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Chromium, cadmium, and lead dynamics during winter foliar litter decomposition in an alpine forest river

Kai Yue[1], Wanqin Yang[1], Yan Peng[1], Chuan Zhang[1], Chunping Huang[1,2], and Fuzhong Wu[1,*]

[1]Long-term Research Station of Alpine Forest Ecosystem, Key Laboratory of Ecological Forestry Engineering, Institute of Ecology and Forestry, Sichuan Agriculture University, No. 211, Huimin Road, Wenjiang District, Chengdu 611130, People's Republic of China
[2]College of Life Science, Sichuan Normal University, No. 1819, 2nd Section, Chenglong Avenue, Longquanyi District, Chengdu 610101, People's Republic of China
[*]Corresponding author's email: wufzchina@163.com

ABSTRACT

Little information is currently available about heavy metal dynamics during litter decomposition in areas receiving few inputs of exotic metals. A field litter decomposition experiment was conducted during the winter in an alpine forest river on the eastern Tibetan Plateau. Concentrations, release rates, and release rate per day of chromium (Cr), cadmium (Cd), and lead (Pb) were investigated in the foliar litter of willow (*Salix paraplesia*), azalea (*Rhododendron lapponicum*), cypress (*Sabina saltuaria*), and larch (*Larix mastersiana*) during the prefreezing, freezing, and thawing periods. Concentrations of Cr in willow, cypress, and larch; Cd in all foliar litter types; and Pb in azalea foliar litter increased following incubation over an entire winter. Both Cr and Pb showed patterns of accumulation during the prefreezing period and patterns of release in the freezing and thawing periods, but Cd showed accumulation in all three periods. Water temperature, pH, flow velocity, conductivity, and nutrient availability in the river were significantly related to the dynamics of these heavy metals in the decomposing foliar litter. The heavy metal accumulation pattern in running water suggested an absolute increase in metal mass, indicating that litter may act as an efficient metal "cleaner" and contribute to an ecosystem's capacity for self-purification.

Introduction

The ever-increasing amounts of heavy metal waste in the biosphere and their consequent accumulation in terrestrial ecosystems may have far-reaching implications for the maintenance of ecosystems due to the negative impacts of these elements on essential ecological processes, such as litter decomposition and nutrient cycling (De Santo et al., 2002). Chromium (Cr), cadmium (Cd), and lead (Pb) are common heavy metals that, even at relatively low levels, are related to various human diseases, such as oral cancer (Chiang et al., 2011), neurocognitive decline (Ciesielski et al., 2013), bone and cardiovascular disease, and renal dysfunction (Calderon, 2000; Watt et al., 2000). These heavy metals have also been reported to significantly damage the physiological activities of plants (Lyubenova et al., 2013; Kováčik et al., 2014). Litter decomposition in alpine forest rivers, which are an important link between upper reaches and downstream ecosystems, is not only an important component of the circulation of materials and energy flow in forest ecosystems (Gessner et al., 1999) but also a main input pathway of heavy metals from terrestrial to aquatic ecosystems. It is generally acknowledged that litter decomposition and element release rates in running waters (e.g., rivers) are much higher than those on forest floors due to stronger flushing and leaching effects (Perakis and Hedin, 2002), and these processes could be affected by their microenvironments and water characteristics (Rueda-Delgado et al., 2006; Martínez et al., 2014). However, most studies have been conducted near smelters or metal processing plants where heavy metal concentrations are extremely high, and there are few data from areas with low concentrations of anthropogenic exotic metal inputs (e.g., from metal processing plants), especially alpine forest rivers, which are important water sources.

The cycling of heavy metals is a complex process because many factors influence the behavior of metals, including biotic and abiotic chemical processes, hydrology, climate, and the properties of the metals themselves (Huser et al., 2012). During the process of litter decomposition in a river, water characteristics (e.g., pH, flow velocity, and nutrient availability), organic matter mineralization, and chemical processes may alter metal solubility and mobility, as a previous study suggested that temporal coherence can occur among dissolved organic carbon, sulfate, and metals in running water (Landre et al., 2009). Alpine forests, which are subjected to low temperatures and undergo considerable seasonal freezing and thawing events, receive low inputs of exotic pollution due to the relatively weak influence of anthropogenic activities. The formation, coverage, and thawing of snow cover, as well as the process of soil freezing and thawing in winter, could both alter the water characteristics of an alpine forest river (Leroy and Marks, 2006) and reduce the communities and activities of decomposers as low temperatures slow the rate of litter decomposition and element cycling (Baldy et al., 2007). More importantly, most litters fall in late autumn before the soil completely freezes over (Moore, 1983;Yang et al., 2005), so large portions of such litters are transported into rivers through forest surface runoff, which makes litter decomposition in rivers during winter important and of interest.

As a result of the strong retention of heavy metals by organic material, metals may be released slowly and thus increase during litter decomposition, and they can potentially reach levels high enough to affect the decomposers in terrestrial ecosystems (Laskowski and Berg, 1993). An early study suggested that Cd and Pb concentrations increased during litter decomposition in all of the investigated litter types in the floor of a coniferous forest, and the absolute amounts of Cd increased as well (De Santo et al., 2002). Similar patterns have also been observed in other studies of the fate of heavy metals in decomposing litter in terrestrial ecosystems (Inman and Parker, 1978; Lyngby and Brix, 1989; Jonczak et al., 2014). However, as a result of the intense leaching and flushing effects of running waters, the heavy metals in the decomposing litter of such ecosystems may exhibit a different release pattern than found in terrestrial ecosystems. Moreover, recent studies have suggested that the type of plant litter and plant functional traits are the predominant controls of litter decomposition both at local and global scales (Cornwell et al., 2008; Makkonen et al., 2012), so litter type may also be an important moderator of the release of heavy metals during litter decomposition. However, little information is available on the heavy metal dynamics in rivers during litter decomposition at sites receiving low inputs of exotic pollution, which makes it difficult to draw definitive conclusions about the roles of heavy metals in the processes of litter decomposition and nutrient cycling.

