

Supplementary Materials: Elucidating Decade-Long Trends and Diurnal Patterns in Aerosol Acidity in Shanghai

Zhixiao Lv ¹, Xingnan Ye ^{1,*}, Weijie Huang ¹, Yinghui Yao ¹ and Yusen Duan ²

¹ Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), National Observations and Research Station for Wetland Ecosystems of the Yangtze Estuary, Department of Environmental Science and Engineering, Fudan University, Shanghai 200438, China; 21210740069@m.fudan.edu.cn (Z.L.); 21110740007@m.fudan.edu.cn (W.H.); 19110740008@fudan.edu.cn (Y.Y.)

² Shanghai Environmental Monitoring Center, Shanghai 200235, China; duanys@sheemc.cn

* Correspondence: yexingnan@fudan.edu.cn

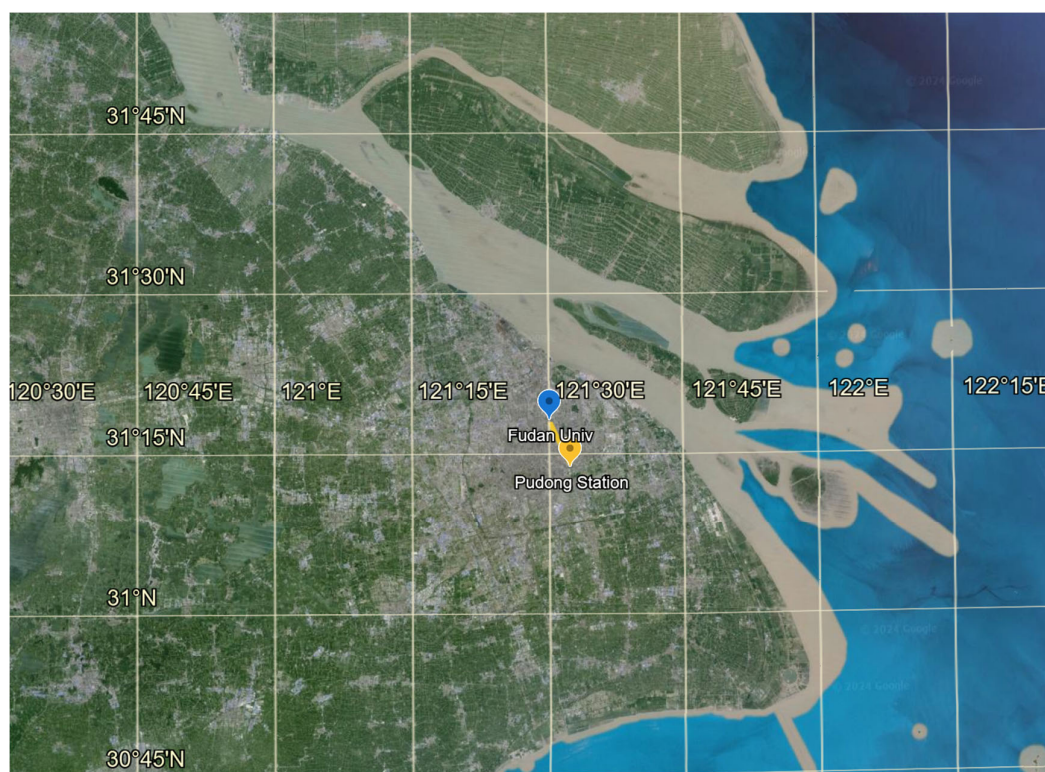


Figure S1. Geographical location of the sampling sites.

