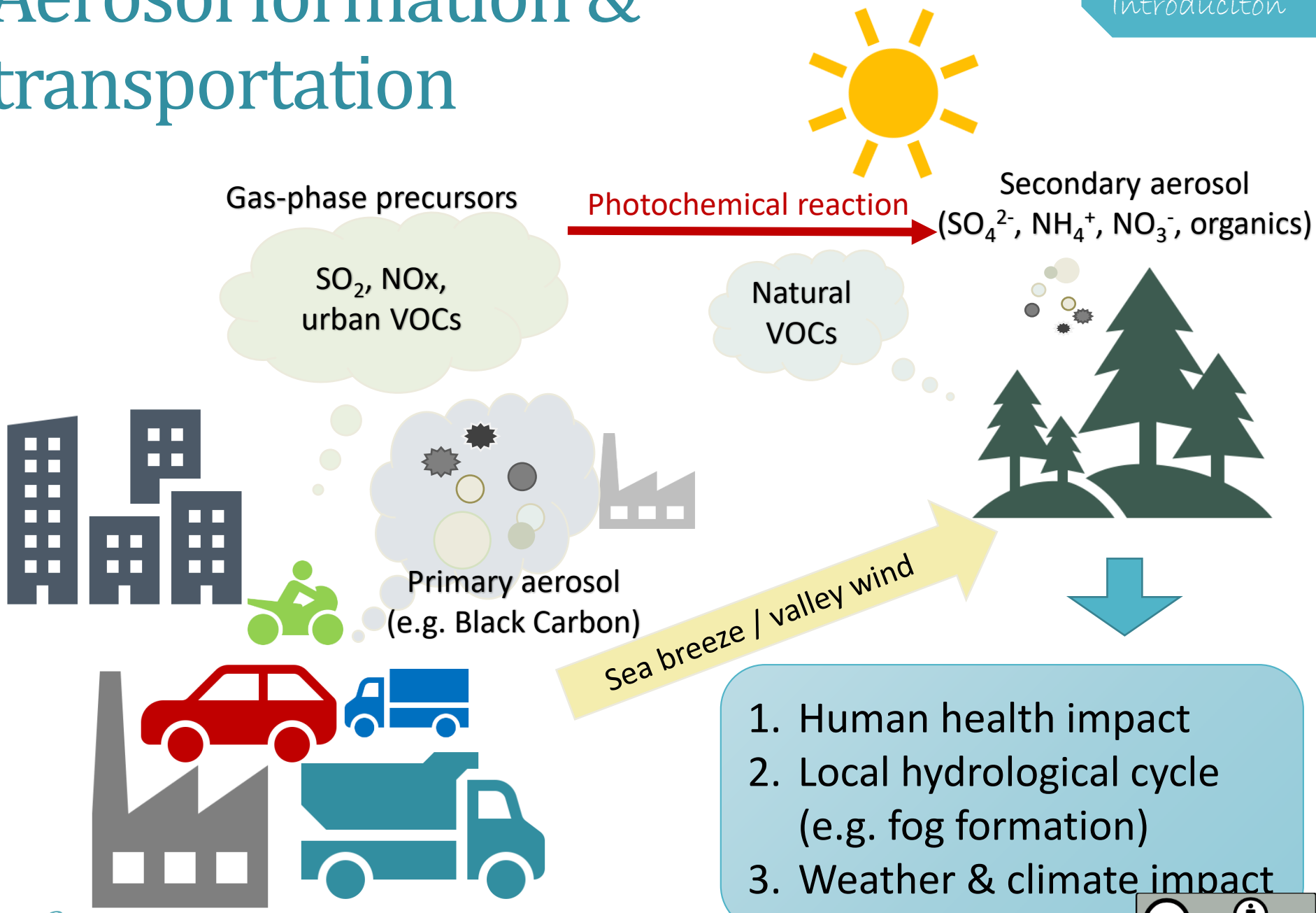
Aerosol Composition, Physiochemical Properties, and Source Apportionment at a Forest Site in Taiwan

Ting-Yu Chen[1], Chia-Li Chen[1], Hui-Ming Hung[1,*], Yi-Chi Chen[2], Haojia Ren[2], Wei-Nai Chen[3], Charles C. -K. Chou[3]

May 6th, 2020

[1] Department of Atmospheric Sciences, National Taiwan University, Taipei 10617, Taiwan
[2] Department of Geosciences, National Taiwan University, Taipei 10617, Taiwan
[3] Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan

Aerosol formation & transportation



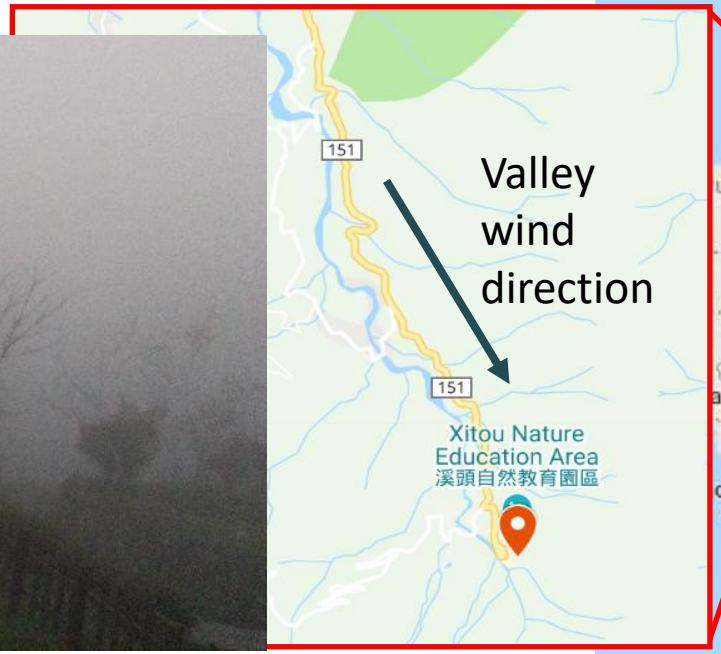
1. Human health impact
2. Local hydrological cycle (e.g. fog formation)
3. Weather & climate impact

