# Submicrometer Water-Soluble Organic Aerosols in Marine Boundary Layer Over the Eastern Equatorial Pacific

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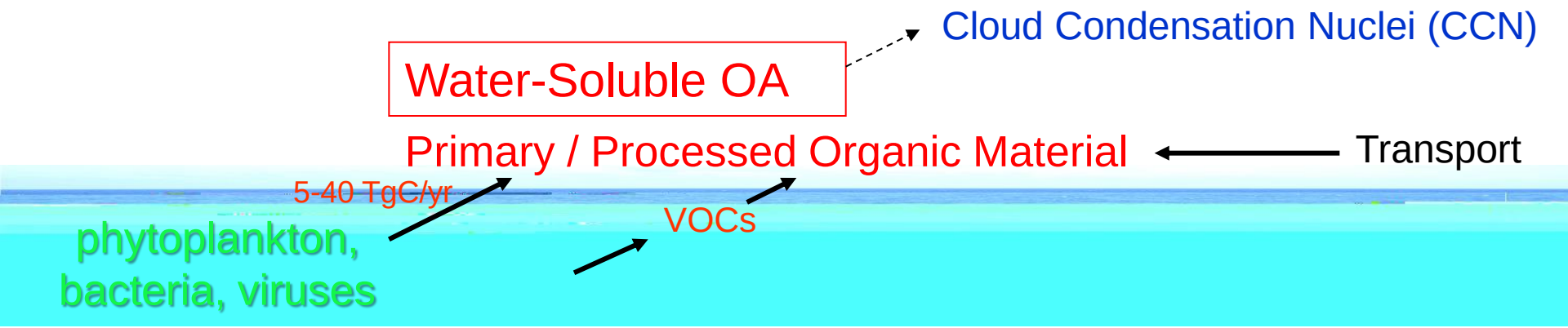
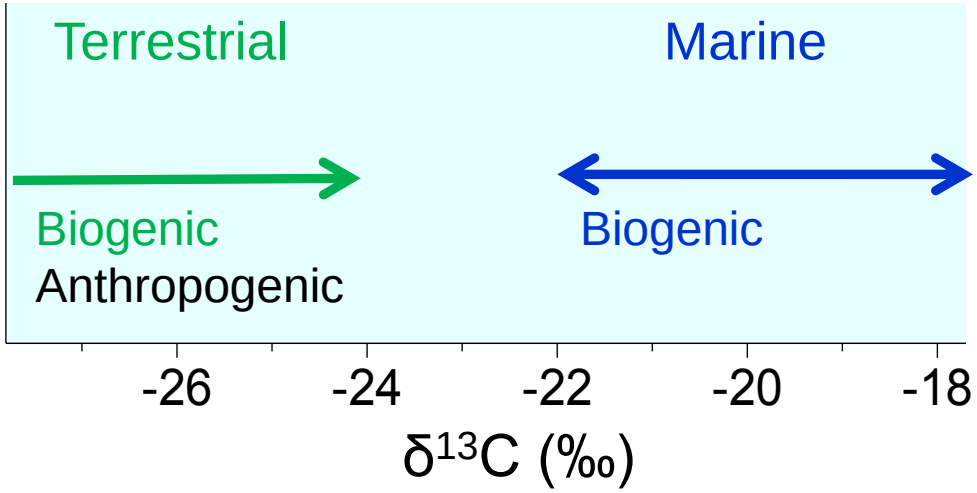
TORERO Data Workshop

# Stable Carbon Isotopic Compositions ($\delta^{13}C$) of Aerosol




$\delta^{13}C$ of fossil fuels (e.g., petroleum): −28‰ to −24‰




Upwelling areas-
Planktonic tissues
can be enriched in $^{13}C$:
**−20‰ to −14‰**
(DOC ~ −22‰ to −20‰
In surface seawater)

- The most common aerosol $\delta^{13}C$ application is for the total carbon (TC)
- Very few studies employ $\delta^{13}C$ in WSOC ($\delta^{13}C_{WSOC}$) aerosols for the source apportionment (i.e. Marine DOC/POC vs. Terrestrial)
- Organic molecular markers support the source apportionment

# Outline

Evaluation of the contribution of marine biogenic sources to water-soluble organic carbon (WSOC) in submicrometer aerosols during the TORERO cruise observation (aboard RV Ka'imimoana):

(1) Isotopic compositions of WSOC ($\delta^{13}C_{WSOC}$) vs. TC ($\delta^{13}C_{TC}$)

(2) Organic molecular markers in WSOC:

Diacids, α-dicarbonyls, and fatty acids

Oxidation products of isoprene, and MSA

# Sub-μm Aerosol Sampling over the Eastern Tropical Pacific

RV Ka'imimoana KA-12-01

Sampling Period: 1 Feb. –29 Feb. 2012

Aerosol Sampling: ~24 hours × 21 samples

- A four-stage cascade impactor attached to a high-volume air sampler (Flow rate ~1,100 L $min^{-1}$)

Submicrometer aerosols on quartz fiber filters were analyzed

- A nine-stage Andersen-type cascade impactor (Flow rate ~120 L $min^{-1}$)

# Stable Carbon Isotopic Compositions ($\delta^{13}C$) of Aerosol WSOC

$\delta^{13}C_{WSOC}$ : $\delta^{13}C$ of WSOC

Miyazaki et al., *ACP*, (2012)

Acidification of filter samples (decarbonated) Only for $\delta^{13}C$

↓

Extracted with ultrapure water

↓

Concentrated → *Elemental Analyzer(EA)* → *Isotope Ratio MS* (Finnigan MAT Delta Plus)

Recovery > 85%, Uncertainty ~ 0.2‰

Some minor isotope fractionating processes ~ 0–2‰

C, N

$\delta^{13}C_{TC}$: $\delta^{13}C$ of Total Carbon

$\delta^{13}C$, $\delta^{15}N$

**Water-soluble OC (WSOC)**:

- A filter cut was extracted with ultra-pure Milli-Q water and the total extracts were then filtrated. Dissolved OC in the extracts was then determined by a total organic carbon (TOC) analyzer (model 810, Sievers).

**Total carbon (TC)**:

- Elemental analyzer (EA) (NA 1500, Carlo Erba)

# Measurements of Organic Molecular Markers

**Diacids, ketoacids, and α-dicarbonyls**:

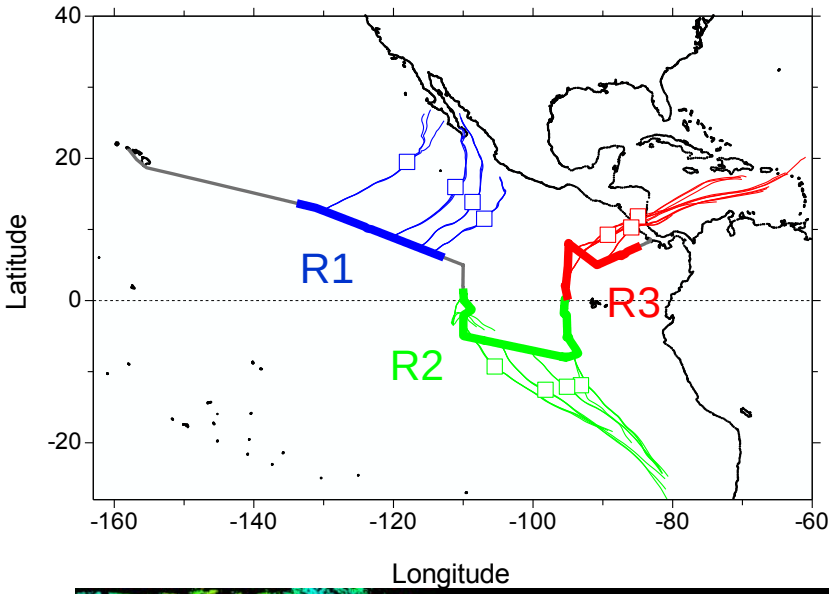
- Filter samples extracted with pure water
- Derivatized to dibutyl esters or dibutoxy acetals
- Measured with a capillary GC (Hewlett-Packard GC7890N)/MS

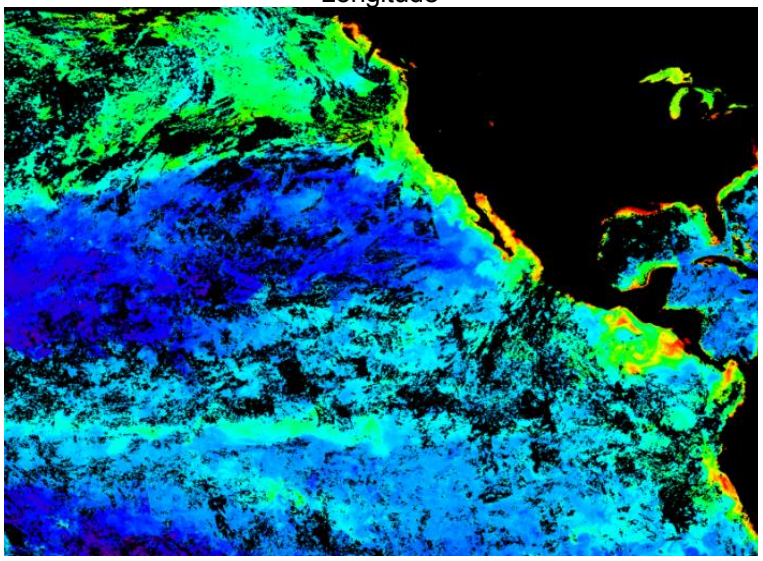
**Biogenic molecular markers of SOA**
**(Oxidation products of isoprene, MSA, etc.):**

