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Occurrence, distribution and risk assessment of heavy metals in agricultural soil and water around a lead-zinc mine in Southwest China

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Abstract

Mining activities could induce severe heavy metal pollution in soil and surface water, which would consequently pose potential ecological environment risks and human health risks. In this research, total 82 agricultural soil samples and 34 water samples were collected from a special area that surrounding a lead-zinc mine. Pollution level, source apportionment, ecological and health risks of heavy metals were evaluated based on the concentrations of cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). According to the results, Cd and Zn were obviously enriched metals in agricultural soil in the study area, meanwhile, the potential risks which calculated by geo-accumulation index were showed a high ecological risk due to high concentration of Cd found in local agricultural soil. Additionally, heavy metal sources analyzed by the PMF model could be classified into four categories: mining activity (Mn), parent material (Cr, Ni), atmospheric deposition caused by industrial and mining activities (Pb, Zn, Cd) and agricultural activities (Cu). Compared with the values specified by corresponding water quality standard, the heavy metals content in surface water were below these values except Cd, while the content of seven heavy metals in drinking water was within the safe limits. The bioavailability of Cd, Pb and Zn in soil were higher than other metals, and when the bioavailability of metals was consideration into health risk assessment, the total HI and TCR values were far below the accepted risk levels. Though human health risks were within the safe margin, the toxic hazards of heavy metals to residents and ecological should be taken into consideration.

Keywords: Heavy metals; Mining area; Agricultural soil; Water body; Source apportionment; Risk assessment

1. Introduction

As the basic industries of the national economy, mineral resources are the essential material foundation for social and economic development of human society (Li et al. 2014). However, mining could lead to occupation of lands, the previous statistics have shown that the wasteland in China, that generated by mining activities, was growing at a rate of 46,700 ha per year (Zhuang et al. 2009). Meanwhile, due to the wastes like mining tail and beneficiation wastewater discharged from the process of ore mining and processing (Hu et al. 2014), high concentration of heavy metals from these wastes were released and diffused into the surrounding environment even though the cessation of mining activity (Xue et al. 2017; Yan et al. 2015), therefore, mining activities also pose a great harm. Heavy metals enter human body via various pathways, which can damage the human tissues after the concentration attains a level, causing various kind of diseases (e.g. cancer, dermal lesions, immune system damage and so on) even death (Shraim 2017; Zhuang et al. 2016). In present, due to the continuous development of industrial and mining, heavy metals contaminated soil and water resource have become a rigorous global environment issue (Koki et al. 2018; Zhou and Wang 2019).

Heavy metals including metals and metalloids as densities greater than 5 g cm^{-3} such as Pb, Zn, Cd, Hg and As (Oves et al. 2012), which could transported into plants and crops from soil due to non-biodegradable characteristic and its persisted for a long period in environment (Boularbah et al. 2006). Additionally, a wide range of sources of heavy metals in soil, such as industry and mining activities, transportation, as well as agricultural activities like wastewater irrigation and fertilizer application (Acosta et al. 2011; Zhang et al. 2018a), among them, mining activity was one of the most significant sources for heavy metals accumulation in soil especially for rural areas (Sun et al. 2018). In the past years, studies on metals in agricultural soils adjacent mining areas have done in many nations, including Cyprus (Barkett and Akün 2018), Germany (Antoniadis et al. 2017) and China (Fei et al. 2017; Zhang et al. 2018b), they were more focused on the source apportionment, spatial distribution and ecological risk evaluation. Meanwhile, mining activities have also led to metal pollution in the surrounding surface or ground water environment. For example, high concentration of As and Cd in ex-mining ponds in Klang Valley were association with ex-mining activities (Koki et al. 2018), researches by Ebenezer Gyamfi also shown that artisanal mining activities have increased the content of heavy metals in streams and exceeded the drinking water standard due to the water in mine pits has pumped into the stream (Gyamfi et al. 2019).

Two factors, environmental pollution and human health were considered into environmental health risk assessment, which quantitatively describe the risk of pollution harming human health (Jiang et al. 2017). In present, health risk assessment model developed by USEPA is the commonly used method for assessing human health risk, it was applied to calculating the non-carcinogenic risk and carcinogenic risk for humans exposed to pollutants from different environmental media such as soil, dust, water body and food (Koki et al. 2018; Ma et al. 2018; Wu et al. 2018a). However, it has been demonstrated that total concentration of metals, which used to calculate the human health risk, would highly overestimate the risk values associated with accidental

soil ingestion (Izquierdo et al. 2015), meanwhile, the model parameters from USEPA probably affect the accuracy of evaluation results due to regional difference (Li et al. 2017a). Therefore, in this research, the bioavailability of soil heavy metals and some exposure parameters of local residents were used to evaluate human health risks in study area.

The objectives of this study were: (i) to determine and analysis the concentration of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) in soil and water body, (ii) to investigate the possible sources of metals in soil, and (iii) to evaluate potential ecological and health risks surrounding the Pb-Zn mine.

2. Materials and methods

2.1. Study area

The study area is located at Sichuan province, Southwest China (Fig. 1), which has a subtropical monsoon humid climate with topography mountain and deep valley. The closed terrain and special climate are formed a dry and hot valley, causing the thin soil and scarce plants with more bare rock, as well as 17.9 degrees of average annual temperature and 741.8 mm of annual rainfall. In study area, the fluctuates of elevation in is large, the drop between the highest and the lowest elevation was 2000m. There are several small Pb-Zn mines which have been in operation at least 10 years. In addition, some processing industrial and mining enterprises are near the mining area, which mainly produces zinc baking sand, sulfuric acid, refined zinc and other products. According to our field survey, the intermediate region of valley is a long stream, the factories and mines are located on both sides of the riparian. Due to the topography, special climate and the construction of the industrial and mining sites, no paddy field is planted in the study area, and the land-use type is dominated by garden plots. Villages are mainly located on the mountains of the valley, all soil, drinking and tributary water samples were collected in these villages.

2.2. Sample collection

Soil samples: along the river in the study area, agricultural soil samples within 5 km around the Pb-Zn mine in the middle reaches of the basin areas were collected. Based on the sizes of agricultural areas, 82 soil samples from 24 sampling sites were collected, using a stainless-steel shovel to avoid contamination, each site contains 1-9 soil samples. In each sample, at least four subsamples were collected randomly, mixed to obtain bulk representative samples (Qu et al. 2013), sample positions were recorded by Geographic Position System (GPS). The collected surface soil samples (0-10cm in depth) were preserved in clean sampling bags, then taken to the laboratory and air dried. When this process was finished, removing the stones, dry branches, fallen leaves and other sundries in soils, all the samples were passed through 2mm polyethylene sieve (Luo et al. 2012). A portion of each soil sample for pH determination, then grinding the remaining soil again, and sieved through 0.15mm for heavy metal and organic matter analysis.

Water samples: water samples were collected from top to bottom along the stream. A control point was set up at the source of the stream, and other sampling points were set up at every 300-400 meters downstream of the industrial and mining areas and the

confluence of stream and lake. In the villages, 2-3 sampling points were set for each tributary that flows into the stream, local drinking water came from the same source, so a drinking water sampling point was set at every 2-3 villages. A total of 34 samples were analyzed, including 13 stream water samples, 11 tributary water samples and 10 drinking water samples. The pH and dissolved oxygen (DO) of water were measured on site, then placed water samples into a polyethylene bottle, acidified with HNO_3 to pH < 2 and stored at 4°C.

2.3. Chemical analysis

Soil pH was analyzed in 2.5:1 water/soil suspension with pH meter (PHS-3C, Shanghai INESA Scientific Instrument Co., Shanghai, China). Soil organic matter (SOM) was tested by the potassium dichromate volumetric method. The soil heavy metals were disposed with tetra-acid digestion (about 0.2000g soil sample, and 10 ml HCl, 5ml HNO_3, 5ml HF, 3ml $HClO_4$) by electric hot plate (Song et al. 2018). Water heavy metals were digested using mixed acids HNO_3 and $HClO_4$ (Hu et al. 2014). The digestion solutions concentration of seven metals were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Intrepid II XSP). The standard solution for drawing the standard curve comes from the national standard sample (GSB 04-1742-2004; Nonferrous Metals and Electronic Materials Analysis and Testing Center, China).

The in vitro digestion test of soil heavy metal was performed according to the methods described by Cheng et al. (2013) and Li et al. (2017a), it extracted the oral heavy metal bioavailability, that was the soluble in the gastrointestinal environment available for absorption. it provides a better measurement of its potential impacts on human health when the oral bioavailability applied to human health risk assessment (Turner 2011).

