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Experimental study of terrestrial plant litter interaction with aqueous solutions

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Abstract

Quantification of silicon and calcium recycling by plants is hampered by the lack of physico-chemical data on reactivity of plant litter in soil environments. We applied a laboratory experimental approach for determining the silica and calcium release rates from litter of typical temperate and boreal plants: pine (*Pinus laricio*), birch (*Betula pubescens*), larch (*Larix gmelinii*), elm (*Ulmus laevis* Pall.), tree fern (*Dicksonia squarrosa*), and horsetail (*Equisetum arvense*) in 0.01 M NaCl solutions, pH of 2–10 and temperature equals to 5, 25 and 40 °C. Open system, mixed-flow reactors equipped with dialysis compartment and batch reactors were used. Comparative measurements were performed on intact larch needles and samples grounded during different time, sterilized or not and with addition or not of sodium azide in order to account for the effect of surface to mass ratio and possible microbiological activity on the litter dissolution rates. Litter degradation results suggest that the silica release rate is independent on dissolved organic carbon release (cell breakdown) which implies the presence of phytoliths in a pure “inorganic” pool not complexed with organic matter. Calcium and DOC are released at the very first stage of litter dissolution while Si concentration increases gradually suggesting the presence of Ca and Si in two different pools. The dry-weight normalized dissolution rate at circum-neutral pH range (approx. 1–10 μmol/g_{DW}/day) is 2 orders of magnitude higher than the rates of Si release from common soil minerals (kaolinite, smectite, illite). Minimal Ca release rates evaluated from batch and mixed-flow reactors are comparable with those of most reactive soil minerals such as calcite and apatite, and several orders of magnitude higher than the dissolution rates of major rock-forming silicates (feldspars, pyroxenes). The activation energy for Si liberation from plant litter is approx. 50 kJ/mol which is comparable with that of surface-controlled mineral dissolutions. It is shown that the Si release rate from the above-ground forest biomass is capable of producing the Si concentrations observed in soil solutions of surficial horizons and contribute significantly to the Si flux from the soil to the river. © 2009 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

A strong impact of plant litter degradation on the flux and speciation of dissolved organic carbon (DOC) in rivers, especially during the flood events or rains, is widely recognized in boreal (Rember and Trefry, 2004; Prokushkin, 2005, 2007), temperate (Ross and Sherrell, 1999) and tropical (Lorieri and Elsenbeer, 1997; Olivé-Lauquet et al.,

2001; Viers et al., 2000) environments. The increase of DOC concentration with the discharge increase is usually explained by the leaching of soluble organic compounds from degrading plant litter in forest floor and topsoil horizons. Although significant part of some major (Si, Ca, Mg, K) and trace (Al, Fe, Mn, Zn, Cu, Pb, etc.) elements may also originate from plant litter, the impact of the latter on elements fluxes in rivers has been rarely quantified.

Indeed, it has been widely argued that degrading plant litter is an important source of the dissolved major and trace elements found in river water (Polynov, 1944; Kovda, 1956; Glazovskaya, 1977; Pokrovsky et al., 2005, 2006). This has been clearly demonstrated for Si cycle in the Amazonian

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forest: the Si input (41 kg/ha/yr) from the rain forest on top of the soil is about four times greater than the Si leached out of the system (11 kg/ha/yr, Lucas et al., 1993). In a temperate ecosystem, Gérard et al. (2008) calculated that an average 60% of the biogeochemical cycle of Si is controlled by Si-uptake and dissolution of phytoliths. Studies of granite (Millot et al., 2002) and basalt environments (Gislason et al., 1996; Moulton et al., 2000) demonstrated that the chemical weathering fluxes can be several times higher in vegetated areas compared to that of bare rocks. It is known that the majority of the nutrients taken up by trees on an annual basis is recycled. Two major sinks for nutrients are storage in plants and secondary mineral precipitation in soil including also the ion exchange. There is also an annual net loss of nutrients from ecosystems due to superficial flow, especially pronounced in the permafrost-dominated landscapes via suprapermafrost flow (e.g., Pokrovsky et al., 2005b). Much less is known about the recycling of non-nutrient (non-limitant) elements. Although several recent studies used isotopic techniques in an attempt to resolve the sources of elements in Hawaiian and Siberian rivers (Derry et al., 2005; Reynolds et al., 2006), the contribution of mineral versus plant litter remains poorly constrained particularly for boreal watersheds.

Recently, the contribution of plant litter degradation to river water concentrations has been assessed from the analysis of the litter composition and the annual Net Primary Productivity (NPP), and it was estimated that annual contribution of Ca, Mg, Na and SiO₂ fluxes due to plant litter degradation to the total river-borne fluxes may be as high as 30–60% (Pokrovsky et al., 2005b; Zakharova et al., 2007). It has been argued that the net Ca mineralization from decomposing litter is responsible for high Ca flux within temperate forest ecosystems (Likens et al., 1998; Dijkstra, 2003). Extensive work on major element recycling by boreal and temperate plants, their loss from soil litter and tree biomass has been performed by Russian research institutes in 1950–1960 (Remezov et al., 1959; Rodin and Bazilevitch, 1965). Several studies quantified net Ca mineralization rates of plant litter using litter bags technique showing that Ca release is closely related to weight loss (Attwill, 1968; Gosz et al., 1973) and thus indicating that Ca is a structural litter component. However, up to present time, there was no quantitative laboratory evaluation of major petrogenic element release from the plant litter.

Although from the mass balance evaluation, the plant litter is able to significantly influence the chemical erosion and river element transport, quantitative assessment of this pool of chemical elements is hampered by the lack of experimental physico-chemical data on the reactivity of plant litter in aqueous solution, i.e., its residence time in soils, decomposition rates and their dependence on environmental parameters (pH, temperature, presence of fungi and bacteria). Indeed, in contrast to relatively good knowledge of plant phytoliths surface chemistry and reactivity (Bartoli, 1981, 1983, 1985; Frayse et al., 2006, 2009a), the rates of whole plant litter degradation has been mostly studied for “biogenic” elements such as C, N, P (Chauvet, 1988) whilst the release rate of lithogenic elements such as Ca or Si remains very poorly known. In the first part of this work, it

was established that there is no effect of the nature of plant species on dissolution rates of phytoliths extracted from these plants (Frayse et al., 2009a). Since phytoliths represent the major pool of Si in plants, it can be hypothesized that the release of Si from plant biomass should be similar among different species. This work is aimed at verifying this hypothesis and testing it for another major biological element, calcium, using physico-chemical experimental approach.

Building on this information, the purposes of this study are twofold. First, we would like to quantify the rates of Ca and Si release from freshly collected litter of typical temperate and boreal plants and its dependence on temperature and pH. In this regard, we would like to evaluate the minimal possible impact of litter on elements release to soil solution as our experiments are conducted under sterile conditions or with sterilized plant litter. Secondly, we aimed at assessing the relative role of soil mineral versus plant litter dissolution in chemical weathering. It is anticipated that assessing these sources is essential for predicting the response of terrestrial ecosystems to the global warming as the plant primary production and biomass degradation respond more rapidly to small temperature variation than soil mineral dissolution.

2. MATERIALS AND METHODS

2.1. Materials

Several representative plant litter samples collected throughout the world were used in experiments (see plant litter initial chemical composition in Appendix 1.1). Pine needles (*Pinus laricio*) were collected from trees in autumn in the North-East of France (near Nancy). Freshly fallen larch tree (*Larix gmelinii*) needles were collected in September 2005 from the 80 to 100 years old trees during the litter-fall period in Central Siberia, on the slope of the Kochechuma river valley (see territory description in Pokrovsky et al., 2005b). Birch leaves (*Betula pubescens*) were collected from the tree in October in the Central Pyrenees national park. European white elm (*Ulmus laevis* Pall.) dry leaves were collected in autumn from lower branches of 250-year old elm tree in Askania Nova national wildlife reserve (Ukraine). Dry bottom fronds of the New Zealand Tree Fern (*Dicksonia squarrosa*) were collected in January (middle of the summer) in the national park located in the central part of the South Island (New Zealand). Horsetail (*Equisetum arvense*) biomass was collected in the riparian zone of the Garonne River, 10 km SW of Toulouse (France). Leaves color was typical brown/yellow and there was no any visible fragmentation or fungal attack. Therefore, given the maximal possible freshness of sampled material, the native biodegradation degree of all leaves, needles and fronds was minimal. Typical secondary soil minerals of studied sites are clays (smectite, illite and kaolinite).

