Analysis of the spatial and temporal characteristics and sources of heavy metal pollution in arable soils in rapidly urbanizing cities in western China

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Abstract

For the purpose of heavy metals' spatial-temporal trends and source allocation in arable soil with the rapid urbanization in Western China, samples were collected in two stages (2008 and 2017) in Chengdu city which was chosen for the case study. Positive Matrix Factorization (PMF) receptor models and Multivariate statistical analysis were used to understand the heavy metals' spatial-temporal variability. The results showed that Cd, Cr, and As in arable soil were presented with an increasing trend during the 10-year period. Semi-variation analysis showed that the block basis ratios of the five heavy metals (Pb, As, Cr, Hg, and Cd) showed an increasing trend, which suggests that the spatial distribution of heavy metals in arable soil is more influenced by human disturbances. The source analysis shows that the enrichment of As is closely related to agricultural activities in both phases (2008 and 2017). Further source analysis showed that source of As did not change, but the contribution increased significantly. The main sources of Hg pollution changed from agricultural activities to medical equipment manufacturing, Cd changed from soil parent material sources to chemical industry waste emissions, and the sources of Pb and Cr expanded from single transportation sources to multiple sources such as road traffic and human construction. In this study, the examining of the temporal and spatial patterns of heavy metal contamination in farmland of typical rapidly developing cities in China can also provide a basis for the conservation and management of arable soil in similar areas in the context of rapid urbanization in China.

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Abstract: For the purpose of heavy metals' spatial-temporal trends and source allocation in arable soil with the rapid urbanization in Western China, samples were collected in two stages (2008 and 2017) in Chengdu city which was chosen for the case study. Positive Matrix Factorization (PMF) receptor models and Multivariate statistical analysis were used to understand the heavy metals' spatial-temporal variability. The results showed that Cd, Cr, and As in arable soil were presented with an increasing trend during the 10-year period. Semi-variation analysis showed that the block basis ratios of the five heavy metals (Pb, As, Cr, Hg, and Cd) showed an increasing trend, which suggests that the spatial distribution of heavy metals in arable soil is more influenced by human disturbances. The source analysis shows that the enrichment of As is closely related to agricultural activities in both phases (2008 and 2017). Further source analysis showed that source of As did not change, but the contribution increased significantly. The main sources of Hg pollution changed from agricultural activities to medical equipment manufacturing, Cd changed from soil parent material sources to chemical industry waste emissions, and the sources of Pb and Cr expanded from single transportation sources to multiple sources such as road traffic and human construction. In this study, the examining of the temporal and spatial patterns of heavy metal contamination in farmland of typical rapidly developing cities in China can also provide a basis for the conservation and management of arable soil in similar areas in the context of rapid urbanization in China.

Keywords: arable soil; heavy metals; spatial and temporal variability; source analysis

1. Introduction

Agricultural land is the material basis and source of wealth for human survival and development, as well as an important site for the migration, transformation, and deposition of heavy metals. Over the past decades, China's rapid urbanization and industrialization have generated significant emissions of heavy metal pollutants, and the accumulated heavy metals are transformed into organic complexes through organisms in the soil, which are persistent, non-degradable and bioaccumulative, posing a serious threat to the health of urban and rural habitats and the ecological and environmental security of agricultural land.(Dai et al., 2018; Zang et al., 2017) It poses a serious threat to the environmental health of urban and rural people and the ecological safety of agricultural land. Due to the rigidity of the demand for food and agricultural products caused by the huge population in China, agricultural production has to rely on intensive farming and high rates of fertilizer and pesticide application to ensure yield, thus causing a decline in the quality of agricultural land and a further increase of risk of heavy metal contamination in the soil.(Shang, Xu, Zhang, & Huang, 2018; G. Wang et al., 2017) About 10% of China's arable soils are contaminated with heavy metals to varying degrees, according to research findings, and the exceedance rate of heavy metals in arable soils in the main grain-producing regions of China is 21.49%, which is highly concentrated in urban areas, especially in the peripheral urban agricultural areas where pollution is relatively low.(Chabukdhara & Nema, 2013; Shang et al., 2018; Q. Yang et al., 2018) The rate of exceedance was 21.49% and was highly concentrated in urban areas, especially in agricultural areas in the periphery of cities with relatively low pollution.

While arable soil in the urban periphery play an important role in providing a daily supply of agricultural products for residents and in the health of urban and rural ecosystems, the level of heavy metal contamination in arable soil is directly related to food safety and the well-being of agroecosystems.(Fujita et al., 2014; Lu & Yu, 2018) Therefore, the potential heavy metal contamination in peri-urban agricultural land has become an important challenge in the rapid urbanization process in China, and its changes in content, sources, and spatial and temporal distribution patterns should be of great concern.

At present, studies on heavy metals in arable soil mainly focus on content characteristics, spatial distribution, pollution level, source analysis, and health risks.(Dong et al., 2019; Ismail Umer, Younis Fatah, Ramadhan Abdo, Abdulaziz Karim, & Nabil Abdulrahman, 2021; Mapani et al., 2010) The spatial pattern of soil heavy metals is largely caused by present and past human activities, such as industrial agriculture, due to their significant cumulative nature.(Y. Wang, Duan, & Wang, 2020) . Therefore, the application of multi-period heavy metal content measurement, spatial and temporal variation analysis of pollution, and pollution source analysis can more accurately reveal sources and spatial and temporal distribution patterns of heavy metal pollution in soils, and can effectively curb the deteriorating trend of soil pollution(H. Y. Chen, Teng, Wang, Song, & Zuo, 2013) It can effectively curb the deterioration of soil pollution. The study of spatial and temporal variability of soil heavy metal pollution can be carried out by comparing spatial interpolation maps of different periods based on geostatistical methods through GIS characterization.(X. Li et al., 2012; Y. Yang, Wu, & Christakos, 2015) Heavy metal spatial variability can be studied by GIS characterization and geostatistical method comparing spatial interpolation maps in different periods. Soil heavy metal pollution source analysis methods include the Emission inventory method, Chemical massbalance (CMB) in receptor model, Hybrid approach, Positive Matrix Factorization (PMF), UN-MIX model, etc.(Lang, Li, Wang, & Peng, 2015; Y. Liu, Liu, Yousaf, Zhang, & Zhou, 2020; Wu, Li, Teng, Chen, & Wang, 2020) Among them, PMF was first used for source of atmospheric airborne particulate matter analysis in the 1990s, and in recent years it has also been widely used for soil analysis.(Tan et al., 2016) It is a new and effective method for source analysis of heavy metals, which is easy to operate and effective in identifying the sources and assigning their contribution to each heavy metal.(Chai et al., 2021) It is a simple and effective method to analyze source heavy metals.

Chengdu is a central city in western China and a typical representative of the fast-growing cities in China in recent years. At the same time, as an important food and agriculture production base in China, it also carries the important responsibility of food security in China. However, there are still ecological risks of soil heavy metals in this region. Numerous scholars have conducted studies to assess the pollution of cultivated soils in Chengdu.(Pang, Li, Zhang, Wang, & Yu, 2011; S, H, Q, Y, & H, 2013) .However, current studies on soil contamination in the region are mainly limited to specific administrative regions, specific periods, or specific soil use types, while there are relatively few systematic studies on the levels, sources, spatial and temporal patterns of hazardous metals on agricultural land in different urban circles in the context of rapid urbanization. The Chinese government has proposed a strategy to build the Chengdu-Chongqing City Cluster to guide the growth of west China and to boost the integration and interplay with the 'Belt and Road' and Yangtze River Economic Belt construction strategies. The research can give useful direction to the development of relevant policies. In addition, the study of heavy metal contamination in arable soils in Chengdu will not only improve the understanding of arable soils in the Yangtze River upstream area, but also provide a basis for arable soil conservation and management in the rapidly urbanizing areas of China.

