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Shoot litter breakdown and zinc dynamics of an aquatic plant, *Schoenoplectus californicus*

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ABSTRACT
Decomposition of plant debris is an important process in determining the structure and function of aquatic ecosystems. The aims were to find a mathematic model fitting the decomposition process of *Schoenoplectus californicus* shoots containing different Zn concentrations; compare the decomposition rates; and assess metal accumulation/mobilization during decomposition. A litterbag technique was applied with shoots containing three levels of Zn: collected from an unpolluted river (RIV) and from experimental populations at low (LoZn) and high (HiZn) Zn supply. The double exponential model explained *S. californicus* shoot decomposition, at first, higher initial proportion of refractory fraction in RIV detritus determined a lower decay rate and until 68 days, RIV and LoZn detritus behaved like a source of metal, releasing soluble/weakly bound zinc into the water; after 68 days, they became like a sink. However, HiZn detritus showed rapid release into the water during the first 8 days, changing to the sink condition up to 68 days, and then returning to the source condition up to 369 days. The knowledge of the role of detritus (sink/source) will allow defining a correct management of the vegetation used for zinc removal and providing a valuable tool for environmental remediation and rehabilitation planning.

KEYWORDS
decomposition; zinc mobility; macrophytes

1. Introduction

Wetlands are highly productive systems, associated with a high nutrient load from adjacent rivers and/or emergent areas. Wetlands contribute as much as 40% to the earth's renewable ecosystem services [see (Constanza et al. 1997)], the retention of pollutants being an important contribution of natural wetlands. Moreover, in recent decades considerable interest has been expressed about the use of these natural biological systems for also contributing to the purification of effluents through artificial wetlands in a controlled manner. However, biomass disposal problem is a limitation in the transfer of phytoremediation technology from the laboratory to the field (Rai 2008) because wetland plants could stop behaving like a sink of metals [see (Arreghini, de Cabo, and Fabrizio de Iorio 2006)] to become a source of pollutants as the decomposition process of the detritus advances. Zinc is one of the main industrial pollutants of terrestrial and aquatic environments [see (Barak and Helmke 1993)] particularly in highly contaminated urban areas, such as Reconquista and Matanza-Riacuelo basins of Argentina (Rendina et al. 2001; Harper, Bertram, and Graedel 2006; Blacksmith Institute 2007; Rendina and Fabrizio de Iorio 2012). Anthropogenic action is also manifested by the degradation of river margins and the removal of native macrophytes, (Basílico, de Cabo, and Faggi 2015), which decreases the ability of aquatic ecosystems to detoxify pollutants. Zinc and other metals come from urban waste and as runoff from the agricultural industry, the rubber industry, and galvanoplasty and also by atmospheric deposition. On the other hand, zinc constitutes a micronutrient for all organisms. However, it can affect plant growth when absorbed in large amounts by interfering with metabolic processes such as photosynthesis and the generation of oxidative stress (Castiglione et al. 2007). Although, the belowground biomass of emergent macrophytes has been reported as the main structure of metal accumulation (Arreghini, de Cabo, and Fabrizio de Iorio 2006; Cheng et al. 2002; Cardwell, Hawker, and Greenway 2002; Yoon et al. 2006; de Cabo et al. 2015) metal levels in aboveground biomass in polluted sites were higher than in non-contaminated environments (Hozhina et al. 2001; Kamel 2013; Mendoza et al. 2015).

Schoenoplectus californicus is indigenous to coastal regions from southern North America (Mason 1957) south to Chile and Argentina [see (Wagner, Herbst, and Sohmer 1990)] and forms monoespecific stands known as "marshes." In marshes, the dynamics of the aboveground biomass of *Schoenoplectus californicus* depends on tidal cycles (Pratolongo, Kandus, and Brinson 2008). Since many phytoremediation studies focus on phytoextraction of metals and/or stabilization in sediments, it is very important to evaluate the relationship between the decomposition rates of the plant biomass and the release of the pollutants originally immobilized. Frequently, most of the organic matter production of aquatic macrophytes is decomposed before it enters the food chain (Mitsch and Gosselink 1993). Decomposition of organic matter is one of the most important processes that determines the structure and function

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of aquatic systems, since it is the process that controls the cycling of C and the availability of nutrients. The process of detritus decomposition in aquatic systems is regulated by environmental factors, such as temperature, redox conditions, nutrient concentration, and the quality of the detritus (nitrogen, phosphorus, lignin and/or polyphenol content, etc.), and it is affected by the presence of degradation agents like shear stress, fungi and shredders (Gessner 1999). Several authors have studied the influence of these factors on the decomposition rate of organic matter (Lambers, Stuart Chapin III, and Pons 1998; Kalburtji, Mosjidis, and Mamolos 1999; Cross et al. 2003; Lecerf et al. 2007; Balasubramanian et al. 2012). Some studies have reported a decrease in the rate of decomposition of detritus in soils [see (Chew, Obbard, and Stanforth 2001; Boucher et al. 2005)] and streams [see (Sridhar et al. 2001; Duarte et al., 2008)] that are contaminated with metals due to the negative effect on the diversity and activity of decomposing microorganisms.

