Spatial Distributions of Organic Carbon and Organic Nitrogen with their Isotopic Compositions and Biogenic Tracer Compounds in Marine Aerosols

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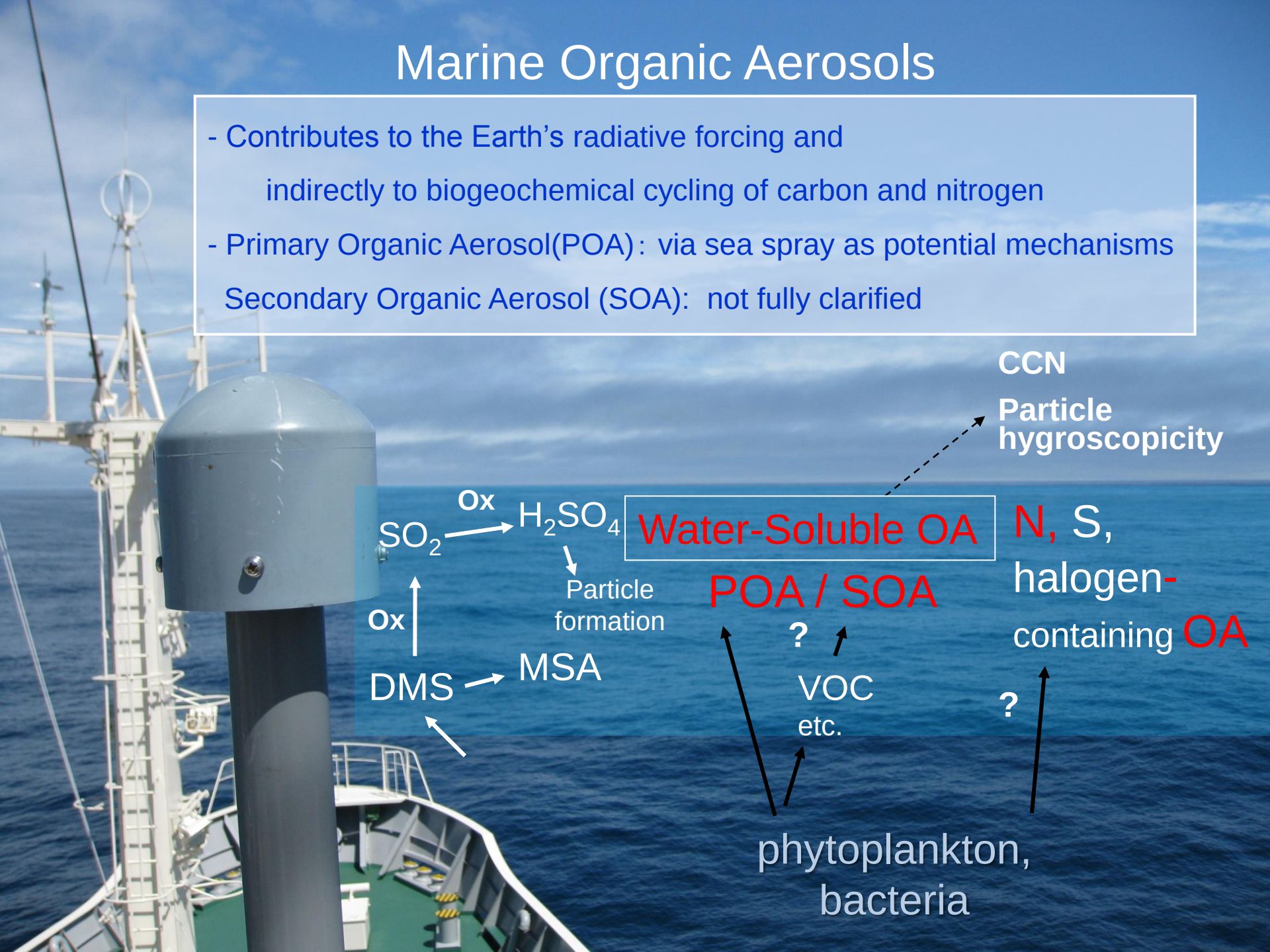
TORERO Data Workshop

Marine Organic Aerosols

- Contributes to the Earth's radiative forcing and
  indirectly to biogeochemical cycling of carbon and nitrogen
- Primary Organic Aerosol(POA) : via sea spray as potential mechanisms
  Secondary Organic Aerosol (SOA): not fully clarified



Outline

➢ We focus on chemical characterization of water-soluble organic carbon (WSOC) and organic nitrogen (ON) in sub-μm marine aerosols collected during the KA-12-01 cruise

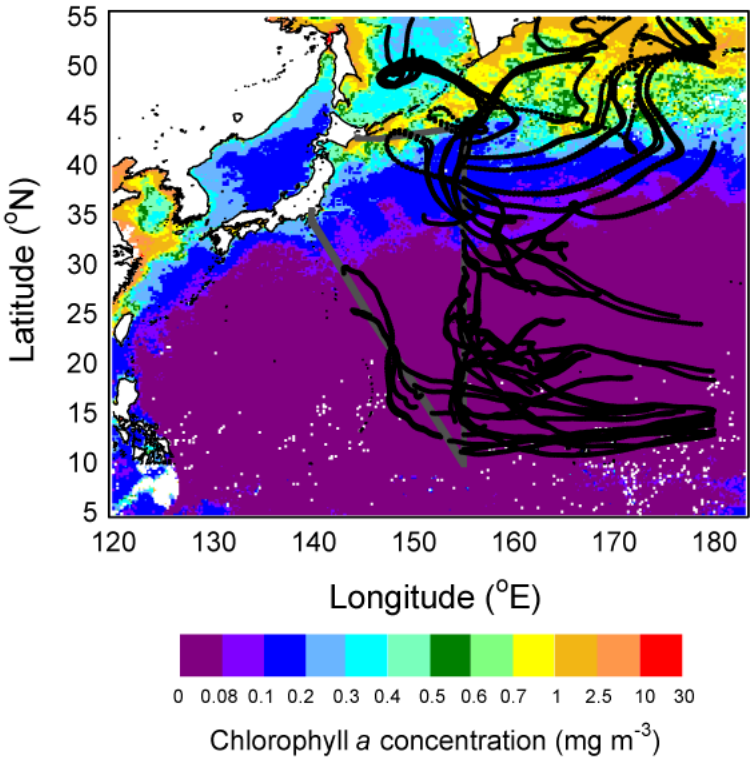
➢ To evaluate the contribution of marine biological sources to organic aerosol (OA) over the eastern equatorial Pacific, we investigate:

(1) Isotopic compositions of WSOC

(2)Organic molecular compositions (biogenic tracers) in WSOC
(Isoprene-derived SOA, α-/β-pinene-SOA, sugars, etc.)

(3) Chemical budget of aerosol N

Marine Biological Activity and Aerosol OC and ON in the western North Pacific in Summer

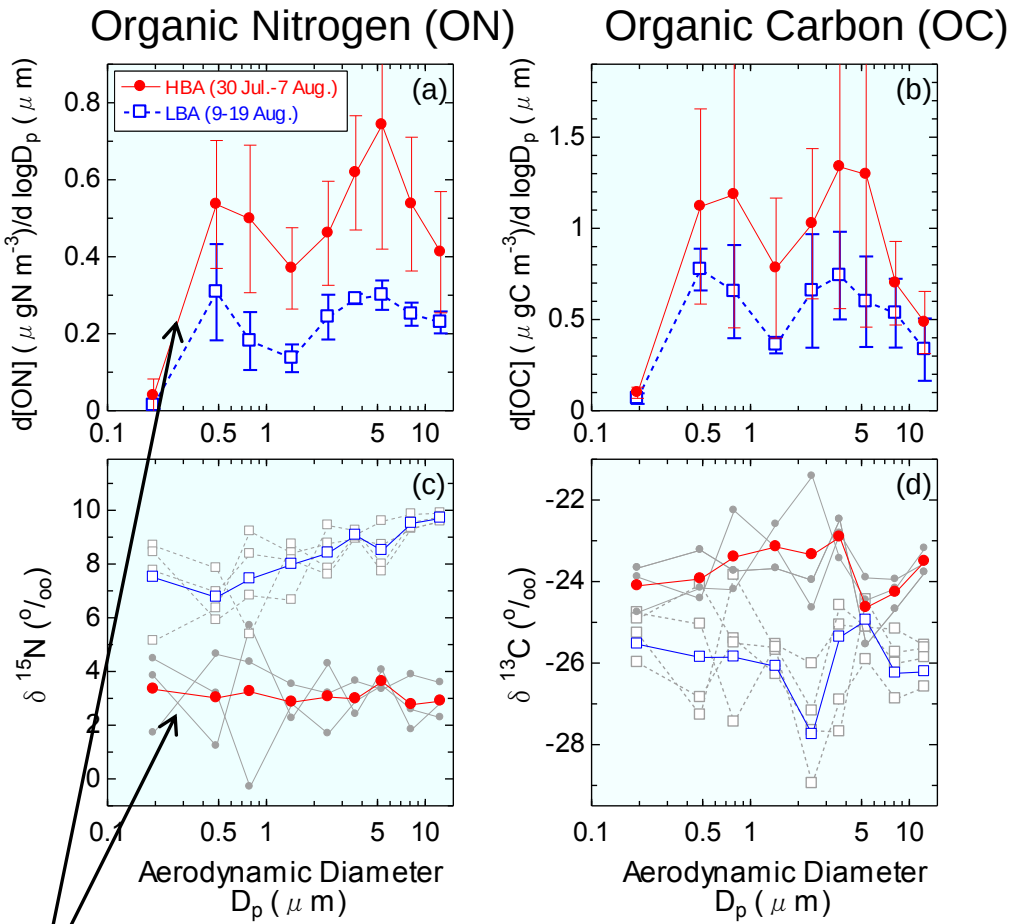


Marine Aerosol Sampling:

R/V JAMSTEC/Hakuho maru (KH08-2 cruise)

Period:

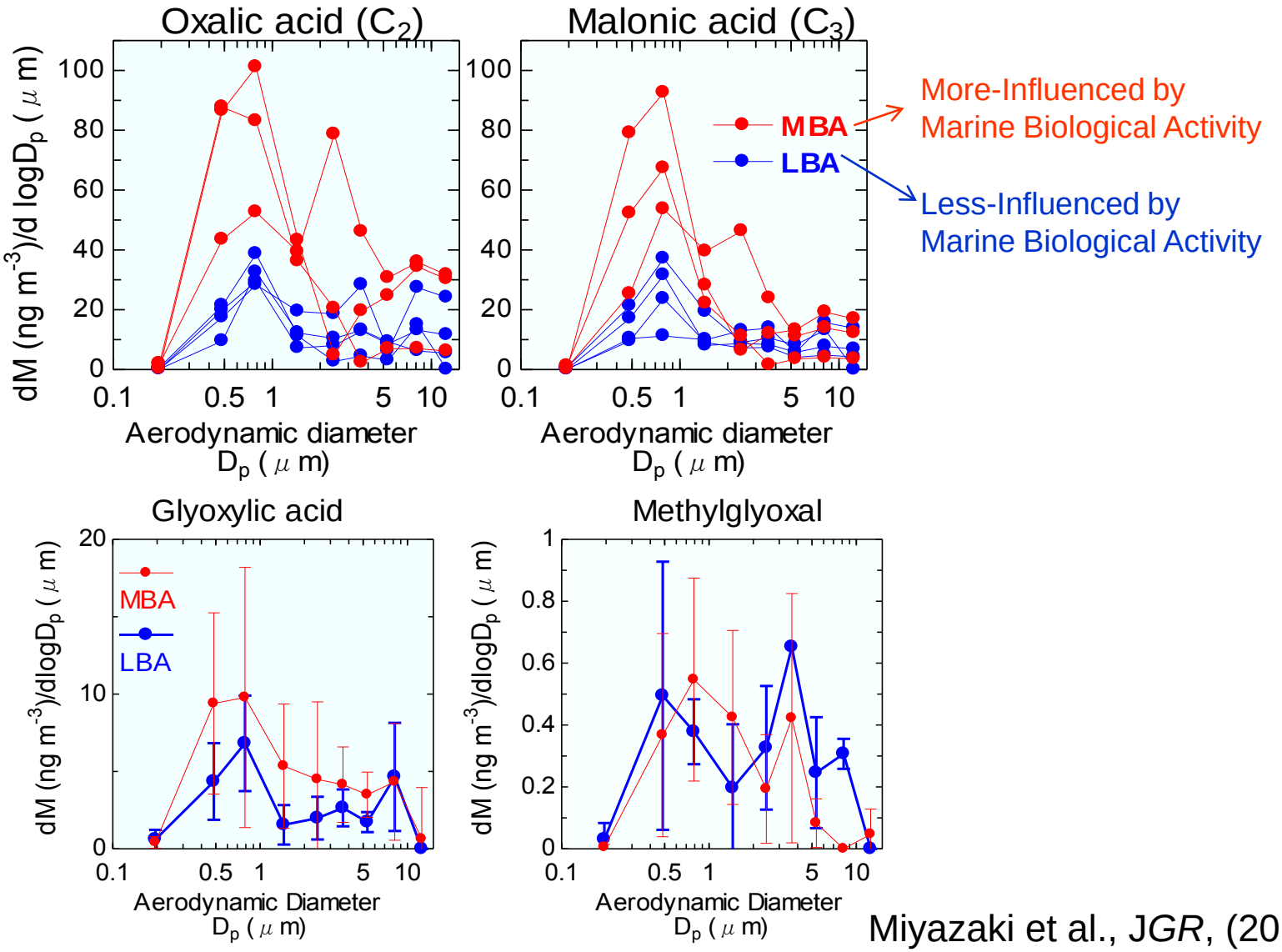
31 Jul. –13 Sep. 2008



Marine Biologically Influenced Aerosols

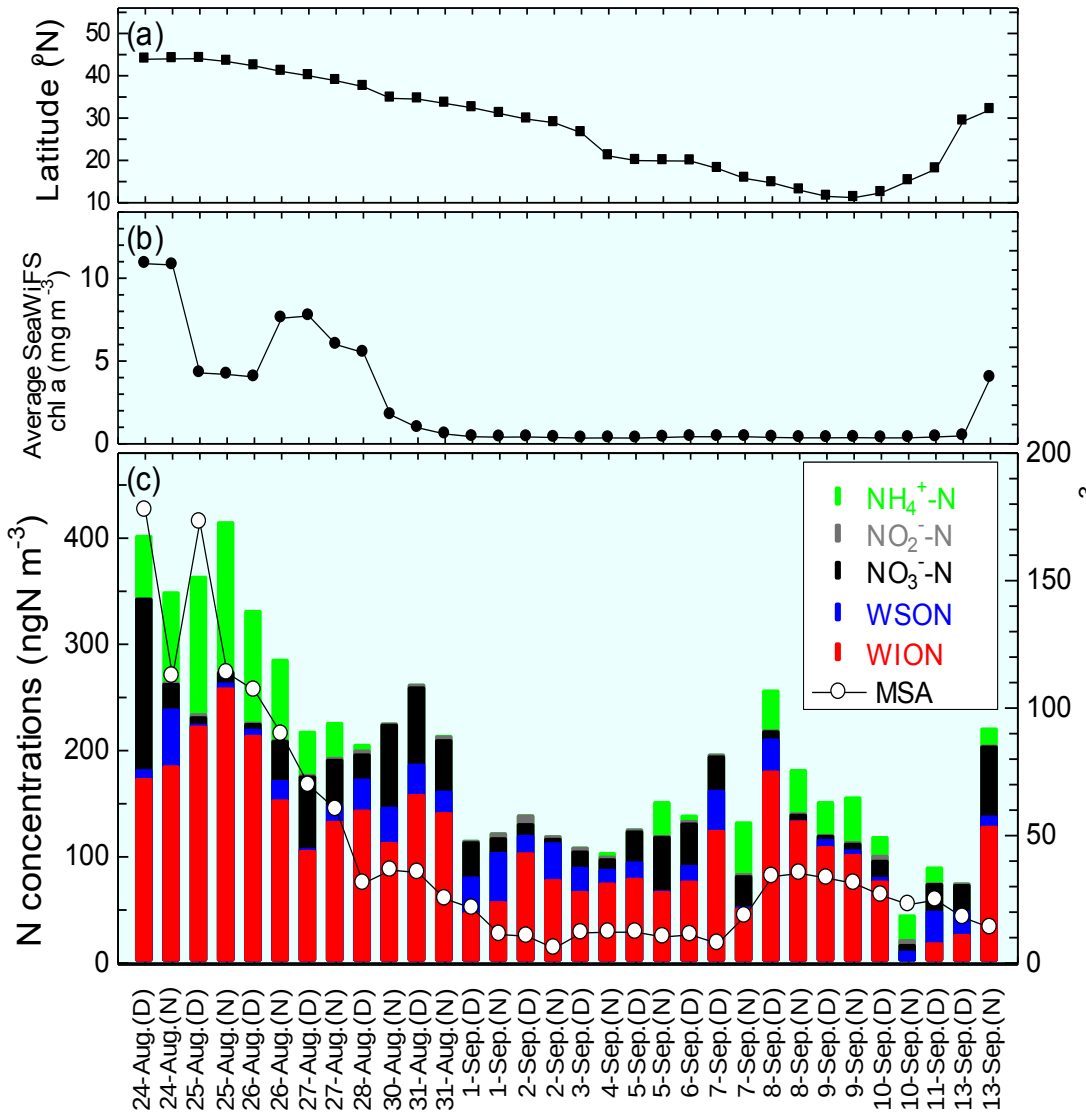
Miyazaki et al., *GRL*, (2010)

