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Full Length Research Paper

Bioaccumulation of eight heavy metals in cave animals from Dashui and Malang caves, Guizhou Province, China

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Eight heavy metals content in the dominant animal groups, soil and water in Malang and Dashui caves were examined. The results showed that zinc contents in *Porcellio scaber* from Dashui and Malang caves were 448.80 and 598.00 mg/kg, respectively, which is the highest among all these 8 metals, while Pb was not detected in *Diestrammena marmorata* and *Rhinolophidae pearsoni*, suggesting that both animals were incapable of or poor in Pb accumulation. The highest average value of enrichment coefficient for soil-born Cd in animals from Dashui cave was 4.15, while that for water-born Zn was 91723.84. By contrast, the highest average value of enrichment coefficient for soil-born Cd in animals from Malang cave was 8.48, and that for water-born Zn was 708102.64.

Key words: Bioaccumulation, heavy metal, cave animals, China.

INTRODUCTION

Cave animals in karst areas are subjected to academic attention (Boris, 2008; Katie et al., 2010; Salin et al., 2010). Several cave eco-environmental factors affect cave animals, such as the light intensity (Ramsey, 1901; Charlton, 1933; Steven and Aldemaro, 1997; Wilkens et al., 2000; Sguanci et al., 2010), temperature and humidity (Studier and Lavoie, 1990; Chapman, 1983; Lavoie et al., 2007). Heavy metals are stable in the environment (Masonrp et al., 2000) and reserved in animal and human bodies through food chains (Rod and Akastair, 1995; Abudul and Bouche, 1997; Klein and Paulus, 1995; Hsu et al., 2006; Vlado et al., 2011), which is one of the important eco-environmental factors. In the karst area, karst caves and water systems in the caves are well developed. So, heavy metals can contaminate cave environment and affect cave animals. Karst topography is widely distributed in Guizhou province, China, accounting for 73.8% of the total land area. So, the examination of heavy metal pollution in cave soil and water and the bio-accumulation of heavy metals in cave animals is an important basis for quality evaluation of cave soil and water.

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MATERIALS AND METHODS

Sampling site

Dashui cave is situated in the urban zone of Guiyang City, Guizhou, and Guizhou Aluminum Plant is a main pollutant source. It is a blind cave (26°36′37.0″ N, 106°36′55.6″ E) with an elevation of 1257 m, the light belt is 16.2 m long, the temperature, humidity and pH value in light belt are 18°C, 90% and 6.0, respectively. The weak-light belt is 5.6 m long and no plant is distributed. The temperature, humidity and pH value are 17°C, 92% and 5.5, respectively. The dark belt is 49.4 m long and no plant is present. The temperature, humidity and pH value are 16°C, 95% and 5.4, respectively.

Malang cave lies in Dongkou Zai, Xiangshan village, Yanshan town, Guiding County, Guizhou. This is a through hole with two openings. Elevation of the cave entrance (26°24′52.8″N, 107°08′-15.3″E) is 1063 m. There is a 28 m long light belt in the entrance of the cave. The temperature, humidity and pH value are 25°C, 80% and 6.0, respectively, the weak-light belt is 3.3 m long, the temperature, humidity and pH value are 24°C, 84% and 6.2, respectively. The dark belt is about 13.6 m long, the temperature, humidity and pH value are 20°C, 90% and 6.0, respectively. The light belt in the exit of the cave is 6.2 m long. The temperature, humidity and pH value are 25°C, 80% and 6.3, respectively. The weak-light belt consists of a 7.8 m-long hall. The temperature, humidity and pH value are 24°C, 90% and 6.5, respectively.

Table 1. Content of eight heavy metals in dominant animals from Dashui and Malang caves.

Study object	Pb	Cd	Hg	As	Cu	Cr	Ni	Zn
	(mg/kg)							
Snails I	8.08	0.88	0.07	6.40	18.06	9.30	26.69	63.53
Snails II	2.50	1.10	0.11	1.33	10.10	17.21	27.75	50.25
Porcellio scaber I	0.96	0.74	0.09	2.06	287.50	14.32	14.23	448.80
Porcellio scaber II	9.30	0.77	0.31	0.98	166.00	12.21	12.30	598.00
Diestrammena marmorata I	ND	0.30	0.34	1.41	37.82	10.96	1.29	128.30
Rhinolophus pearsoni II	ND	0.11	0.68	1.68	9.87	31.34	4.74	84.79

I, Dashui cave; II, Malang cave; ND.

