Supplyment for

Measurement Report: Seasonal variation and anthropogenic influence on cloud condensation nuclei (CCN) activity in the South China Sea: Insights from shipborne observations during summer and winter of 2021

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Text S1-S2, Figure S1-S12, and Table S1-S3

Text S1 Data quality control

In order to mitigate the influence of research vessel emissions on the data and obtain authentic atmospheric measurements in the South China Sea, we applied the following data processing procedures.

1. In the summer cruise, the exhaust emissions from the ship were released at the stern while the observation station was located at the bow. To account for this, and utilizing the accurate relative wind direction information provided by the meteorological station, we adopted method in Huang et al. (2018) to exclude data within the range of 170 to 250 degrees of relative wind direction and with relative wind speeds exceeding 1 m s^{-1}. Additionally, we removed data during abnormal periods (greater than three times the standard deviation) based on the measurements of black carbon (BC) and pollutant NO_X according to Sun et al. (2023).
2. In the winter expedition, the ship's exhaust emissions were released at the stern while the observation station was located at the bow. However, due to the lack of accurate relative wind direction information, we employed a similar approach as mentioned above (Sun et al., 2023). We removed abnormal data (greater than three times the standard deviation) based on the measurements of pollutant NOx and BC during periods identified as anomalies.

Text S2 CE selection of the Tof-ACSM

The selection of collection efficiency (CE) was based on previous observation conducted in the South China Sea using the Tof-ACSM (Sun et al., 2023). We primarily considered the influence of two factors: aerosol acidity and the impact of nitrate. The calculation was performed using the following formula (Middlebrook et al., 2012):

Effect of high ammonium nitrate fraction (ANMF):

$$ANMF = \frac{NO_3^- \times \left(\frac{80}{62}\right)}{SO_4^{2-} + NO_3^- + Cl^- + NH_4^+ + Organics} \quad (1)$$

$$CE_{est,ANMF} = 0.0833 + 0.9167 \times ANMF \quad (2)$$

$$CE_{dry,ANMF} = \max\left(0.5, CE_{est,ANMF}\right) \quad (3)$$

Effect of acidity:

$$\frac{NH_4^+{}_{measurd}}{NH_4^+{}_{predicted}} = \frac{NH_4^+/18}{\left(2\times\left(\frac{SO_4^{2-}}{96}\right)+\left(\frac{NO_3^-}{62}\right)+\left(\frac{Cl^-}{35.5}\right)\right)} \quad (4)$$

$$CE_{est,acidity} = 1 - 0.73 \times \left(\frac{NH_4^+{}_{measurd}}{NH_4^+{}_{predicted}}\right) \quad (5)$$

$$CE_{dry,acidity} = \max\left(0.5, CE_{est,acidic}\right) \quad (6)$$

As shown in Fig. S2, the ANNF is higher in winter compared to summer, although the impacts are not highly pronounced. On the other hand, the effect of aerosol acidity is more significant in summer and relatively lower in winter. Taking into account these factors and referring to Crenn et al. (2015), we employed temporal-varying $CE_{dry,acidic}$ according to eq. (6) in this study, as shown in Fig. S2.

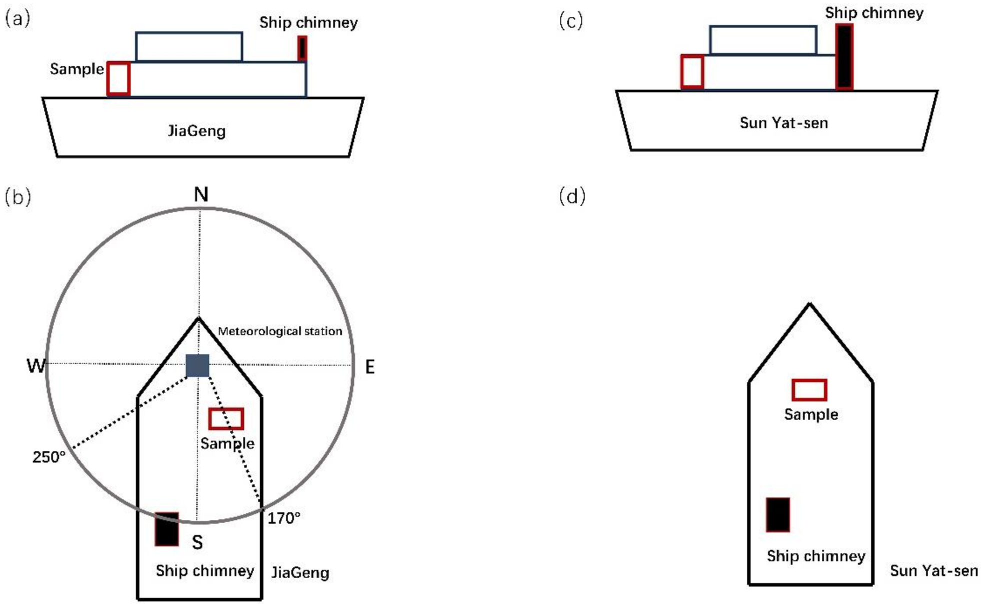

Figure S1. Instrument and ship chimney loaction in two cruise.

