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Headwater Streams Contain Amounts of Heavy Metal in an Alpine Forest in the Upper Reaches of the Yangtze River

(Aliran Kepala Air Mengandungi Amaun Logam Berat di Hutan Alpin di Bahagian Hulu Sungai Yangtze)

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ABSTRACT

Headwater streams are an essential link in the source and sink dynamics of heavy metals between terrestrial and aquatic ecosystems and are also critically important for downstream ecosystem processes and water quality. However, there is little available information about headwater streams. Therefore, the stream storage and distribution patterns of Cd, Pb, Ni, Cr, Cu, Mn and Zn were investigated in ten headwater streams of an Alpine forest located in the upper Yangtze River during the rainy season. The results indicated that the heavy metal storage per unit area of the investigated streams was as follows: 0.95 mg·m^{-2} for Cd, 8.36 mg m^{-2} for Pb, 1.98 mg m^{-2} for Ni, 136.98 mg m^{-2} for Cr, 9.29 mg m^{-2} for Cu, 433.39 mg m^{-2} for Mn and 29.07 mg m^{-2} for Zn; while the heavy metal storage per unit area of the catchment was as follows: 1.19 mg hm^{-2} for Cd, 10.47 mg hm^{-2} for Pb, 2.48 mg hm^{-2} for Ni, 171.62 mg hm^{-2} for Cr, 11.64 mg hm^{-2} for Cu, 542.99 mg hm^{-2} for Mn and 36.42 mg hm^{-2} for Zn. Headwater streams present remarkable potential for contamination, and plant debris from riparian forests may be the most important source of heavy metals, while the stream sediment acts as a significant sink for heavy metals. These results provide new perspectives and data for understanding the ecological links between alpine forests and watersheds.

Keywords: Headwater streams; heavy metal storage; plant debris; sediment; water conservation land

ABSTRAK

Aliran kepala air adalah satu pautan penting dalam dinamik sumber dan sink logam berat antara ekosistem daratan dan akuatik dan juga amat penting bagi proses hiliran ekosistem dan kualiti air. Walau bagaimanapun, terdapat sedikit maklumat tentang aliran kepala air. Oleh yang demikian, aliran penyimpanan dan pengedaran corak Cd, Pb, Ni, Cr, Cu, Mn dan Zn dikaji dalam sepuluh aliran kepala air untuk hutan Alpin yang terletak di bahagian hulu Sungai Yangtze. Hasil menunjukkan bahawa menyimpanan logam berat setiap kawasan unit aliran dikaji adalah seperti berikut: 0.95 mg·m^{-2} untuk Cd, 8.36 mg m^{-2} untuk Pb, 1.98 m mg^{-2} bagi Ni, 136.98 mg m^{-2} untuk Cr, 9.29 mg m^{-2} untuk Cu, 433.39 mg m^{-2} untuk Mn dan 29.07 mg m^{-2} untuk Zn; sementara penyimpanan logam berat setiap unit luas kawasan tadahan adalah seperti berikut: 1.19 mg hm^{-2} untuk Cd, 10.47 mg hm^{-2} untuk Pb, 2.48 mg hm^{-2} untuk Ni, 171.62 mg hm^{-2} untuk Cr, 11.64 mg hm^{-2} untuk Cu, 542.99 mg hm^{-2} untuk Mn dan 36.42 mg hm^{-2} untuk Zn. Aliran kepala air menunjukkan potensi yang luar biasa bagi pencemaran dan sisa loji dari hutan riparia mungkin menjadi sumber terpenting logam berat, sementara endapan sungai bertindak sebagai sinki yang ketara bagi logam berat. Keputusan ini memberikan perspektif yang baru dan data untuk memahami hubungan ekologi antara hutan Alpin dan tadahan air.

Kata kunci: Aliran kepala air; penyimpanan logam berat; sedimen; sisa loji kawasan pulihara air

INTRODUCTION

Headwater streams are not only a fundamental component of forest ecosystems (Richardson & Danehy 2007), but also represent an essential link in the transfer of organic material and energy source-sink dynamics between terrestrial and aquatic ecosystems (Lepori et al. 2005; Tank et al. 2010). There is a strong interaction between streams and riparian areas (Souza et al. 2013). Leaves, bark, twigs and other woody debris in riparian forests are removed with the canopy litter, transported by the wind, and enter streams through surface runoff, thus constituting the carbon, nutrient and heavy metal element output of the forest system (Burrows et al. 2012; Gonçalves & Callisto 2013; Wallace et al. 1997). Headwater streams have a profound influence on downstream water quantity and quality (Alexander et al. 2007), because these systems are intimately linked (Gomi et al. 2002).