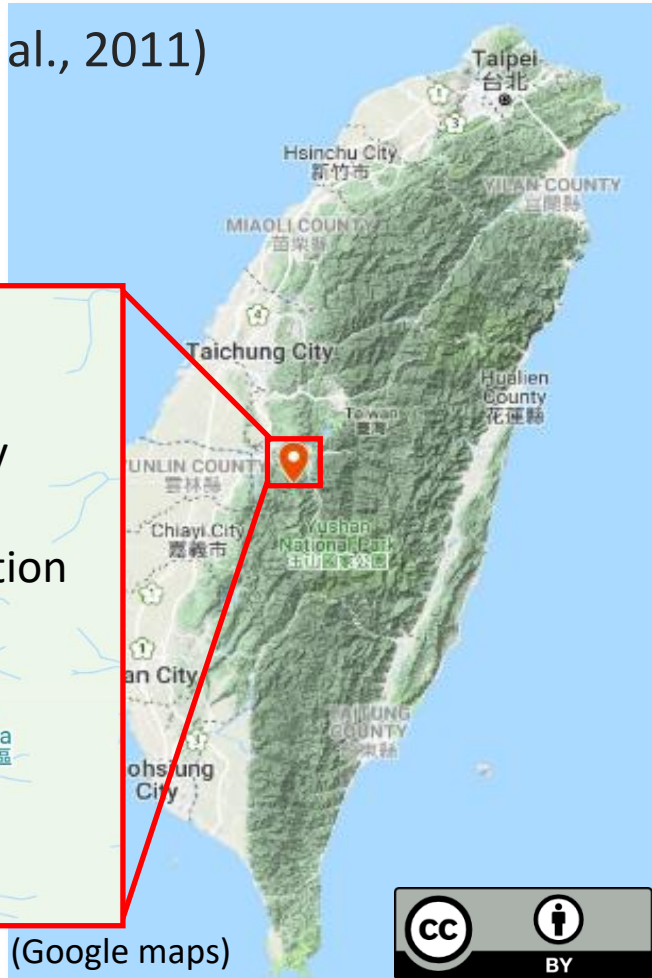
Study site

Xitou Experimental Forest

- 23.40°N, 120.47°E, 1,178m asl
- River valley toward Taichung/Changhua metropolitan
- Mountain-valley wind dominates the local circulation
- Frequent fog formation (292 fog days/year) (Wei et al., 2011)
- Forest Park – biogenic source + human activities

Sampling period: Dec.1-Dec.24, 2018





(Google maps)

Instrumentation

- Temperature
- RH
- Wind
- Visibility
- Solar radiation

Meteorological data

- SO_2, NOx, NOy
- NO, CO
- O_3

Gas pollutant measurement

- Scanning Mobility Particle Sizer (SMPS)
- Condensation Particle Counter CPC
- CCN counter

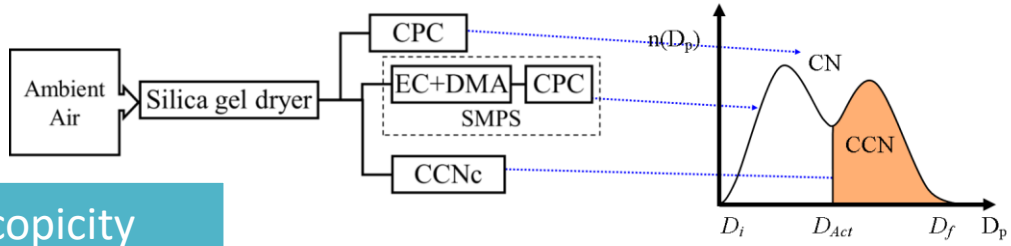
Real-time PM measurements

- Multi Orifice Uniform Deposit Impactor (MOUDI)

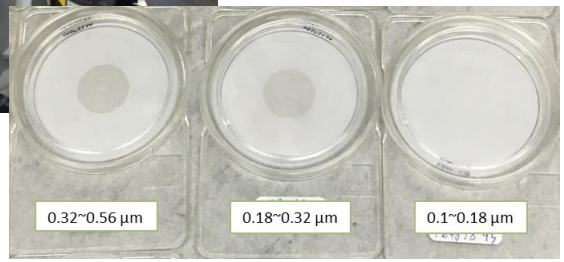
✓ *FTIR, isotope analysis*

Aerosol sample collection

Experimental processes



- CCNc, CPC, SMPS
  - Hygroscopicity coefficient κ
- MOUDI sample collecetion
  - FTIR-ATR
    - Concentration of NH_4^+, NO_3^-, SO_4^{2-}, and black carbon (BC)
  - Denitrifier isotope analysis
    - NH_4^+
      - $\delta^{15}N$
        - Sources of aerosol
    - NO_3^-
      - $\delta^{15}N$
        - Sources of aerosol
      - $\delta^{18}O$
        - Formation Pathways



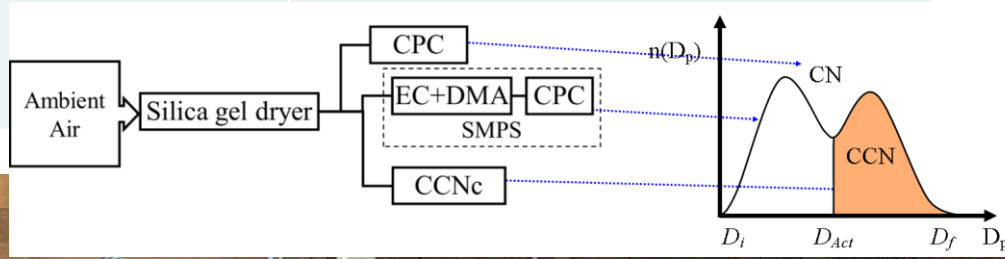
Hygroscopicity κ derivation

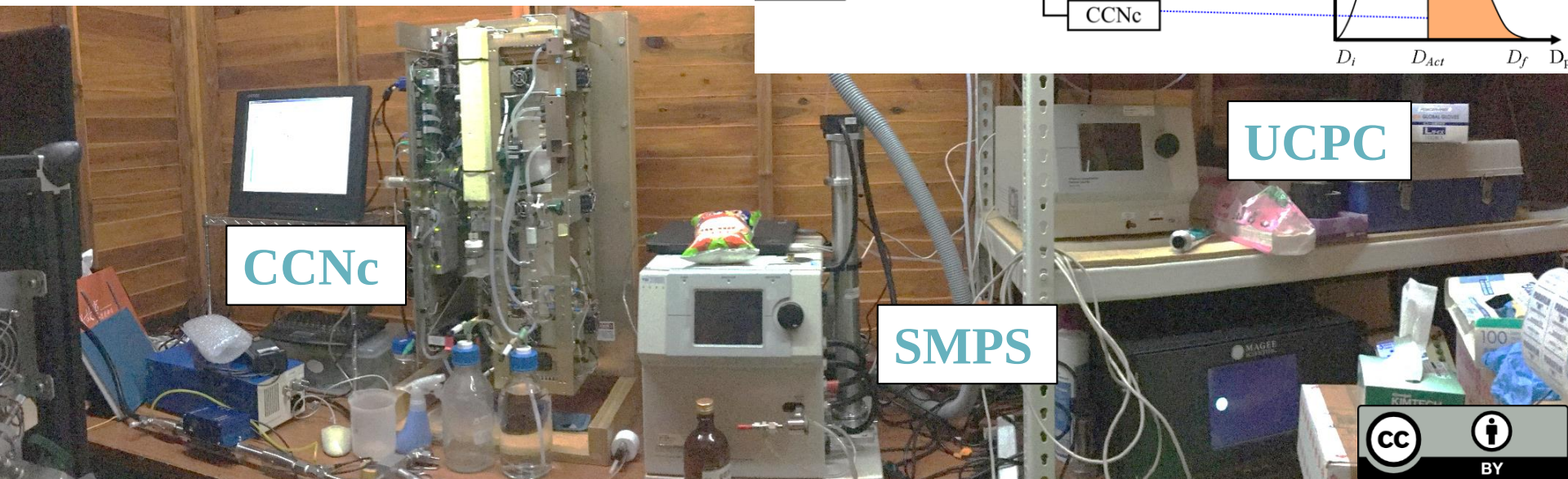
Cloud Condensation Nuclei counter (CCNc)	Scanning Mobility Particle Sizer (SMPS)	Ultrafine Condensation Particle Counter (UCPC):
Number of CCN	5-min size distribution	real-time PM concentration

