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# Atmospheric heavy metal deposition in agro-ecosystems in China

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## Abstract
Atmospheric deposition has become one of the main sources of heavy metals in crops in developed and industrial zones in China for the past several years. However, lack of data of the agro-ecosystems on the vast areas of China makes it difficult to assess the impacts of air pollution on the heavy metal accumulation in crops. In this study, with deposit samples from 67 sites located at different agro-ecosystems (typical, factory nearby, town nearby, roadside, and remote) of four natural regions [Huanghuai (HH), Southeast (SE), Southwest (SW) and upper-mid Yangzi River (Up-mid YR)], atmospheric heavy metal deposition in agro-ecosystems on a large scale in China was studied. The results showed that during the growing season, the deposition fluxes of Cr, Ni, As, Cd, and Pb in typical agro-ecosystems were 0.60–36.86, 0.65–25.37, 0.05–8.88, 0.12–5.81, and 0.43–35.63 $\mu$g m$^{-2}$ day$^{-1}$, respectively, which varied greatly between the four different regions. The average deposition fluxes of Cr, Ni, Cd, and Pb in the HH region, as well as the fluxes of As in the SW region, were significantly higher than those in the SE region. Heavy metal deposition rates among agro-ecosystems were very similar, except for the sites around cement factory in flat HH region. In mountainous SW region, however, deposition rates varied widely with sites nearby towns relatively higher and remote regions much lower. Higher correlation coefficients were observed between Cr, As, Pb, and Ni deposition rates, suggesting that they had similar sources. Samples from the SW and SE regions exhibited higher $^{207}$Pb/$^{206}$Pb and $^{208}$Pb/$^{206}$Pb ratios than those from the HH and Up-mid YR regions. Airborne Pb in SW agro-ecosystems were mainly derived from vehicle exhaust and local smelting, whereas that in the HH region from burning of northern Chinese coal.

**Keywords** Atmospheric deposition · Heavy metals · Agro-ecosystem · Pb isotope

## Introduction

Rapid industrialization and urbanization have made heavy metal contamination in crop foods an increasing public health

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Responsible editor: Gerhard Lammel

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problem in China during the past several years (Zhang et al. 1998; Liu et al. 2017; Wang et al. 2001). Samples of cereals and soybeans from the market of northeastern China (Zhang et al. 1998), coarse grains produced in south China (Liu et al. 2017; Huang et al. 2008), and vegetables from different cities (Wang et al. 2001, 2012) have been found exhibiting higher heavy metal concentration and potential health risks for human health. Many efforts have been made to evaluate and alleviate heavy metal contamination in crops in China (Zhou et al. 2000; Zhao et al. 2015).

Heavy metal in crops comes from soil, water, atmosphere, and cultivar practices such as fertilizer and pesticide by absorption, translocation, and deposition (Kabata-Pendias and Pendias 2000). Due to industrialization and global population growth, atmosphere deposition has become one of the main sources of heavy metal such as Pb, As, Hg, and Cr in crops (Pandey et al. 2012; Dalenberg and van Driel 1990; Ylaranta 1996; Termmerman and Hoenin 2004; Peris et al. 2007; Bermudez et al. 2012; Li et al. 2012). The impacts of

atmospheric deposition on the inputs to agricultural land have been widely investigated in developed countries (Nicholson et al. 2006; Zhang 2003; Keller et al. 1999; Rautengarten et al. 1995). It was reported that the atmospheric deposition had elevated the levels of heavy metal in dietary vegetables and presented a significant threat to the health of users (Pandey et al. 2012) which contributed considerably (73–95%) to the Pb concentrations not only for the leafy plants such as spinach but also for cereals (Dalenberg and van Driel 1990).

Although many attempts have been made to prevent air pollution, the air pollution emissions in China have continually increased since 2000 (Apte et al. 2015). The influence of air pollution has exceeded specified districts and becomes an unavoidable problem in a vast area of China (Wang et al. 2017). In 2010, more than 80% of the population lived in a region where air quality did not reach the air quality standard (Apte et al. 2015). However, as the atmospheric deposition of heavy metals is expected to be higher in urban and industrial areas than in remote districts (Pan and Wang 2015; Pandey et al. 2008), previous studies have focused on urban and industrial districts (Chen et al. 2005; Mukai et al. 1993; Zhu et al. 2017; Tan et al. 2014; Sun et al. 2009; Li et al. 2012) as well as some specific regions such as roadside (Feng et al. 2011) and smelting factories around (Tao et al. 2014). Recently, the impacts of air pollution on the inputs of heavy metal to agro-ecosystems have also attracted more and more attention (Lei et al. 2009; Wong et al. 2003; Tang et al. 2007; Cong et al. 2008; Deng et al. 2012; Lai et al. 2008; Li et al. 2010). Using the data collected from agricultural land areas conducted from 1999 to 2006, Lei et al. (2009) estimated the total trace element deposition to agricultural soils in China. However, most sampling sites in the above studies located in developed or industrial areas such as the Pear Rivar Delta (Wong et al. 2003), Chengdu Economic Region (Tang et al. 2007), the plain area of Beijing Municipality (Cong et al. 2008), and the southern plain of Hebei province (Li et al. 2010). There is only one report about agro-ecosystem in less-developed areas (Deng et al. 2012). This will make the element inputs to agro-ecosystems be overestimated and make it difficult to assess exactly the impact of air pollution on heavy metal accumulation in crops which, as a result, will hinder the efforts to control the levels of heavy metal in food chain.