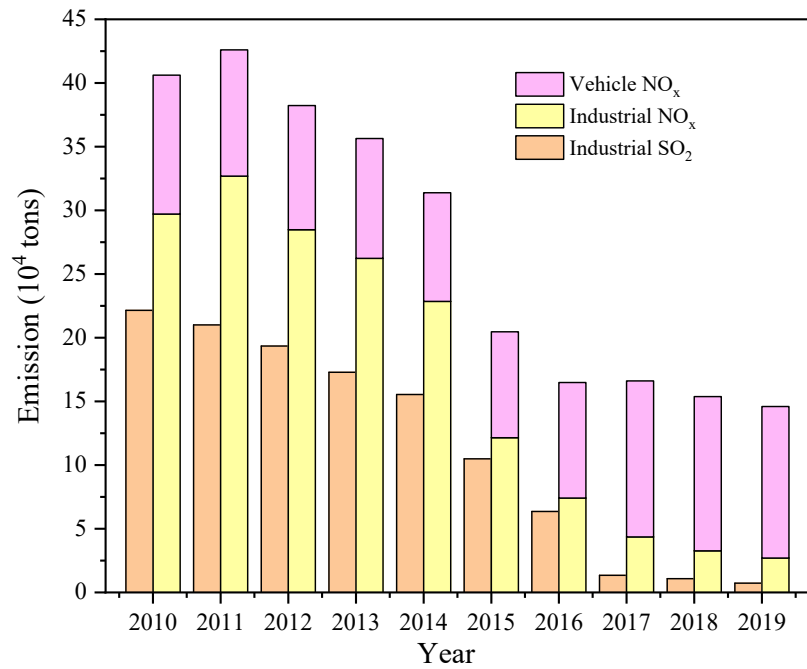


Figure S2. Annual variation of SO₂ and NO_x emissions. The data is from the China Statistical Year-book on Environment, 2011–2021 and partly from ABaCAS-EI v2.0.

Table S1. Aerosol pH of 2010–2020 with seasonal mean values input.

Summer											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.362	9.610	12.480	7.153	1.775	0.823	0.385	0.091	0.75	301.00	2.97
2012–2013	0	7.120	12.827	2.699	1.489	1.275	0.335	0.273	0.76	302.54	3.37
2014	0.236	10.784	13.578	8.965	0.590	0.082	0.849	0.061	0.80	298.95	2.97
2015	0.334	11.039	15.622	7.794	1.542	0.350	1.106	0.057	0.78	299.58	3.05
2016	0.041	6.836	11.468	5.156	0.450	0.084	0.022	0.019	0.78	301.32	2.59
2017	0.105	6.652	12.651	5.102	0.623	0.093	0.065	0.017	0.74	302.16	2.54
2018	0.135	6.016	7.758	3.953	0.554	0.042	0.054	0.021	0.78	301.10	2.35
2019	0.105	6.230	9.787	4.917	0.470	0.016	0.026	0.012	0.78	300.47	2.53
2020	0.216	4.750	10.071	4.159	0.468	0.067	0.043	0.030	0.78	301.82	2.56
Winter											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.02	8.678	9.493	7.162	2.420	1.695	0.766	0.254	0.76	280.80	3.96
2012–2013	0	12.144	15.003	15.556	1.959	0.295	0.702	0.024	0.73	278.64	3.95
2014	0.317	13.992	15.531	17.354	2.644	0.242	1.516	0.087	0.70	279.55	3.76
2015	0.274	13.520	15.732	19.371	2.418	0.240	1.370	0.070	0.72	279.84	3.75
2016	0.198	9.931	11.625	14.094	1.639	0.128	0.433	0.036	0.71	280.80	3.50
2017	0.054	10.008	12.344	17.244	1.842	0.064	0.282	0.024	0.72	278.86	3.58
2018	0.231	7.586	9.510	12.921	1.482	0.138	0.311	0.036	0.75	279.86	3.51
2019	0.147	7.405	10.412	12.965	1.268	0.109	0.389	0.030	0.74	281.75	3.51
2020	0.179	8.211	10.146	12.669	1.344	0.108	0.462	0.037	0.73	281.45	3.45

Table S2. Aerosol pH of 2010–2020 with seasonal mean values input except for Ca²⁺.