To understand the pattern of heavy metal release during litter decomposition in running water at sites receiving low amounts of exotic metal pollutants, a field litter decomposition experiment was conducted to investigate the winter dynamics of Cr, Cd, and Pb in decomposing foliar litter in an alpine forest river on the eastern Tibetan Plateau. To potentially differentiate between the heavy metal dynamics during litter decomposition of different periods of winter, the present study designated the stage from litterfall to the time when the soil completely freezes as the "prefreezing period." During this time, frequent freezing and thawing events occur as temperatures fall to the freezing point. The next stage was designated the "freezing period," which is characterized by temperatures remaining below the freezing point; following the freezing period was the soil "thawing period" that takes place with the increase in temperature during the early spring but in which frequent, repeat freezing and thawing events also occur (Wu et al., 2010; Zhu et al., 2012). Heavy metal dynamics were investigated using the naturally and freshly fallen leaves of dominant riparian species (willow: *Salix paraplesia*, azalea: *Rhododendron lapponicum*, cypress: *Sabina saltuaria*, and larch: *Larix mastersiana*) during these three decomposition periods. Considering the intense leaching and flushing effects of running waters, we hypothesized that Cr, Cd, and Pb will display release patterns during litter decomposition throughout winter incubation but that this process could be modulated by the types of litter and the different periods of winter. The objectives of this study were to examine heavy metal dynamics and the factors that influence them in decomposing foliar litter in running water at a site receiving less exotic metal pollution than typical of anthropogenic activities. The results will be useful for further explaining the mechanisms driving heavy metal dynamics in decomposing litter. This new knowledge could be applied to the control of the turnover of heavy metals and the reduction of toxic heavy metal effects on organisms.

Materials and Methods

Study Site Description

The field experiment was conducted in a forested river in the Bipenggou Valley of the Miyaluo Nature Reserve (102°53′–102°57′E, 31°14′–31°19′N, 2458–4169 m a.s.l.), which is located in Li County, Sichuan Province, southwest China. This is a transitional area situated between the Tibetan Plateau and the Sichuan Basin. The annual mean air temperature is 3°C with absolute maximum and minimum air temperatures of 23 °C in July and −18 °C in January, respectively. The annual mean precipitation is approximately 850 mm including snowfall, and most of the precipitation falls between May and August. The freeze-thaw season starts in November when snow covers the ground and soil temperatures drop below 0 °C; the soil remains frozen until the following April (Zhu et al., 2012). The river is located in a typical alpine forest with an altitude of approximately 3600 m a.s.l. The dominant tree species in the riparian forest are fir (*Abies faxoniana*), larch, and cypress interspersed with azalea (*Rhododendron* spp.), willow, and barberry (*Berberis sargentiana*) shrubs; the herbaceous plants are primarily fern (*Cystopteris montana*), *Carex* spp., and *Cyperus* spp.

River Water Characteristics

The study river is a main drainage line in the forest where most of the small forest streams converge and has an average width of approximately 4 m. On three sampling occasions from November 2013 to April 2014, water physicochemistry was characterized in the forested river. Each time, conductivity (HI 98311, Hanna Instruments, Woonsocket, Rhode Island, U.S.A.), pH (pH 320, WTW GmbH, Weilheim, Germany), and river flow velocity (Martin Marten Z30 Current Meter) were measured in situ. Meanwhile, water samples were collected from each sampling point with prepared polyethylene bottles and transported to the laboratory in refrigerated chambers for nutrient analysis. In the laboratory, water samples were immediately filtered on a GF/F glass fiber filter (Whatman International, Florham Park, New Jersey, U.S.A.; 0.7-μm retention) for the determination of soluble reactive phosphorus (SRP) by the molybdate method. Nitrate concentration was measured by capillary ion electrophoresis (Agilent CE), and the quantification of ammonium was performed with the indophenol blue method (Rice et al., 2012). The concentrations of Cd, Cr, and Pb in river water were determined by inductively coupled plasma spectroscopy (ICP-MS, IRIS Advantage 1000, Thermo Elemental, Waltham, Massachusetts, U.S.A.) (Table 1).

Litterbag Experiment

Heavy metal release during litter decomposition was determined with the widely used litterbag method. In October 2013, naturally and freshly fallen leaves from willow, azalea, cypress, and larch were collected from the riparian forest floor in the sampling plots. In the laboratory, the foliar litter was air-dried for more than two weeks at room temperature to avoid structural damage during oven-drying. Subsamples of the foliar litter from each species were oven-dried at 65 °C for 72 hours to determine the moisture correction factor and then analyzed for their initial nutrient concentrations (Table 2).

TABLE 1

River water physicochemical characteristics in the research area during various winter periods (mean ± SE, n = 3).

Index	Pre-freezing period	Freezing period	Thawing period
Flow velocity (m s^{-1})	1.08 ± 0.21	0.71 ± 0.16	1.63 ± 0.24
pH	7.14 ± 0.04	7.21 ± 0.02	7.08 ± 0.02
Conductivity (μS cm^{-1})	51.6 ± 0.33	52.4 ± 0.43	51.3 ± 0.29
Bicarbonate (HCO_3) (mg C L^{-1})	17.43 ± 0.12	17.01 ± 0.09	17.40 ± 0.27
Soluble reactive phosphorus (SRP) (μg P L^{-1})	7.01 ± 0.33	8.04 ± 0.26	7.15 ± 0.31
Ammonium (NH_4-N) (mg N L^{-1})	0.04 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
Nitrate (NO_3-N) (mg N L^{-1})	0.30 ± 0.13	0.31± 0.09	0.32 ± 0.11
Chromium (Cr) (μg L^{-1})	31.10 ± 1.73	26.53 ± 0.38	22.93 ± 1.21
Cadmium (Cd) (μg L^{-1})	0.53 ± 0.09	0.40 ± 0.06	0.23 ± 0.03
Lead (Pb) (μg L^{-1})	16.6 ± 0.15	13.77 ± 1.02	12.30 ± 0.72

