

## Progress and prospects of atmospheric environmental sciences in China

Fahe Chai, Abdelwahid Mellouki, Yujing Mu, Jianmin Chen, Huiwang Gao, Hong Li



Sponsored by

Research Center for Eco-Environmental Sciences  
Chinese Academy of Sciences

## CONTENTS

### **Special Issue: Progress and prospects of atmospheric environmental sciences in China**

#### Preface

|   |     |
|---|-----|
| Fahe Chai, Abdelwahid Mellouki, Yujing Mu, Jianmin Chen, Huiwang Gao, Hong Li .....   | 1   |
| Haze insights and mitigation in China: An overview  |     |
| Xuliang Zhuang, Yuesi Wang, Hong He, Jianguo Liu, Xinming Wang, Tingyu Zhu, Maofa Ge, Ju Zhou, Guiqian Tang, Jinzhu Ma .....                                | 2   |
| Effectiveness of national air pollution control policies on the air quality in metropolitan areas of China  |     |
| Shuxiao Wang, Jia Xing, Bin Zhao, Carey Jang, Jiming Hao .....  | 13  |
| Fast increasing of surface ozone concentrations in Pearl River Delta characterized by a regional air quality monitoring network during 2006–2011            |     |
| Jinfeng Li, Keding Lu, Wei Lv, Jun Li, Liuju Zhong, Yubo Ou, Duohong Chen, Xin Huang, Yuanhang Zhang .....  | 23  |
| Hygroscopicity and optical properties of alkylaminium sulfates  |     |
| Dawei Hu, Chunlin Li, Hui Chen, Jianmin Chen, Xingnan Ye, Ling Li, Xin Yang, Xinming Wang, Abdelwahid Mellouki, Zhongyang Hu .....                          | 37  |
| Photochemical properties and source of pollutants during continuous pollution episodes in Beijing, October, 2011  |     |
| Jian Gao, Yuechong Zhang, Meng Zhang, Jingqiao Zhang, Shulan Wang, Jun Tao, Han Wang, Datong Luo, Fahe Chai, Chun Ren .....                                 | 44  |
| Dry deposition of PM <sub>10</sub> over the Yellow Sea during Asian dust events from 2001 to 2007   |     |
| Han Yan, Xiaohuan Liu, Jianhua Qi, Huiwang Gao .....  | 54  |
| Seasonal and diurnal variations of atmospheric peroxyacetyl nitrate, peroxypropionyl nitrate, and carbon tetrachloride in Beijing                           |     |
| Gen Zhang, Yujing Mu, Junfeng Liu, Chenglong Zhang, Yuanyuan Zhang, Yujie Zhang .....   | 65  |
| Spatial and temporal variation of particulate matter and gaseous pollutants in 26 cities in China   |     |
| Fahe Chai, Jian Gao, Zhenxing Chen, Shulan Wang, Yuechong Zhang, Jingqiao Zhang, Hefeng Zhang, Yaru Yun, Chun Ren .....                                     | 75  |
| Wintertime peroxyacetyl nitrate (PAN) in the megacity Beijing: Role of photochemical and meteorological processes   |     |
| Hualong Zhang, Xiaobin Xu, Weili Lin, Ying Wang .....   | 83  |
| Modeling study on seasonal variation in aerosol extinction properties over China  |     |
| Yi Gao, Meigen Zhang .....  | 97  |
| Compositions and sources of organic acids in fine particles (PM <sub>2.5</sub> ) over the Pearl River Delta region, south China                             |     |
| Xiuying Zhao, Ximeng Wang, Xiang Ding, Quanfu He, Zhou Zhang, Tengyu Liu, Xiaoxin Fu, Bo Gao, Yunpeng Wang, Yanli Zhang, Xuejiao Deng, Dui Wu .....         | 110 |
| Carbonyl emissions from heavy-duty diesel vehicle exhaust in China and the contribution to ozone formation potential  |     |
| Dong Dong, Min Shao, Yue Li, Sihua Lu, Yanjun Wang, Zhe Ji, Dagang Tang .....   | 122 |
| Hygroscopicity of particles generated from photooxidation of $\alpha$ -pinene under different oxidation conditions in the presence of sulfate seed aerosols |     |
| Biwu Chu, Kun Wang, Hideto Takekawa, Junhua Li, Wei Zhou, Jingkun Jiang, Qinxing Ma, Hong He, Jiming Hao .....  | 129 |
| Gas separation using porous cement membrane   |     |
| Wei Qi Zhang, Maria Gaggl, Gregor J. G. Gluth, Frank Behrendt .....   | 140 |
| Characteristics of atmospheric particles and heavy metals in winter in Chang-Zhu-Tan city clusters, China   |     |
| Kai Zhang, Fahe Chai, Zilong Zheng, Qing Yang, Juansheng Li, Jing Wang, Yujie Zhang .....   | 147 |
| Mechanism and rate constants for complete series reactions of 19 fluorophenols with atomic H  |     |
| Rui Gao, Xiaoyan Sun, Wanni Yu, Qingzhu Zhang, Wenxing Wang .....   | 154 |
| Emission factors of polycyclic aromatic hydrocarbons from domestic coal combustion in China   |     |
| Geng Chunmei, Chen Jianhua, Yang Xiaoyang, Ren Lihong, Yin Baohui, Liu Xiaoyu, Bai Zipeng .....   | 160 |
| Oxidative capacities of size-segregated haze particles in a residential area of Beijing   |     |
| Zhenquan Sun, Longyi Shao, Yujing Mu, Ying Hu .....   | 167 |
| Impact of emission control on regional air quality: An observational study of air pollutants before, during and after the Beijing Olympic Games             |     |
| Shulan Wang, Jian Gao, Yuechong Zhang, Jingqiao Zhang, Fahe Cha, Tao Wang, Chun Ren, Wenxing Wang .....   | 175 |
| Mechanism and kinetics study on the ozonolysis reaction of 2,3,7,8-TCDD in the atmosphere   |     |
| Jing Bai, Xiaomin Sun, Chenxi Zhang, Chen Gong, Jingtian Hu, Jianghua Zhang .....   | 181 |
| Size distribution, characteristics and sources of heavy metals in haze episod in Beijing  |     |
| Jingchun Duan, Jihua Tan, Jiming Hao, Fahe Chai .....   | 189 |
| Estimation of PM <sub>10</sub> in the traffic-related atmosphere for three road types in Beijing and Guangzhou, China                                       |     |
| Yu Wang, Jiong Li, Xiang Cheng, Xiaoxiu Lun, Dezhong Sun, Xingzu Wang .....   | 197 |
| Trace metals in atmospheric fine particles in one industrial urban city: Spatial variations, sources, and health implications                               |     |
| Shengzhen Zhou, Qi Yuan, Weijun Li, Yaling Lu, Yangmei Zhang, Wenxing Wang .....  | 205 |
| Pollution characteristics and health risk assessment of benzene homologues in ambient air in the northeastern urban area of Beijing, China                  |     |
| Lei Li, Hong Li, Xinmin Zhang, Li Wang, Linghong Xu, Xuezhang Wang, Yanling Yu, Yujie Zhang, Guan Cao .....   | 214 |
| CH <sub>4</sub> emission and conversion from A <sup>2</sup> O and SBR processes in full-scale wastewater treatment plants                                   |     |
| Yan Liu, Xiang Cheng, Xiaoxiu Lun, Dezhong Sun .....  | 224 |



