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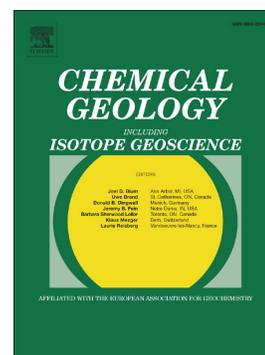
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Dynamic of boron in forest ecosystems traced by its isotopes: A modeling approach

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Keywords: Boron isotopes, nutrients, forest ecosystems, modeling, plant demand

Highlights:

1. We developed a model to assess the dynamic of boron and its isotopes in forest ecosystems
2. Responses of B dynamic to natural and anthropogenic forcings are reflected in the B isotopic compositions of the different ecosystem's pools
3. B isotopes reveal a potential tracer of nutrient cycling and a promising proxy for tracing the global functioning of terrestrial biosphere

Abstract

Understanding the factors that control the cycling of nutrients in terrestrial ecosystems is of fundamental importance given its role for example in nutrient availability to sustain forest productivity, and ultimately in soil carbon storage.

In this paper, we developed a model to assess the dynamic of boron in forest ecosystems and to appraise how the impacts on boron cycling by internal or external factors should be reflected in the changes of its isotopic compositions across an ecosystem. Despite the scarcity of data, we tested this model on two case studies and were able to reproduce the distribution of boron isotopes between the different pools of these two contrasted ecosystems. The model shows a time dependency of the boron isotopic composition of the different biotic and abiotic compartments of the ecosystem. When the forest grows, a transient enrichment in the heavy isotope up to 20‰ relative to the values at steady-state is observed in the biomass and the soil solutions. The magnitude of this enrichment, and the return time to steady state, are sensitive to B supply and plant demand for boron. Responses of B dynamic to natural or anthropogenic disturbances is well reflected in the variations of the B isotopic compositions of the different pools that make B isotopes a good potential tracer of nutrient cycling and by extension make boron isotopes a promising proxy for tracing the global functioning of terrestrial biosphere at present and in the past.

1. Introduction

Boron is an essential micronutrient for the growth of higher plants. A large fraction of boron in plants is located in cell walls where it ensures the formation and stabilization of its structure via the formation of cross-linked pectic network (O'Neill et al., 2001)

Beside ensuring cell wall structure and possibly influencing its biochemical properties (Fleisher et al., 1999), boron is involved in various physiological processes in vascular plants. It has been proposed to play a role in plant nitrogen assimilation (Bolanos et al., 2004), the development of root nodules in N-fixing plant (Yamagishi and Yamamoto, 1994), metabolism of phenolic compounds (Pfeffer et al., 1998) and to be involved in the expression levels of a number of genes (Camacho-Cristóbal et al., 2008).

Apart from these physiological roles, boron may influence litter composition and decomposition (Lehto et al., 2010) thus affecting nutrients turnover and ultimately carbon cycle in forest ecosystems.

Although the fundamental role of boron for the growth of plants has been recognized since 1920's (Warington, 1923), its biogeochemical cycle in ecosystem has retained little attention. It has been proposed that boron along with K was the most important nutrient influencing tree species distribution in tropical regions (John et al., 2007; Steidinger et al., 2015) although this conclusion has been recently refuted by Turner et al. (2017).

Studies on the status of boron and importance of vegetation cycling in forest ecosystem have also led to contrasting results.

For instance, Turner et al. (2017) estimated that the flux of boron supplied by rainfall to tropical forest ecosystem in Panama was equivalent to the annual amount of B returning to the forest floor in litter fall, suggesting that B was not a limiting nutrient. They concluded that the plant requirement for B was considerably less than for phosphorus for example

By contrast, Gaillardet and Lemarchand (2018) reported fluxes for vegetation cycling 5 to 10 times greater than the total B supply to the ecosystems by atmospheric depositions and chemical weathering for two ecosystems developed under tropical and temperate climates. These large biological fluxes are in line with the estimation at the global scale by Park and Schlesinger (2002) who estimated that the internal recycling of boron by vegetation on land was one order of magnitude larger than the inputs of boron and its export by large rivers.

As for other nutrients like K or Si, the distribution and seasonal variation of B between plant tissues, soil organic matter, soil solutions and surface water are probably influenced by biotic processes but the connection between plant demand and boron cycling in ecosystems needs to be elucidated. Contribution from external inputs by atmospheric depositions, loss of soil organic matter by erosion or feedback between supply by chemical weathering and plant demand along with responses to anthropogenic disturbances for examples remain to be established.

In this regard, mass dependent fractionation of stable isotopes can be used effectively to trace processes which transfer matter to or out and from one compartment to another in an ecosystem (Bouchez et al., 2013). For instance, stable isotopes of Ca and Si have been successfully used to trace the cycling of these elements in forested ecosystems (Holmden and Belanger, 2010, Riotte et al., 2018).

With the exception of rare magmatic environments, boron is always bound with oxygen and can be three or four coordinated. For example, in aqueous solution boron forms an acid base couple ($pK_a = 9.24$ at 25°C , Baes and Mesmer, 1976) where boric acid, $\text{B}(\text{OH})_3$, is trigonal and borate ion, $\text{B}(\text{OH})_4^-$, is tetrahedral. Boron has two stable isotopes, ^{10}B and ^{11}B and the higher bond strength of the trigonal coordination, explains its enrichment in ^{11}B relative to the tetrahedrally coordinated boron. For instance, boric acid is enriched in ^{11}B by about 27‰ compared with borate ion (Klochko et al., 2006). Thus, changes of coordination between different phases induce large isotopic fractionations for example during incongruent dissolution of minerals, adsorption onto mineral or organic surfaces. Moreover,

boron isotopes are potentially fractionated during its uptake by roots (Marentes et al., 1997; Cividini et al., 2010; Geilert et al., 2019) and strong evidences exist that intra-plant isotopic fractionations exist (Geilert et al., 2015; Gaillardet and Lemarchand, 2018). At the scale of the ecosystem, the B isotopic compositions, expressed in the classical δ notation, of different compartments cover a range up to 80‰ (Cividini et al., 2010; Gaillardet and Lemarchand, 2018) and vegetation (leaves) and leaf exudates appear to be enriched in the heavy isotope relative to atmospheric inputs and soil.

This paper is an attempt, through a modeling approach, to predict the δ isotopic signatures of different pools during the development of a forested ecosystem and how the impacts on boron cycling by external factors are reflected in the changes of its isotopic compositions across the ecosystem. Especially we examined the distribution of B isotopic compositions of soil solutions and by extension those of streams or rivers, as a signature of biotic demand in terrestrial ecosystems under different boron supply rates and anthropogenic forcings. The results of the model show the strong promise of boron isotopes in ecosystems as a proxy for terrestrial biosphere functioning.

2. Methods

2.1. General description of the model

A synthetic view of the model with the different pools and fluxes is illustrated Figure 1. A list and a description of the pools, fluxes, and parameters are given in Tables SI_1 and SI_2. The model starts from a bare ground and the forest develops through time till the living biomass reaches an equilibrium for which the biomass remains constant. We do not explicitly model the forest development and the evolution of the carbon stocks but we model the evolution of the different boron stocks and their isotopic compositions till the system reaches a steady-state.

Figure 1: Schematic description of the model with the different pools and fluxes considered. A list and a description of the pools, fluxes, and parameters are given Tables SI_1 and SI_2

The soil compartment is divided into three soil layers of different sizes, two being located in the root zone and one below the root zone. The upper soil layer, in the following the soil organic layer (SOL), which includes the forest floor and whose thickness increases with the development of the vegetation (Supporting information SI_1), only receives external inputs from the atmosphere (F_{atm}). This layer exchanges dissolved boron with the lower soil mineral layer (SML) within the root zone via the downward percolation of water. Boron is supplied to the soil mineral layer by chemical weathering (CW) and exported out of the root zone to a mineral layer (ML) by percolation. This layer is also supplied in boron by chemical weathering at the same rate, CW , as the SML. Dissolved boron is leached out of this layer as drainage.

Vegetation takes up boron from the two upper layers and we assumed that the uptake rate of boron by the vegetation is partly driven by the water transpiration rate (passive uptake) which is a function of soil moisture (Porporato et al., 2003; Buendia et al., 2010) and depends on climate and vegetation characteristics (Porporato et al., 2003; Schlesinger and Jasechko, 2014).

To take into account the root distribution with depth (Jackson et al., 1996), we assumed that 50% of the roots are located in the upper soil layer.

2.2. Boron supply rates by atmospheric depositions and chemical weathering

In the model, inputs of boron by atmospheric depositions and chemical weathering are taken as variables. Especially, dissolution of primary minerals and precipitation of secondary minerals like clays or oxides oxides (incongruent dissolution) are not explicitly described or modeled. Hence, the input of B by chemical weathering is a net flux. As a consequence, the fractionation of B isotopes during the co-precipitation of boron from the soil solution with secondary minerals (Gaillardet and Lemarchand, 2018

and references therein) is not modeled either as we consider here that this process occurs over timescales greater than the timescale of ecosystem development. Thus, the $\delta^{11}\text{B}$ value associated to the chemical weathering flux is also a variable which implicitly takes into account the B isotopes fractionation during the incongruent dissolution of minerals in the soil.