Summer											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.362	9.610	12.480	7.153	1.775	0	0.385	0.091	0.75	301.00	2.760
2012–2013	0	7.120	12.827	2.699	1.489	0	0.335	0.273	0.76	302.54	2.930
2014	0.236	10.784	13.578	8.965	0.590	0	0.849	0.061	0.80	298.95	2.962
2015	0.334	11.039	15.622	7.794	1.542	0	1.106	0.057	0.78	299.58	3.006
2016	0.041	6.836	11.468	5.156	0.450	0	0.022	0.019	0.78	301.32	2.583
2017	0.105	6.652	12.651	5.102	0.623	0	0.065	0.017	0.74	302.16	2.527
2018	0.135	6.016	7.758	3.953	0.554	0	0.054	0.021	0.78	301.10	2.346
2019	0.105	6.230	9.787	4.917	0.470	0	0.026	0.012	0.78	300.47	2.534
2020	0.216	4.750	10.071	4.159	0.468	0	0.043	0.030	0.78	301.82	2.589
Winter											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.02	8.678	9.493	7.162	2.420	0	0.766	0.254	0.76	280.80	2.929
2012–2013	0	12.144	15.003	15.556	1.959	0	0.702	0.024	0.73	278.64	3.720
2014	0.317	13.992	15.531	17.354	2.644	0	1.516	0.087	0.70	279.55	3.743
2015	0.274	13.520	15.732	19.371	2.418	0	1.370	0.070	0.72	279.84	3.716
2016	0.198	9.931	11.625	14.094	1.639	0	0.433	0.036	0.71	280.80	3.481
2017	0.054	10.008	12.344	17.244	1.842	0	0.282	0.024	0.72	278.86	3.572
2018	0.231	7.586	9.510	12.921	1.482	0	0.311	0.036	0.75	279.86	3.476
2019	0.147	7.405	10.412	12.965	1.268	0	0.389	0.030	0.74	281.75	3.492
2020	0.179	8.211	10.146	12.669	1.344	0	0.462	0.037	0.73	281.45	3.434

Table S3. Aerosol pH of 2010–2020 with seasonal mean values input except for K⁺.

Summer											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.362	9.610	12.480	7.153	1.775	0.823	0	0.091	0.75	301.00	2.916
2012–2013	0	7.120	12.827	2.699	1.489	1.275	0	0.273	0.76	302.54	3.242
2014	0.236	10.784	13.578	8.965	0.590	0.082	0	0.061	0.80	298.95	2.894
2015	0.334	11.039	15.622	7.794	1.542	0.350	0	0.057	0.78	299.58	2.942
2016	0.041	6.836	11.468	5.156	0.450	0.084	0	0.019	0.78	301.32	2.590
2017	0.105	6.652	12.651	5.102	0.623	0.093	0	0.017	0.74	302.16	2.528
2018	0.135	6.016	7.758	3.953	0.554	0.042	0	0.021	0.78	301.10	2.341
2019	0.105	6.230	9.787	4.917	0.470	0.016	0	0.012	0.78	300.47	2.532
2020	0.216	4.750	10.071	4.159	0.468	0.067	0	0.030	0.78	301.82	2.556
Winter											
Year	Na ⁺	SO ₄ ²⁻	TNH ₃	TNO ₃	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T	pH
2010	0.020	8.678	9.493	7.162	2.420	1.695	0	0.254	0.76	280.8	2.929
2012–2013	0	12.144	15.003	15.556	1.959	0.295	0	0.730	0.73	278.64	3.711
2014	0.317	13.992	15.531	17.354	2.644	0.242	0	0.087	0.70	279.55	3.658
2015	0.274	13.520	15.732	19.371	2.418	0.240	0	0.070	0.72	279.84	3.652
2016	0.198	9.931	11.625	14.094	1.639	0.128	0	0.036	0.71	280.80	3.464
2017	0.054	10.008	12.344	17.244	1.842	0.064	0	0.024	0.72	278.86	3.558
2018	0.231	7.586	9.510	12.921	1.482	0.138	0	0.036	0.75	279.86	3.470
2019	0.147	7.405	10.412	12.965	1.268	0.109	0	0.030	0.74	281.75	3.473
2020	0.179	8.211	10.146	12.669	1.344	0.108	0	0.037	0.73	281.45	3.407

Table S4. Effects of various driving factors on diurnal pH variations in the summer of 2010.

