CCN and INP Abilities of Aerosol Particles Measured during HIWC-2022 and CPEX-CV campaigns

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Outline

1. Introduction
2. Instrumentation, methods, and data
3. CCN ability and aerosol properties
4. INP ability ***(#1)*** measured with Raman spectroscopy (by Mr. Toda)
5. INP ability ***(#2)*** measured with TEM analysis (by Dr. Iwata)
6. Summary

Aerosol-cloud interactions

Fig. 1. Clouds in the presence of anthropogenic haze over the equatorial Indian Ocean. Picture taken on 24 February 1999 at 0.5°N, 73.3°E during the Indian Ocean Experiment campaign. The brownish haze originates from South Asia (see Web fig. 1 for a photo of thick brownish haze over lower Himalayas). The haze reaches close to the top of cumulus clouds located around 5 km in this picture.

Anthropogenic aerosols may alter precipitation patterns and surface temperature structures. [*Ramanathan et al., 2001*]

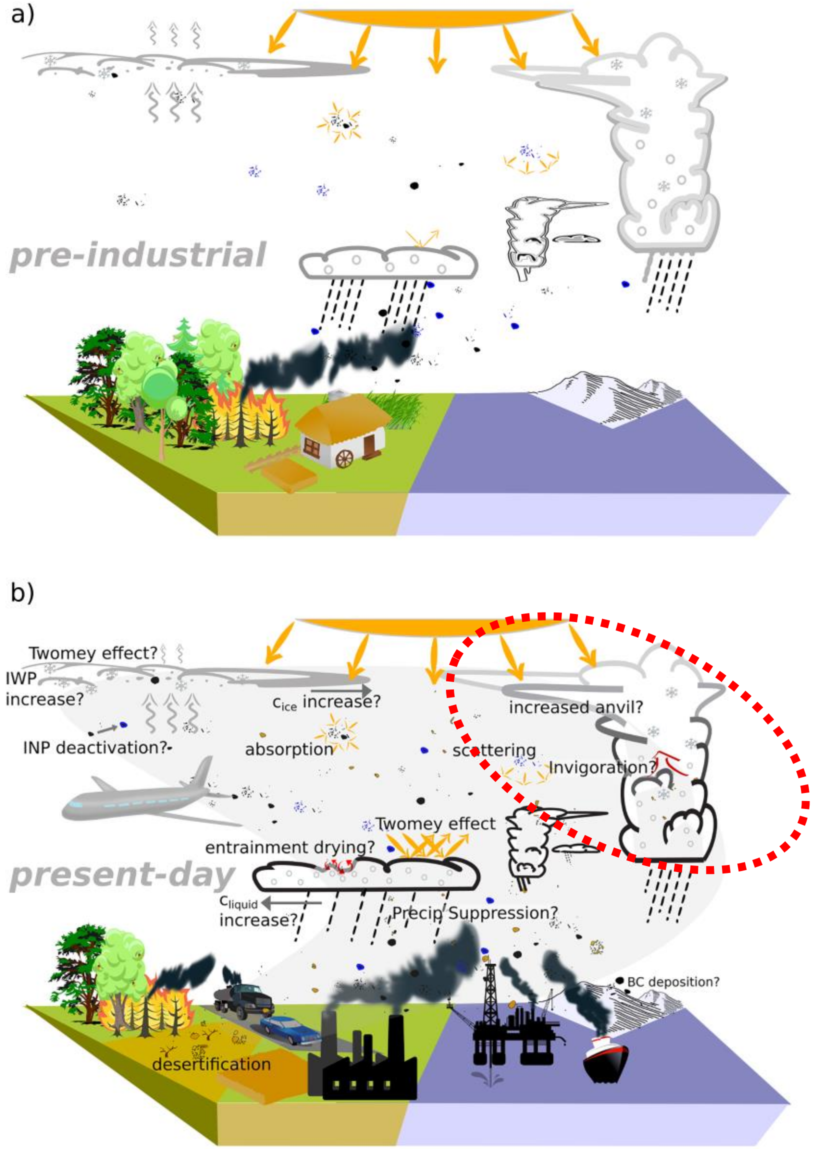


Figure 2. Simplified representation of the impact of anthropogenic aerosol emissions on the Earth system in (a) the preindustrial and (b) the present-day atmosphere. A schematic representation of known processes relevant for the effective radiative forcing of anthropogenic aerosol is summarized for present-day conditions in panel (b), but the same processes were active, with different strengths, in preindustrial conditions. Processes where the impact on the effective radiative forcing remains qualitatively uncertain are followed by a question mark. C_{liquid} and C_{ice} denote liquid and ice cloud fractions, respectively. LWP and IWP stand for liquid and ice water path, respectively. INP stands for ice nucleating particle.

CCN an INPs are important in climate systems via indirect effects on cloud radiative forcing and on precipitation. [*Bellouin et al., 2019*]

CCN concentrations

Northeast Asia

CN Conc.

CCN Conc.

Table 2. Summary of the Measurements in Comparison

Authors	Location	N_{CN}, cm^{-3}	N_{CCN}, cm^{-3}
Kim et al. [2005]	Gosan	2800–5600	
Song and Yum [2004]	Yellow Sea and the South Sea of Korea	1000 (maritime), 2000 (continental)	
	west coast of the Korean Peninsula	5000	
Yum et al. [2005]	west coast of Korean Peninsula	4000–8300	2400–5300 at 1% S
Adhikari et al. [2005]	remote southwest island of Japan	3000–5000	800–2000 at 0.3% S
Hudson and Yum [2002]	Indian Ocean	361	176 at 1% S
Hoppel and Frick [1990]	central Pacific	150–300	
Roberts et al. [2006]	eastern Pacific (pristine-anthropogenic)	<100–10000	20–350 at 0.3% S
Yum and Hudson [2002]	eastern Pacific	252–325	112–157 at 0.6% S
Hudson and Yum [2001]	off the coast of Florida	1200 (maritime), 3600 (continental)	360 (maritime), 1400 (continental) at 1% S
Hoppel et al. [1990]	American Atlantic coast, center of Atlantic, African Atlantic coast, pollution plume in Atlantic	2000, 200, 2000, 10000	
Yum and Hudson [2002]	eastern Atlantic	241–364	126–131 at 0.6% S
Chuang et al. [2000]	eastern Atlantic		27–267 at 0.1% S
O'Dowd et al. [2001]	eastern Atlantic coastal site in Mace Head	400–600 (maritime), 600–1500 (modified maritime air)	
Jennings et al. [1998]	eastern Atlantic coastal site in Mace Head		76–203 at 0.5% S (marine air), 369–1428 at 0.5% S (polluted air)
Eleftheriadis et al. [2006]	coastal site on a remote island in eastern Mediterranean	1300 (background), 3400–4000 (polluted)	
Bates et al. [2000]	Southern Ocean and northeastern Atlantic	300–500	
Yum and Hudson [2004]	Southern Ocean	260–298	32–191 at 1% S
Yum and Hudson [2001]	Artic Ocean	45–497	41–290 at 0.8% S

Pacific

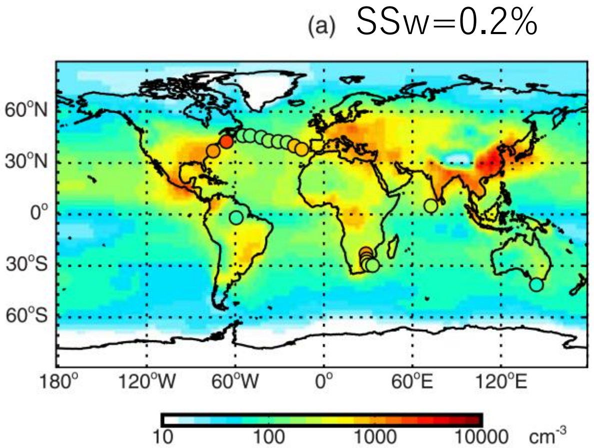
Atlantic

Northeast Asia, polluted in Northern Hemisphere

- **CN Conc. : O(~10^3)**
- **CCN Conc. : (High SSw) O(~10^3)**

Yum et al. (2007) JGR

Spracklen et al. (2008) GRL



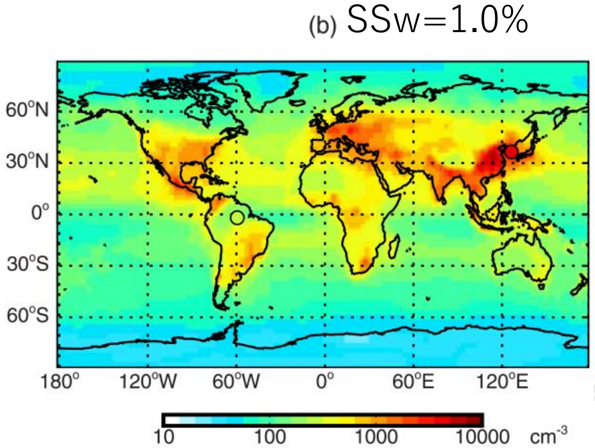


Figure 2. Surface CCN concentrations (cm^{-3}) at (a) 0.2% and (b) 1.0% supersaturation. Model results (background, average for March–May 2000 without BL particle formation) are compared against observations (circles) from Cape Grim (0.23%, March–May) [*Ayers et al.*, 1997], Atlantic Ocean (0.16%, May 1997) [*Hoppel*, 1979], Indian Ocean (0.23%, February–March 1998) [*Cantrell et al.*, 2000], southern Africa (0.3%, March–April 2001) [*Ross et al.*, 2003], Amazonia (0.3% and 1%, May 1999) [*Roberts et al.*, 2003] and Korea (1%, May 2004)[*Yum et al.*, 2005]. Ratio of simulated

Hygroscopicity (*κ*)

κ -Köhler theory

Petters and Kreidenweis, 2007

$$S = a_w \cdot \exp\left(\frac{4\sigma M_w}{RT\rho_w D}\right)$$

$$\frac{1}{a_w} = 1 + \boxed{\kappa \frac{V_s}{V_w}} \longleftrightarrow \boxed{i\,\frac{M_w m_s}{M_s m_w}}$$

Classical Theory

$$\kappa = \sum_i \kappa_i \cdot \frac{V_{si}}{V_s}$$

S : saturation ratio
a_w: water activity
ρ_w : water density
M_w : molecular weight of water
σ : surface tension (solution/air)
R : universal gas constant
T : absolute temperature
D : droplet diamter
V_w : vol. of water
V_s : vol. of dry particulate matter
i : van't Hoff factor
κ : hygroscopicity parameter

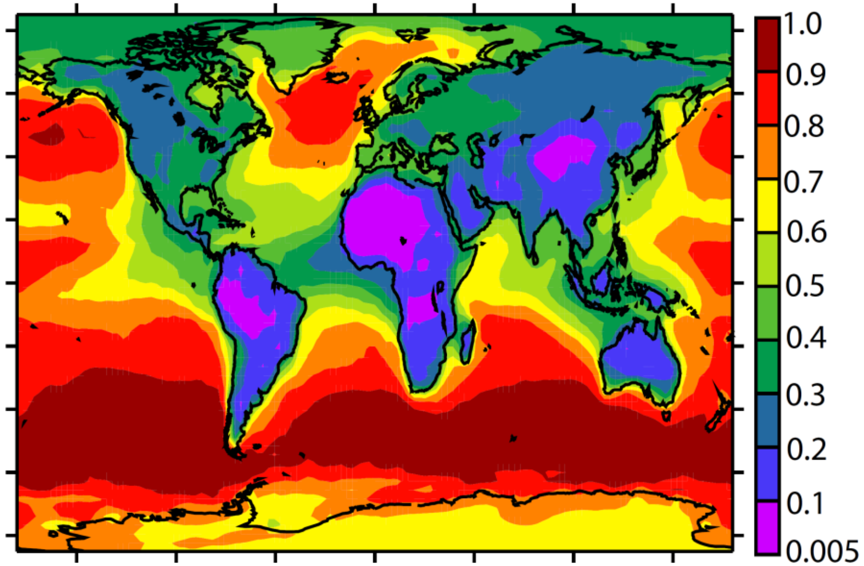


Fig. 1. Annual mean distribution of κ at the surface simulated by EMAC.

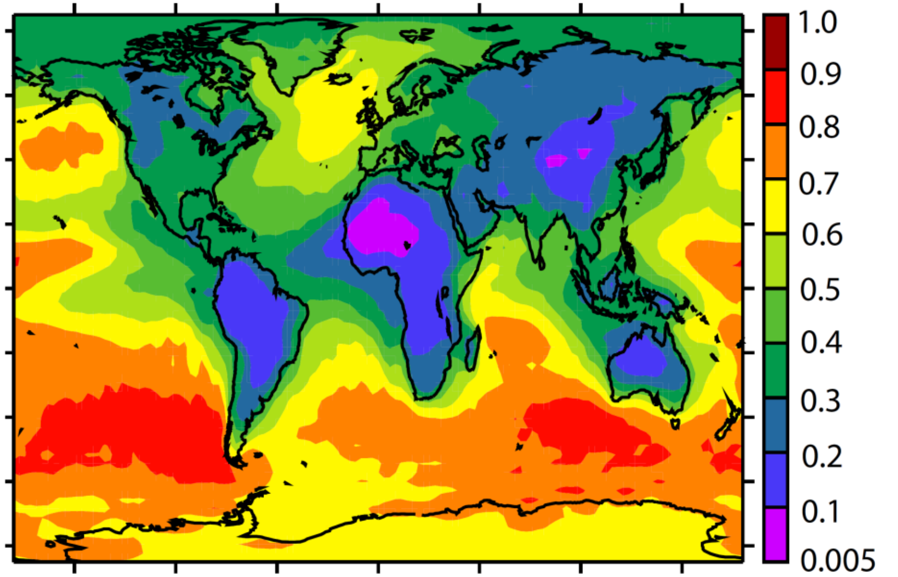


Fig. 2. Annual mean distribution of κ at the altitude of the planetary boundary layer.

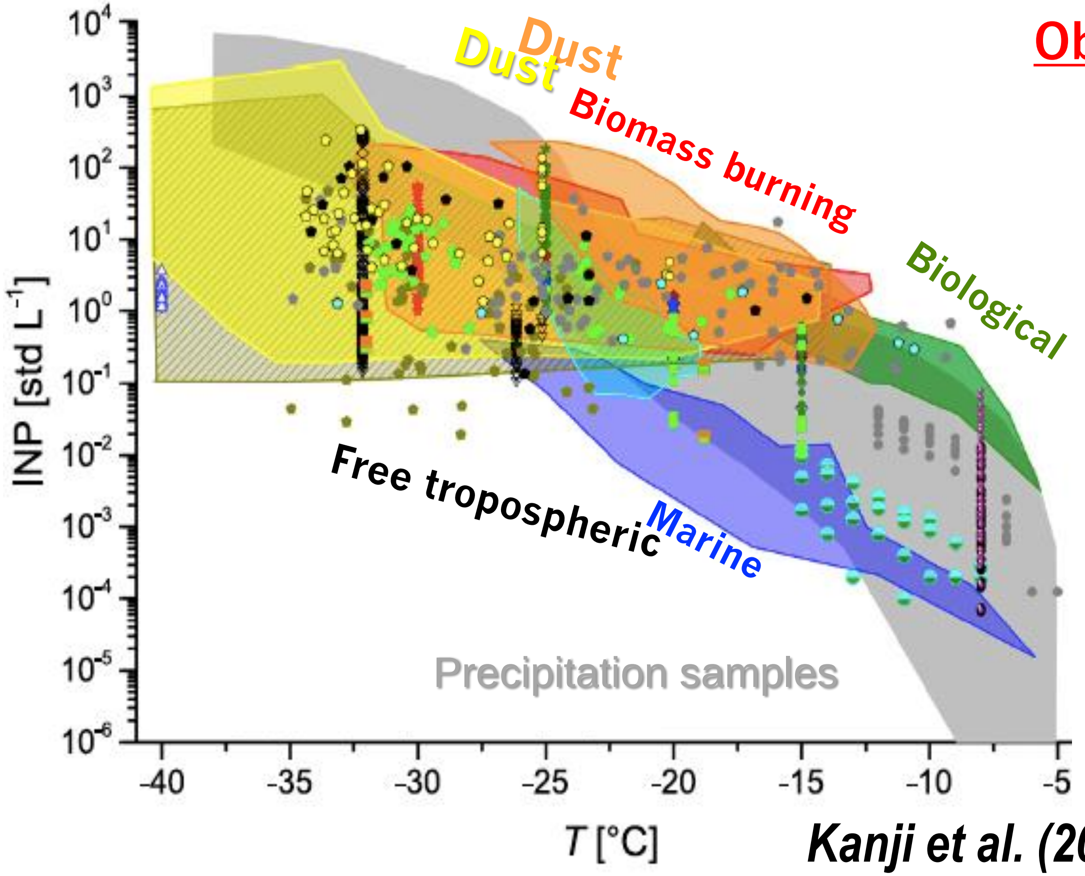
Table 1. Simulated global and regional annual mean κ values (and standard deviation (St Dev)) at the surface and at the simulated PBL height under present day conditions. Standard deviation is calculated for the year from 5-hourly average data. S_c is the critical supersaturation, calculated using the regional mean κ at PBL height. Area column gives total land area for land sites, and marine area for marine sites.

Region	Area (10^{13} m^2)	Mean κ Surface	St Dev Surface	Mean κ PBL height	St Dev PBL height	S_c (%) D_p=60 (nm)	S_c (%) D_p=120 (nm)
Global (Continental)	14.4	0.27	0.21	0.27	0.20	0.48	0.17
Global (Marine)	37.0	0.72	0.24	0.60	0.25	0.33	0.11
N. America	1.61	0.30	0.15	0.29	0.14	0.47	0.17
S. America	1.90	0.17	0.14	0.18	0.13	0.59	0.21
Africa	3.48	0.15	0.12	0.17	0.11	0.61	0.22
Europe	1.14	0.36	0.16	0.33	0.15	0.44	0.15
Asia	3.64	0.22	0.15	0.22	0.13	0.54	0.19
Australia	0.87	0.21	0.16	0.23	0.15	0.52	0.19
N. Atlantic	1.25	0.59	0.18	0.47	0.18	0.37	0.13
Southern Ocean	1.56	0.92	0.09	0.80	0.17	0.28	0.10

- **Evaluated by simulations, but sparce observations.**
- **Requires more study on size-dependency of CCN ability.**

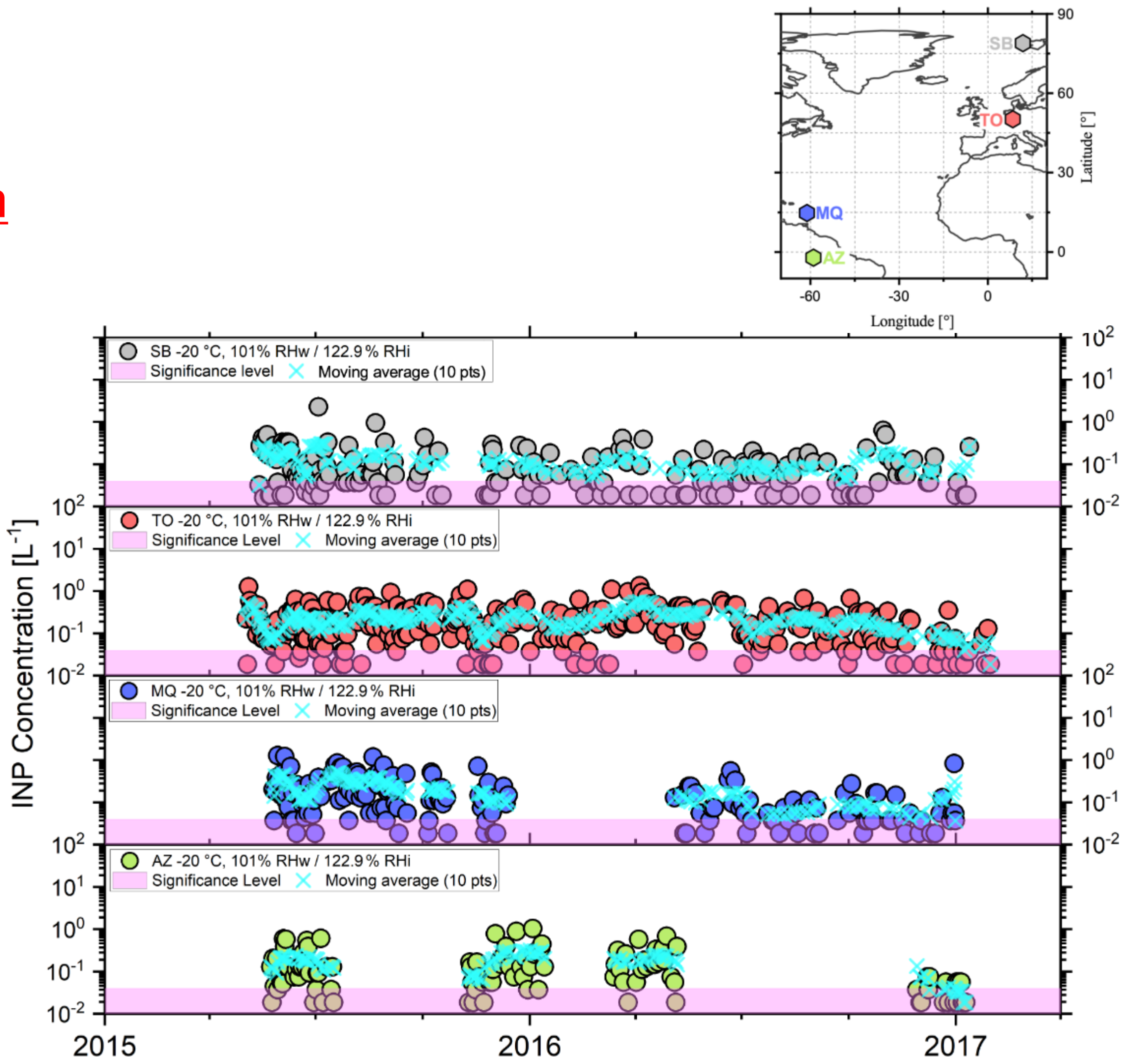
Pringle et al. (2010) ACP

INP concentrations



Kanji et al. (2017)

Observation



Schrod et al. (2020)

- More diverse concentrations at any supercooled T in real atmospheric conditions, compared to specific conditions or events.
- Complicated chemical composition and mixing state in real atmospheric conditions.

