Bulletin of Environmental Contamination and Toxicology (2020) 104:532–537
https://doi.org/10.1007/s00128-020-02810-3

Distribution and Bioavailability of Heavy Metals in Soil Aggregates from the Fenhe River Basin, China

Minxia Liu[1] **· Zhiqiang Han**[2]

Received: 27 June 2019 / Accepted: 17 February 2020 / Published online: 30 March 2020

Abstract

Accumulation, bioavailability and potential ecological risk of seven heavy metals – chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd) and lead (Pb) – have been analyzed in agricultural soil aggregates with particle size of > 1 mm, 0.25–1 mm, 0.05–0.25 mm, and < 0.05 mm from the Fenhe River Basin (FRB). Accumulation factor (AF) analysis demonstrated that heavy metals tend to be enriched in < 0.05 mm soil aggregate. The bioavailability to plants of Cu, Zn, and Cd was higher than that of other metals and increased with the decrease in soil aggregate particle sizes. Risk assessment code (RAC) of Ni, Cu, Zn and Cd were 13.84%–21.08%, 7.13%–13.74%, 32.08%–51.82% and 29.38%–43.82%, indicating that Cu, Zn, Cd and Ni had a low to very high risk to other ecosystems, and the smaller the particle size (0.05–0.25 mm and < 0.05 mm), the greater ecological risk.

Keywords Heavy metals · Fenhe river basin · Soil aggregate · Particle size

With the rapid development of industrialization and urbanization in China, heavy metal pollution in agricultural soil has become an important problem (Niu et al. 2013). Once they enter ecosystems, heavy metals cannot be degraded by microorganisms, and can only migrate, transform, disperse, and enrich in different environmental media with different forms (Alloway 2013). During rainfall, heavy metals in agricultural soil can migrate to groundwater and surface water (Xu et al. 2007). Due to the characteristics of high toxicity and easy accumulation, heavy metals in agricultural soil cannot only reduce the buffering capacity of the soil but also affect human health through the food chain (Upadhyay et al. 2019). Heavy metals interact strongly with proteins and some enzymes in organisms, making them inactive and harmful to organisms (Kabatapendias 2000; Lee et al. 2018; Tang et al. 2013).

✉ Minxia Liu
liumx@sxau.edu.cn

Zhiqiang Han
hanzq@sxau.edu.cn

[1] College of Forestry, Shanxi Agricultural University, No.1 Mingxian Street, Taigu County 030801, Shanxi, China

[2] Periodical Press of Shanxi, Agricultural University, Taigu 030801, China

Total concentrations cannot reflect the bioavailability and migration ability of heavy metals. Previous studies found that the bioavailability and migration ability of heavy metals depend on heavy metal speciation. The Tessier sequential extraction method (Tessier et al. 1979) and BCR sequential extraction method (Rauret et al. 2000) are the two common methods for extract different heavy metal speciation in soils (Bastami et al. 2018; Thinh et al. 2018), sediment (Gu et al. 2015; Kang et al. 2017; Yong and Gao 2015) and dusts (Yıldırım and Tokalıoğlu 2016). Heavy metal speciation extracted by Tessier sequential extraction method includes: exchangeable fraction, acid soluble (carbonates) fraction, reducible (Fe–Mn oxide bound) fraction, oxidizable (organically bound + sulfide bound) fraction and residual fraction. Exchangeable fraction and acid soluble fraction were related to the migration ability of heavy metals, and the bioavailability of heavy metal was the sum of exchangeable fraction, acid soluble fraction, reducible (Fe–Mn oxide bound) fraction and oxidizable (organically bound + sulfide bound) fraction (Ma et al. 2016).

Aggregates are the basic structural units of soil. Due to the differences in physical and chemical properties, soil aggregates with different particle sizes have different adsorption capacities for heavy metals. Many studies have proved that heavy metal concentrations increased with the decrease of soil aggregate particle sizes (Li et al. 2017; Parra et al.