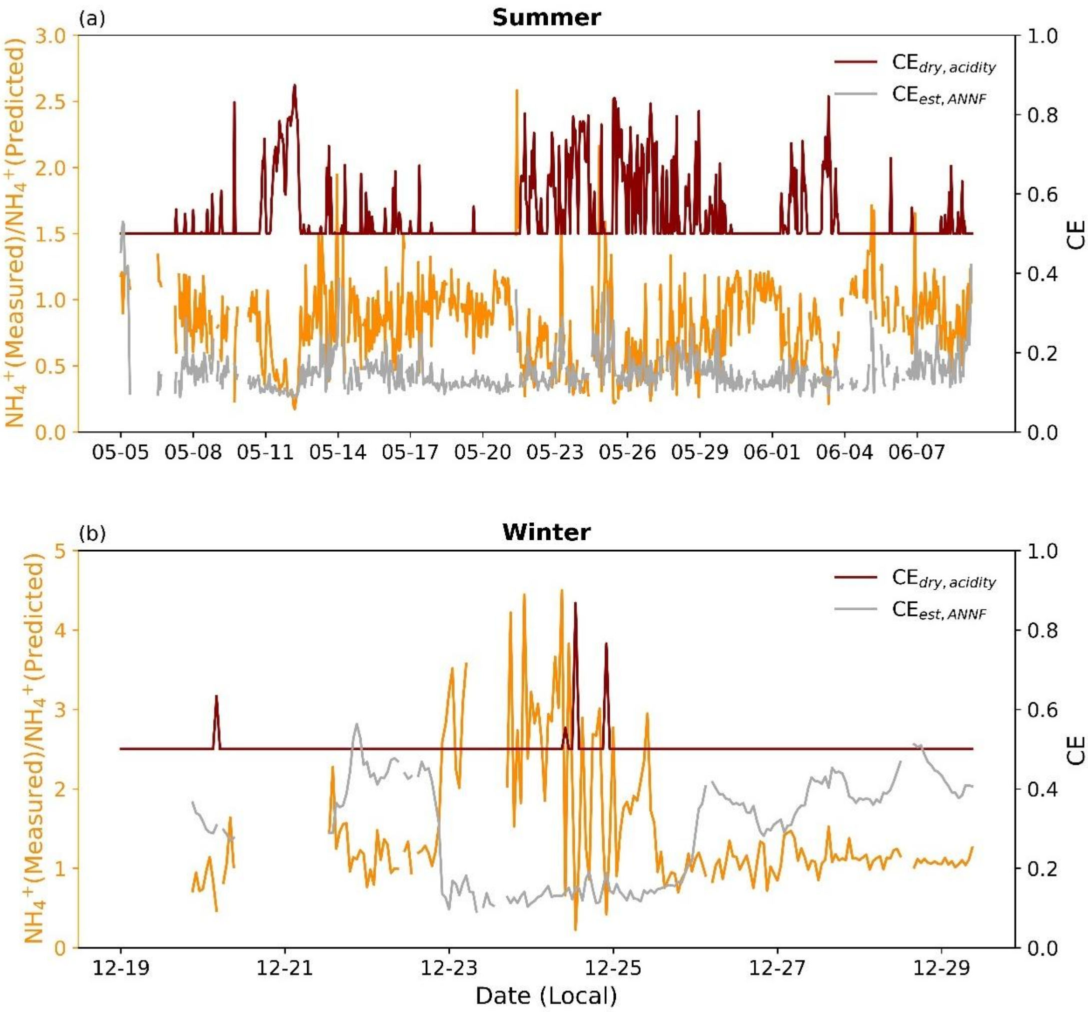

Figure S2. Timeseries of $CE_{dry,acidity}$, $CE_{est,ANNF}$, and $NH_4^+{}_{,Measured}/NH_4^+{}_{,predicted}$.

