Seasonal Changes in Molecular and Stable Isotopic Compositions of Dicarboxylic Acids and Related Polar Compounds in the Northeast Asian Atmosphere

(driven by Biological Activity & Secondary Processes)

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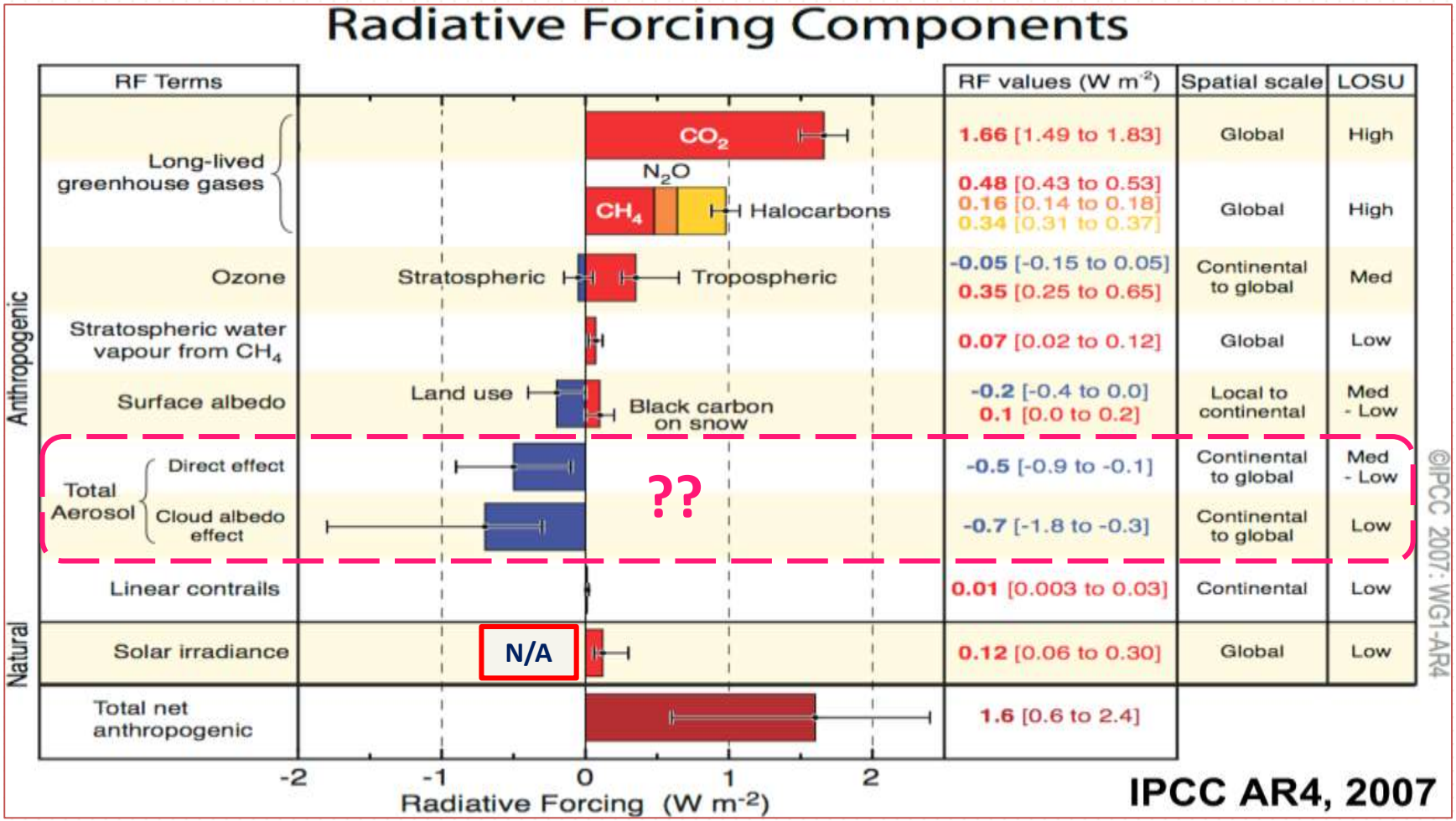
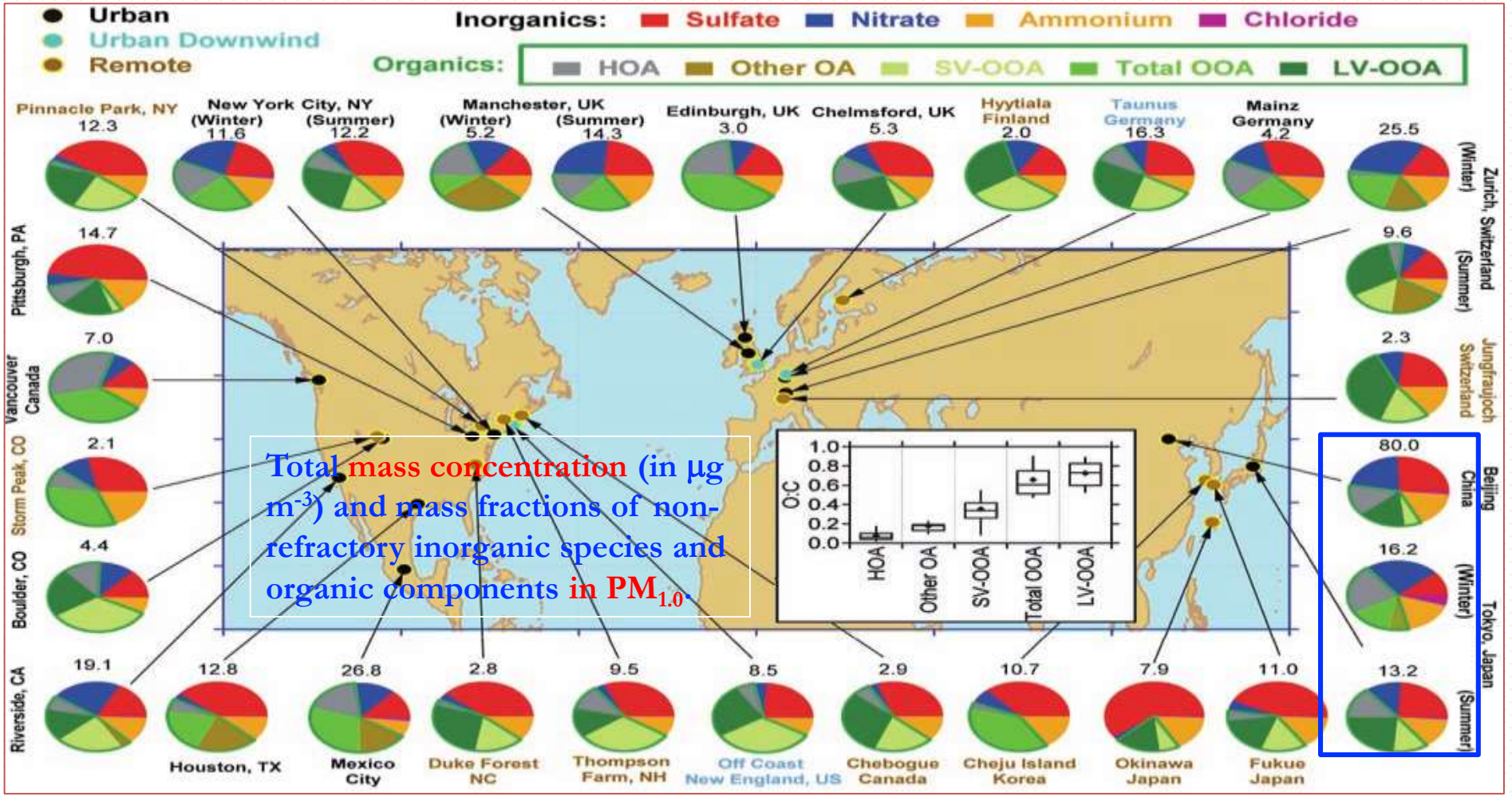
The experiments were done at ILTS, Hokkaido University, Sapporo, Japan

Uncertainty in Aerosol Impact Assessment



- Due to lack of organic aerosol data and their source info. !!!

Aerosol Composition over World



Adopted from ***Jimenez et al., Science, 2009***

- In fact, OA fraction accounts about 50% or even more (up to 90% in submicron aerosols *(Kanakidou et al., 2005)*) at some locations.