Enrichment coefficient

The enrichment coefficient is the ratio of heavy metal content in animals to that in other environmental factors, which is an indicator of heavy metal accumulation in animals. Higher enrichment coefficient of a metal in animal suggests higher absorption capacity of such animal to corresponding heavy metal.

Field investigation and indoor sample determination

We visited Dashui and Malang caves in August, 2008. Visible cave animals seen with naked eyes including mollusks, arthropods and chordates were investigated. Classification of light belts and arrangement of sampling sites are based on our previous work (Xu et al., 2010). 1 kg of mixed soils and 500 ml of dropping water were collected from typical sites of each light belt and taken to the laboratory for examination. Animal species were identified and classified microscopically in the laboratory. Heavy metal contents in soil, water and animal were determined with AA800 atomic absorption spectrometry and 6300 atomic fluorescence spectrometry. Eight heavy metal elements listed in the Environmental Quality Standard for Soils in China including mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), copper (Cu) and nickel (Ni) were examined in the current study.

RESULTS

Heavy metal contents in animals

Snails, *Porcellio scaber* and *Diestrammena marmorata* from Dashui cave, and snails, *P. scaber* and *Rhinolophus pearsoni* from Malang cave were used for analysis (Table 1). No Pb was detected in *D. marmorata* and *R. pearsoni*. The contents of Zn and Cu were high. The contents of Pb and Cd in animals were very low. The contents of different elements in the same animal group from different caves were different. For example, Zn content in snails from Dashui cave was the highest, followed by Ni, Cu, Cr, Pb, As, Cd and Hg, respectively, while the ranking of different elements in snails from Malang cave was Zn, followed by Ni, Cr, Cu, Pb, As, Cd and Hg, respectively. The content of same element in the same animal group also differed in different caves. For example, Pb content in *P. scaber* from Dashui cave was 9.30, while that from Malang cave was 0.96.

Heavy metal contents in soils

The contents of eight heavy metals in soil samples of different belts from Dashui and Dalang caves were measured (Table 2). The content of same element in soil sample from different light belts of different caves differed. For example, Hg content in the light belt of Dashui cave was the highest, followed by weak-light belt and dark belt, while the highest Hg content in Malang cave was observed in the light belt, followed by dark belt and weak-light belt, respectively. The content of different element in the same light belt of different caves differed even greatly. For example, the ranking in the dark belt of Dashui cave was Zn > Cu > Pb > Ni > Cr > As > Hg > Cd, while that in Malang cave was Zn > Cr > Ni > Cu > Pb > As > Cd> Hg. As seen from the average value of each element in the three light belts of both caves, it was above the corresponding background value in China, which probably was correlated with heavy metal contamination in surrounding area outside the caves. In particular, the contents of Zn, Cu, Pb and Hg in Dashui cave were much higher than those in Malang cave. A possible reason may be that Dashui cave lies in city zone, and there is a pollutant source, Guizhou Aluminum Plant in this zone.

Heavy metal contents in water

Heavy metal contents in water samples were determined (Table 3). Except for Cr element, other seven heavy metal elements were all detected in water samples. The content of same element in water in the same light belt of different cave was different. For example, Pb content in light belts of Dashui and Malang caves were 8.17 and 3.41, respectively. Pb content in the former was 2.39 higher than that in the latter; Zn content in light belts of Malang and Dashui caves were 1.97 and 0.77, respecttively, and the content in former was 2.56 times higher than that in the latter. The ranking of average of heavy metal contents in the three light belts in Dashui cave was Ni>Pb>As>Cu>Zn>Cd>Hg, while that in Malong cave

Table 2. Contents of eight heavy metals in soil samples from in Dashui cave and Malang cave.

