Supplementary Materials

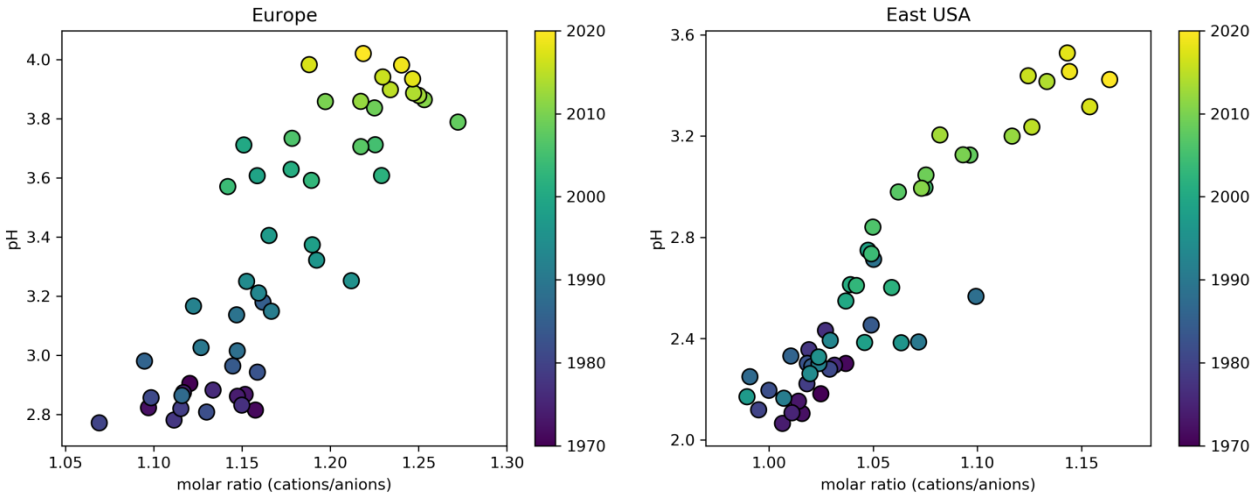

Figure S1: Time evolution of annual average pH as a function of cation/anion molar ratio over Europe (left) and the Eastern USA (right) during the period 1970-2020.

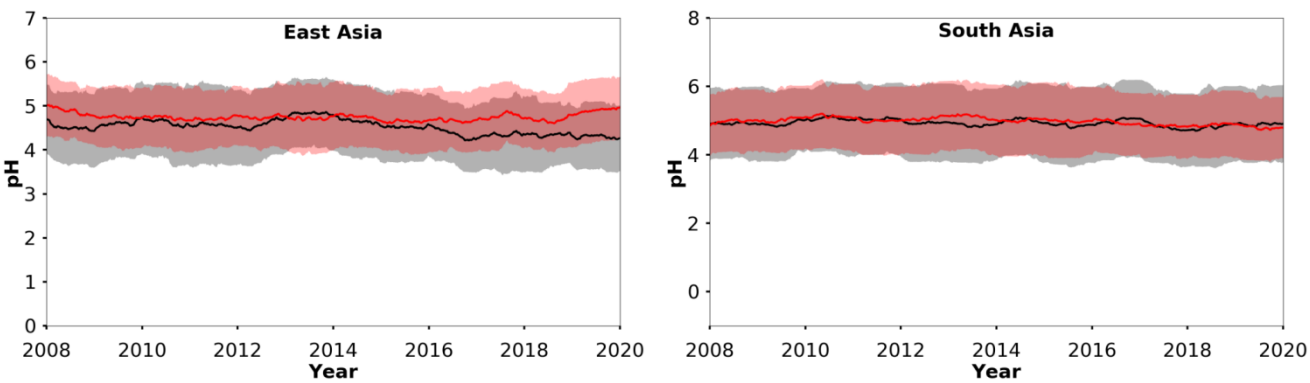

Figure S2: Temporal pH evolution in East and South Asia during the period 2008-2020. Black lines represent the reference simulation. Red lines show the sensitivity simulation in which SO_2 emissions are reduced by 75% in East Asia and increased by 50% in South Asia. Ranges represent the 1σ standard deviation.