A unique procedure was applied for treatment of samples prior the experiments. The biomass was cleaned manually to remove all large foreign substances and the insects. It was thoroughly rinsed in MilliQ water (approx. 5 L of water for 100 g of biomass) and dried at 50 °C during

48 h. Dry material was grounded in automatic agate mortar during 3 min to produce sufficiently fine powder. In some experiments, this powder was sterilized in an autoclave (30 min at 121 °C). We used vapour sterilization without mixing with water. Specific surface area (SSA) of dry (grounded and whole) plant litter was measured using multiple point N₂ adsorption (Micrometrics ASAP 2010 apparatus) after degassing during 48–72 h at 85 °C (Appendix A1.1). Because of their lower SSA, whole needles of *Larix gmelinii* were measured using multiple point Kr adsorption after sample degassing 4 days at 85 °C.

Reacting fluids were comprised of deionized degassed H₂O, Merck reagent grade HCl, NaOH, NaHCO₃, Na₂CO₃, and NaCl. Most experiments were performed at an ionic strength of 0.01 M maintained by a mixture of NaCl, HCl and NaOH. In CO₂-free experiments, fresh input solution was purged of CO₂ by bubbling with pure nitrogen for 10–12 h; this bubbling was repeated once every two days during long-term dissolution experiments. Regular control of alkalinity and pH in inlet solutions for CO₂-free experiments did not reveal any detectable dissolution of atmospheric CO₂ via diffusion through polyethylene walls of the container in the course of experiments. All solutions were prepared from 18 MΩ ultrapure sterile water (MilliQ Plus system) having a blank of dissolved organic carbon <0.05 ppm.

2.2. Litters degradation experiments

Two types of litter degradation experiments were performed in the present study. Short-term and long-term batch reactors were used for quantifying Si, Ca and DOC release rate at various temperatures while open-system mixed-flow reactors equipped with dialysis compartment were used to monitor the long-term steady-state dissolution rates at 25 °C. Both types of experiments were performed in 0.01 M NaCl. The ionic strength was maintained constant within ±10% and pH adjustment was performed using HCl and NaOH solutions. To decrease the microbial respiratory activity, 5 mM sodium azide (NaN₃), known to inhibit microbial respiration activity via stopping the ATP pump, was added for several mixed-flow and long-term batch reactor experiments. All short-term batch experiments have been performed without NaN₃ addition. The batch reactor experiments were performed in the following way. Each batch experiment was performed in sterile polypropylene of 30 ml capacity. In each reactor, 0.2 g of dry plant material was placed in contact with 25 ml of 0.01 M NaCl solution and shaken in the thermostated incubators at 25 ± 0.2 °C and 40 ± 0.5 °C or in the refrigerator at 5 ± 0.5 °C. The total amount of suspension was used for analysis of pH, DOC, Ca and Si concentrations with replicates. Upon interaction with plant litter, the release of complex and simple organic acids contribute to the solution acidity and brings the pH to stable values of 4.5–6.5 (Köhler et al., 2000; 2002). As such, no additional buffers was necessary to keep the pH constant during the experiments. The reaction progress was monitored by measuring dissolved silica, calcium and dissolved organic carbon (DOC) concentration as a function of time. In each sample, pH was measured;

suspension was centrifuged during 10 min at 1500g and filtered through a 0.22 μm cellulose ester membrane before analysis. The dissolution rate was calculated from the slope of [Si]—time dependence using the equation.

$$R = \left(\frac{d[M]}{dt} \right) / m \quad (1)$$

where m is mass of dry material in g_{DW}/L, where t (s) designates the elapsed time, $[M]$ (mol/L) stands for the amount of Ca, Si or organic carbon (moles) released from the solid. This residence time of solution in the mixed-flow reactor depends on reactor volume and on the flow rate as $t_r = V/Q$ (with t_r , V and Q for the residence time of solution in the reactor, volume of the reactor and the flow rate of solution, respectively).

Plant litter dissolution rates were also measured in continuously stirred mixed-flow reactors. Steady-state dissolution rates were obtained at distinct solution compositions and pH using a reaction vessel equipped with a dialysis bag held at a constant temperature of 25.0 ± 0.5 °C by immersion in a thermostated water bath. The input fluid was stored in a polyethylene container protected against CO₂ uptake from the atmosphere. It was injected into the reaction vessel using a Gilson® peristaltic pump at typical flow rates 0.05–0.1 mL/min. The reactor consisted of a 250 mL Azlon® polypropylene beaker which was continuously stirred with a floating Teflon supported magnetic stirrer. The reactive solution left the reactor through a 2.5 μm pore size polycarbonate filter. Approximately 10 mL of plant litter suspension (8 g_{DW}/L) were enclosed in a 10-mL dialysis bag (1 kDa, Cellu-Sep® H1 High Grade or Spectra Por® 7). This dialysis bag was sealed and fixed between the stirrer and the reactor head. Similar design has been used by Köhler et al. (2003, 2005) and Golubev et al. (2006) during their long-term study of illite and smectite dissolution, respectively. Dialysis membrane does not allow the plant debris or colloids to clog the filter while it insures the identical composition of truly dissolved aqueous species (H₄SiO₄, Ca²⁺) inside the bag and in the outlet solution. Over long-term dissolution experiments, the equilibrium distribution of solutes between the content of the dialysis bag and the external solution was not a limiting factor for steady-state attainment: it has been verified in a series of preliminary experiments with CaCl₂ and H₄SiO₄ solutions that it takes typically 48–72 h to establish the dialysis equilibrium while the mechanical steady state in the reactor system is achieved only after 200 h. For most experiments lasting 30–40 days each, one sampling per day was performed.

Steady-state dissolution rates ($R_{Si,Ca}$, mol/cm²/s) were computed from measured solution composition using.

$$R_i = -q \cdot \Delta[i(aq)]_{tot} / s, m \quad (2)$$

where q (L/s) designates the fluid flow rate, $\Delta[i(aq)]_{tot}$ (mol/L) stands for the difference between the input and output solution concentration of i -th element, and s , m (cm²) refers to the total plant mass or B.E.T. surface area present in reactor, respectively. The mass and surface area used to calculate the rates was that measured on the fresh (unreacted) plant litter prepared as described in Section 2.1. Uncertainties on the

steady-state rate constants are dominated by the uncertainty on the standard deviation on average Si or Ca concentration at steady-state ($\pm 10\%$ and $\pm 15\%$, respectively).

2.3. Analytical methods

Solution pH was measured using a combination glass electrode (Mettler Toledo) calibrated with NIST buffers (pH 4.01, 6.865, 9.18 at 25 °C). Precision of pH measurements was ± 0.005 units. Aqueous silica concentration was determined using the molybdate blue method with an uncertainty of 2% and a detection limit of 3.6×10^{-7} M with a High Resolution Digital Colorimeter, Bran + Luebbe Auto-analyser III using control software AACE 6.03. Calcium was measured by flame atomic absorption with an uncertainty of ± 1 percent and a detection limit of 4×10^{-8} and 7×10^{-8} M, respectively. The dissolved organic carbon (DOC) was determined using SHIMADZU ASI 5000A-TOC auto-analyser with an uncertainty of 3% and a detection limit of 0.1 mg/L.

3. RESULTS

3.1. Short-term batch dissolution experiments

Results of seven short-term (≤ 8 h) litter degradation experiments are listed in the [Electronic Annex \(A1\)](#) and illustrated in [Figs. 1A–C](#) where the Si, Ca and DOC concentrations in solution are plotted as a function of time for acidic, neutral and basic conditions at 25 °C. The dissolution rates expressed in mol/g_{DW}/day are listed in [Table 1](#). In neutral solutions, over the investigated reaction time (5–500 min), a constant rate of Si release is observed with the order elm > horsetail >> larch >> birch > pine ([Fig. 1A](#)). This indicates that the contribution of reaction products (backward reaction) to the overall dissolution rate is insignificant, in particular, the rates are unaffected by Si concentration in solution at constant pH. The release of Si is the fastest in basic conditions and the slowest in acidic conditions ([Table 1](#)). The measured order of Si release rate is comparable with Si content in the plant biomass: horsetail > elm >> birch \geq pine ([Appendix 1](#)) which suggests the governing role of plant phytoliths in Si release from plant material.