2014). Aggregates with different particle sizes, to a great degree, determine the toxicity, migration ability and concentrations of heavy metals (Acosta et al. 2011; Zhao et al. 2010). The soil erosion process is a selective process which will take away the finer soil particles order of priority, and the migration distance of fine soil particles in soil runoff is also longer (Quinton and Catt 2007; Uusitalo et al. 2001). It is very important to understand the distribution of heavy metals speciation in the soil aggregates with different particle sizes for providing strategies to repair and control heavy metal pollution, and the transformation of heavy metals.

The Fenhe River is the second largest tributary of the Yellow River, which is approximately 713 km long with a watershed area of approximately 7.9×10^4 km^2. FRB is a highly intensive agricultural production area, accounting for 64% of the agricultural output of Shanxi province. In recent years, agricultural non-point pollution and soil erosion in this area are serious, threatening the crop yield and soil quality of the FRB (Ding et al. 2015; Liu et al. 2008). Once soil erosion occurs, pollutants in the soil migrate with surface runoff, affecting the downstream environmental security and the ecological security of the downstream environment. Previous studies concentrated only on the total heavy metal levels in bulk soils, and the heavy metal speciation and soil aggregates with different particle sizes were neglected. Therefore, the objectives of the paper are to: (1) determine the distribution of heavy metal concentrations in soil aggregates with different particle sizes; (2) analyze the migration and bioavailability of heavy metals in soil aggregates with different particle sizes by examining the chemical speciation of heavy metal; (3) assess the ecological risk of heavy metals using risk assessment code. The results of this study can provide some information on the evaluation of heavy metal pollution in developed areas of agriculture and industry.

Materials and Methods

Fifty agricultural soil samples (0–20 cm sampling depth) from the FRB were collected in July 2017 during the crop-growing season (Fig. 1). Each sample was bulked from five subsamples, which were randomly taken approximately 20 m apart. All the soil samples were packed into self-styled bags for return to the laboratory. Soil samples were air-dried and sieved through a 2-mm sieve prior to further analysis.

Mechanical stable soil aggregates were separated by the dry-sieve method (Institute of Soil Science 1978). Each soil sample (200 g) treated above was sieved through an electric plastic nylon sieve (TTF-100) with pore diameter of 1, 0.25, and 0.05 mm for 10 min. Then, soil aggregates with different particle sizes (> 1 mm, 0.25–1 mm, 0.05–0.25 mm and < 0.05 mm) were obtained. After separation, all the particle sizes were weighted.

For heavy metal analysis, a soil sample (0.15 g) was weighted and transferred into a Teflon beaker, then 5 mL HNO_3, 2 mL HF and 2 mL HCL were added. The Teflon

