

# Long-term records of strontium isotopic composition in tree rings suggest changes in forest calcium sources in the early 20th century

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## Abstract

Many studies made in Europe and North America have shown an increasing depletion of exchangeable base cations that may cause tree nutritional deficiencies in sensitive soils. We use radial variation of strontium isotope in tree-rings ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratio) to monitor possible changes in Ca sources for tree nutrition (Sr is used as an analog to Ca). The two main sources of Ca in forest stands are mineral weathering release and atmospheric inputs. Measurements in several forest stands in temperate regions show a steep decrease from pith to outer wood of the Sr isotope ratio from ~ 1870 to ~ 1920 except for stands developed on soils with a higher Ca status. This suggests a decrease of the weathering contribution (high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio) when cations are displaced from the soil exchange complex by acid deposition at a rate faster than the replenishment of the cation pool by mineral weathering. This displacement enhances the atmospheric contribution, which is characterized by a low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Tree-ring chronologies are an exceptional historic-timing record of chemical changes in the soil environment induced by atmospheric pollution. The reliability of the tree-ring recorder has been verified with a well-controlled nutritional perturbation in the context of a limed forest stand (with a known liming Sr isotopic signature). Our data suggest that forest ecosystems were affected by atmospheric inputs of strong acids earlier than previously thought.

*Keywords:* acid deposition, atmospheric deposition, calcium, dendrochemistry, *Fagus sylvatica*, forest ecosystem, natural Sr isotopes, *Quercus robur*, strontium, weathering

Received 14 March 2005; revised version received 15 May 2005; accepted 20 April 2005

## Introduction

The two main sources of Ca delivered to trees in forest ecosystems are mineral weathering release and atmospheric inputs. The measurement of natural variations of the Sr isotopic composition, expressed by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, constitutes a useful tool to determine the origin and the fluxes of Ca in forest stands because there is no significant chemical or biological fractionation (Gosz *et al.*, 1983; Miller *et al.*, 1993; Blum *et al.*, 2002; Kennedy *et al.*, 2002; Drouet *et al.*, 2005). Strontium is used as a proxy for Ca because the ions  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  have a similar chemical structure and hence, behave similarly in the soil–plant system. Over

the past century, increased acidic deposition (Falkengren-Grerup *et al.*, 1987; Schulze, 1989; Likens *et al.*, 1996; Thimonier *et al.*, 2000; Tomlinson, 2003) and reduction in atmospheric base cations (Hedin *et al.*, 1994; Wesselink *et al.*, 1995) have caused detrimental effects on forest ecosystems in temperate regions of Europe and North America. Acidic deposition is suspected to have a negative effect on the Ca status of sensitive forest ecosystems (i.e. forest stands growing on very acid soils with low weatherable mineral reserve), because of both depletion of soil exchangeable Ca and mobilization of monomeric and phytotoxic aluminum species (Ulrich, 1980; Lawrence *et al.*, 1995).

However, very few data present a historical and continuous record of the soil acidification process, and its impact on tree nutrition. Tree-ring analysis of Sr isotopes provides information on past conditions and

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on the evolution of Ca availability over time (Åberg, 1995; Poszwa *et al.*, 2003; Bullen & Bailey, 2005). Dendrochemistry assumes that a change in tree-ring chemistry reflects the historical pattern of change in the soil solution.

The main objective of the present study is therefore to evaluate the contribution over time of mineral weathering and atmospheric deposition to soil exchange Sr and Ca pools. To this end, strontium isotope ratios were measured in tree-ring chronologies higher than 100 years of beech (*Fagus sylvatica* L.) and oak (*Quercus robur* L.) growth rings from four forest stands located in Central and High Belgium. These stands were chosen because they grow on soils with contrasting Ca contents. Moreover, the soil mineral Sr isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.712$ ) is well separated from atmospheric inputs ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.709$ ) in all the studied sites, providing a good opportunity to apply the Sr isotope method to sites that are more or less susceptible to Ca depletion under acid atmospheric deposition (Drouet *et al.*, 2005). A parallel is also drawn between our own data and those published previously by Åberg (1995) and, more recently, by Bullen & Bailey (2005), with the intention to detect: (1) whether general trends are revealed on a large geographic scale in sensitive forest ecosystems affected by acidic deposition; and (2) whether temporal trends of these long-term chronologies show evidence of a similar historic timing. In addition, we analyze the radial Sr isotopic composition of a beech forest stand of Central Belgium, which has experienced a controlled nutritional perturbation (addition of calcareous improvement of known  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in 1972). The aim is to test the reliability of the tree-ring record and to determine the importance of the lateral re-equilibration process of base cations in tree trunks (Houle *et al.*, 2002; Momoshima & Bondietti 1990), which could have a foredating effect on the historic timing.