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

Journal of Environmental Sciences

[www.jesc.ac.cn](http://www.jesc.ac.cn)



## Emission factors of polycyclic aromatic hydrocarbons from domestic coal combustion in China

Chunmei Geng\*, Jianhua Chen, Xiaoyang Yang, Lihong Ren, Baohui Yin, Xiaoyu Liu, Zhipeng Bai

State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

### ARTICLE INFO

#### Article history:

Special issue: Progress and prospects of atmospheric environmental science in China

#### Keywords:

domestic coal combustion  
emission factor  
polycyclic aromatic hydrocarbons  
potential toxicity risk  
diagnostic ratio

DOI: 10.1016/S1001-0742(13)60393-9

### ABSTRACT

Domestic coal stove is widely used in China, especially for countryside during heating period of winter, and polycyclic aromatic hydrocarbons (PAHs) are important in flue gas of the stove. By using dilution tunnel system, samples of both gaseous and particulate phases from domestic coal combustion were collected and 18 PAH species were analyzed by GC-MS. The average emission factors of total 18 PAH species was 171.73 mg/kg, ranging from 140.75 to 229.11 mg/kg for bituminous coals, while was 93.98 mg/kg, ranging from 58.48 to 129.47 mg/kg for anthracite coals. PAHs in gaseous phases occupied 95% of the total of PAHs emission of coal combustion. In particulate phase, 3-ring and 4-ring PAHs were the main components, accounting for 80% of the total particulate PAHs. The total toxicity potency evaluated by benzo[a]pyrene-equivalent carcinogenic power, sum of 7 carcinogenic PAH components and 2,3,7,8-tetrachlorodibenzodioxin had a similar tendency. And as a result, the toxic potential of bituminous coal was higher than that of anthracite coal. Efficient emission control should be conducted to reduce PAH emissions in order to protect ecosystem and human health.

## Introduction

In 2010,  $3.12 \times 10^9$  tons of coal were consumed in China and it was 68% of the primary energy consumption. In the composition of total consumption of energy, household consumption was the second-biggest sector ( $9.16 \times 10^7$  tons), just below industry ( $2.96 \times 10^9$  tons) (China Statistical Yearbook, 2012). Domestic coal-stove combustion is one popular direct combustion manner, especially for heating and cooking in suburban and rural area of northern China in winter (Chen et al., 2004a, 2004b, 2005; Liu et al., 2009). A significant amount of these combustion takes place indoors without efficient emission control and results in serious indoor and outdoor air pollution (Chen et al., 2006; Zhi et al., 2008). Polycyclic aromatic hydrocarbons (PAHs) are a kind of important compounds mainly emitted from incomplete combustion of fossil fuels, which are toxic and carcinogenic to human health (Douben, 2003; Zhang

et al., 2008). In order to accurately assess the contribution of domestic coal combustion to atmospheric pollution and the human health risk, detailed characteristics of PAHs from domestic coal combustion are needed.

Some studies have reported the emission factors (EFs) for some domestic coal under the particular combustion conditions and high uncertainty for domestic coal combustion still exists (Chen et al., 2004a, 2004b, 2005; Xu et al., 2006; Tao et al., 2006; Shen et al., 2010). For example, EFs of total 15 or 17 PAH species ranged from 6.25 to 1434.8 mg/kg (Shen et al., 2010; Liu et al., 2009). Because organic compounds can present in both gaseous and particulate phases and the partitioning between the gaseous and particulate phase is influenced by several factors, such as flue gas resident time, dilution ratio, sampling temperature, the gas/particle concentration, organics' vapor pressure and so on (Baker and Eisenreich, 1990; Tuominen et al., 1988), dilution sampling system is often used to obtain representative samples (Chen et al., 2004a, 2004b, 2005; Geng et al., 2012; Liu et al.,

\* Corresponding author. E-mail: [gengcm@craes.org.cn](mailto:gengcm@craes.org.cn)

2009; Wang et al., 2010). Thereby EFs of PAH usually are dependent on coal category, coal origin, stove type, combustion conditions, dilution technologies and so on.

Coal resource is rich in China and widely distributed. But only a few studies about the emission characteristics of PAHs from domestic coal combustion were reported (Shen et al., 2010; Liu et al., 2009; Chen et al., 2004a, 2005; Xu et al., 2006). Therefore, five kinds of widely used raw coal were selected and burned in a domestic coal-stove to study the emission characteristics of PAHs, in which three kinds of raw coal haven't been studied before (Bituminous coals from Yinchuan and Dongsheng, anthracitic coal from Zhijin). PAHs in both gaseous and particulate phases emitted from domestic coal combustion were measured for the investigation of emission characteristics, including EFs, gas-particulate distribution and the potential toxicity risk.