Influence of Marine Biological Activity on Di-/Keto-acids and α-Dicarbonyls in marine aerosols



Miyazaki et al., J*GR*, (2010)

Budget of Aerosol Nitrogen in Marine Aerosols



Aerosol organic nitrogen (ON):
Linked to water-solubility, acidity, and light-absorbing properties of ambient aerosols

- Water-insoluble organic nitrogen (WION) : the most abundant aerosol N (55±16% of TN)
- Maxium WION conc. (~260 ngN m^{-3}) at 40–44°N, 135°E (the western North Pacific) where marine biological influences on the aerosols were large

Miyazaki et al., *ACP*, (2011)

Approach

For PM_1 samples collected during the KA-12-01cruise

(1) Isotopic compositions of WSOC
measured by Elemental Analyzer (EA)-
Isotope Ratio (IR) MS

(2)Organic molecular compositions (biogenic tracers)
in WSOC determined by GC-MS

(3) Chemical budget of aerosol N
– importance of marine-derived ON

PM_1 Filter Sampling on Pre-baked Quartz Fiber Filters

Sub-μm Aerosol Samplings:

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

- The bottom stage of the impactor (PM_1) has been analyzed

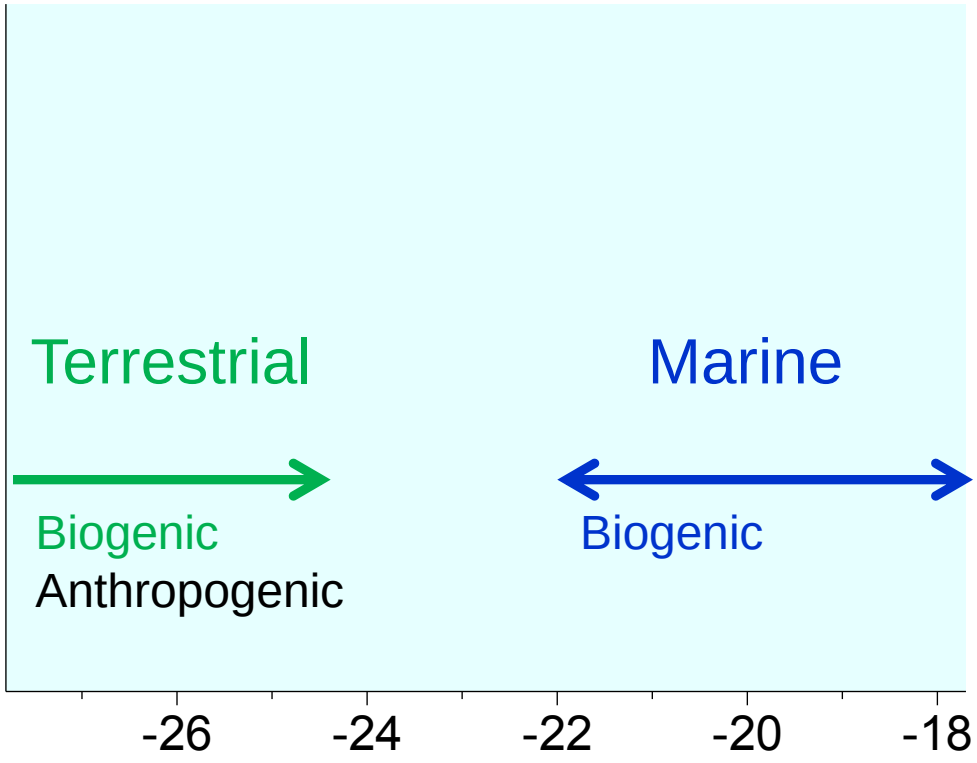
RV Ka'imimoana KA-12-01 Cruise

Period: 1 Feb. –29 Feb. 2012

Sampling: ~ 24 hours × 25 samples

(21 samples are available)

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 $\delta^{13}C$ (-20‰ to -14‰)

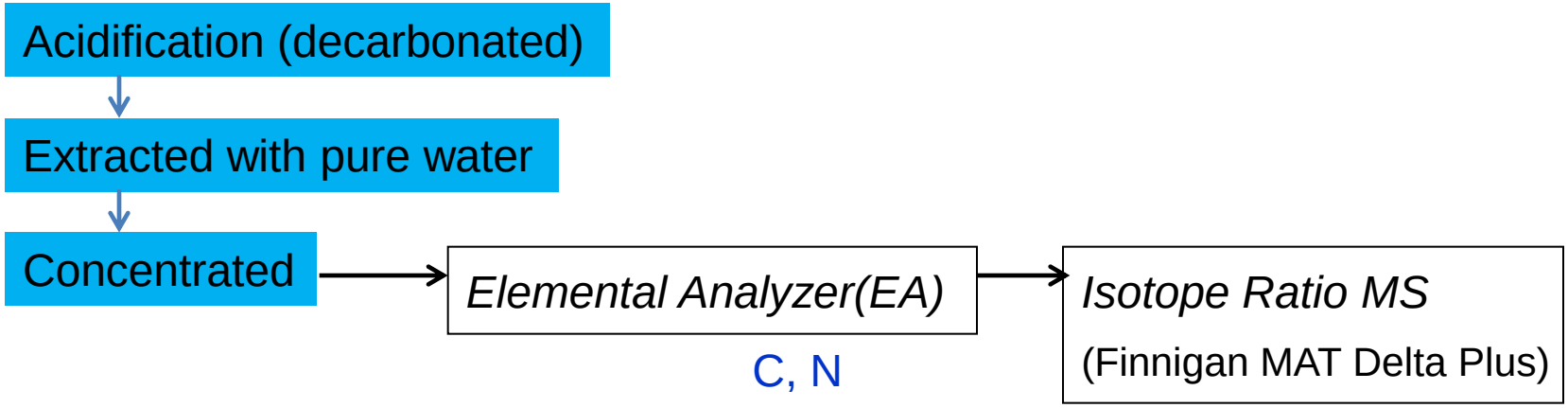
$\delta^{13}C_{TC}$: $\delta^{13}C$ of Total Carbon

$\delta^{13}C_{WSOC}$: $\delta^{13}C$ of Water-Soluble OC

Aerosol Chemical Analysis

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

- The most common aerosol carbon isotopic application is for the bulk total carbon (TC), whereas very few studies employ $\delta^{13}C$ in WSOC aerosols for the source apportionment

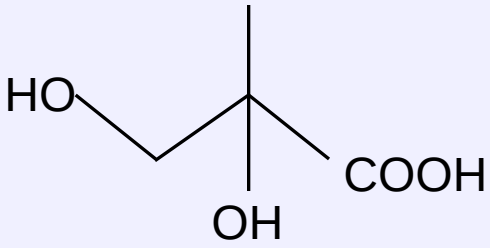


Recovery > 85%, Meas. uncertainty ~ 0.2‰

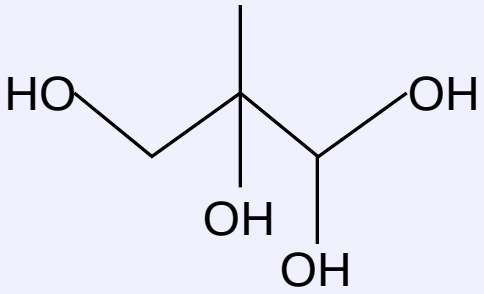
Some minor isotope fractionating processes is on the order of 0-2‰

WSOC mass conc. : Shimadzu TOC/TN analyzer (Model TOC-Vcsh)