In this study, deposit samples were collected from different agro-ecosystems of the four natural regions [Huanghuai (HH), Southeast (SE), Southwest (SW), and upper-mid Yangzi River (Up-mid YR) regions] in China during crop-growing season, the atmospheric heavy metal deposition in agro-ecosystems in China was evaluated on a large scale, and the diversities of atmospheric heavy metal deposition among different agro-ecosystems (typical, factory nearby, roadside, and remote) were investigated both in HH and SW regions. Meanwhile, the sources of heavy metals deposited in agro-ecosystems were traced with Pb isotopic signature. The impacts of air pollution on the heavy metal inputs to agro-ecosystems were also discussed.

# Material and methods

## Sampling sites

This study was carried out in the agro-ecosystems of four natural regions (HH, SE, SW, and Up-mid YR area) in China in 2015. The basic information of the agro-ecosystems in the four regions is listed in Table 1.

To study the heavy metal deposition of the agro-ecosystems on a large scale, 32 sampling sites were arranged in the typical agro-ecosystems—characterized with representative cropping systems without obvious pollution sources—in the four regions. Thirty-two atmospheric deposition samples were collected during the main crop seasons—Jun.–Jul. in the SE and Jun.–Sep. in the HH, SW, and Up-mid YR regions.

To study the distribution of heavy metal deposition within the same region, another 35 sampling sites were arranged in different agro-ecosystems in the flat HH and mountainous SW regions, respectively. The definition of different agro-ecosystems is listed in Table 2. Thirty-five samples were also collected during the main crop season. The detail information of all sampling sites is listed in Table 3 and displayed in Fig. 1.

## Sampling

Atmospheric deposition samples were collected during the main crop seasons with one sample for each site. Totally 67 samples were completed according to the monitoring guide from the Chinese Ecosystem Research Network (CERN). The procedure was as follows: At the sampling sites, polymethyl methacrylate buckets (diameter 15 cm, height 60 cm) were installed 2.0 m above the ground to avoid splashing and contamination from the ground. Before installation, buckets were cleaned carefully with distilled water and added with 60 ml glycol to prevent algal growth. Dry and wet deposits were collected together continuously from June to July in the SE region and from June to September in the other regions. The collectors were replaced with a new one if necessary. Deposits collected were stored at 4 °C for temporary conserve. At the end of collecting, the deposits collected at the same sampling site were combined to a mixed sample, transported to the laboratory, and stored at 4 °C for determination.

## Sample digest and measurement

Mixed samples were dried in a boiling water bath until nearly drying and transferred to a 50-ml polytetrafluoroethylene digestion tank; a microwave-assisted acid digestion (Milestone ETHOS One) of the residue in the tank was performed for 100 minutes, during which time the temperature was slowly increased to 190 °C. The acid mixture was 65% $HNO_3$ (Emsure®, Merck), 30% $H_2O_2$ (Emsure®, Merck), and 40% HF (Emsure®, Merck), with a volume ratio 6:2:1. Quality

**Table 1**  Basic information of the agro-ecosystem in the four natural regions

| Regions | Sampling provinces | Sampling ranges | Landforms | Crop seasons |
|---|---|---|---|---|
| SW | Guizhou | E 106.91–107.04 N 27.01–27.21 | Mountainous | May–Sep. |
| HH | Henan | E 113.01–113.35 N 33.84–34.06 | Plain | |
| Up-mid YR | Shanxi | E 110.05–110.22 N 34.04–34.21 | Mountainous | |
| SE | Fujian | E 117.31–117.53 N 27.27–27.36 | Low mountains and hills | Apr.–Oct. |

control of metal analysis was done by using duplicate samples and standard reference material (GBW07407 from the Chinese Academy of Measurement Sciences). Concentrations of Cd, Pb, As, Cr, and Ni and the lead isotopic ratios were determined using an inductively coupled plasma mass spectrometer (Agilent ICP-MS 7900). An Agilent® internal standard ($^{72}$Ge, $^{115}$In, and $^{209}$Bi) was used as internal standard, and an Agilent® environmental multi-element standard solution was used for the external calibration. The ratios of $^{207}$Pb/$^{206}$Pb and $^{208}$Pb/$^{206}$Pb were analyzed, and the measurements of Pb isotopes were corrected using lead isotopic standard reference material NIST 981. Method detection limits were 15 ng g$^{-1}$ for Cr, Ni, and Pb and 13 ng g$^{-1}$ for As and Cd, respectively. The metal concentrations of blanks were all below detection limits. Analytical precision of replicates ($n = 3$) differed within 5% relative to standard deviation.