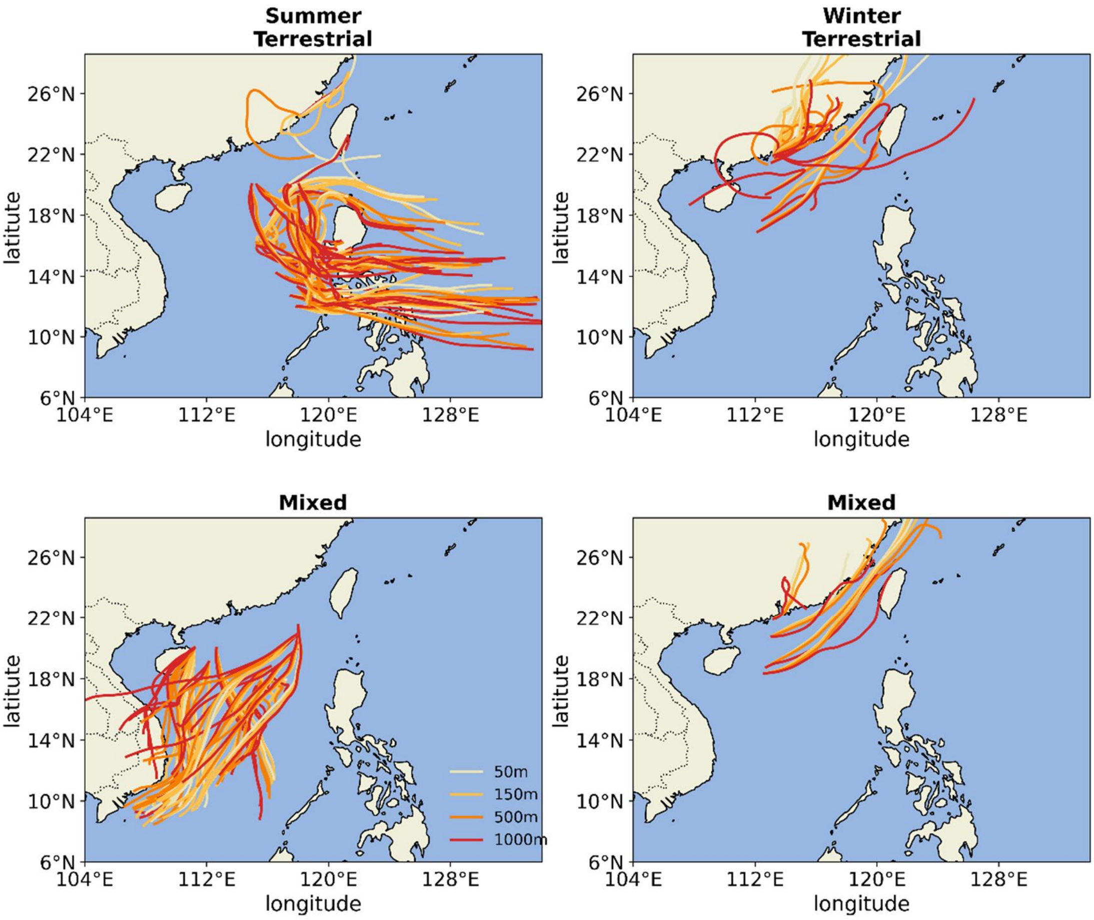

Figure S3. Backward trajectories on 50m, 150m, 500m, and 1000m in summer and winter.

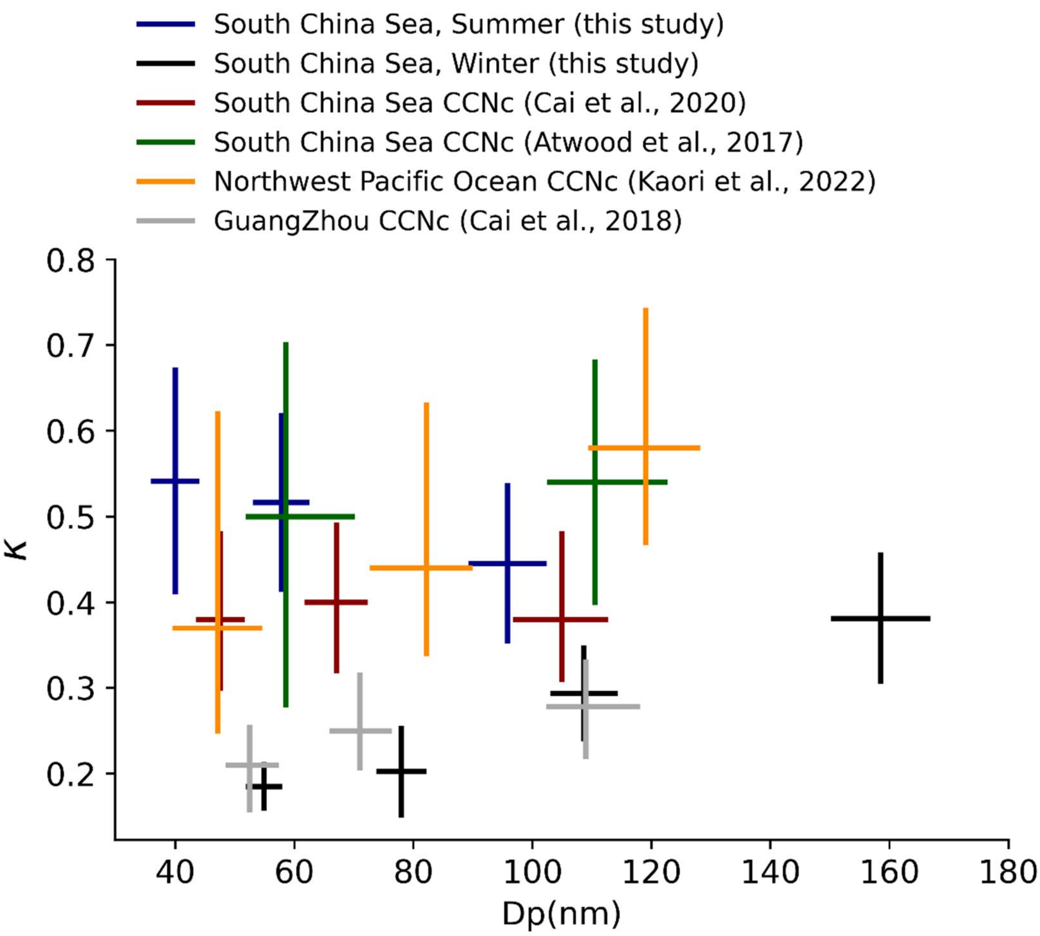

Figure S4. Comparison of activation diameter and κ in this Study with other Studies.

