



## Strontium isotope composition as a tracer of calcium sources in two forest ecosystems in Belgium

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### Abstract

The two main sources of Ca in forest ecosystems are mineral weathering release and atmospheric inputs. We use the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio (Sr is used as a proxy for Ca) to determine the Ca contribution from atmospheric deposition input in two forest ecosystems (beech stands) growing on soils formed from parent materials with contrasting total Ca contents and isotopic ratios: Pleistocene loess in Central Belgium (acid leached soil) and Lower Devonian shales in the Ardenne Massif of High Belgium (ochreous brown earth). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and the Ca and Sr contents were measured in bulk precipitation, in vegetation (beechwood growth rings and leaves) and in main soil horizons (total, acid-extractable and labile pools). The relative contributions of atmospheric input and soil mineral weathering to vegetation were calculated using mixing equations.

Calculations based on Sr isotope ratios of bulk precipitation (end-member 1;  $^{87}\text{Sr}/^{86}\text{Sr}$  close to ocean water: 0.7090), 0.1 M HCl-extractable soil fraction (end-member 2) and beech wood (mixing compartment) indicate that about 43% (Central Belgium) and 39% (Ardennes) of Sr uptake originates from atmospheric inputs. For Ca, the contributions of atmospheric input are 75% and 78%, respectively. These estimations are, however, very sensitive to the choice of the appropriate  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca ratios for the weathering end-member. The isotopic composition of the mineral source is estimated from the soil mineralogical composition and the relative weatherability of the Sr-bearing minerals. Due to soil processes (mineral weathering, element recycling) and geomorphological events (addition of allochthonous minerals to the autochthonous pool inherited from the local bedrock), the distribution of minerals in both soil profiles is heterogeneous and varies from horizon to horizon. Which horizons are relevant and which soil pool (total soil, acid-extractable fraction or labile pool) should be selected for isotopic measurement of the weathering end-member, is therefore open to uncertainty. The choice of the appropriate  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca ratios for the weathering end-member is discussed.

Our results emphasize the importance of the atmospheric contribution of Ca for tree mineral nutrition in the studied forest stands, suggesting that these ecosystems on acid soils are sensitive to chemical changes in the atmospheric environment, e.g. acid depositions associated with decreasing input of atmospheric cations. Our results support therefore

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the conclusion of Hedin et al. [Hedin, L.O., Granat, L., Likens, G.E., Bulshand, T.A., Galloway, J.N., Butler, T., Rodhe, H., 1994. Steep declines in atmospheric base cations in regions of Europe and North America. *Nature*, 367: 351–354], suggesting that the atmospheric base cation trends in Europe and North America are ecologically relevant on the scale of decades for poorly buffered ecosystems. This is a serious possibility of depletion of the soil available cation pool of the High Belgium beech forest, which grows on a bedrock with extremely low levels of total calcium.

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## 1. Introduction

Acidification of forest soils by atmospheric deposition involving depletion of alkaline earth cations is still an active subject of research. Works undertaken in Western Europe and North America suggest that tree nutritional deficiencies may result from an increasing depletion of exchangeable base cations (mainly Ca and Mg) in sensitive soils, caused by inorganic acid inputs (Shortle and Smith, 1988; Åberg et al., 1990; Bondietti et al., 1990; Åberg, 1995; Shortle et al., 1997; McLaughlin, 2000; Likens et al., 1998). Moreover, Hedin et al. (1994), Wesselink et al. (1995) and Likens et al. (1998) consider that base cation decreases in atmospheric precipitation observed in North America and Europe may contribute to decline of forest health by increasing the sensitivity of poorly buffered ecosystems. Excess of anion deposition affects the ecosystem balance by depleting the pool of cation buffers more rapidly than the buffers can be replaced, leading to an aluminisation of the exchange complex, which interferes with the uptake of calcium by trees (Ulrich et al., 1980; Lawrence et al., 1995; Shortle et al., 1997). In soils with a low weatherable mineral reserve, weathering inputs may not be sufficient to replace the accelerated losses of basic cations associated with disturbances such as acidic deposition or intensive forest harvest. To estimate the real impact of such processes, natural isotopes of strontium are recognized to be a powerful tool as a tracer of nutrient sources in forest ecosystems (Capo et al., 1998). In particular, the Sr isotopic studies of Åberg et al. (1989), Miller et al. (1993) and Kennedy et al. (2002) have provided evidence that atmospheric inputs may be quantitatively important as a source of base cations to vegetation under nutrient-poor conditions. Although Sr is in itself of little significance as

a nutrient, it is ubiquitous in nature and is one of the most abundant trace elements in surficial deposits and rocks. Moreover, it acts as a proxy for Ca because both are alkaline earth elements with similar ionic radius and the same valence (Capo et al., 1998). For this reason, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios of natural materials can be used to identify and to quantify the contribution of different Sr sources (and, by inference, of Ca) to the forest vegetation pool. Any possible change of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio by biological or chemical processes would be corrected for mass dependant fractionation during the mass spectrometric measurement. Variations in the Sr isotopic composition in the different components of forest ecosystems are therefore caused entirely by the mixing of Sr derived from different sources with specific isotopic compositions. Within the soil-vegetation system, Ca fluxes are subject to considerable internal circulation but there are only two important inputs into this system: atmospheric deposition and mineral weathering release (Graustein and Armstrong, 1983). If a component of an ecosystem derives its strontium from two sources, which have distinct and internally uniform isotopic compositions, then it is possible to determine the proportions of the strontium derived from each source (Capo et al., 1998). The contribution of each end-member (weathering vs. atmospheric sources) to a two-component mixture (vegetation pool) may be determined using a Sr mixing model.

It is however important to point out that this approach has associated with it uncertainties and site specific difficulties. The Sr isotope method assumes that the two end-members are homogeneously mixed and constant in space and in the considered time interval. This is generally true for the atmospheric end-member, especially in coastal regions, where the Sr

isotopic ratio of atmospheric aerosols is controlled by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oceans ( $0.70923 \pm 0.00001$ ; DePaolo and Ingram, 1985). Continental dust sources impart spatial and temporal variations on this value inland. The main uncertainty comes however from the isotopic composition of the mineral sources, as pointed out by Åberg et al. (1989), Bain and Bacon (1994), Bailey et al. (1996) and Blum and Erel (1997). The soil  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio depends on the Rb/Sr ratio and on the age of the parent material, because  $^{87}\text{Sr}$  is produced by the radioactive  $\beta^-$  decay of  $^{87}\text{Rb}$  (half-life  $\sim 48.8 \times 10^9$  years; decay constant  $\lambda = 1.42 \times 10^{-11} \text{ year}^{-1}$ ) whereas  $^{86}\text{Sr}$  is non-radiogenic (Faure, 1986). However, the variation with depth of the mineralogical composition of soil profiles and the susceptibility of Sr-bearing minerals to weathering largely complicates the assessment of the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio released into soil solution.

The Sr isotope method has been used in forest ecology by different authors (e.g., Graustein and Armstrong, 1983; Gosz et al., 1983; Åberg et al., 1989; Miller et al., 1993; Bailey et al., 1996; Poszwa, 2000; Blum et al., 2002; Kennedy et al., 2002; Dijkstra et al., 2003; Poszwa et al., 2004). The aim of the

present study is to determine the Ca contribution from atmospheric input in two forest ecosystems growing on acid soils with a low weatherable mineral reserve and formed from parent materials with low but distinct total Ca content and contrasting isotopic ratios. In the studied forest stands (one in Central Belgium, the other in High Belgium), the soil mineral Sr isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.712$ ) is well separated from atmospheric inputs ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.709$ ), providing an opportunity to apply the Sr isotope method to sites that are likely susceptible to cation depletion. Moreover, we postulate that the extremely low total Ca content of the soil and the bedrock in the High Belgium forest site strongly reduces the possibility of replenishing the soil exchange complex (the 'labile' pool) through mineral weathering and, consequently, is likely to promote atmospheric influences in tree mineral nutrition. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and the Ca and Sr contents were measured in bulk precipitation, in vegetation, in major soil horizons (bulk soil, 'acid-extractable' soil fraction, 'labile' pool) and in parent materials or bedrock. The relative contributions of atmospheric input and soil mineral weathering to vegetation are calculated using mixing equations.

## 2. Materials and methods

### 2.1. Sites description

Two forest stands were selected for this study, one in the loess belt of Central Belgium (Soignes Regional Forest), the other in the Palaeozoic Ardenne massif in High Belgium (Herbeumont State Forest).

The Soignes Regional Forest, southeast of Brussels, covers 4400 ha of a loessic plateau at about 120 m above sea level. The climate is of Atlantic-type, with an average annual rainfall of 780 mm, evenly distributed throughout the year, and a mean annual temperature of 9.8 °C. The natural vegetation is a deciduous forest with oaks (*Quercus robur* L. and *Quercus petraea* (Mattuschka) Lieblein) and European beech (*Fagus sylvatica* L.) as co-dominant species, but beech has been extensively introduced since the end of the 18th century. The study site is an even-aged beech high forest, planted in 1860–1865 ('Mésanges' site, hereafter MES) (I.G.N.: Tervuren 31/8 N, 50°47'N, 4°27'E). The ground layer consists mainly of *Pteridium aquilinum* (L.) Kuhn, *Dryopteris dilatata* (Hoffm.) A. Gray, *Carex pilulifera* L. and *Milium effusum* L. The presence of a seasonal perched water table is induced locally by compaction under repeated logging traffic. *Juncus effusus* L. and *Carex remota* Jul. ex L., are good indicators of this local soil hydromorphic degradation (Herbauts et al., 1996). Prevailing soils are Leached and Hydromorphic leached soils (French Classification: Sols lessivés and Sols lessivés hydromorphes; FAO-UNESCO: Podzoluvisols; Abc soils series of the Belgian Soil Map), with an  $A_hEB_{(g)}C$  soil profile. The parent material is a Pleistocene niveo-eolian loess which is composed of more than 70% of 2–50 µm silt-size particles. In the studied site, the loess deposit is at least 6 m thick and, in its upper part, dated from the end of the Würm (Weichsel) glaciation (Pleniglacial B: 'Brabantian' loess, ~20,000 years BP; Haesaerts and Bastin, 1977). Beneath the loess lie Tertiary marine sediments (Oligocene clayey sands). The

loess is mainly composed of quartz (~60%), muscovite, K-feldspar, plagioclase, chlorite, and both 1:1 and 2:1 clay minerals. The loess also contains around 13% CaCO<sub>3</sub>, but is decarbonated up to 250 cm in depth. As a result, in the upper 2 m, the pH-H<sub>2</sub>O is <5.0 and in the upper 80 cm of the soil, the effective base cation saturation is very low (<25%); correlatively, aluminium saturation is high (>75%). The humus layer is of the moder-mor type (pH-H<sub>2</sub>O<4.0, mean C/N=18.8). These soils are moreover characterized by an illuvial argillic B<sub>t</sub> horizon (clay-leaching ratio around 2 in the B<sub>2t</sub> horizon), frequently mottled due to unfavourable drainage conditions in the winter. Main soil analytical data are given in Table 1. Morphological, chemical and mineralogical data of similar soils of the Belgian loess belt were published by Van Ranst et al. (1982) and, more