## 1 Materials and methods

### 1.1 Fuel and stove

Five raw coals were selected for the combustion experiment. Bituminous coals were from Yinchuan (YC, Ningxia Province), Datong (DT, Shanxi Province) and Dongsheng (DS, Inner Mongolia), anthracite coals were from Zhijin (ZJ, Guizhou Province) and Jingxi (JX, Beijing). These coals were prepared into 5 to 8 cm diameter pieces before being used. The characteristics of the coals are shown in **Table 1**.

The coal-stove used for the experiment, was purchased from the local market. This type of coal stove is widely used for domestic cooking and heating in China. It has a metallic outer cover and thermal-insulated ceramic liner. The cylindrical inner volume is 0.01 m<sup>3</sup>.

### 1.2 Sampling system

The dilution system has been described in detail elsewhere (Geng et al., 2012; Wang et al., 2010, 2013). Coal com-

bustion flue gas from the stove entered the dilution tunnel through a small stack at the top of the stove. The dilution tunnel consisted of two main parts (made of stainless steel including an orthogonal pipe and a horizontal cylindrical tunnel) and a suction fan. The orthogonal pipe of length 1 m and radius 20 cm was connected to the stove for flue gas introduction and first-step dilution with filtered air. At the end of the orthogonal pipe, a horizontal cylindrical tunnel of length 4 m and radius 40 cm was connected for second-step dilution. At the end of the tunnel, there were several orifices for suction fans and sampling. The flow rate of the suction fan was controlled by Venturi tube and fixed at 5800 L/min. The residence time of flue gas in the dilution tunnel was 5.5 sec. After second-step dilution, the temperature of diluted flue gas was 30°C. The particulate PAHs were collected on quartz fiber filters by a middle-volume particle sampler (Dickel-80, Beijing Geological Instrument-Dickel Cooperation limited, China). The gaseous PAHs were collected on a XAD-4 resin packed in a column with poly urethane foam (PUF) in the two end, which was directly connected under the above filter.

### 1.3 Sampling procedure

Raw coal samples were ignited in the stove using pre-weighed charcoal (0.5 kg). To avoid the interference of charcoal combustion, the raw coal sample (1.0 kg for each experiment) was put into the stove until smoking from charcoal combustion stopped. It has been proved that both gaseous and particulate emissions after the smoking period of charcoal combustion were very small and could be neglected (Geng et al., 2012). Sampling started when the raw coal bricks were put into the stove and ended until the combustion finished. This process lasted for one hour. The produced ash did not contain visible unburned fuel residues. The weight of the coals was recorded before and after combustion to obtain the actual weight of coal burned.

Considering the uncertainty of the domestic coal combustion, the sampling of gaseous and particulate PAHs was repeated three times for each coal. Three samples of each

**Table 1** Analytical characteristics of the studied coals

|                                       |                             | Yinchuan | Dongsheng | Datong | Zhijin | Jingxi |
|---------------------------------------|-----------------------------|----------|-----------|--------|--------|--------|
| Proximate analysis<br>(air dry basis) | Moisture (%)                | 1.30     | 7.46      | 6.98   | 0.94   | 3.02   |
|                                       | Volatile matter (%)         | 19.74    | 30.82     | 32.07  | 5.76   | 4.44   |
|                                       | Ash (%)                     | 23.28    | 6.68      | 9.50   | 9.08   | 26.34  |
|                                       | Fixed carbon (%)            | 55.68    | 55.04     | 51.45  | 84.22  | 66.20  |
|                                       | Lower heating value (MJ/kg) | 19.51    | 27.51     | 26.19  | 31.23  | 22.73  |
| Elemental analysis<br>(air dry basis) | Carbon (%)                  | 62.68    | 68.72     | 64.60  | 81.86  | 68.26  |
|                                       | Hydrogen (%)                | 2.16     | 3.76      | 3.56   | 2.76   | 0.79   |
|                                       | Nitrogen (%)                | 0.62     | 0.90      | 0.84   | 1.04   | 0.26   |
|                                       | Oxygen (%)                  | 9.60     | 12.28     | 14.31  | 2.08   | 1.08   |
|                                       | Sulfur (%)                  | 0.36     | 0.20      | 0.21   | 2.24   | 0.25   |

kind of coal were combined for PAH analysis.

#### 1.4 Analytical method

PUF and XAD-4 resin were purified respectively by dichloromethane for 24 hr. Quartz fiber filters were baked at 650°C for 2 hr, and stored in a desiccator.

The pretreatment and analysis were conducted by China University of Petroleum (Beijing) (Yu et al., 2008). The filter samples were extracted ultrasonically three times with 150 mL of dichloromethane, and each extraction lasted 30 min. PUF and XAD-4 resin samples were extracted for 48 hr with dichromethane in a Soxhlet apparatus, respectively. Surrogate deuterated PAHs (chrysene-*d*12, acenaphthene-*d*10, naphthalene-*d*8, phenanthrene-*d*10, pyrene-*d*12, Supelco, USA) were added prior to the extraction. The extracts were concentrated on a rotary evaporator and fractionated using silica-alumina column chromatography. The PAH fractions were concentrated using rotary evaporation followed by a gentle stream of nitrogen, and internal standard (hexa-methylbenzene, Supelco, USA) was added for quantification of individual PAHs by GC-MS.

Eighteen kinds of PAHs were analyzed in this study, including 16 US EPA priority PAHs, Benzo[*e*]pyrene and coronene. The basic information is shown in **Table 2**. BaPeq is the index of benzo[*a*]pyrene-equivalent carcinogenic power (Cecinato, 1997). TCDD-IEFs is the index of 2,3,7,8-tetrachlorodibenzo-dioxin induction equivalency factors (Bosveld et al., 2002).

