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Contact CEH NORA team at noraceh@ceh.ac.uk

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1	Hazard Posed by Metals and As in PM <sub>2.5</sub> in Air of Five Megacities in the
2	Beijing-Tianjin-Hebei Region of China during APEC
3	Linlin Zhang <sup>a,</sup> , Xiaowei Jin <sup>a,*</sup> , Andrew C Johnson <sup>b</sup> , John P. Giesy <sup>c,d,e</sup>
4	<sup>a</sup> China National Environmental Monitoring Center, Beijing 100012, China
5	<sup>b</sup> Centre of Ecology and Hydrology, Wallingford, Oxfordshire, UK
6	<sup>c</sup> Department of Veterinary Biomedical Sciences and Toxicology Centre, University of
7	Saskatchewan, Saskatoon, Saskatchewan, Canada
8	<sup>d</sup> School of Biological Sciences, University of Hong Kong, Hong Kong, SAR, China
9	<sup>e</sup> State Key Laboratory of Pollution Control and Resource Reuse, School of the
10	Environment, Nanjing University, Nanjing, People's Republic of China
11	
12	
13	*Corresponding author:
14	Xiaowei Jin
15	Department of Analytical Technique, China National Environmental Monitoring
16	Center, Anwai Dayangfang No.8, Chaoyang District, Beijing 100012, China
17	Email: jinxiaowei07@mails.ucas.ac.cn
18	

#### 19 Abstract

Airborne fine particulate matter (PM<sub>2.5</sub>) from five megacities including Beijing, 20 21 Tianjin, Shijiazhuang, Baoding, and Jinan were collected during November 2014 and compared with similar periods in 2012 and 2013. The November 2014 period 22 23 coincided with the Asia Pacific Economic Cooperation (APEC) Leaders meeting during which measures to control pollution of the air were introduced. 24 Concentrations of eleven elements in PM2.5 were quantified by ICP-MS after 25 microwave-assisted digestion. Potential effects of five toxic trace metals including 26 27 Mn, Ni, Cu, Zn, Pb and the metalloid As on health were assessed. In 2014, concentrations of  $PM_{2.5}$  were significantly less than during the same period in 2012 28 and 2013. Mean concentrations of 6 elements ranked in decreasing order: Zn>Pb> 29 30 Cu≈Mn>As>Ni and spatial concentrations ranked in decreasing order: Shijiazhuang >Baoding>Tianjin>Jinan>Beijing. Risks of the five metals and the metaloid As to 31 health of humans were small, except for Mn in Shijiazhuang. Risks to health posed 32 33 by other elements were less during the period of study. Risks posed by the five metals and As in Beijing were greater to varying degrees after the APEC meeting. Risks to 34 health of humans during the APEC were overall lesser than the same period in 2012 35 36 and 2013, mostly due to lesser emissions due to the short-term control measures.

39 **1. Introduction** 

Beijing is the political, economic and cultural center of China. Rapid 40 41 economic development, urbanization and industrialization of the Beijing-Tianjin-Hebei region during recent decades have been linked with poor air 42 quality. Pollution of air includes particulate matter, dust-haze, photochemical smog, 43 and concentrations of metals potentially adverse to human health (Chan and Yao, 44 2008; Zhang et al., 2013; Zhao et al., 2013). Airborne fine particulate matter (PM 45 with aerodynamic diameter  $<2.5 \mu m$ , PM<sub>2.5</sub>) has been considered a particularly 46 47 harmful air pollutant, which brings a challenges to China (Chan and Yao, 2008; Hu et al., 2010). Concentrations of metals in air in China have been well documented with 48 potentially toxic concentrations of metals or metalloids such as As, found in urban 49 50 regions present in aerosols related to anthropogenic processes (Fang et al., 2010; Wei and Yang, 2010). The International Agency for Research on Cancer (IARC) has 51 classified arsenic (As) and arsenicals, cadmium (Cd) and cadmium compounds, 52 hexavalent chromium (Cr) and nickel (Ni) compounds as "carcinogenic to humans" 53 (Group 1); inorganic lead (Pb) compounds as "probably carcinogenic to humans" 54 (Group 2A). Several other metals and As were classified as "possibly carcinogenic 55 to humans" (Group 2B) (IARC, 2006). Concentrations of metals can be enriched in 56 aerosols especially in and on surfaces of particulates, such as PM<sub>2.5</sub>, which can 57 penetrate the human respiratory system and can be associated with cardio-pulmonary 58 59 diseases. Metals, once inhaled, can also be distributed to organs, such as liver and kidney, where they can cause other adverse effects on health. Thus, exposure to 60