2.4. QA/QC

To reduce experimental error, the container that used in the experiment should be soaked one night (about 6 hours) in a 20% HNO_3 solution, and rinsed with ultrapure water. All the reagents and chemicals used for digestion were guaranteed reagent, every sample was repeated at least three times (the deviation between parallel samples was less than 10%). The dilution of the solution and the configuration of the standard curve were carried out with ultra-pure water. Every batch soil samples must have reagent blanks and standard reference (GBW07428; Center for Certified Reference Materials, China) to guarantee the accuracy of the results, and the recoveries of each heavy metal were within the range from 85% - 115%.

2.5. Risk assessment

2.5.1. Geo-accumulation index (I_{geo})

The geo-accumulation index assesses the degree of soil which contaminated by external sources under the background value (BV) conditions (Doabi et al. 2018). The equation of I_{geo} was as follows:

$$I_{geo}=\log_2 \frac{C_i}{1.5B_i} \quad (1)$$

where the C_i was the measured soil metals concentration and B_i was the soil background value in study area. The values of I_{geo} were divided into seven grades according to

pervious study (Doabi et al. 2018; Wang et al. 2017).

2.5.2. Health risk assessment

In this research, Human Health Risk Assessment Guide and Exposure Factors Handbook from US Environmental Protection Agency (USEPA 1989) was used to assess the health risk of study area residents. According to previous study and Exposed Factors Handbook (USEPA 2011), humans exposure to water and agricultural soil heavy metals by three mainly ways: (1) direct ingestion of soil and water, (2) inhalation of soil particles, (3) soil and water through dermal absorption, and the heavy metal average daily intake ADD which received through the three pathways were expressed by Eqs.(2)-(5) (USEPA 2011)

$$ADD_{ing}=\frac{C\times IR\times EF\times ED}{BW\times AT}\times ABS_{GI}\times 10^{-6} \quad (2)$$

$$ADD_{inh}=\frac{C\times IRi\times EF\times ED}{BW\times AT\times PEF}$$

$$ADD_{dermal\text{-}S}=\frac{C\times AF\times SA_S\times ABS\times EF\times ED}{BW\times AT}\times 10^{-6}$$

$$ADD_{dermal\text{-}W}=\frac{C\times Kp\times t\times Ev\times SA_W\times EF\times ED}{BW\times AT}\times 10^{-6}$$

The non-carcinogen risks were calculated by hazard quotient (HQ), which was expressed by divided ADD by the corresponding reference dose (*RfD*) for different metals. *RfD* is an estimate of the maximum allowable risk of daily exposure during a person's lifetime (Li et al. 2017b). The carcinogen risks (CR) were derived from ADD multiplied by heavy metals carcinogenic slope factor (*SF*), CR appraised by calculating the probability of a person who developing cancer during a whole life on account of exposure to the potential carcinogen (Xu et al. 2016). The HI and TCR were the sum of HQ and CR, respectively, these parameters values were calculated by Eqs.(6) - (9). When the HQ or HI >1, that means there is a high chance of non-carcinogenic effects in the local population. For CR and TCR, if CR(TCR)< 10^{-6}, the cancer risk in this area is very slight and can be ignore, however, there is considered unacceptable harmful to local people when RC(TRC)>10^{-4}, the value of RC(TRC) within a range from 10^{-6} to 10^{-4} indicates a tolerable risk (USEPA 2011). The description as well as values of factors were list in Table 1.

$$HQ_i=ADD_i/RfD \quad (6)$$

$$HI=\sum HQ_i \quad (7)$$

$$CR_i=ADD_i\times SF \quad (8)$$

$$TCR=\sum CR_i \quad (9)$$

2.6. PMF model

PMF receptor model was extensively applied in source apportionment of pollutants, which has outstanding features superior to principal component analysis (PCA) such as no non-negativity constraints and using uncertainty to analyze each concentration data individually (Liang et al. 2017). The PMF model has been authenticated excellent performance by previous researcher (Jiang et al. 2017), in this research, it was used to ensure the primary sources and its contribution rates of agricultural soil in study region.

2.7. Statistical analysis

Standard statistical analyses were performed using EXCEL. Pearson correlation analysis was conducted by SPSS, along with PMF 5.0 model were analyzed the sources of soil heavy metals. The spatial distribution of heavy metals of water were generated by ArcGIS. All data analysis diagrams were drawn by Origin.

3. Results and discussion

3.1. Soil characteristics

Physic-chemical parameters and heavy metals concentrations of agricultural soil were revealed in Table 2. In study area, about 35.4% of soils showed weakly alkaline, that possibly because the alkaline parent material, additionally, 25.6% of sample points was faintly acidity, the lower in soil pH mainly caused by fertilization (Ding et al., 2016). Previous research has showed that the processes related to nitrogen cycling released plenty of hydrogen ion (H^+), therefore, heavy application of inorganic fertilizer especially N fertilizer will generate soil acidification, which has demonstrated by Guo et al. (2010). According to field survey, more inorganic fertilizer would be applied into agricultural soil every year to ensure yield, that is the reason for lower pH values in study area. SOM is a physic-chemical indicator which related to soil total organic carbon, it is a vital component of the soil and a good marker of soil quality and fertility (Tang et al. 2018). In study area, the values of SOM were within a wide range 14.88 g kg^{-1} to 107.77g kg^{-1} with average value of 43.86 g kg^{-1}. SOM derives from countless sources like composted farmyard manure and litter decomposition (Sradnick et al. 2013). During the sampling time, agricultural soils with rich organic matter in study area were caused by the entering of ripe or rotten fruits, fallen leaves straw turnover and organic manures.

In 81 soil samples, the average concentrations of metals were 6.21 mg kg^{-1} for Cd, 129.84 mg kg^{-1} for Cr, 47.66 mg kg^{-1} for Cu, 965.48 mg kg^{-1} for Mn, 23.37 mg kg^{-1} for Ni, 74.55 mg kg^{-1} for Pb and 555.96 mg kg^{-1} for Zn. Among this metals, Zn and Mn have the highest concentrations, while Cd with the lowest. Except Ni, the average concentrations of other heavy metals were much greater than the China and Sichuan province soil BVs (CNEMC 1990). Seriously, the mean content of Cd was about 60 times higher than that of China BV in soil, indicating a strong Cd contamination of soil in this area. Meanwhile, in compared with Soil Environmental Quality Risk values of China, 98.8% of Cd, 3.7% of Cr, 12.2% of Cu, 12.2% of Pb and 84.1% of Zn were exceeded the screening value, and 67.0% of Cd were exceeded the intervention value, moreover, the average concentrations of Cd and Zn have partially higher than the specified value of Finland soil criteria and Dutch soil criteria (Table 2). By comparison, the mining and industrial activities relatively frequent areas reported by Wu et al. (2018b), Liu et al. (2020) and our study, were far higher concentration of metals in soil than normal farmlands studied by Zhang et al. (2018c), the results in these researches showed that the majority of higher metal contents in soils were stemmed from mining and industrial areas.

I_{geo} was calculated and applied to appraise soil contamination level. The average I_{geo} values of Cd, Cr, Cu, Mn, Ni, Pb and Zn were 3.43, 0.14, -0.05, -0.05, -1.12, 0.66,

and 2.15, respectively, ranging from “unpolluted” to “extremely polluted” (Fig. 2), with order of Cd > Zn > Pb > Cr > Cu = Mn > Ni. Except Cd and Zn, the I_{geo} values of other metals were below the levels of moderately polluted, however, about 17% of Zn and 67% of Cd of I_{geo} values were exceeded 3.0, showing a heavily pollution level. The ecological risks in study area mainly attributed by the high concentration of Cd. Cd, as the important component in Pb-Zn ore, will be emitted from the surrounding environment as a by-product during ore smelting process. Meanwhile, according to previous research, Cd has a strongly association with industrial activities (Zhou and Wang 2019), while the survey region is located in the industrial parks concentrated. A wide range of source pathways of Cd can lead to a massive accumulation in soils, and eventually result in a high ecological risk.

3.2. Source apportionment of heavy metals

The results of soil characteristic parameters relationships and their correlation with elevation were shown in Fig. 3. pH has negatively significant related to Cr (r^2=-0.522, P<0.01) and Ni (r^2=-0.616, P<0.01), low pH may decrease adsorption of metals by soil negative surfaces and make metals easier used by biological (Zhang et al. 2018c). As a whole, the soil in study area was weakly alkaline, which can help weaken the leaching effects and plant extraction functions, so as to reduce the harm of heavy metals. Meanwhile, Cd, Cu, Pb and Zn were positively significant correlated with SOM (P<0.01), SOM could influence these heavy metals binding or chemical fractions via strong adsorption, ion exchange and chelate effect of humus (Hu et al. 2018a). In addition, a significant correlation among Cd-Pb-Zn, Cr-Ni-Cu and Cu-Mn was performed, indicating a similar source or pollution pathway for these pairs of heavy metals (Xia et al. 2018). Moreover, there was significant correlation between ASL and most heavy metals, manifesting that topographic factors also affected the distribution and migration of metals in agricultural soil.