Heavy metals such as cadmium and lead are non-essential for biological functions but show persistence and bioaccumulation, in addition to being non-biodegradable and highly toxic, even at low concentrations (Gadd 2010). Certain metals, such as copper, zinc and manganese, are essential trace elements that are necessary for normal cell growth and metabolism at low concentrations but are toxic above specific threshold concentrations (Soares & Soares 2013). These metals can cause environmental hazards and may represent serious risks to ecological safety (Colin et al. 2012; Hu et al. 2017). Heavy metals are transported, assimilated or deposited in streams (Tokatli et al. 2013) and as a result of self-purification (Peng et al. 2015), are accumulated in the stream sediment and enter the food chain (Farkas et al. 2007; Loska & Wiechuła 2003). Moreover, the heavy metals in sediment are potentially dangerous through resuspension and bioturbation (Caplat et al. 2005; Stead-dexter & Ward 2004). Some studies have shown that Cd and Cr have higher susceptibility and bioavailability, their higher environmental risk to the aquatic biota, and Pb, Ni and Cu can complex with humic substances in sediments (Ma et al. 2016). The river water showed a high percentage of mobile and eco-toxic forms of Zn, Cu and Pb (Wojtkowska et al. 2016). Factors such as the density of ground cover, surface vegetation, stream characteristics and topography can all affect the heavy metal storage in streams by altering input and collection characteristics, greatly limiting the current understanding of the ecological links between alpine forests and watersheds.

Headwater streams of alpine forests located in western Sichuan, along the eastern edge of the Tibetan Plateau in the upper Yangtze River, play an important role in both soil and water conservation and regional water balance regulation (Yang & Wang 2003). The characteristics of heavy metal storage in headwater streams are closely tied to the security of the downstream aquatic environment. Therefore, we investigated heavy metal storage and distribution patterns in headwater streams of an alpine forest located in the upper Yangtze River. The study has two objectives: To determine the storage of heavy metals in the headwater streams as well as their distribution and removal patterns; and to elucidate the source-sink patterns of heavy metals within the streams.

MATERIALS AND METHODS

STUDY SITES

The study was conducted at the Bipenggou Long-term Research Station of Alpine Forest Ecosystems, Miyaluo Nature Reserve (102°53′-102°57′E, 31°14″-31°19′N, 2458-4169 m a.s.l.), Li County, Sichuan, southwest China, which is located along the eastern edge of the Tibetan Plateau, the western edge of the Sichuan Basin, and the upper Yangtze River. The annual mean air temperature is 2-4°C, with maximum and minimum temperatures of 23.7°C and -18.1°C, respectively. Mean annual precipitation is approximately 850 mm. Canopy forest vegetation is dominated by fir (*Abies faxoniana*) with some understory shrubs (e.g. *Salix paraplesia*, *Rhododendron* spp.) and grasses (e.g. *Cystopteris montana*, *Carex capilliformis*, and *Cacalia auriculata*), and the mean tree age is approximately 120 a. The sampling sites included ten representative headwater streams (labelled A-J in Figure 1) in a typical alpine forest. The distribution and descriptions of these streams are provided in Figure 1.

SAMPLING

Previous investigation determined that the peak water season for alpine forest streams occurs in August, following summer rainfall and snow melt. Therefore, we conducted sampling during August 2015. The study area was 54 ha and the catchment area was 431 ha. The area of investigated streams refers to total water surface area of all streams, and the area of catchment refers to the total area that includes the region of streams and their surrounding rainwater landing and confluence (Allan & Castillo 2007). We selected 10 representative headwater streams at an altitude of 3,600 m a.s.l. (Table 1) according to their topography and vegetation and avoiding the impact of human interference. We measured the length, width and

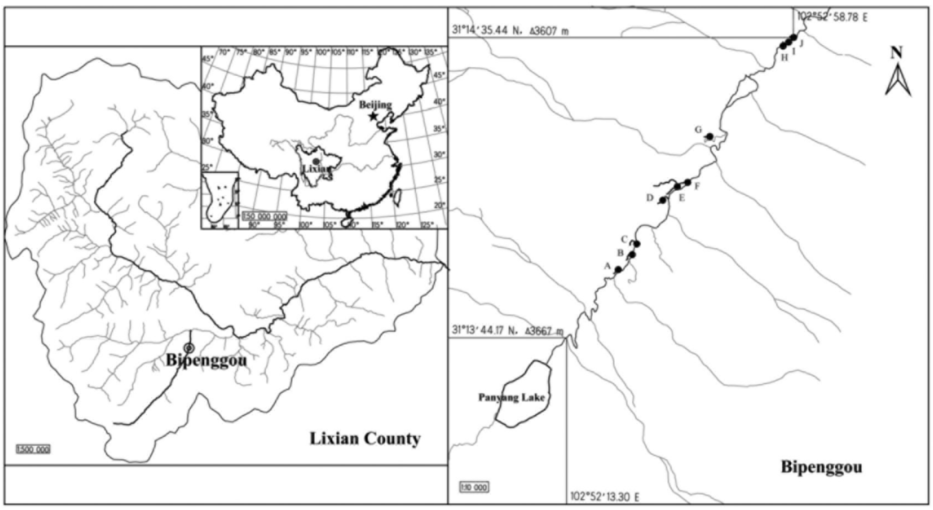

FIGURE 1. Location of the study area and the distribution of sampled streams (A-J)