2.3. Passive vs active boron uptake by the vegetation

The hypothesis that the uptake of B by plants is passive and only driven by transpiration has been challenged (e.g. Pfeffer et al., 1999). A term describing the active uptake of boron when the plant demand in boron is not fulfilled by the passive uptake only has therefore been introduced in the model. The uptake of boron by plants is regarded as an additive process between passive uptake and active uptake (Porporato et al., 2003).

$$\text{Upt}_B = \text{Upt}_B^{\text{passive}} + \text{Upt}_B^{\text{active}} \quad (1)$$

Passive uptake is proportional to the water uptake by plants and the concentration of dissolved boron in the considered soil layer taking into account the root distribution with depth.

As we consider two soil layers, the total uptake of boron, Upt_B is the sum of the uptake from the two soil layers, SOL and SML, thus the total passive uptake is given by:

$$\text{Upt}_B^{\text{passive}} = f(t) \times \eta \times (X \times [B_{\text{SOL}}] \times s_{\text{SOL}} + (1 - X) \times [B_{\text{SML}}] \times s_{\text{SML}}) \quad (2)$$

where s is the soil moisture, η is the maximum transpiration rate which is assumed to depend on climate and vegetation (Porporato et al., 2003), X the fraction of water absorbed from the soil organic layer, $[B_{\text{SOL}}]$ and $[B_{\text{SML}}]$ are the concentrations of dissolved boron in the soil organic layer and the soil mineral layer, respectively. The function $f(t)$ describes the production of biomass with time according to:

$$f(t) = (1 - e^{-t/T_{\text{max}}})^n \quad (3)$$

where t is the time, and in the simulations n was chosen equal to 0.952 and T_{max} to 15 insuring that the biomass production will reach a constant value after less than 100 years.

We used in the case of boron a similar formalism as proposed by Porporato et al. (2003) to simulate the active uptake of soil nitrogen by vegetation.

Importantly, we defined a boron demand term (Dem), as the optimum flux of boron ensuring optimal growth (expressed in mol/m²/yr), scaled with the function f(t) (i.e. the boron demand of the vegetation increases with the biomass production). In the case where the passive uptake does not satisfy the plant demand, an active uptake compensates for the deficit.

Active uptake is assumed to obey Michaelis-Menten type kinetics (Stangoulis et al., 2001; Silberbush et al., 2005) when the influx of boron is limiting or equal to the difference between the plant demand and the passive uptake otherwise. Active uptake of B can then be defined mathematically as:

$$Upt_B^{active} = \begin{cases} 0 & \text{if } Dem \times f(t) - Upt_B^{passive} < 0 \\ \frac{J_{max} \times f(t) \times ([B_{soil}] - [B_{min}])}{K_m + ([B_{soil}] - [B_{min}])} & \text{if } \frac{J_{max} \times f(t) \times ([B_{soil}] - [B_{min}])}{K_m + ([B_{soil}] - [B_{min}])} < Dem \times f(t) - Upt_B^{passive} \\ Dem \times f(t) - Upt_B^{passive} & \text{if } \frac{J_{max} \times f(t) \times ([B_{soil}] - [B_{min}])}{K_m + ([B_{soil}] - [B_{min}])} > Dem \times f(t) - Upt_B^{passive} > 0 \end{cases} \quad (4)$$

Where J_{max} , K_m and $[B_{min}]$ are maximum influx, Michaelis–Menten coefficient and minimal B concentration (at which $Upt_B^{active} = 0$), respectively. J_{max} is a function of root surface area (Dannel et al., 2001; Stangoulis et al., 2001) thus is scaled by f(t), i.e. J_{max} increases with the production of biomass and will depend on the root distribution for the soil layers considered (see Supporting information SI_1 for the estimation of the demand and the different parameters).

2.4. Allocation of boron to the coarse roots/woody part and leaves

A fraction of the boron taken by the vegetation is allocated to the roots/wood (f_{wood}) and the leaves (f_{leaves}) whereas the remaining return to the forest floor soil solution as leaf exudates (f_{ex}). The fraction of boron exudated (f_{ex}) is fixed at 0.5, about half of the flux boron returning annually to the forest floor associated to leaf litter fall (Gaillardet and Lemarchand, 2018). The fractions of boron allocated to root/wood (f_{wood}) and to the leaves (f_{leaf}) are either kept constant through the run to reach a predefined

ratio between the stock of boron in the root/wood compartment and that in the leaf compartment ($B_{\text{wood}}/B_{\text{leaf}}$) or f_{wood} and f_{leaf} can be adjusted at each step to keep a nearly constant $B_{\text{wood}}/B_{\text{leaf}}$ ratio. For instance, the ratio between the living coarse root/wood biomass and the leaf biomass varies from 3 to 8 for birch, pine and spruce stands between 40 years old and 100 years old on drained mire in Finland (Finer, 1989). In addition, Turner et al. (2017) report a ratio of nearly 9 for a lowland tropical forest in Panama of at least 200 years old.

Litter fall and mineralization of soil organic matter

Boron also returns to the forest floor layer as leaf litter fall and wood debris. The fraction of boron returning each year to the soil as litter is taken proportional to the stocks of B in leaves and roots/wood. The rate of boron returning to the floor as leaf litter fall, k_{leaf} , was chosen between 0.5 year^{-1} and 1 year^{-1} , ensuring that the boron residence time in the leaf pool is equal to the leaves turnover i.e. 1 year for broadleaf deciduous forests and 2 years for tropical broadleaf evergreen forests and needleleaf evergreen forests. The boron residence time in the woody parts, equal to the inverse of the rate of boron returning to the floor as wood litter fall, k_{wood} , is fixed and is assumed to be that of the woody biomass. Residence time of woody biomass is highly variable from one ecosystem to another (Xue et al., 2017) and can vary from about 20 years to 130 years for tropical forests solely (Galbraith et al., 2013). In the model, we chose the woody biomass residence time equal to 100 years.

We distinguish in the model the leaf litter pool from the wood litter pool. The organic boron associated to these two distinct pools has different fates. Whereas, the organic boron associated to the leaf litter pool is rapidly released to the SOL solution via litter decomposition, the wood litter decays more slowly so the associated organic B is characterized by a longer residence time before it is released into the SOL solution. We assumed different decay rates, k_{min} , for the wood litter and leaf litter of 0.006 year^{-1} for the wood litter and equal to 0.3 year^{-1} for the leaf litter (Pietsch et al., 2014). In the model, litter decay rates vary as a function of the temperature and soil moisture (Lloyd and Taylor, 1994) (Supporting information

SI_1). In a series of simulations, we examined the effects of soil erosion on the B dynamic. For these simulations, we assumed that the loss of soil organic boron by erosion was proportional to the stocks of B in the leaf and roots/wood litter/humus pools (Supporting information SI_1).

2.5. Isotopic fractionation during B root uptake, B translocation and organic matter mineralization

In the model, evolution of the B isotopic compositions of the different pools is controlled by the isotopic fractionation associated to the different processes which control the B fluxes. Only few studies focused on B isotopic fractionation during the transfer of boron from the soil to the plant and during the translocation of boron within the plant. Marentes et al. (1997) shown that for the three plant species they studied, two were enriched in ^{11}B relative to the nutritive solution whereas one shown no enrichment. However, the enrichment in ^{11}B measured seems to be unrealistic which results in isotopic fractionations between the solution and the plant in the order of the percent. In contrast, Cividini et al., (2010), concluded on the absence or a slight preference for the light isotope (less than 5‰) during the uptake of B by the vegetation and Lemarchand et al. (2005) shown large isotopic fractionations associated to the complexation of boron by organic matter in favor of ^{10}B . More recently, Geilert et al. (2019) suggested the preferential root uptake of ^{11}B during passive uptake and ^{10}B during active uptake. In the following, we assumed that the boron isotopes absorbed by the roots are potentially fractionated relative to the solution only in the case where the uptake of boron by roots is active. We performed different series of simulation with different isotopic fractionation factors i.e. 0.990-0.995 (the light isotope is preferentially absorbed by the roots) and 1 (no isotopic fractionation). In addition, we associated an isotopic fractionation factor of 0.973 to the incorporation of boron into the wood/root (similar to isotopic fractionation factor associated to B complexation by humic acids at pH =5-7, Lemarchand et al. (2005)) and an isotopic fractionation of 0.99 to the allocation of boron to the leaves. The difference between the two isotopic fractionation factors can be explained by the fact that a

fraction of boron allocated to the leaves is not structurally bound (Camacho-Cristobal et al., 2008; Stangoulis et al., 2010) resulting in an apparent fractionation factor closer to 1. We modeled the evolution of the isotopic composition between the different organs from the root/wood to the leaves by a Rayleigh distillation as it was observed in the case of Si isotopes for example (Ding et al., 2005). Hence, the isotopic composition of B in solution transported into the plant becomes gradually heavier in the course of the incorporation of boron into plant tissue and progressively increases from the root to the leaves as observed by Geilert et al. (2015). The remaining boron returns to the forest floor by leaf exudation without additional isotopic fractionation. To take into consideration the greater mobility of non-structurally bound boron during organic matter remineralization, we associated an isotopic fractionation factor in favor of the preferential release of the heavy isotope equal to 1.01 during the leaf litter decay. On the contrary, for the mineralization of the wood litter, we did not associate any isotopic fractionation.