- Observed INP Conc. do not differ greatly from site to site, in spite of diverse geographical climates, transport patterns, aerosol characteristics, and anthropogenic impacts.
- Short-term variability overwhelms long-term trends and/or seasonality.
- Spatio-temporal distributions of INPs are still poorly understood.

Ice Nucleation Active Surface-site (*INAS; n_s*) density

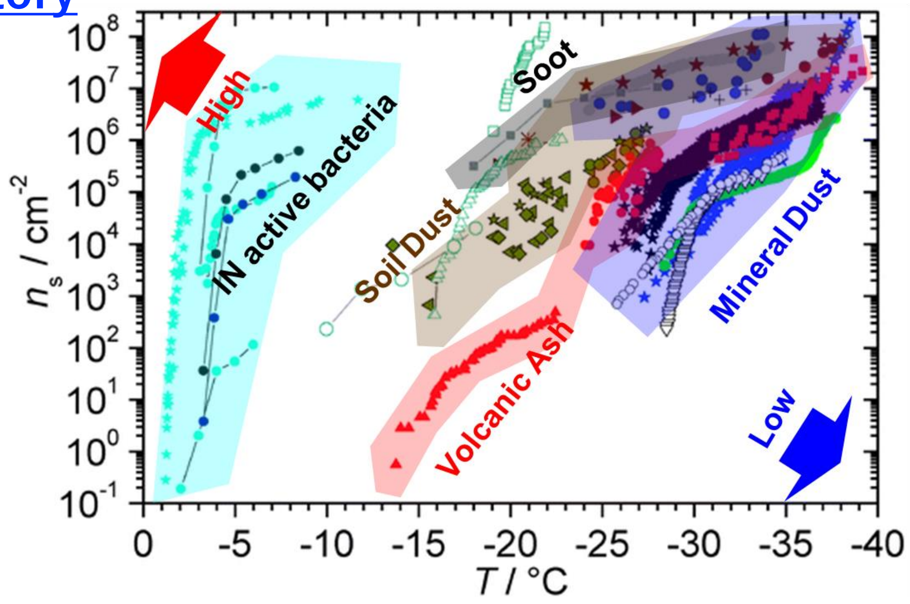
INAS

Connoly et al. 2009; Hoose and Möhler 2012; Kanji et al. 2017; etc.

TABLE 1-1. Definitions of metrics used to summarize and discuss ice nucleation results presented in this chapter.

Metric	Definition
AF **Activated Fraction**	AF = N_{ice}/N_{tot}, where N_{ice} = no. of ice crystals, N_{tot} = total particle no.
F_{ice} **Frozen Fraction**	$F_{ice} = N_{ice}/(N_{ice} + N_{droplets})$, where $N_{droplets}$ is no. of unfrozen drops
n_s and n_m monodisperse aerosol experiments	$n_s(\#\,cm^{-2}) = -\ln(1-AF)/A\,(cm^2)$; A = surface area of 1 particle; $n_m(\#\,mg^{-1}) = -\ln(1-AF)/m_{INP}(mg)$; m = mass of 1 particle
n_s and n_m approximation for experiments with polydisperse aerosol valid for AF < 0.1	$-\ln(1-AF) \cong AF$; for AF < 0.1, $\Rightarrow n_s(\#\,cm^{-2}) = \frac{AF}{A\,(cm^2)} = \frac{N_{ice}}{N_{tot}\times A\,(cm^2)} = \frac{N_{ice}}{A_{total}(cm^2)}$ A_{total} = SA of polydisperse size distribution. For n_m, A_{total} is replaced with the equivalent mass distribution
Ice onset	Defined variably, ranging from first appearance of ice to AF of 1. Typical values include AF = 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1}

Laboratory



- **Various INP ability in each aerosol type.**
- **Higher INAS in dust and biogenic aerosols.**

Murray et al. (2012)

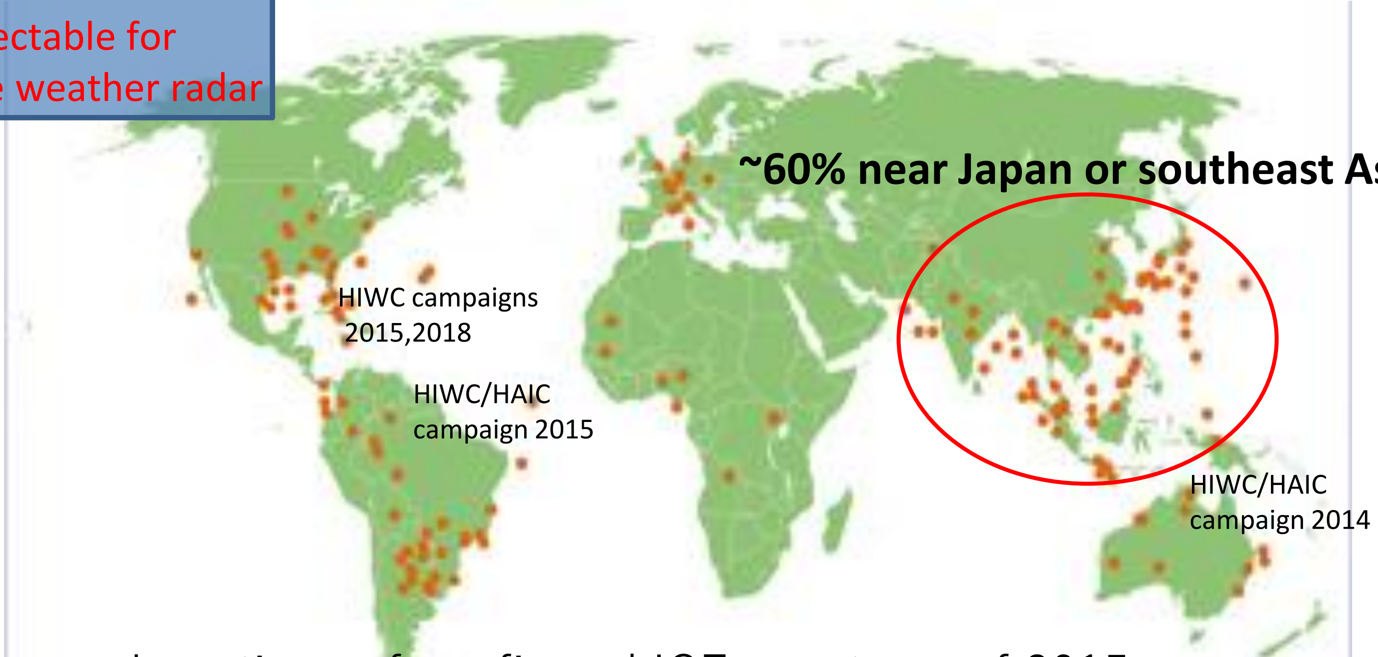
Ice crystal icing (ICI) occurrence

High-level ice clouds sometimes consists of many small ice crystals, which contain high ice water content (HIWC)

Not detectable for airborne weather radar

→ Pilots keep flying in those clouds, not recognizing the aviation hazard of ICI.

→ Incidents have frequently occurred under such conditions.
- Engine icing
- Instrument icing



● Locations of confirmed ICE events as of 2015.
Adapted from *Bravin et al. (2015)*

Objectives

(1) HIWC2022 Flight Campaign (2022/Jul/5-Aug/1, FL, USA)

- Understanding of the actual HIWC conditions in subtropical West Atlantic region
- Investigating of the impact of high concentrations of aerosols on the HIWC conditions
- Microphysical properties of aerosols and clouds in towering cumulus and in marine boundary layers

(2) HIWC Supplementary Campaign (CPEX-CV Flight Campaign) (2022/Sep/5-Sep/30, Cabo Verde)

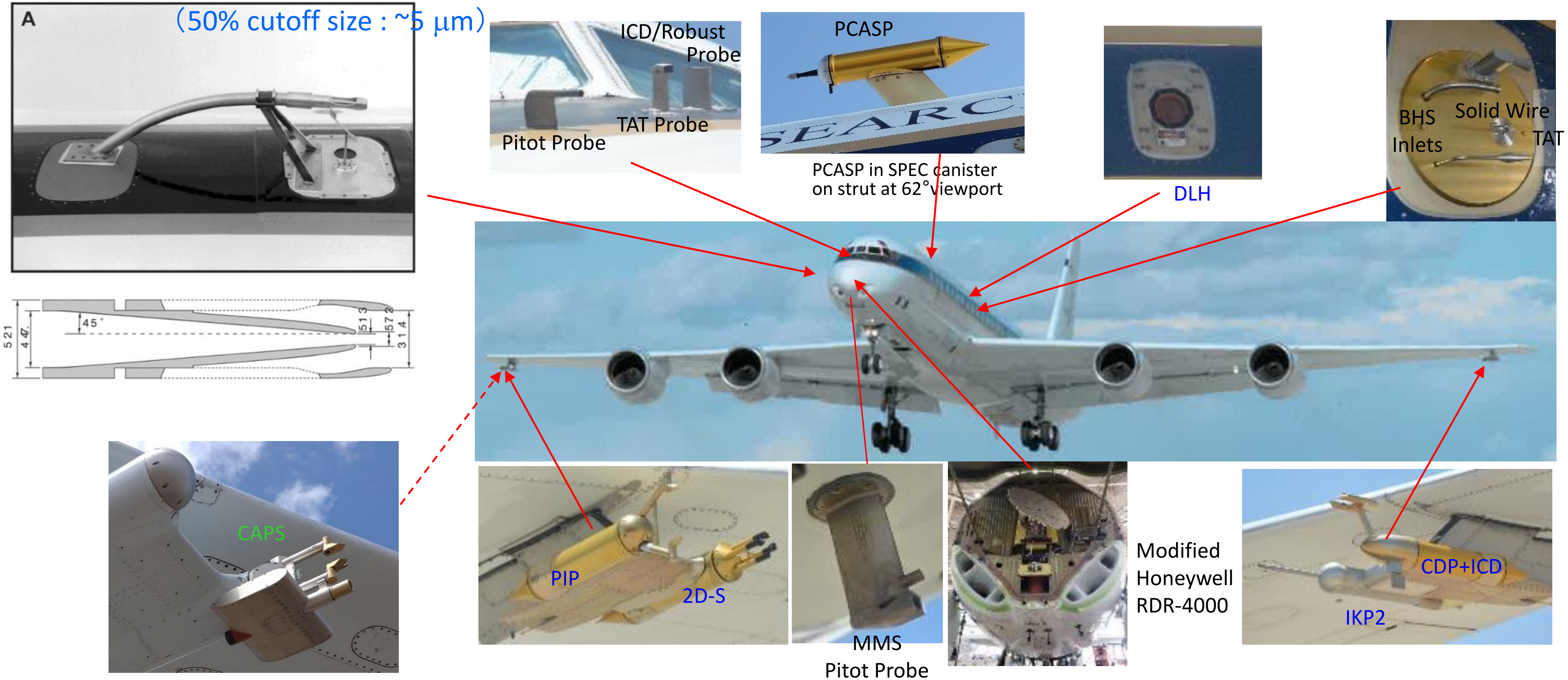
- Understanding of the interactions between large-scale environmental forcings and lifecycle and properties of convective cloud systems in tropical East Atlantic region
- Assessing the impact of observations (winds, thermodynamics, clouds, aerosols) on prediction of tropical weather systems
- Validation of remote-sensing observations via spaceborne sensors vs airborne ones

- Understanding of the actual HIWC conditions in tropical East Atlantic region
- Microphysical properties of aerosols and clouds in high aerosol conditions (Saharan dust layers etc.)

Overview of NASA DC-8 with HIWC-2022 Instrumentation

CPEX-CV

UH Inlet ← *McNaughton et al. 2007*



- Cloud particle spectra: CDP-2, 2D-S, PIP, CAPS
- Cloud Water Content: IKP2, SEA TWC/LWC
- RDR-4000 Wx Radar

Strapp et al. 2016

- Diode Laser Hygrometer, Licor/WVSS2 for background water vapor
- UH Inlet and supporting aerosol instrumentation

- Aerosol : PCASP, SMPS(3080+3081), OPC(KC-01E), CCN-200, Impactors(for TEM grid, Silicon Wafer grid), Membrane Filter sampler

Configuration of Aerosol Rack

OPC

Laptop PC for OPC & SMPS

Laptop PC for IN Counter (INC)

Inlet Pressure Control for
CCN Counter (CCNC)

Electrostatic Classifier (EC),
Differential Mobility Analyzer (DMA)

A/D Converter

Membrane Filter (MF) holder sampler

Laptop PC for two Impactors

Impactor#1
(AS-TEM)

Impactor#2
(AS-SW)

Monitor & Keyboard
for M300

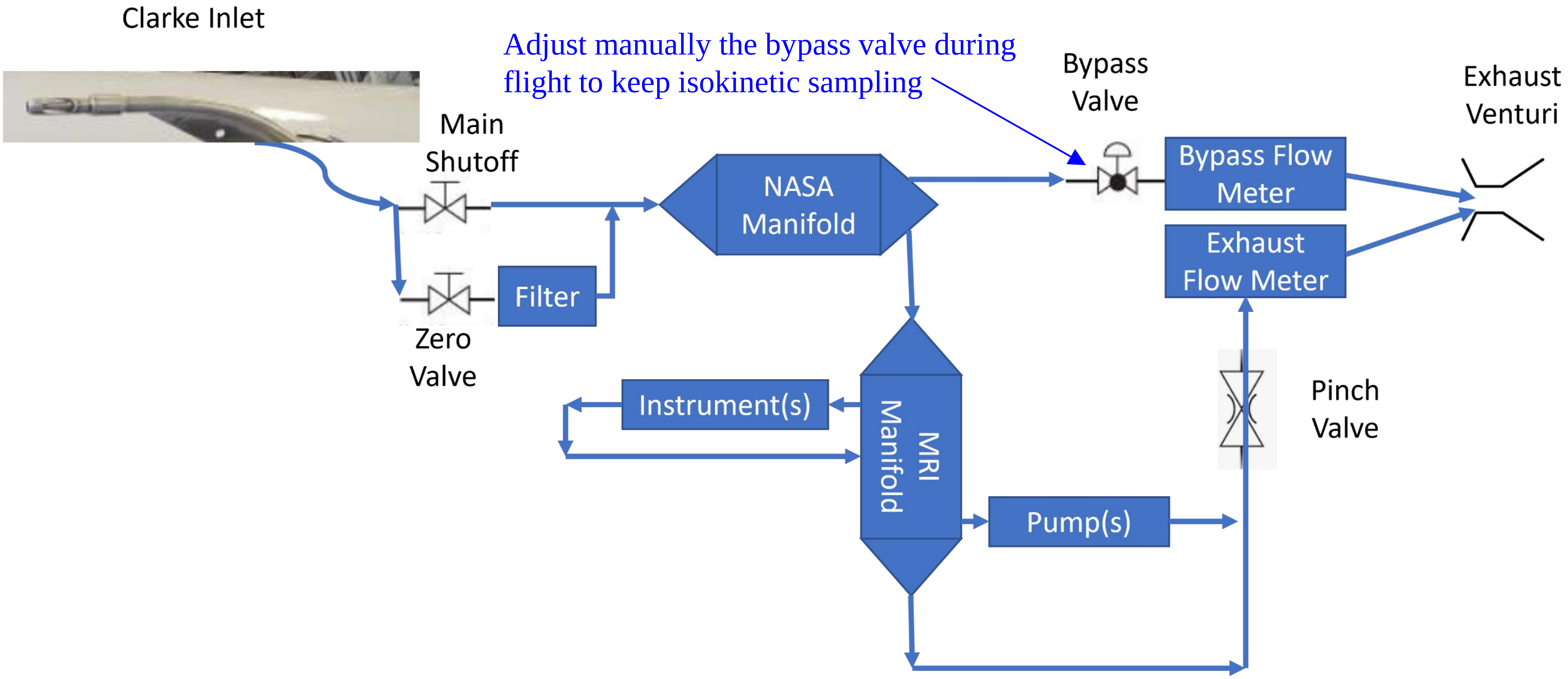
M300

CPC

Bypass valve to keep isokinetic sampling

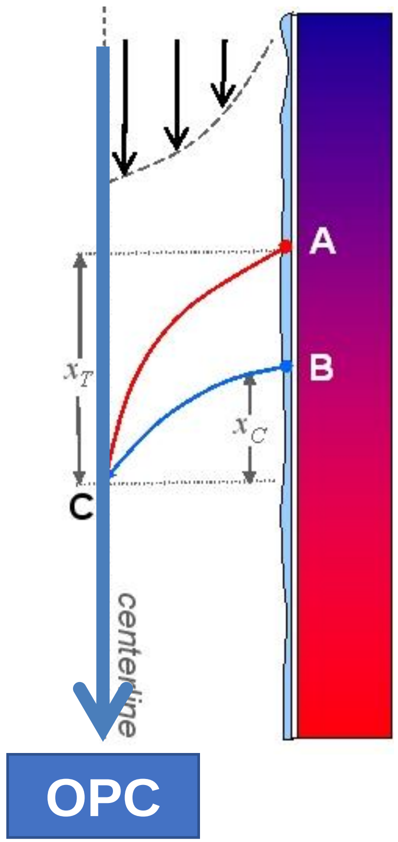
CCNC Rack

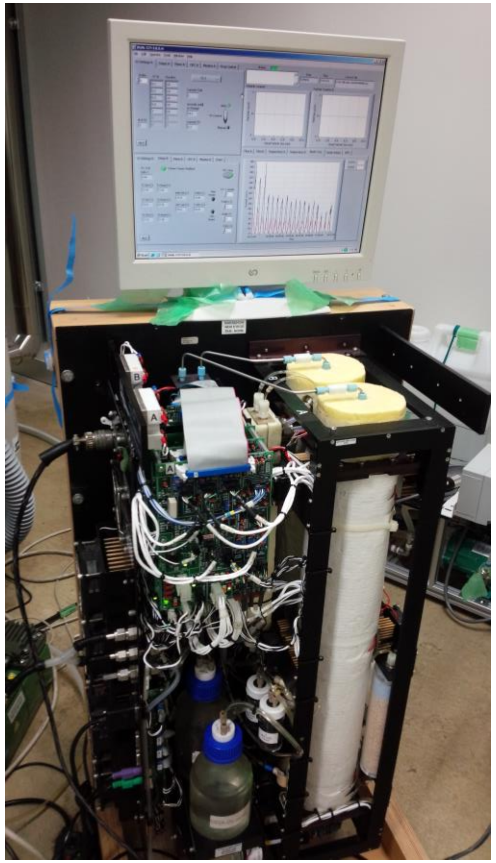
Sampling diagram from inlet to exhaust



CCN counter

(Continuous-Flow Streamwise Thermal-Gradient Chamber)