elevated concentrations of metals in respired air represents a serious concern forhuman health (Duan and Tan, 2013).

Research on airborne particulate contaminants has tended to focus on their physical properties (Duan et al., 2003; Feng et al., 2005; Novák et al., 2013; Okuda et al., 2008; Qu et al., 2012; Sun et al., 2004; Xu et al., 2005; Zhang et al., 2014) but, there have been few assessments of risks posed by metals carried in PM<sub>2.5</sub> in polluted air events in China (Li et al., 2015).

The 22<sup>nd</sup> annual Asia Pacific Economic Cooperation (APEC) Leaders Meeting 68 69 was convened in Beijing in November, 2014. To ensure good quality of ambient air during the meeting, many of the primary combustion sources of PM<sub>2.5</sub> were controlled 70 (MEP, 2014a, b, c). Cessation of many combustion activities over this period 71 72 provided an excellent opportunity to assess changes in air quality when compared to the same period in previous years when no control occurred. This information could 73 be used to calibrate changes in quality of the air related to remedial actions and serve 74 75 as a guide for future corrective actions.

The objectives of this study were, first to determine concentrations of five metals: Nickel (Ni), lead (Pb), zinc (Zn), copper (Cu) and manganese (Mn) and the metalloid arsenic (As) present in PM<sub>2.5</sub> from five megacities including Beijing (20 million people), Tianjin (14 million people), Shijiazhuang (10 million people), Baoding, and Jinan in the Jing-Jin-Ji region and surrounding areas during the APEC meeting. Second, to assess risks to health of humans posed by metals associated with PM<sub>2.5</sub> during this period. Third, to compare concentrations with those during the same period in 2012 and 2013 when no controls were imposed.

### 84 2. Materials and Methods

### 85 2.1 Sample collection

A total of 55 samples of PM<sub>2.5</sub> were collected in Beijing, Tianjin, Shijiazhuang, Baoding and Jinan, during the period November 2 - 20, 2014 (Figure 1). Samples were collected from the local Atmospheric Boundary-layer Observation Stations, which were located along roadways in commercial-residential areas. There are no high buildings or factories in the vicinity, and no "special" sources of contamination at these sample sites but included exposure to natural patterns of wind. Devices for sampling particulate matter were situated on flat roofs 10~20 m above the ground.

93

# 94 Figure 1 near here

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Samples of PM<sub>2.5</sub> were collected daily by use of "middle-flow", impact 96 particulate samplers (Wuhan Tianhong TH-150A) with  $\phi$ 90 mm quartz filter 97 membrane. The rate of airflow during sampling was 100 L/min. Quartz filters were 98 preheated in a muffle furnace at 600 °C for 3 h to remove volatile components before 99 being used for sampling. Before use, filter membranes were placed into a 100 temperature and humidity controlled chamber for 24~48 h at 15~30 °C, with relative 101 humidity of 45%~55% until it achieved a constant weight. An electronic balance 102 with accuracy of 0.01 mg (Mettler Toledo Inc., Switzerland) was used to weigh the 103 membranes before and after sampling. After collection and determination of mass of 104

105 particulates, samples were sealed and kept in a refrigerator at 4  $^{\circ}C$  until analysis.