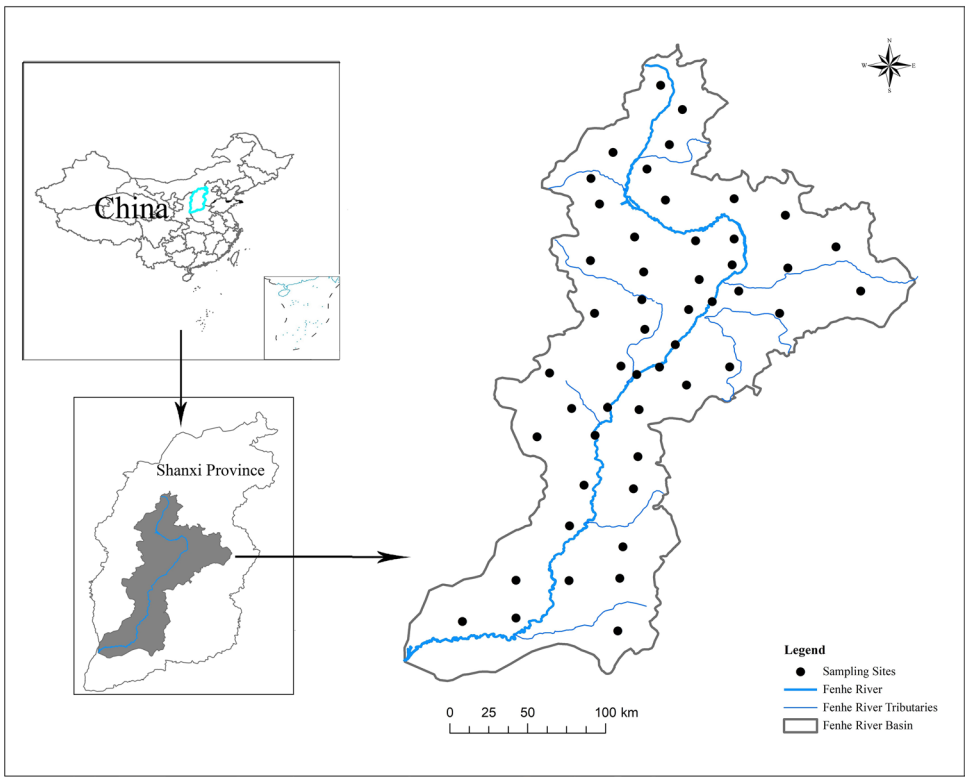

Fig. 1 Soil sampling locations of the study area

beaker was digested in a Microwave Digestion System (Milestone ETHOS ONE). After digestion, the Teflon beaker was uncapped and placed on a hot plate (140 °C) until the sample solution was vaporized nearly to dryness. Afterward, the resulting solution was transferred to a 50 mL volumetric flask and deionized water was added to bring the solution to 50 mL. Inductively coupled plasma source mass spectrometer (Thermo X SERIES2, Massachusetts, USA) was used to determine the heavy metal (Cr, Ni, Cu, Zn, As, Cd and Pb) concentrations in the digested final solution. Each sample replicates 3 times. Quality assurance and quality control (QA/QC) procedures were conducted throughout the whole digestion-measurement process. One standard reference soil (GBW07404, provided by the Chinese Academy of Measurement Science) and one blank with each batch sample (20 soil samples) were digested and measured. Heavy metal recoveries in the standard reference soil were 87% to 115%, which met the needs of the experiment.

The Tessier sequential extraction method was used to extract the heavy metal speciation. A soil sample (1 g) was weighted and transferred to a 100 mL centrifuge tube, extractant was added and shaking on oscillator under certain conditions was performed. After the shock, the sample was centrifuged at 4 000 rpm for 5 min and the supernatant was collected. Residues were washed with 50 mL deionized water, shaken for 15 min and centrifuged at 4 000 rpm for 5 min, then the supernatant was discarded and the next heavy metal speciation was extracted. Each sample replicates 3 times. The extraction scheme of Tessier is shown in Table 1.

Accumulation factor (AF) was used to represent the accumulation of heavy metal in soil aggregates with different particle sizes. The AF can be calculated using Eq. (1):

$$\mathrm{AF} = \frac{C_{aggregates}}{C_{bulk}} \quad (1)$$

where $C_{aggregates}$ is the total heavy metal concentration in soil aggregates with different particle size (mg kg^{-1}) and C_{bulk} is the total heavy metal concentration in bulk soil (mg kg^{-1}).

The ecological toxicity of heavy metals was mainly dependent on their chemical speciation. Therefore, the risk assessment code (RAC), which was based on the acid soluble (carbonates) fraction, was introduced to assess the ecological risk and migration of heavy metal (Ke et al. 2017). The RAC assessed heavy metal ecological risk by calculating the percentage for the acid-soluble fraction of heavy metal. Classification of RAC was: RAC < 1%, no risk; 1% ≤ RAC ≤ 10%, low risk; 11% ≤ RAC ≤ 30%, medium risk; 31% ≤ RAC ≤ 50%, high risk; 51% ≤ RAC ≤ 75%, very high risk.

One-way anova was used to examine the effect of particle size on heavy metal concentration. Least significant difference (LSD) multiple comparison method was used to compare the differences of heavy metals in aggregates with different particle sizes. Before one-way anova, a logarithmic transformation was carried out to ensure that the dataconformed to the normal distribution. SPSS software v.23.0 was performed for the one-way anova.

