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# **B and $\delta^{11}\text{B}$ biogeochemical cycle in a beech forest developed on a calcareous soil: Pools, fluxes, and forcing parameters**

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## 1 **Abstract**

2           Rock weathering and biological cycling hold the development and sustainability of  
3 continental ecosystems, yet the interdependence of macro- and micro-nutrients biogeochemical  
4 cycles and their implications for ecosystem functioning remains unclear, despite being of particular  
5 importance in the context of global changes. This study focuses on the stocks, fluxes and processes  
6 constituting the biogeochemical cycle of boron. Vegetation, soils and solutions were monitored for a  
7 full year in a temperate beech forest developed on calcareous soil. Despite an overwhelmingly large  
8 B pool in soils, this study points to limited influence of weathering emphasizing the importance of  
9 vegetation cycling on this site. The biological imprint on the B cycle is marked by (1) a strong  $^{11}\text{B}$   
10 enrichment of solutions compared to the mineral source and (2) systematic correlations observed  
11 between B and other strongly recycled elements in all water samples. B isotopes are fractionated  
12 within the beech stand with higher values in leaves (23.5‰) and lower in fine roots (-11.7‰),  
13 suggesting that the light  $^{10}\text{B}$  isotope is preferentially assimilated during plant growth. B isotopic data  
14 are consistent with a Rayleigh-like behaviour during xylem transfer leading to an  $^{11}\text{B}$  enrichment in  
15 the higher parts of the trees, putting internal B transfer as the main driver of the large range of  
16 isotopic compositions between plant tissues. B apparent isotopic fractionations are observed in the  
17 annually produced biomass and total beech stand, albeit with different values:  $\alpha_{\text{xylem-biomass}} =$   
18  $0.980 \pm 0.009$  and  $0.990 \pm 0.002$ , respectively, suggesting  $^{11}\text{B}$  transfer from old to new tissue. The  
19 developed model also points to an isotopic fractionation factor during B uptake much higher than  
20 previously evaluated ( $0.979 < \alpha_{\text{uptake}} < 0.994$ ). Overall, this study demonstrates that B isotopes appear  
21 as a promising tracer of soil-plant interactions with particular emphasis on tree adaptation to B  
22 bioavailability in soil.

23 Keywords: boron isotopes, biogeochemical cycle, vegetation cycling, forest ecosystem, plant uptake,

## 24 **1. Introduction**

25 Chemical weathering and biological cycling are two major processes that control soil  
26 formation, nutrient release, and sustainability of continental ecosystems. Their study provides  
27 insights into the processes controlling the transfer of elements across ecosystem compartments and  
28 the balance between external nutrient supply (atmosphere and soil mineral weathering) and  
29 biological cycling, with consequences for ecosystem sustainability and their vulnerability to global  
30 changes. Among tracers used to investigate the transfer of matter in the critical zone, isotopes have  
31 been largely developed these last two decades (e.g. Fantle and DePaolo, 2004; Kimmig et al., 2018;  
32 Lemarchand et al., 2012; Opfergelt et al., 2017; Prunier et al., 2015; Schmitt et al., 2017; Schuessler  
33 et al., 2018; Spivak-Birndorf et al., 2018). B shares chemical properties with neighboring elements in  
34 the periodic table, Al, Si and C, which are major actors of mineralogical and biological reactions. This  
35 special position makes B and B isotopes interesting candidates to provide further understanding of  
36 physiological and bio-geochemical processes (e.g. Blevins and Lukaszewski, 1998; Gaillardet and  
37 Lemarchand, 2018).

38 B is a trace element with concentration in soil constituents varying from  $\text{mg.kg}^{-1}$  level in  
39 quartz to tens of  $\text{g.kg}^{-1}$  in some phyllosilicates and accessory minerals like tourmaline (Hu and Gao,  
40 2008). B is considered to be a mobile element, similarly to K or Na, as shown by its long residence  
41 time in seawater (Lemarchand et al., 2000), but also shows enrichment in some secondary phases  
42 such as clay minerals or metal oxides compared to the continental crust (Goldberg, 1997). The large  
43 range of B isotopic compositions observed in soils and rivers is interpreted as the result of different  
44 weathering regimes and contributions of the vegetation cycling to B global cycle (Cividini et al. 2010;  
45 Ercolani et al. 2019; Lemarchand et al., 2012; Lemarchand and Gaillardet, 2006; Noireaux et al., 2021;  
46 Rose et al., 2000; Spivack et al., 1987; Schmitt et al. 2012; Williams et al., 2001).

47 In plants, B is an essential micronutrient involved in many fundamental physiological  
48 functions like sugar transport, nitrate assimilation or mycorrhizas development, but it is mostly  
49 known for its cell wall stabilization properties (Blevins and Lukaszewski, 1998; Brown et al., 2002;

50 O'Neill et al., 2001). Its restricted range between deficiency and toxicity makes B the second most  
51 widespread micronutrient worth considering after zinc and requires particular care in many  
52 agricultural systems (Shorrocks, 1997). Plants therefore require a continuous supply of sufficient B ,  
53 but also control over internal B distribution to sustain optimal growth (Reid, 2014). Briefly, B is  
54 primarily passively absorbed by plant roots as uncharged boric acid from soil solutions, with active  
55 absorption only mentioned under B-limiting conditions (Hu and Brown, 1997). Once absorbed, B  
56 follows the transpiration stream (xylem) to the leaves where it is partitioned between soluble  
57 compounds and cell walls (Reid, 2014). During uptake and transfer, diffusional gradient between the  
58 xylem and the surrounding tissue allows passive unloading of B. This process can be facilitated by  
59 boron specific transporters or channels whose activation depends on B availability in soil solutions  
60 (Miwa and Fujiwara, 2010; Shao et al., 2021; Tanaka et al., 2008; Takano et al., 2002, 2006, 2010;  
61 Yoshinari and Takano, 2017). The translocation of B towards the different plant organs after sugar  
62 synthesis remains poorly understood as it is mostly depending on the existence of suitable, plant-  
63 specific, complexing molecules (Gupta, 1993; Reid, 2014).

64 B concentrations vary in plants from a few mg.kg<sup>-1</sup> to hundreds of mg.kg<sup>-1</sup> with large  
65 variations between organs, plant species and soil content (Ozturk et al., 2010). However, most  
66 studies focused on either crop plants or leaves, which makes the partitioning and overall B stock  
67 difficult to assess at the ecosystem scale. First attempts to measure B isotopes in different plant  
68 organs were made through <sup>10</sup>B labeling experiments to assess the transfer mechanisms of B  
69 (Marentes et al., 1997; Vanderpool and Johnson, 1992). To date, authors have determined B isotopic  
70 compositions in plants mostly in the context of food authentication, and the published values span a  
71 large range of values, from -25‰ to +40‰, with most of the variability being related to that of the  
72 local bedrock (Roux et al., 2015; Serra et al., 2005; Vogl et al., 2011; Wieser et al., 2001). To our  
73 knowledge, few studies have focused on intra-plant B isotope variations despite their potential  
74 insight in plant metabolism, crucial to fully understand the role of B in ecosystem functioning.  
75 Recently, a study by Sun et al. (2018) shown strong variations between structural and soluble B

76 within deciduous shrub species and observed a preferential accumulation of  $^{11}\text{B}$  within the structural  
77 part. Geilert et al. (2019), on the other hand, have shown a vertical stratification of  $\delta^{11}\text{B}$  data along  
78 the xylem path with low values in roots and high values in leaves. This is suspected to result from a  
79 preferential loading of  $^{11}\text{B}$  to growing meristems facilitated by B transporters. Nevertheless, whether  
80 B transport network or its partitioning between soluble and structural compounds controls  $\delta^{11}\text{B}$   
81 remains an open question.

82           So far, only few studies attempted to establish the B biogeochemical cycle. Park and  
83 Schlesinger, (2002) as well as Schlesinger and Vengosh, (2016) determined the global B fluxes using  
84 previously published data but did not provide values for biological cycling. Cividini et al. (2010)  
85 monitored the fluxes of B and B isotopes in the Strengbach forest watershed (Vosges mountains,  
86 France) and showed a strong biological cycling of this element, up to 5 times higher than the B flux  
87 from bedrock weathering whereas this ratio rises up to 11 in the Mule Hole forest watershed in India  
88 (Gaillardet and Lemarchand, 2018). However, the mechanisms explaining the differences in terms of  
89 isotopic compositions between vegetation and bulk soil in both studies remain unclear. Chetelat et  
90 al, (2021) have recently modelled B isotopes in forest ecosystems and shown a transient enrichment  
91 in  $^{11}\text{B}$  in biomass relative to that of steady-state caused by plant growth. Nevertheless, this model  
92 remains unconstrained through lack of available data. Finally, recent studies showed rapid B release  
93 during litter decomposition in case of no B deficiency, indicating that B is chemically complexed to  
94 water soluble molecules in leaves, whereas it is mostly bounded to cell walls in B deficiency  
95 conditions (Kot *et al.*, 2016; Lehto *et al.*, 2010a, b)

96           Based on a full year of comprehensive monitoring, this study aims at establishing detailed  
97 pools and fluxes of B and B isotopes within a forest water-soil-plant system developed under  
98 temperate climate. Their relationships with macro-nutrients and environmental forcing parameters  
99 are then discussed.

## 100 **2. Materials and methods**

## 101        **2.1. Study site**

102            This study was conducted at the beech forest experimental site located in Montiers-Sur-  
103    Saulx, Northeastern France (Meuse, France, 48°31'55" N / 5°16'8" E). This experimental site is part of  
104    the AnaEE network (Analysis and Experimentations on Ecosystems, <https://www.anaee-france.fr/>).  
105    This site has been co-managed since 2012 by the French National Research Institute for Agriculture,  
106    Food and Environment (INRAE-BEF) and by the French National Agency for Radioactive Waste  
107    Management (Andra) in the framework of its long-term environmental observatory (OPE). The  
108    Montiers site covers two soil sequences of a total of 143 ha (70 ha and 73 ha) in the forested area at  
109    an altitude ranging from 319 m to 400 m. The local climate is characterized as semi-continental with  
110    an annual temperature of 12.6°C with monthly averages ranging from 4.4 to 21.6°C and an average  
111    precipitation rate of approximately 1100 mm.

112            The vegetation of Montiers is mainly composed of an even-aged beech ( $\approx$  60 years; 88% of  
113    total stems), but other species such as maple (6.1%), whitebeam (1.7 %), Ash tree (1.3 %), oak (1.2%),  
114    Hornbeam (1.0%) and wild cherry (0.4%) are also present. The humus can vary on the site from mull  
115    to acid-mull.

116            The geology of the Montiers study site consists in two geological layers: an underlying  
117    Jurassic (Tithonian) limestone covered by lower Cretaceous (Valanginian) acidic detrital sediments.  
118    The calcareous bedrock contains up to 3.4% of clay making the regolith a clay rich soil layer due to  
119    bedrock decarbonation. The detrital sediments are a combination of clay, silt, coarse sand and iron  
120    oxides that result from multiple deposition events. Due to the differences in thickness of the  
121    sediment layer, the soil type displays an acidic gradient with a *Dystric Cambisol* at the top of the  
122    hillslope, an *Eutric Cambisol* and a *Rendzic Leptosol* on the lower parts of the soil sequence. A  
123    schematic representation of the soil profiles as well as the main characteristics of these different soil  
124    types can be found in Calvaruso et al. (2017) and Kirchen et al. (2017). In this study, we focused on  
125    the calcareous soil (*Rendzic Leptosol*). It is only 30cm deep with a textural distribution strongly

126 enriched in clay (up to 50%). The Jurassic limestone bedrock can be found all along the soil profile  
127 with a rock volume varying from 2.3% at the surface to 36.4% at 30cm. Neither pH nor CEC  
128 parameters vary strongly with values averaging 6.9 and 22.7 cmol.kg<sup>-1</sup>. The soil is covered by an  
129 eutrophic mull humus. More detailed information can be found in Turpault et al. (2018).

## 130 **2.2. Instrumentation and sampling**

131 The *Dystric Cambisol*, *Eutric Cambisol* and *Rendzic Leptosol* have been instrumented since the  
132 end of 2011 to allow the monitoring of the stocks and fluxes of nutrients in soil, vegetation, water,  
133 dust, and litter. Each type of soil covers an area of about 1 ha and is divided in four equal replicates  
134 of 2500 m<sup>2</sup>. Out of the replicates, three are instrumented while one is left intact for future  
135 experimentations.

### 136 **2.2.1. Soil**

137 The soil and subsoil samples were collected in March 2011 down to a maximum depth of 35  
138 cm. The soil profile was divided in layers of varying thickness from 5 cm to 15 cm. After drying at  
139 35°C, soil samples were weighed and sieved at 2 mm to obtain the fine earth (<2 mm). About 10g of  
140 the fine earth fraction were ground and sieved at 50 µm.

### 141 **2.2.2. Humus**

142 Humus samples have been collected in June 2010 using a calibrated metal frame of 0.1 m<sup>2</sup>.  
143 The samples were dried in a ventilated oven at 65°C until complete dryness. Dried samples were then  
144 merged per substation and sieved to obtain a homogeneous average sample. A sub-sample was  
145 ground in a ring roller mill before storage at room temperature.