## Data analysis

Data was analyzed using MS Excel 2010 and IBM SPSS 19.0. Statistical analyses including one-way ANOVA were performed using IBM SPSS19.0. Graphs were plotted using SigmaPlot 12.5, and map was made with ArcGIS 10.0.

## Results

### Atmospheric heavy metal deposition in typical agro-ecosystems

Thirty-two samples from typical agro-ecosystems in the four natural regions in China were firstly analyzed for the general

**Table 2**  Definition of different agro-ecosystems

| Agro-ecosystems | Definition |
|---|---|
| Factory nearby | 500–4000 m away from a cement factory |
| Town nearby | 500–4000 m straight away from a town |
| Roadside | 50–500 m away from a road |
| Remote | 3000 m straight away from a village in mountainous region |

heavy metal deposition rates in agro-ecosystems and their spatial distribution on a national scale.

### General situation of heavy metal deposition

The atmospheric deposition fluxes in the sampling sites of the typical agro-ecosystems ranged from 0.60 to 36.86 µg m$^{-2}$ day$^{-1}$ for Cr, 0.65–25.37 µg m$^{-2}$ day$^{-1}$ for Ni, 0.05–8.88 µg m$^{-2}$ day$^{-1}$ for As, 0.12–5.81 µg m$^{-2}$ day$^{-1}$ for Cd, and 0.43–35.63 µg m$^{-2}$ day$^{-1}$ for Pb, respectively (Table 4). The maximum variance in deposition fluxes among sampling sites was observed for Cd, followed by Ni and Cr, and the minimum variation in deposition fluxes was observed for Pb (Table 4). Cd atmospheric deposition in typical agro-ecosystems showed greater variance compared with the other elements.

### Heavy metal deposition in different areas

Significant differences in heavy metal deposition fluxes in typical agro-ecosystem sites were observed between the four natural regions (Table 5). The average deposition fluxes of Cr, Cd, Ni, and Pb were significantly higher in the HH region than in the other regions (Table 5). The As deposition fluxes in the SW and HH were significantly higher than in the SE and Up-mid YR regions. The average deposition fluxes of Cr, Ni, As, Cd, and Pb in the SE sites were significantly lower. These results suggest that there is large-scale variation in atmospheric heavy metal deposition in typical agro-ecosystems in China. Agro-ecosystems in the HH area exhibited much higher heavy metal deposition than the other regions, whereas in the SE region, deposition was much lower. Agro-ecosystems in the SW area also showed higher As and Pb deposition among the four regions.

### Atmospheric heavy metal deposition in different agro-ecosystems

To detail the spatial distribution of heavy metal deposition rates among different agro-ecosystems and provide targeted methods for crop heavy metal control, atmospheric heavy metal deposition in different agro-ecosystems was further

**Table 3** Detail information of all sampling sites

| Regions | Provinces | Typical | Remote | Town nearby | Roadside | Factory nearby |
|---------|-----------|---------|--------|-------------|----------|----------------|
| SW | Guizhou | 6 | 8 | 8 | – | 5 |
| SE | Fujian | 8 | – | – | – | – |
| Up-mid YR | Shanxi | 8 | – | – | – | – |
| HH | Henan | 10 | – | – | 5 | 9 |
| Total | | 32 | 8 | 8 | 5 | 14 |

explored by using the SW and HH regions as examples of mountain and plain landforms, respectively.

## Atmospheric heavy metal deposition in different agro-ecosystems in the SW region

The deposition rates in the agro-ecosystems of the SW region ranged from 0.24 to 12.75 $\mu g\ m^{-2}\ day^{-1}$ for Cr, 0.57–7.69 $\mu g\ m^{-2}\ day^{-1}$ for Ni, 0.75–6.12 $\mu g\ m^{-2}\ day^{-1}$ for As, 0.09–1.11 $\mu g\ m^{-2}\ day^{-1}$ for Cd, and 1.37–25.12 $\mu g\ m^{-2}\ day^{-1}$ for Pb (Table 6). Similar trends were observed for the five elements among different agro-ecosystems. The highest deposition rates were found in the town nearby sites. The deposition fluxes of Cr, Ni, As, Cd, and Pb were significantly lower in remote ecosystems and were only 20.27, 28.43, 35.77, 25.40, and 24.36% of those in the town nearby sites, respectively. Factory nearby sites also showed lower levels of heavy

metal deposition. These results suggest that in the mountainous SW area, heavy metal deposition varies widely among different agro-ecosystems, with higher deposition in town nearby and much lower deposition in remote areas.