Hygroscopicity parameter κ of aerosol

$$S = a_w \, exp\left(\frac{4\sigma M_w}{RT\rho_w D_p}\right) = \frac{{D_p}^3 - {D_{dry}}^3}{{D_p}^3 - {D_{dry}}^3(1-\kappa)} exp\left(\frac{4\sigma M_w}{RT\rho_w D_p}\right)$$

(Petters & Kreidenweis, 2007)





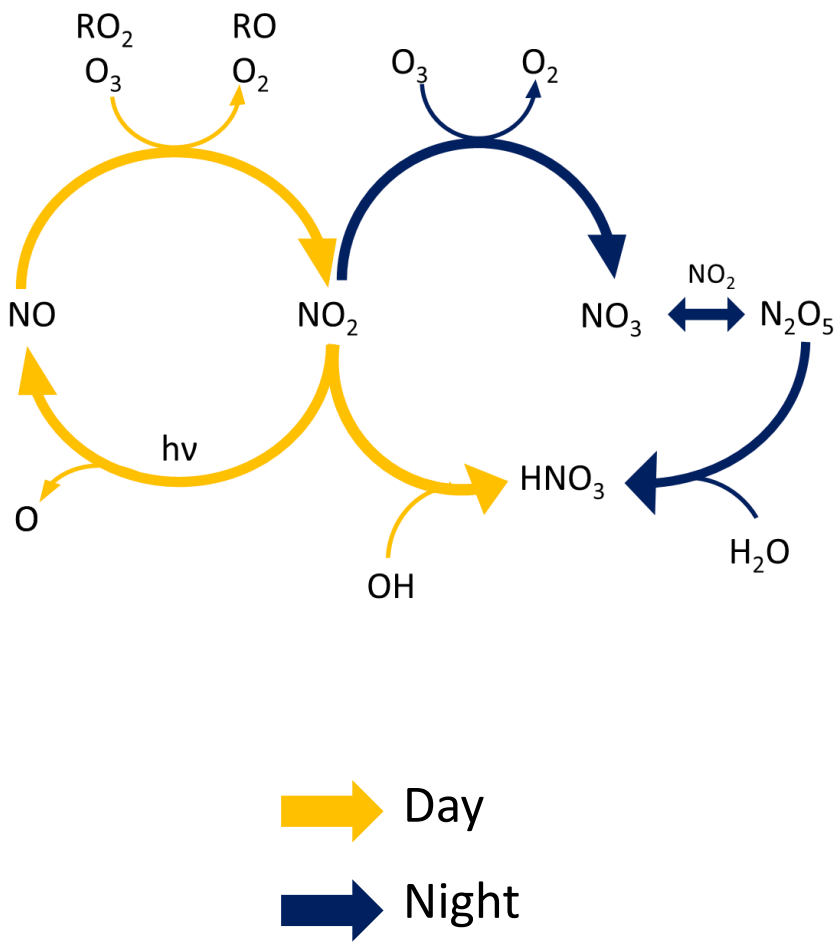
Isotope analysis in aerosol

NH_4^+ — $\delta^{15}N$ — **Sources of aerosol** (Huang et al., 2019; Pan et al., 2018; Savard et al., 2017)

NO_3^- — $\delta^{15}N$ — **Sources of aerosol** (Guha et al., 2017; Kamezaki et al., 2019; Kim et al., 2019; Savard et al., 2017; Siciliano et al., 2018)

NO_3^- — $\delta^{18}O$ — **Formation Pathways** (Fang et al., 2011; Guha et al., 2017; Hastings et al., 2003; Kamezaki et al., 2019)

NO_3^- (HNO_3) formation



N comes from the sources of emission, so $\delta^{15}N$ is **source determined**

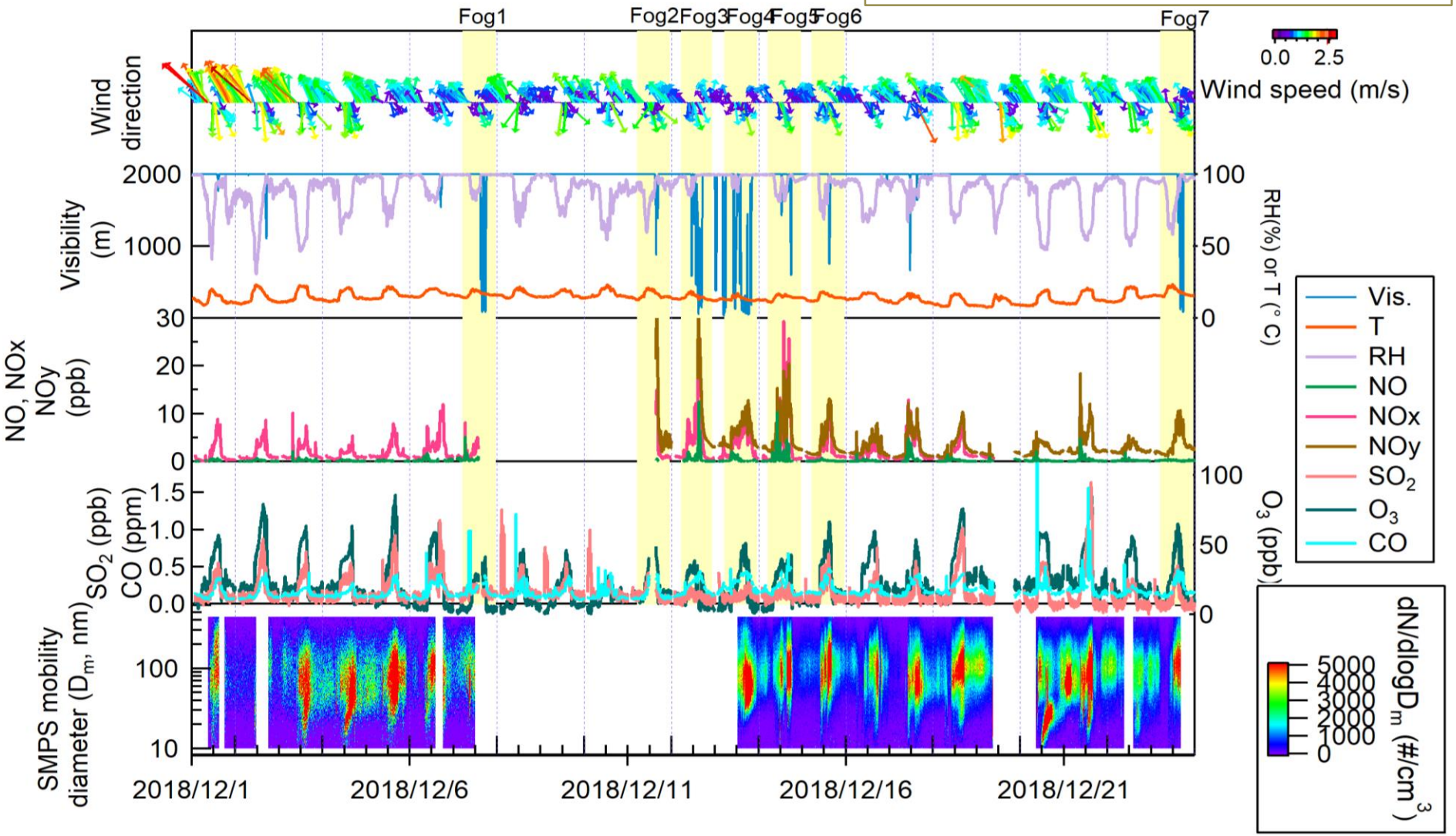
O comes from the interaction with the atmosphere, so $\delta^{18}O$ is **process determined**