### 146 **2.2.3. Beech stand**

147 *Aboveground plant biomass*: In winter 2009, during the establishment of the study site, a  
148 total of 25 trees along the soil sequence were cut down to homogenize stand characteristics,



149 evaluate biomass and establish allometric equations. Additional sampling details can be found in  
150 Calvaruso et al. (2017). 4 trees grown on the *Rendzic Leptosol* were selected for B measurement.  
151 The trees were divided in several parts that were weighted on site. The trunk was separated into  
152 bark and wood samples while the branches were separated into different diameter classes according  
153 to Henry et al. (2011). The selected samples for the characterization of aboveground plant biomass in  
154 this study are: stem wood; stem bark; coarse branches wood (diameter > 7 cm); coarse branches  
155 bark; medium branches wood and bark (4 < diameter < 7 cm) and fine branches wood and bark  
156 (diameter < 4 cm). This separation is essential because of significant differences in the elemental  
157 concentrations, density, and water content.

158 *Roots:* Fine roots were collected in March 2011 in the trenches dedicated for the  
159 establishment of the soil profiles. In each horizon (0-5 cm, 5-15 cm), 100 g of soil containing roots  
160 was collected from 3 sampling points. The separation of roots and soil were performed by shaking.  
161 The roots were then immersed in milli-Q water and placed in an ultrasound bath for 15 min. This last  
162 step was repeated until no soil particles were remaining onto the root after verification by binocular  
163 microscope.

164 *Litterfall:* Litter samples were continuously collected for 12 weeks periods in 2012 except in  
165 autumn when they were sampled every 8 weeks. Each litter sample integrates an entire season:  
166 21/12/11-13/03/12 for winter, 13/03/12 – 05/06/12 for spring, 05/06/12 - 28/08/12 for summer,  
167 28/08/12 – 23/10/12 for the summer-autumn transition and 23/10/12 – 17/12/12 for the second  
168 part of autumn. The samples collected in October and December were merged to constitute an  
169 average autumn sample. Litters were collected in 0.33 m<sup>2</sup> litterbags and were divided in three parts:  
170 leaves (LL), wood (LW) and others (LO), and stored in paper bags at ambient temperature.

171 *Fresh leaves:* Fresh leaves were sampled on the 28/08/12 by shooting and weighed on site.  
172 All vegetation samples were subsequently placed in an oven at 65°C until complete dryness. Dried

173 samples were then ground by a ring roller mill and dried again for two days before storage at room  
174 temperature.

#### 175 **2.2.4. Water compartments**

176 The Montiers experimental site is equipped to allow water sampling from throughfalls to  
177 deep soil solutions. Water samples were collected in tanks that were sampled and emptied every 4  
178 weeks between January and December 2012. In this study, we focused on 4 chosen timeframes:  
179 17/01/12 - 14/02/12 for winter, 10/04/12 - 09/05/12 for spring, 03/07/12 - 31/07/12 for summer  
180 and 24/09/12 - 22/10/12 for autumn. Each period is thereafter respectively labeled Win, Spr, Sum  
181 and Aut. The lack of deep soil solutions for the summer samples imposed an additional sampling  
182 period between 31/07/12 – 28/08/12, hereafter labeled as Sum2. The selected hydrological  
183 compartments are:

184 *Throughfalls (TF)*: Throughfalls were collected by four 0.38 m<sup>2</sup> polyethylene gutters (12 per  
185 station) placed under forest cover, radially to the stems, at 1.2 m above ground and connected to a  
186 120 L polyethylene barrel placed in a pit belowground. The throughfalls collected by the gutters were  
187 then gathered per replicates on site. In this study, 3 replicates were analyzed for boron content and  
188 isotopic composition for each selected timeframe.

189 *Stemflow (SF)* were collected by polyethylene foam wrapped around the stem and connected  
190 to a 120 L, 150 L or 310 L recovery barrel, depending on the size of the tree. 6 collectors were set up  
191 in each substation (18 per station) and distributed among different stem circumferences. During the  
192 winter months (from November to March), only 2 collectors were functioning per replicate and the  
193 recovery barrels were placed underground to avoid water freezing. Before filtration in the  
194 laboratory, the beech stemflows of each substation were mixed to obtain one representative  
195 average sample.

196 *Gravitational water (soil solutions, GW):* soil solutions were sampled by 3 polyethylene  
197 lysimeter plates at 0 cm, -10 cm and -30 cm depth. The lysimeter plates are connected to a 20 L  
198 polyethylene bottle placed below ground.

199 During each sampling period, 250 mL of water was sampled from each collector and stored in  
200 pre-cleaned high-density polyethylene bottles. Within 24 h, the samples were filtered in the lab using  
201 0.45 µm acetate filters (47 mm diameter) and stored in a cold-room at 4°C in pre-cleaned high-  
202 density polyethylene bottles before major elements and boron analyses.

### 203 **2.3. Analytical procedure**

#### 204 **2.3.1. Reagents**

205 Ultra-pure water (18.2 MΩ.cm<sup>-1</sup>) was provided by a Milli-Q Gradient water purification  
206 system (Millipore, Billerica, MA,USA). The HCl and HNO<sub>3</sub> acids used in this study were sub-boiled in a  
207 Teflon DST-1000 Savillex (Eden Prairie, MN, USA) distillation system. The alkali fusion was performed  
208 using Pt-Au crucible and powdered analytical grade K<sub>2</sub>CO<sub>3</sub>. The sample purification steps were  
209 performed in a clean room (class filter h14, class 1000) under a laminar flow box (filter class h15,  
210 class 100) using two types of resin: the cation-specific BioRad AG50W-X12 and the boron specific  
211 Amberlite IRA 743.

#### 212 **2.3.2. Major elements concentration**

213 *Water and vegetation samples:* Concentrations of major cations in water (Al, Ca, Fe, K, Mg,  
214 Mn, Na, P, S, Si) and vegetation samples (Al, Ca, K, Mg, Mn, Na, P, S) were measured by ICP-OES  
215 (Agilent Technologies™ 700 series) at the BEF laboratory (INRAE Grand Est, Nancy) after microwave  
216 acid digestion for vegetation samples (see §2.3.3 for details). Major anions were measured by Ion  
217 Chromatography Dionex™ ICS-2100. TOC, TC, IC, and TN parameters were also determined in water  
218 samples by TOC-L Shimadzu™. The analytical uncertainty is 10% (±2SD).

219 *Soil and humus samples:* Major elements expressed as oxides as well as trace elements were  
220 measured at the SARM laboratory (CNRS, Vandoeuvre-lès-Nancy, France, [http://helium.crpq.cnrs-](http://helium.crpq.cnrs-nancy.fr/SARM/)  
221 [nancy.fr/SARM/](http://helium.crpq.cnrs-nancy.fr/SARM/)) after lithium-borate alkali fusion by Thermo-Fisher ICap 6500 ICP-OES.

### 222 **2.3.3. Boron extraction and purification**

223 *Vegetation samples:* Boron from vegetation and litter was extracted by microwave acid  
224 digestion as described in Roux et al. (2015). Briefly, 100 mg of plant material were digested for 90  
225 min at 800 W ( $\approx$  5000 kPa; 250°C) using 10 mL of 1 N HCl-HNO<sub>3</sub> (1/3 – 2/3). The recovered solution  
226 was centrifuged at 4000 rpm for 20 min before being processed through a double purification  
227 procedure. The first step allowed the removal of most of the cations by ion chromatography using  
228 the resin BioRad AG50W-X12. Since silicon and DOC are not retained by this resin, a final micro-  
229 sublimation step was added to achieve satisfying level of purification.

230 *Soil, humus and water samples:* Boron from soil and humus samples was extracted by K<sub>2</sub>CO<sub>3</sub>  
231 alkali fusion (40 min at 950°C – 50 mg of sample – 250 mg of K<sub>2</sub>CO<sub>3</sub>) and dissolved in 0.2 N HCl before  
232 being processed through a double purification procedure adapted from Lemarchand et al. (2012).  
233 The first step aimed at removing most of the major cation using 1.5 mL of cation exchange Bio-Rad  
234 AG50W-X12 resin (100–200 mesh) while the second step is aimed at extracting boron using 0.5 mL of  
235 the boron-specific Amberlite IRA 743 resin. Boron extraction from water samples was performed only  
236 using the boron specific Amberlite IRA 743 resin. Typically, 500 ng of boron were processed through  
237 the resin to keep the relative contribution of the procedural contamination as low as possible ( $\approx$  12  
238 ng, mainly coming from the alkali fusion step)

### 239 **2.3.4. Boron concentration and isotope**

240 Boron concentration measurements were performed on a quadrupole mass spectrometer at  
241 the Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS, University of Strasbourg) by

242 Isotopic Dilution (ID-ICPMS) following the procedure described in Roux et al. (2015) with a precision  
243 of 1% (2SD).

244 Boron isotopic compositions were determined at LHyGeS by a Finnigan-Neptune MC-ICPMS  
245 (Thermo Scientific, Waltham, MA, USA) using three different reference materials for control: JB2  
246 ( $\delta^{11}\text{B} = 7.74 \pm 0.51\text{‰}$ ,  $2\sigma$ ,  $n = 3$  Geological Survey of Japan, Tokyo, Japan) as rock standards, NIST  
247 SRM 1570a ( $\delta^{11}\text{B} = 25.74 \pm 0.21\text{‰}$ ,  $2\sigma$ ,  $n = 5$ , National Institute of Standards and Technology,  
248 Gaithersburg, MD 20899, USA) for plant material standard and ERM-AE120 ( $\delta^{11}\text{B} = -20.08 \pm 0.28\text{‰}$ ,  
249  $2\sigma$ ,  $n = 12$ , BAM Federal Institute for Materials and Testing, Berlin, Germany) as water standard. The  
250 B reference material NIST SRM 951 ( $^{11}\text{B}/^{10}\text{B} = 4.0437$ , National Institute of Standards and Technology,  
251 Gaithersburg, MD 20899, USA) was used for correction of the instrumental mass bias occurring  
252 during  $^{11}\text{B}/^{10}\text{B}$  measurements. Results are expressed in  $\delta^{11}\text{B}$  (‰) values corresponding to the relative  
253 deviation from the NIST SRM 951 reference material expressed in permil (Eq. 1):

$$\delta^{11}\text{B}_{\text{sample}} = \left( \frac{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{sample}}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{NIST SRM 951}}} - 1 \right) \times 1000 \quad (1)$$

254 The analytical uncertainty for B isotope, based on repeated standards and duplicated samples, is  
255 0.5‰ (2SD).

#### 256 **2.4. B pools and fluxes calculation**

257 Surface normalized B pools and fluxes were obtained by multiplying the mass of solid or  
258 solution given in  $\text{kg}\cdot\text{ha}^{-1}$  by the B concentration in  $\text{g}\cdot\text{kg}^{-1}$ . Pools are therefore expressed in  $\text{g}\cdot\text{ha}^{-1}$ ,  
259 monthly fluxes are expressed on a  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  basis and summed up to a yearly flux expressed in  $\text{g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ . Hereafter, we only detail fluxes and pools for which the calculation differs from the simple  
260 multiplication of B concentration by mass of solid/solution.  
261

##### 262 **2.4.1. Soil**

263 The B stock in the soil profile (in  $\text{g}\cdot\text{ha}^{-1}$ ) is calculated by summing the mass of each soil  
264 horizon ( $\text{kg}\cdot\text{ha}^{-1}$ ) multiplied by its respective B concentration ( $\text{mg}\cdot\text{kg}^{-1}$ ). The mass of a soil layer is  
265 determined by correcting the volume of soil from the rate of stone, bedrock and density as described  
266 in Calvaruso et al. (2017).

#### 267 **2.4.2. Water samples**

268 To transform the water stemflow volumes measured on site into water fluxes, we used the  
269 stem circumference at 130 cm (C130) as the main factor explaining the variability between  
270 individuals. Multiple linear correlations between C130 values and stemflow volumes allow to  
271 distinguish between C130 classes. The stemflow fluxes are then determined for each C130 class by  
272 the equation found in Turpault et al. (2018).

273 Fluxes of dissolved B by soil drainage have been determined using the B concentrations  
274 measured in pore waters of each soil layer and water fluxes calculated by the hydrological BILJOU<sup>®</sup>  
275 model (Granier et al., 1999) and from calibrations determined by Kirchen et al. (2017).

276 Since waters from the different hydrological compartments were not collected continuously  
277 all throughout 2012 (only 5 monthly samples for each compartment, see §2.2.4 for details), we  
278 extrapolated the B concentrations and isotopic compositions of throughfall (TF), stemflow (SF) and  
279 soil solutions (GW0, GW10 and GW30) to fill missing data. Based on strong correlations with B/Na  
280 and  $\delta^{11}\text{B}$  in all ecosystem solutions, the K/Na chemical ratio is used as a proxy. The significance of  
281 these observed correlations will be discussed below. The uncertainties are calculated as the standard  
282 deviation of the difference between the modelled and the measured values for each compartment,  
283 when available. Annual fluxes in throughfalls, stemflows and soil solutions were determined using a  
284 Monte Carlo simulation using observed variability.

#### 285 **2.4.3. Beech stand**

286 The biomass of each forest stand was estimated in 2009 and 2014 using an allometric model  
287 based on tree height, diameter at 130 cm and age of trees (Saint-André et al., 2005). The model was  
288 calibrated, and its robustness verified on site using biomass measurements realized on 24 beech  
289 trees equally distributed on the *Dystric Cambisol* and on the *Rendzic Leptosol*. Allometric equations  
290 were also developed to determine the height of the trees from C130 and diameter at breast height  
291 was measured on a yearly basis, allowing the estimation of the yearly aboveground biomass  
292 production (for details see Calvaruso et al. (2017)). The aboveground biomass production is  
293 calculated as the difference between the biomass calculated in 2014 and 2009 and is considered  
294 linear along this period to derive an annual aboveground biomass production. Since the different  
295 tree compartments were only sampled in 2009 for this study, both B pools in perennial biomass and  
296 B fluxes from biomass production were calculated using the B concentrations measured in the 2009  
297 fallen trees.