The isotopic composition of B taken up by the vegetation is related to that of the soil solution by the relationship

$$R_{\text{upt}} = \alpha_{\text{upt}} \times R_{\text{sol}} \quad (5)$$

Where R_{upt} , R_{sol} and α_{upt} are the isotopic ratios of B taken up by the vegetation, in the soil solution and the isotopic fractionation factor associated to the B uptake.

Calculation of the isotopic composition of boron taken up by vegetation is implemented as follows. Uptake of B by roots occurs in the two soil layers, thus the isotopic composition of boron taken up by vegetation is the average of the isotopic composition of B taken up from the two layers weighted by their uptake fluxes. In addition, we considered that the total uptake is the sum of a passive uptake process which does not induce any isotopic fractionation and an active uptake which favors the uptake of the light isotope. Hence, for each soil layer, the isotopic composition of boron taken up by the roots, is calculated as the average between the passive and active uptakes weighted by their respective contributions.

The isotopic composition of B accumulated into the root/wood is given by

$$R_{wood} = [R_{upt} - R_{upt} \times (1 - f_{wood})^{\alpha_{inc-wood}}] / f_{wood} \quad (6)$$

where R_{wood} is the isotopic composition of B accumulated into the root/wood tissues, $\alpha_{inc-wood}$ the isotopic fractionation factor associated to the incorporation of boron into the wood/roots and f_{wood} the fraction of boron incorporated into root/wood tissues.

The isotopic composition of B lost by exudation is given by

$$R_{ex} = R_{upt} \times \left(\frac{f_{ex}}{1 - f_{wood}} \right)^{\alpha_{inc-leaf} - 1} \times (1 - f_{wood})^{\alpha_{inc-wood} - 1} \quad (7)$$

where R_{ex} is the isotopic composition of B returning to the soil by exudation, f_{leaf} , the fractionation of boron incorporated into leaf tissue and $\alpha_{inc-leaf}$ the isotopic fractionation factor associated to the incorporation of boron into the leaf tissue.

The isotopic composition of B accumulated into the leaves is given by

$$R_{leaf} = \frac{R_{upt} \times \left[(1 - f_{wood})^{\alpha_{inc-wood} - 1} - f_{ex} \times \left(\frac{f_{ex}}{1 - f_{wood}} \right)^{\alpha_{inc-leaf} - 1} \times (1 - f_{wood})^{\alpha_{inc-wood} - 1} \right]}{f_{leaf}} \quad (8)$$

Where R_{leaf} is the isotopic composition of B accumulated into the leaf tissues and f_{ex} the fraction of boron lost by exudation.

Pools and fluxes along with the different parameters and equations are provided in the Supporting Information SI_1, Tables SI_1 and SI_2.

We tested the model on the two case studies (Cividini et al., 2010; Gaillardet and Lemarchand, 2018) of small watersheds, in which a rather comprehensive distribution of boron and its isotopes between different pools of an ecosystem has been measured. The distribution of the isotopic compositions within the different pools of the ecosystems estimated by the model are in line with the isotopic compositions reported by the authors. A description of the simulations is detailed in the Supporting

Information SI_2, the values of the different parameters are listed in Tables SI_3 and SI_4 and the results are illustrated in Figures SI_1, SI_2, SI_3 and SI_4.

3. Results and discussion

3.1. Dynamic of boron in forest ecosystems under different supply rates of boron

We fixed the atmospheric inputs at $0.03 \text{ mmol/m}^2/\text{yr}$ and made the inputs from chemical weathering vary from 0.1 to 60 times the atmospheric supply resulting in total inputs of boron to the ecosystem ranging from about $0.036 \text{ mmol/m}^2/\text{yr}$ to $3.63 \text{ mmol/m}^2/\text{yr}$. For comparison, the export rates by large rivers of dissolved boron vary from $0.037 \text{ mmol/m}^2/\text{yr}$ for the Amazon to $2.22 \text{ mmol/m}^2/\text{yr}$ for the Salween (Lemarchand et al., 2002). This formulation of the total B inputs to the ecosystem is in agreement with the conclusions of Lemarchand et al. (2002) that globally the export of dissolved boron by rivers are dominated by rock weathering and with the general view that atmospheric depositions are the main source of nutrients for limited ecosystems. The boron isotopic compositions of the atmospheric and weathering inputs are chosen equal to 20‰ and 0‰, respectively. The relatively high $\delta^{11}\text{B}$ value chosen for the atmospheric inputs is compatible with the values measured in continental rainwater (Cividini et al., 2010, Foux et al., 2017).

For all the runs, the boron demand of the vegetation and the maximal influx, J_{max} , were fixed at values of $3 \text{ mmol/m}^2/\text{yr}$ and $20 \text{ mmol/m}^2/\text{yr}$, respectively, in the range of the values reported for B uptake in forest ecosystem and estimated for J_{max} (Supporting Information SI_1). In addition, we performed the same simulations for different values of the isotopic fractionation factor during the active uptake by plants (i.e. $\alpha_{\text{upt}}=1$ and $\alpha_{\text{upt}}=0.99$) (Table SI_5).

3.1.1. Evolution of the boron stocks and isotopic compositions of the different pools during the forest development.

Relative evolutions through time of the stocks of boron in the leaving biomass will depend on how boron taken up by the vegetation is allocated to the coarse root/wood biomass and the leaf biomass. In the case where the fraction of boron allocated to the wood is kept constant to attain a fixed ratio (e.g. 8) between the stocks of boron in the woody biomass and in the leaves when the system has reached a steady state, during the early stages of development, the leaf pool dominates the stock of boron in the living biomass. Progressively, the stock of boron in the leaving wood biomass increases to reach the final ratio of 8 between the stock of boron in the woody biomass and the stock of boron in the leaf biomass (Figure SI_5). In the case where the ratio between the stock of boron in the wood biomass and the leaf biomass is fixed to a constant value, the fraction of boron allocated to the coarse root/wood biomass progressively decreases to value chosen in the first case (Figure SI_5). The time for the system to reach a steady state is a function of the B supply by chemical weathering and atmospheric depositions. In the conditions of the simulations, stocks and fluxes of boron attain constant values in less than 200 years for systems characterized by relatively high supplies of boron whereas for the most limited systems, steady values are not yet reached after 1000 years.

Dynamics of the B isotopic compositions of the vegetation and the soil solutions under different boron supply rates are illustrated in Figures 2 and 3.

Figure 2: Evolution of the B isotopic composition of the soil solution in 3 different soil layers with the development of a forest for different supply rates of boron (atmospheric inputs, F_{atm} and chemical weathering, CW) and different B fractionation factors associated (ϵ) to the active uptake of boron by roots

In the case where the active uptake of boron by roots does not fractionate its isotopes, all the simulations show a transient enrichment in ^{11}B of the soil solutions relative to the inputs. This enrichment is explained by the transient storage of the light isotope in the living biomass and the soil organic pool, especially in the woody biomass characterized by a lower turnover rate than that of the leaf biomass. Because of the storage of the light isotope in the vegetation tissues, exudates are enriched in ^{11}B , partly controlling the isotopic composition of the soil solution especially in the soil organic layer along with the decay of the leaf litter characterized by a rapid decay rate. Control of leaf exudates or throughfall on the B isotopic composition of the soil solutions can be highlighted by increasing or decreasing the fraction of boron returning to the soil solution as exudate, f_{ex} . Higher(lower) values of f_{ex} results in a smaller(larger) fraction of boron stored in the woody biomass and in consequence, to B isotopic compositions of exudates less (more) enriched in ^{11}B relative to the uptake. Magnitude, up to nearly 20 ‰ for the soil solution in the root zone and duration, from about 50 years to more than 500 years, of this enrichment appear to depend on the B supply to the ecosystem. More exactly, both magnitude and duration depend on the ratio between the net storage of boron in the biomass (living and dead) and the total supply (atmospheric deposition and chemical weathering) of boron to the root zone (Figure SI_6). For ecosystems characterized by low supply of boron, the root uptake of boron and the transient storage of ^{10}B in the biomass have a stronger impact on the isotopic composition of the soil solution than for ecosystems characterized by high supply of boron for which soil solutions are quickly replenished in boron. In the simulations where the ratio between the stock of boron in the woody biomass and the leaf biomass is kept constant during the run, the transient enrichment in ^{11}B is enhanced compared with the simulations where the fraction of boron allocated to the woody biomass is kept constant (not shown). This result is explained by the larger transient net storage of boron in the woody biomass in the former case (Figure SI_6). For ecosystems characterized by low supply rates of boron, the transient increase of $\delta^{11}\text{B}$ values of soil solutions within the root zone is enhanced when the

active uptake of boron by roots favors the uptake of the light isotope because comparatively more ^{10}B is stored in the woody biomass (Figure 2). However, as the B isotopic composition of the soil solution in SOL is controlled by the overall isotopic composition of the vegetation, it is lower than the B isotopic composition of SML and progressively will become enriched in the light isotope relative to the inputs. The propagation of this transient increase of the soil pore water $\delta^{11}\text{B}$ value below the root zone is illustrated in Figure 2 which shows that the signal is time delayed and of lower amplitude, buffered to some extent by the B input from chemical weathering. In line with the conclusions of Gaillardet and Lemarchand (2018), the isotopic composition of soil pore water varies with depth reflecting the more important contribution of vegetation cycling in the top soil layer relative to the deeper layers controlled by weathering reactions.

