Annals of Forest Science (2016) 73:547–557
DOI 10.1007/s13595-016-0549-2

ORIGINAL PAPER

Dynamics of multiple metallic elements during foliar litter decomposition in an alpine forest river

Kai Yue[1] · Wanqin Yang[1,2] · Yan Peng[1] · Chuan Zhang[1] · Chunping Huang[1,3] · Zhenfeng Xu[1,2] · Bo Tan[1,2] · Fuzhong Wu[1,2]

Received: 1 December 2015 / Accepted: 16 February 2016 / Published online: 23 March 2016

Abstract
• ***Key message*** **Compared with previously reported data, we found that plant litter decomposes faster in river ecosystem than on forest floor in a comparable period, but the dynamics of metallic elements during litter decomposition in river are likely to share common patterns with the corresponding ones in decomposing litter on forest floor**.
• ***Context*** Litter decomposition in terrestrial lotic ecosystem is one of the most important pathways for metallic elements cycling, while little information is currently available about the dynamics of metallic elements in the decomposing litter of lotic ecosystems.
• ***Aims and methods*** The concentrations and release rates of potassium (K), calcium (Ca), sodium (Na), magnesium (Mg), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), and aluminium (Al) were investigated in the decomposing foliar litter of four dominant species in an alpine forest river.
• ***Results*** Over a 1-year period of decomposition, K, Ca, and Mg were released from virtually all types of litter, whereas Na, Fe, Mn, Zn, Cu, and Al were released from willow litter but accumulated in azalea, cypress, and larch litters during litter decomposition. Litter species, decomposition period, and river water characteristics (e.g., temperature, pH, flow velocity, and nutrient availability) were significantly related to the dynamics of these metallic elements in decomposing litter.
• ***Conclusion*** Our results suggested that the similarity between the dynamics of metallic elements in the decomposing litter of lotic ecosystems reported here and previously for forest floors indicates a general pattern for the cycling of metallic element across different ecosystem types, and the net accumulation patterns for elements such as Zn, Cu, and Al during litter decomposition suggested that some litter species may act as efficient "cleaner" for metal purification in future ecological engineering.

Keywords Element cycling · Litter decomposition · Metal concentration · Release rate · Decomposition period · Water physicochemical characteristic

Handling Editor: Gilbert Aussenac

Contribution of the co-authors K.Y., F.W., and W.Y. conceived the project. All author conducted the field work. K.Y. and Y.P. conducted the laboratory analyses. K.Y. and F.W. contributed to analysis and interpretation of the data, and wrote the manuscript. All authors critically reviewed the manuscript.

Electronic supplementary material The online version of this article (doi:10.1007/s13595-016-0549-2) contains supplementary material, which is available to authorized users.

✉ Fuzhong Wu
wufzchina@163.com

1 Long-term Research Station of Alpine Forest Ecosystem, Provincial Key Laboratory of Ecological Forestry Engineering, Institute of Ecology and Forestry, Sichuan Agriculture University, 211 Huimin Road, Wenjiang District, Chengdu 611130, People's Republic of China

2 Collaborative Innovation Centre of Ecological Security in the Upper Reaches of the Yangtze River, Chengdu 611130, People's Republic of China

3 College of Life Science, Sichuan Normal University, Chengdu 610101, People's Republic of China

1 Introduction

Metallic elements, such as potassium (K), calcium (Ca), and magnesium (Mg), are essential plant nutrients that are crucial to plant physiology, whereas other metallic elements, such as zinc (Zn), copper (Cu), and aluminium (Al), can have toxic effects on organisms when they exceed certain levels. Thus, the dynamics of metallic elements are highly important for plant communities and ecosystem function (Chapin et al. 2002). The decomposition of litter as a mechanism of nutrient release is a key process in the functioning of both natural and modified ecosystems (Jonczak 2013; Berg and McClaugherty 2014). Plant litter decomposition in inland waters contributes significantly to global nutrient cycles (Tranvik et al. 2009), particularly in flowing waters, such as forest streams and rivers (Battin et al. 2008, 2009). In forest rivers, plant litter is an essential part of the food web and ecological functioning (Wallace et al. 1997; Gessner et al. 1999) because it provides large inputs of energy and nutrients to an aquatic ecosystem that typically exhibits low levels of primary productivity (Wallace et al. 1997). Litter decomposition in forest rivers is not only an important component of the material cycling and energy flow of the entire forest ecosystem but also plays a critical role in nutrient exchange between aquatic and terrestrial ecosystems. However, most studies investigating metallic element dynamics in decomposing litter have been conducted on forest floors, and little information is currently available regarding the dynamics of such elements during litter decomposition in forest rivers, particularly in alpine forest rivers, which are important water sources.

Rates of litter decomposition in running water and the simultaneous release of elements are much higher than those in upland ecosystems because of stronger leaching and flushing effects (Perakis and Hedin 2002) and that the process of element release could be affected by multiple factors, such as an element's chemical characteristics (Staaf and Berg 1982), litter quality (Leroy and Marks 2006), microenvironments, and water characteristics (Rueda-Delgado et al. 2006; Martínez et al. 2014). Major elements, such as K, Ca, and Mg, were reported to release during litter decomposition on forest floors (Staaf and Berg 1982; Edmonds and Tuttle 2010), whereas trace elements, such as sodium (Na), manganese (Mn), Zn, and Cu, preferentially retain and show increasing concentrations during the early stages of litter decomposition on forest floors (Edmonds and Tuttle 2010; Jonczak et al. 2014; He et al. 2015). Plant litter species and plant functional traits are the predominant factors controlling litter decomposition at both local and global scales (Cornwell et al. 2008; Makkonen et al. 2012); litter quality should thus significantly influence the dynamics of elements in decomposing litter. Specific elements can show different release patterns in different types of litter (Jonczak et al. 2014). Moreover, litter species can affect the microbial and invertebrate assemblages in rivers and thus exert indirect effects on litter decomposition and element release (Leroy and Marks 2006; Abelho 2008).

Some of the water physicochemical characteristics, such as pH, flow velocity, and nutrient availability, may affect the release of metallic elements (Landre et al. 2009). Alpine forests are usually subjected to low temperatures and undergo considerable freeze-thaw cycles. The formation, coverage, and thawing of snow cover and the accompanying freeze-thaw cycles in winter could influence the characteristics of river water (e.g., flow velocity and nutrient availability) and the communities and activities of decomposers, which could further alter the rate of litter decomposition and the pattern of element release (Baldy et al. 2007). Thus, elements may display different release patterns in different seasons and over different periods. However, the available data primarily focus on the process of litter decomposition on forest floors or in small forest streams; few studies have documented this process in forest rivers, particularly in alpine forest ecosystems, which makes it difficult to draw definitive conclusions about the role of litter decomposition in the processes of nutrient cycling in forest ecosystems.