DMT CCN-200
(dual-column version)

Column-A:
SSw = 0.5% (fix)

Column-B:
SSw = 0.1 (11), 0.3 (4), 1.0 (5min)%

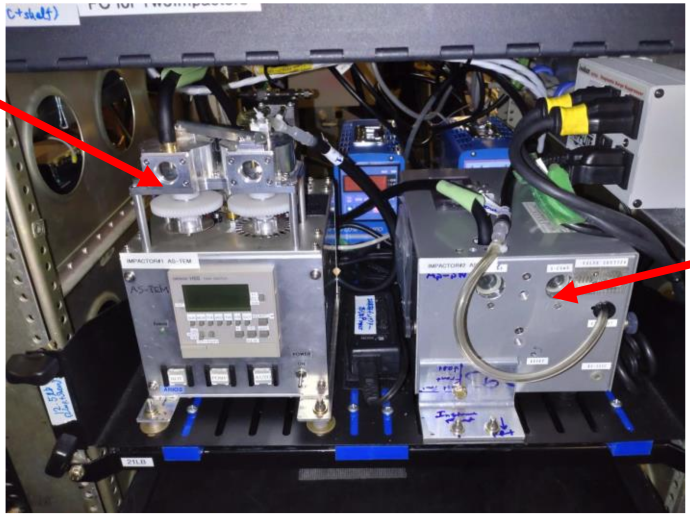
- water supersaturation in chamber with wetted wall and longitudinal thermal gradient
  (Thermal diffusivity ＜ Molecular diffusivity of water vapor)
- some aerosols acivated to water droplets, counted with OPC

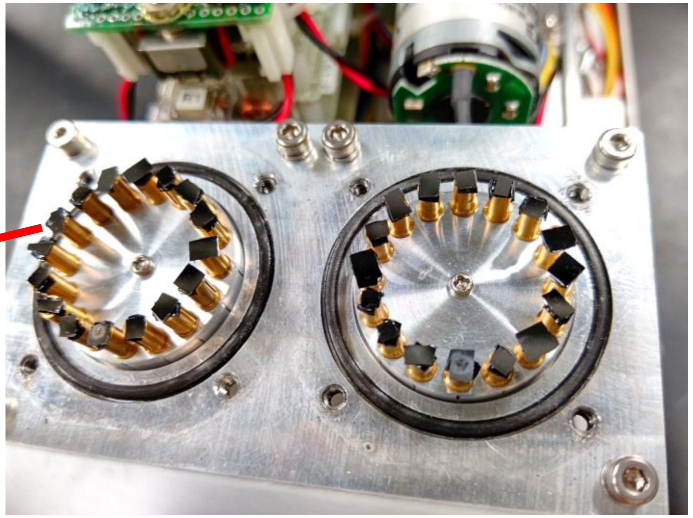
Aerosol Sampling Devices

Impactor sampling (2 types)

TEM grid

cutoff size:
0.7, 0.2 µm

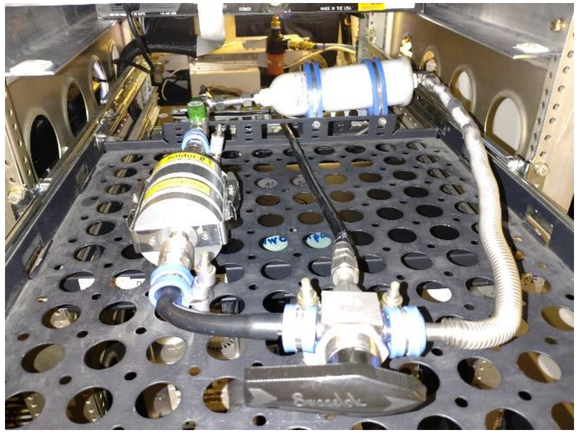




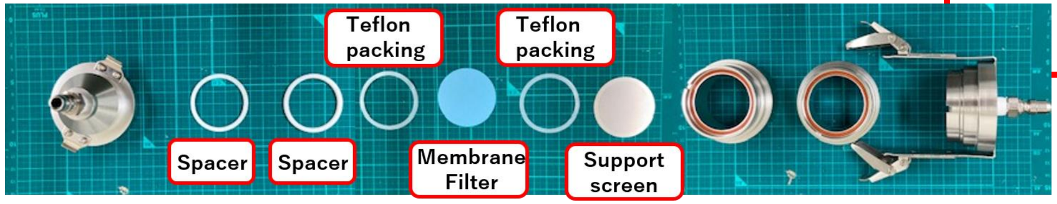
Silicon wafer

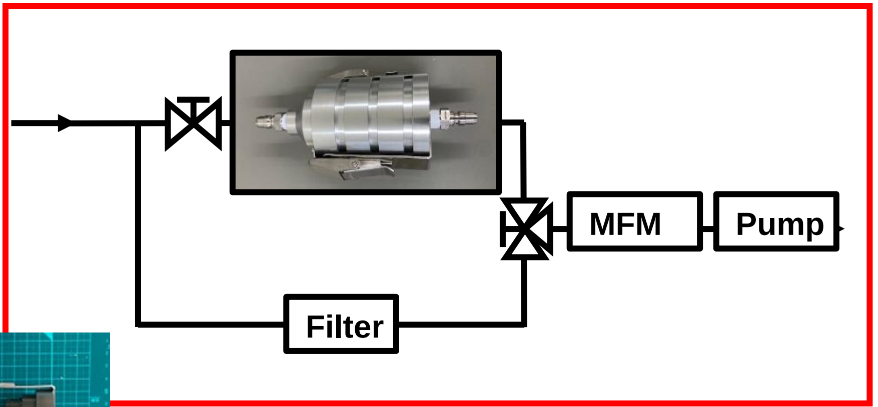
cutoff size: 1 µm

Filter sampling



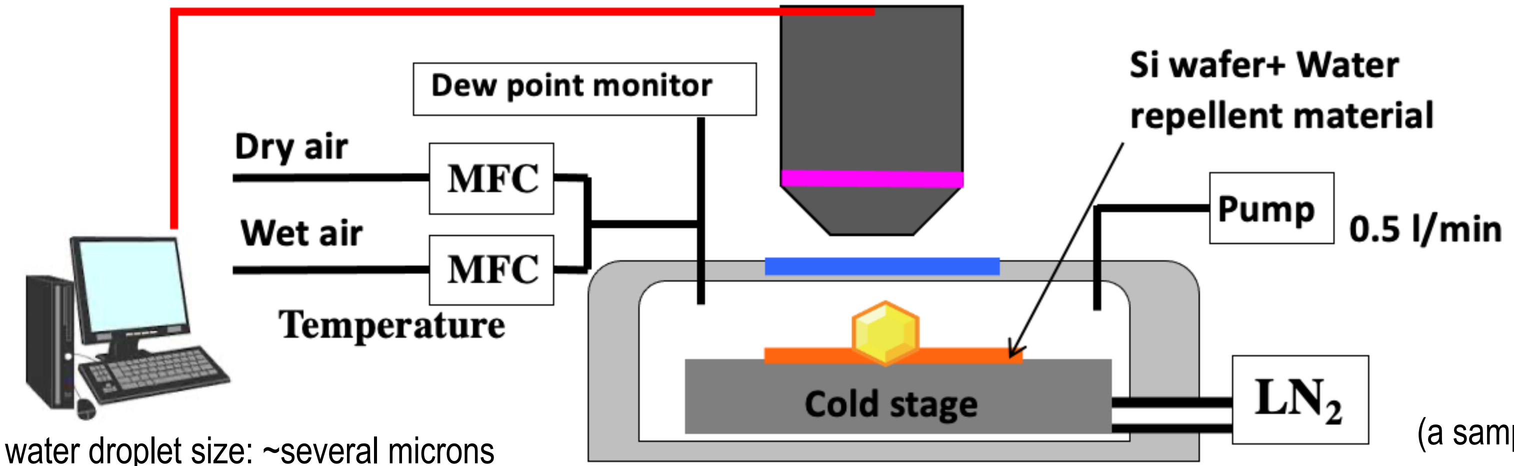
Sartorius PTFE filter
(φ47 mm, pore size 0.45 µm)





Individual Droplet Freezing Method (IDFM)

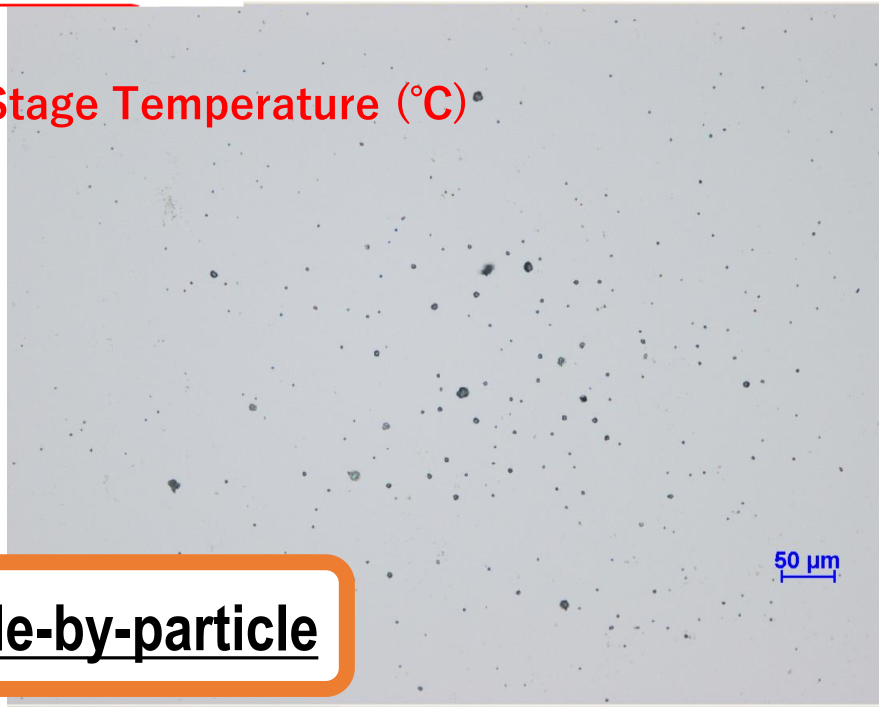
Iwata and Matsuki, 2018



water droplet size: ~several microns

(a sample of the same scale as the motion pictures on your left)

Stage Temperature (℃)



Identify aerosol activated to ice particle, INP, particle-by-particle

Single INP identification and analysis

IDFM

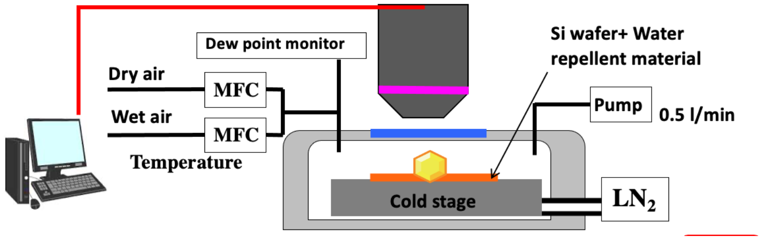
cooling to -22°C*

▼

wait 10 sec in case of non-freeze

▼

cooling to -30°C



*ATD freezes at -22°C

Spectrometer systems

INP

▼

Raman : chemical compounds

▼

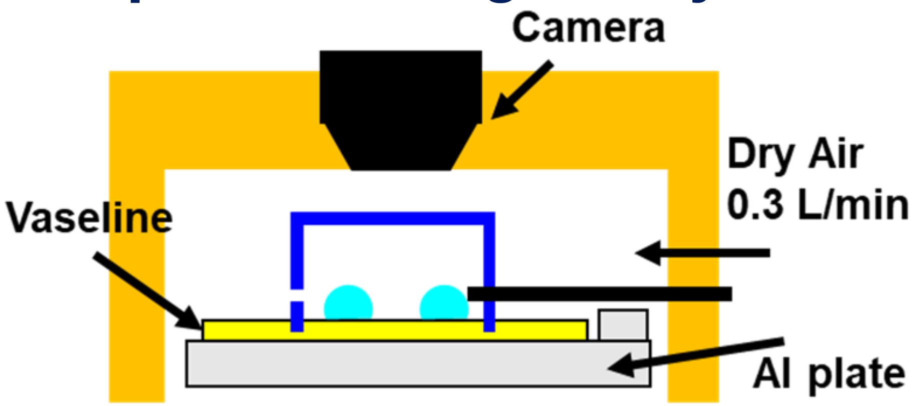
SEM-EDX : morphology, elemental composition

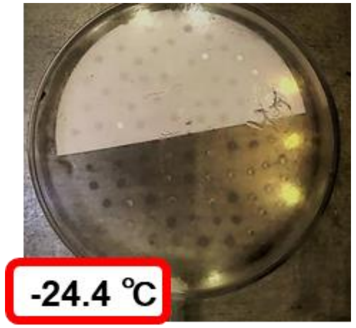
(Nanofinder, Tokyo Instruments)

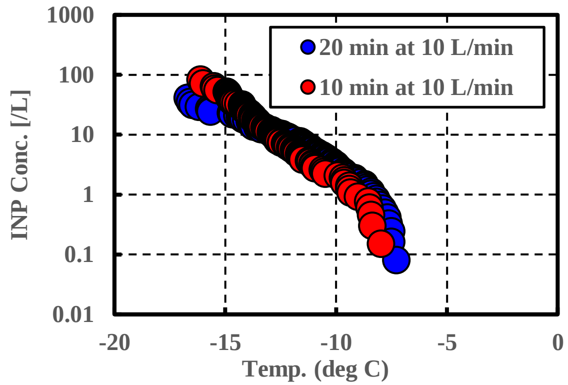
(JSM-7100F, JEOL)

cf. Price et al., 2018

Droplet Freezing Assay on Filter



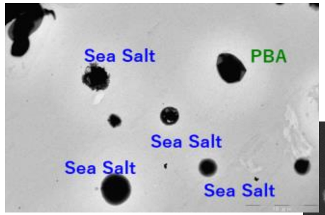




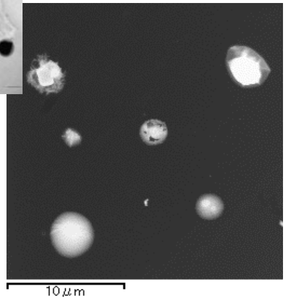
- place an array (~100 #) of ultrapure water droplets (1 μL) onto PTFE MF
- cooling rate: -1 ℃/min, record the freezing T for each droplet
- contact angle between MF and droplets: α=131.6 °
- the number of INP in every 0.5℃ intervals -> calculate INP conc., INAS

Individual Particle Analysis

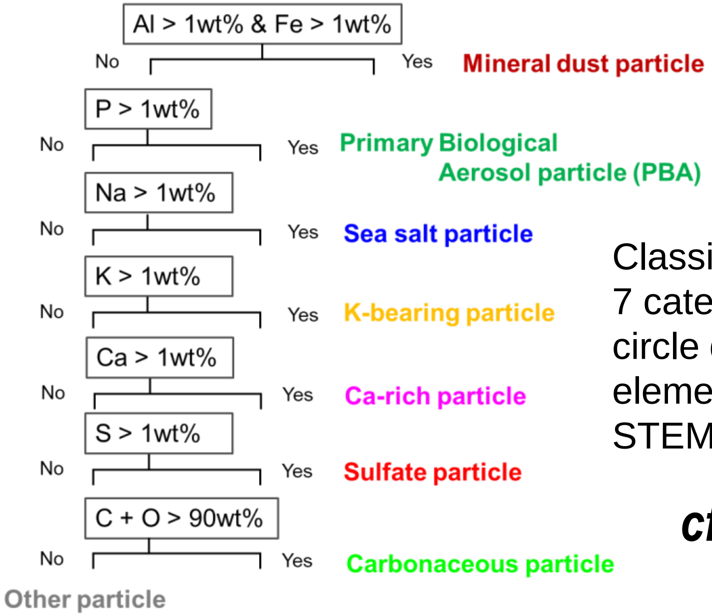
TEM (JEM-1400, JEOL, Tokyo)
+ SEM/EDX (Oxford Inst., Tokyo)



TEM mode



STEM mode

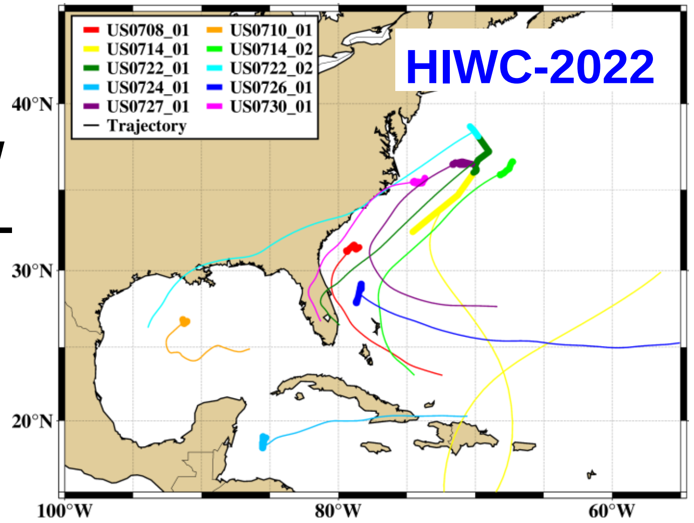


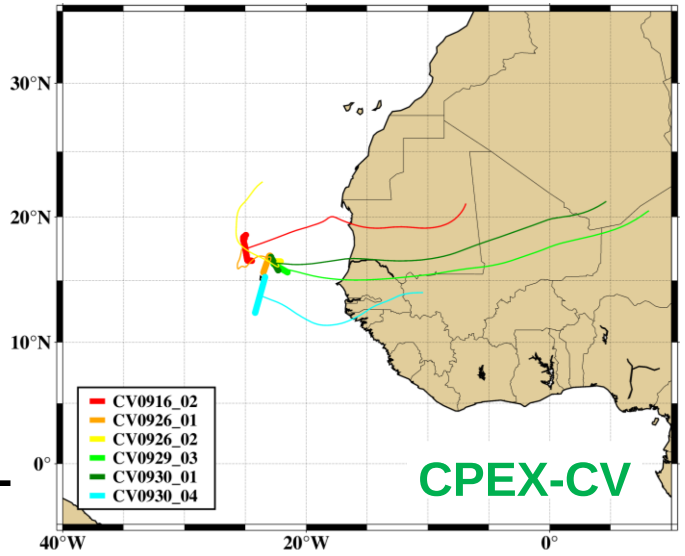
Classify individual particles into 7 categories through equivalent circle diam. by TEM mode and elemental composition by STEM mode (120 kV, 20 sec)

cf. Adachi et al., 2020

Sampling Data (filters)