106 Two filed blanks were performed at each site.

107 *2.2 Sample analysis* 

One-fourth of each filter was extracted with HNO<sub>3</sub>-HCl in a microwave digestion system (CEM Co. Ltd., U.S.A) for 15 min at 200 °C (HJ 657-2013) (MEP, 2013). The 10 metals including Al, Fe, Zn, Mn, Ni, Cu, Se, Pb, Ba and V and the metalloid As were quantified by use of inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technology Co. Ltd., U.S.A) (Zhang et al., 2014.).

113 *2.3 QA/QC* 

Acids and other chemicals used in this study were of highest-purity. Two field 114 blanks and one laboratory blank were prepared and analyzed. Concentrations of 115 116 metals and As in the blanks were generally less than 5% of those in samples. Four internal standard elements were used to compensate for matrix suppression and drift 117 of sensitivity of the ICP-MS. Concentrations of metals and As were calculated by 118 use of a five-point, external calibration curve with linearity as determined by 119 coefficients of determination  $(R^2)$  of greater than 0.999. A standard was run after 120 every 10 samples to monitor stability of the ICP-MS. The relative standard 121 deviations (RSDs) of concentrations of elements were typically less than 5%. 122 Precision and bias were less than 10%. 123

124 2.4 Health risk assessment

125 The model used in this study to assess risk to humans was that recommended by126 the United States Environmental Protection Agency (US EPA). Concentrations of

five metals (Ni, Pb, Zn, Cu Mn) or As were introduced into the model based on the 127 data collected during the APEC 2014 meeting as well as the same period in 2012 and 128 129 2013. Exposure concentrations for trace metals in 2012 and 2013 were from the national air quality monitoring program. The main route of exposure was considered 130 to be the human respiratory system into lungs. The risks induced by digestive tract, 131 dermal absorption and others were ignored since their calculated risks would be less 132 than the actual exposure. Assessments of risks to health of the five metals and As 133 were calculated separately for men, women or children. Suitable exposure 134 135 parameters were introduced into the model used to assess risks to health were based on characteristics of the population of China. As and Ni are recognized carcinogens, 136 while Pb, Zn, Cu and Mn were non-carcinogens (Dong et al., 2014). 137

Risk was predicted based on the assumption of lifetime exposure to the levels of pollutants measured in this study. Lifetime average daily dose (LADD) was used to express exposure to carcinogens, while Incremental life time Cancer Risk (ILCR) was used to express the risk of carcinogens (Equation 1; USEPA, 1989). This would result in predicted risks that were greater than that incurred for the period of exposure, but could be used to make comparisons among periods.

$$ILCR = LADD \times SF = \frac{c \times IR \times EF \times ED}{BW \times AT} \times SF$$
(1)

The ILCR predicts incidence of cancer, as the probability of patients with additional cancers, relative to the background rate. If the ILCR was between  $10^{-6} \sim 10^{-4}$  (1 per 10,000 to 1 per 1,000,000 additional cancers), indicated it posed *de minimis* risk of cancer (Ma and Singhirunnusorn, 2012). The cancer slope factor (SF) [mg·(kg

 $bm \cdot d$ )<sup>-1</sup> <sup>-1</sup> indicated maximum probability of cancer due to exposure to each metal or 149 The values examined here were mean daily exposures or doses (ADD; As. 150  $mg \cdot (kg \cdot d)^{-1}$ ), life, mean, daily exposure doses (LADD;  $mg \cdot (kg \cdot d)^{-1}$ ), the 151 concentration of heavy metal (C;  $mg \cdot m^{-3}$ ), respiratory rate (IR;  $m^3 \cdot d^{-1}$ ), exposure 152 frequency (EF;  $d \cdot a^{-1}$ ), exposure duration (ED; a), body masst (BM; kg), average 153 exposure time (AT; d). The ADD was used to express exposures to non-carcinogens. 154 The Hazard Quotient (HQ) was used as the measure of hazard posed by 155 The non-carcinogen hazard posed by single pollutants was non-carcinogens. 156 calculated (Equation 2; USEPA, 1989). 157

$$HQ = \frac{ADD}{RfD} = \frac{c \times IR \times EF \times ED}{BW \times AT \times RfD}$$
(2)

159 Where: ADD= Average Daily Dose of non-carcinogen  $[mg \cdot (kg \cdot d)^{-1}]$  and RfD= 160 Reference Dose  $[mg \cdot (kg \cdot d)^{-1}]$  associated with a particular level of effect. If HQ was 161 less than 1.0, hazard associated with the RfD would not be exceeded and hazard was 162 considered to be *de minimis*, whereas values of HQ>1 the hazard posed by the 163 non-carcinogen would be of concern.

