvic acid, ω-oxoacids and α-dicarbonyls in fine aerosols (Fig. 2b,c,d). In contrast, concentrations of total diacids and other species in the coarse fraction did not show a sharp increase at polar sunrise (Fig. 2d).

Concentration changes are presented in Fig. 3 for selected diacids and related compounds in fine aerosols. During winter (January to early March), concentrations of oxalic acid (C_2) were relatively low and fluctuated considerably. Then, in the middle of March immediately after polar sunrise (March 5), it peaked and then relaxed to a lower level that was still higher than in the winter. In contrast, malonic (C_3), succinic (C_4), glutaric (C_5) acids and branched chain iC_4 and iC_5 acids increase abruptly in mid-March and remain high even into April. Adipic (C_6) acid concentrations varied differently with two peaks in late January and early March (Fig. 3d). During 3-9 March, C_6 became the most abundant diacid. No significant peak of C_6 was found in the coarse aerosol fraction. Such high concentrations of C_6 have not been found in aerosol samples previously studied, except in Southeast Asia (Narukawa et al., 1999). C_6 diacid is produced by ozone oxidation of cyclic hexene (Hatakeyama et al., 1987).

Straight-chain C_7 to C_{12} diacids in fine aerosol fraction showed a seasonal variation different from C_2-C_5 diacids typified by that of C_9 (Fig. 3e). Although their concentrations are low (< 5 ng m^{-3}), they had very high concentrations in mid February and late March. It has been proposed that these longer chain diacids are the product of atmospheric oxidation of unsaturated fatty acids that originate either from marine biota or terrestrial higher plants (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Kawamura et al., 1996b; Kawamura and Sakaguchi, 1999).

Unsaturated diacids showed different patterns to the saturated diacids discussed above. Maleic acid, a *cis*-unsaturated C_4 diacid (Fig. 3g), was more abundant in winter than in spring, and did not show any significant peak during polar sunrise. Maleic acid may be produced abundantly during polar sunrise by the photochemical oxidation of aromatic hydrocarbons

(Kawamura et al., 1996a), but is quickly transformed to fumaric acid (F, positional isomer of maleic acid) and/or further oxidized. In fact, F showed an increase in the concentrations from January to late February peaking in March (Fig. 3h). Phthalic acid, an aromatic diacid, may be produced by the oxidation of naphthalene and other polycyclic aromatic hydrocarbons (Kawamura and Ikushima, 1993). It increased from winter to mid March (Fig. 3j), being similar to small diacids (C_2-C_5), and then decreased into April. The decrease in April was possibly due to the further oxidation in the atmosphere and/or a decreased atmospheric transport of organic pollutants from mid latitudes to the Arctic toward early summer (Barrie, 1986). In April, the behavior of phthalic acid is in contrast to that of short-chain C_3-C_5 diacid, which continued to increase.

Concentrations of ketomalonic acid (kC_3) and 4-ketopimelic acid (kC_7) were low in winter, but increased greatly in mid or late March (polar sunrise) (Fig. 3k,l), suggesting photochemical-related production. After a slight decrease in April, they again increased by mid April. Concentrations of ketodiacids seem to be largely controlled by the photochemical oxidation of precursor compounds. Malic acid (hC_4) also increased in March and April with a peak at polar sunrise (Fig. 3m), again suggesting a photochemical production of this hydroxylated diacid. Production of malic acid may be associated with oxidation of succinic acid (C_4, Fig. 3b) initiated by OH radicals (Kawamura and Sakaguchi, 1999).

Glyoxylic acid (ωC_2, Fig. 3n) also fluctuated in a way similar to pyruvic acid (Fig. 2b) and phthalic acid (Fig. 3j), suggesting that ωC_2 is produced *in situ* in the Arctic atmosphere from aromatic pollutants. ωC_3 also showed a seasonal trend similar to ωC_2 (data are not shown here). However, ωC_4, ωC_5 and ωC_6 did not give a clear peak in the middle of March, rather they peaked in late March to April (see Fig. 3o for ωC_4). The longer chain oxoacids may have different sources than shorter ω-oxoacids. The coincidence of the peaks in ωC_6 with those of the C_7 to C_{12} diacids is consistent with the hypothesis that long-chain ω-oxoacids are produced by the oxidation of unsaturated fatty acids from marine sources. For example, oxidation of unsaturated fatty acids having a double bond at C-6 position can produce C_6 ω¬oxoacid (Kawamura and Gagosian, 1987). Concentrations of glyoxal and methylglyoxal show a decrease from January to March with a peak in mid March (see Fig. 3p for glyoxal).

In summary, although most organic species showed a peak at polar sunrise (mid to late March), the seasonal patterns of organics largely depends on the type of functional group and chain lengths. These patterns can be interpreted by long-range atmospheric transport and photochemical production/transformation as discussed in section 3.4.

3.3. Fine and coarse mode distributions of individual diacids, ketoacids and dicarbonyls

In Figure 4, the fraction of total mass that was in the coarse aerosols is displayed for selected diacids. Although most diacid species (e.g., C_2-C_5) were found mostly on fine mode, they had an almost constant apportionment between fine and coarse modes. In contrast, C_6-C_{12} diacids, branched chain diacids (iC_4 and iC_5), unsaturated (maleic and fumaric) diacids and tri-functional diacids such as kC_3, kC_7 and hC_4 were occasionally more abundant in the coarse fraction. Interestingly, during winter malic acid (hC_4) existed mostly in the coarse fraction, but thereafter, it shifted to the fine aerosol fraction (Fig. 4f). An explanation is that during dark winter, malic acid is transported as relatively large primary aerosol particles from polluted regions, but in sunlight during transport to the north, it was produced by photochemical reactions and accumulated on fine mode.

The ketoacids also show interesting temporal variations in coarse to fine particle partitioning. Pyruvic and glyoxylic acid (ωC_2) were mostly in the fine aerosol fraction (>90%) (e.g. Fig. 4g). However, often more than 30 % of ωC_3 and ωC_4 were present in the coarse fraction (e.g. Fig. 4h). In general, relatively more was present in the coarse aerosol fraction in the dark winter, and episodically in late March to early April. C_3-C_4 ω-oxoacids may have a different source than ωC_2 and are transported over the Arctic as relatively large particles. In contrast, ωC_2 that is mostly in the fine fraction may be converted to other species such as oxalic acid during the atmospheric transport with shorter residence time (Kawamura et al., 1996a; Warneck, 2003). The atmospheric lifetime of ωC_2 may be shorter than that of ωC_3 and ωC_4. ωC_5 also showed higher abundance in the coarse fraction (20-60% in the spring, data are not presented here). These ω-oxoacids may be produced on sea-salt by the oxidation of unsaturated fatty acids containing a double bond at different position that may be produced by marine bacteria or other biota.

3.4. Long-range atmospheric transport and in situ production of diacids and related compounds: comparison to the oil combustion tracer (vanadium)

In Fig. 5, observed concentrations of total diacids and vanadium in the fine and coarse fractions are compared. In winter, there was a strong correlation of total diacids with V concentration from Barrie et al (1994c), which was not clearly evident in weekly observations reported by Kawamura et al.(1996a). Fine fraction vanadium in the Arctic is primarily from anthropogenic emissions of oil combustion at mid-latitudes (Barrie, 1986). In contrast, there was no correlation between fine fraction V and total diacids after polar sunrise on March 5 (Fig. 5a). Concentrations of diacids increased in early March whereas those of V decreased. This strongly suggests that diacids are produced even under the relatively weak solar radiation on the transport pathway from the southern source regions to the north. For the coarse fraction, contrasts in correlation of diacid and V before and after sunrise are still evident (Fig. 5b) but much weaker than for the fine aerosol fractions. Thus heterogeneous production of diacids also involves coarse aerosols but to a lesser extent than the fine aerosols.