Figure 3: Evolution of the B isotopic composition of the living biomass and the leaf exudate with the development of a forest for different supply rates of boron (atmospheric inputs, F_{atm} and chemical weathering, CW) and different B fractionation factors (ϵ) associated to the active uptake of boron by roots

Differences in the evolution of the isotopic compositions of the different vegetation pools (i.e. wood vs leaf) is partly explained by the different turnover rates. Because of the high turnover rate of the leaf pool, the isotopic composition of the leaves responds quickly to the change of the isotopic composition of the soil solution whereas changes of the isotopic composition of the woody biomass are delayed (Figure 3).

3.1.2. Boron distribution and isotopic compositions of the different pools after the ecosystem has reached a steady-state.

In the conditions of the simulations, after the ecosystem has reached a steady-state, the stock of boron in the living biomass varies from 9.5 mmol/m² (103 mg/m²) to 12 mmol/m² (130 mg/m²) when the uptake of boron is active and obeys Michaelis-Menten type kinetics. In these cases, boron is “limiting” as the plant demand is not fulfilled by the root uptake. When the uptake of boron is active and controlled by the demand, (in that case boron is not “limiting”) the stock of boron in the living biomass reaches a value of 12.5 mmol/m² (135 mg/m²). Data on B stock in living biomass for forest ecosystems are scarce but seems to widely vary across different ecosystems. For instance, Finer (1989) reported stocks of B in above and below ground tree biomass ranging from 15 to nearly 77 mg/m² for tree stands developed on drained mire in Finland whereas Turner et al. (2017) reported stocks of B for lowland tropical forests in Panama of nearly 800 mg/m². Hence the values predicted by the model are in the same order of magnitude with the stocks of boron reported so far in the literature.

Figure 4: Relationships at steady state between the demand normalized to the inputs and (a) the vegetation cycling, (b) the ratio between active uptake and the passive uptake of boron by roots, (c) and (d) the enrichment in B of the organic soil layer and the bottom layer of the root zone. The limit for boron limitation has been fixed arbitrarily and marks the transition between the two formulations for active B uptake by roots (see text for details)

As expected, at steady-state, the degree of boron cycling by vegetation expressed as the ratio between the total uptake of boron by vegetation and the B hydraulic loss at the base of the SML (equal at steady-state to the total B inputs) increases with the ratio between the total inputs and the plant demand (Figure 4a). In a same way, the ratio between the B active uptake and the B passive uptake by roots increase with the ratio between the total inputs and the plant demand (Figure 4b). Hence, in conditions of low B supply, boron is intensively recycled by the biomass before being exported out of the root zone

by drainage. This intense recycling of boron by the biomass coincides with a more important contribution of the soil organic layer to the total boron uptake by roots (Figure 4c)

In the case where the uptake by the vegetation is active, the model predicts a progressive boron enrichment in SOL relative to SML along with the increase of boron cycling by vegetation which is in turn controlled by the ratio between the total inputs and the plant demand (Figure 4d). This is in agreement with the general observation that limiting nutrients accumulate in the top soil through vegetation cycling via litter decay and throughfall (Jobbagy and Jackson, 2001, Cividini et al., 2010).

In the case where the active uptake of boron favors the light isotope, at steady state, evolutions of the difference between the B isotopic compositions of the vegetation pools and the inputs show a decrease with the ratio between the demand and the inputs (Figure SI_7a). Because the B isotopic composition of the SOL is mainly controlled by the inputs from the vegetation, the difference between the B isotopic compositions of the SOL and the inputs follows a similar evolution with the demand normalized to the inputs (Figure SI_7b). The SOL and the vegetation become progressively enriched in ^{10}B along with the increase of the ratio. In the case where boron is limiting (i.e. for low supply rates), the B uptake by roots is essentially active (thus resulting in a larger isotopic fractionation) whereas for higher B supply rates, a significant fraction of boron is absorbed passively (resulting in a smaller isotopic fractionation).

In the case where no isotopic fractionation is associated to the active uptake of boron by roots, isotopic composition of the soil pore water within the root zone is homogenized by vegetation cycling and is controlled by the $\delta^{11}\text{B}$ value of the inputs.

Leaves are enriched in the heavy isotope by about 20‰ relative to the root/wood compartment (Figure SI_7a), in agreement with the observations of Geilert et al., (2015) and Geilert et al. (2019) who measured for various plant species isotopic differences between the upper leaves and the roots between 24‰ and 27‰. The model predicts an enrichment in ^{11}B of the leaf exudates relative to the leaves of about 14‰, also in agreement with the observations of Cividini et al. (2010) and Gaillardet and

Lemarchand (2018).

3.2. Effects of plant demand on B cycling for B limited ecosystems

Due to the relative large range of boron uptake rates measured or estimated for forest ecosystems (Finner, 1998; Cividini et al., 2010; Turner et al., 2017; Gaillardet and Lemarchand, 2018), we tested the effects of plant requirement on the boron dynamic in relation with inter species variability and/or in responses to various stresses. For different plant demands, Dem , we postulated that the maximal influx of boron, J_{max} , will change accordingly. We carried out a series of simulations for a B limited ecosystem where Dem takes the values of 3 mmol/m²/yr and 6 mmol/m²/yr and the associated values of J_{max} are 20 mmol/m²/yr and 40 mmol/m²/yr, respectively (Table SI_6). In the two cases, the plant requirement is not satisfied and the active uptake obeys Michaelis-Menten kinetics. Hence, the value of the maximal influx will control the dynamics of boron and its isotopes. A higher plant demand and thus a higher value of J_{max} results in an enhancement of the vegetation recycling and in a larger biomass pool of boron as well. At steady state, the stock of boron in the living biomass is 8 μ mol/m² (about 90 mg/m²) when the Dem and J_{max} values are equal to 3 mmol/m²/yr and 20 mmol/m²/yr, respectively, whereas it reaches 23 μ mol/m² (about 250 mg/m²) for a Dem value equal to 6 mmol/m²/yr and a J_{max} value equal to 40 mmol/m²/yr. Hence, high plant demand increases the transient storage of ¹⁰B in the biomass and delays the return to steady-state of the system. For instance, given a demand of 6 mmol/m²/yr and maximal influx of 40 mmol/m²/yr, an enrichment in ¹¹B of the soil solutions relative to the inputs lasting for about 1000 years is predicted by the model propagated to other B pools of the ecosystem (Figure 5a). In the case where the active uptake of boron by roots does not fractionate B isotopes, $\delta^{11}B$ values higher than 35 ‰ are predicted for soil solution within the root zone. This enrichment in the heavy isotope is even more marked for the leaf exudate characterized by isotopic compositions reaching 45 ‰ (Figure 5b) whereas the composition of the total inputs is about 18 ‰.

Figure 5: Evolution with time of the B isotopic compositions of (a) the soil solutions and (b) living biomass as well as the leaf exudate for a B limited ecosystem characterized by different values of the plant demand and maximum B influx.

These high values for the soil pore water and leaf exudate are in line with the range of the isotopic compositions from 28‰ to 44‰ measured in the dissolved load of some tropical large rivers (Lemarchand et al., 2002; Louvat et al., 2011; Louvat et al., 2014). Both the fluxes of boron at the base of the SOL and associated to leaf exudation are much larger than the inputs by chemical weathering and atmospheric deposition (Figure SI_8). Hence, the high isotopic compositions of these tropical large rivers could be explained by the control of overland flow of the riverine dissolved boron budget. This would imply that boron and along with other nutrient is lost from the ecosystem, aggravating its boron deficiency. If so, boron isotopes reveal to be a good probe of the nutrient dynamic in ecosystems.

3.3. Consequences of the loss of soil organic boron by physical erosion in forest mountain ecosystems

Removal of soil organic nutrient by physical erosion can exert an important control on nutrient cycling. For instance, Hilton et al. (2013) highlighted the role of physical erosion on the loss of nitrogen from forest mountain ecosystem, evidenced by the relationship between the N isotopic composition of soil organic matter and the slope of the catchment.