298 *Fine root biomass* - The total biomass in fine roots is calculated in each soil layer by summing the  
299 fine-root biomass collected in the different soil aliquots and then multiplied by their respective mass  
300 ratio to total soil.

301 *Fine root decay flux* – The fine-root turnover rate depends on the fine-root biomass and annual  
302 production. In this study, The B flux from fine roots decay to the soil nutrient pool is calculated by  
303 multiplying the B stocks in fine roots by the fine root turnover rate:  $1.11 \text{ y}^{-1}$  as determined for *Fagus*  
304 *sylvatica* in Europe by Brunner et al. (2013).

305 *Harvest and exploitation of residuals* – The French National Forestry Office carries out a thinning of  
306 the aboveground biomass every 7 years, which consist of thinning approximately  $35 \times 10^3 \text{ kg.ha}^{-1}$  on  
307 the *Rendzic Leptosol* (Turpault et al., 2018). However, only the stem (69.2% of the biomass) and  
308 coarse branches (8.5%) are exported while the smaller compartments (i.e. medium and small  
309 branches, 22.3%) are left on the forest floor. Details are available in Calvaruso et al. (2017) and  
310 Turpault et al. (2018).

311 **2.4.4. Mass and isotope budget in the soil-plant system**

312 The comprehensive dataset provided in this study allows quantifying the major B fluxes and  
313 associated isotopic compositions in forest ecosystems. Calculations are made on yearly fluxes and  
314 uncertainties are determined by Monte Carlo simulation. The terms used in the different equations  
315 are reported in *Table 1*.

316 *Table 1: Definitions for equations and system components*

317 *Interactions with the canopy* - Interactions between canopy and atmosphere are considered as B  
318 transfers through leaching of atmospheric particles/aerosols/gases, leaf exudation and canopy  
319 uptake via stomatal absorption (Adriaenssens et al., 2012). So far, gaseous B exchanges between  
320 atmosphere and leaves have never been reported and are therefore not considered here. The B flux  
321 and isotopic composition originating from canopy interactions can be expressed as follows:

$$F_{CL} = F_{TF} + F_{SF} - F_{AW} \quad (2)$$

322

$$R_{CL} \approx \frac{(F_{TF}R_{TF} + F_{SF}R_{SF} - F_{AW}R_{AW})}{F_{CL}} \quad (3)$$

323 *Humus layer* - The humus layer integrates the fluxes coming from canopy leaching, atmospheric  
324 deposition, organic matter mineralization, vegetation uptake and weathering processes (Dincher et  
325 al., 2020). Since neither vegetation uptake (Kirchen et al., 2017) nor any significant weathering flux  
326 (Dincher et al., 2020) have been observed within the humus layer, the B flux by mineralization of the  
327 humus layer is reduced to the difference between B export to the top soil (at 0 cm) and B inputs from  
328 throughfalls and stemflow. Furthermore, no significant variations in stock of major element had been  
329 observed between 2010 and 2018 (Dincher et al., 2020). Therefore, we assume that the humus layer



330 is at steady state, therefore inducing no isotope fractionation during decomposition, which lead to  
 331 the following mass balance equations:

$$F_{\text{hum\_min}} = F_{0cm} - (F_{TF} + F_{SF}) \quad (4)$$

332

$$R_{\text{hum\_min}} \approx \frac{F_{0cm}R_{0cm} - (F_{TF}R_{TF} + F_{SF}R_{SF})}{F_{\text{hum\_min}}} \quad (5)$$

333

334 *Vegetation uptake* - The B flux absorbed by the tree roots is assumed mostly occurring in the shallow  
 335 soil layer as it corresponds to the maximum root density zone (0-30cm) and no significant amount of  
 336 fine roots have been quantified below 30cm (Turpault et al., 2018). It is calculated by summing the  
 337 net biomass production and the cycling flux:

$$F_{\text{upt}} = F_{\text{growth}} + F_{\text{cycling}} \quad (6)$$

with  $F_{\text{cycling}} = F_{CL} + F_{\text{litterfall}} + F_{\text{fine root decay}} \quad (7)$

### 338 **3. Results**

339 All B pools, annual fluxes and isotopic compositions constituting the B biogeochemical are  
 340 reported in *Table 2* and *Figure 1*.

341 *Table 2: B stocks (g.ha<sup>-1</sup>), yearly flux (g.ha<sup>-1</sup>.y<sup>-1</sup>) and isotopic compositions (‰) constituting the B*  
 342 *biogeochemical cycle in the Montiers temperate forest ecosystem*

343 *Figure 1: Biogeochemical cycle of B and B isotopes in the Montiers temperate forest ecosystem.*

#### 344 **3.1. Soil**

345 B concentrations in the soil range between 42 mg.kg<sup>-1</sup> and 83 mg.kg<sup>-1</sup> (*Table 3*), which are  
 346 high compared to the mean continental crust (≈ 10 mg.kg<sup>-1</sup>), but within the 10-100 mg.kg<sup>-1</sup> range of

347 typical soil minerals (Lemarchand et al., 2012). Along the soil profile, B concentrations increase with  
348 depth from 0 cm to 30 cm followed by a decrease in the deepest subsoil layers, which is interpreted  
349 as the dilution of the B-rich clay minerals and Fe-oxides by the B-poor limestone. Despite strong  
350 variations in B concentrations,  $\delta^{11}\text{B}$  values are homogenous along the soil profile as they range from -  
351 6.1‰ to -7.1‰. These  $\delta^{11}\text{B}$  values are consistent with previous published work on shales (Noireaux  
352 et al., 2021). The isotopic compositions and concentrations of the bulk B-rich soil layers are also  
353 consistent with on-site clay minerals (220 mg.kg<sup>-1</sup>; -5.0‰). All soil horizons show higher B  
354 concentrations than the underlying calcareous bedrock by at least a factor 5 ([B]<sub>limestone</sub> = 8.2 mg.kg<sup>-1</sup>,  
355 Table 3). The overall B stock within the profile was determined at 135 kg.ha<sup>-1</sup> and a B isotopic  
356 composition of -6.9‰. Because of the general nature of soils and the large B pool compared to the  
357 other compartment (Table 2), we don't expect the sampling date between soil the other fluxes  
358 sampling to induce significant changes in the overall B biogeochemical cycle.

359 *Table 3: B concentration (mg.kg<sup>-1</sup>) and isotopic composition (‰) of soil, soil constituents, humus,*  
360 *beech stand and litter samples collected in the Montiers forest ecosystem.*

### 361 **3.2. Humus**

362 Compared to the rest of the soil profile the mull samples show significantly lower B  
363 concentration of 19 mg.kg<sup>-1</sup> (Table 3). The humus B isotopic composition (+6.7‰) is significantly  
364 different from those of the soil profile. In terms of B budget, much less B is present in the humus  
365 (0.17 kg.ha<sup>-1</sup>) than in the soil minerals by more than two orders of magnitude.

### 366 **3.3. Beech stand**

367 B concentrations vary over one order of magnitude between plant compartments, from 2.4  
368 mg.kg<sup>-1</sup> in the stem wood to 33.6 mg.kg<sup>-1</sup> in the stem bark (Table 3). The B concentration in leaves, 26  
369 mg.kg<sup>-1</sup>, is consistent with previous studies on beech and other deciduous species (Cividini et al.,  
370 2010; Kot et al., 2016; Rosner et al., 2011). The B concentration decreases from the small branches  
371 (10.9 - 12.2 mg.kg<sup>-1</sup>) to the coarse ones (2.4 – 3.2 mg.kg<sup>-1</sup>, Fig. 2). B concentrations in fine roots are

372 intermediate compared to the other plant compartments and tend to slightly decrease with depth  
373 from 12.2 mg.kg<sup>-1</sup> at 0 - 5 cm to 9.2 mg.kg<sup>-1</sup> at 5 - 15 cm. The isotopic compositions of the different  
374 tree compartments sampled in this study range from -11.7‰ for the deepest fine roots to 23.5‰ in  
375 the leaves, thus covering approximately 30% of recorded B natural isotopic variations (*Fig. 2* and  
376 *Table 3*). δ<sup>11</sup>B values increase vertically from roots to shoots through stem and branches, but also  
377 radially from wood to bark.

378 *Figure 2: Boron concentration (mg.kg<sup>-1</sup>) and isotopic composition (‰) of the different compartments*  
379 *of the beech stand.*

380

381 The calculated B pools in the different beech stand compartments are reported in  
382 *Supplementary material, Table A.1*. The overall B stock in the perennial part of forest stand (stem and  
383 branches) is calculated at 571 ± 119 g.ha<sup>-1</sup> with a mean isotopic composition of 5.0 ± 2.0‰. About  
384 61% of the total B stock is in the stem (349 ± 78 g.ha<sup>-1</sup>) and 39% in the branches (222 ± 41 g.ha<sup>-1</sup>) with  
385 the small branches reaching 28% (160 ± 24 g.ha<sup>-1</sup>). Because the perennial biomass integrates 50 years  
386 of development, we don't expect the 3 year gap with the fluxes sampling to significantly impact the  
387 overall B biogeochemical cycle.

388

### 389 **3.4. Vegetation uptake, perennial and annual growth**

390 From Eq.6 and 7, we calculate a vegetation uptake of 276.1 g.ha<sup>-1</sup>.y<sup>-1</sup>. The yearly B uptake by  
391 perennial biomass growth is estimated at 32.6 g.ha<sup>-1</sup>.y<sup>-1</sup> integrated between 2009 and 2014  
392 (*Supplementary material, Table A.1*), which splits into 59% to the stem (19.2 g.ha<sup>-1</sup>.y<sup>-1</sup>), 25% to the  
393 young and small branches (8.0 g.ha<sup>-1</sup>.y<sup>-1</sup>) and the remaining 16% to the coarse branches (5.7 g.ha<sup>-1</sup>.y<sup>-1</sup>).  
394 However, perennial biomass only represents 14% of the total B vegetation demand while foliage  
395 production involves 119.8 g.ha<sup>-1</sup>.y<sup>-1</sup> (53%) and fine roots accumulate 73.6 g.ha<sup>-1</sup>.y<sup>-1</sup> (33%) of B. The  
396 fine root decay flux to the soil is estimated at 81.6 g.ha.y<sup>-1</sup> (*Table 2, Fig. 1*) with a turnover rate of  
397 1.11 y<sup>-1</sup> (Brunner *et al.*, 2013).

398 **3.5. Exploitation exportation and residues**

399 The latest cut in 2016 led to a total removal of 184.5 g of B among which, 115.4 g were  
400 exported while the remaining 69.2 g have been left on site. This leads to a yearly exportation flux of  
401 16.5 g.ha<sup>-1</sup>.y<sup>-1</sup> and an exploitation residues flux of 9.9 g.ha<sup>-1</sup>.y<sup>-1</sup> of B with a respective isotopic  
402 composition of 3.0‰ and 8.4‰ (Table 2).

403 **3.6. Litterfall**

404 B concentrations and isotopic compositions of the different types of litter are reported in  
405 Table 3. B concentrations in leaf litter samples display little variation throughout the year from 15.3  
406 mg.kg<sup>-1</sup> in spring to 18.8 mg.kg<sup>-1</sup> in autumn (LL,  $\bar{x} = 16.8 \pm 1.5$  mg.kg<sup>-1</sup>, 1SD, n = 4). The wood litter has  
407 B concentrations ranging from 11.9 to 22.4 mg.kg<sup>-1</sup> (LW,  $\bar{x} = 16.6 \pm 4.3$  mg.kg<sup>-1</sup>, 1SD, n = 4) with the  
408 highest value in summer. The other litter components (LO) range from 5.6 to 20.0 mg.kg<sup>-1</sup> (LO,  $\bar{x} =$   
409 12.5 ± 5.9 mg.kg<sup>-1</sup>, 1SD, n = 4) with the highest value during winter. The B isotopic compositions span  
410 a large range of values from -0.2 to 21.3‰ related to the type of litter with leaf litter showing the  
411 highest values (6.9 to 21.3‰) followed by the LO samples (1.4 to 11.9‰) and the wood litter (-0.2 to  
412 6.9‰). B concentrations and isotopic compositions show slight but parallel seasonal evolutions in  
413 leaf litter with higher values in summer and autumn, lower in winter, and lowest in spring. For the  
414 other type of litter, we observe a decrease from 20.0 to 5.6 mg.kg<sup>-1</sup> of the B concentrations  
415 throughout the sampling period while the isotopic compositions continuously increase from 1.4 to  
416 11.9‰. The corresponding B fluxes from the litterfall vary over two orders of magnitude with values  
417 ranging from 0.1 to 52.6 µg.m<sup>-2</sup>.d<sup>-1</sup> (Supplementary material, Table A.2). B fluxes follow the seasonal  
418 growth with a maximum in spring for the LO samples (bud scales) and in autumn for the LL samples  
419 (senescence). The overall B flux and isotopic composition from litter samples constantly increases  
420 from winter (2.1 µg.m<sup>-2</sup>.d<sup>-1</sup>, 2.5‰) to autumn (53.4 µg.m<sup>-2</sup>.d<sup>-1</sup>, 19.1‰) and amount to a total of 72.3  
421 g.ha<sup>-1</sup>.y<sup>-1</sup> with an integrated isotopic composition of 17.3‰ (Table 2).