We presume that both organics and V in the Arctic aerosols have in principle the same source from mid-latitudes. Because V cannot be produced in the atmosphere, any changes in the organics/V ratios clearly support *in situ* photochemical production of particulate diacids either in the gas phase or particles. Fig. 6 presents temporal variations of the ratios of selected diacids and ketoacids to V in both fine and coarse aerosol fractions. Although the ratios for C_2-C_5 diacids in the fine fraction are generally low in January to mid March, they gradually increase from mid-March onward (Fig. 6a-d). Similar seasonal trends were obtained for branched diacids (see Fig. 6e,f). The gradual increase in the ratios even in winter suggests that the precursors are in part oxidized in the atmosphere during the transport from lower latitudes to the Arctic, although it is completely in darkness in January to late February. Similar trends were obtained for coarse aerosols, but the increase in organic acid/V ratios seem to be less than those of fine mode. This again suggests that photochemical production of small diacids in spring is more significant on fine than coarse mode. Although the concentration peak of C_2 is consistent with that of V (see Fig. 3a, Fig. 5a), C_2/V ratios maximized in mid April. The mid April maximum was observed for C_3-C_5 diacids (Fig. 6b-d). These results reinforce the photochemical production of the small diacids even after a polar sunrise as discussed in section 3.2.

Adipic acid/V ratios showed a strong isolated peak in early March, whereas the ratios increased in April (Fig. 6g). This suggests that this peak is not involved with petroleum combustion or other associated anthropogenic activity. Long-chain C_7-C_{12} diacids including azelaic (C_9) acid on both fine and coarse mode showed peaks in the middle and late February and late March (Fig. 6h). The C_9/V ratios also increased toward early summer (Kawamura et al., 1995). These results also support the hypothesis that long-chain diacids are not derived from the fossil fuel combustion sources. Rather, they are produced by atmospheric oxidation of unsaturated fatty acids that are emitted from terrestrial higher plants and/or marine phytoplankton (Kawamura and Gagosian, 1987).

Unsaturated diacids showed temporal patterns in their ratio to V that are different than those of the saturated diacids (Fig. 6i-k). The ratios for maleic, methylmaleic and fumaric acids in both fine and coarse aerosols increased in mid to late February and decreased toward mid-March. The M/V ratios also increased in late March and mid April, as well as the F/V ratios. However, F/V ratios did not increase in mid-April although they increased on coarse mode (Fig. 6j). The peaks in February suggest these unsaturated diacids are produced in the lower latitudinal atmosphere on the way to the Arctic. They should also be produced in the Arctic during polar sunrise and after, but their residence time may be shorter than saturated ones due to the presence of a double bond that is selectively oxidized. Aromatic diacid/V ratios showed a seasonal trend similar to that of M (Fig. 6i). However, the ratios seem to continuously increase in April. These results suggest that aromatic diacid is more refractory to atmospheric oxidative degradation than aliphatic unsaturated diacids (i.e., M, mM, F), but is less stable than saturated diacids (C_2-C_4) (see Fig. 6a-c).

Abundances of tri-functional acids (i.e., kC_3, kC_7, hC_4) relative to V showed a seasonal pattern similar to C_2-C_5 diacids, with enhanced diacid/V ratios in late March to April (see Fig. 6l,m). Third functional groups (additional keto or hydroxyl) may be more efficiently introduced to the parent diacids under a stronger solar radiation in late March to April. Interestingly, the enhanced diacid/V ratios of oxomalonic and malic acids in April were clearly found only in the fine fraction: the ratios in the coarse fraction were low especially for kC_3 (Fig. 6l). Production of kC_3 and hC_4 may be associated with fine particles, possibly via a gas-to-particle conversion, although Kerminen et al. (1999) reported high abundance of malonic and succinic acids in super-micrometer aerosols in the Arctic atmosphere. In contrast, kC_7 in the coarse fraction showed an increase in the ratios although the ratios are lower than those of the fine aerosol fraction (data are not shown here). This suggests that kC_7 is produced by heterogeneous oxidation of C_7 diacid on aerosol surfaces as well as by gas to particle conversion.

Ratios of pyruvic acid and glyoxylic acid over V showed an increase from January to February (Fig. 6n-p), being similar to unsaturated diacids. Then, the ratios decreased toward mid March and again increased in April. The higher ratios in February may suggest that these ketoacids are long-range transported from the lower latitudes to the high Arctic. However, they are produced in copious amounts within the Arctic atmosphere in March to April. C_3-C_5 ω-oxoacids also showed similar seasonal trend (see Fig. 6p for ωC_4). However, they often gave higher ratios for coarse particles than fine particles, again suggesting a heterogeneous production of oxoacids on the aerosol surface through the oxidation of unsaturated fatty acids, which may be emitted from the microlayer in the ocean surface.

3.5. Compositional changes of water-soluble organic compounds from winter to spring

During the polar sunrise, we found significant changes in the composition of major diacids in both fine and coarse fractions. Fig. 7 presents relative abundance of selected diacids in the fine aerosol fraction. The relative abundance of oxalic acid decreased from winter (January) to spring (April) (Fig. 7a), although its absolute concentration increased (see Fig. 5a). In contrast, the relative abundance of malonic, succinic and methylmalonic acids increased from winter to spring (Fig. 7b,c,f), indicating that C_3-C_4 diacids are produced preferentially over C_2 diacid after polar sunrise. The relative abundance of diacids with additional functional group (hC_4, kC_3 and kC_7) also showed an increase (see Fig. 7j-l). Evidence for selective production of hC_4 over C_4 has been reported in the marine aerosols in the western Equatorial Pacific (Kawamura and Sakaguchi, 1999), where solar radiation is stronger than mid latitudes.

In contrast, the relative abundance of unsaturated diacids such as M, mM, Ph in the fine aerosol fraction decreased greatly from winter to spring (see Fig. 7g,h). These results may suggest that unsaturated diacids are produced by the oxidation of aromatic hydrocarbons (Kawamura and Ikushima, 1993), but are further oxidized to result in oxalic acid. This is in contrast to saturated diacids, which accumulate in the arctic air at and after polar sunrise. Relative abundances of C_7-C_{12} diacids showed a peak from middle to late February and late March (see Fig. 7d and 7e for C_9 and C_{11}, respectively). Interestingly, kC_7 also peaked at the same time (Fig. 7l) as the C_7-C_{12} diacids. As described above, peaks of C_7-C_{12} diacids and kC_7 may be associated with a long-range atmospheric transport of unsaturated fatty acids either from continental or oceanic sources and are subjected to subsequent photochemical oxidation during the transport and in the Arctic atmosphere.

The ratio of unsaturated diacid (M) to saturated diacid (C_4) decreased from winter to spring, although higher ratios are seen in early to mid March (data are not shown here). This result again suggests that unsaturated structures are subjected to atmospheric oxidation over saturated structures in spring. We also found that ratios of keto and hydroxy diacids to their parent diacids (hC_4/C_4, kC_3/C_3 and kC_7/C_7) increase from winter to spring, suggesting that the keto and hydroxy diacids are produced by the atmospheric oxidation of C_3, C_4 and C_7 diacids at the polar sunrise and after.

3.6. Relationship of water-soluble organic acids to sulfate

Sulfate is a major constitute of arctic aerosols that is produced by gas-to-particle conversion of SO_2. The major source of SO_2 at Alert is mainly derived from combustion of fossil fuels that contain sulfur as well as smelters in the mid latitudes (Sirois and Barrie, 1999; Norman et al, 1999). In the Arctic, SO_2 is converted to SO_4^{2-}, where the conversion rate increases from 20 % in January to 80 % in early April (Barrie et al., 1994a). In contrast, small diacids such as C_2 are mainly produced by the photochemical oxidation of organic precursors from anthropogenic and natural sources either in the gas phase or aerosols. Thus, it is of interest to compare the individual diacid concentration to SO_4^{2-} in the daily aerosol samples in order to better understand the secondary production of water-soluble dicarboxylic acids and related compounds during light spring, in which photochemical reactions are significant.