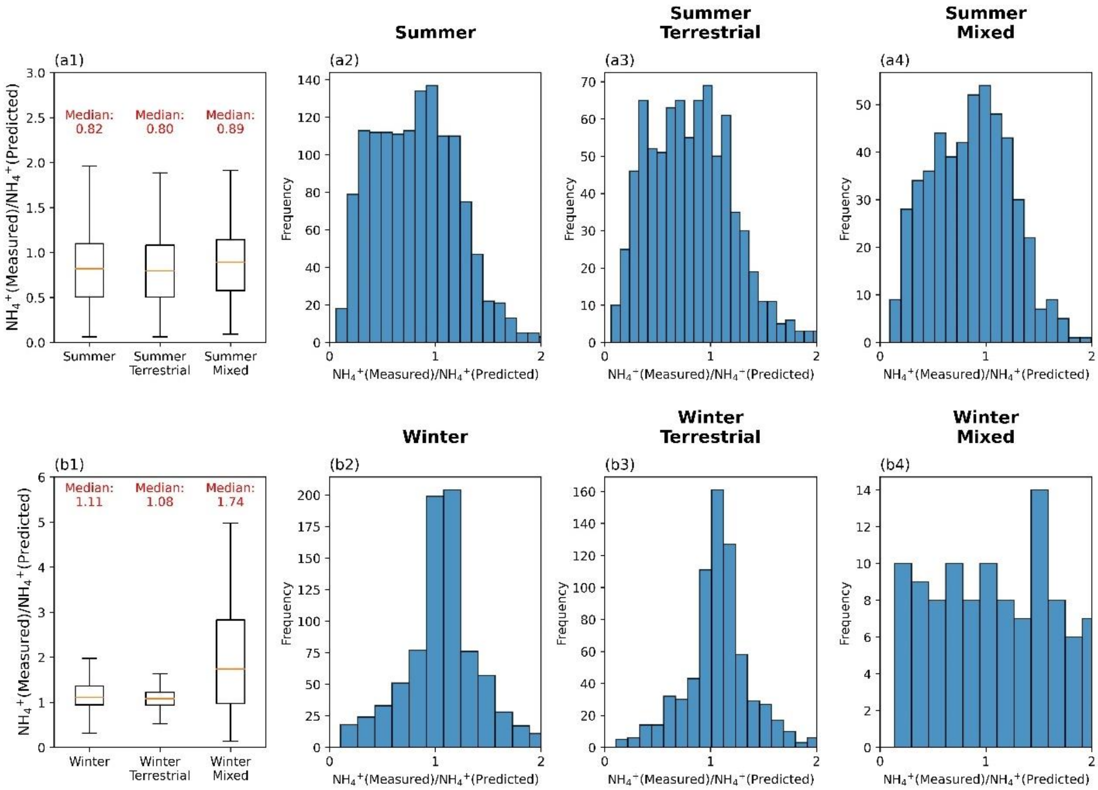

Figure S5. The value of $NH_4^+$$_{,Measured}$/$NH_4^+$$_{,predicted}$ in all observation and under effect of terrestrial and mixed air masses in summer and winter.

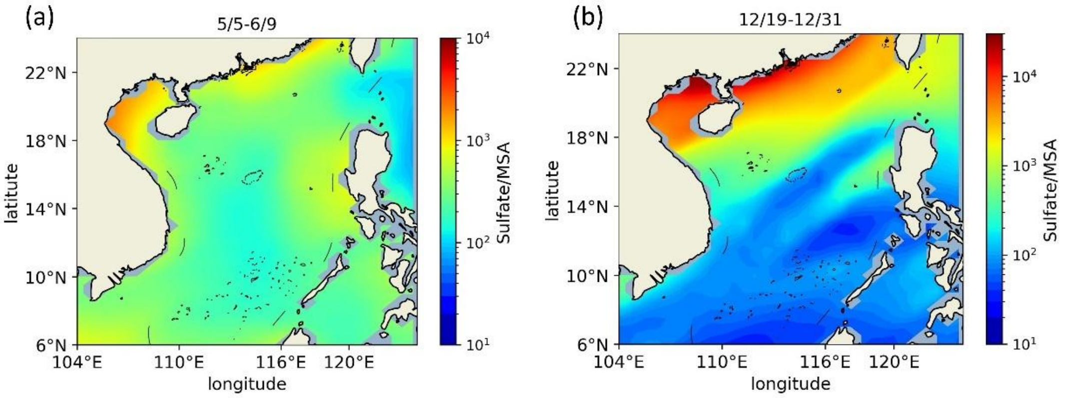

Figure S6. The ratio of sulfate to MSA in summer (a) and winter (b).