TABLE 1. Summary of basic information for the investigated streams

Stream	Longitude	Latitude	Length(m)	Width(m)	Flow(cm^3/s)	Depth(cm)	Altitude(m)
A	102°52′E	31°14′N	66	0.51	20287.35	3	3658
B	102°52′E	31°14′N	13.2	0.42	69.31	6	3625
C	102°52′E	31°14′N	92.4	0.9	1775.51	8	3620
D	102°52′E	31°14′N	186	0.66	7064.98	7	3621
E	102°52′E	31°14′N	108	0.86	79.46	7	3634
F	102°52′E	31°14′N	225.6	0.98	13480.46	6	3634
G	102°52′E	31°14′N	18	1.09	4743.8	6	3620
H	102°52′E	31°14′N	36	0.67	6630.55	14	3607
I	102°52′E	31°14′N	11.3	0.56	211.54	6	3607
J	102°52′E	31°14′N	27.6	0.42	82.15	5	3607

flow of all streams. Based on the length of a stream from its head to end, samples were collected at intervals 5-10 m along the stream from plots with a length of 1 m and width corresponding to the actual width of the stream at that sampling location.

We collected water samples in pre-cleaned polyethylene bottles at half the depth of the stream and preserved these samples at a low temperature for less than one week until analysis, according to the National Standard of the People's Republic of China (HJ 494-2009). Water samples were filtered in the laboratory and stored in glass bottles. The length, width and depth of the water in each sample was measured, and the volume of water (V_w) was calculated using the cuboid model:

$$V_w = L_w \times W_w \times D_w$$

The length, width and depth of the sediment in each sample was plotted, and the volume of sediment (V_1) was calculated using the quadrangular frustum pyramid model:

$$V_1 = \frac{\left[S_1 + \sqrt{(S_1 \times S_2)} + S_2\right] \times H}{3}$$

Then, all of the calculated sediment volumes were summed to estimate the total stream sediment volume (V). It was found that the sediment depth was shallow, therefore, we used the annular sword test with 'five-point sampling method', in which samples were stored in a pre-cleaned, wide-mouth polyethylene bottle and sealed to prevent moisture loss. In the laboratory, we sampled a specific volume (V_m) of sediments to obtain the measured mass (M_m), density (ρ_m) and moisture content (Mc) and calculated the sediment standing crop of streams as M_s:

$$M_s = \rho_m \times V(1 - M_c)$$

The woody debris included coarse and fine woody debris, such as snag, log, branch, root, twig and fine root debris. The non-woody debris included other fine litter or litter fall that was not woody debris, such as leaf litter, flower drop, fruit drop and bark debris (Harmon & Sexton 1996; Stevens 1997). The harvest method was used to estimate the biomass of woody and non-woody debris (West 2009). We collected all of the debris in the streams and measured the fresh weight (M_w) and subsequently determined the dry weight (M_{w2}) in the laboratory after drying. The woody and non-woody debris biomass (W) was calculated as:

$$W = \frac{M_{w2}}{S}$$

In which S includes the investigation area and catchment area.

ANALYSIS AND CALCULATION

Each sample was digested using CEM-Mars 5, and the digestion conditions were set according to the National Standard of the People's Republic of China (HJ 678-2013) as follows:- For water samples, the heat-up time was 10 min; the temperature was 180°C; and the hold time was 15 min. For sediment samples, the heat-up time was 15 min, temperature was 180°C, and the hold time was 25 min. For plant debris samples, the heat-up time was 15 min, temperature was 180°C, and the hold time was 35 min. After digestion was complete, Cd, Pb, Ni, Cr, Cu, Mn and Zn were determined using atomic absorption spectrometry (AAS, AA-7000, Shimadzu Corporation, Kyoto, Japan).

For each sampling site:

$$M_w = \frac{C \times V_w}{S}$$

$$M_s = \frac{C \times V_s}{S}$$

$$M_{wd} = C \times W_w$$

$$M_{nwd} = C \times W_{nw}$$

where M_w is the heavy metal storage in water for each sampling site; M_s is the heavy metal storage in sediment for each sampling site; M_{wd} is the heavy metal storage in woody debris for each sampling site; M_{nwd} is the heavy metal storage in non-woody debris for each sampling site; C is the concentration of heavy metals in different samples; V_w is the estimated volume of water for each sampling site; V_s is the estimated volume of sediment for each sampling site; S is the area of each sampling site; W_w is the estimated biomass of woody debris for each sampling site; W_{nw} is the estimated biomass of non-woody debris for each sampling site.