We conducted a same series of simulations for ecosystems where the plant demand for boron is fixed but which are characterized by different supply rates of boron and various loss rates of soil organic boron. In the simulations, the export rate, k_{loss} , varies from 0.01 yr^{-1} to 0.05 yr^{-1} (Supporting Information SI_1, Table SI_7). In other way, between 1% and 5% of the soil organic boron stock is lost annually by physical erosion.

A comparison of the temporal evolutions of B isotopic compositions of the different compartments of the ecosystem in the absence or not of erosion is illustrated in Figure 6.

Figure 6: Comparison of the temporal evolutions of B isotopic compositions for different supply rates of boron of the different compartments of the ecosystem in the absence (dashed curves) or not (full curves) of erosion. The upper panels show the evolutions of the isotopic compositions of the soil solutions and the lower panels the evolutions of the isotopic compositions of the living biomass and the leaf exudates.

Because the biomass is enriched in the light isotope, the removal of soil organic boron by soil erosion leads to a further increase of the B isotopic composition of the soil solutions relative to the inputs and consequently of the compositions of the different compartments of the ecosystem. The system will eventually reach a steady state but for which the isotopic compositions of boron leaving the root zone will be fractionated relative to the inputs and enriched in the heavy isotope. For all the simulations, we assumed an absence of isotopic fractionation associated to the active uptake of boron by roots. In the case where the active uptake would favor the light isotope, enrichment in the heavy isotopes of the different pools would be enhanced.

At steady-state, as the efficiency of the B cycling by the vegetation increases with the decrease of the boron supply rate, for a given export rate, the ratio between the export of soil organic boron and the inputs increases with the decrease of B supply rates (Figure SI_9a). In addition, increase of the loss of soil organic boron might shift the status of an ecosystem from B non-limited to B limited (Figure SI_9a).

When the system has reached a steady-state, for a given loss rate of organic boron by physical erosion, the magnitude of the shift of the $\delta^{11}\text{B}$ values compared with the composition of the inputs depends on the B status of the ecosystem. For B limited ecosystem, the model predicts enrichment in the heavy isotope of the SOL and SML dissolved boron between 12‰ and 19‰ for soil organic boron erosion rates

of $19 \mu\text{mol}/\text{m}^2/\text{yr}$ ($200 \mu\text{g}/\text{m}^2/\text{yr}$) and $130 \mu\text{mol}/\text{m}^2/\text{yr}$ ($1,400 \mu\text{g}/\text{m}^2/\text{yr}$) (Figures 8b and 8c). When boron is not limiting, this shift varies from less than 1‰ to nearly 12‰ for organic B losses between $53 \mu\text{mol}/\text{m}^2/\text{yr}$ ($570 \mu\text{g}/\text{m}^2/\text{yr}$) and $150 \mu\text{mol}/\text{m}^2/\text{yr}$ ($1,620 \mu\text{g}/\text{m}^2/\text{yr}$) (Figures SI_9b and SI_9c).

Similar evolution trends are predicted for the living biomass with enrichment in the heavy isotope compared with the values predicted in the absence of erosion between 15‰ and 20‰ for strongly B limited ecosystems (not shown).

For comparison, Hilton (2017) compiled the biospheric organic carbon export rates by physical erosion from worldwide forested mountain catchments with values ranging from $1 \text{ gC}/\text{m}^2/\text{yr}$ to $87 \text{ gC}/\text{m}^2/\text{yr}$. Assuming that soil organic matter contains 50% carbon in mass (Folgarait, 2010) and that its B content is around 10 ppm, similar to the value measured in litter (Finer, 1998), between $20 \mu\text{g}/\text{m}^2/\text{yr}$ and about $1,750 \mu\text{g}/\text{m}^2/\text{yr}$ of soil organic boron would be exported by physical erosion, in the range of the values predicted by the model.

3.4. Responses of boron cycling to natural and anthropogenic disturbances

In another series of simulations, we explored the effects of forest disturbances (natural or anthropogenic) on the boron dynamic. We performed runs where the whole tree stand was replaced (wood/root and leaf biomass) for different return times (time interval between two perturbations) between 50 years and 1000 years (Tables SI_8 and SI_9). These two periods are assumed to be characteristic of return times for temperate heavily managed forests and for undisturbed evergreen tropical forests (Pugh et al., 2019). For each simulation, the model is run for 500/1000 years to initialize the stocks and isotopic compositions of the different boron pools of the ecosystem.

Effects of successive tree stand replacements on the B dynamic are illustrated in Figure 7 for two ecosystems, analogous of a temperate ecosystem heavily managed (e.g. clear cut logging) and a tropical evergreen forest faced with perturbations characterized by different return times.

Figure 7: Boron dynamic for non-perturbed (a,b) and for highly perturbed (c,d) forested ecosystems characterized by return times (T_{return}) of 1000 years and 50 years. For the non-perturbed ecosystem, initial values have been set by running the model for 1000 years whereas for the highly perturbed, initial values have been set by running the model for 500 years. The different figures show the evolution with time of the stocks of boron in the living biomass and the soil organic matter (a and c) and the isotopic composition of dissolved boron in the soil solutions as well as of the leaf exudates in the case the active uptake of boron by roots does not fractionate B isotopes (b and d).

The years following the clearing of the tree stand show a rapid decline of the B soil pore water pool and the soil organic pool as boron in soil solution and in soil organic matter is not sustained by vegetation cycling which results in hydraulic loss of boron associated to organic matter decay. This trend lasts till the growth of a secondary forest limits the water loss of boron from the soil solution and partially replenishes the soil organic pool. Because of the mineralization of the soil organic matter, the B isotopic compositions of the soil solutions decrease during the first years following the deforestation till the regrowth of a secondary forest promotes the accumulation of ^{10}B in the biomass.

As expected, the difference between the return time and the time needed for the ecosystem to reach a steady state controls the B stocks of the different compartments and the dynamic of boron. When the return time is long enough (i.e. 1000 years), the stocks of boron in the biomass will recover from the perturbations and even exceed the stocks at the end of the initializing run. This can be explained by the decay of the soil organic boron pool accumulated during the initializing run which became an additional source of boron. Not surprisingly, for heavily managed ecosystems with short return times (i.e. 50-years), the system does not have time to fully recover. However, in this case, although the initial soil organic boron pool will decay providing an additional source of boron, because of the short return time, this pool will continuously decrease to near a steady value. The other observation is that in all the

simulations after several perturbations, the system will reach a pseudo steady state where after each perturbation, the system returns to the pre-perturbation conditions.

Schlesinger and Vengosh (2016) highlighted the role of human disturbances on the global boron biogeochemical cycle. In this perspective, natural and anthropogenic disturbances are major drivers of the structure and function of terrestrial ecosystems, modifying biotic and abiotic patterns and processes (Bowd et al., 2019). Clear cut logging, for example is associated, to a rapid decline of soil dissolved and organic boron till the growth of a secondary forest limits the hydraulic loss of boron from the soil solution and partially replenishes the soil organic pool.

This is in-line with the evolution of the soil biogenic silica pools as loss of dissolved silica following deforestation and replacement of the original forest by crops has been highlighted in the Scheldt basin (Struyf et al., 2010), illustrating the sensitivity of nutrients pools and fluxes to land use changes and their impacts on ecosystems. The consequences of successive disturbances is to maintain to a certain degree, depending on the return time and the size of the pools, the boron cycle out of steady state even if the forest has reached its 'maturity' (ie for return times of 1000 years) sustaining high isotopic compositions of the soil pore water.

4. Conclusions and perspectives

We developed a model to investigate the boron dynamic during the development of forested ecosystems and to explore how the B stocks and associated isotopic compositions of different compartments will evolve with time. The aim of model is to simulate the dynamic of boron and its isotopes on relatively short time-scales, especially we focused on the response of the dynamics of boron and its isotopes to different B supply rates, plant demands, soil erosion and natural or anthropogenic disturbances.

The overall conclusion of the sensitivity analysis developed in this paper is that the isotopic signature of boron in the ecosystem is characterized by a transient storage of ^{10}B in biomass during the growth of the biosphere which enriches the soil solution within the root zone in the heavy isotope. This increase of the B isotopic composition of the root zone soil solution is propagated to the different compartments of the ecosystem. Enrichment in ^{11}B relative to the inputs as high as 15‰-20‰ can be produced for the leaf pool and soil pore water pool. This transient enrichment can last between 100 years to more than 500 years. Magnitude and duration of the transient increase of the isotopic compositions of the different B pools in the ecosystem appear to decrease with the increase of B supply. Thus, for ecosystems not limited by the supply of B from chemical weathering, vegetation cycling will have probably a limited impact on the B isotopic compositions of the different pools which will be in turn driven by the composition of the inputs, mainly controlled in this case by chemical weathering processes (dissolution of rock minerals and neoformation of clays and oxides). In stable tectonic settings, like tropical lowlands, chemical weathering is limited by the supply of fresh minerals resulting in higher B limitation and more efficient vegetation recycling. Atmospheric inputs constitute probably a significant supply of boron to these ecosystems thus relatively high B demand by vegetation and relatively high B isotopic composition of the inputs would be responsible for the enrichment in ^{11}B of the soil solution and of the B flux associated to vegetation cycling (e.g. leaf exudation). Hence, one output of this model is that the interconnection between weathering regimes, B limitation and vegetation recycling can be potentially fingerprinted by boron isotopes.