To understand the effects of industrial and mining activities on agricultural soil heavy metals, centered on the Pb-Zn mine in the middle reaches of stream, exploring the relationships between distance from sampling point to center point and metal concentration. The distribution of Pb, Zn and Cd were certain similarity, high concentration of these metals were discovered in the downstream 4 km, 1 km and upstream 1-2 km (Fig. 4), which mainly located near the dense areas of industry and mining. Meanwhile, the high concentrations of Cr and Ni were concentrated on the downstream of study area, and the two heavy metal concentrations gradually decreases with the increasing ASL. The distribution of Mn and Cu were different from other heavy metals, concentrations of Cu in soil from downstream were obviously higher than that from upstream, while Mn was relatively uniform distributed in upstream of study area. Additionally, the distribution trend of Cr, Cu, Mn and Ni was no apparent related with the location of Pb-Zn mining areas and metallurgical plants, which preliminarily determined that they possibly derived from other sources like parent material.

Pearson correlation could preliminary explain the homologous of correlated metals, the PMF model was used for the further sources analysis and its contribution rate of heavy metals (Liang et al. 2017). The soil heavy metal concentration data and uncertainty data were input into the model, the value of Q (Robust) was stable when

the number of factors was set as 4, in this condition, the model fitting R^2 were exceeded 0.9 except Cd (R^2=0.674) and Pb (R^2=0.663), showing that the result of model was reliable. The results of PMF model were shown in Fig. 5.

The first factor represented 15.1% of the total variance, accompany with strong loadings by Mn. Studies have shown that Mn in soils main came from soil parent material (Liang et al. 2017), on the other hand, Mn is generally used as a reference element (Wu et al. 2018b), which occurred surrounding the mining area along with high concentration (Antoniadis et al. 2017), suggesting that these high concentration of Mn in study area was likely from local closed Mn ore. Particularly, the mean value of Mn was far higher than the BV of Sichuan. Therefore, factor 1 was ascribed mining activity (Mn ore).

The second factor accounted for 27.63% of the total variance and with strong loadings by Cr and Ni, which could be deemed to natural source. According to previous research, the accumulation Cr and Ni were mostly associated and existed in all kinds of rocks (Kumar and Maiti 2015), besides, compared with other heavy metals, the CVs of Cr and Ni (0.29 and 0.39) were belong to the category of low spatial variability (Liang et al. 2017). Meanwhile, the average value and median value of Cr and Ni was similar, respectively, indicating an evenly distributed of Cr and Ni concentrations in the study area. Previous studies have also shown that non-point source contamination of heavy metals was more evenly distributed, hence, parent material was dominated the source of Cr and Ni in study area (Li et al. 2018; Sun et al. 2013).

The third factor was mostly loaded by Cd, Pb and Zn, which contributed the highest (34.07%) of the total variance. Pb and Zn is the major product of Pb-Zn ore, so this factor was attributed to anthropogenic source mainly related to Pb-Zn mining and industry activities. Cd as a naturally occurring non-essential element (Kumar and Maiti 2015), which could cause serious toxicity to the human body, for instance kidney damage, acute intoxication, carcinogenetic and so on (Zhuang et al. 2016). There was a certain content of Cd in Pb-Zn ores, and it was also an important raw material for industrial processes (Zhou and Wang 2019). In addition, the windblown fine granule material that from mining, plant operation, metal smelting and traffic fumes release, such as Pb aerosols and metal-contained dust, were the largely sources of atmospheric heavy metals (Huang et al. 2007). Due to wind direction and closed terrain, these atmospheric pollutants tend to accumulated in downwind soil through atmospheric subsidence (Pan et al. 2016). According to the Fig. 4, the high concentration area located in the downwind direction of mining areas and smelters, therefore, factor three could be attributed to atmospheric deposition.

The fourth factor was most loaded by Cu, accounting for 21.14% of the total variance. Agricultural activity was also a vital cause for the heavy metal accumulation in agricultural soil (Hu et al. 2018b), according to field survey, the application agricultural production materials for garden plot were far higher than plowland, while the high concentrations of Cu were concentrated in garden plot downstream of study area, so factor four could be reduce to agricultural activities. Commercial feeds are often contained with this trace element, while it is rarely absorbed by animals, that will cause high levels of Cu in animal manures (Wang et al. 2013). Previous data revealed

that the poultry excrement pollution in agricultural was serious, the discharge of livestock manure will up to 2.52×10^{9}t and eventually the polluted farmland will reach 3.83 $t^{-1}.hm^{-2}$ (Zhang et al. 2018d). Besides, the results of correlation analysis shown that Mn and Cu was significant correlation, which mainly because of the same source of Mn and Cu in some cases, excessive application of fungicides or pesticides may result accumulation of metal elements such as Mn and Cu in topsoil (Qu et al. 2013). Garden plot will applicate pesticides with 3-5 times a year to prevent pests in study area, which causes high values of Mn and Cu in some areas.

3.3. Heavy metals in water body

The concentration of heavy metals in stream water, tributary water and well water were listed in Table 3. The pH and DO in water were ranged from 7.4 - 8.6 and 3.0 - 8.0 with the averages that meet the surface water quality standard. In stream and tributary water samples, the concentrations of heavy metals were far below surface water threshold limit value (TLV) except Cd. The mean of Cd in stream water was 9.80E-03 mg/L, exceeding about twice of surface water TLV (5.00E-03 mg/L), and the concentration of Cd in tributary water ranged from 1.00E-04 to 1.41E-02 mg/L with 36.4% samples exceeded the surface water TLV (Table 3). In addition, compared to the guideline values of China and WHO for drinking water, the concentrations of heavy metals for well water were below the TLV. Moreover, the concentrations of Cd in stream and tributary water were significantly greater than that in well water, while Cu performed obviously opposite (P<0.01). High content of Cd in stream water mainly attributed to regional industrial and mining activities (Koki et al. 2018), the process of industrial and mine pits wastewater emissions, as well as the mining minerals came into contact with oxygen and water, could be cause high concentration of metals move into water body (Gyamfi et al. 2019; Omwene et al. 2018), while the source of well water is located in a mountain with high altitude, which has a less affected by industrial and mining activities in low altitude areas. Meanwhile, the reason for higher concentration of Cu in well water might be due to the corrosion of internal copper water pipes (WHO 2011). Heavy metals concentration in surface water in study area was similar to a Pb-Zn mine in Huayuan (Du et al. 2019), but lower than that from sphalerite mine in North China (Lu et al. 2019).

The spatial distribution of seven metals for stream water were shown in Fig. 6. Taken the source region of water as the reference point, the mean concentration values of Cr, Ni and Pb in stream water were closed to the reference point ones, indicating these three metals probably related to nature source. Cd and Zn have the similar spatial distribution, which high concentrations located in the downstream or nearby of the industrial and mining areas in connection with pollutants released from operations of factories and mines. Simultaneously, the position of high concentration of Mn for stream water and soil was identical, which mainly discharge from ore weathering during mineral mining, while Cu probably originated from agricultural activities for the average of Cu content from village tributary was higher than that from stream (Table 3). During the rainfall, the soil particles carried into the stream by surface runoff (Wang et al. 2018), these particles flow with stream and eventually deposited in the flat downstream because of the terrain in study area (Lu et al. 2019). When the water

environmental conditions change, heavy metals could be dissolved into water from deposited particles again (Han et al. 2017), causing a higher concentration in downstream (Fig .6). Generally, measures should be focused on heavy metal pollution in surface water to ensure the safety of water environment system in study area.

3.4. Human health risk assessment

The average oral bioavailability of in vitro simulation was decreased by the order of Cd > Zn > Pb > Mn > Ni > Cu > Cr (Table 1). In this research, bioavailability of Cd, Pb and Zn was apparently higher compared to other metals. The bioavailability of different heavy metals varies greatly, that probably because they are affected by many important factors like the origin of metals, their geochemical behavior and so on (Hiller et al. 2017). Meanwhile, previous studies have shown that bioavailability metals were likely associated with pollution degree, and anthropogenic sources of metals generally with higher bioavailability (Liu et al. 2018), that proved the accumulation of Cd, Pb and Zn in soil was more related to metals imported by anthropogenic activities.