Aerosol Composition/Loading over Asia

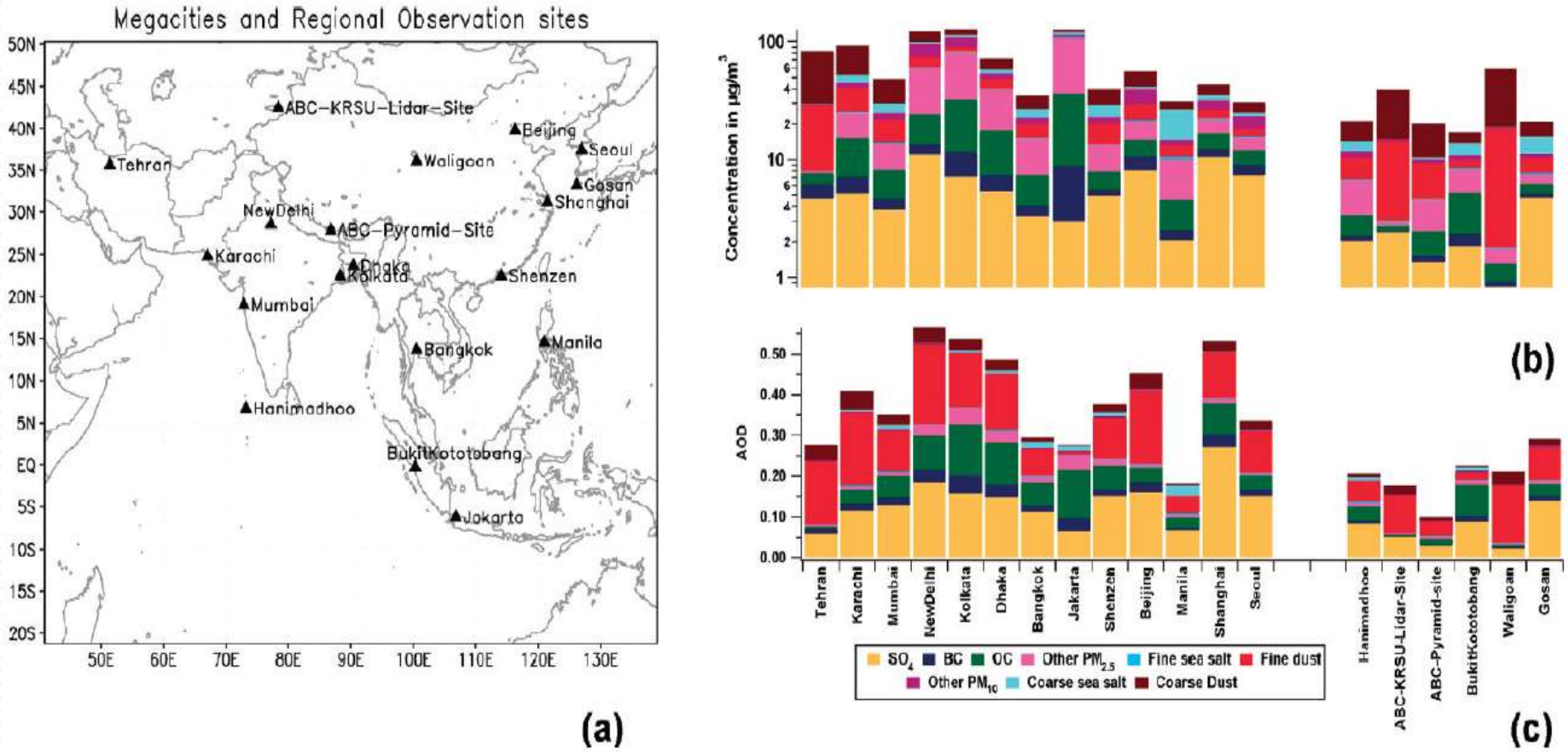


FIGURE 2. Location of the megacities and regional observation sites (a); species contribution to $PM_{2.5}$ mass ($\mu g/m^3$) (b) and AOD (c) at the megacities and regional observation sites. The $PM_{2.5}$ is plotted using a log scale to highlight the pollution related aerosols, which are the major contributors to AOD.

Adopted from ***Carmichael et al., 2009***

- Interestingly, OC is much higher than SO_4^{2-} at some locations, e.g., Kolkata, Dhaka, Jakarta, etc., in Asia.

Aerosol Composition in India

Atmos. Chem. Phys., 11, 8215–8230, 2011
www.atmos-chem-phys.net/11/8215/2011/
doi:10.5194/acp-11-8215-2011

Atmospheric Chemistry and Physics

Characteristics, seasonality and sources of carbonaceous and ionic components in the tropical aerosols from Indian region

C. M. Pavuluri[1], K. Kawamura[1], S. G. Aggarwal[1,2], and T. Swaminathan[3]

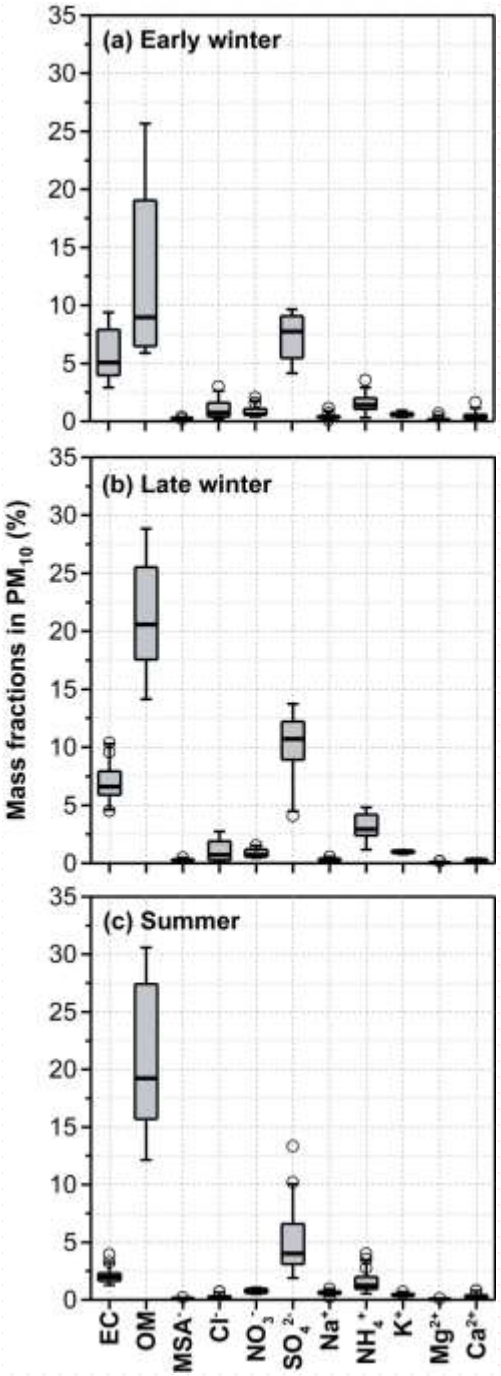
Average concentration of

EC: 6.5 & 1.6 μg m^{-3}

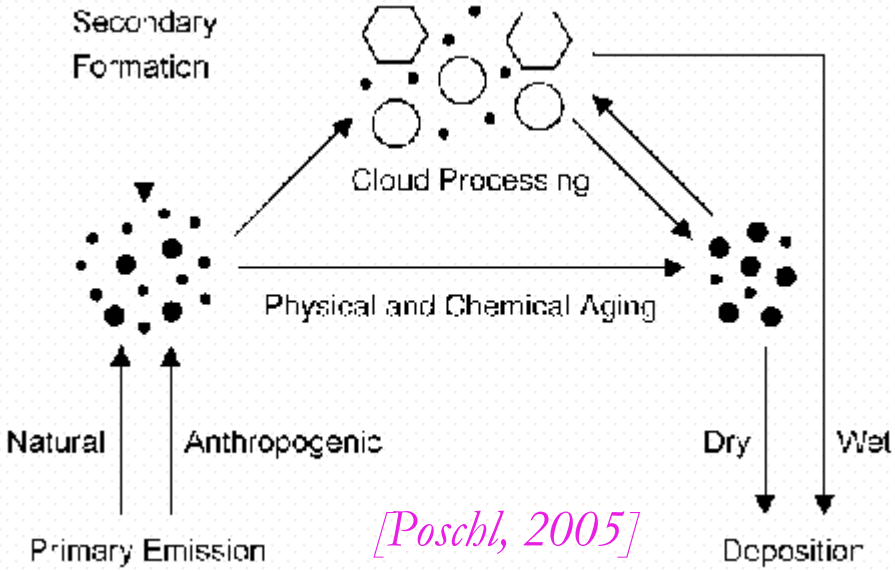
OC: 9.1 & 9.7 μg m^{-3}

SO_4^{2-}: 8.8 & 4.1 μg m^{-3}

in winter and summer, respectively.



