

## **Appendix: Supplementary materials**

**Economic and industrial development significantly contribute to acidity  
and ionic compositions of rainwater in China**

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**Table S1.** The mean of pH and ions concentration in rainwater of each site in China.

City	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup> (μeq/L)	K <sup>+</sup> (μeq/L)	Na <sup>+</sup> (μeq/L)	SO <sub>4</sub> <sup>2-</sup> (μeq/L)	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup> (μeq/L)	F <sup>-</sup> (μeq/L)	pH	Year	reference
Beijing	19.29±140.59	44.84±44.69	195.43±108.47	19.70±13.84	31.68±19.31	236.62±143.99	83.92±44.82	50.25±30.38	17.95±9.48	5.50±0.87	1992-2015, 2017-	[59–67]
Shanghai	148.37±101.80	22.51±16.35	96.84±33.71	13.65±10.03	41.23±31.71	177.66±111.32	37.75±10.53	55.26±34.65	16.46±10.36	5.16±0.54	1980, 1990-2010,	[59], [61], [68–73]
Hangzhou	137.00±123.51	12.15±8.44	68.20±10.02	16.91±17.77	19.11±11.49	69.29±50.89	29.64±13.42	21.71±6.69	21.60	5.27±1.33	1985-1997, 2006-	[22], [74,75]
Nanjing	147.83±117.14	22.13±10.58	111.65±66.82	20.28±4.45	30.81±17.63	83.12±77.99	45.51±5.03	79.93±50.16	15.74±12.23	5.89±0.50	1992-2003, 2016-	[59], [61], [74], [76]
Jinan	218.51±82.81	45.78±21.05	208.36±74.44	15.67±9.76	43.44±28.40	263.41±147.73	114.26±43.68	48.37±25.84	11.43±10.02	6.12±0.95	2001-2020	[59], [77,78]
Yantai	309.00	73.30	88.90	41.30	183.90	188.50	76.30	221.40	5.30	6.82	2016-2020	[79]
Shenzhen	50.69±29.97	6.79±4.02	33.40±12.49	3.69±2.92	20.65±12.90	68.04±15.43	27.10±14.71	31.04±15.26	6.07±7.38	4.45±0.11	1986-2009	[16], [21], [73], [80–81]
Guangzhou	100.13±57.15	13.25±5.98	52.34±25.10	14.53±9.65	36.33±21.20	155.21±66.24	43.43±27.81	39.87±32.36	12.60±6.92	4.56±0.23	2003-2006	[16], [22], [69], [74], [80], [82,83]
Zhuhai	30.16±14.94	12.17±5.13	32.39±19.35	5.67±4.40	41.11±18.46	38.84±14.65	19.78±4.45	43.50±18.01	-	4.97±0.22	2000-2020	<a href="#">EANET</a>
Xiamen	59.44±124.32	8.52±5.47	34.24±9.49	6.30±7.59	20.29±13.11	56.06±27.62	27.57±8.47	28.86±17.37	-	4.85±0.43	2000-2020	[22], <a href="#">EANET</a>