**Table 2** Abbreviation of studied PAHs and its toxic factors

| Name                                   | Ring | BaPeq | TCDD-IEFs  |
|--|------|-------|------------|
| Naphthalene (NAP)                      | 2    | –     | –          |
| Acenaphthylene (ACY)                   | 3    | –     | –          |
| Acenaphthene (ACE)                     | 3    | –     | –          |
| Fluorene (FLO)                         | 3    | –     | –          |
| Phenanthrene (PHE)                     | 3    | –     | –          |
| Anthracene (ANT)                       | 3    | –     | –          |
| Fluoranthene (FLA)                     | 4    | –     | 0.00000001 |
| Pyrene (PYR)                           | 4    | –     | –          |
| Benz[ <i>a</i> ]anthracene (BaA)       | 4    | 0.06  | 0.00001    |
| Chrysene (CHR)                         | 4    | –     | 0.0001     |
| Benz[ <i>b</i> ]fluoranthene (BbF)     | 5    | 0.07  | –          |
| Benz[ <i>k</i> ]fluoranthene (BkF)     | 5    | 0.07  | –          |
| Benzo[ <i>e</i> ]pyrene (BeP)          | 5    | –     | –          |
| Benzo[ <i>a</i> ]pyrene (BaP)          | 5    | 1     | 0.0001     |
| Indeno[1,2,3- <i>cd</i> ]pyrene (IcdP) | 6    | 0.08  | –          |
| Dibenz[ <i>a,h</i> ]anthracene (DahA)  | 5    | 0.6   | 0.0001     |
| Benzo[ <i>g,h,i</i> ]perylene (BghiP)  | 6    | –     | 0.00000001 |
| Coronene (COR)                         | 7    | –     | –          |

–: no data.

BaPeq: index of benzo[*a*]pyrene-equivalent carcinogenic power;

TCDD-IEFs: index of 2,3,7,8-tetrachlorodibenzo-dioxin induction equivalently factor.

## 2 Results and discussion

### 2.1 Emission factors

EFs of the identified 18 PAHs in gaseous and particulate phases were calculated on a coal-weight basis and shown in **Table 3** with some data cited from other reports for comparing. For bituminous coals, the EFs of total PAHs varied from 140.75 to 229.11 mg/kg, with average of 171.73 mg/kg, while for anthracite, the EFs of total PAHs varied from 58.49 to 129.47 mg/kg, with average of 93.98 mg/kg. The EFs of total PAHs for bituminous coal was 82.73% higher than that for anthracite. Gaseous and total PAH EFs of DS were 220.53 and 229.11 mg/kg, the highest value among the tested five coals. While, the lowest values of gaseous and total PAH EFs (51.87 and 58.49 mg/kg) were from JX anthracite coal. The EFs of PAHs of bituminous coal reported in literature were also much higher than that of anthracite. Therefore, it will be very helpful for reducing PAH emissions from domestic coal combustion by using anthracite coal instead of bituminous coal.

It should be noted that most gaseous PAH emission factors in this study were higher than other study, especially for bituminous coal. On the one hand, the detail compounds contained in PAHs from different publications were not exactly same. For example, NAP was analyzed in this study while it was not analyzed in others. On the other hand, the residence time of flue gas before being collected was also different. The residence time in this study was 5.5 sec while it was 54 sec and 14 sec in Chen's study (Chen et al., 2005) and 60 sec in Dou's study (Dou et al., 2007). Residence time is very important for the condensation of volatile compounds. As for bituminous coal, much volatile compounds evaporated into air. Shorter residence time led to less condense on particulate phase.

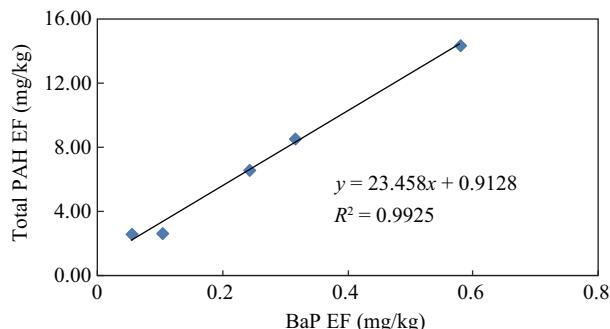
The concentration of BaP ranged from 38.13 µg/m<sup>3</sup> (YC) to 855.10 µg/m<sup>3</sup> (DT) (data not shown). In Beijing, the standard maximum concentration limit of BaP is 0.3 µg/m<sup>3</sup> (DB11/501-2007). The BaP concentration from the emission of studied domestic coal was 126–2849 times higher than the standard value, which indicated the pollution of domestic coal combustion to the atmosphere was serious. Therefore, efficient emission control should be conducted to reduce PAHs emissions, such as domestic coal selection, flue gas treatment and so on.

As shown in **Fig. 1**, good correlation between BaP EFs and the total PAH EFs in particulate phase was observed ( $R^2 = 0.9925$ ). Therefore, the EF of the total PAHs can be derived from the EF of BaP by multiplying the slope in **Fig. 1**, which can be used to estimate the total PAHs when BaP value is available.

**Table 3** Emission factors (EFs) of PAHs emitted from domestic raw coal combustion

| Coal            | Coal district             | EF <sub>gas</sub> (mg/kg) | EF <sub>pm</sub> (mg/kg) | EF <sub>total</sub> (mg/kg) | Reference           |
|-----------------|---------------------------|---------------------------|--------------------------|-----------------------------|---------------------|
| Bituminous (YC) | Ningxia, China            | 138.13                    | 2.62                     | 140.75                      | This study          |
| Bituminous (DS) | Inner Mongolia, China     | 220.53                    | 8.58                     | 229.11                      | This study          |
| Bituminous (DT) | Shanxi, China             | 130.94                    | 14.41                    | 145.35                      | This study          |
| Bituminous      | Beijing, China            | 76                        | 249                      | 325                         | Douhan et al., 2007 |
| Bituminous      | China                     | 66                        | 94                       | 160                         | Chen et al., 2005   |
| Bituminous      | China                     | —                         | —                        | 373                         | Shen et al., 2010   |
| Bituminous      | Beijing and Shanxi, China | 76.4–357.6                | 248.8–1077.2             | 325.3–1434.8                | Liu et al., 2009    |
| Sub-bituminous  | China                     | 28                        | 40                       | 68                          | Chen et al., 2005   |
| Anthracite (ZJ) | Guizhou, China            | 126.8                     | 2.67                     | 129.47                      | This study          |
| Anthracite (JX) | Beijing, China            | 51.87                     | 6.62                     | 58.49                       | This study          |
| Anthracite      | Hunan, China              | 0.108                     | 0.009                    | 0.117                       | Chen et al., 2004   |
| Anthracite      | Beijing, China            | 63                        | 1                        | 64                          | Douhan et al., 2007 |
| Anthracite      | China                     | —                         | —                        | 4.78                        | Shen et al., 2010   |
| Anthracite      | Beijing and Shanxi, China | 47.2–134.5                | 1.4–21.3                 | 52.8–155.8                  | Liu et al., 2009    |