The primary goals from the study were to (1) analyze the spatial and temporal patterns of soil heavy metal contamination in farmlands of typical rapidly developing cities in China; and (2) analyze causes and effects between soil pollution sources and soil pollution and environmental variables in agricultural fields of different circles of rapidly developing cities. We hypothesize that "rapid urban development and human activities are the key drivers of increasing soil heavy metal pollution over time and space" in the study area. Management decisions require a process-based analysis of pollution sources and capture key factors in terms of their spatial and temporal dimensions.

2. Materials and methods

2.1. study area

Chengdu is a key hub city in China's west, located in the hinterland the Chengdu Plain. The area is mainly formed by the alluvium of Minjiang River, Tuojiang River and its tributaries, and some gullies and valleys, and the soil-forming parent material is mainly gray alluvium of Hori River and gray-brown alluvium of Tuojiang River in the primary terrace, and ice carbon and ice water sediment in the old alluvium of the Fourth Pleistocene in the secondary and tertiary terraces, with flat terrain, fertile soil and various parent materials, and rice soils and purple soils are the main types of soil. (Figure 1). The area is dominated by a humid monsoon climate in the subtropics, with an average annual population of 15.2-16.5°C and 900-1300 mm of precipitation correspondingly, making it a major production base for agricultural products such as grain and fruits in the Sichuan basin (Zhang et al., 1999; Hu et al., 2004; Huang, 2011).

2.2. sample collection and analysis

Samples of soils were sampled in September 2008 and September 2017, respectively. Sampling points were set up according to the distance from the central city and the economic development, which were divided into suburban, suburban, and distant suburban strata. The suburban stratum includes: Wenjiang District, Shuangliu County, Pixian County, and Longquanyi; the suburban stratum includes: Qingbaijiang, Xindu; the distant suburban stratum includes: Xinjin County, Jintang County, Pujiang County, etc. In the two phases of data, 226 soil samples were collected in September 2008, and the sampling points were collected according to the three major circles of suburbs, suburbs, and distant suburbs, with a density of about 1 sample per km; on this basis, to further investigate the characteristics of spatial variability of heavy metals, 389 soil samples were taken in September 2017, about 2 samples per km. in the 2017 sampling, in addition to being able to collect soil samples at the original sampling point positioning to collect soil samples, but also fully considered urban development, land use type change, spatial structure characteristics, and other factors, as far as possible corresponding or close to the original sampling point of the agricultural land to collect soil samples. Collection of soil samples from the 0-10 cm surface layer of the tillage layer with a wooden shovel, and collected according to the plum sampling method, and the soil samples were thoroughly mixed and 1.5 kg of soil samples were retained according to the quadrat method. The coordinates of the sample points were located with a handheld GPS from Garmin, USA during the sampling process, and sampling points are distributed as shown in Figure 2.

The samples were dried by natural air in indoor drying stalls, picked up to remove stones, plant roots, and other foreign matters, ground and sieved through 200 mesh nylon mesh for analytical tests. The samples were determined by atomic fluorescence spectrometry (AFS) for As and Hg, by flame atomic absorption spectrometry (AAS/ FAAS) for Cr and Pb, and the Cd was detected by graphite furnace atomic absorption spectrophotometry (GF-AAS).

2.3. data collection and analyses

In this study, Microsoft Excel 2007 was used to calculate and analyze the elemental concentration data, SPSS 13.0 was used to carry out statistical analysis, ArcGis 10.2 and Kriging interpolation methods were used for spatial analysis, and use the positive matrix factorization (PMF) model (USEPA PMF 5.0) to assess the origin of the resolved heavy metals.

3. Results and discussion

3.1. Descriptive statistics of soil heavy metal concentrations in farmland

Representative statistical data on heavy metal levels in the samples of topsoil in agriculture and the respective context data are shown in Table 1. The mean soil heavy metal concentrate in both periods was above the Chengdu soil element context values (CNEMC, 1990). Geological conditions determine to some extent the concentration of heavy metals in soils, but humans can also influence their content in soils(G. Liu et al., 2013) . From 2008 to 2017, the average contents of Cd, As, and Cr in soil increased from 0.18, 6.85, and 42.73 $mg \cdot kg^{-1}$to 0.28, 9.18, and 88.41 $mg \cdot kg^{-1}$, indicating that human activities affected and caused a build-up of these heavy metals during the rapid development of the city, while the mean levels of Pb and Hg increased from 42.71 $mg \cdot kg^{-1}$ and 0.083$mg \cdot kg^{-1}$ to 39.24$mg \cdot kg^{-1}$ and 0.057$mg \cdot kg^{-1}$, which indicates that some heavy metal accumulation in the soil has been controlled during the urban development. According to the coefficient of variation (CV) classification of Nielsen and Bouma(Nielsen & Bouma, 1985), we observed that most of these five heavy metals from the two periods mentioned above belong to moderate and high variability, except for soil Cr, CV of the other four heavy metals increased, among which the coefficient of variation of Pb content increased the most in the two periods, reaching 227%, indicating that Pb content was most disturbed by human activities. The results indicate that urban modernization significantly affects the heavy metal content of arable soils and its variability increases.

3.2. Spatial and temporal distribution of heavy metals in soil

The spatial structure of regional variables was analyzed by calculating and fitting the variance functions of five heavy metals from arable soils of the research area in 2008 and 2017 using GS+9.0 geostatistical software, and we use the residuals (RSS) and the coefficient (R^2) of determination to judge the degree of model fit. The goodness of the model fit depends on whether the residuals are close to 0 and whether the coefficient of determination is close to 1.(Sakata, Ashida, & Tanaka, 2010) . In this paper, the coefficient of determination as well as the residuals meet the criteria for a better model fit. Therefore, it is possible to carry out interpolation in Kriege's space. Normality tests were performed using the K-S method before performing the fit. After model fitting, the fits of the five heavy metals in the two periods are shown in Table 2. The block-base ratio $[C_0 /(C_0 +C)]$ is a measure of the strength of correlation in space between samples, and comparing the block-base ratio values between two periods, the block-base ratios between the same elements showed an increasing trend, indicates that the distribution of heavy metals on the soil in the area studied has been disturbed by some anthropogenic factors(Zou, Dai, Gong, & Ma, 2015).

The results of the spatial distribution of soil heavy metal contents in the study area are shown in Fig. 3. The overall spatial distribution of soil Pb, Cr, and Hg contents in 2008 were similar, with the high-value areas mainly at study area in the east, they all showed a gradual decrease from east to west, While Cd and As are mainly concentrated in the second circle of the study area, their heavy metal contents gradually decrease from the second circle to the remaining two circles.

In 2017, the western part of the study area was the main area of soil Pb, Cr, and Hg accumulation, and the trend of the 10-year time scale change was from the east to the west, while Cd and As were similar to the spatial distribution in 2008, mainly concentrated in the second circle. The space distributed content of Pb, Cr and Hg in soils may be related to the "electronic information industry cluster" and the "one area and two belts" development planning strategy in the study area, while the spatial distribution of Cd and As is similar in both periods. This could be due to the effect of prolonged human interference, which is related to the industrial clustering in the second circle of the study area. Therefore, they become mainly influenced by structural variability factors.(Zou et al., 2015) .

After nearly 10 years of rapid urbanization, mean contents of Cd, As and Cr in the arable soils of research area showed an increasing trend, and the spatial variation of As and Cr was large, and the results were analyzed by the spatial variation of the content of these three heavy metals as shown in Figure 4. where: the absolute increase (AI) is calculated as X_{2017} -X_{2008}; the relative increase (RI) is calculated as (X_{2017}-X_{2008})/$X_{2008}\times100\%$, and where X is the raster layer corresponding to the distribution of heavy metals (He et al., 2019). The spatial distribution of the high values of AI and RI of soil Cd and As contents were similar and mainly concentrated in the second ring, showing that soil Cd showed a serious accumulation trend, while the high values of AI of soil Cr contents showed a point distribution in the central part, but the RI values of Cr show a large surface distribution in the middle of the study area, which indicates that Cr shows a strong spatial and temporal variability in the area. This indicates a significant accumulation of soil Cr in the central part of the study area with urbanization.

