Competitive uptake of dimethylamine and trimethylamine against ammonia on acidic particles in marine atmospheres

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Text S1. Detection limits for ions during the cruise study

Table S1. The detection limits for NH_4^+, $DMAH^+$, $TMAH^+$, NO_3^- and SO_4^{2-}

Table S2. The comparison of DL/2 substitution and Kaplan－Meier (KM) procedure to process the ratios of data that include nondetects(ND).

Figure S1. Time series of the gas and particulate ion concentrations, as well as ambient conditions and modeled pH.

Figure S2. Modeled [DMA] and [TMA] versus the observations in Period 2-B.

Text S1 Detection limits for ions during the cruise study

The detection limits (DL) in concentration were determined using the conventional approach, i.e., DL=(Q/V)*(3*N)/I, in which Q was the quantity of a sample with the lowest concentration used in the calibration; V was the injection volume; N was the noise of the sample while I was the signal response of the sample; the value of I/N was calculated directly by the Thermo Scientific Chromeleon Chromatography Data System (CDS).

The detection limits of NH_4^+, $DMAH^+$, $TMAH^+$, NO_3^- and SO_4^{2-} were listed in Table S1, in which both DL of ions in injection solution and the corresponding concentration in the ambient air were provided.

Table S1. The detection limits of NH_4^+, $DMAH^+$, $TMAH^+$, NO_3^- and SO_4^{2-}

	DL of ions in injection solution ($\mu g\ L^{-1}$)	Corresponding concentration in the ambient air ($\mu g\ m^{-3}$)
NH_4^+	0.04	$2*10^{-3}$
$DMAH^+$	0.08	$4*10^{-3}$
$TMAH^+$	0.04	$2*10^{-3}$
NO_3^-	1	$5*10^{-2}$
SO_4^{2-}	0.3	$1.5*10^{-2}$

Half of the detection limits were used to represent the concentrations of ions below those limits in this study. Recently, Helsel reported that the Kaplan–Meier procedure should be used to compute the ratios of data that include nondetects[1]. The comparison between the use of half of the detection limits and the Kaplan–Meier procedure were provided in the Table S2 below.

Table S2. The comparison of DL/2 substitution and Kaplan－Meier (KM) procedure to process the ratios of data that include nondetects (NDs).

	Ratios of data	DL/2	KM	NDs as a percentage of the total	multiple of ratios between two procedure
the whole campaign	DMA/NH_3	$(8±6)*10^{-3}$	$(8±6)*10^{-3}$	7.2%	-
	$DMAH^{+*}/NH_4^+$	$(4±8)*10^{-2}$	$(4±0.4)*10^{-2}$	9.1%	-
	$DMAH^{+*}/(DMAH^{+*}+DMA)$	0.56±0.25	0.59±0.24	15%	0.054
	TMA/NH_3	$(3±3)*10^{-3}$	$(3±3)*10^{-3}$	2.1%	-
	$TMAH^{+*}/NH_4^+$	$(5±12)*10^{-3}$	$(8±19)*10^{-3}$	40%	0.6
	$TMAH^{+*}/(TMAH^{+*}+TMA)$	0.34±0.16	0.44±0.15	41%	0.29
when $[NH_3]>$ 1.8 μg m^{-3}	DMA/NH_3	$(2±1)*10^{-3}$	$(2±1)*10^{-3}$	0	-
	$DMAH^{+*}/NH_4^+$	$(5±6)*10^{-4}$	$(6±9)*10^{-4}$	28%	0.2
	$DMAH^{+*}/(DMAH^{+*}+DMA)$	0.31±0.16	0.37±0.17	28%	0.19
	TMA/NH_3	$(5±3)*10^{-4}$	$(5±3)*10^{-4}$	3%	-
	$TMAH^{+*}/NH_4^+$	$(1±1)*10^{-4}$	$(1±3)*10^{-3}$	98%	9
	$TMAH^{+*}/(TMAH^{+*}+TMA)$	0.21±0.08	0.39±0.56	98%	0.86
when $[NH_3]<$ 0.3 μg m^{-3}	DMA/NH_3	$(1±0.6)*10^{-2}$	$(1±0.6)*10^{-2}$	11%	-
	$DMAH^{+*}/NH_4^+$	$(1±1)*10^{-1}$	$(1±1)*10^{-1}$	0	-
	$DMAH^{+*}/(DMAH^{+*}+DMA)$	0.80±0.15	0.80±0.15	11%	-
	TMA/NH_3	$(7±2)*10^{-3}$	$(7±2)*10^{-3}$	1.9%	-
	$TMAH^{+*}/NH_4^+$	$(1±2)*10^{-2}$	$(1±2)*10^{-2}$	14%	-
	$TMAH^{+*}/(TMAH^{+*}+TMA)$	0.45±0.15	0.49±0.10	15%	0.089
when 0.3 μg m^{-3} $<[NH_3]<$ 1.8 μg m^{-3}	DMA/NH_3	$(8±4)*10^{-3}$	$(8±3)*10^{-3}$	8.9%	-
	$DMAH^{+*}/NH_4^+$	$(2±2)*10^{-2}$	$(2±2)*10^{-2}$	4.4%	-
	$DMAH^{+*}/(DMAH^{+*}+DMA)$	0.56±0.19	0.55±0.19	9.9%	-0.018
	TMA/NH_3	$(3±1)*10^{-3}$	$(3±1)*10^{-3}$	2%	-
	$TMAH^{+*}/NH_4^+$	$(4±7)*10^{-3}$	$(5±8)*10^{-3}$	25%	0.25
	$TMAH^{+*}/(TMAH^{+*}+TMA)$	0.35±0.16	0.41±0.13	26%	0.17