For each stream:

$$M_t = \frac{\Sigma M \times S}{S_t}$$

where M_t is the heavy metal storage in water, sediment, woody debris and non-woody debris for each stream; S_t is the area of each stream; M is the heavy metal storage in water, sediment, woody debris and non-woody debris for each sampling site; and S is the area between each sampling site.

The data were statistically analyzed using SPSS 22.0 software.

RESULTS

TOTAL STORAGE

The heavy metal storage per unit area of the water, sediment, woody debris and non-woody debris and the total storage for the investigated stream area and the catchment area are shown in Table 2. The mean heavy metal concentrations of each component for all sampling sites in each stream of the alpine forest are shown in Table 3. The heavy metal storage per unit area of each component in the alpine forest streams is shown in Table 4. The correlation coefficients of heavy metal storage in each component of the streams with the length, width, depth and flow are shown in Table 5. The proportion of heavy metal storage in each component of the alpine forest streams is shown in Figure 2. The results indicated that the total heavy metal storage per unit area of the investigated stream and catchment areas showed the following descending order: Mn > Cr > Zn > Cu > Pb > Ni > Cd, ranging from 0.95 to 433.39 mg m^{-2} and 1.19 to 542.99 mg hm^{-2}, respectively.

WATER

The results indicated that the heavy metal storage per unit area of water in the streams showed the following descending order Cu > Mn > Pb > Cr > Zn > Cd > Ni, ranging from 0.12 to 1.52 mg/m^2 for Cu, 0.06 to 0.74 mg/m^2 for Mn, 0.08 to 0.59 mg/m^2 for Pb, 0.05 to 0.59 mg/m^2 for Cr, 0.006 to 0.05 mg/m^2 for Zn, 0.004 to 0.10 mg/m^2 for Cd and 0.006 to 0.07 mg/m^2 for Ni, respectively. The proportion of the total heavy metal storage in stream waters among all components was not more than 10%. Correlation analysis showed that Cu and Ni storage in water increased with an increasing stream depth and with a reducing stream flow; Mn and Cd storage in water increased with an increasing stream depth; Pb storage in water increased with an increasing stream length and depth; and Zn storage in water increased with an increasing stream width. However, the stream characteristics had little effect on Cr storage.

SEDIMENT

The results indicated that heavy metal storage per unit area of sediment in the streams showed the following descending order: Mn > Zn > Pb > Cr > Cu > Cd > Ni, ranging from 5.37 to 73.71 mg m^{-2} for Mn, 0.79 to 7.28 mg m^{-2} for Zn, 0.87 to 10.28 mg m^{-2} for Pb, 0.38 to 4.38 mg m^{-2} for Cr, 0.22 to 2.60 mg m^{-2} for Cu, 0.06 to 1.30 mg m^{-2} for Cd and 0.05 to 0.59 mg m^{-2} for Ni, respectively. In addition to the proportions of Cd and Pb storage in sediment were larger among all components, other heavy metals were smaller. The correlation analysis showed that the Mn, Zn, Cd and Ni storage in sediment increased with a reducing stream length, width and depth; Pb storage in sediment increased with a reducing stream length and width; Cr storage in sediment increased with a reducing stream

TABLE 2. Heavy metals storage in alpine forest stream

	Storage per unit area of the investigated stream area (mg·m^{-2})					Storage per unit area of the catchment area (mg·hm^{-2})				
	water	sediment	woody debris	non-woody debris	total	water	sediment	woody debris	non-woody debris	total
Cd	0.02	0.27	0.44	0.21	0.95	0.03	0.34	0.55	0.26	1.19
Pb	0.18	2.62	2.65	2.91	8.36	0.23	3.28	3.31	3.65	10.47
Ni	0.02	0.21	0.61	1.15	1.98	0.02	0.26	0.76	1.44	2.48
Cr	0.13	1.53	39.85	95.47	136.98	0.16	1.92	49.93	119.61	171.62
Cu	0.33	1.00	3.84	4.11	9.29	0.42	1.26	4.81	5.15	11.64
Mn	0.28	32.1	176.13	224.88	433.39	0.35	40.21	220.67	281.75	542.99
Zn	0.03	2.62	11.85	14.57	29.07	0.04	3.29	14.85	18.25	36.42