To understand the dynamics of metallic elements during litter decomposition in alpine forest rivers, a litter decomposition experiment was conducted to investigate the release patterns of K, Ca, Na, Mg, iron (Fe), Mn, Zn, Cu, and Al in decomposing foliar litter in an alpine forest river on the eastern Tibetan Plateau. Based on the freezing and thawing dynamics determined from our previous investigations at the study site, we divided an entire year into five periods (Zhu et al. 2012; Wu et al. 2014). Specifically, we divided winter into three periods, which were designated as the "pre-freezing period," the "freezing period," and the "thawing period," according to our previous investigations (Wu et al. 2014). In addition, we designated April to August as the "growing season" and August to early November as the "late growing season." Element dynamics were investigated using freshly fallen leaves of the dominant riparian species (willow, *Salix paraplesia* Schneid; azalea, *Rhododendron lapponicum* (L.) Wahl.; cypress, *Sabina saltuaria* (Rehd. et Wils) Cheng et W. T. Wang; and larch, *Larix mastersiana* Rehder & E. H. Wilson) during the designated decomposition periods. The results will further our understanding of the mechanisms driving the dynamics of metallic elements in decomposing litter within flowing water. This new knowledge will also be useful for exploring the patterns of element cycling between forest aquatic and riparian ecosystems.

2 Materials and methods

2.1 Study site description

This study was conducted at the Long-term Research Station of Alpine Forest Ecosystem within the Miyaluo Nature Reserve (102° 53′–102° 57′ E, 31° 14″–31° 19′ N; 2458–4169 m a.s.l.) in Li County, Sichuan Province, southwestern China. This region is a typical cold zone situated between the Sichuan Basin and the Tibetan Plateau and is regularly exposed to subfreezing temperatures. The mean annual temperature is 3 °C with a range from −18 to 23 °C and a mean annual precipitation of approximately 850 mm. The forest age is approximately 130 years. The soil is classified as Cambisol (IUSS Working Group WRB 2006) and is frozen by early November, with accumulated snow until late April of the following year (Zhu et al. 2012). The study river is the primary drainage with a width ranging from approximately 3 to 7 m in a typical alpine forest into which small forest streams feed. Three plots were established as replicate sampling points along the river at an altitude of approximately 3600 m a.s.l. The riparian forest is a temperate coniferous forest, and the dominant tree species are larch, cypress, and fir (*Abies faxoniana*) interspersed with azalea (*Rhododendron* spp.), willow, and barberry (*Berberis sargentiana*) shrubs. The herbaceous plants are primarily fern (*Cystopteris montana*), *Carex* spp., and *Cyperus* spp. (Wu et al. 2014).

2.2 River water characteristics

On each sampling occasion during the 1-year experiment, the river water physicochemistry of the three selected plots was characterized: pH (pH 320, WTW GmbH, Weilheim, Germany), conductivity (HI 98311, Hanna Instruments, Woonsocket, RI, USA), and flow velocity (Martin Marten Z30 Current Meter) were measured in situ. Water samples were also collected from each plot using polyethylene bottles and were transported to the laboratory in refrigerated chambers for further analysis. The water samples were immediately filtered (GF/F glass fiber filter with 0.7-μm retention; Whatman International, Florham Park, NJ, USA) upon arrival at the laboratory. The pre-processed water samples were used to determine the bicarbonate concentration using the double indicator-neutralization method, phosphate (PO_4) concentration using the molybdate method, nitrate concentration using capillary ion electrophoresis (Agilent CE), and ammonium concentration using the indophenol blue method (Rice et al. 2012) (Table 1).

2.3 Experimental design

In October 2013, freshly fallen leaves from willow, azalea, cypress, and larch were collected from the riparian forest floor of the explored study site in two days at the time when the majority of the leaves fell. The collected foliar litter was air-dried for more than 2 weeks at room temperature. Firstly, we weighed 10 g air-dried samples for each species with three replicates, and then oven-dried these samples at 65 °C for 72 h to calculate the moisture correction factor and then analyzed to determine the initial nutrient concentrations and ratios (Table 2). And then, for each litterbag of each litter species, air-dried foliar litter with a mass equivalent to 10 g of the oven-dried sample was weighed and placed into 20 × 20 cm nylon bags (mesh size 0.5 mm). In total, 540 litterbags (4 litter species × 3 plots × 3 replicates × 15 sampling events) were placed in the forest river. Three sample plots were selected along the upper reaches of the river, and the sample plots were approximately 2–3 km from adjacent plots. For each sample plot, 180 litterbags (4 litter species × 3 replicates × 15 sampling events) were placed in the river and tied to ropes that were fastened to stainless steel rods encased by polyvinyl chloride tubes. The litterbags floated on the river water and could move up and down with the wave action, similar to naturally fallen litter. On 23 December 2013 (pre-freezing period, 41 days of exposure), 10 March 2014 (freezing period, 118 days of exposure), 24 April 2014 (thawing period, 163 days of exposure), 4 August 2014 (growing season, 265 days of exposure), and 13 November 2014 (late growing season, 366 days of exposure), three litterbags were retrieved from each plot. By the fifth sampling time on 13 November 2014, most of the litterbags had been destroyed because of the strong current. As a result, we only collected data for five sampling periods during the first 1-year decomposition experiment. The temperatures of litterbags and the air were measured every 2 h during the year-long incubation (Fig. 1) using a DS 1923-F5 iButton logger (Maxim Integrated Products Inc., San Gabriel Drive, Sunnyvale, USA).

2.4 Analytical methods and calculations

Oven-dried foliar litter from the initial samples was ground (using a 0.3-mm mesh screen) to quantify the starting total C, total nitrogen (N), and total phosphorus (P) concentrations. Total C concentration was determined using the dichromate oxidation-ferrous sulfate titration method, and N and P was analyzed using the Kjeldahl method (KND, Top Ltd.,

Table 1 River water flow velocity, pH, conductivity, bicarbonate (HCO_3), phosphate (PO_4), ammonium (NH_4-N), and nitrate (NO_3-N) in the study site during different periods (mean ± SE, $n = 3$)

Period	Flow velocity (m/s)	pH	Conductivity (μ S/cm)	HCO_3 (mg/L)	PO_4 (μg/L)	NH_4-N (mg/L)	NO_3-N (mg/L)
Pre-freezing period	1.08 ± 0.21	7.14 ± 0.04	51.6 ± 0.3	17.4 ± 0.1	7.0 ± 0.3	0.04 ± 0.01	0.30 ± 0.13
Freezing period	0.71 ± 0.12	7.21 ± 0.02	52.4 ± 0.4	17.0 ± 0.1	8.0 ± 0.2	0.02 ± 0.00	0.31 ± 0.09
Thawing period	1.63 ± 0.18	7.08 ± 0.02	51.3 ± 0.3	17.4 ± 0.3	7.2 ± 0.3	0.03 ± 0.01	0.32 ± 0.11
Growing season	1.72 ± 0.37	7.10 ± 0.03	41.9 ± 0.3	17.2 ± 0.5	7.2 ± 0.3	0.02 ± 0.00	0.31 ± 0.08
Late growing season	1.23 ± 0.28	7.12 ± 0.02	46.4 ± 0.3	17.3 ± 0.2	7.1 ± 0.2	0.03 ± 0.00	0.31 ± 0.06

Table 2 Initial nutrient concentrations and chemistry of fresh willow, azalea, cypress, and larch foliar litters (mean ± SE, $n = 3$)