3.3. Source analysis of heavy metals

3.3.1. Correlation analysis

To further investigate the causes driving the variation of five heavy metals in arable soil and their relationships with environmental variables, correlation analysis was conducted for the above five heavy metals (B. Wang, Xia, Yu, Jia, & Xu, 2012). The results showed that in 2008, Cd and Pb were significantly positively correlated ($P<0.01$) in the arable soil, suggesting that these two heavy metals probably share a common supplier, while Cr and As were significantly negatively correlated, indicating that their sources in arable soils are different, while As and Hg were not significantly correlated to any other element. Therefore, the source of As and Hg is probably unique. and In 2017, the correlation between Cd and Pb in arable soil in the study area was weakened ($0.01<P<0.05$) and there was no significant correlation with Cr, Pbwas significantly positively correlated with Cr, so the two may have the same source, As and Hg had no significant correlation with each element in 2008 became significantly positively correlated, Cd had no significant correlation with other elements The correlation between Cd and other elements was not significant, so they may have a single source (Figure 5). The above results indicate that after 10 years of rapid urbanization, the sources of element in arable land have been changed by human activities.

3.3.2. Quantitative source with PMF

In order to get the quantification of the contributing of various pollution sources to the heavy metal content in arable land, we used the PMF model to quantify it(Qingyu Guan et al., 2018). This study was based on EPA PMF5.0 software, with factor numbers setting to different numbers respectively. The number of optimal factors was determined by comparing the Qrob/Qexp different factor counts. We found the smallest difference between Q_{robust} and Q_{true} when the factor number was 4, with most residuals between -3 and 3. Figures 6 and 7 show the fitting performance for the two period models. In 2008, the determining Co-efficient of the five heavy metals were Cd(0.89), Pb(0.42), As(0.97), Cr(0.99), and Hg(0.99); in 2017, the determining Co-efficient of the five heavy metals were Cd(0.99), Pb(0.73), As (0.99), Cr (0.62), and Hg (0.99). The determining Co-efficient of the five elements in both periods were above 0.6 except for Pb in arable soil in 2008, showing an excellent fit of this model. Thus, the model can achieve the purpose of the study and the fitted results can adequately contain the messages of the raw data (Z. Chen et al., 2022).

The source resolution of the five farmland soil heavy metals shows that both 2008 and 2017 have four main sources (Figure 8). In the source resolution in 2008, factor 1 had a relatively high contribution of 92.1% to Hg, and Hg was primarily located at the east of the study area (Fig. 3), which had a clear spatial correlation with the construction of efficient agricultural production base in the study area in 2008, so that humans were the major source of mercury, not a nature origin. Studies have shown Hg is a key ingredient of agrochemical fertilizer, which is evaporative and migratory in nature. (Giersz, Bartosiak, & Jankowski, 2017). Thus, the high usage of pesticides and fertilizers will pollute the arable soil. It has been reported that more than 50 million tons of fertilizers find their way onto arable land annually of China due to the massive and irrational use of chemical fertilizers. For this reason, factoring 1 could be regarded as a source of agricultural activity.

Factor 2 represented 65.8% the As concentration. The areas with high As content were spread over the south part (Figure 3), and the southern part of the study area was distributed with the most high-tech enterprises and key pollution source sewage treatment plants in the whole Chengdu city, and the structure of the river water system and irrigation canal network was similar to the high-value area of As. Therefore, it was speculated that the soil As pollution in the high-value area might be caused by long-term river sewage irrigation. Hence, factor 2 could be treated in terms of a sources of industrial activity.

Factor 3 was responsible for 66.3% with well above other factors of total chromium concentration. It is generally accepted that heavy metals associated with soil parent materials are usually low contaminating elements, It could be explained by the overall low-lying topography over the area and influence from the river (G. Liu et al., 2013). In addition, as can be seen in Table 1, the Cr content is below the local background value. Many studies point out that chromium arises primarily in the maternal matrix (Nanos & Rodríguez Martín, 2012). Consequently, factor 3 could be assumed to stand for maternal material, i.e., natural origin.

The contribution of factor 4 to the concentration of Cd and Pb was 59% and 45%, respectively. One correlation analysis (Figure 5) showed that Cd and Pb were remarkably related to each other, indicating they might have the same source. It is shown that Pb is the main contributor to transportation releases, which could result from vehicle tire friction and fuel combustion in vehicle engines (Qingyu Guan et al., 2018; Venkatalaxmi, Padmavathi, & Amaranath, 2004). During the present research, great numbers of agricultural fields were scattered alongside transportation roads, and this may have resulted in significant levels for Pb to enter the cultivated soils. This is especially true in the most congested traffic areas of Wuhou and Jinjiang. In addition, Cd is also associated with vehicles and is present in high levels of vehicle emissions. Such contamination is accumulated by a series of atmospheric activities in the land (Pardyjak, Speckart, Yin, & Veranth, 2008). As a result, factor 4 may be recognized to be an origin of transportation.

The same four potential sources were resolved in the 2017 source resolution. The contribution of factor 1 to As concentration was 83.5%, an increase of 17.7% relative to the contribution to As concentration in 2008. Based on the comparison of AI and RI values of As concentrations (Figure 4), As showed a trend of severe accumulation in the second rim of the study area, and the spatial location distribution was similar to that of 2008, so factor 1 was considered to have the same source as in 2008, i.e., agricultural sources.

The contribution of factor 2 to Pb and Cr concentrations was 50.1% and 46.1%, respectively. Similar distributions of the two heavy metals were found spatially (Figure 3), with two high values of point pollution zones at the northern center, whose spatial distribution is related to the "electronic information industry cluster" and the "one area and two zones" key development planning strategy in the urban tourism planning of the study area, and there is obvious The spatial correlation is obvious. In the source analysis in 2008, Cr was considered as a "natural source" related to the parent material of soil formation, and Pb was considered to come from vehicle fuel combustion and tire wear. The planning and construction of the tourist area will certainly accelerate the weathering of the parent material and the change of soil properties, and according to the survey, from the completion of the scenic area to 2017, the reception of tourists increased by 11% year-on-year, which greatly enhanced the regional vehicle circulation. Therefore, it can be assumed that factor 2 represents the origin of human intervention.

Consideration of factor 3 represents 85.5% for Cd concentration. Table 1 shows that the mean content of Cd increased by 55.56%. Cd is widely used in various chemical industries and is also a major by-product of paint production, and some studies have shown that these heavy metals can cause enrichment of Cd in the soil through the emission of waste gas, wastewater, and sludge, through atmospheric deposition, surface runoff and solid waste piles(Huang et al., 2020). Meanwhile, the spatiotemporal variation on Cd shows an accumulation characteristic along a circle of urban areas, which may be related to the industrial upgrading in a sub-ring in the rapid urbanization stage of the study area and the out-migration of industrial parks. Therefore, factor 3 represents industrial sources.

The contribution of factor 4 to the Hg concentration was as high as 98.1%, but its mean concentration decreased to 0.057 $mg \cdot kg^{-1}$ compared to 2008, a decrease of 31.32%. Moreover, the spatial distribution of Hg has changed significantly, with the high-value area migrating from the eastern part of the study area to the western part, where medical device manufacturing enterprises such as Chengdu Medical City and Chengdu Medical Device Creation Center are located according to the survey, while some studies have shown that the great deal of healthcare facilities can be a significant source of Hg as well. Examples include clinical equipment like thermometers and sphygmomanometers that carry Hg (Y. Li et al., 2016). Unless properly handled, this would lead indirectly to soil by several pathways. Accordingly, factor 4 would qualify as a contributor to medical devices.