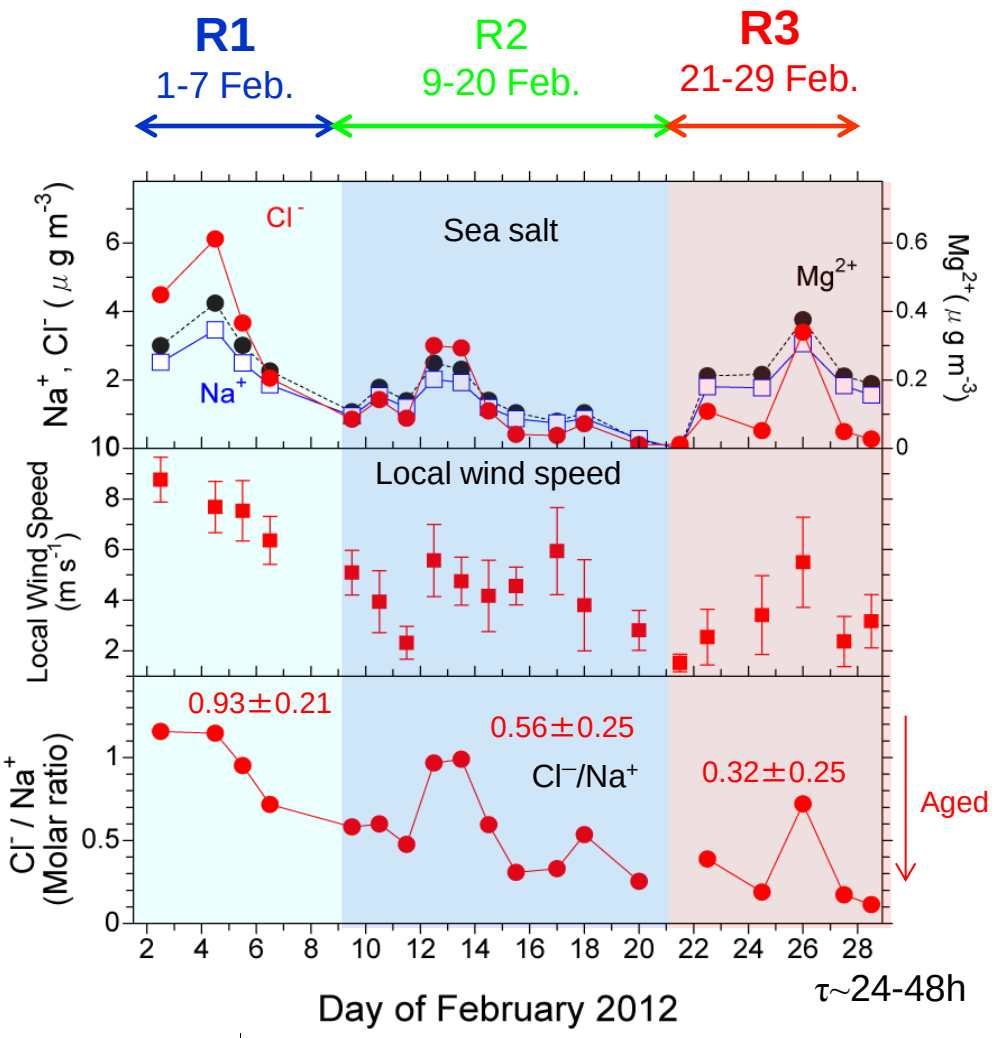
- Aerosol filter samples extracted with methanol/dichloromethane mixture
- Derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA):
  the -COOH and -OH functional groups
  were converted to TMS esters and TMS ethers, respectively
- Measured with a capillary GC (Hewlett-Packard GC7890N)/MS

- MSA was measured with ion chromatography (IC)

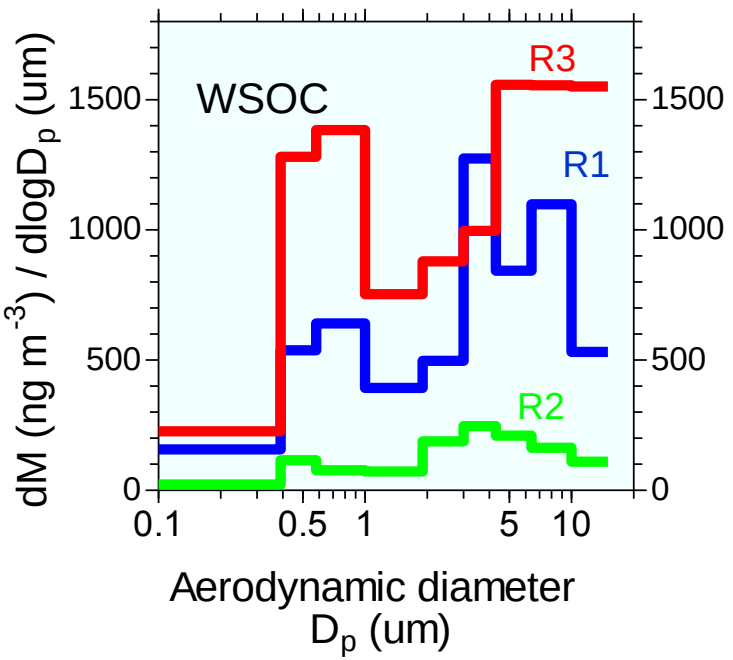
# Sea-salt particles observed during the cruise