In contaminated environments, a significant fraction of metals is rapidly fixed to the solid phase through sorption mechanisms, where the different physical and chemical properties determine their retention force. In this way, the strong association with the solid phase and the low proportion of metals available to plants decrease their mobility towards the water column (Chen et al. 2000; Du Laing et al. 2006). An organism that accumulates metals during its vital phase constitutes a sink of metals and becomes a source of contaminants when its biomass is degraded. The metal, temporarily immobilized in the tissues, may be released to the medium once chemical bonds have broken and new ones of higher thermodynamic stability have been formed. Thus, partitioning of metals between solution and solid phases may indicate whether degraded biomass behaves as a source or sink of contaminants. Since high concentrations of metals are toxic to the decomposer organisms it is considered that the low decay rates minimize the release of pollutants immobilized by plants during early stages of phytorremediation. Nevertheless, the influence of metal contamination on litter decomposition and the resulting change in the source/sink condition of the detritus are aspects of the process that have yet to be elucidated (Schaller et al. 2011).

The decomposition analysis can be performed through mathematical functions to obtain constants that describe the loss of biomass over time, and provide valuable information about the characteristics of the process. The objectives of the present work are: (i) to evaluate the decay process of *Schoenoplectus californicus* detritus contaminated with Zn through mathematical models; (ii) to evaluate the effect of Zn concentration over detritus decay rates; and (iii) to analyze the behavior of the detritus as a sink/source of Zn.

2. Materials and methods

Decomposition in ecosystems is typically studied through the use of litterbags. Although this method may underestimate the actual decomposition, it is assumed that the results obtained from these experiments reflect the characteristic trends of unconfined litter and so species, sites, and experimental manipulations can be compared (Wieder and Lang 1982). Because *S. californicus* is a perennial plant, the aboveground biomass periodically fall so we consider that the shoots are the main structure that could contribute to decomposing organic matter in the sediments and thus, it would act as a sink or a source of metals.

The batch experiment was carried out in darkness and at ambient temperature. At the beginning of the experiment, live shoots of *Schoenoplectus californicus* were cut into 10-cm-length pieces and oven dried at 70°C until constant weight. Dry litter (approximately 4 g) was placed into plastic bags of 10 × 15 cm and 2 mm of mesh. Shoots of *S. californicus* with three levels of Zn were used: shoots collected from an unpolluted river (RIV) obtained from a background area at the Durazno Stream in the upper basin of the Reconquista river (Buenos Aires, Argentina) 34°42'18''S-58°55'48''W (Arreghini et al. 2007). The shoots of low (LoZn) and high (HiZn) Zn concentrations (Table 1) were obtained from plants grown in pots during 90 days in sediments with two levels of zinc added. Litterbags were placed in glass containers of 20×14×20 cm (length:width:height) and were submerged in nonpolluted water collected from Durazno stream (0.018 $mgZn.L^{-1}$) (Arreghini et al. 2007). All treatments were carried out in triplicate, and the following scheme of removal was: three replicate bags were removed periodically after 8, 15, 33, 68, 148, and 369 days of incubation; six removals were for RIV and HiZn treatments and five for LoZn treatment (except for the removal of bags at 148 days in this treatment). Then, the content of each bag was dried at 70°C until constant weight and weighed, and the Zn concentration was determined. At each removal time, the remaining water volume, dissolved oxygen concentration (DO), pH, electrical conductivity (EC), redox potential (Eh), and temperature in water were measured, and the Zn concentration was determined. The concentrations of zinc in litter and water samples were determined through atomic absorption spectrophotometry (Perkin Elmer AAnalyst 200), with previous acid mineralization with HNO_3 and $HClO_4$ (2:1).

The remaining litter mass after 369 days of incubation was compared by one-way ANOVA; normal distribution and homogeneity of variance were examined using Lilliefors and Levene tests, respectively.

Table 1. Initial characteristics of litter for each treatment. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

		RIV	LoZn	HiZn
Zn	($\mu g.g^{-1}$)	19,6	106,3	324,5
Ashes	(%)	14,35	13,36	13,77
C	(%)	41,7	42,9	42,8
N	(%)	1,14	2,49	1,52
Hemicellulose	(%)	37,71	32,64	35,58
Cellulose	(%)	32,84	32,18	34,16
Lignin	(%)	2,14	2,25	4,60
Total fibres	(%)	72,69	67,07	74,34
C:N		37:1	17:1	28:1
Lignin:N		2:1	1:1	4:1

Three models were applied to describe the loss of litter mass over time:

a) Lineal model:

$$m_t = m_0 - k{\cdot}t$$

b) Simple exponential model:

$$m_t = m_0{\cdot}e^{-k{\cdot}t}$$

c) Double exponential model:

$$m_t = LOM\left(e^{-k_1{\cdot}t}\right) + ROM\left(e^{-k_2{\cdot}t}\right)$$

where m_0 is the initial proportion of litter dry mass, k is the decay rate (k_1 and k_2 for double exponential model) (day^{-1}), and m_t is the proportion of litter dry-mass remaining at t days of incubation estimated with each model. Besides, LOM and ROM represent the initial proportion of labile and refractory organic matter in the detritus, respectively, estimated by fitting the dataset to the double exponential model. Goodness of fit was evaluated using the coefficient of determination (R^2).