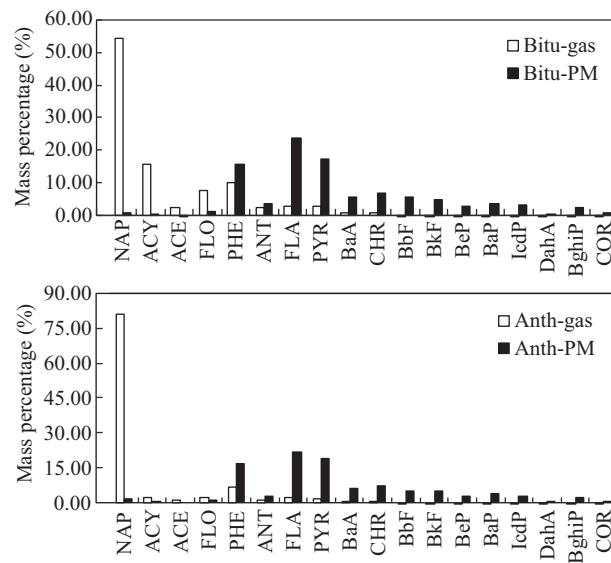
EF<sub>gas</sub>, EF<sub>pm</sub>, EF<sub>total</sub>: PAH emission factor in gaseous phase, particulate phase and both in gaseous and particulate phase, respectively; —: no data.



**Fig. 1** Correlation of BaP EFs with the total PAH EFs in particulate phases.

## 2.2 PAH compositions

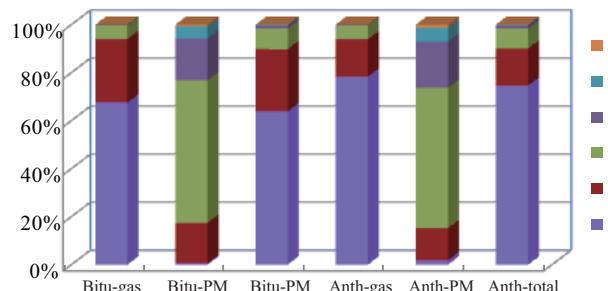
The mass percent distributions of individual PAHs from bituminous coal combustion was similar to those from anthracite coal combustion, while the mass percent distributions in gaseous phase were greatly different from those in particulate phase (Fig. 2). The abundant PAHs in the gaseous phase were those with molecular weight lighter than PHE, while the sum of the other PAHs with heavier mass accounted for less than 10% of the total mass. NAP was the most abundant PAHs in gaseous phase which accounted for 54.54% for bituminous coal and 81.03% for anthracite coal. As for PAHs in particulate phase, the percent of individual PAH was not so concentrated. The mass distribution in particulate phase was dominated by PHE, FLA, PYR, BaA and CHR, in which each species was above 5% and the sum of above PAHs was over 70%. The most abundant PAH in particulate phase was FLA and it accounted for 23.76% for bituminous coal and 21.61% for anthracite coal. For the PAHs other than PHE, FLA, PYR, BaA and CHR, the percentages were mostly from 2% to 5%. The percentage of gaseous PAHs in total were 95% both for bituminous and anthracite coals. That



**Fig. 2** Mass percentage distribution of PAHs.

is, the amount of PAHs in gaseous phase dominated the total PAHs emission of domestic coal combustion. The similar result was also reported by other studies. Chen et al. (2004b) found that the ratio of vapor phase to the sum of both phases was 93% for honeycomb coal briquette combustion. When investigated the atmosphere around an oil furnace carbon black manufacturing plant, Tsai et al. (2002) found the gaseous-phase PAHs accounted for 96.3% to 99.7% of the total PAHs.

Among the detected 18 PAHs, the content of NAP, PHE, FLO, PYR were abundant, which was similar to other studies. Dou et al. (2007) studied the PAH EFs of domestic coal combustion and found that PHE and ACY were abundant, followed by FLO and BbF. Xu et al. (2006) estimated the annual emission of PAHs in China and found the emission of PHE was also plentiful.



**Fig. 3** EFs of PAHs with different rings for flue gas of domestic coal combustion.

The EFs of PAHs species with different rings both in gaseous and particulate phases are given in **Fig. 3**. Differences between gaseous and particulate phases can be found in both bituminous and anthracite coals. In gaseous phases, PAHs with low rings were the main part of total PAHs, among which the percentage of PAHs with 2-ring were the richest compounds, followed by 3-ring PAHs. Those compounds with 2-ring and 3-ring took up more than 85% of total PAHs in gaseous phase. In particulate phase, the distributions of PAHs with different ring numbers were not uniform. However, in the combustion of both bituminous and anthracite coals, the average percentage of 4-ring PAHs showed the highest values (57.38% and 56.62%) while the average percentage of 7-ring PAHs was the lowest (0.72% and 0.79%). PAHs in particulate phase with 3-ring and 4-ring were the main components and took up about 80% of total PAHs. Dou et al. (2007) also indicated that 4-ring species were the main part of PAHs in particulate phase emitted from bituminous coals. The total amount of 2-ring and 3-ring PAHs was 90% of the total PAHs, which was similar to the proportion (85%) of 2-ring and 3-ring PAHs in total PAHs for anthracite coal.