In summary, we can know that heavy metal pollution of arable soils is becoming increasingly serious due to the impact from mankind's activity, and pollution sources tend to be complex and diversified. In the urbanization stage carried out in China, taking Chengdu city as an example, while the economy and infrastructure are developing rapidly, the environmental problems brought about by it should be given full attention, because when it is enriched in the soil it will not only seriously affect the growth of crops, but also further endanger human health and ecological environment through the food chain. Therefore, it is essential to understand the spatial and temporal characteristics of heavy metal pollution changes during urbanization construction for sustainable socio-economic development and construction of green cities.

4. Conclusion

Multivariate statistical analysis, multiple spatial distribution indicators,, correlation analysis, , and correlation analysis have been used for evaluating space-time patterns underlying heavy metal pollution in arable soils in typical rapidly urbanizing areas of China and to assess the relationships between pollution sources and environmental variables of soil heavy metals. Compared with 2008, the accumulation trend of Cd, As and Cr contents in arable soil was obvious in 2017, with the mean contents exceeding the soil background values by 1.69, 1.43, and 1.26 times, respectively, and the relative increases RI were all in areas exceeding 100%. While the levels of lead and mercury remain stable, heavy metals from arable land soils were strongly affected from human industry and agriculture activities. The block-base ratios $[C_0/(C_0 + C)]$ ranged from 50% to 93.5% in both periods, and the block-base ratios of all five soil heavy metals increased to some extent, indicating that the spatial autocorrelation of these elements decreased in 2017, and the variation was enhanced by anthropogenic random disturbance, forming a structural spatial distribution for an example of heavy metal Cd. Correlation analysis and PMF analysis showed four potential sources. However, after 10 years of rapid urbanization, heavy metal sources in arable land have changed considerably due to human activities, among which: 92.1% of Hg elements came from agricultural sources, 65.8% of As concentrations came from industrial activities such as sewage pollution, 66.3% of Cr came from the soil parent material, and transportation activities represented major contributors to Cd and Pb, contributing 59% and 45%, correspondingly, in 2008. and 45%.The source of Hg changed in 2017, 98.1% came from medical equipment, the source of As was the same as in 2008, but the contribution rate increased by 17.7%, 50.1% of Pb and 46.1% of Cr came from human activities, including the source of 2008 while increasing the source and contribution rate of pollution, and Cd changed from the source of soil parent material to industrial sources such as gold refining accounting for 85.5%.

Acknowledgment

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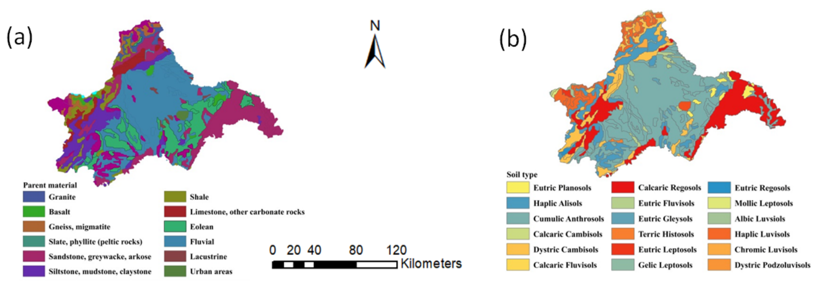

Figure 1 Distribution of (a) parent materials in the study region and (b) soil types

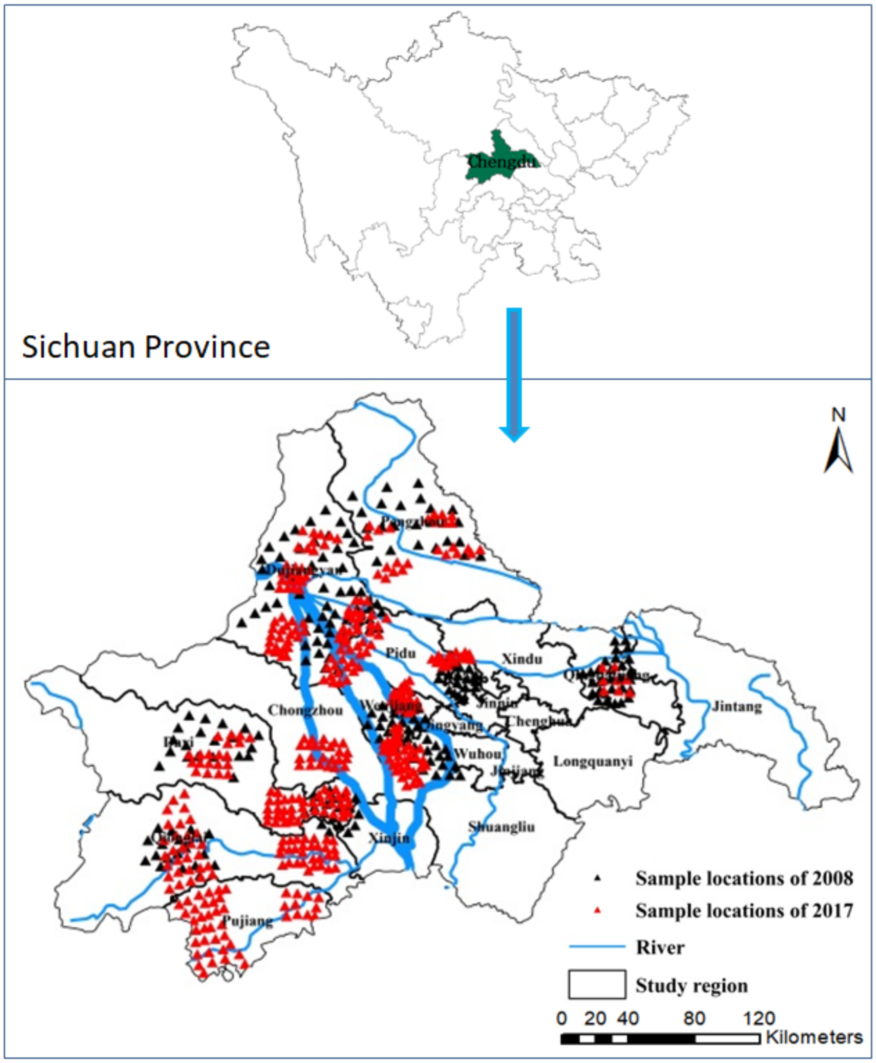

Figure 2 Distributions of study region

Table 1Descriptive statistics of heavy metal concentrations and background values in farmland topsoil in the study region

Element	Year	Max	Min	Average	Standard deviation	Coefficient of variation	Kurtosis	Skewness	Standar
Cd	2008	0.52	0.05	0.18	0.06	0.328	4.553	0.973	0.172
	2017	0.90	0.04	0.29	0.12	0.415	3.213	1.153	
Pb	2008	101.04	17.60	42.71	10.13	0.237	6.368	1.292	23.1
	2017	299.13	14.61	39.24	30.42	0.775	38.339	5.720	
As	2008	27.34	0.34	6.85	2.66	0.389	17.042	2.619	6.42
	2017	21.10	-	9.18	4.17	0.454	0.208	0.106	
Cr	2008	551.96	16.70	42.73	37.13	0.888	158.542	11.613	70.3
	2017	241.25	47.80	88.41	24.03	0.271	8.231	2.452	
Hg	2008	0.99	-	0.08	0.12	1.447	16.191	3.144	0.181
	2017	0.89	-	0.06	0.09	1.595	29.723	4.576	

"-" indicates that the heavy metal was not detected in the soil sample.

a. Average background of Chengdu(CNEMC, 1990).

except for kurtosis, skewness, and coefficient of variation, the units are mg·kg^{-1}.