For each species, samples of air-dried foliar litter equal to 10 g dry mass were then placed into separate 20 × 20 cm nylon bags (0.5 mm mesh size). In total, 36 litterbags (four species × three replicates × three sampling dates) were placed in the forest river. On 13 November 2013, three environmentally similar sampling points were selected as replicates along the upper reach of the river, and at each replicated sampling point, 12 litterbags (four species × three sampling dates) were fastened to a safety rope tied to a riparian tree. Litterbags at the sampling points were randomly sampled at the end of each winter period. The selection of sampling dates was based on changes in the freezing and thawing dynamics determined from previous field observations (Wu et al., 2011; Zhu et al., 2013), and on each sampling date, three litterbags of each litter type were retrieved. In the laboratory, the foliar litter samples were gently rinsed with demineralized water over a 0.3 mm mesh sieve to remove sediment and exogenous matter, and the cleaned samples were then oven-dried at 65 °C to a constant mass to calculate mass loss. Litter mass loss was calculated as the difference between initial dry mass and the actual dry mass of foliar litter on each sampling date. The temperatures in the litterbags were measured every two hours between 13 November 2013 and 24 April 2014 (Fig. 1) using a DS 1923-F5 iButton logger (Maxim Integrated Products, Sunnyvale, California, U.S.A.).

Analysis and Calculations

For the initial samples, oven-dried foliar litter was ground (using a 0.3 mm sieve) to be used for the analysis of carbon (C), nitrogen (N), and phosphorus (P). Carbon content was determined using the dichromate oxidation-ferrous sulfate titration method, and N and P analyses were performed with the Kjeldahl (KND, Top Ltd., Zhejiang, China) and

TABLE 2

Initial litter chemistry of each tree species expressed as potential litter quality variables (mean ± SE, n = 3).

Species	C (g kg–1)	N (g kg–1)	P (g kg–1)	C/N	C/P	N/P
Willow	337.59 ± 0.71a	26.69 ± 1.08a	1.75 ± 0.03a	12.04 ± 0.51a	194.13 ± 3.88a	16.13 ± 0.47a
Azalea	390.97 ± 11.07a	6.59 ± 0.86b	0.97 ± 0.11b	49.68 ± 9.74b	409.60 ± 35.70b	8.24 ± 1.46b
Cypress	492.96 ± 14.99c	10.42 ± 0.51c	1.54 ± 0.03c	52.44 ± 3.82c	310.33 ± 4.59c	5.92 ± 0.44b
Larch	378.11 ± 1.05b	15.70 ± 1.01d	1.25 ± 0.02d	22.65 ± 1.61a	312.94 ± 5.19d	13.82 ± 0.87a

Different lowercase letters in the same column indicate statistically significant differences among species for the corresponding variable (P < 0.05). C: carbon, N: nitrogen, P: phosphorus, C/N: carbon to nitrogen ratio, C/P: carbon to phosphorus ratio, N/P: nitrogen to phosphorus ratio.

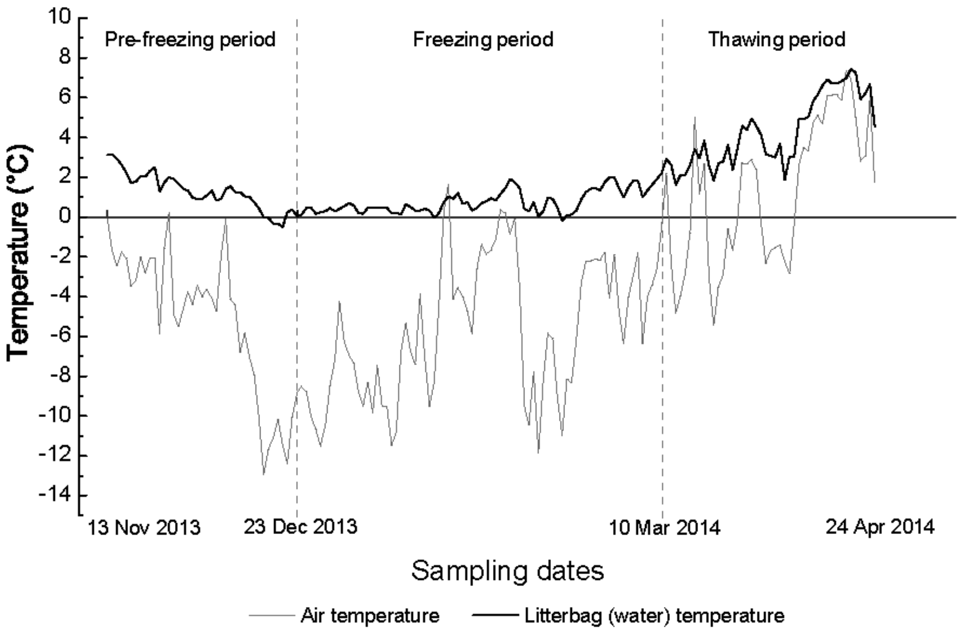

FIGURE 1. Temperature dynamics in the litterbags and the air from 13 November 2013 to 24 April 2014. Sampling stages were partitioned according to freezing and thawing characteristics as the temperature changed.

phosphomolybdenum yellow spectrophotometry methods (TU-1901, Puxi Ltd., Beijing, China), respectively (Ni et al., 2015). For each sampling date and sampling point, litter samples of the same type were retrieved for chemical analyses following the determination of mass loss. The powdered foliar litter of both the initial and remaining samples was digested with a concentrated acid mixture of HNO_3-$HClO_4$ (5:1, v/v) and heated at 160 °C for 5 hours (Xu et al., 2012). Cd, Cr, and Pb concentrations were determined by inductively coupled plasma spectroscopy (ICP-MS, IRIS Advantage 1000, Thermo Elemental, Waltham, Massachusetts, U.S.A.).