## Atmospheric heavy metal deposition in different agro-ecosystems in the HH region

The deposition fluxes in the three agro-ecosystems in the HH area ranged from 4.38 to 36.86 $\mu g\ m^{-2}\ day^{-1}$ for Cr, from 3.75 to 25.37 $\mu g\ m^{-2}\ day^{-1}$ for Ni, from 0.41 to 14.10 $\mu g\ m^{-2}\ day^{-1}$ for As, from 0.48 to 7.26 $\mu g\ m^{-2}\ day^{-1}$ for Cd, and from 9.35 to 64.50 $\mu g\ m^{-2}\ day^{-1}$ for Pb (Table 7). Agro-ecosystems around cement factory had the highest As and Pb deposition fluxes, with averages of 6.96 and 39.94 $\mu g\ m^{-2}\ day^{-1}$, respectively. No remarkable differences in Cr, Ni, and Cd deposition fluxes were observed between the
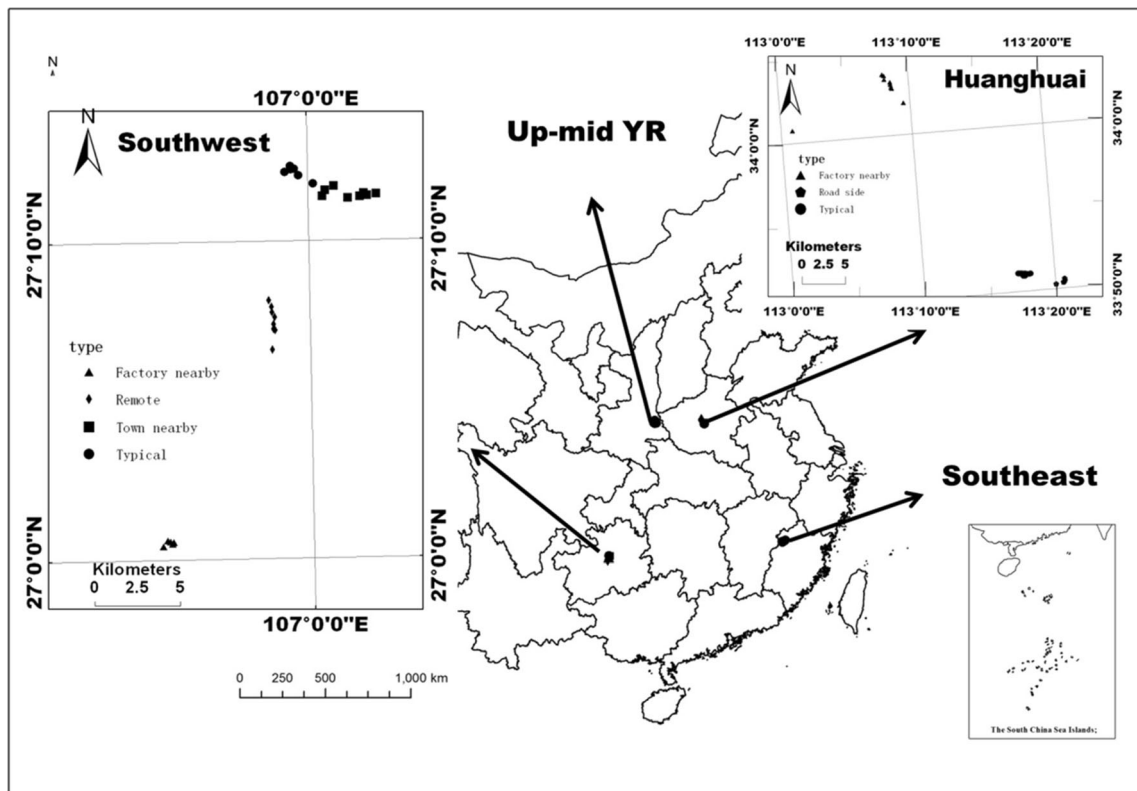


**Fig. 1** The schematic diagram of the distribution of the sampling sites

**Table 4** Atmospheric heavy metal deposition fluxes ($\mu g\ m^{-2}\ day^{-1}$) in typical agro-ecosystems ($n = 32$)

| Indexes | Cr | Ni | As | Cd | Pb |
|---|---|---|---|---|---|
| Mean | 8.30 | 4.25 | 2.02 | 0.73 | 13.07 |
| Median | 3.73 | 1.97 | 1.64 | 0.57 | 9.51 |
| Max | 36.86 | 25.37 | 8.88 | 5.81 | 35.63 |
| Min | 0.60 | 0.65 | 0.05 | 0.12 | 0.43 |
| SD | 9.50 | 5.50 | 1.97 | 1.00 | 10.01 |
| CV (%) | 114.42 | 129.31 | 97.91 | 136.65 | 76.64 |

three agro-ecosystems. These results indicate that in the HH Plain, heavy metal deposition rates are very similar between agro-ecosystems, except for significantly higher Pb and As deposition in the sites around cement factory.

## Correlation between heavy metals in the deposits

Using deposit samples from typical agro-ecosystems, the relationship between the deposition fluxes of different heavy metals was explored (Table 8). The deposition fluxes of Cr, Ni, As, and Pb were significantly positively correlated with each other ($P < 0.01$), which indicated that these metals are derived from similar sources. Significant positive correlations were also observed between the deposition fluxes of Cd-Pb ($r = 0.516$, $P < 0.01$), Cd-Cr ($r = 0.431$, $P < 0.05$), and Cd-Ni ($r = 0.438$, $P < 0.05$); however, these correlation coefficients were relatively low. This suggests that the source of airborne Cd in agro-ecosystems is different from the other metals.