Secondary Formation & Transformations with Aging



[Poschl, 2005]

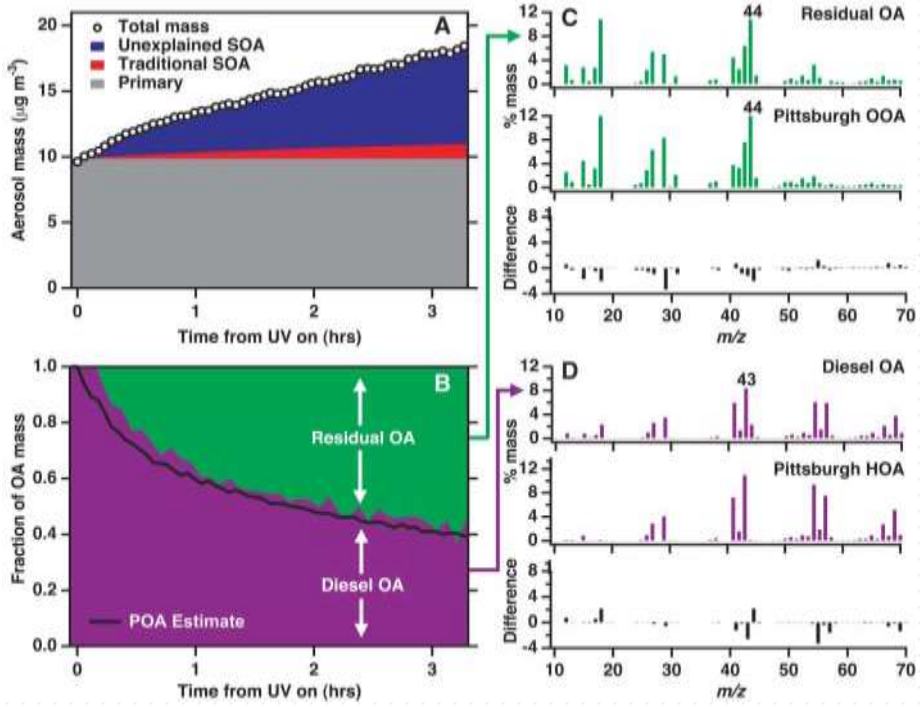


Fig. 2. Results from the photochemical oxidation of diesel exhaust in an environmental chamber. (**A**) The wall-loss–corrected aerosol mass, measured with a scanning mobility particle sizer, assuming a density of 1 g cm^{-3}. The wall-loss correction is based on measured loss of the particle number, accounting for the effects of coagulation, and it assumes that semivolatile vapors are in equilibrium with both the suspended aerosol and the material deposited on the wall during the experiment (*19*). The gray area indicates the primary aerosol (POA + other species). The red area shows the upper-bound estimate of the contribution of known SOA precursors to the suspended aerosol mass (*19*). We attribute the blue area to SOA formed from SVOC and/or IVOC oxidation. AMS results are shown in (**B**) to (**D**). The AMS OA spectrum can be described by two components: the initial diesel spectrum (diesel OA) and an oxidized residual spectrum (residual OA). The relative contribution of these two components to the overall OA spectrum is shown in (B). The spectra of these two components are compared to reference spectra obtained from factor analysis of ambient AMS data in (C) and (D). The spectrum of the diesel OA component is quite similar to the hydrocarbonlike OA (HOA) factor (*8*, *9*). By the end of the experiment, the spectrum of the oxidized residual OA component is quite similar to that of the OOA factor (*8*, *9*). The solid line in (B) indicates the fractional contribution of POA to the suspended OA, based on the initial particle mass and the wall-loss rate and analogous to the results shown in (A). The excellent agreement between this line and the relative contribution of the two AMS components indicates that these two independent approaches yield the same estimate of SOA. *m/z*, mass/charge ratio.

From ***Robinson et al.****, Science, 2007*

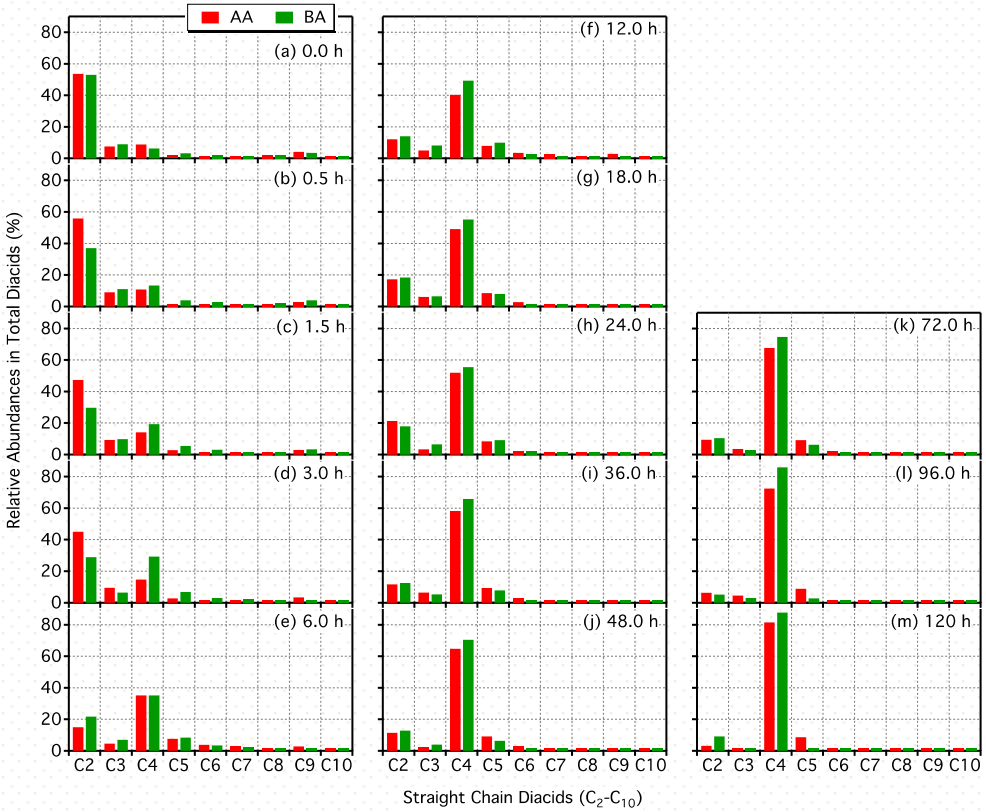
- The composition of organics significantly change with aging

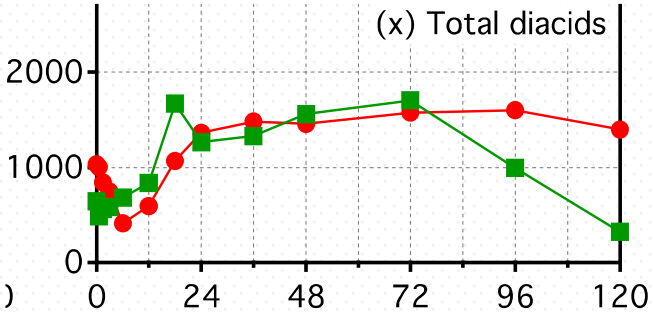
Atmos. Chem. Phys., 15, 7999–8012, 2015
www.atmos-chem-phys.net/15/7999/2015/
doi:10.5194/acp-15-7999-2015

Atmospheric Chemistry and Physics Open Access

Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls

C. M. Pavuluri[1], K. Kawamura[1], N. Mihalopoulos[1,2,3], and T. Swaminathan[4]





- When precursors are not available, degradation (to CO_2) become dominant.

Figure 5. Changes in relative abundances of straight-chain diacids (C_2–C_{10}) to total diacids as a function of UV irradiation time in AA and BA.

Objective

Objective of our research is to identify the sources and atmospheric processing of aerosols during long-range atmospheric transport as well as their variations with time over Northeast Asia through the measurements of:

(i) radiocarbon (^{14}C) in TC & WSOC, and organic tracers, and ^{13}C and ^{15}N isotopic ratios in bulk and water-soluble contents

(ii) diacids and related polar compounds (ketoacids, α-dicarbonyls and fatty acids) &

(iii) compositions of trace elements, inorganic ions & carbonaceous components,

in atmospheric aerosols (collected from Sapporo, Japan & in currently in Northeast China).

