

EqPOS

Jan 29, 2012 – Feb 19, 2012 (22 days)

**Equatorial Pacific Ocean and
Stratospheric/Tropospheric Atmosphere Study**

Sky, Ocean, and In-Between

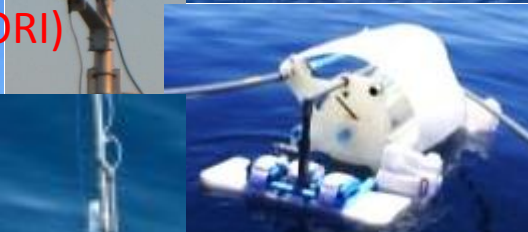
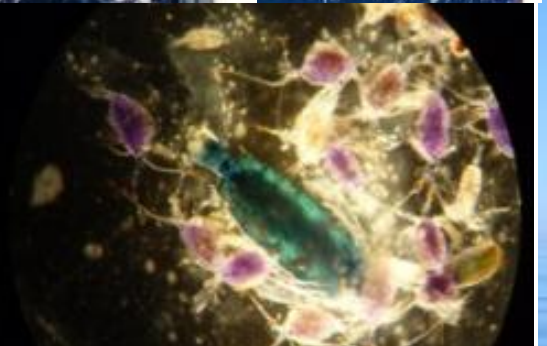
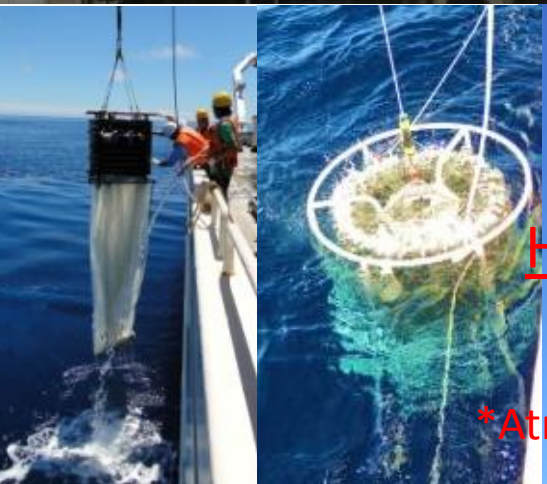
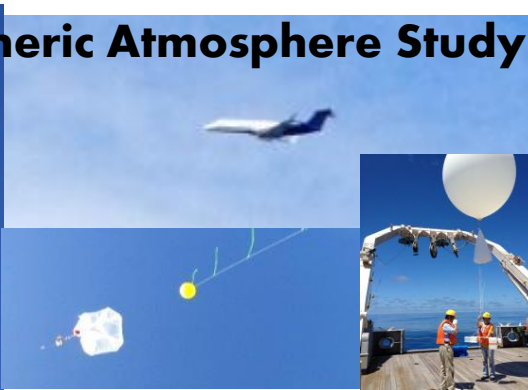
Preliminary Results

Hiroshi Furutani*, Mitsuo Uematsu*
and EqPOS Science Team

*Atmosphere and Ocean Research Institute (AORI)
Univ. of Tokyo



東京大学
THE UNIVERSITY OF TOKYO

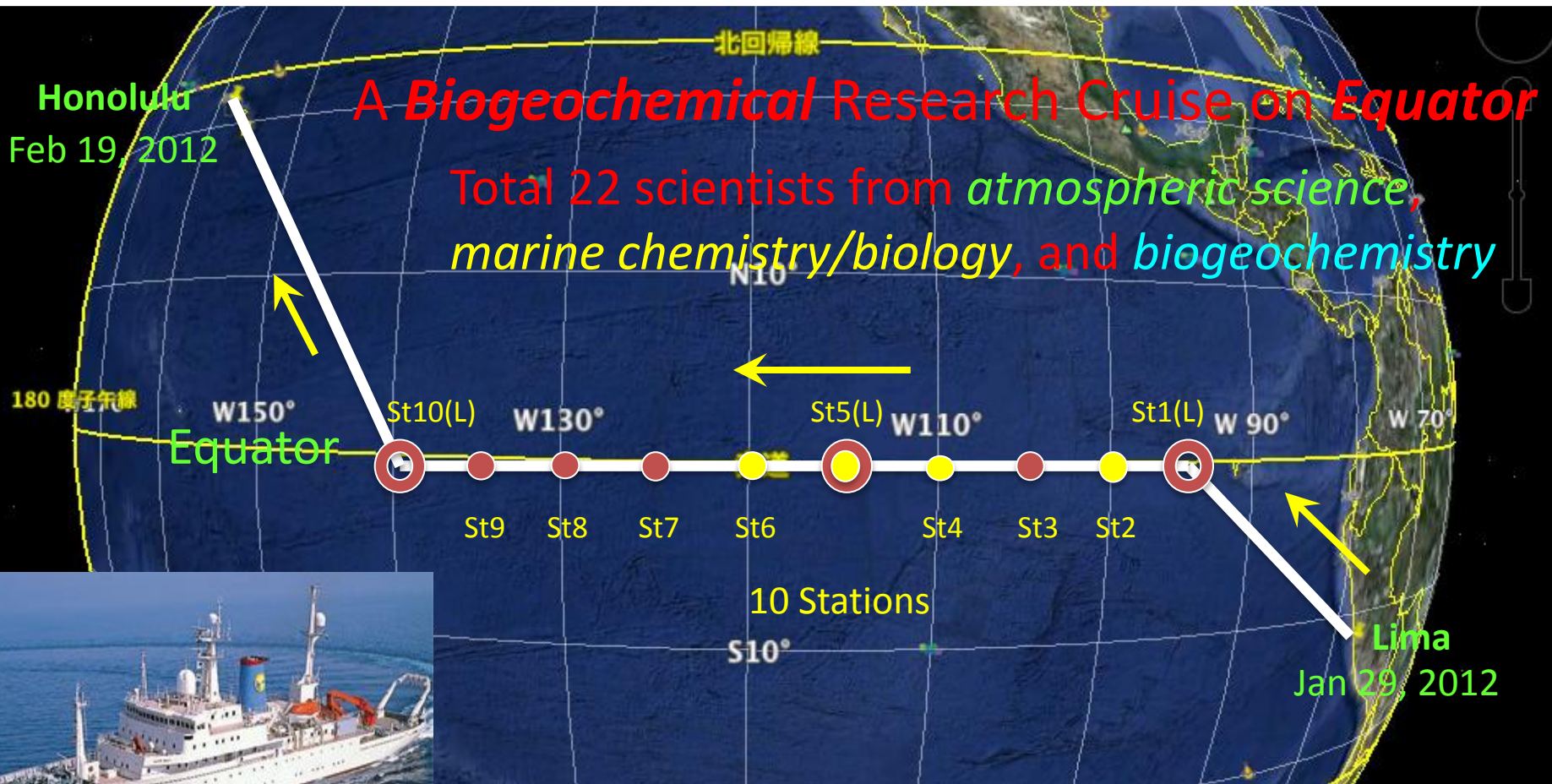


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**Equatorial Pacific Ocean and Stratospheric/
Tropospheric Atmosphere Study**

PI: Prof. Uematsu (AORI)

Jan 29, 2012 – Feb 19, 2012 (22 days)



Stratosphere (30 km)



EqPOS

O₃, CO₂, H₂O
Profiling



Stratospheric
Air Sampling
(Alt = 19-30 Km)

Atmospheric Aerosols
(Size Dist., CCN, Comp., Morphology)

Trace Gas
(DMS, VOCs, CO₂
CO, O₂)

Bubble Bursting

Surface
Microlayer
Sampling

Eddy
Covariance

Gradient
Profile

Air-Sea
Flux

CO₂

Dissolved Gas
(DMS, DMSP, VOCs,
pCO₂, O₂)

N-Fixation

Phytoplankton

Bacteria

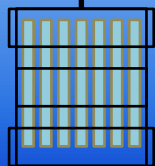
Non-living
Particles

DMS VOCs
CO₂

Microbial
Abundance,
Speciation,
Community

Incubation
Exp.
Zooplankton

Nutrients, Chl-a
TOC
DOC, DON



Ocean Floor (- 6 km)



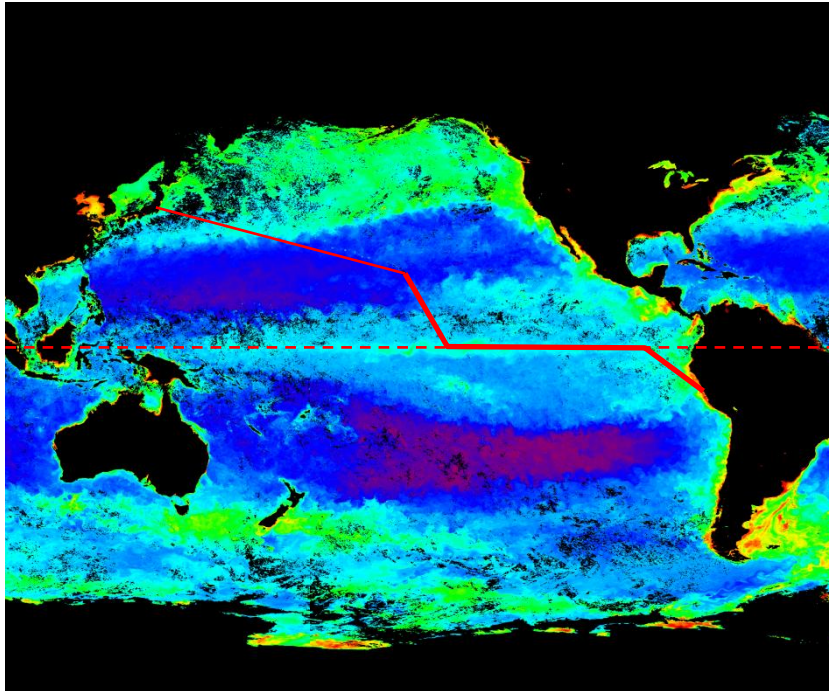
EqPOS

Equatorial Pacific Ocean and Stratospheric/ Tropospheric Atmosphere Study

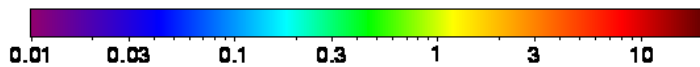
PI: Prof. Uematsu (AORI)

Jan 29, 2012 – Feb 19, 2012 (22 days)

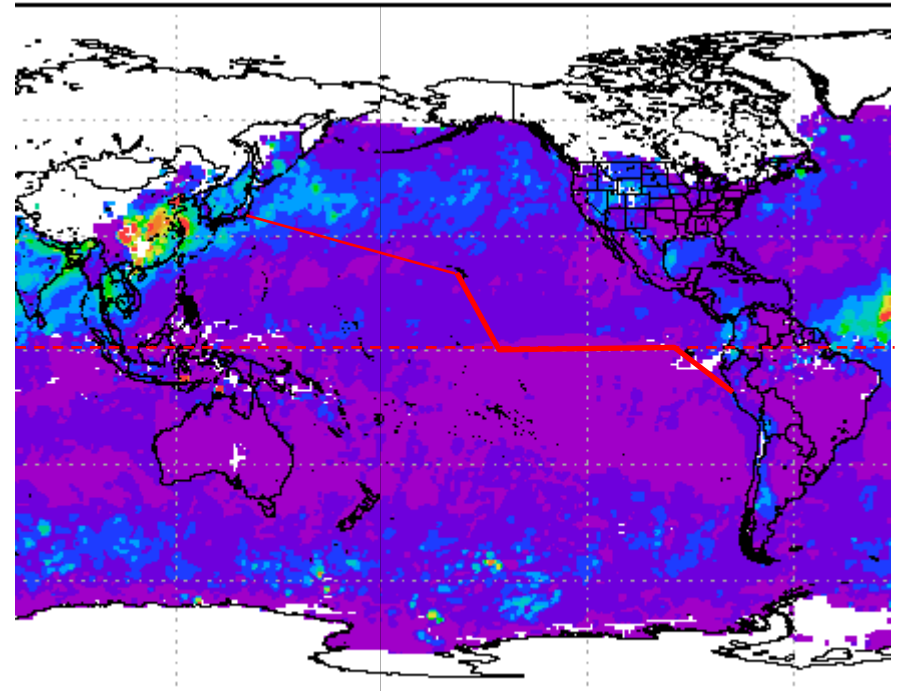
MODIS Surface Chl-a (Feb 2012)



Chlorophyll a concentration (mg / m³)



MODIS AOD (Feb 2012)

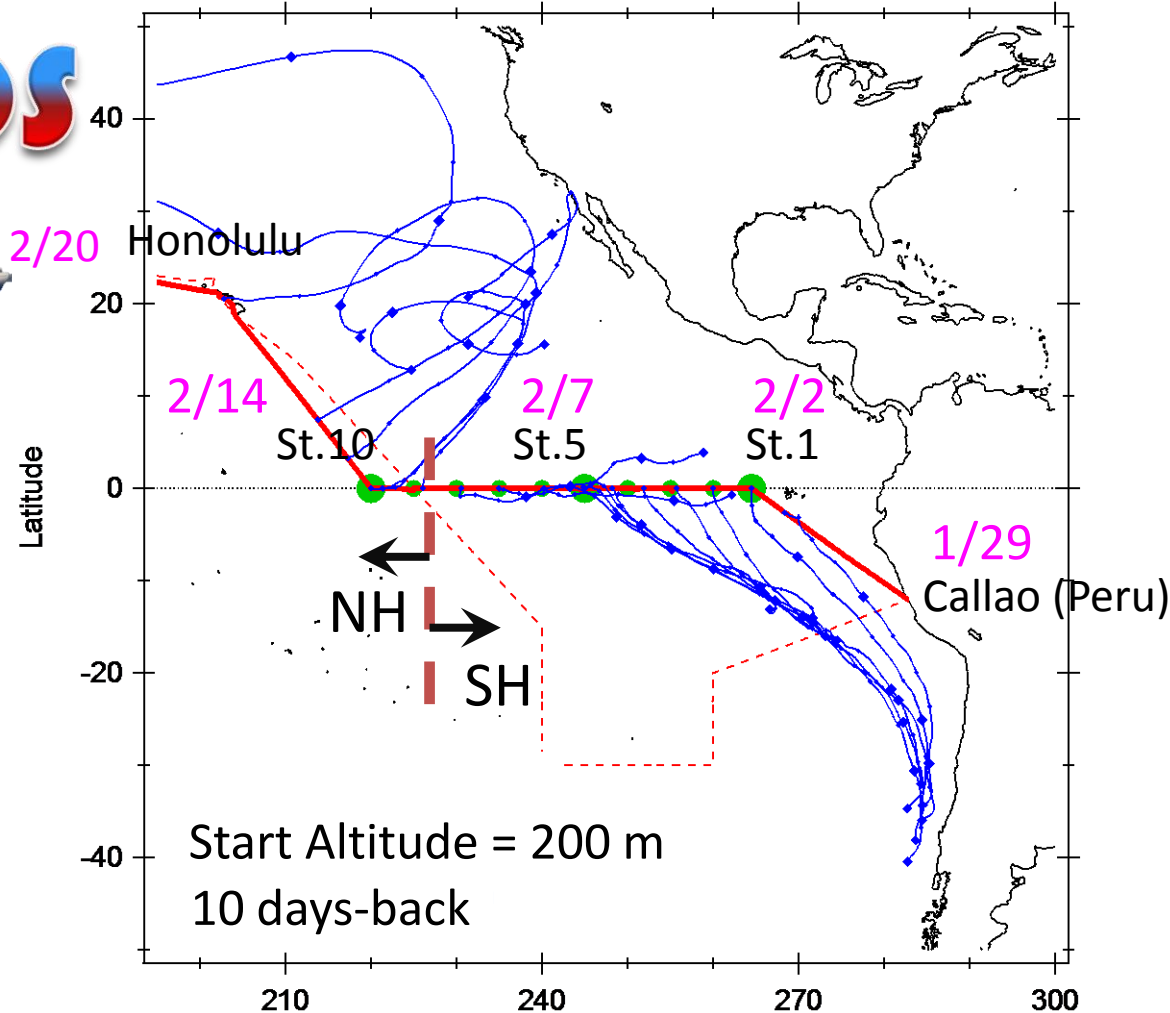


120E 130 120W 60W

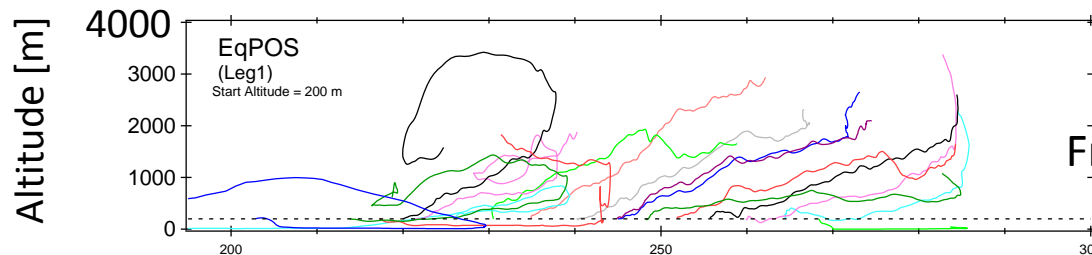


Back Air Trajectories (10 days back)

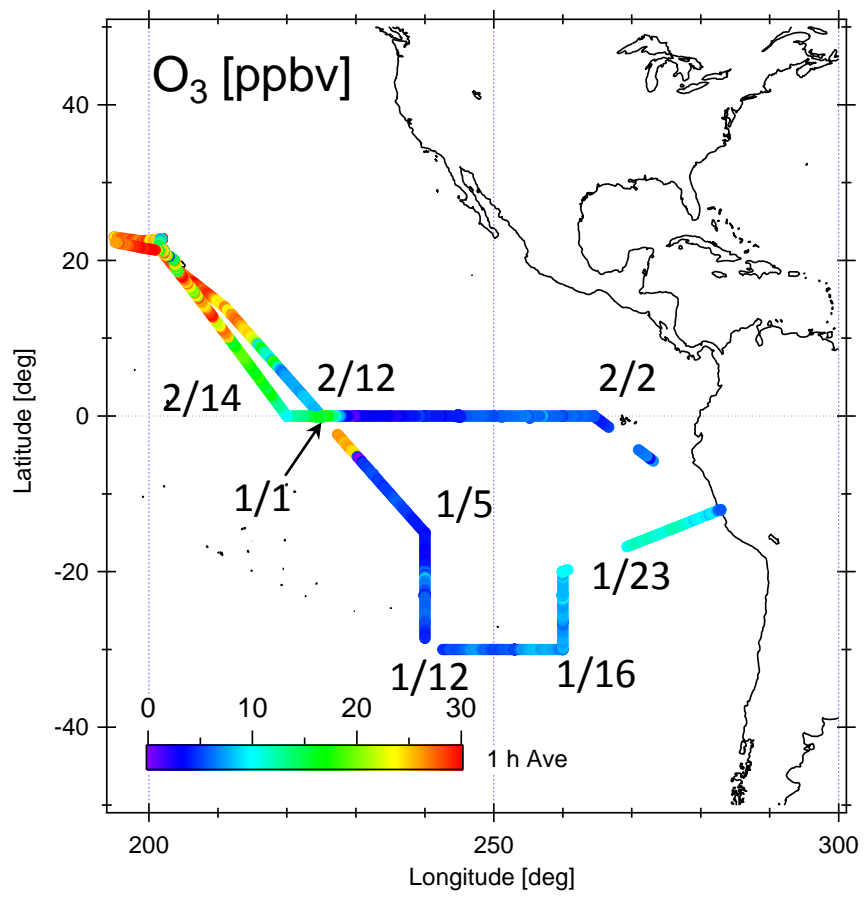
EqPOS

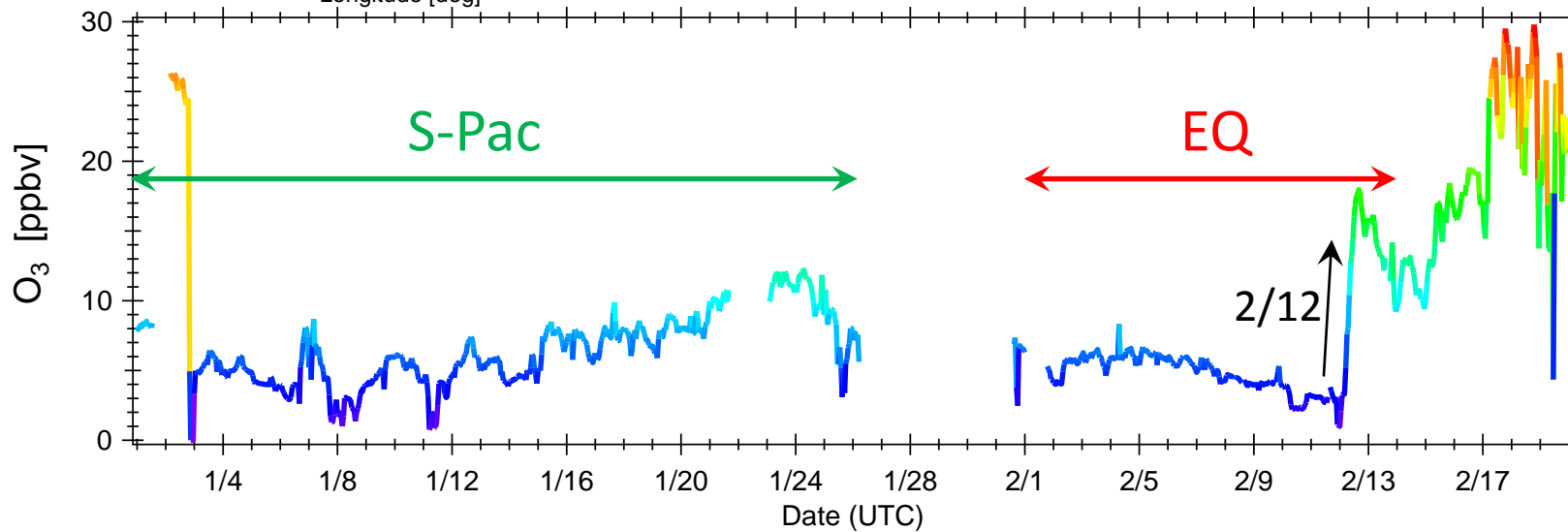
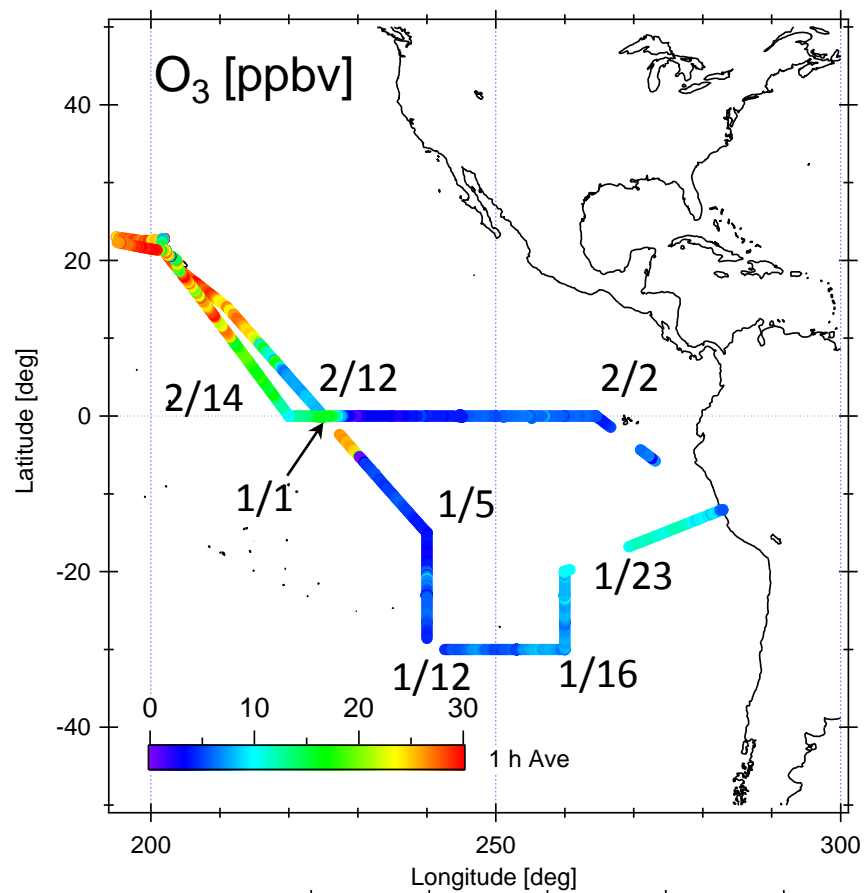