422 **3.7. Water samples**

423 B concentrations in throughfalls range from 2.7 to 11.7  $\mu\text{g.kg}^{-1}$  ( $\bar{x} = 11.4 \pm 8.3 \mu\text{g.kg}^{-1}$ , 1SD,  
424  $n=9$ ) and from 6.4 to 38.3  $\mu\text{g.kg}^{-1}$  in stemflows (Table 4). The isotopic compositions in throughfalls  
425 show seasonal variations with the lowest values during spring and winter (18.8 to 25.5‰) and the  
426 highest during autumn (33.6 to 37.2‰). Stemflows follow the same evolution than that of  
427 throughfalls but in a narrower range with 26.7‰ in winter and 34.7‰ in autumn.

428 The soil solutions have similar range of B concentrations than stemflows and higher than  
429 throughfalls with values ranging from 7.4 to 28.5  $\mu\text{g.kg}^{-1}$  (with a mean value of  $21.2 \pm 5.7 \mu\text{g.kg}^{-1}$ , 2SE,  
430  $n=16$ , Table 4) and isotopic composition ranging from 17.6 and 31.0‰ (with a mean value of  $24.8 \pm$   
431  $2.8$ ‰, 2SE,  $n=14$ ).

432 *Table 4: B concentration ( $\mu\text{g.kg}^{-1}$ ) and isotopic compositions (‰) in throughfall, stemflow and soil*  
433 *solutions collected at 5 chosen timeframes: 17/01/12 - 14/02/12 for winter, 10/04/12 - 09/05/12 for*  
434 *spring, 03/07/12 - 31/07/12 and 31/07/12 – 28/08/12 for summer and 24/09/12 - 22/10/12 for*  
435 *autumn.*

436 *Figure 3: Modelled B fluxes ( $\mu\text{g.m}^{-2}.\text{d}^{-1}$ , in black) and isotopic compositions (‰, in grey) in (a)*  
437 *throughfalls, (b) soil solutions at 0 cm, (c) -10 cm and (d) -30 cm. The line corresponds to the modelled*  
438 *values, the dots to the measured values and the shaded area to the associated uncertainties (1SD).*

439  
440 The corresponding calculated B fluxes are summarized in *Supplementary material Appendix*  
441 *1, Table A.3 and Figure 3*. Throughfall fluxes strongly vary over 2 orders of magnitude with values  
442 ranging from 3.7  $\mu\text{g.m}^{-2}.\text{d}^{-1}$  to 103.6  $\mu\text{g.m}^{-2}.\text{d}^{-1}$ . In soil solutions, fluxes vary between 8.3 and 114.3  
443  $\mu\text{g.m}^{-2}.\text{d}^{-1}$  in the humus layer (0 cm), between 1.7 and 69.6  $\mu\text{g.m}^{-2}.\text{d}^{-1}$  at -10 cm and from 0.1 to 87.4  
444  $\mu\text{g.m}^{-2}.\text{d}^{-1}$  at -30 cm. All solution fluxes exhibit a bimodal evolution with higher values towards the  
445 end of Spring and during Autumn/Winter, and low (to very low) values during the summer.

### 446 **3.8. Canopy leaching and humus mineralization**

447 Using the data published in Roux et al. (2017) for  $F_{\text{AW}}$  and  $R_{\text{AW}}$ , we calculate a canopy leaching  
448 flux ( $F_{\text{CL}}$ ) of 89.6  $\text{g.ha}^{-1}.\text{y}^{-1}$  with an isotopic composition of 30.8‰ and a humus mineralization/litter  
449 leaching flux of 69.1  $\text{g.ha}^{-1}.\text{y}^{-1}$  with an isotopic composition of 30.3‰ (Table 2, Fig. 1).

450

## 451 **4. Discussion**

### 452 **4.1. Tracing B in water fluxes**

453 Above- and under-ground water fluxes integrate multiple sources and biogeochemical  
454 mechanisms. In the following, we combine major elements with B contents and isotope to decipher  
455 the contribution of the different compartments of the soil/plant system to the B biogeochemical  
456 cycle.

#### 457 **4.1.1. Atmospheric inputs**

458 Na and Cl are strongly correlated along the hydrological profile keeping a mass ratio close to  
459 the seawater value (*Fig. 4a*), which suggests that Na principally originates from atmospheric inputs  
460 and behaves conservatively along the water pathway. Since Na is not affected by canopy leaching,  
461 throughfalls integrate both wet atmospheric deposits and the soluble fraction of atmospheric dust  
462 deposits, including marine aerosols. The 2-fold increase in both Na and Cl concentrations observed  
463 directly under the canopy compared to rainfall only occur in winter and can therefore be attributed  
464 to a higher sea salt deposition (Roux et al., 2017). As waters pass through the humus and the mineral  
465 soil, Na concentrations remain equivalent to that of atmospheric inputs and therefore exhibit a  
466 conservative behavior when interacting with ground litter, humus layer and the different soil  
467 constituents. This is consistent with the very low Na concentration in the different litter samples and  
468 fresh leaves (respectively  $0.13 \pm 0.03$  and  $0.07 \text{ mg.kg}^{-1}$ ), the low  $\text{Na}_2\text{O}$  content ( $<0.3\%$  dry weight,  
469 *Supplementary material Appendix 1, Table A.4*) and overall lack of Na-bearing mineral phases (data  
470 not shown) in the soil. However, some soil solution samples at 0 cm and 30 cm deviate from the  
471 seawater line, possibly as a result of HCl gaseous deposition or fertilizers (Staelens et al., 2008; Roux  
472 et al., 2017). The lack of correlation between Cl and K in the throughfall samples rules out canopy  
473 leaching as a cause for Cl enrichment (Cole and Rapp, 1981).

#### 474 **4.1.2. From the canopy to the humus layer**

475 Interactions with the canopy and the litter/humus layer leads to strong B enrichment in  
476 surface solutions (*Table 4*). The trends between B/Na and Ca/Na (*Fig 4b*), K/Na (*Fig 4c*) Si/Na (*Fig 4d*)  
477 and the seasonal evolution of B fluxes and isotopic compositions within the water-soil-plant system  
478 (*Fig 5*) emphasize (1) the primary control of vegetation over the B cycling like other macronutrients  
479 (e.g. Ca, Si, K) and (2) this enrichment varies in intensity for each element depending on seasonal  
480 activity and recycling process.

481 The B/Na molar ratio increases over one order of magnitude from 0.012 in rainfall to  
482  $0.09 \pm 0.02$  (1SD, *Fig. 4*) in throughfalls with a significant increase of the B flux during the senescence  
483 period, which puts canopy leaching as a dominant source of B to the forest floor (*Fig. 5*). In parallel,  
484 K/Na, Ca/Na and Si/Na drastically increased in October from 0.2, 0.4 and 0.02 in rainfall (Roux et al.,  
485 2017) to  $4.2 \pm 0.6$ ,  $1.9 \pm 0.8$  and  $0.62 \pm 0.08$  (2SD) in throughfalls and 7.2, 0.95 and 0.78 in stemflows,  
486 respectively (*Fig. 4*). This evolution is accompanied by different trends between B/Na and Ca/Na in  
487 throughfalls and stemflows that could be explained by the influence of calcareous dust deposit on  
488 the canopy, common in this region of France and increases the Ca/Na in throughfalls (Lequy et al.,  
489 2013; Roux et al., 2017). However, this source remains of secondary importance for B as the range of  
490  $\delta^{11}\text{B}$  values within throughfalls/stemflows (18.9 - 37.2‰, *Table 4*) is incompatible with a significant  
491 contribution of dust particle leaching ( $340 \text{ mg.kg}^{-1}$ , -0.3‰) in solutions (Roux et al., 2017).

492 As solutions pass through the humus layer, Ca and Si are further enriched with values as high  
493 as 16.8 for Ca/Na and 3.5 for Si/Na during summer (*Fig. 4b and d*). At the same time, both K/Na and  
494 B/Na increase from  $0.040 \pm 0.014$  and  $0.092 \pm 0.014$  (2SD) in throughfalls to 0.067 and 0.111 on the  
495 soil solutions, respectively (*Fig. 4c*). Litter decomposition is strongly influenced by environmental  
496 conditions and soil microfauna activity, which usually leads to high mineralization in Spring and  
497 Summer (d'Annunzio et al., 2008). However, elemental ratios and B flux significantly increase in  
498 October and February. Riotte et al. (2014) have suggested litter leaching to be the main process

499 controlling the elemental release on the forest floor, which is consistent with the B flux in soil  
500 solutions during senescence. Other studies have also shown microbial communities responsible for N  
501 fixation from complex organic molecules to be active from November to February (Kaiser et al., 2010,  
502 2011), which is consistent with the relatively high TOC content observed in our study during this  
503 period (GW0: 18.5 – 25.2 mg.L<sup>-1</sup>, *Supplementary material Appendix 1, Table A.5*).

504 *Figure 4: Comparison between (a) Na (mg.L<sup>-1</sup>) and Cl (mg.L<sup>-1</sup>); (b) B/Na and Ca/Na; (c) K/Na and (d)*  
505 *Si/Na molar ratios in all water samples collected in the Montiers forest ecosystem. TF = throughfalls;*  
506 *SF = stemflow; Aw = atmospheric dissolved deposition (data from Roux et al, (2017)); GW0 = soil*  
507 *solution at 0 cm; GW10 = soil solution at -10 cm; GW30 = soil solution at -30 cm. lines represent linear*  
508 *fit to help identifying similarities of differences between sub-datasets (doesn't include Aw data).*

509

#### 510 **4.1.3. Through the soil profile**

511 B, Ca, Si and K show a relative depletion compared to Na in soil solutions from summer  
512 onward, resulting from the uptake by plant roots. Additionally, both B concentrations and isotopic  
513 compositions exhibit strong seasonal variations, especially under the root maximum density at -  
514 10cm. In the first 10 cm,  $\delta^{11}\text{B}$  values exhibit a significant decrease as waters infiltrate soil layers in  
515 February and April, respectively from 24.1‰ to 17.6‰ and from 28.2‰ to 21.7‰. In February, the  
516 significant decrease in both B concentrations and isotopic compositions cannot be explained by  
517 vegetation uptake processes as plants are in dormancy. Similar variations have been reported in  
518 another study who proposed dissolution/precipitation processes of poorly crystallized mineral  
519 phases leading to a <sup>10</sup>B removal in summer and input during winter (Cividini *et al.*, 2010). However,  
520 this appears inconsistent with our observations as soil solutions appear still under a tight control of  
521 biology-derived processes (no significant shift from their correlations with other major nutrient, *Fig.*  
522 *4b, c and d*). A possible explanation could be the mineralization of fine roots whose turnover have  
523 been shown to be an important flux to the bulk soil every year (Turpault et al., 2018). While their  
524 mineralization rate isn't documented, some studies suggested lignin and cellulose degrading  
525 microbial communities to be active during winter (Kaiser et al., 2010, 2011) which is consistent with



526 the high TOC content, an indicator of soil organic matter degradation, in soil solutions during this  
527 period (33.6 mg.kg<sup>-1</sup>, *Supplementary material Appendix 1, Table A.4*). B role in bacterial development  
528 has been suggested during N fixation processes and biofilm formation (Bolaños et al., 2004; Chen et  
529 al., 2002). The development of bacterial communities could consume B in the first 10cm of the soil,  
530 thereby explaining the B flux decrease, and in turn, lower the isotopic composition of the solution by  
531 promoting fine root mineralization (-9.8‰, *Table 3*).

532 *Figure 5: Seasonal variability of B fluxes and isotopic compositions evolution along the*  
533 *hydrological profile (from atmospheric dissolved deposition to soil solutions at -30 cm). Data from*  
534 *atmospheric dissolved deposition are from Roux et al. (2017).*

#### 535 **4.1.4. B fluxes: an overwhelming biological control**

536 The systematic correlations observed in all compartments between B and strongly recycled  
537 macronutrients (*Fig. 4*) as well as evolution of  $\delta^{11}\text{B}$  values from throughfalls to soil solutions (*Fig. 5*)  
538 allow using Eq. (2) – (7) to assign B to different fluxes of the biological cycle (*Table 2*). With an  
539 integrated B flux of 313 g.ha<sup>-1</sup>.y<sup>-1</sup>, biology controls most of the B cycle of forested ecosystems: 159  
540 g.ha<sup>-1</sup>.y<sup>-1</sup> transits as dissolved B either via canopy leaching (56%) or humus mineralization (44%), 72  
541 g.ha<sup>-1</sup>.y<sup>-1</sup> are associated to litterfall and 82 g.ha<sup>-1</sup>.y<sup>-1</sup> are associated with fine root decay. When  
542 compared to the beech stand B stock (571 g.ha<sup>-1</sup>, *Table 2*), we observe that in 2012, the amount of B  
543 released by vegetation corresponds to about 55% of the total B in perennial biomass. Consistently,  
544 with an uptake flux of 276 g.ha<sup>-1</sup>.y<sup>-1</sup>, half of the B stock is being exchanged each year, with an almost  
545 perfect balance between uptake and release by the vegetation. These values point to a very dynamic  
546 biological cycle.

#### 547 **4.2. Boron isotope fractionation and implications for B mobility in forest ecosystem**

##### 548 **4.2.1. B distribution in plants: soluble and structural-bound pools**

549 Canopy leaching as well as early stage of biomass mineralization have in common to both  
550 release the most soluble components (Adriaenssens et al., 2012; Berg, 2000; Staelens et al., 2008).  
551 This results to a large release of B to solutions, preferentially <sup>11</sup>B as shown by the gradual decrease of

552 both B concentration and isotopic composition from the fresh leaves (26.1 mg.kg<sup>-1</sup>, 23.5‰, *Table 3*)  
 553 to the fresh litter in autumn (18.8 mg.kg<sup>-1</sup>, 19.4‰, *Table 3*) and to the 2 litter layers on the forest  
 554 floor (surface litter: 17.1 mg.kg<sup>-1</sup>, 14.3‰; deep litter: 14.1 mg.kg<sup>-1</sup>, 6.6‰, *Table 3*). A large fraction of  
 555 B is therefore not bound to the cell wall, contrarily to what had been suggested by previous studies  
 556 (Lehto et al., 2010b; González-Fontes et al., 2008). Structural-bound B therefore appears  
 557 preferentially enriched in <sup>10</sup>B while soluble B would be enriched in <sup>11</sup>B. This observation is consistent  
 558 with the findings of O'Neill et al. (2001) who showed that B stabilizes cell wall under its tetrahedral  
 559 form, which accumulates the light isotope <sup>10</sup>B (Klochko et al., 2006). Speciation would therefore be  
 560 the main parameter controlling B isotopic fractionation occurring during cell wall synthesis.

