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Hazard Posed by Metals and As in $PM_{2.5}$ in Air of Five Megacities in the Beijing-Tianjin-Hebei Region of China during APEC

Linlin Zhang[a], Xiaowei Jin[a,*], Andrew C Johnson[b], John P. Giesy[c,d,e]

[a] *China National Environmental Monitoring Center, Beijing 100012, China*

[b] *Centre of Ecology and Hydrology, Wallingford, Oxfordshire, UK*

[c] *Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada*

[d] *School of Biological Sciences, University of Hong Kong, Hong Kong, SAR, China*

[e] *State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, People's Republic of China*

*Corresponding author:

Xiaowei Jin

Department of Analytical Technique, China National Environmental Monitoring Center, Anwai Dayangfang No.8, Chaoyang District, Beijing 100012, China

Email: jinxiaowei07@mails.ucas.ac.cn

Abstract

Airborne fine particulate matter ($PM_{2.5}$) from five megacities including Beijing, Tianjin, Shijiazhuang, Baoding, and Jinan were collected during November 2014 and compared with similar periods in 2012 and 2013. The November 2014 period coincided with the Asia Pacific Economic Cooperation (APEC) Leaders meeting during which measures to control pollution of the air were introduced. Concentrations of eleven elements in $PM_{2.5}$ were quantified by ICP-MS after microwave-assisted digestion. Potential effects of five toxic trace metals including 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 and 2013. Mean concentrations of 6 elements ranked in decreasing order: Zn＞Pb＞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 health of humans were small, except for Mn in Shijiazhuang. Risks to health posed 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 health of humans during the APEC were overall lesser than the same period in 2012 and 2013, mostly due to lesser emissions due to the short-term control measures.

Keywords: Human Health; Risk assessment; APEC; Asia; Air Pollution

1. Introduction

Beijing is the political, economic and cultural center of China. Rapid economic development, urbanization and industrialization of the Beijing-Tianjin-Hebei region during recent decades have been linked with poor air quality. Pollution of air includes particulate matter, dust-haze, photochemical smog, and concentrations of metals potentially adverse to human health (Chan and Yao, 2008; Zhang et al., 2013; Zhao et al., 2013). Airborne fine particulate matter (PM with aerodynamic diameter <2.5 μm, $PM_{2.5}$) has been considered a particularly 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 potentially toxic concentrations of metals or metalloids such as As, found in urban 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 classified arsenic (As) and arsenicals, cadmium (Cd) and cadmium compounds, hexavalent chromium (Cr) and nickel (Ni) compounds as “carcinogenic to humans” (Group 1); inorganic lead (Pb) compounds as “probably carcinogenic to humans” (Group 2A). Several other metals and As were classified as “possibly carcinogenic to humans” (Group 2B) (IARC, 2006). Concentrations of metals can be enriched in aerosols especially in and on surfaces of particulates, such as $PM_{2.5}$, which can penetrate the human respiratory system and can be associated with cardio-pulmonary 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 elevated concentrations of metals in respired air represents a serious concern for human 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 $PM_{2.5}$ in polluted air events in China (Li et al., 2015).

The 22nd annual Asia Pacific Economic Cooperation (APEC) Leaders Meeting was convened in Beijing in November, 2014. To ensure good quality of ambient air during the meeting, many of the primary combustion sources of $PM_{2.5}$ were controlled (MEP, 2014a, b, c). Cessation of many combustion activities over this period 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 be used to calibrate changes in quality of the air related to remedial actions and serve 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 $PM_{2.5}$ 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 $PM_{2.5}$ during this period. Third, to compare concentrations with those during the same period in 2012 and 2013 when no controls were imposed.

2. Materials and Methods

2.1 Sample collection

A total of 55 samples of $PM_{2.5}$ 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.

Figure 1 near here

Samples of $PM_{2.5}$ were collected daily by use of “middle-flow”, impact particulate samplers (Wuhan Tianhong TH-150A) with ϕ90 mm quartz filter membrane. The rate of airflow during sampling was 100 L/min. Quartz filters were preheated in a muffle furnace at 600 °C for 3 h to remove volatile components before being used for sampling. Before use, filter membranes were placed into a temperature and humidity controlled chamber for 24~48 h at 15~30 °C, with relative humidity of 45%~55% until it achieved a constant weight. An electronic balance with accuracy of 0.01 mg (Mettler Toledo lnc., Switzerland) was used to weigh the membranes before and after sampling. After collection and determination of mass of particulates, samples were sealed and kept in a refrigerator at 4 °C until analysis. Two filed blanks were performed at each site.

2.2 Sample analysis

One-fourth of each filter was extracted with HNO_3-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.).

