Proceedings of the 3rd International Conference on Green Energy, Environment and Sustainable Development (GEESD2022), X. Zhang et al. (Eds.)

doi:10.3233/ATDE220338

Concentration, Speciation and Risk of Migration and Transformation of Soil Metals Around a Pb-Zn Mine

Zhicheng DONG[a,b], Chenhao XU[a], Lin WANG[a], Shuxing LIU[c] and Lina ZHANG[a,b,1]
[a] *School of Geographic Sciences and Tourism, Jiaying University, Meizhou 514015, Guangdong, China*
[b] *Guangdong Provincial Key Laboratory of Conservation and Precision Utilization of Characteristic Agricultural Resources in Mountainous Areas, Jiaying University, Meizhou 514015, Guangdong, China*
[c] *School of Resources and Environmental Engineering, Ludong University, Yantai 264025, Shandong, China*

Abstract. The migration and transformation of soil heavy metals around mines is a hot issue of global concern. In order to evaluate the potential risk of migration and transformation, investigation and surface soil sample collection were conducted around a Pb-Zn mine. Contents of fourteen metals in four different fields were analyzed. And speciation of As, Cd, Cr, Cu, Ni, Pb and Zn was detected by sequential extraction procedures. Then, characteristics of them are discussed. Moreover, the risk of migration and transformation was evaluated based on the risk index (RI), bioavailability index (BI), easier migration index (EMI), harder migration index (HMI). The results show that metal contents in Field 2, Field 3 and Field 4 are higher than the background values. And they are also higher than that in the cleaning and control field (Field 1), except for Co, Mo, Th, Tl and U. The results also indicate that the speciation contents of exchangeable and carbonate bounds in Field 3 and Field 2 are higher than that in Field 4. Furthermore, the RI and the HMI in Field 4 are higher than that in Field 2 and Field 3, with the values of 21.2, 18.8, 10.2 and 1.95, 1.72, 1.49. Nevertheless, the BI and the EMI in Field 3 are higher than that in Field 2 and Field 4, with the values of 1.22, 1.00, 0.85 and 1.823, 1.816, 1.765. This indicates that based on element migration, transformation and bioavailability, more attention should be paid to Field 3 and Field 2 than Field 4. Finally, the results also show that Zn, Cd and Pb should be concerned in order. All of these above not only aid to determine the priority order of soil heavy metals, but also provide a basis for the selection and decision making of remediation strategies.

Keywords. Heavy metals, speciation, migration, transformation, risk

1. Introduction

Exploitation of metal mines usually causes negative impacts on the ecology and the environment [1-3]. Pb-Zn mines were no exception. Discharge of three wastes of Pb-Zn mines industry is an important pollutant source [2, 4], owing to their contribution of making the soil rich in metals, especially heavy metals [4], such as Cu, Pb, Zn and Cd

[1] Corresponding Author, Lina ZHANG, School of Geographic Sciences and Tourism, Jiaying University, Meizhou 514015, Guangdong, China; Email: Zhanglina_2005@126.com.

etc. These heavy metals consist of different speciation [5], such as exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic-bound and residual fractions [6, 7]. Some of them are bioavailable while others are non-bioavailable [6]. In other words, some of them are active while others are inactive [5]. Those metals of bioavailable and/or active speciation could migrate from soils to other components of the ecosystem, such as groundwater and plants [2, 8]. Furthermore, they can cause harm to ecosystem and human health through biological amplification [1, 2, 4], and even cause public hazards, such as the itai-itai disease occurred in Jinzu River Basin in Toyama of Japan last century [9]. Therefore, it is necessary to evaluate their speciation, bioavailability, activity, and capacity of migration and transformation, together with their risk [10, 11]. This is the premise of risk assessment, identification of the priority control metal(s), selection of remediation measures and environmental protection strategies [11]. And it is of great theoretical and practical significance.

It is generally known that metal speciation not only directly affects the migration and the transformation ability, but also directly affects the accumulation ability and the biological toxicity [5-7, 12]. Some research proposes that the ratio of the sum content of acid extracted fraction and reduced fraction to the total content of all speciation could be used as activity coefficient [13, 14]. And the activity coefficient could be applied to evaluate the availability of heavy metals [13, 14]. Other studies assess the ecological risk of soil heavy metals by using the potential ecological risk index proposed by Hakanson in 1980 [11, 15, 16]. There are also some researchers advise that the ratio of content of acid extracted fraction to the total content of all speciation could be used as potential migration index (PMI) to evaluate the migration capacity of heavy metals from soil to other materials, such as water bodies, plants, and so on [8, 17, 18]. Besides, other indexes including the enrichment factor (EF), mobility factor (MF), pollution load index, potential ecological risk index (PERI), individual contamination factor (ICF) and global contamination factor (GCF) were employed for the assessment of soil contamination and ecological risks [19]. However, there is no consensus on how to evaluate the migration and/or potential and risk of heavy metals at present. It still remains to be further studied.