## Airborne Pb isotope composition in agro-ecosystems

### Pb isotope composition of samples from typical agro-ecosystems

Airborne Pb isotope composition varied greatly in the typical agro-ecosystems of the studied regions. Pb isotope ratios for the 32 samples ranged from 0.8463 to 0.8655 for $^{207}Pb/^{206}Pb$ and 2.0528–2.1167 for $^{208}Pb/^{206}Pb$. The average Pb isotope ratios of samples from the SE, SW, HH, and Up-mid YR regions were 0.8547, 0.8593, 0.8512, and 0.8512, respectively, for $^{207}Pb/^{206}Pb$ and 2.1006, 2.0974, 2.0825, and 2.0688, respectively, for $^{208}Pb/^{206}Pb$ (Fig. 2a). Samples from the SW

and SE regions had higher $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios than the other two regions. A scatter plot showed this trend more clearly (Fig. 2b). According to the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ values, the 32 samples could be roughly divided into two clusters. Of the samples from the SW and SE regions, 78.57% had $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ values above 0.850 and 2.08, respectively. For the Up-mid YR and HH regions, however, 88.89% of the samples exhibited $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ values lower than 0.855 and 2.09, respectively.

### Pb isotope composition of samples from different agro-ecosystems in the HH and SW regions

In the SW region, the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios ranged from 0.8538 to 0.8655 and 2.0831–2.1073, respectively, in typical agro-ecosystems, from 0.8364 to 0.8704 and 2.0600–2.1092, respectively, in remote agro-ecosystems, from 0.8418 to 0.8714 and 2.0641–2.1081, respectively, in town nearby agro-ecosystems, and from 0.8500 to 0.8569 and 2.0700–2.0962, respectively, in factory nearby agro-ecosystems (Fig. 3a). The highest variance in Pb isotope composition was observed among samples from remote ecosystems. No obvious differences in $^{207}Pb/^{206}Pb$ ratios were observed between the other three agro-ecosystems. Similar results were obtained in the HH region. Pb isotope ratios in the HH region ranged from 0.8464 to 0.8603 for $^{207}Pb/^{206}Pb$ and from 2.0629 to 2.1287 for $^{208}Pb/^{206}Pb$. The ratios of most samples fell into the ranges of 0.84–0.86 for $^{207}Pb/^{206}Pb$ and 2.06–2.12 for $^{208}Pb/^{206}Pb$. No difference was observed between typical, roadside, and factory nearby agro-ecosystems (Fig. 3b).

## Discussion

### Atmospheric heavy metal deposition in agro-ecosystems in China

With air pollution becoming an unavoidable problem in vast areas of China (Wang et al. 2017), atmospheric heavy metal deposition in agricultural lands has elevated in the past several years (Lei et al. 2009; Wong et al. 2003; Tang et al. 2007; Cong et al. 2008; Lai et al. 2008; Li et al. 2010). The results of developed and industrial areas in China have exhibited a

**Table 5** Atmospheric heavy metal deposition fluxes ($\mu g\ m^{-2}\ day^{-1}$) for typical agro-ecosystems located in different regions

| Regions (samples) | Cr | Ni | As | Cd | Pb |
|---|---|---|---|---|---|
| SW (6) | $3.94 \pm 3.92$ b | $1.51 \pm 0.70$ b | $3.59 \pm 1.00$ a | $0.55 \pm 0.24$ ab | $15.43 \pm 6.85$ b |
| SE (8) | $1.49 \pm 1.08$ b | $1.39 \pm 1.12$ b | $0.12 \pm 0.14$ b | $0.25 \pm 0.28$ b | $3.17 \pm 1.37$ c |
| Up-mid YR (8) | $3.91 \pm 1.05$ b | $1.92 \pm 0.39$ b | $1.01 \pm 0.55$ b | $0.56 \pm 0.16$ ab | $8.65 \pm 2.22$ c |
| HH (10) | $19.43 \pm 9.24$ a | $9.78 \pm 7.02$ a | $3.40 \pm 2.18$ a | $1.35 \pm 1.62$ a | $23.1 \pm 9.69$ a |

Different lowercase letters in the same column indicate significant differences at the $P < 0.05$ level

**Table 6** Heavy metal deposition fluxes ($\mu g\ m^{-2}\ day^{-1}$) for different agro-ecosystems in the SW region

| Agro-ecosystems (samples) | Cr | Ni | As | Cd | Pb |
|---|---|---|---|---|---|
| Typical (6) | 3.94 ± 3.92 ab | 1.51 ± 0.70 a | 3.59 ± 1.00 a | 0.55 ± 0.24 ab | 15.43 ± 6.85 ab |
| Remote (8) | 0.90 ± 0.51 b | 0.85 ± 0.24 a | 1.32 ± 0.56 b | 0.16 ± 0.06 c | 4.59 ± 2.86 c |
| Town nearby (8) | 4.44 ± 3.64 a | 2.99 ± 2.09 a | 3.69 ± 1.44 a | 0.63 ± 0.34 a | 18.84 ± 7.33 a |
| Factory nearby (5) | 1.61 ± 0.45 ab | 1.04 ± 0.26 a | 2.16 ± 0.89 b | 0.32 ± 0.14 bc | 11.22 ± 4.06 b |