## Materials and methods

### Study area

Seven forest stands were selected for this study. Five are located in the loess belt of Central Belgium (Soignes Regional Forest), and the two others in the Palaeozoic Ardenne massif of High Belgium (Herbeumont State Forest and Smuid Wood) (Table 1).

The Soignes Regional Forest, southeast of Brussels, covers 4400 ha of a loessic plateau at about 120 m above sea level. The natural vegetation is a deciduous forest with oaks (*Quercus robur* L. and *Q. Petraea* (Mattuschka) Lieblein) and European beech (*Fagus sylvatica* L.) as codominant species, but beech has been extensively

introduced since the end of the 18th century. The study sites are even-aged beech high forests: *Mésanges* site (MES) planted between 1860 and 1865; *Comte de Flandre* (CTE) planted between 1810 and 1820; *Tir aux pigeons* (PIG) planted in 1967; *Tambour* (TAM) planted in 1976; and *Bonne Odeur* (ODE) planted between 1830 and 1835. The last forest stand (ODE) was experimentally limed in 1972 by foresters to determine the growth response of the beech to enrichment. Around  $12 \text{ t ha}^{-1}$  of crushed limestone, containing 96% of  $\text{CaCO}_3$  and 2.3% of  $\text{MgCO}_3$ , were applied. In all the stands, the ground layer consists mainly of *Pteridium aquilinum* (L.) Kuhn, *Dryopteris dilatata* (Hoffm.) A. Gray, *Carex pilulifera* L., and *Milium effusum* L.; *Lamium galeobdolon* (L.) L., an indicator of a mull humus type, is locally present in the limed stand. Prevailing soils are acid-leached soils (FAO-UNESCO: Podzoluvisols), with an  $A_hEB_{t(g)}C$  soil profile. These soils are characterized by a clay-enriched  $B_t$  horizon. The parent material is a Pleistocene niveo-eolian loess that is composed of more than 70% of 2–50  $\mu\text{m}$  silt-size particles. In the studied sites, the loess deposit is at least 3.5 m thick and dated from the end of the Würm glaciation ('Brabantian' loess,  $\sim 20,000$  years BP: Haesaerts & Bastin, 1977). The loess sheet is underlain by Tertiary marine sediments (Oligocene clayey sands). The soil profiles are mainly composed of quartz ( $\sim 60\%$ ), muscovite, K-feldspar, plagioclase, chlorite, and both 1:1 and 2:1 clay minerals. The unweathered loess contains around 13%  $\text{CaCO}_3$ , but is decarbonated down to 250 cm (MES site) or 350 cm (CTE site) in depth. As a result, in the upper 2 m of the soil, the pH- $\text{H}_2\text{O}$  is  $< 5.0$  and in the upper 80 cm, the effective base cation saturation is very low ( $< 25\%$ ); correlatively, aluminum saturation is high ( $> 75\%$ ) (Table 1). The humus type is a moder-mor (pH- $\text{H}_2\text{O} < 4.0$ , C/N  $\sim 18$ , base cation saturation  $< 30\%$ ). In the limed beech stand (ODE), the pH- $\text{H}_2\text{O}$  and the effective base cation saturation of the humic layer ( $A_h$ ) are, on average, higher ( $4.9 \pm 1.2$  and  $78 \pm 23$ , respectively,  $n = 20$ ); the C/N ratio and the aluminum saturation rate are lower ( $15.0 \pm 0.8$  and  $20 \pm 20$ , respectively;  $n = 5$  and 20, respectively). Very locally, where residues of the 1970s liming remain, the pH- $\text{H}_2\text{O}$  of the humic layer is around 7.5. In the underlying E horizon, the differences with the non-amended sites are still well marked and decrease only in the  $B_t$  horizons (Table 1).

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. The forest stand studied is a selection high-forest of European beech (*F. sylvatica* L.) and pedunculate oak (*Q. robur* L.) (*Poursumont* site, hereafter POUR). Beech is the dominant species (90%) and the floristic composi-

Table 1 General characteristics and selected soil properties of the forest stands used in dendrochemical analyses