3. Results and discussion

3.1. Litter breakdown over time

There were clear differences in the remaining litter dry mass over time between treatments (Figure 1). The amount of shoot material remaining after 369 days of incubation in RIV was higher than those in the other treatments ($p < 0.05$), attaining 38, 18, and 16% of initial dry mass at RIV, LoZn, and HiZn, respectively.

Different mathematical models have been used in order to describe the decay as weight loss of the detritus over time and to find a function that adequately describes this process. The linear model, which corresponds to zero-order kinetics, is the simplest and it implicitly assumes that the decay rate k is independent of the amount of residual detritus. It has the disadvantage of considering that the absolute decay rate remains constant, so that the relative decay rate increases with time. These considerations are difficult to justify biologically [see (Wieder and Lang 1982)] since the proportion of refractory residual biomass increases as the decomposition process draws on, a situation that would imply a decrease in decomposition velocity. However, this model may show a good fit in cases where the loss of biomass is very low, as can occur in areas with low temperatures or highly reducing conditions, or in the case of detritus with very low proportion of labile material (high percentage of lignin or waxes). Villar et al. (2001) have applied the linear model to describe their experimental data on the decomposition of aquatic macrophytes in the Paraná delta (*S. californicus* and *Cyperus giganteus*) and have obtained good adjustments by maintaining that the differences between the linear and exponential models are minimal after 1 year. Table 2 shows the decay rate k and the determination coefficients (R^2) for each treatment. The linear model fitted to data of the RIV treatment, but not to the LoZn and HiZn treatments in which the determination coefficients were as low as 0.10. However, if only the data for the first 68 days were considered then the treatments LoZn ($R^2 = 0.81$) and HiZn ($R^2 = 0.85$) showed a good fit to the linear model (Figure 2a).

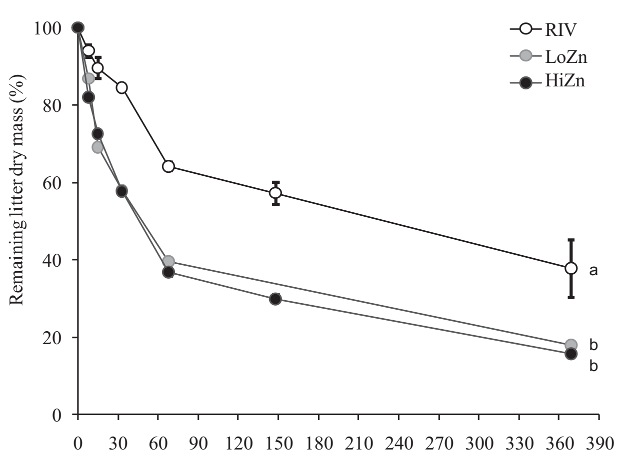

Figure 1. Percentage of remaining litter dry mass (mean ± standard deviation) for each treatment over time. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

The simple exponential model is widely used, firstly proposed by Jenny, Gessel, and Bingham (1949) and then discussed in considerable detail by Olson (1963). In exponential models the absolute decay rate decreases linearly as the amount of remaining substrate diminishes, and the relative decay rate remains constant, these considerations are more realistic in biological terms (Wieder and Lang 1982). That is, as the decomposition progresses, the soluble and labile compounds are leached rapidly whereas the more refractory materials degrade at lower rates. For all treatments, the determination coefficients obtained with the simple exponential model were greater than or equal to 0.88 (Table 2). This model represents the decay of the organic matter more accurately than the linear model, although after 68 days it overestimates the weight loss, and the remaining mass estimated after one year is markedly lower than measured, with an error of estimation of 30% in RIV and higher than 95% in LoZn and HiZn (Figure 2b). Nevertheless, the shoots of *S. californicus* of the RIV treatment exhibited a decay rate of the same order of magnitude as those obtained for *S. californicus* and other species of Cyperaceae in the natural marshes, (Villar et al. 2001; Webster and Benfield 1986; Longhi, Bartoli, and Viaroli 2008) which supports the idea that the decomposition rates of the control treatment correspond to those of the natural environment.