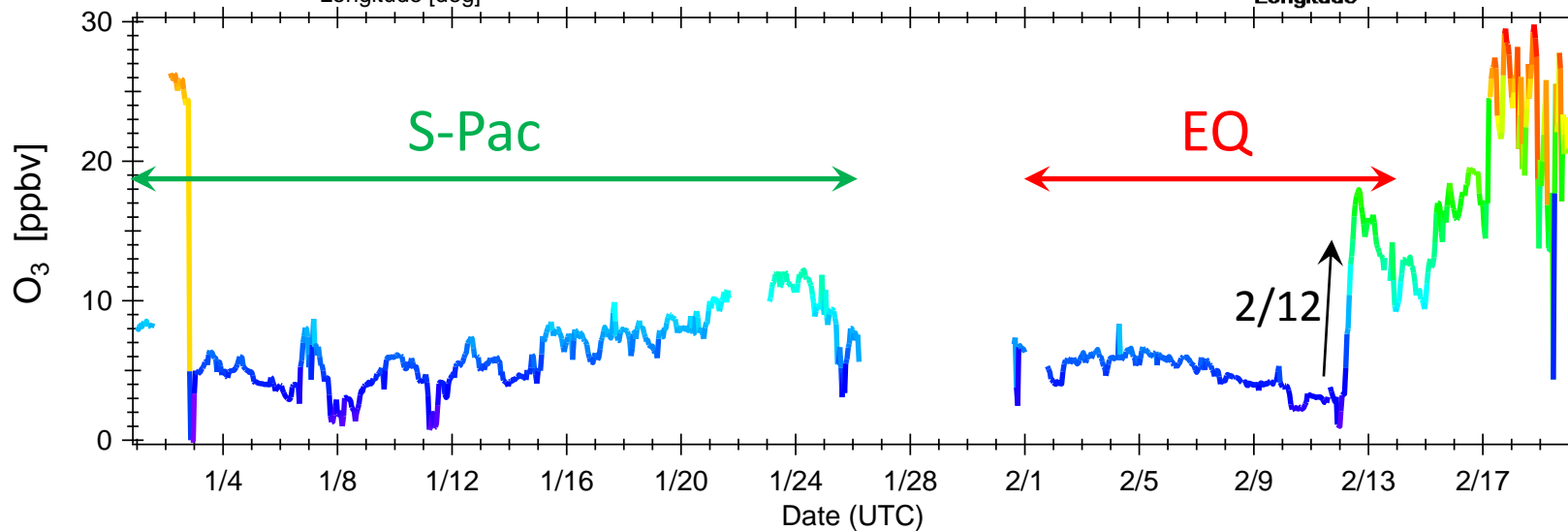
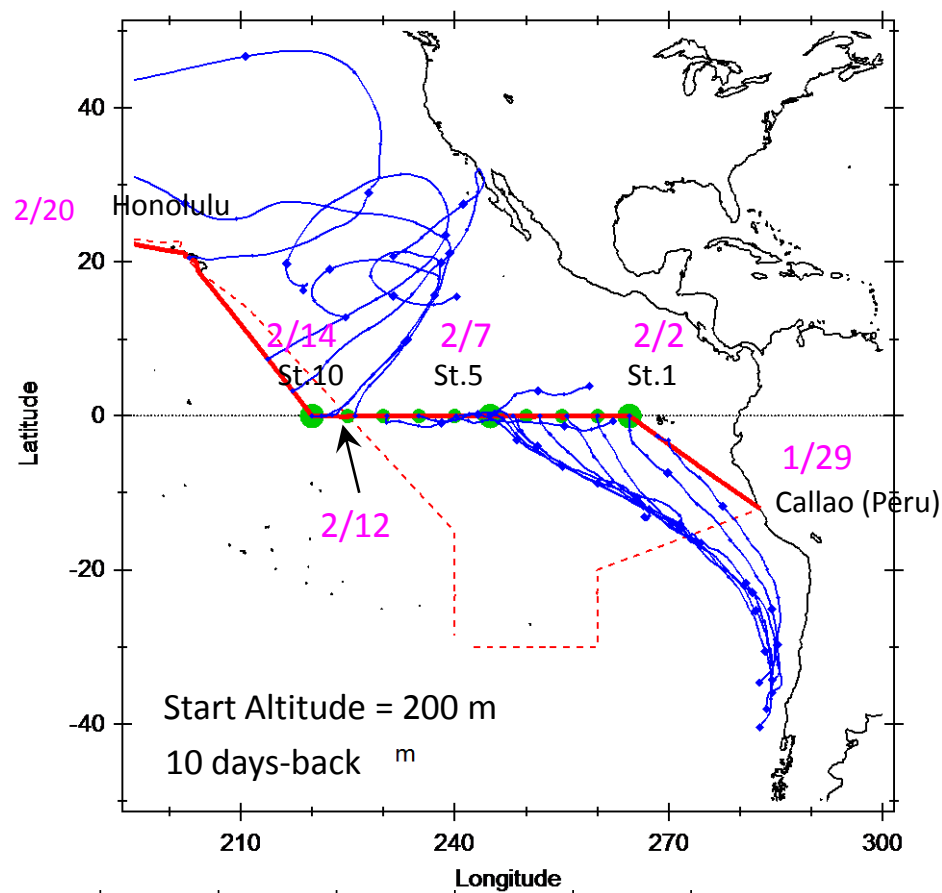
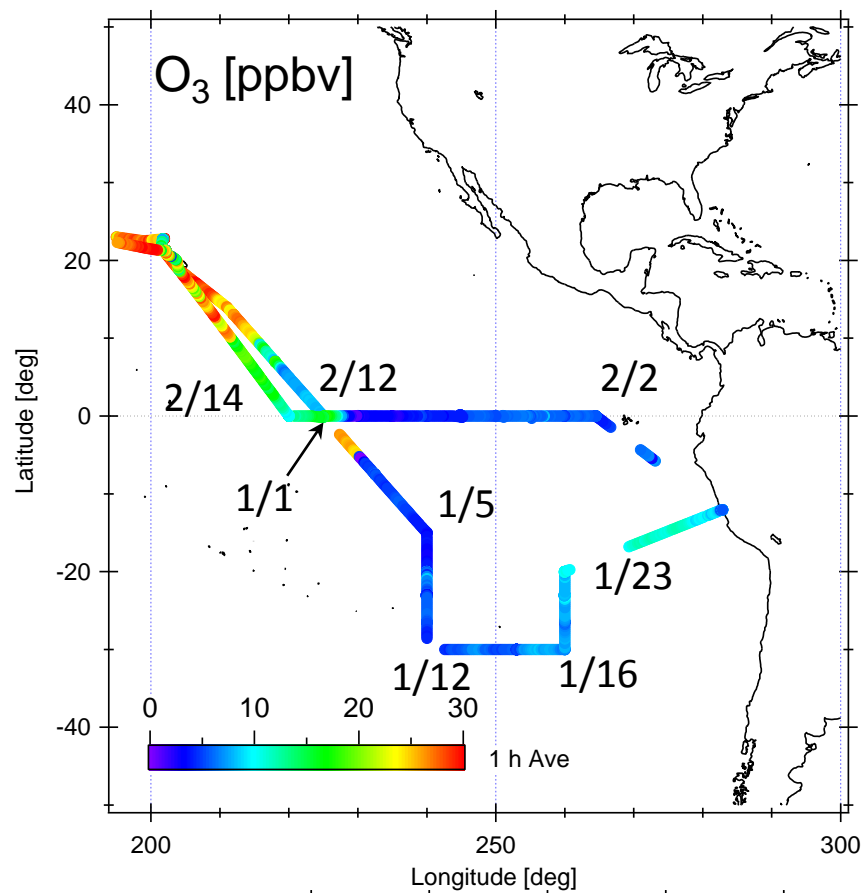
Calculated using HySPLIT

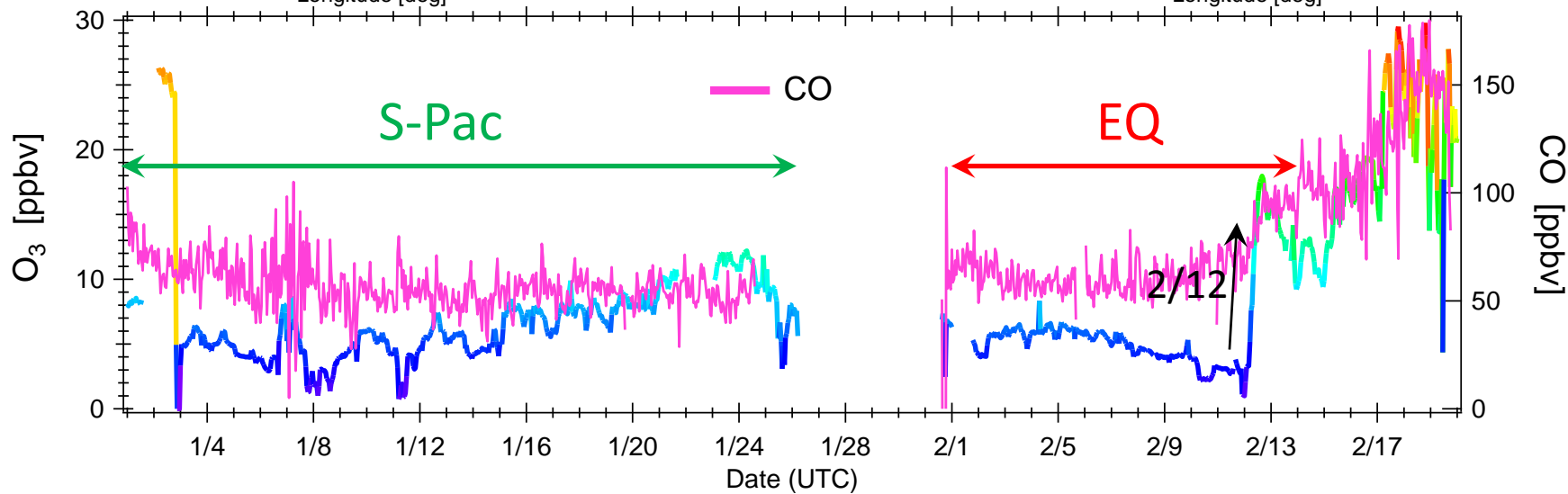
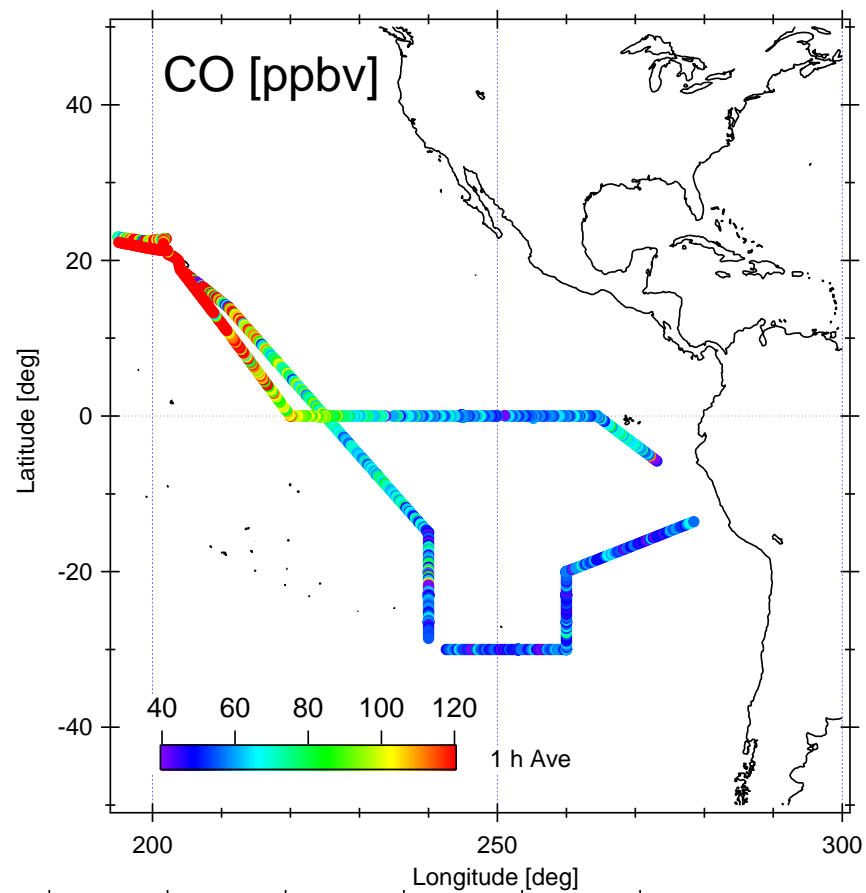
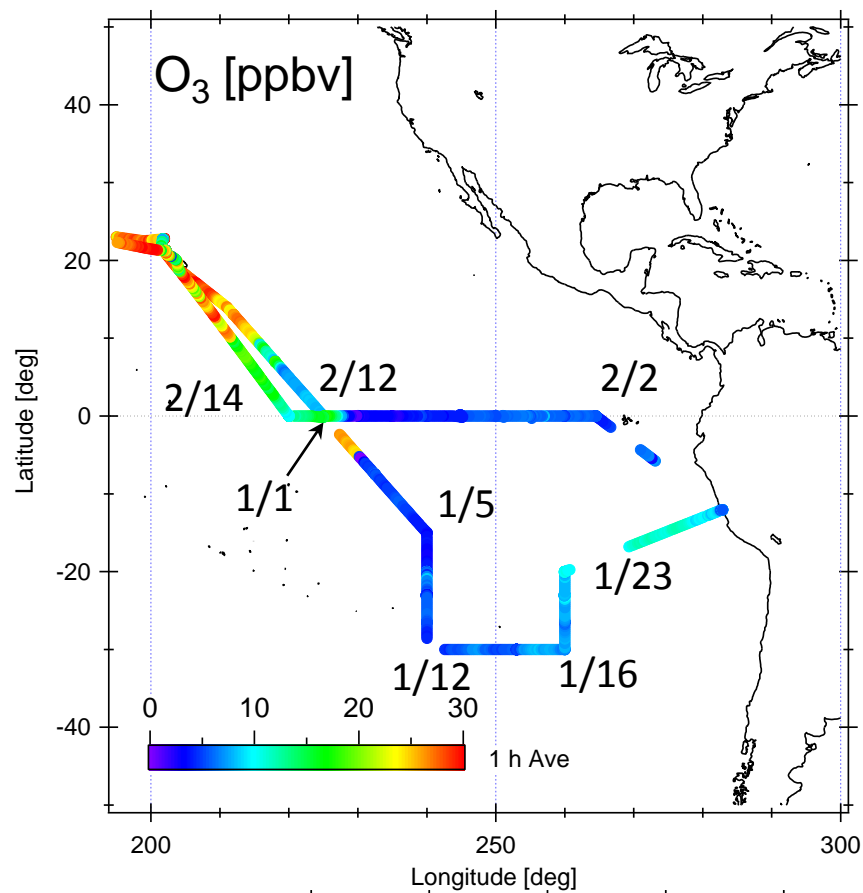


Free Troposphere Origin



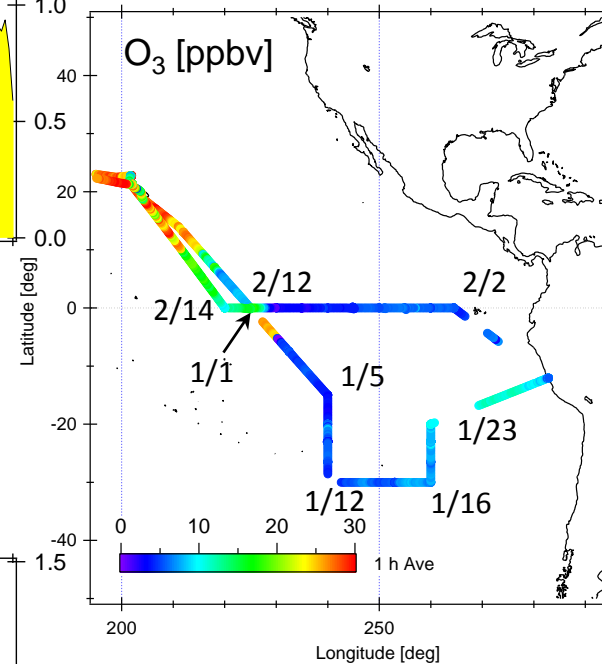
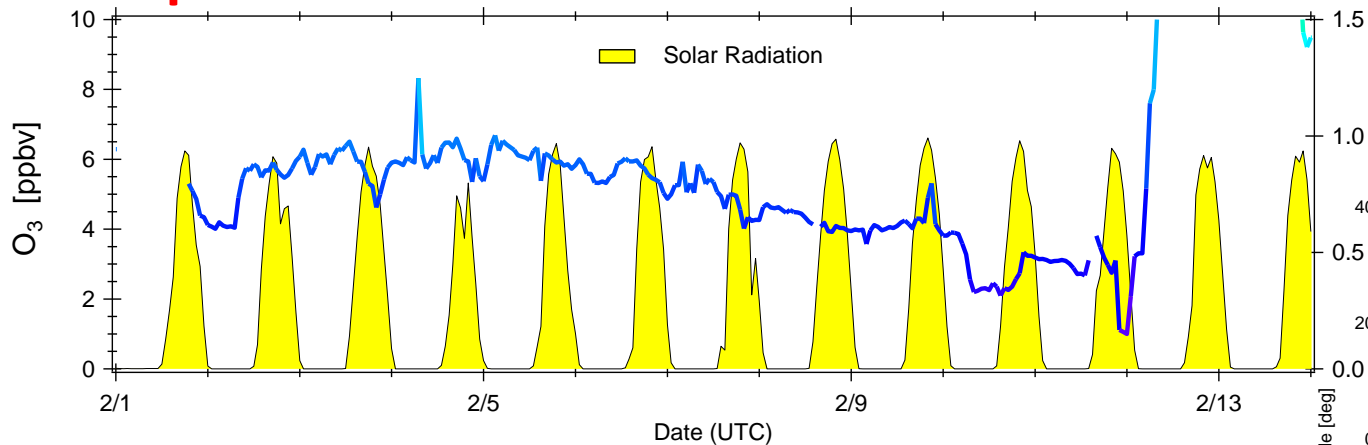




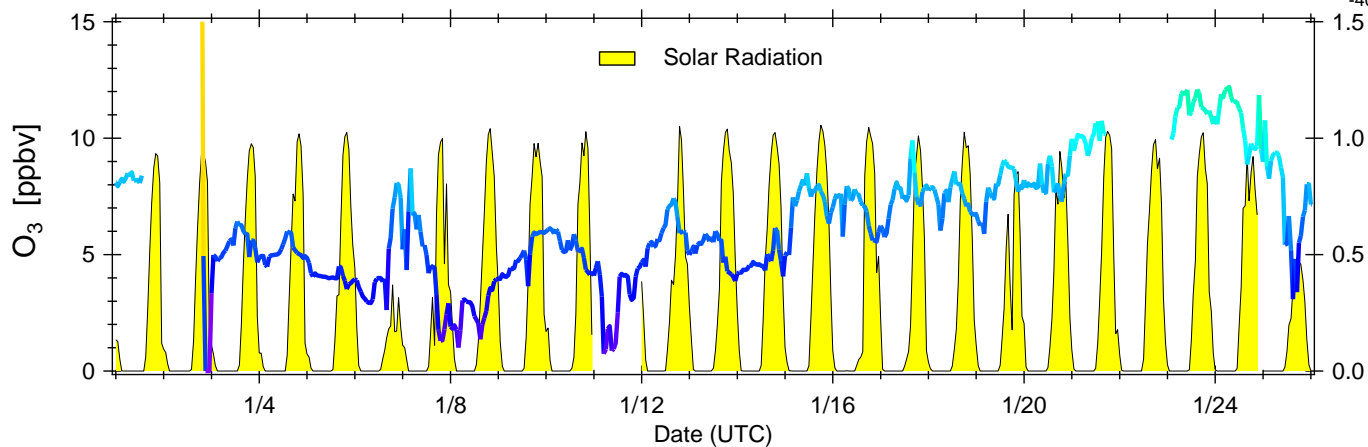


Diurnal Variation of O₃

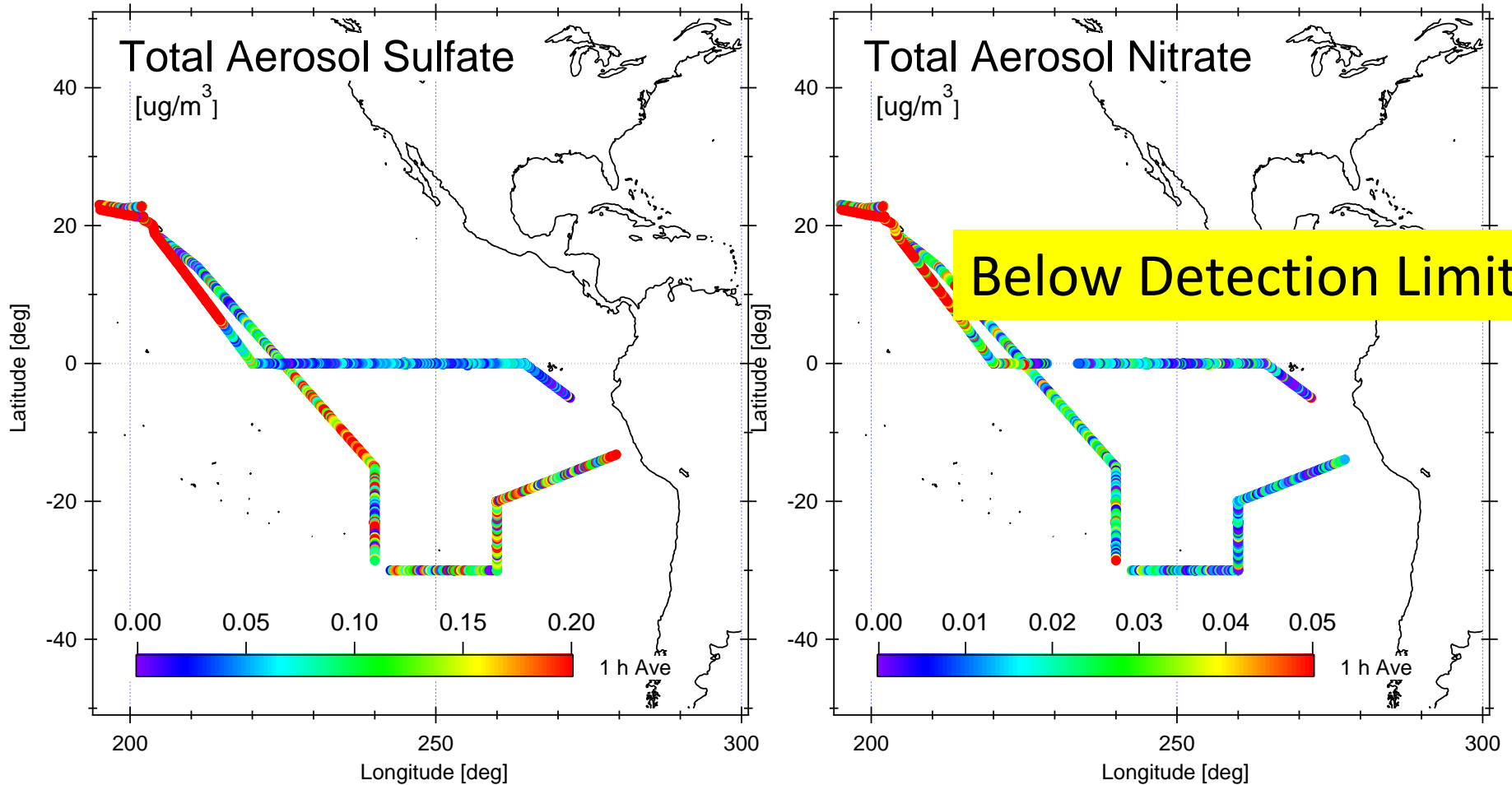
Equator



S-Pacific Ocean



Measured with Particulate Sulfate and Nitrate Monitor (R&P)



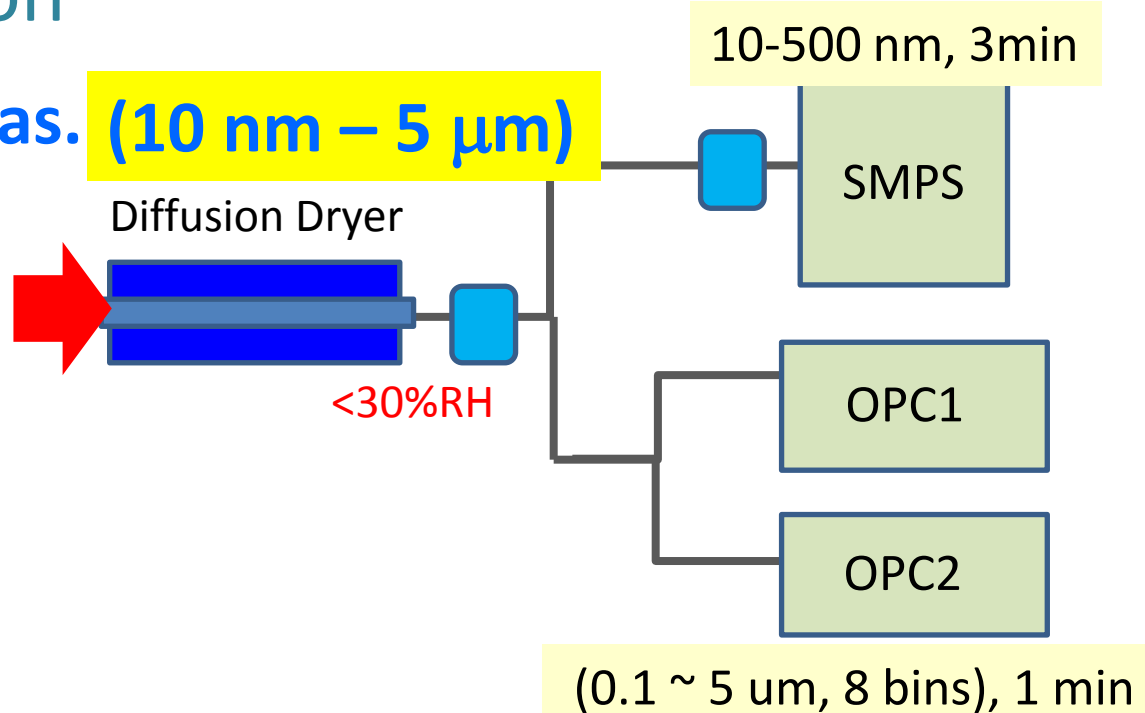
Filter samples (daily) will provide accurate MSA, nss-SO_4^{2-} , NO_3^- concentrations (coming soon..)

Aerosol Size Distribution

Small Ion (+/-) Counting
TEM Sample Collection

Miura Group
(Tokyo Univ of Sci)

(1) Size Distribution Meas. (10 nm – 5 μm)



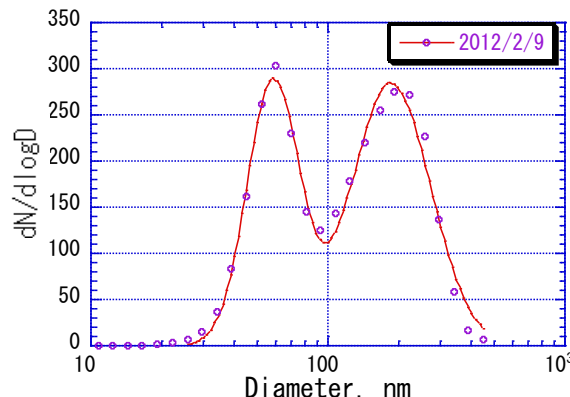
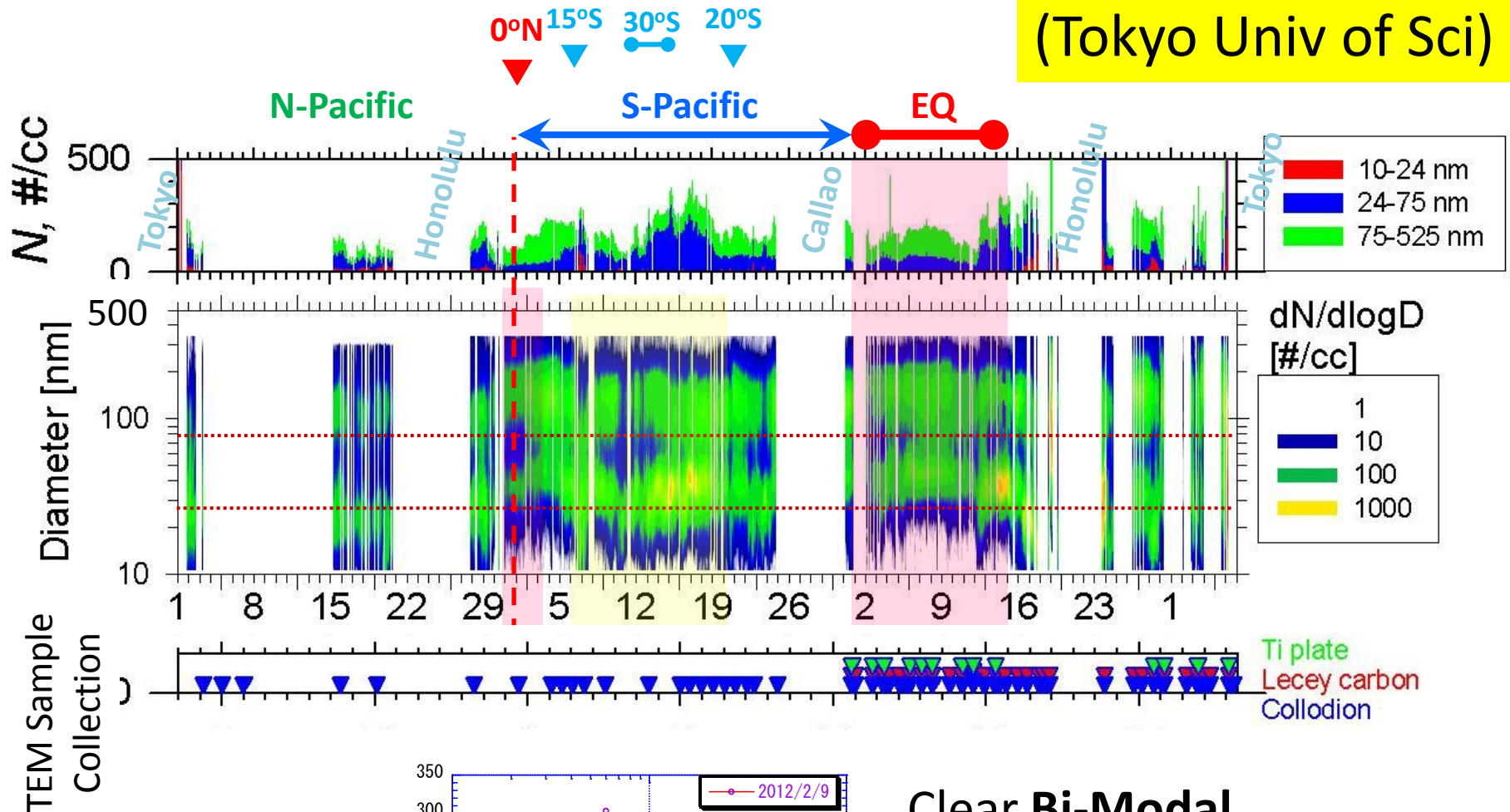
(2) Ion Counting