substance	$\delta^{18}O$ value of O (vs. SMOW)
atmospheric O_2	+23.5 ‰
RO_2	+23.5 ‰
O_3	+90 - 122 ‰
H_2O	-15 ~ 0 ‰ (Southeast Asia)
OH radical	+37.5 ~ 61‰ (½ from O_3 and ½ from H_2O)

Therefore, the $\delta^{18}O$ of HNO_3:
lower if RO_2 is the main oxidant
(+28.17~42.21)
higher if O_3 is the main oxidant
(+72.50 ~ 101.67‰)

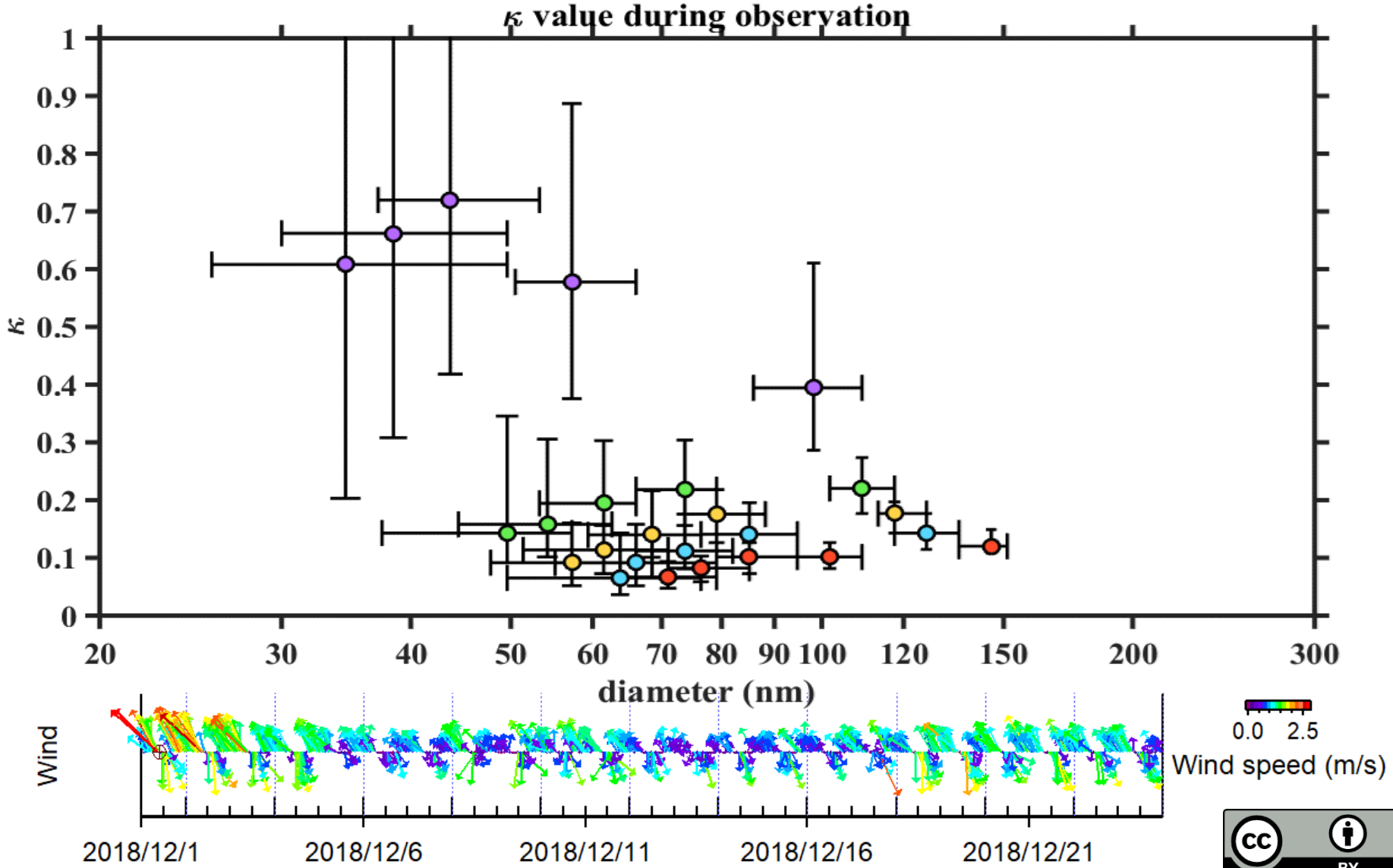
Weather & Pollutants

Pollutants were carried to Xitou by Sea-breeze and Valley wind from 10 am to 5 pm