In present study, the evaluation results of non-carcinogenic and carcinogenic risks for local adults and children were shown in Fig. 7. The heavy metal concentration, which used to calculate the ADD, is the upper limit of 95% confidence interval for the average soil or water concentration (USEPA 1989). Health risks through water ingestion and directly contact were calculated only by metal concentrations of well water due to the residents mainly contact well water. According to the result, the HI of all heavy metals, as well as total HI values (0.12 for adults and 0.36 for children), were far below than 1, that suggests the residents exposed to the local soil and well water environment with no or slight non-carcinogenic health risk. Same as the result above, the exposure cancer risks for local people were also within acceptable levels. TCR caused by Cd, Cr and Ni in soil were 1.15E-06, 1.26E-05 and 5.00E-06 for adults, 1.62E-06, 9.27E-06 and 5.66E-06 for children, followed the decreased order of Cr > Ni > Cd.

As is shown in Fig. 7, for both adults and children, Mn, Cd, Cr and Pb were the main heavy metals for non-carcinogenic risk, and Cr and Ni were contributed most to the carcinogenic risk, which accounted for more than 90% of the combined values of HI and TCR. Mn is a benefit element to the human body (Shraim 2017), the greater non-carcinogenic risk of Mn mainly due to its high concentration, while the HI value for Mn has far less than 1, so the risks caused by Mn could be ignored. Cr as a carcinogenic element for humans, its hexavalent oxidation state Cr(VI) was considered to be the most potentially threat compounds (Nickens et al. 2010), Cd was regarded as a cumulative toxic heavy metal (Zheng et al. 2010), while exposed to Pb environment could cause great harm to the human body especially for children, such as damaging the kidneys and reducing memory (Shraim 2017), inhabitants were more exposed to Cd, Cr and Pb in study area because of the low *RfD* value of the three metals (Li et al. 2014). Though the health risks of Cd, Cr and Pb were within the safe margin, its toxic hazards to humans should be taken into consideration. Moreover, direct ingestion and dermal contact were the main pathways for residents exposed to soil and water heavy metals, the health risks from inhalation could be negligible (Fig. 7). Meanwhile, the health risks of children were significantly higher than of adults, indicating that children were more affected by environmental pollutants, this result mainly due to the special activity and

lower body weight for children (Glorennec et al. 2016). Human health risk results are accordance with previous studies (Koki et al. 2018; Wu et al. 2018a; Xu et al. 2016).

4. Conclusion

The contamination situation of agricultural soil and water body heavy metals in a Pb-Zn mining area was analyzed. In this research, there were varying degrees of heavy metals contamination in the study area, of which the most polluted metal was Cd whether in soil or in surface water, and the high concentration of Cd in soil results a strong potential ecological risk. Source apportionment revealed that soil heavy metals were originated from natural and anthropogenic sources, while the latter dominate in the soil metals contamination. However, the high concentration of Cd, Mn and Zn have no significant correlation with agricultural activity in study area, indicating the main reason for the accumulation of metals in soil was industrial and mining activities. The concentrations of heavy metals in stream and tributary water were greater than that in well water due to the wastewater emission from industrial and mining activities, and heavy metals in well water were far below the guideline values of drinking water. Human health risks which calculated by soil and well water metals concentration was within safe levels, manifesting no or little potential health risks for local inhabitants. In conclusion, there is a certain degree of Cd contamination in study area, so it is necessary to control the waste generated from industrial and mining activities.

Author contributions YJ and HL designed the experiments and wrote the paper. YJ, ZL1, YL and ZL2 collected the soil samples and performed the experiments. JS, XZ1, YY and ZY processed the data and investigated the sampling area. XZ2 and CW reviewed this paper. XZ2 acquired the funding. All the authors contributed to the submitted the manuscript.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Reference

Acosta JA, Faz A, Martínez-Martínez S, Zornoza R, Carmona DM, Kabas S (2011) Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. Journal of Geochemical Exploration 109:8-17

Antoniadis V, Shaheen SM, Boersch J, Frohne T, Du Laing G, Rinklebe J (2017) Bioavailability and risk assessment of potentially toxic elements in garden edible vegetables and soils around a highly contaminated former mining area in Germany. Journal of Environmental Management 186:192-200

Barkett MO, Akün E (2018) Heavy metal contents of contaminated soils and ecological risk assessment in abandoned copper mine harbor in Yedidalga, Northern Cyprus. Environmental Earth Sciences 77

Boularbah A, Schwartz C, Bitton G, Aboudrar W, Ouhammou A, Morel JL (2006) Heavy metal contamination from mining sites in South Morocco: 2. Assessment of metal accumulation and toxicity in plants. Chemosphere 63:811-817

Cheng Z, Nie XP, Wang HS, Wong MH (2013) Risk assessments of human exposure to bioaccessible phthalate esters through market fish consumption. Environmental International 57-58:75-80

CNEMC (1990) The Backgrounds of Soil Environment in China. China National Environmental Monitoring Centre, Beijing, China: China Environmental Science Press (In Chinesee)

Doabi SA, Karami M, Afyuni M, Yeganeh M (2018) Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. Ecotoxicology and Environmental Safety 163:153-164

Du Y, Chen L, Ding P, Liu L, He Q, Chen B, Duan Y (2019) Different exposure profile of heavy metal and health risk between residents near a Pb-Zn mine and a Mn mine in Huayuan county, South China. Chemosphere 216:352-364

Fei JC, Min XB, Wang ZX, Pang ZH, Liang YJ, Ke Y (2017) Health and ecological risk assessment of heavy metals pollution in an antimony mining region: a case study from South China. Environmental Science and Pollution Research International 24:27573-27586

Glorennec P, Lucas JP, Mercat AC, Roudot AC, Le Bot B (2016) Environmental and dietary exposure of young children to inorganic trace elements. Environmental International 97:28-36

Guo JH et al. (2010) Significant Acidification in Major Chinese Croplands. Science 327:1008-1010

Gyamfi E, Appiah-Adjei EK, Adjei KA (2019) Potential heavy metal pollution of soil and water resources from artisanal mining in Kokoteasua, Ghana. Groundwater for Sustainable Development 8:450-456

Han D et al. (2017) Spatial distribution, risk assessment and source identification of heavy metals in sediments of the Yangtze River Estuary, China. Marine Pollution Bulletin 115:141-148

Hiller E et al. (2017) Occurrence of selected trace metals and their oral bioaccessibility in urban soils of kindergartens and parks in Bratislava (Slovak Republic) as evaluated by simple in vitro digestion procedure. Ecotoxicology and Environmental Safety 144:611-621

Hu C, Yang X, Dong J, Zhang X (2018a) Heavy metal concentrations and chemical fractions in sediment from Swan Lagoon, China: Their relation to the physiochemical properties of sediment. Chemosphere 209:848-856

Hu W et al. (2018b) Source identification of heavy metals in peri-urban agricultural soils of southeast China: An integrated approach. Environmental Pollution 237:650-661

Hu X-F, Jiang Y, Shu Y, Hu X, Liu L, Luo F (2014) Effects of mining wastewater discharges on heavy metal pollution and soil enzyme activity of the paddy fields. Journal of Geochemical Exploration 147:139-150

Huang SS et al. (2007) Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. Chemosphere 67:2148-2155

Izquierdo M, De Miguel E, Ortega MF, Mingot J (2015) Bioaccessibility of metals and human health risk assessment in community urban gardens. Chemosphere 135:312-318

Jiang Y, Chao S, Liu J, Yang Y, Chen Y, Zhang A, Cao H (2017) Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu Province, China. Chemosphere 168:1658-1668

Koki IB, Low KH, Juahir H, Abdul Zali M, Azid A, Zain SM (2018) Consumption of water from ex-mining ponds in Klang Valley and Melaka, Malaysia: A health risk study. Chemosphere 195:641-652

Kumar A, Maiti SK (2015) Assessment of potentially toxic heavy metal contamination in agricultural fields, sediment, and water from an abandoned chromite-asbestos mine waste of Roro hill, Chaibasa, India. Environmental Earth Sciences 74:2617-2633

Li H et al. (2017b) Distribution of heavy metals and metalloids in bulk and particle size fractions of soils from coal-mine brownfield and implications on human health. Chemosphere 172:505-515

Li HH et al. (2017a) Pollution characteristics and risk assessment of human exposure to oral bioaccessibility of heavy metals via urban street dusts from different functional areas in Chengdu, China. Science of the Total Environment 586:1076-1084

Li K, Gu Y, Li M, Zhao L, Ding J, Lun Z, Tian W (2018) Spatial analysis, source identification and risk assessment of heavy metals in a coal mining area in Henan, Central China. International Biodeterioration & Biodegradation 128:148-154

Li Z, Ma Z, van der Kuijp TJ, Yuan Z, Huang L (2014) A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Science of the Total Environment 468-469:843-853

Liang J et al. (2017) Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China. Environmental Pollution 225:681-690