Study area	Latitude longitude	Elevation (m a.s.l.)	MAT* (°C)	MAP† (mm)	Stand species	Tree age class‡	Tree		Stand age (year)	Soil type§	BS <sub>e</sub> ¶ (%)	Ca <sup>2+</sup> SR   (%)	Total soil		Exchangeable Ca reserve (kg ha <sup>-1</sup> m <sup>-1</sup> )
							<sup>87</sup> Sr/ <sup>86</sup> Sr ± 2σ × 10 <sup>-6</sup>	±					Ca reserve (kg ha <sup>-1</sup> 0.5 m <sup>-1</sup> )	Ca reserve (kg ha <sup>-1</sup> m <sup>-1</sup> )	
Central Belgium															
Mésanges (MES)	50°47'13"N 4°27'01"E	115	9.8	780	<i>Fagus sylvatica</i>	M (1879-84) M (1969-74)	0.711227 ± 6 0.711104 ± 9		170-175	Dd	31.3	20.3	14 700	29 800	3300
Tir aux Pigeons (PIG)	50°49'41"N 4°28'11"E	110	9.8	780	<i>Fagus sylvatica</i>	M	0.711663 ± 5**		40	Dd	42.1	20.5	14 900	30 800	3600
Tambour (TAM)	50°47'37"N 4°26'41"E	105	9.8	780	<i>Fagus sylvatica</i>	M	0.711348 ± 5**		30	Dd	30.8	15.2	-	-	3000
Comité de Flandre (CTE)	50°48'06"N 4°26'34"E	95	9.8	780	<i>Fagus sylvatica</i>	M (1824-28) M (1949-53)	0.712032 ± 5 0.712109 ± 5		180-190	Dd	63.5	33.8	15 600	31 400	2900
Bonne Odeur (ODE)	50°47'07"N 4°26'58"E	120	9.8	780	<i>Fagus sylvatica</i>	M (1915-19) M (1975-79)	0.711237 ± 10 0.710083 ± 7		170-175	Dd	48.5	30.6	-	-	4700
High Belgium															
Poursumont (POUR)	49°47'57"N 5°16'26"E	410	7.8	1200	<i>Fagus sylvatica</i>	M Y	0.714599 ± 6 0.713532 ± 6**		~160	Bd	5.1	1.7	1700	2100	50
Smuid (SMD)	50°02'07"N 5°15'52"E	360	8.2	1100	<i>Quercus robur</i> <i>Fagus sylvatica</i>	M (1985-89) M	0.714570 ± 5 0.715591 ± 5		~160	Bd	9.4	1.8	3000	4200	80
European Nordic countries (Åberg, 1995)															
Stockholm	59°21'N 18°04'E	0-100	3	500-750	<i>Quercus robur</i>	M	-			Bv	-	-	-	-	-
Oslo	59°56'N 10°44'E	100-200	3	750-1000	<i>Pinus sylvestris</i>	M	-			Po	-	-	-	-	-
USA, New Hampshire (Bullen & Bailey, 2005)															
Cone Pond	43°54'N 71°36'W	480-650	5	1300	<i>Picea rubens</i>	M	-		~185	Po	8.9-27.6**	0.8-5.8**	800-1200	-	-

\*MAT, mean annual temperature.

†MAP, mean annual precipitation.

‡M, mature tree; Y, young tree; P, plantlets. The 5-year growth intervals analyzed are given between parentheses.

§Dd, Dystric Podzolusol; Bd, Dystric Cambisol; Bv, Vertic Cambisol; Po, Orthic Podzol.

¶BS<sub>e</sub>, mean effective soil base saturation for the upper meter depth.||Ca<sup>2+</sup> SR, mean soil calcium saturation rate for the upper meter depth.\*\*Calculated for four sites using the data in Bullen & Bailey (2005) and Bailey *et al.* (1996).

††Foliar samples; other measurements are made on wood (recent growth increment samples).

tion of the herbaceous layer is characteristic of the climax forest association (*Luzulo-Fagetum typicum*) with acidity indicators including *Luzula luzuloides* (Lam.) Dandy et Wilmott, *Deschampsia flexuosa* (L.) Trin., *C. pilulifera* L., and *Polytrichum formosum* Hedw. The soil, with an  $A_hB_wCR$  profile, is an ochreous brown earth (FAO-UNESCO: Dystric Cambisol). The humus is a moder (pH-H<sub>2</sub>O = 3.7, mean C/N = 16.8). The soil is developed in a ~1 m thick loamy and stony solifluction sheet in which weathering products of the bedrock were mixed with added loess in a periglacial environment during the Pleistocene. The bedrock is composed of Lower Devonian clastic rocks, mainly Praguian shales and siltstones. The main minerals in the soil are quartz, muscovite, chlorite, K-feldspar, plagioclase, and both 1:1 and 2:1 clay minerals. Silt-size particles (2–50 µm) are dominant, amounting to more than 50% in all horizons. Because of 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% by weight close to the bedrock and decreases slightly towards the topsoil (60%). Soil acidity is strong in  $B_w$  and C horizons (pH-H<sub>2</sub>O around 4.5) and very strong in the organic horizons ( $A_h$  and  $A_hB$ ; pH-H<sub>2</sub>O < 4.0), corresponding to a very low effective cation saturation (mostly <10%) and a very high exchangeable aluminum saturation (mostly >80%) (Table 1).