The analysis of the results, in particular in the LoZn and HiZn treatments, clearly identifies two stages in the decomposition process. The double exponential model represents the sum of two exponential equations and improves the adjustment in each of the stages (Wieder and Lang 1982). This model assumes that the detritus can be divided into two components, a relatively easy to degrade or labile fraction (LOM) and a more refractory fraction (ROM). The decomposition of each of these stages presents its corresponding decay rate, by definition k_1 being greater than k_2. In the first stage of the decomposition

Table 2. Decay rates from lineal and simple exponential model (k) (days^{-1}) and from double exponential model (k_1 and k_2); M_f: proportion of litter dry-mass remaining measured at 369 days of incubation; m_f: proportion of litter dry-mass remaining at 369 days of incubation estimated with double exponential model; R^2: coefficient of determination; LOM: initial proportion of labile organic matter in litter and ROM: initial proportion of refractory organic matter in litter, both estimated with double exponential model. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply. Different letters denote significant differences between treatments.

	Treatment	k	k_1	k_2	LOM	ROM	M_f	m_f	R^2
Lineal	RIV	0,0020	—	—	—	—	0,3760	0,2620	0,6943
model	LoZn	0,0026	—	—	—	—	0,1777	0,0406	0,1283
	HiZn	0,0029	—	—	—	—	0,1557	−0,0701	0,1013
Simple	RIV	0,0043	—	—	—	—	0,3760	0,2662	0,8776
Exponential	LoZn	0,0190	—	—	—	—	0,1777	0,0029	0,9049
model	HiZn	0,0165	—	—	—	—	0,1557	0,0062	0,8780
Double	RIV	—	0,0253	0,0019	0,3211a	0,6789a	0,3760	0,3784	0,9707
Exponential	LoZn	—	0,0510	0,0030	0,5536b	0,4464b	0,1777	0,1773	0,9929
model	HiZn	—	0,0459	0,0031	0,5837b	0,4163b	0,1557	0,1603	0,9943

process of the *S. californicus* shoots, which lasted approximately 2 months (68 days), the decay rate k_1 exhibited values from 0.0256 to 0.0495 days^{-1} for all treatments (Table 2). In the second stage, the values of k_2 ranged from 0.0019 to 0.0031 days^{-1} for all treatments, and extended up to 369 days. The lowest values of the decay constants were found in the RIV treatment. Unlike the other two models, the double exponential model showed a very good fit to the data (coefficients of determination greater than 0.97) even in those corresponding to the second stage. Therefore, the double exponential model is the one that best represents the decomposition process of the *S. californicus* shoots for the three treatments. Although there are not yet many studies that apply this model to the decomposition process, the number has increased in recent times (Bianchini Jr and Cunha Santino 2011; Hildebrandt, Pastor, and Dewey 2012).

The values of k_1 and k_2 obtained in RIV were within the range obtained by Robertson (1988) for mangroves in the field and similar to those reported by Hildebrandt, Pastor, and Dewey (2012) for a wild rice species.

The ratio of refractory material (ROM) of the RIV treatment was found to be greater than twice the ratio of labile material (LOM) and higher than the ROM fraction of the LoZn and HiZn treatments ($p<0.05$) (Table 2). On the other hand, in the