Table 1

Physical and chemical properties of two representative soil profiles in the studied forest stands

| Horizon  | Sampling depth (cm) | Particle size distribution  |  |  |  | Stoniness (vol.%)   | O.M. (%)  | N (%)                         | C/N                         | pH-H <sub>2</sub> O           | CaCO <sub>3</sub> (%) |
|--|---------------------|---|--|--|--|---|---|-------------------------------|-----------------------------|-------------------------------|-----------------------|
|  |                     | 2000–50 μm (%)  | 50–20 μm (%)   | 20–2 μm (%)  | <2 μm (%)  |   |   |                               |                             |                               |                       |
| <i>Acid leached soil (Dystric Podzoluvisol), Soignes Regional Forest</i> |                     |   |  |  |  |   |   |                               |                             |                               |                       |
| A <sub>h</sub>   | 0–5                 |   |  |  |  | 0   | 21.3  | 0.55                          | 18.3                        | 3.7                           |                       |
| E  | 5–25                | 6.0   | 57.9   | 26.0   | 10.1   | 0   | 2.2   | 0.08                          | 14.8                        | 4.0                           |                       |
| B <sub>1t</sub>  | 25–35               | 8.8   | 52.4   | 22.7   | 16.1   | 0   | 1.8   |                               |                             | 4.1                           |                       |
| B <sub>21t</sub>   | 55–75               | 6.1   | 53.0   | 21.8   | 19.1   | 0   | 0.2   |                               |                             | 4.2                           |                       |
| B <sub>22t</sub>   | 80–90               | 5.2   | 55.9   | 22.9   | 16.1   | 0   | 0.1   |                               |                             | 4.4                           |                       |
| B <sub>3t</sub>  | 175–200             | 7.1   | 50.6   | 24.0   | 18.3   | 0   |   |                               |                             | 4.9                           |                       |
| C <sub>k</sub>   | 300–320             | 7.4   | 62.4   | 15.1   | 15.1   | 0   |   |                               |                             | 7.4                           | 15.1                  |
| <i>Ochreous brown earth (Dystric Cambisol), Herbeumont State Forest</i>  |                     |   |  |  |  |   |   |                               |                             |                               |                       |
| A <sub>h</sub>   | 0–3                 |   |  |  |  | 28.5  | 29.8  | 0.75                          | 19.9                        | 3.7                           |                       |
| A <sub>h</sub> /B  | 3–10                | 23.1  | 12.2   | 31.1   | 30.1   | 39.5  | 13.7  | 0.30                          | 22.7                        | 3.9                           |                       |
| B <sub>1w</sub>  | 10–25               | 26.8  | 15.7   | 34.5   | 23.1   | 46.6  | 6.4   |                               |                             | 4.5                           |                       |
| B <sub>2w</sub>  | 30–40               | 28.5  | 19.8   | 37.0   | 14.8   | 59.2  | 4.7   |                               |                             | 4.4                           |                       |
| B <sub>2w</sub> /C   | 45–55               | 30.2  | 22.8   | 37.6   | 9.4  | 77.2  | 2.5   |                               |                             | 4.5                           |                       |
| C  | 70–85               | 45.4  | 12.5   | 29.1   | 12.9   | 75.9  | 0.6   |                               |                             | 4.4                           |                       |
| Horizon  | Sampling depth (cm) | Exchangeable acidity <sup>a</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) | Exchangeable cations <sup>b</sup>                      |  |  | Exchangeable Al <sup>3+ a</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) | Effective CEC (cmol <sub>c</sub> kg <sup>-1</sup> ) | Effective saturation rate (%) | Calcium saturation rate (%) | Aluminium saturation rate (%) |                       |
|  |                     |   | Ca <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) | Mg <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) | K <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) |   |   |                               |                             |                               |                       |
| <i>Acid leached soil (Dystric Podzoluvisol), Soignes Regional Forest</i> |                     |   |  |  |  |   |   |                               |                             |                               |                       |
| A <sub>h</sub>   | 0–5                 | 3.28  | 0.73   | 0.29   | 0.29   | 2.69  | 4.59  | 28.5                          | 15.9                        | 58.6                          |                       |
| E  | 5–25                | 2.59  | 0.14   | 0.06   | 0.09   | 2.59  | 2.88  | 10.1                          | 4.9                         | 89.9                          |                       |
| B <sub>1t</sub>  | 25–35               | 2.98  | 0.14   | 0.06   | 0.13   | 2.98  | 3.30  | 10.0                          | 4.2                         | 90.3                          |                       |
| B <sub>21t</sub>   | 55–75               | 3.05  | 0.55   | 0.18   | 0.15   | 3.05  | 3.92  | 22.4                          | 14.0                        | 77.8                          |                       |
| B <sub>22t</sub>   | 80–90               | 2.26  | 1.97   | 0.93   | 0.21   | 2.26  | 5.37  | 57.9                          | 36.7                        | 42.1                          |                       |
| B <sub>3t</sub>  | 175–200             | 1.29  | 4.19   | 1.35   | 0.22   | 1.29  | 7.05  | 81.7                          | 59.4                        | 18.3                          |                       |
| <i>Ochreous brown earth (Dystric Cambisol), Herbeumont State Forest</i>  |                     |   |  |  |  |   |   |                               |                             |                               |                       |
| A <sub>h</sub>   | 0–3                 | 8.41  | 0.69   | 0.48   | 0.33   | 6.75  | 9.91  | 15.1                          | 7.0                         | 68.1                          |                       |
| A <sub>h</sub> /B  | 3–10                | 6.94  | 0.14   | 0.19   | 0.18   | 5.75  | 7.45  | 6.8                           | 1.9                         | 77.2                          |                       |
| B <sub>1w</sub>  | 10–25               | 3.37  | 0.05   | 0.05   | 0.07   | 2.99  | 3.54  | 4.8                           | 1.4                         | 84.5                          |                       |
| B <sub>2w</sub>  | 30–40               | 2.44  | 0.05   | 0.03   | 0.06   | 2.27  | 2.58  | 5.4                           | 1.9                         | 88.0                          |                       |
| B <sub>2w</sub> /C   | 45–55               | 1.74  | 0.03   | 0.02   | 0.05   | 1.66  | 1.84  | 5.4                           | 1.6                         | 90.2                          |                       |
| C  | 70–85               | 2.68  | 0.04   | 0.02   | 0.06   | 2.53  | 2.80  | 4.2                           | 1.4                         | 90.4                          |                       |

<sup>a</sup> 1 M KCl extraction.<sup>b</sup> 1 M CH<sub>3</sub>COONH<sub>4</sub> pH 7 extraction.

recently, by Brahy et al. (2000). The evolution of soils in relation to periglacial processes in the Soignes Regional Forest was also studied by Langohr and Sanders (1985).

The Herbeumont State Forest covers 1543 ha of a 400 m high plateau between the Semois and Vierre river valleys in the southern Belgian Ardenne region. Mean annual precipitation is 1200 mm, and mean annual temperature is 7.8 °C. The forest stand studied is a selection high-forest of European beech (*Fagus sylvatica* L.) and pedunculate oak (*Quercus robur* L.) ('Poursumont' site, hereafter POUR) (I.G.N.: Herbeumont-Suxy 67/3-4, 49°48'N, 05°16'E); beech is the dominant species (90%). The floristic composition of the herbaceous layer is characteristic of the climax forest association (*Luzulo-Fagetum*) with acidity indicators including *Luzula luzuloides* (Lam.) Dandy et Wilmott, *Deschampsia flexuosa* (L.) Trin., *Carex pilulifera* L. and *Polytrichum formosum* Hedw. The soil, with an A<sub>h</sub>B<sub>w</sub>CR profile, is an ochreous brown earth (French Classification: Sol brun ocreux; FAO-UNESCO: Dystric Cambisol; Gbbfq and Gbbfi soils series of the Belgian Soil Map). The humus is a moder (pH-H<sub>2</sub>O=3.7, mean C/N=16.8). The soil is developed in a loamy and stony material, about 1 m thick, derived from Lower Devonian clastic rocks, mainly Praguian shales and siltstones with sandstones locally. The main minerals are quartz, muscovite, chlorite, K-feldspar, plagioclase, and both 1:1 and 2:1 clay minerals. Silt-size particles (2–50 µm) are prevalent, amounting to more than 50% in all horizons (Table 1). Due to physical weathering of the shales, the clay content (<2 µm) increases from the C horizon (~10%) to the upper layers (~30%), whereas the sand fraction decreases. The gravel fraction (>2 mm) is around 80% in weight close to the bedrock and decreases slightly towards the top horizons (60%). Soil acidity is strong in B<sub>w</sub> and C horizons (pH-H<sub>2</sub>O around 4.5) and very strong in the organic horizons (A<sub>h</sub> and A<sub>h</sub>B: pH-H<sub>2</sub>O<4.0), corresponding to very low effective cation saturation (mostly <10%) and very high exchangeable aluminium saturation (mostly >80%). Very low levels of total calcium (CaO~0.03%) in the parent rock are critical to explaining the deficiency of this base cation in the soil. Forest decline is well documented in this region (Weissen et al., 1992).

## 2.2. Sampling

### 2.2.1. Bulk precipitation

Bulk precipitation samples were collected in three open sites situated nearby the forest stands studied, one in Central Belgium (Brussels, Meteorological station of the 'Jardin expérimental Jean Massart', Université Libre de Bruxelles) and the two others in High Belgium (Vaux-sur-Sûre and Offagne open sites; the second belongs to the 'Réseau de Surveillance de la Qualité de l'Environnement' of the Walloon Region). The Meteorological station of the University of Brussels is situated 3 km apart from the MES forest stand and the two collecting sites of High Belgium are situated 12 km (Offagne) and 28 km (Vaux-sur-Sûre) apart from the POUR forest stand.

### 2.2.2. Vegetation

Beech trees (~130–160 years old) were randomly sampled in MES site (five boles, hereafter *Fagus* A to *Fagus* E) and POUR site (four boles, hereafter *Fagus* I to *Fagus* IV) during a forest clearing in winter period (1995 and 1997, respectively). Discs of about 20 cm thick were cut from the top of the boles (~30 and 20 m height of the ground in Central Belgium and High Belgium, respectively) and were used for dendroecological and dendrochemical measurements (Penninckx et al., 1999, 2001; Herbauts et al., 2002). Leaves were also collected in four beech crowns in the MES site in September 2000. In the POUR forest stand, leaves of one adult beech (~160 years old), one younger beech (~10 years old) and a composite sample of five beech plantlets (2 years old) were sampled in October 2002.

### 2.2.3. Soils, parent materials and bedrocks

Two individual soil profiles were sampled within the MES site of the Soignes Regional Forest (MES I and MES II). Soil sampling was extended to three complementary even-aged beech stands, selected close to the

main MES stand and developed on the same parent material, leading to a total of five soil profiles under beech in the Soignes Regional Forest. Soil samples were taken at different levels corresponding to the major soil horizons: A<sub>h</sub> (0–5 cm), E (5–25 cm), B<sub>1t</sub> (25–35 cm), B<sub>21t</sub> (55–75 cm), B<sub>22t</sub> (80–90 cm), B<sub>3t</sub> (175–200 cm) and C<sub>k</sub> (300–320 cm). In the Herbeumont State Forest (POUR site), main horizons of one soil profile (POUR I) were sampled: A<sub>h</sub> (0–3 cm), A<sub>h</sub>/B (3–10 cm), B<sub>1w</sub> (10–25 cm), B<sub>2w</sub> (30–40 cm), B<sub>2w</sub>/C (45–55 cm) and C (70–85 cm). Three samples of the bedrock were taken out from the coarse rock fragments packed in a thin soil matrix at a depth >85 cm (R horizon).