Dicarboxylic Acids and Related Polar Compounds

- **Impacts –** hygroscopicity & CCN activity [*Saxena et al.*, 1995]

  indirect radiative effect & hydrological cycle [*Albrecht, 1987*]

- **Loading –** diacids comprise up to 16% of aerosol carbon [*Kawamura & Sakaguchi, 1999*]

- **Sources –** Primary [*Kawamura & Kaplan*, 1987; *Narukawa et al.*, 1999]

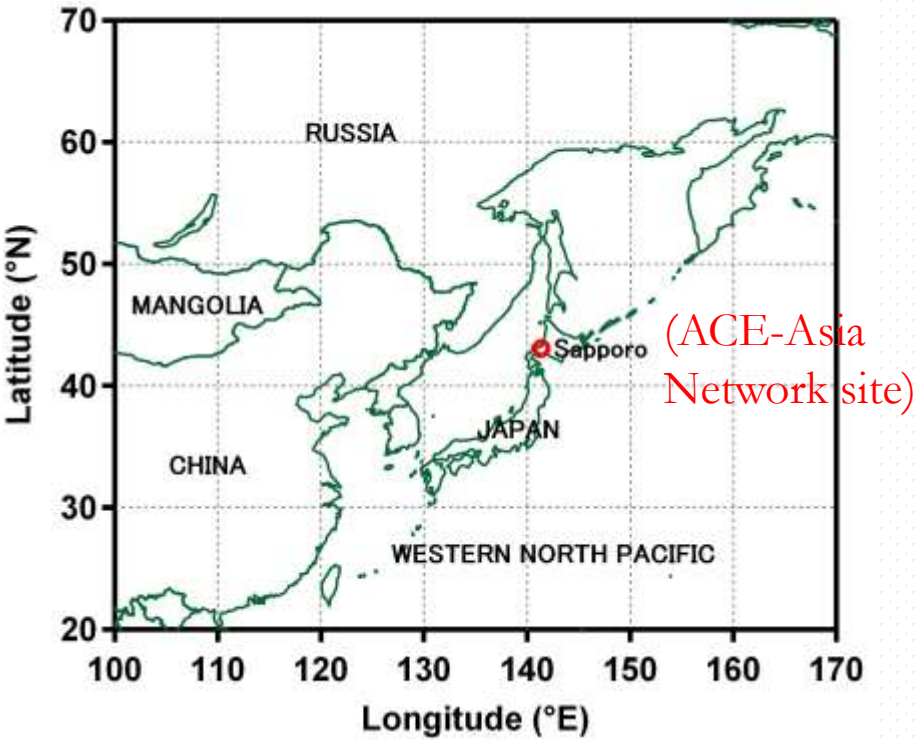
  Secondary [*Kawamura & Sakaguchi*, 1999; *Kawamura et al.*, 1996]

- **Origins –** Global models: biomass burning and SOA from BVOCs are the two major sources of OA [*Kanakidou et al.*, 2005]

  Regional studies: anthropogenic sources contribute ~50% of OA and even more (in Asia) [*de Gouw and Jiminez*, 2009]

  - Thus, there is an ambiguity on anthropogenic and biogenic source contributions of organics (including diacids and related polar compounds) particularly in East Asia.

Ideal Location for Northeast Asian Aerosol Study



(ACE-Asia Network site)

[*Aggarwal and Kawamura*, 2008; *Yamamoto et al.*, 2011]

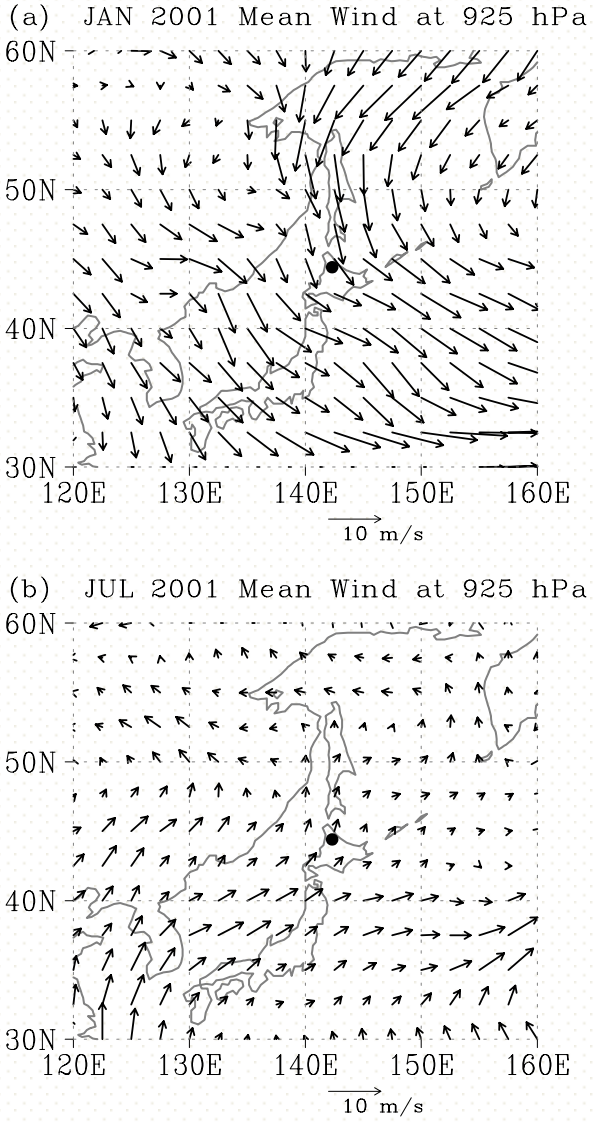


Figure 11. Monthly mean horizontal wind field (m s^{-1}, vectors) at 925 hPa (≈1 km) in (a) January and (b) July (ECMWF 2.5° × 2.5° grid data). The geographic location of Moshiri observatory is also shown (solid circle).

- **Generally, wind regimes are:**

Westerly & NW	**in autumn**
Northerly	**in winter**
Westerly	**in spring**
Southwesterly & SE	**in summer**

[from *Koike et al.*, 2006]

Aerosol Sampling

- TSP & ~2 weeks each (n = 21), ILTS building (~20m AGL), Hokkaido University, during September 2009 – October 2010
- Potential artifacts – may be negligible because:
  - adsorbed organics should be negligible [*Turpin et al.*, 2000], production/transformations are unlikely & evaporation should be negligible

Chemical Analysis

- Extracted into organic free Milli Q water, derivatized to butyl esters and/or butoxy acetals, & measured with GC and GC-MS system
- Recoveries were 91% for C_2 and C_3 acids & ~100% for C_4, C_5 & C_6 acids, & analytical errors were >12% for major species
- The data reported here is corrected for field blanks
- Stable carbon isotope ratios were determined using EA-irMS

Concentrations of Diacids & Related Compounds

	Concentration (ng m^{-3})			Relative abundance (%)
	Range	Med.	Ave. ± SD	Ave. ± SD
Diacids				
C_2	101–509	230	232 ± 104	69.3 ± 6.4
C_3	13.4–56.2	34.0	33.0 ± 12.3	10.2 ± 2.3
C_4	6.55–28.5	15.7	17.1 ± 5.74	5.65 ± 1.9
C_5	0.92–5.67	3.65	3.64 ± 1.23	1.25 ± 0.5
C_6	0.82–3.42	2.46	2.38 ± 0.64	0.80 ± 0.3
C_7	0.60–3.12	1.55	1.67 ± 0.67	0.51 ± 0.1
C_8	1.06–8.84	3.31	3.76 ± 2.03	1.11 ± 0.4
C_9	4.5–26.34	13.78	13.8 ± 5.96	4.28 ± 1.5
C_{10}	0.30–5.55	0.95	1.57 ± 1.45	0.46 ± 0.4
C_{11}	0.66–3.05	1.37	1.53 ± 0.57	0.49 ± 0.2
C_{12}	BDL–0.10	BDL	0.02 ± 0.03	0.01 ± 0.0
iC_4	0.18–0.83	0.56	0.51 ± 0.17	0.17 ± 0.1
iC_5	0.21–2.16	0.95	0.94 ± 0.54	0.36 ± 0.3
iC_6	0.10–0.54	0.31	0.32 ± 0.13	0.12 ± 0.1
M	0.25–1.66	0.91	0.95 ± 0.43	0.34 ± 0.2
F	0.16–1.37	0.69	0.70 ± 0.29	0.24 ± 0.1
mM	0.16–1.24	0.56	0.58 ± 0.28	0.21 ± 0.2
Ph	1.28–8.59	3.38	3.99 ± 2.05	1.52 ± 1.2
iPh	0.15–2.89	0.67	0.74 ± 0.54	0.25 ± 0.2
tPh	1.76–5.49	3.88	3.78 ± 1.08	1.30 ± 0.6
hC_4	BDL–0.34	0.15	0.16 ± 0.09	0.06 ± 0.0
kC_3	0.34–4.92	2.31	2.46 ± 1.31	0.90 ± 0.7
kC_7	0.34–5.10	1.43	1.77 ± 1.33	0.53 ± 0.4
Sub total	157–643	313	327 ± 122	
Ketoacids				
ωC_2	10.3–28.1	18.0	18.4 ± 5.8	53.0 ± 11
ωC_3	0.69–3.78	1.54	1.69 ± 0.71	4.80 ± 1.3
ωC_4	1.08–4.65	2.49	2.71 ± 0.97	7.91 ± 2.5
ωC_5	0.33–1.48	0.88	0.92 ± 0.33	2.68 ± 0.9
ωC_7	0.97–5.44	2.58	2.67 ± 1.29	7.75 ± 3.0
ωC_8	1.08–6.07	2.53	2.96 ± 1.28	8.59 ± 3.0
ωC_9	0.71–2.5	1.50	1.58 ± 0.56	4.74 ± 1.9
Pyr	2.23–7.26	3.26	3.64 ± 1.16	10.5 ± 1.6
Sub total	21.8–52.7	34.3	34.5 ± 8.2	