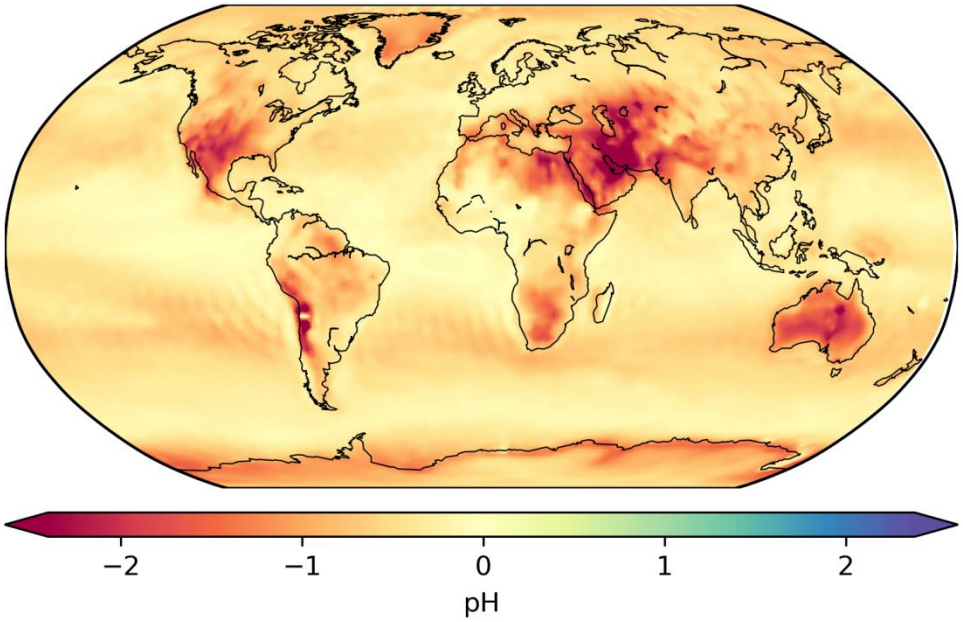

Figure S3: Absolute change in the calculated mean near-surface fine aerosol pH during the period 2010-2015 (cf. central panel in Fig. 1) by assuming that aerosols are always aqueous solution droplets (metastable state). A negative change corresponds to more acidic particles compared to the stable state assumption.

Table S1: Simulated fine aerosol pH compared to observationally-constrained estimates of fine aerosol acidity compiled by Pye et al. (2020).

Location	Latitude	Longitude	Time period	Simulated mean pH	Field derived mean pH	Method used	Reference
Pellston, MI, USA	45.55°N	84.78°W	Jul 2016	3.8	3.5	pH indicator paper/ colorimetric image	Craig et al. (2018)
Ann Arbor, MI, USA	42.28°N	83.74°W	Aug 2016	4.3	3.5	pH indicator paper/ colorimetric image	Craig et al. (2018)
Centreville, AL, USA	32.9°N	87.25°W	Jun 1998 – Aug 2013	6.4	1.2	ISORROPIA (no NH_3)	Weber et al. (2016)
Centreville, AL, USA	32.9°N	87.25°W	Jun – Jul 2013	7.0	1.1	ISORROPIA	Pye et al. (2018)
Egbert, ON, Canada	44.23°N	79.78°W	Jul – Sep 2012	3.9	2.1	E-AIM Model II	Murphy et al. (2017)
Harrow, ON, Canada	42.03°N	82.89°W	Jun – Jul 2007	4.2	1.6	E-AIM Model II	Murphy et al. (2017)
Pasadena, CA, USA	34.14°N	118.12°W	Jun 2010	5.9	2.7	ISORROPIA (metastable)	Guo et al. (2017)
Toronto, Canada	43.66°N	79.40°W	2007-2013	4.0	2.6	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Toronto, Canada	43.66°N	79.40°W	2014-2016	4.1	2.7	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Ottawa, Canada	45.43°N	75.68°W	2007-2016	4.0	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Simcoe, Canada	42.86°N	80.27°W	2007-2016	4.4	2.41	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Montreal, Canada	45.65°N	73.57°W	2007-2016	4.0	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Windsor, Canada	42.29°N	83.07°W	2007-2010	4.4	2.1	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Windsor, Canada	42.29°N	83.07°W	2012-2016	4.5	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
St. Anicet, Canada	45.12°N	74.29°W	2007-2016	4.0	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Sao Paulo, Brazil	23.55°S	46.63°W	Aug – Sep 2012	6.2	4.8	E-AIM	Vieira-Filho et al. (2016)
Po Valley, Italy	45.40°N	12.20°E	Mar 2009 – Jan 2010	4.5	3.1	E-AIM Model IV	Squizzato et al. (2013)
Po Valley,	45.40°N	12.20°E	Spring 2009	4.3	3.6	E-AIM Model IV	Squizzato et al.