	ID	Date	Start [UTC]	Stop [UTC]	Period [min]	Ave. Alt [m]	Ave. Flow [L/min]
HIWC-2022 10 samples	US0708_01	2022/7/8	19:19	19:36	16.8	619.5	12.1
	US0710_01	2022/7/10	19:47	20:15	27.3	302.2	18.5
	US0714_01	2022/7/14	14:50	15:28	37.8	11012.7	3.8
	US0714_02	2022/7/14	17:51	18:16	24.8	340.1	12.1
	US0722_01	2022/7/22	13:45	14:21	36.0	186.7	12.4
	US0722_02	2022/7/22	14:22	14:33	11.0	190.9	12.6
	US0724_01	2022/7/24	14:58	15:28	30.0	189.6	12.1
	US0726_01	2022/7/26	14:02	14:33	31.0	169.4	12.4
	US0727_01	2022/7/27	14:44	15:14	30.6	146.4	12.7
	US0730_01	2022/7/30	17:06	17:36	29.7	168.3	12.5
CPEX-CV 6 samples	CV0916_02	2022/9/16	19:51	20:26	35.0	3109.8	7.3
	CV0926_01	2022/9/26	5:03	5:19	16.3	5562.1	6.6
	CV0926_02	2022/9/26	11:48	11:54	6.3	3185.8	9.6
	CV0929_03	2022/9/29	16:09	16:21	11.6	4007.0	8.7
	CV0930_01	2022/9/30	8:29	8:41	12.0	5669.4	7.0
	CV0930_04	2022/9/30	14:31	14:54	22.9	9389.1	4.6

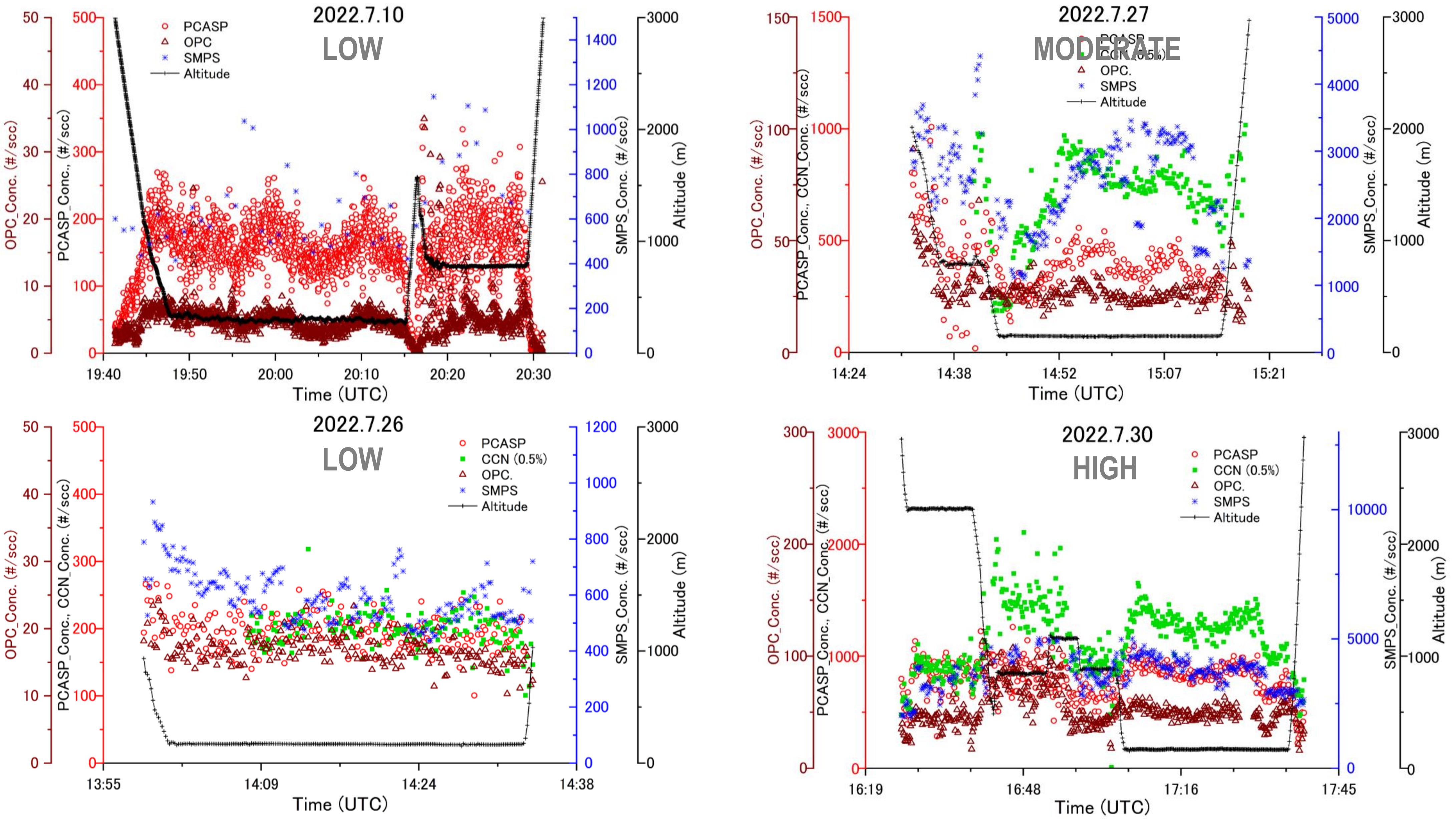




Results(aerosol)

HIWC-2022

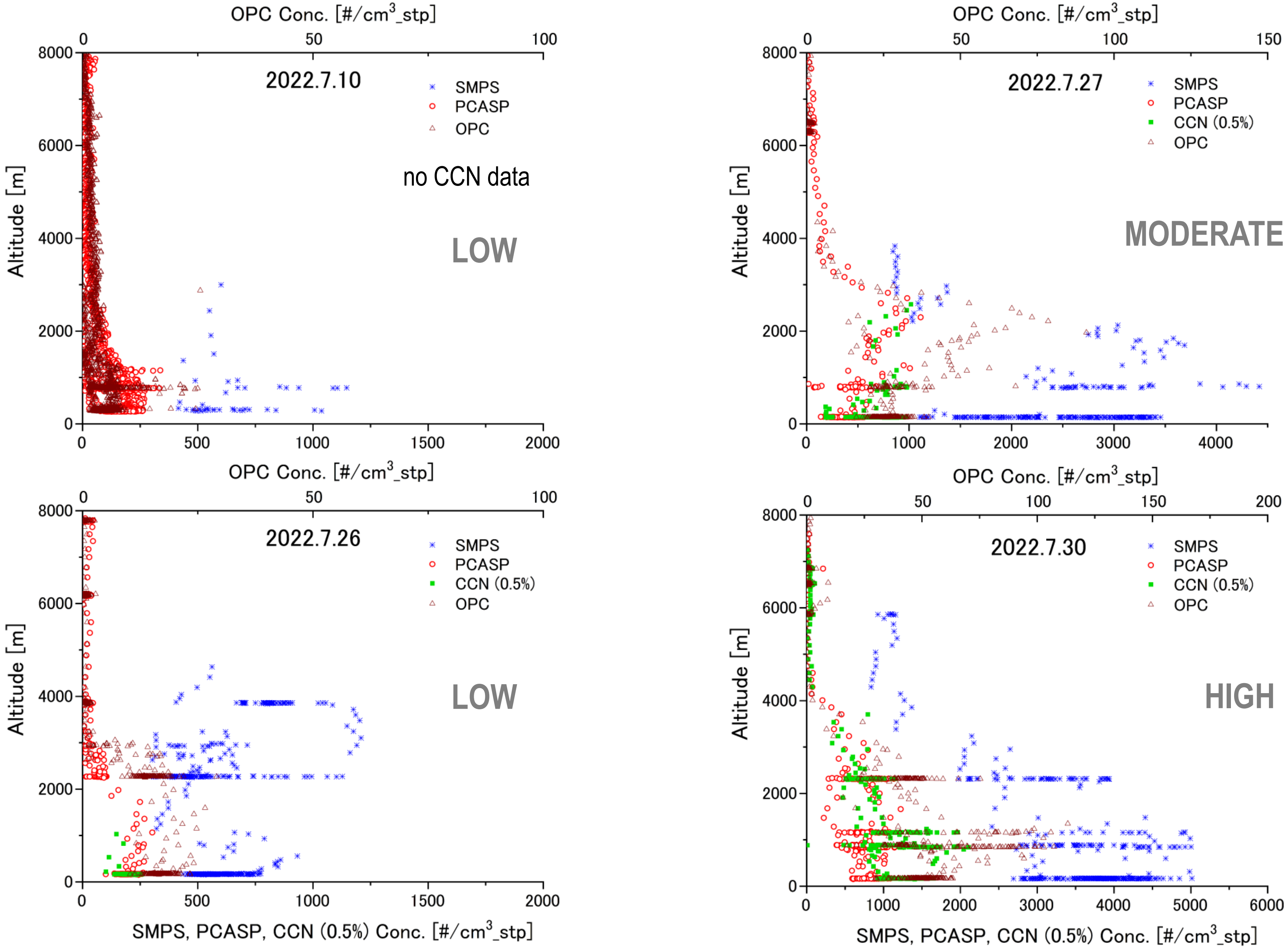
Time series of aerosol conc. (H < 3 km)



Results(aerosol)

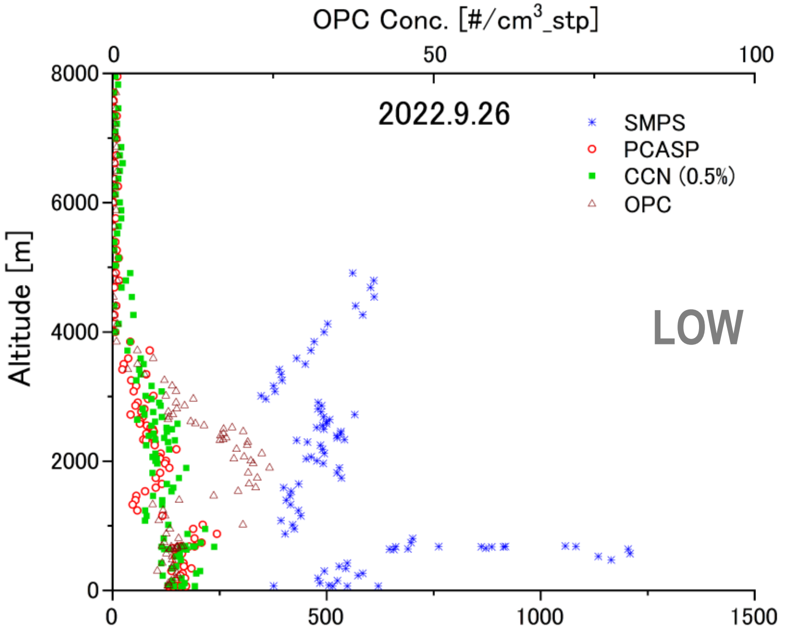
Vertical profiles of aerosol conc. (H < 8 km)

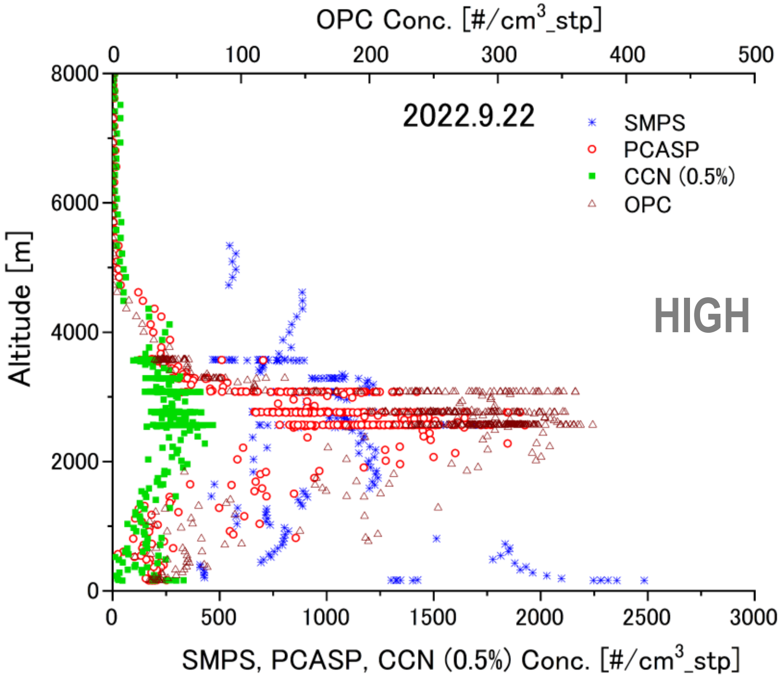
HIWC-2022

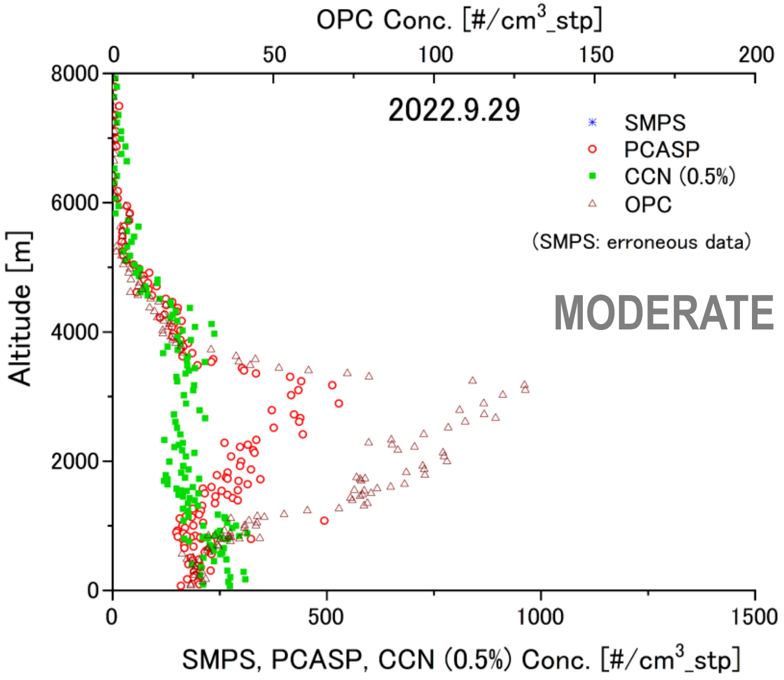


Vertical profiles of aerosol conc. (H < 8 km)

CPEX-CV

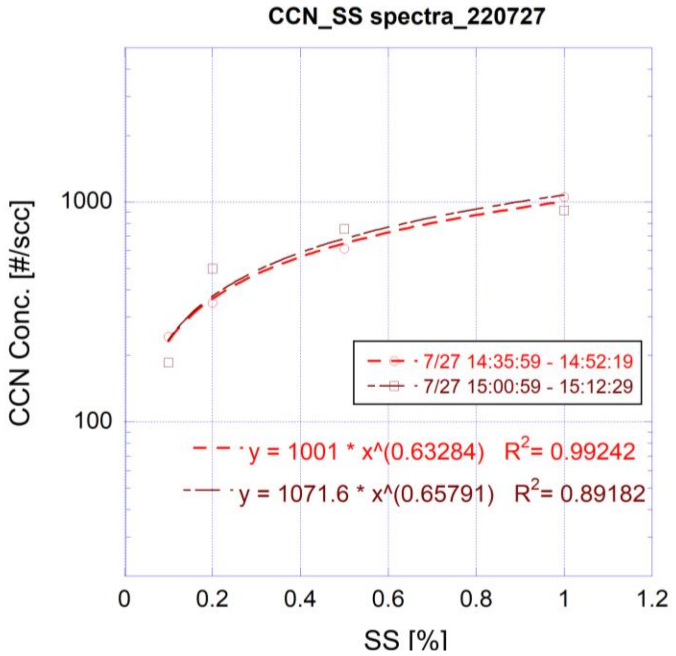


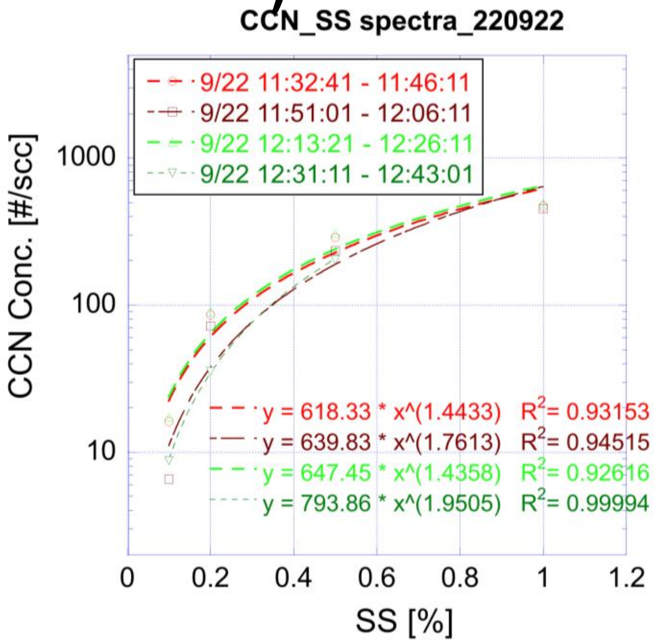


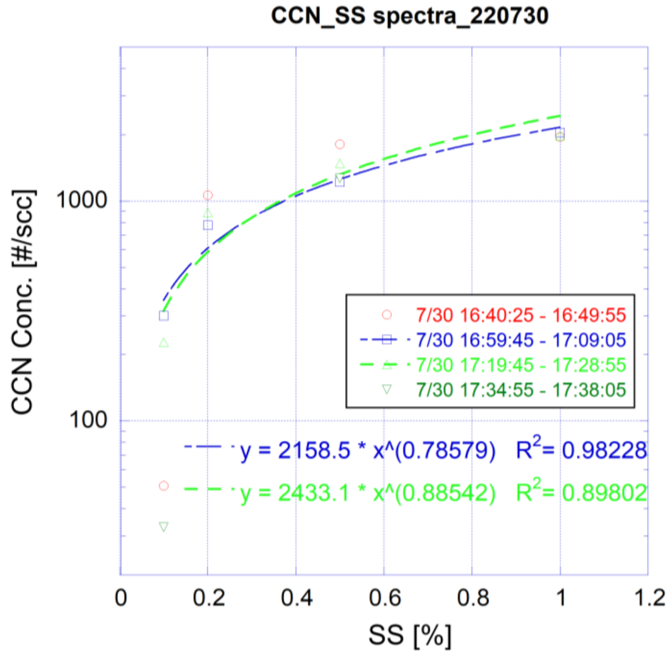


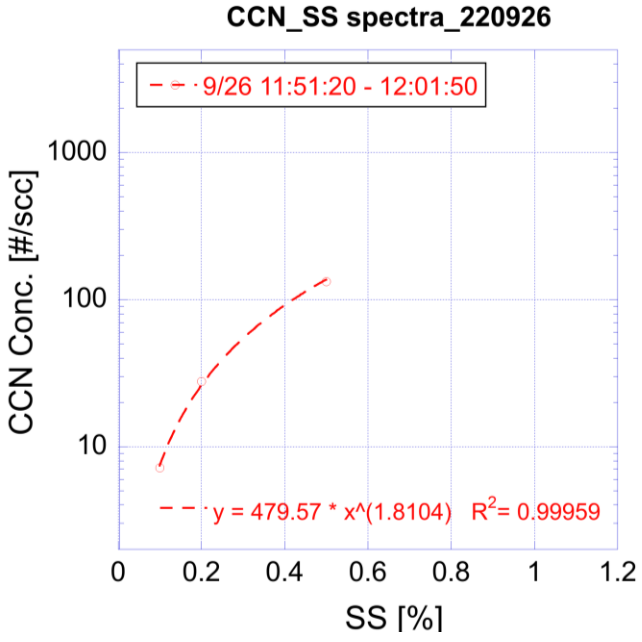
Results(CCN)

CCN SS spectra (at low levels)