### 2.3. Sample preparation and analytical methods

#### 2.3.1. Bulk precipitation

Water samples (up to 1 L) were filtered through a 0.45- $\mu\text{m}$  *Millipore* membrane, evaporated to dryness and brought to a final volume of 50 mL after addition of 1 mL suprapur HCl. Ca and Sr concentrations were determined by ICP-AES.

#### 2.3.2. Vegetation

Wood samples representing the 10 last annual growth rings were cut from polished discs, dried at 65 °C and ground in a Retsch ZM100 mill to pass a 750- $\mu\text{m}$  screen. Beech leaves were prepared in a similar way. Mineralization of about 2 g of ground wood or leaves was done by dry ashing in covered zirconium crucibles (16 h at 450 °C). Ashes were dissolved with 1 mL suprapur HCl and heated on a hot plate for 10 min, avoiding boiling. This solution was brought to a final volume of 50 mL. Ca, Mg, K and Sr concentrations were determined by ICP-AES.

#### 2.3.3. Soils, parent materials and bedrock

**2.3.3.1. Soil chemical and physical analyses.** Soil samples were air-dried, crushed and sieved to a particle size of <2 mm. Common methods were used for the determination of soil pH (stiff paste soil–H<sub>2</sub>O), exchangeable acidity and exchangeable aluminium (1 M KCl extraction; derivative titration curve for H<sup>+</sup> and Al<sup>3+</sup>), exchangeable cations (1 M CH<sub>3</sub>COONH<sub>4</sub> pH 7 extraction; ICP-AES determination of Ca, Mg, K and Sr); carbon (dry combustion; Ströhlein dosimeter) and nitrogen (semi-micro Kjeldahl method).

Iron and aluminium were extracted with ammonium dithionite–oxalate at 60 °C ('free' Fe and Al: [Duchaufour and Souchier, 1966](#)), and with acid ammonium oxalate ('amorphous' Fe and Al: [Schwertmann, 1964](#)); Fe and Al concentrations were determined by ICP-AES.

Total chemical analysis was made by fusion of 100 mg finely ground soil (planetary micro mill Retsch), at 700 °C in Pt–Au crucibles (Claisse-Fluxer) with Li metaborate (Johnson Matthey Spectroflux 100 A); fused samples were dissolved in a 3.25% HNO<sub>3</sub> solution and major elements were determined by ICP-AES. Rb and Sr contents were determined by standard X-ray fluorescence spectrometry techniques on pressed powder pellets (~10 g of sample). Analyses were carried out on ARL9400XP instrument at the 'Collectif de Géochimie instrumentale', Univ. de Liège, following the procedure described by [Bologne and Duchesne \(1991\)](#).

Particle-size distribution was determined by the pipette method after H<sub>2</sub>O<sub>2</sub> pretreatment and dispersion with Na-citrate.

**2.3.3.2. Mineralogical determinations.** The mineralogical composition of clay- and silt-size separates was determined using XRD analyses on powder (silt fraction: 2–50  $\mu\text{m}$ ) or air-dried oriented samples on glass slides (clay fraction: <2  $\mu\text{m}$ ); the diffraction was carried out using a Bruker GADDS diffractometer with Cu K $\alpha$  radiation. The quantitative mineralogical reconstitution of the main soil minerals is based on the total chemical analysis of

the clay, silt and sand fractions, in the same way as in the isoquartz assessment method of [Lelong and Souchier \(1970\)](#).

The mineralogical composition of the Praguian shales (bedrock of the POUR site) was determined by classical petrographic microscope techniques on thin sections and, for the very fine-grained material, by XRD after grinding the rock in a planetary micro mill.

**2.3.3.3. Soil extracts.** The ‘labile’ soil fraction is defined as the sum of cations present in the soil solution and of ‘exchangeable’ cations adsorbed on mineral and organic soil colloids. In practice, it is extracted from the soil by leaching with a cation exchange reagent ([Capo et al., 1998](#)). This cation pool was extracted with suprapur  $\text{CH}_3\text{COONH}_4$  (10 g soil+50 mL 1 M  $\text{CH}_3\text{COONH}_4$  at pH 7). The acetate extract was dried and ashed in covered zirconium crucibles (16 h at 450 °C) to eliminate ammonium acetate. Ashes were dissolved with 1 mL suprapur HCl, heated on a hot plate for 10 min, avoiding boiling, and brought to a final volume of 50 mL; Ca and Sr concentrations were determined by ICP-AES.

‘Acid-extractable’ fraction: the aim is to simulate natural Sr release by weathering in dissolving selectively the more weatherable minerals ([Miller et al., 1993](#)). Four successive acid extracts were obtained by shaking 5 g of soil with 50 mL suprapur 0.1 M HCl for 2 h. Prior to this acid treatment, exchangeable Sr was eliminated of the sample by suprapur 1 M  $\text{CH}_3\text{COONH}_4$  leaching. Ca, Mg, K, Na, Al, Fe and Sr concentrations were determined by ICP-AES. In the MES site, surface horizons containing organic matter ( $A_h$  and E horizons) were at first treated with hot suprapur  $\text{H}_2\text{O}_2$  and afterwards with suprapur 1 M  $\text{CH}_3\text{COONH}_4$  to eliminate exchangeable and organically bound Sr; only the  $\text{CH}_3\text{COONH}_4$  leaching pretreatment was applied to the  $A_h$  and  $A_h/B$  soil samples of the POUR site.

**2.3.3.4. Isotope analysis.** Bulk soil and rock samples were totally digested in sealed Teflon vessels using a HF– $\text{HNO}_3$  (10:1) acid mixture. The carbonated fraction of the  $C_k$  horizon of the loessial soil was leached using 0.5 M  $\text{CH}_3\text{COOH}$  (only a partial dissolution was carried out to caution against a possible acid attack of the silicate residue). Chemical separation of Sr was carried out by cation exchange chromatography. Sr isotopic ratios were measured on a VG Sector 54 multicollector thermal ionisation mass spectrometer housed at the “Laboratoire de Géochimie isotopique, Université Libre de Bruxelles”. The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$ . Measurements of the NBS-987 Sr standard yielded on average  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.710272 \pm 0.000007$  ( $2\sigma$ ,  $n=18$ ). Additional details on the analytical procedure can be found in [Ashwal et al. \(2002\)](#).

**2.3.3.5. Calculation.** Because of their geochemical similarities, Sr is often used as a proxy for Ca in ecosystem studies (e.g., [Graustein and Armstrong, 1983](#); [Åberg et al., 1990](#); [Capo et al., 1998](#)). As long as the proportion of each cation in the source materials is known, Sr isotope ratios allow calculation of the proportion of Ca derived from each source.

The proportion of Sr in a mixture (in this case, the vegetation) derived from two sources (atmosphere and weathering) is calculated using a two-component mixing equation ([Capo et al., 1998](#)):

$$X(\text{Sr})_{\text{Atm}} = \frac{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Veg}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Wea}}}{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{Atm}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Wea}}} \quad (1)$$

where  $X(\text{Sr})_{\text{Atm}}$  represents the mass fraction of Sr derived from atmospheric source. Atm and Wea subscripts refer to the atmospheric and the weathering end-members, respectively. Veg indicates the vegetation mixture component.

In most cases, the calculated Sr contribution cannot directly be related to the Ca contribution to vegetation feeding because the proportion of these elements (Sr/Ca ratio) is not the same in the two sources.

Nevertheless, the fraction of calcium contributed by the atmospheric end-member ( $X(\text{Ca})_{\text{Atm}}$ ) in a two-component system can be calculated from the Sr isotope data, provided the Sr/Ca concentration ratio is known for

each component (Capo et al., 1998). The Sr/Ca ratios of the two sources are incorporated into Eq. (1) to determine the proportion of Ca derived from each source. The relative contribution of Ca from soil mineral weathering and atmospheric sources to vegetation is given by a mixing equation (Eq. (2)):

$$X(\text{Ca})_{\text{Atm}} = \frac{[(^{87}\text{Sr}/^{86}\text{Sr})_{\text{veg}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{wea}}] (\text{Sr}/\text{Ca})_{\text{wea}}}{[(^{87}\text{Sr}/^{86}\text{Sr})_{\text{veg}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{wea}}] (\text{Sr}/\text{Ca})_{\text{wea}} + [(^{87}\text{Sr}/^{86}\text{Sr})_{\text{atm}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{veg}}] (\text{Sr}/\text{Ca})_{\text{atm}}} \quad (2)$$

where  $X(\text{Ca})_{\text{Atm}}$  represents the mass fraction of Ca derived from the atmospheric source.

### 3. Results and discussion

#### 3.1. Isotopic composition (Table 2a and 2b)

##### 3.1.1. Bulk precipitation

Sr content in rainwater is around  $1.5 \mu\text{g L}^{-1}$  and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the rainwater collected in the open site nearby the MES site in Central Belgium (Brussels) is 0.709101 ( $n=2$ ). This value is, not surprisingly, close to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the seawater ( $0.70923 \pm 0.00001$ ; DePaolo and Ingram, 1985), the site being only 100 km away from the North Sea coast. The isotopic composition of the rainwater measured in High Belgium (Vaux-sur-Sûre open site ~250 km from the sea coast) is also very similar ( $^{87}\text{Sr}/^{86}\text{Sr}=0.709238$ ) and, apparently, is also strongly controlled by sea-salt aerosols with constant marine  $^{87}\text{Sr}/^{86}\text{Sr}$  values. Bain and Bacon (1994) have pointed out that rainwater has a similar strontium isotope composition over all of Scotland, even for sites as much as 300 km apart. The Sr/Ca ratio of rainwater is, on average,  $0.0043 \pm 0.0010$  (mean  $\pm$  S.D.,  $n=9$ ; Table 2a) in Central Belgium. This value is very close to the mean Sr/Ca ratio ( $0.0047 \pm 0.0022$ ; mean  $\pm$  S.D.,  $n=73$ ) given by Nakano et al. (2001), based on compiled data on Sr and Ca concentrations in rain from various areas in the world. In High Belgium, the Sr/Ca measured in the Offagne site is lower:  $0.0023 \pm 0.0010$  (mean  $\pm$  S.D.,  $n=14$ ; Table 2a).

##### 3.1.2. Vegetation

The average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measured on beech growth rings of the last decade is 0.7111 (mean for five beech boles) in the MES site and 0.714793 (composite mixed sample;  $n=4$ ) in the POUR site. On average, the Sr content is around 3 ppm (Table 2a) in both sites and the Sr/Ca ratios are respectively 0.0046 and 0.0064. Isotopic ratios measured on the 10 last

annual growth rings of individual beeches show a narrow range of variation in the MES site (from 0.711023 to 0.711326;  $n=5$ ) and a broader range in the POUR site (from 0.713755 to 0.716134;  $n=4$ ). Differences between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured in beech wood from Central and High Belgium (MES and POUR sites, respectively) are logically related to the isotopic composition of their respective bedrocks (see hereafter Section 3.1.3.).