### 2.3 PAH diagnostic ratio

By comparing several PAH diagnostic ratios between sources and receptors, some can be used for source apportionment (Watson, 1984; Yunker et al., 2002; Zhang et al., 2008). In this study, several frequently-used PAHs diagnostic ratios were calculated (**Table 4**). These values were generally comparable to those reported in some other studies for domestic coal combustion (Chen et al., 2004a, 2004b, 2005; Oanh et al., 2005; Yunker et al., 2002; Shen et al., 2010). For gaseous phase, most diagnostic ratios were consistent with each other and the relative standard deviation (RSD) was around or below 20% for the studied five kinds of coals, except BaP/BeP, BaP/(BaP+BeP), BeP/COR, BeP/BghiP. For particulate phase, except FLU/(FLU+PYR), the RSD for all the others PAH ratios were below 50%. For some ratios, the difference was significant between that in gaseous phase and in particulate phase, such as FLU/(FLU+PYR), BaP/COR, PYR/BaP, BaA/BaP, BaP/(BaP+CHR). Thus, the diagnostic ratios in gaseous and in particulate phases need to be investigated separately when these diagnostic ratios are used.

### 2.4 Potential toxicity risk

To assess the potential toxicity risk to ecosystems and human beings, benzo[a]pyrene-equivalent carcinogenic power (BaPE), a sum of 7 carcinogenic PAH components ( $\Sigma\text{PAH}_7$ , BaA, CHR, BbF, BkF, BaP, IcdP and DahA) and 2,3,7,8-tetrachlorodibenzodioxin (TCDD)-based total toxicity potency (TEQ) were utilized in many studies (Larsen and Lasen, 1998; Lu et al., 2008; Bhargava, 2004; Liu et al., 2009). The calculated results of potential risk of PAHs emitted from bituminous coals and antracite coals are listed in **Table 5**.

**Table 4** PAH diagnostic ratios for five studied domestic coal combustion

|                 | Gaseous phase      |         | Particulate phase  |         |
|-----------------|--------------------|---------|--------------------|---------|
|                 | Average $\pm$ S.D. | RSD (%) | Average $\pm$ S.D. | RSD (%) |
| ANT/(ANT+PHE)   | 0.17 $\pm$ 0.03    | 18.37   | 0.14 $\pm$ 0.05    | 36.97   |
| FLU/(FLU+PYR)   | 0.64 $\pm$ 0.12    | 19.15   | 0.06 $\pm$ 0.03    | 56.61   |
| BaA/CHR         | 0.91 $\pm$ 0.09    | 10.21   | 0.82 $\pm$ 0.20    | 24.43   |
| BbF/BkF         | 1.19 $\pm$ 0.23    | 19.65   | 1.04 $\pm$ 0.16    | 15.44   |
| IND/BghiP       | 1.36 $\pm$ 0.07    | 4.96    | 1.33 $\pm$ 0.10    | 7.19    |
| IND/(IND+BghiP) | 0.58 $\pm$ 0.01    | 2.10    | 0.57 $\pm$ 0.02    | 3.08    |
| BaP/COR         | 0.10 $\pm$ 0.01    | 11.31   | 0.48 $\pm$ 0.22    | 45.95   |
| PYR/BaP         | 32.81 $\pm$ 7.44   | 22.67   | 5.84 $\pm$ 2.37    | 40.69   |
| BaA/(BaA+CHR)   | 0.47 $\pm$ 0.02    | 5.27    | 0.45 $\pm$ 0.06    | 14.02   |
| BaA/BaP         | 9.45 $\pm$ 1.00    | 10.57   | 2.00 $\pm$ 0.86    | 43.05   |
| BaP/(BaP+CHR)   | 0.09 $\pm$ 0.01    | 10.34   | 0.31 $\pm$ 0.11    | 36.47   |
| BaP/BeP         | 1.45 $\pm$ 1.20    | 82.49   | 1.32 $\pm$ 0.58    | 44.03   |
| BaP/(BaP+BeP)   | 0.51 $\pm$ 0.22    | 42.89   | 0.55 $\pm$ 0.12    | 21.29   |
| BeP/COR         | 0.13 $\pm$ 0.12    | 93.16   | 0.36 $\pm$ 0.09    | 25.14   |
| BeP/BghiP       | 2.77 $\pm$ 2.28    | 82.20   | 1.30 $\pm$ 0.34    | 26.04   |

**Table 5** Potential toxicity risk of PAHs emitted from domestic coal combustion

|                      | Bituminous |             |        | Anthracite |             |        |
|----------------------|------------|-------------|--------|------------|-------------|--------|
|                      | Gaseous    | Particulate | Total  | Gaseous    | Particulate | Total  |
| $\Sigma\text{PAH}_7$ | 1.644      | 2.148       | 4.410  | 1.177      | 1.382       | 2.560  |
| BaPE                 | 0.132      | 0.333       | 0.532  | 0.092      | 0.235       | 0.327  |
| TEQ                  | 0.0002     | 0.0004      | 0.0007 | 0.0001     | 0.0003      | 0.0004 |

The results of BaPE,  $\Sigma\text{PAH}_7$  and TEQ exhibited a similar tendency that the potential health risk of bituminous coals was higher than that of anthracite coals. Although PAHs in gaseous phase took up most part of PAH mass, its contribution to the total toxicity was still less than PAH in particulate phase. For each coal, the carcinogenic power was different. The total toxicities of DS and DT were high, which was coincident with the high PAHs EFs.

### 3 Conclusions

Using dilution system, gaseous and particulate samples from domestic coal combustion were collected to analyze 18 kinds of PAHs. Both of bituminous and anthracite coals showed high EFs and potential toxicity, and the concentration of BaP was 126 to 2849 times higher than the emission standard value of Beijing (DB11/501-2007). Therefore, efficient emission control should be conducted to reduce PAHs emissions, such as domestic coal selection, flue gas treatment and so on. Gaseous PAHs from the domestic coal combustion accounted for the most part of total PAHs emission and the potential toxicity risk of gaseous PAHs was almost comparable to that of particulate PAHs. Previous studies mainly focused on particulate PAHs measurement and would greatly underestimate the impact on atmospheric PAHs. In the future, relevant study should be enhanced to master the comprehensive characteristics of PAHs emissions from domestic coal combustion.