Thus, soil metals in different fields around a Pb-Zn mine were detected in this study. And the speciation is extracted and analyzed by sequential extraction procedures. Based on the characteristics of metal contents and speciation, risk index (RI), bioavailability index (BI), easier migration index (EMI), harder migration index (HMI) were calculated to evaluate the risk of migration and transformation.

2. Materials and Methods

Field investigations were conducted around a Pb-Zn mine in September 2019, especially in Field 1, Field 2, Field 3 and Field 4. Field 1 is the clean control field far away from the Pb-Zn mine. Other three fields such as Field 2, Field 3 and Field 4 are located in the downstream valley of the Pb-Zn mine. A total of 20 surface soil samples (five samples in each field) were collected a depth of 0-20 cm. The sampling and pretreatment procedures are based on the Technical Specification for soil Environmental monitoring (HJ/T166-2004). Contents of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Th, Tl, U and Zn were analyzed by ICP-AES (Agilen 5110) and ICP-MS (Agilen 7900). The speciation of As, Cd, Cr, Cu, Ni, Pb and Zn was separated into exchangeable, carbonate-bound, Fe-Mn oxide-bound, organic-bound and residual fractions. The speciation contents were measured by using ICP-MS (Agilen 7900). Certified material of GBW07405 (GSS-5) was used to guarantee the accuracy of analytical quality.

Data processing, statistical analysis and charts were conducted by using STATISTICA 6.0 and Excel 2010.

3. Results

3.1. Characteristics of Metal Contents in Different Fields around the Pb-Zn Mine

3.1.1. Content Level of Soil Metals

As shown in Table 1, differences of the ranges, standards deviations, kurtosis and skewness coefficients vary little among different metals. And it implies that the dispersion of these content data is small, and there are almost no outliers.

Table 1. Basic statistics of element contents in different soils around a Pb-Zn mine.

Field no.		As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Se	Th	Tl	U	Zn
1	Mean	16.82	0.09	5.92	84.40	25.36	1.55	22.40	36.20	1.52	1.60	20.90	0.61	4.32	70.6
	Min	12.30	0.06	3.20	79.0	22.60	1.33	19.00	29.00	1.25	1.00	18.40	0.47	3.90	61.0
	Max	20.20	0.12	8.30	89.0	28.20	1.75	26.00	44.00	1.74	2.00	23.80	0.76	4.80	82.0
	SD	3.00	0.03	2.12	3.97	2.03	0.16	2.70	5.50	0.22	0.55	2.16	0.12	0.33	9.18
	Skew	-0.78	0.34	-0.14	-0.37	0.09	-0.40	0.18	0.24	-0.42	-0.61	0.36	-0.01	0.42	0.30
	Kurt	0.55	-2.69	-1.83	-1.10	1.03	0.13	-0.68	0.80	-2.59	-3.33	-1.31	-1.58	1.22	-2.42
2	Mean	28.02	2.59	97.10	80.60	51.12	12.24	63.32	525.6	2.71	1.20	18.28	0.88	6.96	538.8
	Min	25.40	2.51	90.60	74.0	48.70	10.73	60.10	515.0	2.44	1.00	15.86	0.77	6.40	514.0
	Max	30.10	2.75	101.00	95.0	55.10	14.26	66.40	543.0	2.96	2.00	20.38	0.97	7.50	553.0
	SD	1.99	0.10	4.59	8.50	2.66	1.51	2.30	11.08	0.20	0.45	1.80	0.08	0.42	17.14
	Skew	-0.35	1.18	-0.81	1.70	0.96	0.61	-0.12	1.05	-0.22	2.24	-0.35	-0.37	-0.05	-0.89
	Kurt	-1.83	-0.001	-1.56	2.98	-0.44	-2.00	0.80	1.10	-1.08	5.00	-1.21	-0.95	-0.17	-1.23
3	Mean	25.92	1.62	10.74	65.6	60.20	1.22	23.88	223.4	3.35	1.60	16.39	0.70	4.38	263.4
	Min	23.40	1.10	9.10	63.0	57.30	1.00	23.30	205.0	3.16	1.00	14.65	0.60	4.10	257.0
	Max	30.30	1.93	13.20	68.0	66.10	1.38	24.40	245.0	3.52	2.00	18.63	0.88	4.80	276.0
	SD	2.82	0.33	1.71	2.07	3.44	0.15	0.47	15.7	0.15	0.55	1.76	0.12	0.31	7.60
	Skew	1.00	-1.08	0.61	-0.24	1.80	-0.67	-0.01	0.45	-0.02	-0.61	0.18	1.13	0.56	1.50
	Kurt	0.72	0.76	-0.71	-1.96	3.61	-0.70	-2.06	-0.84	-1.48	-3.33	-2.16	0.68	-1.92	2.38
4	Mean	57.74	3.01	19.08	68.4	148.82	3.69	44.94	348.6	4.53	1.80	17.73	0.99	4.90	371.0
	Min	51.30	2.90	17.50	65.0	143.30	3.47	43.70	327.0	4.38	1.00	15.44	0.87	4.70	358. 0
	Max	62.40	3.16	20.40	72.0	155.40	3.94	46.30	386.0	4.75	2.00	19.57	1.21	5.30	384.0
	SD	4.32	0.10	1.19	2.7	5.01	0.17	1.05	23.1	0.16	0.45	1.55	0.13	0.23	9.75
	Skew	-0.79	0.71	-0.48	0.18	0.45	0.48	0.18	1.35	0.74	-2.24	-0.62	1.72	1.74	-0.03
	Kurt	0.11	0.66	-1.72	-0.68	-1.86	0.63	-1.43	1.75	-1.59	5.00	0.47	3.50	3.32	0.03
Background values [20]		8.9	0.056	7.0	50.5	17.0	7.70	14.4	36	0.54	0.288	27.92	0.68	5.51	47.3
Risk screening vales [21]		30	0.3		250	50.0		70.0	100						200
Risk control values [21]		150	1.5		850				500						