2.3 QA/QC

Acids and other chemicals used in this study were of highest-purity. Two field blanks and one laboratory blank were prepared and analyzed. Concentrations of 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 of sensitivity of the ICP-MS. Concentrations of metals and As were calculated by use of a five-point, external calibration curve with linearity as determined by coefficients of determination (R^2) of greater than 0.999. A standard was run after every 10 samples to monitor stability of the ICP-MS. The relative standard deviations (RSDs) of concentrations of elements were typically less than 5%. Precision and bias were less than 10%.

2.4 Health risk assessment

The model used in this study to assess risk to humans was that recommended by 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 data collected during the APEC 2014 meeting as well as the same period in 2012 and 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 to be the human respiratory system into lungs. The risks induced by digestive tract, dermal absorption and others were ignored since their calculated risks would be less than the actual exposure. Assessments of risks to health of the five metals and As were calculated separately for men, women or children. Suitable exposure 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, while Pb, Zn, Cu and Mn were non-carcinogens (Dong et al., 2014).

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.

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

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

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

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

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).

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 $PM_{2.5}$ during APEC (MEP, 2014d).

3. Results and discussion

3.1 Averaged daily concentrations of $PM_{2.5}$

Mean, daily concentrations of $PM_{2.5}$ during the APEC varied among the five megacities (Figure 2) and on each day of the APEC meeting. Two maxima were observed simultaneously in five cities during haze episodes that occurred on November 4 and 9 2014. The greatest concentration of 236 μg $PM_{2.5}$ m^{-3} was observed in Beijing on November 4, while a concentration of 225 μg $PM_{2.5}$ m^{-3} was observed in Tianjin on November 9 2014. After the haze episodes, mean, daily concentrations of $PM_{2.5}$ in the five cities was less than 45 μg m^{-3} respectively between November 6 ~ 7 and 11 ~ 12 which were less than the National air quality standard (MEP, 2012).

Figure 2 near here

In November 2014, when measures were introduced to minimize emissions during the APEC, concentrations of $PM_{2.5}$ 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 $PM_{2.5}$ were, 16.4 and 48.7% and 5.0 and 57.7% less, respectively. Reductions in $PM_{2.5}$ 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^{-3} (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＞

Jinan＞Beijing.

Figure 3 near here

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

3.2 Metal concentrations in $PM_{2.5}$

It was expected that with lesser concentrations of PM2.5 during the APEC meeting concentrations of metals would also be less. This lesser concentration in airborne metal pollution was clearly seen in Beijing (Fig. 4) and Tianjin (Fig. 5) but to a limited extent in Shijiazhuang (Fig. 6). Of the metals associated with particulates, the greatest concentrations were for Al, Fe, Zn and Pb which ranged from 10^2 to 10^3 ng m^{-3} with lesser concentrations of Cu, Ba, Mn, As and Se, concentrations of which ranged from 10 to 10^2 ng m^{-3}. Concentrations of Ni and V, which ranged from 1 to 10 ng m^{-3} were the least observed. Overall the cities were ranked in decreasing order of pollution of air by metals: Baoding＞Tianjin＞Shijiazhuang＞Jinan＞Beijing, and in order of years of decreasing pollution: 2013＞2012＞2014.

Figure 4 near here

Figure 5 near here

Figure 6 near here

Mean concentrations of five metals and As ranked in decreasing order were: Zn＞Pb＞Cu≈Mn＞As＞Ni. The concentration of Zn was greatest with a range of 0.174~0.554 μg m^{-3} and maximum of 3.76 μg m^{-3} in $PM_{2.5}$ from Shijiazhuang. The concentration of Ni was least with a range of 0.0002~0.008 μg m^{-3}, but was less than the LOD in Jinan and Tianjin. Concentrations of metals and As, ranked in decreasing order was: Shijiazhuang＞Baoding＞Tianjin＞Jinan＞Beijing. However, differences among cities were small.

3.3 Hazard Posed by Five Metals and As in $PM_{2.5}$

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

Figure 7 near here

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

The ILCR for both As and Ni were less than 10^{-4}, which suggested risks of additional cancers caused by these elements were small. Mn has a potential non-carcinogen hazard for human health, and hazards of the other five metals were *De 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. , Due to lesser emissions during APEC in November 2014, risks to health of humans of the five metals and As were lesser than those for the same period in 2012 and 2013.

Figure 8 near here

Control measures imposed for the APEC November 2014 were effective at lessening concentrations of $PM_{2.5}$ and associated metals, particularly for As and Ni 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

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

Figure 9 near here

4. Conclusions

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

$PM_{2.5}$ and metals were less during APEC following control measures with predicted health benefits was encouraging and demonstrated that China could improve the health outcomes for its urban residents with further efforts.

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Table 1. Human exposure parameters via respiratory system intake.

Parameter [a]	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(carcinogen)/a	70 × 365	70 × 365	70 × 365
AT(non-carcinogen)/a	30 × 365	30 × 365	6 × 365

Note: [a] IR refers to respiration rate; BW refers to body weight; EF refers to exposure frequency; ED refers to exposure day; AT refers to average time;

Table 2. Dose-response parameters of 5 metals and As via inhalation.