Gerden type ion counter (+/-), 4 min

(3) TEM Sample for Individual Analysis

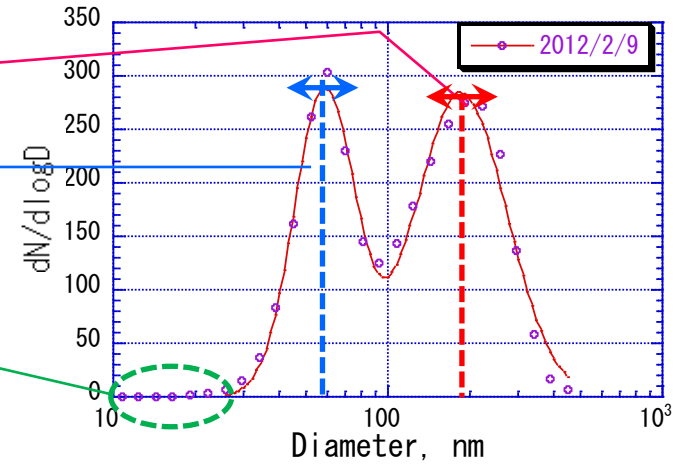
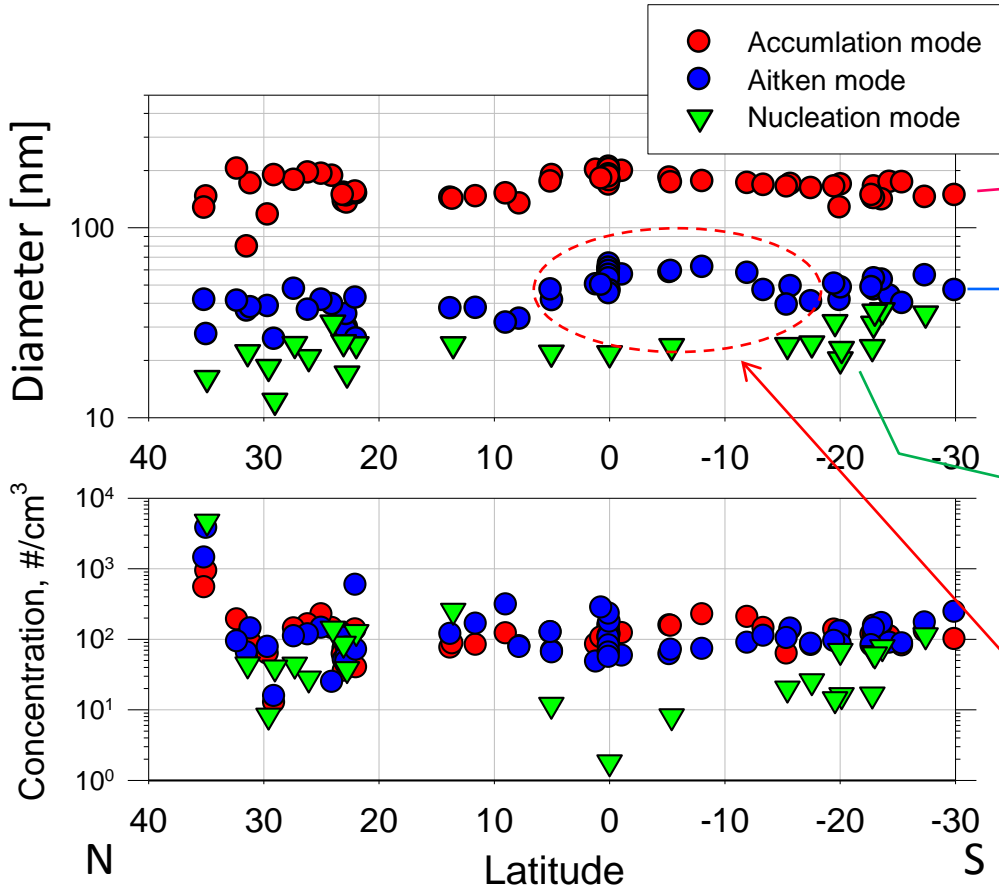
Collection with impactor, 1~3 per day

Miura Group (Tokyo Univ of Sci)



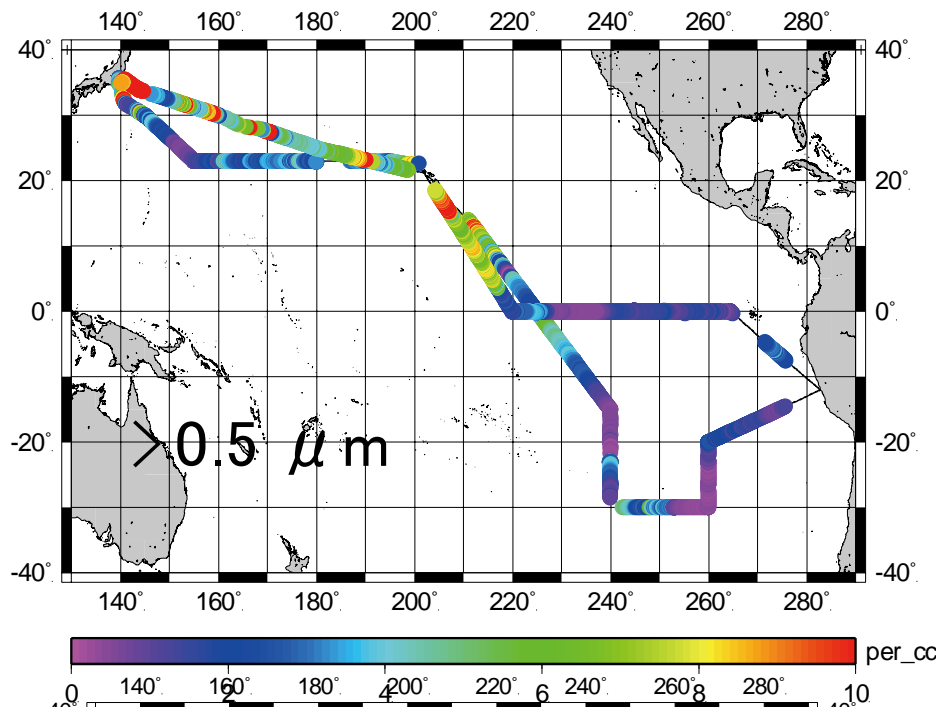
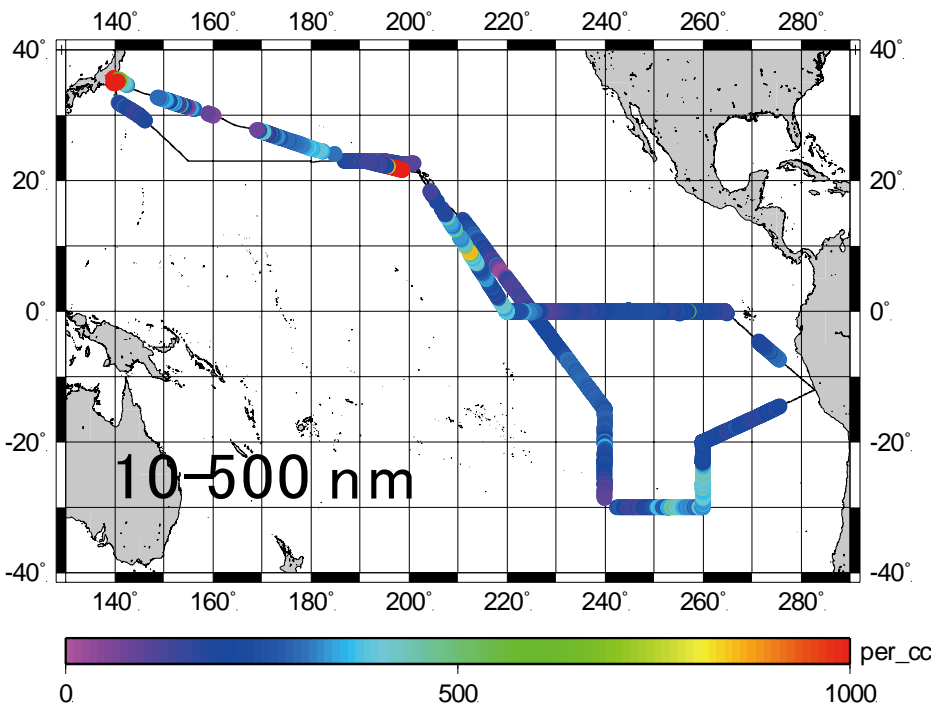
**Clear Bi-Modal
Size Distribution
In EQ and S-Pacific
=> Indication of Cloud
Processed Aerosols**

Miura Group (Tokyo Univ. of Sic.)

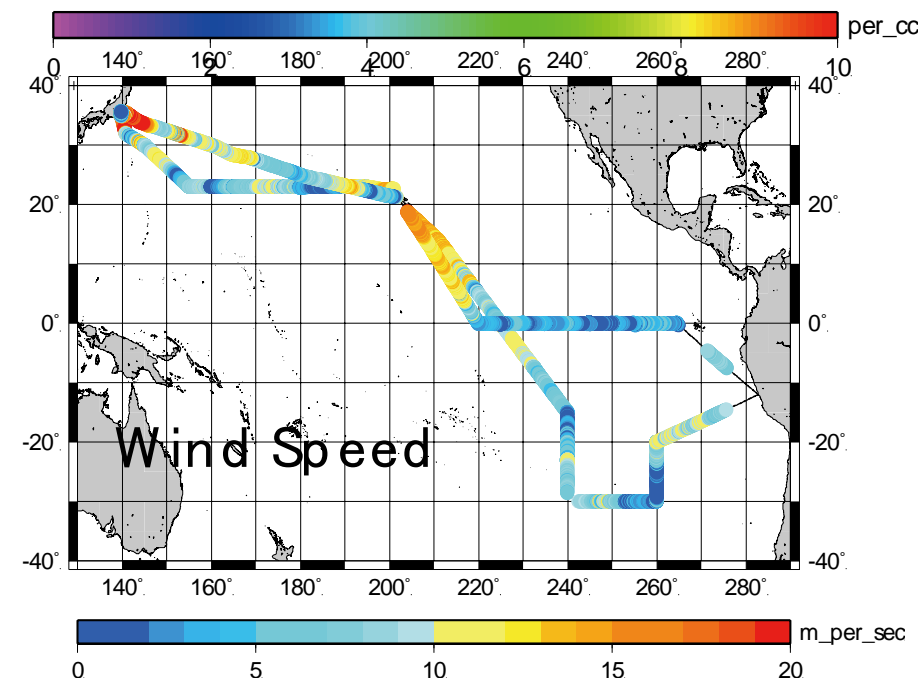


● Aitken mode diameters is large in 0° ~ -15°S

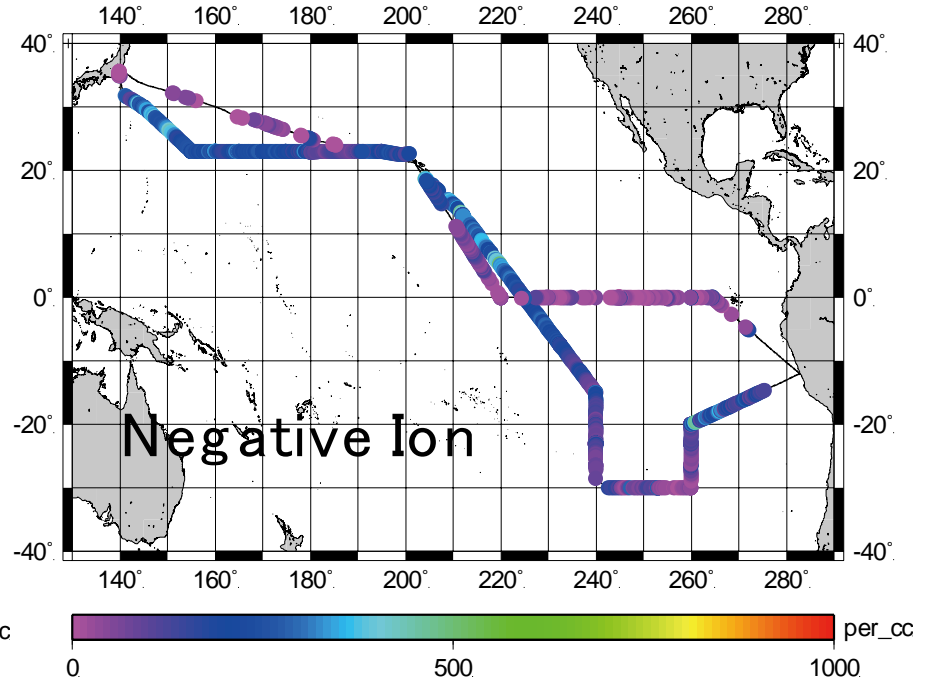
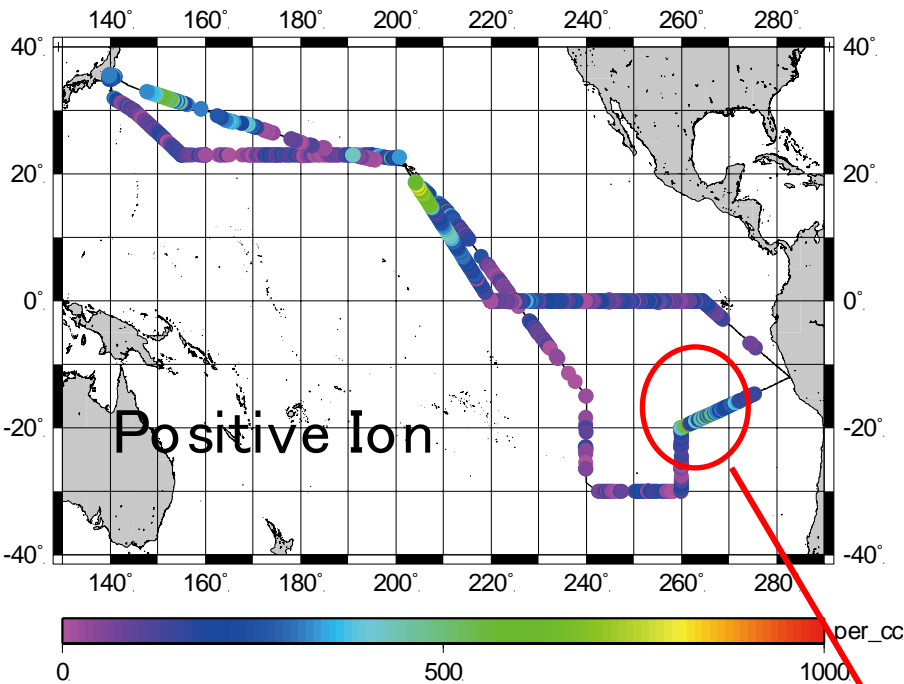
Horizontal distribution of aerosol concentration



Miura Group
(Tokyo Univ. of Sic.)



Positive & Negative Ion concentrations



High concentration

Ion relate with concentration of nucleation mode aerosols?

Miura Group
(Tokyo Univ. of Sic.)

Other Aerosol Data Coming Soon...

Category	Type	Instrument	Time Resolution	Note	Target
Aerosol	Size distribution	OPC(KC01D)	3 min	0.5-5 μm , 5 size bin	
		OPC(KC18)		0.3-0.5 μm , 5 size bin	
		SMPS3034		10-487 nm, 54 size bin	
	Chemical composition	Filter Sampler 1	12 hour	whole size	Ionic Spcies MSA Trace Metals Phosphorus (Org-P and Inorg-P)
		Filter Sampler 2	1 day	2 size fraction	
		Filter Sampler 3	3 day	($d < 2.5 \mu\text{m}$, $2.5 \mu\text{m} < d$)	
		Cacade Filter Impactor	6 or 12 days	0.06-12 μm , 12 size bin	
		Sampling by PILS	12 or 24 hours	Aerosol samples in liquids	
	Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS)	Real-time	Single particle size-resolved mass spectrometry, $d = 100 \text{ nm} \sim 3 \mu\text{m}$	Org-N, Metals, Phosphorus, Oxy-Organics, Dust etc	
	TEM Single Particle Observation	1-3 per day		Morphology, Elemental Composition	
Mass concentration	EC/OC analyzer	2 - 33hours	PM2.5		
	Nitrate Monitor	10 min			
	Sulfate Monitor	1 hour			
Number concentration	Water-CPC	1 sec	Total concentradtion for $d > 5 \text{ nm}$	CCN Activity	
	CCN Counter	1 hour	SS = 0.1, 0.2, 0.3, 0.4, 0.6 (%)		
	Small Ion Concentration	4 min			

Omori and Tanimoto
(NIES)

EqPOS

Yuko Omori and Hiroshi Tanimoto 
(National Institute for Environmental Studies)

Stratosphere (30 km)



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O₃, CO₂, H₂O
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Stratospheric
Air Sampling
(Alt = 19-30 Km)

Atmospheric Aerosols
(Size Dist., CCN, Comp., Morphology)

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Bubble Bursting

Surface
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Non-living
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Phytoplankton

Bacteria

N-Fixation

Incubation
Exp.

Zooplankton

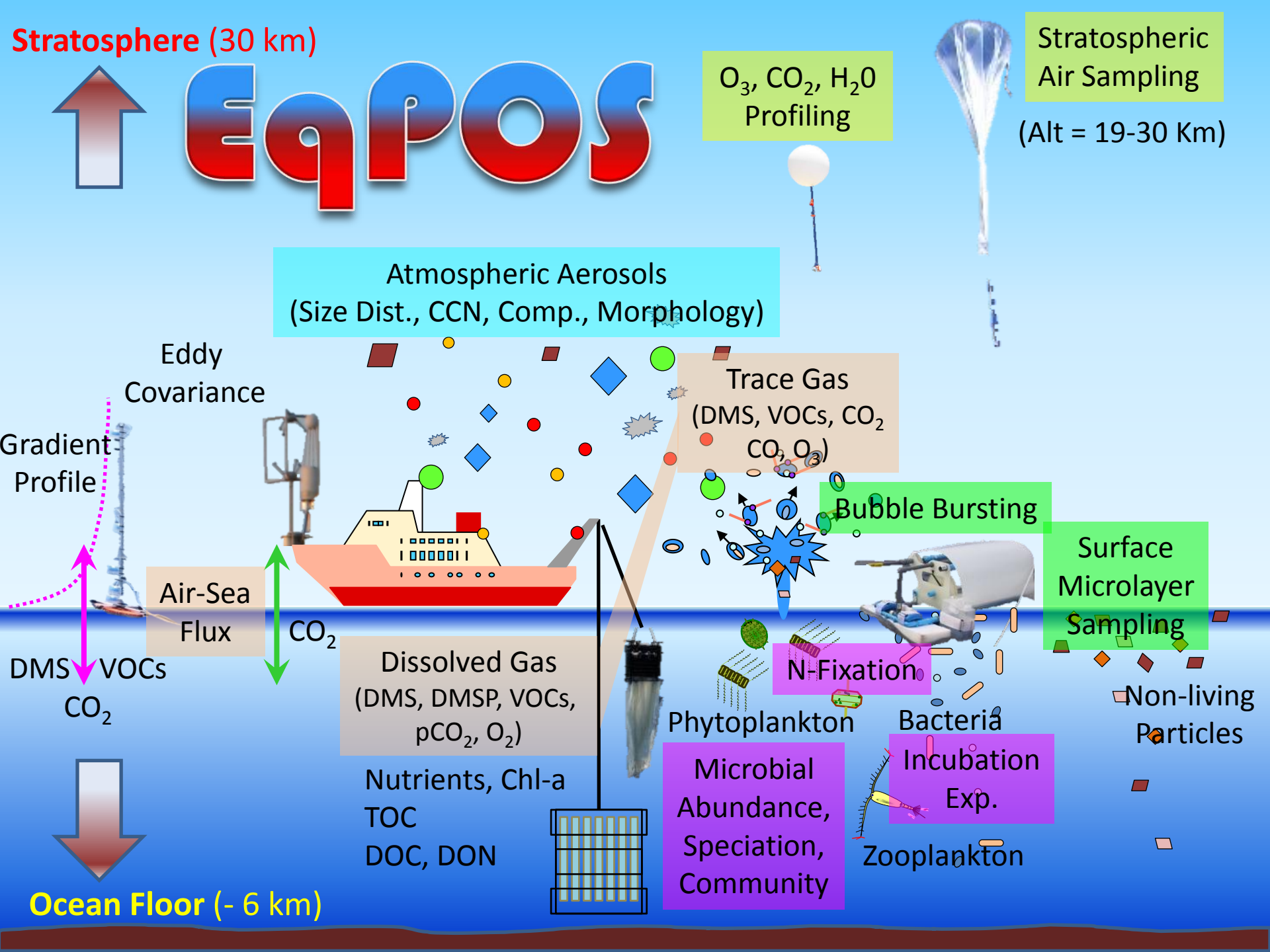
Microbial
Abundance,
Speciation,
Community

Nutrients, Chl-a
TOC
DOC, DON

DMS VOCs
CO₂



Ocean Floor (- 6 km)

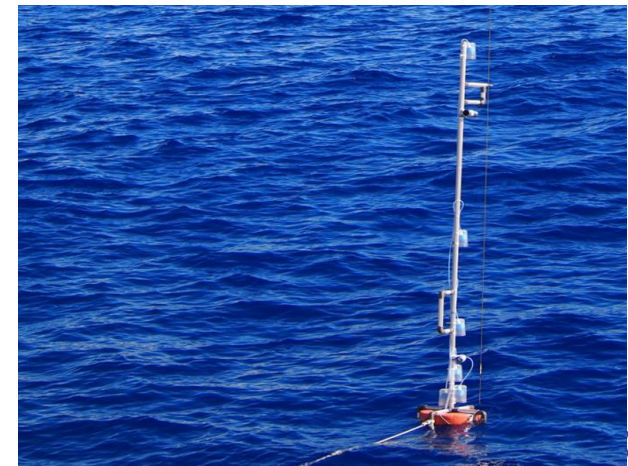
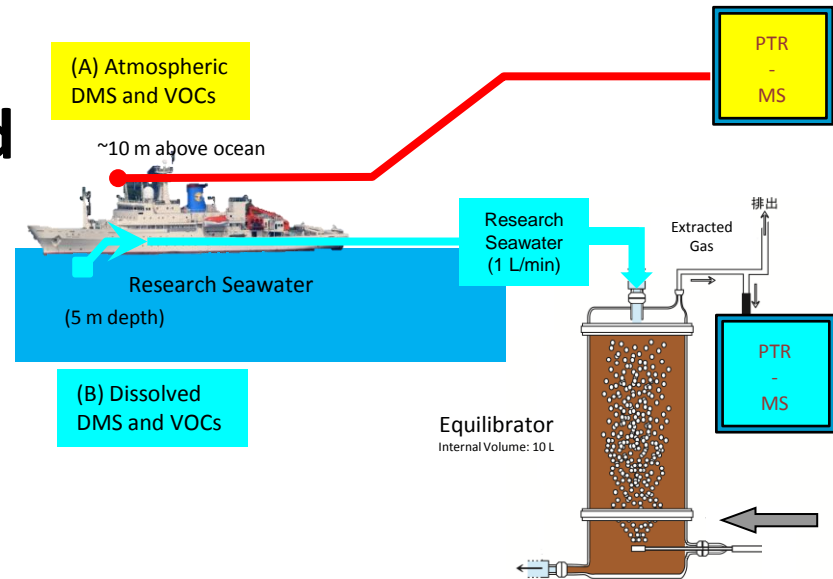


Subjects (NIES)

Omori and Tanimoto
(NIES)

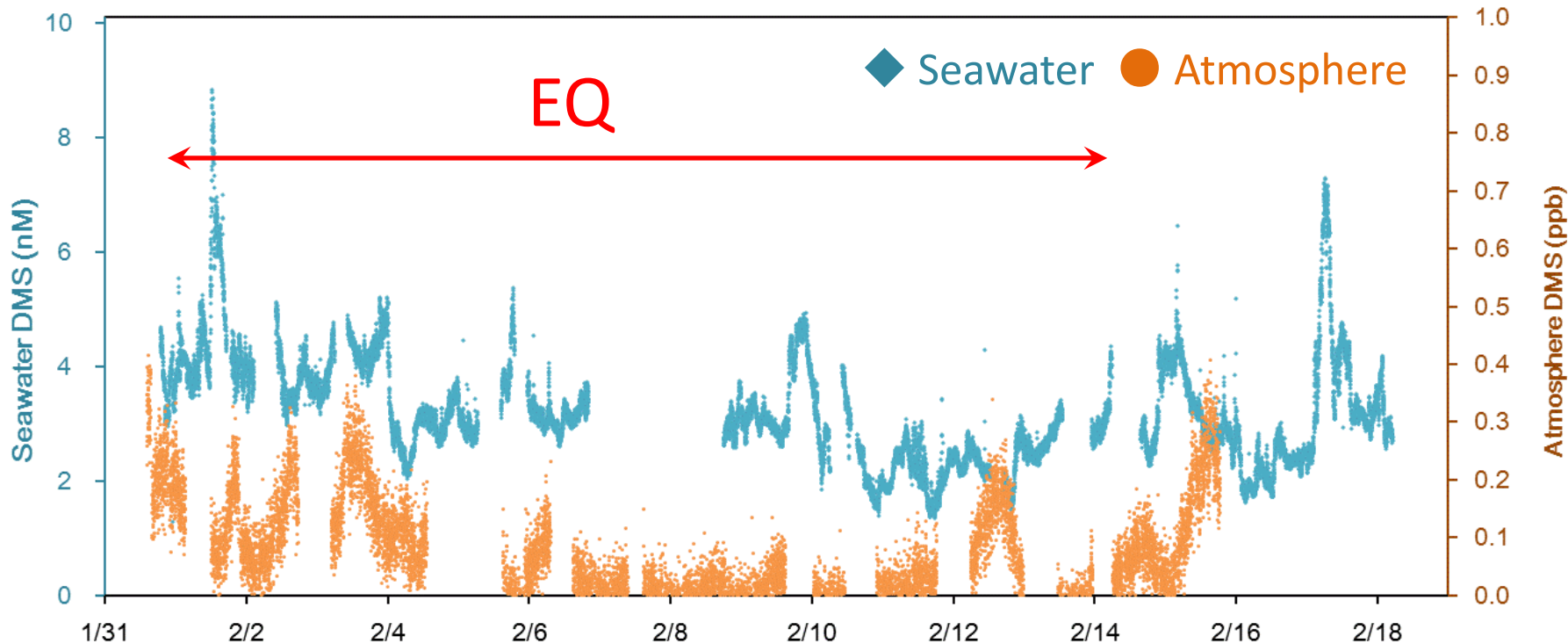
1. Underway measurement for DMS and other VOC dissolved in surface seawater with equilibrator-inlet-PTR-MS (EI-PTR-MS)

2. DMS and other VOC flux measurement with “profiling buoy” system



DMS distribution

Omori and Tanimoto
(NIES)



DMS concentration	Seawater (nM)	Atmosphere (ppb)
Min	1.3	0.00
Max	8.8	0.42
Ave (SD)	3.2 (1.0)	0.07(0.08)

5 sec int. for each gas
30 sec/per cycle
Detection limit ~0.02 nM

Comparison with previous observations

DMS (nM) (SD)	Min-Max	Area	Ref
3.4 (0.9)	1.4-10.1	10S-0N, 85-115W	this observation
3.1		0-5N, 80-140 W	Andrea & Raemdonck (1983)
2.0 (0.70)	0.6-4.2	15N-10S, 145-165 W	Bates et al.(1993)
2.4	1.7-3.3	5.6-5.7S, 107 W	Turner et al. (1996)
1.58 (0.6)		Equatorial upwelling	Marandino et al. (2007)
0.95 (0.40)		Gyre	Marandino et al. (2007)
1.88		5-20N, 140W	Andrea & Raemdonck (1983)
2.22	0.94-4.06	Sargasso Sea, 25N	Andrea & Barnard (1984)

高時間分解能でのDMS測定によって、これまで観測されてこなかったDMS濃度の局所的なピークを捉えることが出来たのかもしれない

Omori and Tanimoto
(NIES)