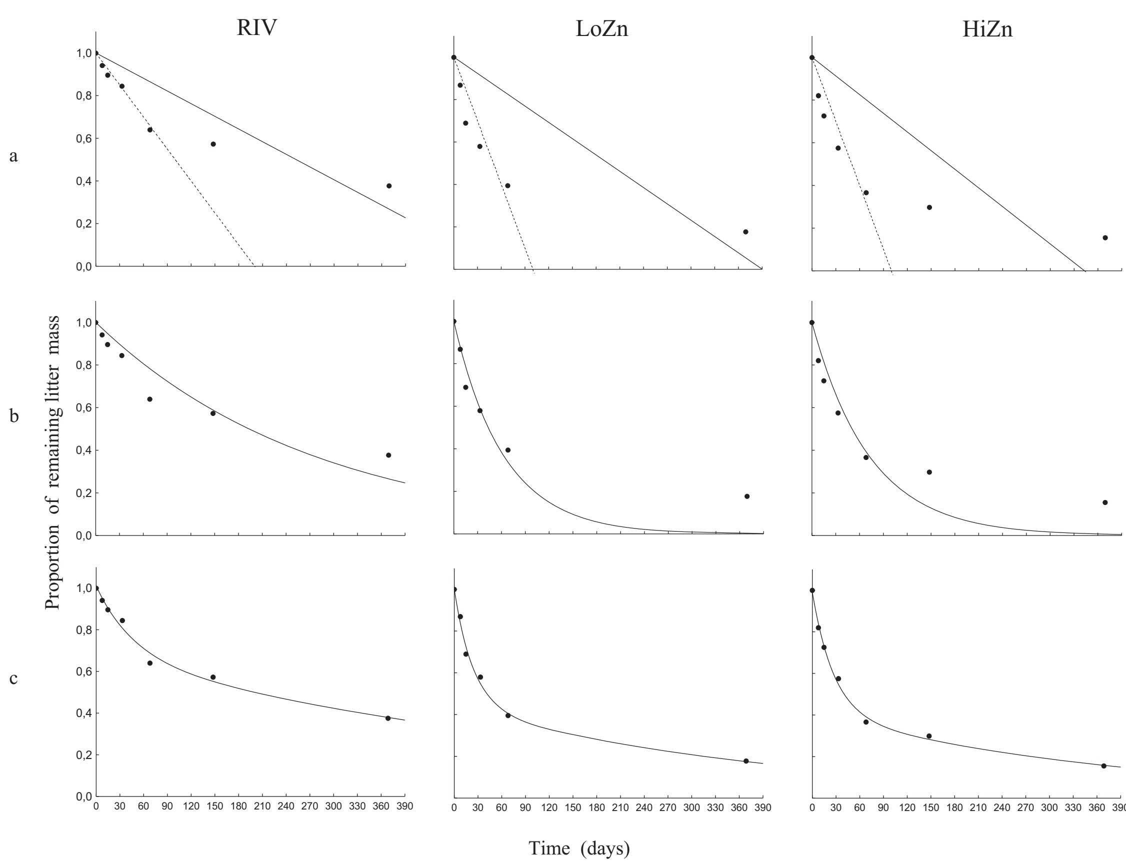

Figure 2. Proportion of remaining litter dry mass during litterbag decomposition experiment for each treatment (dots). Decomposition curve (solid line) according to (a) linear model, (b) simple exponential model, and (c) double exponential model. For linear model, dash line corresponds to the first 68 days. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

LoZn and HiZn treatments, the labile fraction was slightly higher than the refractory proportion. According to Gessner (1999), in all phases of the decomposition process several mechanisms operate simultaneously that lead to the loss of weight and that can interact in varying degrees, although one in particular dominates in each phase. In the first phase, the dominant mechanism is the rapid leaching of soluble or weakly bound materials, and implies the rapid disappearance of nutrients by the different macrophytes. Thus, a faster leaching in the debris with higher labile material (LoZn and HiZn treatments) can be expected which was shown by its higher k_1. The second phase, which can last for more than 300 days, is dominated by the degradation of organic matter carried out by fungi and bacteria with the leaching of the resulting products and where the slow degradation of the less labile materials predominates. After 369 days, the remaining mass in LoZn and HiZn was half that obtained in the RIV treatment (Table 2). The difference in the detritus quality could be one of the causes of the higher decay rate and consequently a smaller remaining mass is obtained in the LoZn and HiZn treatments. Several factors, such as climate, nutrient levels, chemical composition of the detritus, organisms present in the medium, stream morphology, etc., control the detritus decay rate (Gessner 1999; Aerts and De Caluwe 1997). It is generally accepted that decomposition occurs more rapidly in materials with high N content and low levels of lignin and other refractory organic compounds (Aber and Melillo 1980). Godshalk and Wetzel (1978) argue that the total content of structural materials (hemicellulose, cellulose, and lignin) of plants controls their decay rate, being higher when the content of these compounds are lower. However, the total contents of these structural components and the content of hemicellulose and cellulose separately were similar in the three treatments, while the lignin content of the shoots of HiZn was twice that of RIV and LoZn and lower than 5% in all cases (Table 1). In low-lignin detritus (less than 7%), the effect of lignin on the decay rate does not appear to be a determinant of decomposition (Aerts and De Caluwe 1997). Due to the lack of a clear pattern, these litter components did not explain the higher rate of decomposition found in LoZn and HiZn during the decomposition process.

The carbon content was similar in all three treatments, and the N content was lower in RIV (Table 1). As a consequence, the C:N ratio was higher in the latter. Godshalk and Wetzel (1978) argue that the low initial contents of N and the high C: N ratios reduce the rate of decomposition. Also, Villar et al. (2001) found that the community structure dominated by high C/N species in the Paraná deltaic marshes and the low oxygen concentration prevailing determine the slow decomposition rates. However, the C:N ratios obtained in the treatments did not fully explain the differences between decay rates. It must be considered that in analytical measures of total carbon the labile and refractory fractions are not usually differentiated. From the double exponential model, it was observed that RIV detritus—with the lowest decay rate (k_1 and k_2)—had the highest proportion of refractory biomass (ROM) (Table 2). In this way, the LOM: ROM ratio could give additional information for estimating the biomass biodegradability and the availability of binding sites for metals as the decomposition process advances, both useful features in phytoremediation technologies.

3.2. Variations of pH, redox potential, dissolved oxygen, and conductivity in water

During the experiment, marked variations in pH, dissolved oxygen concentration and redox potential were observed, as well as a progressive increase in electrical conductivity (Figure 3).