In the course of litter dissolution experiments, DOC concentration remains constant being the lowest for horsetails (~ 100 mg/L) and the highest for elm (around 300 mg/L, [Fig. 1C](#)). Both pH and the nature of plant material are responsible for [DOC] in batch experiments. Released DOC concentration increases in the order horsetail < pine < birch < larch < elm ([Fig. 1C](#)). The comparison of the order of Si ([Fig. 1A](#)) and DOC ([Fig. 1C](#)) release demonstrates that the silica release rate is independent on DOC production due to cellulose hydrolysis and the breakdown of cellular organelles and components and cytoplasm, i.e., the phytoliths and/or dispersed Si in pure “inorganic” pool are not complexed with majority of the organic matter. Ca release rate cannot be quantified in these experiments. This release is very fast during the first several minutes of reaction, and only in basic solutions for larch needles

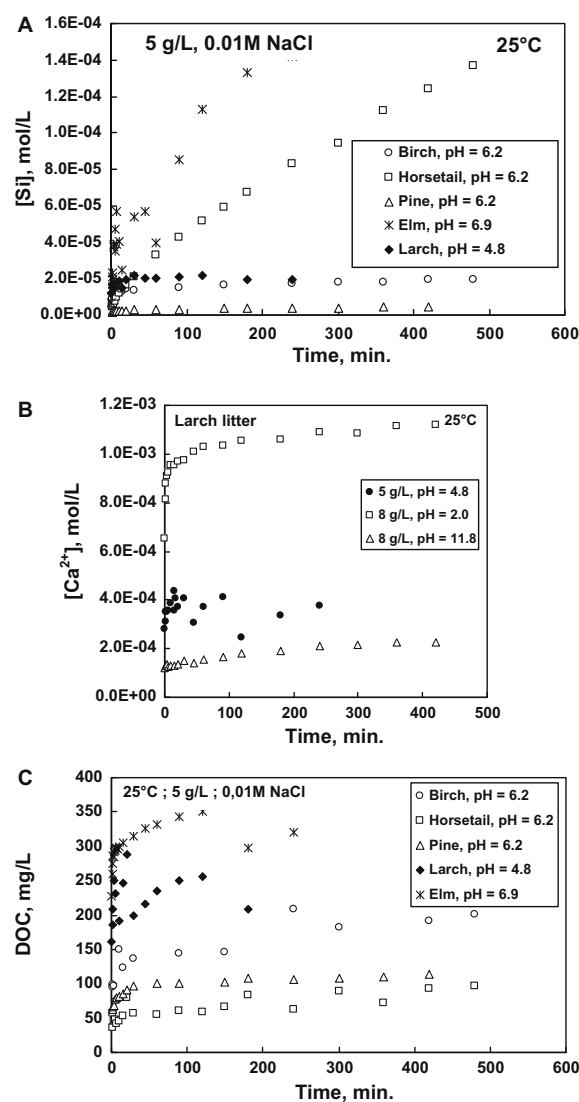


Fig. 1. Examples of short-term (A), calcium (B) and DOC (C) release rate from plant litter dissolving in batch reactors.

dissolution, the rate could be approximated as 4.8×10^{-5} mol_{Ca}/g_{DW}/day ([Fig. 1B](#)).

Note that the sterilized biomass of larch and elm exhibits a factor of 2.5 and 10 lower Si release rate, respectively, compared to non-sterilized material ([Table 1](#)). Although such a comparison is not straightforward since the non-sterile short-term (4 h) experiments may reveal the dissolution of most labile dispersed Si pool and the sterilized biomass long-term (38–46 h) experiments correspond to phytoliths dissolution (see a discussion in [Section 4.1](#) below), this difference indicates on possible role of microbial processes and/or the effect of cell degradation during autoclaving. Our preliminary results demonstrate that the presence of heterotrophic bacteria exhibits weak or slightly accelerating effects on Si release from larch and fern biomass ([Frayse et al., 2009b](#)). Noteworthy that this is not so for most trace metals and cations, whose release from plant litter in laboratory is suppressed by microbial uptake of organic complexes of these elements.

Table 1

Dissolution rates determined in short and long-term batch experiments of plant litter degradation. Note different temporal scale used to calculate element fluxes.

Litter	T , °C	Time, h	$V_{\text{susp.}} > \text{g}_{\text{DW}}/\text{L}$	pH	Si fluxes, $\text{mol}_{\text{Si}}/\text{g}_{\text{DW}}/\text{day}$	Ca fluxes, $\text{mol}_{\text{Ca}}/\text{g}_{\text{DW}}/\text{day}$
Pine	25	7	5	6.2	0–0.25 h: 1.15E-05 0.25–7 h: 1.44E-06	ND
Birch	25	8	5	6.2	0–0.25 h: 9.10E-05 0.25–8 h: 3.83E-06	ND
Horsetail	25	8	5	6.2	8.04E-05	ND
Elm	25	4	5	6.9	0–10 min: 1.08E-03 10 min–4 h: 1.50E-04	ND
Larch	25	4	5	4.8	0–0.5 h: 6.42E-05	ND
	25	7	8	2.0	0–0.25 h: 7.65E-05 0.25–7 h: 3.46E-06	ND
	25	7	8	11.8	0–0.5 h: 3.44E-03 0.5–7 h: 5.4E-06	0–7 h: 4.77E-05
Larch (sterilized)	5	38	8	4.7	3.74E-07	1.85E-03 (first min)
	25				1.42E-06	1.73E-03 (first min)
	40				4.89E-06	1.78E-03 (first min)
Elm (sterilized)	5	46	8	6.8	3.59E-06	ND
	25				1.15E-05	
	40				3.50E-05	
Fern (sterilized)	5	70	8	5.6	3.43E-06	ND
	25				1.14E-05	
	40				3.97E-05	
Horsetail	25	122	8	2.5	0–35 days: 7.49E-07 35–122 days: 4.48 E-07	ND
				6.3	0–35 days: 6.6E-06	
				8.4	0–12 days: 4.81E-06	
	40	122	8	2.4	0–35 days: 2.11E-06 35–122 days: 1.33E-06	ND
				6.4	0–35 days: 6.83E-06	
				8.3	ND	
Pine	25	87	8	2.0	1.81E-08	ND
				4.5	1.45E-08	
				8.0	4.48E-08	
	40	87	8	1.9	4.56E-08	ND
				4.6	6.81 E-08	
				7.4	3.91 E-08	
Birch	25	104	8	3.0	2.44E-08	1.50E-06
				6.4	2.98E-08	ND
				8.0	2.69E-08	ND
	40	104	8	3.3	4.74E-08	1.82E-06
				6.3	4.49E-08	ND
				7.5	4.54E-08	ND

3.2. Long-term batch dissolution experiments

Results of long-term (≤ 3 days and ≤ 120 days) litter degradation experiments (Table 1) are illustrated in Figs. 2 and 3 and listed in Electronic Annex A2. Si release rates from horsetail, pine and birch biomass at 25 and 40 °C, in acidic and neutral solutions are illustrated in Fig. 2A–C for horsetail, pine and birch, respectively. For all plants, there is a net increase of both the slope [Si]—time dependence and the Si concentration in solution with the increase of temperature from 25 to 40 °C. At all temperatures, the increase of pH from 2.5–3 to 6.3 brings about similar effect for horsetail and birch

(Fig. 2A and C, respectively). The pH increase from 2 to 4.6 does not produce any rate increase (Fig. 2B for pine), despite the fact that there is a minimum of phytoliths dissolution rate at pH around 2 (Fraysse et al., 2009a).

Linear [Si]—time dependencies over almost 3 months of exposure time were observed allowing computing far from equilibrium dissolution rates (Table 1) and activation energies of dissolution (Fig. 2D and Table 2). The activation energy (E_a) of Si release from plant litter ranges from 53 ± 2 kJ/mol for horsetail to 80 ± 2 kJ/mol for pine needles with a pH value equals to 2.5 and 4.6 ± 0.1 for horsetail and pine needles, respectively (Table 2). The