Liu B, Ai S, Naeem S, Ding J, Ji W, Zhang Y (2018) Metal bioaccessibility in a wastewater irrigated soil-wheat system and associated human health risks: Implications for regional thresholds. Ecological Indicators 94:305-311

Liu K, Li C, Tang S, Shang G, Yu F, Li Y (2020) Heavy metal concentration, potential ecological risk assessment and enzyme activity in soils affected by a lead-zinc tailing spill in Guangxi, China. Chemosphere 251:126415

Lu J, Lu H, Lei K, Wang W, Guan Y (2019) Trace metal element pollution of soil and water resources caused by small-scale metallic ore mining activities: a case study from a sphalerite mine in North China. Environmental Science and Pollution Research International 26:24630-24644

Luo X-s, Yu S, Li X-d (2012) The mobility, bioavailability, and human bioaccessibility of trace metals in urban soils of Hong Kong. Applied Geochemistry 27:995-1004

Ma W, Tai L, Qiao Z, Zhong L, Wang Z, Fu K, Chen G (2018) Contamination source apportionment and health risk assessment of heavy metals in soil around municipal solid waste incinerator: A case study in North China. Science of the Total Environment 631-632:348-357

Nickens KP, Patierno SR, Ceryak S (2010) Chromium genotoxicity: A double-edged sword. Chemico-

Biological Interactions 188:276-288

Omwene PI, Oncel MS, Celen M, Kobya M (2018) Heavy metal pollution and spatial distribution in surface sediments of Mustafakemalpasa stream located in the world's largest borate basin (Turkey). Chemosphere 208:782-792

Oves M, Khan MS, Zaidi A, Ahmad E (2012) Soil Contamination, Nutritive Value, and Human Health Risk Assessment of Heavy Metals: An Overview. In: Toxicity of heavy metals to legumes and bioremediation. pp 1-27. doi:10.1007/978-3-7091-0730-0_1

Pan LB, Ma J, Wang XL, Hou H (2016) Heavy metals in soils from a typical county in Shanxi Province, China: Levels, sources and spatial distribution. Chemosphere 148:248-254

Qu M-K, Li W-D, Zhang C-R, Wang S-Q, Yang Y, He L-Y (2013) Source Apportionment of Heavy Metals in Soils Using Multivariate Statistics and Geostatistics. Pedosphere 23:437-444

Shraim AM (2017) Rice is a potential dietary source of not only arsenic but also other toxic elements like lead and chromium. Arabian Journal of Chemistry 10:S3434-S3443

Song Y et al. (2018) Multivariate linear regression model for source apportionment and health risk assessment of heavy metals from different environmental media. Ecotoxicology and Environmental Safety 165:555-563

Sradnick A, Murugan R, Oltmanns M, Raupp J, Joergensen RG (2013) Changes in functional diversity of the soil microbial community in a heterogeneous sandy soil after long-term fertilization with cattle manure and mineral fertilizer. Applied Soil Ecology 63:23-28

Sun C, Liu J, Wang Y, Sun L, Yu H (2013) Multivariate and geostatistical analyses of the spatial distribution and sources of heavy metals in agricultural soil in Dehui, Northeast China. Chemosphere 92:517-523

Sun Z, Xie X, Wang P, Hu Y, Cheng H (2018) Heavy metal pollution caused by small-scale metal ore mining activities: A case study from a polymetallic mine in South China. Science of the Total Environment 639:217-227

Tang H et al. (2018) Impact of long-term fertilization practices on the soil aggregation and humic substances under double-cropped rice fields. Environmental Science and Pollution Research International 25:11034-11044

Turner A (2011) Oral bioaccessibility of trace metals in household dust: a review. Environmental Geochemistry and Health 33:331-341

USEPA (1989) Risk Assessment Guidance for Superfund Vol.I: Human Health Evaluation Manual (Part A). Office of Emergency and Remedial Response.

USEPA (2011) Exposure Factors Handbook. U. S. Environmental Protection Agency, Washington, DC.

Wang H, Dong Y, Yang Y, Toor GS, Zhang X (2013) Changes in heavy metal contents in animal feeds and manures in an intensive animal production region of China. Journal of Environmental Sciences 25:2435-2442

Wang X, Zhang L, Zhao Z, Cai Y (2018) Heavy metal pollution in reservoirs in the hilly area of southern China: Distribution, source apportionment and health risk assessment. Science of the Total Environment 634:158-169

Wang Y, Wang R, Fan L, Chen T, Bai Y, Yu Q, Liu Y (2017) Assessment of multiple exposure to chemical elements and health risks among residents near Huodehong lead-zinc mining area in Yunnan, Southwest China. Chemosphere 174:613-627

WHO (2011) Guidelines for Drinking-water Quality, 4th edition. World Health Organization.

Wu J, Lu J, Li L, Min X, Luo Y (2018b) Pollution, ecological-health risks, and sources of heavy metals

in soil of the northeastern Qinghai-Tibet Plateau. Chemosphere 201:234-242

Wu W, Wu P, Yang F, Sun D-l, Zhang D-X, Zhou Y-K (2018a) Assessment of heavy metal pollution and human health risks in urban soils around an electronics manufacturing facility. Science of the Total Environment 630:53-61

Xia F et al. (2018) Distribution and source analysis of heavy metal pollutants in sediments of a rapid developing urban river system. Chemosphere 207:218-228

Xu Z, Li J, Pan Y, Chai X (2016) Human health risk assessment of heavy metals in a replaced urban industrial area of Qingdao, China. Environmental Monitoring and Assessment 188:229

Xue S et al. (2017) Cadmium, lead, and arsenic contamination in paddy soils of a mining area and their exposure effects on human HEPG2 and keratinocyte cell-lines. Environmental Research 156:23-30

Yan W et al. (2015) The spatial distribution pattern of heavy metals and risk assessment of moso bamboo forest soil around lead–zinc mine in Southeastern China. Soil & Tillage Research 153:120-130

Zhang J, Li H, Zhou Y, Dou L, Cai L, Mo L, You J (2018c) Bioavailability and soil-to-crop transfer of heavy metals in farmland soils: A case study in the Pearl River Delta, South China. Environmental Pollution 235:710-719

Zhang P et al. (2018b) Risk assessment and source analysis of soil heavy metal pollution from lower reaches of Yellow River irrigation in China. Science of the Total Environment 633:1136-1147

Zhang Y, Li S, Chen Z, Wang F, Chen J, Wang L (2018a) A systemic ecological risk assessment based on spatial distribution and source apportionment in the abandoned lead acid battery plant zone, China. Journal of Hazardous Materials 354:170-179

Zhang Y, Yin C, Cao S, Cheng L, Wu G, Guo J (2018d) Heavy metal accumulation and health risk assessment in soil-wheat system under different nitrogen levels. Science of the Total Environment 622-623:1499-1508

Zheng N, Liu J, Wang Q, Liang Z (2010) Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. Science of the Total Environment 408:726-733

Zhou X-Y, Wang X-R (2019) Impact of industrial activities on heavy metal contamination in soils in three major urban agglomerations of China. Journal of Cleaner Production 230:1-10

Zhuang P, McBride MB, Xia H, Li N, Li Z (2009) Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Science of the Total Environment 407:1551-1561

Zhuang P et al. (2016) Assessment of influences of cooking on cadmium and arsenic bioaccessibility in rice, using an in vitro physiologically-based extraction test. Food Chemistry 213:206-214