Table 2 Semi-variance function model of soil heavy metals and corresponding parameters

Element	Years	Theoretical model	Nugget (C_0)	Still (C_0 +C)	[C_0 / (C_0 +C)]	Range/m	RSS	R^2
Cd	2008	Exponential	0.00181	0.00363	0.501	21200	8.405E-07	0.643
	2017	Exponential	0.0009	0.0138	0.935	5700	2.837E-06	0.922
Pb	2008	Gaussian	0.02505	0.0547	0.542	32900	3.789E-04	0.724
	2017	Spherical	0.0481	0.1482	0.675	7400	2.618E-04	0.716
As	2008	Exponential	0.1082	0.2714	0.601	135000	1.419E-03	0.754
	2017	Exponential	0.22	0.582	0.662	105000	1.136E-03	0.952
Cd	2008	Gaussian	0.0814	0.2948	0.724	56900	4.216E-03	0.845
	2017	Spherical	0.242	2.234	0.892	61400	0.036	0.990
Hg	2008	Spherical	0.82	1.641	0.50	41200	0.158	0.783
	2017	Gaussian	0.00451	0.001342	0.664	53900	4.33E-06	0.920

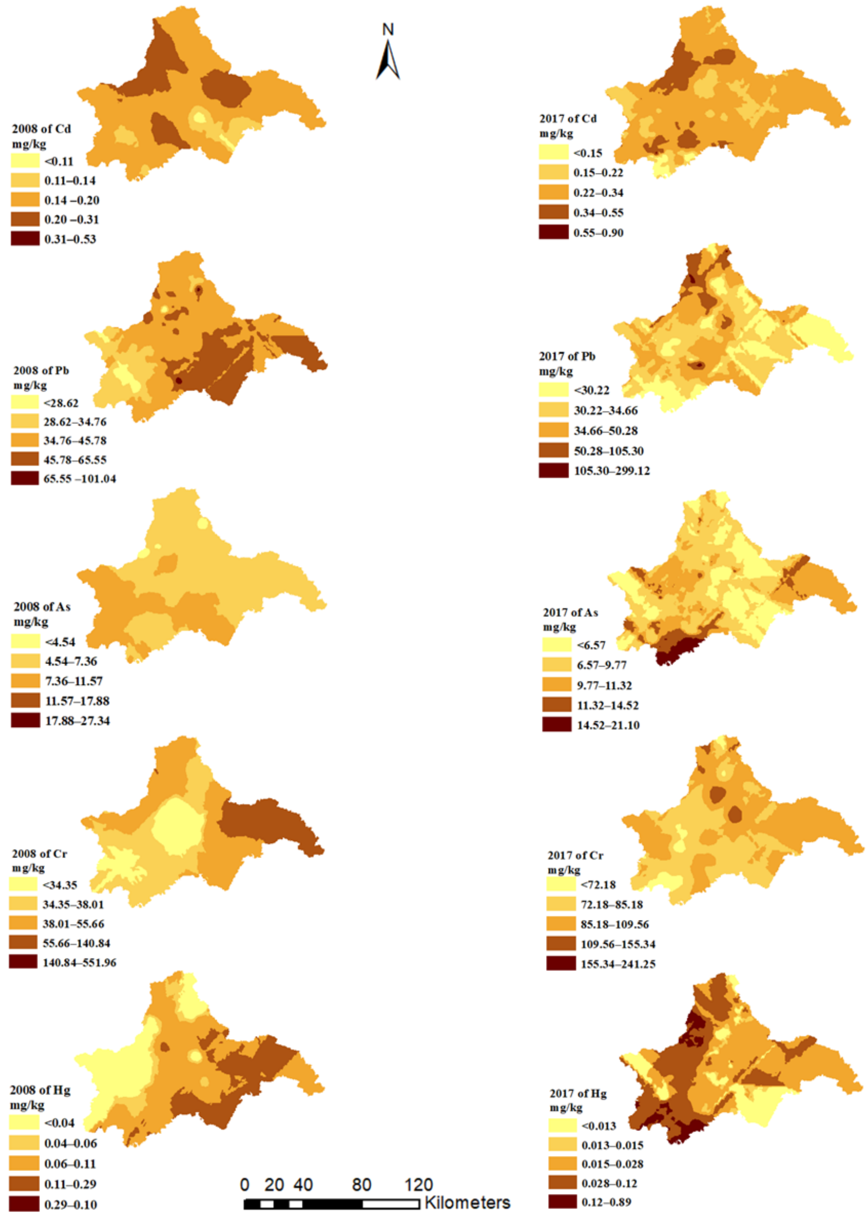

Figure 3 Spatiotemporal distributions of heavy metal concentrations of farmland soil in the study region

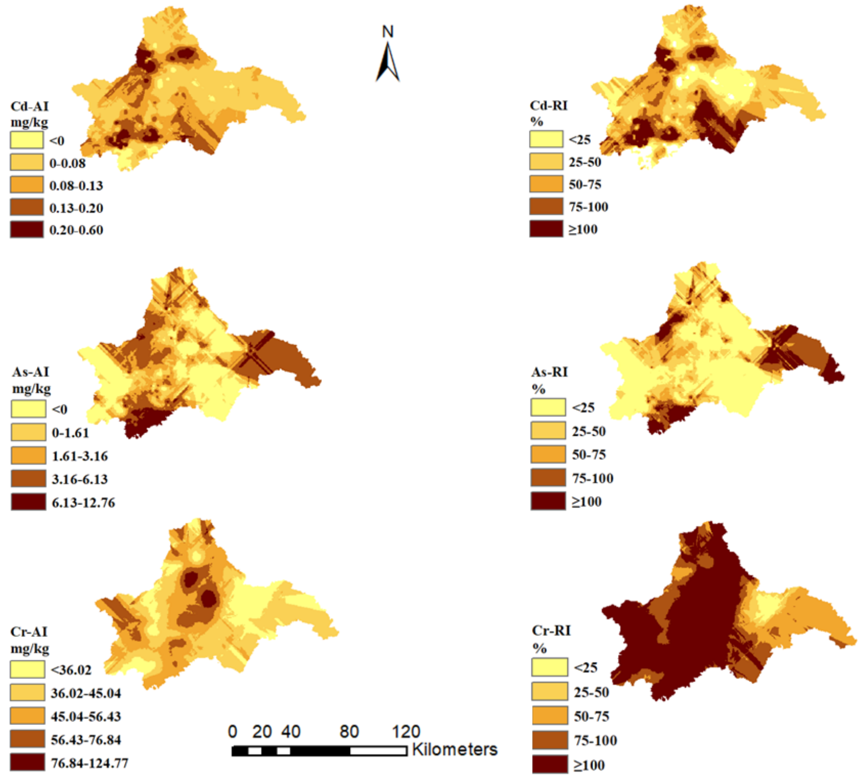

Fig. 4 Spatiotemporal distributions of soil heavy metal relative increments (RI) and absolute increments (AI)

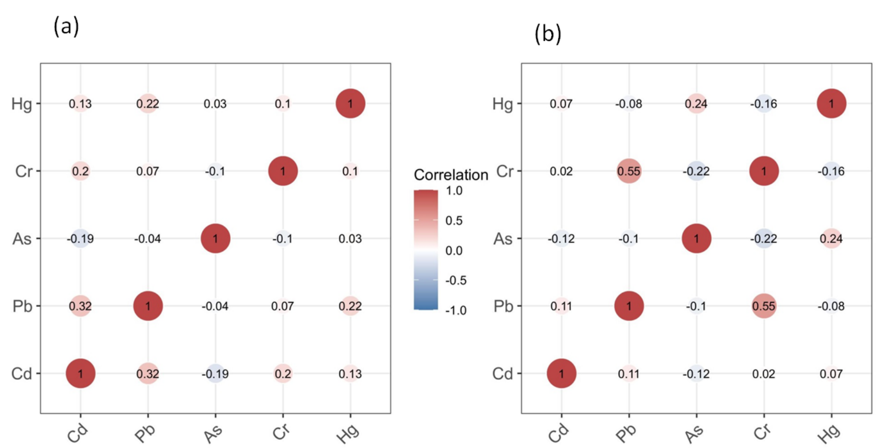

Figure 5 (a) Correlation analysis of heavy metals in agricultural soils in 2008, (b) Correlation analysis of heavy metals in agricultural soils in 2017