TABLE 3. Mean concentration of heavy metals in alpine forest streams

stream		Concentration									
		A	B	C	D	E	F	G	H	I	J
Water (mg L^{-1})	Cd	0.04	0.04	0.01	0.03	0.04	0.02	0.04	0.04	0.03	0.03
	Cr	0.27	0.15	0.15	0.09	0.22	0.17	0.09	0.25	0.20	0.19
	Cu	0.40	0.56	0.70	0.29	0.48	0.37	0.62	0.65	0.51	0.64
	Mn	0.20	0.24	0.41	0.38	0.11	0.59	0.16	0.32	0.29	0.46
	Ni	0.02	0.05	0.03	0.02	0.03	0.03	0.04	0.03	0.02	0.04
	Pb	0.24	0.20	0.26	0.25	0.23	0.25	0.24	0.25	0.19	0.23
	Zn	0.05	0.01	0.03	0.05	0.05	0.04	0.09	0.02	0.02	0.07
Sediment (mg kg^{-1})	Cd	2.23	2.17	2.76	6.02	2.98	1.40	3.93	2.06	2.58	4.74
	Cr	11.68	21.93	15.33	12.79	22.78	17.63	13.52	21.40	14.33	16.00
	Cu	10.18	9.28	8.64	10.78	13.61	10.53	11.84	15.05	6.47	9.50
	Mn	151.90	194.08	307.11	1224.88	279.52	124.77	370.05	128.95	154.33	196.00
	Ni	2.19	2.29	2.15	2.28	2.55	2.45	2.13	2.17	1.99	2.17
	Pb	22.39	24.62	34.83	34.19	28.37	23.22	31.98	49.50	38.41	31.95
	Zn	34.00	28.63	31.62	27.96	33.86	24.80	33.50	26.20	27.21	23.97
woody debris (mg kg^{-1})	Cd	0.27	0.23	0.77	0.53	0.26	0.50	0.14	0.22	0.11	0.55
	Cr	88.81	9.22	43.13	41.44	75.00	117.87	10.34	22.06	99.06	27.91
	Cu	5.21	4.79	5.95	3.84	5.25	4.39	3.75	4.21	4.28	3.46
	Mn	58.61	66.80	96.99	256.55	138.52	179.85	308.30	266.05	1015.61	191.56
	Ni	0.99	0.33	0.63	0.59	0.48	1.29	0.59	0.60	2.22	0.60
	Pb	4.88	5.27	1.94	4.84	4.38	3.78	1.54	1.31	0.57	1.54
	Zn	4.05	2.68	4.42	8.52	21.20	25.32	12.21	10.26	17.50	73.95
Non-woody debris (mg kg^{-1})	Cd	0.29	0.09	0.80	0.42	0.09	0.42	0.39	0.30	0.33	1.43
	Cr	508.44	136.84	168.76	262.20	608.63	256.84	59.88	105.13	145.31	76.76
	Cu	8.30	12.77	23.10	10.14	9.96	19.24	5.85	6.64	6.07	5.06
	Mn	215.74	356.72	190.49	603.01	352.57	350.58	1245.41	648.28	1529.95	768.84
	Ni	4.73	3.18	1.81	2.07	5.02	3.17	2.32	2.03	3.59	3.91
	Pb	10.39	11.12	3.26	6.64	11.05	6.75	2.06	2.00	1.27	4.19
	Zn	18.46	19.86	16.43	27.37	41.19	39.32	31.70	27.66	29.81	119.33

TABLE 4. Heavy metal storage in alpine forest streams

Stream		Storage (mg m^{-2})									
		A	B	C	D	E	F	G	H	I	J
Water	Cd	0.01	0.02	0.00	0.02	0.03	0.01	0.02	0.10	0.01	0.01
	Cr	0.09	0.08	0.05	0.07	0.16	0.10	0.05	0.59	0.09	0.10
	Cu	0.12	0.28	0.24	0.22	0.36	0.20	0.36	1.52	0.22	0.33
	Mn	0.06	0.12	0.14	0.29	0.08	0.32	0.09	0.74	0.13	0.23
	Ni	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.07	0.01	0.02
	Pb	0.08	0.10	0.09	0.19	0.17	0.14	0.14	0.59	0.08	0.12
	Zn	0.02	0.01	0.01	0.04	0.04	0.02	0.05	0.05	0.01	0.04
Sediment	Cd	0.42	0.13	0.07	0.36	0.42	0.06	0.28	0.23	0.69	1.30
	Cr	2.18	1.33	0.38	0.77	3.24	0.76	0.96	2.41	3.84	4.38
	Cu	1.90	0.56	0.22	0.65	1.93	0.45	0.84	1.70	1.73	2.60
	Mn	28.32	11.80	7.65	73.71	39.71	5.37	26.16	14.55	41.31	53.60
	Ni	0.41	0.14	0.05	0.14	0.36	0.11	0.15	0.24	0.53	0.59
	Pb	4.17	1.50	0.87	2.06	4.03	1.00	2.26	5.59	10.28	8.74
	Zn	6.34	1.74	0.79	1.68	4.81	1.07	2.37	2.96	7.28	6.55
Woody debris	Cd	0.08	0.03	0.74	0.50	0.11	0.38	0.03	0.64	0.01	0.34
	Cr	23.95	1.21	46.34	32.82	19.07	42.15	2.52	51.38	9.40	31.07
	Cu	1.57	0.62	5.73	2.94	1.53	3.04	1.16	12.67	0.77	2.77
	Mn	17.08	8.73	170.04	186.23	32.84	150.44	79.99	677.92	167.72	185.41
	Ni	0.26	0.04	0.92	0.41	0.16	0.52	0.14	2.24	0.20	0.36
	Pb	2.04	0.69	1.66	3.42	1.32	2.44	0.37	4.68	0.06	1.22
	Zn	1.17	0.35	3.45	5.43	5.35	15.89	4.48	26.64	2.69	56.02
Non-woody debris	Cd	0.08	0.09	0.23	0.26	0.07	0.11	0.42	0.18	0.11	1.04
	Cr	105.00	61.35	43.67	111.42	196.97	42.70	42.30	43.45	23.69	54.36
	Cu	2.10	6.51	3.79	5.01	4.48	2.23	5.08	4.95	1.56	4.17
	Mn	51.17	260.36	61.99	306.48	145.58	102.92	982.18	422.37	432.05	617.09
	Ni	0.97	1.64	0.48	1.02	2.03	0.56	1.78	1.30	0.75	2.74
	Pb	2.63	5.35	1.01	3.45	5.46	1.54	1.52	1.54	0.37	2.86
	Zn	4.37	12.21	5.62	13.13	18.28	7.93	29.18	16.46	8.01	96.11