# 164 *2.5 Exposure parameters*

Exposure parameters used in the current study were selected based on China's population characteristics (Dong et al., 2014; Wang et al., 2009). Exposure to metals in air was assessed by predicting inhalation and subsequent exposure to the respiratory system (Table 1). The SF and RfD were those suggested by USEPA's Integrated Risk Information System (IRIS) (Table 2) (USEPA, 1999).

170

*Table 1 near here* 

#### *Table 2 near here*

To ensure air quality during the November 2014 APEC meeting, the government of China adopted several, long-term, permanent mitigation measures including shutting down some coal-fired power plants, renovation of obsolete boilers burning the equivalent of 5400 tons of coal to more efficient systems; Removing 391,000 older motor vehicles from highways, and closing of 300 polluting enterprises as well as other measures to control some of the primary sources of air pollutants, which were completed by the end of October 2014. In addition, during the APEC, use of cars was restricted by implementation of the odd and even number rule and temporary suspension of operations of some key industrial enterprises, large-scale infrastructure construction that were known periodic sources of particulates. In addition, overall activities and transportation were reduced by large portions of people taking vacation. All these measures sharply reduced the concentration of PM<sub>2.5</sub> during APEC (MEP, 2014d).

**3. Results and discussion** 

*3.1 Averaged daily concentrations of PM*<sub>2.5</sub>

192 Mean, daily concentrations of  $PM_{2.5}$  during the APEC varied among the five

193	megacities (Figure 2) and on each day of the APEC meeting. Two maxima were
194	observed simultaneously in five cities during haze episodes that occurred on
195	November 4 and 9 2014. The greatest concentration of 236 $\mu g~PM_{2.5}~m^{-3}$ was
196	observed in Beijing on November 4, while a concentration of 225 $\mu g \; PM_{2.5} \; m^{\text{-3}}$ was
197	observed in Tianjin on November 9 2014. After the haze episodes, mean, daily
198	concentrations of $PM_{2.5}$ in the five cities was less than 45 µg m <sup>-3</sup> respectively between
199	November 6 ~ 7 and 11 ~ 12 which were less than the National air quality standard
200	(MEP, 2012).

202 Figure 2 near here

203

In November 2014, when measures were introduced to minimize emissions during the APEC, concentrations of PM<sub>2.5</sub> in Beijing were 20.8% and 33.1% less than they were during the same period in November 2012 and 2013, respectively (Figure 3). Similarly, in Tianjin and Shijiazhuang, mean, daily concentrations of PM<sub>2.5</sub> were, 16.4 and 48.7% and 5.0 and 57.7% less, respectively. Reductions in PM<sub>2.5</sub> between 2014 and 2012 and 2013 were most significant in Shijiazhuang.

During the period of the APEC meeting in November, 2014, mean, daily concentrations of  $PM_{2.5}$  were slightly greater than the National air quality standard of 75 µg m<sup>-3</sup> (MEP, 2012). Concentrations of  $PM_{2.5}$  among five megacities were ranked: Baoding > Tianjin > Shijiazhuang > Jinan > Beijing during the APEC. Concentrations of  $PM_{2.5}$  showed that a spatial trend existed with Shijiazhuang> 215 Jinan>Beijing.