Species	C (g/kg)	N (g/kg)	P (g/kg)	C/N	C/P	N/P
Willow	338 ± 1a	26.6 ± 1.1a	1.75 ± 0.03a	12.7 ± 0.5a	193 ± 4a	15.2 ± 0.47a
Azalea	382 ± 11a	6.59 ± 0.86b	0.97 ± 0.11b	60.4 ± 9.7b	403 ± 35b	7.13 ± 1.46b
Cypress	463 ± 15c	10.4 ± 0.5c	1.54 ± 0.03c	44.8 ± 3.8c	301 ± 5c	6.80 ± 0.44b
Larch	378 ± 1b	15.7 ± 1.0d	1.25 ± 0.0d	24.3 ± 1.6a	303 ± 6d	12.6 ± 0.9a

C total carbon, *N* total nitrogen, *P* total phosphorus. Different lowercase letters in the same column indicate statistically significant differences among the different litter types ($P < 0.05$)

Zhejiang, China) and spectrophotometry (TU-1901, Puxi Ltd., Beijing, China) method after digestion with sulphuric acid and hydrogen peroxide at 360 °C, respectively (Lu 1999; Ni et al. 2015). Once retrieved, the foliar litters were transferred to the laboratory, and the foreign materials in which were carefully selected by hand. After that, the litters were cleaned using deionized water and air-dried, and then oven-dried at 65 °C to a constant mass and weighed. The oven-dried samples were ground in a mill with a 0.3-mm mesh screen to measure the elemental concentrations. The powdered foliar litter of both the initial and field samples was digested with a concentrated acid mixture of HNO_3-$HClO_4$ (5:1, *v*/*v*) and heated at 160 °C for 5 h (Xu et al. 2012). The concentrations of K, Ca, Mg, Fe, Mn, Zn, Cu, Na, and Al were determined using inductively coupled plasma spectroscopy (ICP-MS, IRIS Advantage 1000, Thermo Elemental, Waltham, MA, USA).

The element release rate (*R*, % initial mass/month) throughout the litter decomposition process for each period was calculated as follows:

$$R(\%) = \frac{M_{t-1}C_{t-1} - M_tC_t}{M_0C_0\Delta T_t} \times 100\% \quad (t = 1, 2, 3, 4, 5)$$

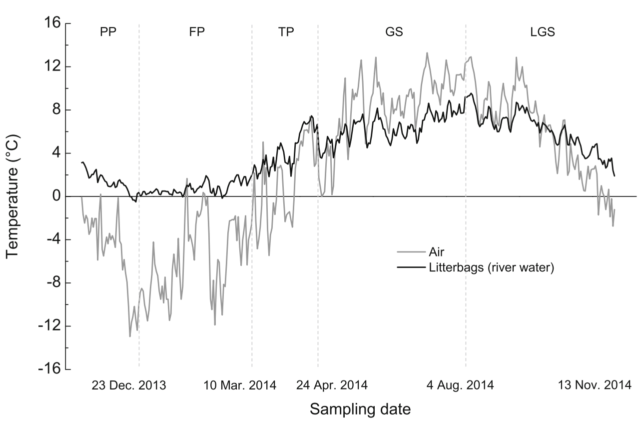

Fig. 1 Dynamics of daily mean temperature in litterbags and air throughout the entire year of litter exposure. The entire year was divided into five periods based on the freeze-thaw dynamics according to our previous investigations at the study site, and the samplings were conducted at the end of each period. The five periods are *PP* pre-freezing period, *FP* freezing period, *TP* thawing period, *GS* growing season, *LGS* late growing season

where M_0 and C_0 are the dry mass and element concentration of the initial foliar litter, respectively; M_{t-1} and M_t are the dry mass of the litter remaining in the litterbags at the sampling times of "t-1" and "t" ($t = 1, 2, 3, 4, 5$), respectively; C_{t-1} and C_t are the element concentrations in the remaining litter at the sampling times of "t-1" and "t" ($t = 1, 2, 3, 4, 5$), respectively; and ΔT_t is the time interval (month) of each period ($t = 1, 2, 3, 4, 5$).

The element release rates per month for the entire winter (R_w), entire growing season (R_g), and entire year (R_y) were calculated as follows:

$$R_w(\%) = \frac{M_0C_0 - M_3C_3}{M_0C_0\Delta T_w} \times 100\%$$

$$R_g(\%) = \frac{M_3C_3 - M_5C_5}{M_0C_0\Delta T_g} \times 100\%$$

$$R_y(\%) = \frac{M_0C_0 - M_5C_5}{M_0C_0\Delta T_y} \times 100\%$$

where M_0, M_3, and M_5 are the litter dry masses of the initial, third, and fifth sampling times, respectively; and C_0, C_3, and C_5 are the litter element concentrations of the initial, third, and fifth sampling times, respectively; and ΔT_w, ΔT_g, and ΔT_y is the time interval (month) of the winter, the growing season, and the entire year.

2.5 Statistical analysis

A one-way ANOVA with Fisher's least significant difference (LSD) test was used to identify significant ($P < 0.05$) differences in initial litter chemistry among the four litter species and the concentrations, contents, and release rates of elements among the different decomposition periods. A repeated measurement ANOVA with Greenhouse-Geisser correction was employed to test the effects of time, litter species, and their interactions on the release rates of elements throughout the entire year. Pearson correlation was conducted to test the relationship between water physicochemistry and element release rate across the whole year's incubation. Statistical analyses were carried out using SPSS 18.0 (SPSS Inc., Chicago, Illinois, USA) for Microsoft Windows.

3 Results

3.1 Remaining litter mass

After 1 year of incubation, the four litter species underwent relatively rapid mass loss, with the average remaining dry mass ranging from 0 to 61.52 % of the initial dry mass depending on litter species (Fig. 2). Willow was consistently the most rapidly decomposed litter, regardless of the decomposition period. Cypress litter followed with 46.06 % of its initial dry mass remaining after 1 year of incubation in the forest river, whereas the remaining dry masses of azalea and larch litter were similar at the end of the 1-year incubation.

3.2 Metallic element concentrations

K concentrations showed a consistent decrease during the year-long incubation regardless of litter species (Fig. 3a). Ca concentrations increased during the pre-freezing period in all types of litter and then decreased, although a minor increase was observed during the thawing period (Fig. 3b). Na concentrations increased in winter, reaching their highest levels during the thawing period but then decreasing in the ensuing growing season (Fig. 3c). Mg concentrations in willow and azalea litters decreased at the end of the late growing season but increased in cypress and larch litters (Fig. 3d). The concentration dynamics of Fe, Mn, Zn, Cu, and Al were similar throughout litter decomposition, showing a statistically significant ($P<0.05$) increase at the end of the late growing season compared with the initial values, although some fluctuation was observed in other periods (Fig. 3e, f, g, h, i).