Radial variation of the strontium isotope ratio across growth rings is currently being investigated. The first results show that, in the MES site,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio remains constant over a 120-year time period, whereas in the POUR site, the ratio significantly decreases from pith ( $^{87}\text{Sr}/^{86}\text{Sr}=0.715823$ ) to outer rings ( $^{87}\text{Sr}/^{86}\text{Sr}=0.714793$ ) over a chronology of 130 years. The decrease of the Sr/Ca ratio from wood to leaves (0.0046 vs. 0.0016 in the MES site and 0.0064 vs. 0.0019 in the POUR site, Table 2a) is related to a biopurification process as described by Elias et al. (1982), Blum et al. (2000), Poszwa et al. (2000) and Blum et al. (2002).

##### 3.1.3. Soils

Sr contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the main soil horizons of the two studied forest stands are given in Table 2b.

**3.1.3.1. Soil parent materials.** In Central Belgium (MES site), the Sr content of the carbonated Pleistocene loess ( $C_k$  horizon of the leached soil) is around 170 ppm and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is 0.716592. The isotopic ratios of the carbonated fraction ( $\text{CH}_3\text{COOH}$  leachate) and of the silicate residue are 0.708255 and 0.725714, respectively.

In High Belgium, the Lower Devonian bedrock (POUR site) contains only about 25 ppm of Sr, but it is much more radiogenic with a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of

Table 2a

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios  $\pm 2\sigma \times 10^{-6}$ , Sr and Ca concentration data for bulk precipitation ( $\mu\text{g L}^{-1}$ ) and vegetation ( $\text{mg kg}^{-1}$ , 100 °C heated material) in the studied sites

| Bulk precipitation (0.45 $\mu\text{m}$ filtered)                    |                                  |   |                                       |                                |                                |   |                               |                               |                                |      |        |
|---|----------------------------------|---|---------------------------------------|--------------------------------|--------------------------------|---|-------------------------------|-------------------------------|--------------------------------|------|--------|
| Location  | Sampling date                    | $^{87}\text{Sr}/^{86}\text{Sr}$<br>$\pm 2\sigma \times 10^{-6}$ | Sr<br>( $\mu\text{g L}^{-1}$ )        | Ca<br>( $\mu\text{g L}^{-1}$ ) | Sr/Ca<br>( $\text{g g}^{-1}$ ) |   |                               |                               |                                |      |        |
| Central Belgium BP1   | 28-XI-2001                       | 0.709026 $\pm$ 10   | 1.3                                   | 250                            | 0.0052                         |   |                               |                               |                                |      |        |
| Central Belgium BP2   | 29-XII-2002                      | 0.709175 $\pm$ 7  | 1.4                                   | 292                            | 0.0048                         |   |                               |                               |                                |      |        |
| High Belgium BP3 (Vaux-sur-Sûre)                                    | 23-I-2003                        | 0.709238 $\pm$ 7  | 2.4                                   | 1112                           | 0.0021                         |   |                               |                               |                                |      |        |
| Central Belgium mean bulk precipitation ( $n=9$ ; mean $\pm$ S.D.)  |                                  |   | 1.1 $\pm$ 0.3                         | 279 $\pm$ 83                   | 0.0043 $\pm$ 0.0010            |   |                               |                               |                                |      |        |
| High Belgium mean precipitation (Offagne, $n=14$ ; mean $\pm$ S.D.) |                                  |   | 3.6 $\pm$ 2.0                         | 1847 $\pm$ 1547                | 0.0023 $\pm$ 0.0010            |   |                               |                               |                                |      |        |
| Vegetation  |                                  |   |                                       |                                |                                |   |                               |                               |                                |      |        |
| Location  | Wood years growth interval       | Beech boles   |                                       |                                |                                | Beech leaves  |                               |                               |                                |      |        |
|   |                                  | $^{87}\text{Sr}/^{86}\text{Sr}$<br>$\pm 2\sigma \times 10^{-6}$ | Sr $^{-1}$<br>( $\text{mg kg}^{-1}$ ) | Ca<br>( $\text{mg kg}^{-1}$ )  | Sr/Ca<br>( $\text{g g}^{-1}$ ) | $^{87}\text{Sr}/^{86}\text{Sr}$<br>$\pm 2\sigma \times 10^{-6}$ | Sr<br>( $\text{mg kg}^{-1}$ ) | Ca<br>( $\text{mg kg}^{-1}$ ) | Sr/Ca<br>( $\text{g g}^{-1}$ ) |      |        |
| MES   | <i>Fagus</i> A                   | 1990–1994   | 0.711023 $\pm$ 9                      | 2.9                            | 552                            | 0.0053  | <i>Fagus</i> 1                | 0.711025 $\pm$ 14             | 16.8                           | 9410 | 0.0018 |
|   | <i>Fagus</i> B                   | 1990–1994   | 0.711158 $\pm$ 10                     | 1.9                            | 359                            | 0.0053  | <i>Fagus</i> 2                | 0.711259 $\pm$ 10             | 10.6                           | 7060 | 0.0015 |
|   | <i>Fagus</i> C                   | 1985–1989   | 0.711326 $\pm$ 9                      | 1.5                            | 467                            | 0.0032  | <i>Fagus</i> 3                | 0.711506 $\pm$ 10             | 15.2                           | 9530 | 0.0016 |
|   | <i>Fagus</i> D                   | 1985–1989   | 0.711002 $\pm$ 10                     | 2.8                            | 698                            | 0.0040  | <i>Fagus</i> 4                | 0.711169 $\pm$ 9              | 16.3                           | 9850 | 0.0017 |
|   | <i>Fagus</i> E                   | 1990–1994   | 0.711128 $\pm$ 10                     | 3.9                            | 741                            | 0.0053  |                               |                               |                                |      |        |
|   | Mean                             |   | 0.7111                                | 2.6                            | 563                            | 0.0046  |                               |                               |                                |      |        |
|   | S.D.                             |   | 0.0001                                | 0.9                            | 159                            | 0.0010  |                               |                               |                                |      |        |
|   | <i>Fagus</i> composite ( $n=5$ ) | 1960–1964   | 0.711117 $\pm$ 7                      | 3.4                            | 732                            | 0.0047  |                               |                               |                                |      |        |
|   | <i>Fagus</i> composite ( $n=5$ ) | 1970–1974   | 0.711104 $\pm$ 9                      | 3.5                            | 810                            | 0.0043  |                               |                               |                                |      |        |
| POUR  | <i>Fagus</i> I                   | 1975–1979   | 0.713755 $\pm$ 6                      | 2.3                            | 309                            | 0.0076  | <i>Fagus</i> (mature)         | 0.714599 $\pm$ 6              | 12.2                           | 6429 | 0.0019 |
|   | <i>Fagus</i> I                   | 1994–1996   | 0.713827 $\pm$ 6                      | 2.5                            | 334                            | 0.0074  | <i>Fagus</i> (10 yrs)         | 0.713532 $\pm$ 6              | 5.6                            | 2772 | 0.0020 |
|   | <i>Fagus</i> II                  | 1975–1979   | 0.714653 $\pm$ 8                      | 3.5                            | 575                            | 0.0061  | <i>Fagus</i> (plantlets)      | 0.713679 $\pm$ 6              | 6.5                            | 4560 | 0.0014 |
|   | <i>Fagus</i> II                  | 1994–1996   | 0.714603 $\pm$ 8                      | 2.5                            | 422                            | 0.0059  |                               |                               |                                |      |        |
|   | <i>Fagus</i> III                 | 1975–1979   | 0.715042 $\pm$ 7                      | 3.7                            | 573                            | 0.0064  |                               |                               |                                |      |        |
|   | <i>Fagus</i> III                 | 1994–1996   | 0.714765 $\pm$ 7                      | 2.8                            | 459                            | 0.0061  |                               |                               |                                |      |        |
|   | <i>Fagus</i> IV                  | 1975–1979   | 0.715977 $\pm$ 7                      | 2.3                            | 361                            | 0.0064  |                               |                               |                                |      |        |
|   | <i>Fagus</i> IV                  | 1994–1996   | 0.716134 $\pm$ 7                      | 2.4                            | 472                            | 0.0051  |                               |                               |                                |      |        |
|   | Mean                             |   | 0.7148                                | 2.8                            | 438                            | 0.0064  |                               |                               |                                |      |        |
|   | S.D.                             |   | 0.0009                                | 0.6                            | 102                            | 0.0008  |                               |                               |                                |      |        |
|   | <i>Fagus</i> composite ( $n=4$ ) | 1975–1979   | 0.714809 $\pm$ 7                      | 3.4                            | 526                            | 0.0065  |                               |                               |                                |      |        |
|   | <i>Fagus</i> composite ( $n=4$ ) | 1994–1995   | 0.714793 $\pm$ 10                     | 3.0                            | 572                            | 0.0052  |                               |                               |                                |      |        |

Sr/Ca mass ratios are given for each compartment.

S.D. for standard deviation.

Table 2b

 $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  $\pm 2\sigma \times 10^{-6}$ , Sr and Ca concentration data ( $\text{mg kg}^{-1}$  of air dried soil) for bulk soil, labile pool ( $\text{CH}_3\text{COONH}_4$  extracted), HCl soil leachate in the two studied sites