Note: SD stands for standard deviation; Skew stands for Skewness; Kurt stands for Kurtosis.

As described in Table 1, contents of almost all soil metals in the four fields were higher than the soil background values. Specifically, compared to background values, contents of these 14 soil metals are all higher in Field 2, Field 3 and Field 4. And they are also higher than in Filed 1, except for Co, Mo, Th, Tl and U.

3.1.2. Variation of Soil Metals in Different Fields

As demonstrated in Figure 1, soil metal contents vary among different fields. Contents of Pb, Zn, Cu, Cd, U, Co, Ni, Tl, As and Sb are higher in Field 2, Field 3 and Field 4 than in the cleaning and control field (Field 1). And content variations of Mo and Se are generally similar to those metals just mentioned. In contrast, contents of Cr and Th are lower in Field 2, Field 3 and Field 4 than in Field 1. Specifically, contents of Pb, Zn, U, Co and Ni decrease in Field 2, Field 4, Field 3 and Field 1 in order. And contents of Cd, Tl and As decrease in Field 4, Field 2, Field 3 and Field 1 in order. Similarly, contents of Sb and Cu follow the order of Field 4 > Field 3 > Field 2 > Field 1. And contents of Mo and Se follow the order of Field 2 > Field 4 > Field 1 > Field 3 and Field 4 > Field 3 = Field 1> Field 2, respectively. However, contents of Cr and Th decrease in Field 1, Field 2, Field 4 and Field 3 in order.

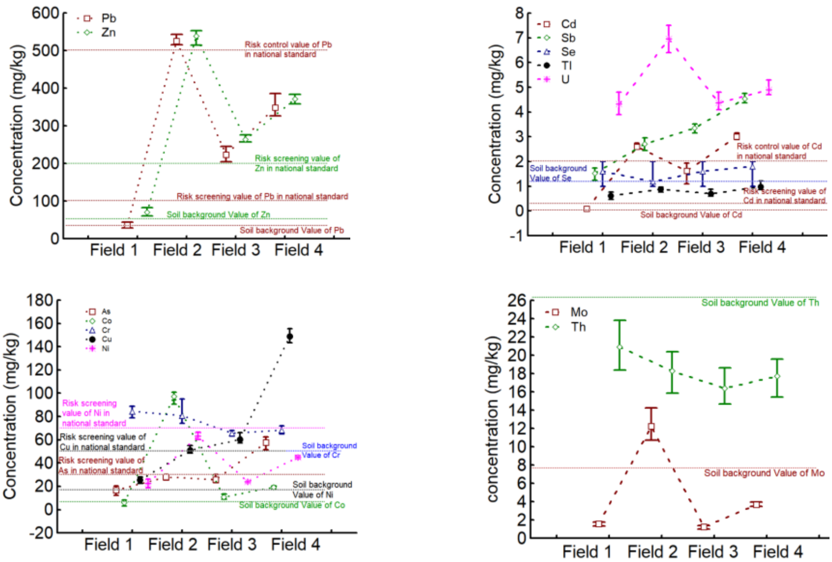

Figure 1. Soil element contents in different fields.

As illustrated in Figure 1, metal contents vary among different elements in the same field. In detail, metal contents follow the order of Cr > Zn > Pb > Cu > Ni > Th > As > Co > U > Se > Mo > Sb > Tl > Cd in Field 1, Zn > Pb > Co > Cr > Ni > Cu > As > Th > Mo > U > Sb > Cd > Se > Tl in Field 2, Zn > Pb > Cr > Cu > As > Ni > Th > Co > U > Sb > Cd > Se > Mo > Tl in Field 3, and Zn > Pb > Cu > Cr > As > Ni > Co > Th > U > Th > U > Sb > Mo > Cd > Se > Tl in Field 4, respectively. Especially, for Zn, Pb and Cd, whose contents exceed the risk screening values of the risk control standard for soil contamination of agricultural land (GB15618-2018), they get better rankings in Field 2, Field 3 and Field 4 than in Field 1. Specifically, contents of Zn in Field 2, Field 3 and Field 4 are all ranked in the first place, followed by contents of Pb. And contents of Cd are also not the last, but getting better ranking than Tl and Se. In comparison, contents of Zn and Cd get lower ranking than Cr, with the ranking in second and third places in Field 1. And content of Cd also gets lower ranking than Tl and Se, with the ranking in the last place.

