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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

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*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):

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

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 | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fixed effects | Random | Zn | | | Cd | | | Fe | | | Cu | | | Pb | | | Mn | | |
| Test variable | Control variables | Variable | $\chi^2$ | Df | p | $\chi^2$ | Df | p | $\chi^2$ | Df | p | $\chi^2$ | Df | p | $\chi^2$ | Df | p | $\chi^2$ | 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.