	Concentration (ng m^{-3})		
	Range	Med.	Ave. ± SD
Tricarboxylic acid			
Cit	BDL–4.18	0.48	0.82 ± 1.00
α-Dicarbonyls			
Gly	1.03–8.70	2.5	3.19 ± 1.91
mGly	1.04–12.13	2.4	3.53 ± 2.78
Sub total	2.07–16.34	4.62	6.72 ± 3.82
Fatty acids			
C_{14}	2.18–12.5	6.54	7.06 ± 2.94
C_{16}	5.56–76.5	32.0	34.5 ± 16.4
C_{17}	0.24–6.91	1.88	2.40 ± 1.84
C_{18}	1.68–24.55	17.1	15.4 ± 6.17
$C_{18:1}$	BDL–43.9	10.5	15.3 ± 15.7
C_{20}	1.13–5.97	2.41	2.94 ± 1.33
C_{21}	BDL–0.74	0.46	0.45 ± 0.16
C_{22}	1.58–6.79	3.08	3.17 ± 1.45
C_{23}	0.14–1.56	0.71	0.73 ± 0.32
C_{24}	1.71–7.08	3.52	3.60 ± 1.61
C_{25}	BDL–0.99	0.46	0.47 ± 0.25
C_{26}	BDL–6.14	2.49	2.74 ± 1.80
C_{27}	BDL–0.41	BDL	0.07 ± 0.11
C_{28}	BDL–4.41	1.55	1.63 ± 1.14
C_{29}	BDL–0.14	BDL	0.01 ± 0.03
C_{30}	BDL–2.64	0.39	0.75 ± 0.87
Sub total	33.0–173	83.2	91.3 ± 41.8

- Oxalic (C_2) acid – most abundant
- $C_3 > C_4 > C_9 >$ Ph acids
- Even C numbered fatty acids are abundant

Implication for Long-range Transported (Aged) Aerosols

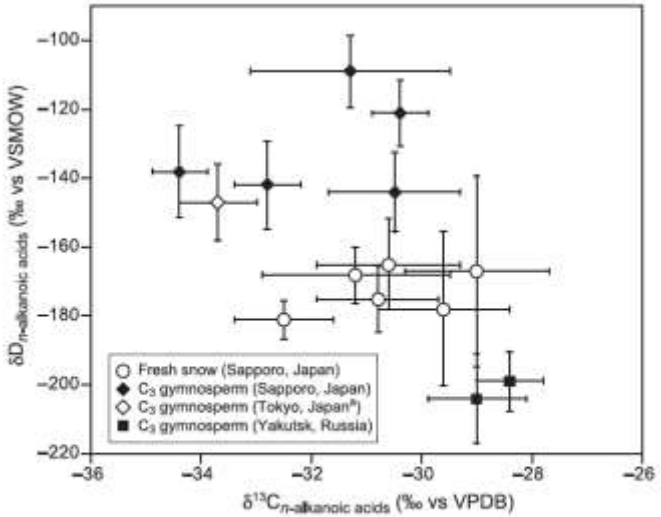
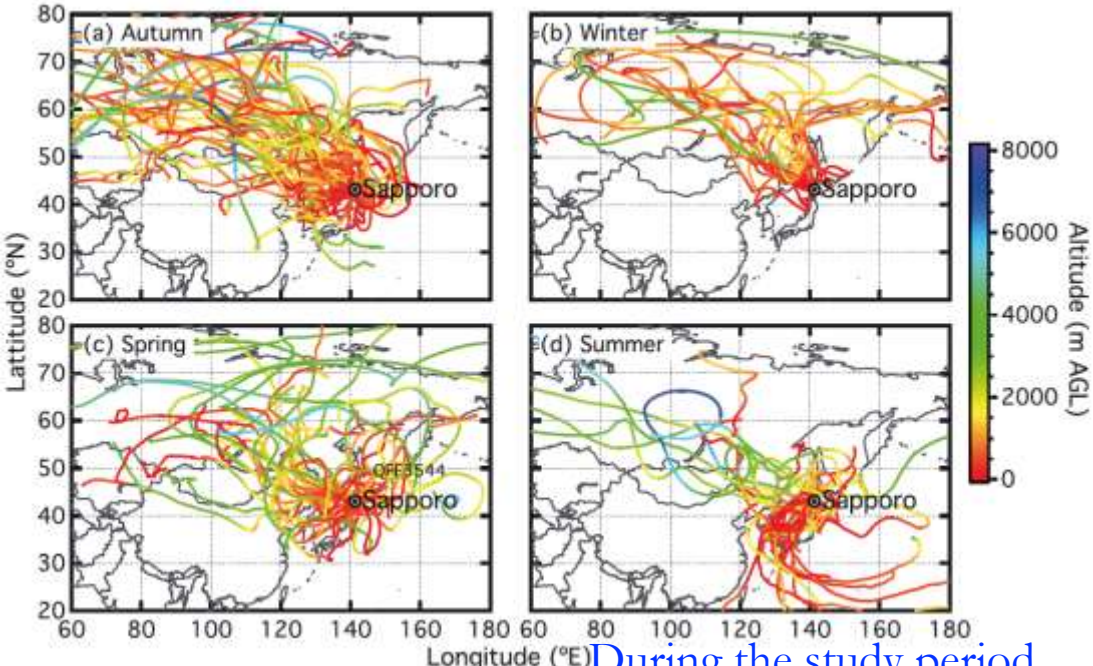


Fig. 6. Cross plot of weighted mean $\delta^{13}C$ and δD values of C_{22}–C_{28} even carbon-numbered *n*-alkanoic acids in snow and plant leaves from Sapporo and Tokyo, Japan and Yakutsk, Russian Far East. Error bars indicate a standard deviation. [a]Data from Chikaraishi and Naraoka (2007).

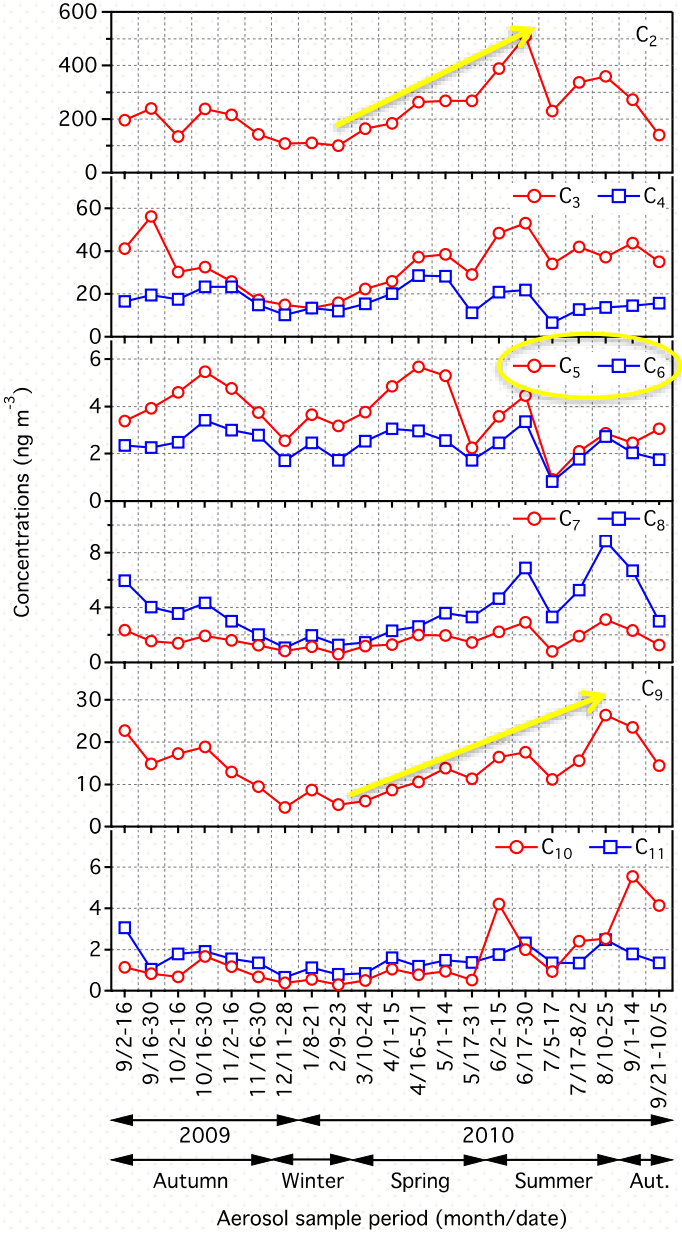
[*Yamamoto et al.*, 2011]