Molecular Characterization (Biogenic Tracers) of WSOC

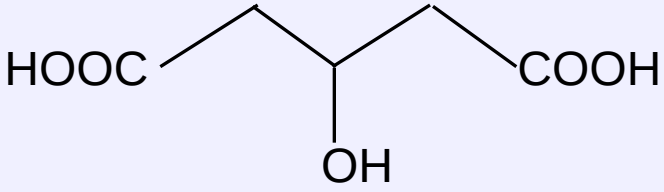


2-methylglyceric acid

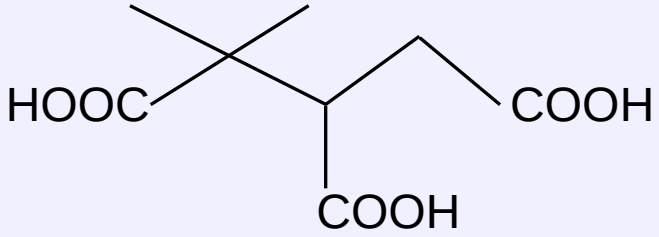


2-methyltetrols

Isoprene SOA tracers



3-hydroxyglutaric acid



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

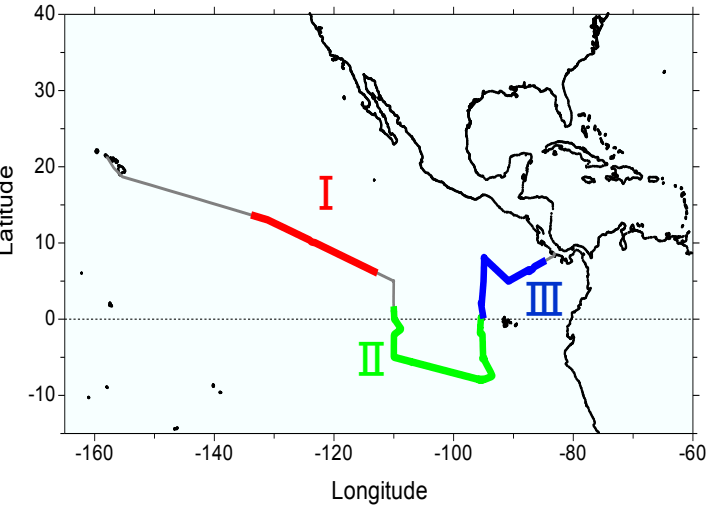
α-/ß-pinene SOA tracers

Extracted with dichloromethane/methanol

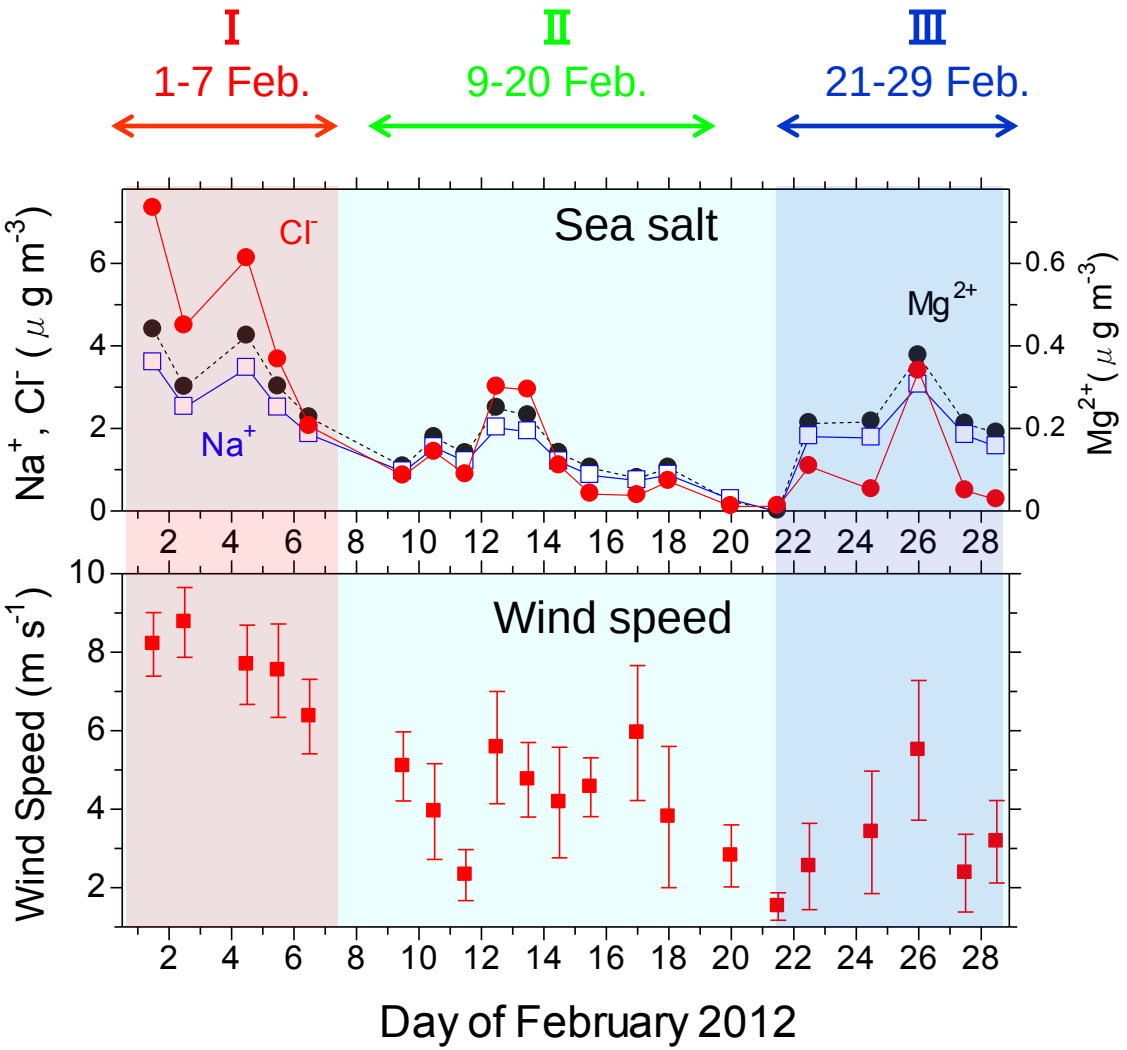
– COOH → TMS esters / –OH →TMS ethers → *GC-MS*