3.3 Metallic element release rates

Potassium showed relatively consistent release pattern, regardless of decomposition period and litter species, with 81.64–100 % of the initial content released depending on litter species at the end of the year; the release rate during winter was usually significantly ($P<0.05$) higher than that in the ensuing growing season, with the exception of azalea litter (Fig. 4a). Ca showed release pattern for the entire year, although negative release (accumulation) rates were observed in the pre-freezing period for azalea, cypress, and larch litters (Fig. 4b). Na generally displayed negative release rates in the winter period but subsequent positive release rates in the ensuing growing season, regardless of litter species (Fig. 4c). The release rate of Mg was much more dynamic, varying with litter species and decomposition period (Fig. 4d). Mg was significantly released from willow and azalea litter for the entire year but showed minimal release from cypress litter. However, Mg accumulated in larch litter during almost all of the decomposition periods (Fig. 4d). Fe, Mn, Zn, Cu, and Al in willow litter generally showed obvious release rate during the year-long incubation, but significant ($P<0.05$) differences in release rates were observed among different periods (Fig. 4e, f, g, h, i). These metallic elements in azalea, cypress, and larch litters generally showed substantial negative release rates during winter, the entire growing season, and the entire year, and the content of which could be as high as 100–1151 % of the initial content after the 1-year incubation, depending on the element and the litter species (Fig. 4e, f, g, h, i).

River water characteristics significantly correlated with the metallic element release rates during litter decomposition throughout the year-long incubation (Table 3). The temperature of the river water was one of the most important variables and significantly influenced virtually all of the element release

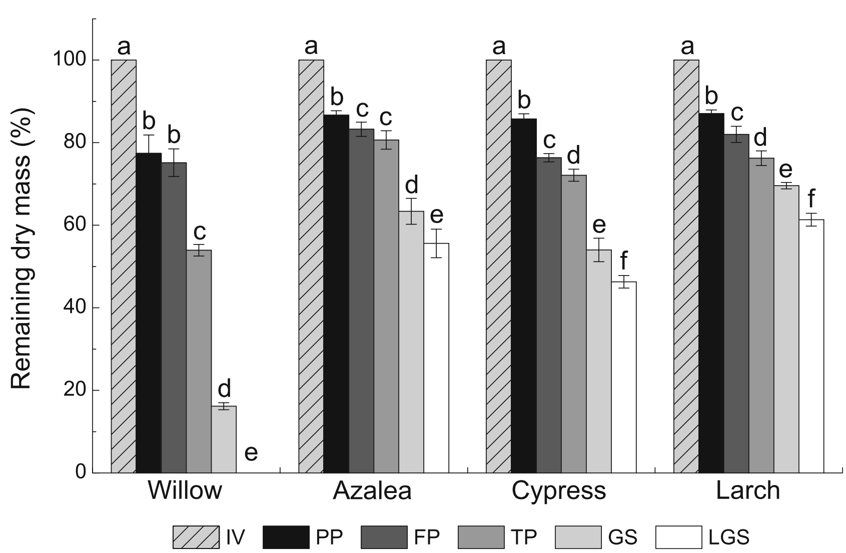

Fig. 2 Dry masses of the remaining litter in litterbags at each sampling event in the forest river throughout the entire year of incubation. Values are means, with *error bars* representing standard deviations ($n=9$). Different *lowercase letters* indicate statistically significant differences among different periods for a specific litter species ($P<0.05$). *IV* initial value, *PP* pre-freezing period, *FP* freezing period, *TP* thawing period, *GS* growing season, *LGS* late growing season

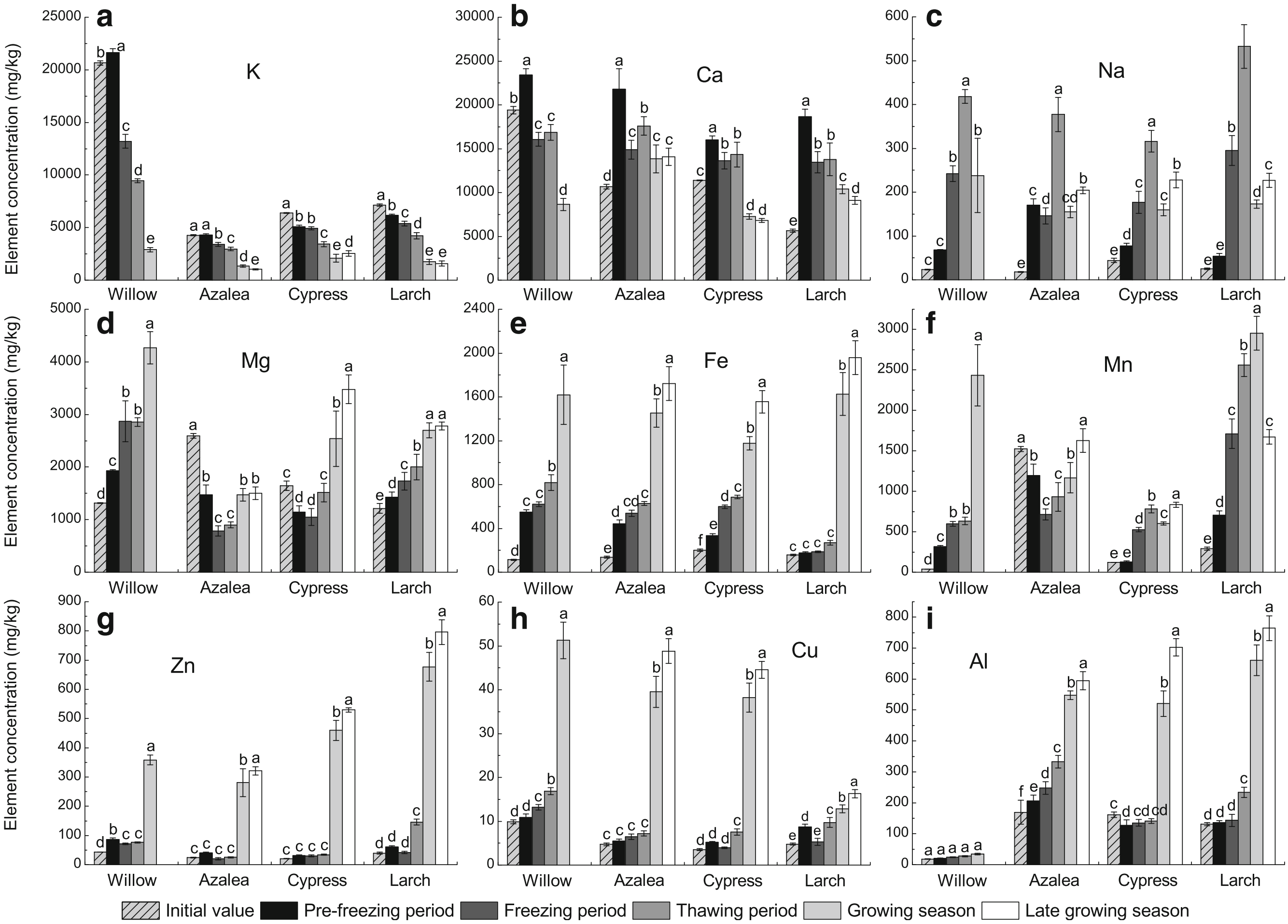

Fig. 3 Dynamics of metallic element concentrations in decomposing foliar litter during different periods (mean ± SD, $n = 9$). Different *lowercase letters* indicate that the metallic element concentration in the foliar litter type differed significantly among different periods ($P < 0.05$). The designated periods were divided based on the freeze-thaw dynamics according to our previous investigations at the study site

rates in all litter species. Water conductivity, flow velocity, and nutrient availability (e.g., HCO_3, PO_4, NH_4-N, and NO_3-N) were obviously related to element release rates, and were modulated by both element type and litter species (Table 3).