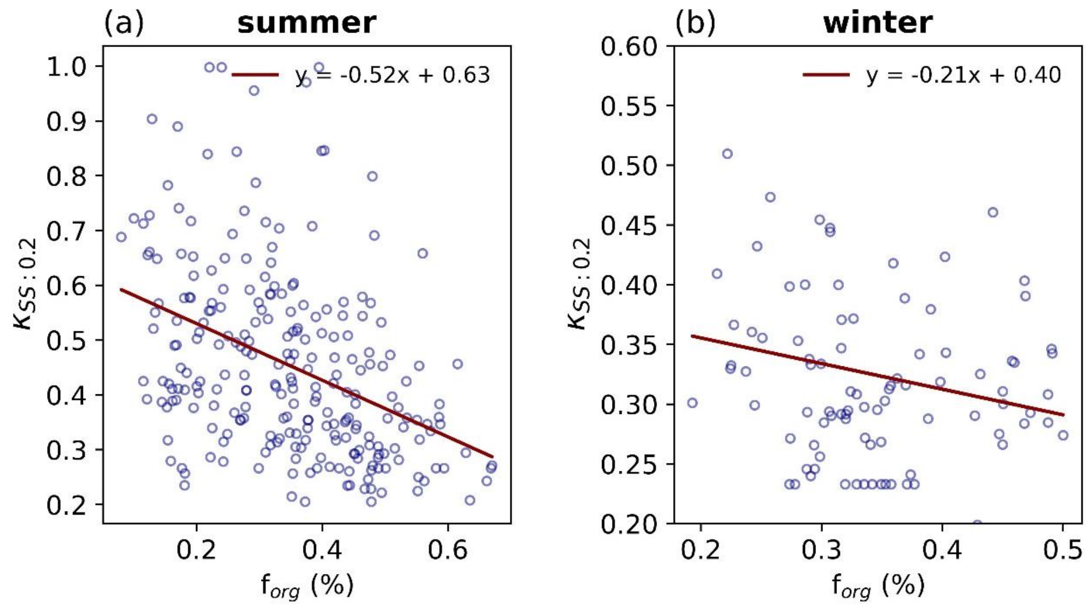

Figure S7. Scatter plot of κ under the supersaturation of 0.2% and organic mass fraction with linear regression.

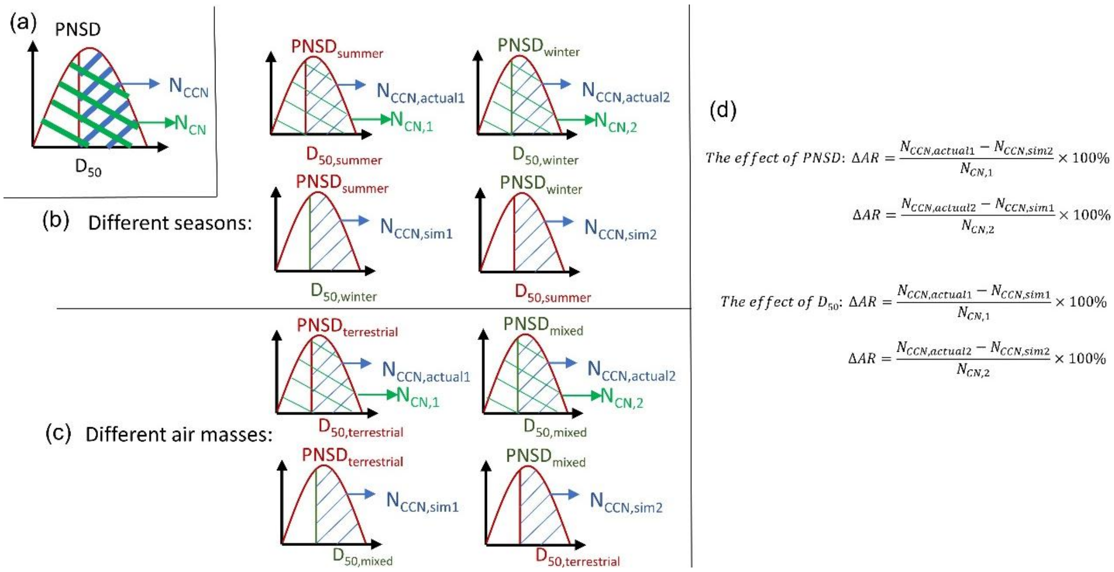

Figure S8. The Calculation Scheme of investigating the effect PNSD and aerosol hygroscopicity (D_{50}) on the activation ratio (AR). (a) The example of total particle and cloud condensation nuclei number concentration calculation; (b) The calculation scheme for different seasons; (c) The calculation scheme for different air masses; (d) the formula of delta AR.