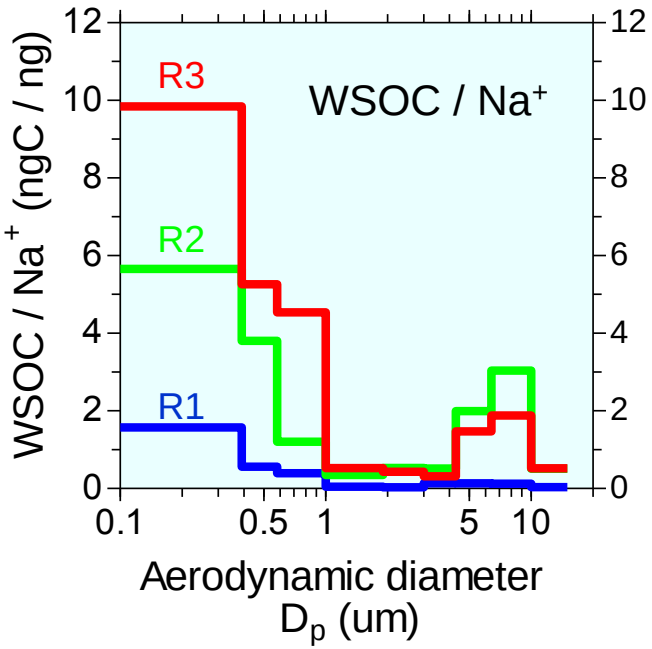


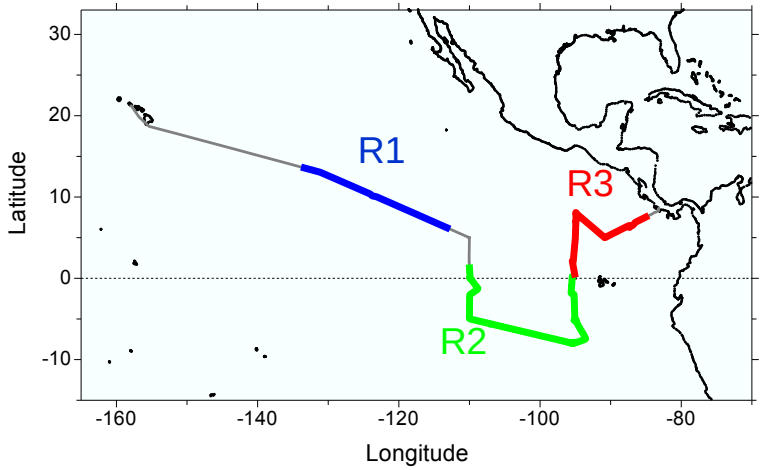





# WSOC enriched in submicrometer particles

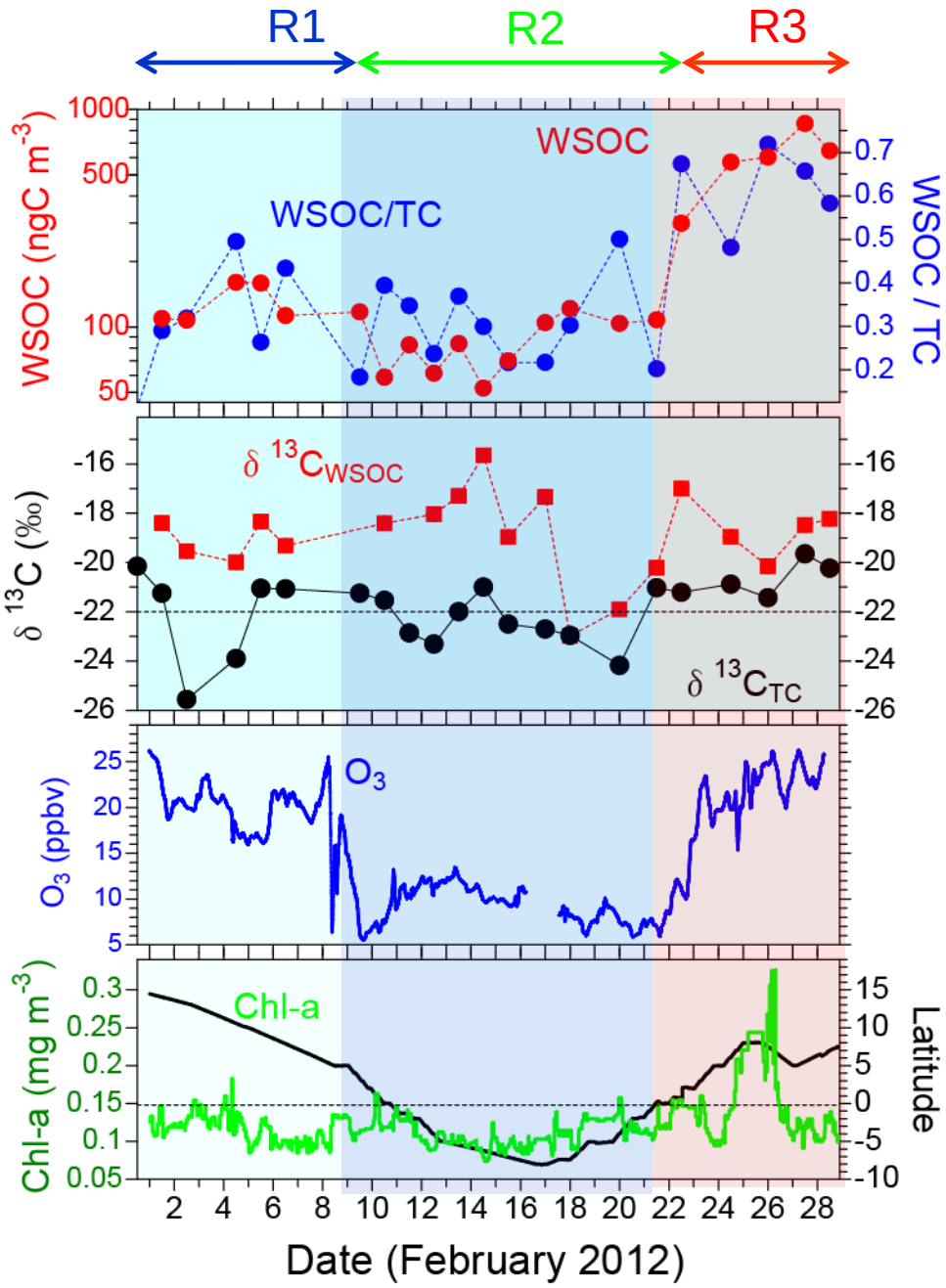


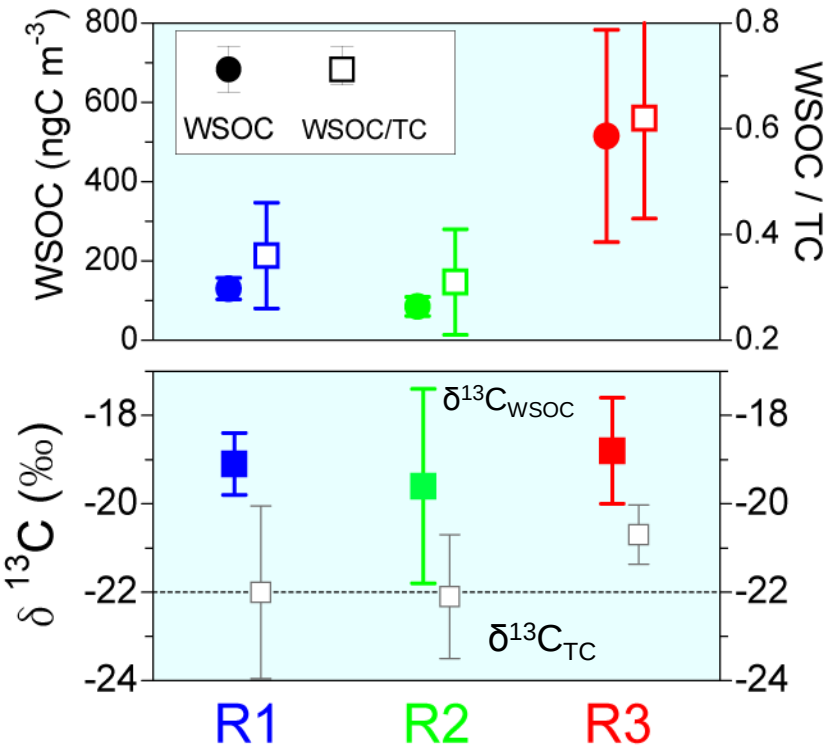




Water-soluble organics enrirhed in sub-μm particles in R3

# Time Series of Aerosol WSOC and $\delta^{13}C_{WSOC}$ vs. $\delta^{13}C_{TC}$



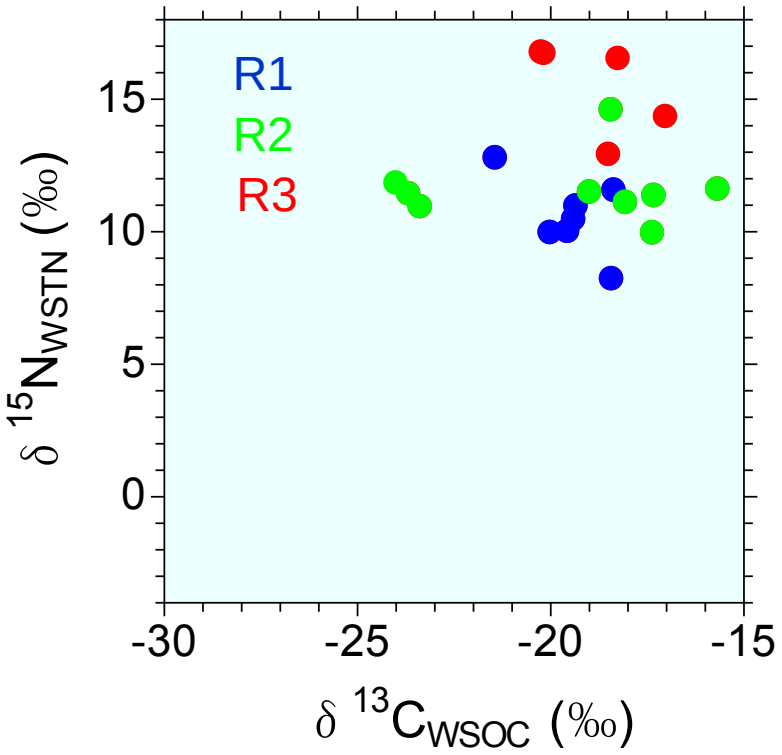




$\delta^{13}C_{WSOC}$ : −19.8±2.0‰
> $\delta^{13}C_{TC}$ : −22.2±1.9‰

-Close to typical $\delta^{13}C$ for DOC in SSW over tropical oceans

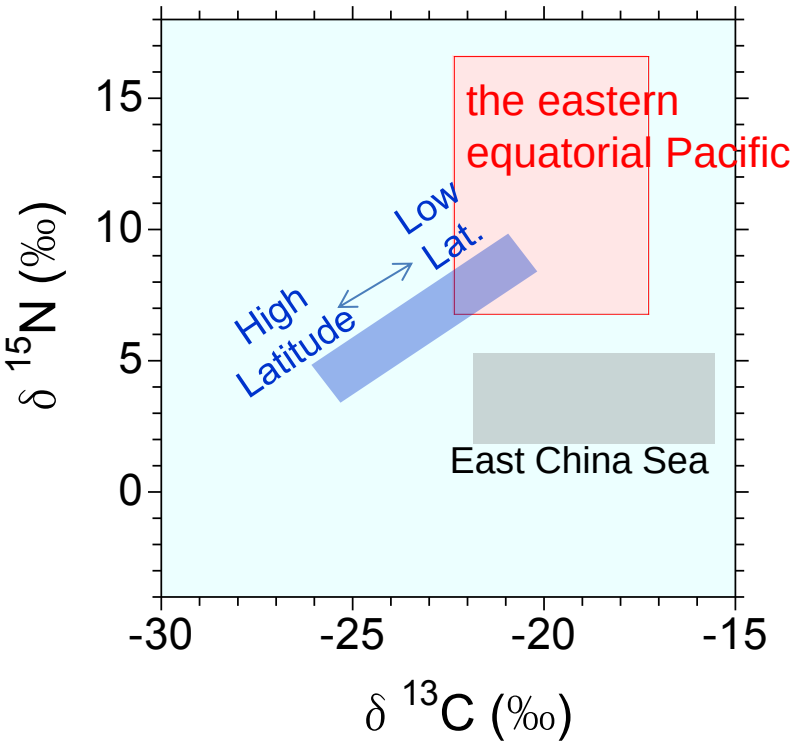
- Attributable to planktonic tissues more enriched in $^{13}C$ regardless of the sampling region