Calculation for sea-air DMS flux

$$\text{Flux} = k_{\text{DMS}} \times (\text{DMS}_{\text{seawater}} - \text{DMS}_{\text{Air}}) \doteq k_{\text{DMS}} \times (\text{DMS}_{\text{seawater}})$$

$$k_{\text{DMS}} = 0.31 \times U^2 \times (\text{Sc}_{\text{DMS}}/660)^{-0.5} \quad (\text{Wanninkhof et al. 1992})$$

$$\text{Sc}_{\text{DMS}} = 2674.0 - 147.12t + 3.726t^2 - 0.038t^3 \quad (\text{Saltzman et al. 1993})$$

DMS: DMS concentration

k_{DMS} : exchange velocity of DMS

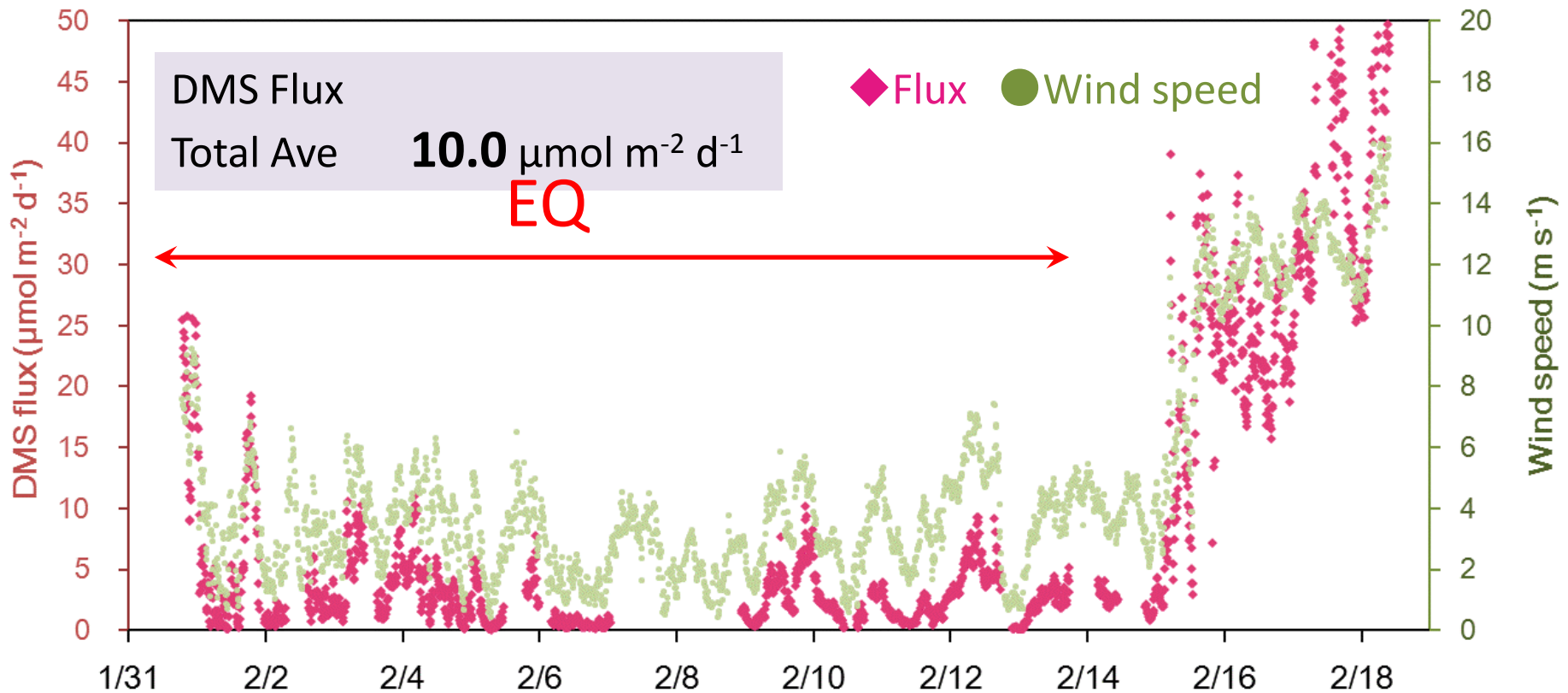
Sc_{DMS} : schmidt number of DMS

t: seawater temperature ($^{\circ}\text{C}$)

U: wind speed (m s^{-1})

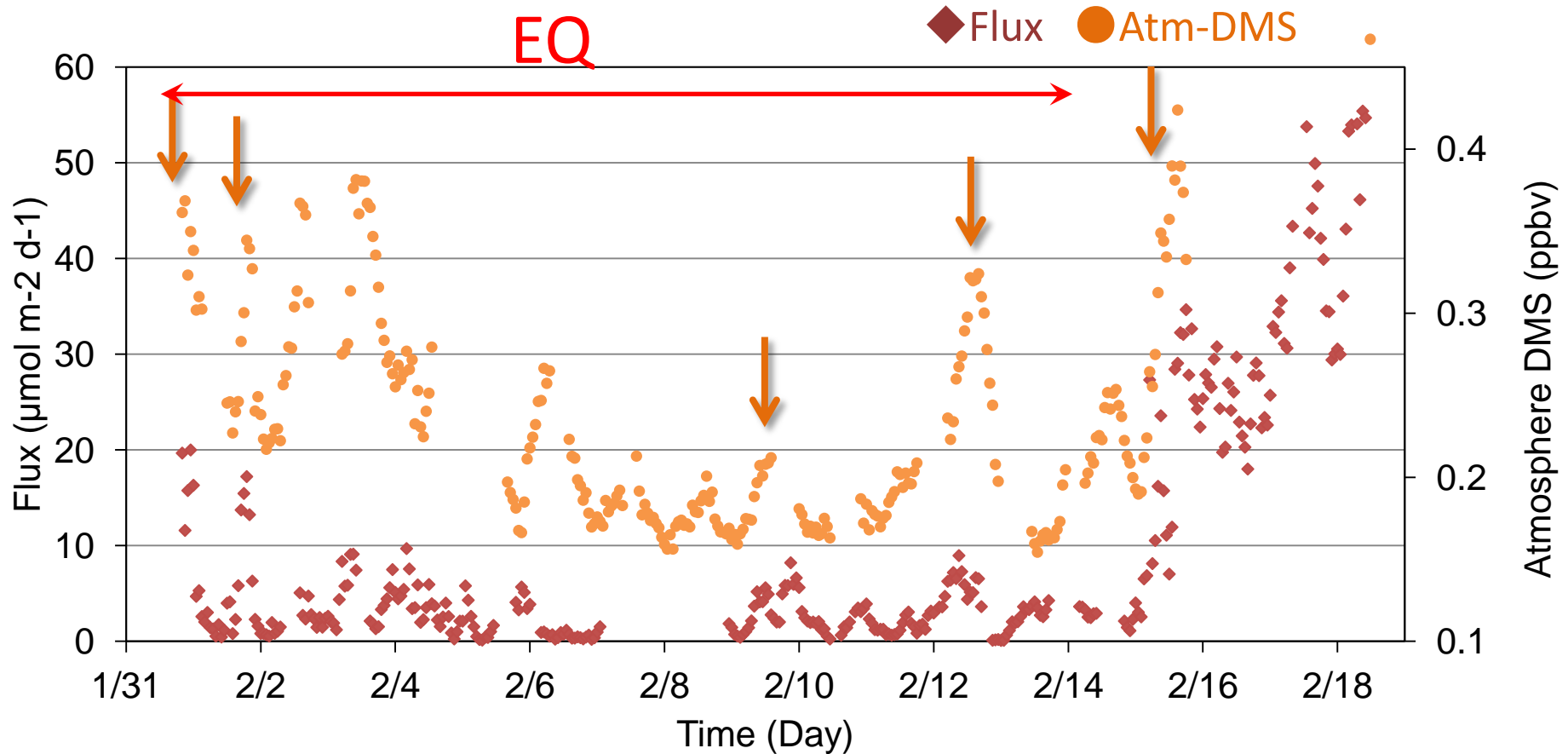
Omori and Tanimoto
(NIES)

DMS flux and wind speed



Omori and Tanimoto
(NIES)

DMS Flux vs. Atm-DMS



フラックスが大きい → 大気DMS濃度が増加する傾向を確認

今後、フラックスバイ観測との整合性を確認・エアロゾルなどのデータとも比較し、大気中の粒子形成とDMSの関係をみていきたい

2. “Profiling Buoy” observation

Subject of profiling buoy observation

- Measurement of flux from of DMS and other VOC profiles
- Gas exchange velocity estimation

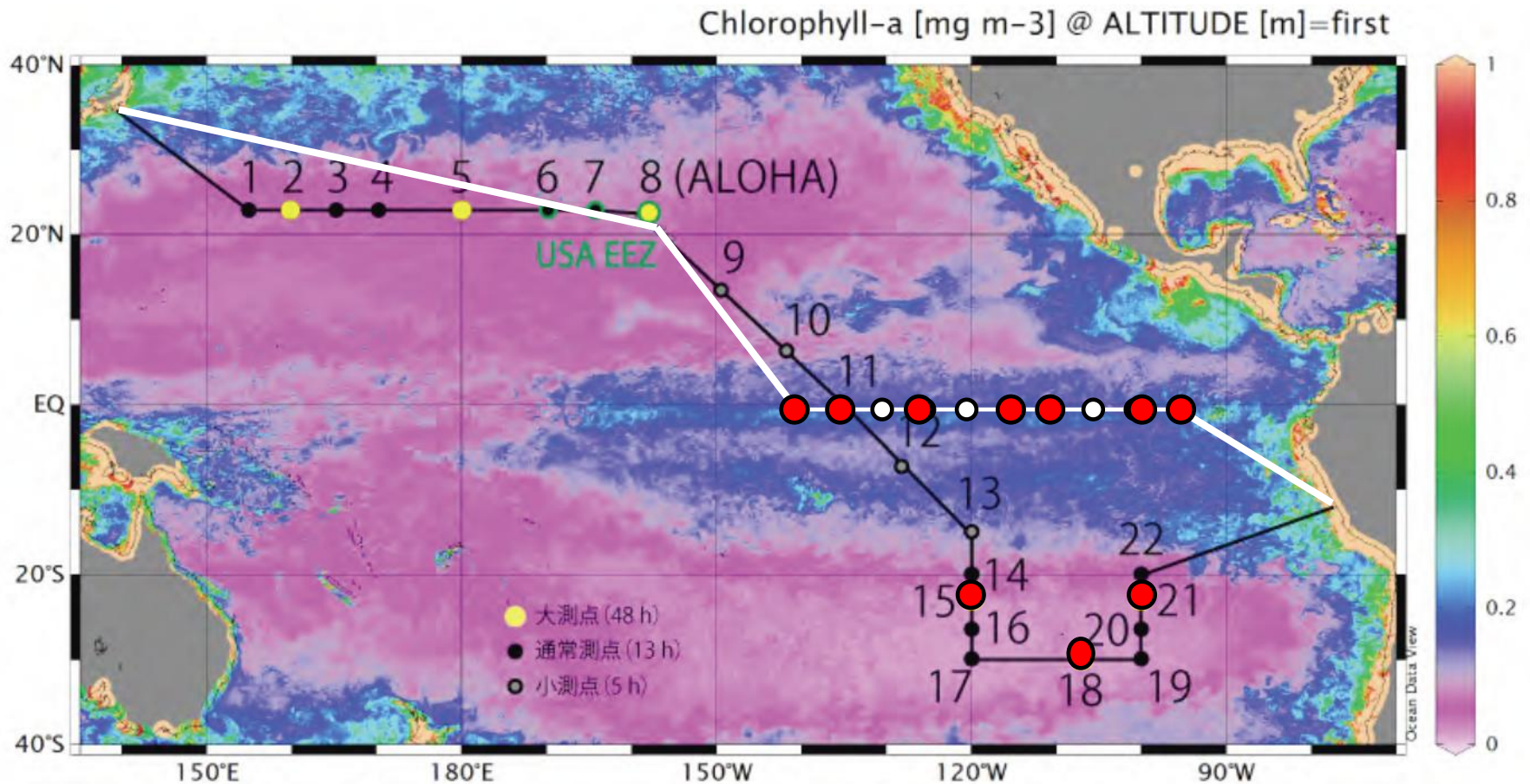
Omori and Tanimoto
(NIES)

PTR-MS
(DMS, acetone)



Location of Flux Buoy Measurement

(● Flux Buoy)

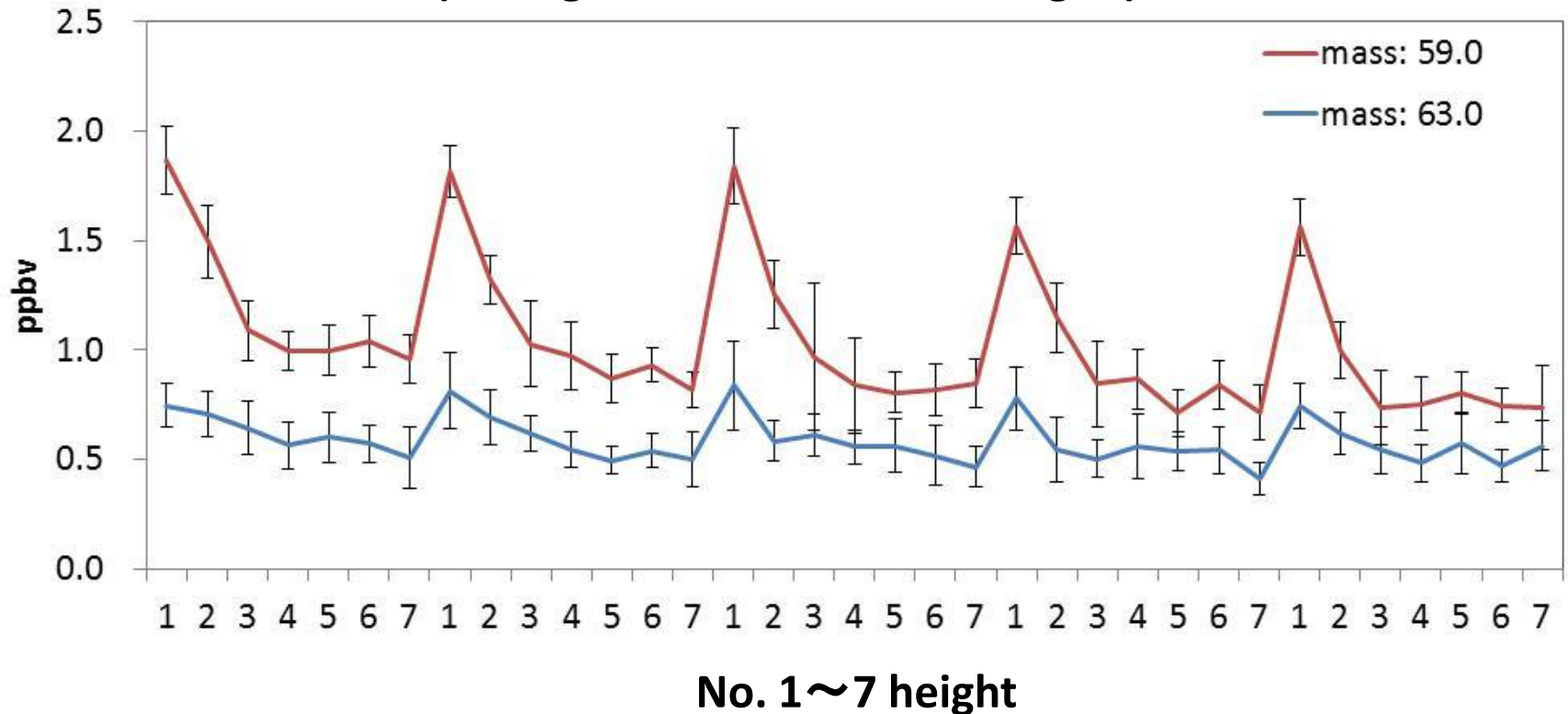


DMS and acetone concentration

Each height from sea surface : 1.2, 5.0, 20, 53, 120, 258, 1400 (upper deck) cm

DMS(m/z = 63), Acetone(m/z = 59) (ppbv)

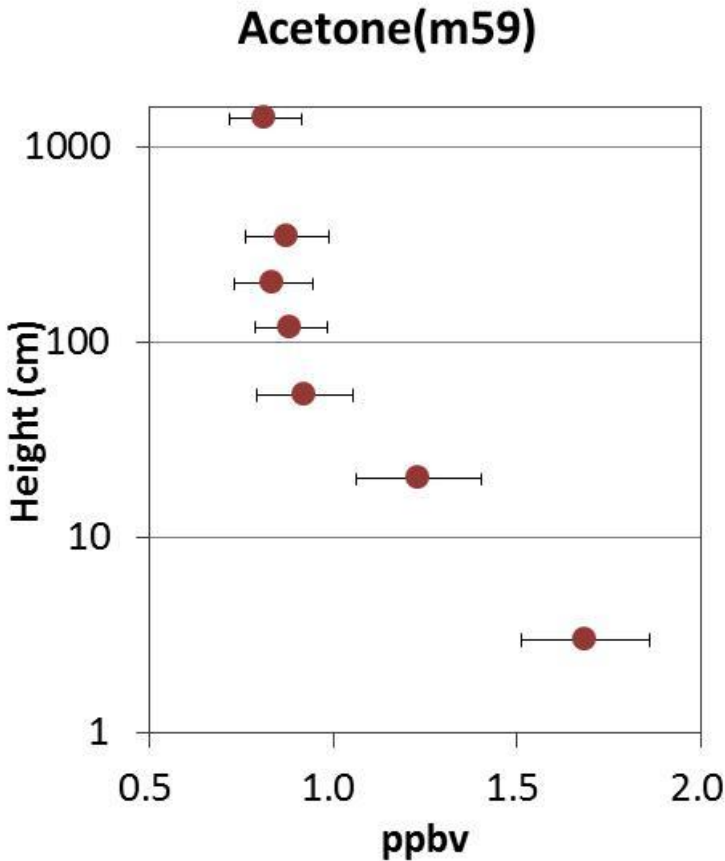
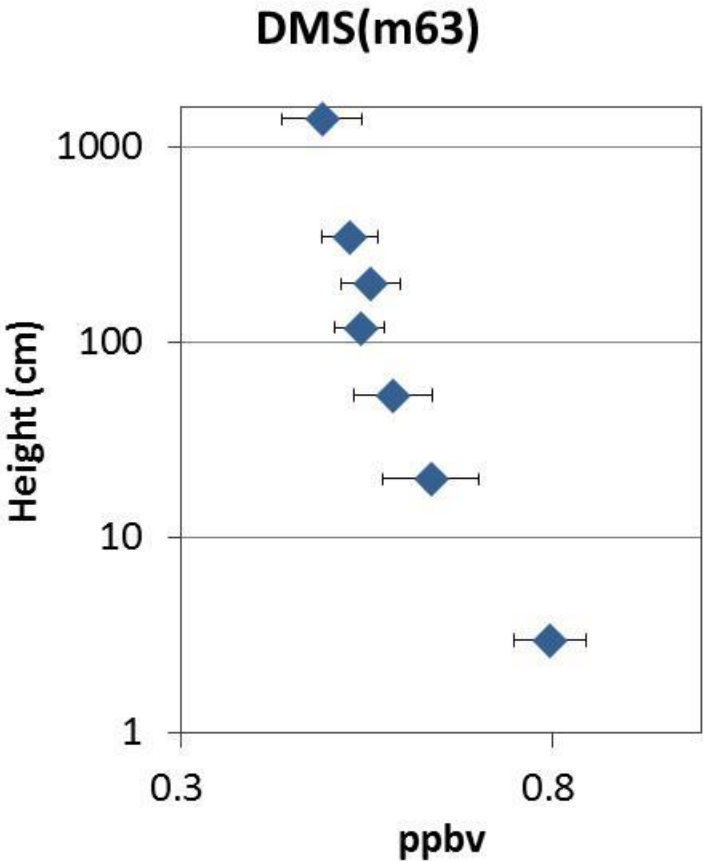
(average for 30 sec at each height)



Profiles of DMS and acetone

Omori and Tanimoto
(NIES)

Average of 5 profiles (\pm SD)



Future Work

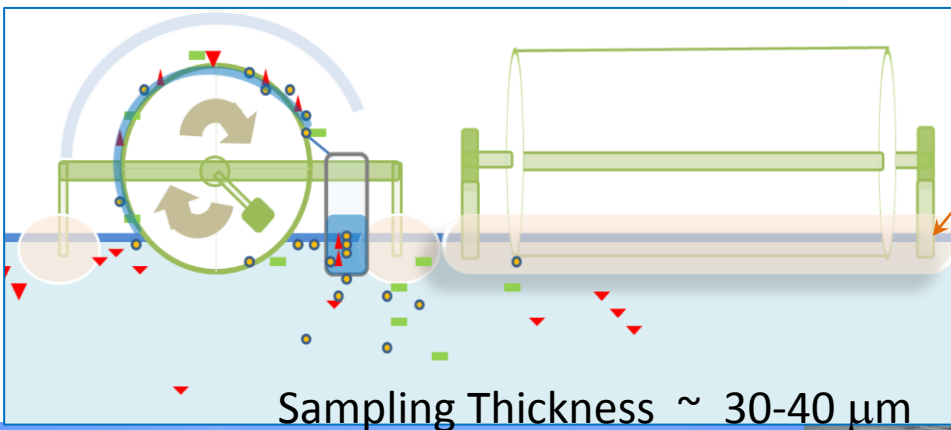
- Comparison of flux observed by “flux buoy” and estimated from DMS air/sea concentrations.
 - =>Factor controlling DMS flux
- Relationship with microorganisms and DMS concentration
 - => Microbial structure/functional gene vs. DMS concentration.
- Relationship with Atmospheric Aerosols

Characterization of Sea Surface Microlayer

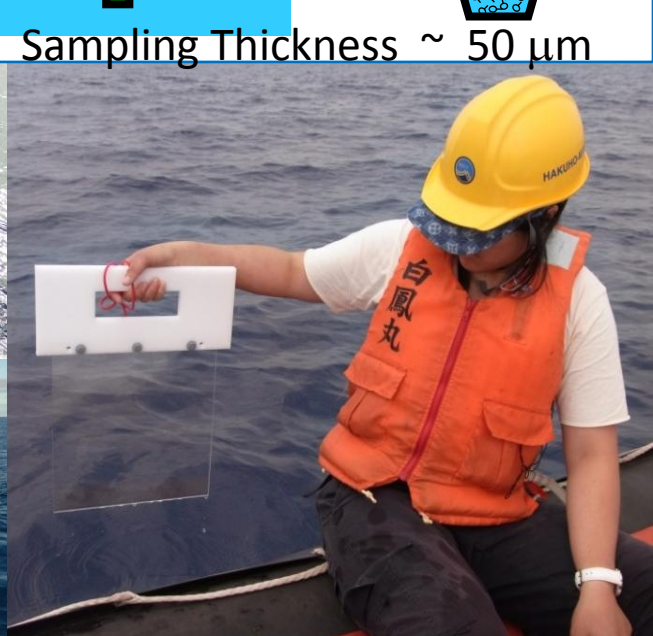
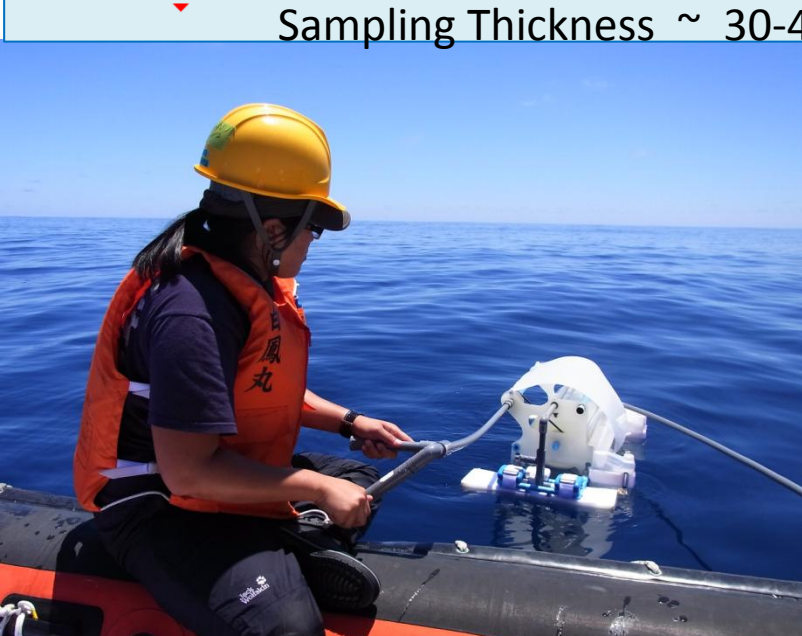
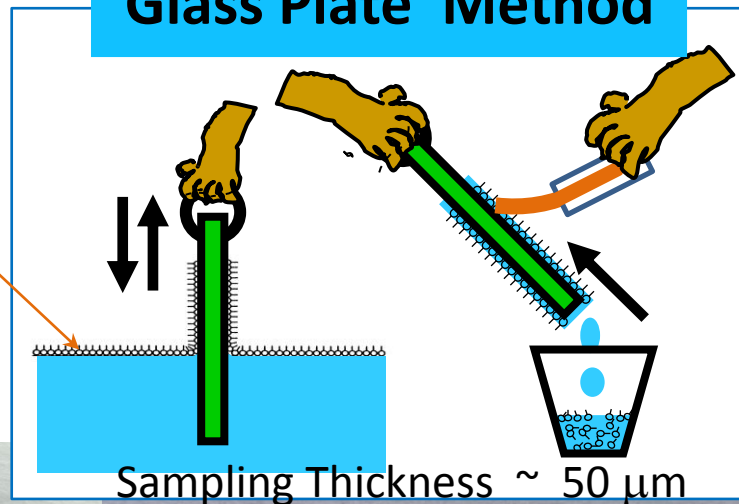
Sea-Surface Microlayer (SML) Sampling

Top thin layer of ocean surface (air-liquid interface)

