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Chemical characteristics of cloud water and the impacts on aerosol properties at a subtropical mountain site in Hong Kong SAR

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Table S1. Comparison of glyoxal and methylglyoxal in cloud water [μM] and their gas-phase precursors [ppb] as well as pollutants concentrations [ppb] at Mt. TMS and other sites.

	Glyoxal	Methyl glyoxal	Isoprene	Benzene	Toluene	Xylene	NO_x	O_3	Ref
Mt. TMS	6.7	19.1	0.16	0.5	2.3	0.9	3	31	this study
Whistler, Canada	0.6-1.8	0.5-7.4	0.6	0.05	0.1		4	25	(Ervens et al., 2013)
Davis, USA	1.3-8.7	0.1-0.9	0.2	2	4		20	70	(Ervens et al., 2013)
Mt. Schmücke, Germany	0.8-11.3	0.4-3.3							(van Pinxteren et al., 2005)
Puy de Dôme, France	0.13-0.89	0.01-0.22		up to 1.1 [a]					(Deguillaume et al., 2014;Barbet et al., 2016)

[a] sum of observed benzene, toluene and ethylbenzene (Barbet et al., 2016)

Table S2. Description of six cloud events at Mt. TMS in November 2015. Sampling time, sample number (n), liquid water content (LWC), pH values, equivalent molar ratios of chloride, potassium, calcium and magnesium to sodium and non-sea-salt sulfate (nss-SO_4^{2-}) to nitrate, formic-to-acetic acid (F/A) ratio in cloud water and in the corresponding gas phase (calculated), and trace gases are included.

Events	Day	Sampling duration	n	LWC ($g\ m^{-3}$)	pH	Cl^-/Na^+ (1.16*)	K^+/Na^+ (0.02*)	Ca^{2+}/Na^+ (0.04*)	Mg^{2+}/Na^+ (0.23*)	nss-SO_4^{2-} /NO_3^-	F/A (cloud)	F/A (gas**)	SO_2 (ppb)	NO_x (ppb)	Air mass description
E.1	8	15:10-17:30	1	0.08	5.5	2.14	0.41	5.06	0.47	1.03	2.3	0.4	2.7	12.3	Heavily polluted by cold front, continental, altitude <1 km
E.2	9	03:10-15:00	4	0.18	3.82	3.11	0.50	4.15	0.48	1.38	1.6	1.2	1.3	1.9	Clean after cold front passage, continental, <1 km
E.3	11	12:20-21:40	2	0.21	3.3	2.46	0.15	0.58	0.23	0.91	1.2	1.5	1.1	1.6	Circling from sea to PRD region, mixed, <1 km
E.4	15-16	21:10-13:20	6	0.15	3.17	1.62	0.06	0.13	0.22	1.48	1.5	1.9	0.8	1.1	Along the southeast coast of China, mixed, <1 km
E.5	18-19	16:30-13:10	8	0.28	3.56	1.51	0.04	0.04	0.22	1.69	1.7	1.7	0.7	0.8	Deriving from west Pacific Ocean, marine, 1 to 1.5 km
E.6	21-22	12:30-16:00	11	0.35	4.19	1.50	0.04	0.08	0.16	1.51	0.9	0.5	0.9	1.6	Deriving from west Pacific Ocean, marine, > 1.5 km

*: equivalent molar ratio of seawater.

**: refer to Sun et al. (2016) for the calculation of F/A ratio in the gas phase corresponding to the original liquid phase. $[F/A]_M = \frac{K_{H1}(H^+ + K_a)}{K_{H2}(H^+ + K_b)}[F/A]_C$, where $[F/A]_M$ is the measured F/A ratio in the liquid phase and $[F/A]_C$ is the corresponding calculated F/A ratio in the gas phase; $K_{H1} = 5.6 \times 10^3$ M atm^{-1} and $K_{H2} = 8.8 \times 10^3$ M atm^{-1} are Henry constants for formic and acetic acids, respectively; $K_a = 1.77 \times 10^{-4}$ mol L^{-1} and $K_b = 1.76 \times 10^{-5}$ mol L^{-1} are the dissociation constants of formic and acetic acids, respectively.

Table S3. Concentration ratios of formaldehyde/acetaldehyde (C1/C2) and acetaldehyde/propanal (C2/C3) in the gas phase during cloud events. The gas phase carbonyl compounds in E.1 and E.2 were NOT measured.