3.2. Characteristics of Metal Speciation

As illustrated in Figure 2, Cd speciation in Field 2, Field 3 and Field 4 is dominated by exchangeable, Fe-Mn oxide bound and carbonate bound, with the approximate mean value of 0.74 μg/g, 0.76 μg/g and 0.53 μg/g, respectively. Pb speciation is dominated by residual and carbonate bound, with the approximate mean value up to 234.2 μg/g and 96.23 μg/g. Zn speciation is dominated by exchangeable, Fe-Mn oxide bound and carbonate bound, with the approximate mean value up to 169.1 μg/g, 72.0 μg/g and 61.9 μg/g, respectively. This generally consists with previous studies [22]. Cu speciation is dominated by residual, with the approximate mean value up to 48.5 μg/g. Cr speciation is dominated by residual, with the approximate mean value up to 449.0 μg/g. Previous study also concludes that exchangeable Cr is lower while residual Cr is higher [23]. Ni speciation is dominated by residual, with the approximate mean value up to 27.7 μg/g. It is also found that exchangeable Ni was lower while residual Ni is higher in soils [24]. As speciation is dominated by residual, with the approximate mean value up to 26.0 μg/g. Previous research also shows that exchangeable As is lower while residual As is higher [23]. These residual metals are kept inside crystal lattices of their minerals [7], and not easy to be released into the environment [25].

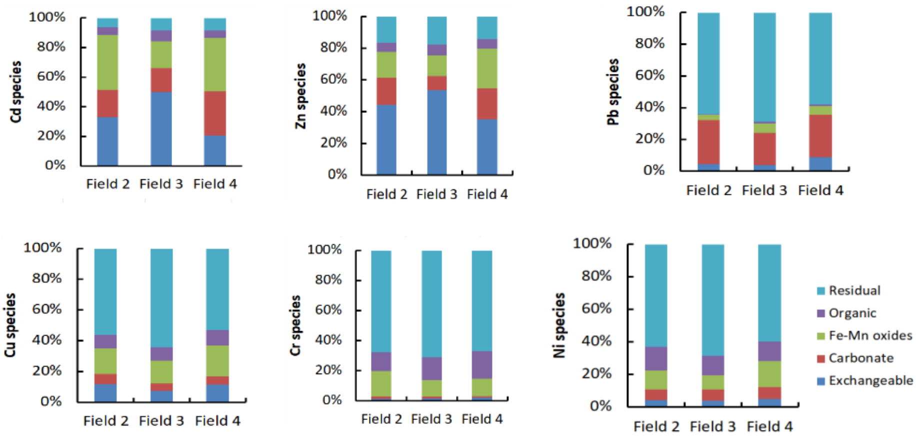

Figure 2. Percentage contents of mental speciation in different fields.

4. Discussions

4.1. Correlation between Content and Speciation of Soil Metals around the Pb-Zn Mine

As demonstrated in Table 2, organic bound Cd, Fe-Mn Oxide bound Pb, carbonate bound Cu, Cr of exchangeable, carbonate and residual, residual Ni, and As of Fe-Mn oxide bound, organic bound and residual are significantly correlated with their total contents in Field 2. And in Field 3, there are also significant correlations between the total content of soil metals and Cd of Fe-Mn oxide bound, organic bound and residual, residual Pb, Fe-Mn oxide bound Cu, together with As of Fe-Mn oxide bound, organic bound and residual. In similar, Fe-Mn oxide bound Cu, carbonate bound and organic bound Cr, together with As of Fe-Mn oxide bound, organic bound and residual are also significantly correlated with their total contents in Field 4. It indicates that some speciation contents are significantly correlated with the total contents of soil metals in these three fields. However, there are not significant correlation between other speciation and the total content. Similar relationships are generally consistent with some existing understandings. For instance, it is found that there is a negative correlation between the total content and speciation content of metals, such as exchangeable Cu and Cd [26]. Nevertheless, it is also found that there is no correlation between the total content and speciation content of metals, such as exchangeable Pb, exchangeable Cr and carbonate bound Cr [26].

Table 2. Correlation coefficients between total content and speciation of soil metals.