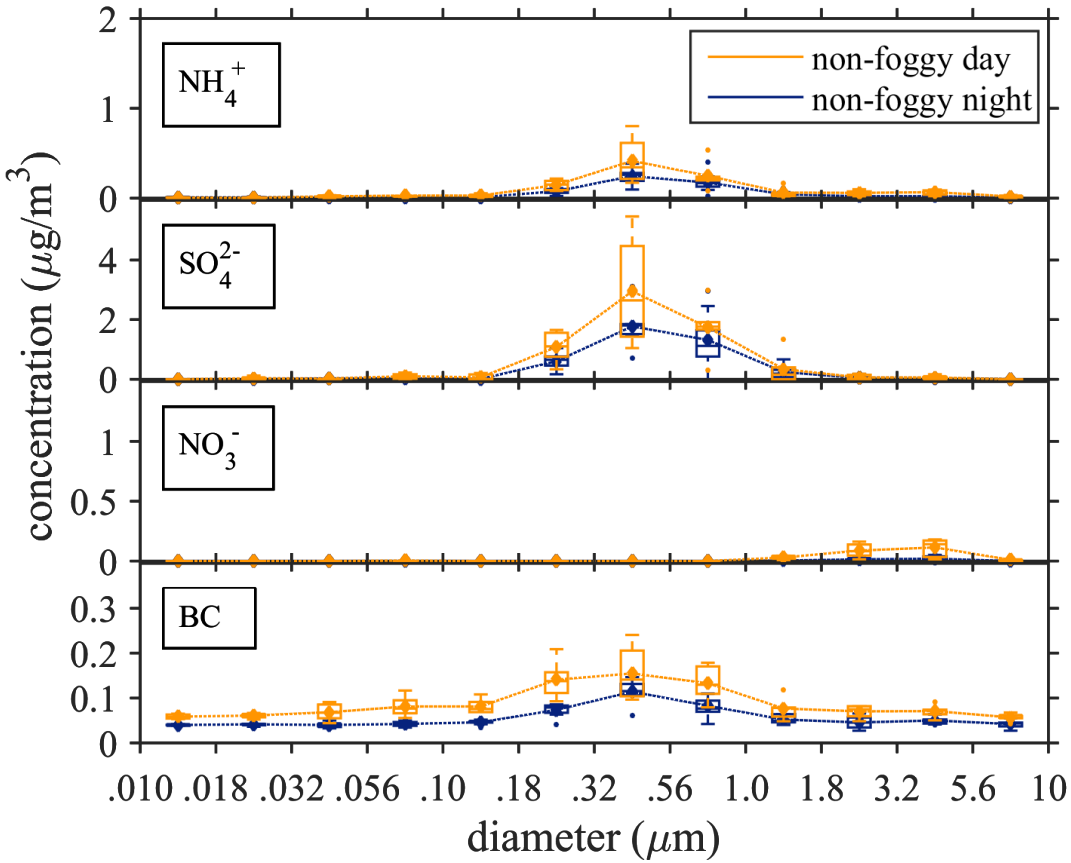


κ from SMPS & CCNc

12/1~3 has higher κ accompanied by stronger southeast wind. Which indicates that aerosol may come from different sources and have distinct properties.

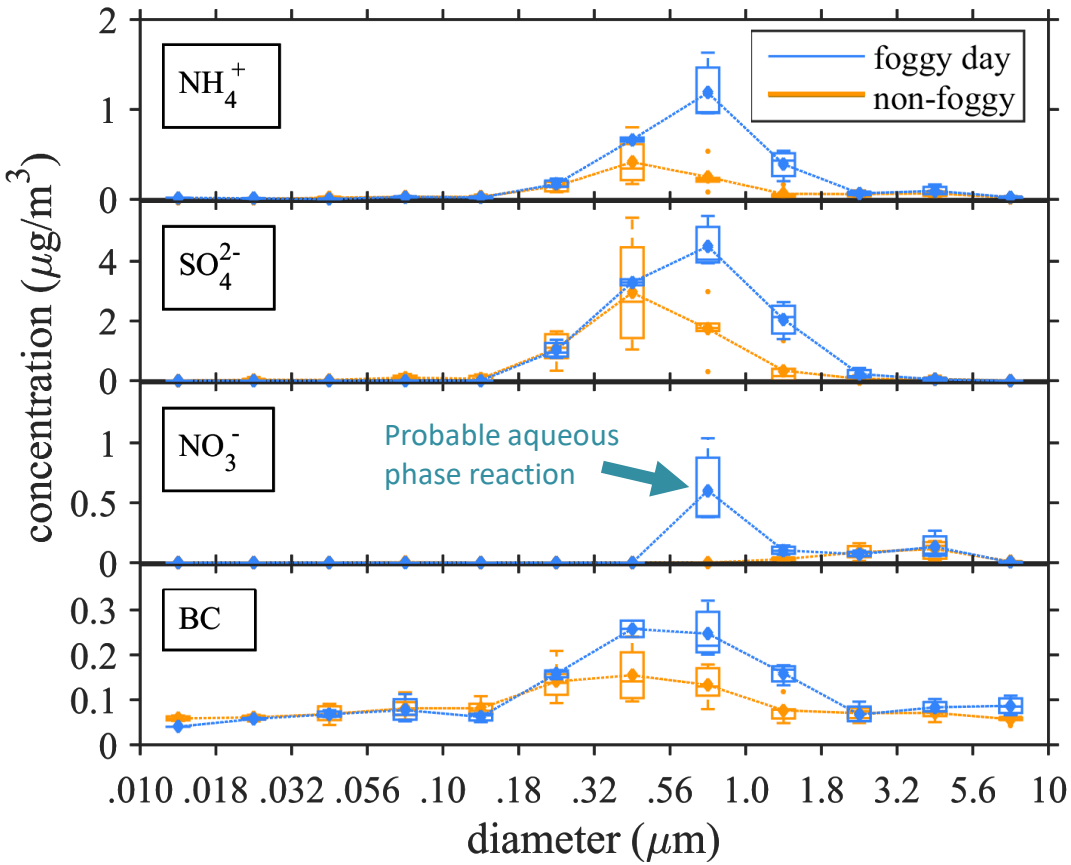


Size distribution of day and night



- Sea/Valley breeze from urban area made conc. of daytime higher
- NO_3^- size distribution is different from NH_4^+, SO_4^{2-}, BC: Secondary $(NH_4)_2SO_4$ aerosol forms prior to NH_4NO_3 in clear days
  → NO_3^- exists in larger sea salt aerosol as $NaNO_3$

Foggy vs. non-foggy days



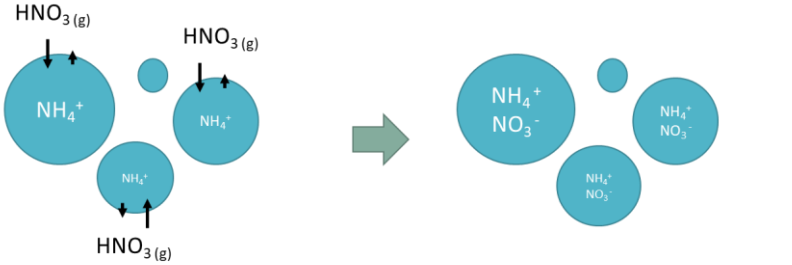
Foggy period has higher concentration

Hygroscopic growth may make aerosol size larger

Fog formation promotes aqueous phase reaction

→ Fine particles (d=0.56~1μm) have high concentration of NO_3^-.