TABLE 5. Correlation coefficients for heavy metal storage in each component of the streams with the length, width, depth and flow of the stream

Stream		Storage				
		water	sediment	woody debris	non-woody debris	total
Length	Cd	-0.115	-0.345	0.685*	-0.055	-0.42
	Pb	0.370	-0.515	0.745*	0.248	-0.139
	Ni	-0.213	-0.515	0.527	-0.285	-0.321
	Cr	0.067	-0.515	0.612	0.442	0.685*
	Cu	-0.297	-0.261	0.636*	-0.115	0.224
	Mn	0.285	-0.139	0.188	-0.576	-0.479
	Zn	0.164	-0.552	0.406	-0.224	-0.042
Width	Cd	0.006	-0.498	0.334	0.158	-0.085
	Pb	0.377	-0.456	0.158	-0.419	-0.529
	Ni	0.076	-0.553	0.231	-0.280	-0.267
	Cr	-0.201	-0.571	0.267	-0.353	-0.018
	Cu	0.146	-0.438	0.340	0.036	0.036
	Mn	0.122	-0.444	0.097	-0.043	0.024
	Zn	0.401	-0.523	0.207	0.000	0.109
Depth	Cd	0.439	-0.395	0.621	0.056	0.332
	Pb	0.609	-0.295	0.433	-0.038	-0.019
	Ni	0.318	-0.508	0.477	-0.182	0.063
	Cr	0.038	-0.314	0.514	0.044	0.339
	Cu	0.470	-0.395	0.514	0.301	0.659*
	Mn	0.452	-0.207	0.508	-0.044	0.176
	Zn	0.163	-0.447	0.245	0.075	0.038
Flow	Cd	-0.212	-0.273	0.358	0.103	0.006
	Pb	0.042	-0.115	0.636*	-0.309	-0.236
	Ni	-0.401	-0.236	0.527	-0.515	-0.345
	Cr	-0.103	-0.430	0.503	-0.115	0.224
	Cu	-0.564	-0.200	0.527	-0.333	-0.188
	Mn	0.236	-0.115	0.224	-0.321	-0.103
	Zn	0.188	-0.224	0.164	-0.455	-0.115

* $P<0.05$, ** $P<0.01$; n=10

length, width, depth and flow; Cu storage in sediment increased with a reducing stream width and depth.

WOODY DEBRIS

The results indicated that the heavy metal storage per unit area of woody debris in the streams showed the following descending order: Mn > Cr > Zn > Cu > Pb > Ni > Cd, ranging from 8.73 to 677.92 mg m^{-2} for Mn, 1.21 to 51.38 mg m^{-2} for Cr, 0.35 to 56.02 mg m^{-2} for Zn, 0.62 to 12.67 mg m^{-2} for Cu, 0.06 to 4.68 mg m^{-2} for Pb, 0.04 to 2.24 mg m^{-2} for Ni and 0.01 to 0.74 mg m^{-2} for Cd, respectively. The proportion of heavy metal storage in woody debris was larger among all components for every stream, and at least 4 streams harboured more than 30% of each heavy metal in this component. The correlation analysis showed that Mn storage in woody debris increased with stream depth; Cr, and Ni storage in woody debris increased with an increasing stream length, depth and flow; Zn storage in woody debris increased with an increasing stream length; and Cu and Cd storage in woody debris increased with an increasing stream width, depth and flow of streams, and distinct increased with an increasing stream length; Pb storage in woody debris increased with an increasing stream depth, and distinct increased with an increasing stream length and flow.