The Smuid Wood covers ~250 ha of a 360 m high plateau near the Lomme river valley in the middle west of the Belgian Ardenne region. The forest management of the stand studied is very similar to that of the POUR site, (i.e. a selection high-forest of European beech) (*F. sylvatica* L.) and pedunculate oak (*Quercus robur* L.) where beech predominates (90%) (Smuid site, hereafter SMD). The forest association (*Luzulo-Fagetum festucetosum*) is characterized by the presence of both *L. luzuloides* (Lam.) Dandy et Wilmott and *Festuca altissima* All. The soil, which is also developed in an ~1 m thick loamy and stony solifluction material, has nearly the

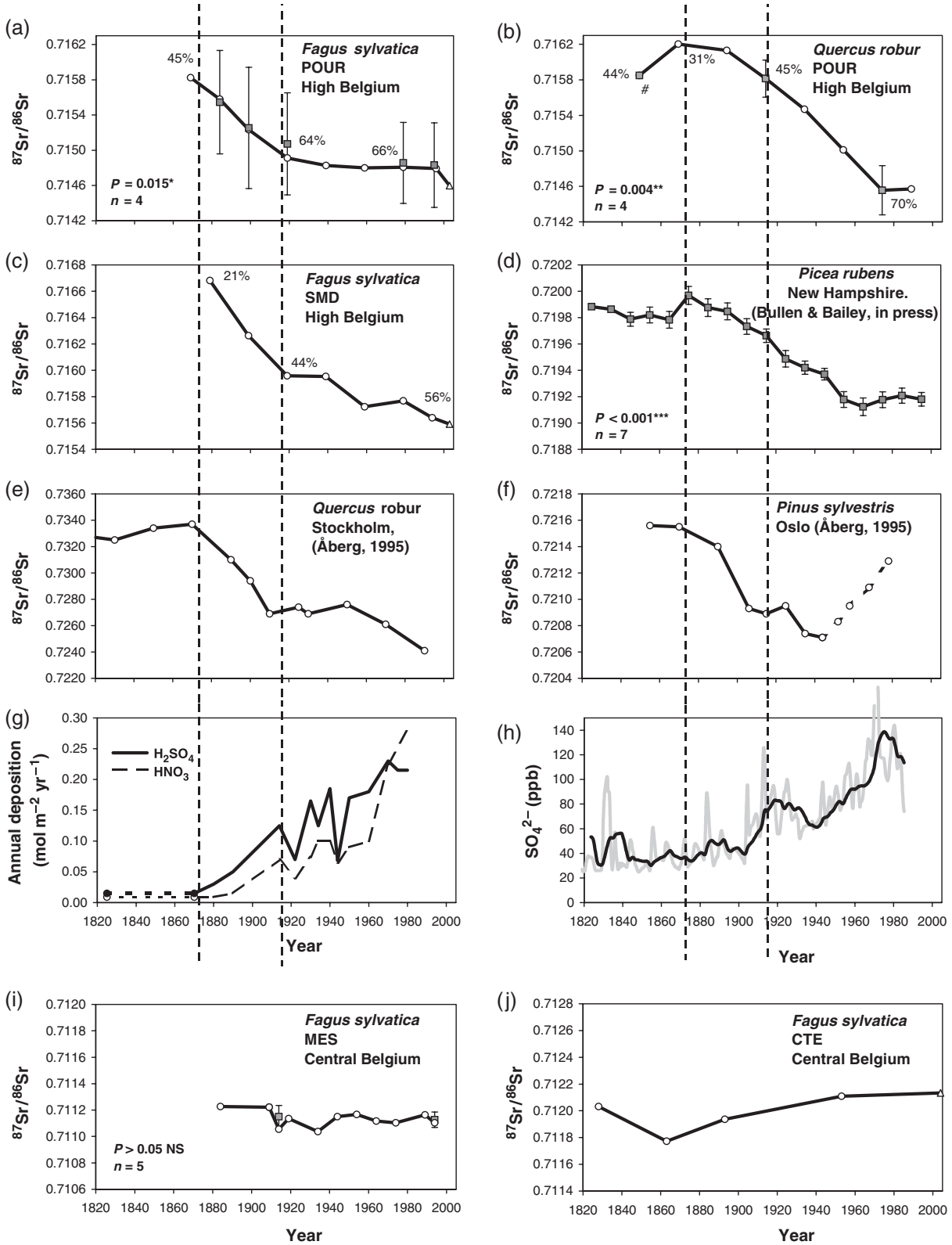
same textural, chemical, and mineralogical properties as the ochreous brown earth of the POUR site (Table 1). The bedrock is composed of Lower Devonian rocks, mainly Lochkovian shales and sandstones.

Very low levels of total Ca in the parent material and bedrock of the two High Belgium forest sites (CaO ~ 0.03% and ~ 0.07% in POUR and SMD sites, respectively) are critical in explaining the deficiency of this base cation in the soil. Forest decline is well documented in this region and related to Ca and Mg deficiencies (Weissen *et al.*, 1992). Additional information on site and stand characteristics is provided in Herbauts *et al.* (1996), Penninckx *et al.* (1999, 2001), and Drouet *et al.* (2005).

