Supporting Information

Atmospheric arsenic deposition in the Pearl River Delta region, South China: influencing factors and speciation

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Number of pages: 20

Number of tables: 5

Number of figures: 7

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1. Stabilization of soluble As compounds carried by atmospheric deposition

The matrix spike/matrix spike duplicates (MS/MSD) were processed to obtain the EDTA amount effectively stabilizing soluble As compounds in the present study. After sampling and filtration, the randomly selected sample filtrates were immediately spiked with specific concentrations of As compounds (1 μg iAs^{III} l^{-1} and 1 μg iAs^{V} l^{-1}) and a series of EDTA concentrations (0, 1.0, 1.25, 5.0, 10.0 mM), and subsequently incubated in the dark and cold environment; meanwhile, the filtrates spiked with the same series of EDTA concentrations but without As standards were incubated in parallel. All of the spiked filtrates were determined by the HPLC–ICP-MS after 7-, 14-, 21- and 28-day incubation, respectively.

Without EDTA stability, the recovery rates for spiked iAs^{III} decreased by about 30% after 28-day incubation, while the level of iAs^{V} increased correspondingly. This indicates that at least 30% of the soluble iAs^{III} carried by the atmospheric deposition could be oxidized to iAs^{V} after one month (SI Figure 1). With EDTA addition, the interconversion between iAs^{III} and iAs^{V} was inhibited effectively. Compared with 1.0mM EDTA spiked, the recoveries of soluble iAs^{III} stabilized by 1.25 mM EDTA spiked were enhanced to about 90% after 28 days (SI Figure 1). However, the stability of soluble As species could not be enhanced significantly by increasing EDTA amounts, when the its concentrations were higher than 1.25 mM. Accordingly, 1.25 mM is considered as the most effective spiked EDTA concentration to stabilize the soluble As compounds carried by atmospheric deposition.

2. Extraction and stabilization of insoluble As compounds

In brief, a filtered membrane was introduced to the digestion tubes with 10 ml 100 mM

H_3PO_4 solution (with 40mM L-ascorbic acid spiked) and submitted to microwave irradiation at 40 W to each tube for 20 min. After cooling down, the extracts obtained were centrifuged at 3000 rpm for 20 min. And the supernatant was filtered through the 0.45 μm syringe filter before instrumental analysis.

The MS/MSD were also processed to obtain the L-ascorbic amount effectively stabilizing insoluble As compounds during microwave assistant extraction. A series of L-ascorbic acid concentrations (0, 20, 40, 60, 80mM) were spiked in H_3PO_4 extraction solution. And the spiked concentrations of As compounds were 1 μg iAs^{III} l^{-1} and 1 μg iAs^{V} l^{-1}. A substantial portion of iAs^{III} would be transformed to iAs^{V} with the low levels of L-ascorbic acid spiked (<40 mM) (SI Figure S2). When the spiked concentration was increased to 40 mM or higher, both iAs^{III} and iAs^{V} could be stabilized with the recovery rates of nearly 100% (SI Figure S2).

3. Concentration of As compounds with the strong anion exchange (SAX) cartridge

A volume of 20.0±0.1 ml of the filtrate or extract was allowed to flow serially through a strong anion exchange (SAX) cartridge (Agilent Technologies, Santa Clara, CA, USA) at a flow rate of 1.0± 0.1 ml min^{-1} (delivered by a peristaltic pump), on which both iAs^{III} and iAs^{V} were retained. Afterwards, the retained As species were eluted by 2.0± 0.1 ml 0.3M H_3PO_4 at a flow rate of 1.0± 0.1ml/min.

Ahead of retention, the SAX cartridges were pre-washed and activated using methyl alcohol and Milli-Q water in sequence, and the pH of all sample solutions were adjusted to 11.2 with NaOH to ensure all of As compounds dissociate. The recovery rates of the 10-time concentration experiment were 92.1±4.6% and 88.7±7.3% for iAs^{III} and iAs^{V}, respectively.

4. Verification of statistic models

In order to verify whether the statistic models (SI Table S3) could be applied to the entire PRD region for further investigation of the characteristics of regional atmospheric As deposition, the z scores of the monthly values of the identified independents (SI TableS3) recorded at study sites standardized from the regional data recorded at meteorological stations and air quality monitoring stations (Figure 1, SI Equations S1-S3, **n=10, m=1 during study period or m=3 from 2013 to 2015**), were employed in the models, and these obtained deposition z scores (Z_{PRD}) were compared with those deposition z scores ($Z_{DH\&GZ}$) calculated from independents' z scores standardized only from the study sites (DH & GZ) SI Equations S1-S3, **n=2, m=1**). The z scores indicate the relative magnitude of monthly deposition. If the monthly Z_{PRD} vary significantly with the $Z_{DH\&GZ}$, it means that the monthly variations of the individual independents recorded at the study sites are consistent with other cities, and this indicates the study sites are representative of the PRD region. Otherwise, if they do not vary with each other, this could be attributed to some different conditions in other cities that were not observed at our study sites.