3.4 Discussion

Our finding that the metal dynamics during litter decomposition in a lotic ecosystem are similar to previous observations on forest floors (Staaf and Berg 1982; Lomander and Johansson 2001) suggests that a general pattern may exist for the fate of metallic elements in decomposing litter in both terrestrial and aquatic ecosystems. However, litter mass loss was much higher in the river compared with the results observed in our previous study (Ni et al. 2015) on the forest floor for a comparable period, and metallic elements in decomposing river litter showed some unique release patterns that could be affected by multiple factors.

K, Ca, and Mg are the essential macronutrients for plant growth. Although Na is not an important nutrient for all plants, it is an essential element for animals and litter decomposers (Geerling and Loewy 2008). K, Ca, and Mg typically show release patterns in decomposing litter that are even more rapid than those of N and P (Prescott 2005), whereas Na is likely to accumulate during litter decomposition (Edmonds and Tuttle 2010). Elements are released from litter by either physical leaching or the breakdown of structural organic components by organisms. Different elements have different patterns of release over time, and elements are retained to different degrees in the litter structure. K could be lost easily through leaching, and it was found to be the most mobile nutrient in decomposing litter, with >80 % of the initial content released after 1 year of incubation on the forest floor (Edmonds and Tuttle 2010), which is similar with our finding in river. The potential mechanisms underlying this high release rate may be the mobile characteristics of K. Similarly, leaching appeared to occur for Ca and Mg. In contrast, Na showed a pattern of accumulation in the early stages of litter decomposition. During litter decomposition, litter consumers must accumulate Na up to approximately 100- to 1000-fold

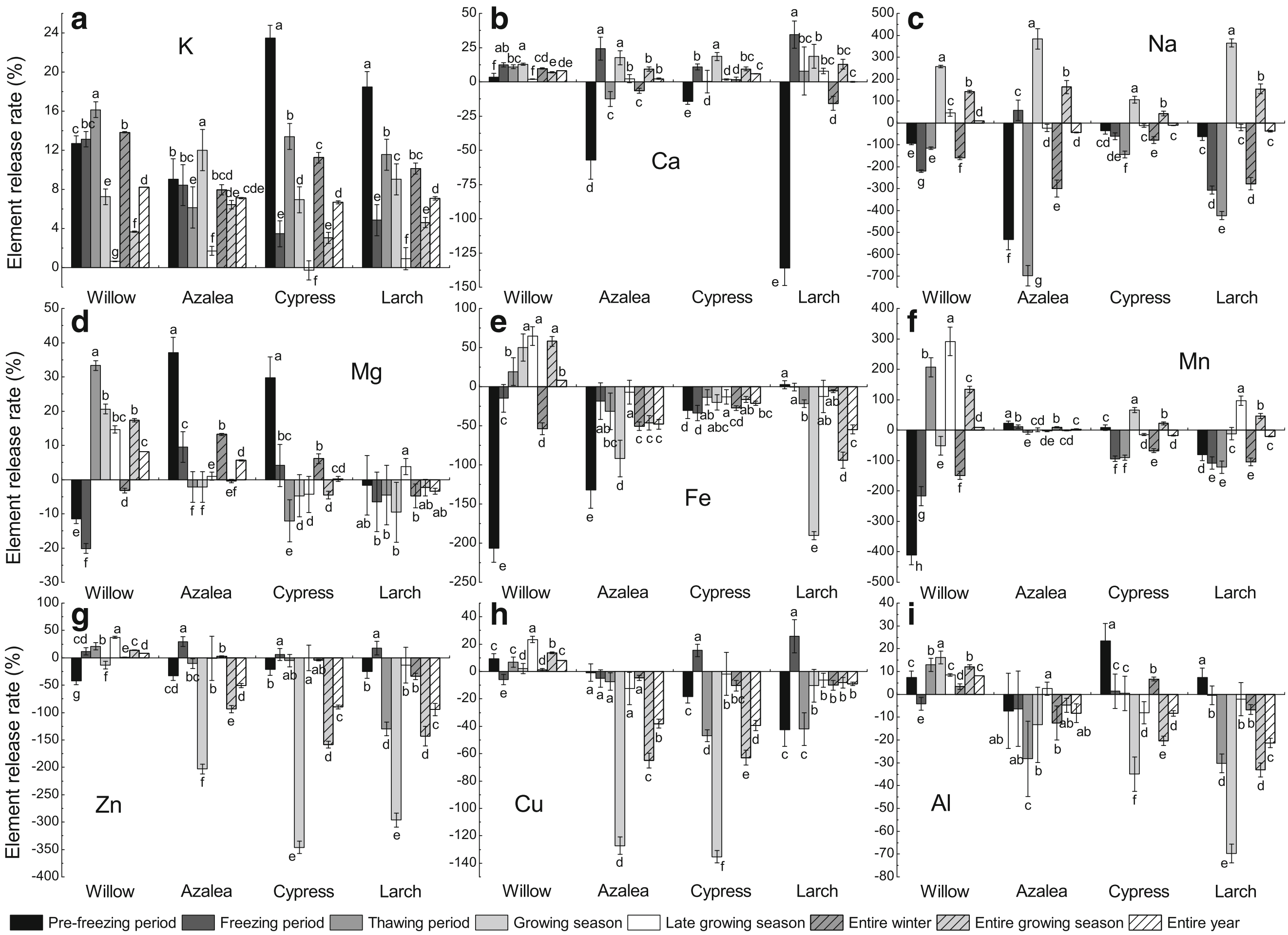

Fig. 4 Metallic element release rates (percent initial mass/month) for the four foliar litter species investigated during different decomposition periods (mean ± SD, $n = 9$). Different *lowercase letters* indicate significant differences of element release rates for a specific litter species among different periods ($P < 0.05$). Negative values indicate accumulation rates during foliar litter decomposition. The designated five periods within 1 year were divided based on the freeze-thaw dynamics according to our previous investigations at the study site

over the litter they consume to maintain Na balance (Cromack et al. 1977). Thus, Na usually showed a pattern of accumulation during litter decomposition and could fluctuate according to the Na balance of litter decomposers and consumers because neither insufficient nor excess Na would be unfavorable for decomposers and consumers and the carbon-release process (Jia et al. 2015).