Event	C1/C2	C2/C3
E.3	2.8 ± 0.5	6.4 ± 1.7
E.4	4.5 ± 2.8	4.4 ± 1.6
E.5	3.8 ± 0.5	5.8 ± 2.6
E.6	3.0 ± 0.6	3.8 ± 0.8

Table S4. Carbonyls concentrations (Mean ± SD) in cloud water and gas phase, as well as measured and theoretical partitioning fraction of carbonyls in the aqueous phase (F_p). The measured carbonyls in cloud water were scaled by LWC to their air equivalent concentrations.

	Cloud water	Gas phase	F_p		K_H	ref
	(ppbv)	(ppbv)	Measured	Theoretical	M atm^{-1}	
Glyoxal	$(5.61 \pm 3.87)\times10^{-2}$	0.05 ± 0.01	5.08×10^{-1}	7.48×10^{-1}	4.19×10^{5}	(Ip et al., 2009)
Methylglyoxal	$(1.22 \pm 1.03)\times10^{-1}$	0.19 ± 0.14	3.14×10^{-1}	2.03×10^{-1}	3.2×10^{4}	(Zhou and Mopper, 1990)
Formaldehyde	$(6.48 \pm 4.42)\times10^{-3}$	1.98 ± 0.34	3.59×10^{-3}	2.60×10^{-2}	3.24×10^{3}	(Sander, 2015)
Acetaldehyde	$(2.16 \pm 1.23)\times10^{-3}$	0.62 ± 0.21	3.83×10^{-3}	1.09×10^{-4}	13.17	(Sander, 2015)
Acetone	$(2.38 \pm 2.10)\times10^{-3}$	2.23 ± 1.32	2.01×10^{-3}	2.26×10^{-4}	27	(Sander, 2015)
Propanal	$(5.05 \pm 5.90)\times10^{-3}$	0.14 ± 0.05	3.24×10^{-2}	9.49×10^{-5}	9.9	(Sander, 2015)