$$Z_{ijk} = \frac{x_{ijk} - \mu}{\sigma}$$

SI Equation S1

$$\mu = \frac{\sum_{k=1}^{m}\sum_{i=1}^{n}\sum_{j=1}^{12} x_{ijk}}{m \times n \times 12}$$

SI Equation S2

$$\sigma = \frac{\sum_{k=1}^{m}\sum_{i=1}^{n}\sum_{j=1}^{12}(x_{ijk} - \mu)^2}{m \times n \times 12}$$

SI Equation S3

where Z_{ijk} is the z score , μ is the mean, σ is the standard deviation, x_{ijk} is the values of independents for a specific month (j) in a specific city (i) within a specific period (k), n is the number of cities, m is the number of study years.

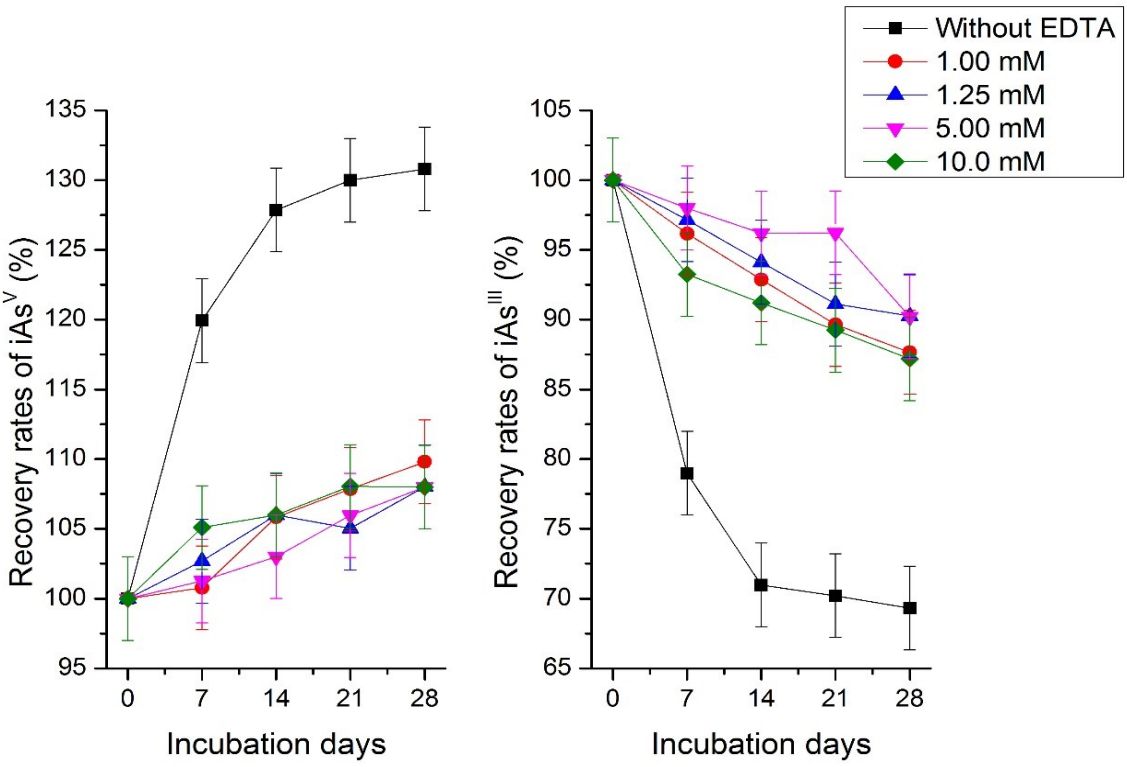
In detail, the z scores of deposition fluxes for the individual cities were calculated on the basis of the meteorological data and the site average of $PM_{2.5}/PM_{10}$ concentrations recorded. The z scores in the area of Guangzhou and Foshan were obtained from the meteorological data recorded in Guangzhou and the site average of $PM_{2.5}/PM_{10}$ concentrations recorded in both cities, as no meteorological data in Foshan city were provided in the Guangdong Monthly Meteorological Dataset [1].

During the sampling period (March 2015 to February 2016), the correlation coefficients between the z scores standardized only from the study sites (SI Equations S1-S3, n=2, m=1) and those standardized from the entire region ((SI Equations S1-S3, n=10, m=1) were 0.993 (p<0.001) and 0.946 (p<0.001) for wet and dry deposition, respectively (Abstract Graphic (B)). From 2013 to 2015, the correlation coefficients between the z scores standardized only from the sampling sites ((SI Equations S1-S3, n=2, March to December 2015) and those standardized from the entire region (except Macao) ((SI Equations S1-S3, n=9, m=3, 2013-2015) were 0.985 (p<0.001) and 0.969 (p<0.001) for wet deposition and dry deposition, respectively (SI Figure S4(a)).