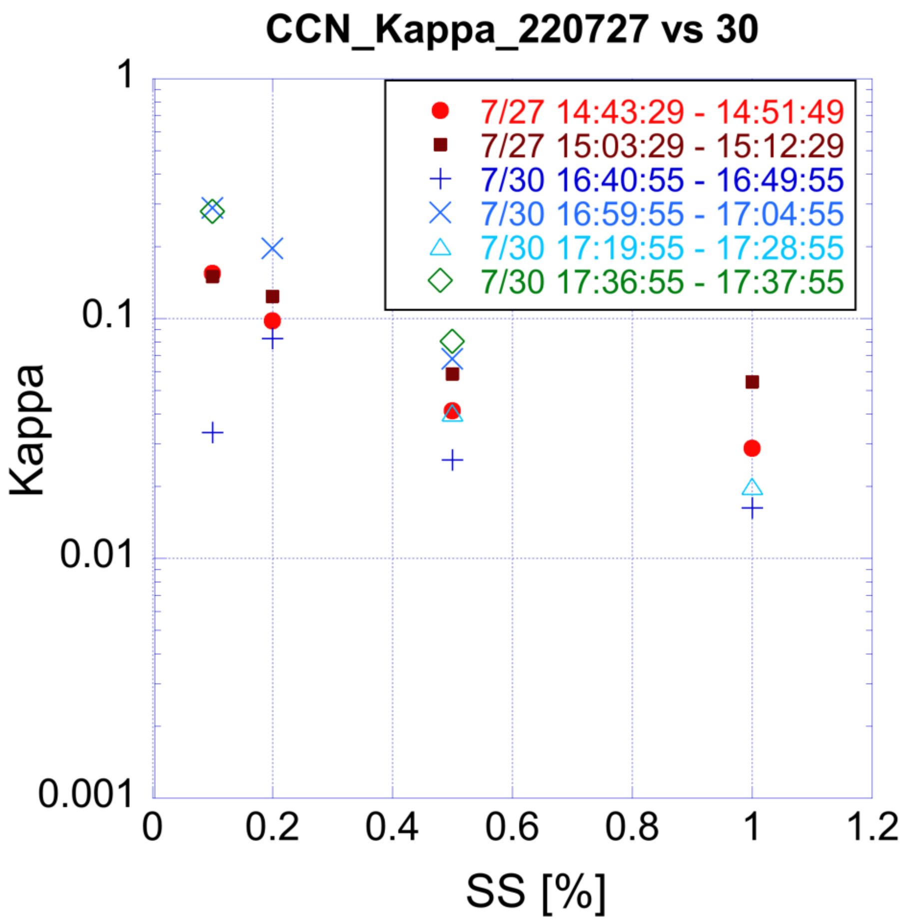




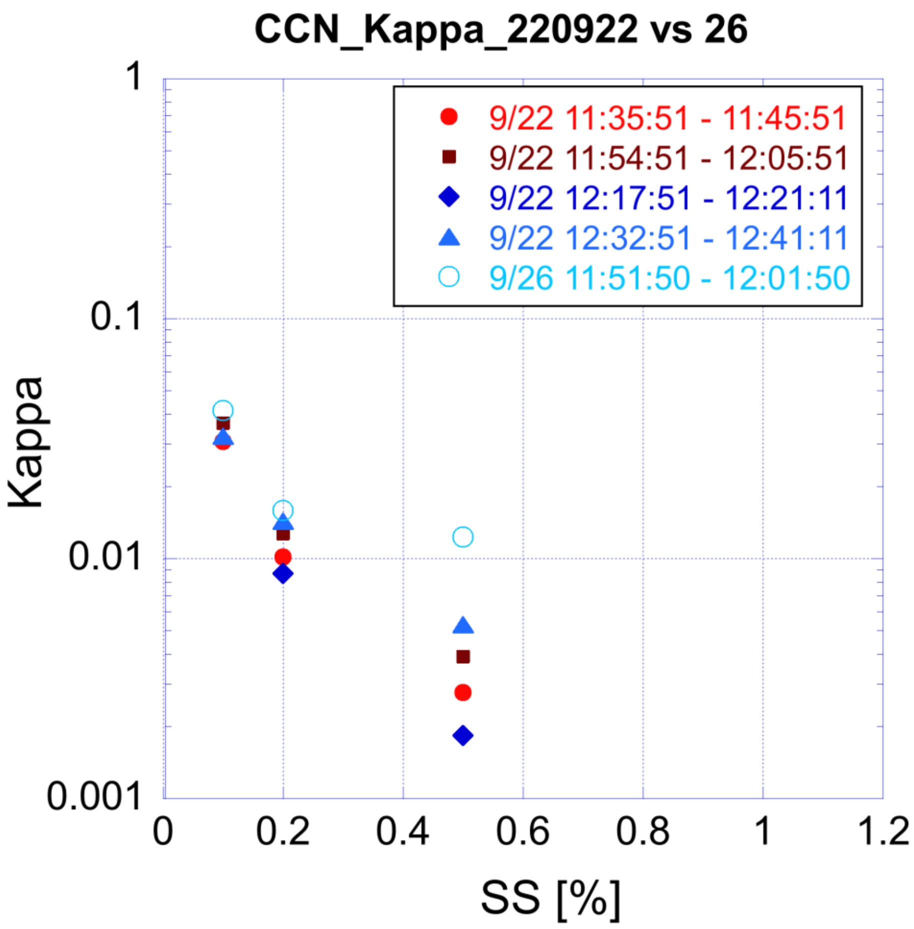
HIWC-2022

CPEX-CV

Hygroscopicity (*K*) (at low levels)



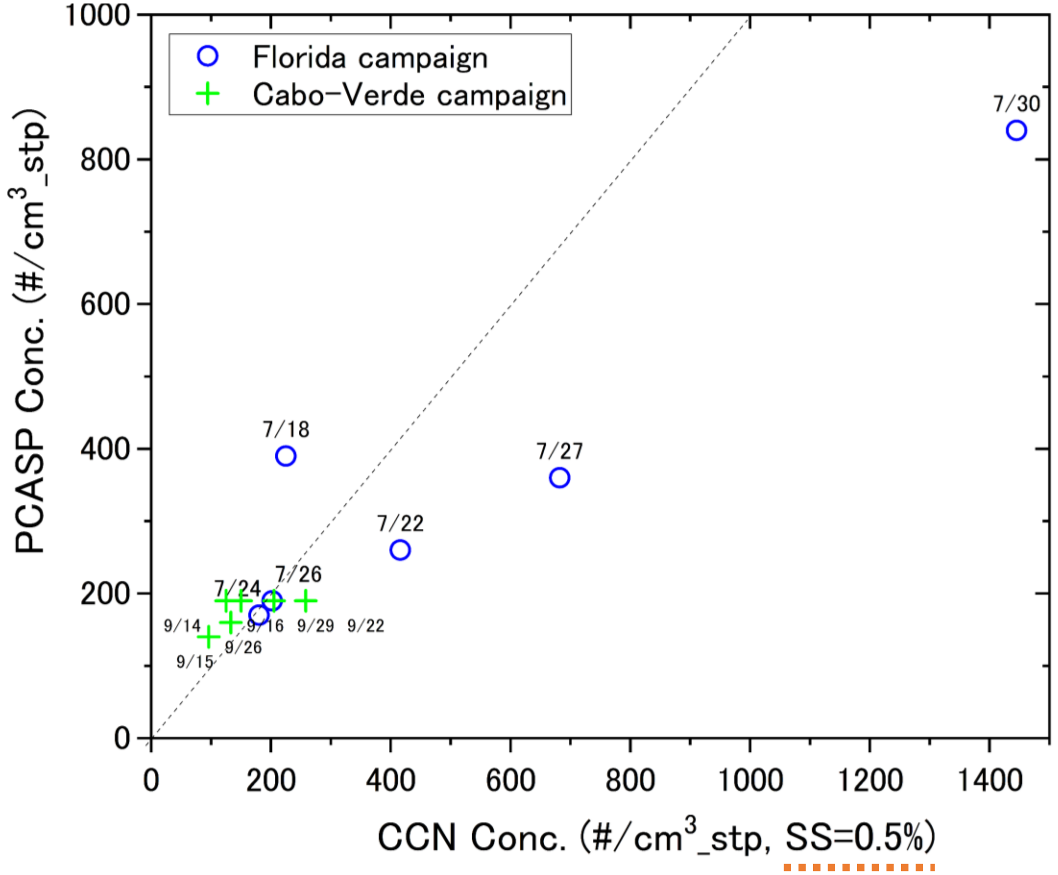
HIWC-2022

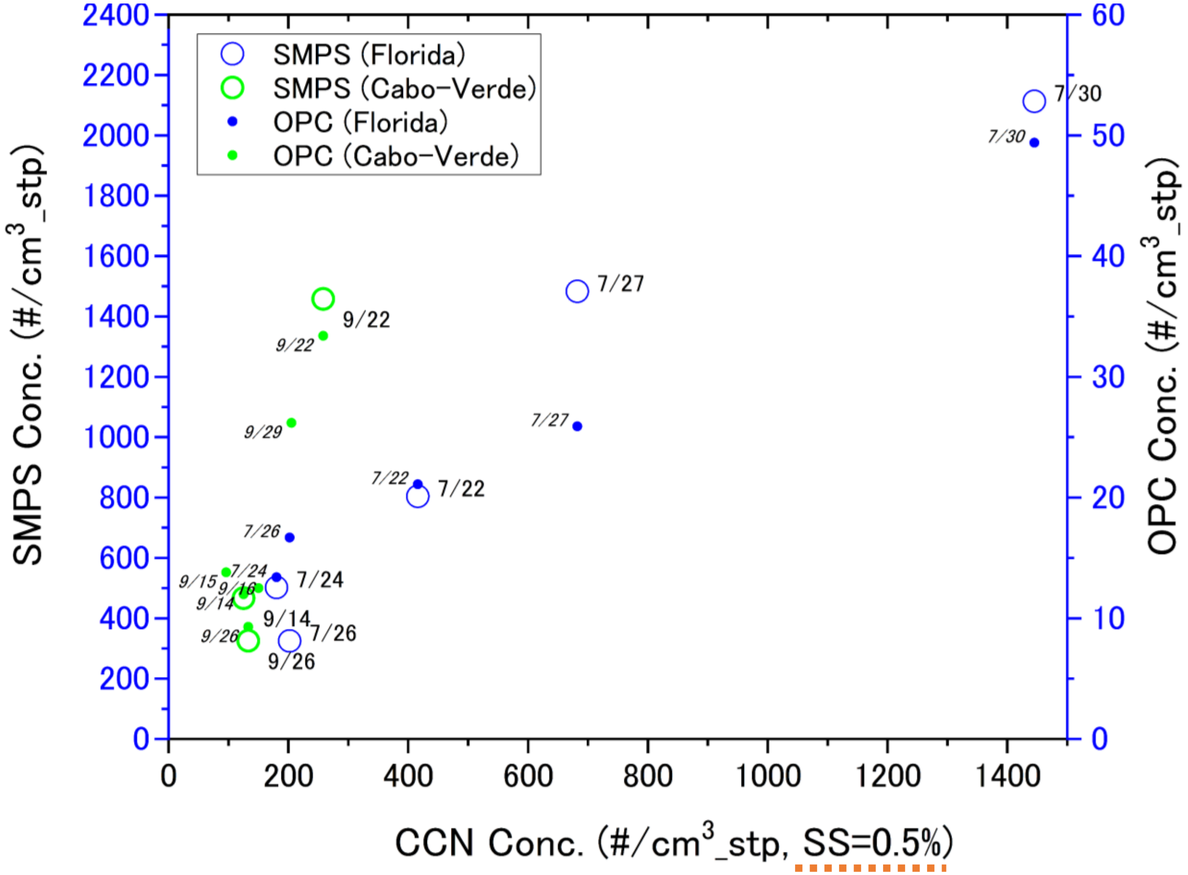


CPEX-CV

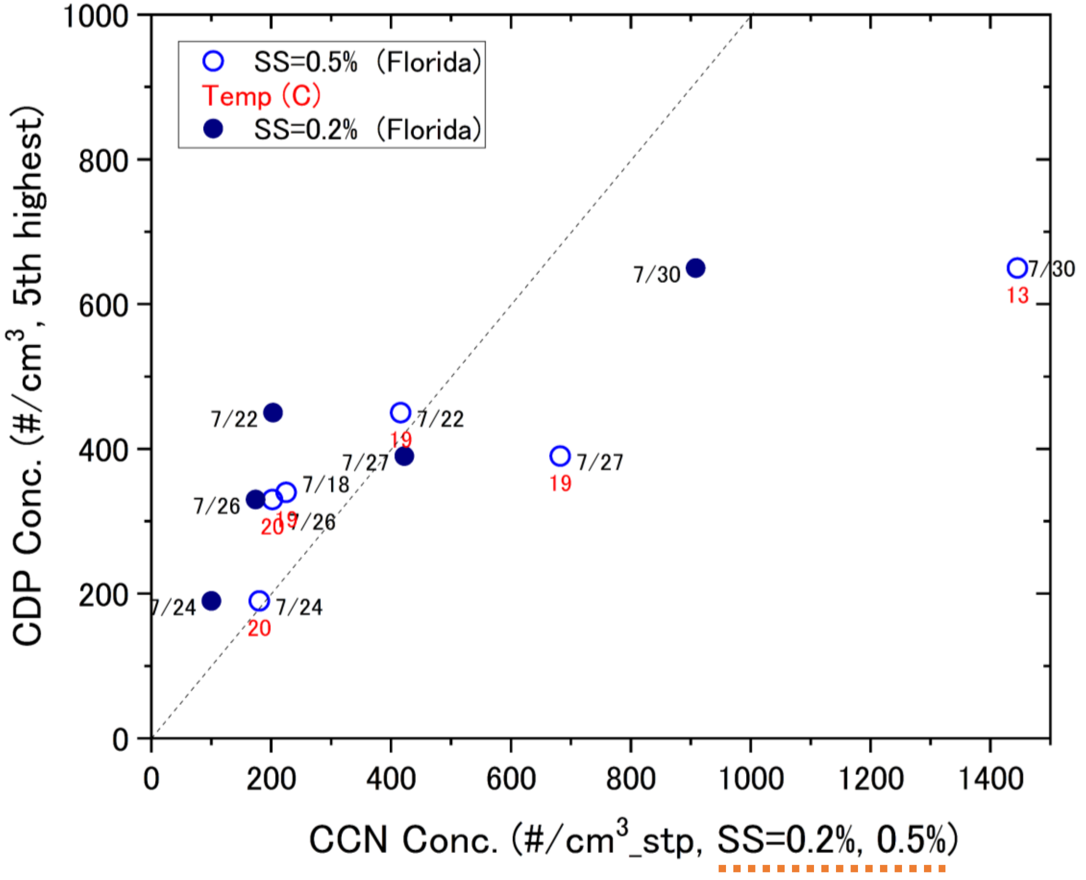
HIWC-2022
CPEX-CV

CCN vs PCASP or SMPS (at low levels, average)

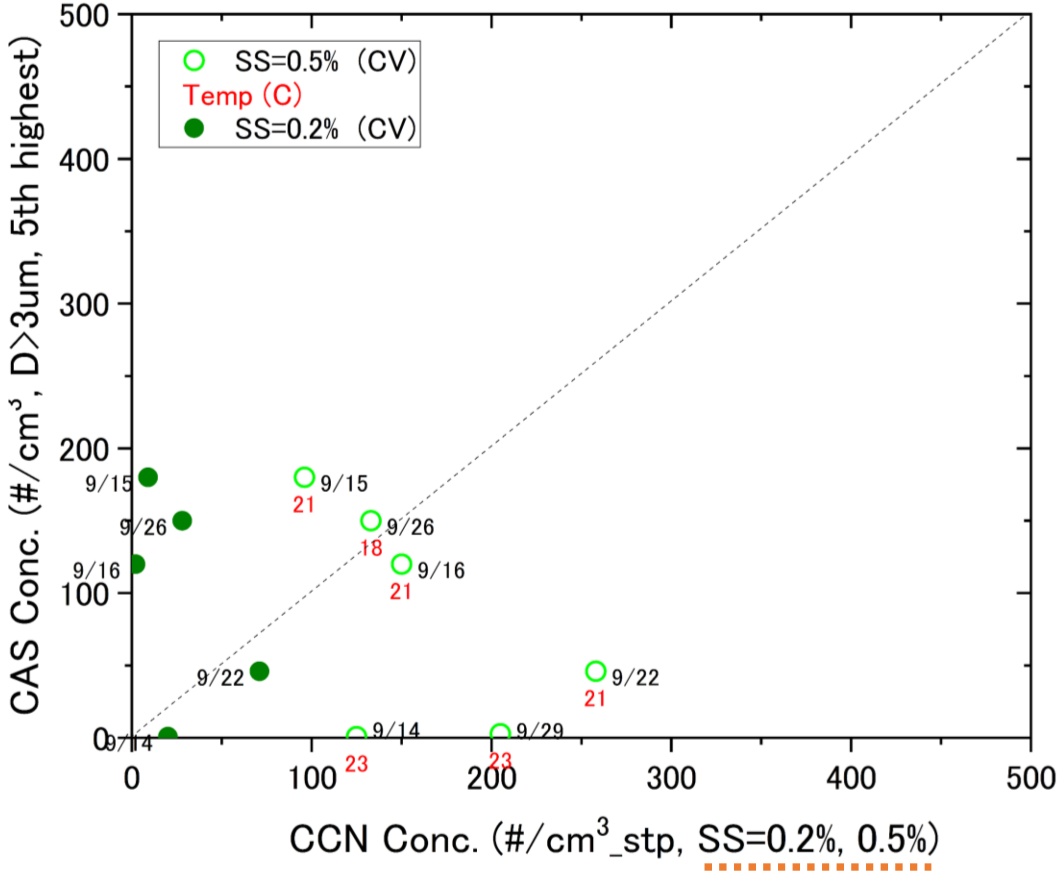




CCN vs CDP or CAS (5th highest)