561 From the B isotopic ratios of leaf litter ( $R_{leaf\ litter}$ ) and leaves ( $R_{leaf}$ ), the progressive loss of  
 562 soluble <sup>11</sup>B during canopy leaching is tentatively modeled by a Rayleigh-like distillation involving the  
 563 isotopic fractionation caused by cell wall synthesis ( $\alpha_{cell\ wall}$ ) and the mass fraction of the residual B  
 564 after canopy leaching ( $f_{leaf\ litter}$ ) as follows:

$$R_{leaf\ litter} = R_{leaf} f_{leaf\ litter}^{(\alpha_{cell\ wall} - 1)} \quad (8)$$

565

566 Since the B budget in august leaves (114.2±7.5 g.ha<sup>-1</sup>, 23.5‰, *Supplementary material, Table*  
 567 *A.1*) equals the sum of leaf litter and canopy leaching fluxes from August to December (122.4±8.2  
 568 g.ha<sup>-1</sup>, 27.6±3.4 ‰), then no B translocation between leaves and perennial biomass occur  
 569 throughout the year. The isotopic ratio of the leaves can therefore be deduced from the B fluxes and  
 570 isotopic ratios of leaf litter and throughfalls corrected from atmospheric inputs as follows:

$$F_{leaf} = F_{TF} - F_{AW} + F_{leaf\ litter} \quad (9)$$

571

$$R_{leaf} \approx \frac{F_{TF} \times R_{TF} - F_{AW} \times R_{AW} + F_{leaf\ litter} \times R_{leaf\ litter}}{F_{TF} - F_{AW} + F_{leaf\ litter}} \quad (10)$$

572 Combining Eq 8 and 10 to calculate the apparent isotopic fractionation factor caused by cell  
 573 wall synthesis gives  $\alpha_{cell\ wall} = 0.9925 \pm 0.0045$ . This fractionation factor is much higher (closer to 1)  
 574 than expected by a speciation-driven mechanism at physiological pH 7-8 ( $\alpha = 0.9728$ , Klochko et al.,  
 575 2006) indicating that the soluble B speciation is not the sole parameter at play.

#### 576 **4.2.2. B isotope fractionation during plant growth**

577 At the beech stand scale, the isotopic composition gradient observed from the deepest fine  
 578 roots (-11.7‰, *Table 3*) to the leaves (23.5‰, *Table 3*) reflects additional fractionation during  
 579 internal B transport. B is known to follow transpiration stream as exhibited by accumulation of  
 580 toxicity symptoms at the margin of leaves, where xylem vessels terminate (Oertli, 1993). This  
 581 transport can be facilitated by B specific channels shown to be most active in B deficiency conditions,  
 582 where B concentrations in the soil solutions are lower than the plant requirements (Shao et al., 2021;  
 583 Tanaka et al., 2008; Takano et al., 2002, 2006, 2010; Yoshinari and Takano, 2017). The B pathway  
 584 from the roots surface to the shoots includes at least three transmembrane processes: (i) import  
 585 from soil solutions to roots, (ii) export from roots to xylem and (iii) export from xylem to shoots  
 586 (Reid, 2014).

587 If we assume that the progressive transfer of B from the xylem to the surrounding tissues  
 588 along the root-to-shoot pathway follows a Rayleigh-like behaviour with a constant isotope  
 589 fractionation factor, then the B isotopic composition of the xylem evolves with its B removal as  
 590 follows:

$$R_{xylem} = R_{uptake} f^{\alpha_{xylem} - 1} \quad (11)$$

591 With  $f$  the residual mass fraction of B in the xylem,  $\alpha_{xylem}$  the isotopic fractionation during B transfer  
 592 from the xylem to the newly produced tissue and  $R_{uptake}$  the isotopic ratio of the B right after uptake

593 by tree roots. Here, we assume 1) a constant apparent B isotopic fractionation factor, which may  
 594 include a mechanism with multiple steps and 2) a single source of B entering the tree by the roots  
 595 and being progressively consumed during the xylem ascent up to the leaves. We also assume that  
 596  $R_{uptake}$  is constant over time, which is supported by the rather constant  $\delta^{11}\text{B}$  values in the soil solutions  
 597 shown in this study and in Cividini et al. (2010). If not constant,  $R_{uptake}$  should be considered as a  
 598 mean value integrated over the period of plant growth.

599 The B isotopic ratio of a growing compartment consuming B from  $f_1$  to  $f_2$  is given by:

$$\overline{R}_i = \frac{\alpha_{xylem} R_{uptake}}{f_2 - f_1} \times \int_{f_1}^{f_2} f^{\alpha_{xylem}-1} df \quad (12)$$

600 Where  $\overline{R}_i$  is the averaged isotopic ratio of the tissues produced after consuming the amount of  
 601 B corresponding to the change of the remaining fractions from  $f_1$  to  $f_2$ . This gives after integration:

$$\overline{R}_i = \frac{R_{uptake}}{f_2 - f_1} \times (f_2^{\alpha_{xylem}} - f_1^{\alpha_{xylem}}) \quad (13)$$

602 Fine roots are the first tissue to take up B, so  $f_2=1$  and  $f_1=f_{fine\ roots}$

$$\overline{R}_{fine\ roots} = \frac{R_{uptake}}{1 - f_{fine\ roots}} \times (1 - f_{fine\ roots}^{\alpha_{xylem}}) \quad (14)$$

603 Leaves are the last tissue to take up B, so  $f_2 = f_{leaves}$ , the residual B fraction left by the other tissues,  
 604 and  $f_1 = 0$ .

$$\overline{R}_{leaves} = \frac{R_{uptake}}{f_{leaves}} \times (f_{leaves}^{\alpha_{xylem}}) \quad (15)$$

605 The B stock and isotopic composition of leaves are calculated as the sum of leaf litter and  
 606 throughfalls corrected from their atmospheric component as described in Eq. (9) and (10). Since our  
 607 data don't allow a precise determination of the B pathway between organs, the wood and bark  
 608 tissues are paired and considered homogenous. This includes the trunk and the large branches, for

609 which the bark has been analysed separately, whereas wood and bark have not been separated in  
610 medium and fine branches.

611 This model was applied at two different scales. (i) Annually, where Eq. (14) and (15) are solved for  
612  $R_{uptake}$  and  $\alpha_{xylem}$  only using data of leaves and fine roots to calculate the isotopic composition of the  
613 intermediate tissues (branches and stem) grown during 2012 (*Fig 6a, b and c*, dotted line). (ii) A long-  
614 term approach based on the bulk B stocks of the beech stand that integrate  $\approx 50$  years of growth,  
615 where  $R_{uptake}$  and  $\alpha_{xylem}$  are optimized to best fit all the B data measured in the different bulk organs  
616 (*Fig. 6a, b and c*, full line). The hypotheses behind the long-term approach are that biomass has  
617 grown with constant B distribution between organs and constant isotopic fractionation or that B  
618 constantly exchanges between organs. None of these two hypotheses seems entirely satisfactory  
619 with respect to our present knowledge of B functions in plants, but this approach is still considered  
620 as a working hypothesis because of its agreement with our dataset (see discussion below). The  
621 uncertainty on  $R_{uptake}$  and  $\alpha_{xylem}$  was determined by Monte Carlo simulation based on the observed  
622 variability of the mass fraction of B being transferred to each organ from roots to leaves and then  
623 used to calculate the different  $f$  values. The results of these two approaches are reported in Table 5  
624 and Fig 6.

625 The long-term approach can reproduce observed data to the exception of the fine roots,  
626 which seem enriched in  $^{10}\text{B}$  (*Fig. 6a and d, scenario 1*), and gives  $R_{uptake} = 6.3 \pm 2.1\%$  and  $\alpha_{xylem} =$   
627  $0.988 \pm 0.003$  (*Table 5*). A pool of coarse roots, which were not sampled in this study, has been  
628 considered as an attempt to reconcile model and data, but has insignificant impact on the model  
629 outputs (*Fig 6b and d, Table 5, scenario 2*). For this calculation, the B stock in coarse roots was  
630 extrapolated from biomass data (Turpault et al., 2018), the B concentration assumed similar to stem  
631 wood ( $[\text{B}]_{\text{coarse roots}} = 2.9 \text{ mg.kg}^{-1}$ ) and the B isotopic composition set as intermediate between fine  
632 roots and stem ( $\delta^{11}\text{B}_{\text{coarse roots}} = 0\%$ ). Sensitivity tests around these extrapolations make the  
633 contribution of coarse roots as a solution unlikely. An alternative explanation could be that the

634 dynamic fine roots pool, characterized by a rapid turnover  $1.1 \text{ y}^{-1}$  (Brunner et al., 2013; Finér et al.,  
635 2011; Montagnoli et al., 2012; Turpault et al., 2018), is subject to seasonal variations in B isotopes so  
636 that a single sampling is not representative of annual production. We calculate that the fine roots  
637 should have an annual B isotopic composition of  $-3\text{‰}$  to make the entire dataset consistent with a  
638 Rayleigh-like B behaviour (*Fig. 6c and 6f, scenario 3*). This scenario gives  $R_{\text{uptake}} = 7.0 \pm 2.1 \text{ ‰}$  and  
639  $\alpha_{\text{xylem}} = 0.990 \pm 0.002$ , not much different from outputs of scenario 1. Here again, consideration of  
640 large roots has no impact on the calculated  $R_{\text{uptake}}$  and  $\alpha_{\text{xylem}}$  values.

641 *Table 5: Results of the Rayleigh like model for B during plant growth*

642 *Figure 6: Results of the Rayleigh like model for B during plant growth. (a) corresponds to the*  
643 *annual and long-term modeling using raw data (scenario 1). (b) adds an hypothetical B stock in*  
644 *coarse roots based on data from Turpault et al, (2018) (scenario 2). (c) changes the  $\delta^{11}\text{B}$  value of the*  
645 *fine root compartment to make the entire dataset consistent with Rayleigh-like behavior ( $\delta^{11}\text{B}_{\text{fine roots}}$*   
646 *=  $-3\text{‰}$ ; scenario 3). (d), (e) and (f) compare the results of modelled value of annually formed biomass*  
647 *to the measured value in bulk intermediate organs (branches and stem) for each scenario.*

648

649 The annual approach, based on fines roots and leaves, only assumes that B is distributed and  
650 isotopically fractionated between fresh tissues using the biomass annual growth data (*Table 3*). Here,  
651 no B transfer between old and young tissues is considered. This allows to calculate the B isotopic  
652 composition of the newly produced intermediate organs (stem and branches) that can then be  
653 compared to their respective measured bulk values. This approach gives  $R_{\text{uptake}} = 11.9 \pm 7.5\text{‰}$  and  
654  $\alpha_{\text{xylem}} = 0.975 \pm 0.010$ , different from those calculated with bulk biomass (see *Table 5 and Fig. 6,*  
655 *scenario 1*). These calculated values are not significantly different under scenario 2 but increase to  
656  $R_{\text{uptake}} = 14.0 \pm 7.1\text{‰}$  and  $\alpha_{\text{xylem}} = 0.980 \pm 0.009$  when fine roots are set at  $\delta^{11}\text{B} = -3\text{‰}$  (*scenario 3,*  
657 *Table 5*). Following the Rayleigh model, the discrepancy shown by these two approaches makes  
658 difficult to explain B isotopes in the perennial biomass from data of the annual products.  
659 Explanations may be found in a preferential  $^{11}\text{B}$  redistribution within perennial biomass via boric acid  
660 transporters, as suggested by Shao et al., (2021) and Tanaka et al., (2008). Environmental changes,  
661 such as atmospheric pollution could also lead to  $^{10}\text{B}$  enrichment of the recent biomass products

662 (Guinoiseau et al., 2018; Roux et al., 2017). Further research on B isotopes in soil/plant interactions  
663 as well as in different part of the wood is still needed to help clarify this point.

664           Regardless of the chosen approach, the model puts vegetation as the main driver of isotopic  
665 composition increase observed between soil and leaves, most likely induced by B internal allocation  
666 and transport network. The magnitude of this increase is therefore dictated by the amount of B  
667 allocated to fine roots and perennial tissues, which accumulate  $^{10}\text{B}$ . The model also points to  
668 additional mechanisms occurring on a longer timescale as shown by the differences between long-  
669 term and annual apparent fractionation factors. Calculated  $\alpha_{xylem}$  varies from  $0.975 \pm 0.010$  for the  
670 annual products to  $0.988 \pm 0.003$  for the bulk biomass. Translocation processes have been  
671 mentioned in previous studies, where channels involved in xylem-phloem transfer allow boric acid,  
672 enriched in  $^{11}\text{B}$ , distribution to growing tissue (e.g. Tanaka et al., 2008).