Major inorganic species including MSA → Metrohm *IC*

Sea-Salt Particles and Wind Speeds during the Sampling Period



Relatively high loadings of sea salt during the period I

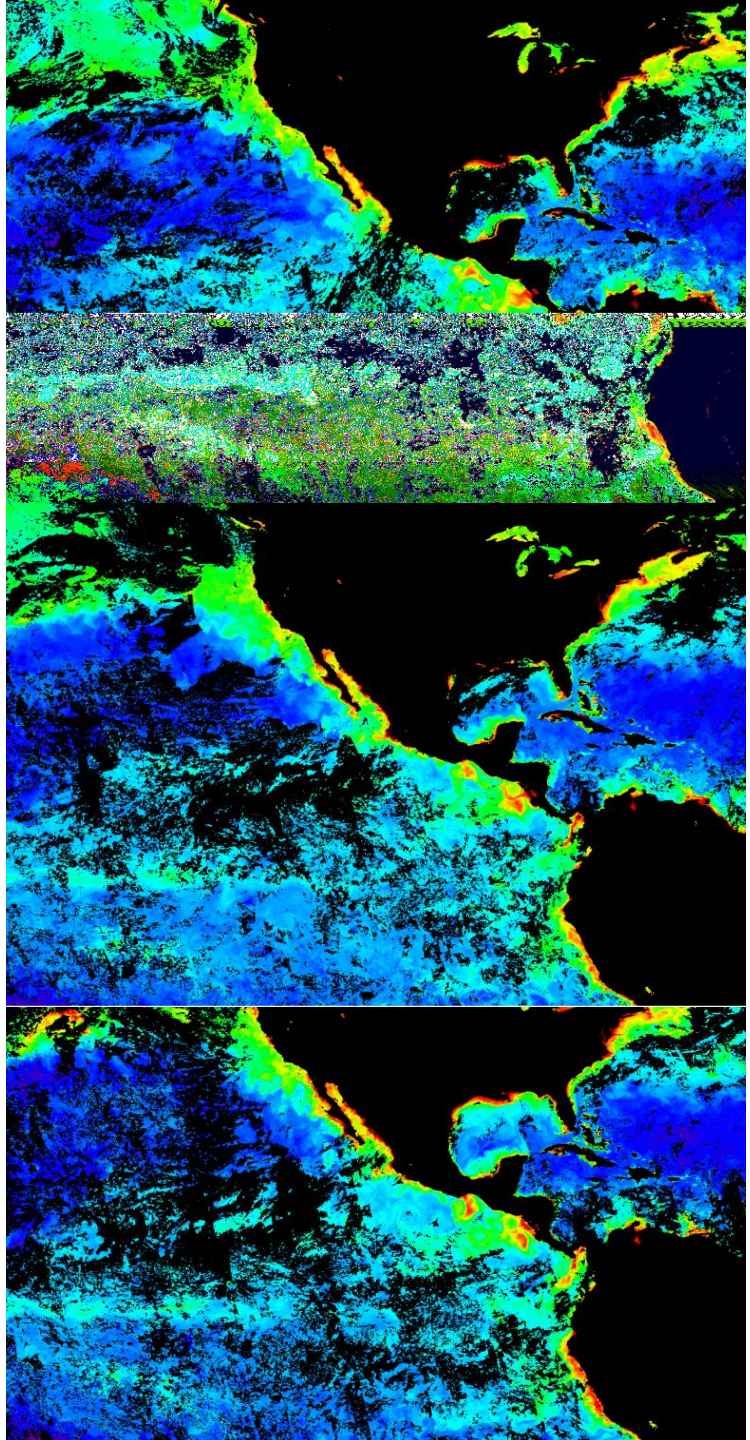


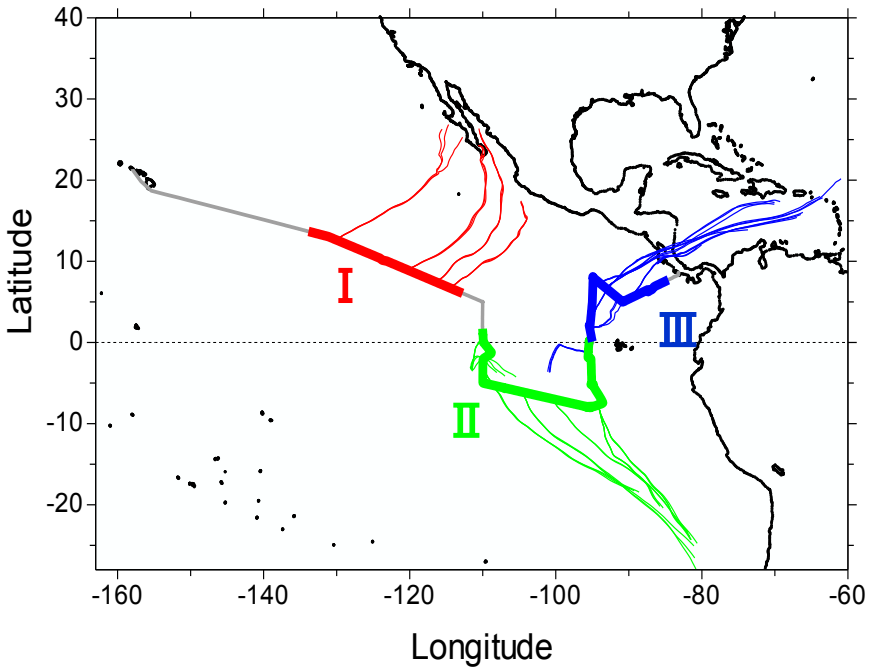
Cruise Track and 5-day Back Trajectories during the KA-12-01 Cruise