The foliar litter decomposition-rate constant (k d^{-1}) for the entire winter was calculated according to Olson (1963):

$$k = -\ln(M\,M_0^{-1})\,t^{-1}, \qquad (1)$$

where M and M_0 are litter dry mass at the end of incubation and initial dry mass, respectively, and t is the number of incubation days (162 d) for the entire winter.

The heavy metal release rate (R) throughout the litter decomposition process for each period was calculated as follows:

$$R\,(\%) = (M_{t-1}C_{t-1} - M_tC_t) \times (M_0C_0)^{-1} \times 100\%\ (t = 1, 2, 3). \qquad (2)$$

To exclude the effects of time length on the heavy metal release rate during each period, the heavy metal release rates per day (V) were calculated as follows:

$$V\,(\%) = R_t\,D_{\Delta t}^{-1}\ (t = 1, 2, 3) \qquad (3)$$

where M_0 and C_0 are the dry mass and heavy metal concentration of the initial litter, respectively; M_{t-1} and M_t are the dry mass of the remaining litter in the litterbags for the sampling times of $t - 1$ and t ($t = 1, 2, 3$), respectively; C_{t-1} and C_t are the heavy metal concentrations in the remaining litter for the sampling times of $t - 1$ and t ($t = 1, 2, 3$), respectively, and $D_{\Delta t}$ is the time interval (day number) of each sampling date.

The heavy metal release rate during the entire winter decomposition experiment (R_0) and the release rate per day during the entire winter (V_0) were calculated as follows:

$$R_0\,(\%) = (M_0C_0 - M_3C_3) \times (M_0C_0)^{-1} \times 100\% \qquad (4)$$

$$V_0\,(\%) = R_0\,D_e^{-1} \qquad (5)$$

where M_0 and C_0 are the dry mass and heavy metal concentration of the initial litter, respectively; M_3 and C_3 are the dry mass and heavy metal concentration of the remaining litter in the litterbags for the third sampling time, respectively; D_e is the number of incubation days (162 d) for the entire winter.

Statistical Analysis

A one-way ANOVA with a Fisher's least significant difference (LSD) test was used to identify significant ($P < 0.05$) differences between the initial litter quality and litter decomposition rate among the different litter types. A two-way ANOVA with a Tukey's HSD test was performed to test the effects of litter type, sampling period, and their interaction on the heavy metal release rate and release rate per day. Pearson correlations were conducted between (1) foliar litter release rate and water characteristics, (2) foliar litter release rate per day and water characteristics, (3) foliar litter release rate and water heavy metal concentrations, and (4) foliar litter release rate per day and water heavy metal concentrations. All statistical tests were performed using SPSS (version 18.0, SPSS Inc., Chicago, Illinois, USA) for Microsoft Windows.

Results

Litter Decomposition

After incubation over the entire winter, the four litter types underwent a relatively rapid loss of 18.9%–45.5% of their initial dry mass depending on litter type (Fig. 2, part a). Mass losses for all of the litter types in the prefreezing period were relatively high. Willow ($k = 0.00375$ d^{-1}) and cypress ($k = 0.00189$ d^{-1}) litter had the fastest decomposition rates with mass losses of 18.1% and 18.8% of initial dry mass, respectively. Initial litter quality showed a remarkable correlation with litter decomposition rate (Fig. 2, part b). Except for C concentration, all of the tested chemical properties affected litter decomposition rate at significantly different levels; N concentration and C/P ratio correlated most significantly with litter decomposition.

Heavy Metal Concentration in Decomposing Litter

Concentrations of Cr and Cd in the decomposing litters primarily increased after incubation over the entire winter, but the Pb concentration primarily decreased (Fig. 3). Cr concentrations in willow, cypress, and larch litters increased significantly in the prefreezing period and then fluctuated before reaching values higher than their respective initial concentrations (Fig. 3, part a). However, the Cr concentration in azalea litter decreased markedly after the entire winter's incubation. Cd concentrations in the four litter types showed a similar pattern of increase although the magnitude varied among the different litter types and periods (Fig. 3, part b). At the end of winter, Cd concentrations in all of the investigated foliar litter types were significantly higher than their respective initial values (Fig. 3, part b). Pb concentrations in willow, azalea, and larch litters increased significantly in the prefreezing period relative to their respective initial values but decreased in the freezing period and then remained relatively steady during the thawing period (Fig. 3, part c). The Pb concentration in cypress litter was relatively steady, and no significant change was observed during the entire incubation period.

Heavy Metal Release Rate and Release Rate per Day

During the entire winter's incubation, the Cr in willow litter displayed an obvious negative release (accumulation) rate in contrast with the release rates of the azalea, cypress, and larch litters (Fig. 4, part a). In the prefreezing period, the Cr in the willow, cypress, and larch litters obviously accumulated but was released in the azalea litter. The Cr in the willow litter showed an accumulation rate during the freezing period but a much higher release rate in the thawing period. In contrast, the Cr in the azalea and larch litters displayed release rates in the thawing period and accumulation rates in the other periods. The Cr release rates per day of these four foliar litters behaved somewhat similarly to the overall release rates (Fig. 5, part a). At the end of the decomposition experiment, foliar litter Cd had enriched from 32.5% to 1530.9% depending on litter type (Fig. 4, part b), and except for the low release rates in the willow and larch litters in the thawing period, the Cd in all of the foliar litter types in the different winter periods showed relatively consistent accumulation rates. In contrast with litter Cd, Pb showed obvious release rates across the whole

