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Short communication

Impacts of human activity modes and climate on heavy metal “spread” in groundwater are biased

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HIGHLIGHTS

- We examined how different groundwater heavy metals responded to human activity modes.
- We assessed the influences of climate change on groundwater heavy metal.
- Impacts of human and climate on heavy metal “spread” in groundwater are biased.

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ABSTRACT

Groundwater quality deterioration has attracted world-wide concerns due to its importance for human water supply. Although more and more studies have shown that human activities and climate are changing the groundwater status, an investigation on how different groundwater heavy metals respond to human activity modes (e.g. mining, waste disposal, agriculture, sewage effluent and complex activity) in a varying climate has been lacking. Here, for each of six heavy metals (i.e. Fe, Zn, Mn, Pb, Cd and Cu) in groundwater, we use >330 data points together with mixed-effect models to indicate that (i) human activity modes significantly influence the Cu and Mn but not Zn, Fe, Pb and Cd levels, and (ii) annual mean temperature (AMT) only significantly influences Cu and Pb levels, while annual precipitation (AP) only significantly affects Fe, Cu and Mn levels. Given these differences, we suggest that the impacts of human activity modes and climate on heavy metal “spread” in groundwater are biased.

1. Introduction

Groundwater quality has been a focus of research because hazardous substances such as heavy metals presented in groundwater can enter the food chain and ultimately harm aquatic organisms and human beings (Järup, 2003; Nouri et al., 2008; Zeng et al., 2013). For hydrosphere, about 13–30% of the total volume of freshwater is groundwater (Dragoni and Sukhija, 2008), which is the source of drinking water for over 50% of the world's population. Thus, the increase of heavy metal contents in groundwater would pose potential threats to human health and survival (Hofmann et al., 2015; Zhang et al., 2015). Also, groundwater is being influenced by climate change (Kløve et al., 2014). There are few studies focused on the variations of heavy metal levels in groundwater under climate change, although it was previously suggested that groundwater quality was related to climate change (Alley, 2001). Dragoni and Sukhija (2008) pointed out that we should not overlook the effect of climate change on groundwater quality. Groundwater management and protection requires sufficient information on the response of groundwater to human activities and climate change.

It has been a major challenge in groundwater studies in

Abbreviations: AMT, annual mean temperature; AP, annual precipitation; AIC, akaike information criterion; Cd, cadmium; Cu, copper; Mn, manganese; Pb, lead; Zn, zinc; Fe, iron.

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revealing variation of groundwater quality in response to human activities and climate change due to human-activity diversity and environmental complexity. Fortunately, an effective approach, named mixed-effect model, has been proposed to account for data dependence, data stratification and relatedness (Korte et al., 2012; Whitehorn et al., 2012; Zhou and Stephens, 2012). It has gained its popularity through a wide range of applications, such as genome-wide association (Korte et al., 2012), biodiversity (Patiño et al., 2013), pharmacogenomics and cancer (Im et al., 2012), health (De Onis et al., 2012), and ecology (Whitehorn et al., 2012). The mixed-effect model not only considers the fixed effect, but also includes random effect. In this study, human activity modes, climate variables and soil properties were identified as fixed effects, while sampled sites were deemed as random effects.

2. Materials and methods

We searched the Google Scholar and the Web of Science by keywords of "groundwater heavy metal", "groundwater quality" and "ground water heavy metal" in March 2015, and found over 1000 matched records. We assembled six large datasets comprising 45 publications selected from over 1000 documents. The datasets include Fe, Pb, Cu, Cd and Mn. We retained only groundwater heavy metal data for which dominant human activities were known along the groundwater. The groundwater with geographical location information (namely longitude and latitude) being unclear was not considered. Groundwater with known geographical information and heavy metal levels was also excluded if their climate data could not be extracted from WorldClim (http://www.worldclim.org). Regarding groundwater heavy metals, we recorded the concentrations of six main heavy metals (Fe, Zn, Cd, Cu, Pb and Mn). In cases where dominant human activity was unknown, it was excluded from the initial assembled data set, so that many data became unavailable. Finally, a total of 349 data points from 26 sites for Fe, 551 data points from 37 sites for Zn, 331 data points from 29 sites for Cd, 515 data points from 37 sites for Cu, 355 data points from 35 sites for Pb, and 356 data points from 28 sites for Mn were adopted. All units for heavy metal concentrations (levels) were converted to $\mu g\ L^{-1}$.