Figure 8 shows seasonal changes in the ratios of selected organic compounds to SO_4^{2-}. In the arctic winter to spring, contribution of sea-salt to total SO_4^{2-} is very small (< 3%) and SO_4^{2-} from oxidation of DMS is negligible (Norman et al, 1999). Oxalic acid/SO_4^{2-} ratios (range: 0.006-0.025) are low from January to April, but show an increase in mid April by a factor of two (Fig. 8a). These values and trend are similar to those reported for the arctic aerosols from Svalbard (78°N) (Hara et al., 2002). In contrast, the ratios for C_3, C_4 and iC_4, which were low in January to February, show a large increase from March to April by a factor of 5-10 (Fig. 8b-d). The behavior of these small diacids are in contrast to SO_4^{2-} whose precursor (SO_2) is mostly reacted away by April (Barrie et al., 1994a). This study also indicates that production of C_3-C_4 diacids continued even after the polar sunrise, suggesting that there are enough organic compounds in the Arctic to serve as precursors of small diacids long after precursors for SO_4^{2-} have disappeared. Although longer-chain saturated diacids such as C_9 are possible precursors of small diacids, they did not show a clear increase from winter to spring, but they showed several isolated peaks in February to March (Fig. 8e).

Hydroxysuccinic (hC_4) and ketodicarboxylic (kC_3 and kC_7) acids also showed an increase in the concentrations relative to SO_4^{2-} (Fig. 8f-h), again suggesting that the tri-functional compounds are produced during arctic polar sunrise and subsequent spring. These tri-functional compounds seem to be relatively stable under strong solar radiation. Interestingly, kC_3/SO_4 ratios that were low in winter extensively increased at polar sunrise in mid April and remained high throughout March and April. A sudden incidence of solar radiation at polar sunrise may provide a sudden increase of oxidants (OH and other radicals), which could induce the production of ketomalonic acid. However, kC_7/SO_4 ratios did not show any significant peak in mid March (Fig. 8h), but gradually increased toward mid April showing three isolated peaks in mid February, late February and late March. Timing of these peaks is consistent to the case of C_9, again suggesting that kC_7 is associated with unsaturated fatty acids of biogenic origin.

The ratios of pyruvic acid and glyoxylic acid to SO_4^{2-} did not show any clear change during the PSE92 (Fig. 8i, j), although pyruvic acid seems to decrease from winter to spring. In contrast, the ratios of ω-oxobutanoic acid (ωC_4) to SO_4^{2-} show an increase from March to April (Fig. 8h). Production of this acid may be involved with enhanced atmospheric transport of precursor compounds (unsaturated fatty acids with double bond at C-4 position) and/or their atmospheric oxidation as discussed above. Glyoxal/SO_4^{2-} ratios gradually decreased from winter to spring (Fig. 8l), suggesting that photochemical production is less important for this organic compound in the Arctic atmosphere.

3.7 Behavior of diacids and related compounds during ozone depletion events

Depletion of surface ozone has often been observed at Alert in March and April after polar sunrise (e.g., Anlauf et al., 1994). Barrie et al. (1988) proposed that O_3 destruction is caused by catalytic reactions involving reactive bromine gases. During ozone depletion, particulate Br, BrO and molecular Br_2 are observed to increase (Barrie et al., 1988; Barrie et al., 1994a; Spicer et al., 2002, Hönninger and Platt, 2002). Kawamura et al. (1995) used weekly samples to show a positive correlation between small diacids (i.e., C_2-C_5) and particulate Br at Alert. This suggests that production of organics is associated with ozone depletion and the production of particulate Br. During the PSE92, strong ozone depletion events were observed in April with an increase of particulate Br and diacids. Figure 9 presents daily variation of particulate Br^-, total diacids and ozone.

Fig. 10 presents the relationship between ozone concentrations and the ratio of succinic acid (C_4) to V in the fine aerosols for winter and spring. As stated above, the atmospheric concentrations of small diacids (C_2-C_5) increased from winter to spring by a factor of 2 to 5 depending on species (Fig. 3). During winter C_4/V ratios (Fig. 6c) are low (< 10) and are positively correlated with ozone (Fig. 10a). This correlation may be due to a long-range transport of polluted air masses originated from the lower latitudes, which are subjected to the mixing or advection in the lower troposphere to the surface in a situation where the mean vertical profile of ozone and the C_4/V ratio increases with height above the ground.

There is good evidence that ozone increases with height above the ground at Alert during dark winter (Bottenheim et al., 2002b). Thus the correlation with ozone in the dark implies that C_4/V increases with altitude. Also, it is well known that arctic haze particles containing V decrease with altitude (Barrie, 1986). More significant however, is the fact that during the ozone depletion event of April the C_4/V ratios are much higher (20-100) and are negatively correlated with O_3 (Fig. 10b). This indicates that in sunlight C_4 diacid is produced relative to V in the lower troposphere that is depleted of O_3 and enriched in particulate Br (Fig. 10c). Similar results were found for other small diacids and ketoacids.

Enhanced production of C_4 diacid has also been reported in the snow pack samples collected in the high Arctic in spring (Narukawa et al., 2002). The production of C_4 may be involved with the formation of gaseous and particulate Br. That is, the oxidation of precursor organics may be initiated by the attack of Br atom and radicals. Bromine oxide radicals (BrO) are produced in spring in the high Arctic (Hausmann and Platt, 1994; Hönninger and Platt, 2002). BrO that has been proposed as an important agent for tropospheric ozone depletion (Barrie et al., 1988) may also act as an important oxidizing agent for organic precursors to produce small diacids (Impey et al., 1999; Behnke et al., 1999). A direct link between halogens and diacids is offered by the observation of Narukawa et al. (2003b) that halogenated C_3 and C_4 dicarboxylic acids were present in arctic aerosols in April and May, but they were not detected in aerosols during dark winter. It is of interest to note that, although bromomalonic acid was detected, chloromalonic acid was not detected in spring. Further, bromosuccinic acid was more abundant than chlorosuccinic acid; the latter is likely produced by nucleophillic substitution of the former acid in aerosols (Narukawa et al., 2003b).

Concentrations of some unsaturated (maleic and phthalic) diacids decreased when particulate Br increased during spring (data are not shown here). This is in contrast to major saturated diacids (C_2-C_5) whose concentrations increased with an increase in Br concentrations in spring. Because of a double bond, the unsaturated diacids may be preferentially decomposed by reaction with reactive halogens (e.g. Br, BrO or Br_2) that are present during ozone depletion. In addition to unsaturated diacids, hydroxyl succinic acid (hC_4 or malic acid) also showed a decrease in the concentration when particulate Br increases in spring (data are not shown here). This suggests that dicarboxylic acids containing additional functional group (such as double bond and OH) are subjected to oxidative degradation involved with bromine atom or radicals. During an O_3 depletion event, we found a preferential production of saturated small diacids and preferential degradation of unsaturated diacids.

As shown in Figure 11, ratios of unsaturated (maleic and phthalic) acids to succinic acid decreased when particulate Br increased during the April ozone depletion period. However, such a clear trend was not observed for particulate Cl. The present result suggests that bromine chemistry degrades unsaturated diacids and produces lower molecular weight saturated diacids as well as particulate bromine. It should be noted that C_3/C_4 and hC_4/C_4 ratios also decrease when Br increases (data are now shown here). This suggests that Br chemistry associated with ozone depletion and particulate Br production also play an important role in decomposing C_3 and hC_4 diacid. Similar but weaker trend was also obtained for the relationships with particulate Cl. Reaction mechanism involved with halogen chemistry needs to be clarified.

4. Conclusion

A unique data set of daily observations of water-soluble organics in size-segregated atmospheric aerosols in the high Arctic at Alert in 1992 during winter/spring was used to study the controls on ambient concentrations and the molecular composition of dicarboxylic acids, ketocarboxylic acids and dicarbonyls. Simultaneous observations of other aerosol constituents enhanced the value of the data set. Concentrations of most saturated diacids were found to peak after polar sunrise. Based on a comparison of the relative abundance of organic acids with vanadium and sulfate, it was concluded that long-range atmospheric transport of polluted air controls the composition of water-soluble organic compounds during dark winter whereas in the sunlight that progressively increases toward spring the chemical composition is greatly influenced by secondary aerosol production mostly in the fine fraction (< 2 µm) but also evident in the coarse fraction. This can take place during transport to the Arctic or in Arctic air close to Alert. During ozone depletion that originates in the surface-based inversion layer over the Arctic ocean off Alert and with which production of reactive bromine gases and particulate bromine is associated, there is enhanced production of small saturated diacids (C_2-C_5) and preferential degradation of unsaturated diacids (maleic and phthalic acids). Independent evidence by Narukawa et al. (2003b) shows the presence of brominated diacids in aerosols at Alert in spring but not in winter. Thus, bromine chemistry plays an important role in the photochemical degradation of aromatic structures and production of small diacids during Arctic ozone depletion.