Fe, Mn, Zn, and Cu are essential trace elements for plant physiology, but excess amounts of these elements, similar to Al, would be harmful. In general, the major pathways for the cycling of these metallic elements in terrestrial ecosystems are root uptake, litterfall, and the ensuing decomposition (Bergkvist 1987; Andersson et al. 1992). A previous study found that the contents of Zn and Mn decreased by 24 and 43 % from the initial values, respectively, after 7 years in decomposing spruce needle litter on the forest floor (Lomander and Johansson 2001). However, recent studies have suggested that a net accumulation of Mn, Zn, and Cu could occur in decomposing litter after 1 year of incubation on forest floors (Jonczak et al. 2014; He et al. 2015), and these elements plus Fe and Al were also found to accumulate during river litter decomposition in this study. Numerous studies have demonstrated that the concentrations of most metallic elements in litter increase considerably as decomposition progresses (Windham et al. 2004; Du Laing et al. 2006), and some studies have also suggested that metallic elements will be released when the content exceeds a certain threshold (Lomander and Johansson 2001; Edmonds and Tuttle 2010; Aponte et al. 2012). The sorption of metallic metals in decomposition litter may be attributed to the potential mechanisms such as the formation of chelates and complexes at active sites on the organic molecules of decomposing detritus (Odum and Drifmeyer 1978). Meanwhile, 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). Consistent with such studies, our research suggested that metallic element dynamics in decomposing river

Table 3 Correlations between metallic element release rate (percent initial mass/month) and river water characteristics across the entire year ($n = 45$)

Metal	Species	DMT	PAT	NAT	FV	pH	Cond.	HCO_3	PO_4	NH_4-N	NO_3-N
K	Willow	−0.638***	−0.814***	−0.302*	−0.089	0.117	0.677***	0.171	0.232	0.110	0.198
	Azalea	−0.195	−0.139	−0.239	0.138	0.095	−0.174	−0.242	0.132	−0.279	−0.244
	Cypress	−0.441**	−0.570***	−0.794***	0.088	−0.192	0.401**	0.696***	−0.464**	0.710***	−0.377*
	Larch	−0.390**	−0.507***	−0.735***	0.155	−0.206	0.299*	0.604***	−0.428**	0.588***	−0.355*
Ca	Willow	−0.022	−0.073	0.440**	0.210	0.065	−0.087	−0.529***	0.504***	−0.734***	0.487**
	Azalea	0.327*	0.425**	0.808***	0.013	0.215	−0.388**	−0.836***	0.619***	0.929***	0.472**
	Cypress	0.408**	0.494**	0.722***	0.226	0.054	−0.557***	−0.762***	0.455**	−0.918***	0.393**
	larch	0.413**	0.411**	0.934***	0.152	0.026	−0.308*	−0.617***	0.523***	−0.859***	0.723***
Na	willow	0.824***	0.880***	0.315*	0.693***	−0.561***	−0.966***	−0.045	−0.484**	−0.250	−0.040
	azalea	0.372*	0.624***	0.426**	−0.007	0.254	−0.706***	−0.799***	0.367*	−0.756***	−0.130
	cypress	0.449**	0.658***	0.073	0.240	−0.057	−0.813***	−0.358*	−0.129	−0.345*	−0.398**
	larch	0.539***	0.707***	0.018	0.382**	−0.235	−0.862***	−0.169	−0.336*	−0.200	−0.408**
Mg	willow	0.772***	0.542***	0.569***	0.861***	−0.870***	−0.456**	0.354*	−0.536***	−0.057	0.663***
	azalea	−0.705***	−0.613***	−0.978***	−0.515***	0.384**	0.492**	0.359*	−0.133	0.683***	−0.825***
	cypress	−0.639***	−0.505***	−0.925***	−0.507***	0.415**	0.366*	0.243	−0.095	0.575***	−0.864***
	larch	0.051	0.055	−0.099	−0.137	−0.037	0.100	0.266	−0.216	0.360*	−0.113
Fe	willow	0.725***	0.694***	0.976***	0.407**	−0.286	−0.546***	−0.439**	0.170	−0.696***	0.718***
	azalea	0.176	0.145	0.702***	−0.170	0.142	0.114	−0.363*	0.446**	−0.410**	0.626***
	cypress	0.675***	0.521***	0.491**	0.581***	−0.655***	−0.362*	0.300*	−0.451**	0.303	0.496**
	larch	−0.621***	−0.658***	−0.373*	−0.663***	0.410**	0.847**	0.281	0.178	0.529***	−0.102
Mn	willow	0.745***	0.594***	0.794***	0.493**	−0.584***	−0.335*	0.099	−0.230	−0.182	0.742***
	azalea	−0.716***	−0.550***	−0.829***	−0.597***	0.574***	0.384**	0.011	0.142	0.355*	−0.807***
	cypress	0.487**	0.615***	−0.177	0.429**	−0.343*	−0.780***	0.081	−0.536***	0.051	−0.503***
	larch	0.670***	0.807***	0.287	0.155	−0.216	−0.654***	−0.049	−0.333*	−0.017	−0.159
Zn	willow	0.392**	0.323*	0.795***	0.026	−0.079	−0.031	−0.235	0.249	−0.355*	0.708***
	azalea	−0.549***	−0.584***	−0.140	−0.659***	0.451**	0.800***	0.091	0.346*	0.302*	0.082
	cypress	−0.549***	−0.614***	−0.246	−0.611***	0.355*	0.837***	0.271	0.192	0.476**	0.036
	larch	−0.636***	−0.554***	−0.364*	−0.845***	0.637***	0.730***	0.022	0.346*	0.374*	−0.283
Cu	willow	0.477**	0.441**	0.003	0.205	−0.446**	−0.223	0.538***	−0.651***	0.531***	−0.078
	azalea	−0.609***	−0.676***	−0.356*	−0.612***	0.354*	0.867***	0.329*	0.148	0.546***	−0.042
	cypress	−0.608***	−0.549***	−0.267	−0.819***	0.616***	0.746***	−0.004	0.388**	0.316*	−0.166
	larch	−0.108	0.116	0.377*	−0.499***	0.662***	−0.092	−0.875***	0.782***	−0.701***	0.005
Al	willow	0.721***	0.562***	0.199	0.898***	−0.887***	−0.608***	0.470**	−0.758***	0.128	0.234
	azalea	−0.045	0.176	−0.149	−0.438**	0.393**	−0.114	−0.235	0.118	0.036	−0.482**
	cypress	−0.758***	−0.802***	−0.737***	−0.567***	0.334*	0.847***	0.479**	−0.025	0.733***	−0.374*
	larch	−0.649***	−0.575***	−0.523***	−0.796***	0.561***	0.723***	0.177	0.187	0.537***	−0.408**

DAT daily average temperature, defined as the mean value of the daily mean temperatures during each period; *PAT* positive accumulated temperature, defined as the sum of the temperature values above 0 °C during each period; *NAT* negative accumulated temperature, defined as the sum of the negative temperature values during each period; *FV* flow velocity, *Cond.* conductivity. $*P < 0.05$; $**P < 0.01$; $***P < 0.001$

litter showed a release pattern similar to that of forest floors, indicating a general pattern for the fate of metallic elements during litter decomposition. Nevertheless, metallic elements displayed different release patterns in different periods and for different types of litter.