| Soil                    |                     | Bulk soil (sieved <2 mm)    |  |                            |                            |                            |                              |  | CH <sub>3</sub> COONH <sub>4</sub> extracted |                            |                              |  | 0.1 M HCl leaching         |                            |                             |  |
|-------------------------|---------------------|-----------------------------|--|----------------------------|----------------------------|----------------------------|------------------------------|--|--|----------------------------|------------------------------|--|----------------------------|----------------------------|-----------------------------|--|
| Location                | Sampling depth (cm) | Horizon                     | $^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma \times 10^{-6}$ | Sr ( $\text{mg kg}^{-1}$ ) | Rb ( $\text{mg kg}^{-1}$ ) | Ca ( $\text{mg kg}^{-1}$ ) | Sr/Ca ( $\text{g g}^{-1}$ )  | $^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma \times 10^{-6}$ | Sr ( $\text{mg kg}^{-1}$ )                   | Ca ( $\text{mg kg}^{-1}$ ) | Sr/Ca ( $\text{g g}^{-1}$ )  | $^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma \times 10^{-6}$ | Sr ( $\text{mg kg}^{-1}$ ) | Ca ( $\text{mg kg}^{-1}$ ) | Sr/Ca ( $\text{g g}^{-1}$ ) |  |
| MES I                   | 0–5                 | A <sub>h</sub>              | 0.731066±11  | 74.1                       | 67.8                       | 2500                       | 0.0296                       | 0.711725±11  | 1.10   | 283                        | 0.0039                       |  |                            |                            |                             |  |
|                         | 10–25               | E                           | 0.732199±14  | 83.5                       | nd                         | 3192                       | 0.0261                       | 0.713040±11  | 0.23   | 65                         | 0.0036                       |  |                            |                            |                             |  |
|                         | 55–75               | B <sub>21t</sub>            | 0.732698±20  | 85.9                       | nd                         | 4429                       | 0.0194                       | 0.713321±13  | 1.44   | 267                        | 0.0054                       |  |                            |                            |                             |  |
|                         | 175–200             | B <sub>3t</sub>             | 0.727883±16  | 92.8                       | nd                         | 3998                       | 0.0232                       | 0.712344±13  | 5.00   | 1017                       | 0.0050                       |  |                            |                            |                             |  |
|                         | 300–320             | C <sub>k</sub>              | 0.716592±12  | 168.0                      | 60.0                       | 52500                      | 0.0032                       |  |  |                            |                              |  |                            |                            |                             |  |
|                         | 300–320             | Carbonates <sup>a</sup>     | 0.708255±7   | 63.7                       | nd                         | 36899                      | 0.0017                       |  |  |                            |                              |  |                            |                            |                             |  |
|                         | 300–320             | C <sub>k</sub> <sup>b</sup> | 0.725714±13  | 77.7                       | 69.5                       | 4012                       | 0.0194                       |  |  |                            |                              |  |                            |                            |                             |  |
| MES II                  | 0–5                 | A <sub>h</sub>              | 0.731109±7   | 78.6                       | 73.1                       | 2035                       | 0.0386                       | 0.712138±6   | 0.89   | 190                        | 0.0047                       | 0.713643±7   | 0.37                       | 32                         | 0.0117                      |  |
|                         | 10–25               | E                           | 0.732115±7   | 73.5                       | 61.0                       | 2161                       | 0.0340                       | 0.712888±7   | 0.12   | 19                         | 0.0062                       | 0.713114±6   | 0.14                       | 8                          | 0.0179                      |  |
|                         | 55–75               | B <sub>21t</sub>            | 0.732764±10  | 75.9                       | 83.2                       | 1962                       | 0.0387                       | 0.715291±6   | 0.48   | 66                         | 0.0073                       | 0.712067±7   | 0.39                       | 15                         | 0.0257                      |  |
|                         | 175–200             | B <sub>3t</sub>             | 0.727066±7   | 82.8                       | 83.0                       | 2929                       | 0.0283                       | 0.712234±7   | 5.29   | 1110                       | 0.0048                       | 0.713571±6   | 1.15                       | 281                        | 0.0041                      |  |
| Soignes Regional Forest |                     |                             | Mean±S.D. (n=5 except <sup>c</sup> , n=4)                  |                            |                            |                            | Mean±S.D. (n=4) <sup>c</sup> |  |  |                            | Mean±S.D. (n=3) <sup>d</sup> |  |                            |                            |                             |  |
|                         | 0–5                 | A <sub>h</sub>              | 0.7301±0.0025  | 77±3                       | 70±2                       | 2093±362                   | 0.038±0.006                  | 0.7121±0.0007  | 0.81±0.29                                    | 200±107                    | 0.0049±0.0021                |  |                            |                            |                             |  |
|                         | 10–25               | E                           | 0.7321±0.0001  | 75±5                       | 61±1 <sup>c</sup>          | 2361±469                   | 0.032±0.004                  | 0.7129±0.0002  | 0.15±0.06                                    | 36±21                      | 0.0043±0.0012                |  |                            |                            |                             |  |
|                         | 55–75               | B <sub>21t</sub>            | 0.7323±0.0005  | 77±5                       | 79±3 <sup>c</sup>          | 2558±1049                  | 0.033±0.008                  | 0.7137±0.0011  | 1.43±0.68                                    | 241±119                    | 0.0062±0.0008                | 0.7125±0.0005  | 0.36±0.04                  | 18±6                       | 0.0211±0.0073               |  |
|                         | 175–200             | B <sub>3t</sub>             | 0.7279±0.0015  | 85±5                       | 81±4 <sup>c</sup>          | 3688±839                   | 0.025±0.002                  | 0.7123±0.0003  | 5.04±0.17                                    | 1092±135                   | 0.0047±0.0005                | 0.7137±0.0002  | 1.3±0.3                    | 377±104                    | 0.0036±0.0004               |  |
| POUR I                  | 0–3                 | A <sub>h</sub>              | 0.747102±9   | 46.0                       | 136.5                      | 929                        | 0.0495                       | 0.714509±9   | 0.69   | 135                        | 0.0051                       | 0.714070±6 <sup>c</sup>                                    | 0.71 <sup>c</sup>          | 69 <sup>c</sup>            | 0.0104 <sup>c</sup>         |  |
|                         | 3–10                | A <sub>h</sub> /B           | 0.751009±10  | 43.6                       | 142.6                      | 786                        | 0.0555                       | 0.715634±9   | 0.12   | 12                         | 0.0098                       | 0.716204±6 <sup>c</sup>                                    | 0.42 <sup>c</sup>          | 37 <sup>c</sup>            | 0.0116 <sup>c</sup>         |  |
|                         | 10–25               | B <sub>1w</sub>             | 0.754042±8   | 42.6                       | 144.3                      | 500                        | 0.0852                       | 0.715427±13  | 0.05   | 5                          | 0.0101                       | 0.717617±6   | 0.46                       | 35                         | 0.0132                      |  |
|                         | 45–55               | B <sub>2w</sub> /C          | 0.755251±5   | 44.3                       | 150.9                      | 533                        | 0.0801                       | 0.717020±5   | 0.03   | 4                          | 0.0075                       | 0.717027±5   | 0.48                       | 35                         | 0.0137                      |  |
|                         | 70–85               | C                           | 0.769918±9   | 35.0                       | 142.8                      | 286                        | 0.1225                       | 0.717845±26  | 0.04   | 5                          | 0.0071                       | 0.715234±6   | 0.53                       | 46                         | 0.0114                      |  |
|                         | 70–85               | R                           | 0.769133±8   | 25.0                       | 89.4                       | 214                        | 0.1167                       |  |  |                            |                              |  |                            |                            |                             |  |
|                         | 70–85               | R (shale)                   | 0.766625±8   | 24.9                       | 84.6                       | nd                         | nd                           |  |  |                            |                              |  |                            |                            |                             |  |
|                         | 70–85               | R (sandstone)               | 0.726022±7   | 20.9                       | 18.1                       | nd                         | nd                           |  |  |                            |                              |  |                            |                            |                             |  |

Element Sr/Ca ratios are given for each soil fraction. Rb concentrations ( $\text{mg kg}^{-1}$  of air dried soil) are given for bulk soil.

S.D. for standard deviation.

<sup>a</sup> Partial 0.5 M CH<sub>3</sub>COOH leaching.

<sup>b</sup> HF digested after 2.5 M HCl leaching.

<sup>c</sup> MES II, TU, PIG, REL sites.

<sup>d</sup> MES II, TU, PIG sites.

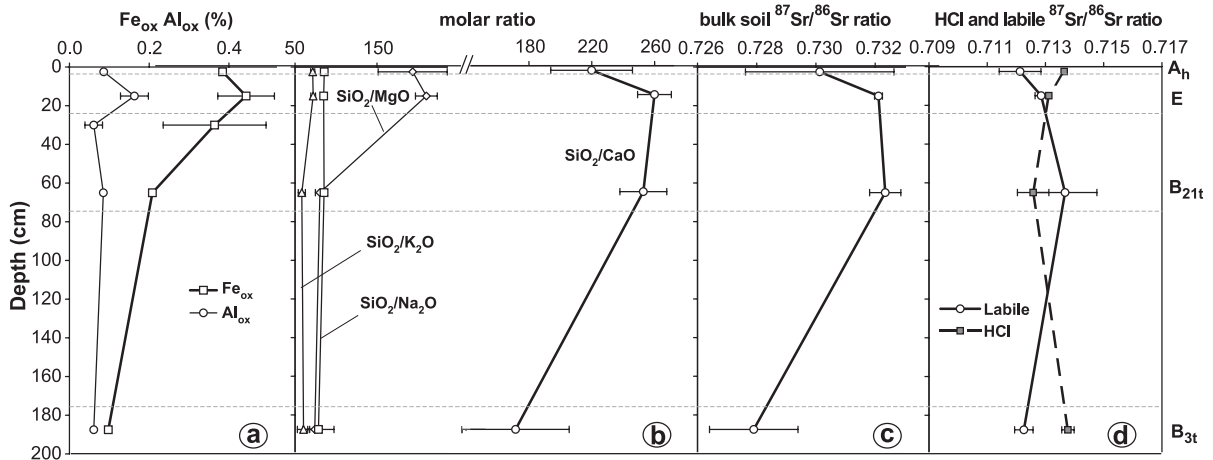


Fig. 1. Central Belgium sites (MES I, MES II<sup>†,‡,§</sup>, TU<sup>‡,§</sup>, PIG<sup>‡,§</sup>, REL<sup>‡</sup>). Soil profile distribution with depth of: (a) mean amorphous Fe and Al contents ( $n=5$ ) extracted by acid ammonium oxalate ( $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$ ); (b)  $\text{SiO}_2/\text{CaO}$ ,  $\text{SiO}_2/\text{MgO}$ ,  $\text{SiO}_2/\text{Na}_2\text{O}$ ,  $\text{SiO}_2/\text{K}_2\text{O}$  molar ratios ( $n=4^{\ddagger}$ ); (c)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of bulk soil ( $n=5$ ); and (d)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the acid extracted pool (0.1 M HCl,  $n=3^{\S}$  except for  $\text{A}_h$  and E horizons:  $n=1^{\dagger}$ ) and labile pool ( $\text{CH}_3\text{COONH}_4$  extracted,  $n=4^{\ddagger}$ ). Error bars show standard deviations.

0.769133 for bulk rock, 0.766625 for the shales and 0.726022 for the sandstones nodules.

### 3.1.3.2. Acid leached soils on Pleistocene loess.

**Bulk soil.** The Sr content of the total digests of soil horizons is around 80 ppm. It slightly decreases upwards from the  $\text{B}_{3t}$  to the E horizon, while the Sr/Ca ratio increases from 0.025 to 0.032 (Table 2b). The distribution pattern of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio with depth is shown in Fig. 1c. In the  $\text{B}_{3t}$  horizons (175–200 cm depth), the Sr isotope ratio is on average  $0.7279 \pm 0.0015$ , slightly higher than the Sr isotope composition of the silicate residue of the carbonated loess ( $^{87}\text{Sr}/^{86}\text{Sr}=0.725714$ ) measured in the MES I soil profile. This slight increase of the isotope ratio can be attributed to mineralogical changes due to weathering of the most weatherable minerals, i.e. Ca-plagioclase (Table 3). This Sr-rich and Rb-poor mineral generally

has a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Faure, 1986) and is well known to be a weakly resistant mineral in acidic soil environments (Franke and Teschner-Steinhardt, 1994). Change in pH from  $\text{C}_k$  (>250 cm; pH- $\text{H}_2\text{O} \sim 7.5$ ) to  $\text{B}_{3t}$  horizon (175–200 cm; pH- $\text{H}_2\text{O} \sim 5.0$ ) can be related to the complete dissolution of the  $\sim 10\%$   $\text{CaCO}_3$  content and to the rapid decrease in calcium saturation ( $\sim 60\%$  in the  $\text{B}_{3t}$  horizon). In the overlying  $\text{B}_{21t}$  and E horizons, the increase of the Sr isotopic ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$  are, on average, 0.732394 and 0.732112, respectively) is consistent with a higher acidity (pH<4.5) and a more severe weathering of the mineral pool. The increasing intensity of weathering processes upwards in the soil profile is clearly shown by the increase of amorphous Fe and Al contents (Fig. 1a) and by the increase of  $\text{SiO}_2/\text{CaO}$  and  $\text{SiO}_2/\text{MgO}$  molar ratios (Fig. 1b) which reflects preferential weathering of plagioclase feldspars and chloritic