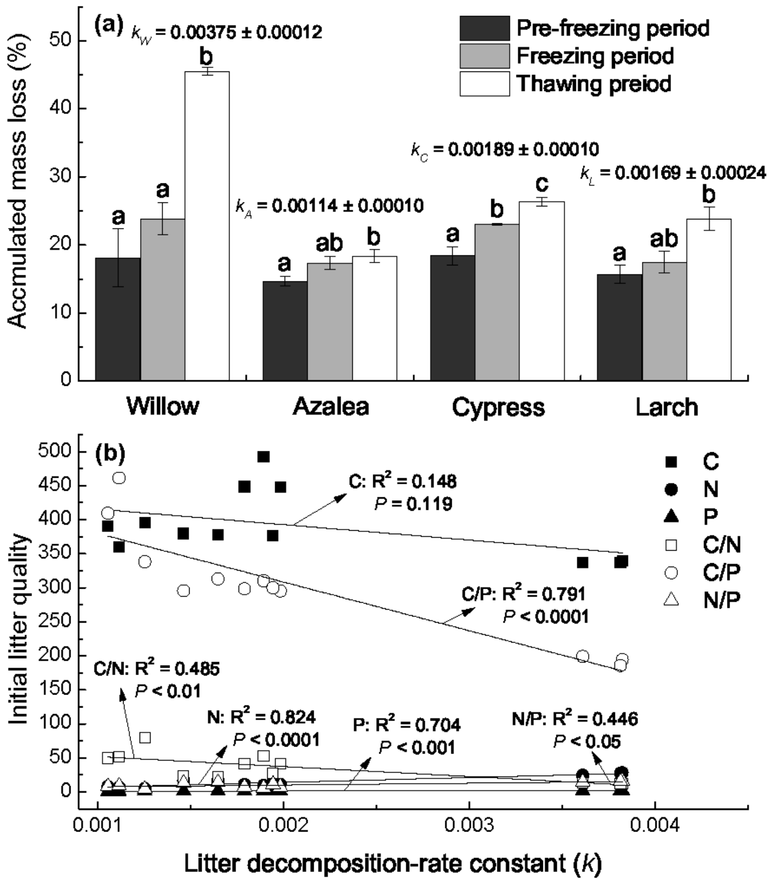

FIGURE 2. (a) Accumulated mass loss of willow, azalea, cypress, and larch foliar litter in different winter periods and the litter decomposition-rate constant for the entire winter (mean ± SE, n = 3). Different lowercase letters indicate statistically significant differences among different periods for a specific litter type (P < 0.05). (b) Correlations between the litter decomposition-rate constant (k d^{-1}) and initial litter quality (n = 12). The coefficients of determination and P-values are shown. C: carbon, N: nitrogen, P: phosphorus, C/N: carbon to nitrogen ratio, C/P: carbon to phosphorus ratio, N/P: nitrogen to phosphorus ratio.

experimental period in the willow, cypress, and larch foliar litters but a low accumulation rate in the azalea litter. However, both accumulation and release rates could be observed in the different winter periods (Fig. 4, part c). Per day release rates of Cd and Pb behaved similarly to their respective overall release rates (Fig. 5, parts b and c).

Temperature significantly affected the heavy metal release rate and/or release rate per day (Table 3); the results of a Pearson correlation analysis suggested that a higher temperature was likely to promote the release of foliar litter heavy metals. In contrast, river flow velocity usually showed a significantly negative correlation with heavy metal release rate and release rate per day. As for the pH and river water nutrient status parameters (HCO_3, SRP, NH_4-N, and NO_3-N), the release rate of Pb seemed to show an opposite response to the effects of these parameters compared with the release of Cr and Cd (Table 3). Moreover, water conductivity was also an important factor affecting heavy metal release, but its effect was modulated by litter type.

Discussion

Partially consistent with our hypothesis, the results from this study indicate that, apart from certain exceptions (e.g., Cr in the azalea foliar litter), foliar litter Cr and Cd show patterns of accumulation during decomposition, but Pb primarily exhibits an overall release pattern during winter incubation (Fig. 4). Our findings for heavy metal dynamics in decomposing litter in running water are similar to previous observations in terrestrial ecosystems, indicating a general pattern for the fate of heavy metals in decomposing litter in both terrestrial and aquatic ecosystems. Previous studies in terrestrial ecosystems have suggested that most heavy metals increase as litter decomposes, even up to an approximately 80% mass loss (Berg and McClaugherty, 2014), but this process could be affected by a variety of factors.

Concentrations of Cr in willow, cypress, and larch; Cd in all of the investigated foliar litter; and Pb in azalea foliar litter increased after an entire

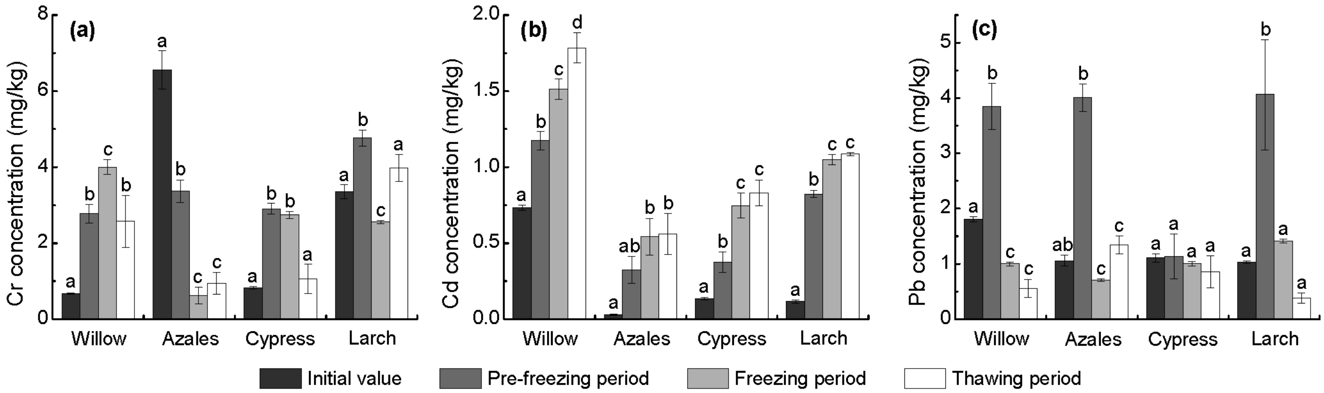

FIGURE 3. Dynamics of heavy metal concentrations ([a] Cr, [b] Cd, and [c] Pb) in decomposing foliar litter during the different winter periods (mean ± SE). Different lowercase letters indicate that the heavy metal concentration of the foliar litter of a specific litter type differed significantly among different periods (P < 0.05).