On the other hand, we attempted to compare the relative magnitudes of deposition between our results and the literature data, in order to further verify our statistic models. To our

knowledge, only one study about the atmospheric deposition flux of total As within the PRD region was published recently, in which the annual wet and dry deposition fluxes in Guangzhou were inferred from the atmospheric deposition fluxes of suspended particulate matters and colloidal matters and their containing As concentrations during the period of 2010-2011 [2],. By applying our statistic models of wet and dry deposition based on the monitoring data of PM_{10} and meteorology during the study period of literature (May 2010 - April 2011), the projected z-scores precisely indicated the relative magnitudes of wet and dry deposition observed in the present study and the above literature (SI Table S4). However, the projected z-scores from the bulk deposition model did not recover their relative magnitudes. This might be attributed to the higher p values for the independents of $PM_{2.5}$ and wind speed involved in the model ($0.05<p<0.1$, SI Table S3).

Hence, the study sites in the present study are representative of the entire PRD region, and the obtained statistic models for wet and dry deposition could be able to investigate the seasonal variation of As deposition and the relative contributions by individual cities to the PRD region.



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120 SI Figure S1. Recovery rates of soluble inorganic As compounds stabilized by EDTA of

121 different concentrations

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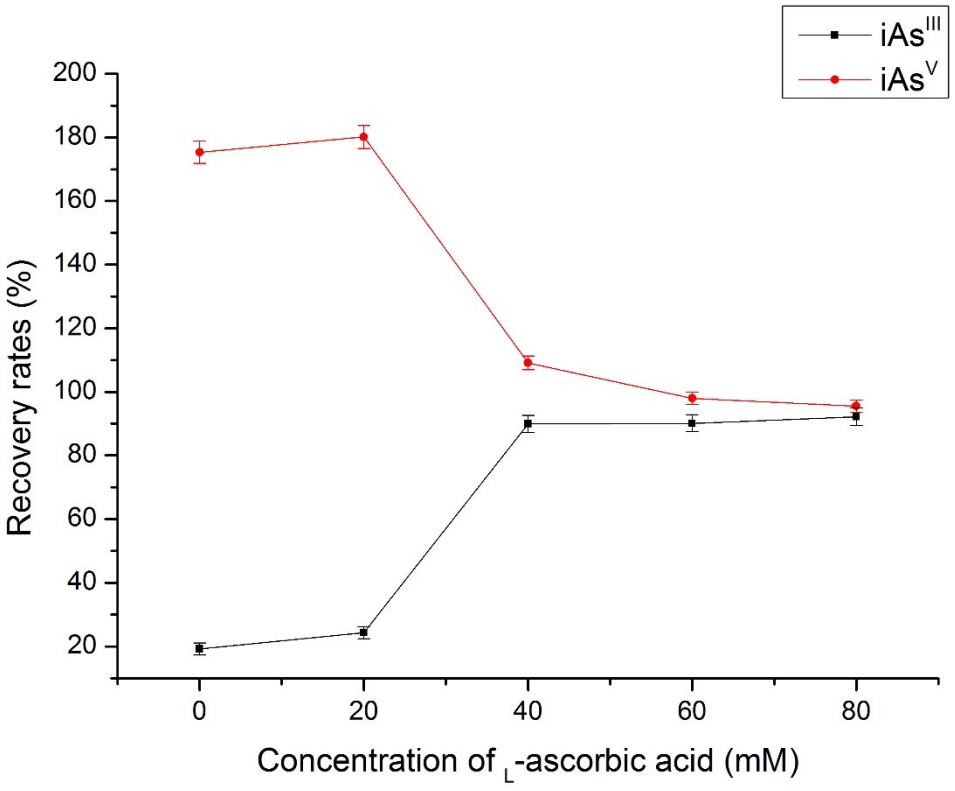
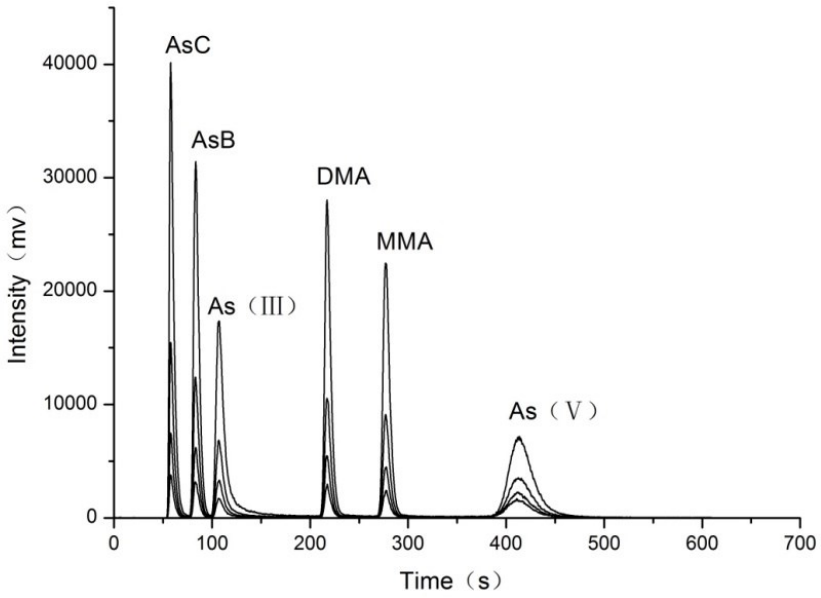