Results and Discussion

On average, the proportion of > 1 mm, 0.25–1 mm, 0.05–0.25 mm and < 0.05 mm soil aggregates were (23.59 ± 9.92)%, (32.19 ± 9.44)%, (39.21 ± 16.99)% and (4.89 ± 2.43)%, respectively. Concentrations of heavy metals in bulk soil and soil aggregates with different particle sizes are presented in Fig. 2. Overall, concentrations of heavy metals increased with the decrease of particle sizes. The results of one-way anova showed that the particle size of soil aggregates had a significant effect on the contents of heavy metals except Cr and Cu ($p = 0.060$ for Cr, $p = 0.008$ for Ni, $p = 0.052$ for Cu, $p = 0.042$ for Zn, $p = 0.037$ for As, $p = 0.043$ for Cd and $p = 0.001$ for Pb). The results of the LSD are shown in Fig. 2. All results are presented in the form of mean ± standard deviation, $^*p < 0.05$. This is consistent with previous studies' finding that heavy metals tend to accumulate in fine particles of soil (Li et al. 2018, 2017). This was mainly due to the increase of soil specific surface area and organic matter content with the decrease of soil particle size. Although the proportion of < 0.05 mm soil aggregate is the lowest, the concentrations for all heavy metals in < 0.05 mm soil aggregate were the highest. For all heavy metals, concentrations in < 0.05 mm and 0.05–0.25 mm soil aggregates were higher than the concentrations in bulk soil.

Table 1 The sequential extraction scheme of Tessier et al. (1979)

Form	Extractant	Extraction condition
exchangeable (F1)	1 M $MgCl_2$	1:8 of soil to solution. 1 h shaking, room temperature
Acid soluble (F2)	1 M CH_3COONa	1:8 of soil to solution. pH = 5; 5 h continuous agitation, room temperature
Reducible (F3)	0.04 M $NH_2OH.HCl$	1:20 of soil to solution. 6 h occasional agitation, (96 ± 3) °C
Oxidizable (F4)	0.02 M HNO_3, 30% H_2O_2	Final volume: 100 mL. pH = 2. 3 h occasional agitation, (85 ± 2) °C
Residual (F5)	Total heavy metal – F1–F2–F3–F4	

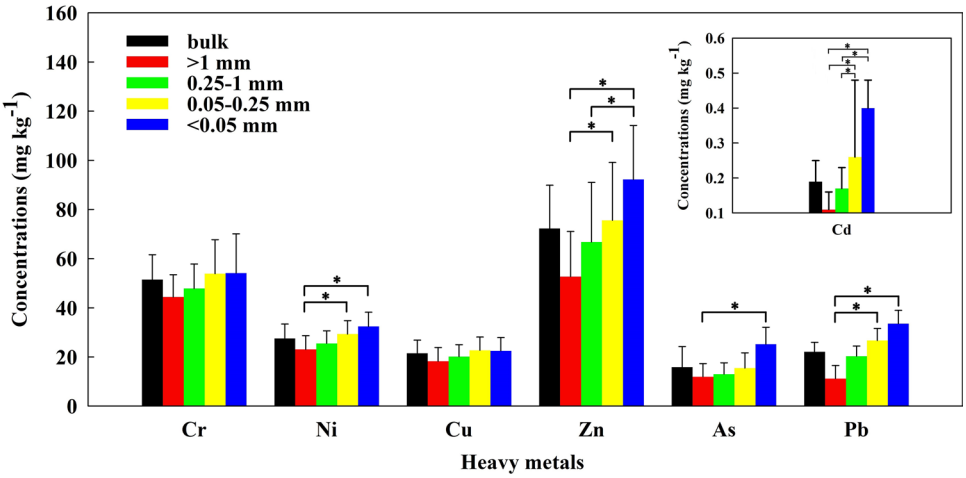

Fig. 2 Heavy metals concentrations in bulk soil and soil aggregates with different particle sizes

It is worth noting that the concentrations of Cr, Ni and Cu in bulk soil were lower than their corresponding background values, but concentrations of Cr, Ni and Cu in < 0.05 mm soil aggregate were higher than their corresponding background values. It is necessary to assess the contribution of soil aggregates with different particle sizes to the risk of heavy metals.