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

Note: [b] RfD refers to reference dose; [c] SF refers to slope factor;

Figure captions:

Figure 1. Areas within five megacities in the Beijing-Tianjin-Hebei Region, from which samples were collected during the APEC in November 2014.

Figure 2 Mean daily concentrations of $PM_{2.5}$ in five megacities during APEC, November, 2014.

Figure 3 Comparison of mean daily concentration of $PM_{2.5}$ 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^{-3}).

Figure 5 Concentrations of 11 elements in $PM_{2.5}$ in Tianjin during 2012 to 2014 (ng m^{-3}).

Figure 6 Concentrations of 11 elements in $PM_{2.5}$ in Shijiazhuang during 2012 to 2014 (ng m^{-3}).

Figure 7 Risks to health of humans due to exposure to five metals and As for men, women and children during the APEC.

Figure 8 Comparison of risks to health posed by five metals and As for men during 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 after the APEC in Beijing.

Figure 1

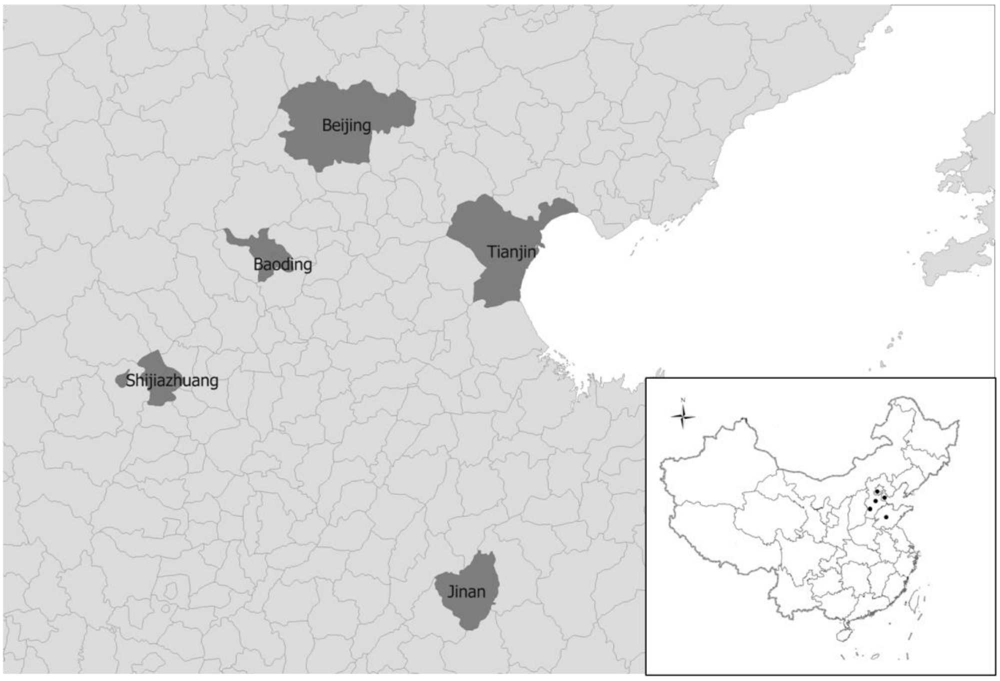
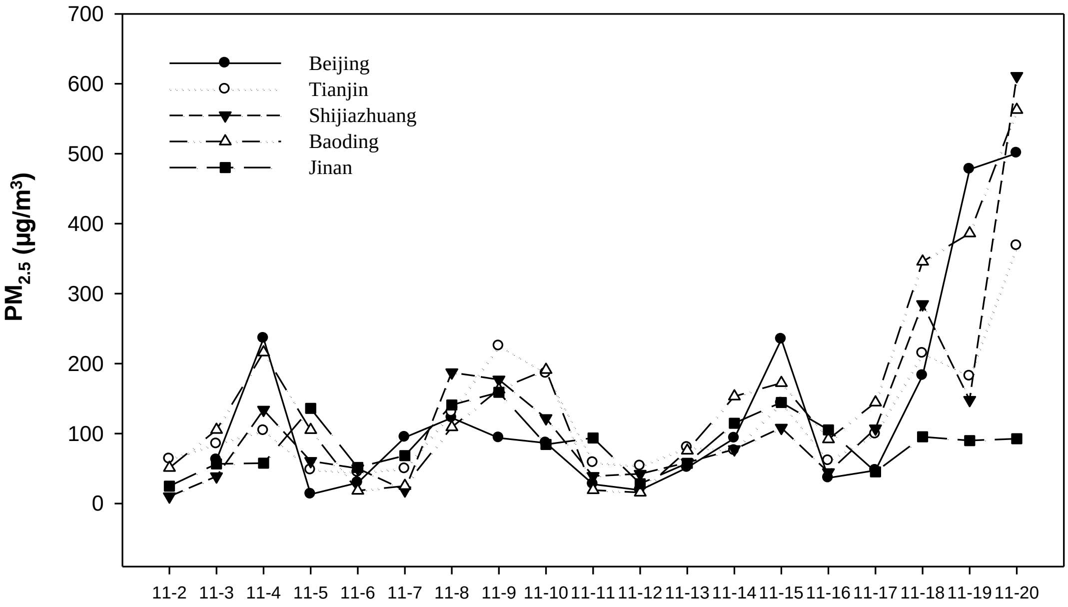