Table 3

Mineralogical composition of the MES I soil profile (<2 mm) in wt.%

| Depth (cm) | Horizon          | Hornblende (wt.%) | K-feldspar (wt.%) | Muscovite (wt.%) | Illite (wt.%) | Na-plagioclase (wt.%) | Ca-plagioclase (wt.%) | Chlorite (wt.%) | Quartz (wt.%) |
|------------|------------------|-------------------|-------------------|------------------|---------------|-----------------------|-----------------------|-----------------|---------------|
| 0–5        | $\text{A}_h$     | 0.28              | 6.78              | 5.29             | 3.26          | 8.36                  | 1.60                  | 4.38            | 68.76         |
| 10–25      | E                | 0.26              | 5.39              | 4.73             | 3.68          | 7.81                  | 1.57                  | 4.12            | 67.40         |
| 55–75      | $\text{B}_{21t}$ | 0.18              | 5.26              | 4.80             | 6.12          | 6.55                  | 1.19                  | 9.73            | 62.50         |
| 175–200    | $\text{B}_{3t}$  | 0.14              | 5.63              | 5.52             | 5.99          | 13.06                 | 2.37                  | 9.46            | 55.72         |
| 300–320    | $\text{C}_k$     | 0.20              | 5.00              | 5.90             | 5.89          | 14.15                 | 2.99                  | 8.92            | 58.81         |

See text for details.

minerals. The close connection between the  $^{87}\text{Sr}/^{86}\text{Sr}$  distribution with depth and the weathering pattern of Ca-plagioclase is especially obvious when the vertical distribution of the  $\text{SiO}_2/\text{CaO}$  molar ratio is compared with isotopic data (Fig. 1). This strikingly confirms that the evolution of the bulk soil isotope composition is mainly determined by the susceptibility to weathering of Sr-bearing minerals, as previously noted by Bain and Bacon (1994), Bailey et al. (1996), Blum and Erel (1997) and Bain et al. (1998). Preferential leaching of Ca/Sr-rich minerals with a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during soil evolution, compared to K/Rb-rich minerals with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, explains most of the Sr isotopic pattern of the studied soils. There is moreover a highly significant correlation ( $r=0.7986$ ,  $P<0.001$ ,  $n=21$ ) between the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio and the  $\text{SiO}_2/\text{CaO}$  molar ratio. Quantitative mineralogical reconstitution (Table 3) indicates that, in this acid leached soil, about half of the Ca-plagioclase initial content in the soil parent material was lost during soil evolution. Above the clay-enriched  $\text{B}_{21t}$  horizon, in the eluvial soil compartment (E horizon), the isotopic ratio tends to stabilize and clearly decreases in the organic-rich humic layer ( $^{87}\text{Sr}/^{86}\text{Sr}$  of the  $\text{A}_h$  horizon=0.730127). This can be explained either by an increasing contribution of organically bound strontium with low isotopic ratio to the total strontium pool ( $^{87}\text{Sr}/^{86}\text{Sr}$  of beech leaves is, on average, 0.711240), as suggested by Bailey et al. (1996), Bain and Bacon (1994) and Poszwa (2000), or by mineralogical changes induced by translocation (i.e. clay illuviation) or destabilization of K- and Rb-bearing minerals (illite and muscovite, with high isotopic ratio), in a more acidic soil environment ( $\text{pH}-\text{H}_2\text{O}<4.0$ ) (Olson et al., 2000; Kohut and Warren, 2000). The strong decrease of micaceous mineral contents in the upper E and  $\text{A}_h$  horizons (Table 3) clearly supports the second hypothesis: losses are around half of the initial content. By contrast, losses are only around 25% in the underlying  $\text{B}_{21t}$  horizon.

*Acid-extractable soil fraction.* Sr isotope ratios of the 0.1 M HCl laboratory leachates measured in MES II soil profile, supported by mean value of the Soignes Regional forest (Table 2b), are, for all horizons, clearly lower ( $<0.7137$ ) than in the bulk soil ( $>0.7271$ ). This can be accounted for by a preferential dissolution of the plagioclase feldspars, which are the most weatherable minerals and which produces

mainly non-radiogenic strontium, lowering the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the HCl leachate. Plagioclase is indeed known to dissolve at relative fast rate and can release significant Sr, even when it is present in relatively low concentrations (Brantley et al., 1998). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the HCl treatment ('simulated weathering') are therefore significantly lower than total soil digests and reflect the differential weatherability of the soil minerals.

*Ammonium acetate extractable soil fraction: 'labile' pool.* The soil 'labile' pool is usually viewed as a mixture of cations (mainly exchangeable cations) derived from mineral weathering, atmospheric deposition and, in surface horizons, organic restitution. It is therefore not surprising that Sr isotope ratios of the ammonium acetate extractable soil fraction ( $<0.7153$ ) are, for all horizons, lower than those of the total digests of soil (Table 2b). More surprising is the fact that the Sr isotope ratios of the 'labile' pool are always close to those of the HCl leachates (Fig. 1d). This clearly suggests that the Sr isotopic composition of the soil cation exchange pool is controlled almost entirely by weathering processes (i.e., by the weatherability of the Sr-containing mineral phases in each horizon). It can also be concluded that input to the soil exchangeable pool of Sr from atmospheric deposition or organic restitutions does not appear to impart a significant effect on the soil exchangeable strontium isotopic composition. In a study on a granitic glacial soil chronosequence, Blum and Erel (1997) had also concluded that there were no appreciable atmospheric contributions of Sr to the soil cation exchange pool at soil depths greater than about 10 cm.

### 3.1.3.3. Ochreous brown earths on Lower Devonian shales.

*Bulk soil.* The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of bulk soils developed on Lower Devonian shales are always significantly higher than those of the loessic leached soils of Central Belgium: the values range from 0.747102 (humic layers) to 0.769918 (C horizons) (Table 2b). This is a direct consequence of high values in the Palaeozoic bedrock (R horizon:  $^{87}\text{Sr}/^{86}\text{Sr}=0.769133$ ). Surprisingly, the Sr isotope ratio (Fig. 2c) increases with depth. The expected pattern was an increase of the isotopic ratio from the parent material (C horizon) to the weathered surface horizons, due to

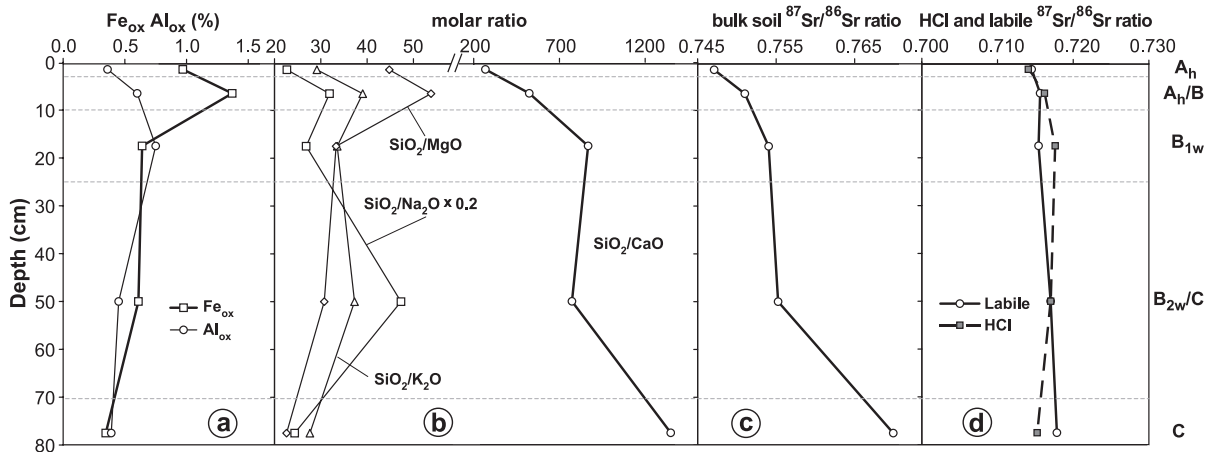


Fig. 2. High Belgium site (POUR I). Soil profile distribution with depth of: (a) amorphous Fe and Al contents extracted by acid ammonium oxalate ( $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$ ); (b)  $\text{SiO}_2/\text{CaO}$ ,  $\text{SiO}_2/\text{MgO}$ ,  $\text{SiO}_2/\text{Na}_2\text{O} \times 0.2$ ,  $\text{SiO}_2/\text{K}_2\text{O}$  molar ratios; (c)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of bulk soil; and (d)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the acid extracted pool (0.1 M HCl) and labile pool ( $\text{CH}_3\text{COONH}_4$  extracted).

more rapid weathering of Ca/Sr-rich minerals compared to K/Rb-rich minerals, as observed in the acid leached soils on loess. The observed isotopic trend is nicely correlated with a decreasing total calcium content with depth (Table 2b). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio and the total Ca content are significantly correlated ( $r = -0.9390$ ,  $P < 0.01$ ,  $n = 6$ ), suggesting that, even if uncommon, the Ca-bearing minerals are again of primary importance in determining the soil isotopic pattern. However, the decrease of the total calcium content with depth and the abrupt increase of the  $\text{SiO}_2/\text{CaO}$  molar ratio between the B<sub>2w</sub>/C and the C horizon are difficult to explain in terms of mineral weathering. This is utterly inconsistent with all the other element ‘weathering’ patterns (amorphous Fe and Al contents,  $\text{SiO}_2/\text{K}_2\text{O}$ ,  $\text{SiO}_2/\text{MgO}$  and  $\text{SiO}_2/\text{Fe}_2\text{O}_3$  molar ratios) that clearly increase upwards (Fig. 2;  $\text{SiO}_2/\text{Fe}_2\text{O}_3$  is not reported). In their soil mineralogical study on ‘phyllites’ and ‘weathering loam’ of High Belgium, Van Ranst et al. (1982) have pointed out that inconsistent distribution or abrupt changes of molar ratios cannot be explained by pedogenetic processes. They hypothesised a contribution of ‘solifluction material’ covering the local weathering product of the bedrock. In High Belgium, gelifluction deposits inherited from the Pleistocene periglacial environment are indeed widely distributed (Pissart, 1976). However, in the present case, particle-size distribution curves, used to test soil homogeneity in four profiles of

the POUR site, fail to reveal with certainty the presence of solifluction material overlying the weathered local shales. Moreover, the presence of a solifluction layer could hardly explain that only the Ca vertical distribution is changed. In soils developed on Devonian shales with extremely low calcium contents ( $< 0.05\%$  CaO in the R horizon; Table 2b), an increase of Ca concentration upwards in the soil could also result from: (1) a high contribution of organically bound and exchangeable calcium to the total calcium pool in the upper horizons, and/or (2) the addition of allochthonous Ca-bearing minerals to the autochthonous pool inherited from the local bedrock. As the sum of Ca associated with organic matter and exchangeable Ca represents less than 6% of the total Ca content in the A<sub>h</sub>/B horizon and less than 1% in the B<sub>w</sub> horizon ( $< 1$  and  $< 0.05\%$ , respectively, for Sr), the first hypothesis seems highly unlikely. The second hypothesis postulates that the soil was enriched by allochthonous inputs of Ca-rich and non-radiogenic Sr-bearing minerals that were not detected by the XRD method. This hypothesis is supported by the Rb–Sr isochron diagram, which plots the Sr isotopic compositions against  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios (Fig. 3). Whereas the age calculated for the three whole rock samples from the bedrock ( $384.9 \pm 7.5$  Ma; MSWD = 0.20) fits reasonably well with the Lower Devonian period, the five horizons of the soil clearly plot off this line, to the right of it. These horizons are nevertheless aligned