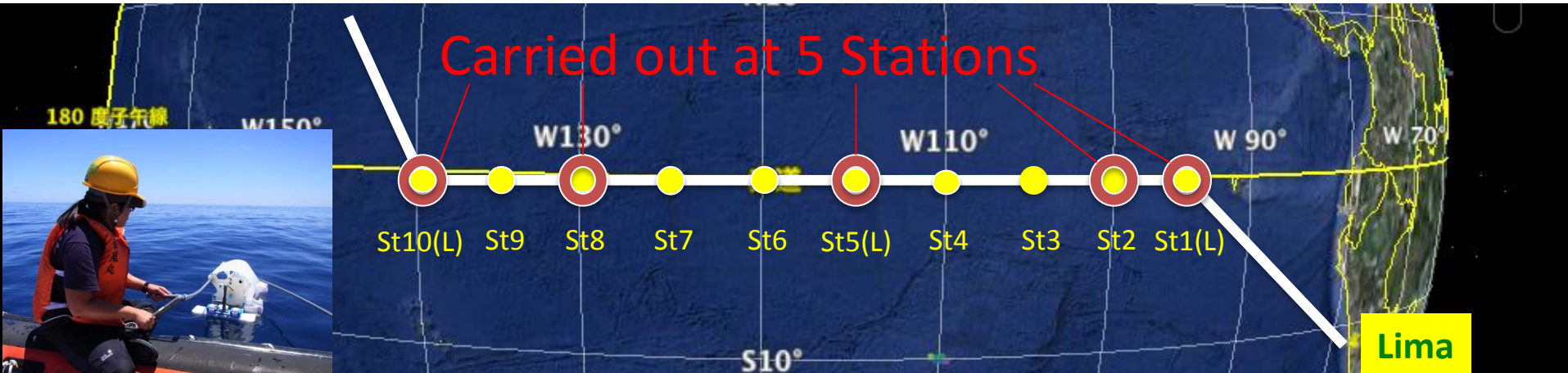
Rotating Drum Method



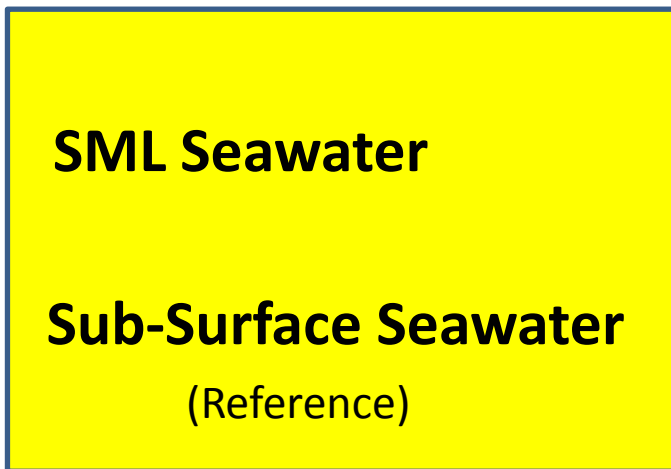
Glass Plate Method



Sea-Surface Microlayer (SML) Sampling



Further Analysis



Chemical Analysis

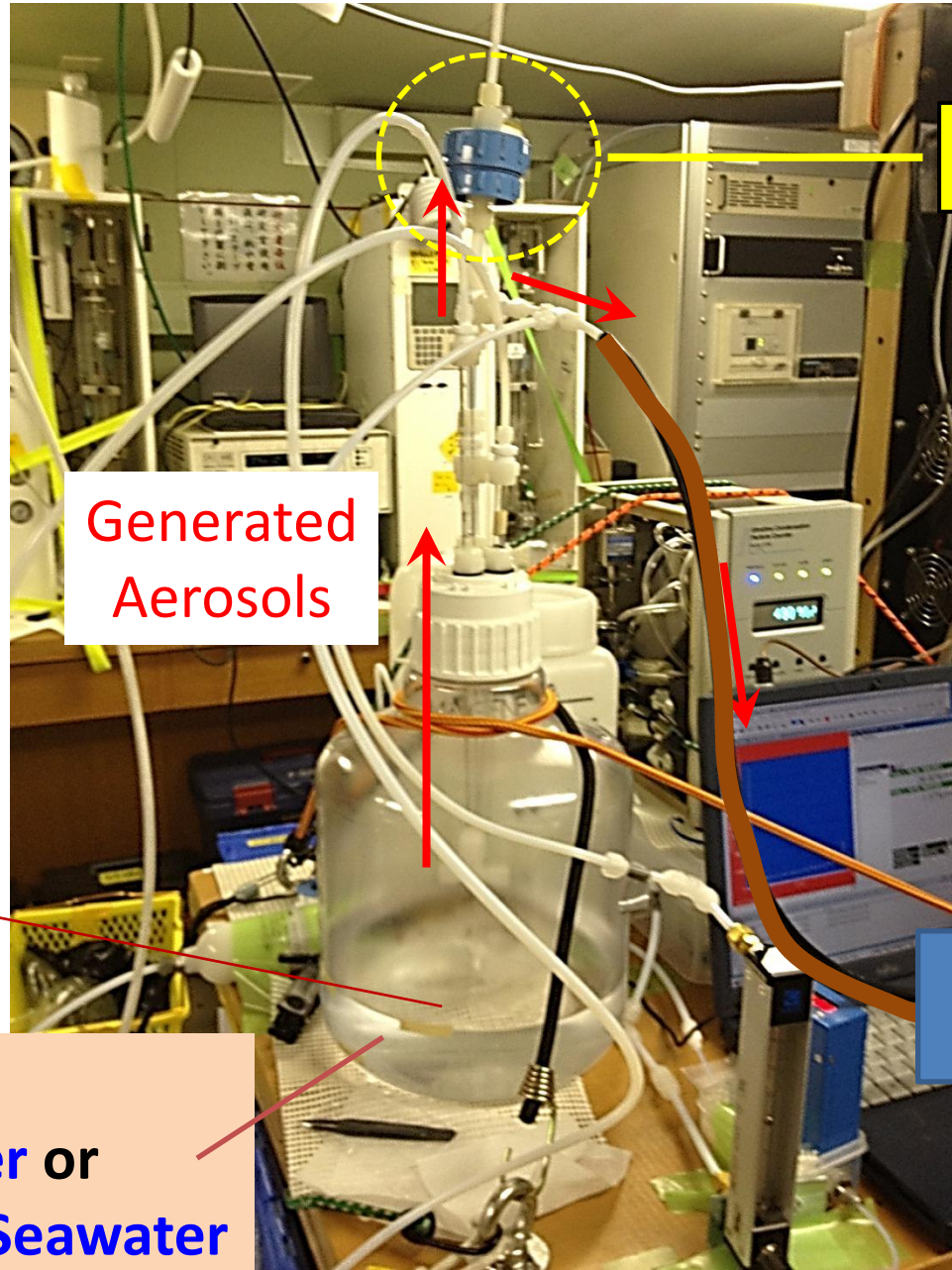
- **Phosphorus**
 - Total
 - Particulate vs. Dissolved
 - Organic vs. Inorganic
- Trace Metals
- Ionic Species

Generated Aerosols

Laboratory
Air Bubble Bursting



Laboratory Bubble Bursting Aerosol Generation Exp.



Teflon Filter Pack

Further Off-Line Analysis

- ⇒ Total Phosphorus
- ⇒ Water Soluble Phosphorus
- ⇒ Total Organic Carbon?
- ⇒ Trace Metals?
- ⇒ Ionic Species

On-Line Analysis

ATOFMS

~0.1 L/min

Silica Gel
Diffusion
Dryer

Pump

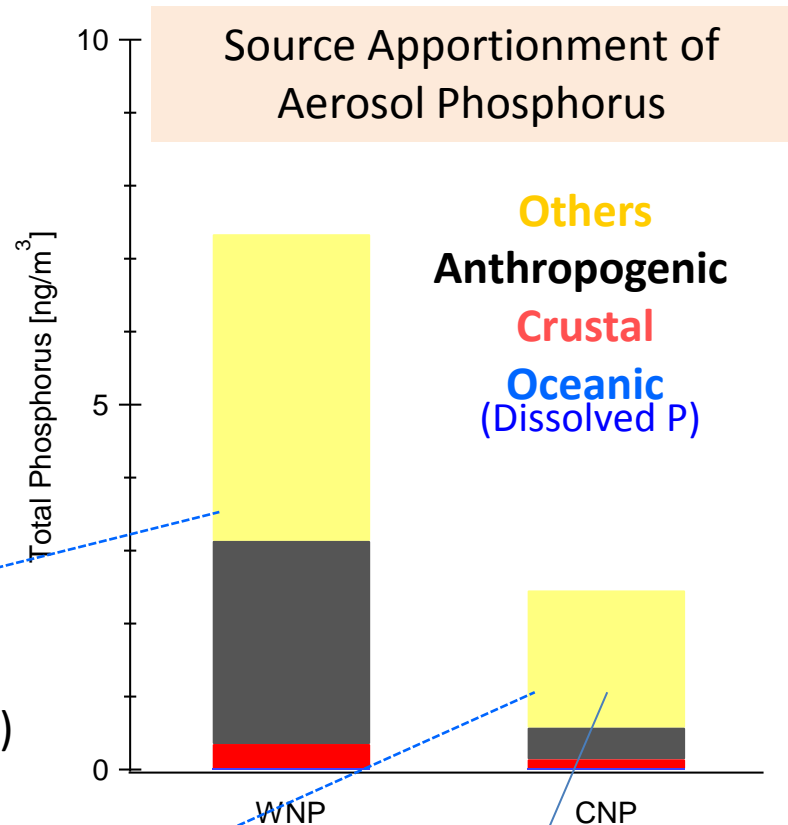
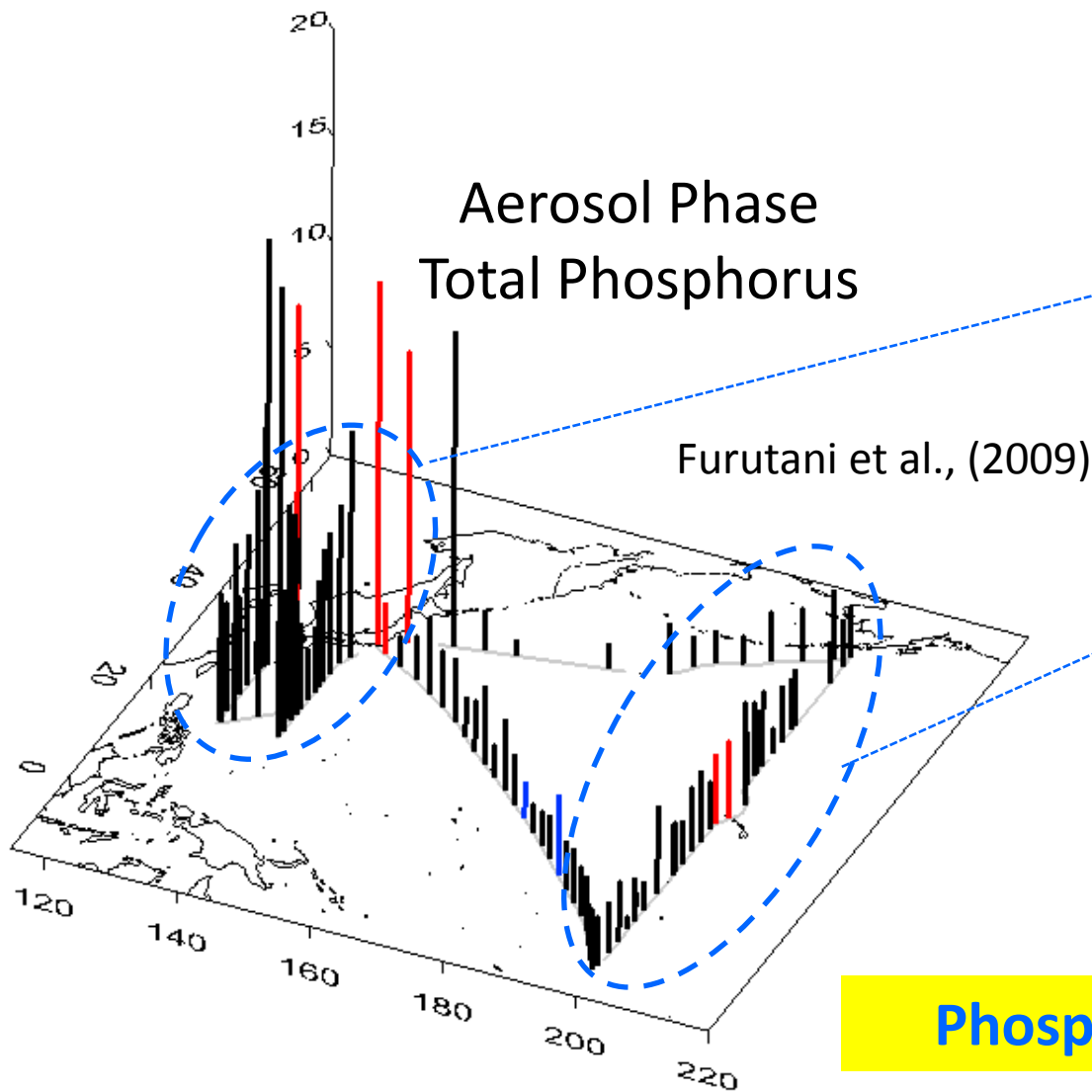
**Generated
Aerosols**

Bubbling Head



Sample:
SML Seawater or
Sub-Surface Seawater

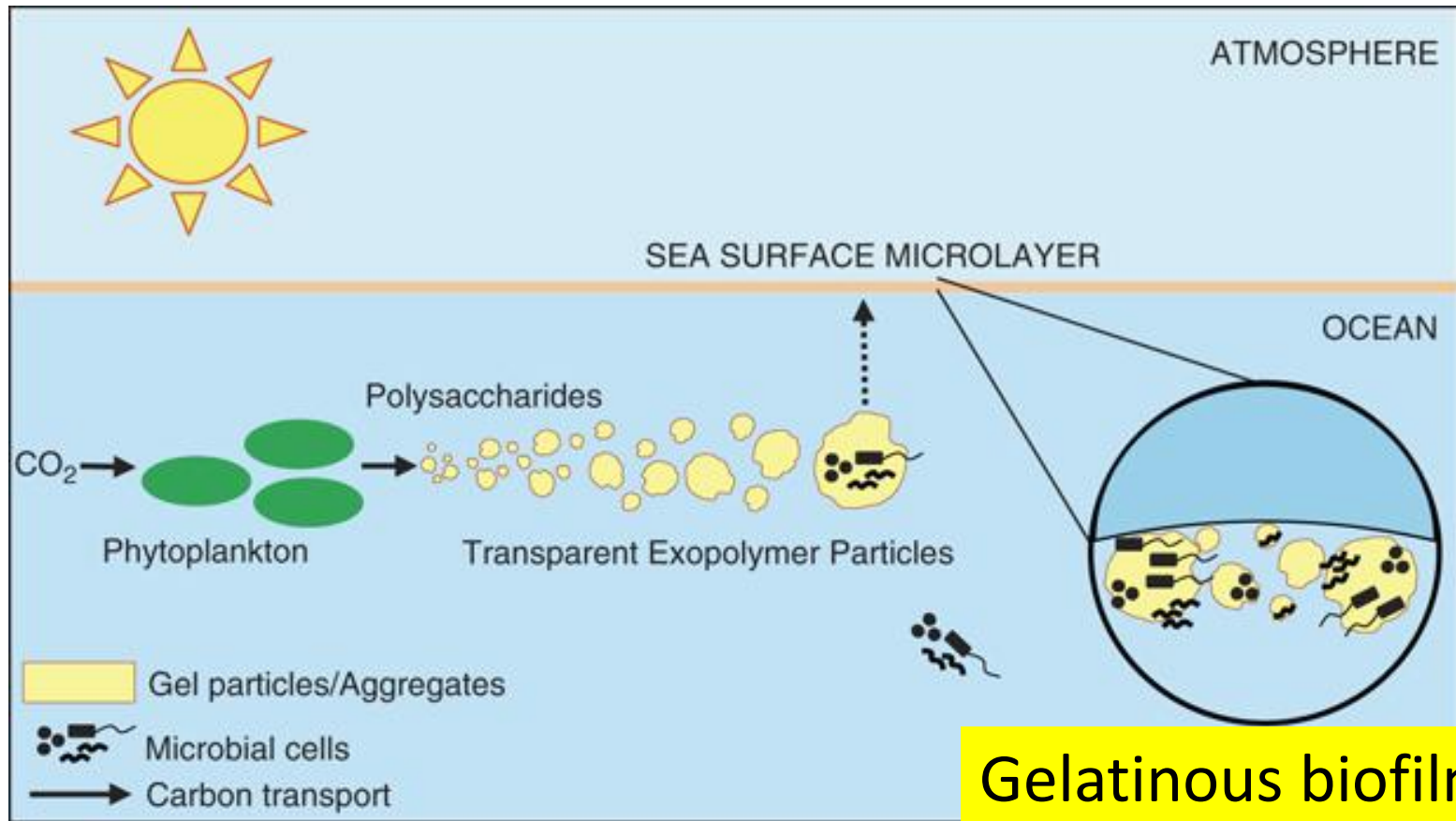
Missing Source of Atmospheric P in open ocean



Unaccounted source other than *dissolved oceanic P*

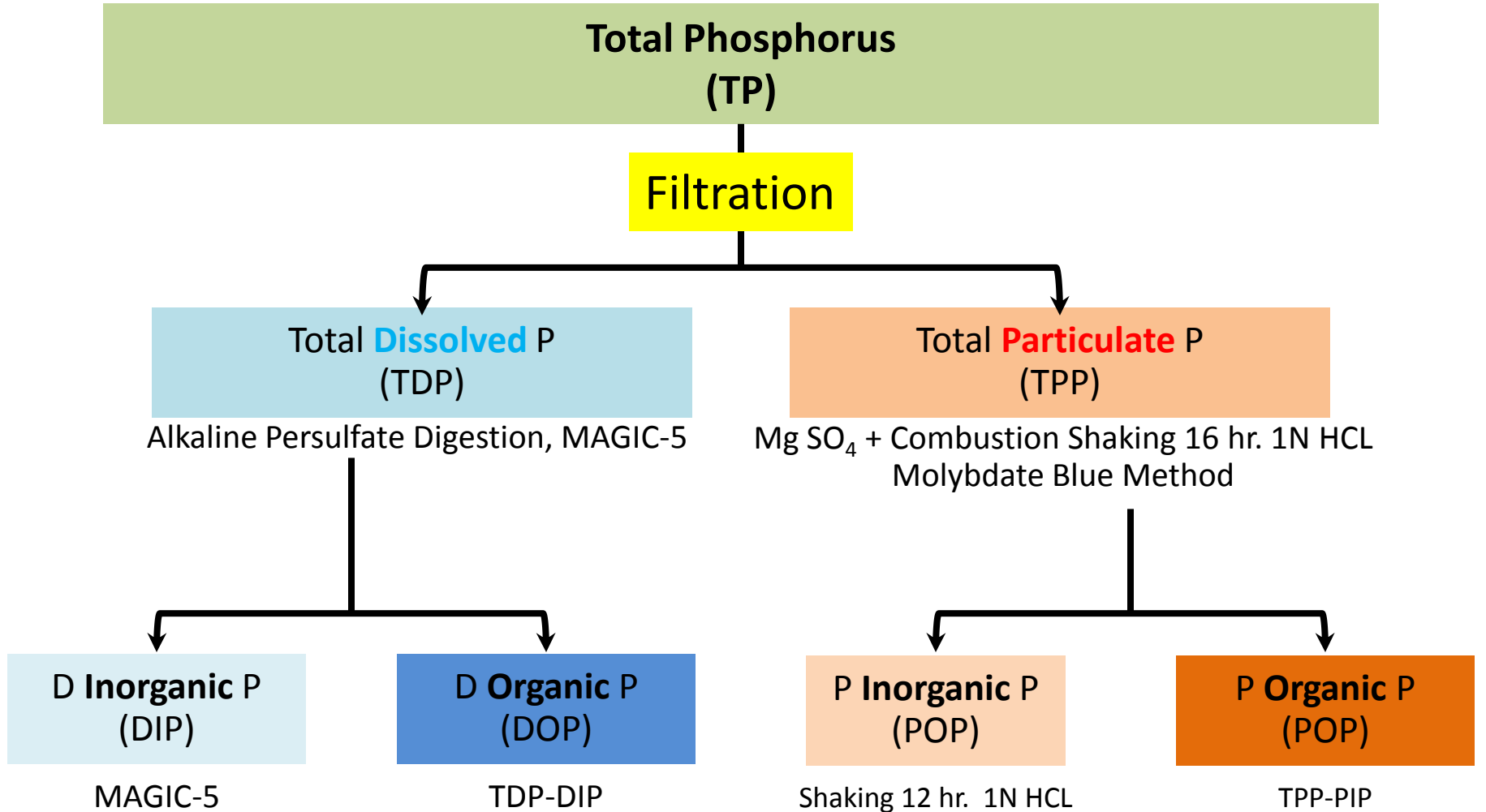
Phosphorus is enriched in SML?

Surface Microlayer: Gelatinous biofilm?



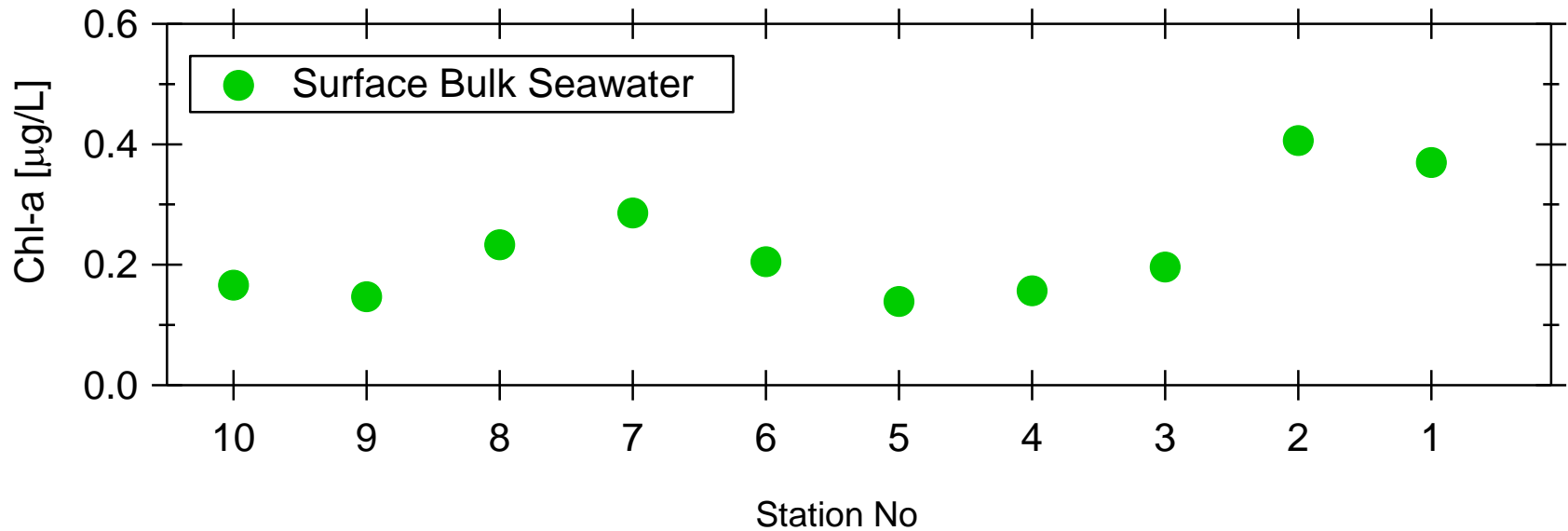
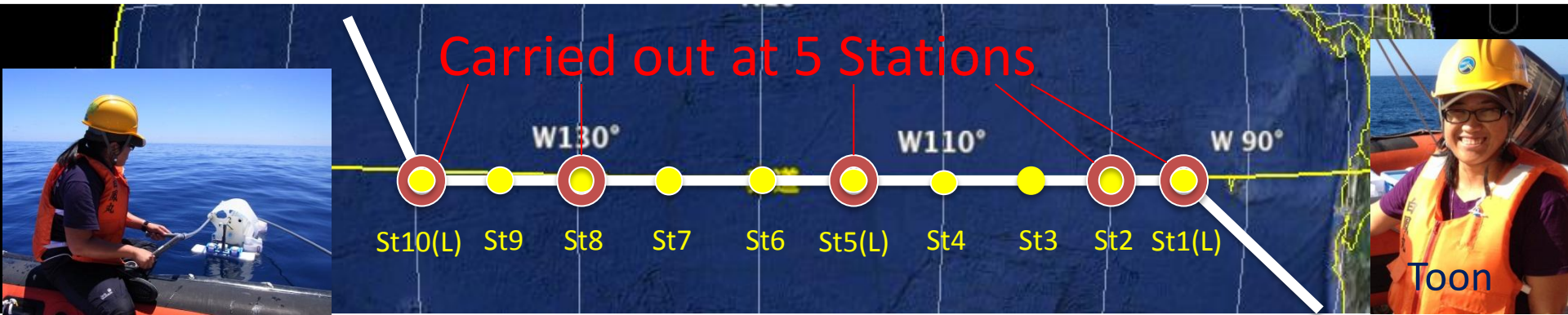
Particulate P \ll Dissolved P in bulk seawater
Particulate P may be enriched in SML?

Chemical Fractionation of Phosphorus

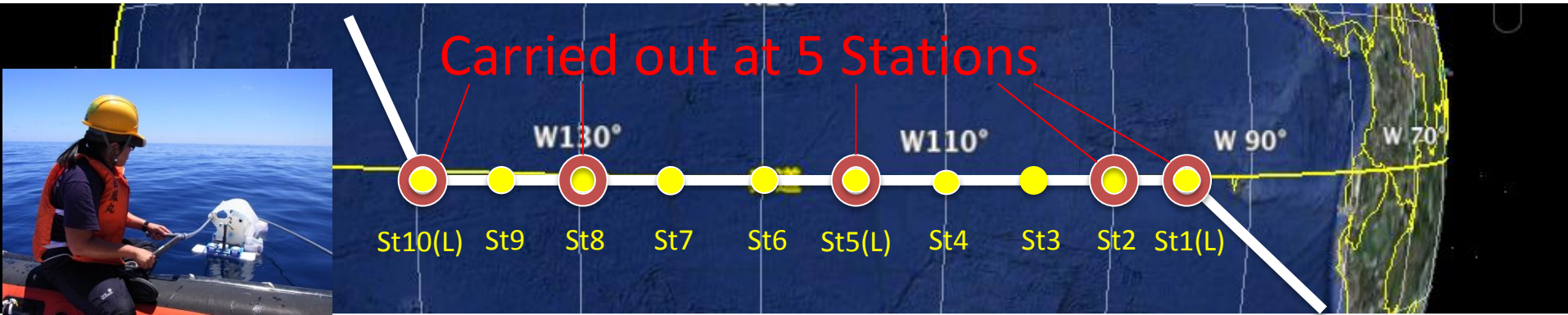


Grasshoff *et al.* (1999), Moutin *et al.* (2005) and Chen *et al.* (2006)

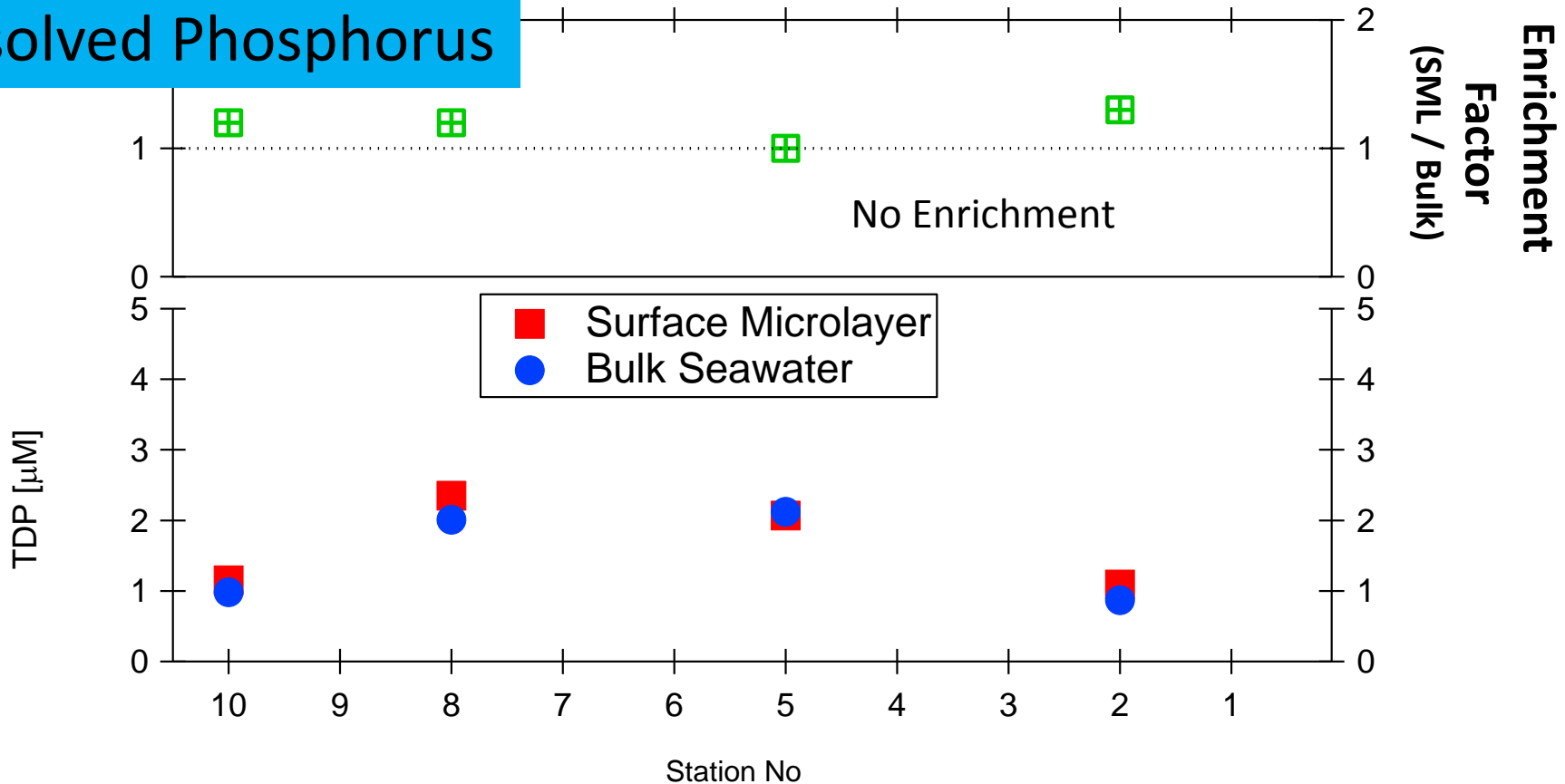
TDP Sea-Surface Microlayer (SML) Sampling