Figure 2



700
600
500
400
300
200
100
0
$PM_{2.5}$ (μg/m³)
Beijing
Tianjin
Shijiazhuang
Baoding
Jinan
11-2
11-3
11-4
11-5
11-6
11-7
11-8
11-9
11-10
11-11
11-12
11-13
11-14
11-15
11-16
11-17
11-18
11-19
11-20

Figure 3

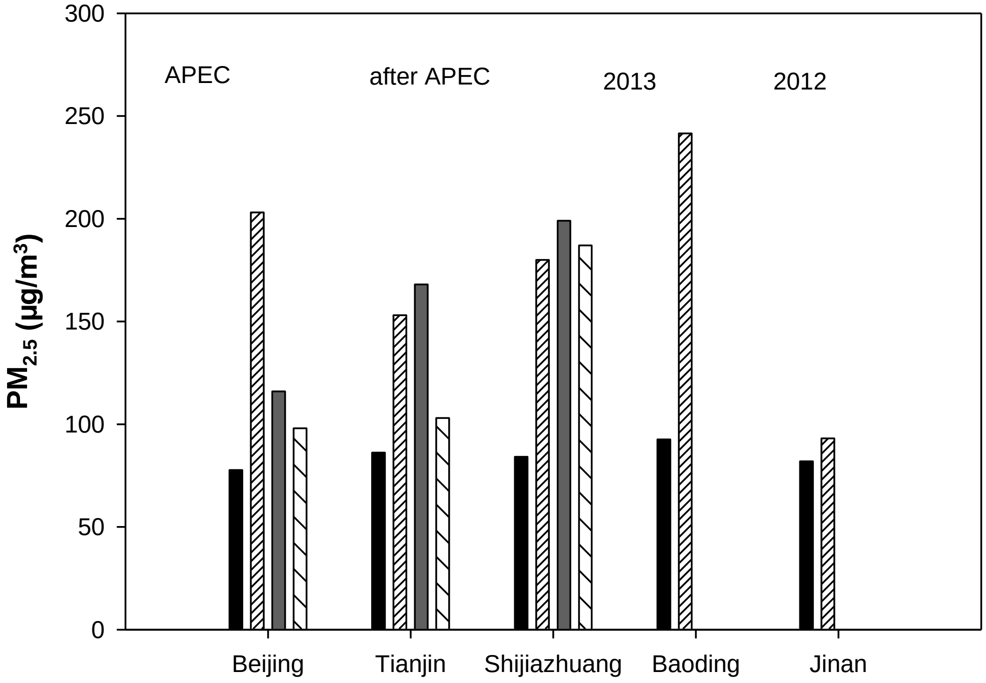
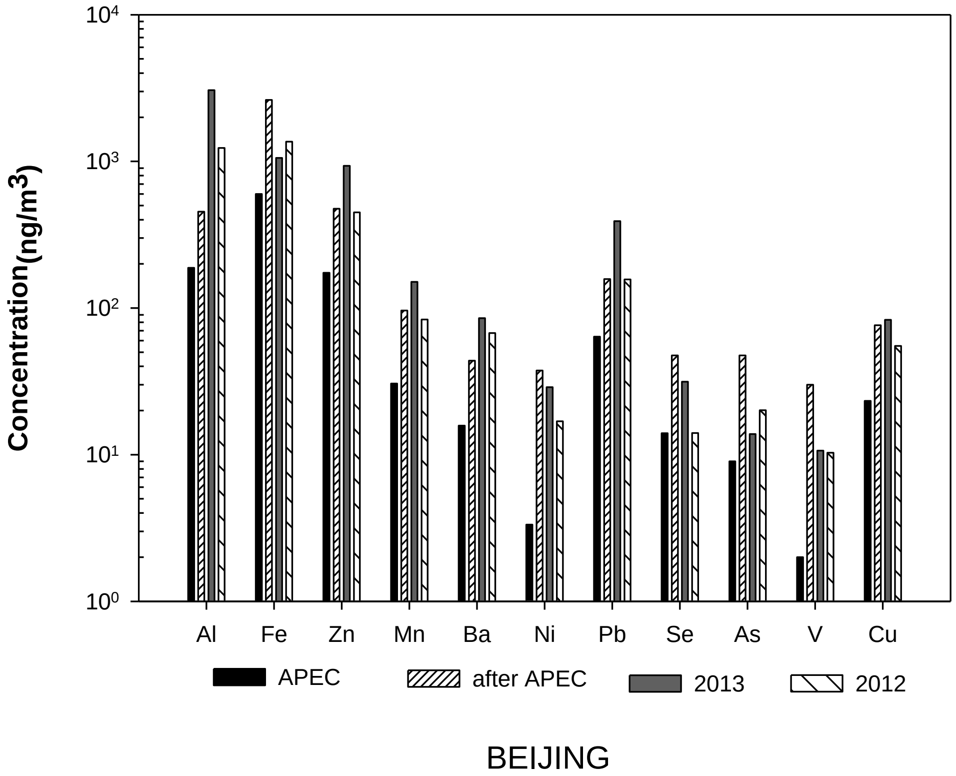
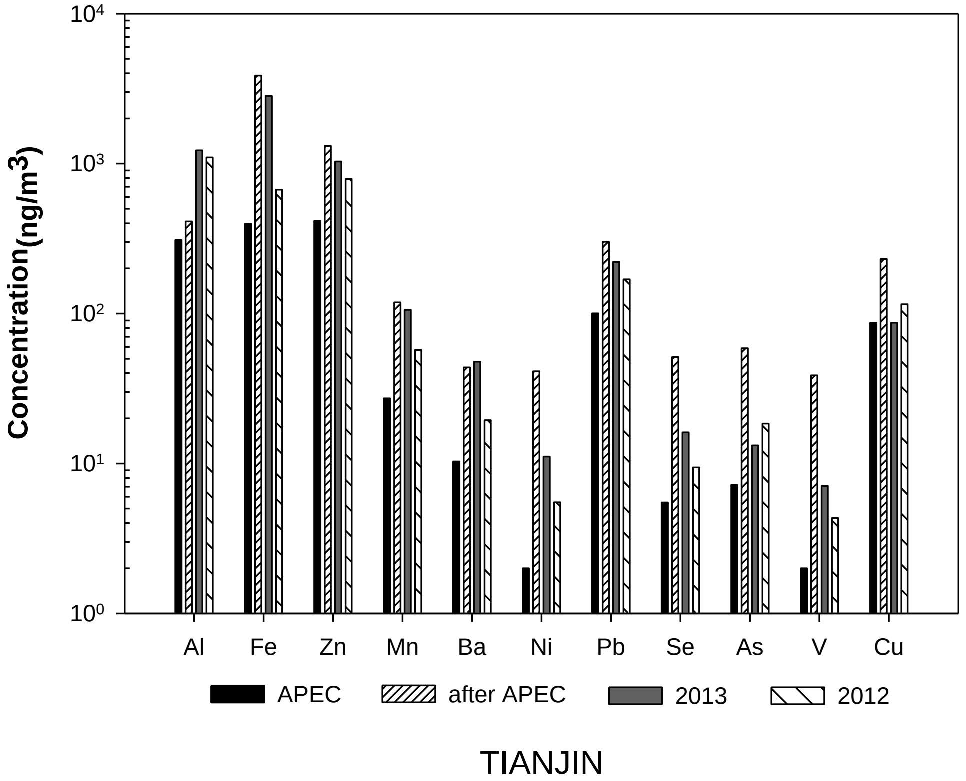