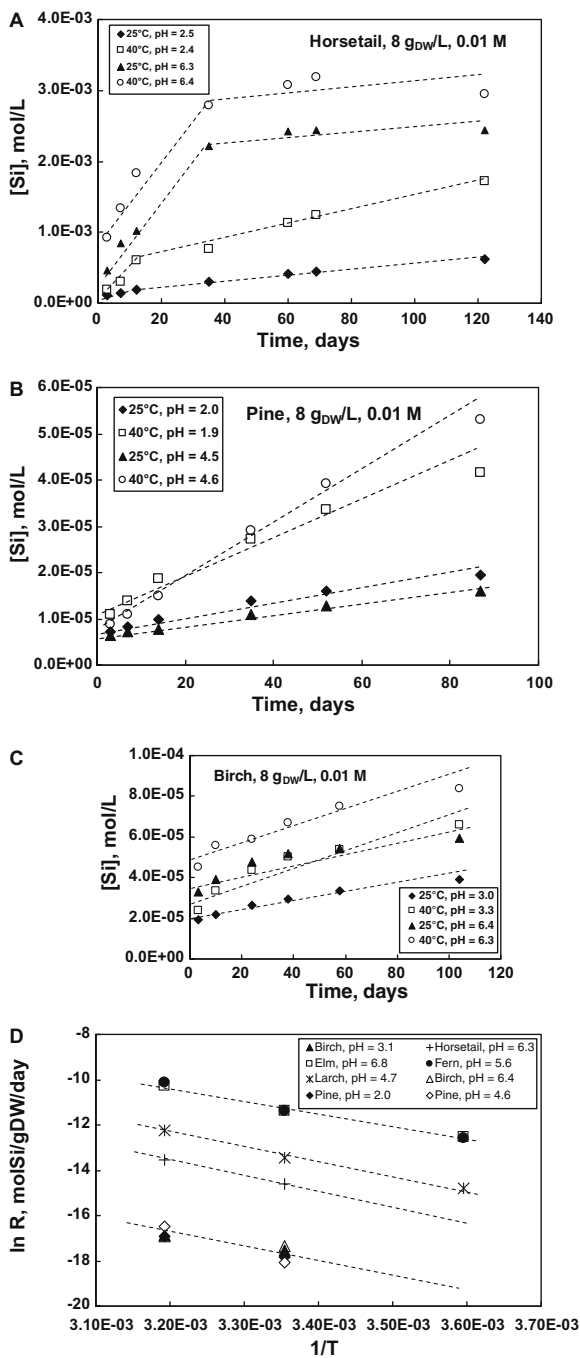


Fig. 2. Long-term Si release rates from horsetail (A), pine (B) and Birch (C) biomass at 25 and 40 °C, in acidic and neutral solutions. (D): Ln R (molSi/gDW/day) as a function of 1/T (K) for litter dissolution experiments.

dissolution of horsetail biomass in alkaline solutions at 40 °C (0.01 M NaOH, pH ~8) yields constant equilibrium

Table 2
Activation energy (E_a) of Si release from plant litter at 5–40 °C, $I = 0.01$ M.

	Horsetail	Pine	Birch	Larch	Elm	Fern
pH	2.5	2.0	3.1	4.7	6.8	5.6
E_a , kJ/mol	53.4	47.8	34.4	52.6	46.6	49.9

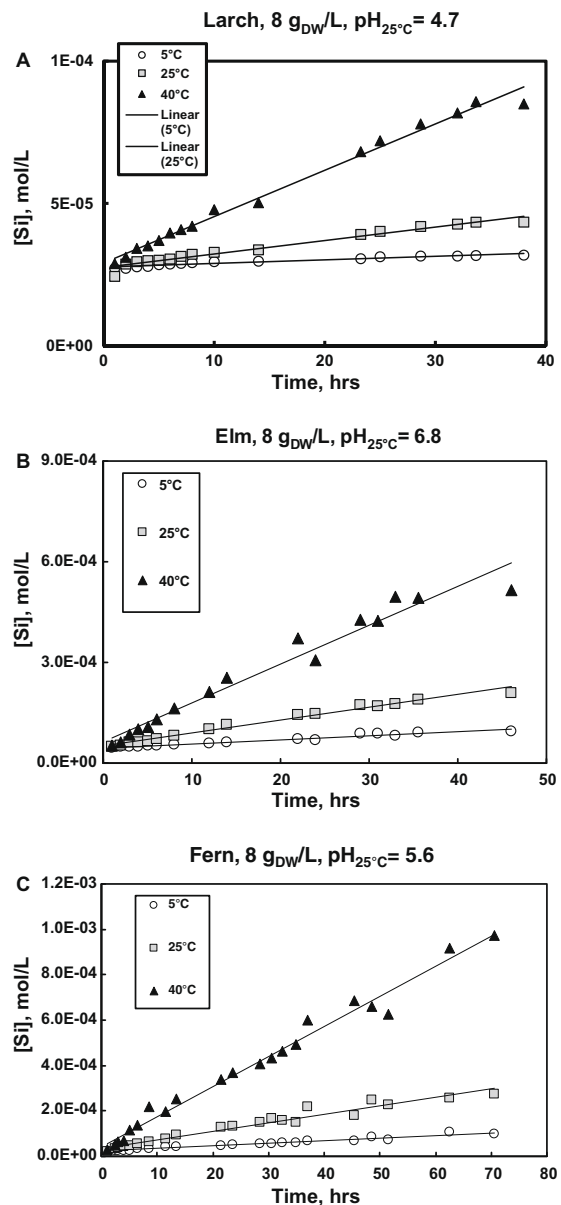


Fig. 3. Silica concentration change as a function of reaction time for larch (A), elm (B), and fern (C) litter degradation at 5, 25 and 40 °C and pH 4.7, 6.8 and 5.6, respectively. The solid line corresponds to linear regression fit and the symbols represent the experimental data.

Si concentration after ~60 days of reaction (3 mM, [Electronic Annex A2](#)), close to the value measured for this plant phytoliths (2.53 mM, [Fraysse et al., 2009a](#)).

The concentration of DOC in long-term plant dissolution experiments remained constant since the first sampling

or even decreased over time reflecting probably colloids coagulation (horsetail at pH 2.5, see [Electronic Annex A2](#)). After first 1–2 days of reaction, no change in DOC concentration was detected; the minimal concentrations were observed in neutral solutions (pH 4.5–6.3) and the maximal ones in slightly alkaline (pH 8) and acidic (pH 2) solutions. For the same plant species in the full range of pH, the DOC release does not demonstrate clear temperature dependence between 25 and 40 °C. Among different plant species, in the full range of investigated pHs and temperatures, the following order of [DOC] was observed: horsetail < pine < birch < larch with a factor of five differences between horsetail and larch. Fully independent behaviour of silica and organic carbon, in accord with short-term degradation experiments (Section 3.1), probably reflects the presence of two different pools of Si and organic matter in the plant litter and their independent release to solution.

The change of Ca concentration in course of long-term degradation of horsetail and pine could not be quantified as [Ca] achieves a constant value upon the first day of the reaction. Only for birch litter dissolution at pH 3.1, this [Ca] change could be measured ([Electronic Annex A2](#)). Long-term (up to 100 days) calcium release rate increases from 1.50 to 1.82 $\mu\text{mol}/\text{g}_{\text{DW}}/\text{day}$ with temperature increase from 25 to 40 °C yielding activation energy of 28.5 kJ/mol for this reaction. The Ca release rate from larch biomass observed during the first 10 min of reaction is around $1.8 \times 10^{-3} \text{ mol}_{\text{Ca}}/\text{g}_{\text{DW}}/\text{day}$ ([Table 1](#)) which is comparable with dissolution rate of 0.1 m^2/g calcite (assuming, for the latter, R equals to $10^{-10} \text{ mol}/\text{cm}^2/\text{s}$ in neutral solutions at far from equilibrium conditions, [Pokrovsky et al., 2005c](#)). Since plant biomass was thoroughly washed prior the experiments, we suggest that these high initial release rates correspond to Ca mobilization from very labile pool present in the near-surface layers, for example, calcium pectate (e.g., [Lodish et al., 1995](#)). The slower release rate of Ca measured over the next 7 h is equal to $4.8 \times 10^{-5} \text{ mol}_{\text{Ca}}/\text{g}_{\text{DW}}/\text{day}$ and may reflect liberation of intracellular Ca pool or dissolution of cellular minerals such as carbonates and oxalates (i.e., [Canti, 2003](#)).

The series of larch, elm and fern biomass dissolution in circum-neutral pH (4.7; 6.8 and 5.6, respectively) at 5, 25 and 40 °C are presented in [Fig. 3A–C](#). Si concentration increases linearly with time allowing calculating the rates and the activation energies: $E_a = 52.6, 46.6$ and 49.9 kJ/mol for larch, elm and fern biomass dissolution, respectively. These values are similar to inorganic mineral dissolution rates and strongly suggest surface chemical reaction (non-transport) control on Si release rate from the solid. Unfortunately, evaluation of activation energy for Ca release rates in batch-reactors experiments was not possible due to fast release of labile Ca pool at the very beginning of reaction.

3.3. Long-term dissolution in mixed-flow (open) reactors

Optical examination of initial and reacted material (whole larch needles) did not reveal any visible changes in the surface morphology as was also confirmed by the Electronic Microscope Observations. Punctual chemical com-

position measurement using energy dispersive technique did not demonstrate any qualitative changes in major constituents presence after long-term dissolution runs. Accordingly, total carbon analysis performed by C-S solid analyzer (Horiba) did not reveal, within the uncertainty of 2%, any systematic trend in total carbon and sulfur analysis of reacted material compared to the initial powder. The total wet chemical analysis of Ca and Si in fresh and reacted plant material revealed systematic decrease of these elements content by a factor of 2–10, and by 20–40%, accordingly ([Appendix 1.2](#)). Transmission FT-IR analysis revealed the disappearance, after 1.5 months of reaction, of some IR-peak characteristic for the Si–OH bands at 3730 cm^{-1} and 1323 cm^{-1} for elm biomass and at 3701 cm^{-1} for the larch samples. In addition, important modifications were detected in the region (1250 – 1100 cm^{-1} , in particular 1072 cm^{-1}) assigned to the stretching vibration of the Si–O group of phytoliths. For reacted samples, a very low intensity of this band was observed compared to the initial material. The bands intensity and position of typical organic constituents (carboxyl ($3400, 1400$ and 1740 cm^{-1}), aliphatic ($1455, 2850, 2930$ and 2960 cm^{-1}), hydroxyl (3400 and 1540 cm^{-1} with interference of water at these particular wavelengths), and polysaccharide (1086 cm^{-1}) have not changed significantly between the reacted and unreacted elm and larch biomass.