winter's decomposition in an alpine forest river (Fig. 3). During litter decomposition, the ratio between the remaining litter mass and the remaining amount of an element in the litter indicates a relationship between the patterns of elemental release and total mass loss (Inman and Parker, 1978). When the concentration of a heavy metal remains constant, the release of a metal element is similar to the loss of litter mass. If the concentration of a heavy metal decreases, the release of the metal element is higher in relation to the loss of litter mass and vice versa. Thus, the increase in the concentration of a heavy metal in decomposing foliar litter over time can result from the following processes: (1) a metal element being released more slowly relative to the litter decomposition rate, (2) the addition of metals via aerial deposition, (3) the upward transport of a metal by soil organisms, and (4) the input of a metal through leaching from overlying litters (Lomander and Johansson, 2001). The difference between the litter decomposition rate and the heavy metal release rate may be the main reason for the increase in Cr and Cd concentrations, as the above explanations are more likely for heavy metal accumulation in decomposing litters on forest floors, and the foliar litter mass loss in rivers seems to be relatively high compared with that on forest floors (Ni et al., 2015). However, it is likely that the im-

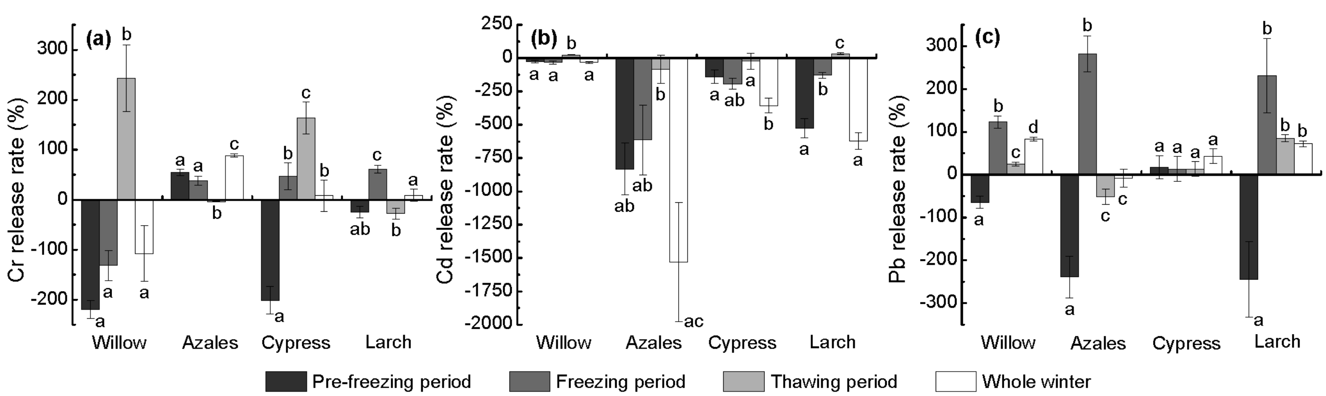

FIGURE 4. Heavy metal ([a] Cr, [b] Cd, and [c] Pb) release rates for four foliar litter types investigated during different decomposition periods (mean ± SE, n = 3). Different lowercase letters indicate significantly different foliar litter heavy metal release rates for a specific litter type among different periods (P < 0.05). Negative values indicate accumulation rates during foliar litter decomposition.

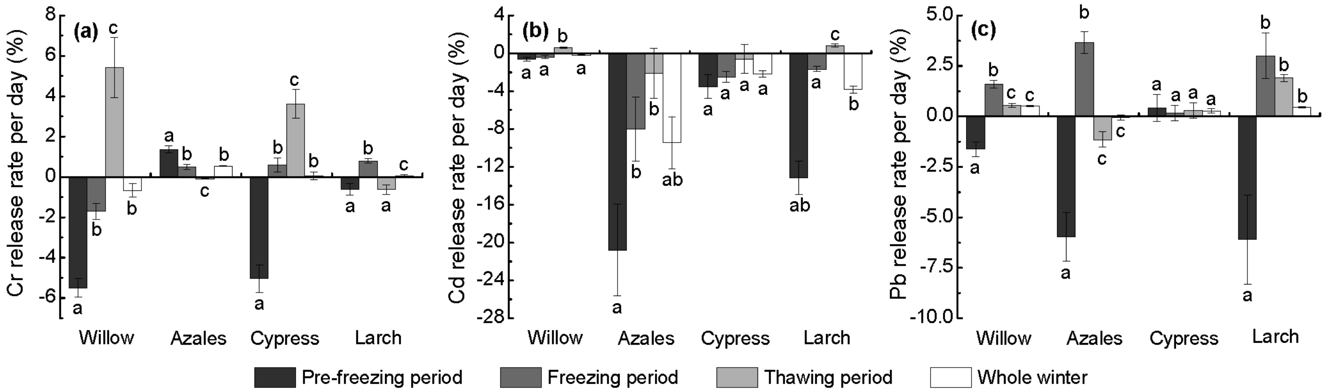

FIGURE 5. Heavy metal ([a] Cr, [b] Cd, and [c] Pb) release rate per day for four foliar litter types investigated during different decomposition periods (mean ± SE, n = 3). Different lowercase letters indicate significantly different foliar litter heavy metal release rates per day for a specific litter type among different periods ($P < 0.05$). Negative values indicate accumulation rates per day during foliar litter decomposition.

port of an exotic metal occurred as well as several of these heavy metal concentrations increased faster than would be suggested by just the conservation of the existing amount (Fig. 4).