### Acknowledgment

This work was supported by the Natural Science Foundation of China (No. 41275135, 41105090), the National High Technology Research and Development Program (863) of China (No. 2012AA063506) and the Open Foundation of Environmental Simulation and Pollution Control State Key Laboratories (Peking University).

### REFERENCES

- Baker J E, Eisenreich S J, 1990. Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. *Environmental Science and Technology*, 24(3): 342–352.
- Bhargava A, Khanna R N, Bhargava S K, Kumar S, 2004. Exposure risk to carcinogenic PAHs in indoor-air during biomass combustion whilst cooking in rural India. *Atmospheric Environment*, 38(28): 4761–4767.
- Bosveld A T C, de Bie P A, van den Brink N W, Jongepier H, Klomp V A, 2002. *In vitro* EROD induction equivalency factors for the 10 PAHs generally monitored in risk assessment studies in the Netherlands. *Chemosphere*, 49(1): 75–83.
- Cecinato A, 1997. Polycyclic aromatic hydrocarbons (PAH), benz(a)pyrene (BaPy) and nitrated-PAH (NPAH) in suspended particulate matter. *Annali Di Chimica*, 87: 483–496.
- Chen Y J, Bi X H, Mai B X, Shen G, Fu J, 2004a. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel*, 83(7–8): 781–790.
- Chen Y J, Bi X H, Mai B Z, Sheng G Y, Fu J M, 2004b. Quantitative study and size distribution of polycyclic aromatic hydrocarbons from honeycomb coal briquette combustion. *Environmental Pollution and Control*, 26(6): 415–423.
- Chen Y J, Sheng G Y, Bi X H, Feng Y L, Mai B X, Fu J M, 2005. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environmental Science and Technology*, 39(6): 1861–1867.
- China Statistical Yearbook, 2010, China Statistics Press, Beijing. 2011.
- Chen Y J, Zhi G R, Feng Y L, Fu J M, Sheng G Y, Simoneit B R T, 2006. Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China. *Geophysical Research Letter*, 33: L20815. DOI:10.1029/2006GL026966.
- Dou H, Chang B, Wei Z C, Qiu W, Liu S Z, Liu Y et al., 2007. Emission factors of PAHs in residential coal combustion in China. *Acta Scientiae Circumstantiae*, 27(11): 1783–1788.
- Douben P E T, 2003. PAHs: An Ecotoxicological Perspective. Wiley, New York.
- Geng C M, Wang K, Wang W, Chen J H, Liu X Y, Liu H J, 2012. Smog chamber study on the evolution of fume from residential coal combustion. *Journal of Environmental Sciences*, 24(1): 169–176.
- Larsen J C, Larsen P B, 1998. Chemical carcinogens. In: Air Pollution and Health (Hester R, Harrison R, eds.). Cambridge, UK: The Royal Society of Chemistry, 33–56.
- Liu W X, Dou H, Wei Z C, Chang B, Qiu W X, Liu Y et al., 2009. Emission characteristics of polycyclic aromatic hydrocarbons from combustion of different residential coals in North China. *Science of the Total Environment*, 407(4): 1436–1446.
- Lu H, Zhu L Z, Chen S G, 2008. Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China. *Environmental Pollution*, 152(3): 569–575.
- Oanh N T K, Albina D O, Ping L, Wang X K, 2005. Emission of particulate matter and polycyclic aromatic hydrocarbons from select cookstove-fuel systems in Asia. *Biomass and Bioenergy*, 28(6): 579–590.
- Shen G, Wang W, Yang Y, Zhu C, Min Y J, Xue M et al., 2010. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmospheric Environment*, 44(39): 5237–5243.
- Tao S, Li X R, Yang Y, Coveney R M, Lu X X, Chen H T et al., 2006. Dispersion modeling of polycyclic aromatic hydrocarbons from combustion of biomass and fossil fuels and production of coke in Tianjin, China. *Environmental Science and Technology*, 40(15): 4586–4591.

- Tsai P J, Shieh H Y, Lee W J, Lai S O, 2002. Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces. *Journal of Hazardous Materials*, 91(1-3): 25–42.
- Tuominen J, Salomaa S, Pyysalo H, Skytta E, Tikkanen L, Nurmela T et al., 1988. Polynuclear aromatic compounds and genotoxicity in particulate and vapor phases of ambient air: effect of traffic, season, and meteorological conditions. *Environmental Science and Technology*, 22(10): 1228–1234.
- Wang K, Geng C M, Wang W, Liu X Y, Liu H J, Ge M F, 2010. Characterization of residential coal combustion: products and in situ photo-oxidation. *Heterogeneous Combustion*, Nova Science Publishers, 2010, ISBN: 978-1-61761-324-1 USA.
- Wang Q, Geng C M, Lu S H, Chen W T, Shao M, 2013. Emission factors of gaseous carbonaceous species from residential combustion of coal and crop residue brikettes. *Frontiers of Environmental Science and Engineering*, 7(1): 66–76.
- Watson J G, 1984. Overview of receptor model principles. *Journal of the Air Pollution Control Association*, 34: 619–623.
- Xu S S, Liu W X, Tao S, 2006. Emission of polycyclic aromatic hydrocarbons in China. *Environmental Science and Technology*, 40(3): 702–708.
- Yu G G, Wang T G, Zhu X L, Wu D P, 2008. Source appointment of PAHs in aerosol of northwest of Beijing. *Environmental Chemistry*, 27(2): 245–250.
- Yunker M B, Macdonald R W, Vingarzan R, Mitchell H R, Goyette D, Sylvestre S, 2002. PAHs in the Fraser River basin: a critical appraisal PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33(4): 489–515.
- Zhang Y X, Schauer J J, Zhang Y H, Zeng L M, Wei Y J, Liu Y et al., 2008. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. *Environmental Science and Technology*, 42(14): 5068–5073.
- Zhi G R, Chen Y J, Feng Y L, Xiong S C, Li J, Zhang G et al., 2008. Emission characteristics of carbonaceous particles from various residential coal-stoves in China. *Environmental Sciences and Technology*, 42(9): 3310–3315.