Concentrations varied greatly among heavy metals, comparison of concentration cannot reflect the enrichment degree of different metals. As a standard parameter, AFs can clearly illustrate the accumulation of heavy metals in soil aggregates with different particle sizes (Acosta et al. 2009; Gong et al. 2014; Zhang et al. 2013). The AFs of heavy metals in soil aggregates with different particle sizes is shown in Fig. 3. The lowest AF value appeared in > 1 mm and 0.25–1 mm soil aggregates, and the lowest AF values were 0.51 for Pb, 0.58 for Cd, 0.73 for Zn, 0.75 for As, 0.84 for Ni, 0.85 for Cu and 0.86 for Cr. The highest AF values were 2.11, 1.60, 1.52, 1.38, 1.28, 1.18, 1.05 for Cd, As, Pb, Zn, Ni, Cu, and Cr, respectively, observed in < 0.05 mm aggregates. Our data are in line with previous studies in soils of Beijing and Bangladesh (Li et al. 2017; Li et al. 2014; Islam et al. 2014). Accumulation factor values for Zn, As, Cd, Pb had a significant change in soil aggregates with different particle sizes ($p < 0.05$); AF values of Cr, Ni and Cu were relatively stable. According to the results of AFs, heavy metals in < 0.05 mm aggregate from agricultural soil of the FRB were polluted more seriously than other particle size soil aggregates.

Bioavailability of heavy metal was the sum of the exchangeable fraction, acid soluble fraction, reducible (Fe–Mn oxide bound) fraction and oxidizable (organically bound + sulfide bound) fraction. As shown in Fig. 4, the percentages of bioavailability of Cr, Ni, Cu, Zn, As, Cd

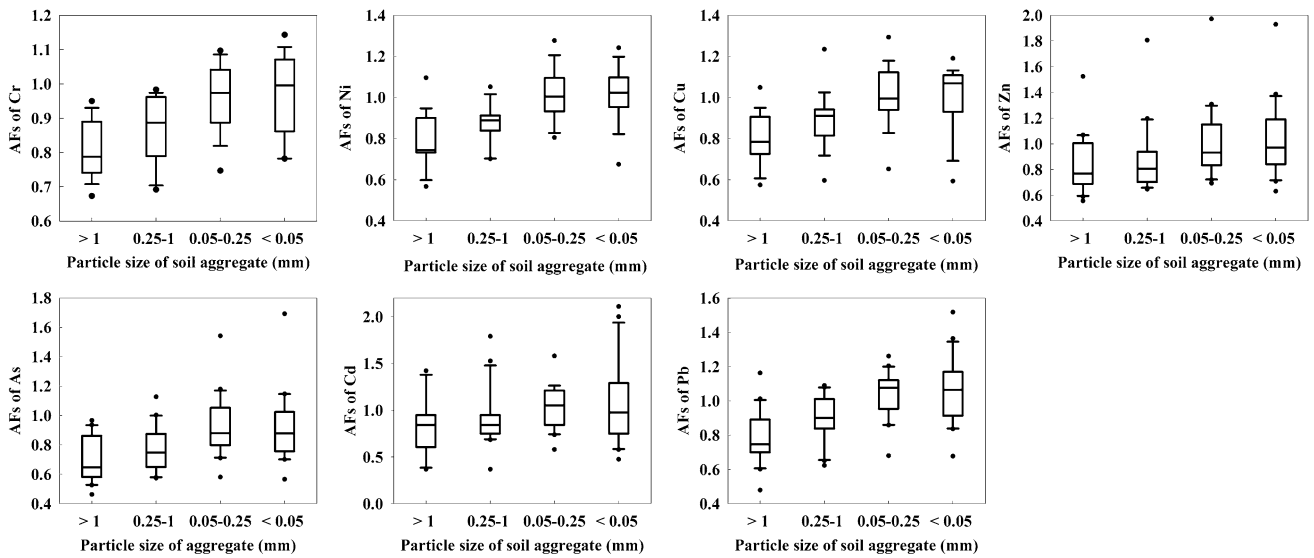

Fig. 3 Accumulation of heavy metals in soil aggregates with different particle sizes