Different lowercase letters in the same column indicate significant differences at the $P < 0.05$ level

higher heavy metal deposition of agro-ecosystems than those abroad which were responsible for 43–85% of the total As, Cr, Hg, Ni, and Pb inputs (Lei et al. 2009). Atmospheric heavy metal deposition in agro-ecosystems of undeveloped areas has only been reported in Heilongjiang (Deng et al. 2012) and exhibited a relatively lower deposition fluxes (Table 9). In the present study, using samples from typical agro-ecosystems in the SW, SE, Up-mid YZ, and HH regions, atmospheric heavy metal deposition in agro-ecosystems of non-developed areas was studied on a national scale. The results showed that similar to the results of Deng et al. (2012), the average deposition fluxes of Cr, Ni, As, Cd, and Pb in agro-ecosystems in this study were much lower and only 23.63–49.67% of those in developed zones in China (Table 9). This suggests that great difference exists on the heavy metal deposition in agro-ecosystems of different areas with those in developed zones much higher than those in undeveloped zones. These results are consistent to the previous studies that heavy metal deposition decreased from industrial and urban areas to suburban, agricultural, and rural sites (Pan and Wang 2015; Pandey et al. 2008). Thus, it is necessary to investigate the atmospheric heavy metal deposition of both developed and undeveloped areas to evaluate the influence of air pollution on agro-ecosystems.

## Distribution of atmospheric heavy metal deposition in agro-ecosystems

Apart from the impacts of economic and development, heavy metal deposition has also been found varying widely due to regional characteristics (Zhu et al. 2016). Similar results were observed in this study. Among the four regions studied, heavy metal deposition rates in agro-ecosystems of the HH region with worse air quality (Xu et al. 2016) and higher heavy metal emissions (Wu and Jiang 2011; Wang et al. 2016) were distinctly higher while those of the SE region with better air quality (Xu et al. 2016) were much lower (Table 5). Atmospheric heavy metal deposition in agro-ecosystems is heavily influenced by the local air quality on a national scale which may reflect the impacts of long distance transport of air pollution.

Meanwhile, the impacts of local air quality on heavy metal deposition in agro-ecosystems varied in different regions. In the plain HH regions with bad air quality, the heavy metal deposition rates were similar among different agro-ecosystems except for the sampling sites within 4 km away from a cement factory. In the mountainous SW region, however, deposition rates varied greatly among different agro-ecosystems with the lowest in remote agro-ecosystems for all five elements. Sites around cement factory also exhibited lower deposition rates. These results suggest that in areas with poorer air quality and plain terrain such as central China, atmospheric deposition air quality is a vital factor influencing heavy metal deposition in the agro-ecosystems. In areas with better air quality and mountainous terrain such as SW China, however, heavy metal deposition in agro-ecosystems is more complex. They can be readily confined to certain districts, which not only results in much lower heavy metal deposition in remote regions but also alleviates the influence of industry activities.

Although having better air quality, sampling sites in SW regions still exhibited the highest As deposition among the four regions (Table 5) which may be due to the use of high arsenic coal in Guizhou province (Tian et al. 2015; Wei et al. 2012). Meanwhile, cement factory increased As and Pb deposition rates in agro-ecosystem within 4 km away in the HH region which is consistent with the results of Liu et al. (2014) and Wang et al. (2000). These results suggest that the

**Table 7** Heavy metal deposition fluxes ($\mu g\ m^{-2}\ day^{-1}$) for different agro-ecosystems in the HH region

| Agro-ecosystems (samples) | Cr | Ni | As | Cd | Pb |
|---|---|---|---|---|---|
| Typical (10) | 19.43 ± 9.24a | 9.78 ± 7.02a | 3.40 ± 2.18b | 1.35 ± 1.62a | 23.10 ± 9.69b |
| Road nearby (5) | 10.61 ± 3.35a | 5.15 ± 2.06a | 1.56 ± 1.08b | 0.60 ± 0.16a | 20.39 ± 11.66b |
| Factory nearby (9) | 17.15 ± 8.99a | 8.23 ± 3.14a | 6.96 ± 2.99a | 1.44 ± 2.19a | 39.94 ± 16.00a |

Different lowercase letters in the same column indicate significant differences at the $P < 0.05$ level

**Table 8** Correlation coefficients of heavy metal deposition fluxes in typical agro-ecosystems ($n = 32$)

| Elements | Cr | Ni | As | Cd |
|----------|---------|---------|--------|----|
| Ni | 0.948** | 1 | | |
| As | 0.792** | 0.790** | 1 | |
| Cd | 0.431* | 0.438* | 0.305 | 1 |
| Pb | 0.828** | 0.753** | 0.787** | 0.516** |

**Significant correlation at the $P < 0.01$ level; *significant correlation at the $P < 0.05$ level

influence of local industrial activities on the heavy metal deposition in agro-ecosystems cannot be neglected especially in the SW region with better air quality.