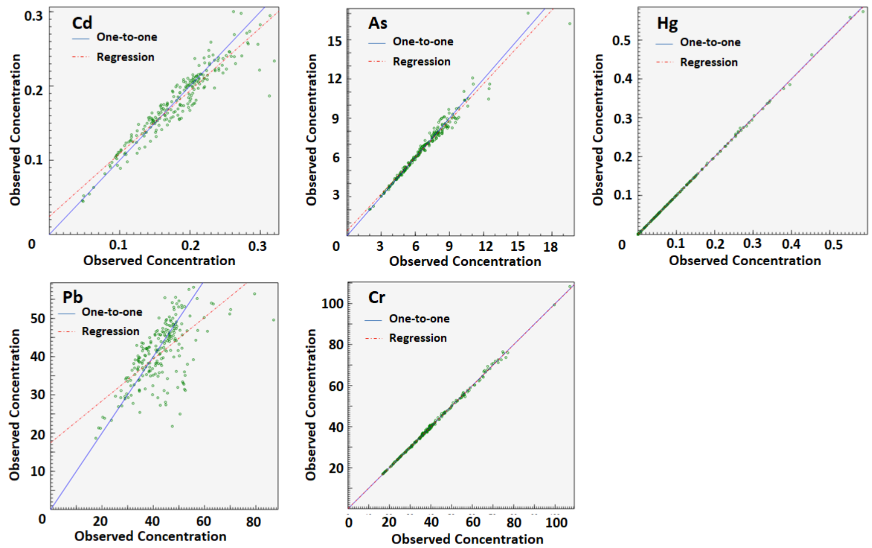

Figure 6 Comparisons of observed concentrations and predicted values in 2008

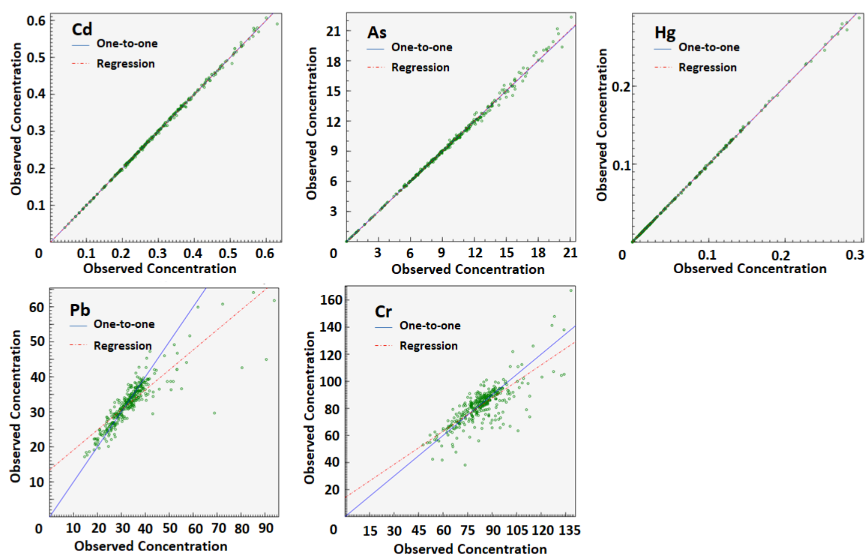

Figure 7 Comparisons of observed concentrations and predicted values in 2017

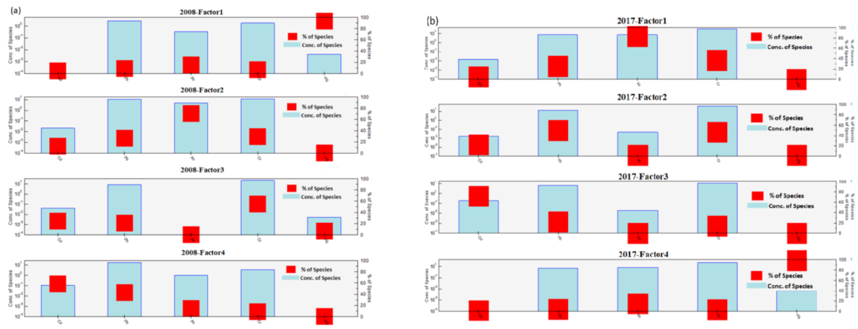

Figure 8 (a) Contributions of factors to each heavy metal in 2008 (b)Contributions of factors to each heavy metal in 2017