	5:00	10:00	14:00	20:00	24:00
pH	3.18	2.58	2.34	2.87	3.16
RH (%)	83	72	64	75	80
T (°C)	25.7	29.4	30.1	26.9	26.1
T _d (°C)	22.5	23.9	22.5	21.9	22.4
SO ₄ ²⁻ (µg m ⁻³)	9.053	9.703	10.174	9.310	8.908
NO ₃ ⁻ (µg m ⁻³)	7.644	5.452	4.362	4.960	6.471
Ca ²⁺ (µg m ⁻³)	0.692	0.806	0.811	0.873	0.824
K ⁺ (µg m ⁻³)	0.325	0.273	0.307	0.381	0.520
NH _x (µg m ⁻³)	13.210	13.014	13.323	11.377	13.398
N/S	1.31	0.87	0.66	0.82	1.12
ΔpH (T)	/	-0.31	-0.4	-0.12	-0.07
ΔpH (RH)	/	-0.30	-0.52	-0.16	-0.05
ΔpH (SO ₄ ²⁻)	/	-0.04	-0.06	-0.02	0.01
ΔpH (NO ₃ ⁻)	/	-0.05	-0.10	-0.02	-0.04
ΔpH (NH _x)	/	-0.01	0	-0.11	0.01

T_d: dew point temperature; ΔpH = pH_{actual} - pH_{fixing the variable with the value at 5:00}.**Table S5.** Effects of various driving factors on diurnal pH variations in the winter of 2010.

	5:00	10:00	14:00	20:00	24:00
pH	3.97	3.97	3.75	3.95	3.99
RH (%)	84	76	65	76	81
T (°C)	6.4	8.0	10.2	7.1	5.5
T _d (°C)	3.8	4.0	3.9	3.2	2.5
SO ₄ ²⁻ (µg m ⁻³)	7.106	8.504	9.200	9.129	9.388
NO ₃ ⁻ (µg m ⁻³)	4.952	6.185	6.223	6.310	6.962
Ca ²⁺ (µg m ⁻³)	1.665	1.804	1.704	1.63	1.647
K ⁺ (µg m ⁻³)	0.258	0.501	0.406	0.867	0.950
NH _x (µg m ⁻³)	8.943	10.240	9.808	9.320	9.273
N/S	1.08	1.13	1.05	1.07	1.15
ΔpH (T)	/	-0.08	-0.18	-0.03	0.04
ΔpH (RH)	/	0.05	0.04	0.05	0.02
ΔpH (SO ₄ ²⁻)	/	-0.12	-0.25	-0.18	-0.15
ΔpH (NO ₃ ⁻)	/	-0.03	0.02	-0.04	-0.07
ΔpH (NH _x)	/	0.10	0.07	0.03	0.03

T_d: dew point temperature; ΔpH = pH_{actual} - pH_{fixing the variable with the value at 5:00}.**Table S6.** Effects of various driving factors on diurnal pH variations in the summer of 2020.