Indeed, the Cr release rate from willow litter, the Cd release rates of all of the litter types, and the Pb release rate of the azalea litter suggest that absolute amounts of these two heavy metals increased after an entire winter's incubation, and Cd was even enriched to as much as 1530.9% of its initial mass (Fig. 4, part b). These results are consistent with a previous laboratory study that reported that heavy metal concentrations increased significantly, and net absorptions were recorded from the surrounding water (Lyngby and Brix, 1989). In our study, a negative correlation was generally observed between litter heavy metal release rate/release rate per day and river water metal concentration (Table 4), indicating a potential transport of heavy metal from river water to litter. Potential mechanisms to account for the sorption of heavy metals in decomposing litter have been proposed, such as the formation of chelates and complexes at active sites on the organic molecules of decomposing detritus (Odum and Drifmeyer, 1978). Drifmeyer and Rublee (1981) suggested that a large fraction of heavy metals in decomposing litter is readily exchangeable and that the carboxylic acid group has an important role in the exchange reaction, which may result in the accumulation of a metal. Furthermore, fungi in decomposing litter have been reported to be capable of accumulating significant amounts of the metals present in their external environment, even in unpolluted areas (Gadd and Griffiths, 1978; Berthelsen et al., 1995). As fungal mycelia can constitute a significant pool of organic material with a high capacity for heavy metal accumulation, they are thus likely to affect the overall mobility of a heavy metal in a litterbag (Krantz-Rülcker et al., 1993). This is an interesting finding that is not only meaningful for explaining the capacity of ecosystems for self-purification but also significant for the control of hazardous materials. A recent study found that the heavy metal concentration in the water of forest streams decreased from stream head to end (Peng et al., 2015), indicating a self-purification capacity that may be attributed to accumulation in litter. Moreover, for heavy metals whose net amount will increase in decomposing litter, this characteristic could be used to decrease the heavy metal content of these types of rivers as the accumulation rates in this study appear to be relatively high (Fig. 4).

However, the Cr in the azalea, cypress, and larch litters and the Pb in the willow, cypress, and larch litters in our study contrasted with most of the previous studies (Inman and Parker, 1978; Lomander and Johansson, 2001); a pattern of decrease was observed in Pb concentrations as the degree of litter decomposition progressed. Usually, Pb is known to be relatively immobile over a wide range of acidities in the environment and is characterized by high increases in concentration (Berg and McClaugherty, 2014), so the decrease in Pb during litter decomposition may be a result of the effects of complex

TABLE 3

Pearson correlations between heavy metal release rates/release rates per day and river water characteristics during foliar litter decomposition (n = 9).

		Species	AT	PAT	NAT	FV	pH	Cond	HCO_3	SRP	NH_4-N	NO_3-N
R	Cr	Willow	**0.909****	**0.946****	**0.729***	**–0.731***	**–0.700***	–0.548	0.267	–0.239	–0.171	**0.900****
		Azalea	**–0.857****	**–0.909****	**–0.768***	**0.771***	0.621	0.459	–0.173	0.145	0.256	**–0.907****
		Cypress	0.628	**0.746***	**0.954****	**–0.955****	–0.261	–0.059	–0.254	0.282	–0.644	**0.946****
		Larch	–0.601	–0.465	0.302	–0.298	**0.850****	**0.971****	**–0.938****	**0.935****	**–0.799****	–0.032
	Cd	Willow	**0.892****	**0.883****	0.490	–0.493	**–0.799****	**–0.697***	0.480	–0.457	0.904	**0.722***
		Azalea	**0.682***	**0.725***	0.618	–0.619	–0.491	–0.361	0.132	–0.109	–0.211	**0.726***
		Cypress	**0.682***	0.651	0.258	–0.261	**–0.688****	–0.615	0.480	–0.464	0.207	0.468
		Larch	0.605	**0.728***	**0.961****	**–0.962****	–0.232	–0.028	–0.285	0.313	**–0.668****	**0.941****
	Pb	Willow	–0.154	0.181	**0.741***	**–0.739***	0.545	**0.704***	**–0.884****	**0.897****	**–0.977****	0.469
		Azalea	–0.282	–0.116	0.641	–0.638	0.646	**0.784***	**–0.926****	**0.934****	**–0.957****	0.344
		Cypress	–0.017	–0.025	–0.046	0.046	–0.003	–0.013	0.027	–0.028	0.041	–0.040
		Larch	0.076	0.230	**0.795***	**–0.794***	0.304	0.474	**–0.691***	**0.708***	**–0.869****	0.603
V	Cr	Willow	**0.850****	**0.915****	**0.826****	**–0.828****	–0.584	–0.410	0.109	–0.080	–0.328	**0.946****
		Azalea	**–0.690***	**–0.796***	**–0.933****	**0.934****	0.344	0.147	0.167	–0.195	0.572	**–0.956****
		Cypress	0.656	**0.771***	**0.956****	**–0.957****	–0.293	–0.091	–0.225	0.254	–0.624	**0.958****
		Larch	–0.554	–0.442	0.313	–0.309	**0.801****	**0.870****	**–0.898****	**0.896****	**–0.777***	–0.005
	Cd	Willow	**0.875****	**0.909****	**0.690***	**–0.693***	**–0.680***	–0.535	0.267	–0.241	–0.152	**0.858****
		Azalea	0.534	0.636	**0.818****	**–0.819****	–0.219	–0.046	–0.222	0.246	–0.555	**0.809****
		Cypress	0.517	0.557	0.504	–0.505	–0.355	–0.249	0.066	–0.048	–0.201	0.576
		Larch	0.515	0.651	**0.972****	**–0.972****	–0.121	0.085	–0.392	0.419	**–0.748***	**0.912****
	Pb	Willow	0.066	0.235	**0.859****	**–0.857****	0.346	0.529	**–0.763***	**0.780***	**–0.950****	0.644
		Azalea	–0.128	0.040	**0.743***	**–0.741***	0.516	**0.675***	**–0.859****	**0.872****	**–0.961****	0.481
		Cypress	0.019	–0.006	–0.111	0.110	–0.077	–0.101	0.128	–0.130	0.143	–0.072
		Larch	0.245	0.392	**0.861****	**–0.860****	0.139	0.322	–0.573	0.594	**–0.819****	**0.720***