126 SI Figure S2. Recovery rates of insoluble inorganic As compounds stabilized by $_{L}$-ascorbic

127 acid



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129 SI Figure S3 Chromatogram of all six arsenic compounds

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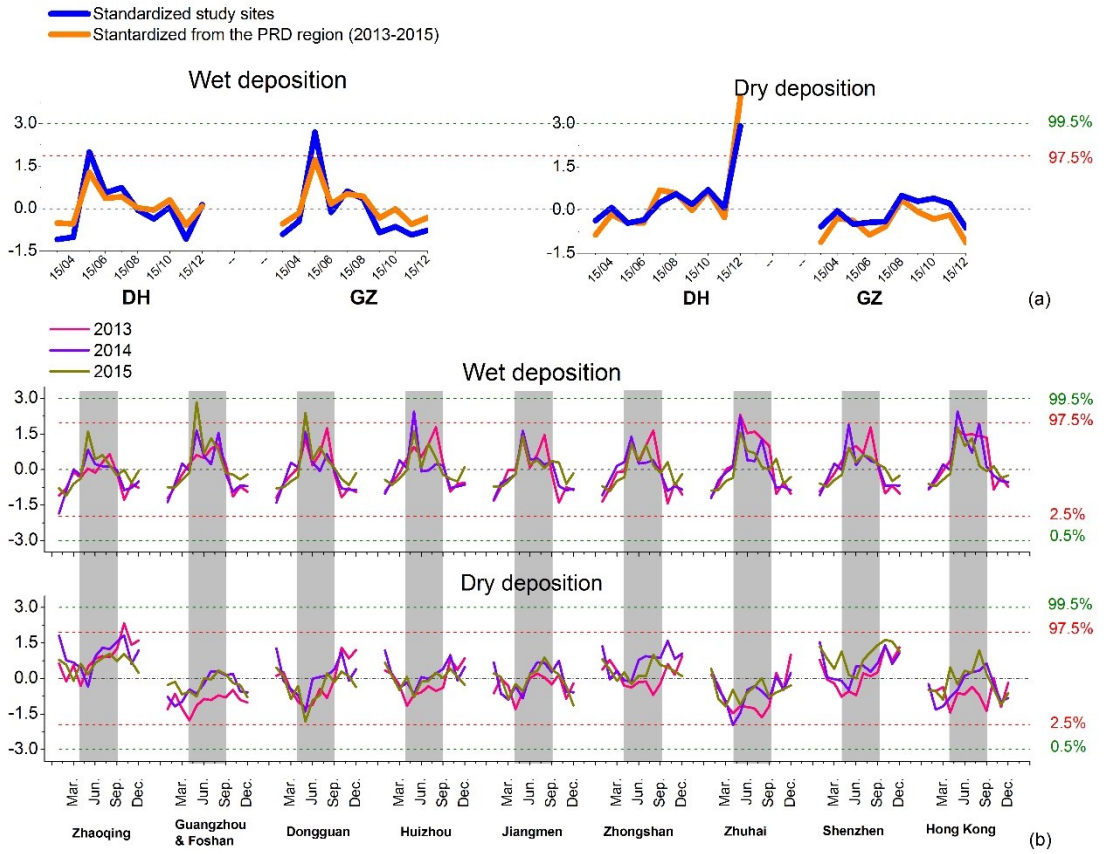
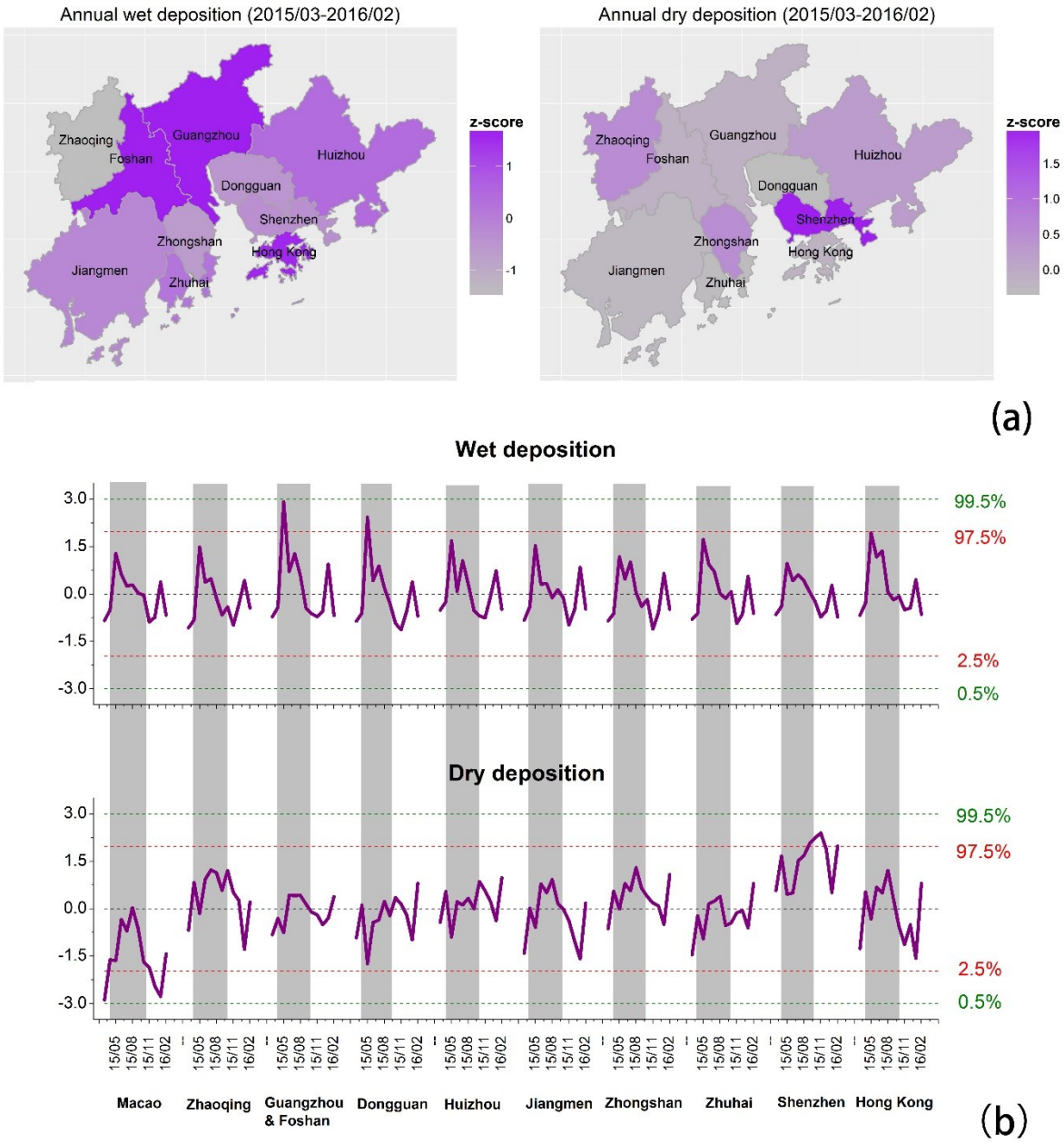