A repeated measurement ANOVA indicated that litter species, decomposition time, and the interaction of these two factors significantly ($P < 0.001$) affected the release rates of all the investigated metallic elements (Table 4). The release rates of metallic elements during litter decomposition typically follow different patterns, although some elements are always released in a similar manner, regardless of the litter species (Jonczak et al. 2014). Litter quality is always the dominant factor influencing litter decomposition (Zhang et al. 2008; Makkonen et al. 2012), and metal-release patterns can also be strongly affected by the chemical composition of the initial

Table 4 *F* values for repeated measurement ANOVA of time and litter species on element release rate (percent initial mass/month) over the entire year

Factor	*d.f.*	K	Ca	Na	Mg	Fe	Mn	Zn	Cu	Al
Time	4	466.68***	468.87***	594.51***	31.93***	232.40***	417.94***	654.99***	284.56***	131.05***
Species	3	160.23***	274.60***	431.45***	65.08***	144.78***	243.08***	85.57***	480.40***	109.79***
Time × species	12	71.32***	129.35***	104.52***	223.29***	173.77***	330.23***	443.03***	104.70***	67.08***

d.f. degree of freedom. ***$P < 0.001$

litter quality (Jonczak et al. 2014). Because element release is usually determined by the breakdown of structural organic components by litter consumers, the rate at which an element is released could thus be expected to be governed largely by the litter decomposition rate. With the progress of decomposition, litter quality changed and thus can vary largely in different decomposition periods, and this in turn can influence the decomposition process and the simultaneous element release pattern. Meanwhile, as bioavailability, decomposer community, and temporally variable environmental conditions can vary significantly during different periods with the progress of decomposition, thus both time and its interaction with litter species were tested to show significant effects on element release rates.

Temperature has always been thought to be a key factor controlling litter decomposition both on forest floors (Aerts 2006; Salinas et al. 2011) and in lotic ecosystems (Martínez et al. 2014). With constant moisture, temperature in lotic ecosystems is likely to be one of the primary factors controlling microbial and decomposer activities (Martínez et al. 2014), thereby modulating the litter decomposition process and the simultaneous process of element release. The dynamics of metallic elements are related to chemical characteristics, such as solubility and mobility (Staaf and Berg 1982), and thus, metallic elements with higher mobility (e.g., Ca and Na) may be less influenced by water flow velocity. Similarly, because pH typically influences the solubility and mobility of metallic elements during litter decomposition, changes in pH may have little influence on Na or Fe but can significantly influence some other metallic elements. Moreover, the release rates of metallic elements could also be significantly affected by other factors, such as conductivity and nutrient availability, because such factors are usually strongly correlated with microbial and litter consumer activities.

4 Conclusion

In summary, the results of this study suggest that K, Ca, and Mg are generally released from nearly all types of litter during the first decomposition year, whereas Na, Fe, Mn, Zn, Cu, and Al are only released from willow litter and accumulate in azalea, cypress, and larch litters after 1 year of incubation. The dynamics of these metallic elements during litter decomposition could be strongly influenced by litter species, decomposition period, and river water characteristics (e.g., temperature, pH, flow velocity, and nutrient availability). The similarity between the dynamic patterns of metallic element release in the decomposing litter of lotic ecosystems and forest floors suggests that a general pattern for the cycling of metallic elements may exist across different ecosystem types. Moreover, given that an excess amount of some metallic elements, such as Zn, Cu, and Al, will be harmful to plants and the ecosystem as a whole, the net accumulation patterns observed for such metallic elements in the decomposing litter of flowing water suggests that some species of litter could act as an efficient metal "cleaner" for ecosystem's metal purification in future ecological engineering. These findings are useful for both further investigations of element cycling across aquatic and terrestrial ecosystems and the control of hazardous materials in water conservation areas, such as alpine biomes.

Acknowledgments We thank the chief editor Dr. Erwin Dreyer, the handing editor Dr. Gilbert Aussenac, and two anonymous reviewers for their insightful comments on the early versions of the manuscript. We are also grateful to Mr. Bin Wang, Dr. Yamei Chen, and Dr. Wei He for their kind help with field work and laboratory analyses.

Compliance with ethical standards

Funding This study was financially supported by the National Natural Science Foundation of China (31270498, 31570445, 31500358, and 31570601) and the Doctoral Scientific Fund Project of the Ministry of Education of China (20135103110002).

References

Abelho M (2008) Effects of leaf litter species on macroinvertebrate colonization during decomposition in a Portuguese stream. Int Rev Hydrobiol 93:358–371. doi:10.1002/iroh.200711019

Aerts R (2006) The freezer defrosting: global warming and litter decomposition rates in cold biomes. J Ecol 94:713–724. doi:10.1111/j.1365-2745.2006.01142.x

Andersson A, Nilsson Å, Håkanson L (1992) Metal concentrations of the mor layer. Report 3990. Swedish Environmental Protection Agency, Solna

Aponte C, García LV, Maranon T (2012) Tree species effect on litter decomposition and nutrient release in mediterranean oak forests changes over time. Ecosystems 15:1204–1218. doi:10.1007/s10021-012-9577-4

Baldy V, Gobert V, Guerold F, Chauvet E, Lambrigot D, Charcosset JY (2007) Leaf litter breakdown budgets in streams of various trophic status: effects of dissolved inorganic nutrients on microorganisms and invertebrates. Freshw Biol 52:1322–1335. doi:10.1111/j.1365-2427.2007.01768.x

Battin TJ, Kaplan LA, Findlay S, Hopkinson CS, Marti E, Packman AI, Newbold JD, Sabater F (2008) Biophysical controls on organic carbon fluxes in fluvial networks. Nat Geosci 1:95–100. doi:10.1038/ngeo101

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ (2009) The boundless carbon cycle. Nat Geosci 2:598–600. doi:10.1038/ngeo618

Berg B, McClaugherty C (2014) Plant litter: decomposition, humus formation, carbon sequestration. Springer, New York

Bergkvist B (1987) Soil solution chemistry and metal budgets of spruce forest ecosystems in S. Sweden. Water Air Soil Pollut 33:131–154

Berthelsen B, Steinnes E, Solberg W, Jingsen L (1995) Heavy metal concentrations in plants in relation to atmospheric heavy metal deposition. J Environ Qual 24:1018–1026

Chapin FS III, Matson PA, Vitousek P (2002) Principles of terrestrial ecosystem ecology. Springer, New York

Cornwell WK, Cornelissen JHC, Amatangelo K, Dorrepaal E, Eviner VT, Godoy O, Hobbie SE, Hoorens B, Kurokawa H, Pérez-Harguindeguy N, Quested HM, Santiago LS, Wardle DA, Wright IJ, Aerts R, Allison SD, Van Bodegom P, Brovkin V, Chatain A, Callaghan TV, Díaz S, Garnier E, Gurvich DE, Kazakou E, Klein JA, Read J, Reich PB, Soudzilovskaia NA, Vaieretti MV, Westoby M (2008) Plant species traits are the predominant control on litter decomposition rates within biomes worldwide. Ecol Lett 11:1065–1071. doi:10.1111/j.1461-0248.2008.01219.x

Cromack K Jr, Sollins P, Todd RL, Crossley DA Jr, Fender WM, Fogel R, Todd AW (1977) Soil microorganism—arthropod interactions: fungi as major calcium and sodium sources. In: Mattson W (ed) The Role of Arthropods in Forest Ecosystems. Springer, Berlin Heidelberg, pp 78–84