We used long-term climate data (1950–2000) to represent the climate conditions of a site, namely mean annual temperature (AMT) and annual precipitation (AP). AMT and AP were extracted from WorldClim (http://www.worldclim.org/). Data on subsoil pH and subsoil bulk density were extracted from Regridded Harmonized World Soil Database v1.2 (FAO-2012; Wieder et al., 2014). In a few of cases, subsoil pH and subsoil bulk density of some sites were unknown. We used data from soils adjacent to these sites.

2.1. Kruskall-Wallis tests

The difference between heavy metal concentrations (levels) in groundwater affected by mining, waste disposal, sewage effluent, agriculture and complex activity was identified through Kruskall-Wallis tests.

2.2. Mixed-effect models

Mixed-effect model refers to the model consisting of the mixture of random effects and fixed effects (Baayen et al., 2008; Winter 2013; Bates et al., 2014). It is useful for the data that is unbalanced and repeatedly measured. Random effect is the probabilistic part of a mixed-effect model related to individual experimental units obtained randomly from a population, while fixed effect is the fixed part of a mixed-effect model.

To reveal how human activity modes and climate influence groundwater heavy metal concentrations (levels), we have adopted a mixed-effect model to address both the fixed and mixed effects (Bates, 2010; Korte et al., 2012; Bates et al., 2014):

$$\boldsymbol{y} = \mathbf{X}\boldsymbol{\beta} + \mathbf{Zb} + \mathbf{e} \tag{1}$$

where $\mathbf{y}$ is a $n \times 1$ vector of response variables, $\boldsymbol{\beta}$ refers to a $p \times 1$ vector of fixed-effect parameters, $\mathbf{X}$ and $\mathbf{Z}$ represent two model matrices, $\mathbf{b}$ is the random-effect vector and $\mathbf{e}$ is a $n \times 1$ vector of error terms that is not explained by the model.

In this study, human activity modes, climate variables and soil properties were identified as fixed effects, while sampled sites were identified as random effects. It should be noted that the predictors (including AMT, AP, subsoil pH and subsoil bulk density) were kept as control variables, and human activity modes were kept as test variable when examining the impact of human activity modes on groundwater heavy metals in mixed-effect models. Analogously, human activity modes and non-test variables were considered as control variables if the test variable was a climate variable.

Akaike information criterion (AIC) is calculated according to the following formula (Akaike, 1974):

$$\mathrm{AIC} = 2k - 2\ln(L) \tag{2}$$

where L is the likelihood function and k is the number of estimated parameters. A model with a smaller AIC value means a better fit.

Conditional R^2 that gives the variance explained by both fixed effect and random effect was calculated following the previous works (Nakagawa and Schielzeth, 2013; Johnson, 2014).

3. Results and discussion

3.1. Impact of human activity modes on heavy metal levels in groundwater

Here, we showed that human activity modes significantly influenced Cu ($\chi^2(4) = 16.48$, $p < 0.01$) and Mn ($\chi^2(4) = 9.92$, $p < 0.05$) levels in groundwater (Table 1). AIC results also indirectly supported this conclusion (Fig. 2), showing that the full models with human activity modes as predictor had smaller AIC than the reduced model without human activity modes (749.66 vs. 758.14 for Cu and 824.77 vs. 826.68 for Mn). A consistent finding for these

Table 1
Mixed-effect models for heavy metals in groundwater.