### Sampling

Beech trees (~130–160 years old) were randomly sampled in the MES, ODE, POUR, and SMD sites (five, six, four, and six boles, respectively) and oak trees (~160 years, four boles) in the mixed stand of the POUR site, during forest clearings in the winter period, between 1995 and 1997. In the CTE site, only one old beech (planted around 1815) was sampled in 2004. Discs 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 previously for dendroecological and dendrochemical measurements (Penninckx *et al.*, 1999, 2001; Herbauts *et al.*, 2002). Leaves were also collected in beech crowns in MES ( $n = 4$ ), PIG ( $n = 5$ ), TAM ( $n = 5$ ), CTE ( $n = 5$ ), ODE ( $n = 5$ ), POUR ( $n = 5$ ), and SMD ( $n = 5$ ) sites. In addition, in the POUR stand, foliage of one adult beech (~160-year old), of younger beech (~10-year old; composite sample,  $n = 10$ ), and of beech plantlets (2 years old; composite sample,  $n = 5$ ) were collected. A composite sample of beech plantlets (2-year old;  $n = 50$ ) was also collected in the SMD forest stand. Soil profiles were sampled within each forest site. Soil samples were taken at different levels corresponding to the major soil horizons (Table 1). Soil samples collected

**Fig. 1** Comparison between Sr isotope signal in tree-rings and estimates of acid deposition since 1820. (a) Mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  $\pm$  SE in beech tree-rings of the *Poursumont* stand (POUR), High Belgium. (b) Oak chronology in the same stand. (c) Beech chronology of the *Smuid* stand (SMD), High Belgium. (d) Spruce chronology of Cone Pond watershed, New Hampshire, USA (Bullen & Bailey, 2005) (with the permission of *Springer Science*). (e) Oak chronology in the Stockholm area (Åberg, 1995). (f) Pine chronology near Oslo (Åberg, 1995) (with the permission of *Springer Science*). (g) Estimation of acid deposition in Germany (Ulrich, 1987). (h) Estimates of non-marine  $\text{SO}_4^{2-}$  deposition, inferred from the GISP2 ice core record (Mayewski *et al.*, 1990), unsmoothed (thin line) and smoothed with a 10-point moving window (bold line) (with the permission of *Nature*). (i) Beech chronology of the *Mésanges* stand (MES), Brussels, Central Belgium. (j) Beech chronology of the *Comte de Flandre* stand (CTE), Brussels, Central Belgium. Symbol (#) indicates an SE bar smaller than the symbol size;  $n$  is the number of individual tree measurements by date (gray squares) and/or the number of samples constituting a composite sample (white circles). White triangles represent measurements on foliar samples. The gray circle in (d) indicates a single tree sample. Vertical dotted lines enclose the time scale of rapid evolution of the Sr isotope ratio. Note the difference in scale for the Sr isotope ratio. All chronologies are displayed on the same time axis (1820–2000). Roman numerals indicate the estimation of Ca percentage derived from the atmospheric source; see text for details.



at MES and POUR sites have been previously discussed in Drouet *et al.* (2005).

#### Analytical methods

The tree discs were polished with a Si carbide abrading band to reveal annual growth rings. For each disc, dated stemwood samples representing 5-year growth intervals were cut off with a band saw and a chisel, and the extremities of these wood 'sticks' were cut off to avoid contamination of rings from the abrasive material and to ensure that interring contamination did not occur. The samples were dried at 65 °C and ground in a centrifugal mill ZM100 (Retsch, Haan, Germany) to pass a 750 µm screen. In four of the five studied stands, composite samples were prepared for the determination of the Sr isotope composition by mixing 5-year growth increment of 4 (POUR site), 5 (MES site), or 6 (SMD and ODE sites) individual trees (shown in Figs 1 and 2). Subsequently, in the MES and the POUR sites, a limited number of quintet of five and four trees, respectively, were individually analyzed to observe the intertree variability and allow statistical analyses.

Mineralization of about 2 g of ground wood or leaves was performed by dry ashing in covered zirconium crucibles (16 h at 450 °C). Ashes were dissolved with 1 mL suprapure HCl and heated on a hot plate for 10 min, avoiding boiling. This solution was brought to a final volume of 50 mL.