Aqueous-phase process:

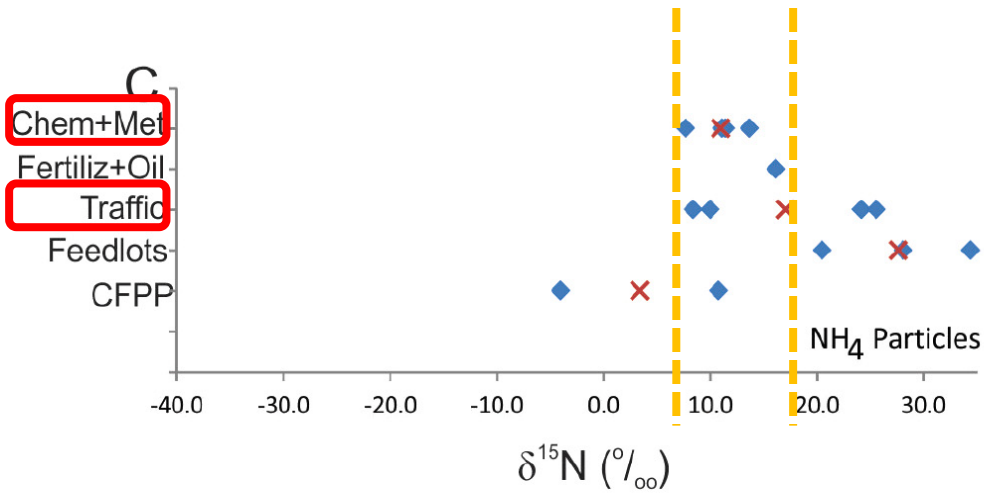


Gas-phase HNO_3 has high Henry's constant, can be easily dissolved in liquid water

Stabilized by ammonium in the droplet, forming nitrate-containing aerosol

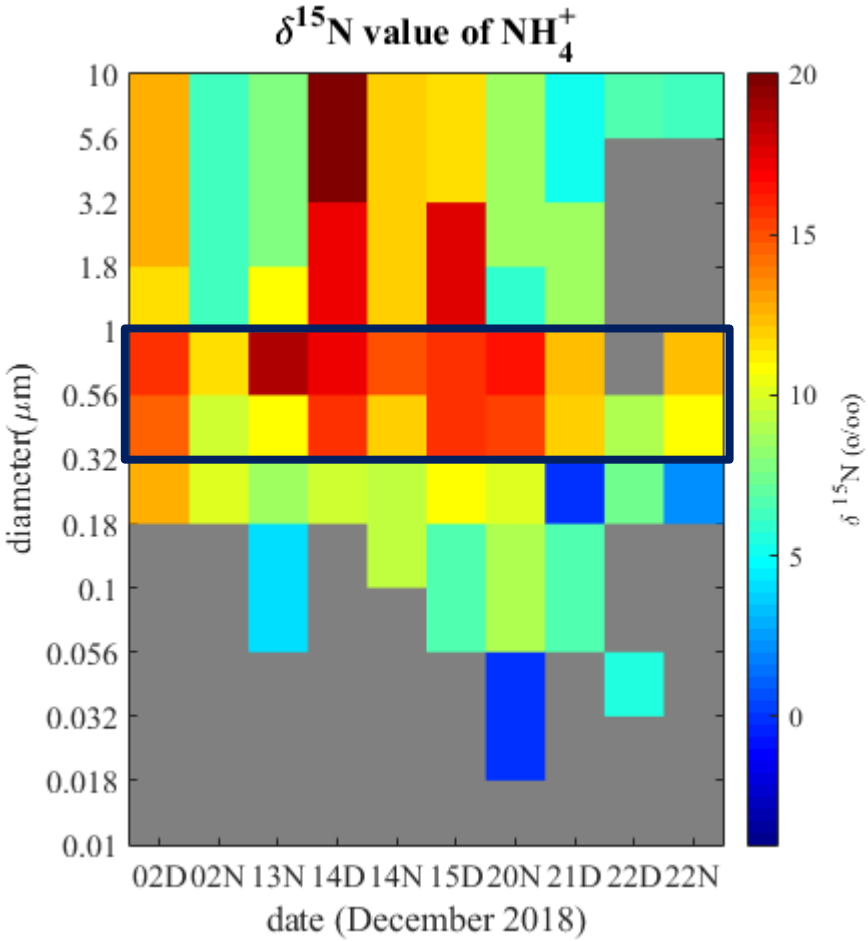
$\delta^{15}N$ size distribution

Aerosol d=0.32~1μm has high p-NH_4^+ concentration. $\delta^{15}N$ of NH_4^+ falls between 8~17‰, indicating that most NH_4^+ was from anthropogenic sources like traffic or factories



(Savard et al., 2017)

* Fog events: 13N, 14D, 15D

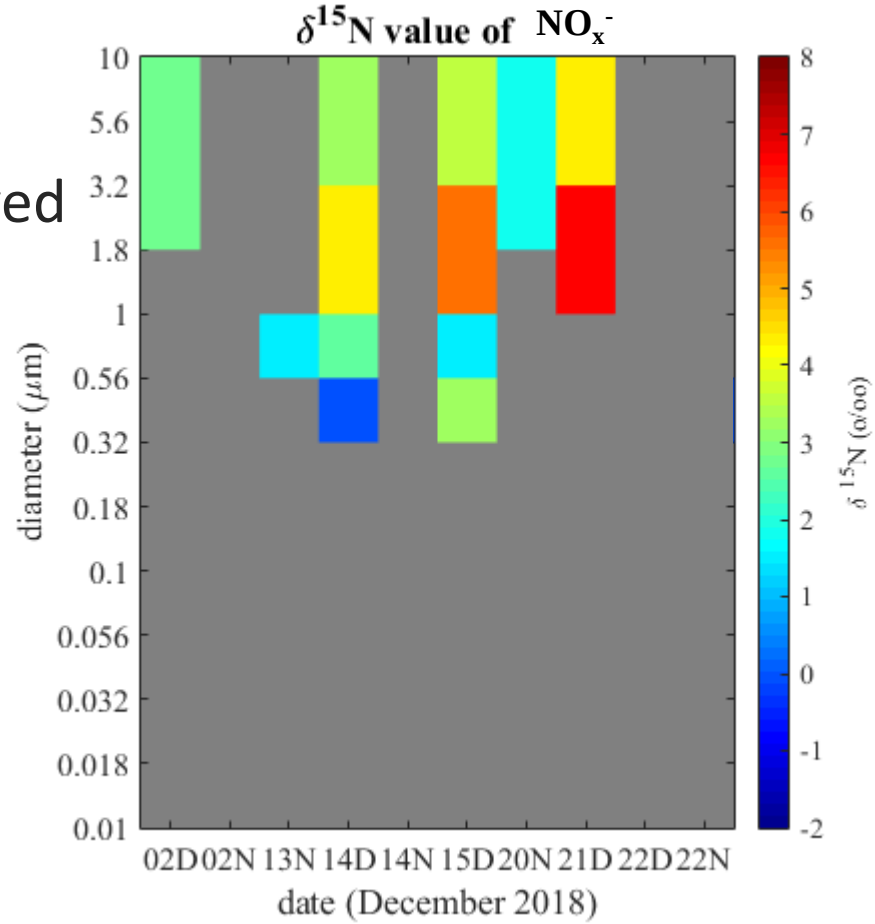


$\delta^{15}N$ size distribution

It is more difficult to distinguish the source of p-NO_x^- by isotope analysis. ($\delta^{15}N$ of p-NO_x^-: -1~+7‰)

Relatively high p-NO_x^- $\delta^{15}N$ was observed in Dec. 21 because of the agricultural activities (mowing, fertilizing)