Model			Zn			Cd			Fe			Cu			Pb			Mn		
	Fixed effects	Random																		
Test variable	Control variables	Variable	χ^2	Df	p	χ^2	Df	p	χ^2	Df	p	χ^2	Df	p	χ^2	Df	p	χ^2	Df	p
HAM[a]	AMT, AP, pH, bulk density	Site	4.16	4	>0.05	7.04	4	>0.05	8.06	4	>0.05	16.48	4	<0.01	5.74	4	>0.05	9.92	4	<0.05
AMT	HAM[a], AP, pH, bulk density	Site	3.43	1	>0.05	2.31	1	>0.05	2.53	1	>0.05	19.57	1	<0.01	9.91	1	<0.01	0.73	1	>0.05
AP	HAM[a], AMT, pH, bulk density	Site	1.56	1	>0.05	0.62	1	>0.05	6.33	1	<0.05	5.44	1	<0.05	1.13	1	>0.05	6.26	1	<0.05

Note: [a] refers to human activity modes; AMT and AP denote annual mean temperature and annual precipitation, respectively; Df denotes degrees of freedom.

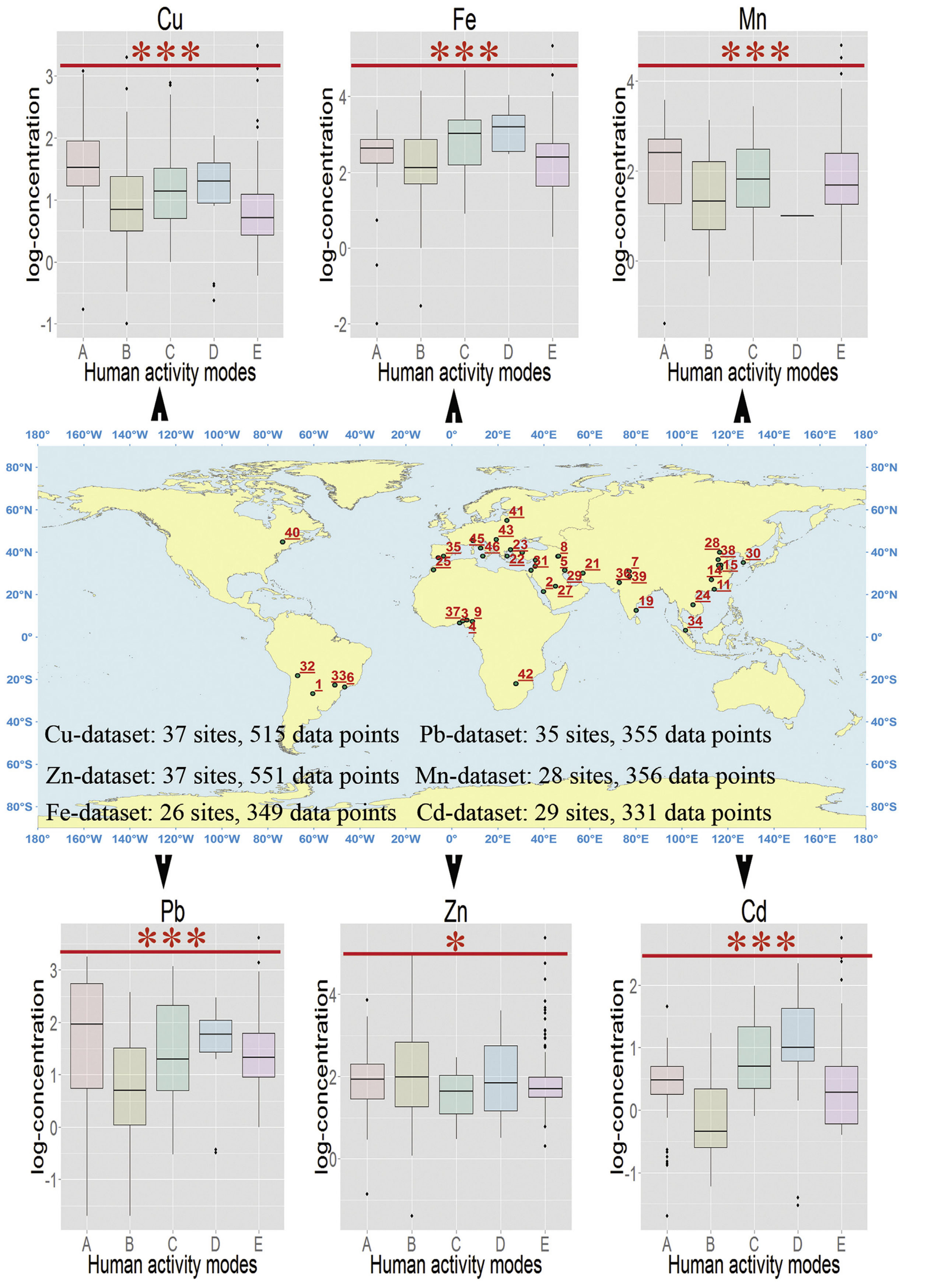

Fig. 1. Groundwater site distribution in this study and human activity modes (A, agriculture; B, complex activity; C, waste disposal; D, sewage effluent; E, mining) occurring along the groundwater. "*", $p < 0.05$; "***", <0.001.

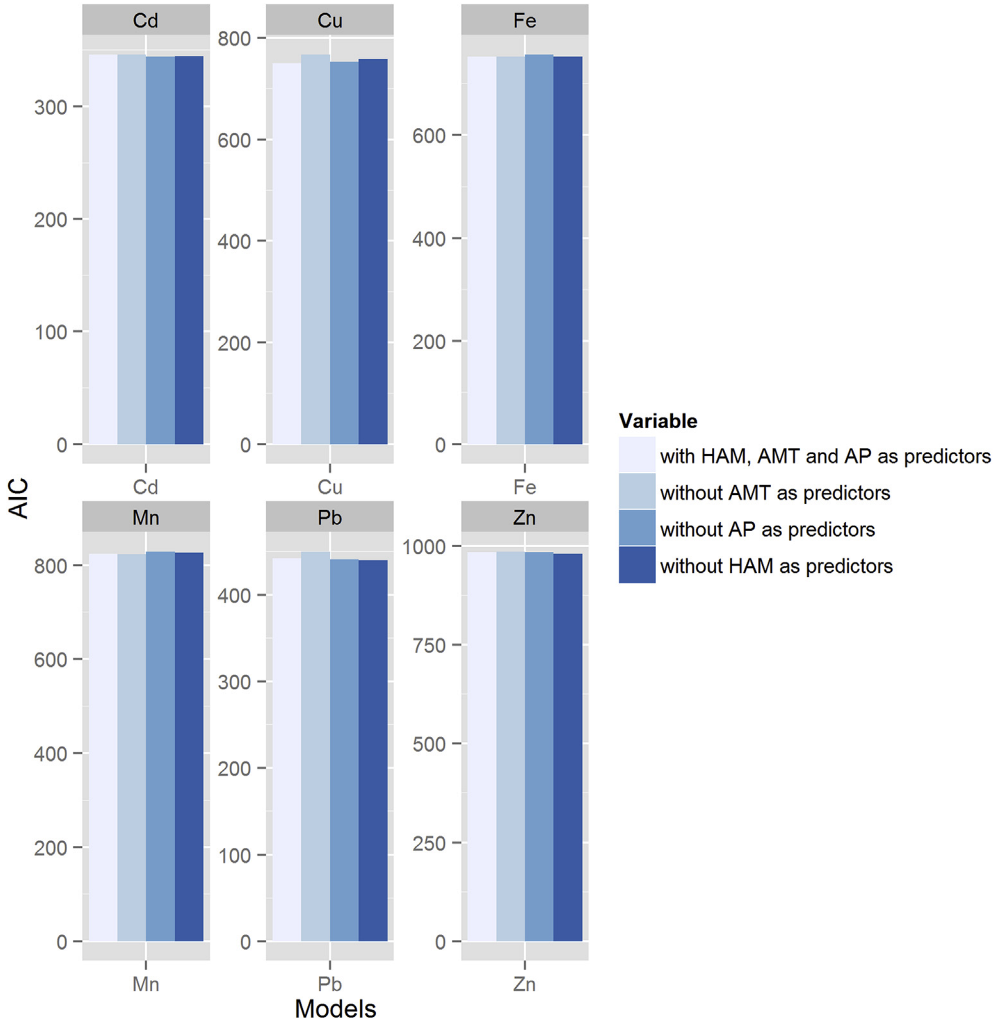

Fig. 2. Akaike information criterion (AIC) for the mixed-effect models of Zn, Cd, Fe, Cu, Pb and Mn that include human activity modes (mining, waste disposal, agriculture, sewage effluent and complex activity) as fixed effects and site as random effect.