#### 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 aluminum (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), carbon (dry combustion; Ströhlein dosimeter), and nitrogen (semi micro Kjeldahl method). Particle-size distribution was determined by the pipette method after H<sub>2</sub>O<sub>2</sub> pre treatment and dispersion with Na-citrate. Total chemical analysis was carried out by fusion of 100 mg finely ground soil (planetary micro mill Retsch), at 700 °C in Pt–Au crucibles (Claisse-Fluxer) with LiBO<sub>2</sub> (Spectroflux 100 A, Johnson Matthey, Paris, France); fused samples were dissolved in a 5% HNO<sub>3</sub> solution and major elements were determined by ICP-OES. Bulk soil samples used for isotope analysis were totally digested in sealed Teflon vessels using a HF–HNO<sub>3</sub> (10:1) acid mixture. The 'acid-extractable' soil fraction was obtained from preconditioned soil samples by suprapure 1 M CH<sub>3</sub>COONH<sub>4</sub> leaching to eliminate the exchangeable

Sr. Surface horizons containing substantial amounts of organic matter (*A<sub>h</sub>* and *E* horizons) were at first treated with hot suprapure H<sub>2</sub>O<sub>2</sub> and afterwards with suprapure 1 M CH<sub>3</sub>COONH<sub>4</sub> to eliminate exchangeable and organically bound Sr. The acid extract consists of four successive extracts, obtained by shaking 5 g of soil with 50 mL suprapure 0.1 M HCl for 2 h. The aim is to simulate natural Sr release by weathering (Miller *et al.*, 1993; Blum *et al.*, 2002, Bullen & Bailey, 2005). The carbonated fraction of the *C<sub>k</sub>* horizon of the loessial soils was leached using 0.5 M CH<sub>3</sub>COOH (only a partial dissolution was carried out to prevent against possible acid attack of the silicate residue); this extract is evaporated to dryness, dry ashed, and re-dissolved with HCl in a similar way as for plant material. All elemental analyses of soil (Ca, Mg, K, Na, Ba, Al, Fe, and Sr) and vegetation (Ca, Mg, K, Ba, and Sr) were determined by ICP-OES.

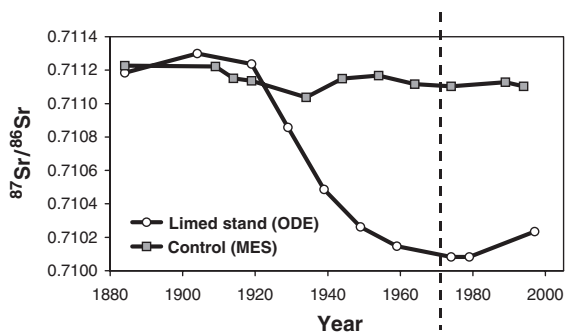
#### Isotope analyses

Chemical separation of Sr from tree core and foliage digests, total soil, 0.1 M HCl, and CaCO<sub>3</sub> dissolutions was carried out by cation exchange chromatography. Sr isotopic compositions were measured on a VG Sector 54 multicollector thermal ionization mass spectrometer housed at the 'Laboratoire de Géochimie isotopique, Université Libre de Bruxelles.' The measured <sup>87</sup>Sr/<sup>86</sup>Sr ratios were normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194. Measurements of the NBS-987 Sr standard yielded on average an <sup>87</sup>Sr/<sup>86</sup>Sr value of 0.710270 ± 0.000009 (2σ, n = 25). Additional details on the analytical procedure can be found in Ashwal *et al.* (2002).

#### Calculations

Because of their geochemical similarities, Sr is often used as a proxy for Ca in ecosystem studies (e.g. Graustein & Armstrong, 1983; Åberg *et al.*, 1990; Capo *et al.*, 1998). Sr isotopes are useful tracers in biological systems because there is no significant fractionation by geochemical or biochemical processes and any small mass-dependent fractionating is eliminated via the normalization procedure during measurement. 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):

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



**Fig. 2** Sr isotope signal of a limed beech stand (*Bonne Odeur*, Brussels, Central Belgium). Circles indicate the limed stand chronology; squares indicates  $^{87}\text{Sr}/^{86}\text{Sr}$  values of a control stand. The stand was limed by a blower in 1972 with  $\sim 12\text{ t ha}^{-1}$  of crushed Frasnian limestone ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratio = 0.707857). The dotted line indicates the liming year.

where Veg, Wea, and Atm subscripts denote the vegetation, weathering, and atmospheric component, respectively.

The calculated Sr contribution cannot directly be related to the Ca contribution to vegetation uptake because the proportion of these elements (Sr/Ca ratio) is not the same in the two sources. Nevertheless, the fraction of Ca 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 Eqn (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 :

$$X(\text{Ca})_{\text{Atm}} = \frac{\left[ (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Veg}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Wea}} \right] (\text{Sr}/\text{Ca})_{\text{Wea}}}{\left[ (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Veg}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Wea}} \right] (\text{Sr}/\text{Ca})_{\text{Wea}} + \left[ (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Atm}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{Veg}} \right] (\text{Sr}/\text{Ca})_{\text{Atm}}}, \quad (2)$$

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

### Statistical analyses

To test whether the *date* or *tree* factors are determinant in explaining the wood Sr isotopic distribution, we performed an analysis of variance (ANOVA). For the POUR site, four singletree samples at five and three dates, for beech and oak, respectively, were used for the test. In the MES site, five single beech trees at two dates

were used. In addition, for the MES chronology, we calculated the amount of change that would be detectable by a *t*-test at a value  $\alpha = 0.05$ , assuming equal sample size and standard deviations. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the most recent tree-ring of each tree was successively incremented in proportion to an increasing Ca atmospheric contribution and compared with the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oldest tree-ring. No tests were applied for chronologies based on composite samples.