216

### 217 Figure 3 near here

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Meteorological conditions during APEC were characterized by a more stable 219 atmosphere conducive to the accumulation of pollutants during the period November 220 2-6, which mainly due to northwest of North China controlled by a Mongolia high 221 pressure cell, the Yangtze River Delta region to the Korean peninsula generated a 222 223 weak high pressure system, meanwhile with Mongolia high pressure and a northeast-west trough of low pressure, a saddle-shaped field system, that covered 224 Inner Mongolia and parts of North China, developed. From November 5 to 6, a 225 226 high-pressure continental atmospheric air mass developed and advanced eastward. This cell, which generated a cold wave system covering the Beijing-Tianjin-Hebei 227 region resulted in dispersion of air pollutants. During the period of November 8 to 10, 228 229 there was always a weak high pressure over the region, which resulted in relatively weak northerly winds originating northwest of Beijing. Also during this period in 230 the eastern part of North China a static, stability weather pattern developed that 231 allowed pollutants to accumulate in the atmosphere. Finally during the period of 232 November 15 to 21, after the APEC, there was an obvious static, pressure field 233 present in North China which did not allow for effective dispersion of pollutants. 234

235 3.2 Metal concentrations in PM<sub>2.5</sub>



It was expected that with lesser concentrations of PM2.5 during the APEC

237	meeting concentrations of metals would also be less. This lesser concentration in
238	airborne metal pollution was clearly seen in Beijing (Fig. 4) and Tianjin (Fig. 5) but to
239	a limited extent in Shijiazhuang (Fig. 6). Of the metals associated with particulates,
240	the greatest concentrations were for Al, Fe, Zn and Pb which ranged from $10^2$ to $10^3$
241	ng m <sup>-3</sup> with lesser concentrations of Cu, Ba, Mn, As and Se, concentrations of which
242	ranged from 10 to $10^2$ ng m <sup>-3</sup> . Concentrations of Ni and V, which ranged from 1 to
243	10 ng m <sup>-3</sup> were the least observed. Overall the cities were ranked in decreasing order
244	of pollution of air by metals: Baoding>Tianjin>Shijiazhuang>Jinan>Beijing, and
245	in order of years of decreasing pollution: $2013 > 2012 > 2014$ .
246	
247	Figure 4 near here
248	Figure 5 near here
249	Figure 6 near here
250	
251	Mean concentrations of five metals and As ranked in decreasing order were: Zn>
252	Pb>Cu≈Mn>As>Ni. The concentration of Zn was greatest with a range of
253	0.174~0.554 $\mu g~m^{\text{-3}}$ and maximum of 3.76 $\mu g~m^{\text{-3}}$ in PM_{2.5} from Shijiazhuang. The
254	concentration of Ni was least with a range of 0.0002~0.008 $\mu g \ m^{\text{-3}}$ , but was less than
255	the LOD in Jinan and Tianjin. Concentrations of metals and As, ranked in
256	decreasing order was: Shijiazhuang>Baoding>Tianjin>Jinan>Beijing. However,
257	differences among cities were small.

258 3.3 Hazard Posed by Five Metals and As in PM<sub>2.5</sub>

259	Risks posed by the five metals and As in $PM_{2.5}$ to humans, varied among
260	elements, location and life stages of humans (Figure 7). Regardless of the location
261	or age group Mn followed by As posed the greatest risks to health of humans. As
262	and Ni were the metals considered to be of greatest carcinogenic concern. As had
263	ILCR values of $10^{-6}$ $\sim$ $10^{-4}$ . These results suggested risks due to cancer was small.
264	Risks to health posed by As ranked in decreasing order of: Shijiazhuang>Jinan>
265	Baoding>Tianjin>Beijing. Risks arranged in decreasing order for life stages were:
266	adults>children. Cancer risks from Ni were less than $10^{-7}$ , which is considered <i>de</i>
267	minimis. Hazards posed by non-carcinogenic toxicity were in decreasing order: Mn
268	>Pb>Zn>Cu. Mn exhibited potential non-carcinogenic hazard (HQ>0.1) to
269	health of humans whereas Pb, Zn and Cu exhibited lesser hazard (HQ $\leq$ 0.1). HQs
270	of Mn for men, women and children in Shijiazhuang, were 1.08, 0.93 and 1.19,
271	respectively. These results suggested that Mn in $PM_{2.5}$ posed risk to the local
272	population. Manganese is a required, trace element for animals and plants, but can
273	be toxic to humans. The main route of exposure of humans to Mn is via respiration.
274	The risks posed by dietary or dermal absorption of Mn were ignored because they
275	were de minimis and much less than those posed by respiratory exposure. In this
276	study, inhalation was the dominating exposure route for local residents to all metals
277	and As. The main potential sources of metals and As in $PM_{2.5}$ were anthropogenic,
278	such as metallurgy, iron and steel industrial production and emission. After
279	accumulation via the lungs, Mn could also be distributed to other tissues, including
280	liver and kidney. Overall, health risks of five metals and As for men, women and