two heavy metals was that their mean concentrations were the highest in agriculture-affected groundwater (mean concentrations: 45.63095 μg L^{-1} for Cu and 97.3953 μg L^{-1} for Mn). The previous studies have shown that the concentrations of groundwater heavy metal could be elevated due to agricultural activities (Ramesh and Elango, 2012; Ağca et al., 2014; Wongsasuluk et al., 2014). Different from Cu and Mn levels, Fe ($\chi^2(4) = 8.06$, $p > 0.05$), Pb ($\chi^2(4) = 5.74$, $p > 0.05$), Cd ($\chi^2(4) = 7.04$, $p > 0.05$) and Zn ($\chi^2(4) = 4.16$, $p > 0.05$) levels were not significantly disturbed by human activity modes. AIC's comparison between models with human activity modes as a predictor and those without human activity modes for these four heavy metals demonstrated that models without human activity modes generally fitted better than those with human activity modes except for the models for Fe where AIC of model without human activity modes was slightly higher than that of model with human activity modes (752.42 vs. 752.36).

Distinctive effects of human activity modes on different heavy metals in groundwater reflected bias of human activity modes towards significant influences on Cu and Mn levels rather than Zn, Cd, Pb and Fe ones. Such a bias might be derived from the fact that the present human activity modes significantly interfered with the transfer of Cu and Mn between groundwater and its surrounding environment, but this interference was not significant for Zn, Fe, Pb and Cd. There were significant differences in Zn ($p < 0.05$), Cd ($p < 0.001$), Fe ($p < 0.001$), Cu ($p < 0.001$), Pb ($p < 0.001$) and Mn ($p < 0.001$) concentrations between all analyzed human activity modes based on Kruskall-Wallis tests (Fig. 1), respectively, suggesting that mining, waste disposal, agriculture, sewage effluent and complex activity had different effects on groundwater heavy metal levels. Mining has a profound effect on local groundwater quality, making the surrounding groundwater being more enriched in heavy metals (El Khalil et al., 2008). Wastewater containing heavy metal and harmful chemicals from many industries discharge may seep into the groundwater (Rattan et al., 2005). With excess heavy metals, the groundwater would directly threaten human health through oral intake or dermal exposure.

Heavy metal contamination of groundwater is one of the most urgent issues today (Schwarzenbach et al., 2006), mainly resulting from anthropogenic activities (Rattan et al., 2005; Leung and Jiao, 2006; El Khalil et al., 2008; Bakis and Tuncan, 2011; Ağca et al., 2014; Wongsasuluk et al., 2014; Hofmann et al., 2015). Many studies have investigated the variations of heavy metals in groundwater in response to each of these human activities, but few have accounted for the overall effect of these activities. Here, using six standardized data sets from multiple countries and areas (Fig. 1 and Figs. S1–S6), we examined how different groundwater heavy metals responded to human activity modes under climate change. Our assembled datasets comprised 349 data points for Fe, 551 data