## Results and discussion

### Radial trends of Sr isotopic composition recorded in growth rings

Dendrochemical curves clearly show a decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio from inner to outer wood in the forest sites of High Belgium (POUR and SMD sites), for both beech and oak (Fig. 1a–c). Dated wood ranges from ca. 1870 to 1990 for beech and ca. 1850 to 1970 for oak. By contrast, the Sr isotopic signal shows a very low variation over the recorded chronologies in the MES beech stand and, to a lesser extent, in the CTE beech stand of Central Belgium (Fig. 1i and j) where dated wood ranges from ca. 1890 to 1990 and ca. 1830 to 1950, respectively. There is a great inter-tree variability in the range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values for beech in the POUR High Belgium stand, which is probably because of 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 relatively shallow soil profiles (Drouet *et al.*, 2005). By contrast, the variability is slight in the MES beech stand of Central Belgium where loessial soil profiles are deeper and developed in a much more

homogeneous parent material. Nevertheless, the two-way ANOVA test shows that the influence of the *date* factor on the variation of the Sr isotopic ratio is significant in the High Belgium POUR site (*Fagus*:  $F_{4,12} = 4.78$ ,  $P = 0.015$ ; *Quercus*:  $F_{2,6} = 16.17$ ,  $P = 0.004$ ); the test is not significant in the MES site of Central Belgium ( $F_{1,4} = 0.15$ ,  $P = 0.716$ ). The influence of the *tree* factor is not significant for the two sites except for *Fagus* in the POUR site (*Fagus* POUR:  $F_{3,12} = 82.36$ ,  $P < 0.001$ ; *Fagus* MES:  $F_{4,4} = 4.66$ ,  $P = 0.083$ ; *Quercus* POUR:  $F_{3,6} = 1.57$ ,  $P = 0.291$ ).

Patterns of decreasing Sr isotope ratio with time in bole wood (similar to those recorded in beech and oak trees of the forest sites of High Belgium) were also observed for *Q. robur* and *Pinus sylvestris* in Scandinavia (Åberg, 1995) (Fig. 1e and f), for *Picea abies* in France (Poszwa *et al.*, 2003), and for *Picea rubens* in New Hampshire, USA (Bullen & Bailey, 2005) (Fig. 1d). A decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio between the core and the outer wood for *P. abies* in Sweden was also pointed out by Åberg *et al.* (1990). Most of these published data cover long-term chronologies (100–160 years), except for the growth ring records of *Picea abies*, which are limited to a growth period of only about 40 years. Data showing no radial variation of the Sr isotopic composition in tree-rings (as those observed in beech trees of Central Belgium) have not been published up to now.

#### *Reliability of the tree-ring recorder*

The reliability of the tree-ring recorder was verified using a well-controlled nutritional perturbation, induced 30 years ago in a forest stand by a liming operation with a known liming Sr isotopic signature. The radial Sr isotopic composition could be an artifact because of lateral re-equilibration of base cation in the tree-rings. This process, pointed out by Momoshima & Bondietti (1990) and more precisely described by Houle *et al.* (2002), implies that ring activity can last tens of years after the ring formation. The conducting cross-section is continuously re-equilibrated with cation from the mineral sap (influenced by current soil solution) until the inactivity of the ring. For example, using the radial distribution of fallout  $^{90}\text{Sr}$  in tree-rings of red spruce, Bondietti *et al.* (1989) have shown that its stem wood may continue to conduct nutrients for up to 30 years following its formation. To assess the importance of the re-equilibration process in European beech and to determine more precisely how many growth rings this process affected, we measured the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in growth rings of six beeches in a forest stand of Central Belgium (ODE site), similar to the MES site, but limed in 1972 with Frasnian limestone ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.707857$ ). The Sr isotopic dendrochemical pattern (Fig. 2) shows that the wood isotopic ratio was influenced about 50 years before the liming application date. Furthermore, this time period is in good agreement with 40 active rings detectable on a fresh disc cut from the bole of a living beech by the IKI method recommended by Hagemeyer & Schäfer (1995). It is also in good agreement with the radial distribution of  $^{90}\text{Sr}$  measured in the American beech (*Fagus grandifolia* Ehrh.) by Momoshima & Bondietti (1994), which shows that the tree-ring record is foredated by around 35 years before the atmospheric deposition of  $^{90}\text{Sr}$  in the northern

hemisphere. Concerning the pedunculate oak of the High Belgium sites, dendroecological and dendrochemical observations (Penninckx *et al.*, 2001) have shown that the active sapwood is composed of around 30 active growth rings. So, lateral re-equilibration could foredate by several decades the period of Sr isotope ratio decrease observed in stands growing on sensitive soils.