131 SI Figure S4 Monthly variations of Z_{PRD} *and* $Z_{DH\&GZ}$ (a), and the monthly variations of z

132 scores of deposition fluxes around the PRD region (b) from 2013 to 2015 (the gray panels:

133 wet season)



134 SI Figure S5 Spatial (a) and monthly (b) variation of z scores of As deposition fluxes around

135 the PRD region during sampling period (the gray panels: wet season)

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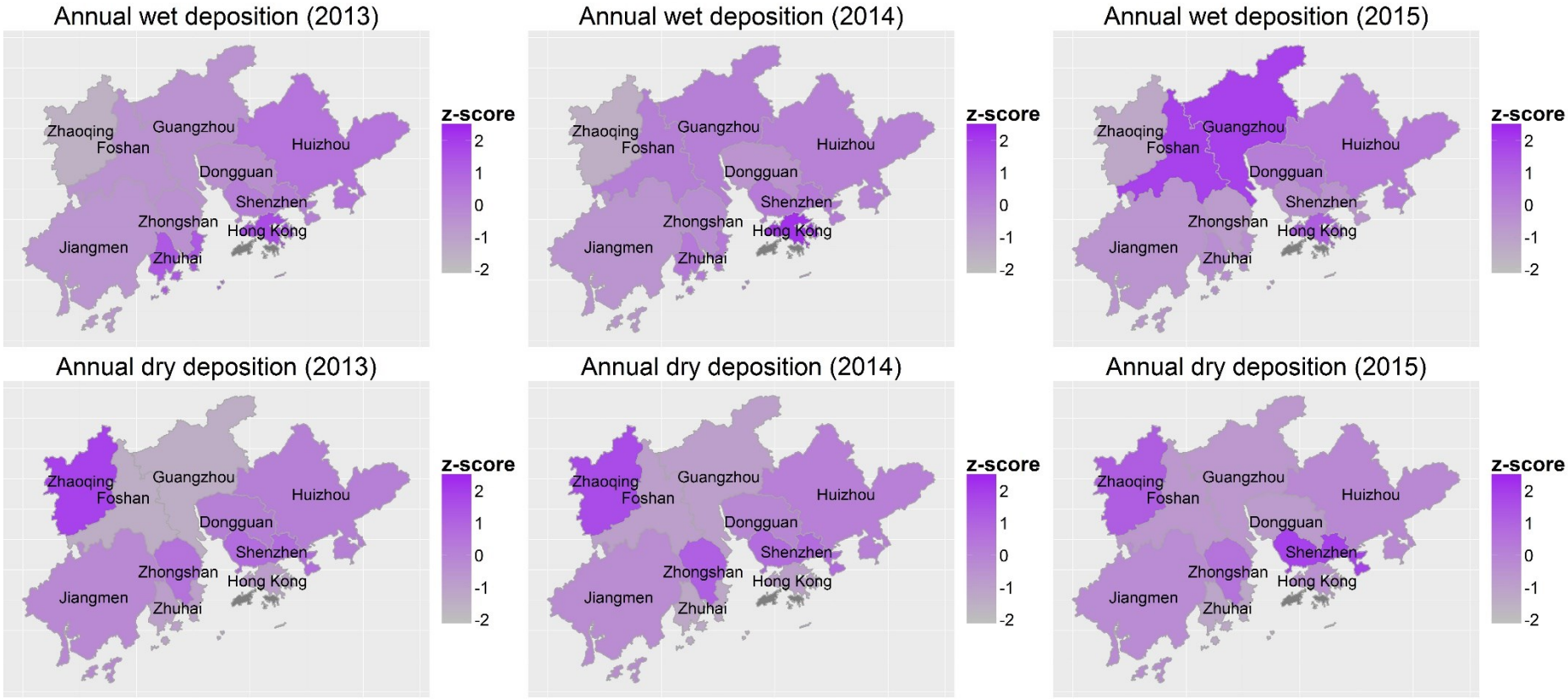