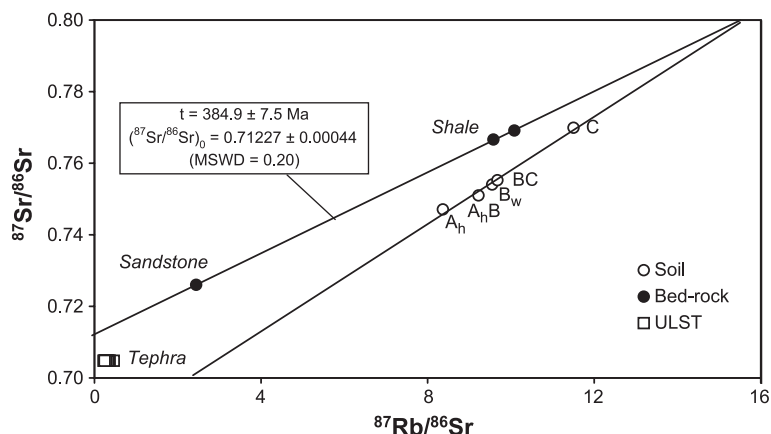


Fig. 3. Rb–Sr isochron plot for bedrock and soil samples of High Belgium (POUR site). The Rb–Sr isotopic systematics of shale and sandstone shows a well correlated isochron. The calculated age ( $384.9 \pm 7.5$  Ma) fits with Lower Devonian epoch. The pseudo-isochron drawn with soil samples reflects the mixing of two materials: the Praguian soil material and an unknown allochthonous deposit with low  $^{87}\text{Rb}/^{86}\text{Sr}$  and low  $^{87}\text{Sr}/^{86}\text{Sr}$ , e.g. niveo-eolian drift or volcanic ashes (see text for details). Upper Laacher See tephra (ULST) data are from Wörner et al. (1983, 1985).

but this line has no chronological meaning at all. Its intercept on the  $y$ -axis (0.683) is indeed lower than the initial ratio of the underlying bedrock and even lower than the initial Sr isotopic composition of the Earth (0.699) 4.55 Ga ago. A similar pattern has been obtained by Bailey et al. (1996) on Silurian metapelites in New Hampshire. The pseudo-isochron line traced out with the soil sample values is not consistent with a weathering pattern and does not square with any weathering profile case reviewed by Brass (1975). This line could be interpreted as a simple binary mixing between two end-members, the lower Devonian shales (and sandstones) and an allochthonous deposit that contained Ca-rich minerals. Different Ca-bearing minerals (Ca-plagioclase, Ca-amphibole, clinopyroxene, etc.) could have been supplied to the local soils by niveo-eolian drift (loess) and/or volcanic ash deposits (Bourguignon, 1955; Bourguignon and Delecour, 1955; Pissart, 1976; Herbauts, 1981; Juvigné, 1999). The heavy-mineral composition of three soil samples of the POUR site ( $A_hB$  horizon, 3–10 cm;  $B_w$ , 15–25 cm and C, 70–85 cm) was determined by E. Juvigné (Univ. de Liège). Allochthonous heavy minerals have indeed been identified in the whole profile (in all three horizons), suggesting deep incorporation in the soil ‘active layer’ by periglacial processes. A loessic contamination was detected by the presence of epidote and green hornblende in the 30–60  $\mu\text{m}$  soil fraction

and a volcanic contribution by the presence of titanite, brown amphibole and augite in the 90–420  $\mu\text{m}$  soil fraction. The volcanic minerals are probably mainly inherited from a late Quaternary tephra layer, widespread in central and northern Europe that results from the explosive eruptions of the Laacher See Volcano (East Eifel volcanic field, West Germany), some 11,000 yr B.P. (van den Bogaard and Schmincke, 1985). Ashes of the southwestern fan (‘Upper Laacher See Tephra’=ULST, with a mafic phonolitic composition) have been detected in Quaternary sediments and late glacial peat deposits of south and eastern Belgium, up to more than 100 km from the vent (Pissart and Juvigné, 1980; van den Bogaard and Schmincke, 1985; Juvigné, 1999). If the presence of ULST minerals in the studied soil is therefore not really surprising, it remains to be seen whether this input of Ca-bearing minerals can account for the high increase of the total Ca content and, consequently, the lowering of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio towards the top of the soil sequence. The  $^{87}\text{Rb}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the ULST material (0.30 and 0.7048, respectively; Wörner et al., 1983 and 1985) are qualitatively consistent with this hypothesis, but nevertheless this material does not plot on the ‘pseudo-isochron’ (Fig. 3).

*Acid-extractable soil fraction.* In all the soil horizons the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the 0.1 M HCl extracts (<0.7176) are significantly lower than the total soil

digests ( $>0.7471$ ; Table 2b). This is easily ascribed to the preferential dissolution of Rb-poor and Ca/Sr-rich minerals with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio.

*'Labile' soil fraction.* As observed in the leached soils of Central Belgium, the Sr isotope ratios of the HCl leachates and the 'labile' pool are strikingly close. The isotopic composition of the labile pool is again clearly governed by weathering processes.

### 3.2. Quantification of calcium atmospheric contribution to vegetation

Sr and Ca contents of the vegetation pool were modelled as mixtures of atmospheric and mineral weathering end-members on the basis of their Sr isotopic composition (Eq. (1)) and Sr/Ca ratio (Eq. (2)) (Tables 2a and 2b). Precision in measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca ratios lead to an uncertainty of 0.8–2.9% (MES) and 0.6–1.3% (POUR) for Sr and Ca, respectively, for each modelled mixture.

#### 3.2.1. Atmospheric end-member

The atmospheric contribution is composed of dissolved cations in rainwater and dust fall. Water-soluble Sr is immediately available for plant uptake, whereas dust minerals must be weathered prior to Sr release. The isotopic ratios measured on bulk precipitation are close to the seawater composition in both sites and, consequently, are thought to be free from local contributions. The Sr/Ca ratios of bulk precipitations used in Eq. (2) are  $0.0043 \pm 0.0010$  ( $n=9$ ) in Central Belgium and  $0.0023 \pm 0.0010$  ( $n=14$ ) in High Belgium (Table 2a).

#### 3.2.2. Weathering end-member

In both the acid leached soil on loess and the ochreous brown earth on Devonian shales, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the 0.1 M HCl extracts are taken as weathering end-member. HCl extracts were previously used by Miller et al. (1993) and Blum et al. (2002). Given the range of the isotopic composition of HCl-extractable Sr in the different soil horizons of both profiles, the choice of the appropriate  $^{87}\text{Sr}/^{86}\text{Sr}$  as weathering end-member is much more critical. The selection of a unique isotopic composition of Sr released to solution is therefore dependent on the localization of the active feeder roots which determines the specific depth of mineral uptake. For

European beech, the main zone of root distribution and activity is commonly thought to be located in the upper meter of the soil (Manil et al., 1977; Tessier du Cros, 1981).

The isotopic composition and the Sr/Ca ratio of the HCl leachates of the  $A_h$  (0–5 cm), E (5–25 cm) and  $B_{21t}$  (55–75 cm) horizons of the acid leached soils of Central Belgium were selected as weathering end-members (Table 2b). Field observations in the Soignes Regional Forest (soil profiles, windfallen trees) suggest effectively that most of the beech roots are located in the upper 80 cm, with a particular high density of fine roots in the upper 10 cm.

In the ochreous brown earth of High Belgium, beech root distribution is constrained by the stoniness of the soil (around 65% of rock fragments  $>2$  mm) and by the presence of the bedrock at a shallow level. Roots can however expand as far deep as about 70 cm, where the more or less weathered shaly bedrock can frequently be observed. Thus, the  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca ratios of HCl leachates of the  $A_h/B$  (3–10 cm),  $B_{1w}$  (10–25 cm) and  $B_{2w}/C$  (45–55 cm) horizons were selected as weathering end-members (Table 2b). The  $\text{H}_2\text{O}_2$  pretreatment was not applied to the  $A_h$  horizon (0–3 cm); the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measured on the  $A_h$  HCl extract is probably influenced by the isotope signature of the organic matter and, hence, has not been integrated to calculations.

#### 3.2.3. Calculation

The relative contribution of Sr and Ca from soil mineral weathering and atmospheric sources to vegetation is calculated using the mixing equations (Eqs. (1) and (2)). Results are shown in Figs. 4 and 5. The different curves are calculated for the provisional weathering end-member as well as for a range of possible measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the HCl leachate to illustrate the effect of the selected end-member on the calculated Ca atmospheric contributions to beech nutrition. On this diagram, various mixtures of two end-members define an hyperbola. The curvature of the mixing lines depends on the differences in Sr isotopic and Sr/Ca ratios of the end-members.

##### 3.2.3.1. Beechwood of Central Belgium (MES site).

Calculations based on Sr isotope ratio and Sr/Ca of rainwater (Atm, end-member 1), Sr isotope ratio and

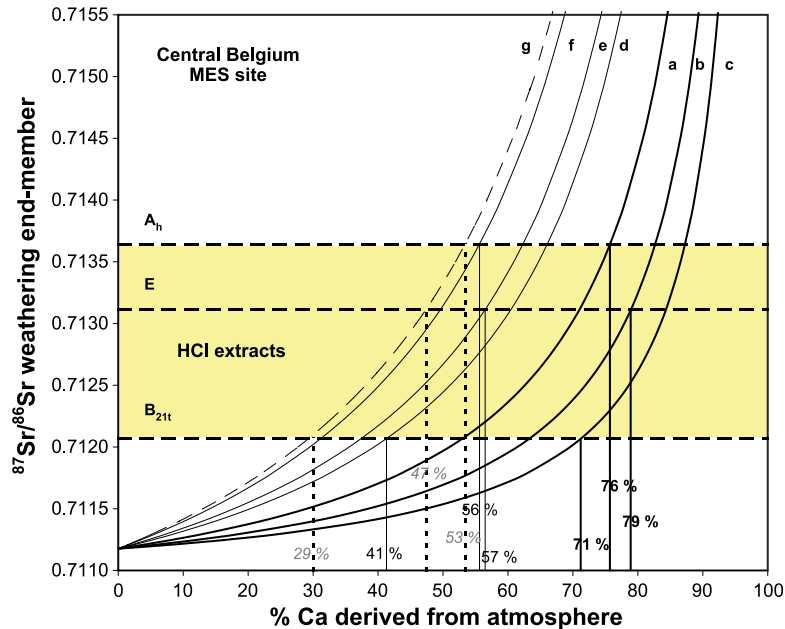


Fig. 4. Calculation of relative contribution to vegetation of atmospheric Ca vs. Ca released by weathering in Central Belgium site (MES). The shaded area indicates the range of HCl leaching  $^{87}\text{Sr}/^{86}\text{Sr}$  values (from 0.712067 to 0.713643) of different horizons (horizontal dotted lines). Atmospheric  $^{87}\text{Sr}/^{86}\text{Sr}=0.709023$  and element Sr/Ca ratio=0.0043 for all curves. We use mean  $^{87}\text{Sr}/^{86}\text{Sr}$  of vegetation, the mean of wood and leaves values (=0.711177) as isotopic value for the mixing component. For curves a, b and c, weathering Sr/Ca ratios measured in the HCl extracts are respectively 0.0257 ( $B_{21t}$ ), 0.0117 ( $A_h$ ) and 0.0179 (E). For curves d, e and f, weathering Sr/Ca ratio are respectively 0.0073 (labile  $B_{21t}$ ), 0.0047 (labile  $A_h$ ) and 0.0062 (labile E). Dotted curve (g) does not take into account the Sr/Ca ratio of the Eq. (2). Intersections of curves a–f with the Sr isotopic composition of their respective horizon weathering end-member (horizontal lines) give the atmospheric Ca proportions (bold and roman values). Intersection of curve g with the labile pool isotopic values represents the atmospheric Sr percentage (Eq. (1); italic values).