The Ratios of data processed by DL/2 substitution and Kaplan－Meier (KM) procedure has been compared in the Table S2. When the numbers of NDs account for less than 20% of the total, the difference between two processes can be ignored. When the percentage of NDs covers over 20% of the total samples, the difference between two processes increases.

The uncertainty for NH_4^+ was 5% when its measured concentration in the injection solution was above 4 μg L^{-1} (corresponding to 0.2 μg m^{-3} NH_4^+ in ambient air) at the beginning, intermediate maintenance and ending of the cruise period. The uncertainties of $DMAH^+$ and $TMAH^+$ were 41% and 13%, respectively, when their concentrations in the injection solution were above 0.2 μg L^{-1} (corresponding to 10 ng m^{-3} $DMAH^+$ and $TMAH^+$ in ambient air). The uncertainty of $DMAH^+$ decreased to 14% when its concentration was over 50 ng m^{-3} in ambient air. Larger uncertainties were expected for the measured concentrations of $DMAH^+$ and $TMAH^+$ below 10 ng m^{-3} in the ambient air, although they were still detected.

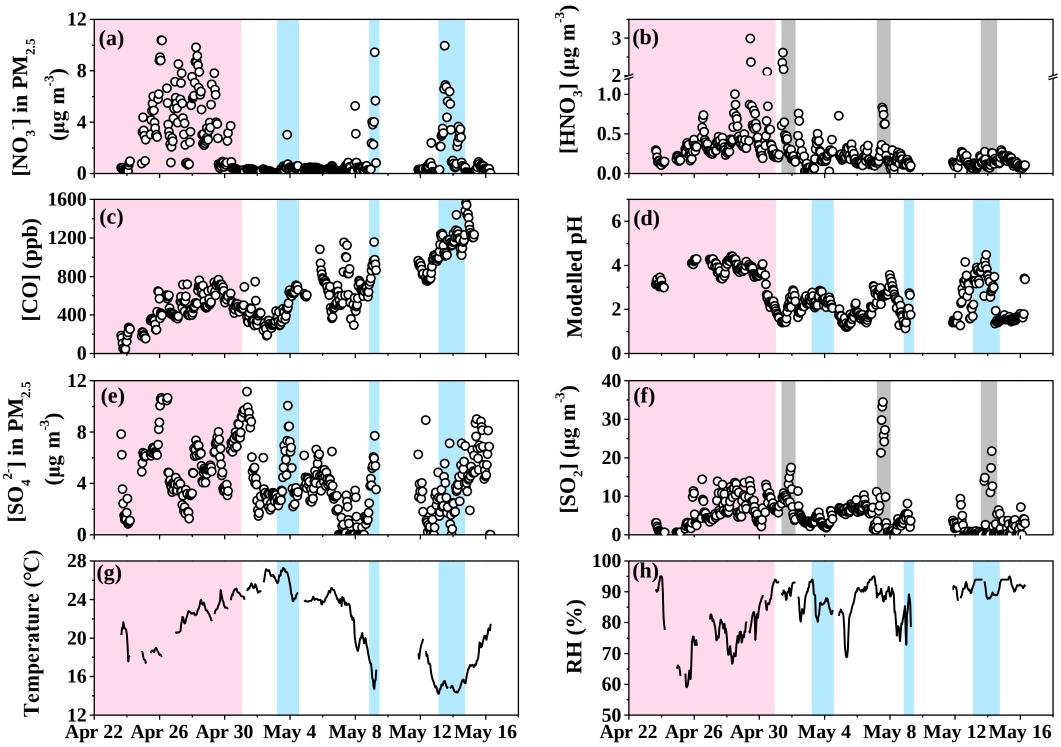

Fig S1. Time series of the gas and particulate ion concentrations, as well as ambient conditions and modeled pH. (a) particulate NO_3^-; (b) HNO_3; (c) CO; (d) modelled pH (e) particulate SO_4^{2-}; (f) SO_2; (g) ambient temperature; (h) RH. Period 1 is highlighted in pink and the remainder is Period 2. Three SO_2 plumes due to emissions from the vessel are highlighted in gray and three troughs of $TMAH^+$ are highlighted in blue.