NON-WOODY DEBRIS

The results indicated that the heavy metal storage per unit area of non-woody debris in the streams showed the following descending order: Mn > Cr > Zn > Cu > Pb > Ni > Cd, ranging from 51.17 to 982.18 mg m^{-2} for Mn, 23.69 to 196.97 mg m^{-2} for Cr, 4.37 to 96.11 mg m^{-2} for Zn, 1.56 to 6.51 mg m^{-2} for Cu, 0.37 to 5.46 mg m^{-2} for Pb, 0.48 to 2.74 mg m^{-2} for Ni and 0.07 to 1.04 mg m^{-2} for Cd, respectively. The proportion of heavy metal storage in non-woody debris was highest among all components in every stream, with the exception of Cd. The correlation analysis showed that Mn storage in non-woody debris increased with a reducing stream length and flow; Cr storage in non-woody debris increased with an increasing stream length and reducing flow; Zn storage in non-woody debris increased with a reducing stream flow; Cu storage in non-woody debris increased with an increasing stream depth and with a reducing stream flow; Pb storage in non-

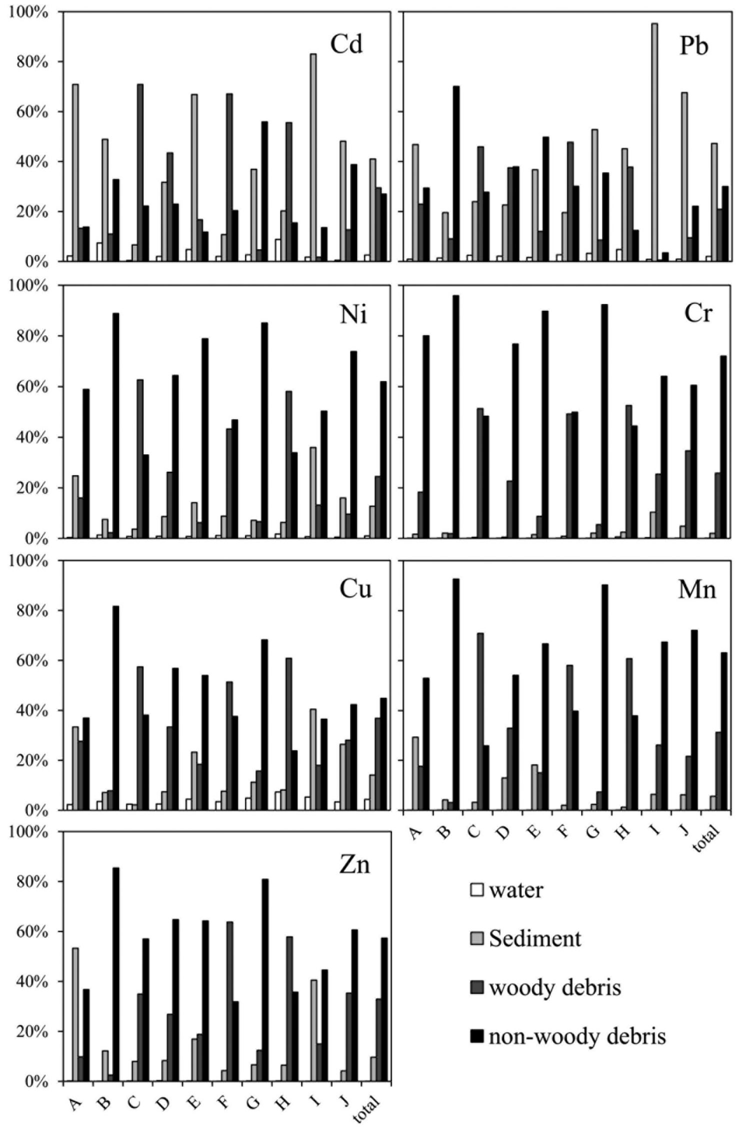

FIGURE 2. The proportion of heavy metal storage in each component of the alpine forest streams

woody debris increased with a reducing stream width and flow; Ni storage in non-woody debris increased with a reducing stream flow. However, the stream characteristics had little effect on Cd storage.

DISCUSSION

Heavy metals accumulate in environments due to both natural causes, such as erosion of bedrock and atmospheric convection, and human activities, such as mining, refining, and excessive use of fossil fuels (Pulatsü & Topçu 2015). It is widely accepted that alpine forest watersheds typically provide high-quality water with little sediment and few pollutants (Singh & Mishra 2014); in particular, headwater streams as the source of the alpine forest watersheds should be located in undisturbed woodland patches that have not been contaminated. The current study showed that heavy metal storage in water increased as stream depth increased, indicating that deeper streams exhibit higher concentrations of dissolved heavy metals. The average heavy metal concentration of water in our all sampling sites was similar to that observed in peatlands in Sudbury, Ontario, Canada (Pennington & Watmough 2015). However, the heavy metal storage in water was the smallest heavy metal component in every stream tested (less than 5%), which may be due to the self-purification of the water. Despite the fact that the heavy metal storage of water in the water of headwater streams is minimal, studies have shown that heavy metals can reach remote alpine forests via long-distance atmospheric transport (Bing et al. 2014). Thus, alpine forests may be a potential source and sink of heavy metals.