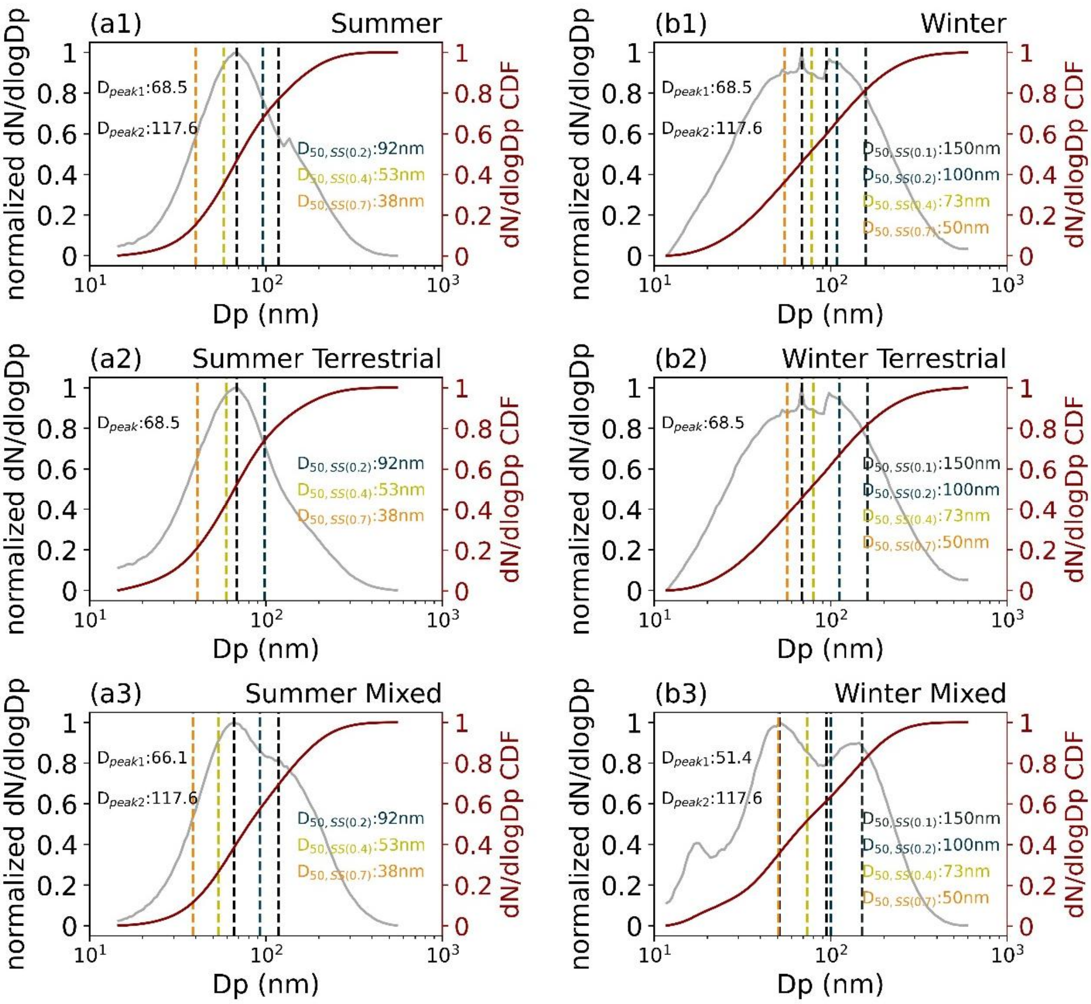

Figure S9. Normalized particle number size distribution and activation diameter at different supersaturation under effect of terrestrial and mixed air masses in summer and winter. Cumulative distribution function (CDF) is a function that represents the accumulation of probabilities for values less than or equal to a given value in a statistical dataset.

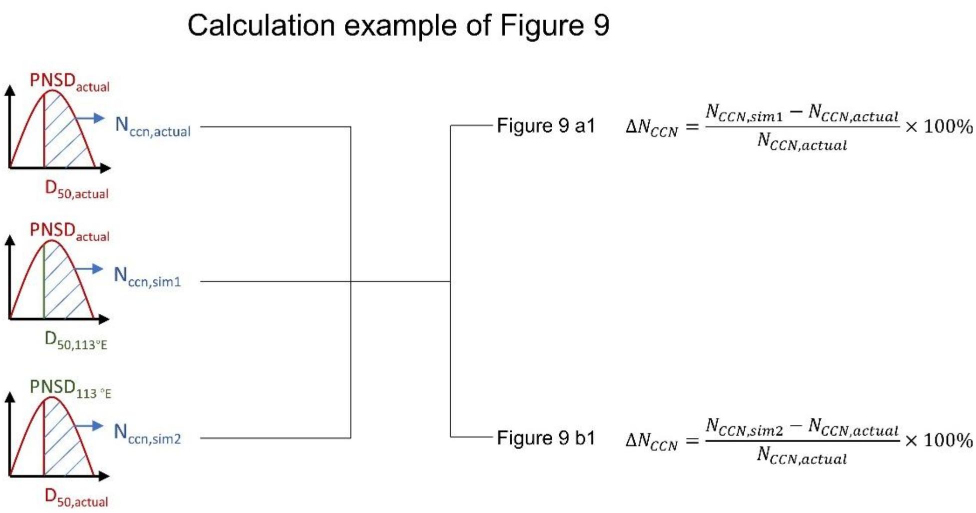

Figure S10. The calculation example of Figure 9; the subscript "actual" denotes the observed values.