# $\delta^{13}C$ & $\delta^{15}N$ in Water-Soluble Fractions of Aerosol and Surface Seawater



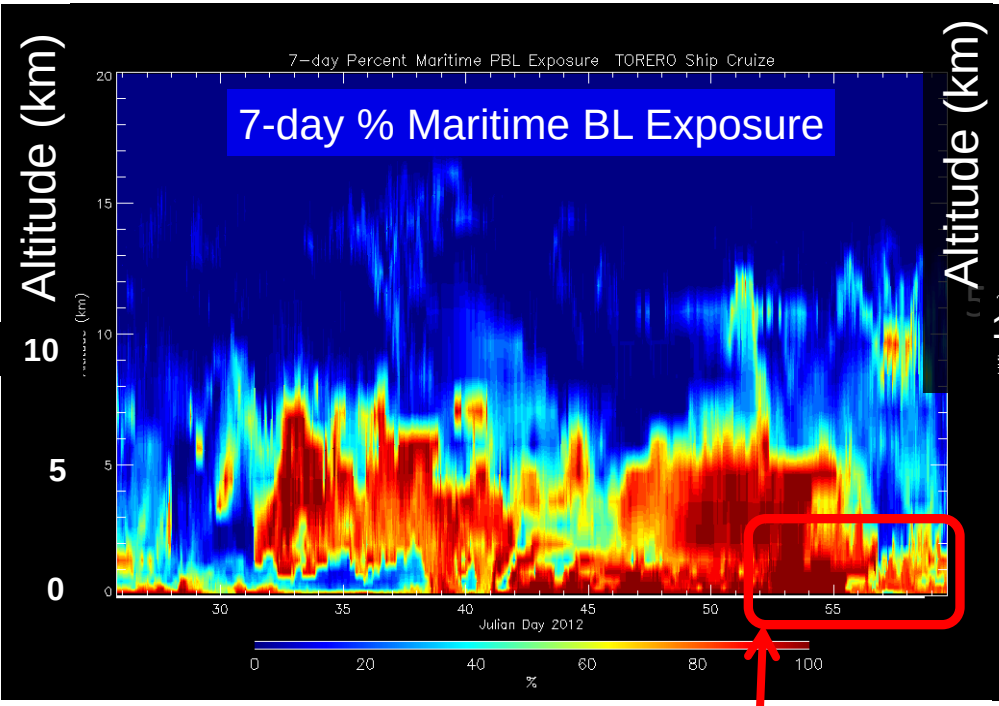

Ambient Sub-μm Aerosol
(this study)

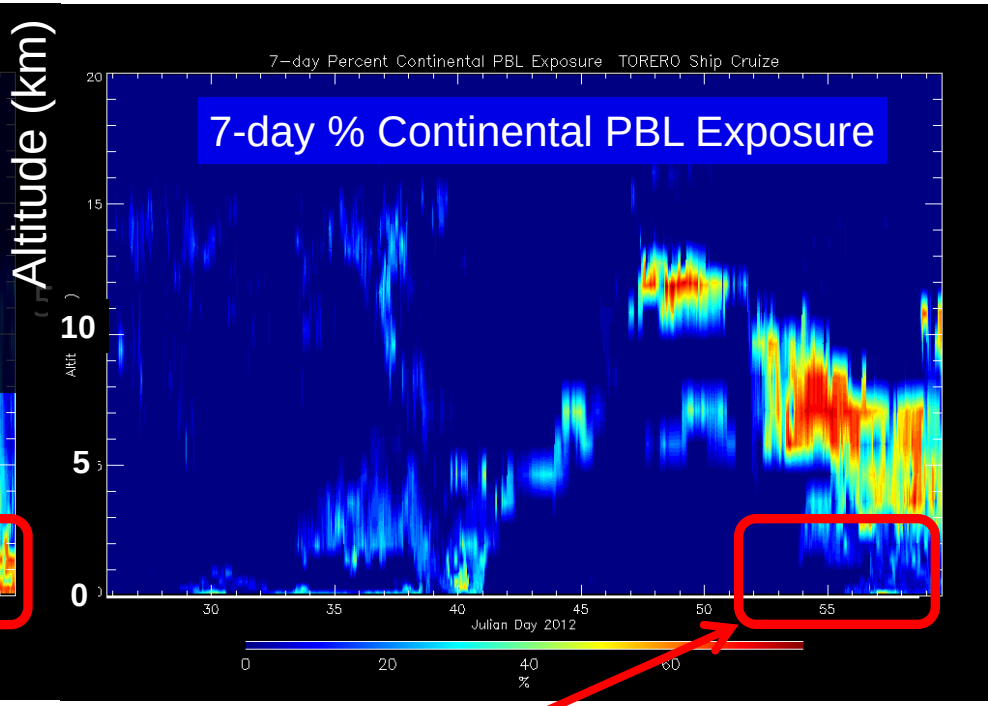
δ15N-δ13C of Phytoplankton
in Surface Seawater
[*Wada et al.*, 1984]



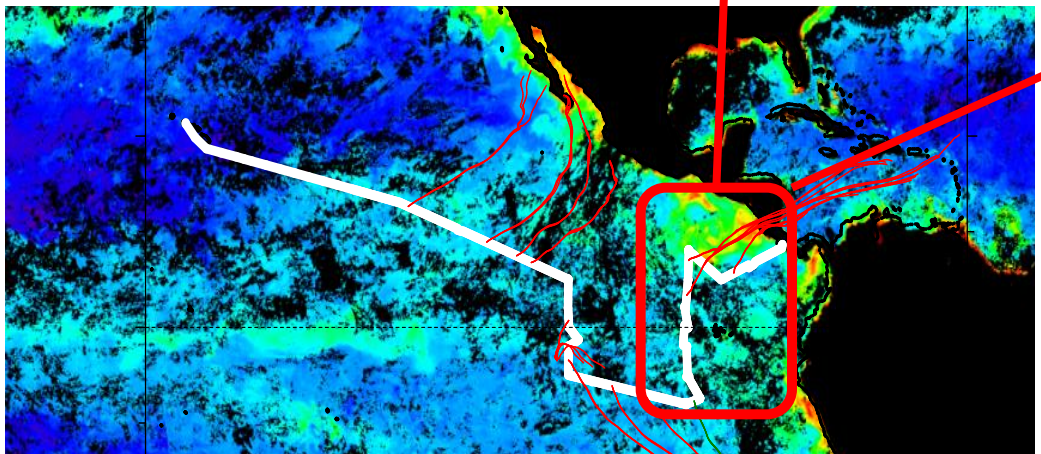

Surface Seawater
(typical ranges from literature)

# Air-Mass Exposure to Ocean Surface vs. Land Surface




RAQMS model



→ More than 80% of air parcels at the sampling points (z < 2km) had been exposed to marine BL air

# Contributions of marine OC sources to WSOC

Relative contributions of marine OC sources to the aerosols calculated using mass balance equation:

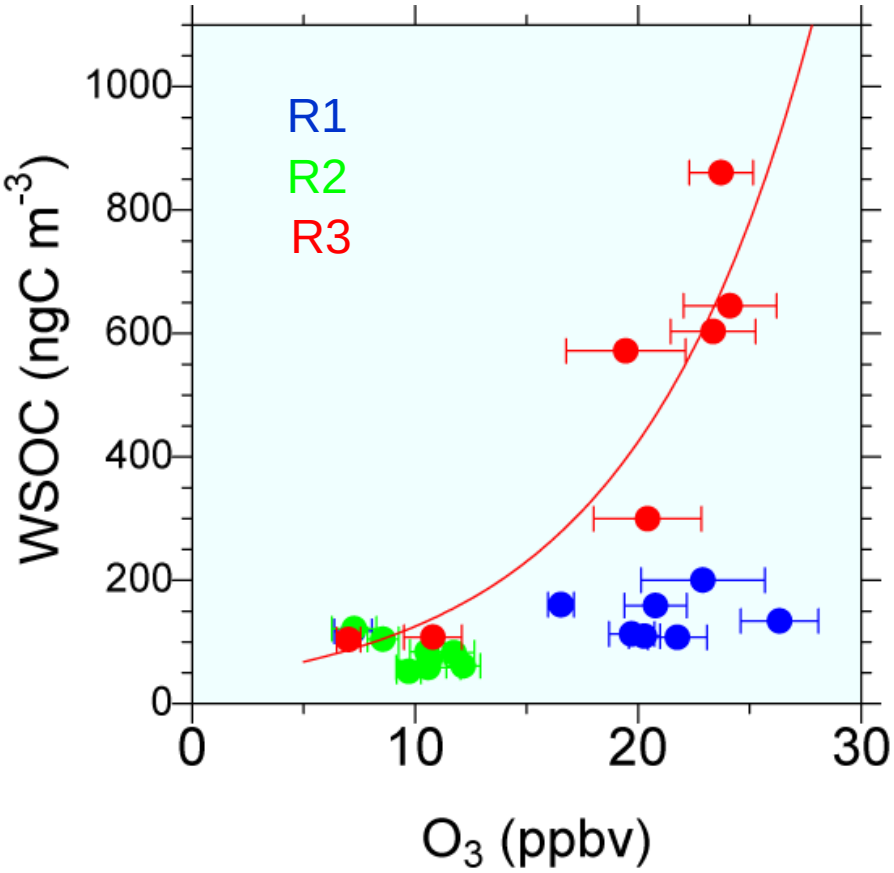
$$\delta^{13}C_{aerosol} = F_{marine} \times \delta^{13}C_{marine} + F_{terrestrial} \times \delta^{13}C_{terrestrial}$$