The initial values of pH were close to neutrality and after 8 days there was a decrease of one unit at all treatments (Figure 3a). The carbon dioxide generated during aerobic decomposition of the organic matter contributes to the system acidification. After 15 days, a progressive increase in the pH was observed reaching slightly alkaline values. As the decomposition process progresses the consumption of dissolved oxygen in water (Figure 3b) generates anoxic conditions that impose the need to use alternative acceptors of electrons, such as NO_3^-, MnO_2, Fe^{3+}, SO_4^{2-}, and CO_2 on the microorganisms (Mitsch and Gosselink 1993). The reduction of these chemical species by the microbial processes tends to increase the pH compensating the acidification with carbon dioxide production (Bastviken, Olsson, and Tranvik 2003).

At the beginning of the experiment the redox potential presented positive values and fell to -315 and -344 mV between 15 and 68 days (Figure 3c) maybe due to the reduction of CO_2 to CH_4. In the second phase of decomposition process, from the 68th day, an increase in redox potential values was observed up to oxidant conditions, at the same time as the dissolved oxygen was recorded in the water (Figure 3b). In this phase, the slowing down of the decomposition process would allow oxygen input by diffusion from the atmosphere predominates over its consumption, increasing the redox potential and oxygen levels in water.

The electrical conductivity increased over time and the highest values were recorded in LoZn and HiZn ($p<0.01$) at the end of the experiment (Figure 3d). This would indicate a greater release of the electrolytes to the water associated with the higher decomposition rates of LoZn and HiZn.

3.3. Dynamics of zinc during the decomposition process

During the first 8 days of the experiment, a rapid and marked decrease of zinc concentration was observed in the detritus in all three treatments (37% in RIV, 86% in LoZn, and 28% in HiZn), attributable to desorption and leachate of the adsorbed or soluble metal in the incubation water (Table 3). In addition, the initial Zn water concentration (18μg/L) doubled in RIV and LoZn and reached 370 μg/L in HiZn. Between 8 and 68 days, an increase in the Zn detritus concentration was observed in the RIV and LoZn treatments (Table 3). The continuous loss of biomass that occurs as the decomposition process progresses (Figure 1) generated a net release of metal into the incubation water, so it can be considered that the detritus of RIV and LoZn continued to behave as a source of metal at this stage. In addition, the decrease in pH could favour the dissolution and/or desorption of soluble forms of metals of plant tissues.

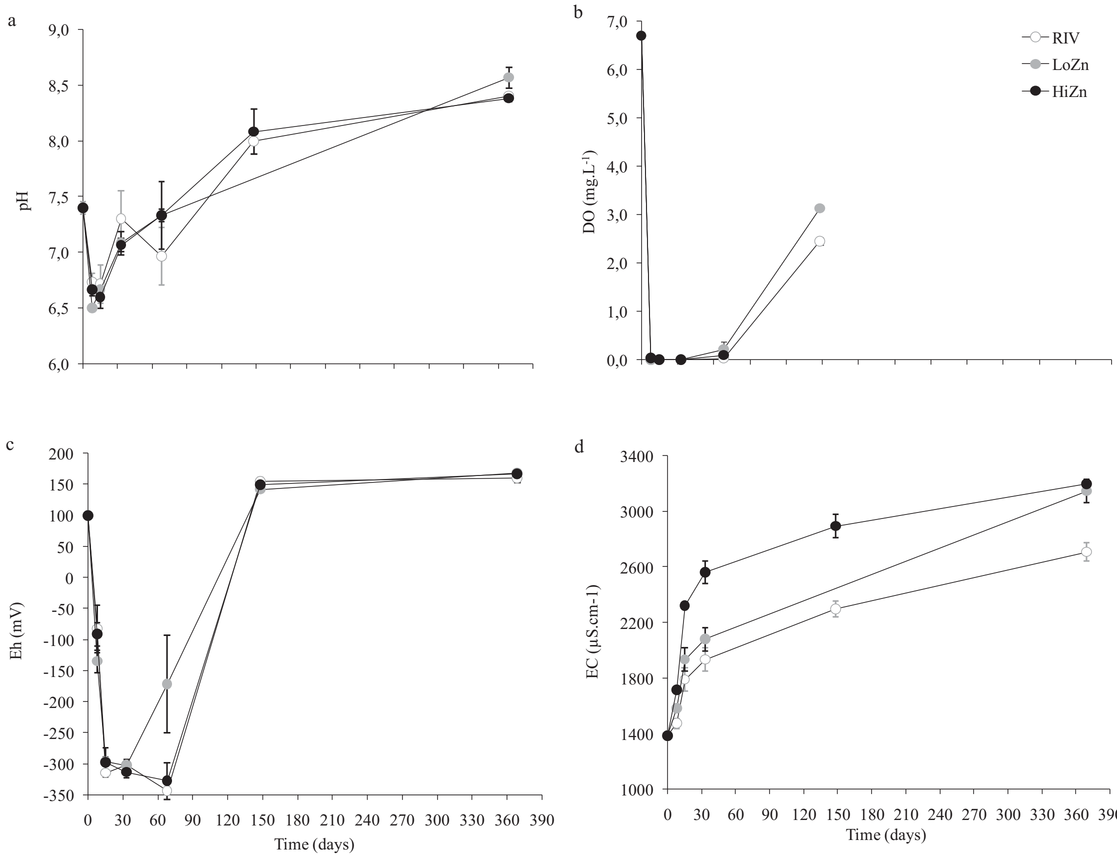

Figure 3. (a) pH, (b) dissolved oxygen (DO), (c) redox potential (Eh), and (d) electrical conductivity (EC) in water of each treatment during litter decomposition experiment. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