Sr/Ca of HCl soil extract of  $A_h$ , E, and  $B_{31t}$  horizons which are prospected by beech roots (Wea, end-member 2) and  $^{87}\text{Sr}/^{86}\text{Sr}$  of beech wood (Veg, mixing compartment) (Tables 2a and 2b) indicate that 29–53% of Sr uptake (Eq. (1)) and 71–79% of Ca uptake (Eq. (2)) originate from atmospheric inputs (Fig. 4).

**3.2.3.2. Beechwood of High Belgium (POUR site).** In this forest stand, the contribution of atmospheric inputs to Sr (Eq. (1)) and Ca (Eq. (2)) uptakes are calculated using the Sr isotope ratio and the Sr/Ca ratio of rainwater (Atm, end-member 1), the Sr isotope ratio and the Sr/Ca ratio of HCl soil extract of  $A_h/B$ ,  $B_{1w}$  and  $B_{2w}/C$  horizons which are prospected by beech roots (Wea, end-member 2) and the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  of beech foliage and *Fagus* 1 wood sample ( $^{87}\text{Sr}/^{86}\text{Sr}=0.713878$ ) (Veg, mixing compartment) (Tables 2a and 2b). Beech leaves and *Fagus*

I tree were selected as representative of the mixing compartment because they were collected in the vicinity of the soil profile used for the Sr isotopic and Sr/Ca ratio determinations of the acetate and HCl extracts. Data of Table 2a show that there is in fact a wide variation of the Sr isotopic composition of individual beech trees in this forest site, which is probably due to the varying depth at which the basement rock or its weathering products with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios come out in the soil profiles. Consequently, the Sr isotopic signature of *Fagus* II, III and IV were not taken into account for calculations, these trees being not close enough from the main soil sampling site. When calculated on the basis of the isotopic ratio of the  $A_h/B$ ,  $B_{1w}$  and  $B_{2w}/C$  horizons, the contribution of atmospheric inputs to Sr and Ca uptake (Eq. (1)) range from 33% to 45% and from 72% to 82%, respectively (Fig. 5).

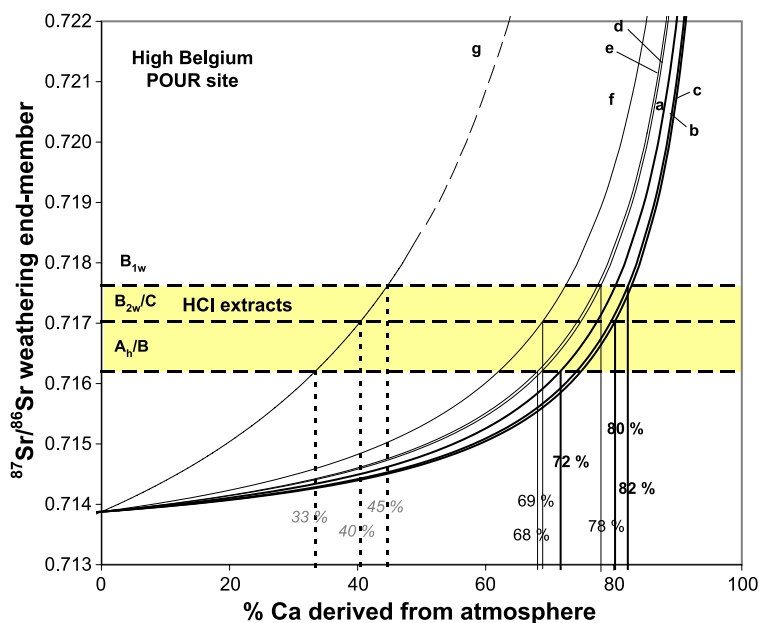


Fig. 5. Calculation of relative contribution to vegetation of atmospheric Ca vs. Ca released by weathering in High Belgium site (POUR). The shaded area indicates the range of HCl leaching  $^{87}\text{Sr}/^{86}\text{Sr}$  value (from 0.716204 to 0.717617) of different horizons (horizontal lines) representing weathering end-member. Atmospheric  $^{87}\text{Sr}/^{86}\text{Sr}=0.709238$  and element Sr/Ca ratio=0.0023 for all curves. We use mean  $^{87}\text{Sr}/^{86}\text{Sr}$  of vegetation, the mean of wood and leaves values (=0.713878) as isotopic value for the mixing component. For curves a, b and c, weathering Sr/Ca ratios measured in the HCl extracts are respectively 0.0132 ( $B_{1w}$ ), 0.0116 ( $A_{1/B}$ ) and 0.0137 ( $B_{2w/C}$ ). For curves d, e and f, weathering Sr/Ca ratios are respectively 0.0101 (labile  $B_{1w}$ ), 0.0098 (labile  $A_{1/B}$ ) and 0.0075 (labile  $B_{2w/C}$ ). Dotted curve (g) does not take into account the Sr/Ca ratio of the Eq. (2). Intersections of curves a to f with the Sr isotopic composition (horizontal lines) of their respective horizon weathering end-member give the atmospheric Ca proportions (bold and roman values). Intersection of curve g with the labile pool isotopic values represents the atmospheric Sr percentage (Eq. (1); italic values).

**3.2.3.3. Comparison between the two sites.** The Ca atmospheric contribution is high and of the same order of magnitude in the two studied forest sites (on average, 75% and 78%, in Central and High Belgium, respectively), in spite of very different total and exchangeable Ca contents in their soils.

In the upper meter, the acid leached soil developed on loess of Central Belgium contains 12 times more total Ca and 30 times more exchangeable Ca than the ochreous brown earth on Devonian shales of High Belgium. Even if only the upper 50 cm of the soil are taken into account (i.e., the depth mainly prospected by beech roots), the Ca contents are still clearly distinct: the loessial soil contains 7 times more total Ca and 15 times more exchangeable Ca than the soil of High Belgium. We had postulated that a very low total Ca content of the soil and the bedrock in the High Belgium forest site would have reduced the possibilities of replenishing the soil

exchange complex (the 'labile' pool) by mineral weathering and, consequently, would have promoted atmospheric influences in tree mineral nutrition. However, our results show that the atmospheric contributions are not related with the soil Ca amounts. There appears to be several possible explanations for this unexpected results: (a) beech trees take up available Sr and Ca preferentially in the soil solution of the upper horizons which are more strongly influenced by atmospheric inputs and organic restitutions than deeper horizons, increasing, in both forest stands, the contribution of the atmospheric end-member and lessening the influence of the soil Ca content; (b) preferential flowpaths and/or a short residence time of rain water in the soil (specially in the upper horizons) reduce the possibility of cation exchange between the soil solution and the exchange complex. The first hypothesis is specially valid for the loessic soils of the 'Soignes

Regional Forest' (MES site) in which the presence at a shallow depth of a 'consolidated horizon' of periglacial origin (Langohr and Sanders, 1985) and, locally, of a 'traffic-damaged horizon' due to logging operations (Herbauts et al., 1996), creates unfavourable conditions to the extension in depth of beech rooting. The second hypothesis is supported by the study of Bullen et al. (1997) on a soil chronosequence on granitoid alluvium, leading to the conclusion that the lack of Sr isotopic equilibrium between exchangeable and soil water Sr, can be ascribed to the inefficiency of Sr exchange between soil waters and the exchange pool. In order to better understand the relation between Ca atmospheric contributions vs. soil Ca amounts and to confirm our estimations, the determination of the relative contributions to vegetation of atmospheric Ca and of Ca released by weathering is currently extended to forest sites growing on contrasted soil types.

**3.2.3.4. Selection of the Sr/Ca ratio in Eq. (2).** Our results have shown that in both the acid leached soil on loess and the ochreous brown earth on Devonian shales the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the 0.1 M HCl and  $\text{CH}_3\text{COONH}_4$  extracts are very close, leading to the conclusion that the Sr exchangeable pool is widely supplied by mineral weathering processes. However, nearly all the Sr/Ca ratios of the labile pool are lower than those of the 0.1 M HCl extract (Table 2b). The lower Sr/Ca ratios of the labile pool cannot be explained by atmospheric depositions or organic restitutions because these sources would also lower the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the exchange pool. Ion exchange (mass action) and/or exchange selectivity process on soil organic colloids (Baes and Bloom, 1988), promoting Ca vs. Sr in the exchange pool, are more adequate processes to explain the decrease of the labile Sr/Ca ratio.

Another point of view is to consider that the cations released by mineral weathering are negligible compared to the large pool of Ca adsorbed on the exchange complex. A total mineral weathering release of  $<1 \text{ keq ha}^{-1} \text{ year}^{-1}$  estimated by Ulrich (1984) for sedimentary material is to be compared with a soil exchangeable pool of  $\sim 40 \text{ keq Ca ha}^{-1} \text{ 0.5 m}^{-1}$  in the MES forest site. More precisely, in soils of High Belgium, a total base cation release of  $\sim 0.1 \text{ keq ha}^{-1} \text{ year}^{-1} \text{ 0.5 m}^{-1}$  has been estimated by Bosman et al.

(2001), which is negligible in regard of the  $2.6 \text{ keq Ca ha}^{-1} \text{ 0.5 m}^{-1}$  of the exchange complex of the POUR forest site. The exchange fraction could therefore be viewed as the effective weathering end-member interacting with the soil solution. Consequently, the Sr/Ca ratio of the labile fraction would be more appropriate for calculation (curves d, e and f in Figs. 4 and 5). On the basis of the Sr/Ca ratio of the labile pool, calculation using Eq. (2) shows that the range of Ca atmospheric contribution would be reduced from 71–79% to 41–57% in the Central Belgium forest stand. In the High Belgium site, the atmospheric contribution are not significantly changed, from 72–82% to 68–78% (Figs. 4 and 5). Based on these new estimations, our conclusion would be that atmospheric contributions to the vegetation may be influenced by the Ca content of the soil. The selection of the appropriate Sr/Ca ratio needs a more precise knowledge of soil exchange processes.

In any case, the Sr/Ca ratio introduced in a theoretical manner by Capo et al. (1998) is poorly used in the literature. To our knowledge, the published estimations are largely established on calculation based on Sr and extrapolated to Ca without any adjustment.

Our results show however that the determination of the relative contributions of atmospheric and weathering end-members to vegetation are very different when calculated with (Eq. (2)) or without adjustment using the Sr/Ca ratio (Eq. (1)).

#### 4. Conclusion

Whatever the parameters used for the calculations, Ca atmospheric contributions take large to major part in the forest stand feeding. In the nutrient-poor forest site of High Belgium, the external inputs are in all cases the main Ca source.

In other respects, a decrease in the basic cations concentration from atmospheric depositions to ecosystems has been observed in Europe and North America (Wesselink et al., 1995; Likens et al., 1998; Lee et al., 1998). Our results support therefore the conclusion of Hedin et al. (1994) which suggest that the atmospheric base cation trends are ecologically relevant on the scale of decades for nutrient-poor ecosystems.

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