#### 673           **4.2.3. Boron isotope fractionation during vegetation uptake**

674           Cividini et al, (2010) estimated the apparent isotopic fractionation factor induced by  
675 vegetation uptake to be of relatively low magnitude in the Strengbach catchment ( $0.990 < \alpha_{\text{uptake}} < 1$ ).  
676 This was mostly based on the drastic decrease in B concentrations in soil solutions at roots depth  
677 without any significant shift in  $\delta^{11}\text{B}$  values. In this study however, comparing the calculated annual  
678  $R_{\text{uptake}}$  to the isotopic composition of soil solutions allows us to give a more representative value since  
679 it solely results from the passage of B from soil solution to root xylem, provided that roots take up B  
680 from gravitational waters rather than porous water (Goldberg, 1997). The soil solutions in the  
681 maximum root density zone (0 – 10 cm) during peak vegetation activity (from March to September)  
682 exhibit a weighed mean value of 27.7‰, which limits the range of possible  $\alpha_{\text{uptake}}$  values to 0.979 -  
683 0.994. This value is much higher than previously reported, but consistent with preferential  
684 absorption of  $^{10}\text{B}$ , especially in deficiency conditions (Cividini et al., 2010; Geilert et al., 2019).  
685 Alternatively, the low B isotopic ratio calculated for  $R_{\text{uptake}}$  may reflect the contribution of at least

686 another source than gravitational waters, which could be found in the pool of B adsorbed on soil  
687 minerals. If so,  $R_{uptake}$  would reflect reflect the bioavailable reserve of B in the soil.

688           The lack of observed effect of the high uptake flux ( $276 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ) on the  $\delta^{11}\text{B}$  with depth  
689 implies a constant and large source of isotopically low B. The systematic correlations observed  
690 between dissolved B and strongly recycled macronutrients doesn't point to a major influence of soil  
691 mineralogical constituents on soil solution chemistry. Rather, fine roots pool have been shown to be  
692 a dynamic soil nutrient pool, including in our study site (Turpault et al., 2018), putting them as the  
693 most likely source of B in soils. It is then surprising that overall limited seasonal and vertical  $\delta^{11}\text{B}$   
694 variations in soil solutions actually hide such a dynamic turnover. This is partly due to the buffering  
695 capacity of throughfalls and stemflows, which are a significant source of B with high  $\delta^{11}\text{B}$  to soil  
696 solutions. Nevertheless, this implies to reevaluate the mechanism of fine roots mineralization, in  
697 particular their contribution to the belowground B budget as well as the B pathway from dead to  
698 living fines roots without visible influence on the soil water chemistry. Unfortunately, the lack of  
699 information about fine root mineralization dynamics and the concomitant isotope fractionation  
700 occurring between the different B pools (structural vs soluble) makes evaluating the contribution of  
701 fine roots challenging and unconstrained.

## 702 **5. Summary and perspectives**

703           Soils constitute the largest B reservoir at the ecosystem scale ( $245 \text{ kg}\cdot\text{ha}^{-1}$ ;  $-6.9\text{‰}$ ). However,  
704 even if soil B is mostly controlled by the B-rich and highly reactive clay phase, our results confirm the  
705 control of biology-related processes on the B cycle in forest ecosystem (canopy exchange  $90 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ,  
706 litterfall  $72 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  and litter leaching/organic matter mineralisation  $69 \text{ g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ). In 2012,  $276$   
707  $\text{g}\cdot\text{ha}^{-1}$  out of the  $571 \text{ g}\cdot\text{ha}^{-1}$  total B-bound perennial biomass has been renewed, thus showing the  
708 extreme reactivity of the vegetation pool with respect to B. The strong biological imprint on the B  
709 cycle is highlighted by the  $^{11}\text{B}$  enriched isotopic compositions of the solutions compared to the  
710 mineral source, but most importantly by the systematic correlations observed in all compartments



711 between B and strongly recycled elements (Ca, K and Si). While the correlation of B with K highlights  
712 the vegetation cycling with clear release/uptake periods, correlations with Ca and Si show different  
713 patterns of nutrient release depending on the considered mechanism (litter leaching/organic matter  
714 mineralisation or canopy exchange), probably as a result of B incorporation into structural or soluble  
715 part of the leaves. This partitioning, most likely due to cell wall synthesis, is further observed with B  
716 isotopes, which exhibit an apparent fractionation factor between structural and soluble forms of  
717  $0.9925 \pm 0.0045$ .

718         The large isotopic composition gradient observed between deeper fine roots (-11.2‰) and  
719 leaves (23.5‰) is consistent with a Rayleigh-like model leading to  $^{11}\text{B}$  enrichment in the leaves,  
720 whose magnitude is dependent on the production of perennial biomass. This shows that plant  
721 internal transport and the allocation of resources is responsible for the large isotopic composition  
722 differences observed in previous studies between leaves and soils. Nevertheless, differences are  
723 observed depending on whether the annual ( $\alpha_{\text{xylem}} = 0.980 \pm 0.009$ ) or total biomass is considered  
724 ( $\alpha_{\text{xylem}}$  of  $0.990 \pm 0.002$ ), suggesting  $^{11}\text{B}$  transfer from old to new tissue within perennial tissue.

725         The Rayleigh model also points to an apparent isotopic fractionation factor induced by  
726 vegetation uptake much higher than previously thought ( $0.979 < \alpha_{\text{uptake}} < 0.994$ ). Surprisingly, soil  
727 solutions don't exhibit any increase in  $\delta^{11}\text{B}$  with depth, implying a dynamic isotopically low B source,  
728 which is hypothesized to be fine roots since soil mineralogical constituents appear to have a limited  
729 influence. Despite the buffering capacity of stemflow and throughfalls, it is surprising that rather  
730 limited seasonal and vertical  $\delta^{11}\text{B}$  variations in soil solutions actually hide such distinct and dynamic  
731 processes. This implies to reevaluate the way fine roots are considered in the belowground budget  
732 calculation and the cycling of dead biomass.

733         Beyond reconciling the large differences in terms of isotopic compositions between  
734 vegetation and bulk soil, which have remained unclear and/or unconstrained to this day (Gaillardet  
735 and Lemarchand, 2018; Cividini et al., 2010; Chetelat et al., 2021), this model highlights how B

736 isotopes could give insight in the status of nutrients and evolution of forest ecosystems. Annual and  
737 long-term parameters provided by the model have shown to be significantly different due to  
738 mechanisms occurring at different timescale with annual tissue representative of the ecosystem's  
739 current status, and perennial tissue representative of its evolution. While this statement may appear  
740 unsurprising to some, such an approach has never been put forward for micronutrients critical in  
741 plant development such as B. Since B internal transport, including the accumulation in woody tissue,  
742 leads to an overall  $^{11}\text{B}$  enrichment of the ecosystem, therefore simple, easy-to-access parameters,  
743 such as the  $\delta^{11}\text{B}$  difference between soil and leaves ( $\Delta^{11}\text{B}_{\text{soil-leaves}}$ ), branches ( $\Delta^{11}\text{B}_{\text{soil-branches}}$ ), or stem  
744 ( $\Delta^{11}\text{B}_{\text{soil-stem}}$ ) could be used to evaluate of the allocation and/or accumulation of resources.

745           Nevertheless, in his current state, the model fails to explain why the beech stand still exhibit  
746 higher values than the soil it originates from ( $\Delta^{11}\text{B}_{\text{beech stand-soil}} = 12\text{‰}$ ). However, high biological fluxes  
747 combined with the  $^{11}\text{B}$  enrichment caused by internal B transport completely overrun the lower  
748 isotopic composition sources such as weathering. This slow shift towards higher values could  
749 therefore be the result of the intensity of the biological cycle over the geologic inputs (atmospheric  
750 deposition and weathering).

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760

761 **Tables and Figures**

762

763 *Table 1: Definitions for equation and system components*

<b>Equation components</b>	
R	Isotopic ratio
F	Flux
$\alpha$	Isotopic fractionation factor
<b>System components</b>	
<i>CL</i>	Canopy leaching
<i>TF</i>	Throughfall
<i>SF</i>	Stemflow
<i>Aw</i>	Atmospheric dissolved deposition
<i>hum_min</i>	Humus mineralization
<i>upt</i>	Vegetation uptake
<i>Ocm</i>	Solutions at 0cm depth
<i>Litterfall</i>	Litterfall
<i>cycling</i>	SF + TF + Litterfall
<i>growth</i>	Perennial biomass growth

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Table 2: B stocks ( $g \cdot ha^{-1}$ ), yearly flux ( $g \cdot ha^{-1} \cdot y^{-1}$ ) and isotopic compositions (‰) constituting the B biogeochemical cycle in the Montiers temperate forest ecosystem

<b>Compartment</b>	<b>B</b>	<b><math>\delta^{11}B</math></b>
<b>Stocks</b>	$g \cdot ha^{-1}$	‰
Soil	<b>135 x 10<sup>3</sup></b>	-6.9
Humus	<b>173</b>	6.7
Vegetation		
- Perennial	<b>571 ± 119</b>	5.0 ± 2.0
- Leaves	<b>114</b>	23.5
- Fine roots	<b>74</b>	-9.3
<b>Fluxes</b>	$g \cdot ha^{-1} \cdot y^{-1}$	‰
Litterfall	<b>72</b>	17.3
Throughfalls	<b>98 ± 6</b>	29.1 ± 2.8
Stemflows	<b>9 ± 0</b>	31.1 ± 0.3
Drainage 0cm	<b>176 ± 6</b>	29.7 ± 1.6
Drainage -10cm	<b>121 ± 6</b>	25.7 ± 2.0
Drainage -30cm	<b>109 ± 27</b>	23.7 ± 10.5
Exportation residuals	<b>10</b>	8.4
Exportation harvest	<b>17</b>	3.0
Fine root decay	<b>82</b>	-9.3
Canopy exchange	<b>90</b>	30.8
Humus mineralization	<b>69</b>	30.3
Vegetation uptake	<b>276</b>	-
Perennial growth	<b>33</b>	-

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Table 3: B concentration ( $\text{mg.kg}^{-1}$ ) and isotopic composition ( $\text{‰}$ ) of soil, soil constituents, humus, beech stand and litter samples collected in the Montiers forest ecosystem.

Sample name	Sample type	Sampling date	B	$\delta^{11}\text{B}$
<i>Soil samples</i>			$\text{mg.kg}^{-1}$	$\text{‰}$
Surf Lit	Surface litter	Spring 2012	<b>17.1</b>	14.3
Deep Lit	Deep litter	Spring 2012	<b>14.8</b>	6.6
Hum	humus	June 2010	<b>18.6</b>	6.7
Soil 0-5	Soil horizon 0-5cm	March 2011	<b>54.6</b>	-6.7
Soil 5-15	Soil horizon 5-15cm	March 2011	<b>63.3</b>	-6.9
Soil 15-30	Soil horizon 15-30cm	March 2011	<b>82.8</b>	-7.1
Soil 30 - 135	Soil horizon 30-135cm	March 2011	<b>75.5</b>	-6.8
Soil >135	Soil horizon >135cm	March 2011	<b>42.4</b>	-6.1
Clay	Decarbonated clay	March 2011	<b>220.0</b>	-5.0
Limestone	Limestone bedrock	March 2011	<b>8.2</b>	-5.4
<i>Beech stand</i>				
Lf	Leaves	28/08/2012	<b>26.1</b>	23.5
B<4a	Branch <4cm	Winter 2009	<b>12.1</b>	8.2
B<4b	Branch <4cm	Winter 2009	<b>12.2</b>	13.6
B<4c	Branch <4cm	Winter 2009	<b>11.7</b>	10.9
B<4d	Branch <4cm	Winter 2009	<b>10.9</b>	6.7
B 4-7a	Branch 4-7cm	Winter 2009	<b>6.8</b>	7.5
B 4-7b	Branch 4-7cm	Winter 2009	<b>5.9</b>	5.6
B 4-7c	Branch 4-7cm	Winter 2009	<b>5.3</b>	3.5
B 4-7d	Branch 4-7cm	Winter 2009	<b>5.7</b>	4.9
BW>7a	Branch wood >7cm	Winter 2009	<b>2.8</b>	7.8
BW>7b	Branch wood >7cm	Winter 2009	<b>3.2</b>	5.4
BW>7c	Branch wood >7cm	Winter 2009	<b>2.4</b>	0.2
BW>7d	Branch wood >7cm	Winter 2009	<b>3.1</b>	4.1
BB>7a	Branch bark >7cm	Winter 2009	<b>33.1</b>	10.3
BB>7b	Branch bark >7cm	Winter 2009	<b>25.9</b>	10.7
BB>7c	Branch bark >7cm	Winter 2009	<b>26.0</b>	3.8
BB>7d	Branch bark >7cm	Winter 2009	<b>29.3</b>	9.3
SWa	Stem wood	Winter 2009	<b>2.4</b>	2.0
SWb	Stem wood	Winter 2009	<b>2.5</b>	3.1
SWc	Stem wood	Winter 2009	<b>2.4</b>	-0.9
SWd	Stem wood	Winter 2009	<b>2.5</b>	1.5
SBa	Stem bark	Winter 2009	<b>33.6</b>	4.7
SBb	Stem bark	Winter 2009	<b>21.0</b>	5.3
SBc	Stem bark	Winter 2009	<b>24.9</b>	1.5
SBd	Stem bark	Winter 2009	<b>31.5</b>	4.4
R 0-15	Root 0-5cm	March 2011	<b>12.2</b>	-7.2
R 5-15	Root 5-15cm	March 2011	<b>9.2</b>	-11.7
<i>Litterfall</i>				
LL win	Leaf litter	21/12/11 - 13/03/12	<b>16.0</b>	13.7
LL spr	Leaf litter	13/03/12 - 05/06/12	<b>15.3</b>	6.9
LL sum	Leaf litter	05/06/12 - 28/08/12	<b>17.1</b>	21.3
LL win	Leaf litter	28/08/12 - 18/12/12	<b>18.8</b>	19.4