In the HiZn treatment, the Zn dynamics were different. The initial increase in the Zn concentration in the incubation water that occurred during the first 8 days was followed by a decrease in this concentration between 8 and 68 days (Table 3). Thus, the HiZn detritus would be undergoing a change from its source condition to behaving like a metal sink. Although an increase in electrical conductivity attributable to ion leaching in the water was observed during the first phase in all treatments (Figure 3), the marked increase observed in HiZn could favor the precipitation of low soluble Zn salts which together with the increase in the detritus surface area will determine a greater metal sorption.

Table 3. Concentration of Zn (mean ± standard deviation) in water (μg/L) and detritus (μg/g) for each treatment over time. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

	Days	Water	Detritus
RIV	0	18 ± 2	20 ± 2
	8	35 ± 3	12 ± 4
	15	54 ± 14	15 ± 3
	33	75 ± 13	13 ± 2
	68	122 ± 33	18 ± 4
	148	72 ± 15	21 ± 10
	369	143 ± 48	40 ± 12
LoZn	0	18 ± 2	106 ± 9
	8	40 ±	15 ±
	15	47 ± 9	20 ± 2
	33	75 ± 7	24 ± 10
	68	125 ± 36	32 ± 5
	148	—	—
	369	146 ± 77	76 ± 2
HiZn	0	18 ± 2	325 ± 12
	8	370 ± 36	234 ± 19
	15	278 ± 43	267 ± 22
	33	191 ± 10	376 ± 38
	68	296 ± 68	870 ± 18
	148	232 ± 62	950 ± 173
	369	587 ± 155	932 ± 315

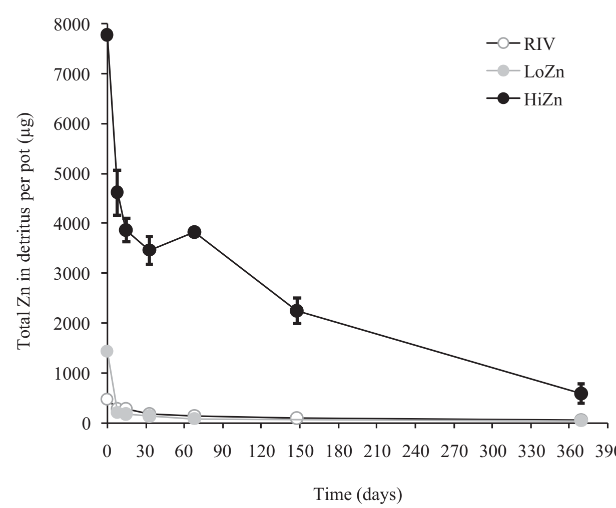

Figure 4. Total amount of Zn in the detritus per pot (μg) of each treatment during the experiment. RIV: shoots collected from an unpolluted river; LoZn: from experimental populations grown at low Zn supply; HiZn: from experimental populations grown at high Zn supply.

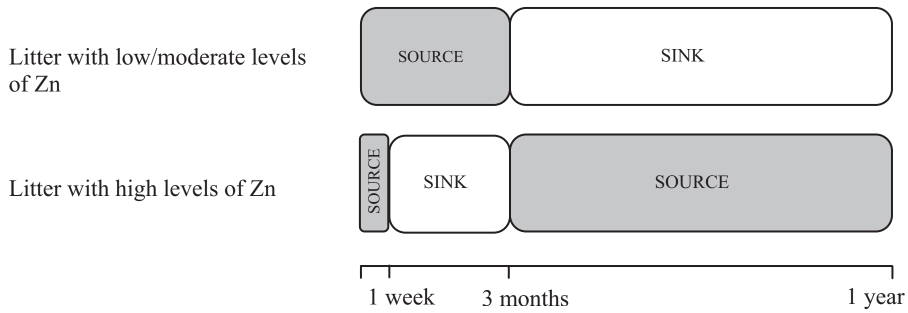

Figure 5. Scheme of sink/source behavior of *S. californicus* litter during decomposition process.