Field no.	Speciation	Cd	Pb	Zn	Cu	Cr	Ni	As
Field 2	Exchangeable	0.17	0.25	0.71	-0.59	0.87**	0.74	0.80
	Carbonate	-0.25	-0.69	-0.62	0.92*	0.82**	0.46	-0.53
	Fe-Mn oxides	-0.21	0.93*	-0.40	0.49	0.72	0.65	0.91*
	Organic	0.95*	0.55	0.30	0.73	0.80	-0.06	0.95*
	Residual	0.45	0.24	0.27	0.53*	0.99*	0.85**	0.92*
Field 3	Exchangeable	0.66	-0.66	0.76	-0.33	0.55	0.43	0.71
	Carbonate	0.78	-0.04	-0.78	-0.18	0.73	-0.32	-0.27
	Fe-Mn oxides	0.87**	0.05	0.42	0.84**	0.44	-0.05	0.97*
	Organic	0.98*	-0.41	0.20	0.72	0.72	0.54	0.94*
	Residual	0.82**	0.87**	0.60	0.93*	0.48	0.57	0.96*
Field 4	Exchangeable	-0.80	0.11	-0.45	0.01	0.63	0.54	0.57
	Carbonate	-0.35	-0.13	0.51	-0.35	0.83**	0.10	0.08
	Fe-Mn oxides	0.58	-0.26	-0.26	0.88*	-0.77	0.59	0.89*
	Organic	0.26	-0.08	0.11	0.04	0.84**	-0.07	0.93*
	Residual	0.21	0.56	0.07	0.69	0.96*	0.38	0.96*

Note: * marked correlations are significant at $p < 0.05000$; ** marked correlations are significant at $p < 0.10000$.

4.2. Pollution Risk of Soil Metals around the Pb-Zn Mine

4.2.1. Pollution Risk of Different Fields

The ratio of soil metal content to its risk screening value (GB15618-2018) could be used as the risk index (RI) to reflect the pollution risk, to some extent. Moreover, total risk index of all metals could reflect the pollution risk of the sample site and/or the whole field, to some extent. As illustrated in Figure 3, total risk index of Cd, Pb, Zn, Cu, Cr, Ni and As is the highest in Field 4, with the mean value of 21.1, and ranges from 20.6 to 22.4. It is followed by Field 2 and Field 3 in order, with the mean values of 18.8 and 10.2. The values range from 17.2 to 18.0 in Filed 2, and from 8.2 to 11.5 in Field3. Likewise, total risk index of Cd, Pb, Zn, and Cu is also the highest in Field 4, with the mean value of 18.4, and ranges from 17.7 to 19.4. It is followed by that in Field 2, with the mean value of 17.6, and ranges from 17.2 to 18.0. And it is the lowest in Field 3, with the mean value of 10.2, and ranges from 8.2 to 11.5.

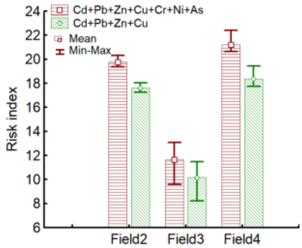

Figure 3. Risk index of different fields.

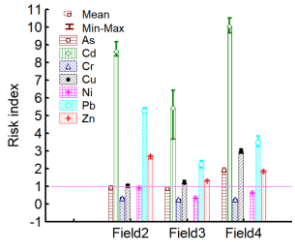

Figure 4. Risk index of different soil metals.

4.2.2. Pollution Risk of Different Metals

As demonstrated in Figure 4, RI of Cd in Field 2 and Field 4, together with Pb in Field 2, are higher, with the mean values of 8.6, 10.0 and 2.2, respectively. And their risk indices range from 8.4 to 9.2, from 9.7 to 10.5 and from 2.05 to 2.45, respectively. This indicates that the pollution risks of Cd, Pb, Cu and Zn in these three fields are higher, especially Cd and Pb. According to risk control standard for soil contamination of agricultural land (GB15618-2018), when the contents of soil metals are higher than risk intervention values, soil pollution risk is high, such as edible agricultural products not up to the quality and safety standards. In this case, strict control measures such as no planting edible agricultural products and returning the grain plots to forestry should be carried out in principle.

4.3. Migration Potentiality (Risk) of Soil Metals

Bioavailability, activity, and capacity of migration and transformation of soil metals are closely related to their speciation [5, 6, 27, 28]. Hence, metals' potentiality (risk) of activity, stability, migration and transformation could be well reflected by their speciation contents and ratios.

4.3.1. Bioavailability Potentiality (Risk) of Soil Metals

Exchangeable metals include water-soluble ones and those adsorbed by soil clay minerals and other components (such as iron hydroxide, manganese hydroxide, humus, etc.). Metals of this speciation have a great impact on the food chain owing to their sensitivity to environmental change, characteristics of easy migration and transformation, and absorptivity by plants [29-31]. Hence, the ratio of exchangeable metal content to the total content of all speciation could be used as the bioavailability index (BI) [18, 32]. And the BI could be applied to compare and determine the bioavailability potentiality (risk) of soil metals.

As demonstrated in Figure 5, sum of BI of Zn, Cd, Cu, Pb, Ni, Cr and As is different in Field 2, Field 3 and Field 4, with the values of 1.00, 1.22 and 0.85, respectively. And for Zn, Cd, Cu, Pb, sum of their BI is also different with the values of 0.94, 1.15 and 0.76, respectively. It indicates that Filed 3 is the most at bioavailability potentiality (risk) of soil metals, followed by Field 2 and Field 4 in order.