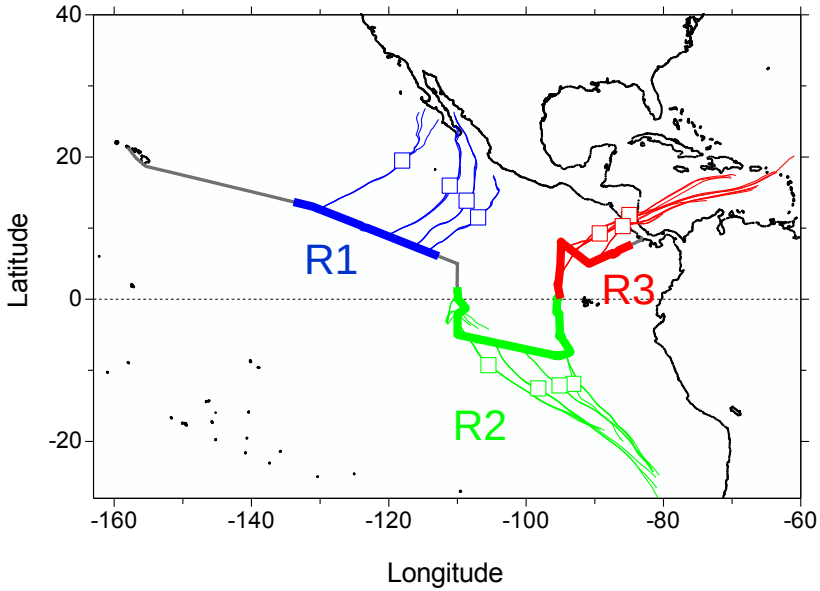
$$F_{marine} + F_{terrestrial} = 1;$$

$\delta^{13}C_{marine} = -18 \pm 2‰$, $\delta^{13}C_{terrestrial} = -25 \pm 2‰$ [e.g., *Turekian et al.*, 2003]

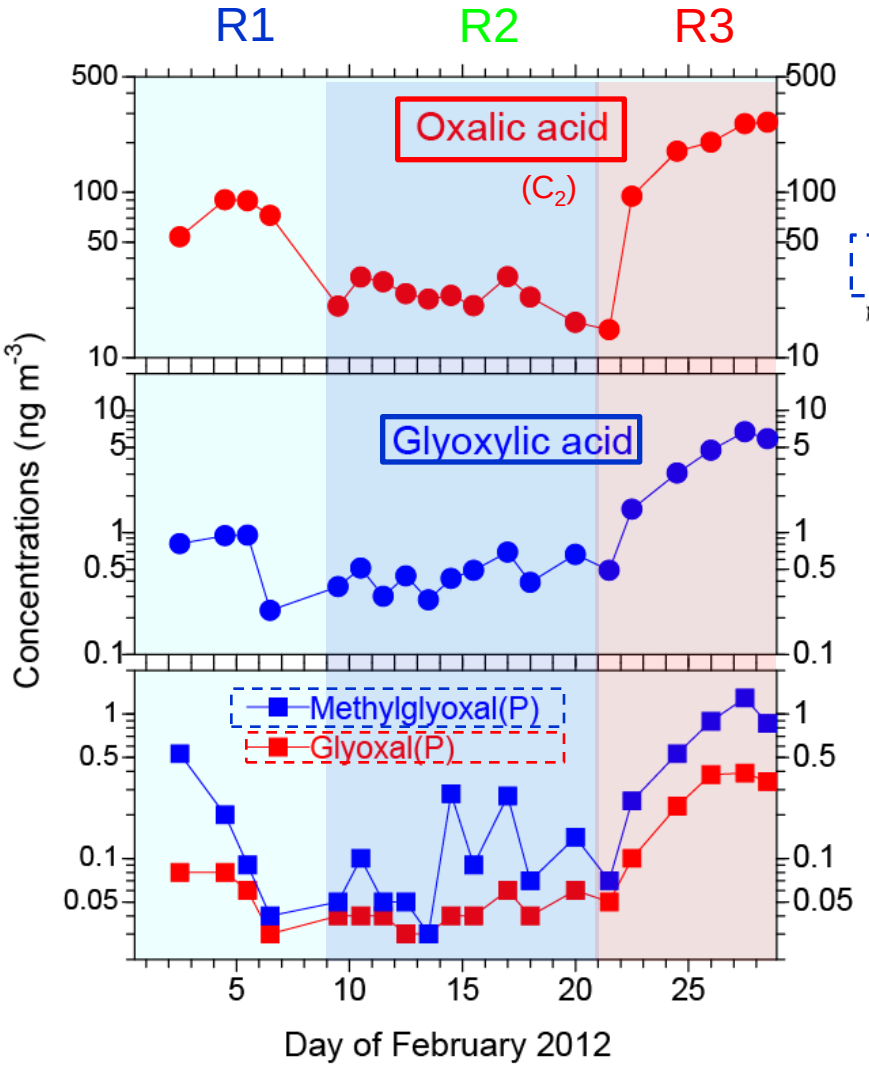
→ Marine OC sources accounted for ~ 90±25% of sub-μm WSOC

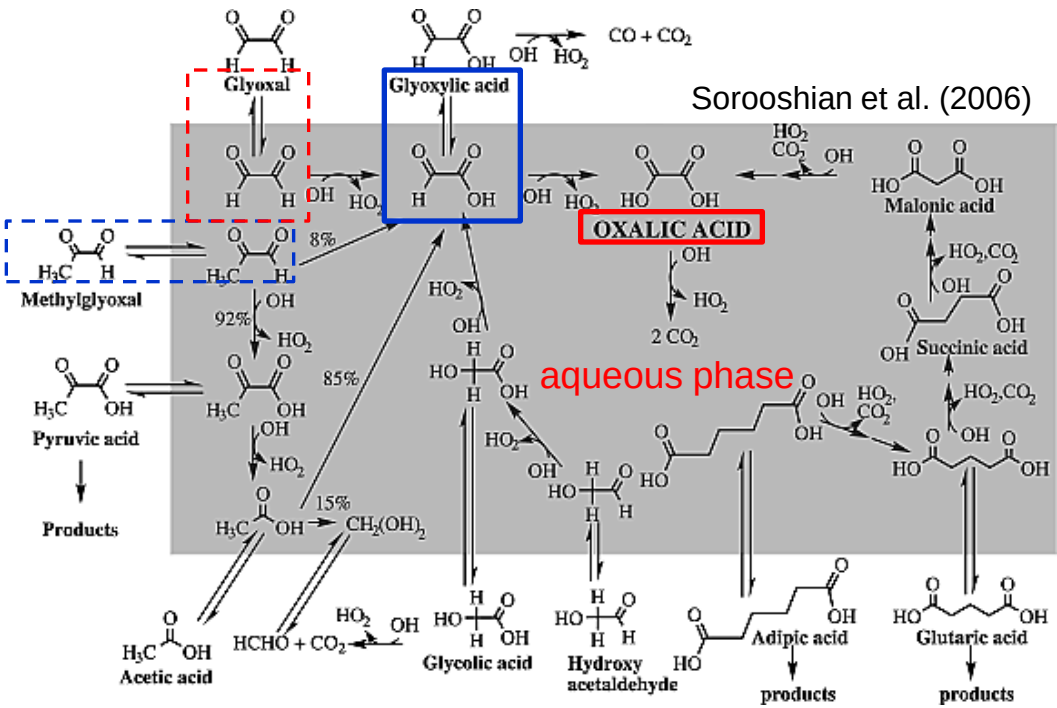
# Sub-μm WSOC over the phytoplankton blooms (R3) is likely processed organic material from the sea surface