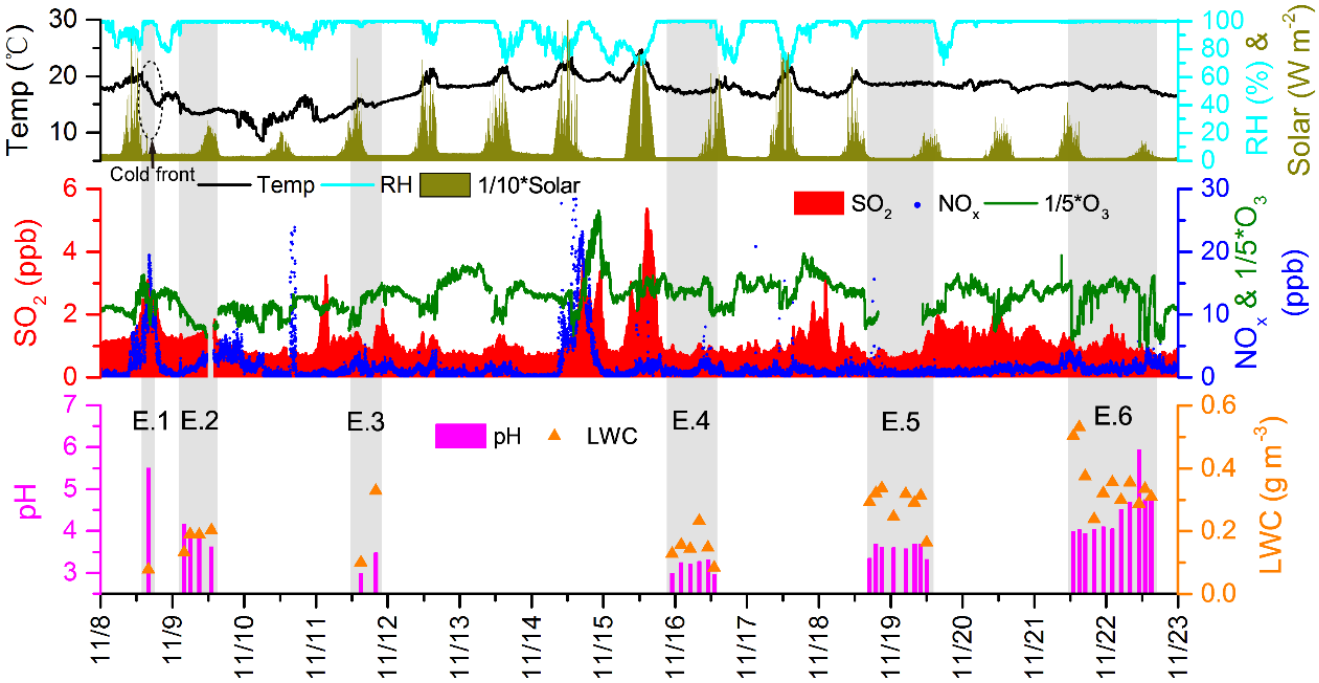

Figure S1. Time series of pH values and LWC of cloud water samples for six events (E.1-6) at Mt. TMS in Hong Kong in November 2016. Gray areas indicate cloud water sampling periods during the campaign. Meteorological parameters including temperature, relative humidity (RH) and solar radiation are shown in the top panel. Trace gases (SO_2, NO_x and O_3) are displayed in the middle panel. A short-time cold front passage (14:00-20:00, 8 November 2016) is labeled by dotted ellipse, which is recorded by Hong Kong observatory (www.weather.gov.hk/contente.htm).

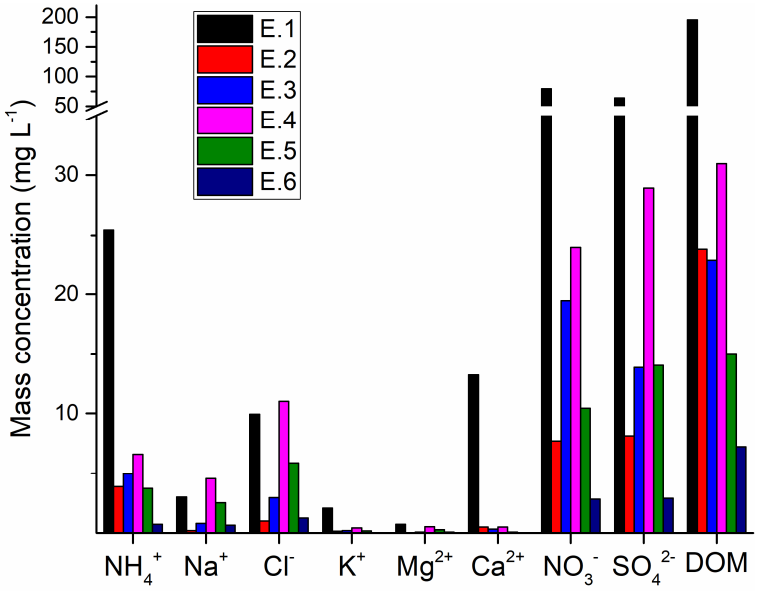

Figure S2. Absolute mass concentrations of major components in cloud water for case E.1-6.