Italy							(2013)
Po Valley, Italy	45.40°N	12.20°E	Summer 2009	4.8	2.3	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Fall 2009	4.5	3	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Winter 2009-2010	4.4	3.4	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Winter 2012-2013	4.2	3.9	ISORROPIA (metastable, no NH_3)	Masiol et al. (2020)
Po Valley, Italy	45.40°N	12.20°E	Spring 2012	4.1	2.3	ISORROPIA (metastable, no NH_3)	Masiol et al. (2020)
Cabauw, Netherlands	51.97°N	4.93°E	Jul 2012 – Jun 2013	4.0	3.7	ISORROPIA	Guo et al. (2018)
Cabauw, Netherlands	51.97°N	4.93°E	Jun – Aug 2013	3.6	3.3	ISORROPIA	Guo et al. (2018)
Cabauw, Netherlands	51.97°N	4.93°E	Dec – Feb 2012	4.1	3.9	ISORROPIA	Guo et al. (2018)
Beijing, China	39.99°N	116.30°E	Nov 2015 – Dec 2016	4.9	4.2	ISORROPIA	Liu et al. (2017)
Guangzhou, China	23.13°N	113.26°E	Jul 2013	2.6	2.5	E-AIM Model IV	Jia et al. (2018)
Beijing, China	39.97°N	116.37°E	Nov 2014 –Dec 2014	4.5	4.6	ISORROPIA	Song et al. (2018)
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	4.7	ISORROPIA (metastable)	He et al. (2018)
Beijing, China	39.99°N	116.31°E	Jan – Dec 2014	4.9	3.0	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Winter 2014	5.5	4.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Fall 2014	6.0	3.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Spring 2014	5.4	2.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Summer 2014	3.1	1.8	ISORROPIA (metastable)	Tan et al. (2018)
Tianjin, China	39.11°N	117.16°E	Dec 2014 – Jun 2015	4.4	4.9	ISORROPIA (metastable)	Shi et al. (2017)
Tianjin, China	39.11°N	117.16°E	Aug 2015	1.4	3.4	ISORROPIA (metastable)	Shi et al. (2017)