Figures

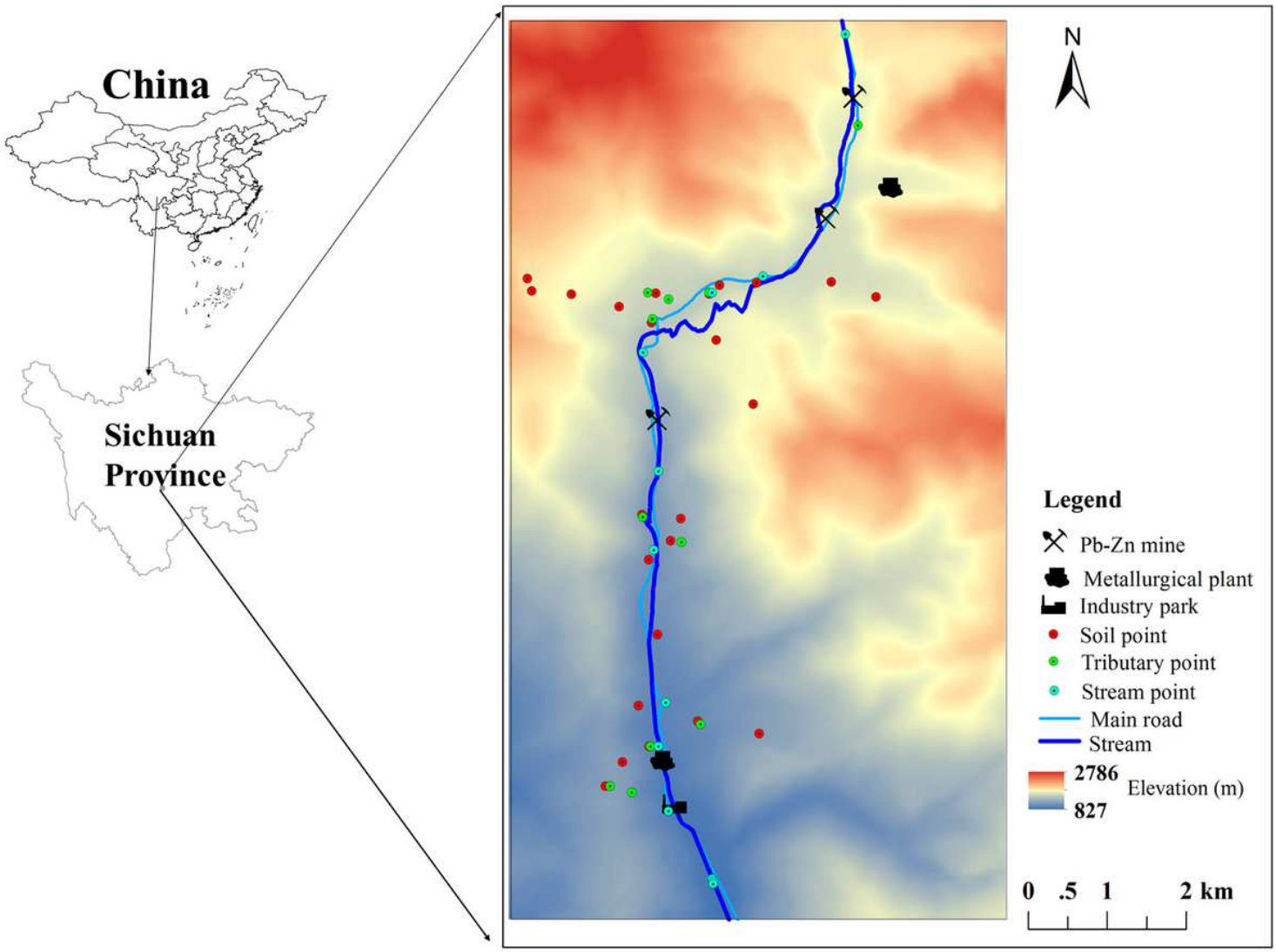


Figure 1

The location of soil sampling sites in study area

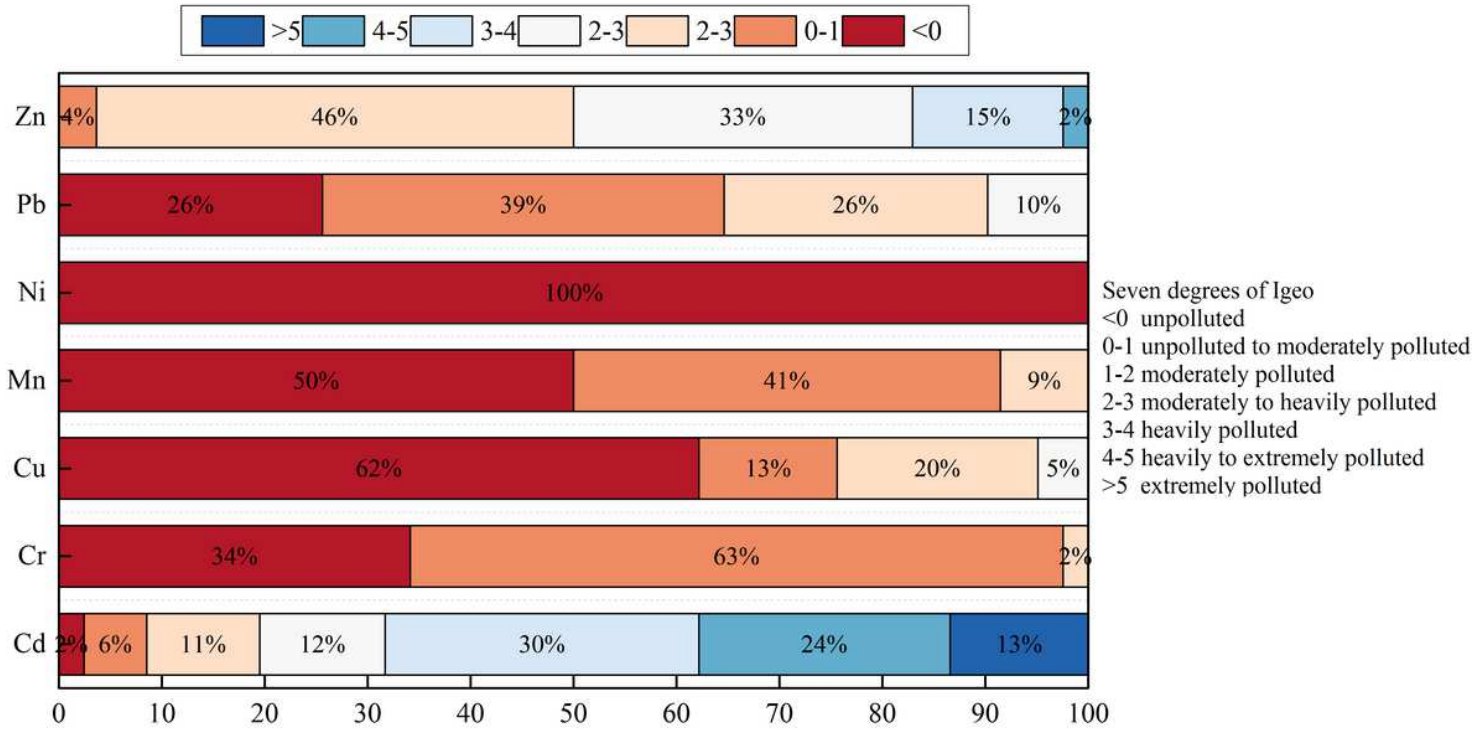


Figure 2

The result of ecological risks assessment: percentage (%) of each class in the Geo-accumulation index of heavy metals