300
250
200
150
100
50
0
PM2.5 (μg/m3)
APEC
after APEC
2013
2012
Beijing
Tianjin
Shijiazhuang
Baoding
Jinan

Figure 4



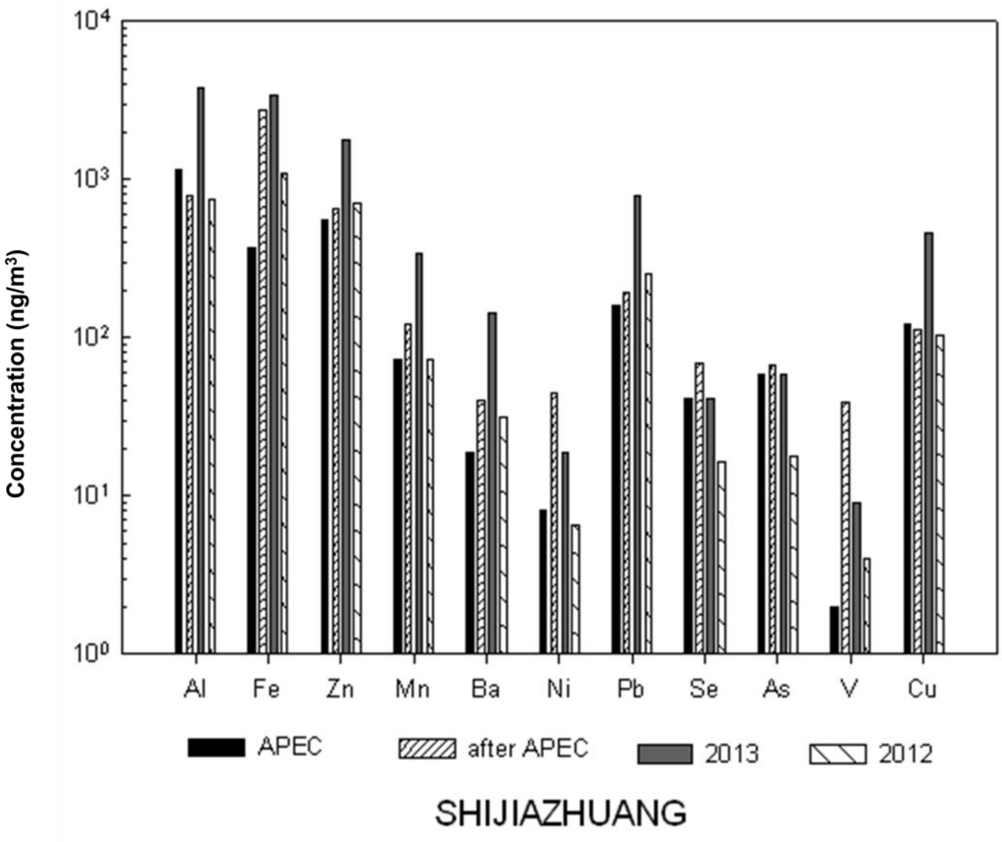
10⁴
10³
10²
10¹
10⁰
Concentration(ng/m3)
Al
Fe
Zn
Mn
Ba
Ni
Pb
Se
As
V
Cu
APEC
after APEC
2013
2012
BEIJING

Figure 5



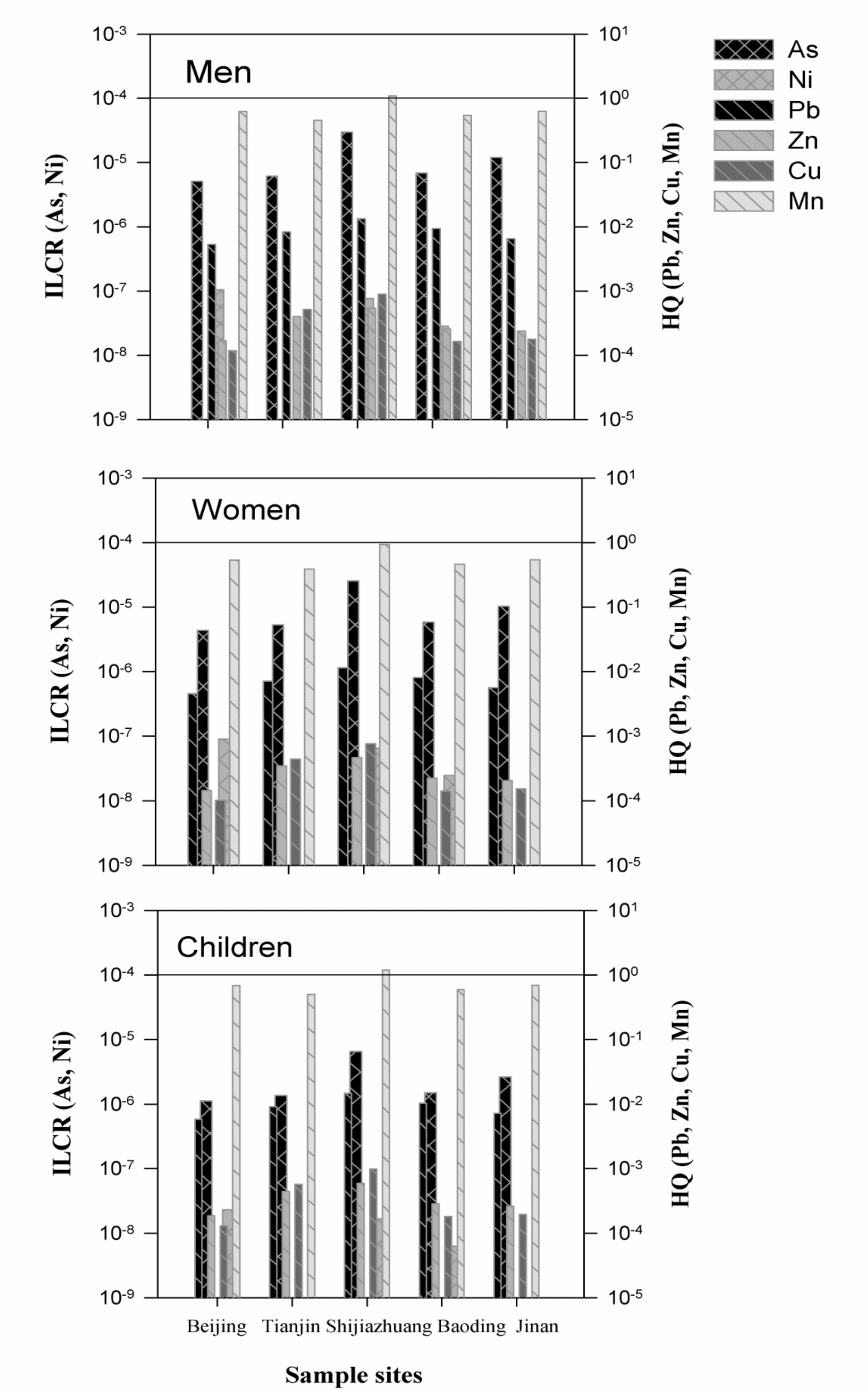
10⁴
10³
10²
10¹
10⁰
Concentration(ng/m3)
Al
Fe
Zn
Mn
Ba
Ni
Pb
Se
As
V
Cu
APEC
after APEC
2013
2012
TIANJIN