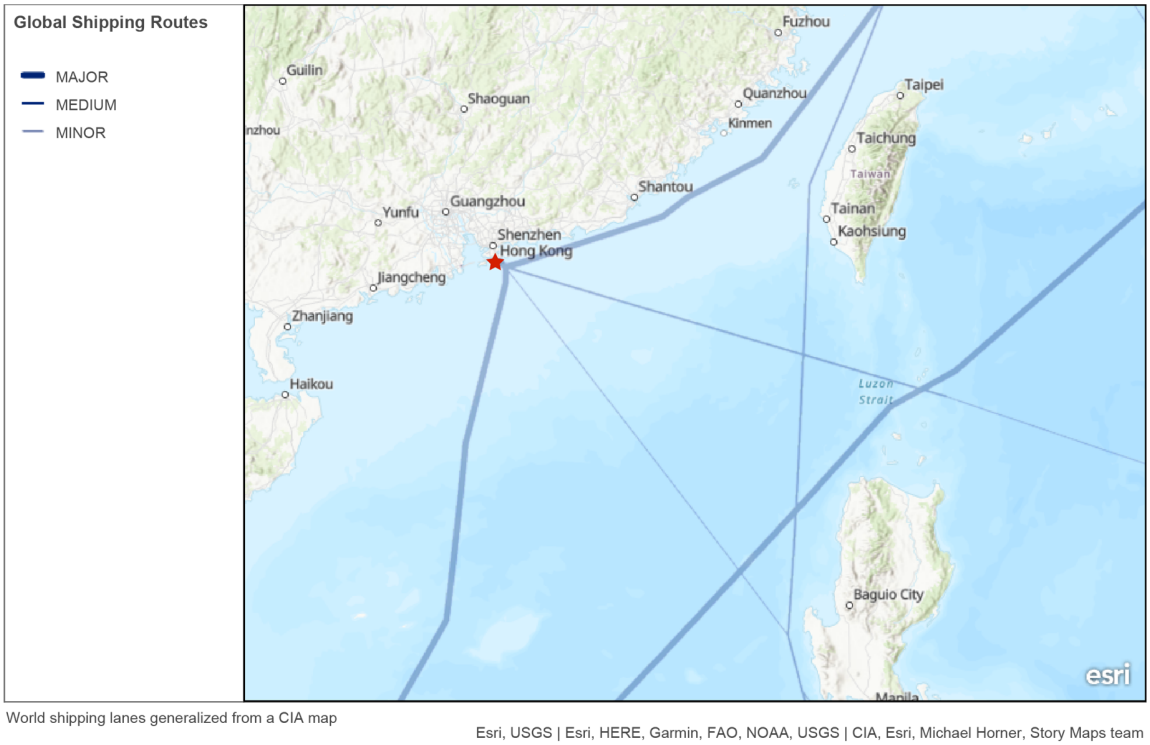

Figure S3. International shipping routes going throgh Hong Kong (red star) in the western Pacific Ocean. The map is reproduced from the ArcGIS Online map of global shipping routes (https://www.arcgis.com/home/index.html) and processed using Adobe Illustrator CS6 software.