Headwater streams are intimately linked with the surrounding riparian forests, and the input of terrestrial litter often exceeds stream primary production, which represents an important energy source for stream production (Nakano & Murakami 2001). Non-woody debris often enters streams due to natural forces such as gravity, wind and rainwater scour, and because of the low mass were light, which with the water flowing to downstream or intercepted easily, and its decomposition rate is faster in water (Chen et al. 2006; Graça 2001). Woody debris affects the pattern of a stream by intercepting sediment and altering the flow rate, while its continued decomposition provides nutrients. However, most woody debris is buried by sediment, reducing its rate of decomposition in water (Jackson & Wohle 2015; Ryan et al. 2014). The average Cd and Pb concentrations of non-woody debris in our all sampling sites were larger than that foliar litter at growing season in the alpine forest in the Miyaluo Nature Reserve in Lixian County, Sichuan, China (He et al. 2015). The present study showed that the Cd and Pb storage in plant debris accounted for 50% of the total; Cu and Ni storage in plant debris was more than 80% of the total; and Cr, Mn and Zn storage in plant debris surpassed 90% of the total. Heavy metal storage in non-woody debris increased with a decreased stream flow, indicating that non-woody debris was more readily deposited in slower-velocity streams. Heavy metal storage in woody debris increased with an increasing stream length, depth and flow, possibly because deeper, longer streams can accumulate more woody debris. Additionally, woody debris can deflect the stream flow and contribute to the formation of debris dams (Baillie & Davies 2002). These features create a drop in water levels, increase the stream flow, and result in further accumulation of plant debris. Both woody and non-woody debris are fundamental outputs of riparian forests and are likely critical sources of heavy metals in headwater streams. Woody and non-woody debris decompose gradually in streams, releasing heavy metals over time, which are ultimately deposited in the sediment (Passos et al. 2011).

Because streams can self-purify, heavy metals are rapidly and efficiently removed from the water by algae and through sedimentation (Mccoll 1974). The average Cr, Cu, Ni, Pb and Zn concentration of the sediment in our all sampling sites were lower than in surface sediment of reservoir on the Yunnan-Guizhou plateau, China and in five aquatic ecosystems in eastern China, but the average Cd concentration was larger relatively (Tang et al. 2014; Wu et al. 2014). Heavy metal storage in each component of streams depends largely on the morphological features of the stream. In this study, we found that the heavy metal storage in sediment increased with decreasing length, width and depth of streams. The shorter, narrower streams accumulated sediment more easily, and shallow streams accumulated heavy metals in their sediment much more readily. This study demonstrated that the Cr, Cu, Mn, Ni and Zn storage in sediment was greater than that in both woody and non-woody debris, although Cd and Pb storage showed the opposite pattern. The proportions of Cr, Cu, Mn, Ni and Zn storage were lower than those of Cd and Pb in the sediment, but higher in both woody and non-woody debris. This is likely because the capacity of woody and non-woody debris to adsorb and release heavy metals varies in water, the decomposition rate of plant debris is closely associated with physicochemical water properties and microbial activity (Perez et al. 2012). Both woody and non-woody debris release Cd and Pb during the decomposition process. It is clear that the heavy metal storage in sediment was much greater than in stream water, suggesting that the stream sediment is the principal sink of heavy metals in headwater streams. However, because bioturbation and resuspension of sediment are likely, stream sediment is also a potential source of secondary pollution in the aquatic environment. Heavy metals storage of plant debris could be a major factor potentially affecting downstream ecosystem and water quality because of the potential for high heavy metal accumulation in headwater streams over time.

Conclusion

Our results indicate that there are amounts of heavy metal stored in the headwater streams of alpine forest in the upper reaches of the Yangtze River. These headwater streams exhibit a remarkable potential for contamination, potentially resulting in downstream aquatic environmental hazards and affecting the ecological security of downstream regions. Compared with water, plant debris from riparian forests is the most important source of heavy metals in headwater streams and in the entire watershed, while the sediment is the most significant heavy metal pool in this system. Plant debris and sediment have potential pollution risks, which constitute a certain ecological threat to the downstream watershed. Because sampling was conducted during rainy season in this study, the results reported here may overestimate heavy metal inputs of woody and non-woody debris to a certain extent. Nevertheless, our findings provide new perspectives and data for understanding the ecological links between alpine forests and watersheds, and for monitoring and controlling heavy metal contamination in streams.

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