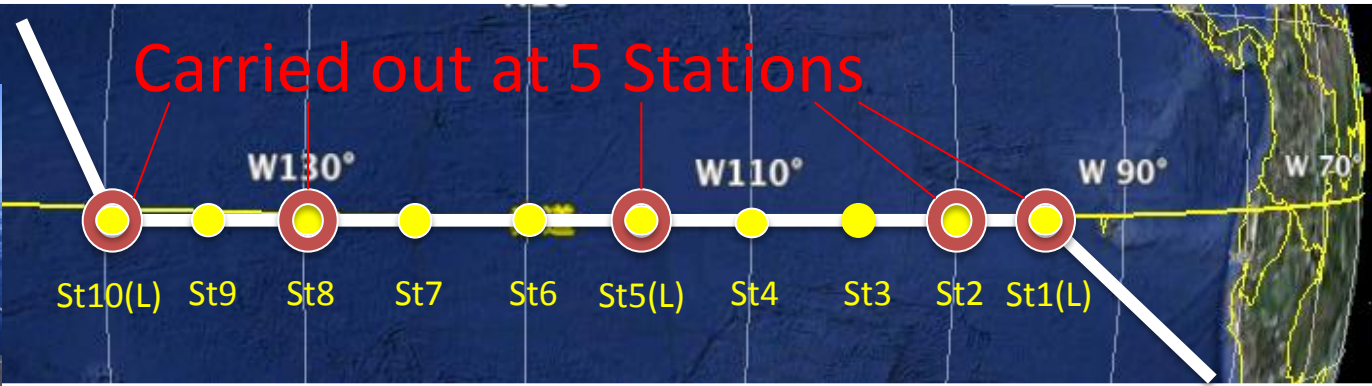
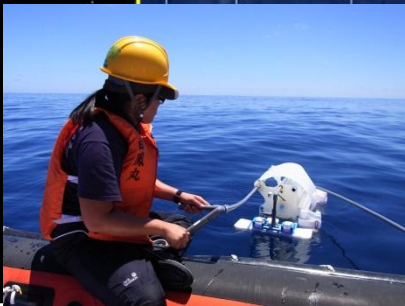
TDP Sea-Surface Microlayer (SML)



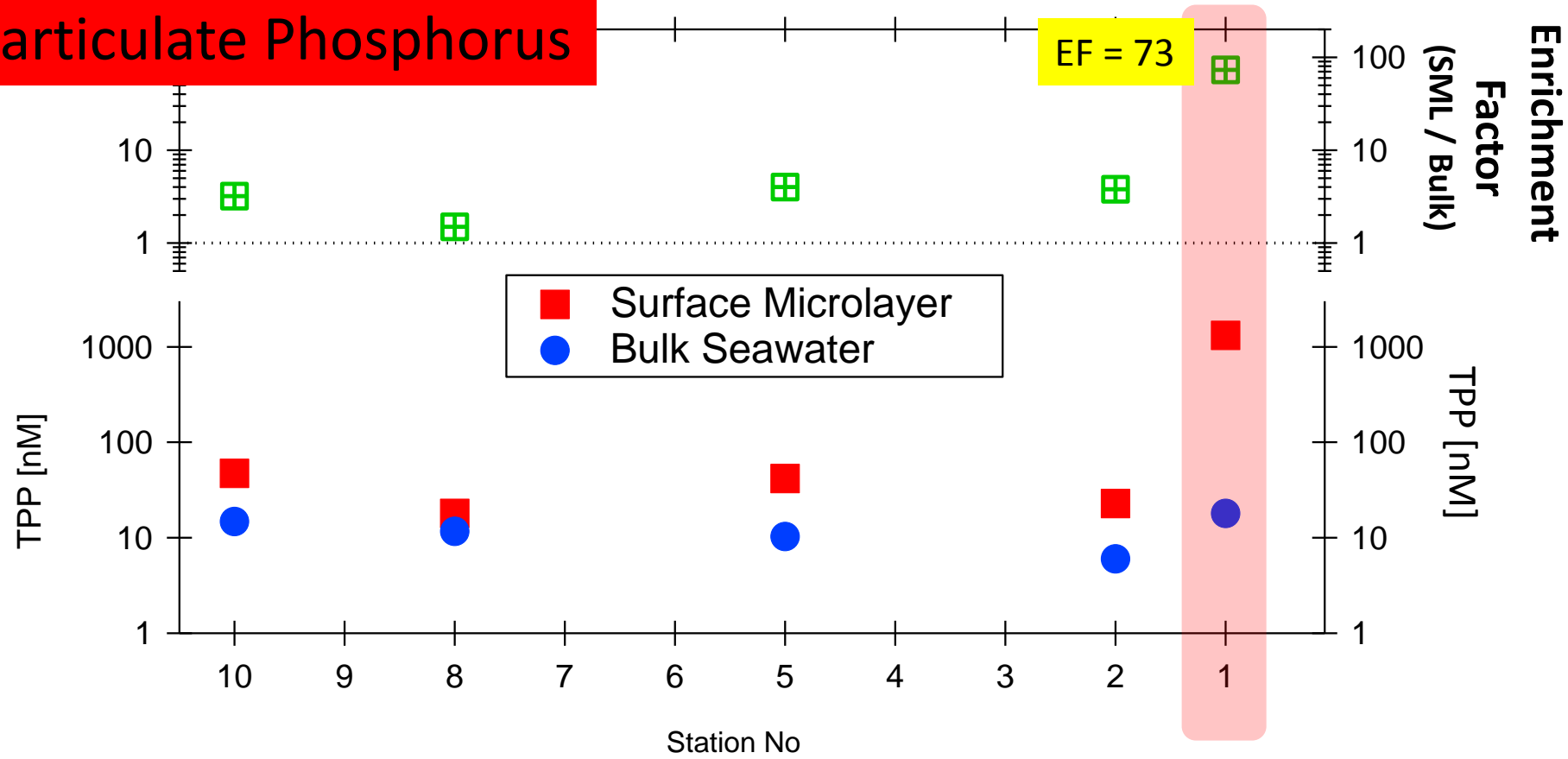
Dissolved Phosphorus



TDP Sea-Surface Microlayer (SML)

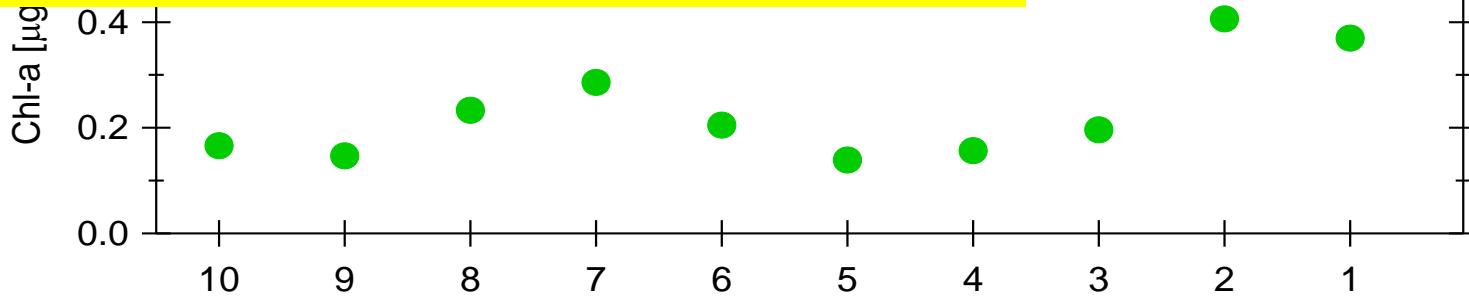


Particulate Phosphorus

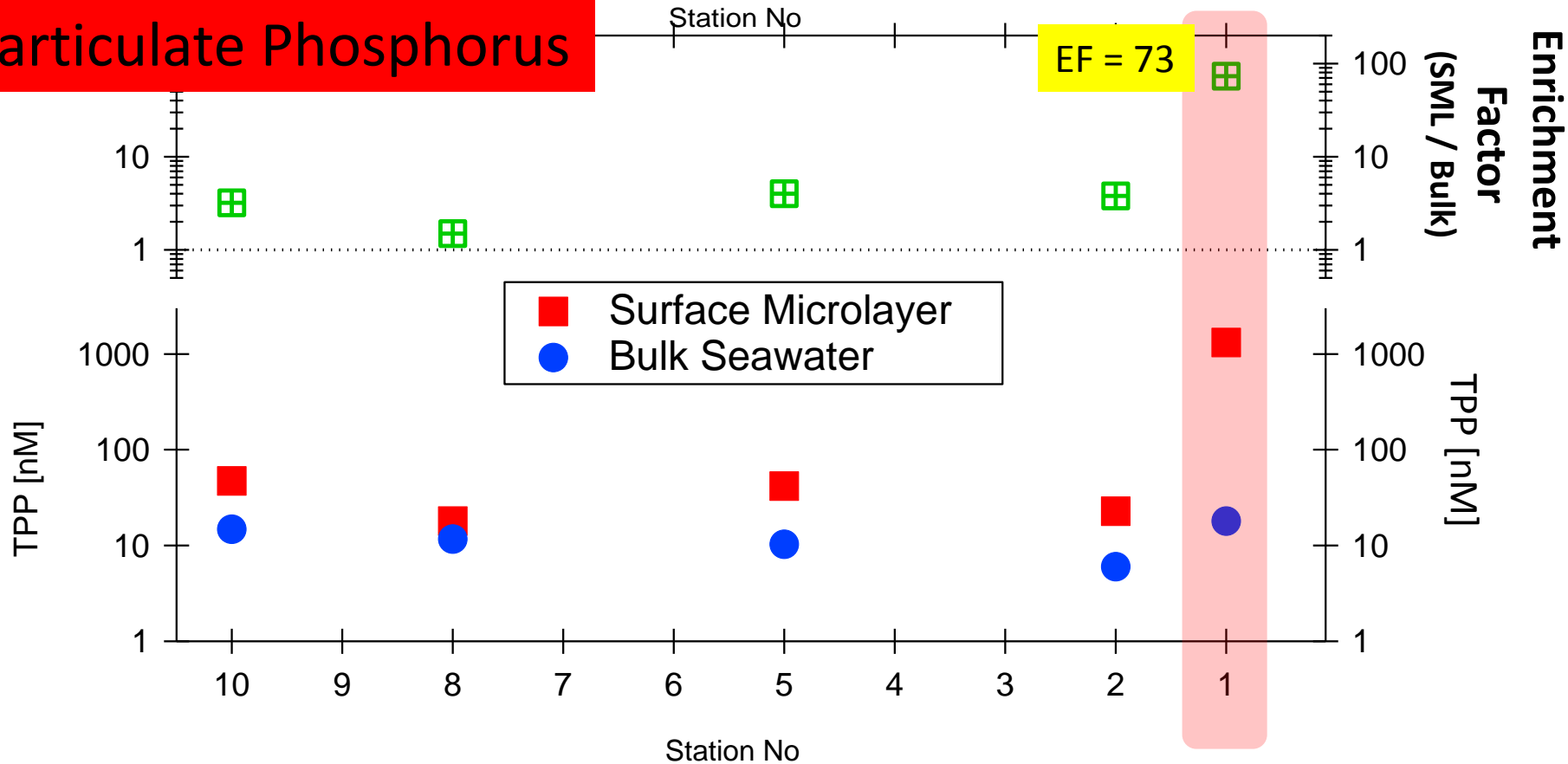


Looks like Only Particulate Phosphorus in SML increased!

Surface Microlayer (SML)

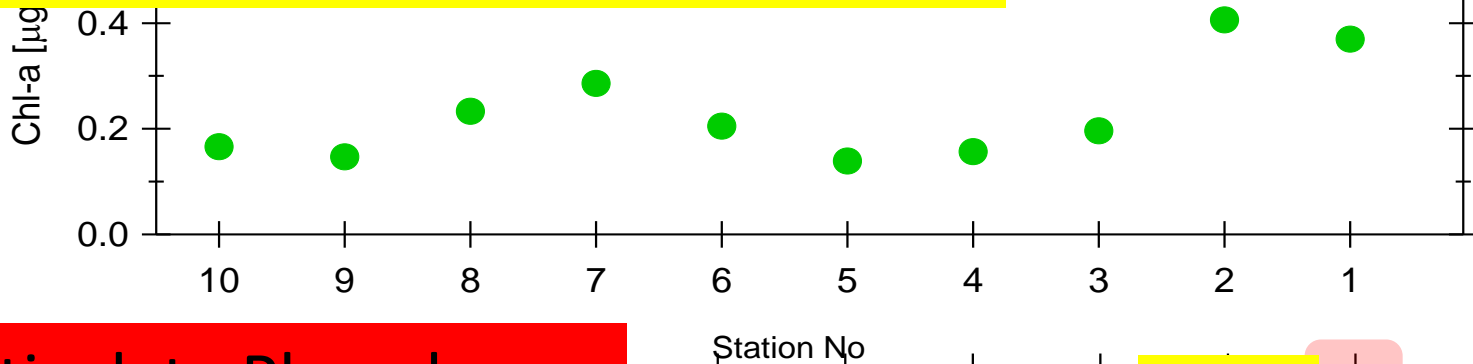


Particulate Phosphorus



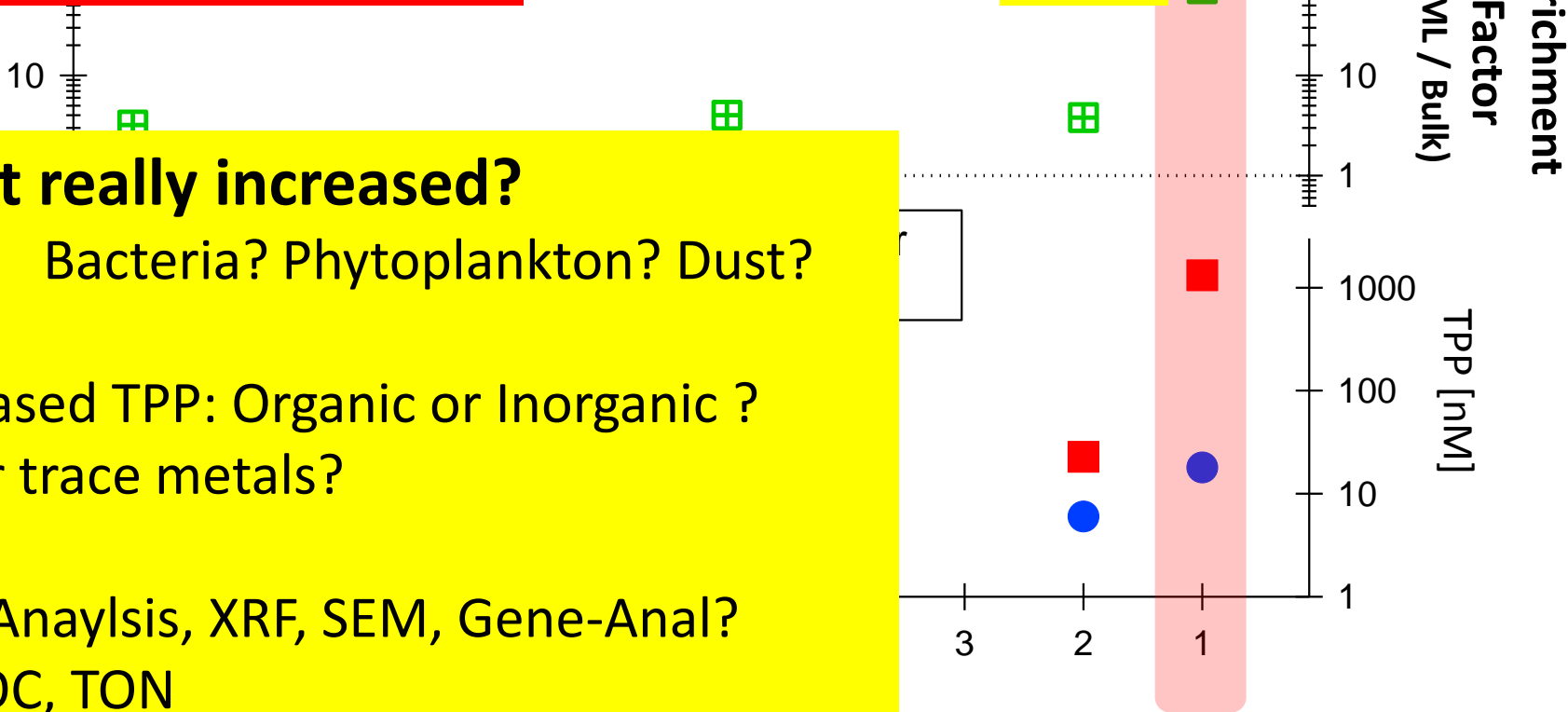
Looks like Only Particulate Phosphorus in SML increased!

Surface Layer (SML)



Particulate Phosphorus

EF = 73



What really increased?

Bacteria? Phytoplankton? Dust?

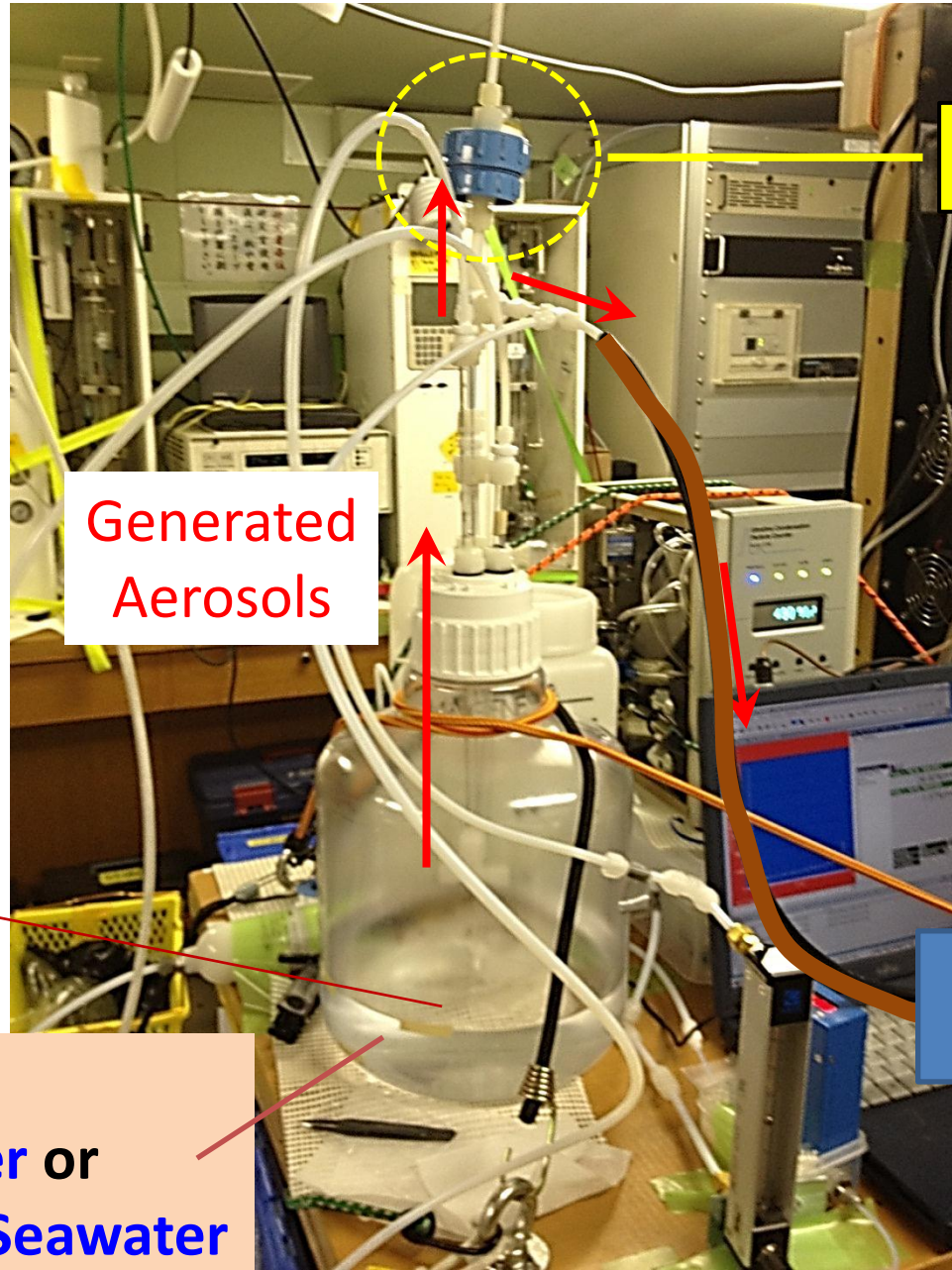
Increased TPP: Organic or Inorganic ?

Other trace metals?

=> P-Analysis, XRF, SEM, Gene-Anal?

TOC, TON

Laboratory Bubble Bursting Aerosol Generation Exp.



Teflon Filter Pack

Further Off-Line Analysis

- ⇒ Total Phosphorus
- ⇒ Water Soluble Phosphorus
- ⇒ Total Organic Carbon?
- ⇒ Trace Metals?
- ⇒ Ionic Species

Generated Aerosols

Bubbling Head



On-Line Analysis

ATOFMS

~0.1 L/min

Silica Gel Diffusion Dryer

Pump

Sample:
SML Seawater or
Sub-Surface Seawater

Single Particle Mass Analysis

SML

D = 100 – 3000 nm

Unaccounted

SS_CN

SS_Plain

NaCl_SiScCoCr

Mg_K_OC_PCN

Mg_K_OC_CN

Mg_K_OC_noNeg

Fe_NaAlK_SiP_OC_PbAg

Fe_NaAlK_OC_noNeg

Ti_OCCN_P_MgAl

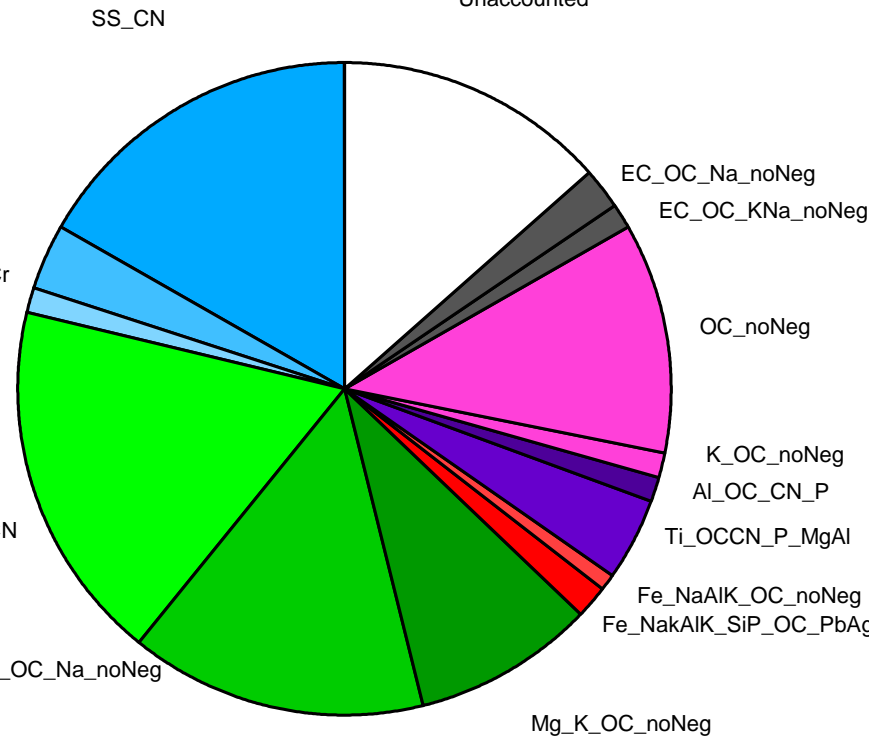
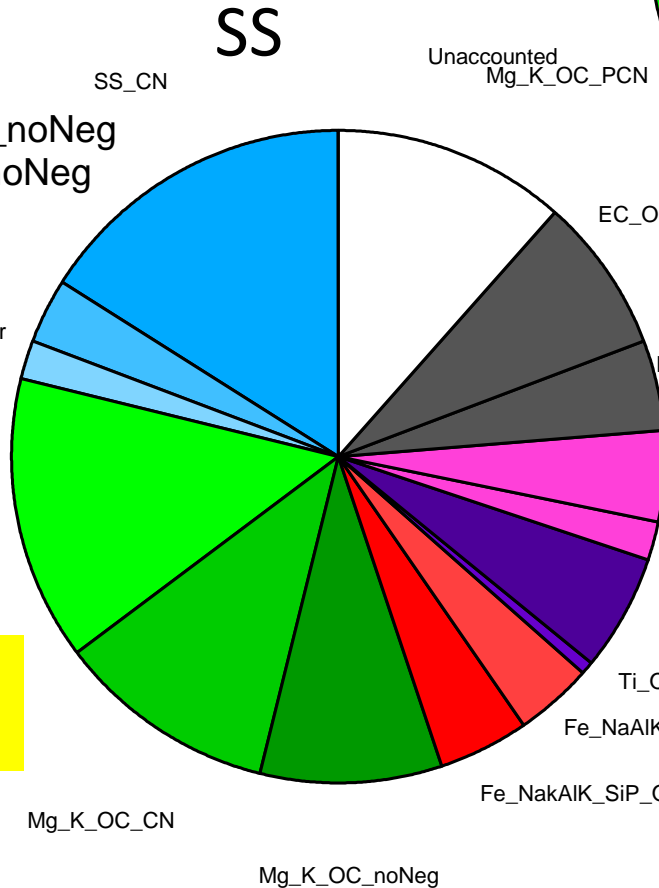
Al_OC_CN_P

K_OC_noNeg

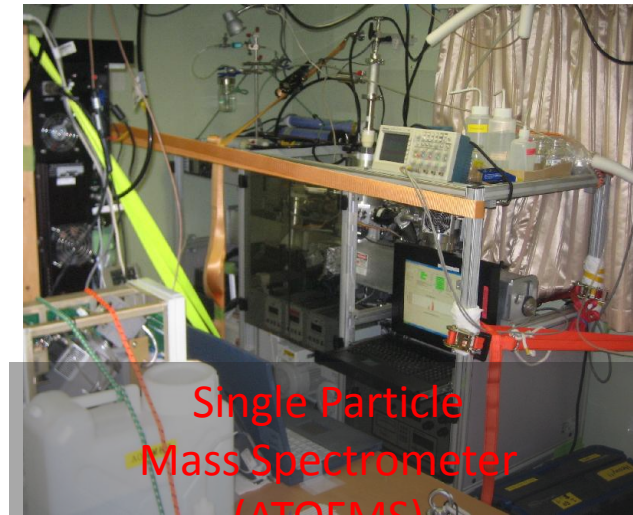
OC_noNeg

EC_OC_KNa_noNeg

EC_OC_Na_noNeg



Filter Samples:
Not much difference



Balloon Launch and Flight Operation from R/V “*Hakuho-Maru*” for Stratospheric Air Sampling over the Equator of Eastern Pacific

S. Aoki, H. Fuke, Y. Inai, H. Honda *et al.*

ISAS/JAXA, Tohoku Univ., National Institute of Polar Research



Sampling of Stratospheric Atmosphere

- Since 1985, stratospheric air sampling has been carried out repeatedly, over Japan (Sanriku, Taiki), Sweden (Kiruna), and Antarctica (Syowa).