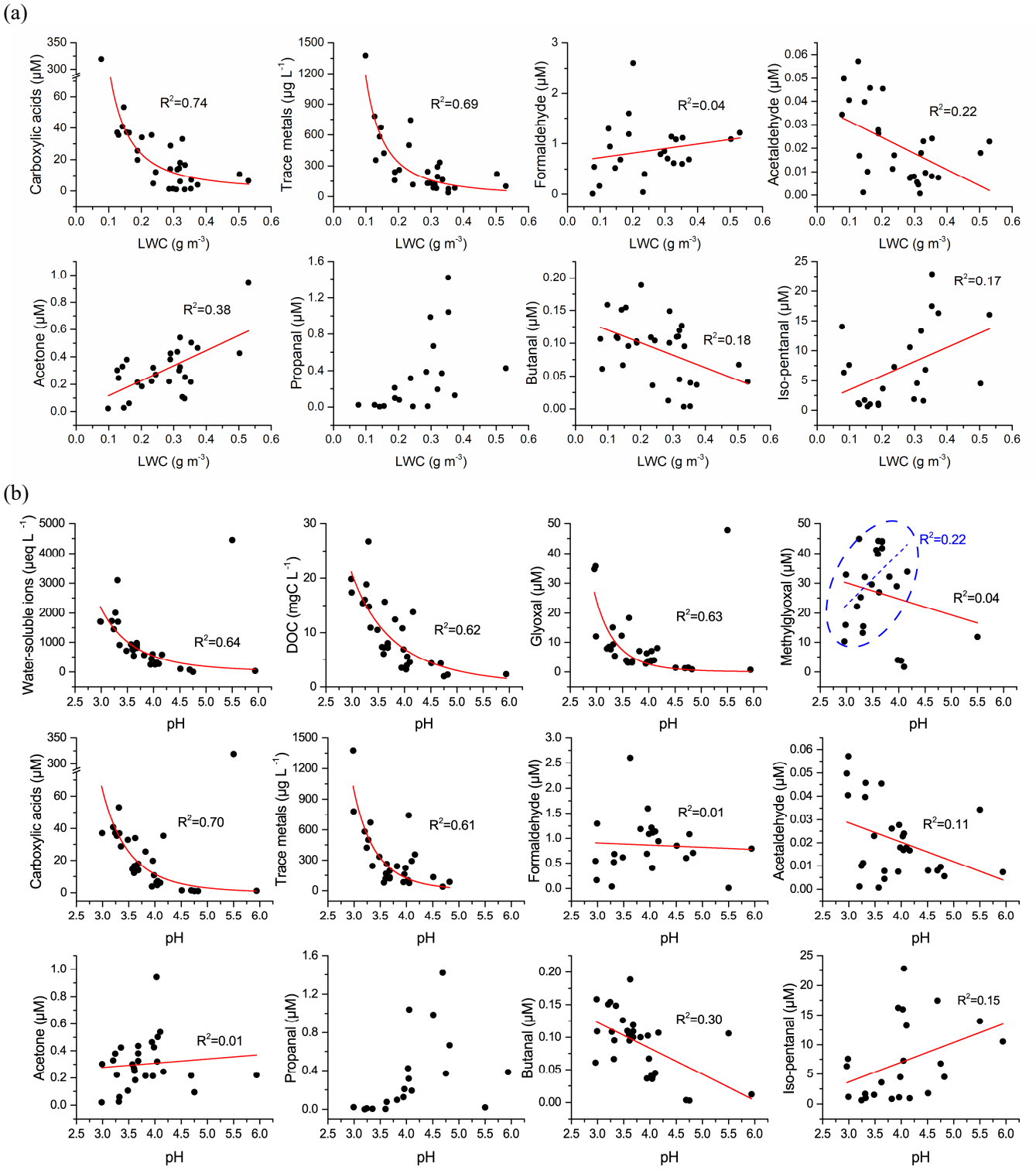

Figure S4. Relationships of water-soluble ions, DOC, carboxylic acids, trace metals and individual carbonyl compounds with (a) LWC and (b) pH in cloud water.

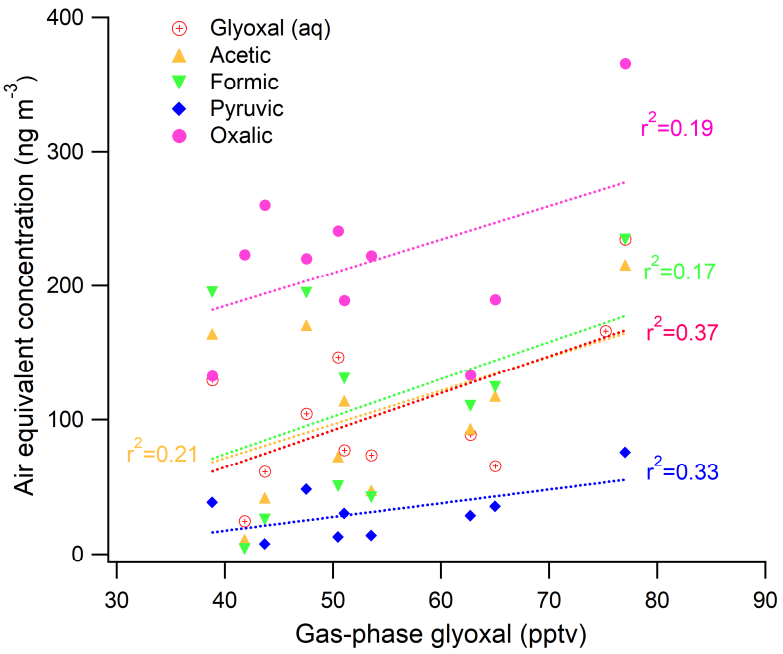

Figure S5. Relationships of the aqueous-phase glyoxal and carboxylic acids with gas-phase glyoxal. Air equivalent concentrations of aqueous phase organics were used to eliminate LWC effects.

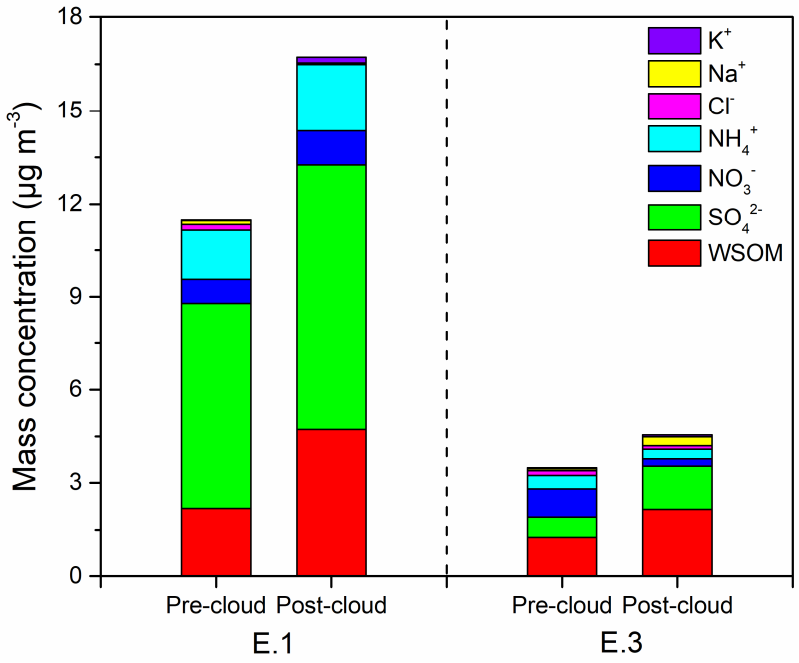

Figure S6. Absolute mass concentration of major water-soluble components in the pre-cloud and post-cloud aerosols for cloud events E.1 and E.3.

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