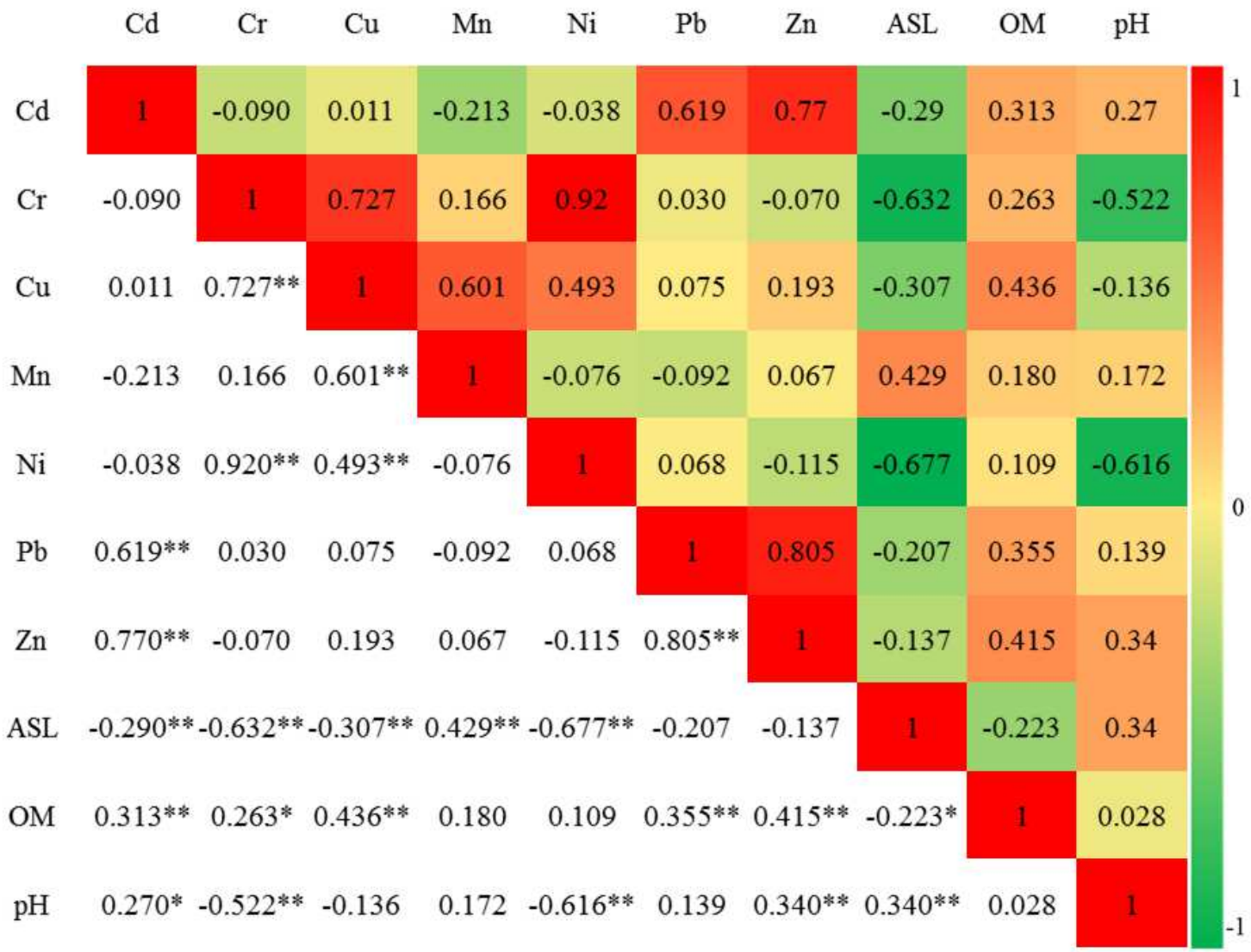


Figure 3

The correlation of heavy metals, pH, OM and ASL and their correlation with each other, * and ** means that a significant correlation between the two at the level of P<0.05 and P<0.01(2-tailed), ASL means the altitude in study area

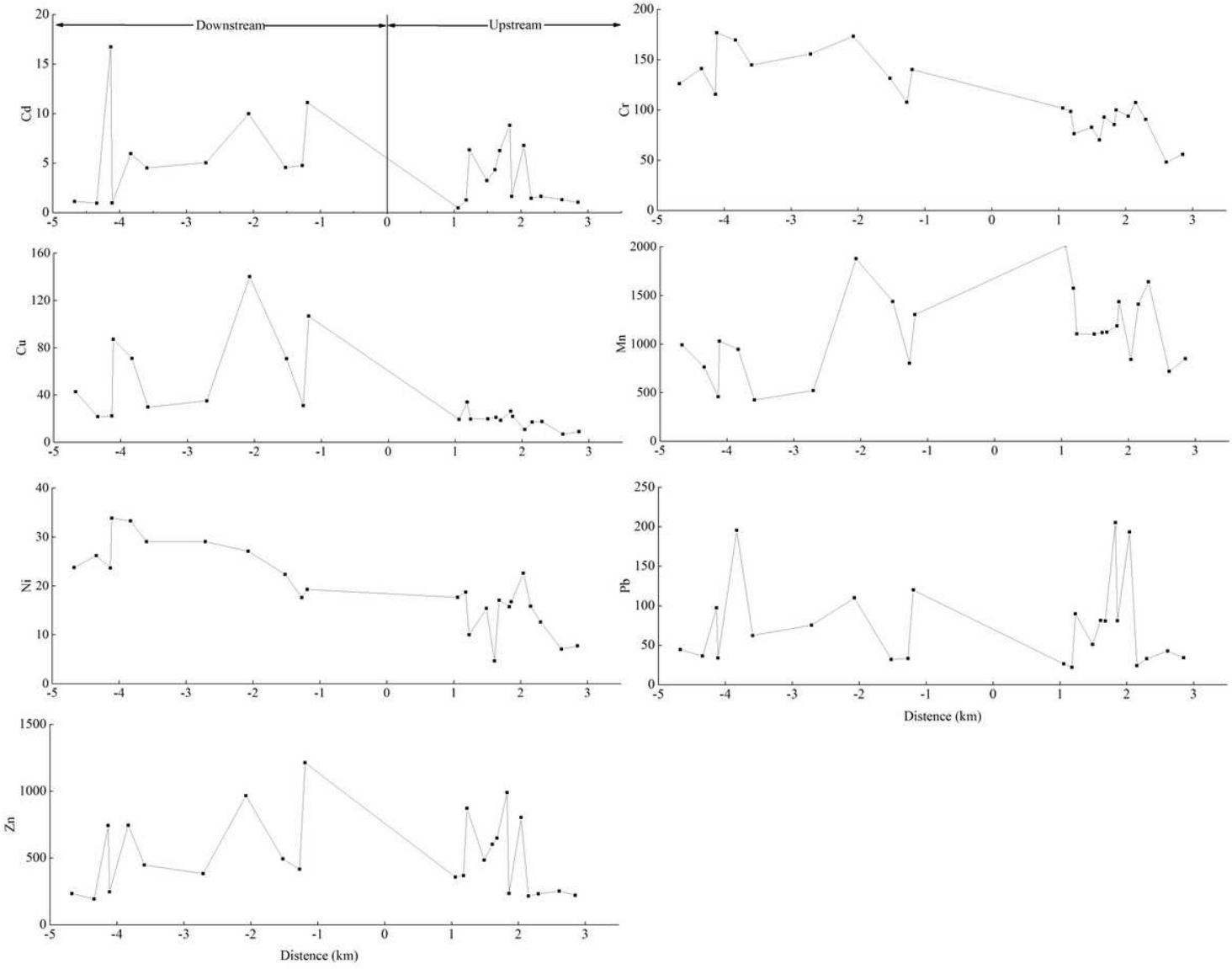
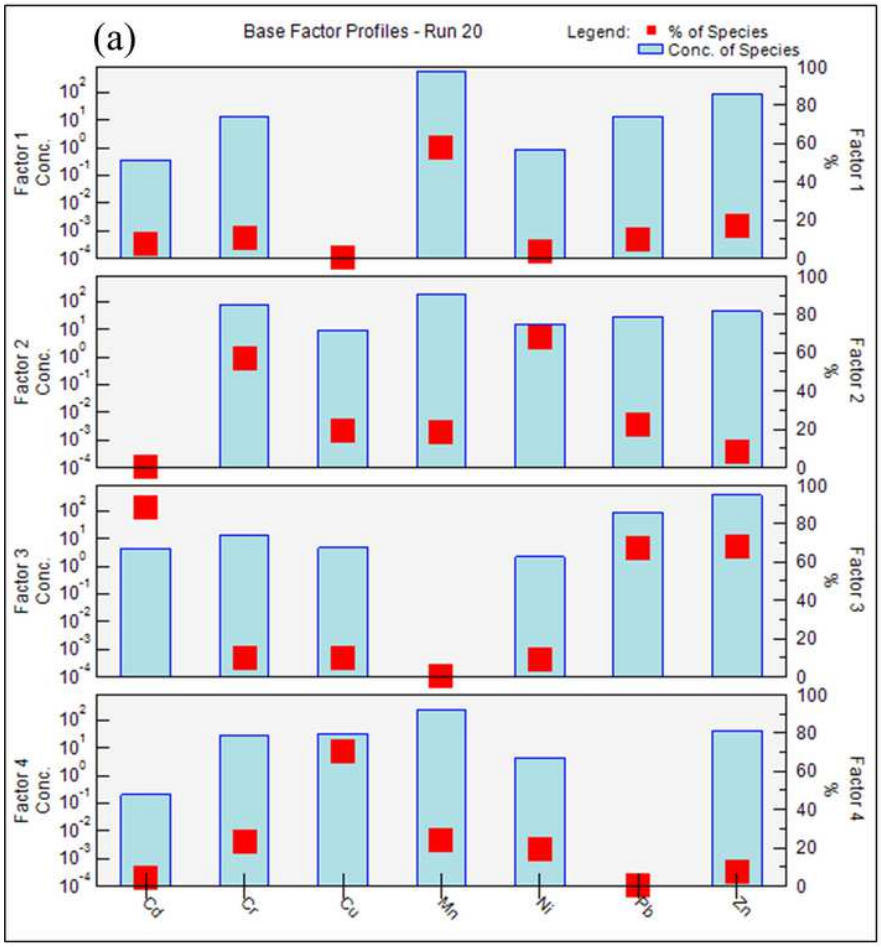
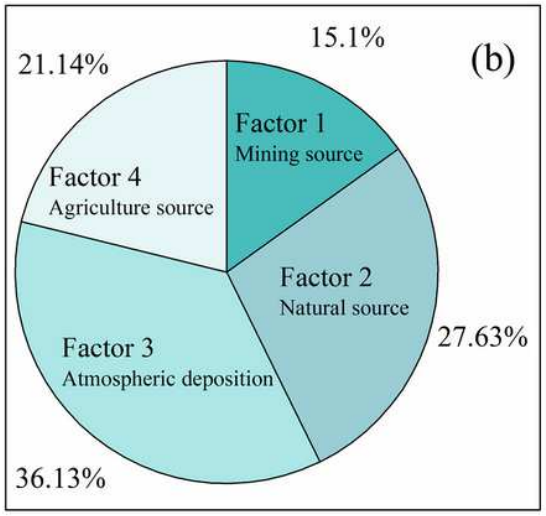