137 SI Figure S6 Annual and spatial variation of z scores of As deposition fluxes in the PRD region (2013-2015)

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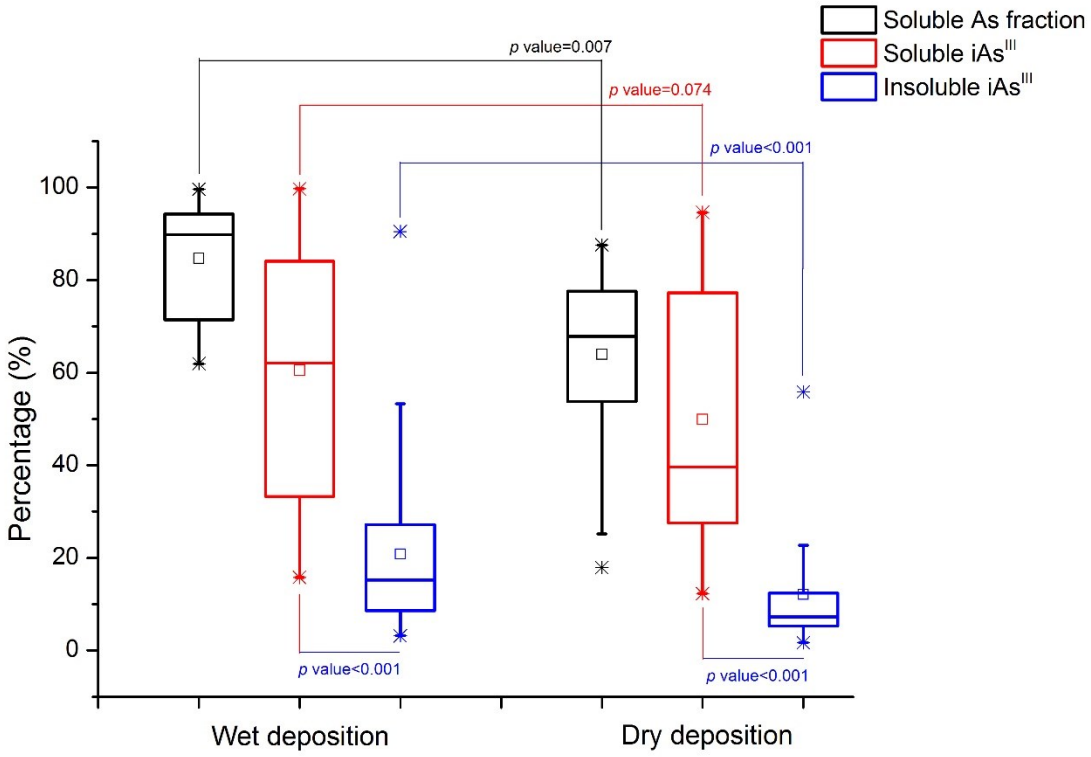