Feb.10-17

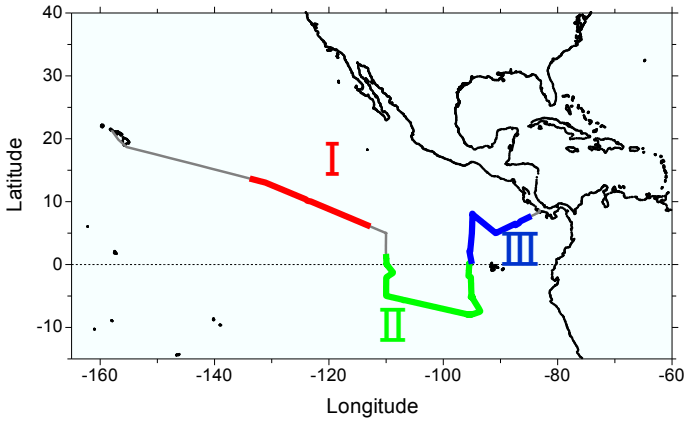
Feb.18-25

Feb.26
-Mar.4





Temporal and Spatial Variations in Sub-μm WSOC

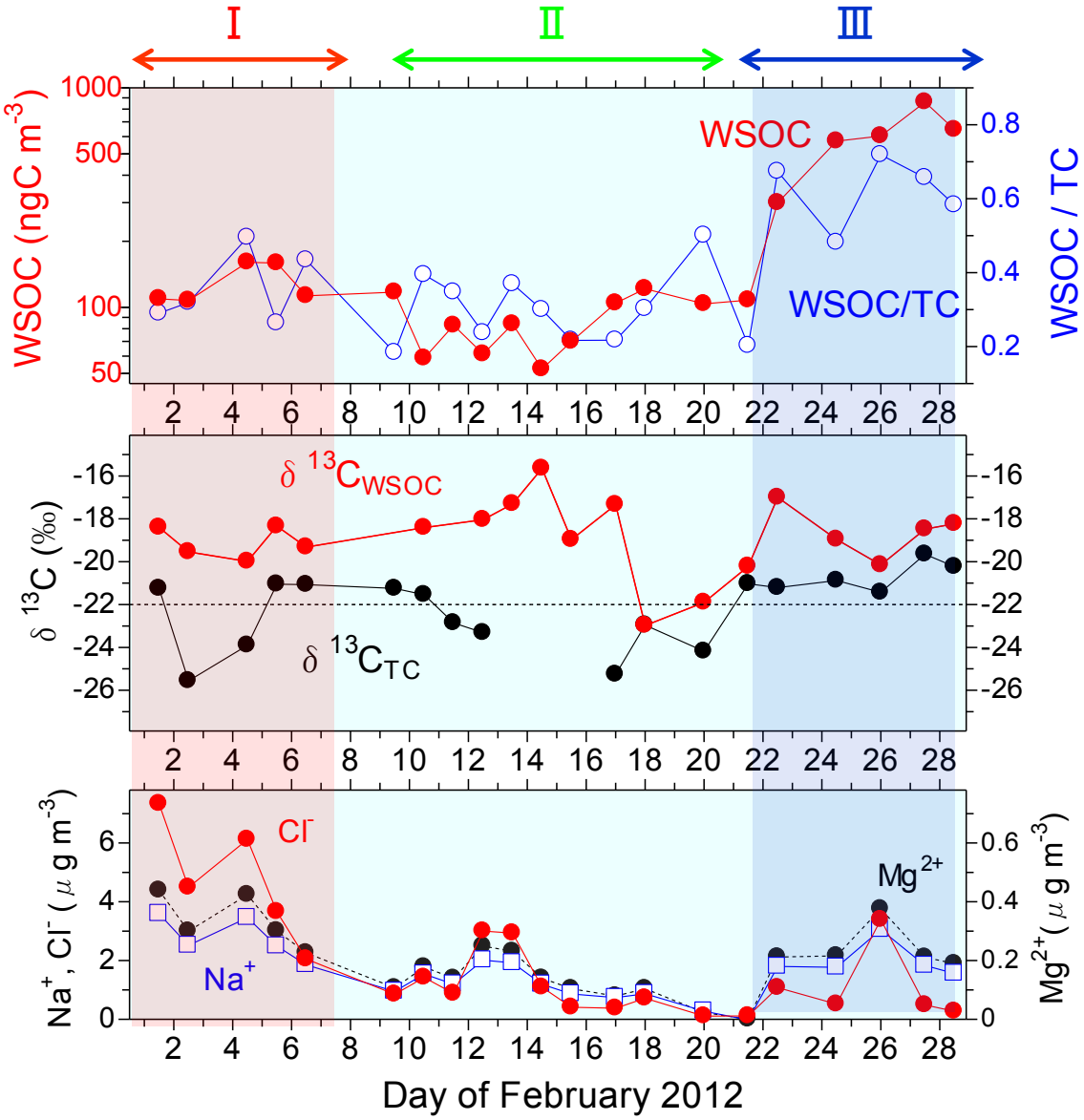


Water-soluble fraction

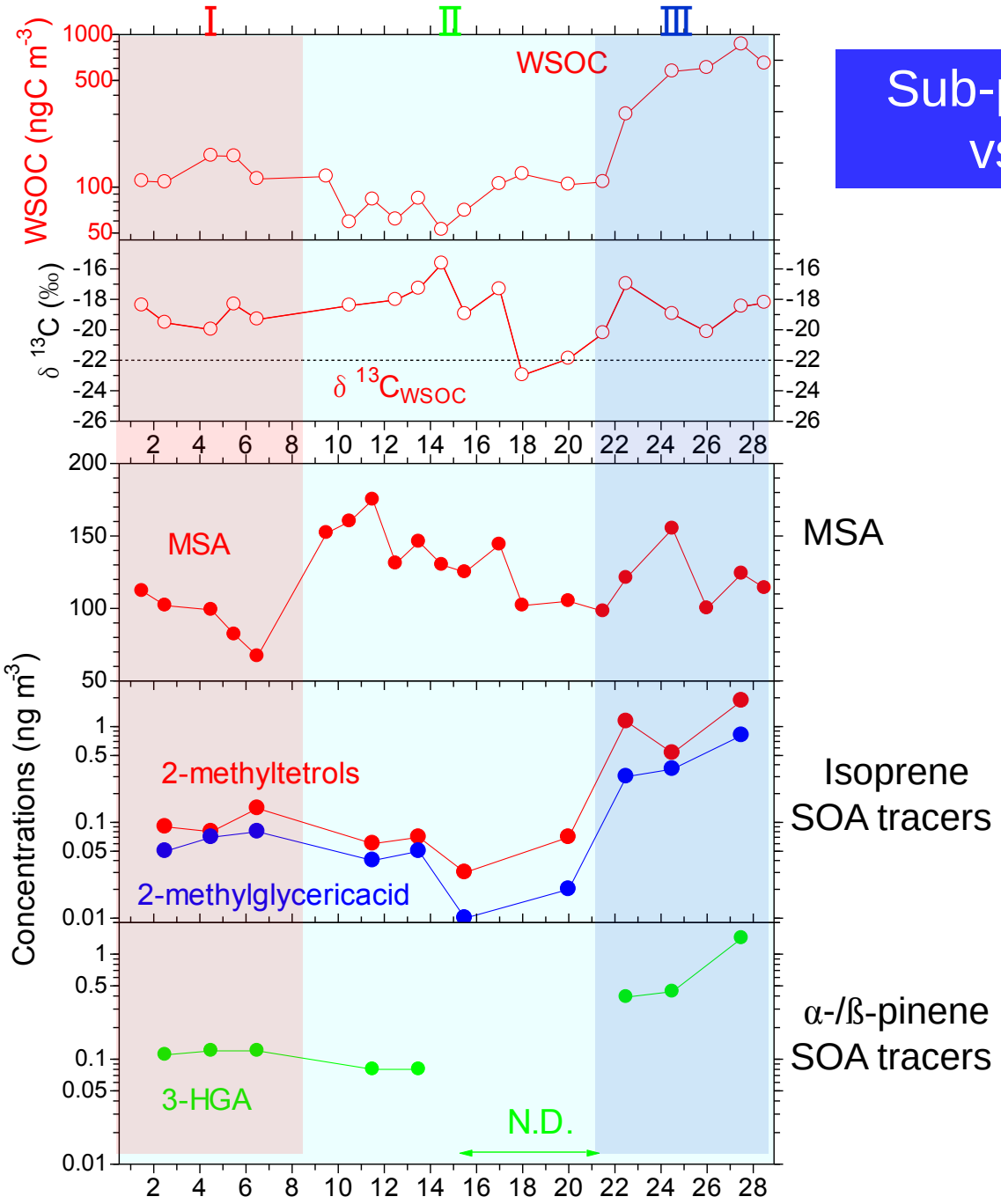
of TC: ~40±16%

$\delta^{13}C_{WSOC}$: −19.8±2.0‰

> $\delta^{13}C_{TC}$: −22.2±1.9‰



Sub-μm WSOC & $\delta^{13}C_{WSOC}$ vs. Biogenic Tracers

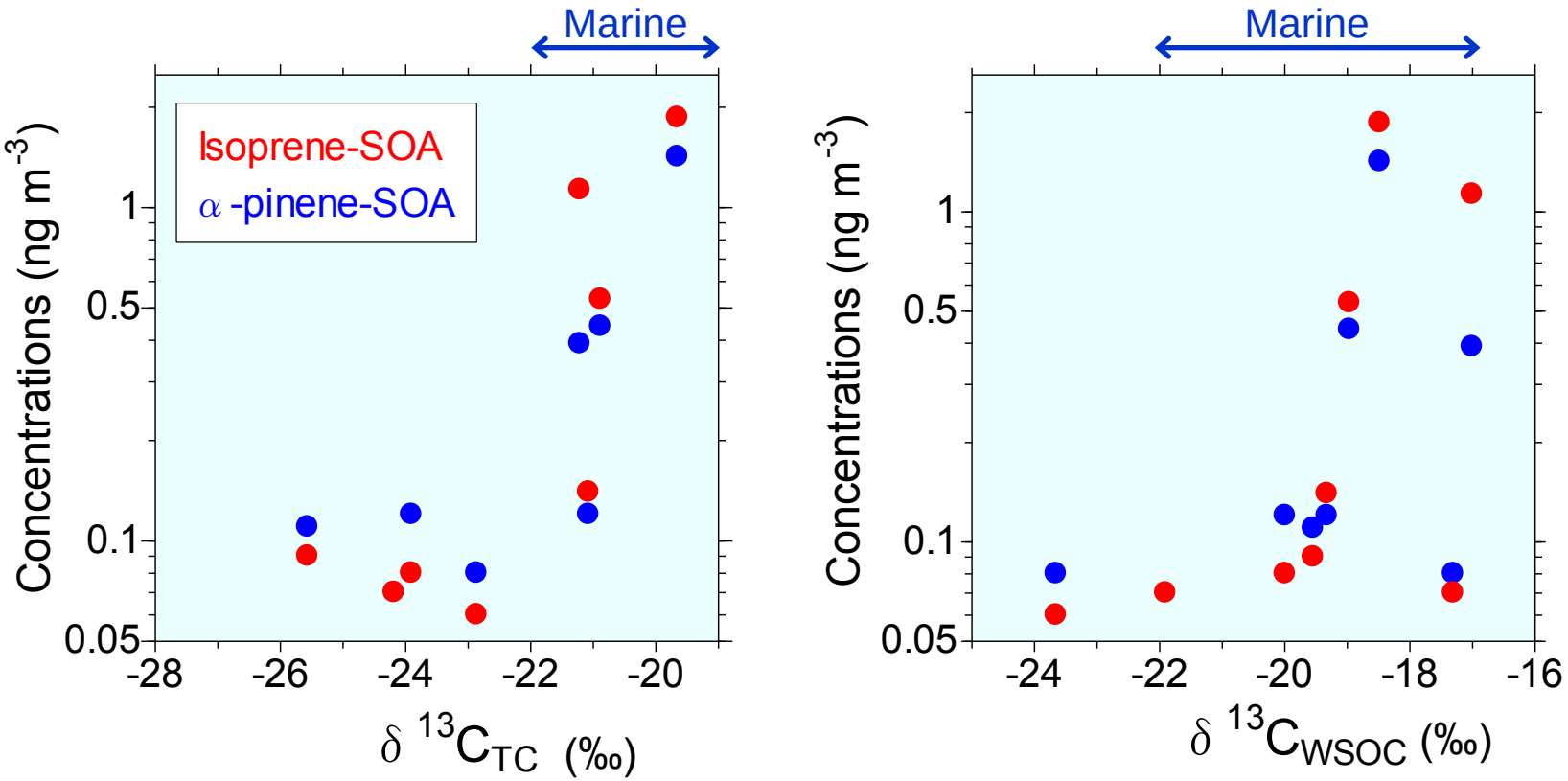


MSA

Isoprene SOA tracers

α-/ß-pinene SOA tracers

$\delta^{13}C$ vs. Biogenic SOA Tracers



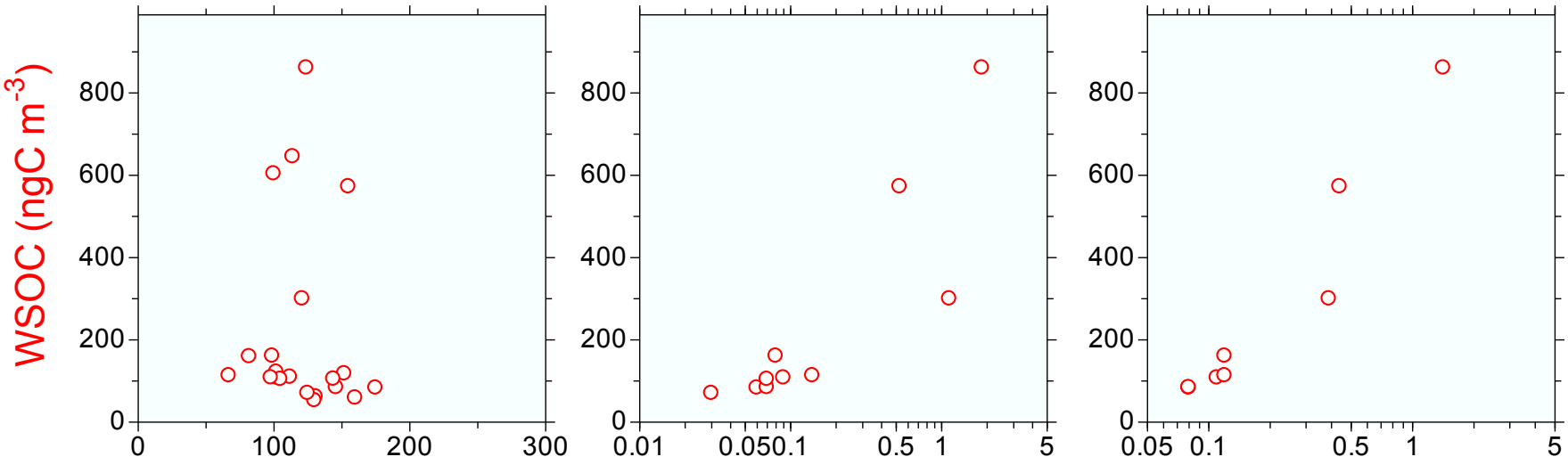
The relative contributions of marine sources to the sampled aerosols using $\delta^{13}C$