Acknowledgements

The authors thank two anonymous reviewers for the critical and useful comments. This work was in part supported by the Japanese Ministry of Education, Science, Sports and Culture through Grant-in-Aid 09304054 and 10144101 and by the Air Quality Research Branch of the Atmospheric Environment Service of Canada (now Meteorological Service of Canada).

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Figure Captions

Fig. 1. Averaged molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the fine (< 2 µm) and coarse (> 2 µm) aerosol fractions collected in the high Arctic for (a) winter (January 26 to February 10) and (b) ozone depletion period after polar sunrise (April 13-22).

Fig. 2. Temporal variations in the concentrations (ngm^{-3}) of (a) total diacids, (b) pyruvic acid and (c) total ω-oxoacids, and (c) total α-dicarbonyls detected in the fine (< 2 µm) and coarse (> 2µm) fractions of the Arctic aerosols.

Fig. 3. Temporal variations in the concentrations (ngm^{-3}) of selected dicarboxylic acids (a-m), ketocarboxylic acids (n-o), and α-dicarbonyl (p) in the Arctic aerosols (fine fraction). See Table 1, for the abbreviations.

Fig. 4. Variations of relative abundance (%) of coarse fraction in the total (fine + coarse) for selected dicarboxylic acids and related compounds. See Table 1, for the abbreviations.

Fig. 5. Temporal changes in the concentrations of total dicarboxylic acids and vanadium in the Arctic aerosols. (a) fine (< 2 µm) fraction, (b) coarse (> 2 µm) fraction.

Fig. 6. Temporal changes in (a-m) diacid/vanadium ratios and (n-p) ketoacids/vanadium ratios for fine (< 2 µm) and coarse (> 2 µm) aerosols.

Fig. 7. Temporal changes in the relative abundance (%) of selected diacids in the total diacid concentrations in the Arctic aerosols (fine: < 2 µm).

Fig. 8.Variation in the concentration ratios of dicarboxylic acid and related compounds to sulfate in the fine (< 2 µm) aerosols collected in the high Arctic.

Fig. 9. Concentration changes of particulate Br and total diacids (fine aerosol mode, ngm^{-3}) and surface ozone (ppbv) in the high Arctic atmosphere from January 22 to April 22, 1992.

Fig. 10. Relationship of concentration ratios of succinic acid (C_4) to vanadium (V) with ozone for (a) winter and (b) spring, and (c) with particulate Br for ozone depletion period in arctic spring. Data for the fine aerosol fraction (< 2 µm).

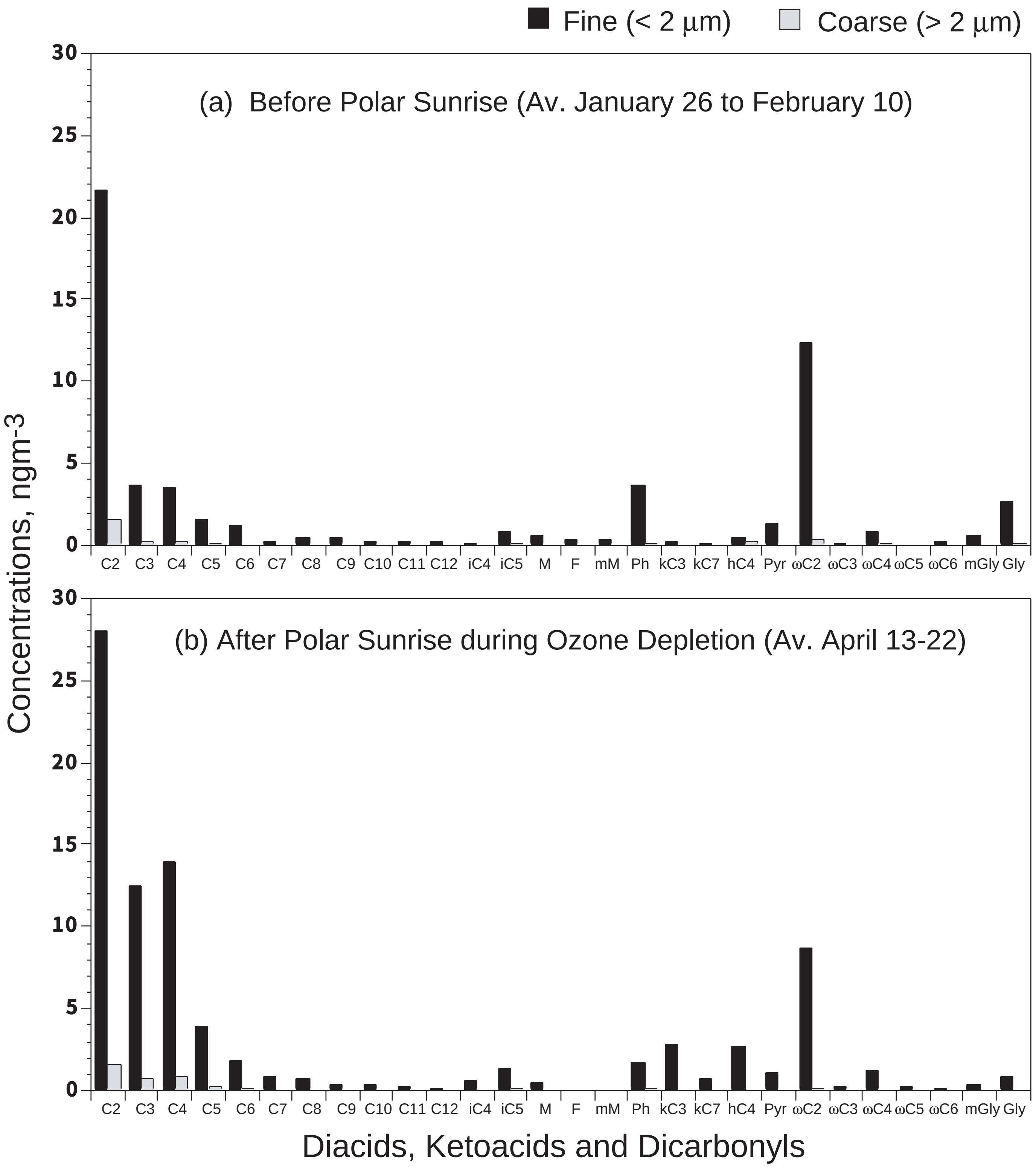
Fig. 11. Relationship of the concentration ratios of (a) maleic acid and (b) phthalic acid to succinic acid with particulate bromine in the high Arctic aerosols during ozone depletion period (April 6-22, 1992).

Table 1. Concentrations (ngm^{-3}) of dicarboxylic acids, ketocarboxylic acids, and dicarbonys detected in the Arctic aerosol samples (n=96) collected on daily basis at Canadian Arctic, Alert in 24 January to 20 April, 1992.

Components	Carbon Nos.	Abbr.	M.W.	Fine (<2 µm)		Coarse (>2 µm)	
				Ave.	range	Ave.	range
Diacids							
Oxalic	2	C_2	90	25.5	6.51-59.1	1.64	<0.001-6.13
Malonic	3	C_3	104	7.60	1.23-20.3	0.36	<0.001-1.12
Succinic	4	C_4	118	7.66	1.64-19.3	0.42	0.037-1.33
Glutaric	5	C_5	132	3.06	<0.01-6.77	0.16	0.008-0.47
Adipic	6	C_6	146	6.98	0.01-83.7	0.15	<0.001-1.65
Pimelic	7	C_7	160	0.76	<0.01-3.56	0.04	<0.001-0.27
Suberic	8	C_8	174	0.87	0.11-4.24	0.05	<0.001-0.23
Azelaic	9	C_9	188	0.63	<0.01-3.35	0.07	<0.001-0.63
Sebacic	10	C_{10}	202	0.52	<0.01-3.35	0.02	<0.001-0.18
Undecanedioic	11	C_{11}	216	0.44	<0.01-2.82	0.02	<0.001-0.18
Dodecanedioc	12	C_{12}	230	0.29	<0.01-2.58	0.02	<0.001-0.35
Methylmalonic	4	iC_4	118	0.32	<0.01-1.01	0.02	<0.001-0.13
Methylsuccinic	5	iC_5	132	1.46	<0.01-21.3	0.10	<0.001-0.89
Maleic	4	M	116	0.59	0.0751.61	0.04	<0.001-0.41
Fumaric	4	F	116	0.39	<0.01-2.75	0.04	<0.001-0.17
Methylmaleic	5	mM	130	0.26	<0.01-3.38	0.05	<0.001-2.86
Phthalic	8	Ph	166	3.55	<0.01-10.5	0.15	<0.001-0.91
Oxomalonic	3	kC_3	118	1.54	<0.01-6.77	0.02	<0.001-0.15
4-Oxopimelic	7	kC_7	174	0.49	<0.01-1.50	0.03	<0.001-0.12
Malic	4	hC_4	134	1.54	<0.01-6.46	0.10	<0.001-0.56
Sub total				64.4	18.3-146	3.49	0.686-10.5
Ketoacids							