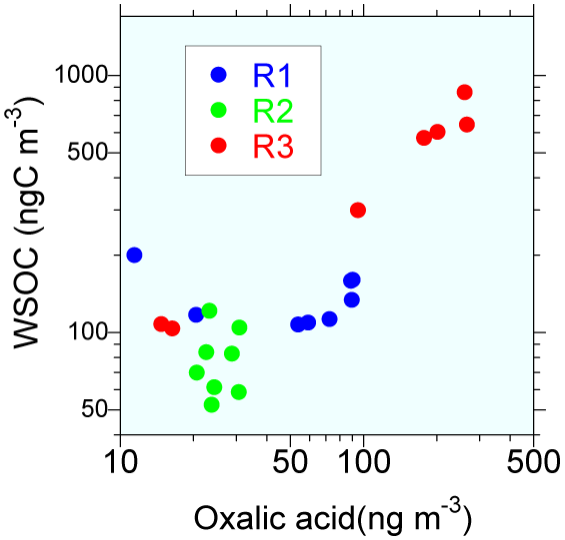


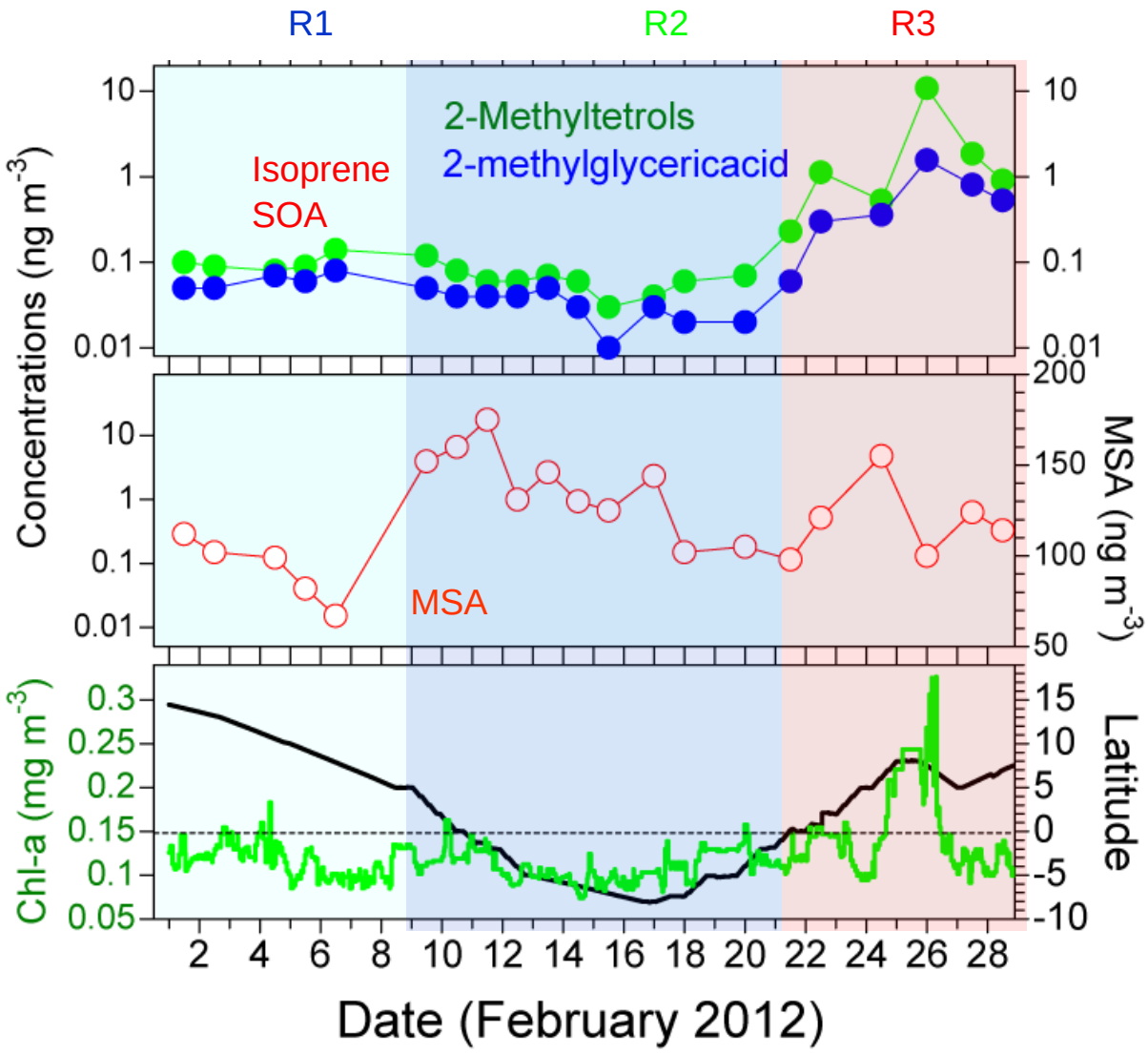
# Low-Molecular-Weight Diacids,Ketoacids and Dicarbonyls

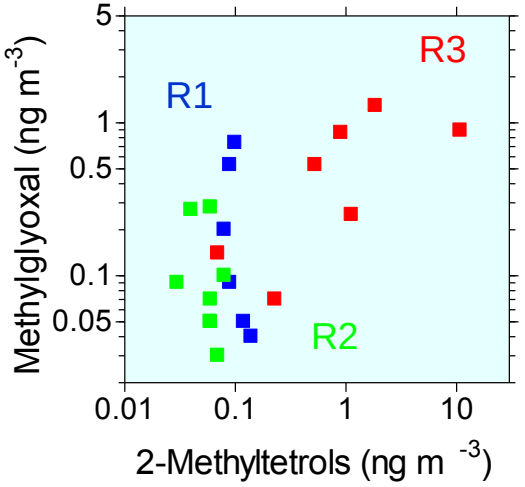


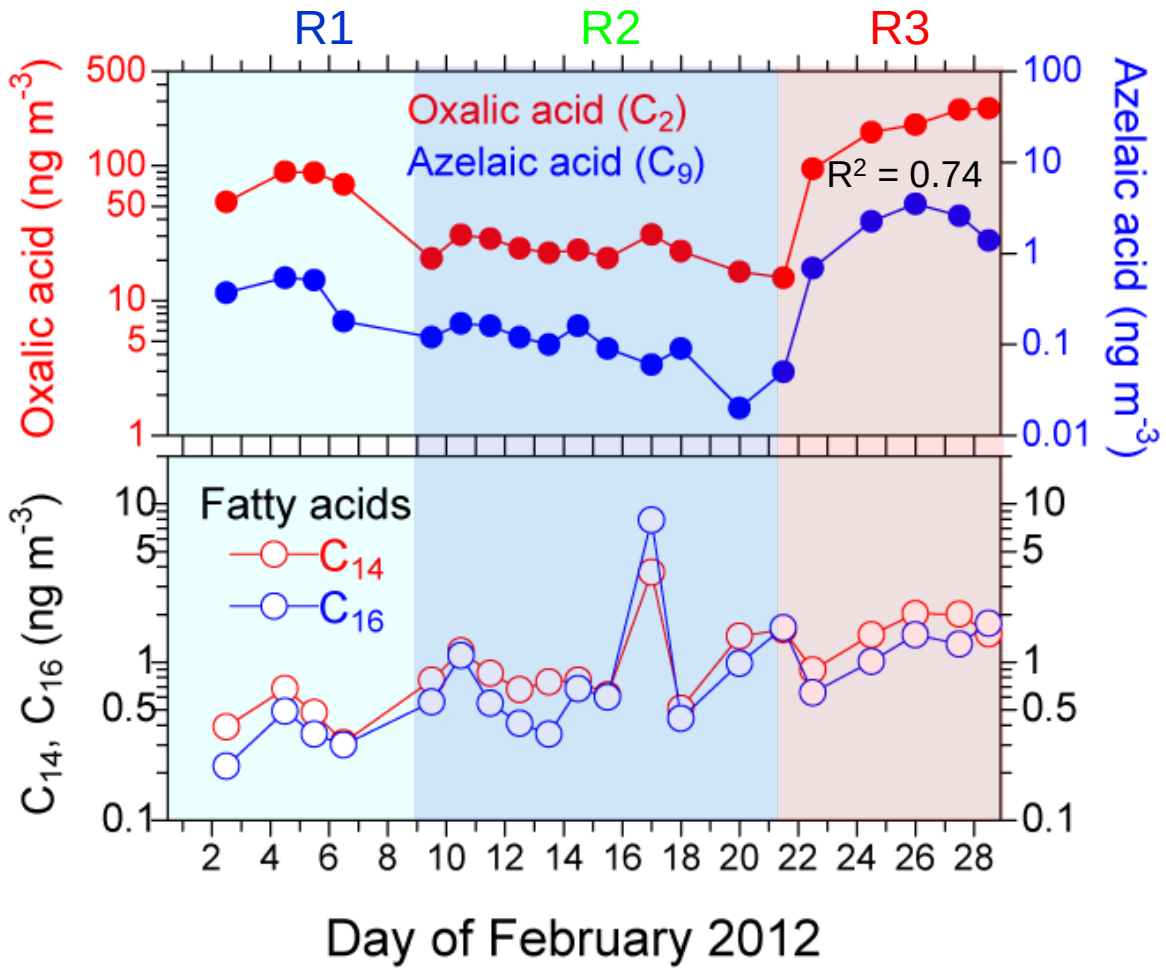



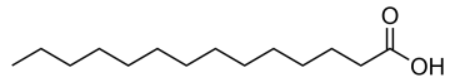
# WSOC vs. Biogenic Marker Compounds



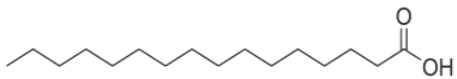



# Oxalic Acid, Azelaic Acid, and Long-Chain Fatty Acids




Myristic acid ($C_{14}$)




Palmitic acid ($C_{16}$)

Most of fatty acids with odd-carbon numbers were below lower detection limits.
The predominance of even-carbon numbers supports that
these fatty acids are of biological origin from marine plants.

# Summary

Submicrometer OA is highly water-soluble over upwelling areas/ phytoplankton blooms.

$\delta^{13}C_{WSOC}$ (−19.8±2.0‰) > $\delta^{13}C_{TC}$ :

- Close to typical $\delta^{13}C$ for DOC in surface seawater in tropical oceans, which is attributable to planktonic tissues more enriched in $^{13}C$.

- Predominant (~90%) marine biogenic sources for submicrometer WSOC particles regardless of the sampling region.

Oxalic acid in sub-μm WSOC:

- Some evidence for production via multi-phase chemistry from α-dicarbonyls as well as photodegradation of long-chain organics.