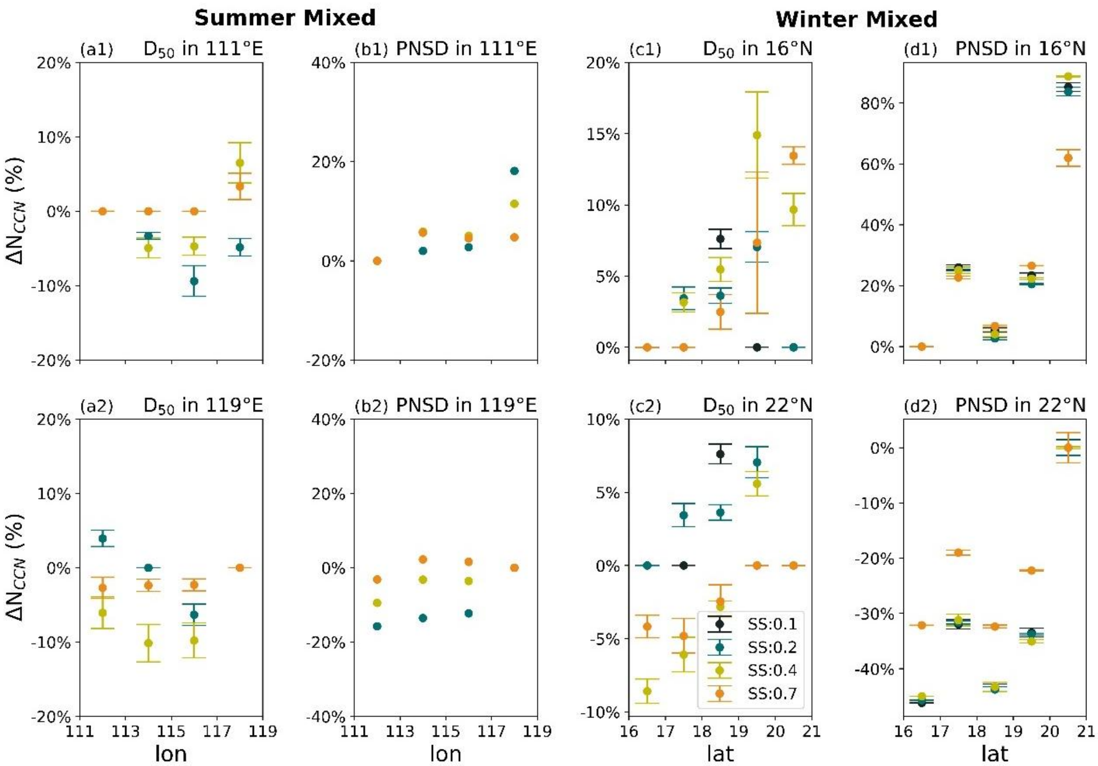

Figure S11. The difference between the calculated cloud condensation nuclei (CCN) concentration using the activation diameters from the farthest and nearest offshore distances, along with the measured particle size distribution, and the measured CCN concentration under the effect of mixed air masses in summer (a1 and a2) and winter (c1 and c2); The difference between the calculated CCN concentration using the particle size distribution from the farthest and nearest offshore distances, along with the measured activation diameter, and the measured CCN concentration under the effect of mixed air masses in summer (b1 and b2) and winter (d1 and d2).

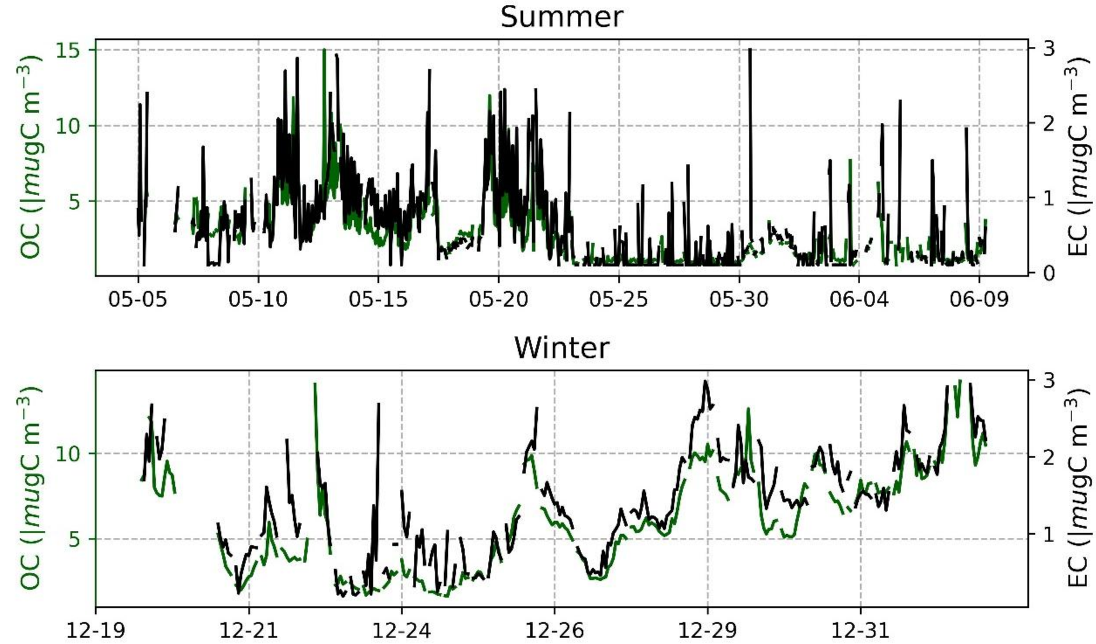

Figure S12. Timeseries of organic carbon and elemental carbon in summer and winter.