As illustrated in Figure 6, the change of BI basically follows as Zn > Cd > Cu > Pb > Ni > Cr > As in these three fields. More specifically, BI of Zn and Cd are higher than other metals, with the approximate mean values of 0.44 and 0.35. And BI of Cu is lower, with the mean value of approximately 0.10. Especially, BI of Pb, Ni, Cr and As are much more lower, with the approximate mean values of 0.06, 0.04, 0.03 and 0.01. It implies that Zn and Cd are the most at bioavailability potentiality (risk). Hence, Zn and Cd in these three fields should be paid more attention.

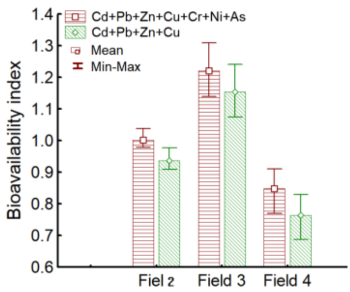

Figure 5. BI of different fields.

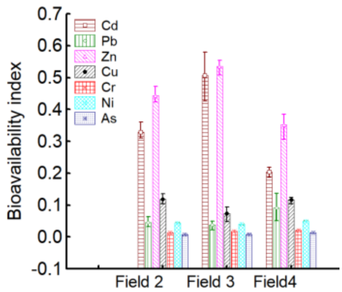

Figure 6. BI of different fields metals.

4.3.2. Easier Migration Potentiality of Soil Metals

As mentioned earlier, exchangeable metals are easy to migrate and transform. Therefore, it is very harmful to the food chain and ecosystem. And carbonates bound metals are those absorbed in carbonates or coprecipitated with carbonates. They are sensitive to pH changes. When the pH value decreases, they are easily released again into environment, and absorbed by organisms. It is also very harmful to the food chain and ecosystem [30, 31]. Hence, the ratio of the sum content of these two kinds of speciation (exchangeable and carbonates bound metals) to the total content of all kinds of speciation could be used as the easier migration index (EMI) to compare and determine the easier migration potentiality of soil metals.

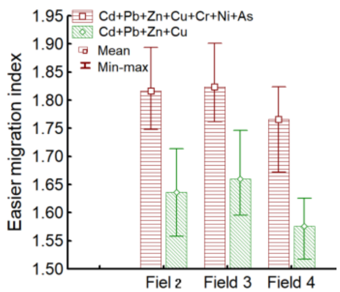

Figure 7. EMI of different fields.

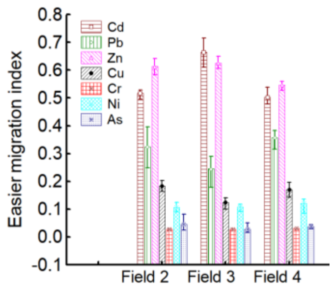

Figure 8. EMI of different metals.

As demonstrated in Figure 7, sum of EMI of Zn, Cd, Cu, Pb, Ni, Cr and As is different in Field 2, Field 3 and Field 4, with the values of 1.816, 1.823 and 1.765, respectively. And for Zn, Cd, Cu, Pb, sum of their EMI is also different in these three fields, with the values of 1.64, 1.66 and 1.58, respectively. It implies that Filed 3 is the most at easier migration potentiality of metals, followed by Field 2 and Field 4 in order.

As illustrated in Figure 8, the change of EMI basically follows as Zn > Cd > Pb > Cu > Ni > As > Cr in these three fields. In detail, EMI of Zn, Cd and Pb is higher than other metals, with the approximate mean values of 0.59, 0.56 and 0.31. And EMI of Cu and Ni is lower, with the mean values of approximately 0.16 and 0.11. Especially, EMI of As and Cr is much lower, with the approximate mean values of 0.04 and 0.03.

It indicates that Zn, Cd and Pb are more of easier migration potentiality. Hence, Zn, Cd and Pb in these three fields should be paid more attention.

4.3.3. Harder Migration Potentiality of Soil Metals

Existing as mineral coatings and fine dispersed particles, Fe-Mn oxides bound metals are absorbed in iron manganese oxides or coprecipitated with them. They are generally released into environment only when the redox potential and/or pH are lower. Meanwhile, organic bound metals refer to those are complexed or chelated by organic matters (such as biological residues, humus, etc.) in soil. They are generally released into environment only when the redox potential is higher. In sum, metals of these two kinds of speciation (Fe-Mn oxides bound and organic bound) are harder to be released into environment and be absorbed by organisms [29, 30]. Hence, the ratio of the sum content of these two kinds of speciation to the total content of all kinds of speciation could be used as the harder migration index (HMI) to compare and determine the harder migration potentiality of soil metals.

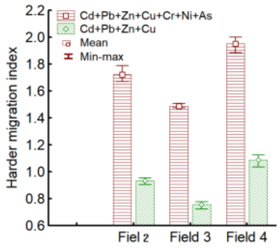

Figure 9. HMI of different fields.

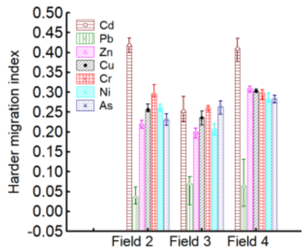

Figure 10. HMI of different metals.