Pyruvic	3	Pyr	88	1.28	0.37-2.76	0.05	<0.001-0.22
Glyoxylic (2-oxoethanoic)	2	ωC_2	74	11.9	<0.01-38.9	0.34	<0.001-2.34
3-Oxopropanoic	3	ωC_3	88	0.20	<0.01-0.576	0.02	<0.001-0.07
4-Oxobutanoic	4	ωC_4	102	1.14	<0.01-3.13	0.11	<0.001-0.76
5-Oxopentanoic	5	ωC_5	116	0.11	<0.01-0.447	0.01	<0.001-0.09
6-Oxohexanoic	6	ωC_6	130	0.27	<0.01-1.08	0.01	<0.001-0.35
Sub total				14.9	4.59-44.1	0.35	0.008-2.81
α-Dicarbonyls							
Glyoxal	2	Gly	58	1.83	0.46-4.53	0.08	<0.001-1.32
Methylglyoxal	3	mGly	72	0.53	<0.01-2.76	0.02	<0.001-0.35
Sub total				2.36	<0.01-5.34	0.11	<0.001-1.34

Fig. 1 (Kawamura et al.)



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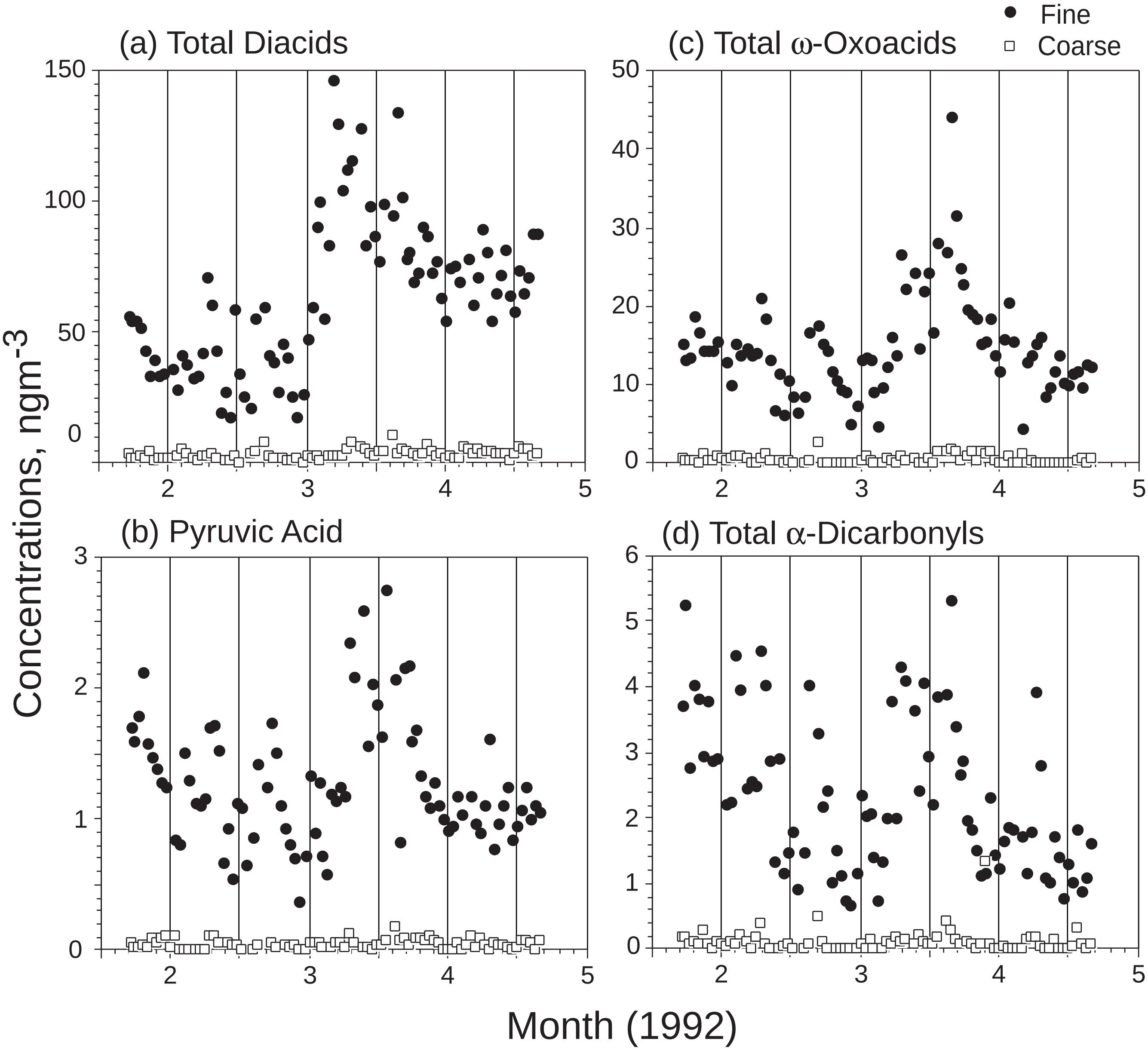

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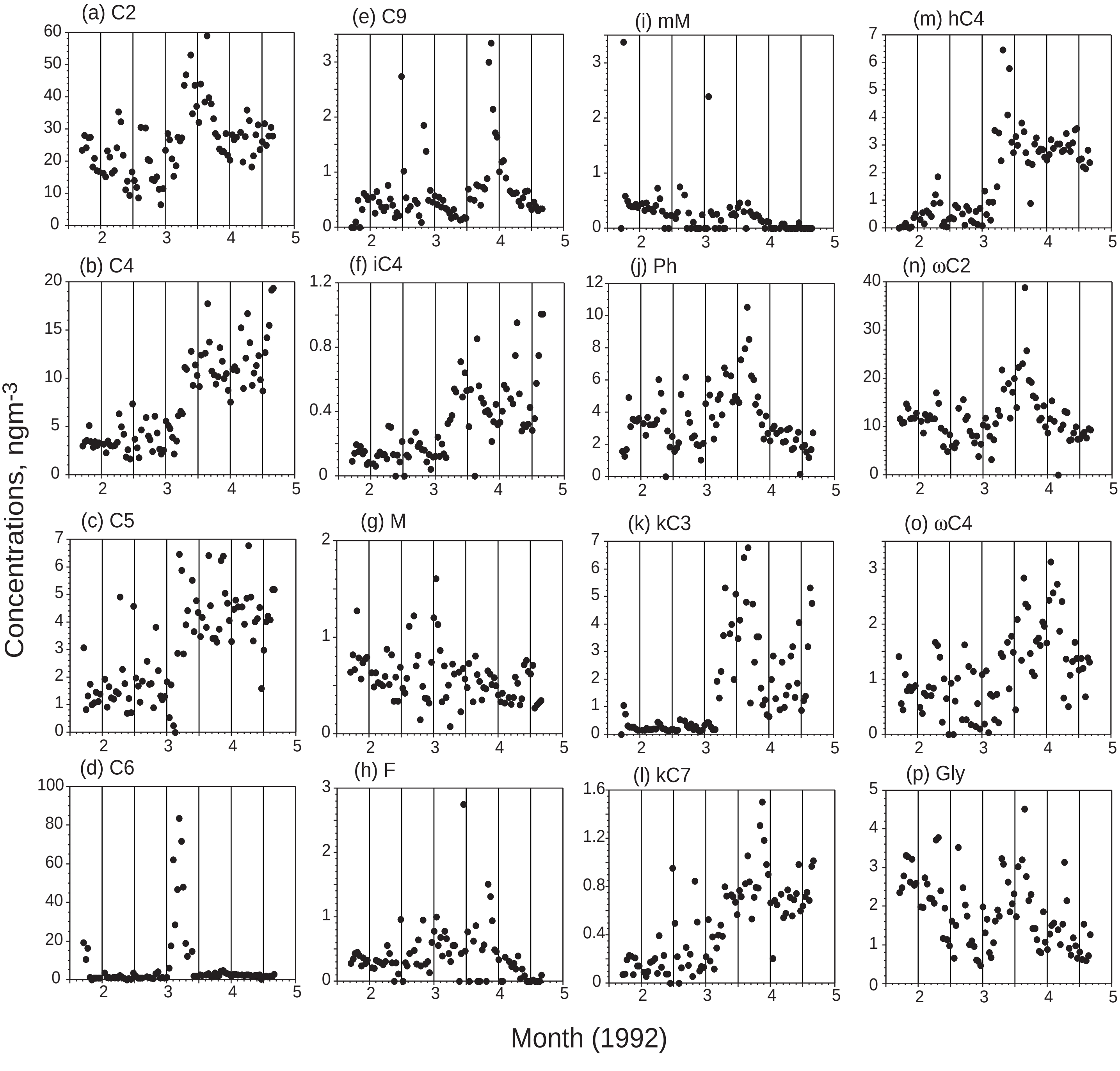