After the system has eventually reached a steady state, significant variation with depth in the root zone of the soil pore water B isotopic compositions is only observable when the adsorption of boron by roots fractionates its isotopes, otherwise the isotopic composition of the soil pore water within the root zone tends to be homogenized by vegetation cycling and is controlled by the $\delta^{11}\text{B}$ value of the inputs.

Loss of soil organic boron by physical erosion would also modify boron dynamic of ecosystems. Because of the more efficient B recycling by the vegetation for limited ecosystem, the loss of boron by soil erosion normalized to the total inputs by chemical weathering and atmospheric depositions is higher than for B non-limited ecosystems. Consequently, after the system has reached a steady state, the partial loss of this pool enriched in ^{10}B results in variable enrichment in the heavy isotope relative to the values in the absence of erosion depending on the degree of B limitation. For B non-limited ecosystems, loss by erosion would probably have less impact on the B isotopic composition of the different pools of the ecosystem than for B limited ecosystems.

In spite of the uncertainties on some parameters, the model developed here can reproduce at a first order, the distribution of B and its isotopes in different ecosystems. Although the number of studies allowing a comparison is still limited, our work provides a conceptual framework necessary to guide future boron isotopic measurement in ecosystem spanning climatic or geological gradients. For instance, assessment of fluxes and pools of boron at different stages of forest development or for forested ecosystems developed on soil chronosequence and hence characterized by different B supply rates, could be used to test the model's predictions and in return, refine it. Impacts of the loss of soil organic boron by erosion on boron dynamic and export of organic boron would need to be quantified by studying ecosystems developed along slope gradient for example. The model developed in this paper is also simple and flexible and could be adapted to other nutrients. However, the main advantage of boron compared with other elements is the relatively large isotopic fractionation associated to vegetation cycling resulting in a large range of isotopic compositions across the different pools which allows to follow the B dynamic at the scale of an ecosystem. Analysis of B isotopes in tree rings might potentially record the dynamic of B during the development of an ecosystem as well as the responses to different perturbations. In addition, recycling of silicon by vegetation has been proposed to sustain clays formation in upper soil horizon even for highly weathered soil profiles (Lucas et al., 1993). As shown

here, vegetation recycling can also maintain relatively high dissolved B concentration in the upper soil, hence, co-precipitation with secondary minerals of boron from soil solution enriched in ^{11}B by vegetation recycling could also potentially record the print of the 'biogenic' origin of these clay minerals.

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Figure 1: Schematic description of the model with the different pools and fluxes considered. A list and a description of the pools, fluxes, and parameters are given Tables SI 1 and SI 2

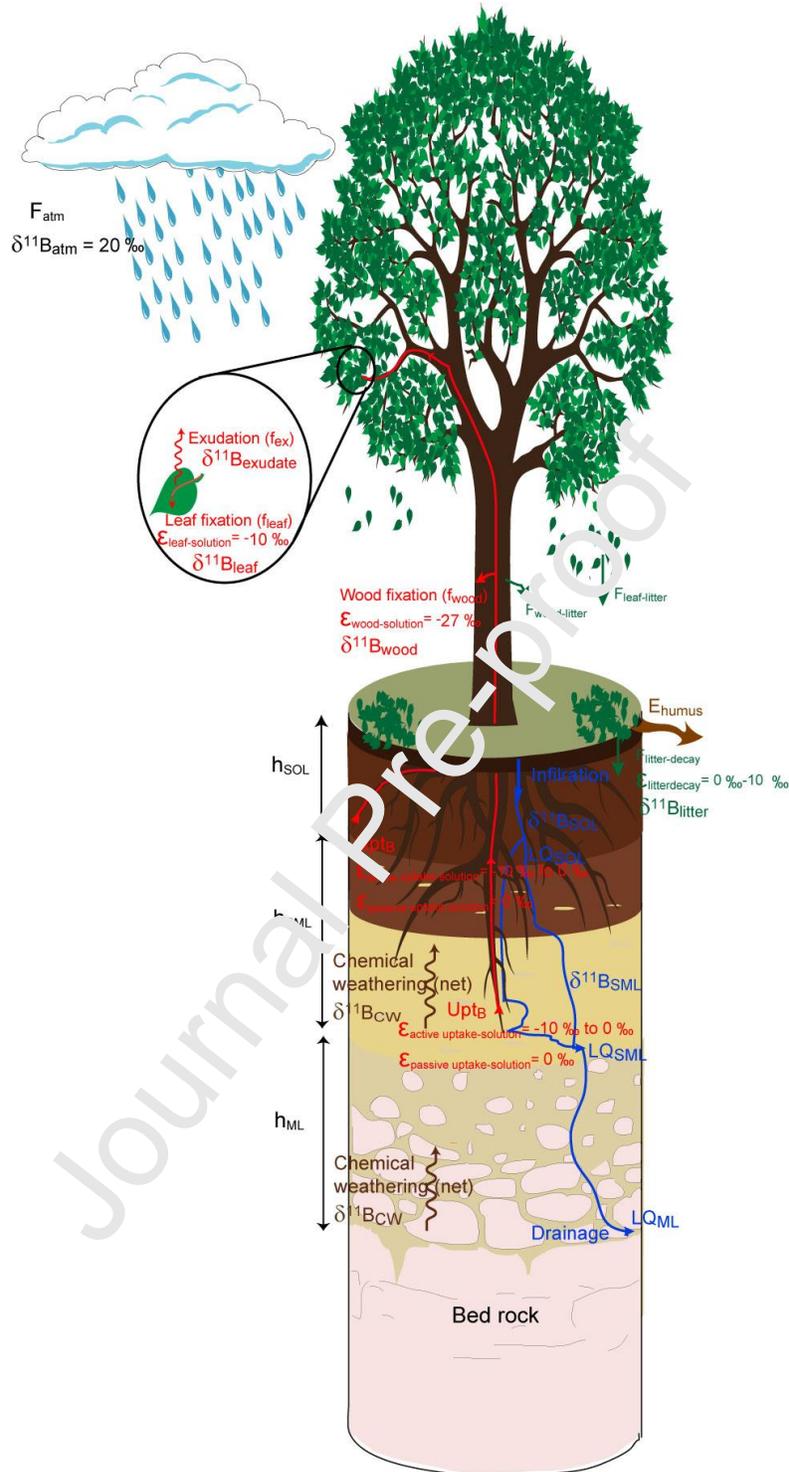


Figure 2: Evolution of the B isotopic composition of the soil solution in 3 different soil layers with the development of a forest for different supply rates of boron (atmospheric inputs, F_{atm} and chemical weathering, CW) and different B fractionation factors associated (ϵ) to the active uptake of boron by roots

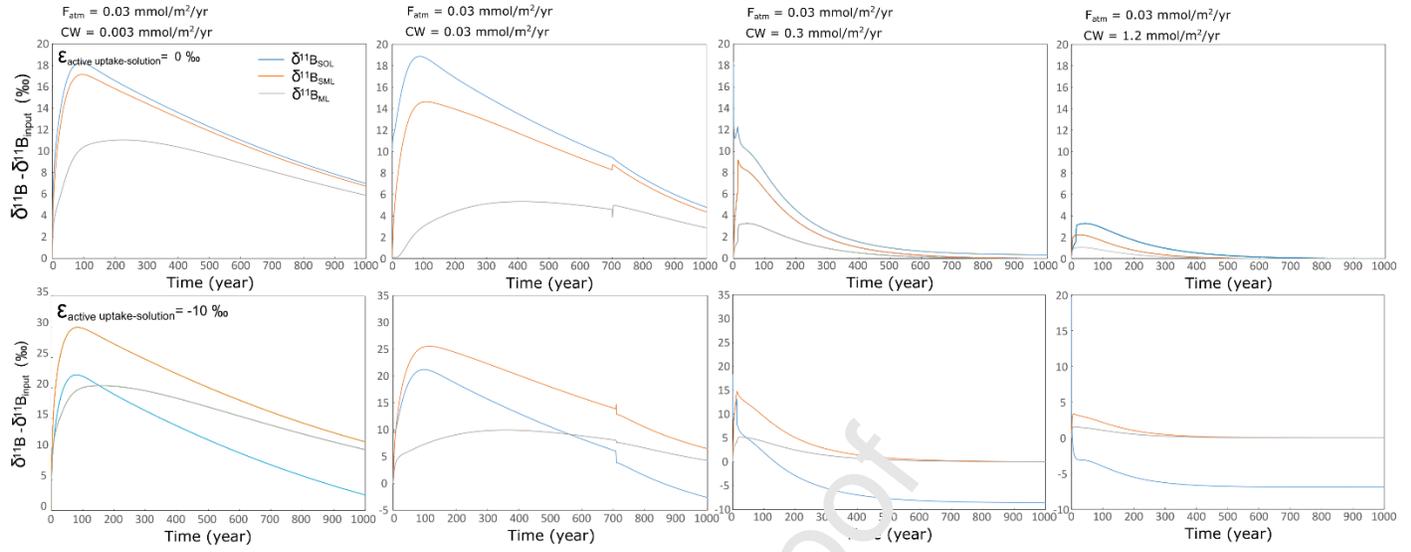


Figure 3: Evolution of the B isotopic compositions of the living biomass and the leaf exudate with the development of a forest for different supply rates of boron (atmospheric inputs, F_{atm} and chemical

weathering, CW) and different B fractionation factors (ϵ) associated to the active uptake of boron by roots