Wuhan	89.25±25.10	38.33±29.47	98.61±9.04	19.87±21.58	33.69±32.89	71.45±11.19	72.25±3.42	25.35±12.75	15.70±4.47	6.21±0.18	2020-2021	<a href="https://sthjt.hubei.gov.cn/">https://sthjt.hubei.gov.cn/</a>
Zhengzhou	357.10±96.81	95.29±105.24	202.95±29.12	32.52±18.53	74.81±37.90	317.20±98.75	89.11±22.83	355.02±224.99	16.68±4.70	5.91±0.71	1995-2006, 2018-	[21], [59], [84]
Nanchang	55.81±18.94	6.55±1.68	61.31±7.18	5.60±2.12	11.09±4.89	74.54±31.89	33.70±7.60	19.37±6.75	11.05±2.39	4.28±0.32	2007-2008, 2013-	[23], [85,86]
Hengyang	40.49±21.84	4.80±3.01	71.65±10.46	3.39±2.91	3.86±3.90	64.15±20.75	32.48±9.03	9.23±3.20	26.99±21.40	5.14±0.37	2015-2019	[87]
Chongqing	115.23±91.91	18.42±38.00	91.34±28.00	12.55±17.18	7.41±6.09	192.02±109.60	43.27±14.91	13.15±10.68	3.68±0.74	4.58±0.51	2001-2020	[73], [74], [79], [88,89], <a href="#">EANET</a>
Chengdu	142.11±76.44	15.52±7.01	180.88±49.12	13.94±10.38	17.83±12.24	168.66±67.90	62.70±41.03	35.90±16.86	21.91±10.59	5.12±0.67	1995-2002, 2008	[90–92]
Kunming	220.30±44.57	33.33±9.45	43.59±24.14	10.07±4.07	16.36±7.48	108.04±32.58	31.38±10.23	24.63±7.87	14.69±4.03	7.41±0.14	2015-2019	[93]
Lasa	181.93±27.66	9.46±3.27	11.50±3.96	9.92±4.83	36.65±45.34	4.61±1.88	5.39±2.94	17.65±6.89	0.40	7.50	1998-2000, 2003	[69], [92], [94]
Lijiang	51.45±59.40	9.32±6.49	10.56±7.69	4.56±5.73	7.59±11.35	27.06±28.18	8.94±11.82	13.80±16.25	0.60	6.26±0.18	1991-1993, 2006,	[69], [93], [95], <a href="#">EANET</a>
Xi'an	333.42±256.38	47.46±34.48	120.95±88.94	23.77±36.82	59.38±54.65	293.86±287.00	53.50±41.58	42.98±56.36	27.77±1.70	6.43±0.48	2000-2020	[21], [59], [69], [96,97], <a href="#">EANET</a>
Wulumuqi	59.98±76.27	5.98±8.12	8.49±11.14	2.72±1.20	11.86±5.60	35.00±12.58	5.65±2.88	11.21±4.82	0.61±0.05	7.71±0.59	2003, 2017-2019	[22], [98]
Lanzhou	775.72±239.73	67.72±25.63	224.10±151.88	61.63±62.49	108.90±99.73	481.80±203.98	177.58±83.22	77.94±31.93	12.50±5.00	7.57±0.10	2009, 2019-2020	[92], 99]
Tianshan	219.07±169.96	24.91±22.73	17.81±14.44	6.46±5.37	24.37±21.28	62.93±44.09	15.83±12.85	25.89±28.24	-	7.13	2003-2004	[94], [100,101]
Wuzhishan	14.05±9.26	3.64±1.36	17.35±3.75	2.78±0.13	8.04±0.91	10.99±3.63	9.61±0.23	7.93±0.70	-	5.92±0.04	2019-2020	<a href="#">EANET</a>