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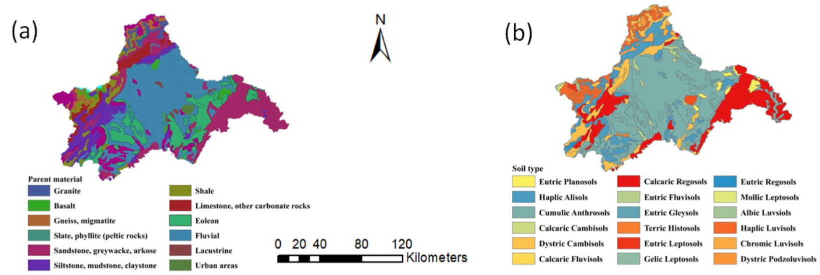
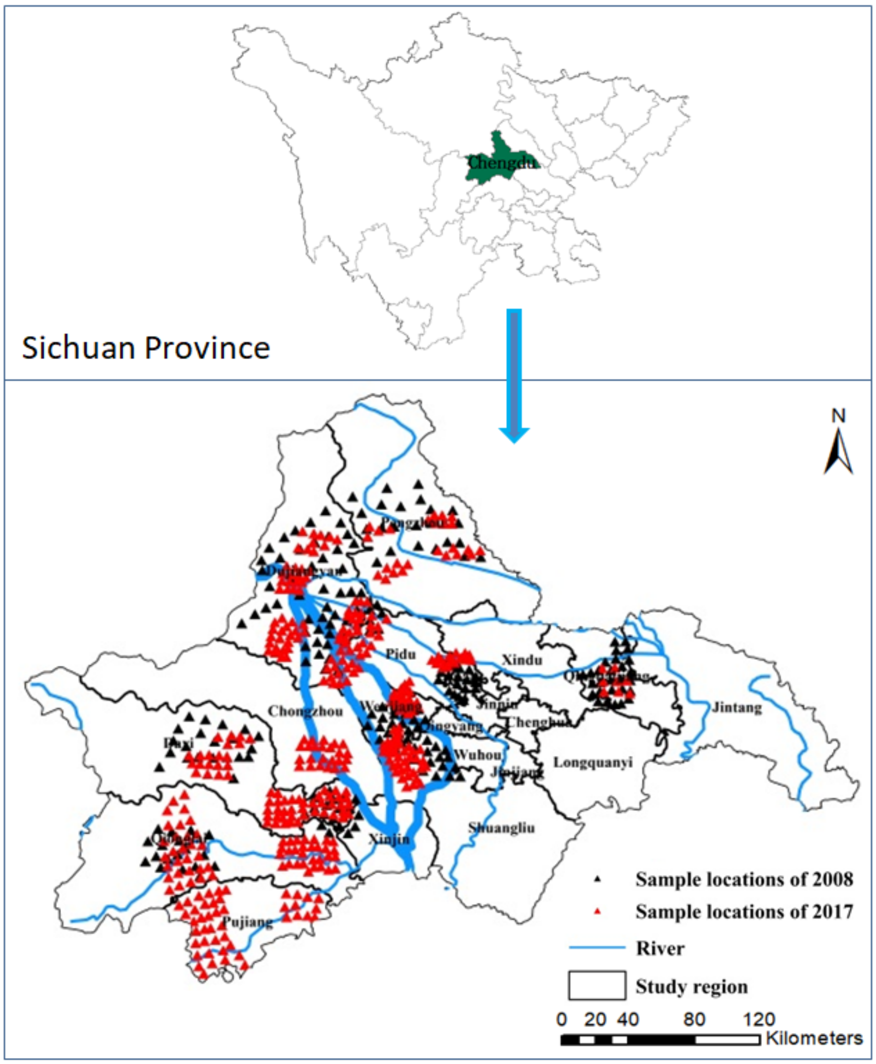
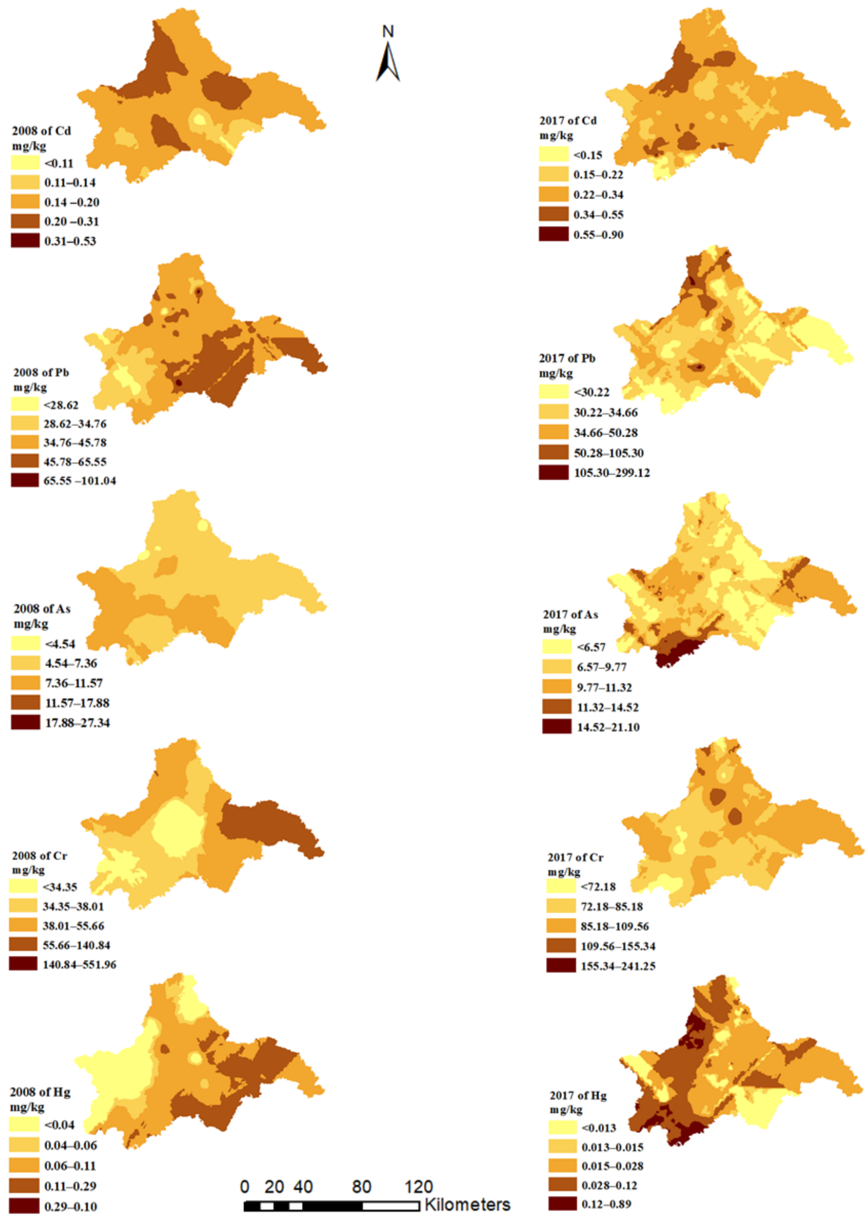
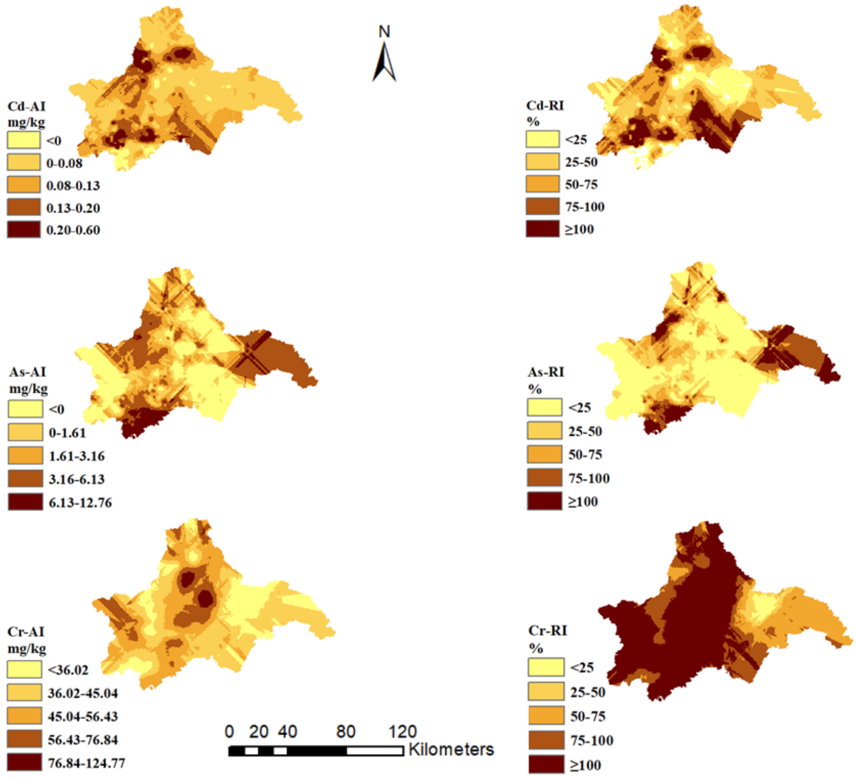
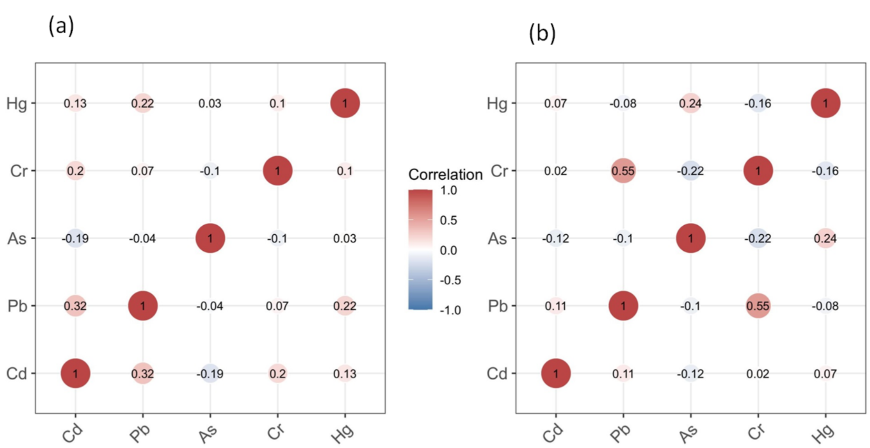

(a)
N
(b)
Parent material
Granite
Basalt
Gneiss, migmatite
Slate, phyllite (peltic rocks)
Sandstone, greywacke, arkose
Siltstone, mudstone, claystone
Shale
Limestone, other carbonate rocks
Eolean
Fluvial
Lacustrine
Urban areas
0 20 40 80 120
Kilometers
Soil type
Eutric Planosols
Haplic Alisols
Cumulic Anthrosols
Calcaric Cambisols
Dystric Cambisols
Calcaric Fluvisols
Calcaric Regosols
Eutric Fluvisols
Eutric Gleysols
Terric Histosols
Eutric Leptosols
Gelic Leptosols
Eutric Regosols
Mollic Leptosols
Albic Luvsiols
Haplic Luvisols
Chromic Luvisols
Dystric Podzoluvisols