As demonstrated in Figure 9, sum of HMI of Zn, Cd, Cu, Pb, Ni, Cr and As is different in Field 2, Field 3 and Field 4, with the values of 1.72, 1.48 and 1.95, respectively. And for Zn, Cd, Cu, Pb, sum of their HMI is also different in these three fields, with the values of 0.93, 0.75 and 1.08, respectively. It indicates that Filed 4 is the most at harder migration potentiality of soil metals, followed by Field 2 and Field 3 in order.

As illustrated in Figure 10, the change of HMI basically follows as Cd >Cr > Cu > As > Ni > Zn > Pb in these three fields. In detail, EMI of Cd is higher than other metals, with the approximate mean values of 0.36. And HMI of Cu, As, Ni and Zn is lower, with the mean value of approximately 0.28, 0.27, 0.26, 0.25 and 0.24. Especially, HMI of Pb is much lower, with the approximate mean values of 0.06. It implies that Cd is more of harder migration potentiality. Hence, Cd in these three fields should be paid more attention.

5. Conclusions

Ecological risk of fields and metals was compared and determined by comprehensive application of metal contents, speciation contents, RI, BI, EMI and HMI, etc.

(1) Metal contents are not higher but the speciation contents of exchangeable and carbonate bounds are higher in Field 3 and Field 2 than in Field 4.

(2) Field 4 is the most at pollution risk and the harder migration potentiality, followed by Field 2 and Field 3 in order. Their RI and HMI are 21.2, 18.8, 10.2 and 1.95, 1.72, 1.48, respectively. However, Field 3 is the most at bioavailability and the easier migration potentiality, followed by Field 2 and Field 4 in order. Their BI and EMI are 1.22, 1.00, 0.85 and1.823, 1.816, 1.765, respectively.

(3) From the perspective of element migration, transformation and bioavailability, Field 3 has the highest ecological risk, followed by Field 2 and Filed 4 in order.

(4) Compared to Field 4, more attention should be paid to Field 3 and Field 2.

(5) Based on the total content, the speciation, the BI and EMI, Zn, Cd and Pb should be concerned in order.

Acknowledgments

This study was supported by Natural Science Foundation of Guangdong Province (2020A1515011077, 2021A1515012597), Yantai Key Research and Development Plan (2019XDHZ103), Scientific Research Projects of Jiaying University (2020KJY05, 2019KJY05), College Students' innovation and entrepreneurship training program of Jiaying University (202110582096).

References

[1] Qian W, Bing W, Yuena M, Xueyang Z, Wenqiang L, Miao C. Stabilization of heavy metals in biochar derived from plants in antimony mining area and its environmental implications. Environ. Pollut. 2022 Jan;300:118902.

[2] Caren AK, Cuthbert LN, George S, Eliakira KN. Assessing phytoremediation potentials of selected plant species in restoration of environments contaminated by heavy metals in gold mining areas of Tanzania. Heliyon. 2021 Sept;7(9):e07979.

[3] Guan QY, Liu Z, Shao WY, Tian J, Luo HP, Ni F, Shan YX. Probabilistic risk assessment of heavy metals in urban farmland soils of a typical oasis city in northwest China. Science of the Total Environment. 2022 Apr;833:155096.

[4] Fagbenro AA, Yinusa TS, Ajekiigbe KM, Oke AO, Obiajunwa EI. Assessment of heavy metal pollution in soil samples from a gold mining area in Osun State, Nigeria using proton-induced X-ray emission. Sci. Afr. 2021 Nov; 14: e01047.

[5] Guo HY, Zhao SF, Xia DP, Shen Y, lv JH, Liu XL, Xu XK. Speciation transformation and bioavailability of heavy metals during biogas production from coal slime. Biochemical Engineering Journal. 2021 Sept;176:108208.

[6] Mor M, Nadia BB, Frédérique BB, Linda AD, Cheikh D, Mamadou F, Nicole G. Speciation of metals by sequential extractions of agricultural soils located near a dumpsite for prediction of element availability to vegetables. Talanta. 2022 Mar;244:123411.

[7] Rodríguez L, Ruiz E, Alonso-Azcárate J, Rincón J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. J. Environ. Manage. 2009 Feb;90(2):1106-1116.

[8] Jiang CL, Zhao Q, Zheng LG, Chen X, Li C, Ren MX. Distribution, source and health risk assessment based on the Monte Carlo method of heavy metals in shallow groundwater in an area affected by mining activities, China. Ecotoxicol. Environ. Saf. 2021 Aug;224:112679.

[9] Kōji N, Arinobu I, Etsuko K. A comparison between health effects of cadmium and cadmium concentration in urine among inhabitants of the Itai-itai disease endemic district. Environ. Res. 1979 Apr;18(2):397-409.