Results of 21 long-term (30–70 days) litter dissolution experiments are listed in [Table 3](#) and illustrated in [Figs. 4–7](#). Si concentrations as a function of time for birch, horsetail, larch, elm and fern biomass dissolution at 25 °C and pH 3–10.7 are shown in [Fig. 4A–E](#). Typically, it takes about 5–10 days to achieve mechanical steady state (depending on the flow rate) and the constant concentration of Si in the outlet solutions were observed after c.a. 1 month of experiment. The outlet Si concentration increases with the increase of pH; in alkaline solutions, the steady state for pine, birch and horsetail biomass could not be achieved, apparently, due to complete removal of Si from the solid phase.

To account for the possible effect of microbial activity, experiments with larch litter in the presence or not of 5 mM NaN_3 at otherwise identical conditions (0.01 M NaCl, pH 5–6) have been conducted (exp. 3–5, [Table 3](#) and [Electronic Annex](#)). Our results demonstrate that, for *Larix gmelinii* biomass the presence of NaN_3 increases Si release rate by 30–40% compared to non-sterile conditions. Another test of microbiological activity on element release rate from the plant litter consisted of dissolving the sterilized and non-sterilized biomass of *Larix gmelinii* and *Ulmus Laevis* Pall. at otherwise similar conditions (0.01 M NaCl, pH 5.6–6.2, exp. 1–4, 1–1, 2–4 and 3–3, [Table 3](#)). It can be seen in [Fig. 5](#) that outlet Si concentration is $\sim 30\%$ lower in sterilized compare to non-sterilized sample which can be explained by the effect of microbial activity. At the same time, the structural changes in organic matter subjected to heating can also increase the biomass degradation intensity via cell breakdown and lysis. However, quantitative evaluation of live activity of bacteria or fungi on plant litter degradation (i.e., [Fang et al., 2005](#); [Bärlocher and Kendrick, 1974](#)) was beyond the goal of the present study. Recently, it has been shown that, for larch biomass in neutral

Table 3

Si and Ca release rates for long-term dissolution in mixed-flow reactor, at 25 °C and $I = 0.01$ M. Experiment 3–5 with larch litter was performed in the presence of 5 mM NaN_3 .

Litter	Exp.	Time, days	Treatment	pH	Si fluxes, $\text{mol}_{\text{Si}}/\text{g}_{\text{DW}}/\text{day}$	Ca fluxes, $\text{mol}_{\text{Ca}}/\text{g}_{\text{DW}}/\text{day}$	Ca/Si mass ratio, Initial litter	Ca/Si mass ratio, After experiment	Si fluxes normalized to phytolith mass, $\text{mol}_{\text{Si}}/\text{g}_{\text{phyto}}/\text{day}$	Phytoliths dissolution rates, $\text{mol}_{\text{Si}}/\text{g}_{\text{phyto}}/\text{day}$ (Frayse et al., 2009a,b)
Pine	8–1	55	Ground 3 min	5.8	1.62E-07	5.31E-07	ND	ND	ND	ND
	8–2	41		8.3	4.21E-07	ND				
Birch	9–1	55	Ground 3 min	5.8	1.71E-07	4.77E-07	ND	ND	ND	ND
	11–1	48		3.0	1.31E-07	8.99E-07				
	11–2	41		10.7	9.72E-07	4.77E-07				
	9–2	41		8.3	3.25E-07	4.77E-07				
Horsetail	7–1	55	Ground 3 min	5.8	3.36E-06	1.72E-06	0.347	ND	4.73E-07	1.03E-04
	7–2	41		8.4	ND	ND			ND	
	10–2	41		10.8	ND	ND			ND	
	10–1	48		3.0	7.88E-07	7.38E-07			1.11E-07	8.08E-06
Larch	1–1	50	Ground 3 min	6.2	1.10E-06	5.06E-07	0.163	0.051	2.00E-08	4.71E-05
	2–2	69	Ground 30 min	6.2	1.29E-06	4.50E-07				
	3–2	69	Intact	5.8	9.26E-06	6.05E-08				
	1–4	54	Ground 3 min + sterilization	5.6	5.91E-07	3.97E-08				
	2–3	36	Ground 30 min	3.0	9.39E-07	4.23E-07				
	3–5	33	Ground 3 min + sterilization	5.8	1.53E-06	ND				
Elm	3–3	38	Ground 3 min	5.8	1.54E-06	1.08E-06	0.486	0.149	5.78E-08	1.00E-04
	3–4	39	Ground 3 min	2.0	ND	ND				
	2–4	40	Ground 3 min + sterilization	5.7	5.24E-07	1.73E-06				
	1–5	33	Ground 3 min + sterilization	6.5	2.24E-06	ND				
	2–5	33	Ground 3 min + sterilization	5.9	9.49E-06	ND				
Fern	2–5	33	Ground 3 min + sterilization	5.9	9.49E-06	ND	0.065	0.058	1.15E-06	6.96E-05