139 SI Figure S7 As solubility and speciation carried by atmospheric deposition in the PRD

140 region

141 SI Table S1 Total As levels (Min. ~ Max., Mean) in rain in this study and other regions around the world

Sites		Study period	Total As levels (μg/l)	References
PRD region, China	Guangzhou	Mar. 2015 ~ Feb. 2016	0.16 ~ 7.91, 0.90	This study
	Dinghu		0.17 ~ 5.88, 1.12	
Singapore		Dec. 2004	0.11~0.17, 0.14	[3]
Vermont, USA	Mt. Mansfield	Aug. ~ Oct. 1998	<MDL ~ 0.26, 0.10	[4]
Southeastern Nigeria	Shale bedrock areas	Jul. ~ Aug. 2009	0.25 ~ 0.74, 0.56	[5]
Central Poland	Poznań	Jan. ~ Mar. 2013	<MDL ~ 1.58, 0.74 *	[6]
California, USA			0.46	[7]

142 *the snow sample

143 SI Table S2 Average bulk deposition fluxes in this study and other regions around the world

Sites		Study period	Flux ($\mu g.m^{-2}.month^{-1}$)	Reference
PRD region, China	Guangzhou	Mar. 2015 ~ Feb. 2016	135.25	This study
	Dinghu		185.09	
Beijing-Tianjin-Hebei region, China	Beijing	Dec.2007 ~ Nov. 2010	310.83	[8]
	Tianjin		459.17	
	Baoding		724.17	
	Tangshan		370	
	Cangzhou		229.17	
	Shijiazhuang		253.33	
Yangtze River Delta Region, China		Dec. 2006 ~ Dec. 2007	130.83	[9]
Shanxi Province, China		Oct. 2005 ~ Oct. 2006	315	[10]
Taiwan	Chiayi, Southern Taiwan	Jan. 2011 ~ June 2012	192	[11]
USA	Lake Superior	1993 ~ 1994	14.08	[12]
	Lake Michigan		11.5	
	Lake Erie		15.17	
Europe	Rural areas	/	2.46 ~ 12.9	[13]
	Urban areas	/	6.6 ~ 102	
Japan	Komae	Dec. 2003 ~ Nov. 2005	131.67	[14]
	Umihotaru		218.33	
	Narashino		372.5	
Australia	Brisbane	Apr. 2007 ~ Mar 2008	29.1	[15]

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145 SI Table S3. Summary of stepwise linear regression models

		Precipitation (mm)	$PM_{2.5}$ ($\mu g.m^{-3}$)	Relative humidity (%)	Wind speed ($m.s^{-1}$)	PM_{10} ($\mu g.m^{-3}$)	Constant
Wet deposition ($\mu g.m^{-2}$)	Coefficient	0.469	-6.469	--	--	--	278.081
	Standardized coefficient	0.640	-0.297	--	--	--	--
	Sig.	<0.001	0.049	--	--	--	0.036
	VIF	1.517	1.517	--	--	--	--
	Regressed annual fluxes ($\mu g.m^{-2}$)	DH: 1597.60, GZ: 1517.18					
	Measured annual fluxes ($\mu g.m^{-2}$)	DH: 1751.53, GZ: 1364.20					
Dry deposition	Coefficients	--	--	-3.005	-34.857	-1.222	401.019
	Standardized coefficients	--	--	-0.773	-0.479	-0.414	--
	Sig.	--	--	<0.001	<0.005	0.016	<0.001
	VIF	--	--	1.282	1.137	1.245	--
	Regressed annual fluxes ($\mu g.m^{-2}$)	DH: 467.81, GZ: 259.91					
	Measured annual fluxes ($\mu g.m^{-2}$)	DH: 469.58, GZ: 258.83					
Bulk deposition	Coefficients	0.431	-7.498	--	-70.092	--	497.207
	Standardized coefficients	0.524	-0.307	--	-0.241	--	--
	Sig.	0.004	0.074	--	0.084	--	0.008
	VIF	1.518	1.545	--	1.024	--	--
	Regressed annual fluxes ($\mu g.m^{-2}$)	DH: 2222.85, GZ: 1624.43					
	Measured annual fluxes ($\mu g.m^{-2}$)	DH: 2221.11, GZ: 1623.03					

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147 SI Table S4. Comparison of the projected z-scores and annual wet/dry deposition fluxes
148 between the literature and our study

		This study		Literature data
		DH	GZ-SYSU	Institute of Geochemistry, CAS, Guangzhou **
Wet deposition*	Annual fluxes ($\mu g.m^{-2}.year^{-1}$)	1751.53	1354.20	910
	z-scores	0.72	0.69	-1.41
Dry deposition	Annual fluxes ($\mu g.m^{-2}.year^{-1}$)	469.58	258.83	1250
	z-scores	0.19	-1.31	1.12

149 *For wet deposition projection, the $PM_{2.5}$ level was calculated from PM_{10} level and the average
150 ratio of $PM_{2.5}/PM_{10}$ monitored at the air quality monitoring station in the center of Guangzhou
151 (Figure 1) from 2013 to 2015, as $PM_{2.5}$ concentration was unavailable before 2013.
152 ** About 10 km away from GZ-SYSU site in the present study (Figure 1)