* Fog events: 13N, 14D, 15D

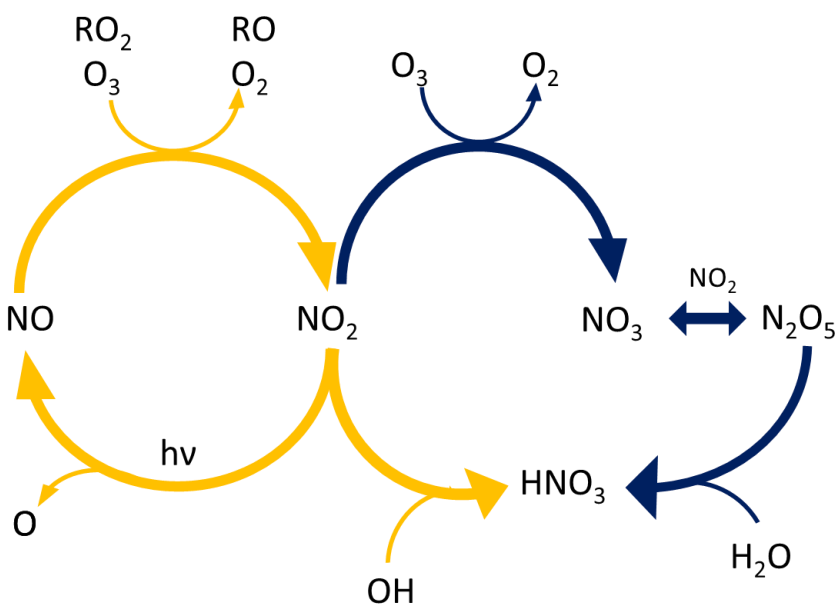


* NO_x^-: NO_3^- or NO_2^-

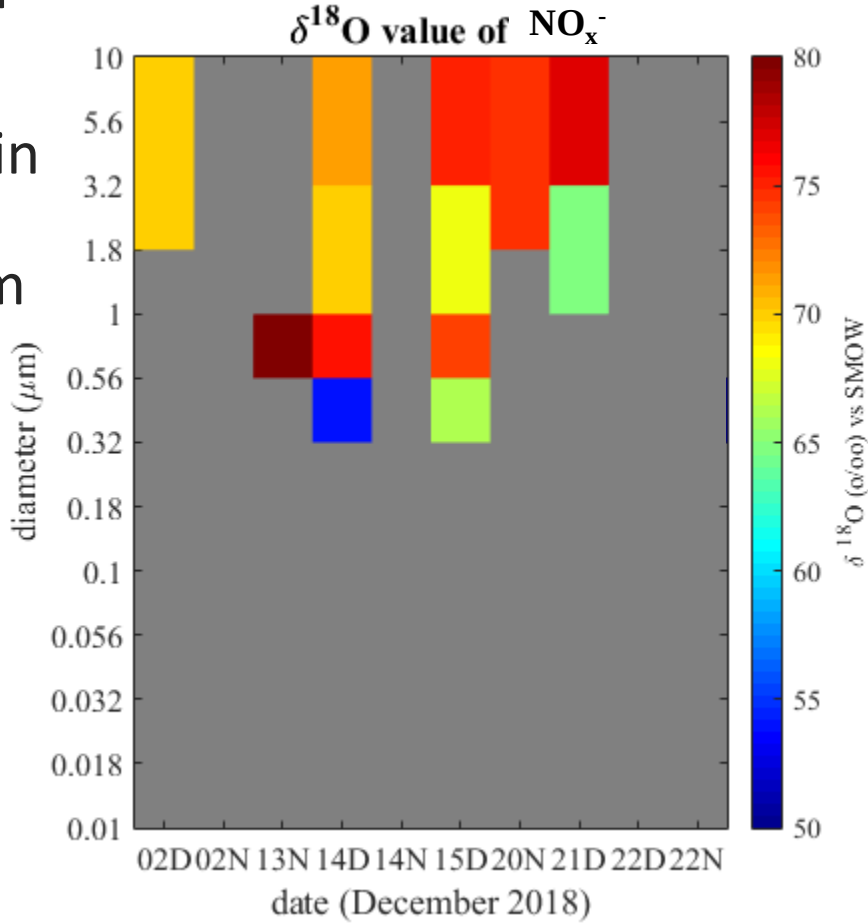
$\delta^{18}O$ size distribution

$\delta^{18}O$ of p-NO_x^- is between +55~80‰
→ O_3 oxidation is the main pathway of HNO_3 formation.

In foggy events, the $\delta^{18}O$ value of NN in diameter 0.56-1 μm is relatively high
→ The NO_3^- formation is different from that of other size bins.

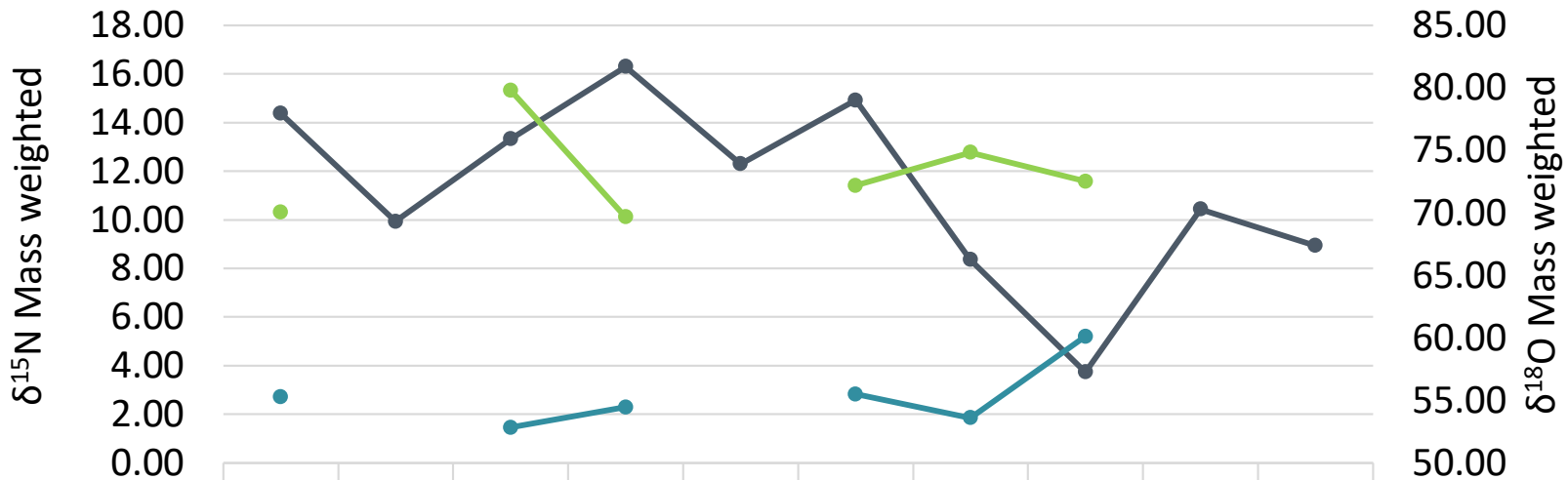


* Fog events: 13N, 14D, 15D



* NO_x^-: NO_3^- or NO_2^-

Mass weighted average of isotope ratio



	181202D	181202N	181213N	181214D	181214N	181215D	181220N	181221D	181222D	181222N
d15N_NH4	14.38	9.93	13.33	16.30	12.30	14.92	8.35	3.73	10.43	8.94
d15N_NN	2.72		1.46	2.29		2.83	1.85	5.20		
d18O_NN	70.05		79.81	69.67		72.18	74.82	72.52		

$\delta^{15}N$ of NH_4^+ is higher in the daytime and foggy periods

181221D may have strong agricultural effect: fertilizing+mowing

$\delta^{18}O$ of NO_x^- in daytime is slightly lower than in nighttime, indicating the radical reactions happened in daytime.