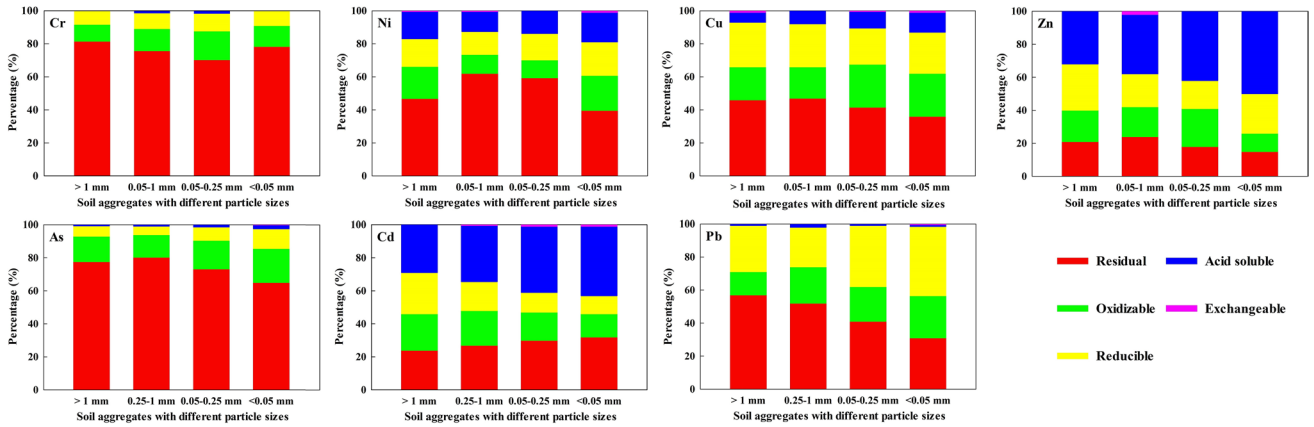

Fig. 4 Chemical speciation of heavy metals in soil aggregates with different particle sizes

and Pb were from 18.71% to 29.84%, 38.01% to 64.17%, 53.82% to 64.17%, 76.03% to 85.92%, 19.81% to 35.11%, 70.42% to 82.51% and 43.05% to 69.48%, respectively. The bioavailability of Ni, Cu, As, Zn and Pb increased from the particle of 0.25–1 mm to < 0.05 mm, suggesting that the smaller the aggregate size of soil, the higher the bioavailability to plants of these heavy metals. It is worth noting that bioavailability of Cd decreased with the decrease of soil aggregate particle size, and the proportion of bioavailability of Cd in < 0.05 mm soil aggregates was as high as 70.42%.

Risk assessment code (RAC) was proved to be associated with the ecological risk and migration of the heavy metals (Chen et al. 2016; Ma et al. 2016; Perin et al. 1985; Singh et al. 2005). According to the classification of RAC, Lead, Cr and As were no potential ecological risk to environment, with their RAC from 0% to 0.98%. The RACs for Ni, Cu, Zn and Cd were 13.84%–21.08%, 7.13%–13.74%, 32.08%–51.82% and 29.38%–43.82%, respectively, in soil aggregates with different particle sizes decreasing from > 1 to < 0.05 mm, suggesting these metals would pose a low to very high risk of migrating to other ecosystems (Fig. 4). In addition, RACs for Cu, Zn and Cd increased with the decrease of soil aggregate particle size, and the RAC for Ni increased from a particle size of 0.25–1 mm to < 0.05 mm. For these four metals, the smaller particle size, the higher the ecological risk, and the easier to migrate to other ecosystems.