Beijing, China	39.98°N	116.28°E	Feb 2017	4.7	4.5	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Apr - May 2016	5.2	4.4	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Jul - Aug 2017	2.2	3.8	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Sep - Oct 2017	4.5	4.3	ISORROPIA	Ding et al. (2019)
Guangzhou, China	23.13°N	113.26°E	Jul – Sep 2013	2.7	2.4	E-AIM Model III	Jia et al. (2018)
Hohhot, China	40.48°N	111.41°E	Summer 2014	5.5	5	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	Autumn 2014	6.8	5.3	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	Winter 2014	5.8	5.7	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	Spring 2015	6.1	6.1	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	2014 - 2015	6.2	5.6	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	7.6	ISORROPIA (stable state)	He et al. (2018)
Xi'an, China	34.23°N	108.89°E	Nov – Dec 2012	5.7	6.7	ISORROPIA	Wang et al. (2016)
Beijing, China	39.99°N	116.30°E	Jan – Feb 2015	5.0	7.6	ISORROPIA	Wang et al. (2016)
Beijing, China	40.35°N	116.30°E	Jun – Aug 2005	4.2	0.6	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Shanghai, China	31.45°N	121.10°E	May – Jun 2005	3.5	0.7	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Lanzhou, China	36.13°N	103.68°E	Jun – Jul 2006	6.8	0.6	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Beijing, China	40.32°N	116.32°E	Jan 2005 – Apr 2006	5.1	0.7	E-AIM Model II (only aerosols)	He et al. (2012)
Chongqing, China	29.57°N	106.53°E	Jan 2005 – Apr 2006	3.6	1.5	E-AIM Model II (only aerosols)	He et al. (2012)
Beijing, China	40°N	116.33°E	Jan 2013	4.6	5.8	ISORROPIA (forward & reverse, estimated NH_3)	Wang et al. (2016)
Singapore	1.3°N	103.78°E	Sep – Nov 2011	3.2	0.6	E-AIM Model IV	Behera et al. (2013)

Hong Kong	22.34°N	114.26°E	Jul 1997 – May 1998	3.3	0.3	E-AIM Model II (for RH >= 70%)	Yao et al. (2007)
Hong Kong	22.34°N	114.26°E	Nov 1996 – Nov 1997	3.4	-1	E-AIM Model II (for RH < 70%)	Yao et al. (2007)
Hong Kong	22.34°N	114.26°E	Oct 2008	5.0	0.6	E-AIM Model III (only aerosols)	Xue et al. (2011)
Hong Kong	22.34°N	114.26°E	Nov 2008	3.7	-0.5	E-AIM Model III (only aerosols)	Xue et al. (2011)
Hong Kong	22.34°N	114.26°E	Jun - Jul 2009	1.6	-0.1	E-AIM Model III (only aerosols)	Xue et al. (2011)
Pacific Ocean	47.5°S	147.5°E	Nov - Dec 1995	7.0	1.0	EQUISOLV	Fridlind and Jacobson (2000)
South Ocean	61°S	45°W	Jan 2015	6.9	1.4	ISORROPIA (no NH_3)	Dall'Osto et al. (2019)
South Ocean	64°S	65°W	Jan – Feb 2015	6.9	3.8	ISORROPIA (no NH_3)	Dall'Osto et al. (2019)

Table S2: Fractional emission factors of aerosol components for biofuel combustion, and savannah and tropical forest biomass burning (Akagi et al., 2011), and for sea salt (Seinfeld and Pandis, 2006).

Source	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
Biofuel combustion	-	0.014	-	-	0.093	0.022	0.073	-
Grassfire burning	0.05	0.04	0.62	0.01	0.62	0.04	0.06	0.01
Forest fire burning	0.25	0.21	0.29	0.01	0.56	0.08	0.16	0.01
Sea salt	0.077	-	0.55	0.306	0.011	0.037	0.012	-

Table S3: Fractional chemical composition of mineral dust emissions (Karydis et al., 2016).

Desert	Na^+	K^+	Ca^{2+}	Mg^{2+}	Other
Great Basin	0.064	0.023	0.053	0.018	0.842
Mojave	0.015	0.027	0.059	0.019	0.880
Sonoran	0.025	0.012	0.037	0.006	0.920
Patagonia	0.012	0.015	0.021	0.013	0.939
Monte	0.023	0.018	0.025	0.009	0.925
Atacama	0.069	0.007	0.018	0.005	0.901
Kalahari/ Namibia	0.030	0.050	0.120	0.090	0.710
Sahara	0.011	0.035	0.075	0.030	0.849
Saudi Arabia	0.010	0.004	0.034	0.006	0.946
Thar/Lut	0.022	0.033	0.082	0.022	0.841
Taklimakan	0.012	0.030	0.120	0.028	0.810
Gobi	0.012	0.021	0.077	0.017	0.873
Great Sandy/ Simpson	0.028	0.001	0.005	0.003	0.963
Other	0.012	0.015	0.024	0.009	0.940

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, 10.5194/acp-11-4039-2011, 2011.