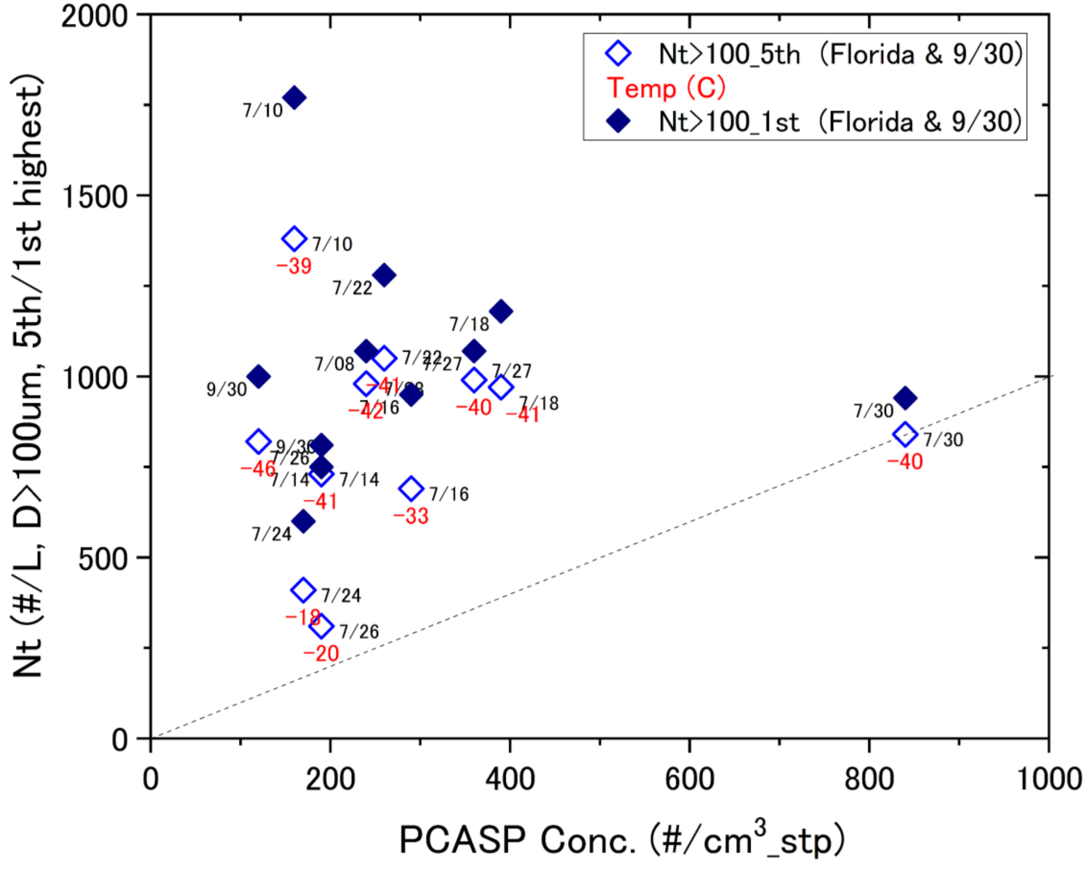
HIWC-2022

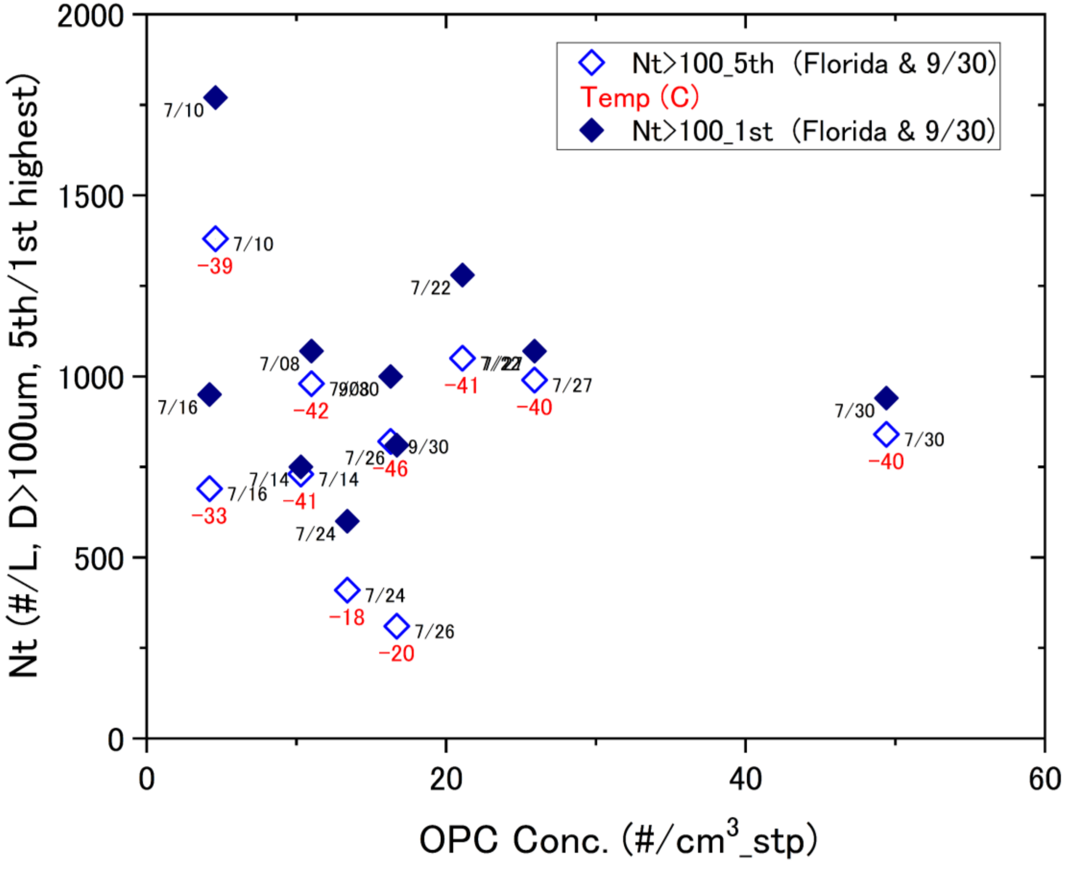


CPEX-CV

Results(aerosol vs ice particles)

HIWC-2022, 9/30 PCASP or OPC vs 2DS+PIP (max.) (CIP for 9/30)



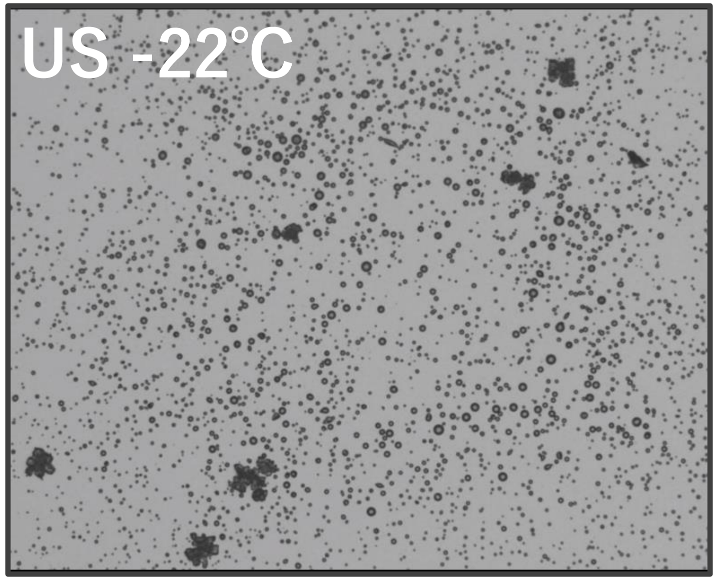


Results(INP) **#1**

IDFM (on Si wafer)

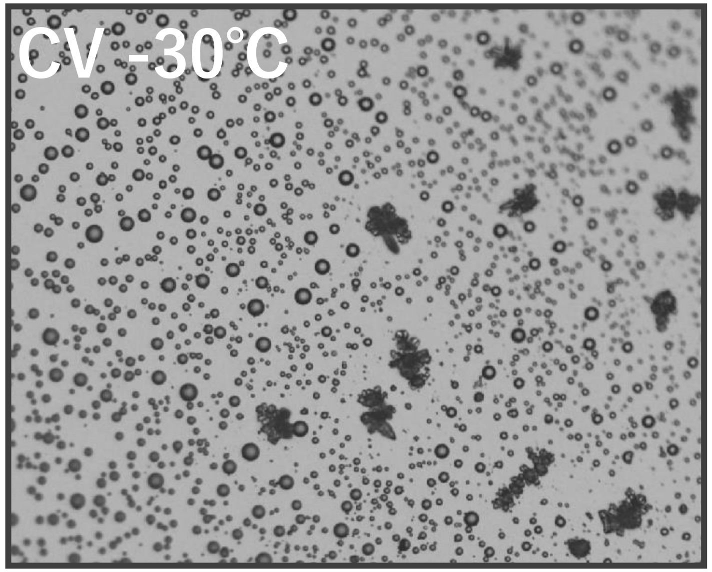
HIWC-2022

- Total [#] ： 46693
- highest T : -19.2°C
- INP (-30<T<-22) [#] : 42
- **INP (T>-22) [#] : 15**

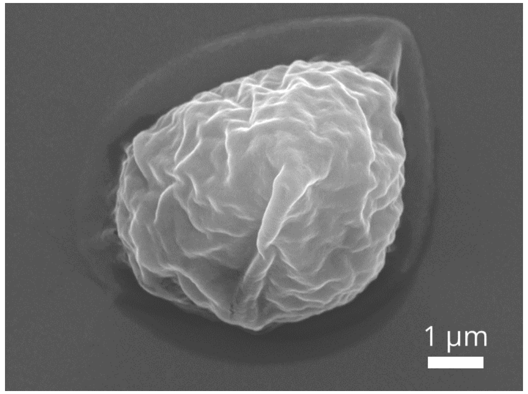


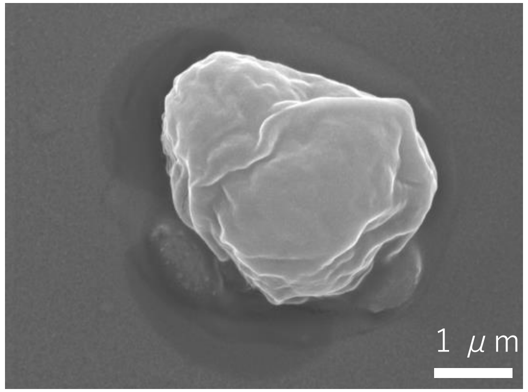
CPEX-CV

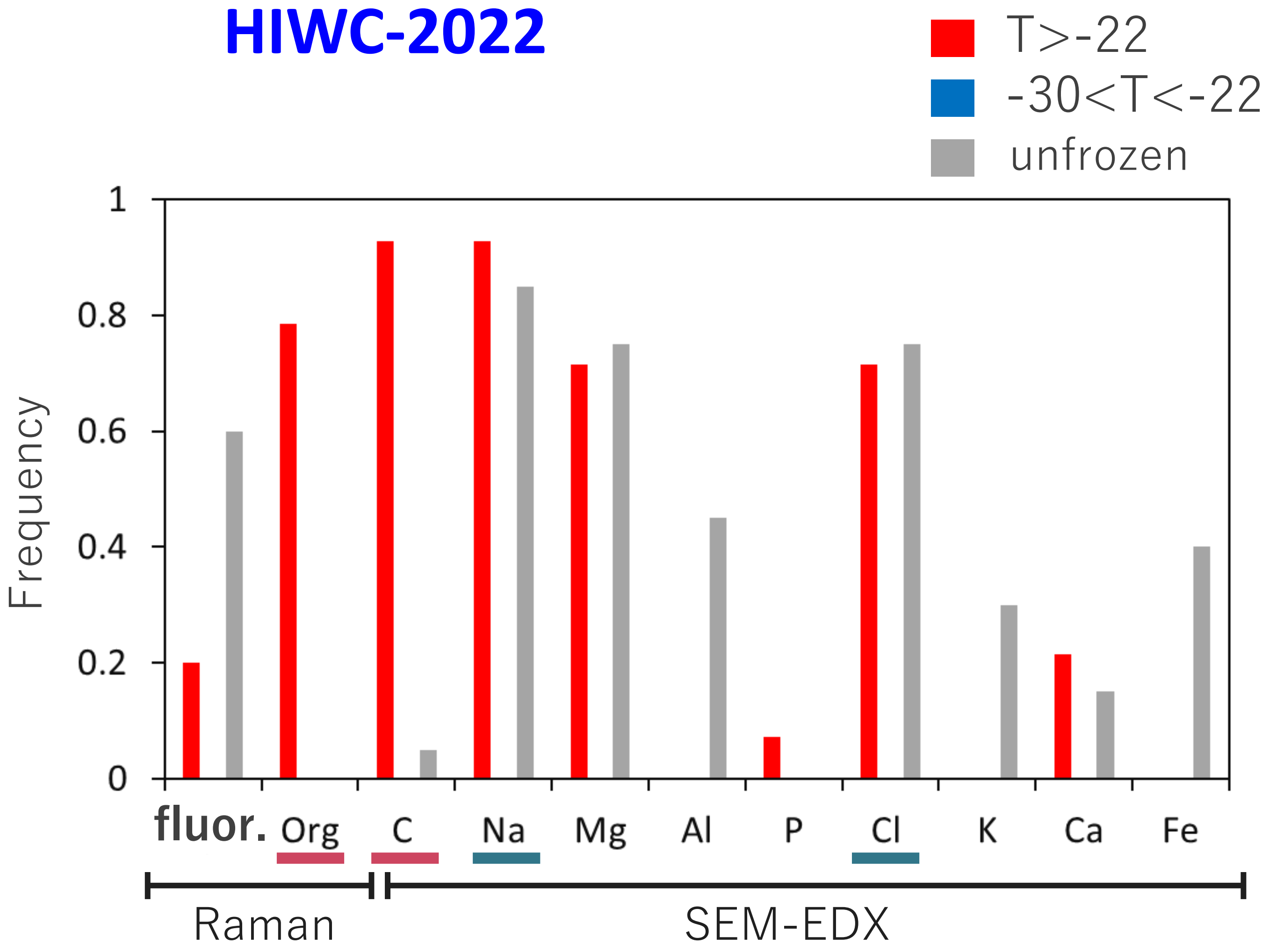
- Total (#) ： 27892
- highest T : -22.4°C
- INP (- 30<T<-22) [#] : 116
- **INP (T>-22) [#] : 0**



INP (T>-22)



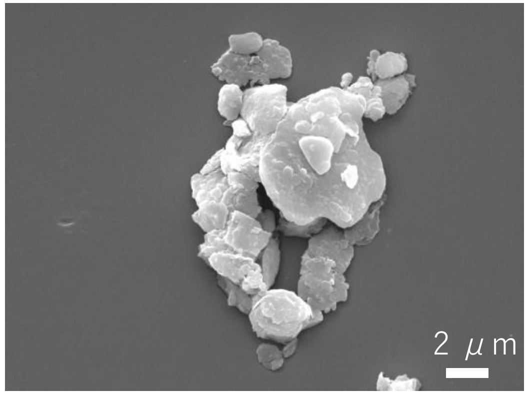


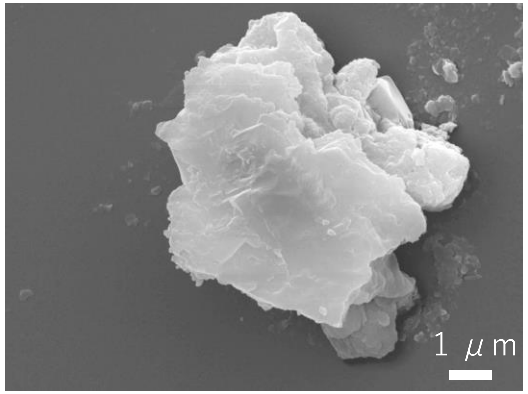


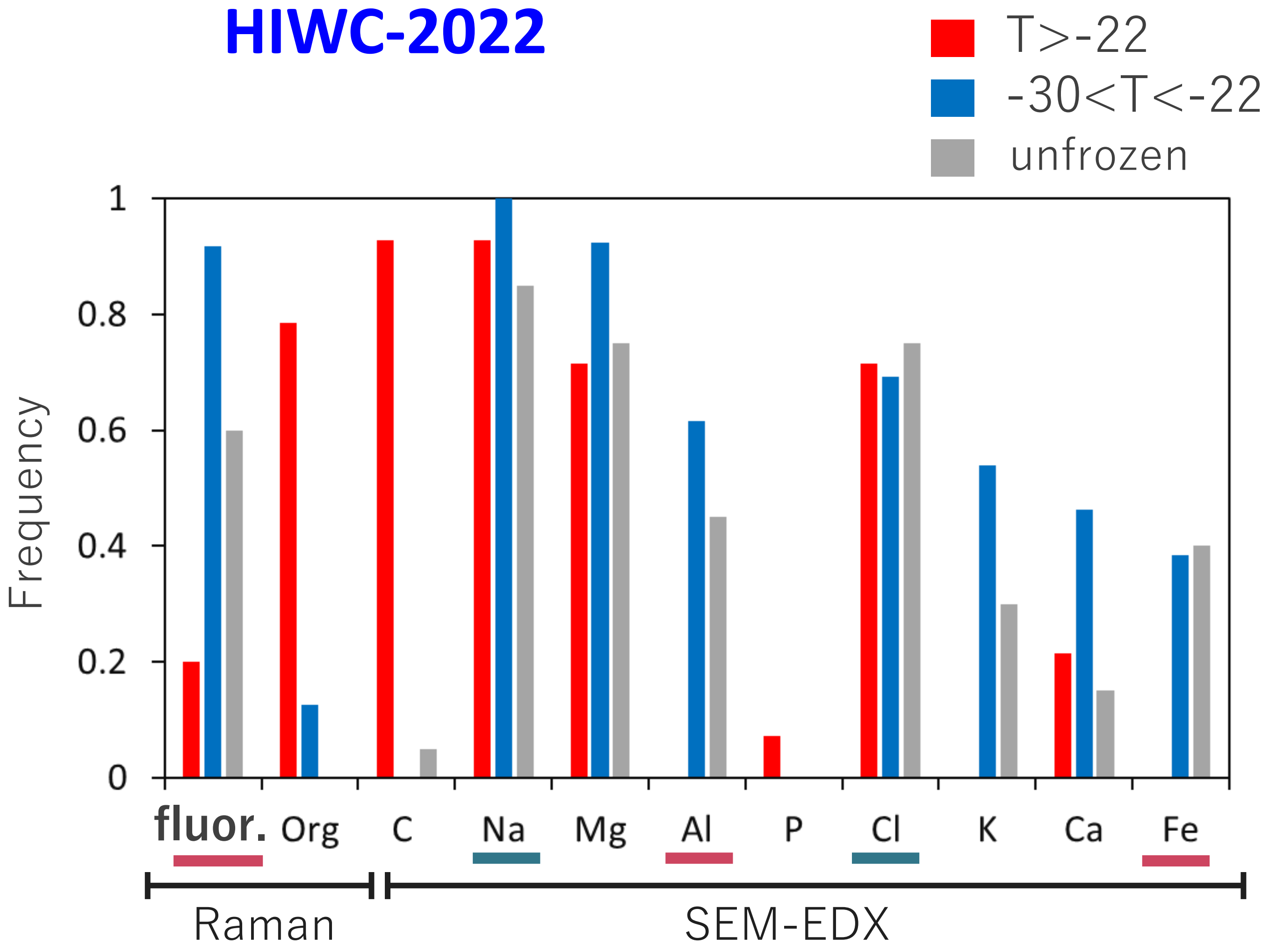
- elliptoid shape, different from sea salt or mineral dust
- C-H band and/or C, which indicates organic substances

  → bio-aerosol internally mixed with sea salt, which may cause higher activated T.