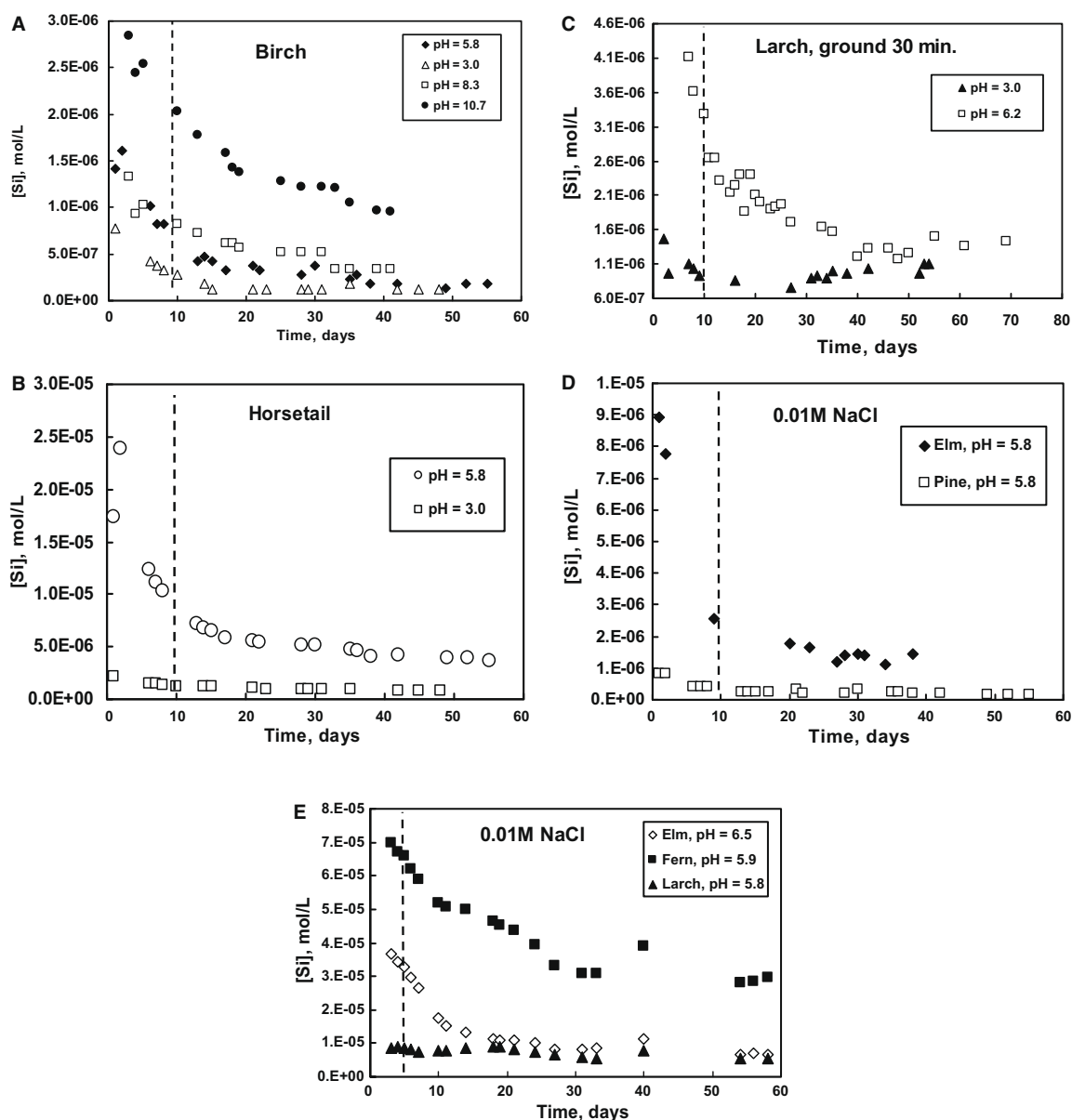


Fig. 4. Si concentration as a function of time in mixed-flow reactor equipped with 1 kDa dialysis bag. (A) Birch biomass at pH 3–10.7; (B) Horsetail biomass at pH 3.0–5.8. Dashed line represents the mechanical steady state corresponding to the time necessary to renew solution in the mixed-flow reactor five times. Experimental conditions: biomass concentration of 0.8 g_{DW}/L , 0.01 M NaCl, 25 °C. Note that the data of the birch dissolution experiment at pH 3.0 and 5.8 are subjected to high uncertainty since they approach the detection limit. (C) Larch biomass at pH 3–6. (D) Pine and elm biomass in neutral solutions. (E) Elm, fern and larch sterilized biomass dissolution at pH 6 ± 0.5 . Experimental conditions: biomass concentration of 68, 74 and 80 g_{DW}/L for fern, larch and elm, respectively; 0.01 M NaCl; 25 °C.

solutions at 25 °C, the silica release rate in sterile conditions is an order of magnitude lower than that in the presence of heterotrophic bacteria whereas for fern, sterile experiment yielded 40% higher Si release rate than that in the presence of bacteria (Fraysse et al., 2009b).

The effect of biomass grain size/dispersivity has been addressed in a series of experiments conducted on the same type of starting material (*Larix gmelinii* needles) that were used as whole (intact needles of 8–10 mm length, $S_{B.E.T.} = 2.1 \pm 0.2$ m^2/g), grounded 3 min to fine powder ($S_{B.E.T.} = 2.7 \pm 0.2$ m^2/g) and grounded 30 min ($S_{B.E.T.} = 3.23 \pm 0.25$ m^2/g). It can be

seen from Fig. 6 that the whole needles produce only $40 \pm 8\%$ lower Si concentration in the outlet solution compared to grounded material while the rates of Si release from larch biomass ground 3 min and 30 min are within ± 10 –15% similar (compare exps. 1–1 and 2–2 in Table 3).

Behavior of DOC during long-term litter dissolution in dialysis compartment is shown in Electronic Annex A3. Outlet concentration of organic carbon in form of small-size organic molecules passed through 1 kDa membrane (1–2 mg/L) is almost two orders of magnitude lower than the DOC concentration in batch experiments (100–200 mg/L).

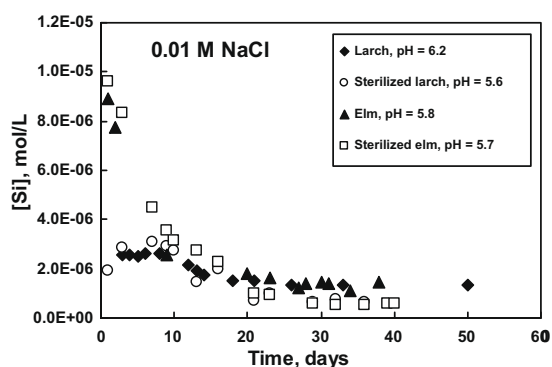


Fig. 5. Comparison of Si release from larch and elm litter biomass: sterilized (circles and squares for larch and elm, respectively) and non-sterilized (diamonds and triangles for larch and elm, respectively).

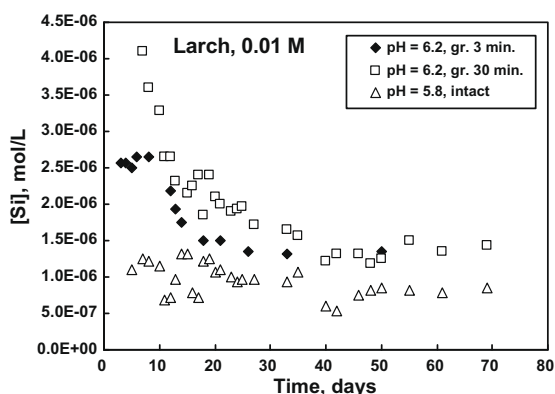


Fig. 6. Effect of the morphology and surface area of starting material on Si concentration in mixed-flow, dialysis-bag reactor, at 25 °C. Experimental conditions: solid diamonds, 3 min grounded, pH 6.2, 2.70 m²/g; open squares, pH 6.2, 30 min grounded, 3.23 m²/g; open triangles, whole intact needles, 2.12 m²/g, pH 5.8.

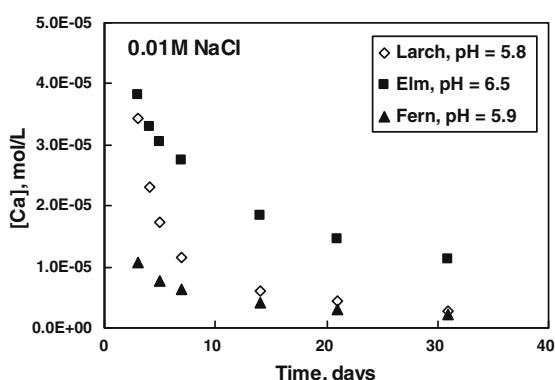


Fig. 7. Ca concentration as a function of time in mixed-flow reactor for litter dissolution experiments at 25 °C with larger amount of biomass (74, 80 and 68 g_{DW}/L for larch, elm and fern, respectively). Uncertainties on pH values are 0.1 pH unit.

Similar to litter dissolution in closed reactors, [Organic Carbon] increases with pH decrease in solution. Note that the release of DOC is not only controlled by the degradation

of the plant litter but might be influenced by the solubility as a function of pH. However, maximal DOC concentration in batch reactors (Fig. 1C and A1 of the Electronic Annex) is not directly linked to pH value and thus the effect of solubility control is not likely to be strongly pronounced in our experiments. We measured the pH, Si, and Ca concentration inside the dialysis bag at the end of the experiment with larch litter and did not find significant variation within ± 0.1 pH units, 10% and 30% of concentration.

Ca release from plant litter in mixed-flow reactor is illustrated in Fig. 7. Extremely low Ca concentrations after 1 month of reaction suggest strong depletion of plant biomass with complete removal of “labile”, highly reactive Ca pool whose presence is pronounced only during the first 5 days of reaction in the open system. In batch dissolution experiments, this labile Ca pool was pronounced after much shorter exposure times (Sections 3.1 and 3.2). It is possible that under acidic conditions aggregation of some organic molecules together with divalent cations could affect the release of divalent cations. In addition, Ca release rate might be affected by the dialysis membrane separation since most organic acids carry a charge that needs to be compensated by a cation. Ca concentration inside the dialysis bag was maximum 30% lower than that in the outlet solution although no systematic effect of pH and biomass type could be detected. We evaluated that the effect of colloidal status of metal inside the dialysis bag decreased the release rate of divalent metals by a factor of 10 (Frayse et al., 2009b). We do not anticipate such an effect to be strongly pronounced for Ca since the colloidal forms of this element in organic-rich natural waters constitute not more than 30% of its total dissolved flux (Dahlqvist et al., 2004; Pokrovsky et al., 2006). However, some colloidal forms of Ca can be responsible for lower dissolution rate in batch and mixed-flow-experiments in this work (Tables 1 and 3, respectively).