children were small except for Mn in Shijiazhuang. 281

282

283 Figure 7 near here

284

Risks to health of five trace metals and As for men during the APEC in 2014 were 285 less than during the other years, although not dramatically so for Beijing and Tianjin 286 than the same time of year in 2012 or 2013 (Figure 8). The lesser risk to health in 287 Shijiazhuang during the APEC in 2014 was limited. 288

The ILCR for both As and Ni were less than 10<sup>-4</sup>, which suggested risks of 289 additional cancers caused by these elements were small. Mn has a potential 290 291 non-carcinogen hazard for human health, and hazards of the other five metals were De 292 minimis. The health risks and hazards of five metals and As to men ranked as 2012>2013>2014 in Beijing and Tianjin, and 2012≈2013>2014 in Shijiazhuang. 293 Due to lesser emissions during APEC in November 2014, risks to health of humans of 294 the five metals and As were lesser than those for the same period in 2012 and 2013.

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#### Figure 8 near here 297

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299 Control measures imposed for the APEC November 2014 were effective at lessening concentrations of PM<sub>2.5</sub> and associated metals, particularly for As and Ni 300 301 where cancer was reduced by more than a factor of 10 (Fig. 9). Reductions in hazard quotients for the other metals were more modest, with the least improvement seen in 302

303 Shijiazhuang (Figure 9). After the APEC meeting and relaxation of control 304 measures, the presence in air particles of As posed a potential cancer risk and Mn 305 posed a potential non-cancer hazard.

306

307 *Figure 9 near here* 

308

#### 309 4. Conclusions

In November 2014, control measures were introduced to minimize emissions 310 311 from combustion of fossil fuels, including coal, emissions from factories and vehicle exhaust during the APEC meeting. Concentrations of PM<sub>2.5</sub> in Beijing were 20-33% 312 less than they were during the same period in November 2012 and 2013, whilst in 313 314 Tianjin and Shijiazhuang, daily, mean concentrations of PM<sub>2.5</sub> were, 16 to 49% and 5 to 58% less, respectively. During the period, during which controls were imposed, 315 concentrations of 10 metals and As present in the PM<sub>2.5</sub> from five megacities 316 including Beijing, Tianjin, Shijiazhuang, Baoding, Jinan from Jing-Jin-Ji were also 317 less. The most dramatic decreases in concentrations were observed for Fe and V. 318 Mean daily concentrations of PM<sub>2.5</sub> in the five megacities were slightly greater than 319 the Chinese National Standard limit of 75 µg m<sup>-3</sup>, but less than the same period in 320 2013 and 2012. Health hazards or risks of five trace metals and As for men, women 321 and children were small for most locations for most metals, except for Mn in 322 Shijiazhuang. Risks posed by five trace metals and As during APEC were overall less 323 than those during the same period in 2012 and 2013. The fact that concentrations of 324

325	PM <sub>2.5</sub> and metals were less during APEC following control measures with predicted
326	health benefits was encouraging and demonstrated that China could improve the
327	health outcomes for its urban residents with further efforts.