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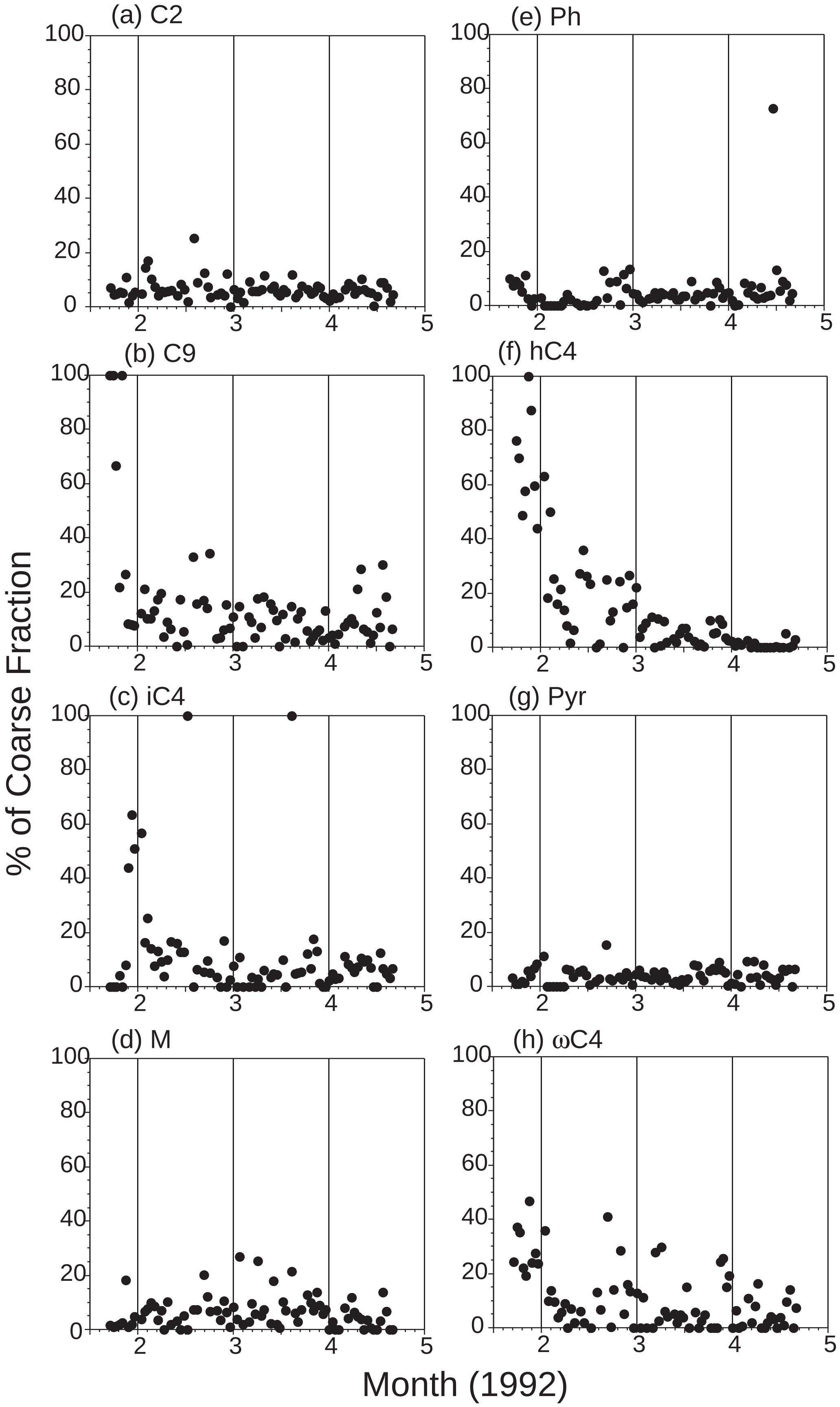

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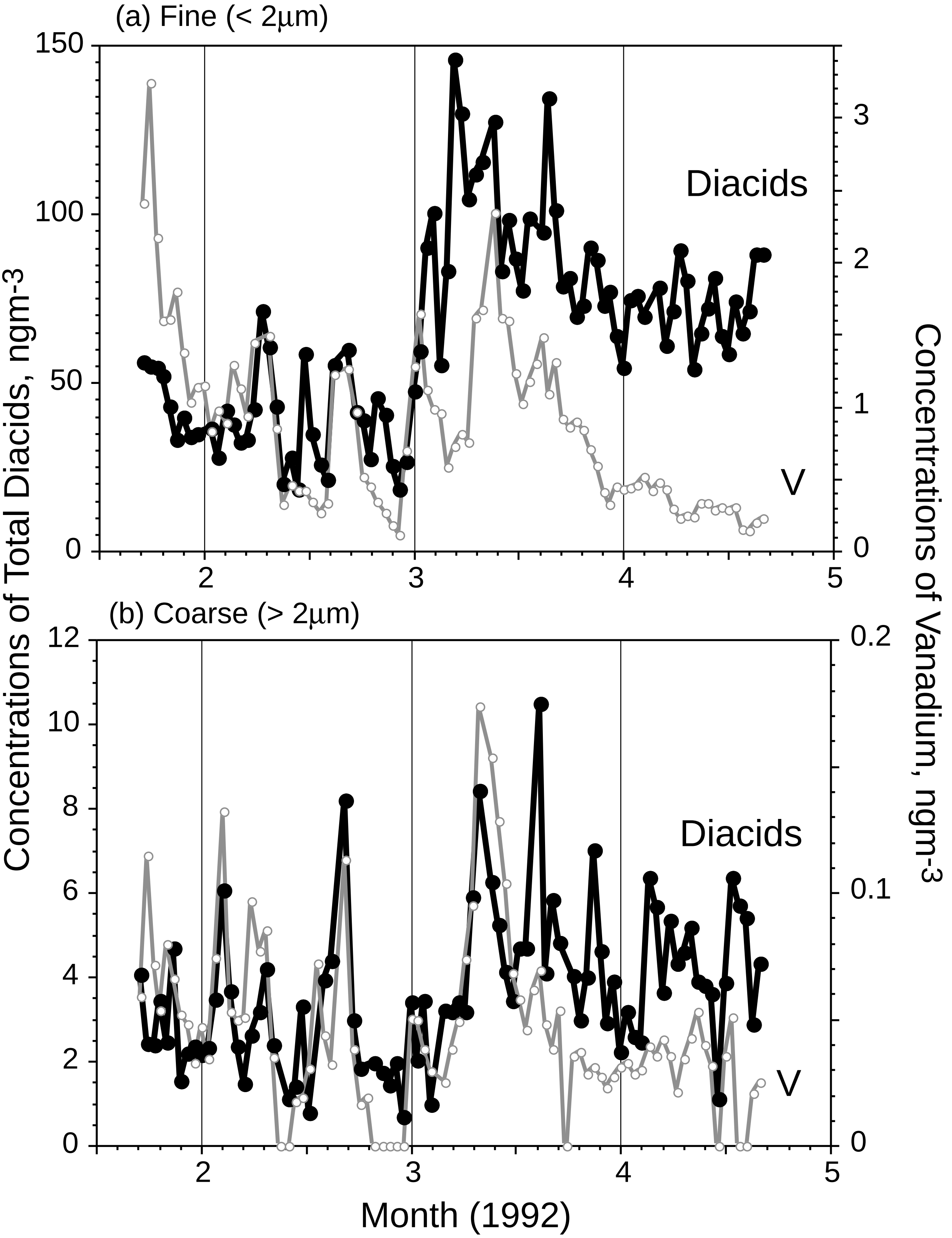