Heavy metal concentrations increased with the decrease of particle size of soil aggregate, and heavy metals in < 0.05 mm soil aggregate created more polluted in the agricultural soil from the FRB according to the AF values. The accumulation order for heavy metals in < 0.05 mm soil aggregate was Cd > As > Pb > Zn > Ni > Cu > Cr. Copper, Zn, and Cd had higher bioavailability to plants: the smaller the particle of the soil aggregate, the higher the bioavailability (except Cd). Copper, Zn, Ni, Cd a low to very high risk of migrating to other ecosystems, and the smaller the particle size, the greater ecological risk. Our study demonstrates that assessment of soil heavy metal enrichment and risk must be based on soil aggregates. The study can give some information on prevention and control of heavy metal pollution in soil in intensive agricultural production area.

Acknowledgements This research was funded by the Applied Basic Research of Shanxi Province of China (No. 201801D221042) and Science and Technology Innovation Fund of Shanxi Agricultural University (No. 2016YJ13).

References

Acosta JA, Faz Á, Karsten K, Boris J, Silvia MM (2011) Heavy metal concentrations in particle size fractions from street dust of Murcia (Spain) as the basis for risk assessment. J Environ Monit Jem 13:3087–3096

Acosta JA, Cano AF, Arocena JM, Debela F, Martínez-Martínez S (2009) Distribution of metals in soil particle size fractions and its implication to risk assessment of playgrounds in Murcia City (Spain). Geoderma 149:101–109

Alloway BJ (2013) Sources of heavy metals and metalloids in soils, 3rd edn. Springer, New York

Bastami KD, Neyestani MR, Molamohyedin N, Shafeian E, Haghparast S, Shirzadi IA, Baniamam M (2018) Bioavailability, mobility, and origination of metals in sediments from Anzali Wetland, Caspian Sea. Mar Pollut Bull 136:22–32. https://doi.org/10.1016/j.marpolbul.2018.08.059

Chen H, Teng Y, Lu S, Wang Y, Wu J, Wang J (2016) Source apportionment and health risk assessment of trace metals in surface soils of Beijing metropolitan, China. Chemosphere 144:1002–1011

Ding G, Fan S, Zhang Y (2015) Pollution and distribution charicteristic of heavy metals in Fenhe river reclaimed water irrigation area of Shanxi Province. J Irrig Drain 34:53–55

Gong C, Ma L, Cheng H, Liu Y, Xu D, Li B, Liu F, Ren Y, Liu Z, Zhao C (2014) Characterization of the particle size fraction associated heavy metals in tropical arable soils from Hainan Island, China. Ecol Environ Sci 139:109–114

Gu YG, Lin Q, Yu ZL, Wang XN, Ke CL, Ning JJ (2015) Speciation and risk of heavy metals in sediments and human health