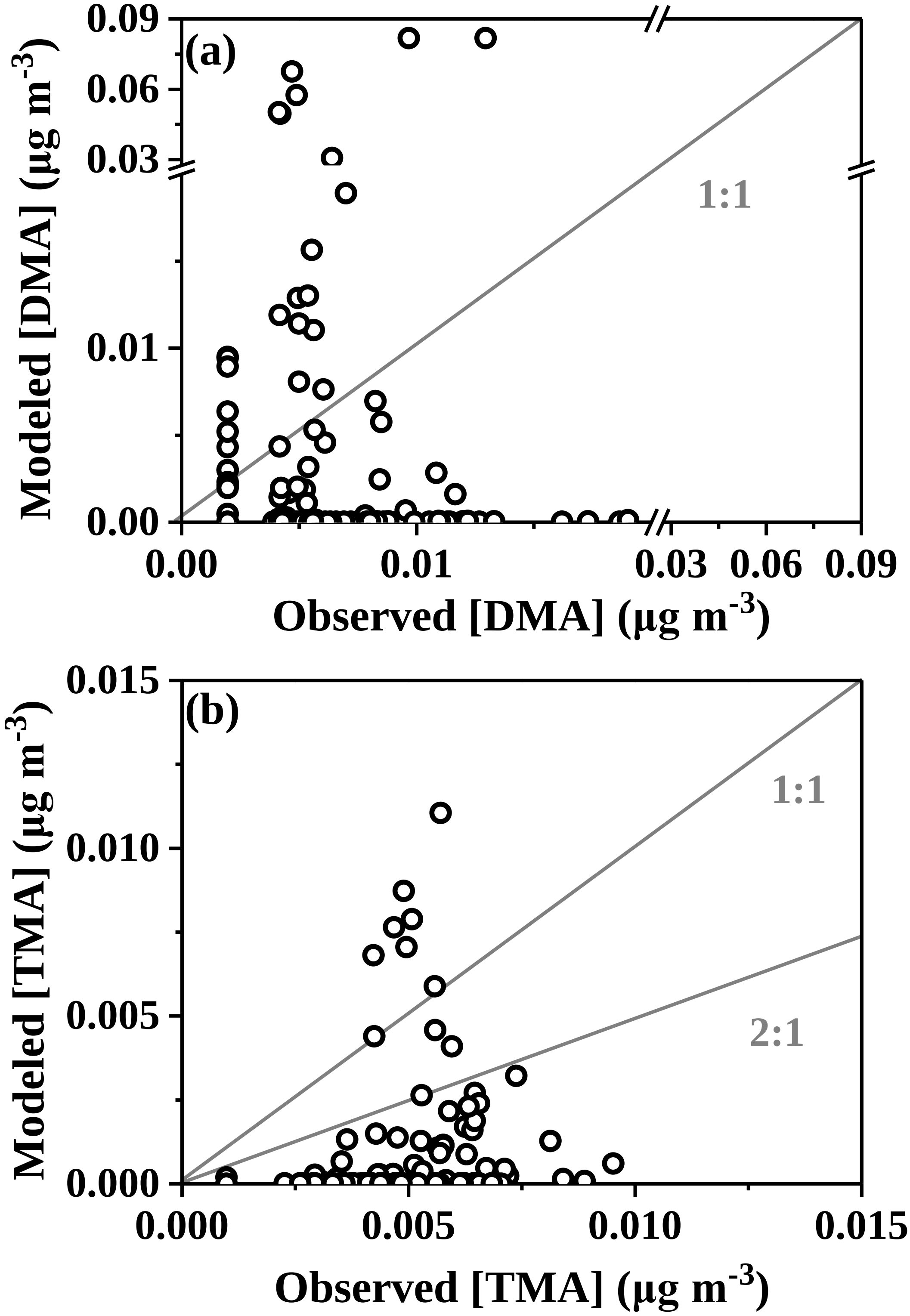

Fig S2. Modeled [DMA] and [TMA] versus the observations in Period 2-B. (a) [DMA] and (b) [TMA].

Reference

1. Helsel, D. R.. Summing nondetects: Incorporating low-level contaminants in risk assessment. Integr. Environ. Asses. 2010, 6(3), 361-366.DOI: 10.1002/ieam.31