Antarctica (2004)



Sanriku (2007)



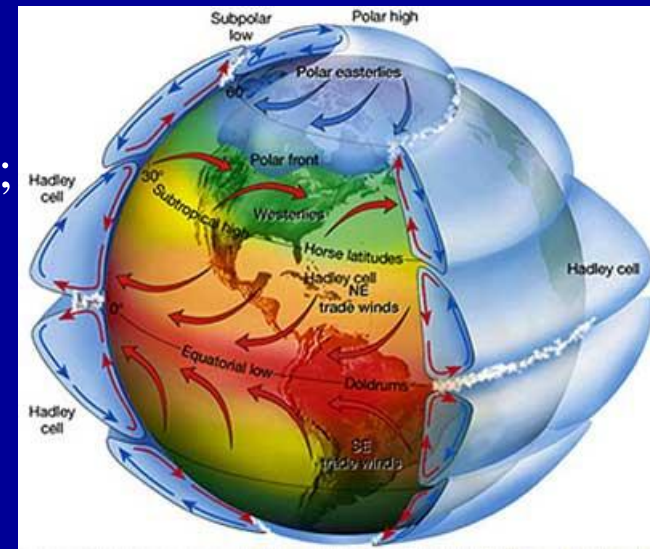
Taiki (2010)



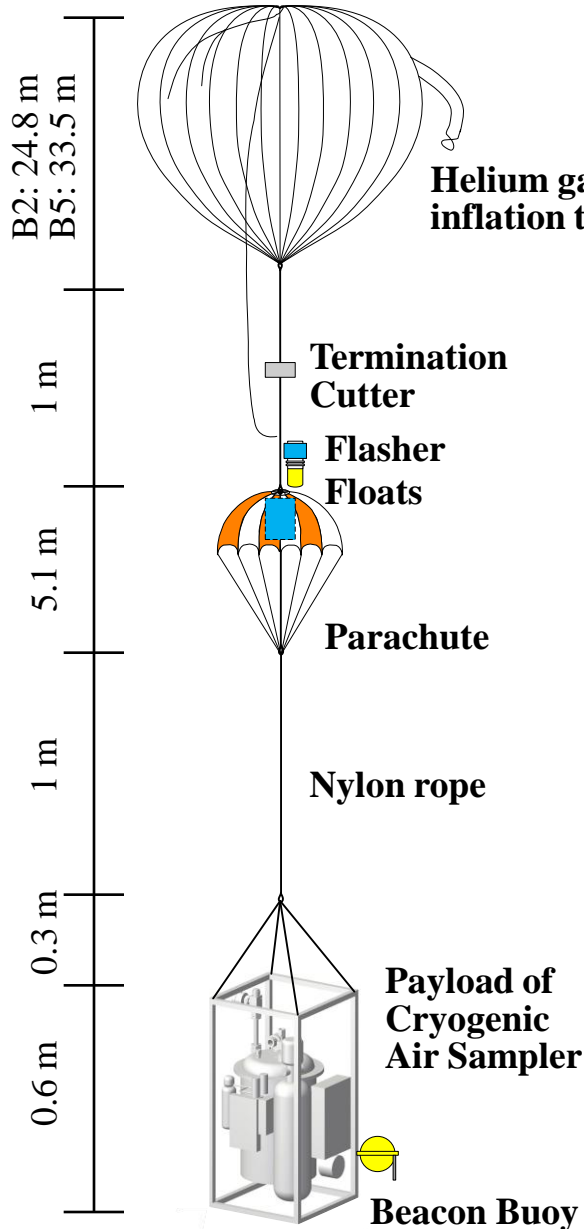
Antarctica (2008)

Sampling of Stratospheric Atmosphere

- Since 1985, stratospheric air sampling has been carried out repeatedly, over Japan (Sanriku, Taiki), Sweden (Kiruna), and Antarctica (Syowa).
- It primarily aims to elucidate the stratospheric transport / chemical processes by direct and long-term sporadic air sampling.
- Concentration of various compounds and isotopes including green-house gases have been monitored;
 - CO_2 , CH_4 , N_2O , SF_6 , etc.
 - $\delta^{15}\text{N}$ of N_2 , $\delta^{18}\text{O}$ of O_2 , CO , H_2 , Ar , etc.
- Gravitational separation of major components has been found in their stratospheric vertical distributions.
- It is essential to sample the air **“over the equator”** to investigate the transport process of greenhouse gases from the troposphere to the stratosphere.
- Air sampling had never been carried out over the equator. (**“data gap”**)



Balloon
B2 (2000m³) or B5 (5000m³)



2000 m³ Balloon

Weight of B2 System

Balloon	21.5 kg
Parachute etc.	4.1 kg
Air Sampler	22.0 kg
Total Weight	47.6 kg
Free Lift (20%)	9.5 kg
Total Buoyancy	57.2 kg

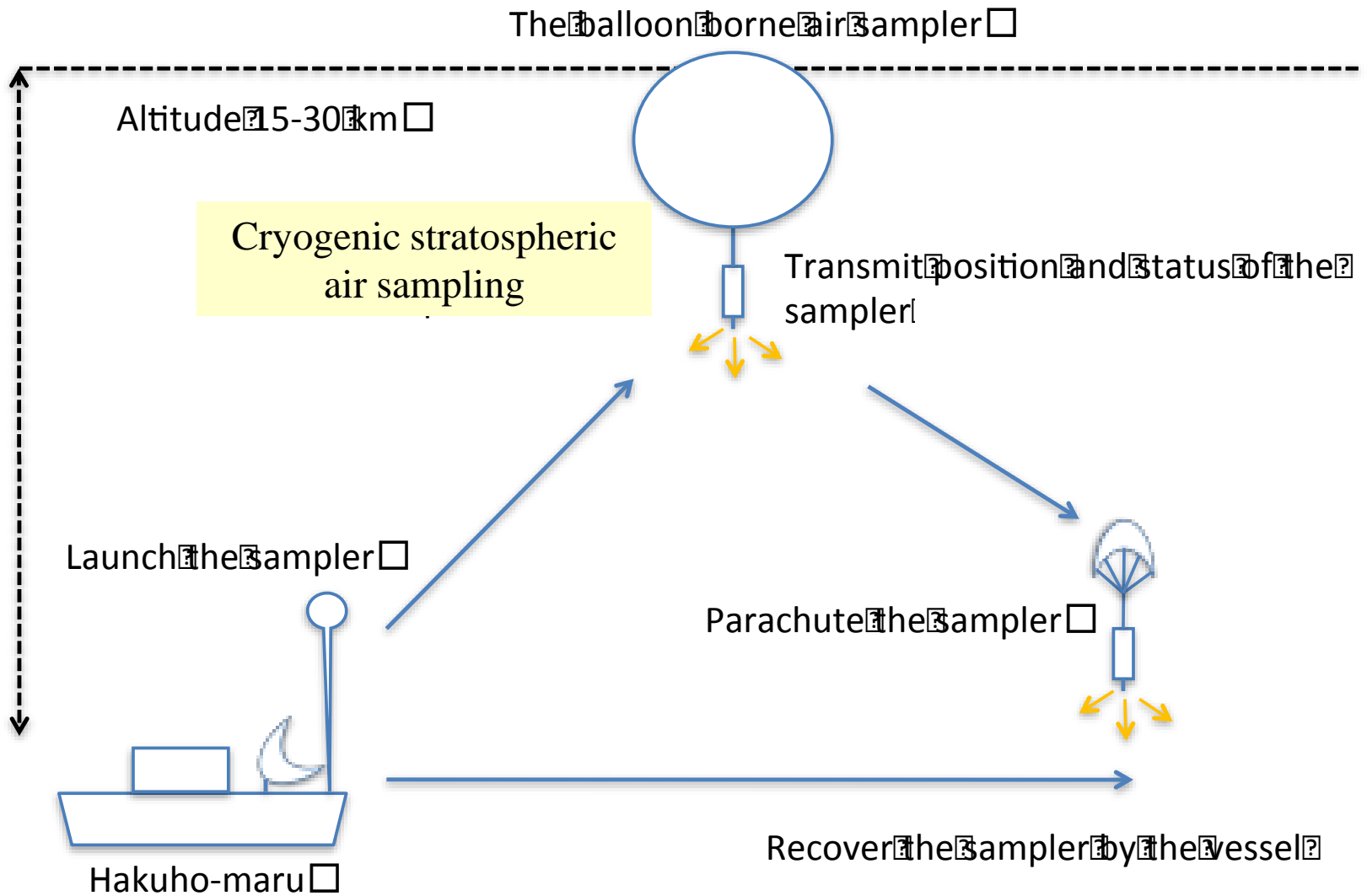
5000 m³ Balloon
Weight of B5 System

Balloon	37.1 kg
Parachute etc.	4.1 kg
Air Sampler	22.0 kg
Total Weight	63.2 kg
Free Lift (18%)	11.4 kg
Total Buoyancy	74.5 kg

Flight Train Configuration



Flight Sequence



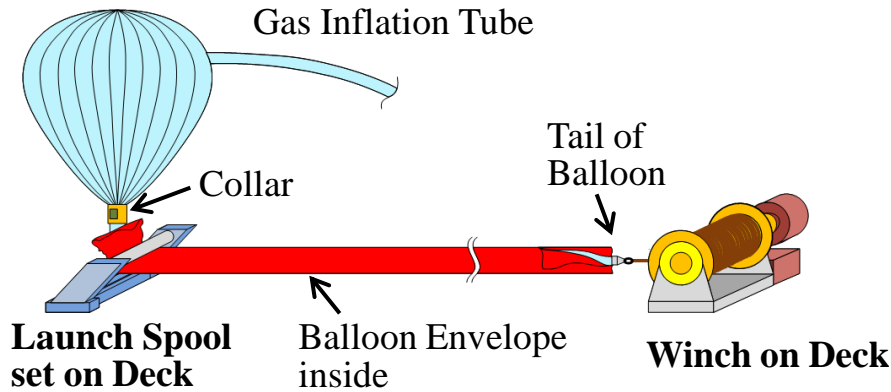
Technical Challenges for Launch

- Narrow deck; The open space of vessel deck is limited to only 20 m^L, 7 m^W.
- Many equipments are located: such as a big crane C-frame, poles, and antennas.
- Minimum cargo; It is important to utilize existing equipments on vessel as much as possible.
- Limited number of people; “a few scientists + crews” (no staff from ISAS balloon office).

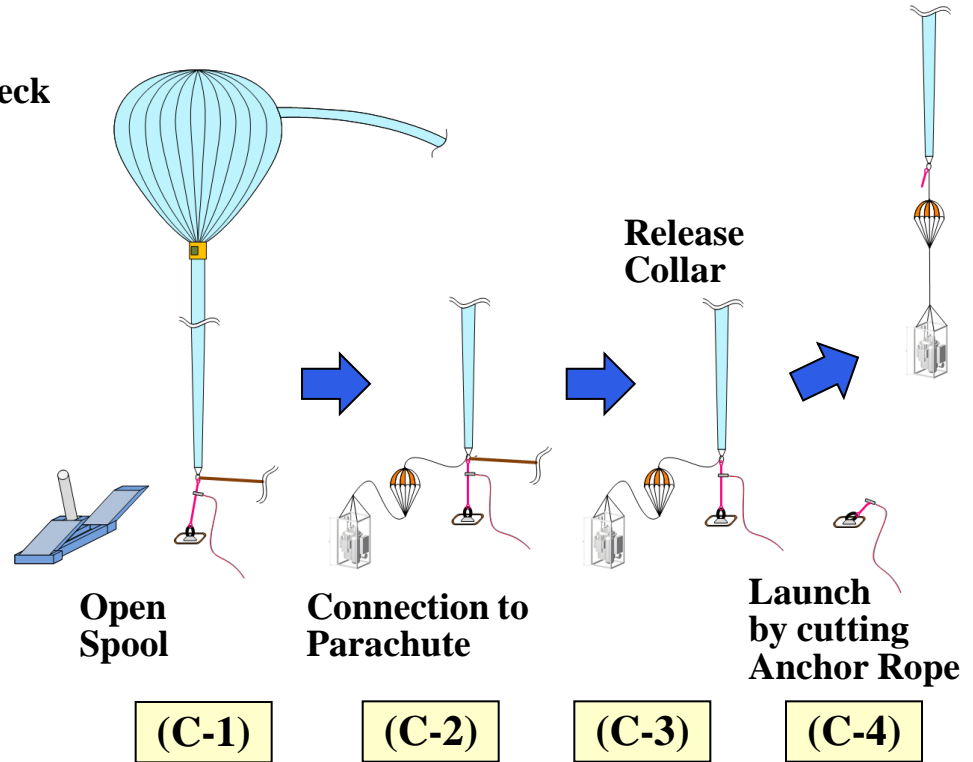
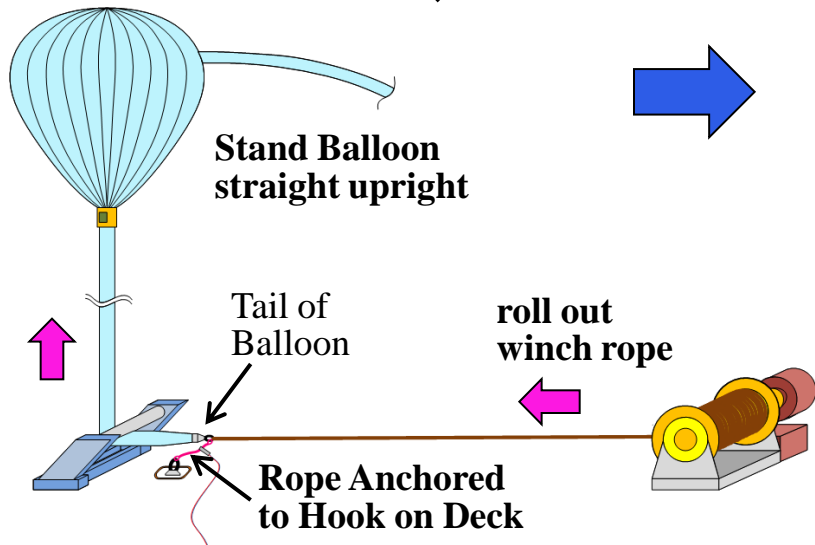


Newly Modified Static Launch Method

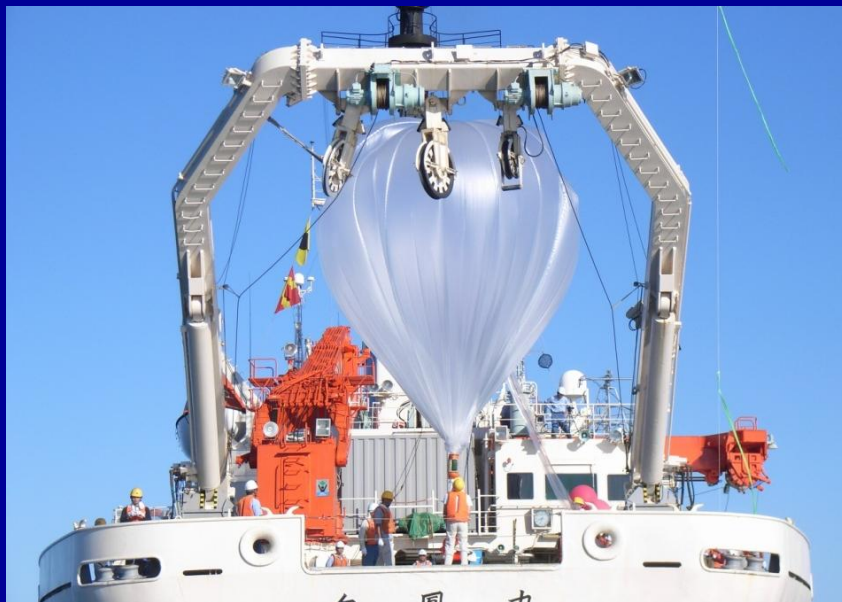
(A)



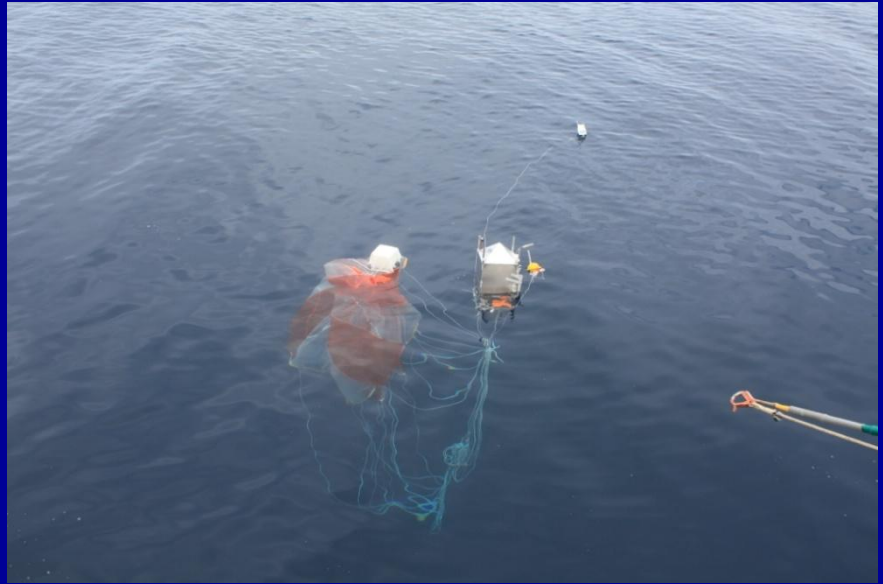
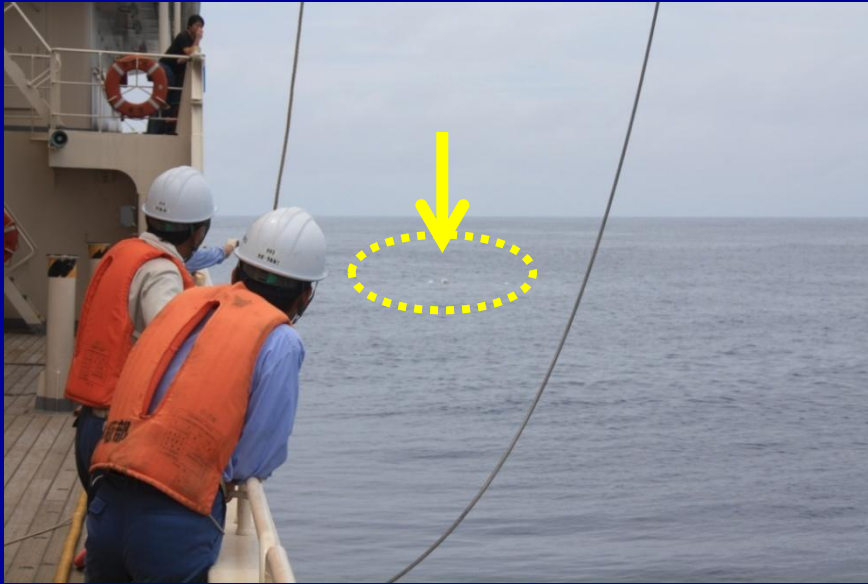
(B)



Launch from “*Hakuho-Maru*”



Payload Recovery by “Hakuho-Maru”



All Four Flights Successfully Done !!

EqPOS

**Stratospheric
Air Sampling
Balloon**

(4 Launches)
Alt = 19-30 km

**O₃, CO₂, H₂O
Sonde**

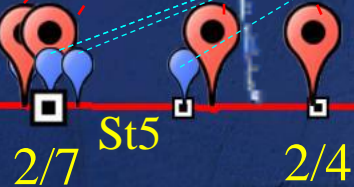
(6 Launches)
Alt = 0-30 km

St10

2/14



2/10



2/7

St5

2/4

2/2

St1

1/29

Callao
(Peru)



Google earth

Chemical Analysis for Stratospheric Air

CO₂

CH₄

N₂O

SF₆

CO

H₂

Ar

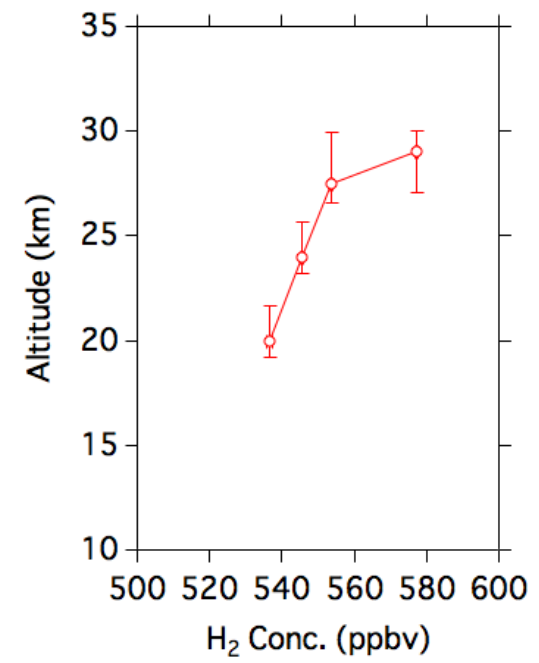
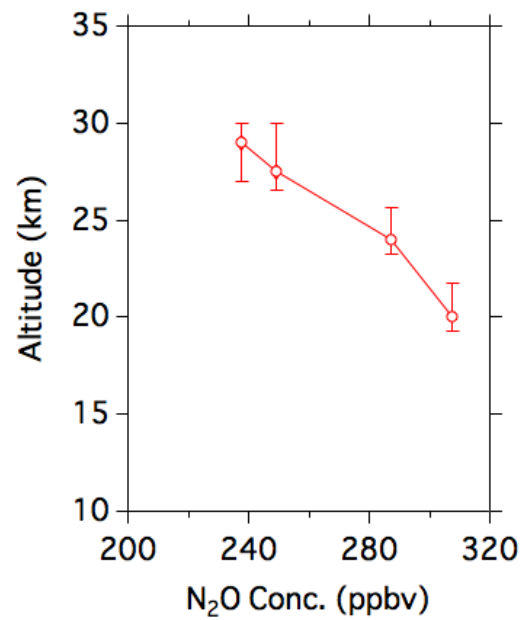
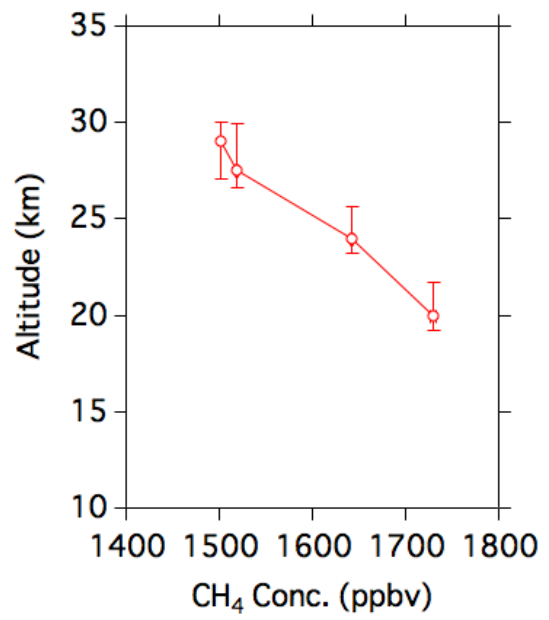
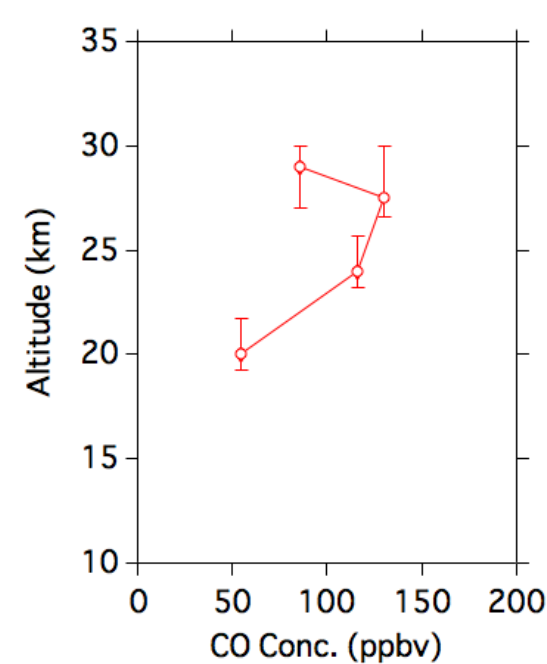
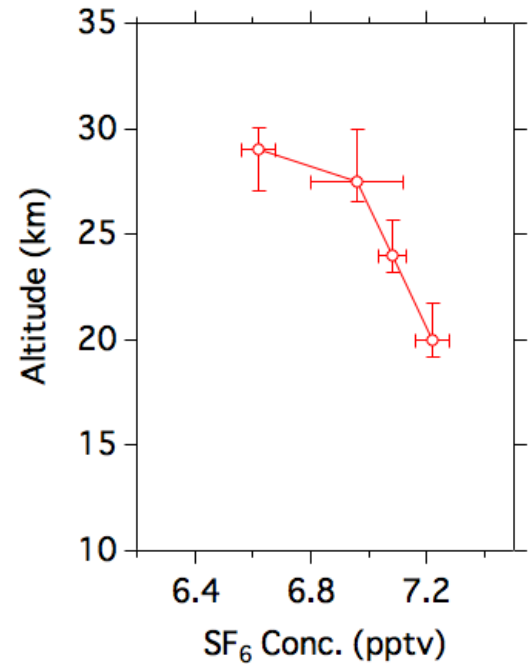
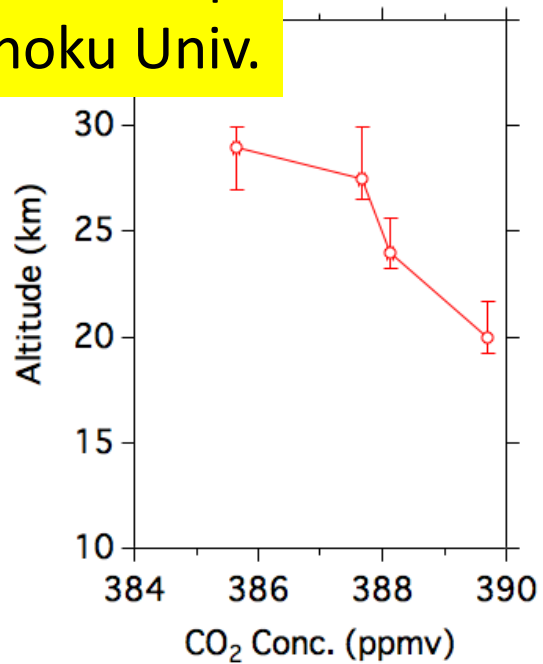
Aoki Group
Tohoku Univ.