implications of heavy metals in edible nekton in Beibu Gulf, China: a case study of Qinzhou Bay. Mar Pollut Bull 101:852–859
Institute of Soil Science CAoS (1978) Soil physical and chemical property analysis. Shanghai science and Technology Press, Shanghai
Islam S, Ahmed K, Al-Mamun H, Masunaga S (2014) Trace metals in soil andvegetables and associated health risk assessment. Environ Monit Assess 186:8727–8739
Kabatapendias A (2000) Trace elements in soils and plants, 3rd edn. CRC Press, Boca Raton
Kang X, Song J, Yuan H, Duan L, Li X, Li N, Liang X, Qu B (2017) Speciation of heavy metals in different grain sizes of Jiaozhou Bay sediments: bioavailability, ecological risk assessment and source analysis on a centennial timescale. Ecotoxicol Environ Saf 143:296–306
Ke X, Gui S, Huang H, Zhang H, Wang C, Guo W (2017) Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. Chemosphere 175:473–481
Lee SG, Da HK, Lee YS, Cho SY, Chung MS, Cho MJ, Kang YW, Kim HJ, Kim DS, Lee KW (2018) Monitoring of arsenic contents in domestic rice and human risk assessment for daily intake of inorganic arsenic in Korea. J Food Compos Anal 69:25–32
Li Q, Ji HB, Qin F, Tang L, Guo XY, Feng JG (2014) Sources and the distribution of heavy metals in the particle size of soil polluted by gold mining upstream of Miyun Reservoir, Beijing: implications for assessing the potential risks. Environ Monit Assess 186:6605–6626
Li H, Ji HB, Shi CJ, Gao Y, Zhang Y, Xu XY, Ding HJ, Tang L (2017) 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 F, Zhang J, Liu C, Xiao M, Wu Z (2018) Distribution, bioavailability and probabilistic integrated ecological risk assessment of heavy metals in sediments from Honghu Lake, China. Process Saf Environ Prot 116:169–179
Liu Y, Zhang H, Yin J (2008) Pollution assessment and spatial distribution of soil Hg and Cr in the Taiyuan area of the Fenhe River (in chinese). Trans CSAE 24:57–60+314.
Ma X, Zuo H, Tian M, Zhang L, Meng J, Zhou X, Chang X, Liu Y (2016) Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere 144:264–272
Niu L, Yang F, Xu C, Yang H, Liu W (2013) Status of metal accumulation in farmland soils across China: from distribution to risk assessment. Environ Pollut 176:55–62
Parra S, Bravo MA, Quiroz W, Moreno T, Karanasiou A, Font O, Vidal V, Cereceda F (2014) Distribution of trace elements in particle size fractions for contaminated soils by a copper smelting from different zones of the Puchuncavi Valley (Chile). Chemosphere 111:513–521
Perin G, Craboledda L, Lucchese L, Orio AA (1985) Heavy metal speciation in the sediments of Northern Adriatic Sea. A new approach for environmental toxicity determination. Heavy Met Environ 5:454–456
Quinton JN, Catt JA (2007) Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. Environ Sci Technol 41:3495–3500
Rauret G, López-Sánchez JF, Sahuquillo A, Barahona E, Lachica M, Ure AM, Davidson CM, Gomez A, Lück D, Bacon J (2000) Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. J Environ Monit 2:228–233
Singh KP, Mohan D, Singh VK, Malik A (2005) Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. J Hydrol 312:14–27
Tang R, Keming MA, Zhang Y, Mao Q (2013) The spatial characteristics and pollution levels of metals in urban street dust of Beijing, China. Appl Geochem 35:88–98
Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particular trace elements. Anal Chem 15:844–851
Thinh NV et al (2018) Chemical speciation and bioavailability concentration of arsenic and heavy metals in sediment and soil cores in estuarine ecosystem, Vietnam. Microchem J 139:268–277
Upadhyay MK, Shukla A, Yadav P, Srivastava S (2019) A review of arsenic in crops, vegetables, animals and food products. Food Chem 276:608–618
Uusitalo R, Turtola E, Kauppila T, Lilja T (2001) Particulate phosphorus and sediment in surface runoff and drainflow from clayey soils. J Environ Qual 30:589–595
Xu S, Guo S, Hu Y, Li F, Wang Y, Ye H, Zhong A, Shi C (2007) Revaluation of soil heavy metals pollution in Zhangshi irrigation area of Shenyang and analysis of Cd forms in soil (in chinese). Chin J Appl Ecol 18:2144–2148
Yıldırım G, Tokalıoğlu Ş (2016) Heavy metal speciation in various grain sizes of industrially contaminated street dust using multivariate statistical analysis. Ecotoxicol Environ Saf 128:266–266
Yong Z, Gao X (2015) Rare earth elements in surface sediments of a marine coast under heavy anthropogenic influence: The Bohai Bay, China. Estuar Coast Shelf Sci 164:86–93
Zhang H, Luo Y, Makino T, Wu L, Nanzyo M (2013) The heavy metal partition in size-fractions of the fine particles in agricultural soils contaminated by waste water and smelter dust. J Hazard Mater 248–249:303–312
Zhao H, Li X, Wang X, Di T (2010) Grain size distribution of road-deposited sediment and its contribution to heavy metal pollution in urban runoff in Beijing, China. J Hazard Mater 183:203–210