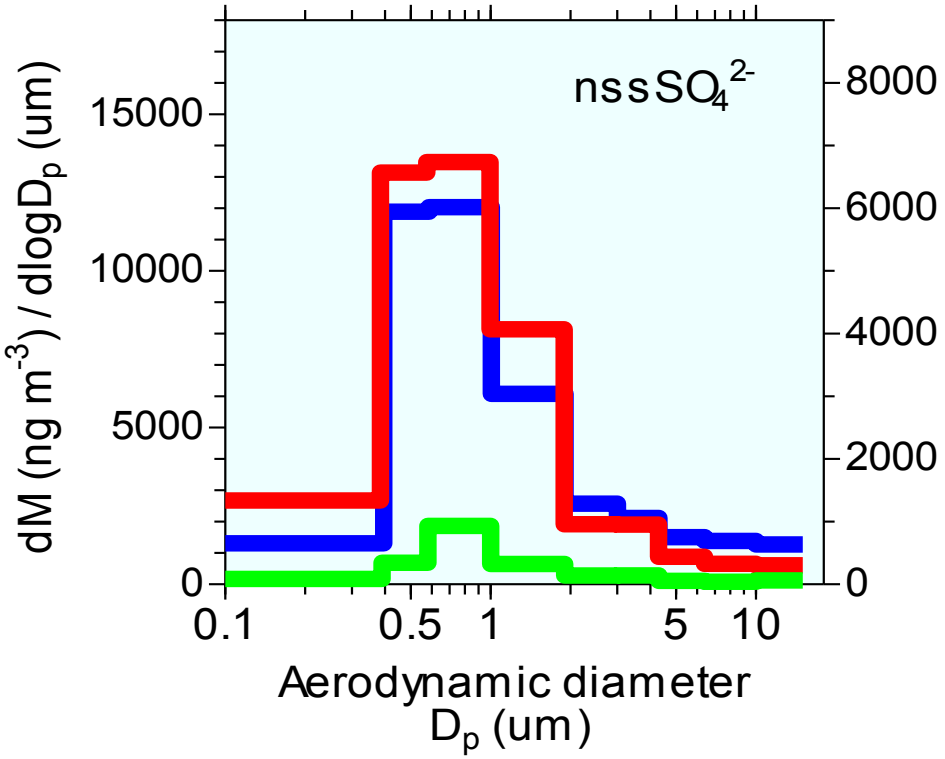
# Manuscripts to be submitted to *ACP/AMT Special Issue*

(1) Source apportionment of sub-μm WSOC using the isotopic compositions ($\delta^{13}C_{WSOC}$) and organic molecular markers during the TORERO cruise

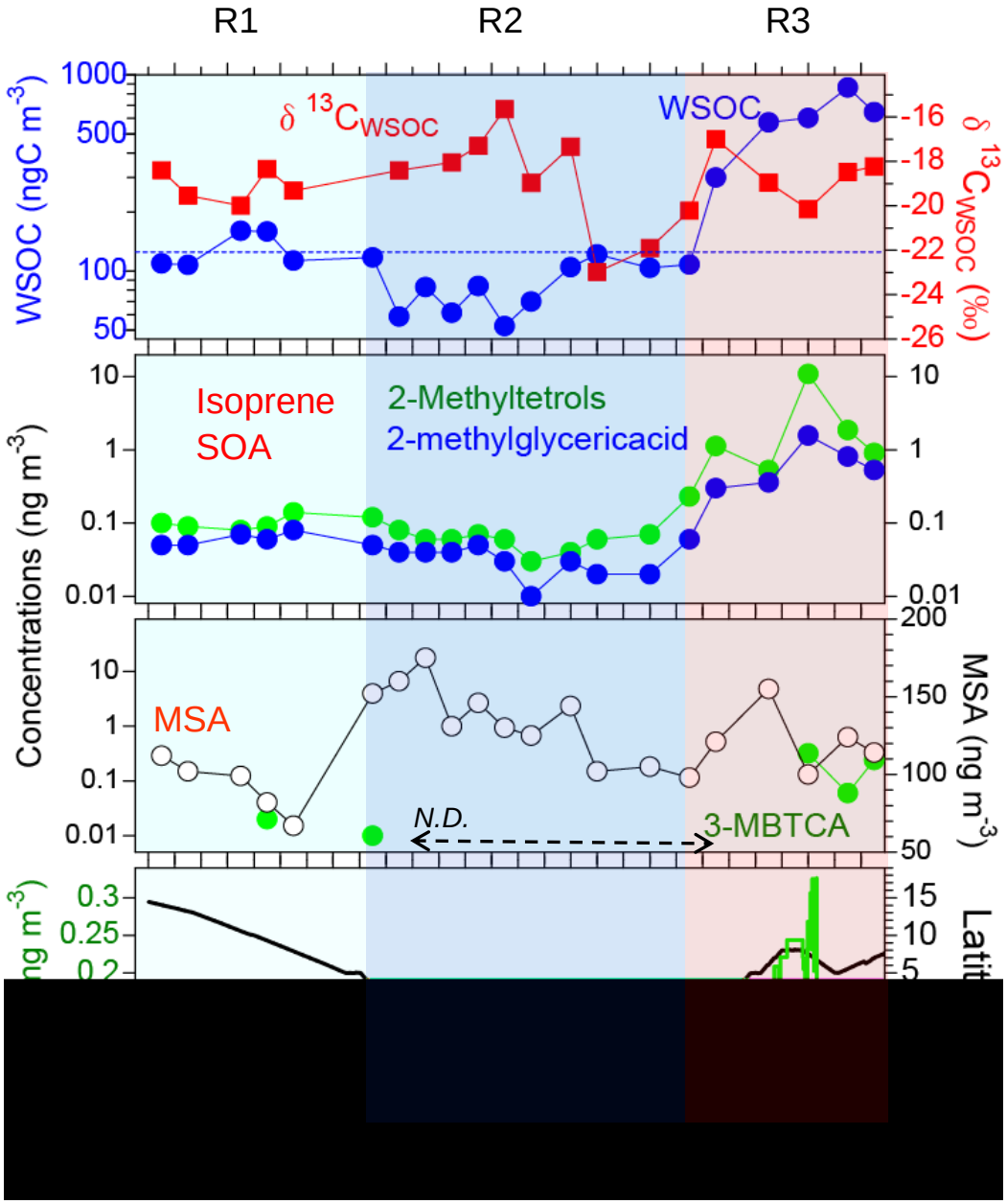
*in preparation*

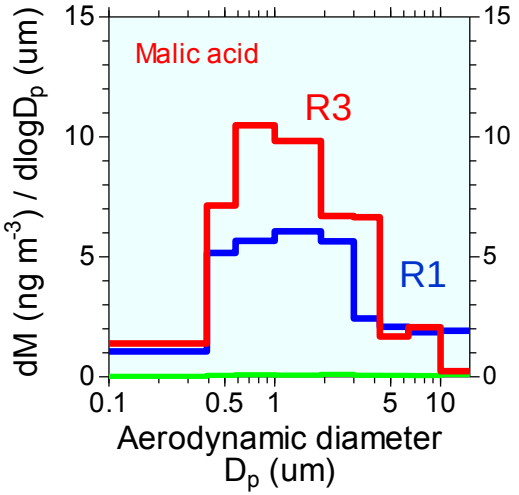
(2)Sources and processes of diacids, dicarbonyls, and long-chain fatty acids in marine aerosols

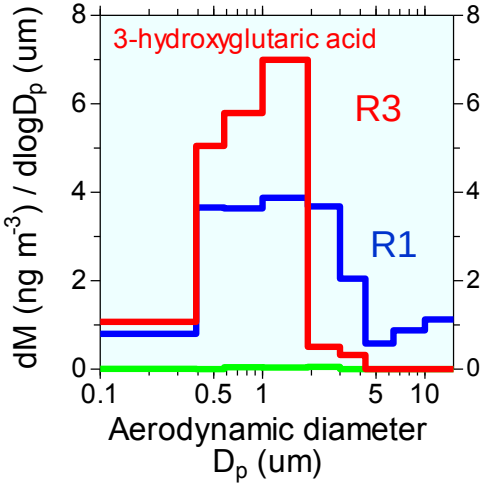
*planned*

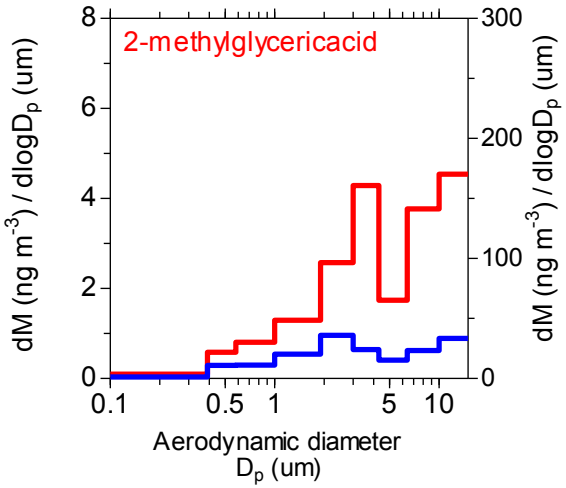

nssSO4 2-
dM (ng m-3) / dlogDp (um)
15000
10000
5000
0
8000
6000
4000
2000
0
0.1
0.5
1
5
10
Aerodynamic diameter
Dp (um)