Study object	Pb	Cd	Hg	As	Cu	Cr	Ni	Zn
	(mg/kg)							
Light belt I	42.95	0.13	0.20	30.17	60.53	37.32	26.96	284.10
Light belt II	12.91	1.15	0.40	4.88	30.47	14.70	34.60	140.20
Weak-light belt I	6.31	0.15	0.86	23.62	180.10	38.54	79.60	568.60
Weak-light belt II	13.70	1.84	0.03	6.70	6.70	49.54	61.66	207.10
Dark belt I	56.11	0.40	1.61	17.58	130.90	35.86	51.69	259.60
Dark belt II	22.91	2.51	0.28	12.64	30.82	68.63	58.00	121.10
Average value I	35.12	0.23	0.89	23.79	123.84	37.24	52.75	370.77
Average value II	16.51	1.83	0.24	8.07	22.66	44.29	51.42	156.13

I, Dashui cave; II, Malang cave; ND, not detected.

Table 3. Content of eight heavy metals in water samples from Dashui and Malang caves.

Study object	Pb	Cd	Hg	As	Cu	Cr	Ni	Zn
	(μg/L)							
Light belt I	8.17	0.76	0.14	6.43	1.70	ND	8.18	0.77
Light belt II	3.41	0.45	0.21	9.49	0.86	ND	12.00	1.97
Weak-light belt I	—	—	—	—	—	—	—	—
Weak-light belt II	3.21	0.45	0.32	4.08	1.01	ND	7.60	0.43
Dark belt I	6.06	0.27	0.29	1.22	1.21	ND	13.27	0.85
Dark belt II	—	—	—	—	—	—	—	—
Average value I	7.12	0.52	0.21	3.83	1.46	ND	10.73	0.81
Average value II	3.31	0.45	0.27	6.79	0.94	ND	9.80	1.20

I, Dashui cave; II, Malang cave; ND, not detected —: No sample.

was Ni > As> Pb> Zn> Cu> Cd> Hg. Ni content in water sample was high, which was different from that in soil samples (Zn content was high in soil sample). Hg content in water sample was usually very low, similar to that in soil samples.

Bioaccumulation of heavy metals

As seen from the enrichment coefficient of soil-born heavy metals of cave animals (Table 4), the enrichment coefficient of different element in the same cave was different. The enrichment coefficient of Cd (4.15) was the highest in Dashui cave, while that of arsenic (0.13) was the lowest. The ranking of the eight heavy metals was Cd > Cu > Zn > Ni > Cr > Hg > Pb >As. The enrichment coefficient of other seven elements was below 1 except for Cd. The enrichment coefficient of Cu (8.48) was the highest in Malang cave, while that of arsenic was the lowest (0.18). The ranking of these eight heavy metals was Cu > Hg > Zn > Cd > Pb > Ni > Cr > As. The enrichment coefficient of Cu, Hg and Zn of cave animals was above 1. The enrichment coefficient of the same element in animals from different cave differed greatly. For example, Cd bioaccumulation in animals from Dashui and Malang caves were 4.15 and 0.45, respectively. The former was 8.83 times higher than the latter. Cu and Hg bioaccumulation of animals from Malong cave was 8.48 and 4.35, while that of animals from Dashui cave was 0.73 and 0.22, respectively. The enrichment coefficient of Cu and Hg in the former was 11.62 and 19.77 times higher than that in the latter.

Cr was not detected in water samples (Table 5). Therefore, the enrichment coefficients of Cr of these animal groups were null. As seen from the average value, the highest enrichment coefficient was Zn in animals from Dashui and Malong caves, 91723.84 and 708102.64, respectively. The enrichment coefficient of different heavy metals in the same animal groups from the same cave differed greatly. For example, the enrichment coefficient of Zn in snails from Dashui cave was 32506.49, while for Hg was 500.00. The former was 65.01 times higher than the latter. The ranking of seven heavy metals were Zn > Cu>Ni>Cd>As>Pb>Hg. The enrichment coefficients of Cu and As in *P. scaber* from Malang cave were 164356.44 and 240.20, respectively. The former was 584.25 times higher than the latter, and the ranking of seven heavy metals was Cu>Zn>Pb>Cd>Ni>Hg>As. The enrichment coefficient of the same heavy metal element in the same

Table 4. Enrichment coefficients of eight soil-borne heavy metals in dominant animals from Dashui and Malang caves.