Figure 6



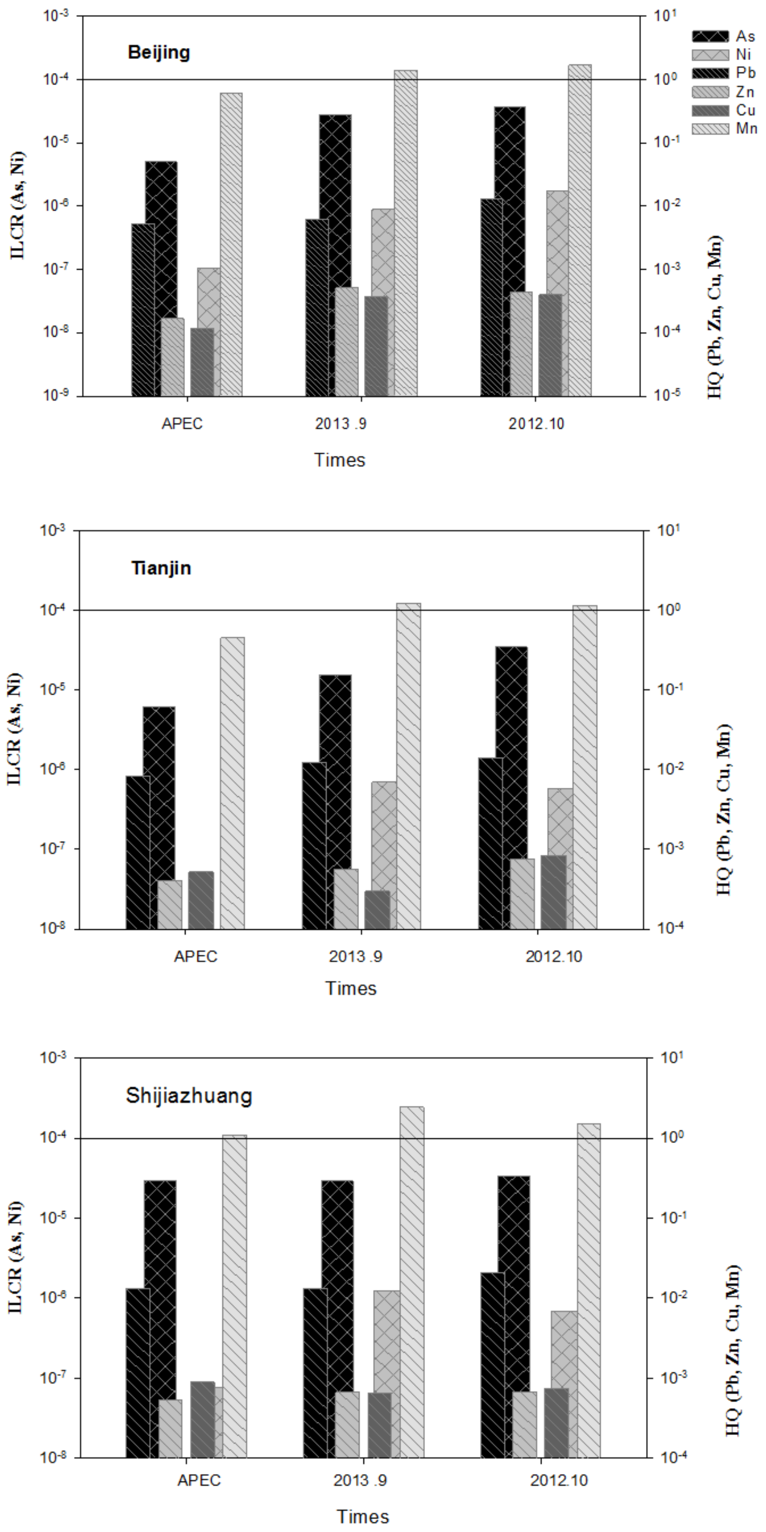
Concentration (ng/m^3)
10^4
10^3
10^2
10^1
10^0
Al
Fe
Zn
Mn
Ba
Ni
Pb
Se
As
V
Cu
APEC
after APEC
2013
2012
SHIJIAZHUANG