153 SI Table S5. The projected annual z scores during study period and 2013-2015

City	Wet deposition				Dry deposition			
	Study period	2013	2014	2015	Study period	2013	2014	2015
Macao	-0.60				-2.03			
Zhaoqing	-1.51	-1.55	-1.49	-1.27	0.54	1.89	1.66	1.15
Guangzhou & Foshan	1.66	-0.52	0.11	1.88	-0.13	-1.42	-0.92	-0.67
Dongugan	-0.54	-0.41	-0.53	0.18	-0.36	0.12	-0.13	-0.81
Huizhou	0.43	0.49	0.06	0.27	0.25	0.13	0.10	-0.16
Jiangmen	-0.19	-0.62	-0.57	-0.59	-0.27	-0.21	-0.32	-0.27
Zhongshan	-0.65	-0.45	-0.36	-0.81	0.50	0.53	1.10	0.54
Zhuhai	0.21	1.28	0.29	-0.33	-0.32	-0.91	-1.27	-1.21
Shenzhen	-0.38	0.16	0.26	-0.50	1.98	0.71	0.73	1.88
Hong Kong	1.58	1.64	2.21	1.18	-0.15	-0.84	-0.96	-0.46

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References

1. NSTI, Guangdong Monthly Meteorologial Dataset http://data.cma.cn/data/cdcdetail/dataCode/SURF_CLI_CHN_MUL_MON.html In China Met. Data Service.
2. Huang, W.; Duan, D.; Zhang, Y.; Cheng, H.; Ran, Y., Heavy metals in particulate and colloidal matter from atmospheric deposition of urban Guangzhou, South China. *Marine Pollution Bulletin* **2014,** *85*, (2), 720-726.
3. Karthikeyan, S.; Balasubramanian, R., Interlaboratory study to improve the quality of trace element determinations in rainwater. *Analytica Chimica Acta* **2006,** *576*, (1), 9-16.
4. Malcolm, E. G.; Keeler, G. J.; Lawson, S. T.; Sherbatskoy, T. D., Mercury and trace elements in cloud water and precipitation collected on Mt. Mansfield, Vermont. *Journal of Environmental Monitoring* **2003,** *5*, (4), 584-590.
5. Nganje, T. N.; Hursthouse, A.; Edet, A. E.; Stirling, D.; Adamu, C. I., Assessment of the Health Risk, Aesthetic and Agricultural Quality of Rainwater, Surface Water and Groundwater in the Shale Bedrock Areas, Southeastern Nigeria. *Water Quality, Exposure and Health* **2014,** *7*, (2), 153-178.
6. Siudek, P.; Frankowski, M.; Siepak, J., Trace element distribution in the snow cover from an urban area in central Poland. *Environmental Monitoring and Assessment* **2015,** *187*, (5), 225-225.
7. Andreae, M. O., Arsenic in rain and the atmospheric mass balance of arsenic. *Journal of Geophysical Research* **1980,** *85*, 4512-4518.
8. Pan, Y.; Wang, Y. S., Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. *Atmospheric Chemistry and Physics* **2015,** *15*, (2), 951-972.
9. Huang, S.; Tu, J.; Liu, H.; Hua, M.; Liao, Q.; Feng, J.; Weng, Z.; Huang, G., Multivariate analysis of trace element concentrations in atmospheric deposition in the Yangtze River Delta, East China. *Atmospheric Environment* **2009,** *43*, (36), 5781-5790.
10. Zhong, C.; Yang, Z.; Jiang, W.; Yu, T.; Hou, Q.; Li, D.; Wang, J., Annual input fluxes and source identification of trace elements in atmospheric deposition in Shanxi Basin: the largest coal base in China. *Environmental Science and Pollution Research* **2014,** *21*, (21), 12305-12315.
11. Lin, L.; Wu, S. H.; Lin, S.; Mwangi, J. K.; Lin, Y.; Lin, C.; Wang, L.; Changchien, G.; Kang, Y.; Styling, F., Atmospheric Arsenic Deposition in Chiayi County in Southern Taiwan. *Aerosol Air Qual. Res.* **2013,** *13*, (3), 932-942.
12. Sweet, C. W.; Weiss, A.; Vermette, S. J., Atmospheric Deposition of Trace Metals at Three Sites Near the Great Lakes. *Water, Air, & Soil Pollution* **1998,** *103*, (1), 423-439.
13. Settimo, G.; Viviano, G., Atmospheric depositions of persistent pollutants: methodological aspects and values from case studies. *Annali dell'Istituto Superiore di Sanità* **2015,** *51*, (4), 298-304.
14. Sakata, M.; Tani, Y.; Takagi, T., Wet and dry deposition fluxes of trace elements in Tokyo Bay. *Atmospheric Environment* **2008,** *42*, (23), 5913-5922.
15. Huston, R.; Chan, Y. C.; Chapman, H.; Gardner, T.; Shaw, G. R., Source apportionment of heavy metals and ionic contaminants in rainwater tanks in a subtropical urban area in Australia.

197 *Water Research* **2012,** *46*, (4), 1121-1132.
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