## Editorial Board of Journal of Environmental Sciences

### Editor-in-Chief

**Hongxiao Tang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

### Associate Editors-in-Chief

**Jiuhui Qu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Shu Tao** Peking University, China  
**Nigel Bell** Imperial College London, United Kingdom  
**Po-Keung Wong** The Chinese University of Hong Kong, Hong Kong, China

### Editorial Board

#### Aquatic environment

**Baoyu Gao** Shandong University, China  
**Maohong Fan** University of Wyoming, USA  
**Chihpin Huang** National Chiao Tung University, Taiwan, China  
**Ng Wun Jern** Nanyang Environment & Water Research Institute, Singapore  
**Clark C. K. Liu** University of Hawaii at Manoa, USA  
**Hokyong Shon** University of Technology, Sydney, Australia  
**Zijian Wang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Zhiwu Wang** The Ohio State University, USA  
**Yuxiang Wang** Queen's University, Canada  
**Min Yang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

#### Terrestrial environment

**Christopher Anderson** Massey University, New Zealand  
**Zuccong Cai** Nanjing Normal University, China  
**Xinbin Feng** Institute of Geochemistry, Chinese Academy of Sciences, China  
**Hongqing Hu** Huazhong Agricultural University, China  
**Kin-Che Lam** The Chinese University of Hong Kong, Hong Kong, China  
**Erwin Klumpp** Research Centre Juelich, Agrosphere Institute, Germany  
**Peijun Li** Institute of Applied Ecology, Chinese Academy of Sciences, China

#### Michael Schloter

German Research Center for Environmental Health, Germany

**Xuejun Wang** Peking University, China

**Lizhong Zhu** Zhejiang University, China

#### Atmospheric environment

**Jianmin Chen** Fudan University, China  
**Abdelwahid Mellouki** Centre National de la Recherche Scientifique, France  
**Yujing Mu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Min Shao** Peking University, China  
**James Jay Schauer** University of Wisconsin-Madison, USA

**Yuesi Wang** Institute of Atmospheric Physics, Chinese Academy of Sciences, China

**Xin Yang** University of Cambridge, UK

#### Environmental biology

**Yong Cai** Florida International University, USA  
**Henner Hollert** RWTH Aachen University, Germany  
**Jae-Seong Lee** Hanyang University, South Korea  
**Christopher Rensing** University of Copenhagen, Denmark  
**Bojan Sedmak** National Institute of Biology, Ljubljana  
**Lirong Song** Institute of Hydrobiology, the Chinese Academy of Sciences, China  
**Chunxia Wang** National Natural Science Foundation of China  
**Gehong Wei** Northwest A & F University, China  
**Daqiang Yin** Tongji University, China  
**Zhongtang Yu** The Ohio State University, USA

#### Environmental toxicology and health

**Jingwen Chen** Dalian University of Technology, China

**Jianying Hu** Peking University, China

**Guibin Jiang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

**Sijin Liu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

**Tsuyoshi Nakanishi** Gifu Pharmaceutical University, Japan

**Willie Peijnenburg** University of Leiden, The Netherlands

**Bingsheng Zhou** Institute of Hydrobiology, Chinese Academy of Sciences, China

#### Environmental catalysis and materials

**Hong He** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Junhua Li** Tsinghua University, China  
**Wenfeng Shangguan** Shanghai Jiao Tong University, China  
**Yasutake Teraoka** Kyushu University, Japan  
**Ralph T. Yang** University of Michigan, USA

#### Environmental analysis and method

**Zongwei Cai** Hong Kong Baptist University, Hong Kong, China  
**Jiping Chen** Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China  
**Minghui Zheng** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Municipal solid waste and green chemistry**

**Pinjing He** Tongji University, China

#### Environmental ecology

**Rusong Wang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

### Editorial office staff

**Managing editor** Qingcai Feng  
**Editors** Zixuan Wang Suqin Liu Zhengang Mao  
**English editor** Catherine Rice (USA)

# JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)  
<http://www.jesc.ac.cn>

## Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

## For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

## For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: [journal@mail.sciencep.com](mailto:journal@mail.sciencep.com), or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

## Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

## Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

## Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: [jesc@263.net](mailto:jesc@263.net), [jesc@rcees.ac.cn](mailto:jesc@rcees.ac.cn). Instruction to authors is available at <http://www.jesc.ac.cn>.

## Journal of Environmental Sciences (Established in 1989)

Vol. 26 No. 1 2014

|                 |   |                          |   |
|-----------------|---|--------------------------|---|
| Supervised by   | Chinese Academy of Sciences   | Published by             | Science Press, Beijing, China   |
| Sponsored by    | Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences   | Distributed by           | Elsevier Limited, The Netherlands   |
| Edited by       | Editorial Office of Journal of Environmental Sciences<br>P. O. Box 2871, Beijing 100085, China<br>Tel: 86-10-62920553; <a href="http://www.jesc.ac.cn">http://www.jesc.ac.cn</a><br>E-mail: <a href="mailto:jesc@263.net">jesc@263.net</a> , <a href="mailto:jesc@rcees.ac.cn">jesc@rcees.ac.cn</a> | Domestic                 | Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China<br>Local Post Offices through China |
| Editor-in-chief | Hongxiao Tang   | Foreign                  | Elsevier Limited<br><a href="http://www.elsevier.com/locate/jes">http://www.elsevier.com/locate/jes</a>     |
| CN 11-2629/X    | Domestic postcode: 2-580  | Printed by               | Beijing Beilin Printing House, 100083, China  |
|                 |   | Domestic price per issue | RMB ¥ 110.00  |

ISSN 1001-0742



9 771001 074147