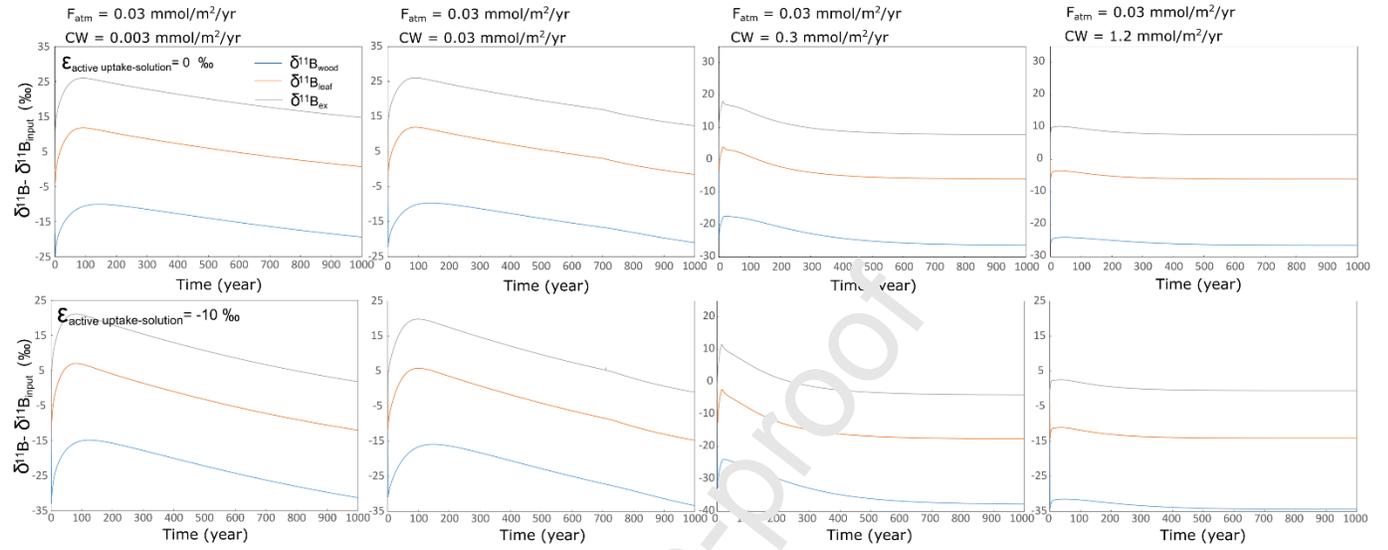


Figure 4: Relationships at steady state between the demand normalized to the inputs and (a) the vegetation cycling, (b) the ratio between the active uptake and the passive uptake of boron by roots, (c) and (d) the enrichment in B of the organic soil layer and the bottom layer of the root zone. The limit for boron limitation has been fixed arbitrarily and marks the transition between the two formulations for active B uptake by roots (see text for details)

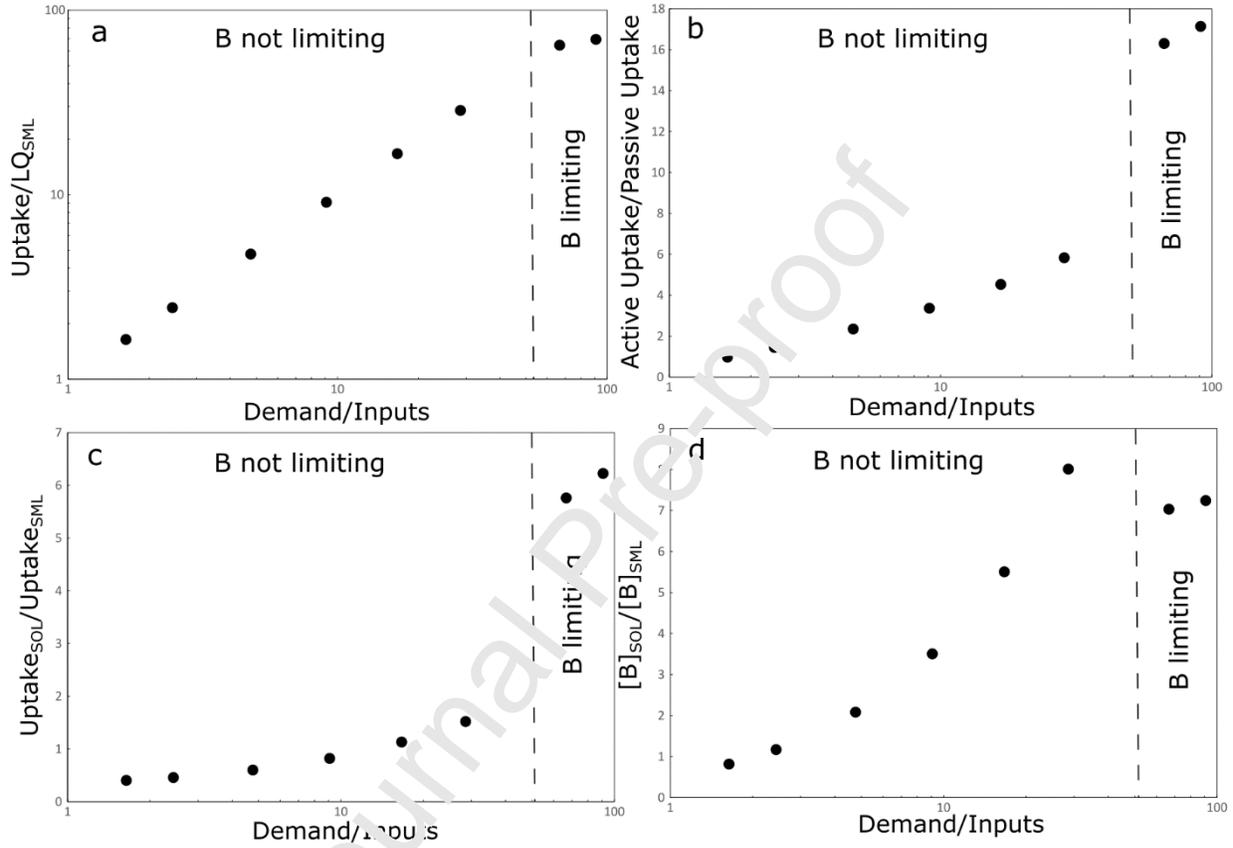


Figure 5: Evolution with time of the B isotopic compositions of (a) the soil solutions and (b) living biomass as well as the leaf exudate for a B limited ecosystem characterized by different values of the plant demand and maximum B influx.