4. DISCUSSION

4.1. Two pools of Si in plant biomass?

While the occurrence of silica in plants is known mostly as phytoliths (amorphous silica particles), the presence of silica associated with organic compounds is still controversial (Epstein, 1994). Ultrastructural observations and the electron energy loss microanalysis showed the presence of silica-organic material in litter and soil (Watteau and Villemin, 2001). Inanaga and Okasaka (1995) suggested, using spectroscopic techniques, that silicon in rice may be bound with lignin-carbohydrate complexes or phenol-carbohydrate complexes in a similar way to calcium. Watteau et al. (2002) demonstrated the presence of two forms of Si in the plant roots: either diffused inside the polyphenolic substance or as a pure silica layer. Analysis of Si behavior in the course of dissolution in short-term batch reactor and in long-term mixed-flow reactors equipped with dialysis compartment demonstrates two dissolution regimes: very fast initial Si release during the first minutes/hours (batch reactor) or 1–10 days (mixed-flow reactor) followed by a slower, long-term silica release. For example, for birch litter degradation (5 g_{DW}/L) in 0.01 M NaCl at pH 6.2, the rate of Si release dur-

ing the first 15 min is equal to 9.1×10^{-5} mol_{Si}/g_{DW}/day whereas the second part of the curve yields 3.83×10^{-6} mol_{Si}/g_{DW}/day (Fig. 1A). Another example is horsetail degradation that yields initial short-term (<30 min) Si release rate in batch reactors that is 5–10 times faster than the later long-term or steady-state release (e.g., 8×10^{-5} mol_{Si}/g_{DW}/day versus 6×10^{-6} mol_{Si}/g_{DW}/day for horsetail in neutral solution, Table 1). When re-normalizing the rates from dry biomass to the weight of phytoliths in the biomass, the “slower” rates of Si release at the second stage of dissolution (in long-term batch reactor) or the “steady-state” rates of plant biomass (in flow-through reactors) are a factor of 2–3 slower (horsetail, larch, elm) or similar to (fern) the steady-state dissolution rates of individual phytoliths (see Table 3 and Fraysse et al., 2009a). This strongly suggests that the reactivity of the main part of biogenic amorphous silica within the organic matrix is close to that of the pure solid, and neither the organic matter–silica bonding nor the diffusion through the organic template limit the Si release from the solid to the solution. Therefore, our results may corroborate the hypothesis of the presence of two pool of silica in the plants: concentrated pool of phytoliths (amorphous silica aggregates of 1–100 μm size) and individual molecules H₄SiO₄ or small polymers dispersed in the organic matrix or complexed with pectin/proteins in the cell wall. Although peptide and amino acids interaction with silicic acid via hydrogen bonds and electrostatic force are widely documented (i.e., Coradin and Livage, 2001) and known to produce a SiO₂·nH₂O–protein matrix in the diatom cell walls (Hecky et al., 1973; Gélalbert et al., 2004), complexation of silica with pectin constituents has yet to be demonstrated. In any case, this pool of Si in plants is extremely labile and its presence explains high initial Si concentration in the dialysis bag experiments (Fig. 4 0–20 days of exposure) as well as the existence of two slopes for Si release in batch reactors. An alternative explanation of the existence of two slopes may be dissolution of ultrafine particles of amorphous silica, non linked to the organic matrix but attached to the phytoliths. This dissolution occurs at the very beginning of reaction thus producing a parabolic dependence of Si concentration on time, which is well documented in oceanographic works. However, such a parabolic dependence of Si release has not been observed for phytoliths plant dissolution at 25 °C at far from equilibrium (Fraysse et al., 2006, 2009a). Roughly, analysis of post-experiment Si content in residual larch and elm biomass (Table A 1.2. of Appendix 1) indicates that not more than 10–20% of total Si may be in most reactive, non-phytolith-like form directly linked to the organic matrix. For birch and pine biomass, contribution of organic matrix-linked Si to the overall Si release is higher than that for the larch, since the proportion of phytoliths in the formers is at least 30 times lower yet the biomass-normalized rates are a factor of 5–10 lower. Note that the simple mass balance approach which takes into account the proportion of phytoliths in plant biomass determined by weight method (65.7, 15.8, and 17.5 g Si/1000 g plant for horsetail, larch, and elm, respectively, Fraysse et al., 2009a) and the Si content measured by analytical technique in dry plant material (64.2, 16.3, and 17.1 g Si/1000 g, Appendix 1 of this work) does not allow quantification of different pools: the dry-ash

treatment with subsequent H₂O₂ rinsing routinely used to extract the phytoliths will inevitably convert the organic matrix-linked silica into mineral form. Therefore, rigorous quantification of the relative proportion of each Si pool in plant litter requires high-resolution microscopic techniques such as TEM and additional long-term experiments in mixed-flow reactors.

4.2. Comparison of Si, Ca and DOC release rate between different materials and different species

Comparison of Si release rates from phytoliths (Fraysse et al., 2009a), and plant biomass (this study, Sections 3.1 and 3.3) normalized to the initial source material—dry plant biomass revealed the following order of rates: pine < birch < elm ~ larch < horsetail < fern. Comparison of Si flux due to dissolution of plant litter (mol Si/g_{DW}/day), and common soil minerals is given in Fig. 8. It can be seen that Si release rate for pine and birch are comparable with that of clays in acidic conditions whereas the rates of elm, horsetail and larch biomass are 1–2 orders of magnitude higher than those of clay minerals. The rates of primary rock-forming mineral dissolution (hornblende, diopside, and olivine) as calculated for the full range of pH from data of Golubev et al. (2005) are lower or comparable with those of plant litter (not shown in Fig. 8). Therefore, results of the present study demonstrate quite high aquatic reactivity of plant litter biomass that can act as important source of silica in surface waters. This conclusion is likely to be most applicable to permafrost-dominated watersheds covered by the larch trees where the surficial waters do not encounter the deep soil mineral horizons (e.g., Pokrovsky et al., 2005b). For other temperate environments, given that the plant litter represents maximum 10% of the overall soil profile containing large amount of clays in the mineral part of the soil column, the effect of plant litter degradation on Si release may be comparable or smaller than that of clays dissolution.

Dijkstra (2003) reported, based on field measurements using the buried polyethylene bag technique, Ca mineralization rates from 5×10^{-8} – 3×10^{-7} mol_{Ca}/g_{DW}/day for 6

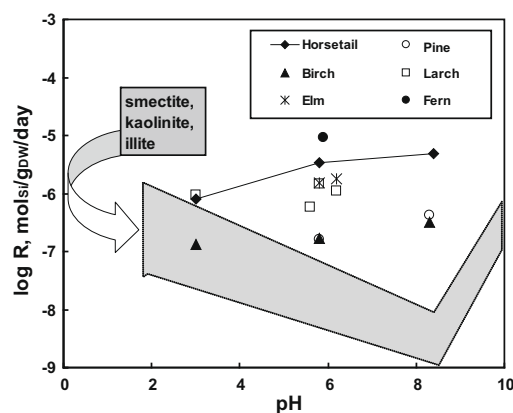


Fig. 8. Si release rates for typical soil clay minerals and plant litter as a function of pH at 25 °C. Soils clays, Köhler et al. (2003, 2005) and Golubev et al. (2006).

different tree species (maple, beech, white ash, oak and hemlock). Thorough field experiments of pine, spruce, birch and oak leaves degradation over the annual cycle in temperate forest yielded the range of Ca loss from plant biomass equal to $(1-3) \times 10^{-7}$ mol_{Ca}/g_{DW}/day (Stepanov, 1940). These values are comparable with fluxes measured in the present study ($\sim(4-5) \times 10^{-7}$ mol_{Ca}/g_{DW}/day for pine, larch and birch (Table 3).

Both short- and long-term types of batch experiments conducted in the present study demonstrated very fast leaching from plant litter of organic carbon, the rates of carbon release being much higher than those of silicon. Therefore, it is anticipated that, in the plant litter subjected to mineralization (dissolution) in the soil horizon, there will be an increase of the relative proportion of Si versus carbon in the solid phase. Indeed, previous results of spruce needles analysis evidenced a nearly linear relationship between the Si content and the age of needles (Höhne, 1963; Sommer et al., 2006).

In contrast to silica, that is present in monomeric non-colloidal form, as also followed from field experiments on plant litter leaching (Hongve et al., 2000), outlet concentration of small-size organic molecules passed through 1 kDa membrane is almost two orders of magnitude lower than the DOC concentration in batch experiments (compare Figs. A3 and A1 of the Electronic Annex). Such low DOC concentrations in <1 kDa fraction compared to <0.22 μ m fraction suggest that the hydrolysis of lignocellulose of plant tissue and plant cell breakdown in reactor does not produce small organic molecules (<1 kDa). At the same time, these organic molecules typically contribute to more than 50–80% of <0.22 μ m DOC in boreal waters draining forest floor of pine, birch and larch (i.e., Pokrovsky and Schott, 2002; Pokrovsky et al., 2005a, 2006). It is possible that the presence of microbes or longer duration of litter decomposition in the topsoil horizons are responsible for much smaller molecular size of the organic molecules in natural environments compared to those produced under laboratory conditions. Detailed characterization of DOC speciation in plant litter leachates (i.e., Hongve et al., 2000) may help to elucidate this issue but was beyond the objectives of the present study.