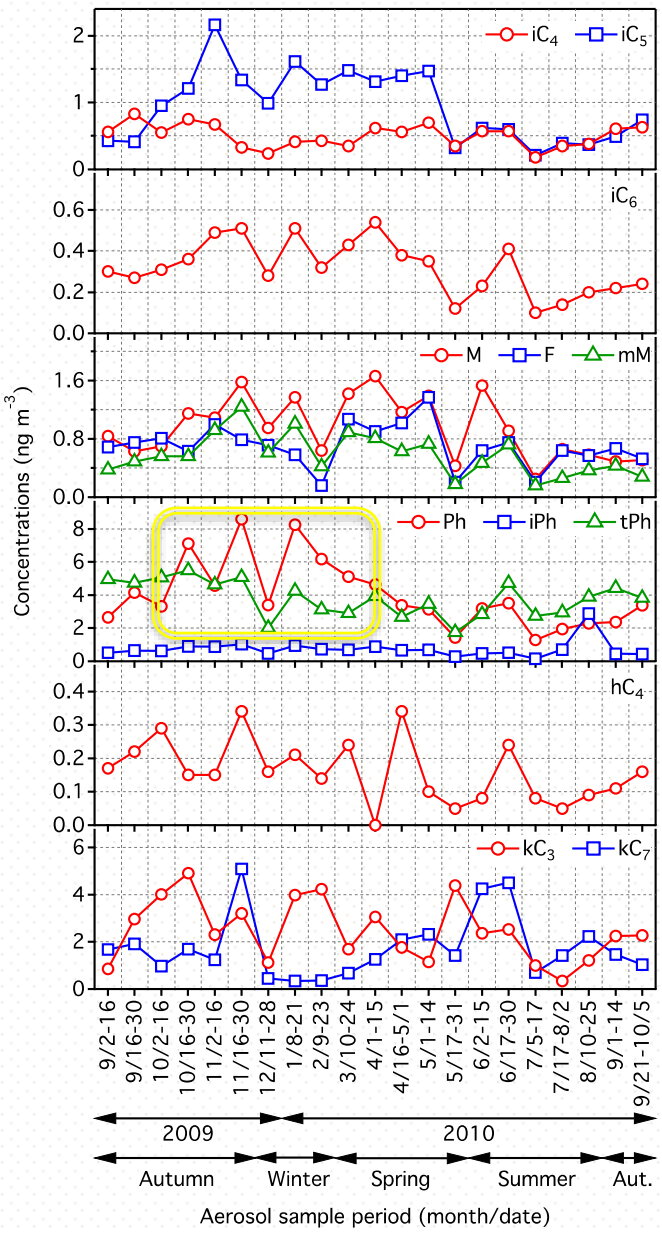


During the study period

Source/Location	Sampling Period	Diacids-C/TC (%)			Diacids-C/WSOC (%)			C_3/C_4			Reference
		Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	
Auto. exhaust								0.25	0.44	0.35	*Kawamura & Kaplan*, 1987
Tokyo, Japan	Apr 1988 to Feb 1989	0.18	1.80	0.95				0.56	2.9	1.60	*Kawamura & Ikushima*, 1993
Sapporo, Japan	May-Jul 2005	0.74	3.60	1.80	2.80	8.10	4.80	0.88	2.40	1.40	*Aggarwal & Kawamura*, 2008
Chennai, India	Jan-Feb & May 2007	0.40	3.00	1.58	4.00	11.0	5.90				*Pavuluri et al.*, 2010
Gosan, Korea	Apr 2001 to Mar 2002	0.80	6.20	3.10							*Kawamura et al.*, 2004
Western Pacific	Aug-Oct 1992	1.10	4.90	3.20	2.10	14.7	8.20				*Sempere & Kawamura*, 2003
Western North to Central Pacific	Sept-Dec 1990	1.10	15.8	8.80							*Kawamura & Sakaguchi*, 1999
Arctic Ocean	Aug 2009	0.28	2.10	0.87							*Kawamura et al.*, 2012
Arctic (Alert)	Feb-Jun 1991	1.50	9.00	4.00							*Kawamura et al.*, 2010
Sapporo, Japan	Sept 2009 to Oct 2010	1.22	3.03	1.95	3.73	16.3	9.20	1.01	5.18	2.08	This study