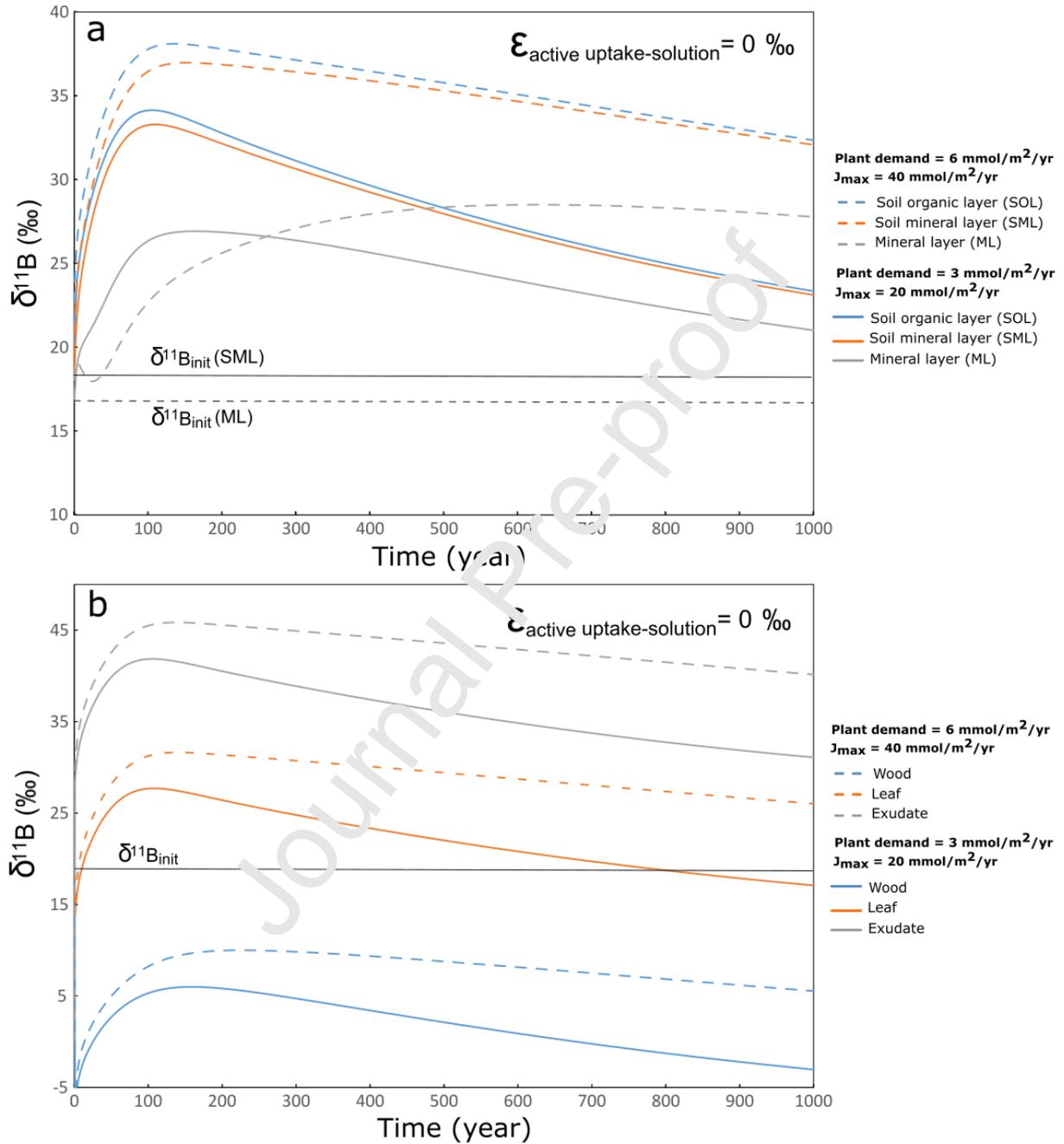


Figure 6: Comparison of the temporal evolutions of B isotopic compositions for different supply rates of boron of the different compartments of the ecosystem in the absence (dashed curves) or not (full curves) of erosion. The upper panels show the evolutions of the isotopic compositions of the soil solutions and the lower panels the evolutions of the isotopic compositions of the living biomass and the leaf exudates.

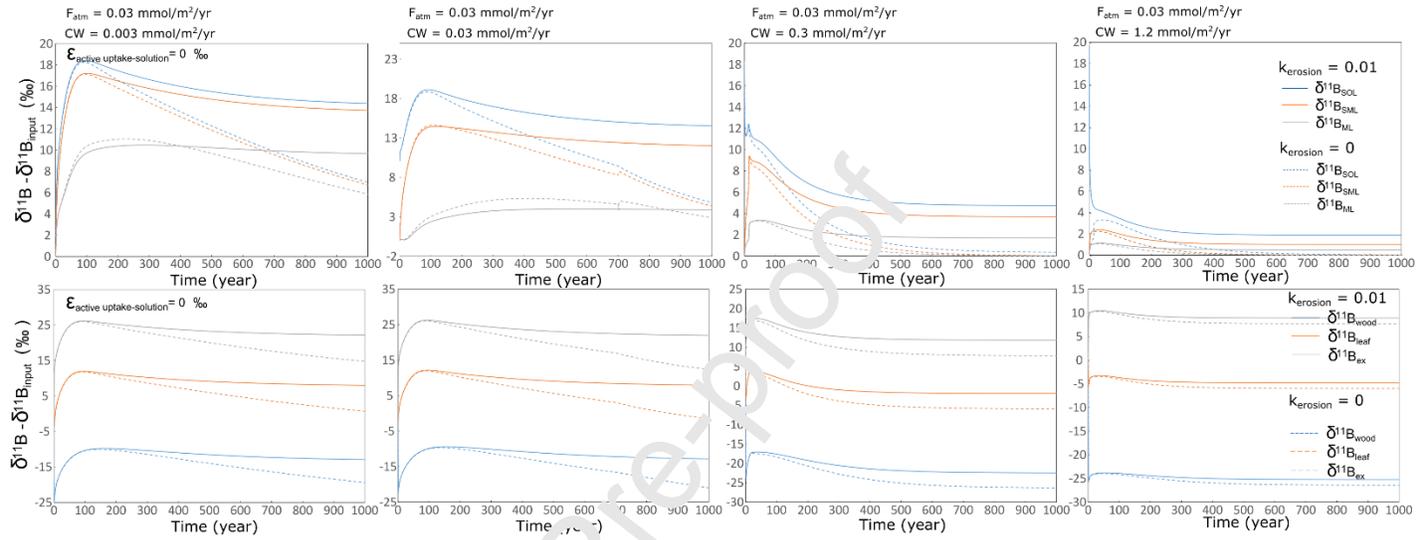
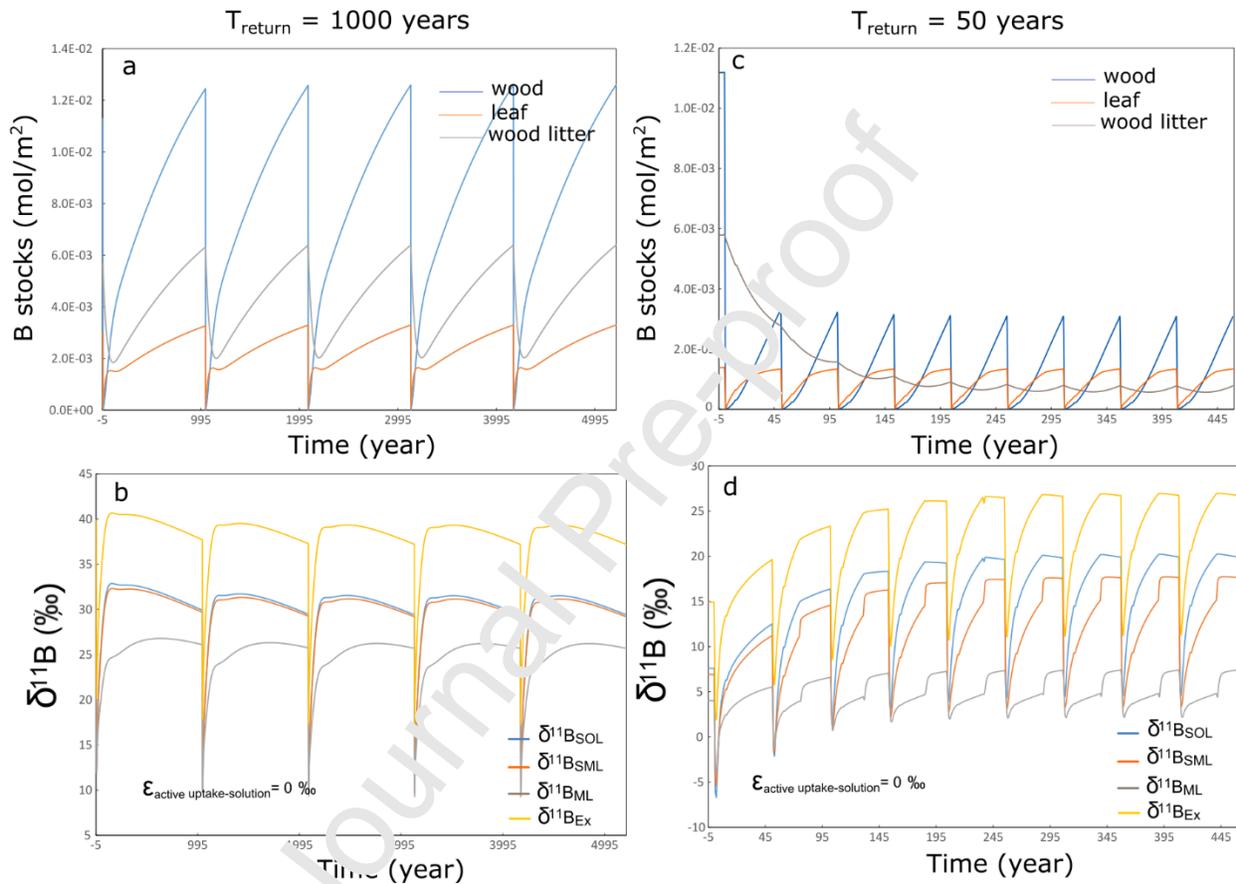


Figure 7: Boron dynamic for non-perturbed (a,b) and for highly perturbed (c,d) forested ecosystems characterized by return times (T_{return}) of 1000 years and 50 years. For the non-perturbed ecosystem, initial values have been set by running the model for 1000 years whereas for the highly perturbed, initial values have been set by running the model for 500 years. The different figures show the evolution with time of the stocks of boron in the living biomass and the soil organic matter (a and c) and the isotopic composition of dissolved boron in the soil solutions as well as of the leaf exudates in the case the active uptake of boron by roots does not fractionate B isotopes (b and d).



Declaration of interest

The authors declare no conflicts of interest.

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