Summary

1. The hygroscopicity κ:

- The κ value for the particle diameter <120 nm showed a strong time dependence likely due to the sources and the chemical processes.
- The κ value of aerosol falls between 0.05~0.2, similar to the value of urban area and behaves more like organic compounds

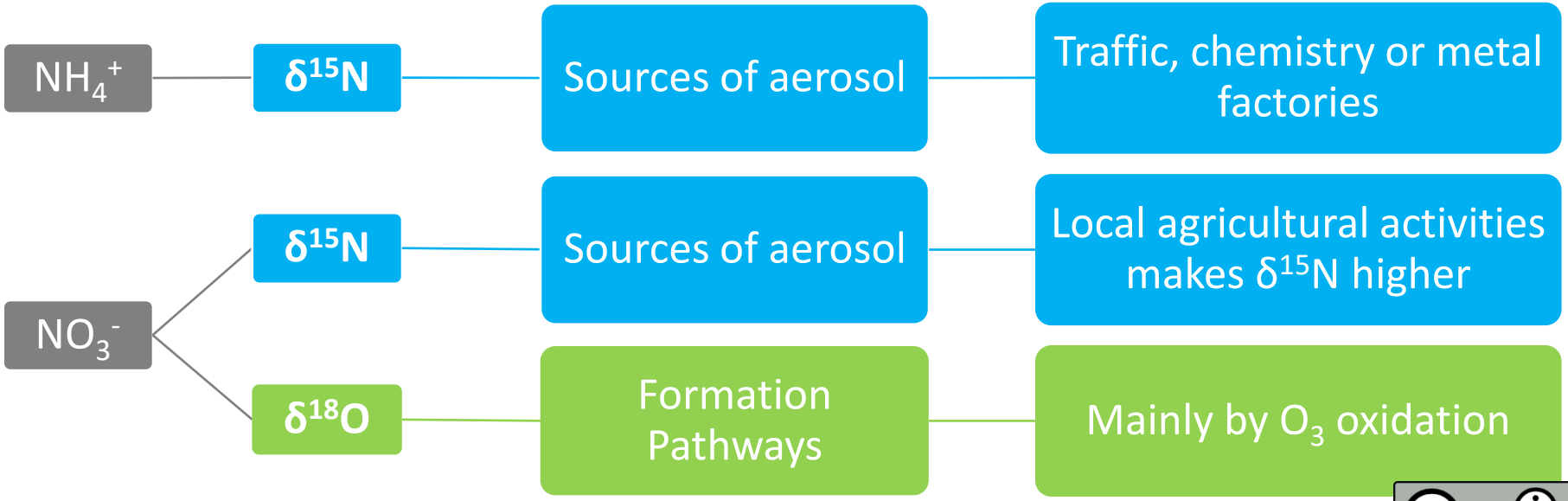
2. Aerosol properties under different weather conditions:

- The valley wind and sea breeze during daytime bring more pollutants to inland during daytime.
- Stronger inversion during foggy period may makes higher concentration of functional groups .
- Fog formation can further affect the aerosol composition:
  1) Hygroscopic growth makes the size distribution of aerosol containing NH_4^+, SO_4^{2-} shifts to a larger mode.
  2) NO_3^- of 0.56-1 μm is much higher during foggy periods, which indicates aqueous phase reaction is included under foggy condition. This can be further supported by isotope results.

Summary

3. Isotope Analysis:

- p-NH_4^+ and p-NO_x^- are likely contributed from anthropogenic sources such as factories and traffic.
- The agricultural activities such as fertilizing and mowing may have strong influence on the local aerosol formation.
- The observed high $\delta^{18}O$ might result from the pathways of the oxidation of NO with O_3 rather than with RO_2



References

Braman, R.S. and Hendrix, S.A., 1989, Nanogram nitrite and nitrate determination in environmental and biological materials by vanadium (III) reduction with chemiluminescence detection. Anal Chem, 61: 2715-2718.

David Felix, J., Elliott, E.M., Gish, T., Maghirang, R., Cambal, L. and Clougherty, J., 2014, Examining the transport of ammonia emissions across landscapes using nitrogen isotope ratios. Atmospheric Environment, 95: 563-570.

Casciotti, K.L., Sigman, D.M., Hastings, M.G., Bohlke, J.K. and Hilkert, A., 2002, Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal Chem, 74: 4905-4912.

Fang, Y.T., Koba, K., Wang, X.M., Wen, D.Z., Li, J., Takebayashi, Y., Liu, X.Y. and Yoh, M., 2011, Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China. Atmospheric Chemistry and Physics, 11: 1313-1325.

Felix, J.D., Elliott, E.M. and Shaw, S.L., 2012, Nitrogen isotopic composition of coal-fired power plant NOx: influence of emission controls and implications for global emission inventories. Environ Sci Technol, 46: 3528-3535.

Guha, T., Lin, C.T., Bhattacharya, S.K., Mahajan, A.S., Ou-Yang, C.-F., Lan, Y.-P., Hsu, S.C. and Liang, M.-C., 2017, Isotopic ratios of nitrate in aerosol samples from Mt. Lulin, a high-altitude station in Central Taiwan. Atmospheric Environment, 154: 53-69.

Hastings, M.G., Sigman, D.M. and Lipschultz, F., 2003, Isotopic evidence for source changes of nitrate in rain at Bermuda. Journal of Geophysical Research: Atmospheres, 108: n/a-n/a.

Maria, S.F., Russell, L.M., Turpin, B.J. and Porcja, R.J., 2002, FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean. Atmospheric Environment, 36: 5185-5196.

Savard, M.M., Cole, A., Smirnoff, A. and Vet, R., 2017, δ 15 N values of atmospheric N species simultaneously collected using sector-based samplers distant from sources – Isotopic inheritance and fractionation. Atmospheric Environment, 162: 11-22.

Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M. and Bohlke, J.K., 2001, A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal Chem, 73: 4145-4153.

Walters, W.W., Chai, J. and Hastings, M.G., 2018, Theoretical Phase Resolved Ammonia–Ammonium Nitrogen Equilibrium Isotope Exchange Fractionations: Applications for Tracking Atmospheric Ammonia Gas-to-Particle Conversion. ACS Earth and Space Chemistry, 3: 79-89.

Weigand, M.A., Foriel, J., Barnett, B., Oleynik, S. and Sigman, D.M., 2016, Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. Rapid Commun Mass Spectrom, 30: 1365-1383.