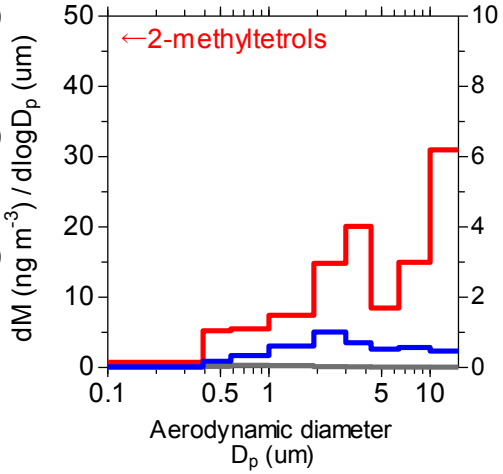
# WSOC vs. Biogenic Marker Compounds

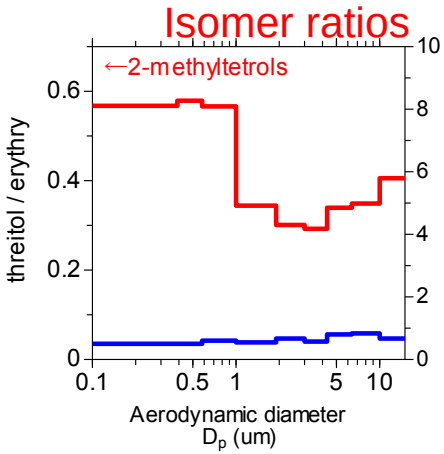


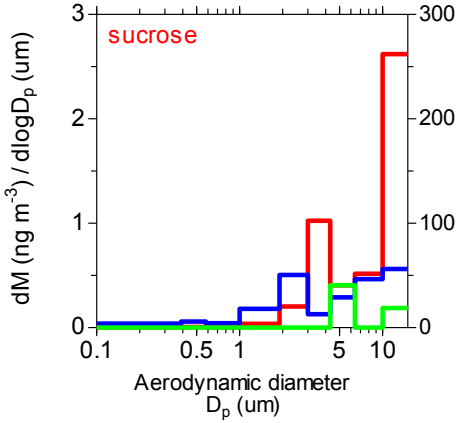




2-methylglycericacid
dM (ng m-3) / dlogDp (um)
Aerodynamic diameter
Dp (um)


←2-methyltetrols
dM (ng m-3) / dlogDp (um)
Aerodynamic diameter
Dp (um)


Isomer ratios
←2-methyltetrols
threitol / erythry
Aerodynamic diameter
Dp (um)

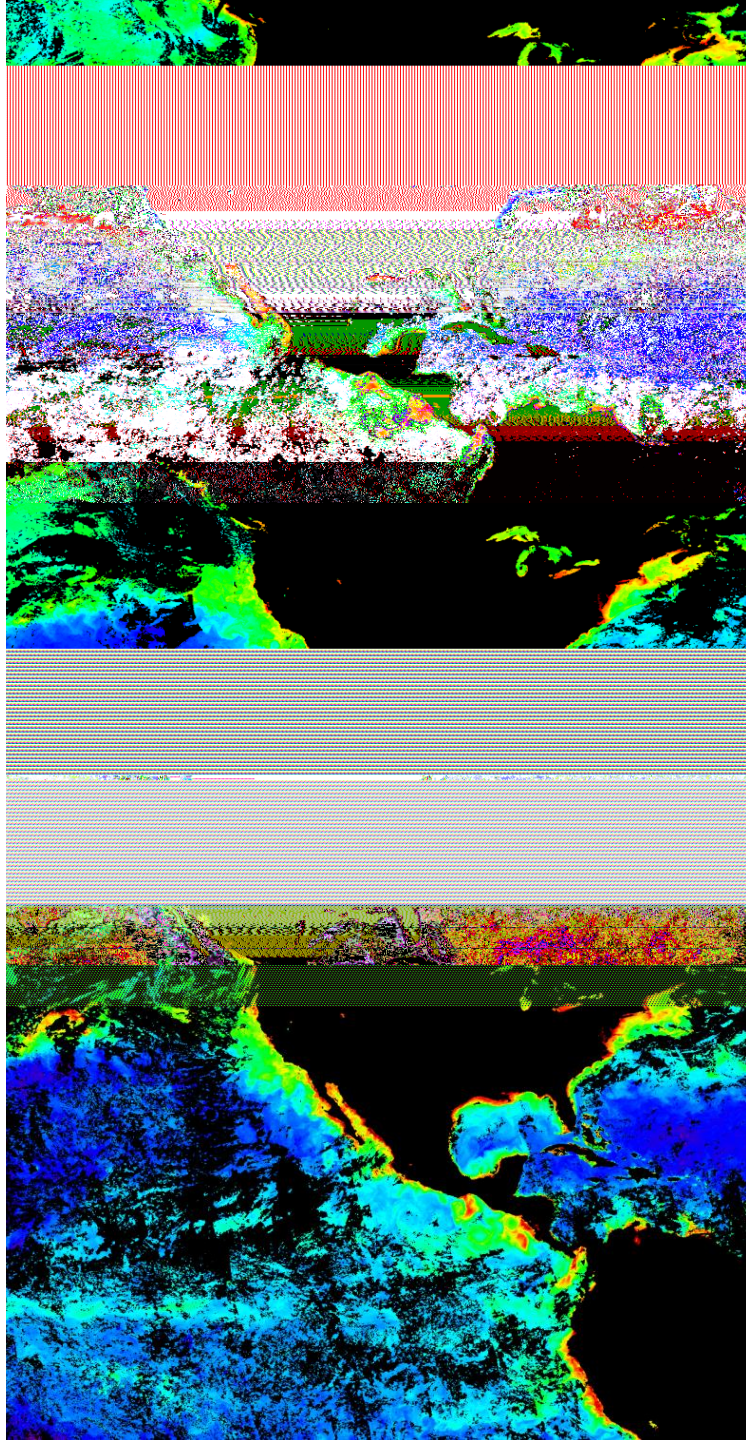

sucrose
dM (ng m-3) / dlogDp (um)
Aerodynamic diameter
Dp (um)

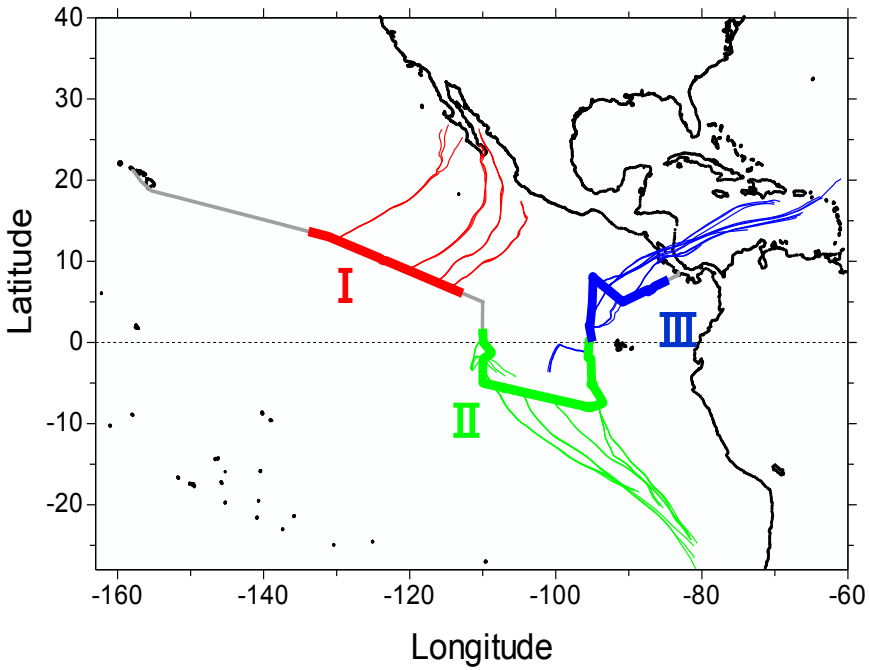
# Cruise Track and 5-day Back Trajectories during the KA-12-01 Cruise

Feb.10-17

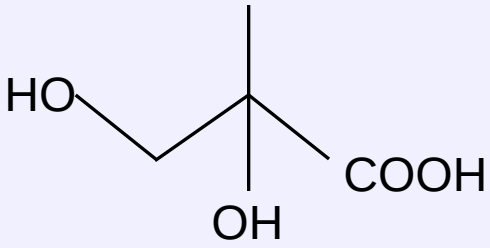
Feb.18-25

Feb.26
-Mar.4

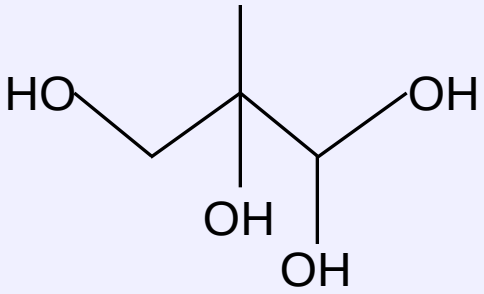




# Molecular Characterization (Biogenic Tracers) of WSOC

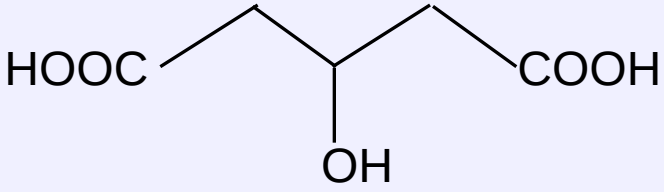



*2-methylglyceric acid*

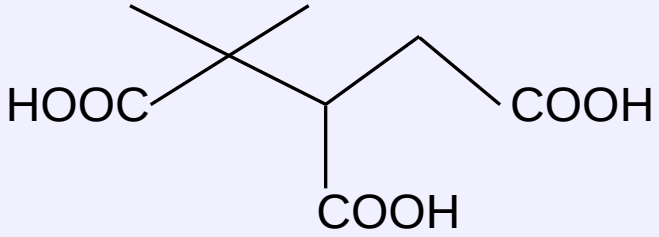



*2-methyltetrols*

Isoprene SOA tracers




*3-hydroxyglutaric acid*




*3-methyl-1,2,3-butane-tricarboxylic acid (MBTCA)*

α-/ß-pinene SOA tracers

Extracted with dichloromethane/methanol

– COOH → TMS esters / –OH →TMS ethers → *GC-MS*

Major inorganic species including MSA → Metrohm *IC*