**Table S2.** The spearman correlation coefficients of social-economic indicators and Cl-normalized equivalent unit ratios in precipitation in China.

	Ca <sup>2+</sup> /Cl <sup>-</sup>	Mg <sup>2+</sup> /Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup> /Cl <sup>-</sup>	K <sup>+</sup> /Cl <sup>-</sup>	Na <sup>+</sup> /Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>	F <sup>-</sup> /Cl <sup>-</sup>	pH	Population	GDP	GDP per capita	Wastewater	Industrial wastewater	SO <sub>2</sub>	Industrial SO <sub>2</sub>
Ca <sup>2+</sup> /Cl <sup>-</sup>	1.00	0.86**	0.45*	0.72**	0.32	0.62**	0.44*	0.11	0.45*	0.04	-0.12	-0.44*	0.40	-0.16	0.02	0.07
Mg <sup>2+</sup> /Cl <sup>-</sup>		1.00	0.60**	0.68**	0.32	0.62**	0.53**	0.17	0.49*	0.27	0.15	-0.22	0.42	-0.13	-0.26	0.07
NH <sub>4</sub> <sup>+</sup> /Cl <sup>-</sup>			1.00	0.64**	-0.27	0.70**	0.93**	0.57**	-0.20	0.61**	0.35	-0.22	0.47	0.09	0.12	0.28
K <sup>+</sup> /Cl <sup>-</sup>				1.00	0.22	0.55**	0.64**	0.35	0.17	0.24	0.12	-0.26	0.54	0.12	-0.14	0.01
Na <sup>+</sup> /Cl <sup>-</sup>					1.00	-0.03	-0.22	-0.34	0.57**	-0.33	-0.09	0.23	-0.13	-0.31	-0.60	-0.20
SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup>						1.00	0.74**	0.35	-0.06	0.39	0.30	-0.15	0.53	-0.05	0.33	0.36
NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>							1.00	0.53*	-0.27	0.48*	0.26	-0.17	0.32	-0.06	-0.26	0.13
F <sup>-</sup> /Cl <sup>-</sup>								1.00	-0.47*	0.42	0.20	0.04	0.19	0.14	0.07	-0.52
pH									1.00	-0.024	-0.05	0.14	-0.12	-0.54*	-0.48	-0.26
Population										1.00	0.73**	-0.05	0.86**	0.49	0.57	0.43
GDP											1.00	0.49*	0.67*	0.38	0.21	0.27
GDP per capita												1.00	-0.62	-0.41	-0.67	-0.49
Wastewater r													1.00	0.73*	0.75	0.48
Industrial Wastewater r														1.00	0.52	0.65*
SO <sub>2</sub>															1.00	0.94**

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Industrial	
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**Table S3.** The comparison of the mean pH values with other mountains.

	Height (m)	Area	Year	pH	Reference
Tianshan	2119	North China	2003-2004	7.13	This study
Wuzhishan	958	South China	2019-2020	5.92	This study
Leigongshan	1630	South China	2003	4.44	[102]
Waliguan	3816	North China	1997	6.38	[103]
Mangdang Mountain	1382	South China	1981-1983	5.41	[104]
Lushan	1150	South China	1987	5.13	[105]
			2007-2009	4.25	[106]

**Table S4.** The value of nss-Ca<sup>2+</sup>, nss-SO<sub>4</sub><sup>2-</sup>, NP, AP and NP/AP of rainwater from 24 sites.

City	nss-Ca <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	NP	AP	NP/AP
Beijing	217.90	232.66	413.33	316.57	1.31
Shanghai	146.56	172.51	243.40	210.25	1.16
Hangzhou	136.16	66.90	204.36	96.54	2.12
Nanjing	146.47	79.27	258.12	124.78	2.07
Jinan	216.60	257.98	424.96	372.24	1.14
Yantai	300.91	165.51	389.81	241.81	1.61
Shenzhen	49.78	65.46	83.18	92.56	0.90
Guangzhou	98.53	150.67	150.87	194.10	0.78
Zhuhai	28.36	33.70	60.74	53.48	1.14
Xiamen	58.55	53.53	92.79	81.10	1.14
Wuhan	87.77	67.24	186.38	139.49	1.34
Zhengzhou	353.80	307.85	556.76	396.96	1.40
Nanchang	55.32	73.15	116.63	106.85	1.09
Hengyang	40.32	63.67	111.97	96.15	1.16
Chongqing	114.91	191.09	206.25	234.37	0.88
Chengdu	141.33	166.43	322.21	229.13	1.41
Kunming	219.58	106.00	263.17	137.38	1.92
Lasa	180.31	0.03	191.81	5.42	35.40
LiJiang	51.12	26.11	61.68	35.05	1.76
Xi'an	330.81	286.44	451.76	339.94	1.33
Wulumuqi	59.46	33.52	67.95	39.17	1.73
Lanzhou	770.93	468.19	995.03	645.77	1.54
Tianshan	217.99	59.88	235.80	75.71	3.11

$$\text{nss-Ca}^{2+} = [\text{Ca}^{2+}]_{\text{rainwater}} - [\text{Na}^+]_{\text{rainwater}} \times ([\text{Ca}^{2+}] / [\text{Na}^+])_{\text{seawater}}; \text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}]_{\text{rainwater}} - [\text{Na}^+]_{\text{rainwater}} \times ([\text{SO}_4^{2-}] / [\text{Na}^+])_{\text{seawater}}; \text{NP/AP} = [\text{nss-Ca}^{2+} + \text{NH}_4^+] / [\text{nss-SO}_4^{2-} + \text{NO}_3^-].$$