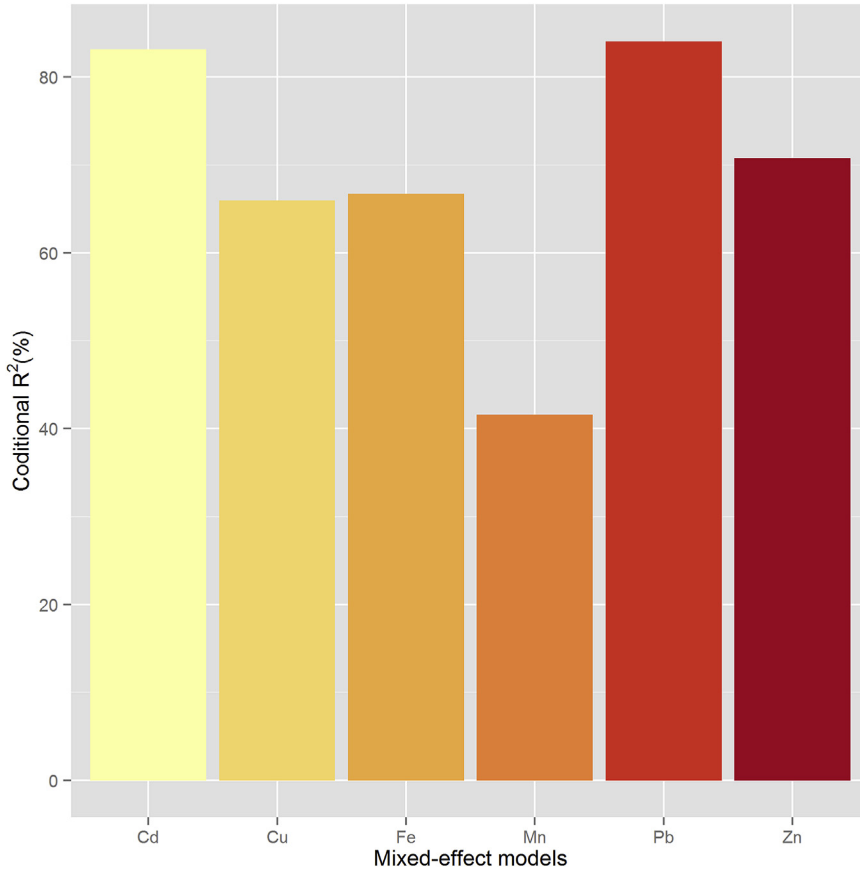

Fig. 3. Conditional R^2 for the mixed-effect models of Zn, Cd, Fe, Cu, Pb and Mn that include human activity modes (mining, waste disposal, agriculture, sewage effluent and complex activity) as fixed effects and site as random effect.

points for Zn, 356 data points for Mn, 355 data points for Pb, 331 data points for Cd, 515 data points for Cu, respectively. Human activities are highly complex. Human activity modes that significantly affect groundwater quality mainly include agriculture, sewage effluent, mining, waste disposal (including landfill and solid waste disposal), and other industrial and urban activities. Although sewage effluent, mining and waste disposal were associated with the development of industry and urbanization, they were identified as single activity due to their strong effects on groundwater quality (El Khalil et al., 2008; Bakis and Tuncan, 2011). Groundwater is often disturbed by several human activities simultaneously. Among these activities, there is often a dominant activity that acts as a key factor influencing groundwater quality. To determine their varying effect on groundwater quality, we used the dominant activity to represent human activities occurring along the surroundings of groundwater. However, in some cases, dominant activity was difficult to identify. For example, the ongoing urbanization was often accompanied by the development of industry. In addition, urbanization and industrialization themselves were composed of many sub-activities. In this regard, we termed the dominant activity as complex activity. That is, complex activity = urbanization or industrialization or (urbanization + industrialization) or (urbanization + industrialization + other). It should be noted that, agricultural activity was not considered as complex activity in this study because agricultural activity was relatively simple as compared to urbanization and industrialization.