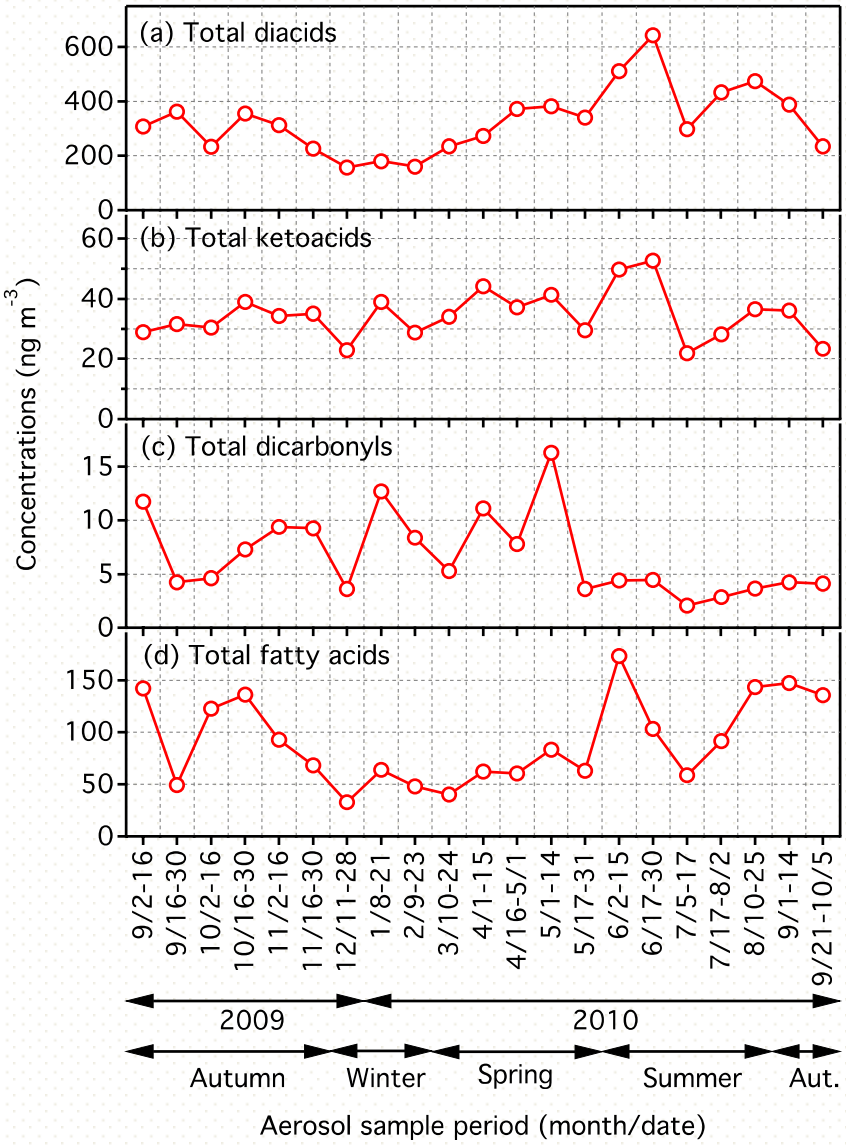
Temporal Variations of Diacids

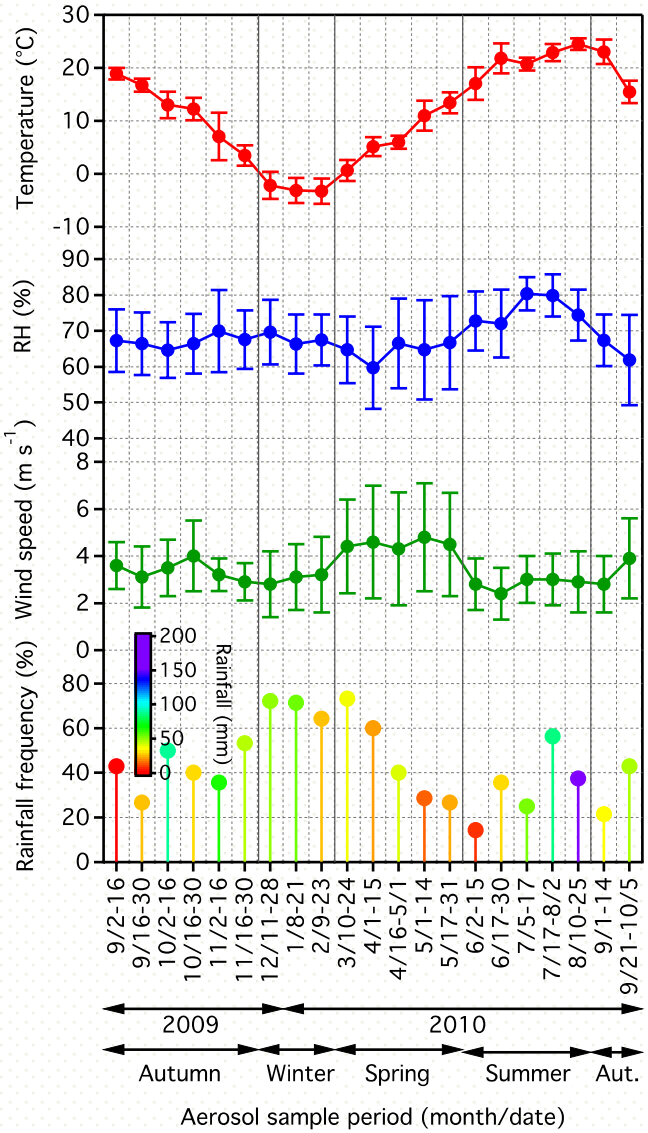




- **Temporal pattern is similar to that of biogenic VOCs [*Guenther et al., 1997*].**
- **Anthropogenic species were higher in winter.**

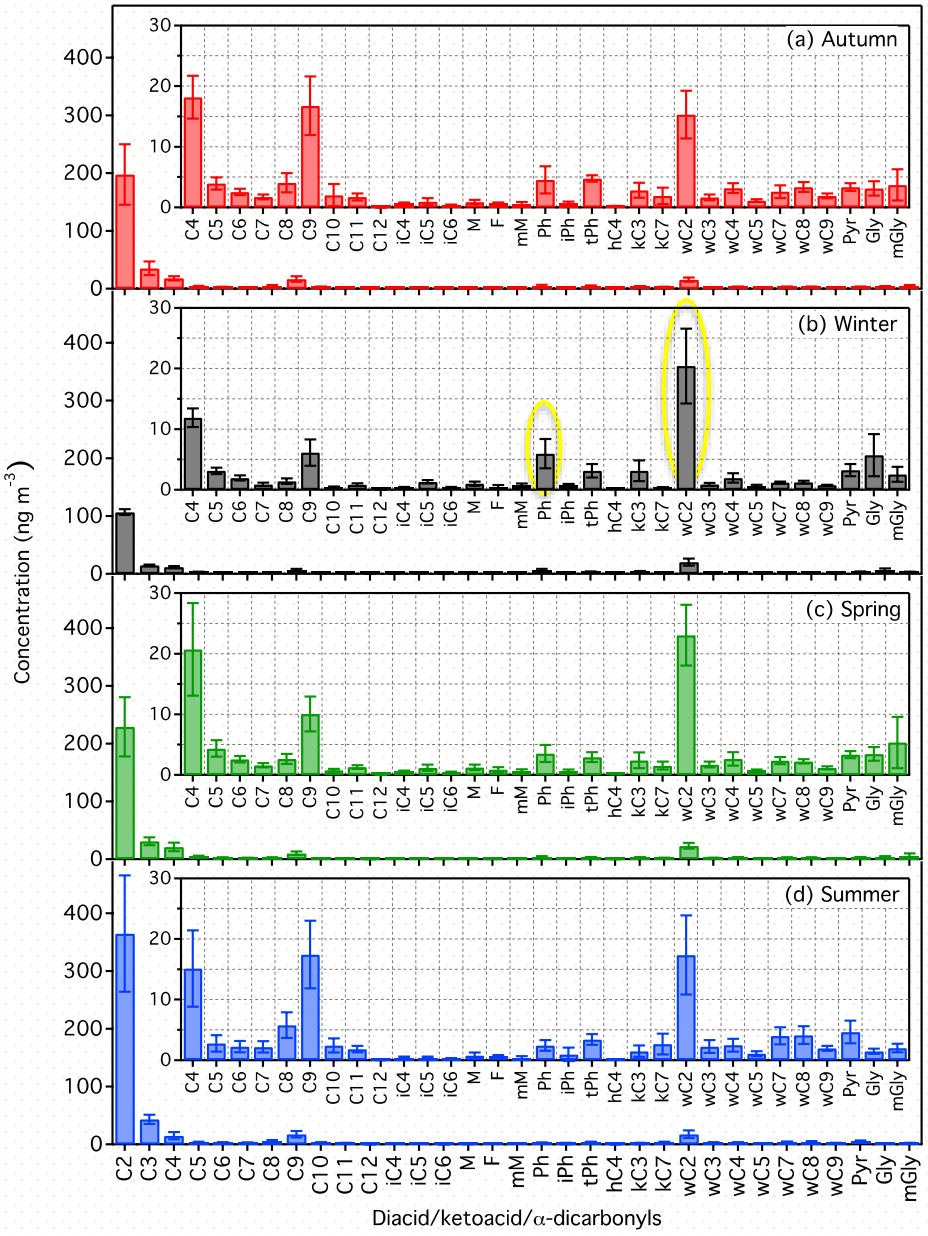
Temporal Variations of Total Diacids & Related Compounds

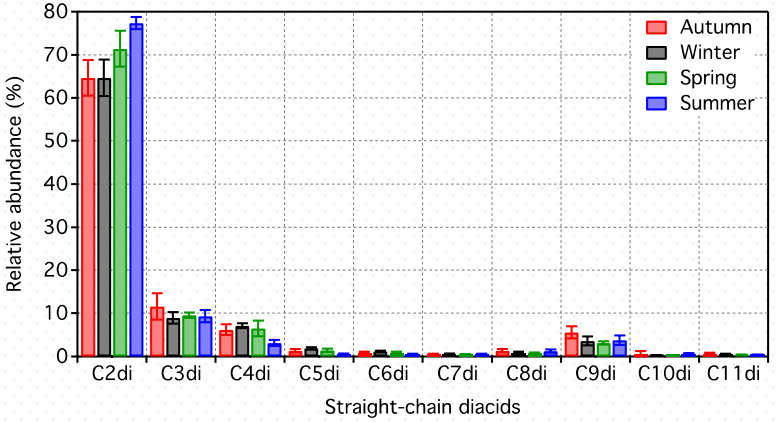




[http://www.data.jma.go.jp]

Seasonal Variations in Molecular Distributions





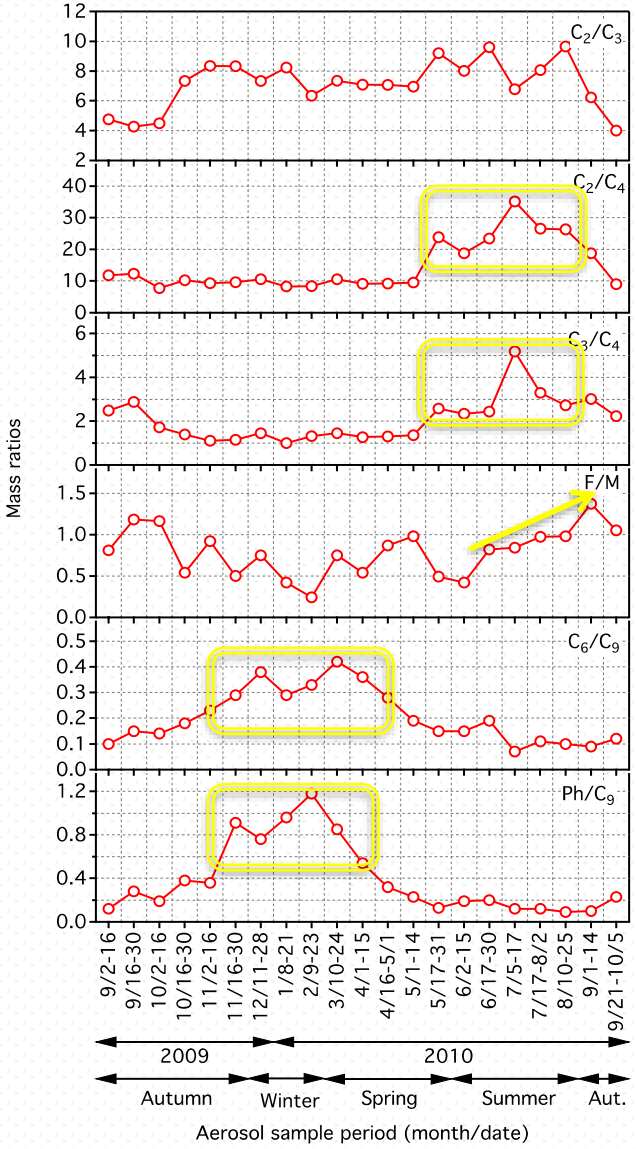
- Biogenic emissions might be the major source of diacids and related compounds in autumn, spring and summer
- Anthropogenic emissions may be significant in winter.
- Marine/terrestrial biogenic emissions and photochemical formation/transformations might be higher in summer.