In the second phase (68–369 days), the considerable decrease in the rate of the more resistant compound decomposition diminishes the rate of metal release into the water, the Zn water concentrations of RIV and LoZn treatments remaining practically constant after one year (from 122–125 μg.L^{-1} to 143–146 μg.L^{-1}). At this phase an increase in the Zn detritus concentration of RIV and LoZn treatments was recorded (Table 3). The change from the source to sink condition in debris with low to moderate initial concentrations of Zn could be due to the formation of a heterotrophic film favored by the forms of dissolved organic carbon and the exudates of the microorganisms during the decomposition process. (Du Laing et al. 2006; Schaller et al. 2011; Komínková et al. 2000). Moreover, in this phase it would favor the readsorption on the detritus of cations of high charge density, like Zn^{2+}, reducing its concentration and total amount in water. Some authors [see (Du Laing et al. 2006; Johnson and Hale 2004; Murray-Gulde et al. 2005; Rearte et al. 2013)] have reported an increase in the concentration of metals in detritus from aquatic and terrestrial plants and have considered that this increase would be a consequence of adsorption processes in which the detritus would be behaving as a cation exchange system. On the other hand, the increase in the Zn water concentration in the HiZn treatment would indicate that detritus with high zinc levels would continue to behave as a metal source for the system even after 1 year.

The total amount of Zn in the detritus per pot decreased in all treatments over time. The percentages of decline were 71%, 94%, and 51% up to 68 days and 88%, 97%, and 93% at one year for RIV, LoZn, and HiZn respectively (Figure 4). Thus, whereas the metal release was dominant in the first stage of the process in the RIV and LoZn treatments, the metal was released to the water almost continuously until the end of bioassay in the HiZn treatment. The Figure 5 schematizes the behavior of *S. californicus* detritus as a source or sink through the decomposition process. In litter with low or moderate initial concentrations of Zn, a net release of metal occurs during the first 2 months of incubation, and then it behaves as a metal sink. In detritus with initial concentrations of Zn higher than 300 μg.g^{-1}, there is a rapid release into the water during the first 8 days, a change to the sink condition up to 68 days, and then a return to the source condition up to 369 days.

The knowledge of the role of detritus will allow defining a correct management of the vegetation used for zinc removal. In natural or artificial wetlands vegetated by *S. californicus* and *S. americanus* that receive low or moderate contributions of Zn, the continuous and fast production of biomass and the low translocation of the metal [see (Arreghini, de Cabo, and Fabrizio de Iorio 2006; Arreghini et al. 2017)] assures a low to moderate concentration of metal in the shoots. These structures are standing for between 1 and 2 years, (Pratolongo, Kandus, and Brinson 2008) and the rhizomes are in continuous growth. Once fallen shoots enter the marsh, the breakage of cell walls, the penetration by fungal hyphae, and the degradation of the structural elements by microbial enzymes combined with feeding by invertebrate shredders enhance leaching that continues for weeks (Wantzen et al. 2008). In the present study, the absence of shredders should decrease the decomposition rates respect to natural wetlands. In addition, redox conditions in anoxic environment limit the complete oxidation of organic matter, promoting its accumulation in the upper layers of the marsh sediment (Villar et al. 2001). Thus, the preservation of river margins will contribute to providing binding sites for dissolved metal released during decomposition process and would represent a starting point for environmental remediation and rehabilitation planning. Besides, in cases where high concentrations of zinc are translocated from roots to shoots phytoextraction—to harvest the standing biomass to avoid the release of metals from the decomposing biomass—could be a most appropriate management strategy.

4. Conclusions

The double exponential model showed the best fit for explaining the decomposition process of *S. californicus*. Unlike other functional approaches (linear or simple exponential), the double exponential model provides additional and valuable information, such as the proportion of labile and refractory material of the detritus with different Zn concentrations. This allows establishing a relationship between the degradability of the biomass and the release of metals to the environment.

The behavior (sink/source) of the detritus varies with its Zn concentration. If the initial concentrations of Zn are low or moderate, they behave as a metal source during the first 2-month releasing the soluble or more labile metal, whereas in the following months they behave as a sink by increasing the surface/volume ratio of the material and generating new binding sites that both favor the adsorption of Zn. On the other hand, if the detritus presents high initial concentrations of Zn (greater than 300 μg.g^{-1}); they behave like a sink for much of the first phase, because the high concentrations of Zn in the water increase the ionic strength and favor precipitation and/or adsorption of metal. Subsequently, during the second phase, the Zn bound to the more refractory structures begins to be released into the water and the detritus becomes a source of contamination again.

The knowledge of the role of detritus (sink/source) will allow defining a correct management of the vegetation used for zinc removal and providing a valuable tool for environmental remediation and rehabilitation planning. In natural or artificial wetlands vegetated with *S. californicus* that receive low or moderate contributions of Zn the *in situ* decomposition of shoots can contribute to diminishing the Zn concentration in the water column and metal mobilization in the environment. On the other hand, in cases where only high concentrations of Zn in shoots are found, the most appropriate management strategy would be to harvest the standing biomass to avoid the release of metals from the decomposing biomass.

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