Behera, S. N., Betha, R., Liu, P., and Balasubramanian, R.: A study of diurnal variations of PM2.5 acidity and related chemical species using a new thermodynamic equilibrium model, Science of The Total Environment, 452-453, 286-295, https://doi.org/10.1016/j.scitotenv.2013.02.062, 2013.

Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A., Cook, R. D., Dutcher, C. S., and Ault, A. P.: Direct Determination of Aerosol pH: Size-Resolved Measurements of Submicrometer and Supermicrometer Aqueous Particles, Analytical Chemistry, 90, 11232-11239, 10.1021/acs.analchem.8b00586, 2018.

Dall'Osto, M., Airs, R. L., Beale, R., Cree, C., Fitzsimons, M. F., Beddows, D., Harrison, R. M., Ceburnis, D., O'Dowd, C., Rinaldi, M., Paglione, M., Nenes, A., Decesari, S., and Simó, R.: Simultaneous Detection of Alkylamines in the Surface Ocean and Atmosphere of the Antarctic Sympagic Environment, ACS Earth and Space Chemistry, 3, 854-862, 10.1021/acsearthspacechem.9b00028, 2019.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.

Fridlind, A. M., and Jacobson, M. Z.: A study of gas-aerosol equilibrium and aerosol pH in the remote marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), Journal of Geophysical Research: Atmospheres, 105, 17325-17340, https://doi.org/10.1029/2000JD900209, 2000.

Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., and Weber, R. J.: Effectiveness of ammonia reduction on control of fine particle nitrate, Atmospheric Chemistry and Physics, 18, 12241-12256, 10.5194/acp-18-12241-2018, 2018.

Guo, H. Y., Liu, J. M., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A., and Weber, R. J.: Fine particle pH and gas-particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, Atmospheric Chemistry and Physics, 17, 5703-5719, 10.5194/acp-17-5703-2017, 2017.

He, K., Zhao, Q., Ma, Y., Duan, F., Yang, F., Shi, Z., and Chen, G.: Spatial and seasonal variability of PM_{2.5} acidity at two Chinese megacities: insights into the formation of secondary inorganic aerosols, Atmos. Chem. Phys., 12, 1377-1395, 10.5194/acp-12-1377-2012, 2012.

He, P., Alexander, B., Geng, L., Chi, X., Fan, S., Zhan, H., Kang, H., Zheng, G., Cheng, Y., Su, H., Liu, C., and Xie, Z.: Isotopic constraints on heterogeneous sulfate production in Beijing haze, Atmos. Chem. Phys., 18, 5515-5528, 10.5194/acp-18-5515-2018, 2018.

Jia, S., Wang, X., Zhang, Q., Sarkar, S., Wu, L., Huang, M., Zhang, J., and Yang, L.: Technical note: Comparison and interconversion of pH based on different standard states for aerosol acidity characterization, Atmos. Chem. Phys., 18, 11125-11133, 10.5194/acp-18-11125-2018, 2018.

Karydis, V. A., Tsimpidi, A. P., Pozzer, A., Astitha, M., and Lelieveld, J.: Effects of mineral dust on global atmospheric nitrate concentrations, Atmos. Chem. Phys., 16, 1491-1509, 10.5194/acp-16-1491-2016, 2016.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophysical Research Letters, 44, 5213-5221, https://doi.org/10.1002/2017GL073210, 2017.