## The sources of airborne heavy metals in agro-ecosystems

Correlation between different metals has been used to speculate the similarity of their sources (Chen et al. 2013; Zhu et al. 2017; Slawomir and Magdalena 2014; Zhang et al. 2015). In this study, there was a high correlation between the deposition fluxes of Cr, Ni, As, and Pb in typical agro-ecosystems. A weak positive relationship was also observed between Cd-Pb, Cd-Cr, and Cd-Ni deposition fluxes. These observations are consistent with the findings for PM2.5 particles (Thomaidis et al. 2003) and for the rainfall in Chinese natural terrestrial ecosystems (Zhu et al. 2016). These results suggest that the airborne Cr, Ni, As, and Pb in the typical agro-ecosystems have similar sources with more complicated sources for Cd.

**Fig. 2** Mean values (**a**) and scatter plot (**b**) of Pb isotope ratio of deposits from typical agro-ecosystems in different regions
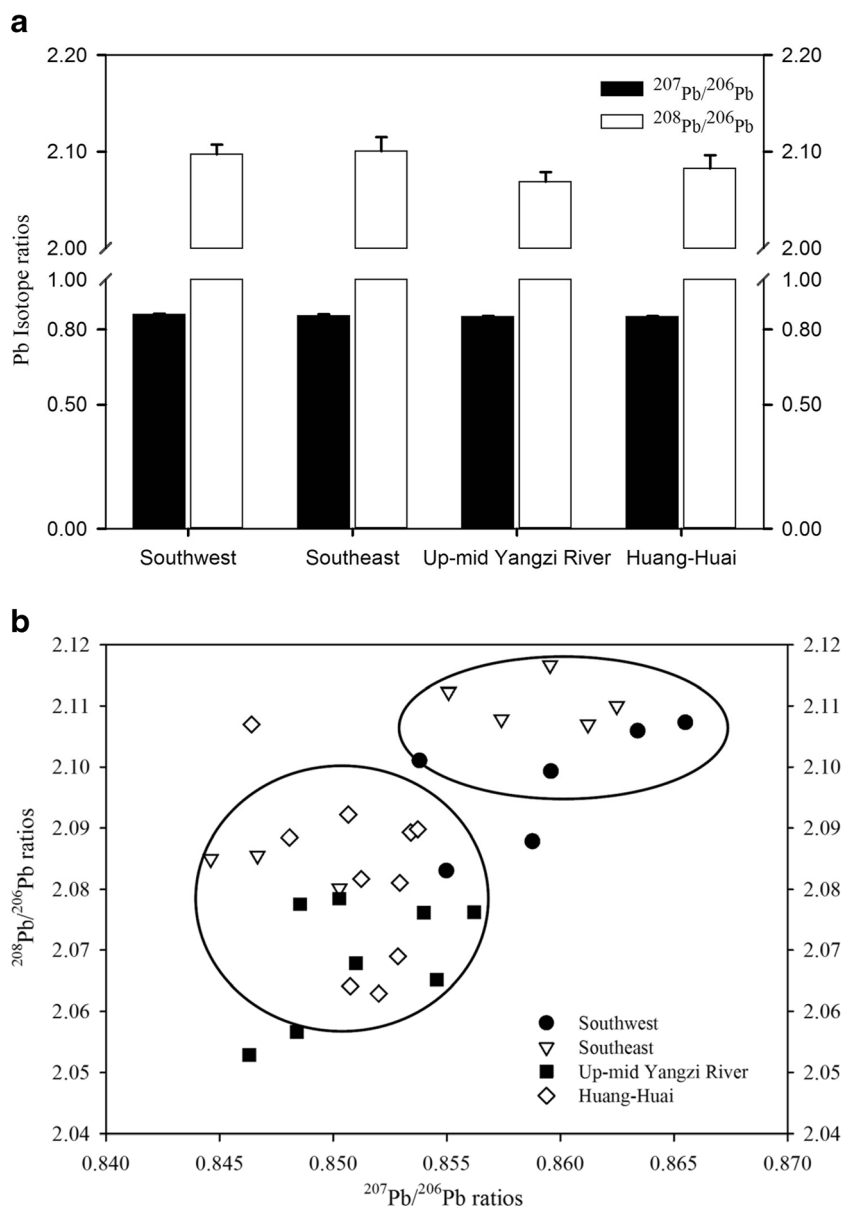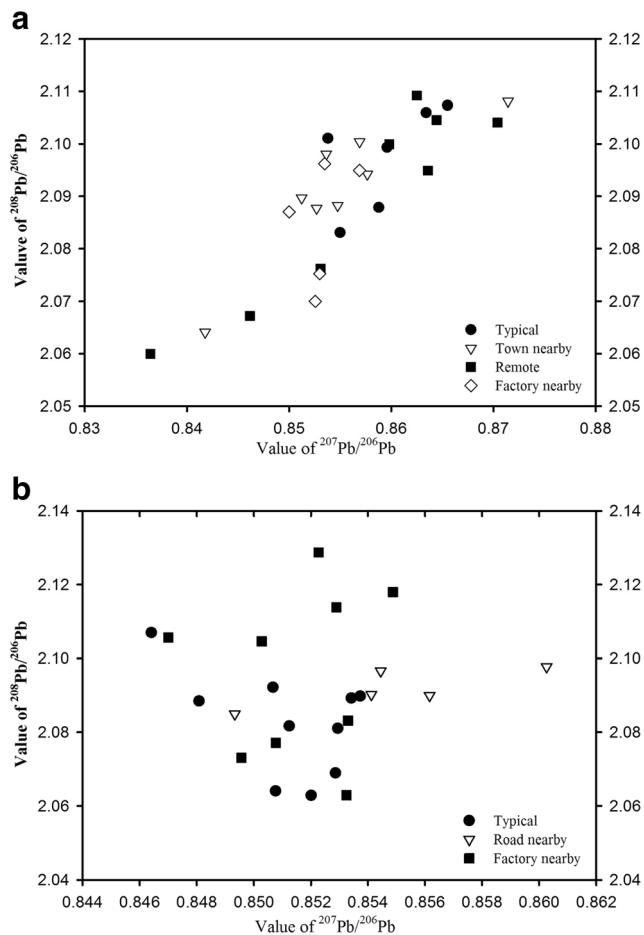
**Fig. 3** $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios of samples from different agro-ecosystems in SW (**a**) and HH (**b**) regions