	5:00	10:00	14:00	20:00	24:00
pH	3.01	2.56	2.22	2.66	3.00
RH (%)	89	74	68	82	88
T (°C)	26.4	29.6	30.6	27.5	26.9
T _d (°C)	24.4	24.5	24.0	24.2	24.7
SO ₄ ²⁻ (µg m ⁻³)	4.263	5.016	5.222	4.542	4.392
NO ₃ ⁻ (µg m ⁻³)	3.592	3.401	2.922	3.036	4.037
Ca ²⁺ (µg m ⁻³)	0.059	0.087	0.066	0.076	0.036
K ⁺ (µg m ⁻³)	0.052	0.043	0.034	0.040	0.041
NH _x (µg m ⁻³)	8.702	12.361	11.106	8.634	9.216

N/S	1.30	1.05	0.87	1.04	1.42
ΔpH (T)	/	-0.22	-0.27	-0.07	-0.02
ΔpH (RH)	/	-0.51	-0.69	-0.25	-0.02
ΔpH (SO_4^{2-})	/	-0.05	-0.05	-0.03	-0.01
ΔpH (NO_3^-)	/	-0.04	-0.01	-0.02	0
ΔpH (NHx)	/	0.22	0.16	0	0.02

Td: dew point temperature; $\Delta\text{pH} = \text{pH}_{\text{actual}} - \text{pH}_{\text{fixing the variable with the value at 5:00}}$.

Table S7. Effects of various driving factors on diurnal pH variations in the winter of 2020.

	5:00	10:00	14:00	20:00	24:00
pH	3.69	3.64	3.51	3.62	3.68
RH (%)	77	69	66	72	74
T (°C)	6.6	10.2	11.6	8.8	7.4
T _d (°C)	2.8	4.9	5.4	4.1	3.1
SO_4^{2-} ($\mu\text{g m}^{-3}$)	4.949	6.180	5.716	4.899	5.359
NO_3^- ($\mu\text{g m}^{-3}$)	11.241	14.227	10.990	10.667	11.845
Ca^{2+} ($\mu\text{g m}^{-3}$)	0.179	0.216	0.144	0.183	0.189
K^+ ($\mu\text{g m}^{-3}$)	0.254	0.242	0.216	0.272	0.310
NHx ($\mu\text{g m}^{-3}$)	8.996	11.280	9.894	8.934	9.426
N/S	3.52	3.56	2.98	3.37	3.42
ΔpH (T)	/	-0.18	-0.25	-0.11	-0.04
ΔpH (RH)	/	0.04	0.04	0.02	0.01
ΔpH (SO_4^{2-})	/	-0.11	-0.07	0.01	-0.04
ΔpH (NO_3^-)	/	-0.03	0	0.01	-0.01
ΔpH (NHx)	/	0.24	0.08	-0.01	0.05

Td: dew point temperature; $\Delta\text{pH} = \text{pH}_{\text{actual}} - \text{pH}_{\text{fixing the variable with the value at 5:00}}$.

Table S8. Effect of elevated TNO₃ on aerosol pH in different seasons.

Case	Original input					Model output			Sensitivity test				
	T	RH	SO_4^{2-}	TNH ₃	TNO ₃	HNO ₃	NO_3^-	pH	TNO ₃	HNO ₃	NO_3^-	pH	ΔpH
1	30.1	64	10.174	13.323	6.770	4.932	1.809	2.34	10.052	7.14	2.862	2.43	0.09
2	29.4	72	9.703	13.014	6.535	3.982	2.512	2.58	8.727	5.178	3.492	2.62	0.04
3	26.9	75	9.310	11.377	6.240	2.668	3.515	2.87	8.924	3.672	5.169	2.89	0.02
4	26.1	80	8.908	13.398	8.421	2.012	6.307	3.16	9.594	2.239	7.238	3.20	0.04
5	11.6	66	5.716	9.893	11.394	0.308	10.910	3.51	11.646	0.314	11.152	3.51	0
6	10.2	69	6.180	11.280	11.753	0.169	11.400	3.67	14.739	0.210	14.298	3.64	-0.03
7	8.8	72	4.899	8.934	11.137	0.161	10.802	3.62	11.711	0.170	11.358	3.61	-0.01
8	7.4	74	5.359	9.426	11.664	0.102	11.379	3.69	12.267	0.108	11.966	3.68	-0.01

case 1–4 in summer; case 5–8 in winter.