Masiol, M., Squizzato, S., Formenton, G., Khan, M. B., Hopke, P. K., Nenes, A., Pandis, S. N., Tositti, L., Benetello, F., Visin, F., and Pavoni, B.: Hybrid multiple-site mass closure and source apportionment of PM2.5 and aerosol acidity at major cities in the Po Valley, Science of The Total Environment, 704, 135287, https://doi.org/10.1016/j.scitotenv.2019.135287, 2020.

Murphy, J. G., Gregoire, P. K., Tevlin, A. G., Wentworth, G. R., Ellis, R. A., Markovic, M. Z., and VandenBoer, T. C.: Observational constraints on particle acidity using measurements and modelling of particles and gases, Faraday Discussions, 200, 379-395, 10.1039/C7FD00086C, 2017.

Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem. Phys., 9, 1711-1722, 10.5194/acp-9-1711-2009, 2009.

Pye, H. O. T., Zuend, A., Fry, J. L., Isaacman-VanWertz, G., Capps, S. L., Appel, K. W., Foroutan, H., Xu, L., Ng, N. L., and Goldstein, A. H.: Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US, Atmos. Chem. Phys., 18, 357-370, 10.5194/acp-18-357-2018, 2018.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G. L., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmospheric Chemistry and Physics, 20, 4809-4888, 10.5194/acp-20-4809-2020, 2020.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2006.

Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A., and Russell, A. G.: pH of Aerosols in a Polluted Atmosphere: Source Contributions to Highly Acidic Aerosol, Environmental Science & Technology, 51, 4289-4296, 10.1021/acs.est.6b05736, 2017.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., and Pavoni, B.: Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy), Atmos. Chem. Phys., 13, 1927-1939, 10.5194/acp-13-1927-2013, 2013.

Tan, T., Hu, M., Li, M., Guo, Q., Wu, Y., Fang, X., Gu, F., Wang, Y., and Wu, Z.: New insight into PM2.5 pollution patterns in Beijing based on one-year measurement of chemical compositions, Science of The Total Environment, 621, 734-743, https://doi.org/10.1016/j.scitotenv.2017.11.208, 2018.

Tao, Y., and Murphy, J. G.: The sensitivity of PM2.5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites, Atmos. Chem. Phys., 19, 9309-9320, 10.5194/acp-19-9309-2019, 2019.

Vieira-Filho, M., Pedrotti, J. J., and Fornaro, A.: Water-soluble ions species of size-resolved aerosols: Implications for the atmospheric acidity in São Paulo megacity, Brazil, Atmospheric Research, 181, 281-287, https://doi.org/10.1016/j.atmosres.2016.07.006, 2016.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F.,

Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proc Natl Acad Sci U S A, 113, 13630-13635, 10.1073/pnas.1616540113, 2016.

Wang, H., Ding, J., Xu, J., Wen, J., Han, J., Wang, K., Shi, G., Feng, Y., Ivey, C. E., Wang, Y., Nenes, A., Zhao, Q., and Russell, A. G.: Aerosols in an arid environment: The role of aerosol water content, particulate acidity, precursors, and relative humidity on secondary inorganic aerosols, Science of The Total Environment, 646, 564-572, https://doi.org/10.1016/j.scitotenv.2018.07.321, 2019.

Weber, R. J., Guo, H. Y., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geoscience, 9, 282-285, 10.1038/ngeo2665, 2016.

Xue, J., Lau, A. K. H., and Yu, J. Z.: A study of acidity on PM2.5 in Hong Kong using online ionic chemical composition measurements, Atmospheric Environment, 45, 7081-7088, https://doi.org/10.1016/j.atmosenv.2011.09.040, 2011.

Yao, X., Ling, T. Y., Fang, M., and Chan, C. K.: Size dependence of in situ pH in submicron atmospheric particles in Hong Kong, Atmospheric Environment, 41, 382-393, https://doi.org/10.1016/j.atmosenv.2006.07.037, 2007.