INP (-30<T<-22)





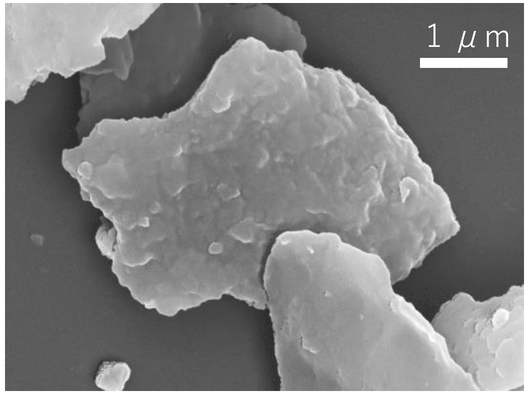


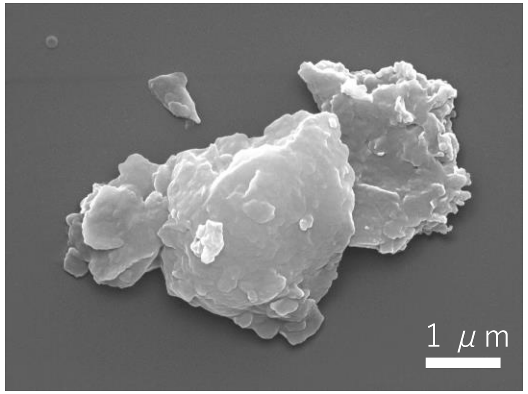
・non-spherical shape with asperity

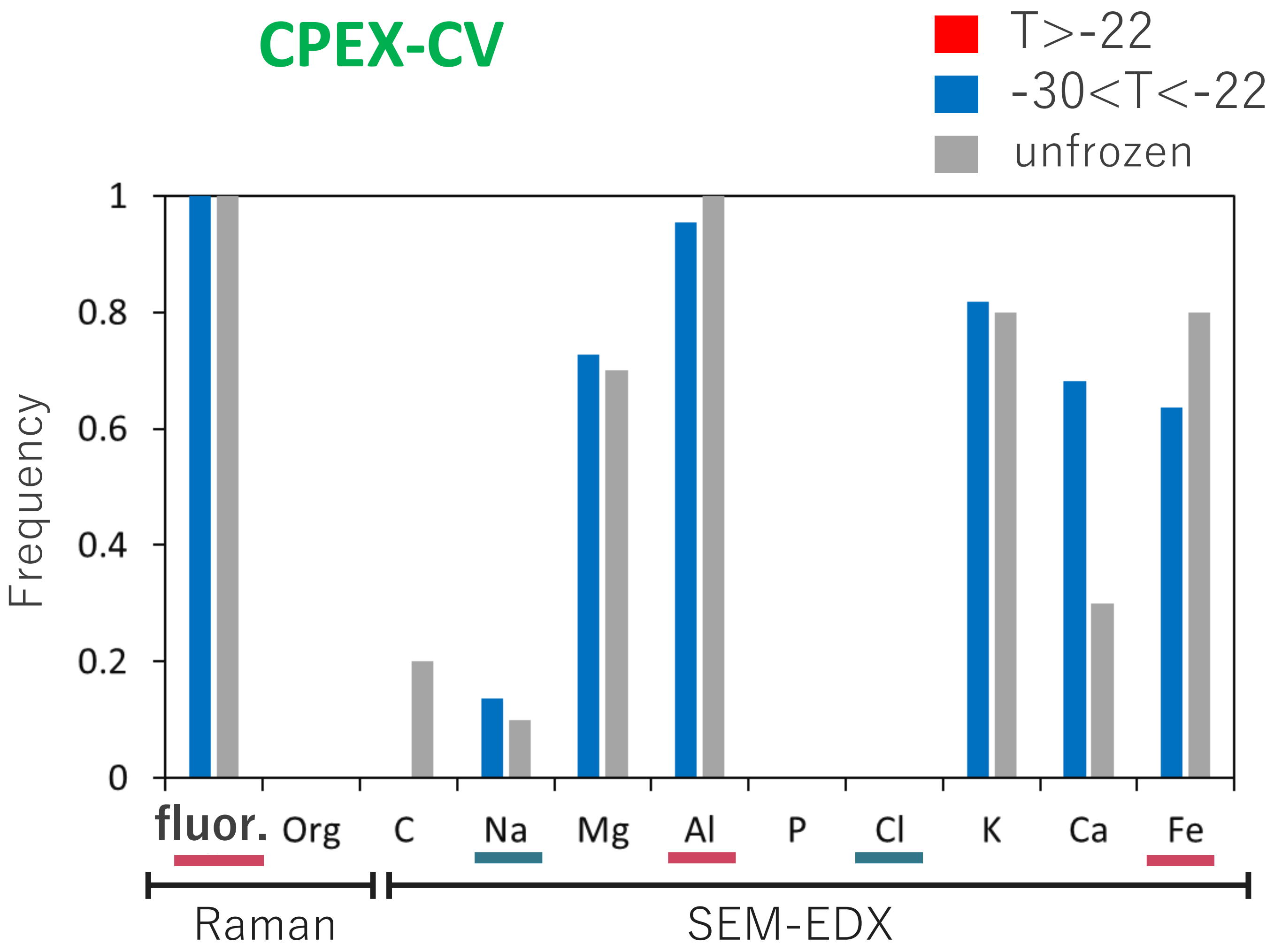
・clay mineral feature: fluorescence, mineral particle feature: Al, Fe

➢ mineral dust internally mixed with sea salt

INP







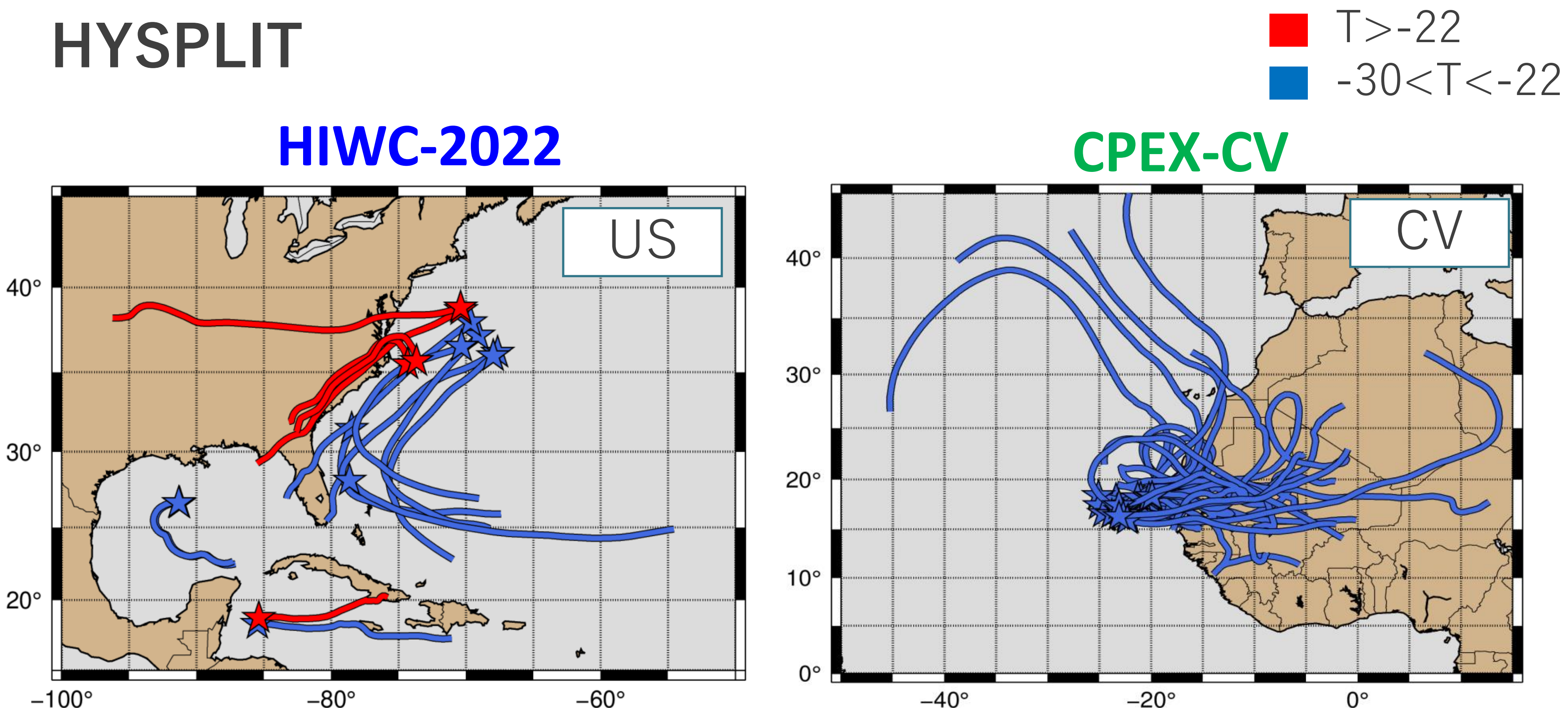
- non-spherical shape with asperity
- clay mineral feature: fluorescence, mineral particle feature: Al, Fe

➢ mineral dust externally mixed with others

Results(INP) #1

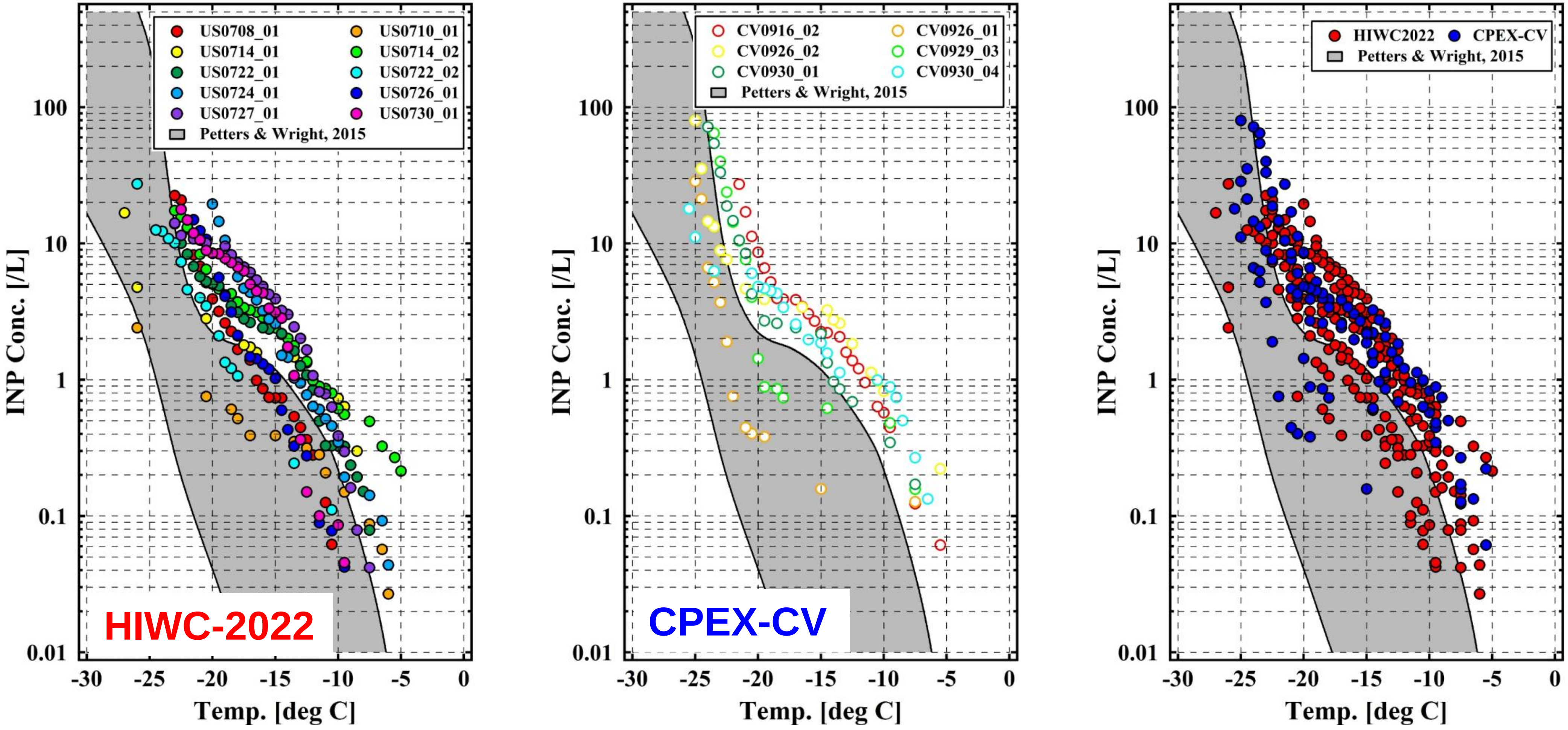
Back Trajectory

HYSPLIT



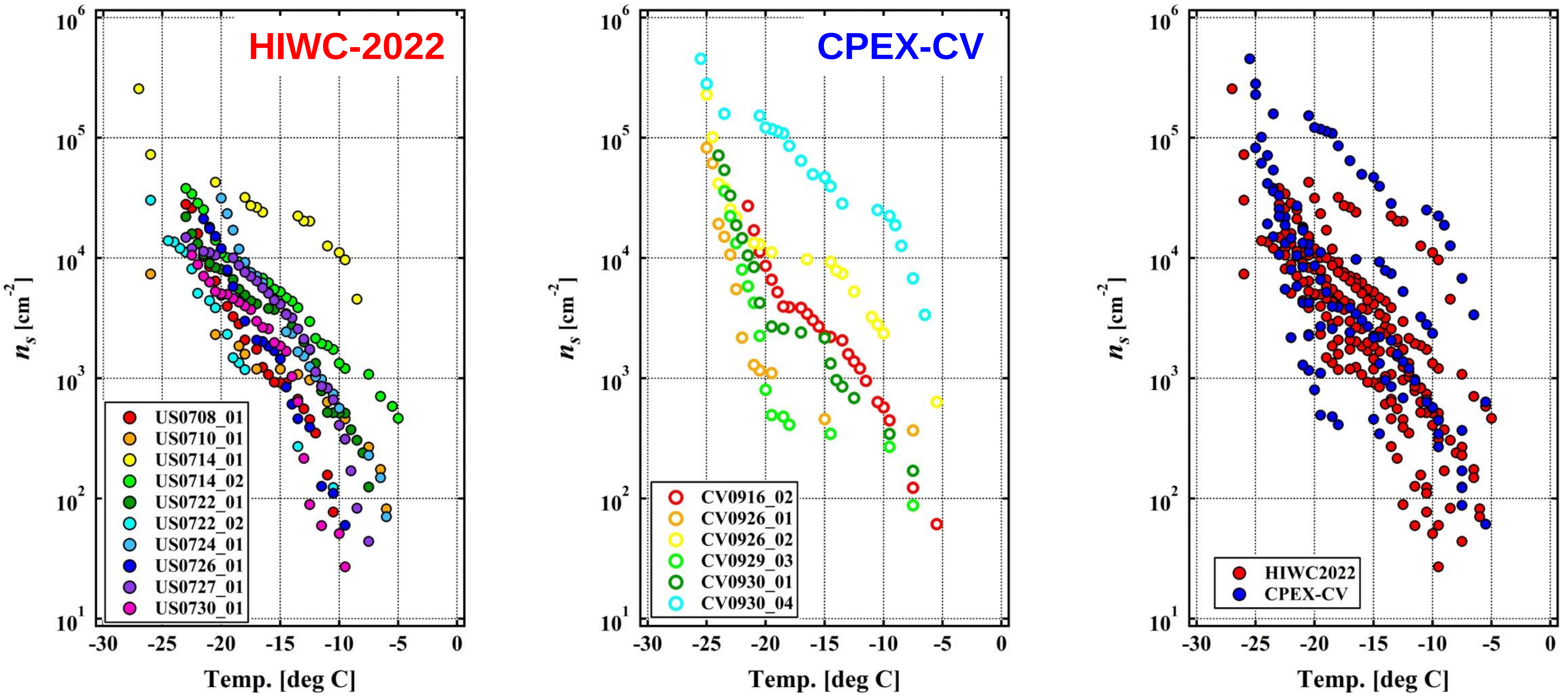
- bio-aerosol originated from the land, which contributed to freeze at higher T (US)
- externally mixed mineral dust originated from the Sahara desert (CV)

INP Conc.



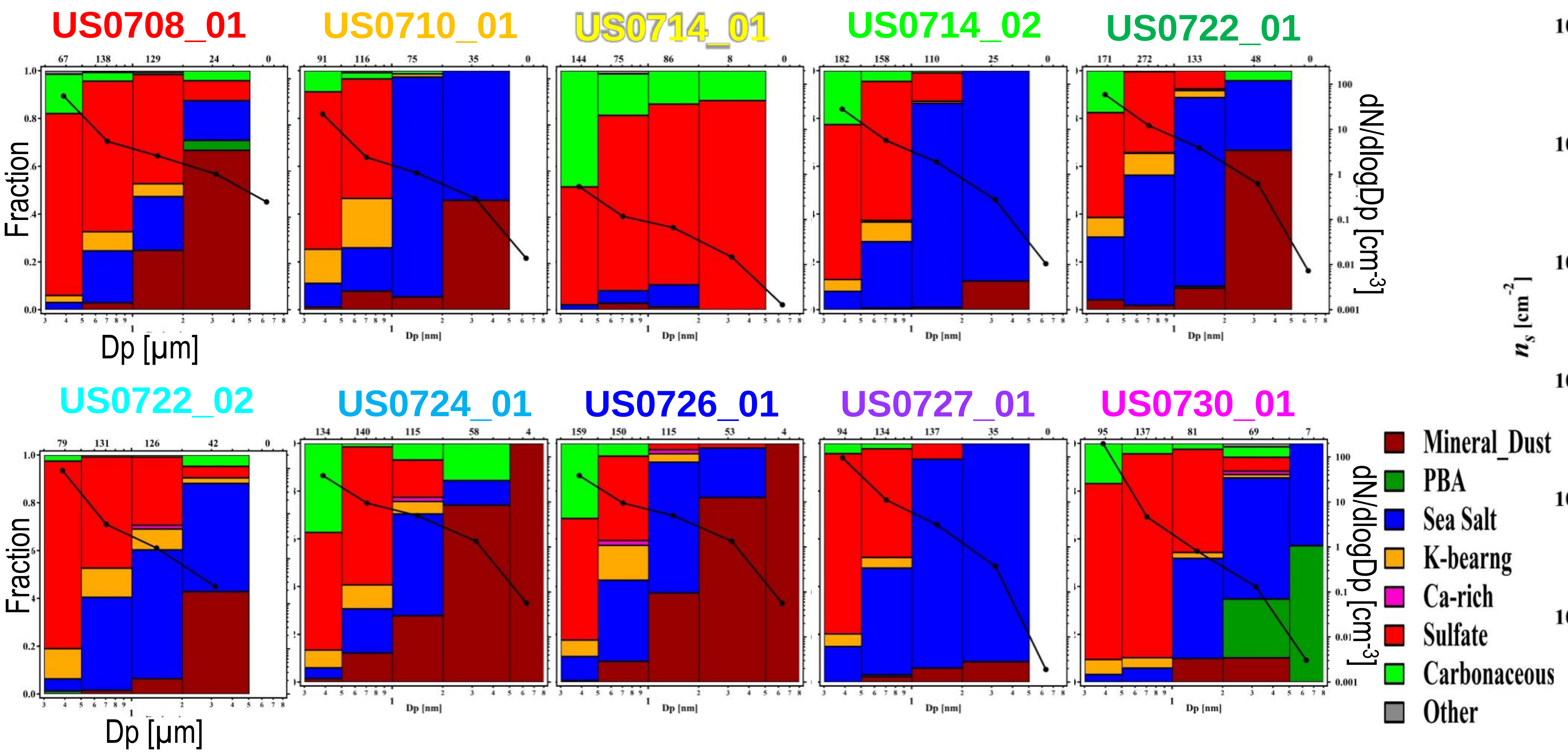
- comparable INP conc. to previous studies (various locations) (Kanji et al., 2017, Price et al., 2018)
- 1 ~ 2 order range in any T in both campaigns
- similar INP conc. between two campaigns, despite of different sampling locations and heights

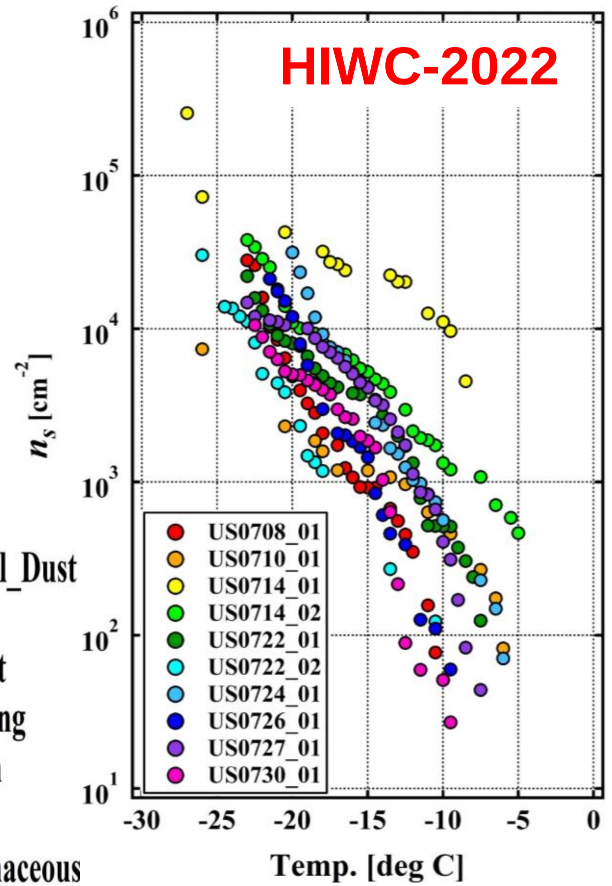
Results(INP) #2 Ice Nucleation Active Site (INAS) Densities



- INAS was calculated based on size ditributions over all ranges (SMPS+OPC)
- no significant differences between two campaigns
- rapid increase at T < -20℃ in CPEX-CV