LW win	Wood litter	21/12/11 - 13/03/12	<b>16.0</b>	-0.2
LW spr	Wood litter	13/03/12 - 05/06/12	<b>16.0</b>	6.9
LW sum	Wood litter	05/06/12 - 28/08/12	<b>22.4</b>	3.1
LW aut	Wood litter	28/08/12 - 18/12/12	<b>11.9</b>	5.8
LO win	Other litter	21/12/11 - 13/03/12	<b>20.0</b>	1.4
LO spr	Other litter	13/03/12 - 05/06/12	<b>12.0</b>	9.0
LO sum	Other litter	05/06/12 - 28/08/12	<b>12.4</b>	11.6
LO aut	Other litter	28/08/12 - 18/12/12	<b>5.6</b>	11.9

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777 *Table 4: B concentration ( $\mu\text{g.kg}^{-1}$ ) and isotopic compositions (‰) in throughfall, stemflow and soil*  
 778 *solutions collected at 5 chosen timeframes: 17/01/12 - 14/02/12 for winter, 10/04/12 - 09/05/12 for*  
 779 *spring, 03/07/12 - 31/07/12 and 31/07/12 – 28/08/12 for summer and 24/09/12 - 22/10/12 for*  
 780 *autumn.*

Sample name	Sample type	Sampling date	B	$\delta^{11}\text{B}$
			$\mu\text{g.kg}^{-1}$	‰
TF1 Win	Throughfall	17/01/12 - 14/02/12	<b>4.6</b>	20.1
TF2 Win	Throughfall	17/01/12 - 14/02/12	<b>2.7</b>	20.6
TF3 Win	Throughfall	17/01/12 - 14/02/12	<b>5.1</b>	25.5
TF2 Spr	Throughfall	10/04/12 - 09/05/12	<b>5.3</b>	18.8
TF2 Spr	Throughfall	10/04/12 - 09/05/12	<b>7.2</b>	19.0
TF2 Spr	Throughfall	10/04/12 - 09/05/12	<b>3.8</b>	22.2
TF1 Sum	Throughfall	03/07/12 - 31/07/12	<b>9.7</b>	31.8
TF2 Sum	Throughfall	03/07/12 - 31/07/12	<b>6.4</b>	32.1
TF1 Sum2	Throughfall	31/07/12 - 28/08/12	<b>11.7</b>	31.0
TF2 Sum2	Throughfall	31/07/12 - 28/08/12	<b>10.5</b>	31.2
TF1 Aut	Throughfall	25/09/12 - 23/10/12	<b>9.3</b>	35.7
TF2 Aut	Throughfall	25/09/12 - 23/10/12	<b>11.0</b>	37.2
TF3 Aut	Throughfall	25/09/12 - 23/10/12	<b>6.3</b>	33.6
SF Win	Stemflow	17/01/12 - 14/02/12	<b>6.8</b>	26.7
SF Spr	Stemflow	10/04/12 - 09/05/12	<b>6.4</b>	27.1
SF Sum	Stemflow	03/07/12 - 31/07/12	<b>27.9</b>	32.3
SF Sum2	Stemflow	31/07/12 - 28/08/12	<b>38.3</b>	30.2
SF Aut	Stemflow	25/09/12 - 23/10/12	<b>13.6</b>	34.7
GW0 Win	Groundwater 0cm	17/01/12 - 14/02/12	<b>15.3</b>	24.1
GW0 Spr	Groundwater 0cm	10/04/12 - 09/05/12	<b>12.1</b>	28.2
GW0 Sum	Groundwater 0cm	03/07/12 - 31/07/12	<b>16.5</b>	27.1
GW0 Sum2	Groundwater 0cm	31/07/12 - 28/08/12	<b>22.4</b>	30.8
GW0 Aut	Groundwater 0cm	25/09/12 - 23/10/12	<b>18.6</b>	30.6
GW10 Win	Groundwater 10cm	17/01/12 - 14/02/12	<b>7.4</b>	17.6
GW10 Spr	Groundwater 10cm	10/04/12 - 09/05/12	<b>14.7</b>	21.7
GW10 Sum	Groundwater 10cm	03/07/12 - 31/07/12	<b>17.4</b>	25.7
GW10 Sum2	Groundwater 10cm	31/07/12 - 28/08/12	<b>19.2</b>	31.0
GW10 Aut	Groundwater 10cm	25/09/12 - 23/10/12	<b>18.0</b>	30.8
GW30 Win	Groundwater 30cm	17/01/12 - 14/02/12	<b>24.0</b>	18.4
GW30 Spr	Groundwater 30cm	10/04/12 - 09/05/12	<b>13.6</b>	18.8
GW30 Sum2	Groundwater 30cm	31/07/12 - 28/08/12	<b>28.5</b>	17.7
GW30 Aut	Groundwater 30cm	25/09/12 - 23/10/12	<b>11.3</b>	24.3

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*Table 5: Results of the Rayleigh like model for B during plant growth*

	Scenario 1		Scenario 2		Scenario 3	
	$R_{\text{uptake}}$	$\alpha_{\text{xylem}}$	$R_{\text{uptake}}$	$\alpha_{\text{xylem}}$	$R_{\text{uptake}}$	$\alpha_{\text{xylem}}$
<b>Long term</b>	6.3±2.1	0.988±0.003	6.3±2.1	0.989±0.002	7.0±2.1	0.990±0.002
<b>Annual</b>	11.9±7.5	0.975±0.010	11.4±7.3	0.976±0.010	14.0±7.1	0.980±0.009

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788 **References**

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Fig 1: 2 columns

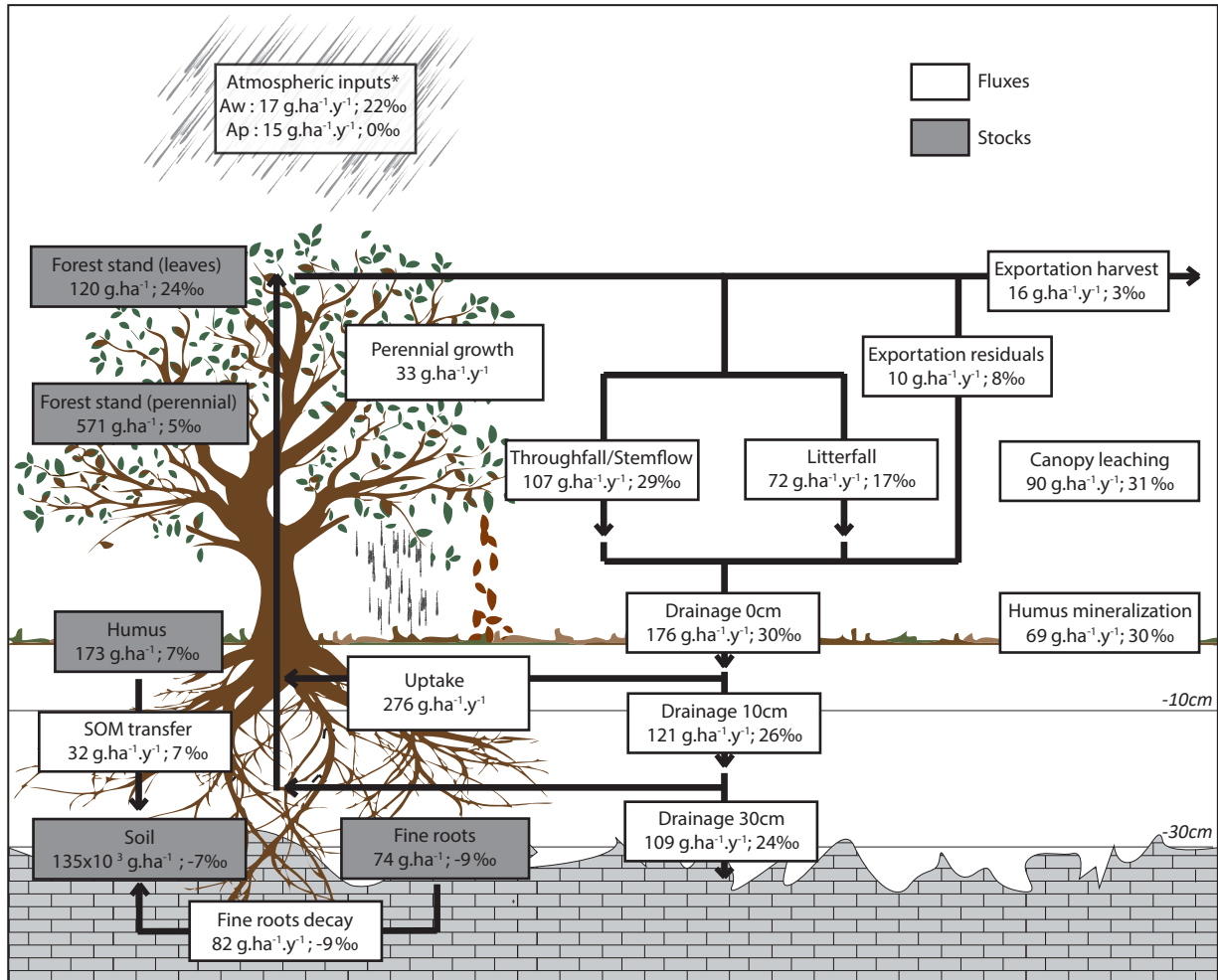


Figure 1: Biogeochemical cycle of B and B isotopes in the Montiers temperate forest ecosystem.

Fig 2: 1 column

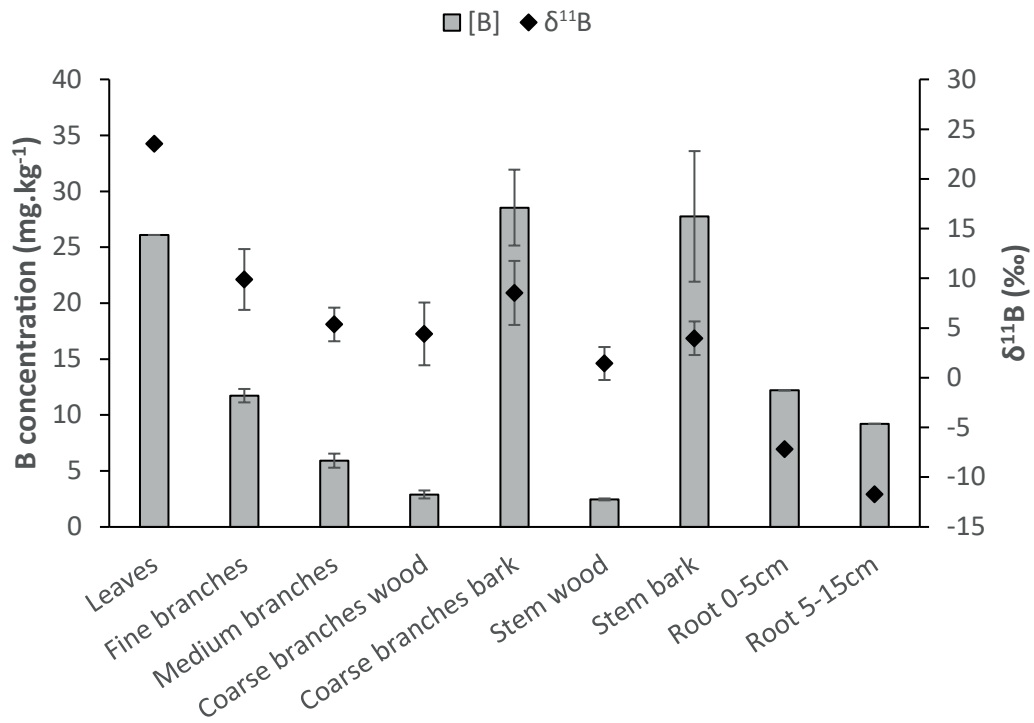


Figure 2: Boron concentration (mg.kg<sup>-1</sup>) and isotopic composition (‰) of the different compartments of the beech stand.