[10] Adebiyi FM, Ayeni DA. Chemical speciation, bioavailability and risk assessment of potentially toxic metals in soils around petroleum product marketing company as environmental degradation indicators. Petroleum Research. 2021 Sept. https://doi.org/10.1016/j.ptlrs.2021.08.006

[11] Cui XW, Geng Y, Sun RR, Xie M, Feng XW, Li XX, Cui ZJ. Distribution, speciation and ecological risk assessment of heavy metals in Jinan Iron & Steel Group soils from China. Journal of Cleaner Production. 2021 Feb;295:126504.
[12] Li Q, Wang YH, Li YC, Li LF, Tang MD, Hu WF, Chen L, Ai SY. Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. Sci. Total Environ. 2022 Feb;825:153862.
[13] Chen L, Wen F, Cheng Y, He BY. Characteristics of Speciation Distribution and Toxicity Leaching of Heavy Metals in Pb-Zn Tailing. J Arid Land Resour Environ. 2017 Mar;31(3):89-94.
[14] Du M, Wang Y, Li CR, Wen CC, Bu D. Analysis on the form and migration potential of heavy metals in iron tailings of a mine in Tibet. Nonferrous met Eng. 2022 Apr;12(4):140-145.
[15] Liang YY, Yi XY, Dang Z, Wang Q, Gao SQ, Tang J, Zhang ZF. Pollution and risk assessment of heavy metals in agricultural soils around a Pb-Zn tailing pond. J. Agro-Environ Sci. 2019 Jan;38(1):103-110.
[16] Zhou R, Qin C, Ren HJ, Zhao Y. Distribution characteristics and potential risk of heavy metals in soil around water source. China Environ Sci. 2022 Feb. https://doi.org/10.19674/j.cnki.issn1000-6923.20220208.008
[17] Jiang J, Li YC, Wang N, Zhang XS. Effect of cyanobacteria aggregation on the migration and release of heavy metals in Lake Chaohu. J. Lake Sci. 2017 May;29(03):558-566.
[18] Ebong GA, Dan EU, Inam E, Offiong NO. Total concentration, speciation, source identification and associated health implications of trace metals in Lemna dumpsite soil, Calabar, Nigeria. J King Saud Univ-Sci. 2019 Feb;31(4):886-897.
[19] Gujre N, Mitra S, Soni A, Agnihotri R, Rangan L, Rene ER, Sharma MP. Speciation, contamination, ecological and human health risks assessment of heavy metals in soils dumped with municipal solid wastes. Chemosphere. 2020 Aug; 262:128013.
[20] China Environmental Monitoring Center. Background Values of Soil Elements in China. Beijing: China Environ. Sci. Press; c1990. 98-100p.
[21] Ministry of Ecology and Environment of the People's Republic of China. Soil environmental quality: Risk control standard for soil contamination of agricultural land: GB 15618-2018 (in Chinese). Beijing: Stand Press China; c2018. 2-3p.
[22] Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G. Assessment of metal mobility in dredged harbour sediments from Barcelona (Spain). Sci. Total Environ. 2004 Apr;321:241-255.
[23] Delgado J, Barba-Brioso C, Nieto JM, Boski T. Speciation and ecological risk of toxic elements in estuarine sediments affected by multiple anthropogenic contributions (Guadiana saltmarshes, SW Iberian Peninsula): I. Surficial sediments. Sci. Total Environ. 2011 Sept;409:3666-3679.
[24] Pérez-López R, Álvarez-Valero AM, Nieto JM, Sáez R, Matos JX. Use of sequential extraction procedure for assessing the environmental impact at regional scale of the São Domingos Mine (Iberian Pyrite Belt). Appl Geochem. 2008 Dec;23:3452-3463.
[25] Nemati K, Bakar NKA, Abas MR, Sobhanzadeh E. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. J. Hazard Mater. 2011 Aug;192:402-410.
[26] Cui XT, Wang XQ, Luan WL. An analysis of modes of occurrence and biological availability of the heavy metal elements in soil of the central and southern plain in Hebei. Geol. in China. 2015 Apr; 42(2):655-663.
[27] Morillo J, Usero J, Gracia I. Potential mobility of metals in polluted coastal sediments in two bays of southern Spain. J. Coastal Res. 2009 Mar;23:353-361.
[28] Sundaray SK, Nayak BB, Lin S, Bhatta D. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—A case study: Mahanadi basin, India. J.. Hazard Mater. 2011 Feb;186:1837-1846.
[29] Ge Y, Murray P, Hendershot WH. Trace metal speciation and bioavailability in urban soils. Environ Pollut. 2000 Jan;107:137-144.
[30] Maiz I, Arambarri I, Garcia R, Millán E. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. Environ. Pollut. 2000 Oct;110:3-9.
[31] Barona A, Aranguiz I, Elías A. Assessment of metal extraction, distribution and contamination by a 3-step sequential extraction procedure. Chemosphere. 1999 Nov;39(11):1911-1922.
[32] Kidd PS, Domínguez-Rodríguez MJ, Díez J, Monterroso C. Bioavailability and plant accumulation of heavy metals and phosphorus in agricultural soils amended by long-term application of sewage sludge. Chemosphere. 2007 Jan;66(8):1458-1467.