INAS Densities vs Particle Types

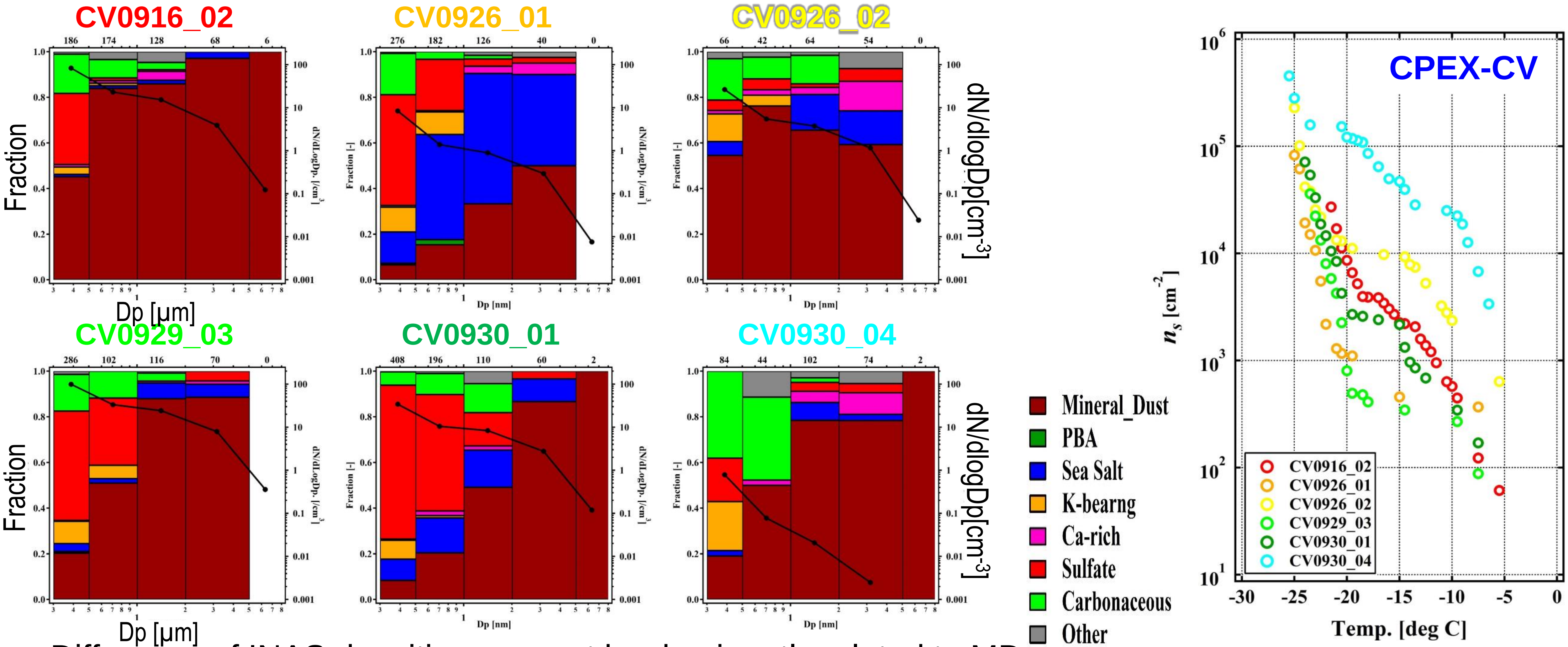




- Difference of INAS desities may not be related to MD and/or biogenic aerosols.
- INAS variations among cases were not clearly understood, although various types were classified.
  → Partly because contributions of INP surface areas to all areas may be small ?

Results(INP) #2

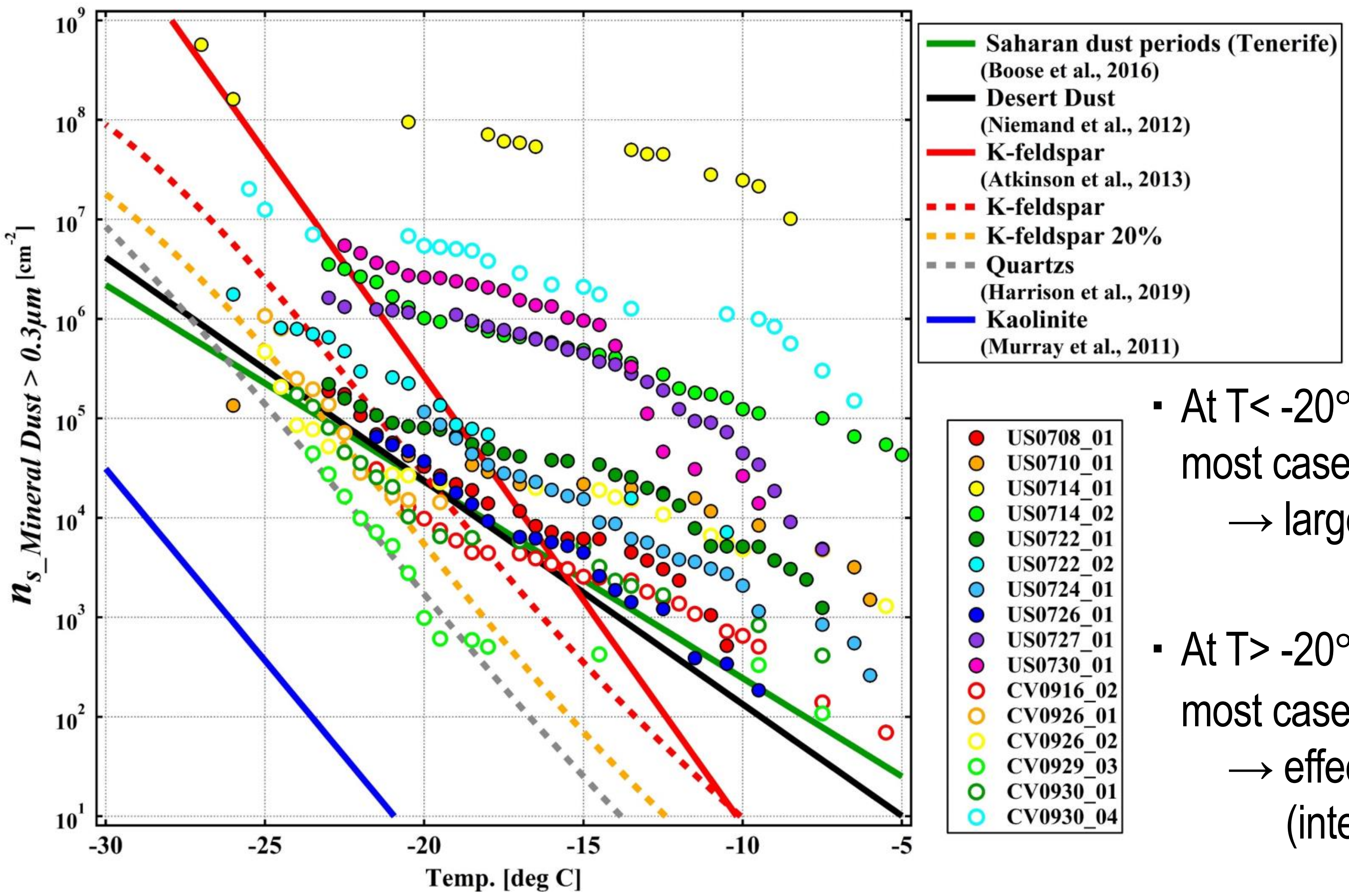
INAS Densities vs Particle types



- Difference of INAS densities may not be dominantly related to MD.
- In CPEX-CV, INAS variations among cases were not clearly understood, although most type was MD.
  → Partly because contributions of INP surface areas to all areas may be small ?

Contributions of Mineral Dust

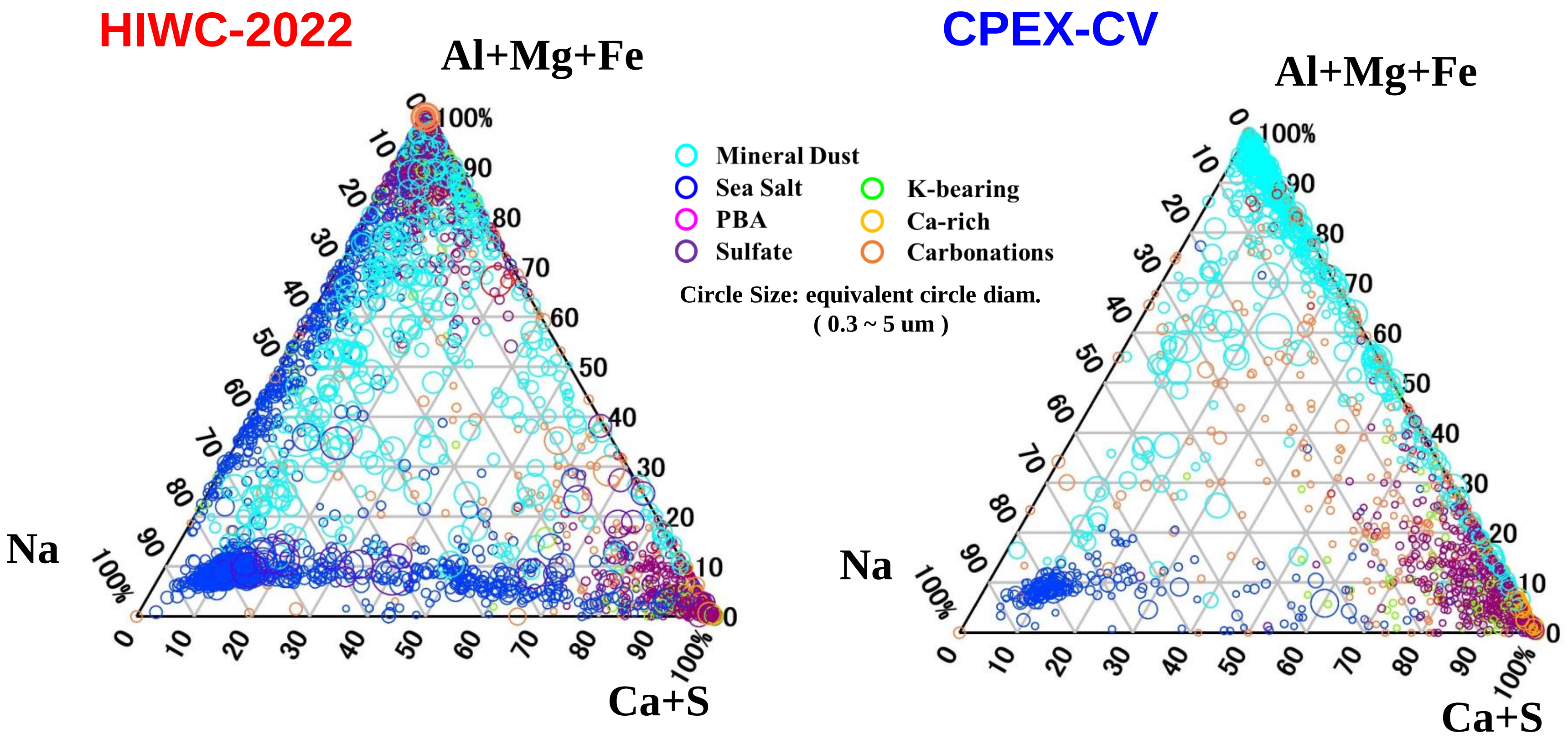
If all INPs were mineral dust (MD), INAS curves converged to those of standard dust particle …
(vertical axis: INAS from the aerosols classified as MD and larger than 0.3um)



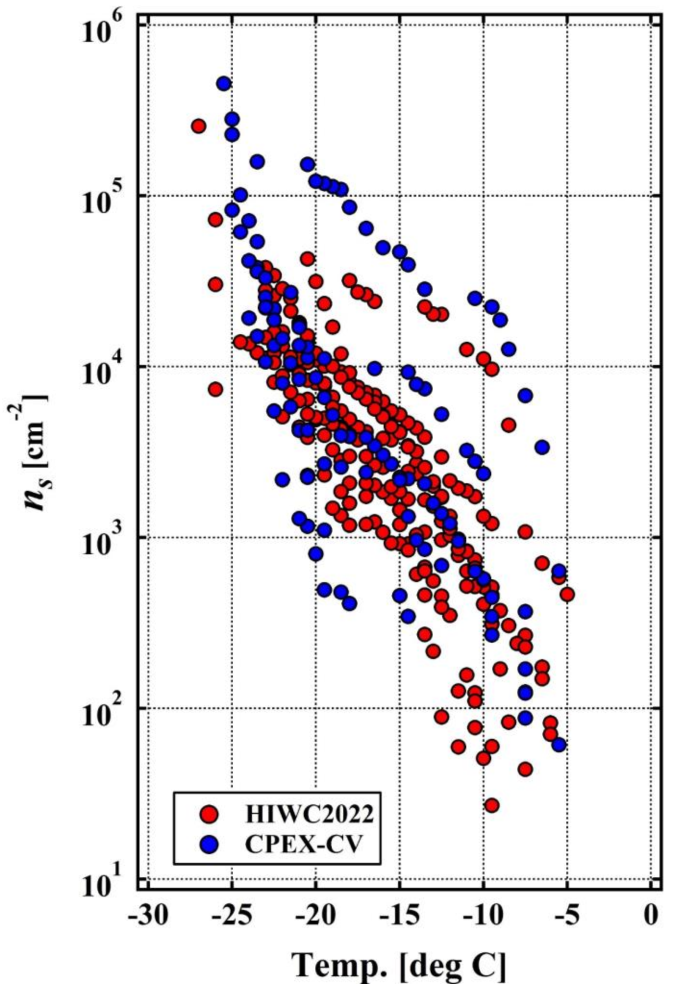
- At T< -20℃, except for some cases, most cases converged to INAS for standard MD
  → large contributions of MD

- At T> -20℃, regardless of primary biogenic aerosols (US0730_1), most cases deviaed from INAS for standard MD
  → effects of other categories than MD ?
  (internally mixed biogenic compounds ?)

Internally Mixed Particles



Ternary diagram for wt % ratios



In HIWC-2022, contrast to CPEX-CV,

- Mineral dust (MD), without detection of Fe or internally mixed with sea salt, was chracteristic.
- Contributions of MD may be underestimated, which caused to weaken the relations between particle classification and INAS.

Summary and future work

(CCN and aerosol)

- Aerosol number concs. were highly variable in both campaigns in terms of vertical and horizontal distributions.
- CCN number concs., as well as CCN spectra, were well-correlated with aerosol loading in HIWC-2022, but not so correlated (mostly low CCN) in CPEX-CV.
- κ was higher at any SS in HIWC-2022 than in CPEX-CV. The values were small compared to typical continental case.

(INP #1)

- Bio-aerosol internally mixed with sea salt, which originated from the land, may cause high activated T in HIWC-2022.
- No particles activated at T>-22C in CPEX-CV. Mineral dust internally mixed with sea salt, which originated from the Sahara desert, activated at T<-22C.

(INP #2)

- INP number concs. in both campaigns were similar and comparable to previous studies.
- INAS at T<-20C may be explained through the dust parameterizations from previous studies.
- INAS at T>-20C was difficult to explain or understand in context of the dust parameterizations.

(Future work)

- Size dependency on CCN and INP activations
- Difference between activated and non-activated aerosol, even in bio-aerosol category
- Evaluation of mineral dust particles internally mixed with other categories

Backup Slides

κ value of a given chemical composition

κ -Köhler theory

Petters and Kreidenweis, 2007

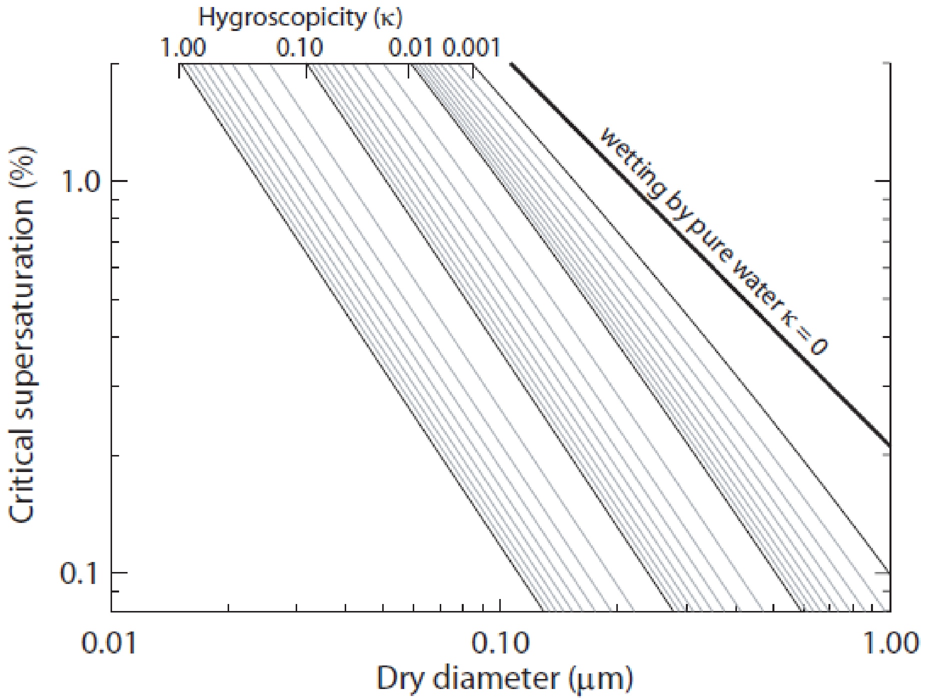
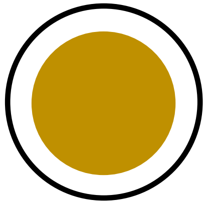


Fig. 1. Calculated critical supersaturation for $0 \leq \kappa \leq 1$ computed for $\sigma_{s/a}$=0.072 J m^{-2} and T=298.15 K. The gray lines are linearly spaced intermediates.

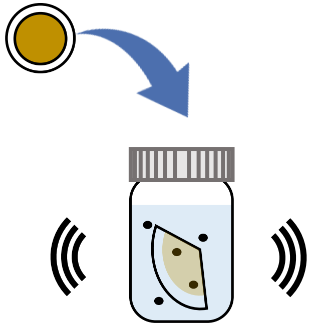
Particle Type	κ
$(NH_4)_2SO_4$	0.61
NaCl	1.28
Arizona Test Dust	0.025
Sahara Dust	0.054

small κ => growth similar to pure water
large κ => larger solute effect
typical value κ (ambient air) : 0.1-0.9

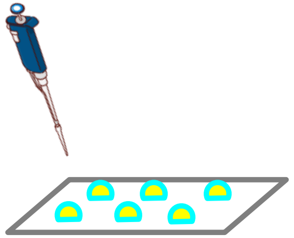
➢ Typical IN assay by cold plate



Polycarbonate Filter



Extraction by submersion and oscillation in ultra pure water (1 mL)



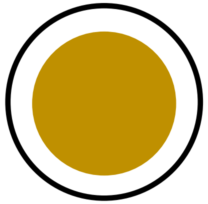
Set suspension droplets on a cold plate coated with Vaseline

Cooled to -50˚C (1˚C/min)

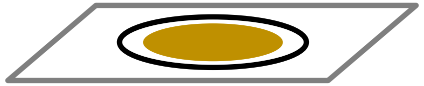
This study !!

Method & Analysis (INP) ***#2***

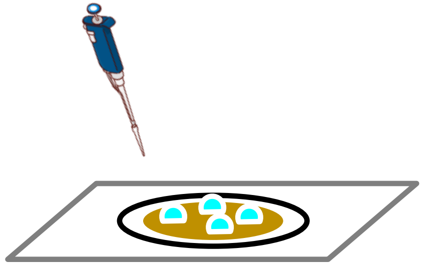
➢ Droplet Freezing Assay on Filter



Hydrophobic PTFE Filter



Set the filter on the cold plate coated with Vaseline



Set ultra pure water droplets on the filter

Cooled to -50˚C (1˚C/min)