Du Laing G, Van Ryckegem G, Tack FM, Verloo MG (2006) Metal accumulation in intertidal litter through decomposing leaf blades, sheaths and stems of Phragmites australis. Chemosphere 63:1815–1823. doi:10.1016/j.chemosphere.2005.10.034

Edmonds RL, Tuttle KM (2010) Red alder leaf decomposition and nutrient release in alder and conifer riparian patches in western Washington, USA. For Ecol Manag 259:2375–2381. doi:10.1016/j.foreco.2010.03.011

Gadd GM, Griffiths AJ (1978) Microorganisms and heavy metal toxicity. Microb Ecol 4:303–317

Geerling JC, Loewy AD (2008) Central regulation of sodium appetite. Exp Physiol 93:177–209. doi:10.1113/expphysiol.2007.039891

Gessner MO, Chauvet E, Dobson M (1999) A perspective on leaf litter breakdown in streams. Oikos 85:377–384

He J, Yang W, Xu L, Ni X, Li H, Wu F (2015) Copper and zinc dynamics in foliar litter during decomposition from gap center to closed canopy in an alpine forest. Scand J For Res. doi:10.1080/02827581.2015.1078405

IUSS Working Group WRB (2006) World reference base for soil resources. FAO, Rome

Jia Y, Kong X, Weiser MD, Lv Y, Akbar S, Jia X, Tian K, He Z, Lin H, Bei Z (2015) Sodium limits litter decomposition rates in a subtropical forest: additional tests of the sodium ecosystem respiration hypothesis. Appl Soil Ecol 93:98–104. doi:10.1016/j.apsoil.2015.04.012

Jonczak J (2013) Dynamics, structure and properties of plant litterfall in a 120-year old beech stand in Middle Pomerania between 2007–2010. Soil Sci Ann 64:8–13. doi:10.2478/ssa-2013-0002

Jonczak J, Parzych A, Sobisz Z (2014) Dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of four types of litter in headwater riparian forests in northern Poland. Leoene Prace Badawcze (For Res Papers) 75:193–200. doi:10.2478/frp-2014-0018

Landre AL, Watmough SA, Dillon PJ (2009) The effects of dissolved organic carbon, acidity and seasonality on metal geochemistry within a forested catchment on the Precambrian Shield, central Ontario, Canada. Biogeochemistry 93:271–289. doi:10.1007/s10533-009-9305-0

Leroy CJ, Marks JC (2006) Litter quality, stream characteristics and litter diversity influence decomposition rates and macroinvertebrates. Freshw Biol 51:605–617. doi:10.1111/j.1365-2427.2006.01512.x

Lomander A, Johansson M-B (2001) Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (Picea abies) needle litter during decomposition. Water Air Soil Pollut 132:165–184

Lu RK (1999) Soil and agro-chemical analytical method. China Agricultural Science and Technology Press (in Chinese), Beijing

Makkonen M, Berg MP, Handa IT, Hättenschwiler S, van Ruijven J, van Bodegom PM, Aerts R (2012) Highly consistent effects of plant litter identity and functional traits on decomposition across a latitudinal gradient. Ecol Lett 15:1033–1041. doi:10.1111/j.1461-0248.2012.01826.x

Martínez A, Larrañaga A, Pérez J, Descals E, Pozo J (2014) Temperature affects leaf litter decomposition in low-order forest streams: field and microcosm approaches. FEMS Microbiol Ecol 87:257–267. doi:10.1111/1574-6941.12221

Ni X, Yang W, Tan B, He J, Xu L, Li H, Wu F (2015) Accelerated foliar litter humification in forest gaps: dual feedbacks of carbon sequestration during winter and the growing season in an alpine forest. Geoderma 241–242:136–144. doi:10.1016/j.geoderma.2014.11.018

Odum WE, Drifmeyer JE (1978) Sorption of pollutants by plant detritus: a review. Environ Health Perspect 27:133–137

Perakis SS, Hedin LO (2002) Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature 415:416–419. doi:10.1038/415416a

Prescott C (2005) Decomposition and mineralization of nutrients from litter and humus. In: BassirRad H (ed) Nutrient Acquisition by Plants: an ecological perspective. Springer, Berlin, pp 125–141

Rice EW, Bridgewater L, American Public Health Association, American Water Works Association (2012) Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC

Rueda-Delgado G, Wantzen KM, Tolosa MB (2006) Leaf-litter decomposition in an Amazonian floodplain stream: effects of seasonal hydrological changes. J N Am Benthol Soc 25:233–249. doi:10.1899/0887-3593(2006)25[233:LDIAAF]2.0.CO;2

Salinas N, Malhi Y, Meir P, Silman M, Roman Cuesta R, Huaman J, Salinas D, Huaman V, Gibaja A, Mamani M, Farfan F (2011) The sensitivity of tropical leaf litter decomposition to temperature: results from a large-scale leaf translocation experiment along an elevation gradient in Peruvian forests. New Phytol 189:967–977. doi:10.1111/j.1469-8137.2010.03521.x

Staaf H, Berg B (1982) Accumulation and release of plant nutrients in decomposing Scots pine needle litter. Long-term decomposition in a Scots pine forest II. Can J Bot 60:1561–1568

Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB (2009) Lakes and reservoirs as regulators of carbon cycling and climate. Limnol Oceanogr 54:2298–2314. doi:10.4319/lo.2009.54.6_part_2.2298

Wallace JB, Eggert SL, Meyer JL, Webster JR (1997) Multiple trophic levels of a forest stream linked to terrestrial litter inputs. Science 277:102–104. doi:10.1126/science.277.5322.102

Windham L, Weis JS, Weis P (2004) Metal dynamics of plant litter of Spartina alterniflora and Phragmites australis in metal-contaminated salt marshes. Part 1: patterns of decomposition and metal uptake. Environ Toxicol Chem 23:1520–1528. doi:10.1897/03-284

Wu F, Peng C, Zhu J, Zhang J, Tan B, Yang W (2014) Impact of freezing and thawing dynamics on foliar litter carbon release in alpine

/subalpine forests along an altitudinal gradient in the eastern Tibetan Plateau. Biogeosciences 11:6471–6481. doi:10.5194/bg-11-6471-2014

Xu Z, Pu X, Yin H, Zhao C, Liu Q, Wu F (2012) Warming effects on the early decomposition of three litter types, Eastern Tibetan Plateau, China. Eur J Soil Sci 63:360–367. doi:10.1111/j.1365-2389.2012.01449.x

Zhang D, Hui D, Luo Y, Zhou G (2008) Rates of litter decomposition in terrestrial ecosystems: global patterns and controlling factors. J Plant Ecol 1:85–93. doi:10.1093/jpe/rtn002

Zhu J, He X, Wu F, Yang W, Tan B (2012) Decomposition of Abies faxoniana litter varies with freeze–thaw stages and altitudes in subalpine/alpine forests of southwest China. Scand J For Res 27:586–596. doi:10.1080/02827581.2012.670726