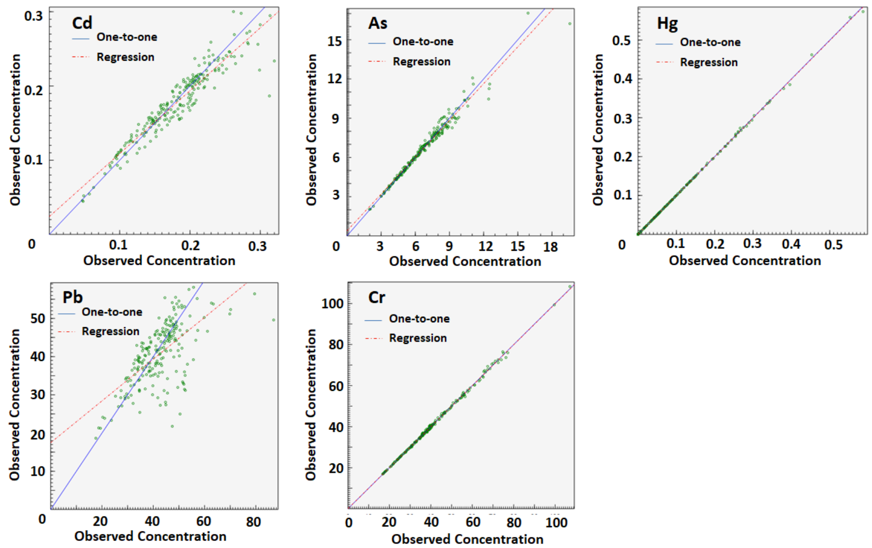

Chengdu
Sichuan Province
N
Pidu
Xindu
Jintang
Chongzhou
Wuhou
Longquanyi
Shuangliu
Xinjin
Pujiang
Sample locations of 2008
Sample locations of 2017
River
Study region
0 20 40 80 120
Kilometers

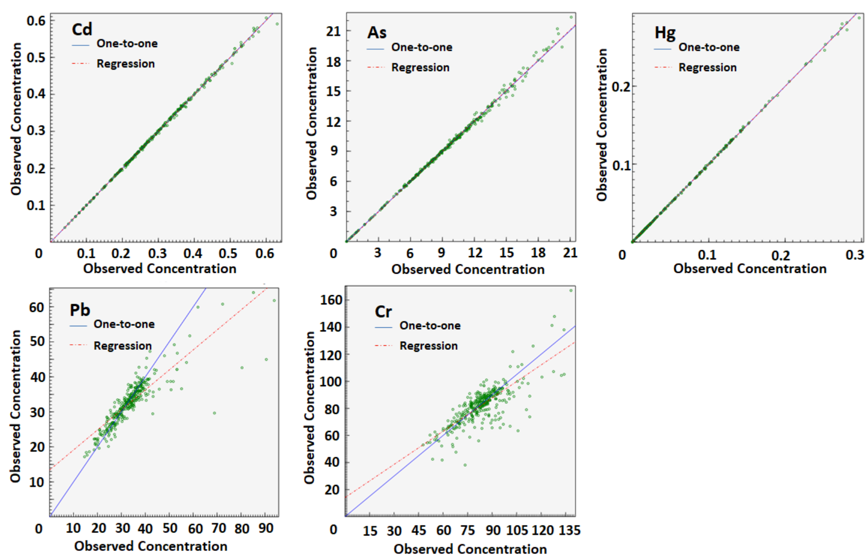


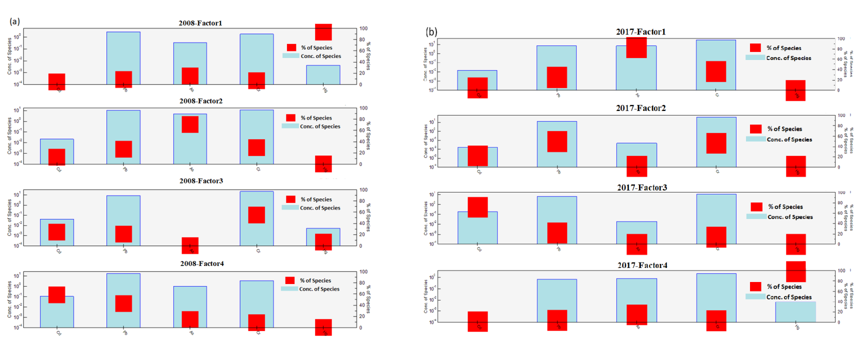
N
2008 of Cd
mg/kg
<0.11
0.11–0.14
0.14 –0.20
0.20 –0.31
0.31–0.53
2017 of Cd
mg/kg
<0.15
0.15–0.22
0.22–0.34
0.34–0.55
0.55–0.90
2008 of Pb
mg/kg
<28.62
28.62–34.76
34.76–45.78
45.78–65.55
65.55 –101.04
2017 of Pb
mg/kg
<30.22
30.22–34.66
34.66–50.28
50.28–105.30
105.30–299.12
2008 of As
mg/kg
<4.54
4.54–7.36
7.36–11.57
11.57–17.88
17.88–27.34
2017 of As
mg/kg
<6.57
6.57–9.77
9.77–11.32
11.32–14.52
14.52–21.10
2008 of Cr
mg/kg
<34.35
34.35–38.01
38.01–55.66
55.66–140.84
140.84–551.96
2017 of Cr
mg/kg
<72.18
72.18–85.18
85.18–109.56
109.56–155.34
155.34–241.25
2008 of Hg
mg/kg
<0.04
0.04–0.06
0.06–0.11
0.11–0.29
0.29–0.10
2017 of Hg
mg/kg
<0.013
0.013–0.015
0.015–0.028
0.028–0.12
0.12–0.89
0 20 40 80 120
Kilometers


N
Cd-AI
mg/kg
<0
0-0.08
0.08-0.13
0.13-0.20
0.20-0.60
Cd-RI
%
<25
25-50
50-75
75-100
≥100
As-AI
mg/kg
<0
0-1.61
1.61-3.16
3.16-6.13
6.13-12.76
As-RI
%
<25
25-50
50-75
75-100
≥100
Cr-AI
mg/kg
<36.02
36.02-45.04
45.04-56.43
56.43-76.84
76.84-124.77
Cr-RI
%
<25
25-50
50-75
75-100
≥100
0 20 40 80 120
Kilometers


(a)
Hg 0.13 0.22 0.03 0.1 1
Cr 0.2 0.07 -0.1 1 0.1
As -0.19 -0.04 1 -0.1 0.03
Pb 0.32 1 -0.04 0.07 0.22
Cd 1 0.32 -0.19 0.2 0.13
Cd Pb As Cr Hg
Correlation
1.0
0.5
0.0
-0.5
-1.0
(b)
Hg 0.07 -0.08 0.24 -0.16 1
Cr 0.02 0.55 -0.22 1 -0.16
As -0.12 -0.1 1 -0.22 0.24
Pb 0.11 1 -0.1 0.55 -0.08
Cd 1 0.11 -0.12 0.02 0.07
Cd Pb As Cr Hg


Cd
One-to-one
Regression
As
One-to-one
Regression
Hg
One-to-one
Regression
Pb
One-to-one
Regression
Cr
One-to-one
Regression
Observed Concentration
Observed Concentration


Cd
One-to-one
Regression
As
One-to-one
Regression
Hg
One-to-one
Regression
Pb
One-to-one
Regression
Cr
One-to-one
Regression
Observed Concentration
Observed Concentration


(a)
2008-Factor1
2008-Factor2
2008-Factor3
2008-Factor4
(b)
2017-Factor1
2017-Factor2
2017-Factor3
2017-Factor4
% of Species
Conc. of Species