Figure 7



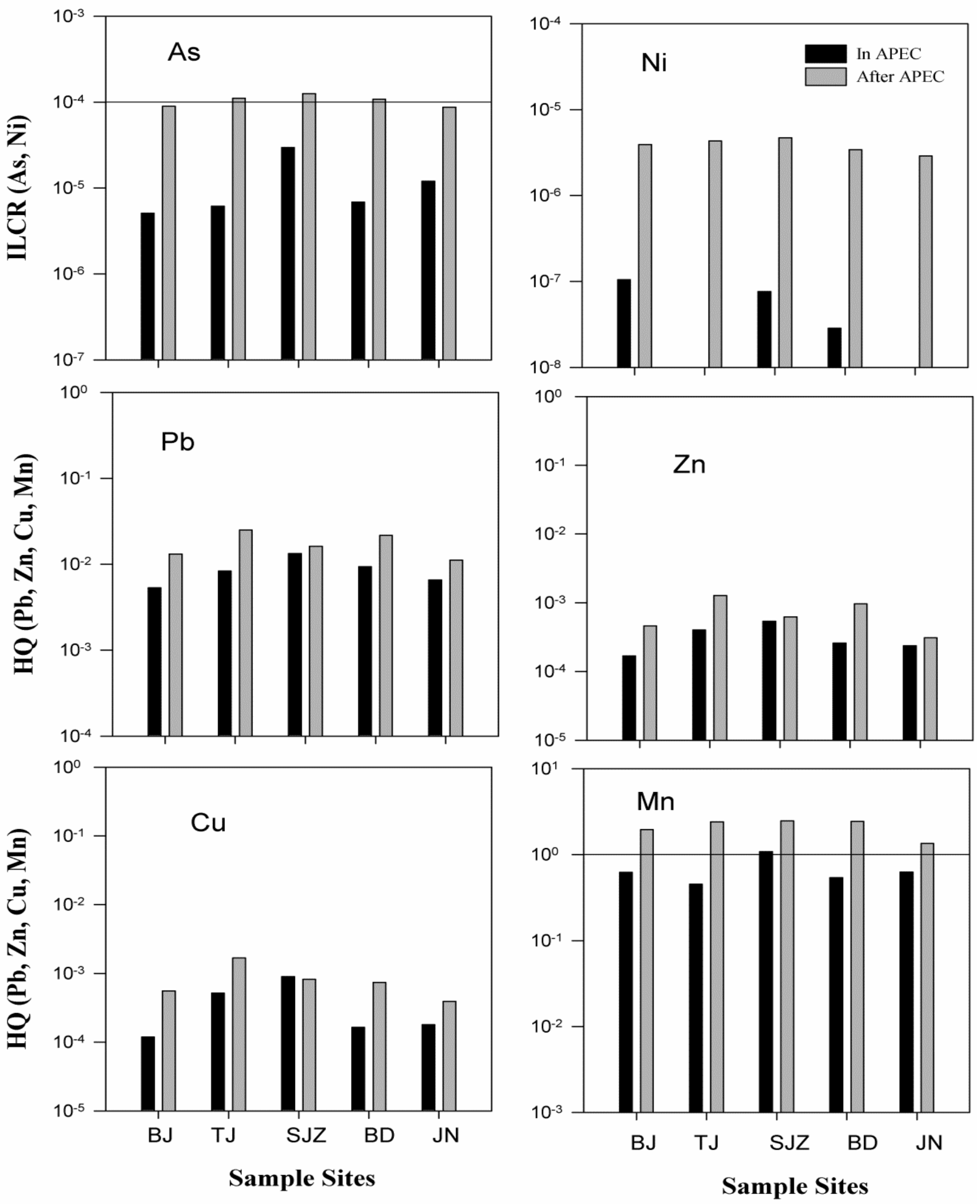
Men
Women
Children
ILCR (As, Ni)
HQ (Pb, Zn, Cu, Mn)
As
Ni
Pb
Zn
Cu
Mn
10-3
10-4
10-5
10-6
10-7
10-8
10-9
10¹
10⁰
10-1
10-2
10-3
10-4
10-5
Beijing
Tianjin
Shijiazhuang
Baoding
Jinan
Sample sites

Figure 8



Beijing
Tianjin
Shijiazhuang
As
Ni
Pb
Zn
Cu
Mn
ILCR (As, Ni)
HQ (Pb, Zn, Cu, Mn)
APEC
2013 .9
2012.10
Times

Figure 9



As
Ni
In APEC
After APEC
Pb
Zn
Cu
Mn
ILCR (As, Ni)
HQ (Pb, Zn, Cu, Mn)
HQ (Pb, Zn, Cu, Mn)
BJ
TJ
SJZ
BD
JN
Sample Sites
Sample Sites