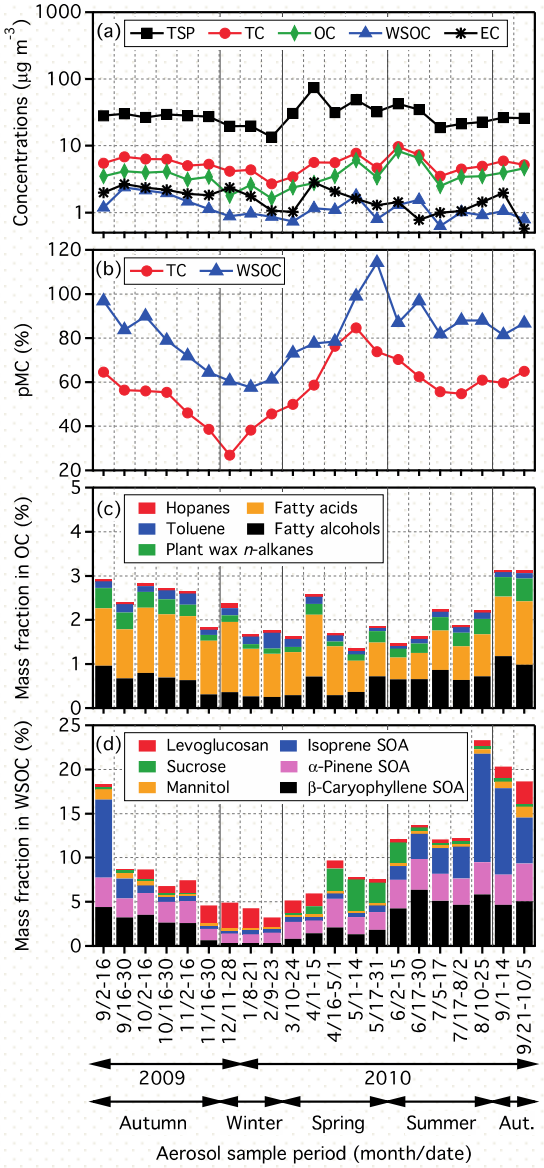
Temporal Changes in Mass Ratios

JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 2362–2371, doi:10.1002/jgrd.50244, 2013

Enhanced modern carbon and biogenic organic tracers in Northeast Asian aerosols during spring/summer

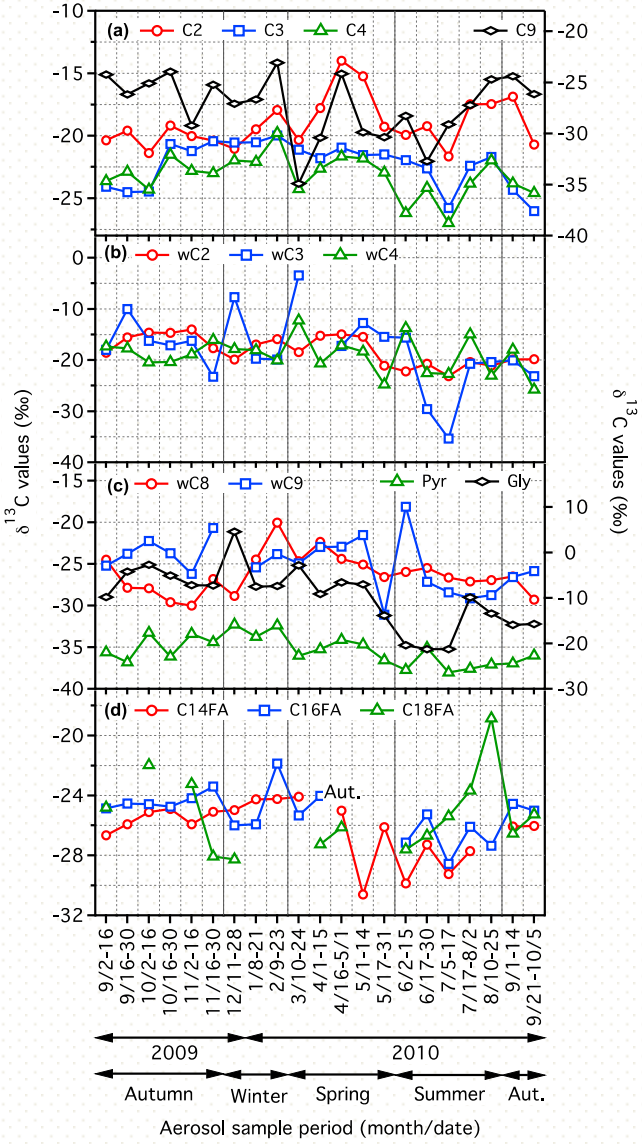
Chandra Mouli Pavuluri,[1] Kimitaka Kawamura,[1] Masao Uchida,[2] Miyuki Kondo,[2] and Pingqing Fu[1,3]

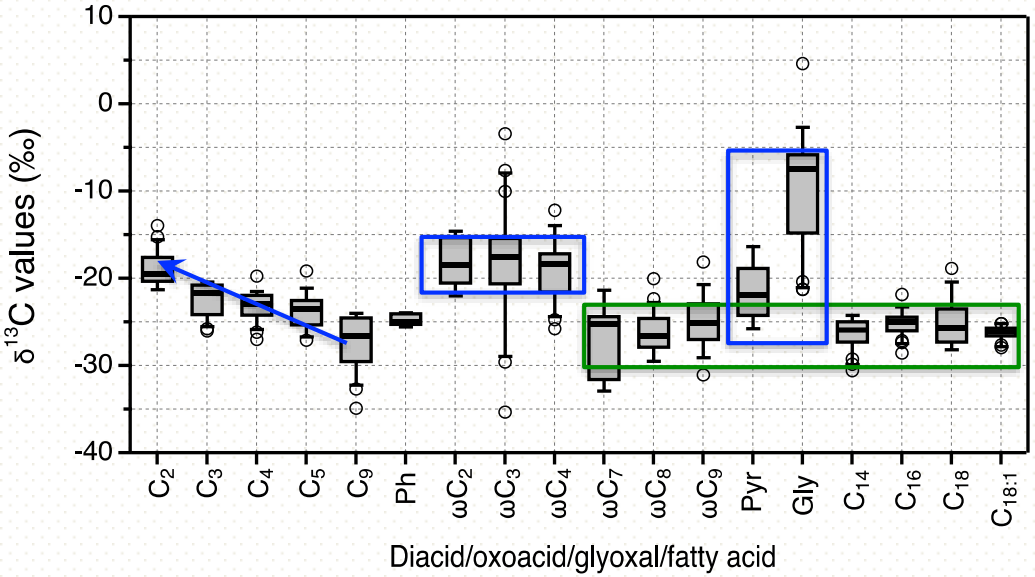




- These trends confirm that the biogenic origin of organics in growing season

Temporal Trends & Distributions of Stable Carbon Isotopic Compositions of Diacids & Related Species





- The "NO" seasonal pattern & distributions in $\delta^{13}C$ & enrichment of ^{13}C infer that the Sapporo aerosols are significantly subjected for photochemical processing (aging) during long-range atmospheric transport over Northeast Asia.

Conclusions

- Our results and their comparisons with the literature, together with the air mass trajectories, indicate that dicarboxylic acids and related polar compounds (as well as other organics) are mainly originated from biogenic emissions over Northeast Asia and significantly aged during long-range atmospheric transport.

- They further suggest that anthropogenic (including biomass burning) emissions are significant in this region, particularly in late autumn to winter whereas the (in situ) photochemical transformations are enhanced in summer.

- Thus, our research warrants that OA contents & their seasonal variations, particularly driven by the biological activity, need to be considered in models for better estimation of aerosol budget and their impacts on Earth's climate system.

Thanks

for Your Attention