It has been widely argued that large initial leaching losses in litter decomposing experiments may be artifacts caused by using artificially dried leaves (i.e., Hongve et al., 2000) since air-drying can both accelerate and depress the rates at which litter decomposes (Bärlocher, 1992; Taylor, 1998). However, the artifacts of sample preparations are unlikely to affect the long-term release rates in this study as comparative experiments were performed with fresh plant biomass dried at moderate temperature (50 °C) and sterilized (120 °C), whole (intact) needles and after grinding during 3 and 30 min. In all cases, similar release rates were observed (Figs. 5 and 6, and Table 3). In contrast, alternating cycles of freezing and thawing typical in temperate and boreal regions are able to effectively disrupt the cells and release soluble components (Harris and Safford, 1996; Bunnell et al., 1977). These may induce important chemical transformations in the plant tissue and thus deserve further laboratory modeling.

4.3. Plant material dissolution in natural environment

The application of obtained results to natural setting can be performed assuming a steady state condition of the forest ecosystem, i.e., constant biomass, not aggraded forest, and no change of soil depth and mineralogical composition with time. The upper soil profile containing plant litter can be viewed as mixed-flow reactor with rainwater input corresponding to annual precipitation or runoff, the mass of litter fall in soils and the rates of their dissolution define the Si (or Ca) concentration in the outlet river water:

$$C = R * M / D \quad (3)$$

where M is the mass of litter in the ecosystem (g_{DW}/ha), D is flow rate or annual precipitation (mm/yr or L/ha/yr) and R is the experimental dissolution rate given in mol_{Si}/g_{DW}/yr. This calculation is based on the assumption that the plant litter is in permanent contact with soil/rain water and thus provides the maximal reactivity of the plant litter in its turnover cycle. To calculate C , we will assume typical parameters of boreal forest: $M = 20$ t/ha of aboveground biomass in the form of needles and leaves (10% of total biomass, ~ 200 t/ha in temperate and boreal forest, Schlesinger, 1997; Rodin and Bazilevitch, 1965), $D = 4.93 \cdot 10^6$ L/ha/yr corresponding to annual precipitation of 500 mm/yr, and $R = 3.7 \times 10^{-5}$ mol_{Si}/g_{DW}/yr corresponding to minimal plant litter dissolution rate in slightly acidic solutions typical for topsoil horizons (pH 3–4.5) measured in this study, see Table 3 and Fig. 8. This yields $C = 4.3$ mg_{Si}/L which is comparable with usual Si concentration in surface waters (4.2–5.0 mg/L, Gaillardet et al., 1999) and in soil solutions of surficial horizons (2.8–14 mg/L, Sommer et al., 2006; Pokrovsky et al., 2005a, b). Interestingly, that the calculated half-life time of plant phytoliths (time necessary to dissolve 50% of initial material) ranges between 0.5 and 3 years (Frayse et al., 2009a) whereas it is known that 30–40% of spruce, birch, and moss biomass degrade completely over the annual cycle (Sloboda, 2009).

Typical fluxes of Si forest throughfall in humid climate are on the order of 5–20 mmol_{Si}/m²/yr (Cornu et al., 1998; Sommer et al., 2006). Assuming the weight of leaves 4.8 t/ha (Lucas et al., 1993), this yields the flux of 1.1×10^{-5} – 4.0×10^{-5} mol_{Si}/g_{DW}/yr, corresponding to Si leaching from the green biomass. This value is comparable with the rates for Si release from temperate plants studied in this work. Taking into account the proportion of Si in biomass, this yields the fluxes of biogenic Si associated with plant litter degradation equal to 0.5–1.0 t/km²/yr, comparable with total annual Si fluxes in rivers of boreal and temperate watersheds (Oliva et al., 2003; Zakharova et al., 2005, 2007). Noteworthy that soil surface of boreal forest contains several times more organic matter in the form of litter than in the form of aboveground biomass (Rodin and Bazilevitch, 1965). Therefore, only partial dissolution of total (litter + aboveground) plant material will be sufficient to provide Si concentrations and fluxes encountered in the river water. However, it is important to keep in mind that some elements are recycled at a high rate within the top soil. Litter soil leachate is not in permanent contact with the soil water moving to the stream and most of the elements in the top soil solutions are taken up again.

The flux of carbon related to terrestrial primary production and respiration is around 60 Gt/yr (IPCC, 2007). With only 1% of Si in the plant biomass (10 g/kg, which is the minimal value for Si content, given Conley (2002) and lays in the range of Si concentration in plants studied in this work, Appendix 1), this yields 1.2 Gt/yr of Si involved in plant uptake and litter degradation. Assuming that 90% of Si is recycled, the resulting output value (0.12 Gt/yr) is of the same order of magnitude as the flux of dissolved Si transported by world rivers due to silicate chemical weathering (around 0.07 Gt/yr, Viers et al., 2007). However, for quantitative estimation of the proportion of plant-derived silica in the river-water, both detailed mass-balance models that take into account the roots location and equilibrium state in the soil solution (Goddéris et al., 2006) or the stable isotopic approaches (Reynolds et al., 2006) are necessary.

The main issue related to the modification of natural cycles due to global warming is the coupling between the carbon and the major element fluxes. It is known that the primary production of land vegetation will increase as the concentration of atmospheric CO₂ rises (Amthor, 1995); the theoretical growth increase should be about 40% when atmospheric CO₂ is double the ambient value (Woodward et al., 1991). This will proportionally increase the biomass involved in Si recycling and possibly the flux of Si from the soil to the river related to plant biomass degradation. At the same time, rise of annual temperature to 0.6–4 degrees over the next 100 years (IPCC, 2007) will increase the rates of inorganic soil mineral dissolution by no more than 5–10% as follows from the Arrhenius equation with corresponding activation energy (40–60 kJ/mol). Therefore, the plant litter degradation process-controlled element fluxes are able to respond in a much faster way to the environmental change compared to inorganic mineral dissolution.

5. CONCLUDING REMARKS

Short-term and long-term laboratory experiments of plant litter degradation allowed to quantify the rates and characterize the mechanisms responsible for Si and Ca release from six plants species (elm, larch, pine, birch, fern and horsetail) upon their interaction with aqueous solutions at various temperatures and pH. The measured order of Si release rate from plant biomass is comparable with Si content in organic matrix: horsetail > elm >> birch ≥ pine which suggests the governing role of plant phytoliths in Si release from plant material. Indeed, organic matter-free weight-normalized Si release rate for horsetail and larch litter is similar to that of phytoliths of this plant. This strongly suggests that the main part of Si present in the form of individual solid phases is not linked to the organic matrix and thus its reactivity is fully controlled by aqueous solution chemistry. Assuming steady-state conditions of the forest ecosystem, it was evaluated that the dissolution (lixiviation) of plant biomass located in the aboveground vegetation pool or the soil litter horizon by rainwater is capable: (i) yielding concentrations of dissolved Si encountered in interstitial soil solutions and (ii) producing the annual river fluxes of Si measured in the forested watersheds. Results obtained in the present study help to quantify the kinetic as-

pect of plant litter degradation and better constrain the factors controlling Si release to the solution from the plant biomass under conditions of environmental change.

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APPENDIX 1

1.1. Chemical composition and SSA measurements of plant litter samples used in the present study.

	Unit	Birch	Larch	Horsetail	Pine
Residual humidity at 103 °C	%	7.62	7.36	8.67	7.21
Ashes at 480 °C	%	6.36	6.58	25.2	1.38
Organic matter	%	93.6	93.4	74.8	98.6
[Si]	g/kg	0.5	16.3	64.2	0.46
[P]	g/kg	1.97	0.469	1.27	0.593
[K]	g/kg	10.6	1.04	1.54	1.06
[Ca]	g/kg	14.8	6.78	23.3	2.8
[Mg]	g/kg	2.78	2.75	1.17	0.446
[Na]	g/kg	0.132	0.036	0.122	0.0628
[Fe]	mg/kg	313	276	327	165
[Zn]	mg/kg	189	20.5	49.7	26.3
[Al]	mg/kg	385	237	433	495
Specific surface area (SSA), m ² /g					
Litter	Treatment			SSA, m ² /g	
Horsetail	Ground 3 min			3.33	
Larch	Intact			2.12	
	Ground 3 min			2.70	
	Ground 30 min			3.23	
Elm	Ground 3 min			2.34	
Fern	Ground 3 min			3.10	

1.2. Ca and Si concentration in fresh and reacted material.

Samples	Type	Ca, g/kg	Si, g/kg
Fern initial	Fresh material	2.37	36.4
Fern exp. 2–5	Post-experiment	1.34	23.3
Elm initial	Fresh material	8.31	17.1
Elm exp. 2–4	Post-experiment	2.61	17.5
Elm exp. 3	Post-experiment	0.64	13.7
Larch initial	Fresh material	6.78	16.3
Larch exp. 1–4	Post-experiment	0.91	14.2

APPENDIX 2. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2009.09.002](https://doi.org/10.1016/j.gca.2009.09.002).

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