Species	Summer			Winter		
	All	**Terrestrial**	**Mixed**	**All**	**Terrestrial**	**Mixed**
Particle number concentration (cm^{-3})						
N_{CN}	7268.85	9921.94	2114.31	4903.73	6336.74	1836.20
PM_1 ($\mu g\ m^{-3}$)						
Sulfate	1.44	1.56	1.27	3.47	4.34	1.58
Organic	1.34	1.42	1.22	7.17	9.36	2.42
Nitrate	0.22	0.26	0.17	4.04	5.75	0.29
Ammonium	0.50	0.52	0.47	3.15	3.73	1.91
Chloride	0.08	0.09	0.07	0.28	0.35	0.12
$PM_{2.5}$ ($\mu g\ m^{-3}$)						
OC	2.85	3.54	1.54	6.05	6.90	2.45
EC	0.64	0.79	0.36	1.39	1.56	0.65
Gas (ppb)						
SO_2	1.61	1.74	1.44	2.25	2.43	1.76
NO_2	9.35	12.82	3.25	47.80	51.06	38.60
NO	32.75	50.73	3.92	9.60	8.66	12.24
CO	279.82	297.54	255.21	69.99	70.02	69.88
O_3	15.79	15.02	17.07	26.64	20.83	40.17

Table S1. Particle number concentration, mass concentration of NR-PM1, OC, and EC, gas concentration under effect of different air masses in summer and winter.

	Summer		**Winter**	
median diameter (nm)	**Terrestrial**	**Mixed**	**Terrestrial**	**Mixed**
All	68.50	66.10	68.5	51.4
Nucleation	19.34±8.01	23.97±7.09	23.95±6.05	20.82±6.76
Aikten	61.40±13.47	60.24±10.50	55.30±18.05	52.51±8.10
Accumulation	151.66±39.75	140.08±27.66	148.59±41.39	144.50±15.98

Table S2. Peak diameter of nucleation, aikten, and accumulation mode under effect of different air masses in summer and winter.

Period	ss	0.1%	0.2%	0.4%	0.7%
Summer					
All	N_{CCN} (cm^{-3})		2899	5451	5771
	D_{50}		96	58	40
	AR		0.39	0.67	0.85
Terrestrial	N_{CCN} (cm^{-3})		3009	6443	7450
	D_{50}		98	60	41
	AR		0.34	0.62	0.81
Mixed	N_{CCN} (cm^{-3})		908	1473	1794
	D_{50}		92	54	39
	AR		0.46	0.76	0.89
Winter					
All	N_{CCN} (cm^{-3})	881	1661	2357	3053
	D_{50}	156	106	77	54
	AR	0.21	0.36	0.49	0.64
Terrestrial	N_{CCN} (cm^{-3})	1049	2209	3341	4445
	D_{50}	158	109	78	56
	AR	0.14	0.29	0.43	0.59
Mixed	N_{CCN} (cm^{-3})	752	1189	1524	1909
	D_{50}	150	100	73	50
	AR	0.25	0.40	0.53	0.67

Table S3. Summary of average N_{CCN}, D_{50}, and AR at 0.1, 0.2, 0.4, and 0.7 % ss under effect of different air masses in summer and winter.

Reference

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Frohlich, R., Belis, C. A., Aas, W., Aijala, M., Alastuey, A., Artinano, B., Baisnee, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillon, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Esteve, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prevot, A. S. H., Jayne, J. T., and Favez, O.: ACTRIS ACSM intercomparison - Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments, Atmos Meas Tech, 8, 5063-5087,doi: 10.5194/amt-8-5063-2015, 2015.

Huang, S., Wu, Z. J., Poulain, L., van Pinxteren, M., Merkel, M., Assmann, D., Herrmann, H., and Wiedensohler, A.: Source apportionment of the organic aerosol over the Atlantic Ocean from 53 degrees N to 53 degrees S: significant contributions from marine emissions and long-range transport, Atmos. Chem. Phys., 18, 18043-18062,doi: 10.5194/acp-18-18043-2018, 2018.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci Tech, 46, 258-271,doi: 10.1080/02786826.2011.620041, 2012.

Sun, Q., Liang, B., Cai, M., Zhang, Y., Ou, H., Ni, X., Sun, X., Han, B., Deng, X., Zhou, S., and Zhao, J.: Cruise observation of the marine atmosphere and ship emissions in South China Sea: Aerosol composition, sources, and the aging process, Environ. Pollut, 316, 120539,doi: https://doi.org/10.1016/j.envpol.2022.120539, 2023.