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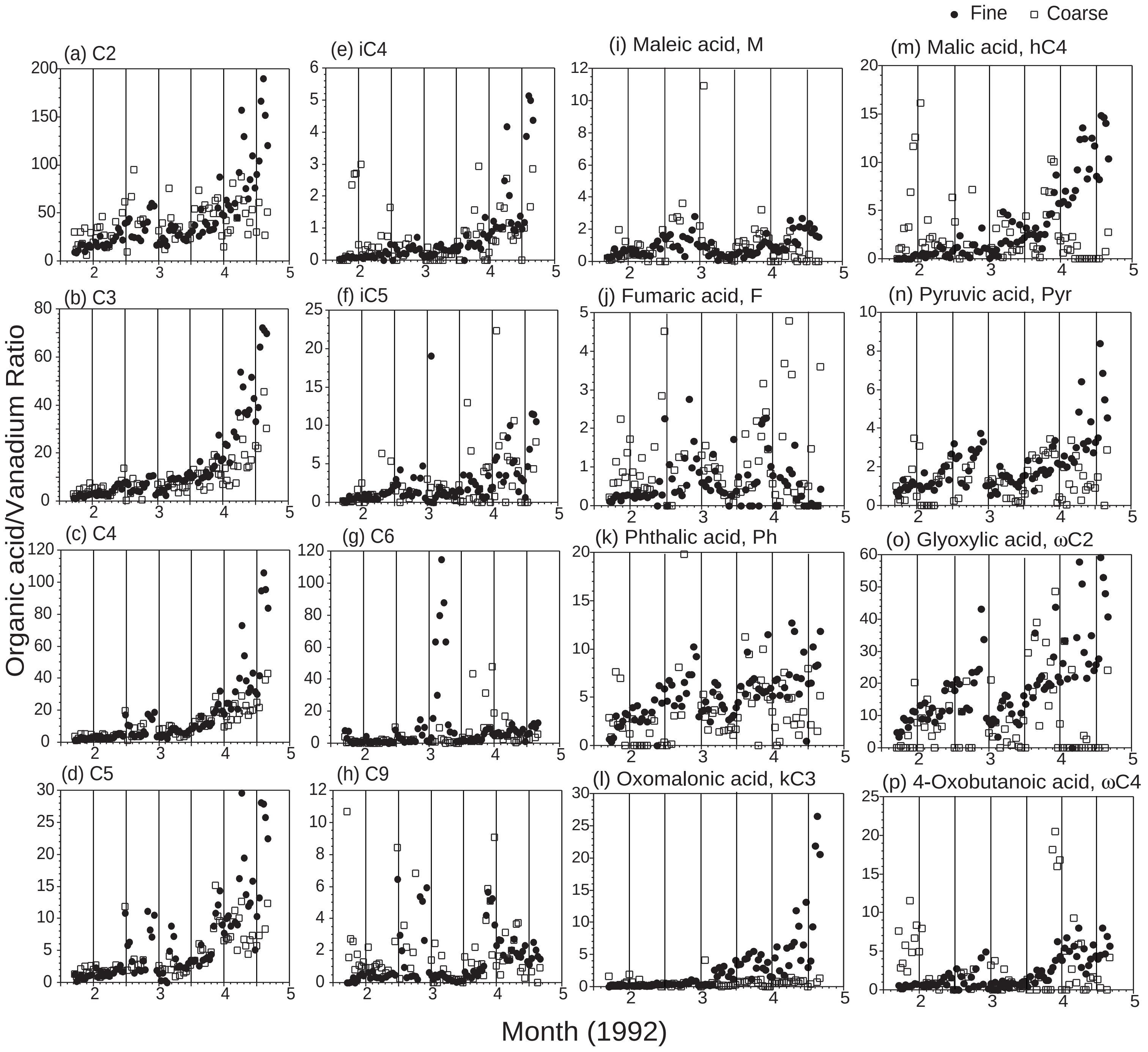

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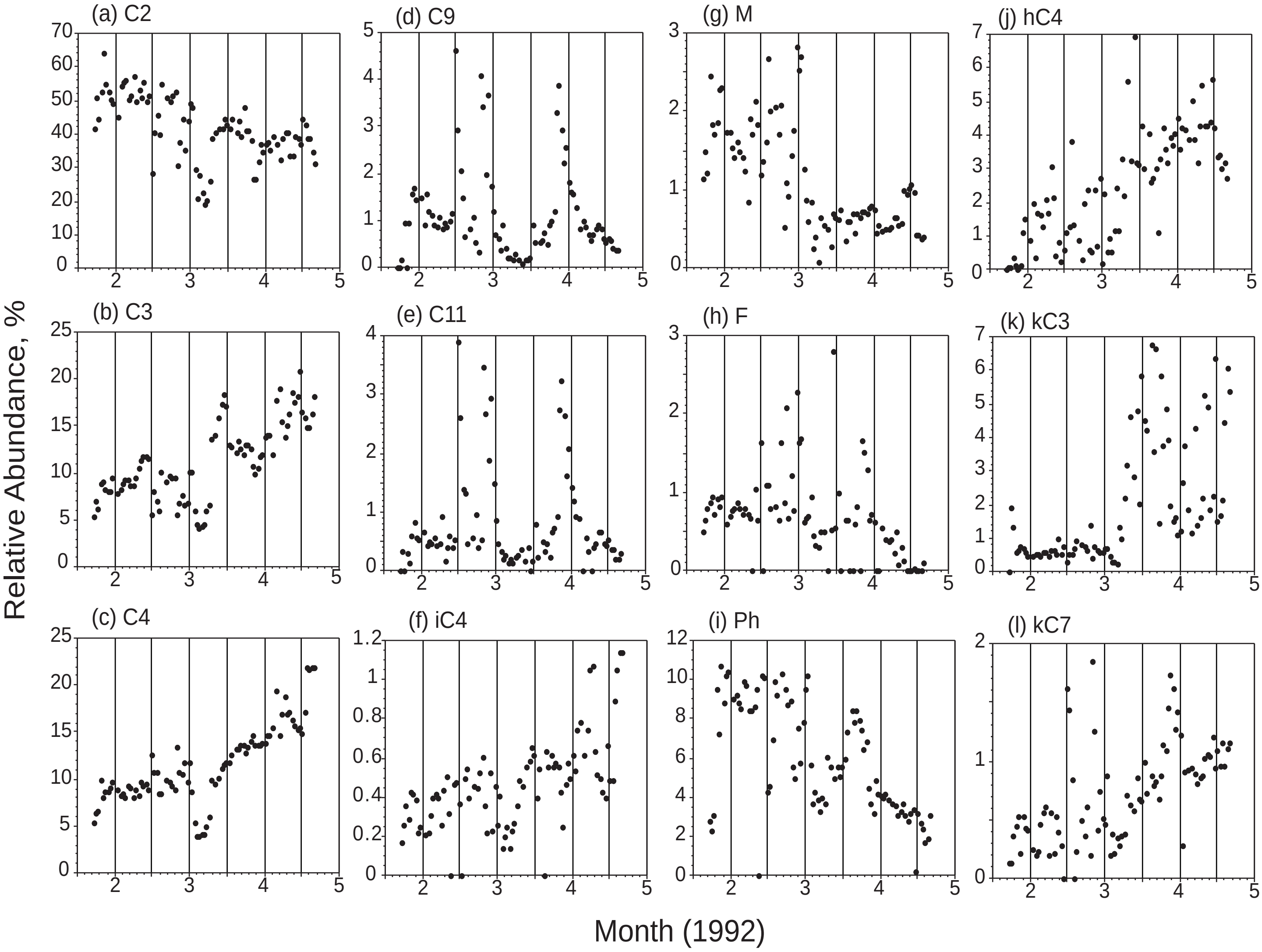