Study object	Pb	Cd	Hg	As	Cu	Cr	Ni	Zn
Snails I	0.19	6.77	0.35	0.21	0.30	0.25	0.99	0.22
Snails II	0.19	0.96	0.28	0.27	0.33	1.17	0.80	0.36
Porcellio scaber I	0.15	4.93	0.10	0.09	1.60	0.37	0.18	0.79
Porcellio scaber II	0.68	0.42	10.33	0.15	24.78	0.25	0.20	2.89
Diestrammena marmorata I	ND	0.75	0.21	0.08	0.29	0.31	0.02	0.49
Rhinolophus pearsoni II	ND	0.04	2.43	0.13	0.32	0.46	0.08	0.70
Average value I	0.17	4.15	0.22	0.13	0.73	0.31	0.40	0.50
Average value II	0.44	0.47	4.35	0.18	8.48	0.29	0.36	1.32

I, Dashui cave; II, Malang cave; ND, not detected.

Table 5. Enrichment coefficients of eight water-borne heavy metals in dominant animals from Dashui and Malang caves.

Study object	Pb	Cd	Hg	As	Cu	Cr	Ni	Zn
Snails I	988.98	1157.89	500.00	995.33	10623.53	ND	3262.84	32506.49
Snails II	733.14	2444.44	523.81	146.35	11744.19	ND	2312.50	25507.61
Porcellio scaber I	—	—	—	—	—	—	—	—
Porcellio scaber II	2897.20	1711.11	968.75	240.20	164356.44	ND	1564.89	1390697.67
*Diestrammena marmorata*I	ND	1111.11	1172.41	1155.74	31256.20	ND	97.21	150941.18
Rhinolophus pearsoni II	—	—	—	—	—	—	—	—
Average value I	988.98	1134.50	836.21	1075.54	20939.87	ND	1680.03	91723.84
Average value II	1815.17	2077.76	746.28	190.18	88050.32	ND	1938.70	708102.64

I, Dashui cave; II, Malang cave; ND, not detected.

animal group from different cave also differed. For example, the enrichment coefficient of As in snails from Dashui and Malang caves were 995.33 and 146.35, respectively. The former was 5.80 times higher than the latter. As seen from the enrichment coefficients of different heavy metal elements in different animal groups, the enrichment coefficients of Cd, Cu, Ni and Zn in snails were all above 1000, and those of Pb, Cd, Cu, Ni and Zn in *P. scaber* were also above 1000. The enrichment coefficients of Cd, Hg, As, Cu and Zn in *D. marmorata* were also above 1000.

DISCUSSION

The investigation of heavy metal content in cave animals, cave soil and cave water facilitates the understanding of the condition and degree of heavy metal contamination in the whole cave. The current study provides scientific evaluation for the cave environment. Heavy metal contents in the main animal groups, soil and water samples from Dashui and Malang caves shows that Pb was not detected in *D. marmorata* and *R. pearsoni*, suggesting that these two animal species are incapable of or poor in Pb accumulation. As seen from the average value of three light belts in two caves, metal content of each element is above the background value for soils in China, which is probably correlated with the types of rocks and parent materials of cave soils. Because the parent rock of soil is dolomite inside the carbonate rocks, the main chemical components are carbonates. Carbonate ore easily react with CO_2 in the presence of water, and cause dissolution and leaching. The relatively accumulated ferric oxide in the soil helps to enrich microelements (Zhu and Yin, 1984), which improves dramatically heavy metal contents in dolomite soils. In addition, it may be correlated with heavy metal pollution outside the cave.

Although, both caves are slightly polluted in terms of heavy metal contents, the household water and irrigation water of farmland for villagers living in remote karst area are directly or indirectly from the cave. Studies on heavy metal pollution in karst caves are non-negligible, especially in mountain areas with widely distributed karst topography and less industry and mining.

Studies of heavy metal pollution in karst caves are of important theoretical and practical significance for the protection of cave environment and animals.

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