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Parameter <sup>a</sup>	Men	Women	Children			
$IR/m^3 \cdot d^{-1}$	19.02	14.17	5			
BM/kg	62.7	54.4	15			
$EF/d \cdot a^{-1}$	350	350	350			
ED/ a	30	30	6			
AT(carcinog	gen)/a 70 × 365	$70 \times 365$	$70 \times 365$			
AT(non-care	cinogen)/a $30 \times 365$	30 × 365	6 × 365			
Note: <sup>a</sup> IR refers	Note: <sup>a</sup> IR refers to respiration rate; BW refers to body weight; EF refers to exposure frequency; ED refer					
exposure day; AT	refers to average time;					
Table 2.	<b>Table 2.</b> Dose-response parameters of 5 metals and As via inhalation.					
RfD <sup>b</sup> (Non-carcinogen) SF <sup>c</sup> (Carcinogen						

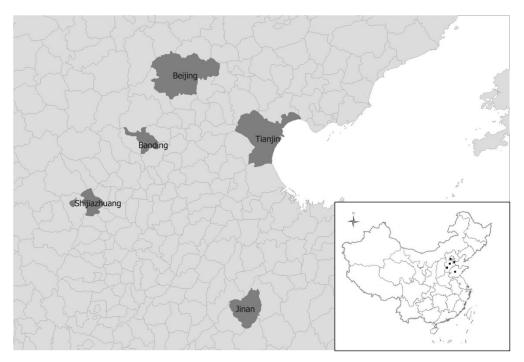
RfD <sup>b</sup> (Non-carcinogen)				SF <sup>c</sup> (Carcinogen)	
$(mg \cdot (kg \cdot d)^{-1})$				(mg·(k	$g \cdot d)^{-1}$
Pb	Zn	Cu	Mn	As	Ni
3.50×10 <sup>-3</sup>	3.00×10 <sup>-1</sup>	4.00×10 <sup>-2</sup>	1.43×10 <sup>-5</sup>	15.10	0.84

Note: <sup>b</sup> RfD refers to reference dose; <sup>c</sup> SF refers to slope factor;

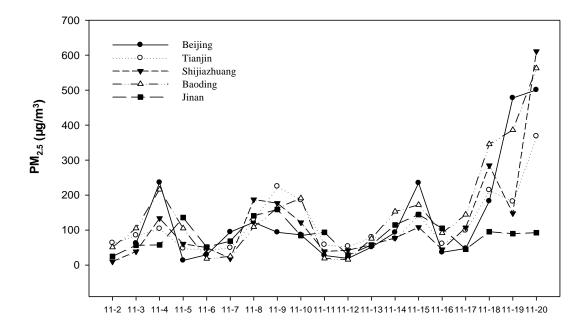
# 438 **Figure captions:**

- Figure 1. Areas within five megacities in the Beijing-Tianjin-Hebei Region, fromwhich samples were collected during the APEC in November 2014.
- 441 Figure 2 Mean daily concentrations of PM<sub>2.5</sub> in five megacities during APEC,
  442 November, 2014.
- Figure 3 Comparison of mean daily concentration of PM<sub>2.5</sub> during the non-heating
  season in autumn 2012 to 2014.
- Figure 4 Concentrations of 11 elements in  $PM_{2.5}$  in Beijing during the period 2012 to 2014 (ng m<sup>-3</sup>).
- Figure 5 Concentrations of 11 elements in  $PM_{2.5}$  in Tianjin during 2012 to 2014 (ng m<sup>-3</sup>).
- Figure 6 Concentrations of 11 elements in PM<sub>2.5</sub> in Shijiazhuang during 2012 to 2014
  (ng m<sup>-3</sup>).
- 451 Figure 7 Risks to health of humans due to exposure to five metals and As for men,452 women and children during the APEC.
- 453 Figure 8 Comparison of risks to health posed by five metals and As for men during454 the APEC with the same period in 2012 and 2013.
- **Figure 9** Comparison of risks to health of humans posed by five metals and As in and
- 456 after the APEC in Beijing.