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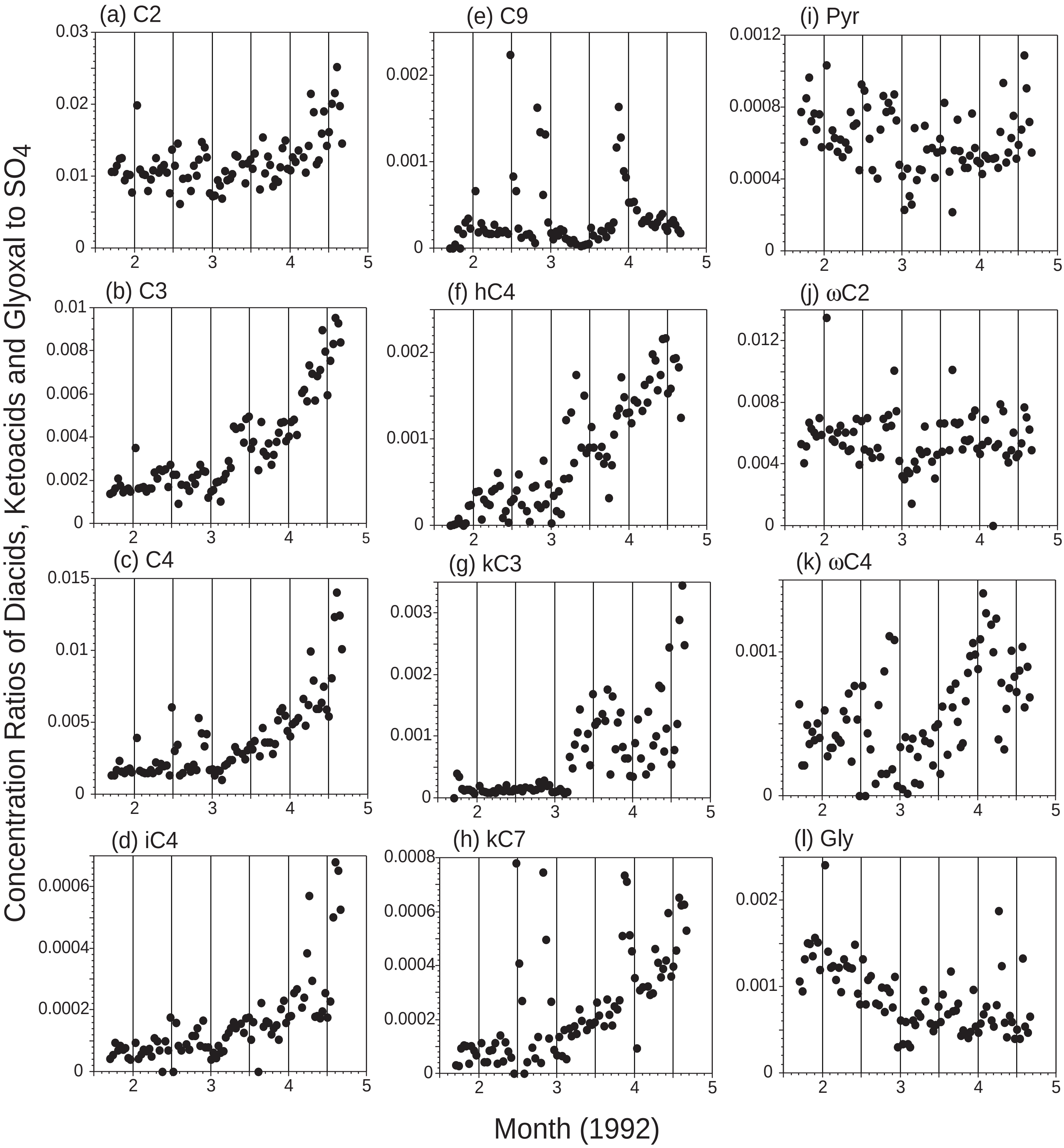

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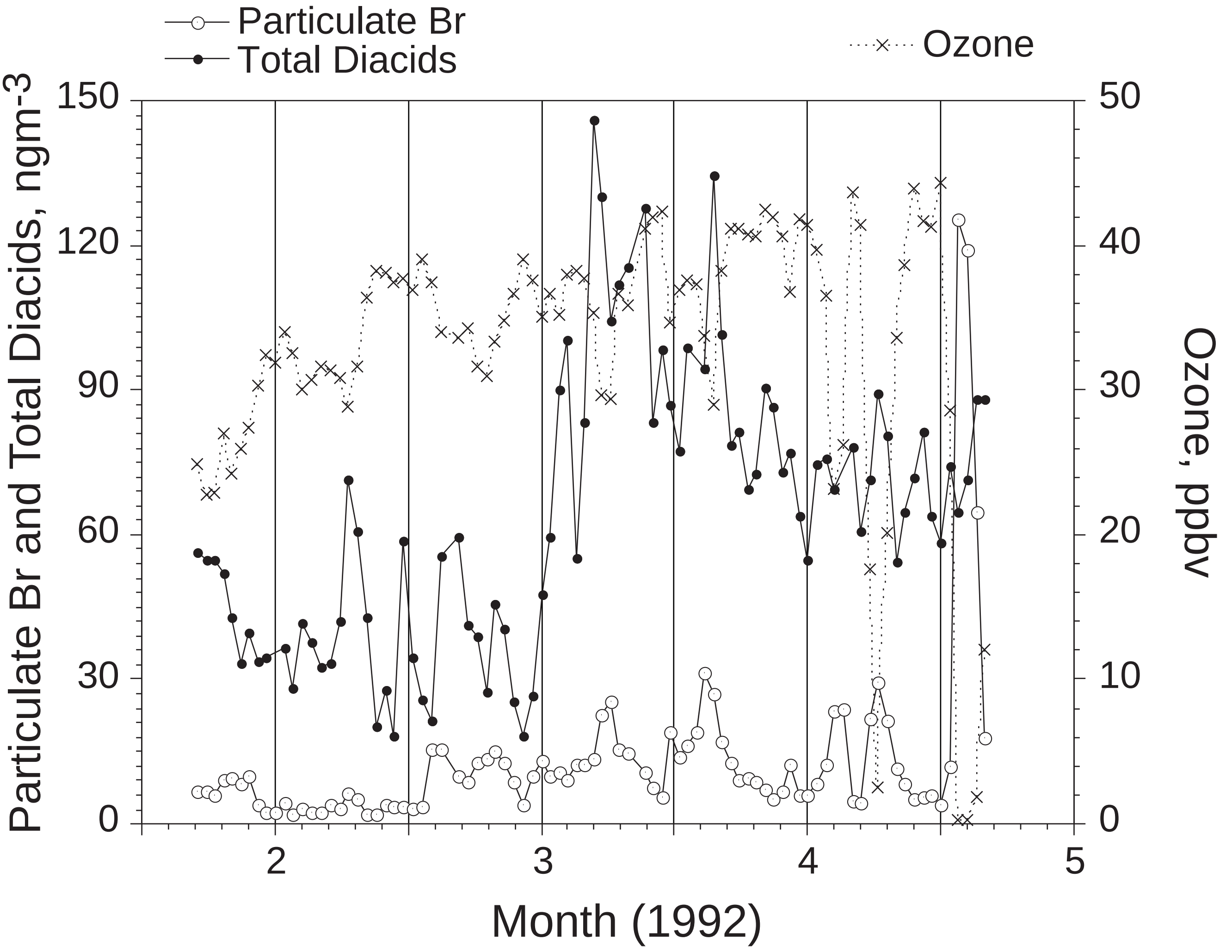

Fig. 10 (Kawamura et al.)