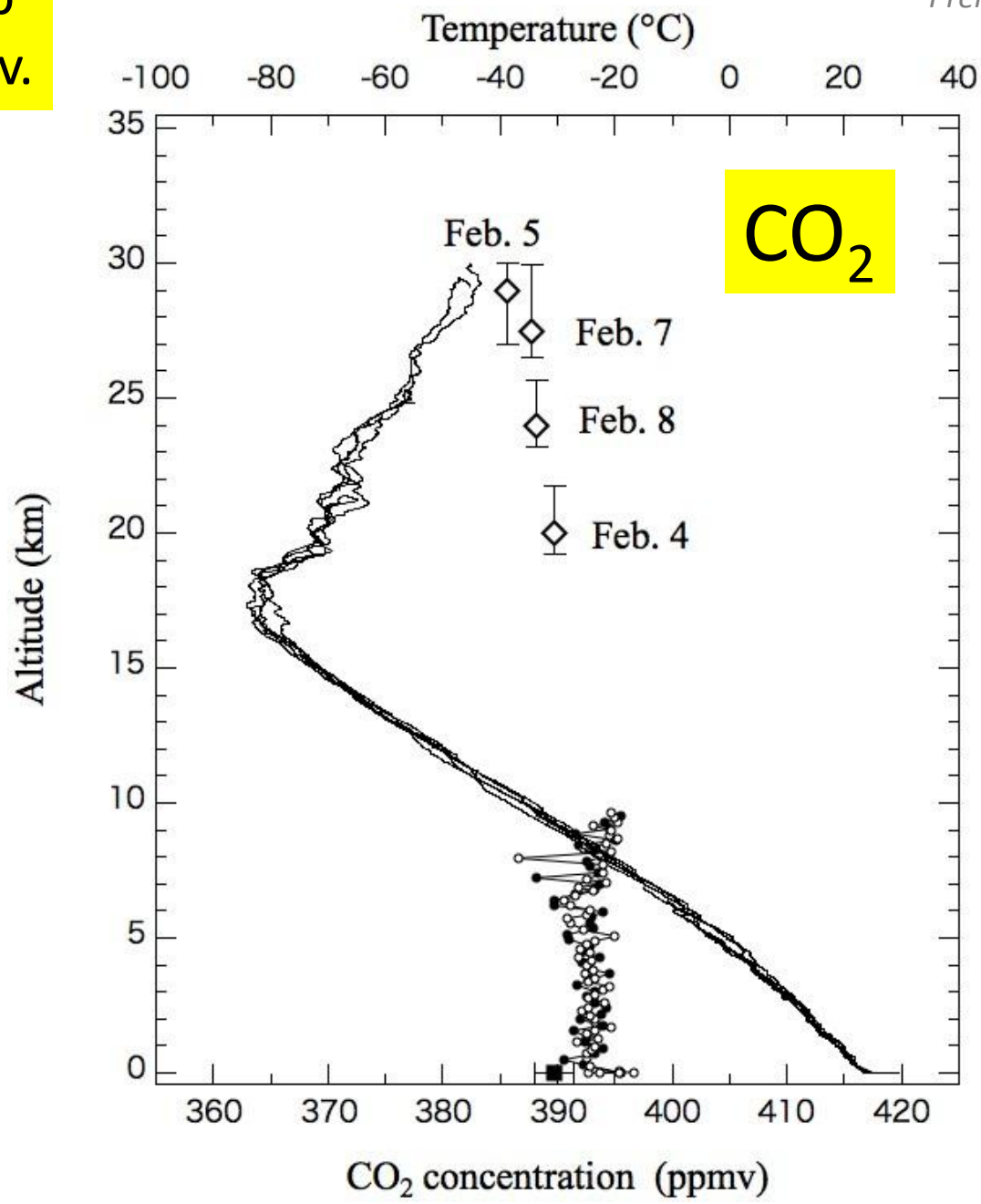
$\delta^{15}\text{N}$ of N₂

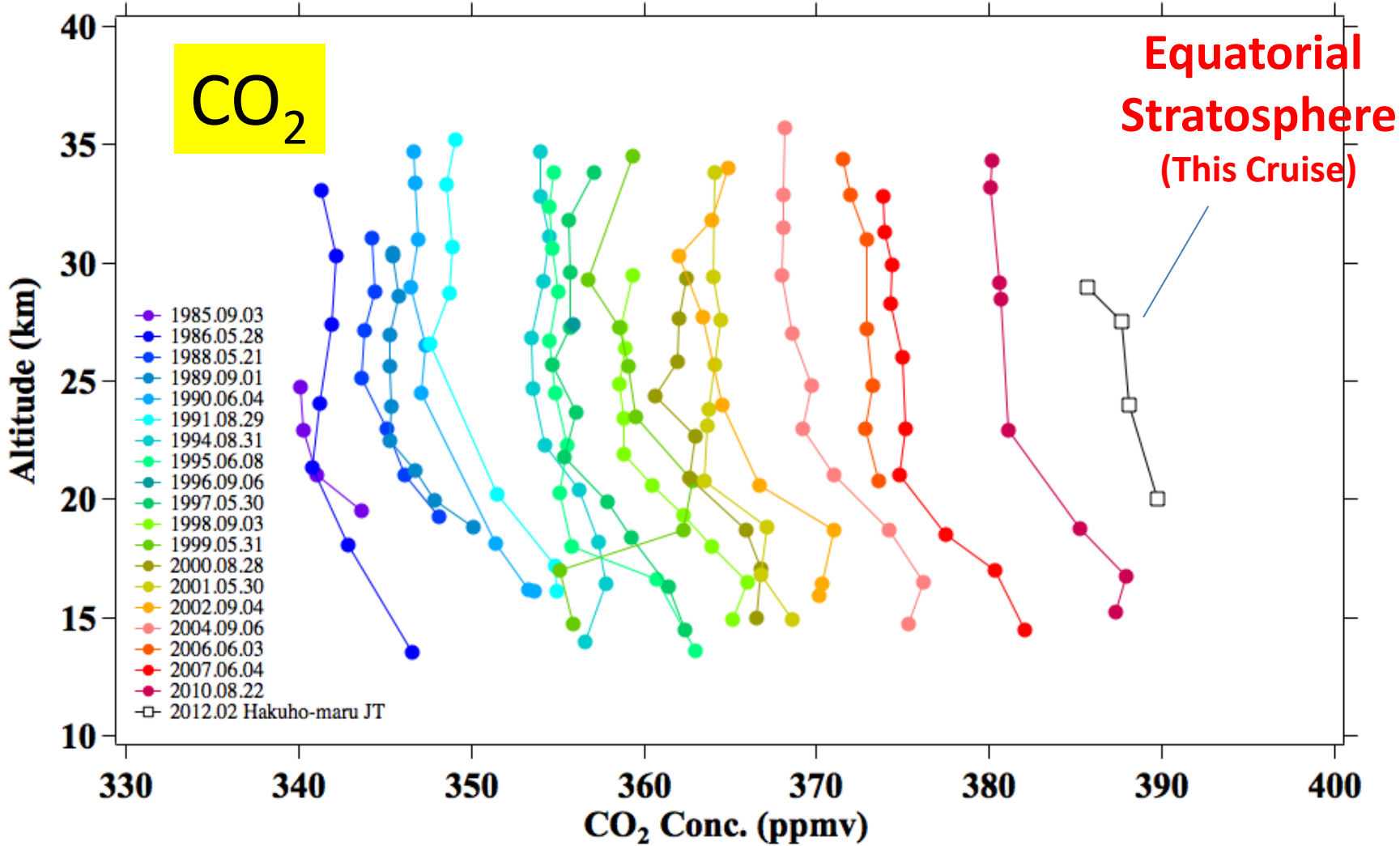
$\delta^{18}\text{O}$ of O₂

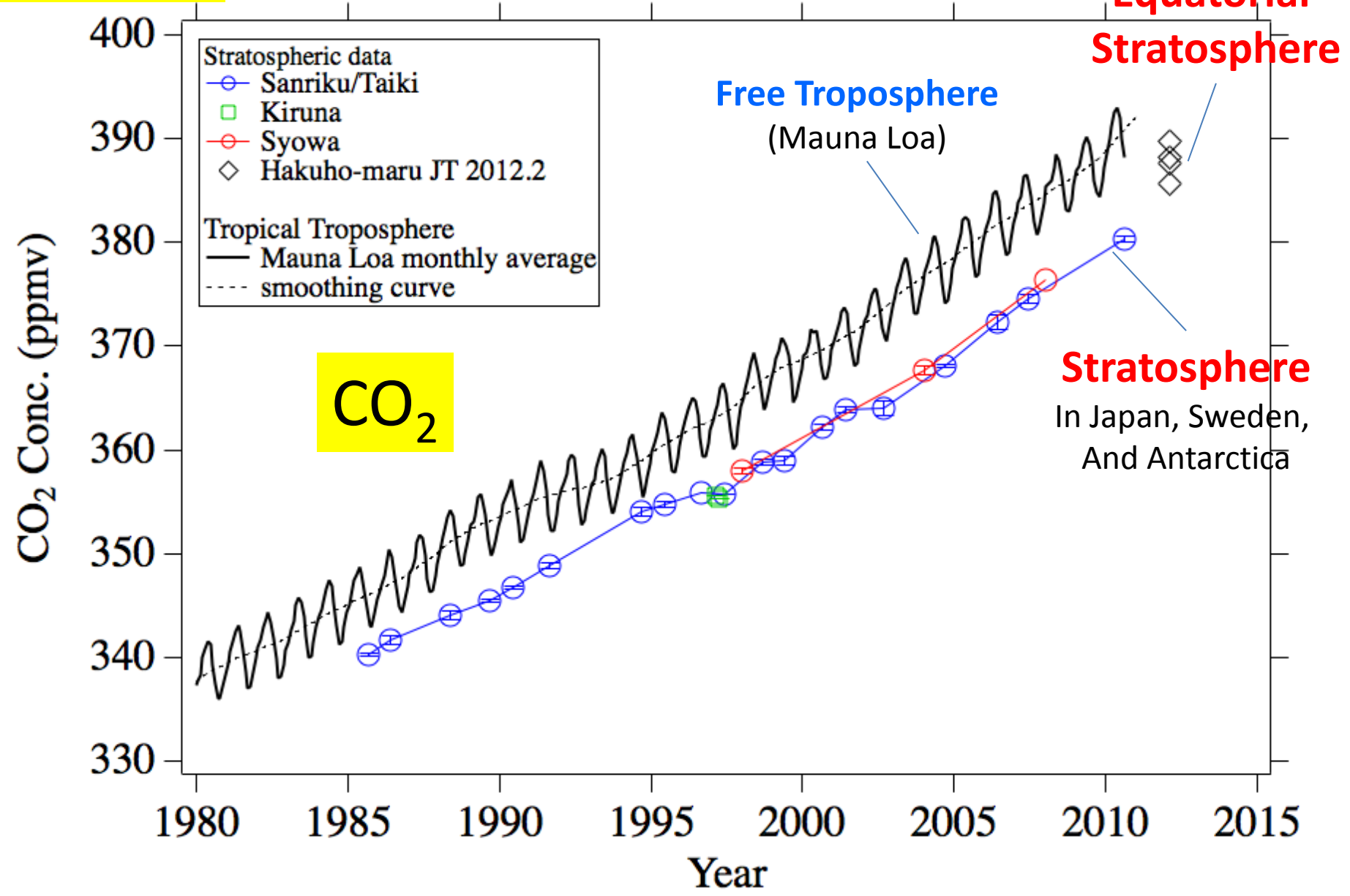
D/H of CH₄

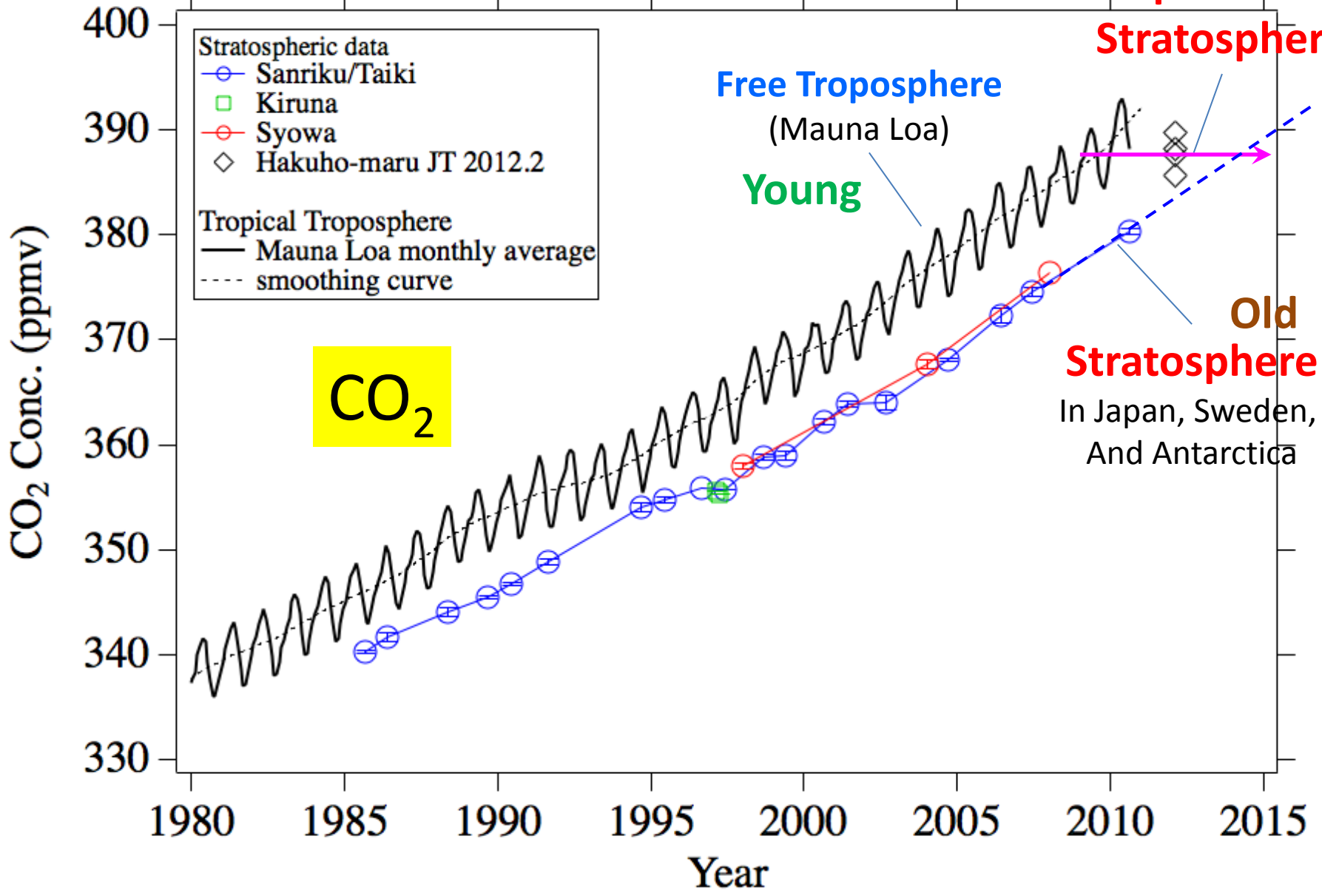
etc.



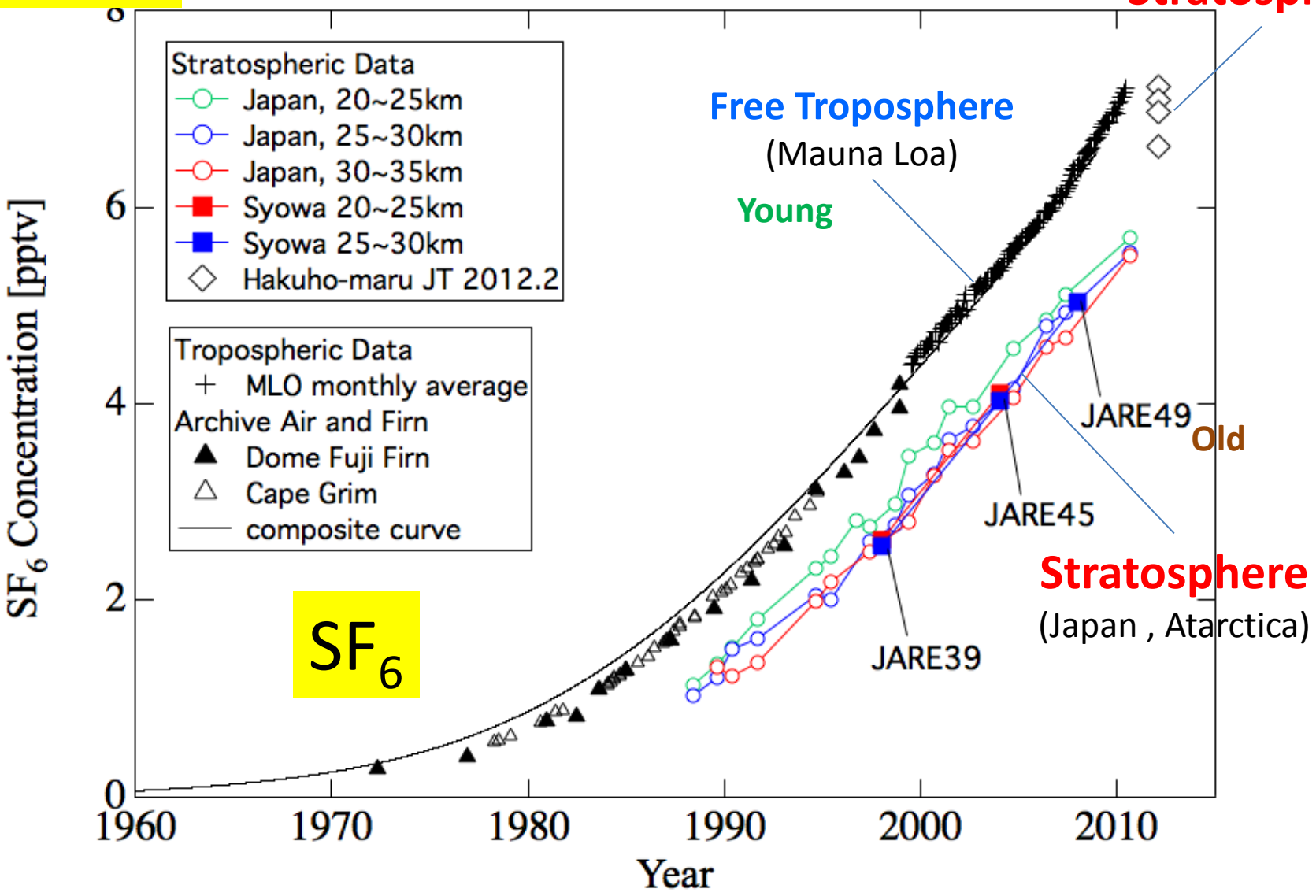








Equatorial
Stratosphere



Chemical Analysis for Stratospheric Air

CO₂

CH₄

N₂O

SF₆

CO

H₂

Ar

$\delta^{15}\text{N}$ of N₂

$\delta^{18}\text{O}$ of O₂

D/H of CH₄

etc.

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Tohoku Univ.



Summary of rubber-balloon soundings

(Total 6 Launches)

CO₂, O₃, H₂O
T, RH, GPS

Altitude = Surface to 30 km

Launch time (LT)	Longitude	Sensors
09:12, Feb. 2, 2012	95.501degW	T, RH, GPS
10:56, Feb. 3, 2012	100.035degW	H2O, O3, T, RH, GPS
17:30, Feb. 5, 2012	110.009degW	CO2, T, RH, GPS
17:14, Feb. 6, 2012	115.000degW	CO2, T, RH, GPS
13:37, Feb. 7, 2012	115.021degW	H2O, O3, T, RH, GPS
17:29, Feb. 7, 2012	115.010degW	CO2, T, RH, GPS



Just before a launch

Preparation for a balloon



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Tohoku Univ.

Instruments for soundings

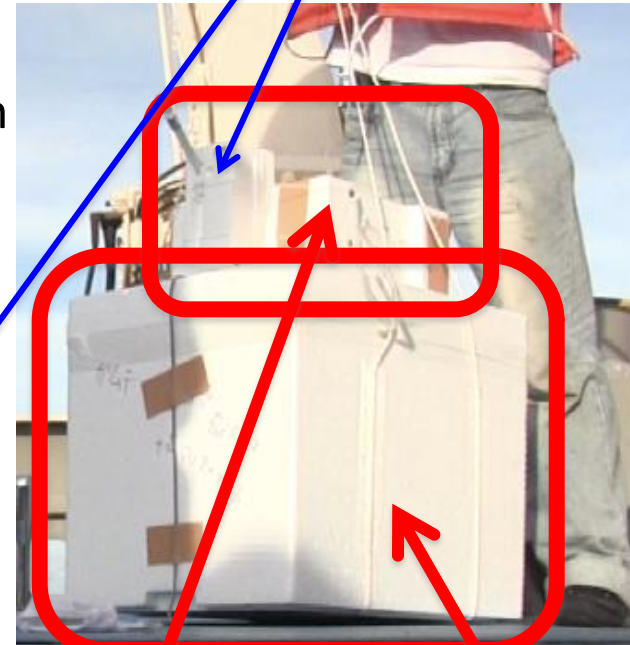
Cryogenic Frostpoint Hygrometer (CFH)

uncertainty: < 9%
vertical resolution: < 100m

Electrochemical Concentration Cells (ECC) ozonesonde

uncertainty: ~10%
vertical resolution: ~100m

Radiosonde



sensor

reference gas container

CO2 sonde

uncertainty: a few ppmv(?)
vertical resolution: ~240m



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Tohoku Univ.

Stratosphere (30 km)



EqPOS

O₃, CO₂, H₂O
Profiling



Stratospheric
Air Sampling
(Alt = 19-30 Km)

Atmospheric Aerosols
(Size Dist., CCN, Comp., Morphology)

Trace Gas
(DMS, VOCs, CO₂,
CO, O₂)

Bubble Bursting

Surface
Microlayer
Sampling

Eddy
Covariance

Gradient
Profile

Air-Sea
Flux

CO₂

Dissolved Gas
(DMS, DMSP, VOCs,
pCO₂, O₂)

N-Fixation

Phytoplankton

Bacteria

Non-living
Particles

Nutrients, Chl-a
TOC
DOC, DON

Microbial
Abundance,
Speciation,
Community

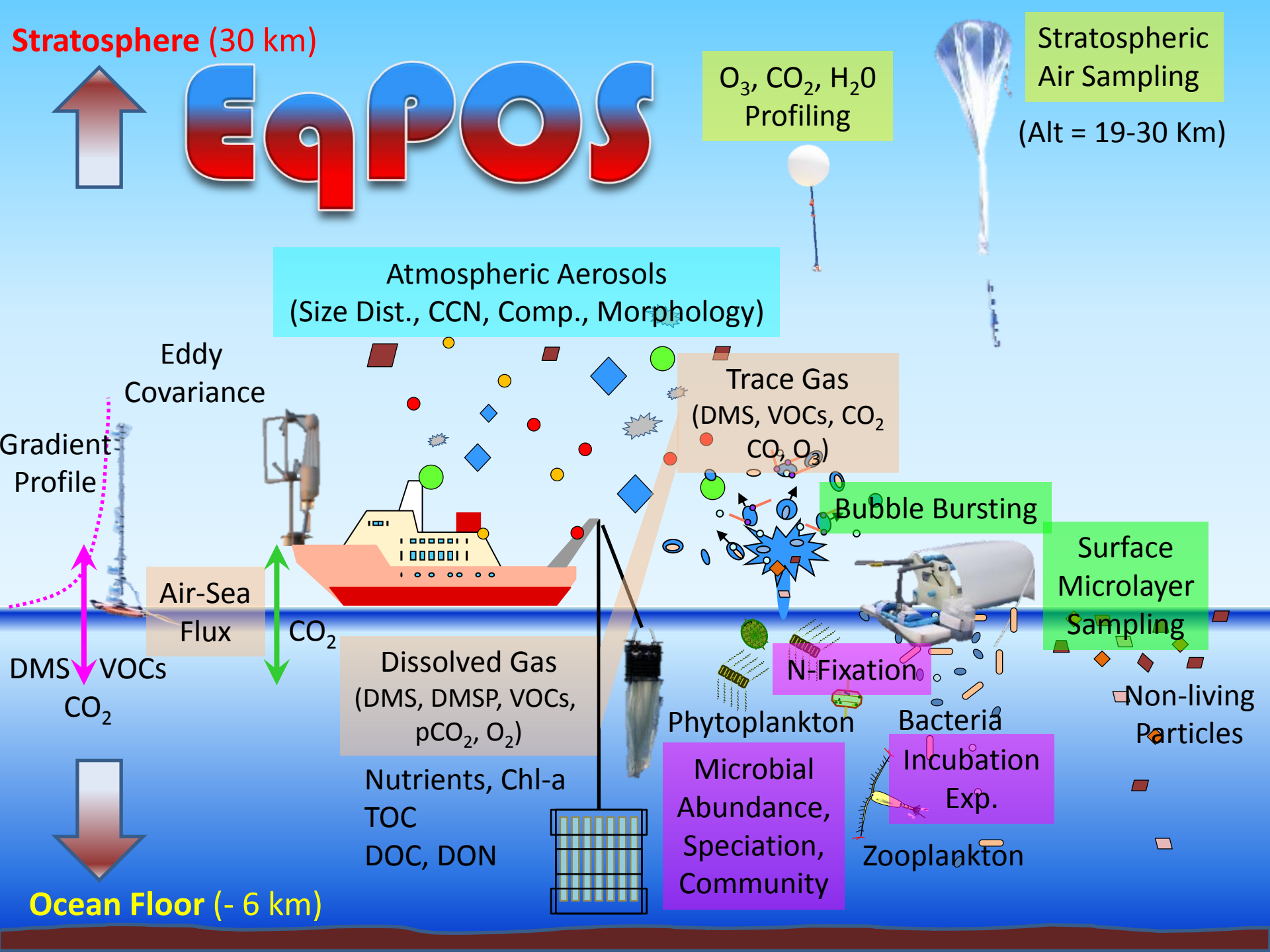
Incubation
Exp.

Zooplankton

DMS VOCs
CO₂



Ocean Floor (- 6 km)



EqPOS

**Equatorial Pacific Ocean and
Stratospheric/Tropospheric Atmosphere Study**

Summary (Preliminary Results)

- **EqPOS** was mainly influenced by SH (South Pacific Ocean) air mass.
- Particulate matter seems to be enriched in SML, but only St. 1 among 5 stations.
- Continuous and simultaneous seawater-DMS and atmospheric DMS were successfully conducted with 30 sec time resolution with EI-PTR-MS.
- Patch-like high seawater-DMS in tropical /EQ Pacific Ocean
- Emission from ocean seems to increase atmospheric DMS
- Stratospheric large balloons were all successfully launched from R/V Hakuho and recovered for the first time.
- Nicely overlaps with TORERO campaign in time and space, and scientific research topics.
- Marine biogeochemical /biogeochemical information would be interesting.

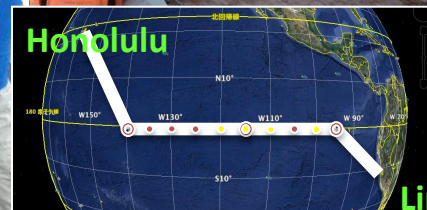
Acknowledgement

- All participants for *more-than-planned* research activity and fun and joy together
- R/V Hakuho crew (Seino captain) for perfect support!
- TORERO (PI Prof. Volkamer) project for excellent collaboration.



PI Prof. Uematsu
(at the end of the cruise)

EqPOS



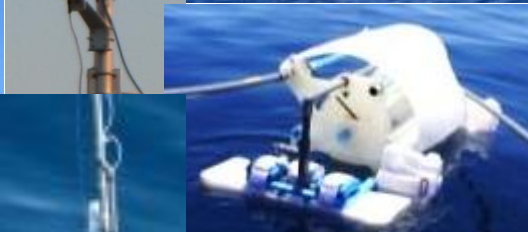
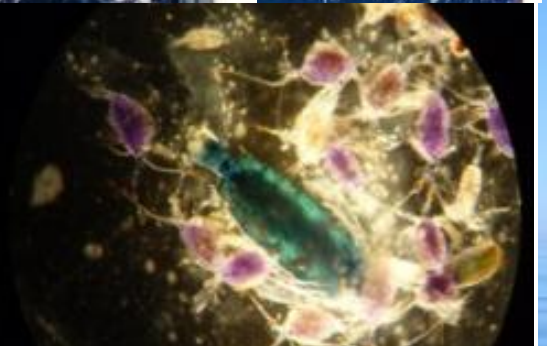
EqPOS

Jan 29, 2012 – Feb 19, 2012 (22 days)

Equatorial **P**acific **O**cean and
Stratospheric/Tropospheric Atmosphere Study

Sky, Ocean, and In-Between

Thank you for your attention!



東京大学
THE UNIVERSITY OF TOKYO