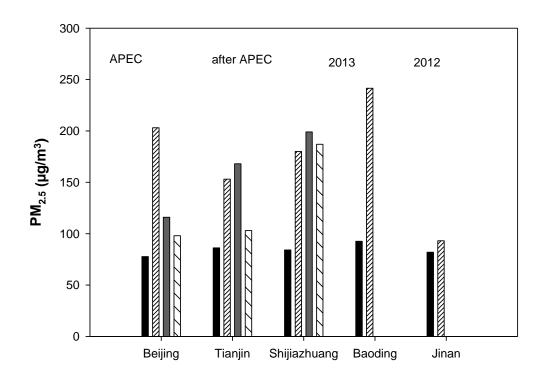


Figure 4

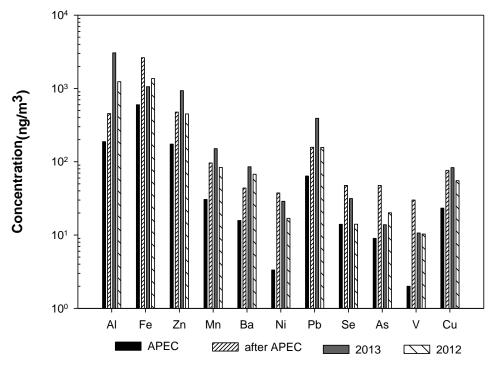




Figure 5

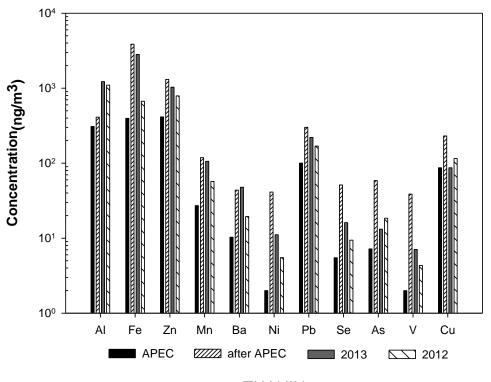




Figure 6

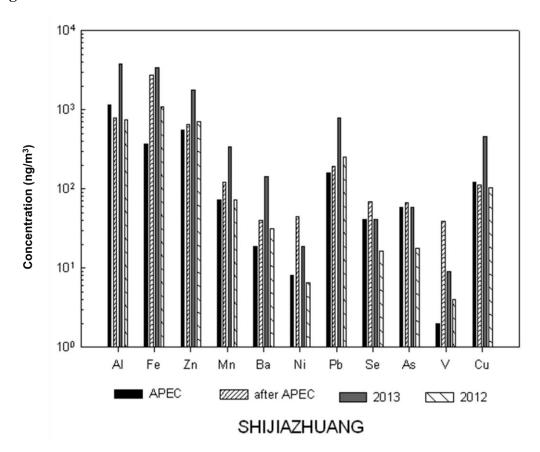
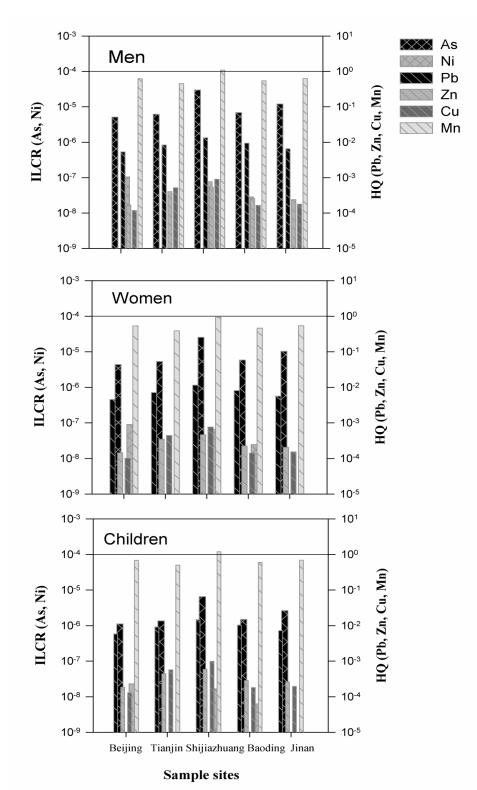


Figure 7



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# Figure 8