Notes: *R*, release rate; *V*, release rate per day; AT, average temperature, defined as the mean value of the daily mean temperatures during the corresponding period; PAT, positive accumulated temperature, defined as the sum of the positive temperature values during the corresponding period; NAT, negative accumulated temperature, defined as the sum of the negative temperature values during the corresponding period (Tourna et al., 2008); FV, flow velocity; Cond, conductivity; SRP, soluble reactive phosphorus. $^{*}P < 0.05$, $^{**}P < 0.01$. Bold indicates significant numbers.

factors and may not just be due to the mobility of the metal. Nevertheless, heavy metals displayed different release patterns in different periods of winter.

A two-way ANOVA suggested that sampling period (prefreezing, freezing, and thawing) significantly ($P < 0.001$) affected both the release rate and release rate per day of heavy metals (Table 5). The release of metal elements during litter decomposition could follow different patterns, although some of the elements are always released in a similar way, regardless of litter type (Jonczak et al., 2014). However, most of the heavy metal elements can be released in different patterns depending on their characteristics, bioavailability at the site, the needs

TABLE 4

Pearson correlations between heavy metal release rates/release rates per day and the respective heavy metal concentration in river water during foliar litter decomposition (*n* = 9).

Species	Release rate			Release rate per day		
	Cr	Cd	Pb	Cr	Cd	Pb
Willow	–0.752*	–6.05	–0.562	–0.795*	–0.762*	–0.675*
Azalea	0.787*	–0.656	–0.474	0.848**	–0.604	–0.555
Cypress	–0.913**	–0.286	0.084	–0.930**	–0.357	0.158
Larch	0.018	–0.867**	–0.501	0.014	–0.827**	–0.630

*$P < 0.05$, **$P < 0.01$.

of living organisms, and temporally variable environmental conditions. During the various winter periods, the water characteristics varied, which would influence the magnitude and even direction (release or accumulation) of heavy metal release as significant correlations have been observed between the pattern of heavy metal release and water characteristics (Table 3). Moreover, litter type is also an important moderator of heavy metal release, and the interaction effects with sampling period seem to be stronger than those of the litter type per se.

Temperature has always been a key factor governing litter decomposition (Aerts, 2006; Salinas et al., 2011), and both the release rate and release rate per day in this study showed significant correlations with temperature (Table 3). In aquatic ecosystems with constant moisture, a warmer temperature is likely to hasten microbial activity and thus accelerate element mobility as the microbial community plays an important role in retaining or importing matter into the decomposing litter-microbe complex (Berg and McClaugherty, 2014). A significantly negative relationship has been observed between most heavy metals and river flow velocity, and water pH seems to play a major role in the release of heavy metals from litter. Previous studies have suggested that Cd shows increasing solubility and mobility with decreasing pH, so it is often leached from litter (Berg and McClaugherty, 2014). However, such a property is not independent of the aquatic microbial population, and at low concentrations when metals are not in excess, a low pH does not necessarily mean a high net mobility. Heavy metal release could also be strongly affected by other factors, such as conductivity and nutrient status (Table 3), and these correlations could be at-

TABLE 5

F-values for two-way ANOVA with Tukey's honest significant difference (HSD) test of the effects of litter type, sampling period (i.e., the designated periods in winter), and their interactions on the heavy metal release rates and release rates per day during winter litter decomposition.

Factor	d.f.	Chromium (Cr)	Cadmium (Cd)	Lead (Pb)
Release rate				
Litter type	3	3.010	12.664***	0.302
Sampling period	2	50.785***	12.684***	47.139***
Litter type × sampling period	6	28.551***	3.079	9.139***
Release rate per day				
Litter type	3	2.333	13.968***	0.183
Sampling period	2	63.733***	21.526***	40.908***
Litter type × sampling period	6	31.623***	4.884**	8.768***

d.f.: degrees of freedom; **$P < 0.01$, ***$P < 0.001$.

tributed to microbial activities related to the physicochemical properties of water. Furthermore, the similar trends in heavy metal release rate and release rate per day suggest that time has little effect on the heavy metal release rate in each period.

Conclusions

In summary, the results of this study suggest that both Cr and Pb show accumulation patterns in the prefreezing period and release patterns in the freezing and thawing periods, but Cd shows an accumulation pattern in all three periods. The dynamics of these heavy metals in decomposing foliar litter could be strongly affected by litter type, stage of decomposition, and the characteristics of river water, such as temperature, pH, flow velocity, conductivity, and nutrient availability. The accumulation patterns for all of the heavy metals in litter in the early stage of decomposition (prefreezing period) indicate that litter in running water could act as an efficient heavy metal "cleaner" that contributes to the self-purification capacity of the ecosystem. Moreover, the similar accumulation pattern between heavy metals in the decomposing litter of running water ecosystems with that of terrestrial ecosystems suggests a general pattern for the fate of heavy metals across different ecosystem types. These findings are useful both in the control of environmental pollution in water conservation areas, such as alpine biomes, and for further investigations into element cycling across terrestrial and aquatic ecosystems.

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