3.2. Impact of climate on heavy metal levels in groundwater

No significant influence was found for AMT on Zn ($\chi^2(1) = 3.43$, $p > 0.05$), Cd ($\chi^2(1) = 2.31$, $p > 0.05$), Fe ($\chi^2(1) = 2.53$, $p > 0.05$) and Mn ($\chi^2(1) = 0.73$, $p > 0.05$) levels in human-disturbed groundwater. Cu ($\chi^2(1) = 19.57$, $p < 0.01$) and Pb ($\chi^2(1) = 9.91$, $p < 0.01$), by contrast, were significantly affected by AMT in groundwater (Table 1). Hence, AMT showed a significant bias toward Cu and Pb levels but against Zn, Cd, Fe and Mn levels. AIC analyses for Cu and Pb showed that the models with AMT as predictor generated smaller AIC values than those without AMT (Fig. 2), suggesting that the models with AMT fitted better than those without AMT. AP's effects on groundwater heavy metals were wider than AMT, because more heavy metal types were influenced by AP in groundwater, including Fe ($\chi^2(1) = 6.33$, $p < 0.05$), Cu ($\chi^2(1) = 5.44$, $p < 0.05$) and Mn ($\chi^2(1) = 6.26$, $p < 0.05$). There were no significant influences for AP on Zn ($\chi^2(1) = 1.56$, $p > 0.05$), Cd ($\chi^2(1) = 0.62$, $p > 0.05$) and Pb ($\chi^2(1) = 1.13$, $p > 0.05$). AP factor's effect on these heavy metal levels was estimated using AIC. The analyses for Fe, Cu and Mn showed that models with AP as a predictor produced smaller AIC values than those without AP, while the analyses for Zn, Cd and Pb indicated an opposite observation, suggesting that AP's biased impacts on heavy metal levels were valid for groundwater. Water quality deteriorations caused by climate change have more profound effects on human and ecosystem than groundwater recharge fluctuation, and thus should receive more attentions.

Climate is changing and will continue to change in the future (Dragoni and Sukhija, 2008). Anthropogenic activities such as the release of CO_2 are accelerating global warming and affecting the hydrological cycle (Maxwell and Kollet, 2008). Several studies were made in groundwater at a regional scale, such as Ontario (Jyrkama and Sykes, 2007) and Belgium (Brouyere et al., 2004) or at a global scale (Doll, 2009). Clearly, these studies are restricted to the influence of climate change on groundwater recharge and levels (Santos et al., 2014). It remains largely unclear how the climate change influences the heavy metal levels in groundwater. In this study, we assessed the influences of climate change on groundwater heavy metal concentrations (levels) using the mixed-effect models. Our results showed that bias was also presented for climate's effects on groundwater heavy metal levels, which was consistent with human activity modes. Kløve et al. (2014) had reviewed the influence of climate on groundwater quality. Climate change could cause the variations in groundwater recharge and levels, and further resulted in groundwater quality changes. For example, increased groundwater recharge might lead to increased risks of leaching of pollutants to groundwater system (Taylor et al., 2013; Kløve et al., 2014).

It should be noted that soil properties (including subsoil pH and subsoil bulk density) were always included in our model whatever the test variables were, because groundwater was close to the soils whose properties were potential factors affecting groundwater quality. Other soil properties were omitted in our model due to shortage of data. For example, data on soil heavy metal contents that may affect groundwater heavy metal levels was unavailable. Such a problem makes it difficult to include all factors related to groundwater in our model. Data unavailability also restricted the assembly of larger-scale datasets. Due to the inherent limitation, our model might not be a perfect version, but was statistically reliable. Our mixed-effect models including human activity modes, AMT, AP, subsoil pH, subsoil bulk density and site explained 70.77% of the variability in Zn concentrations (log-scale), 83.14% in Cd concentrations (log-scale), 66.74% in Fe concentrations (log-scale), 65.96% in Cu concentrations (log-scale), 84.05% in Pb concentrations (log-scale) and 41.60% in Mn concentrations (log-scale) (Fig. 3) based on conditional R^2 (Nakagawa and Schielzeth, 2013; Johnson, 2014). Our results revealed the real presence of bias for the effects of human activity modes and climate on groundwater heavy metal “spread”. Although human activity modes and climate only significantly affect a part of heavy metals in groundwater, it does not mean that we no longer need to keep a cautious eye on those heavy metals that were not significantly influenced. Furthermore, finding the linkage between groundwater quality and human activities as well as climate change is vital to the sustainable use of groundwater. Thus, the present work is also helpful in groundwater health risk assessment, pollution prevention and resources management.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.03.046.

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