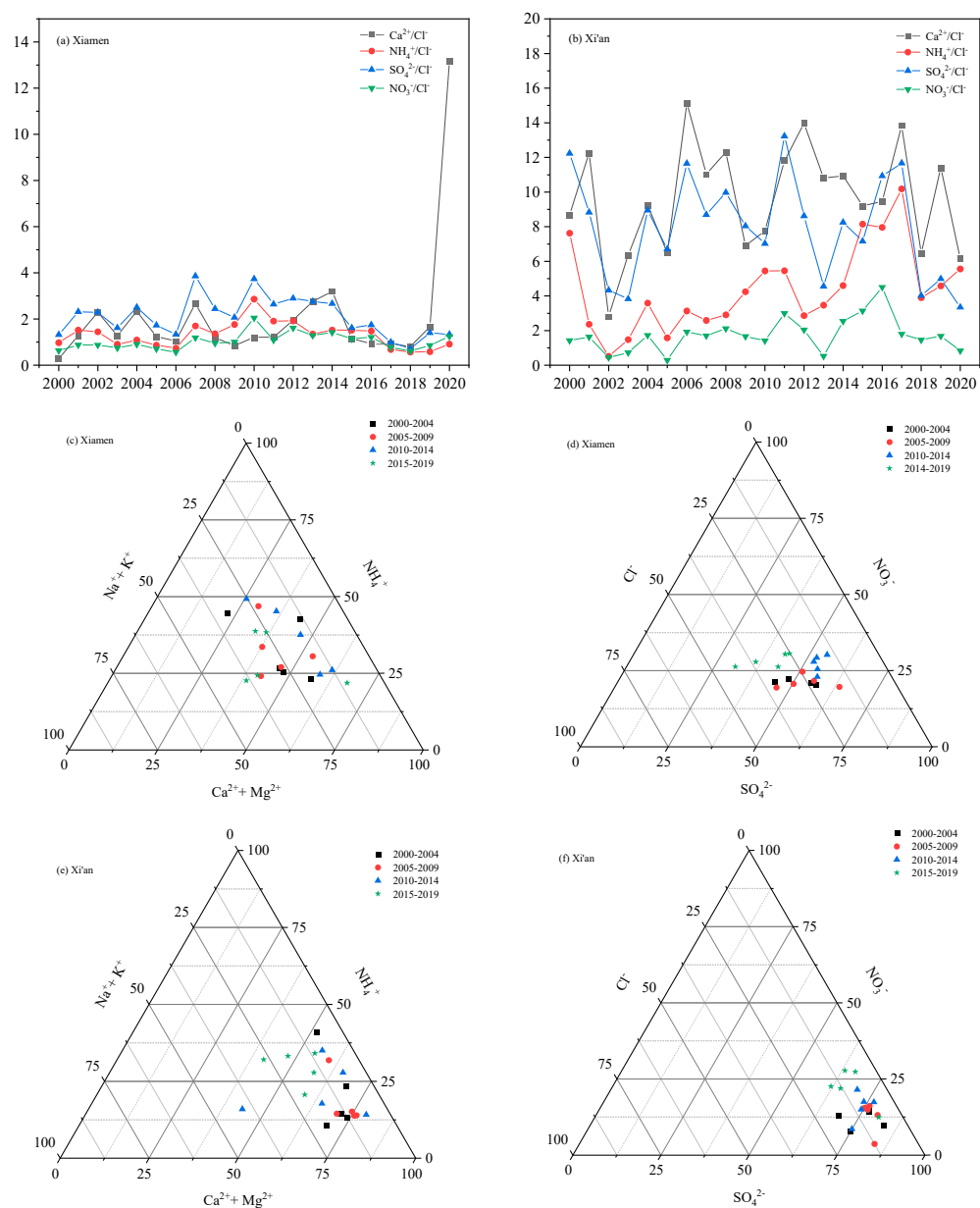
**Table S5.** Cl-normalized equivalent unit ratios in rainwater.