Figure 4

Relationships between distance from sampling point to center point and metal concentration





(c)	Factor 1	Factor 2	Factor 3	Factor 4
Cd	7.3	-	88.6	4.1
Cr	10.6	56.9	9.7	22.9
Cu	-	19.7	9.9	70.4
Mn	57.5	18.3	-	24.2
Ni	3.6	68.0	9.4	19.1
Pb	10.1	22.5	67.4	-
Zn	16.6	8.1	67.9	7.3

Figure 5

(a) Four sources contribution, (b) factor profile and (c) the contribution rate (%) of each factor to a single heavy metal via seven heavy metals in soil analyzed by PMF model, -: the contribution rate was lower than 0.05%

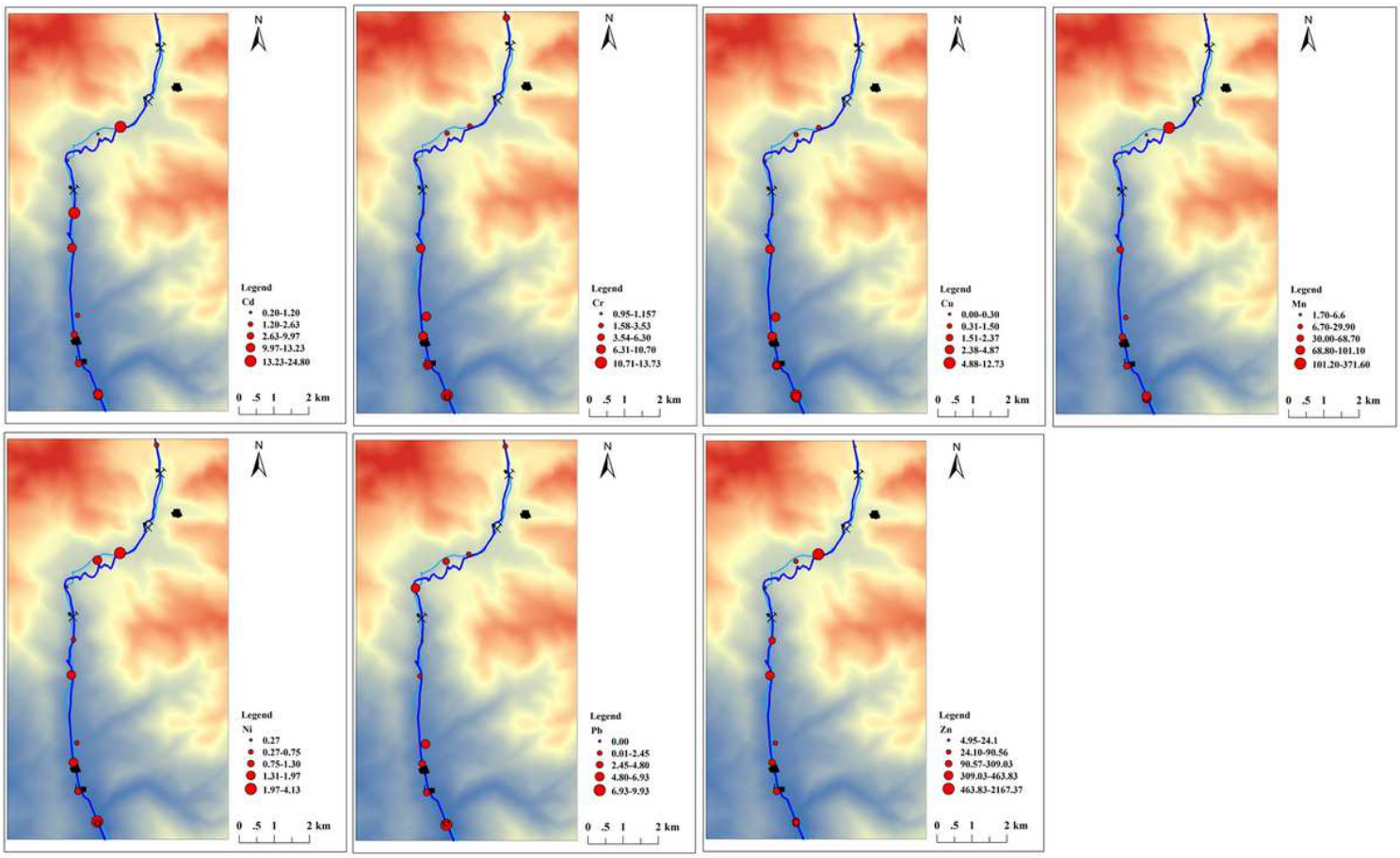


Figure 6

Spatial distribution of heavy metals for stream water, ug/L

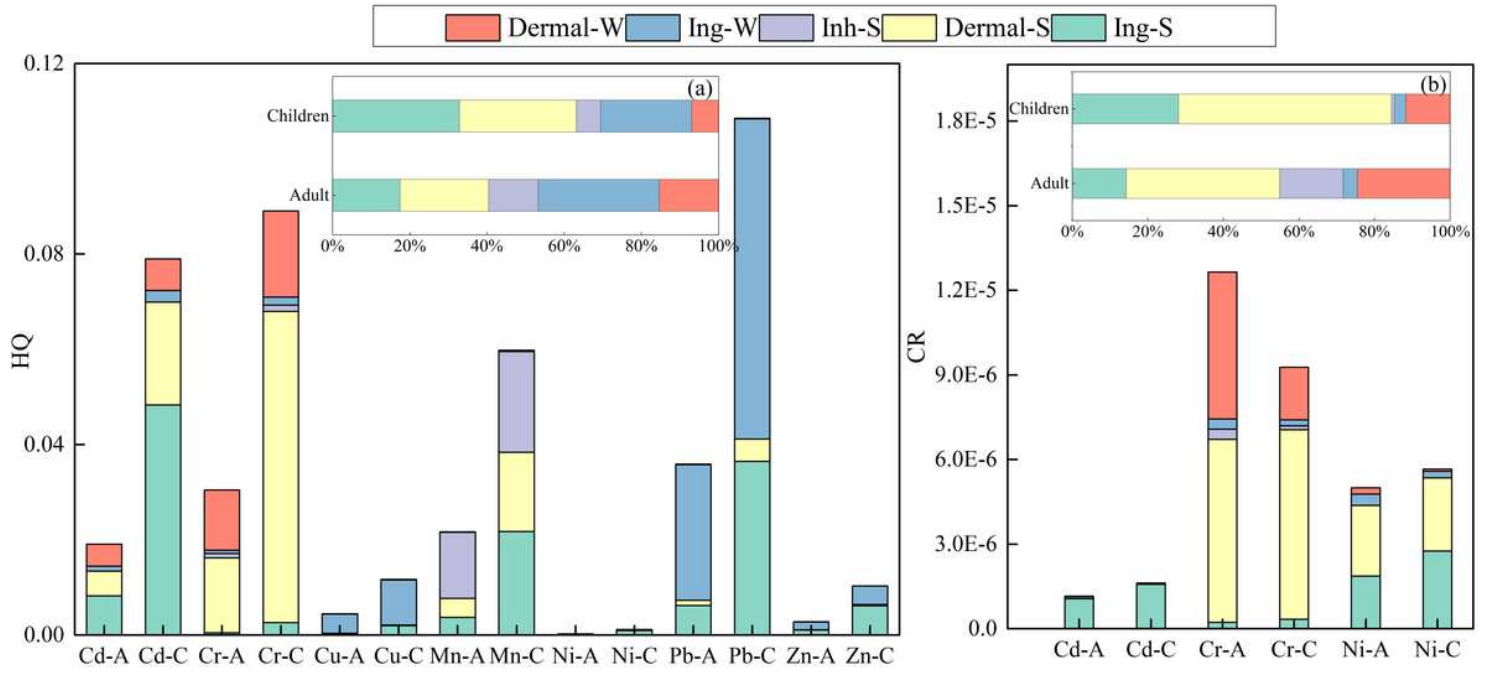


Figure 7

Accumulated health risks of human exposed to different heavy metals in soil and water, while (a) and (b) represented the contribution rates of each pathway to the non-carcinogenic risk and carcinogenic risk, respectively. The suffix letters W, S, A and C stand for water, soil, adults and children, respectively.