Fig 3: 2 column

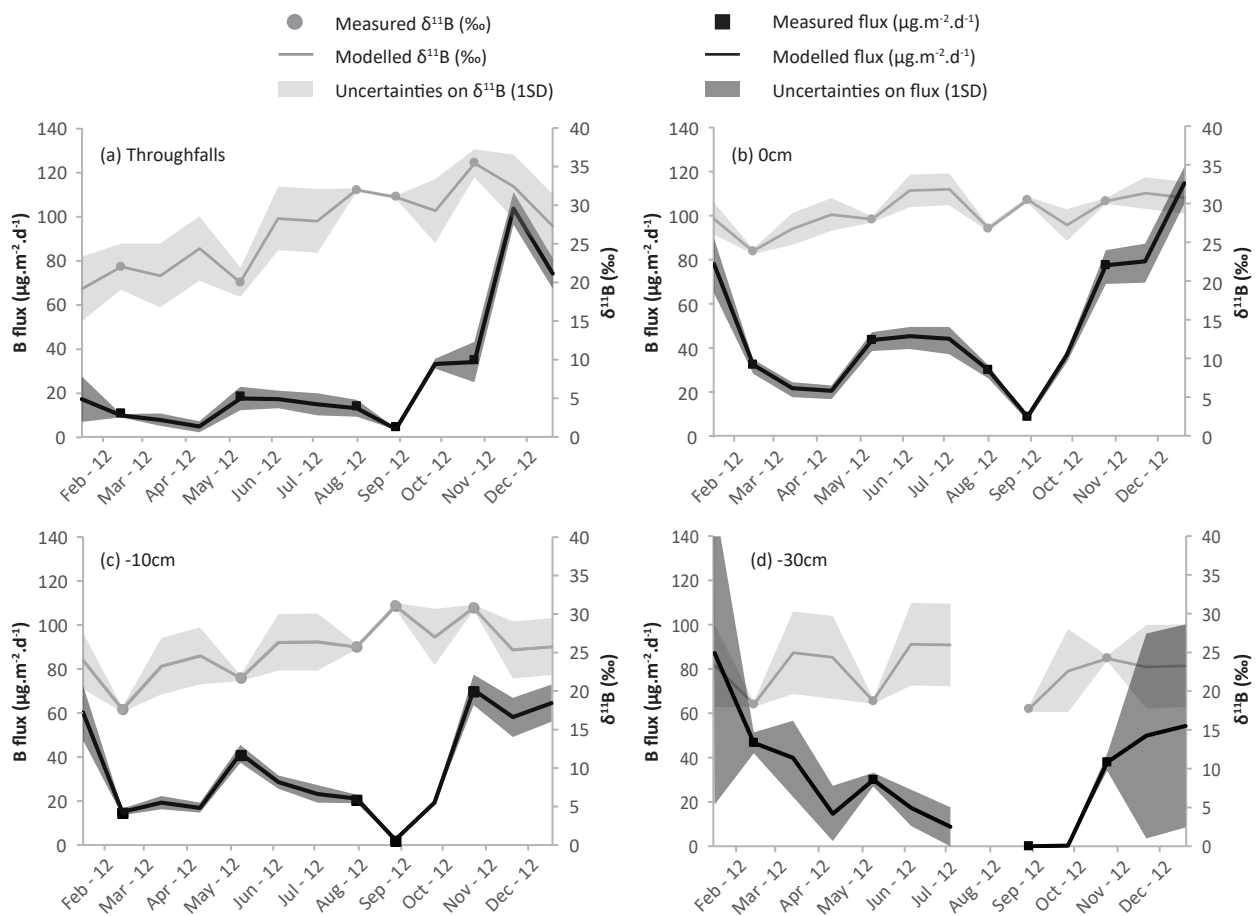


Figure 3: Modelled B fluxes ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , in black) and isotopic compositions (‰, in grey) in (a) throughfalls, (b) soil solutions at 0 cm, (c) -10 cm and (d) -30 cm. The line corresponds to the modelled values, the dots to the measured values and the shaded area to the associated uncertainties (1SD).

Fig 4: 2 columns

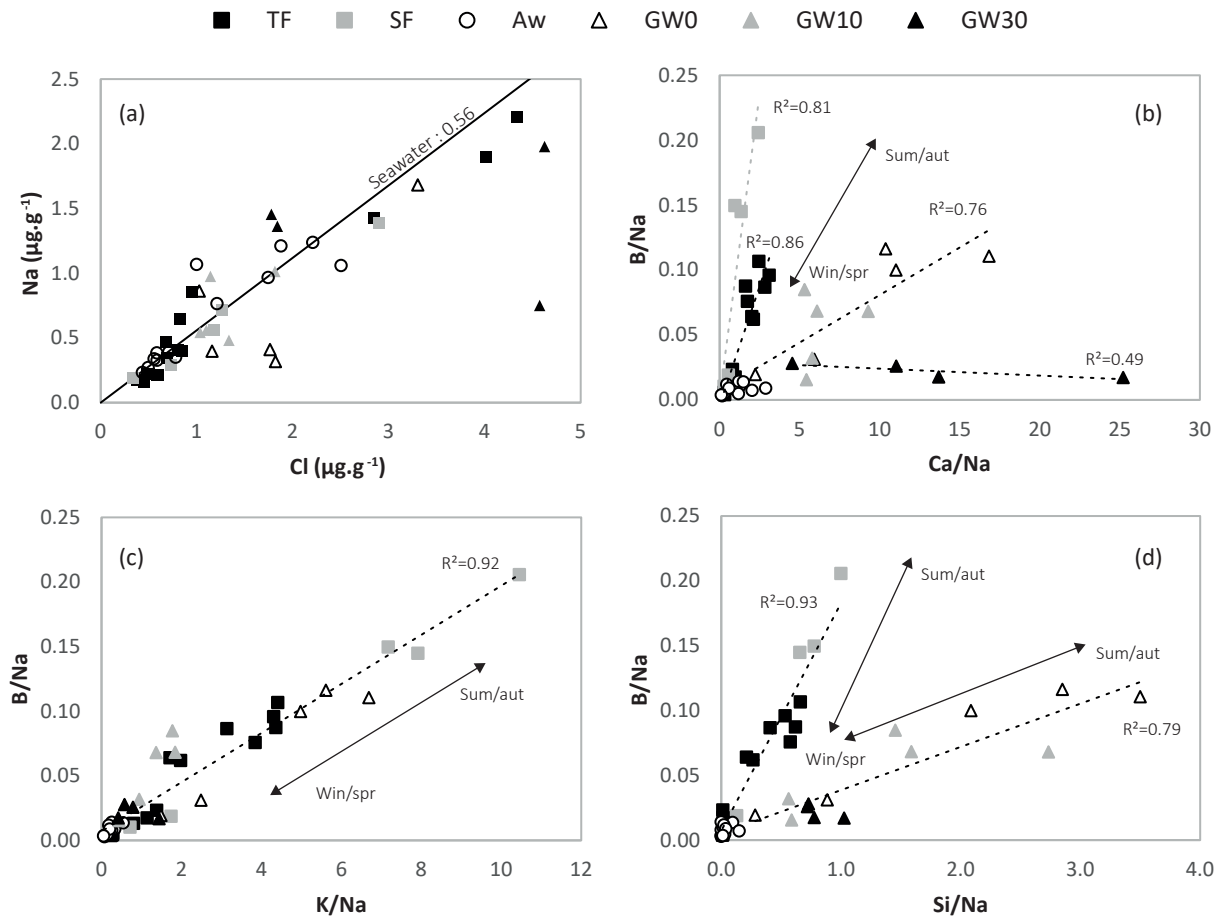


Figure 4: Comparison between (a) Na ( $\text{mg}\cdot\text{L}^{-1}$ ) and Cl ( $\text{mg}\cdot\text{L}^{-1}$ ); (b) B/Na and Ca/Na; (c) K/Na and (d) Si/Na molar ratios in all water samples collected in the Montiers forest ecosystem. TF = throughfalls; SF = stemflow; Aw = atmospheric dissolved deposition (data from Roux et al, (2017)); GW0 = soil solution at 0 cm; GW10 = soil solution at -10 cm; GW30 = soil solution at -30 cm. lines represent linear fit to help identifying similarities of differences between sub-datasets (doesn't include Aw data).

Fig 5: 1 column

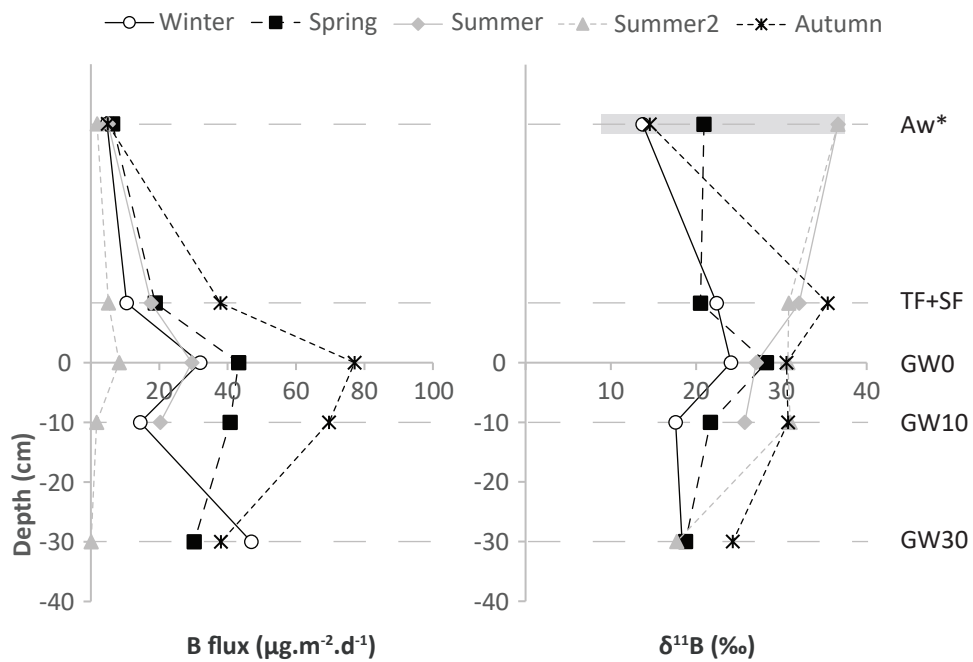


Figure 5: Seasonal variability of B fluxes and isotopic compositions evolution along the hydrological profile (from atmospheric dissolved deposition to soil solutions at -30cm). The above ground part of the hydrological profile displayed isn't to scale. Data from atmospheric dissolved deposition are from Roux et al. (2017). TF = throughfalls; SF = stemflow; Aw = Atmospheric dissolved deposition; GW0 = soil solution at 0cm; GW10 = soil solution at -10cm; GW30 = soil solution at -30cm.

Fig 6: 2 column

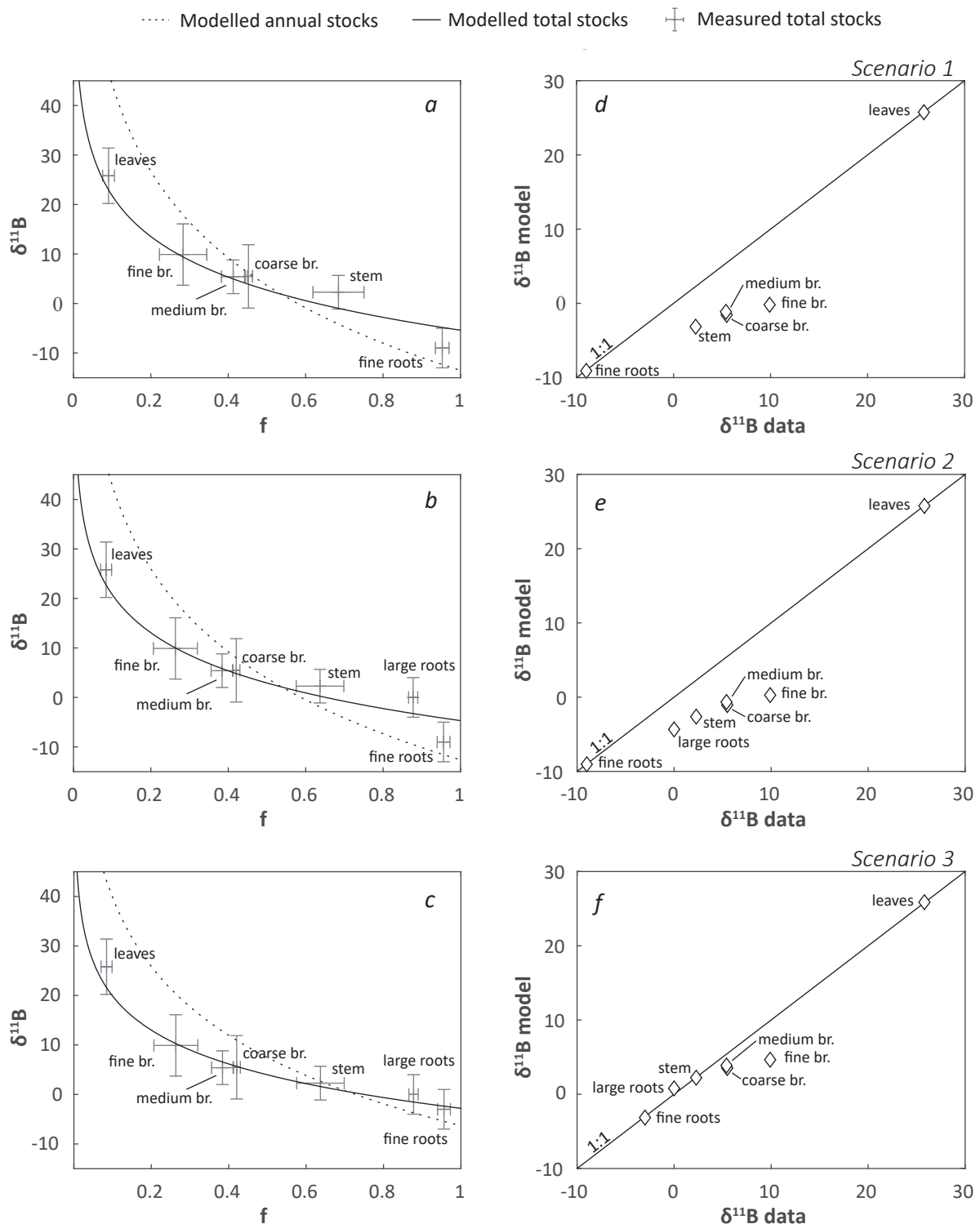


Figure 6: Results of the Rayleigh like model for B during plant growth. (a) corresponds to the annual and long-term modeling using raw data (scenario 1). (b) adds an hypothetical B stock in coarse roots based on data from Turpault et al, (2018) (scenario 2). (c) changes the  $\delta^{11}\text{B}$  value of the fine root compartment to make the entire dataset consistent with Rayleigh-like behavior ( $\delta^{11}\text{B}_{\text{fine roots}} = -3\text{‰}$ ; scenario 3). (d), (e) and (f) compare the results of modelled value of annually formed biomass to the measured value in bulk intermediate organs (branches and stem) for each scenario.