Accurate identification of heavy metal sources in the atmosphere is critical to their control. With specific isotopic composition or fingerprint, Pb isotopic signature has been considered an ideal tool for tracing sources of air pollution (Kurkjian et al. 2002; Mukai et al. 2001; Pandey et al. 2008; Li et al. 2012; Sherman et al. 2015). Air deposits from different sources show different Pb isotope characteristics (Bi et al. 2007; Chen et al. 2005; Mukai et al. 2001). In this study, samples from typical agro-ecosystems of the SW and SE regions exhibited different Pb isotopic composition from those of the HH and Up-mid YR regions which disclosed different sources of air pollution. Case studies of HH and SW regions exhibited similar tendency. The $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios of most samples from the SW region ranged from 0.85 to 0.87 and 2.060–2.109, respectively (Fig. 3). The former ratios were higher than those observed for local smelting and lower than those for vehicle exhausts, and the latter ones were similar to the ratios observed for local smelting (Bi et al. 2007; Chen et al. 2005). This is consistent with the findings of Hu et al. (2005) who found that the heavy metals in rainwater in Guiyang city were predominantly derived from coal burning and vehicle exhaust. Nevertheless, the $^{207}Pb/^{206}Pb$ ratios of

**Table 9** Reported atmospheric heavy metal deposition fluxes in agricultural fields in China (μg m⁻² day⁻¹)

| Elements | Chengdu Economic Region | Beijing Plain | Taiyuan Basin | Ganman County, Heilongjiang | Southern Plain, Hebei | Pearl River Delta | Agro-ecosystem in HH, SW, SE, and Up-mid YZ regions |
|---|---|---|---|---|---|---|---|
| As | 7.59 | 7.94 | 15.17 | 2.99 | 8.68 | – | 2.02 (0.05–8.88) |
| Cd | 4.85 | 0.65 | 1.20 | 0.40 | 2.34 | – | 0.73 (0.12–5.81) |
| Cr | – | 32.46 | – | 19.96 | 42.86 | 17.61 | 8.30 (0.60–36.86) |
| Ni | – | 18.08 | – | 8.74 | 19.83 | – | 7.39 (0.65–25.37) |
| Pb | 125.83 | 60.23 | 84.81 | 21.53 | 83.49 | 34.74 | 13.07 (0.43–35.63) |
| Sources | Tang et al. (2007) | Cong et al. (2008) | Lai et al. (2008) | Deng et al. (2012) | Li et al. (2010) | Wong et al. (2003) | This study |

most samples from the HH region ranged from 0.84 to 0.86 which was similar to those derived from northern Chinese coal (Mukai et al. 2001). Therefore, airborne Pb in the agro-ecosystems of the SW region is mainly derived from vehicle and local smelting, while that of the HH area is mainly derived from northern Chinese coal.

## Conclusions

The atmospheric heavy metal deposition in agro-ecosystems was observed for four natural regions in China. On a national scale, the spatial distribution of Pb, Cd, As, Cr, and Ni deposition rates in agro-ecosystems was found to be consistent with air quality. The variation of heavy metal deposition rates among different agro-ecosystems within the same regions is dependent on both local air quality and topographic features. In the plain regions with bad air quality such as central China, air quality is a vital factor controlling heavy metal deposition in agro-ecosystems. In the mountainous regions with good air quality such as southwest China, however, topographic features play more important role which not only led to much lower heavy metal deposition fluxes in remote regions but also alleviated the influence of pollution sources. Airborne Pb in SW agro-ecosystems was mainly derived from vehicle exhaust and local smelting, whereas that in the HH region from burning of northern Chinese coal.

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