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

$F_{marine} + F_{terrestrial} = 1$; $\delta^{13}C_{marine} = -20 \pm 2‰$, $\delta^{13}C_{terrestrial} = -25 \pm 2‰$ (e.g., *Turekian et al.*, 2003)

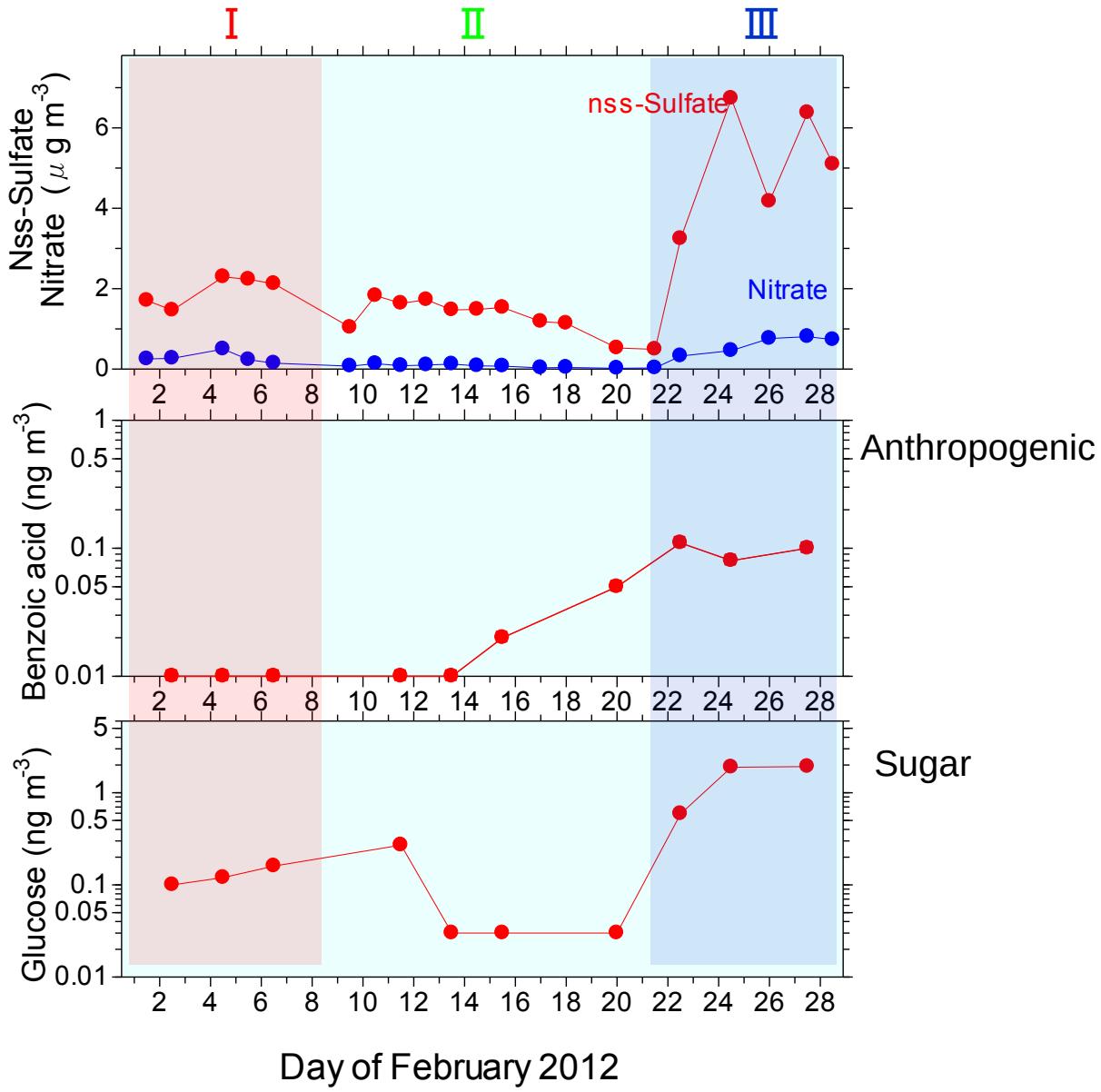
→ Marine biological sources account for ~ 93±26% of WSOC

WSOC vs. Biogenic SOA Tracers



- Isoprene- and α-pinene-oxidation products of marine origin closely linked to the elevated WSOC conc.
- MSA (i.e., DMS oxidation) : not necessarily contribute to the elevated levels of WSOC?

Sulfate, Nitrate & other organic tracers



(1) Isotopic compositions of WSOC

(2)Organic molecular compositions (biogenic tracers) in WSOC

(Isoprene-derived SOA, α-/β-pinene- SOA, sugars, etc.)

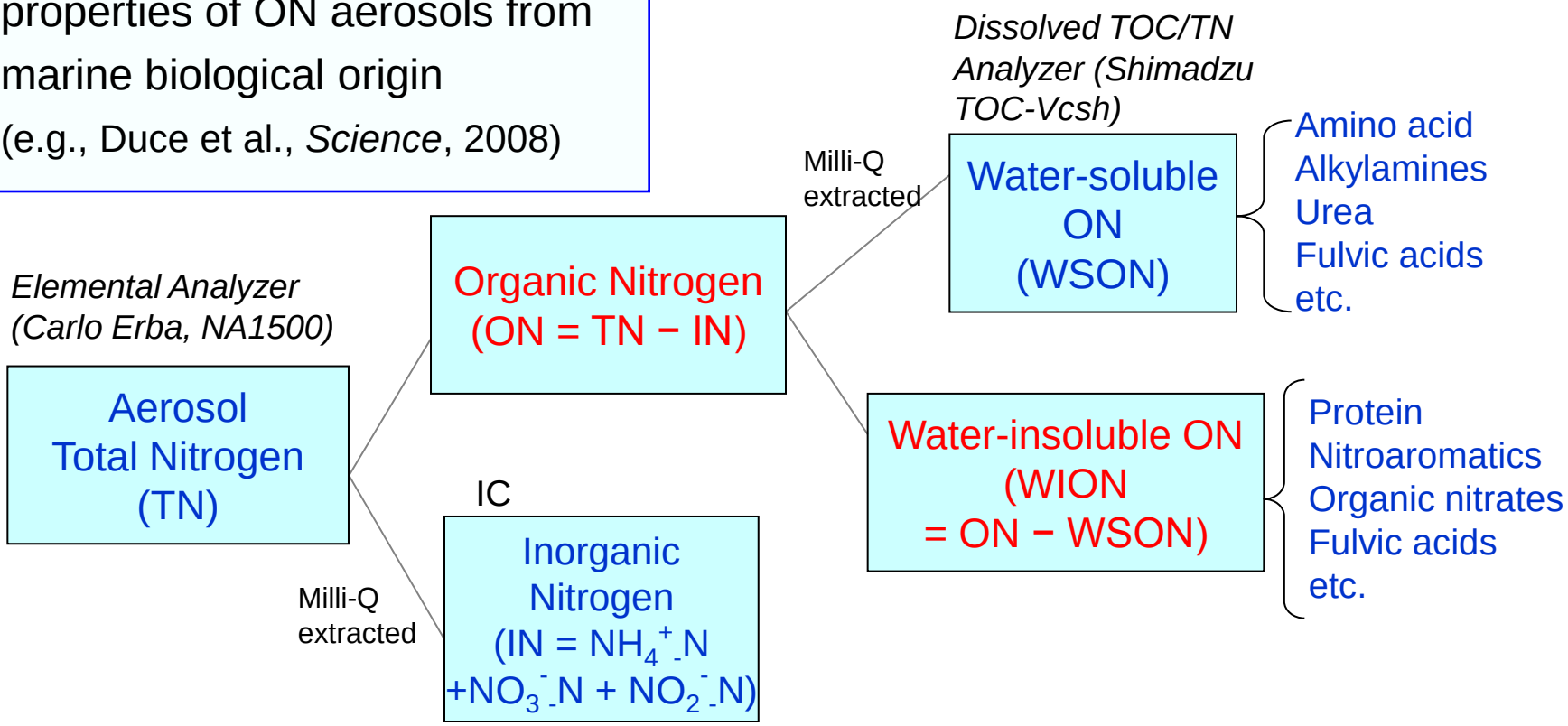
(3) Chemical budget of aerosol N

Analytical Definition of Aerosol Organic Nitrogen

Aerosol ON:

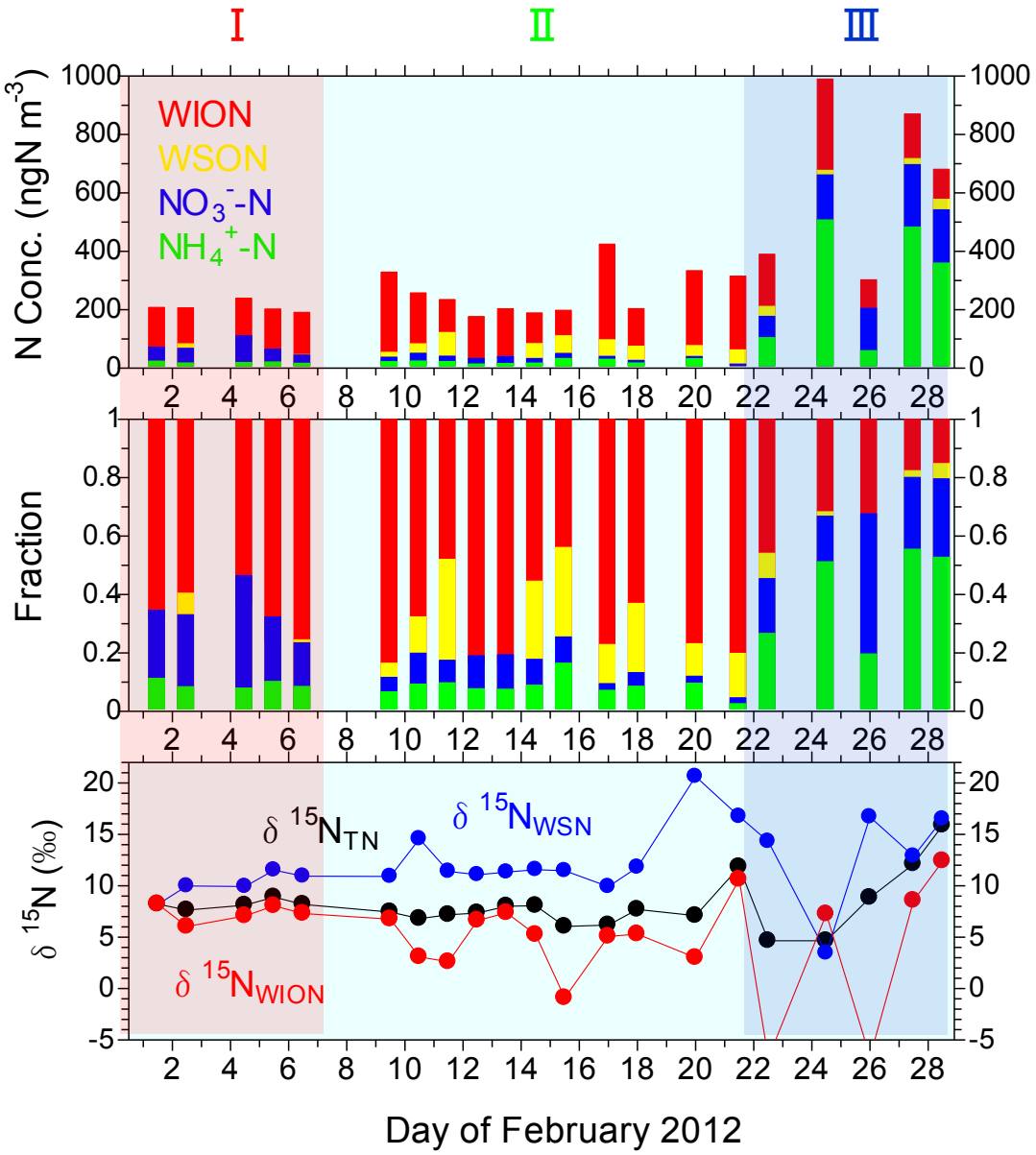
Little is known about chemical properties of ON aerosols from marine biological origin

(e.g., Duce et al., *Science*, 2008)



Nitrogen Isotopic Analysis : EA / Isotope Ratio MS

Budget of Aerosol Nitrogen

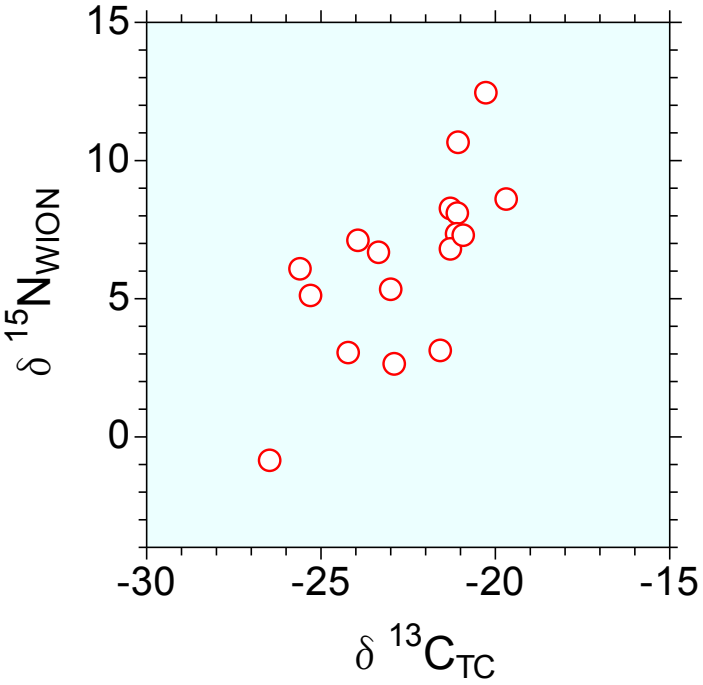


WION was the most abundant aerosol N (70±13% of aerosol N)

Mass concentrations and fractions of WSON elevated during the period Ⅱ

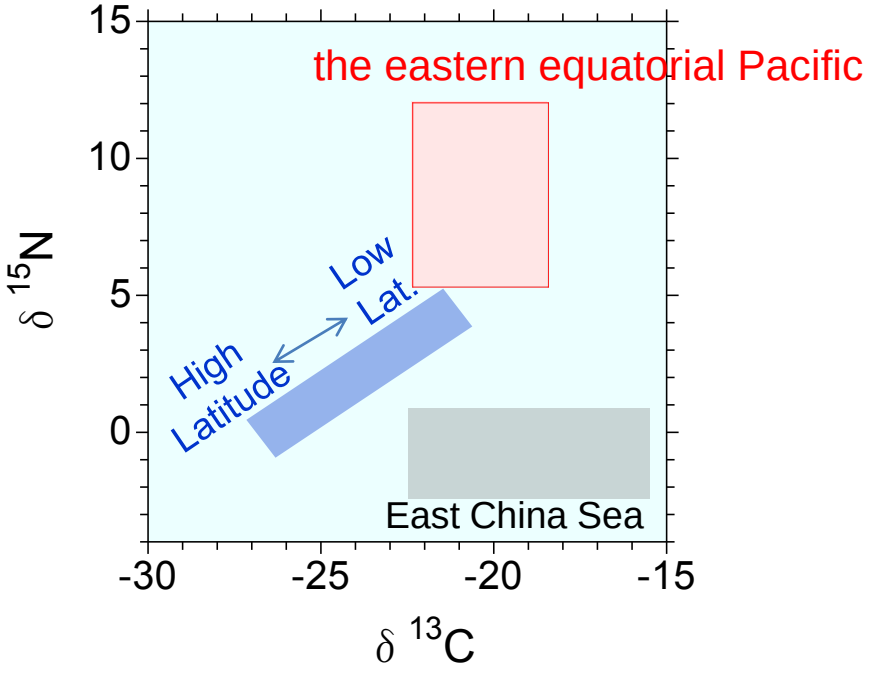
$$\delta^{15}N_{WION} = \frac{([TN] \times \delta^{15}N_{TN} - [WSN] \times \delta^{15}N_{WSN})}{([TN] - [WSN])}$$

$\delta^{15}N$ in Aerosol and Surface Sea Water



Ambient Aerosol
(this study)

$\delta^{15}N$ of Phytoplankton
in Surface Sea Water
[*Wada et al*., 1984]



Surface Sea Water
(typical ranges)

Summary

- Water-soluble fraction of TC in sub-μm aerosols: ~40±16%

- The $\delta^{13}C$ analysis indicates that marine-derived carbon accounted for 93±26% of WSOC

- WSOC and BSOA tracers exhibited higher loadings over the coastal region
- Isoprene- and α-pinene-SOA of marine origin likely contributed to the elevated levels of WSOC

- Water-insoluble organic nitrogen (WION) was the most abundant N (70±13% of total aerosol N)

  → an enrichment of nitrogen in OA originated from the oceanic region

Need to clarify..

- Linkage of OA identified above with types of marine biota (diatoms, etc.,)
- Sea-to-air emissions via sea spray vs. secondary oxidation