City	Ca <sup>2+</sup> / Cl <sup>-</sup>	Mg <sup>2+</sup> / Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup> / Cl <sup>-</sup>	K <sup>+</sup> / Cl <sup>-</sup>	Na <sup>+</sup> / Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> / Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup> / Cl <sup>-</sup>	F <sup>-</sup> / Cl <sup>-</sup>
Beijing	4.92	0.88	5.56	0.44	0.68	6.06	2.34	0.44
Shanghai	2.88	0.40	2.18	0.25	0.75	3.36	0.87	0.34
Hangzhou	6.70	0.60	3.53	0.84	0.93	3.53	1.48	0.82
Nanjing	1.69	0.30	1.54	0.36	0.54	1.11	0.80	0.30
Jinan	4.84	0.98	5.05	0.31	0.85	5.42	2.72	0.22
Yantai	1.40	0.33	1.40	0.19	0.83	0.85	0.34	0.02
Shenzhen	1.71	0.21	1.26	0.12	0.64	2.56	0.93	0.20
Guangzhou	3.47	0.42	1.70	0.43	1.08	5.64	1.38	0.37
Zhuhai	0.78	0.30	0.81	0.14	0.98	1.00	0.53	-
Xiamen	1.89	0.31	1.56	0.23	0.76	2.28	1.19	-
Wuhan	3.74	1.40	4.55	0.65	1.15	3.10	3.22	0.66
Zhengzhou	2.19	0.46	1.55	0.13	0.50	1.48	0.81	0.33
Nanchang	2.94	0.39	3.85	0.37	0.64	4.53	2.12	0.71
Hengyang	5.66	0.69	9.03	0.37	0.44	8.60	4.27	4.10
Chongqing	9.98	1.69	9.08	0.84	0.58	16.34	4.71	0.29
Chengdu	5.59	0.58	7.79	0.62	0.49	3.28	3.10	0.69
Kunming	9.71	1.48	2.01	0.44	0.68	4.83	1.36	0.67
Lasa	12.15	0.64	0.94	0.56	1.90	0.31	0.38	0.04
Lijiang	8.74	1.88	3.96	0.59	0.80	3.82	1.40	0.29
Xi'an	11.58	2.08	4.40	0.93	2.01	9.04	1.77	0.54
Wulumuqi	4.64	0.45	0.65	0.25	1.09	3.44	0.51	0.07
Lanzhou	12.98	1.01	2.96	0.68	1.20	6.50	2.45	0.20
Tianshan	18.05	2.89	1.87	0.31	1.27	3.75	0.92	-
Wuzhishan	1.83	0.47	2.18	0.35	1.02	1.41	1.22	-

**Table S6.** Principal component analysis (PCA) of the major ions. (Maximum variance method was used).

	PC1	PC2	PC3
Ca <sup>2+</sup>	0.64	0.58	0.24
Mg <sup>2+</sup>	0.57	0.39	0.28
NH <sub>4</sub> <sup>+</sup>	0.14	0.93	-0.11
K <sup>+</sup>	0.81	0.37	0.08
Na <sup>+</sup>	0.89	0.21	0.04
SO <sub>4</sub> <sup>2-</sup>	0.47	0.84	-0.02
NO <sub>3</sub> <sup>-</sup>	0.24	0.92	-0.03
Cl <sup>-</sup>	0.80	0.10	-0.12
F <sup>-</sup>	0.23	0.14	-0.68
pH	0.27	0.08	0.78
% variance	51.47%	13.30%	10.44%
% cumulative	51.47%	64.77%	75.21%





**Figure. S1.** Temporal variations of Cl-normalized equivalent unit ratios and triangular diagrams of rainwater chemical ions in Xiamen and Xi'an.