#### *Origin of the radial trends of Sr isotopic composition in tree-rings*

Long-term chronologies suggest that a decreasing trend could be a general feature in forest trees of Europe and North America. Change in the radial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio can be ascribed to: (i) the variation over the tree growth period of the Sr isotope signal of the two main sources of Sr delivered to trees (i.e. atmospheric inputs and mineral weathering release) or (ii) a temporal change of the respective contribution to tree nutrition of these two primary sources.

Two modifications over time of the Sr isotope ratio can be considered: (i) a modification of the atmospheric source and (ii) a modification of the weathering source.

An evolution in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the atmospheric source over time can be discarded given that the current Sr isotope measurements on bulk precipitation in Central and High Belgium (Drouet *et al.*, 2005) are similar to those of present-day seawater (0.70923, constant value for the <200-year interval) (e.g. Capot *et al.*, 1998). This is in good agreement with the monitoring network of wet deposition on a European scale (Van Leeuwen *et al.*, 1996), which shows that nearly the whole Belgian territory is under an oceanic influence as clearly proved by the distribution pattern in precipitation of elements from marine origin, mainly Cl and Na. Bain & Bacon (1994) had already pointed out in Scotland that the isotopic composition of the precipitation in regions situated only 300 km or less from the sea coast is strongly controlled by sea-salt aerosols with constant marine  $^{87}\text{Sr}/^{86}\text{Sr}$  values. It can also be concluded that the Sr atmospheric source is not substantially influenced by human activities, knowing that most of the industrial and agricultural sources of Ca contributing to atmospheric pollution (and, by inference, of Sr) generate strontium with an isotope ratio lower than that of the present-day seawater (Straughan *et al.*, 1981; Simonetti *et al.*, 2000; Böhlke & Horan, 2000). It would also be very surprising that regional industrial activities had the same effect, at the same time, in countries as far as North America, Scandinavia and High Belgium. Moreover, if we assume that the whole modification of the tree-ring  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is because of a change of the isotopic

signal of the atmospheric source, we can estimate what could be the value of the Sr isotopic ratio in precipitation in the 1870s. This calculation is possible if we consider that the proportion of Sr originating from the atmospheric source and stored in the forest biomass (calculated from Eqn. (1)) has not changed over time. Based on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the weathering source, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in recent and old tree-rings, and the current proportion and Sr isotopic ratio of the atmospheric source, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the 1870s precipitation was modeled and gave values of 0.7093, 0.7074, 0.7128, 0.7145, and 0.7148, for the MES, CTE, POUR (beech), POUR (oak), and SMD forest stands, respectively. A similar calculation was extended to the data published for a forest site of central Sweden (Åberg *et al.*, 1989, 1990), for a Norway spruce forest of northeast France (Probst *et al.*, 2000; Poszwa *et al.*, 2003), and for the red spruce forest studied by Bullen & Bailey (2005) in New Hampshire. Modeled  $^{87}\text{Sr}/^{86}\text{Sr}$  precipitations are 0.7230 in Sweden, range from 0.719 to 0.721 in France, and from 0.7130 to 0.7193 ( $n = 7$ ) in North America. Most of these values are clearly too high to be consistent with an oceanic or even continental origin of the precipitation in all these areas. In addition, the calculated  $^{87}\text{Sr}/^{86}\text{Sr}$  values are different between stands, which could only be explained by different local or regional human influences. Our view is that these results are not compatible with the similar decreasing patterns of tree-rings  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio recorded in forest stands with a wide geographic distribution. The lack of evidence of changes over time of the Sr isotopic composition of atmospheric deposition was also suggested by Åberg *et al.* (1990), Dijkstra *et al.* (2002), Poszwa *et al.* (2003) and Bullen & Bailey (in press). Also unlikely is the hypothesis that the steep declines in the atmospheric concentrations of base cations over the past 20 years in Europe and North America (Hedin *et al.*, 1994) could have an effect upon the Sr isotope signal in tree-rings: the consequence would have been a proportional increase of the weathering source in tree nutrition and hence, an increase of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the growth rings during this time period.

Change of the weathering isotopic signal by a variation of the relative weathering contributions is also unlikely, as already pointed out by Bailey *et al.* (1994). Laboratory kinetics, budget studies, and reconstruction of historic weathering by modeling in Swedish catchments over the 12000 years following the last glaciation have shown that no variation of the chemical weathering has been reconstituted for the last century, even if the modeled soil chemistry (e.g. depletion of base cations and decrease of soil solution pH) has changed very rapidly during the same time

period, because of acid deposition effects (Sverdrup & Warfvinge, 1995). But change of the isotope signal of the weathering source could also be explained by changes in the soil layers prospected by tree roots during their growth period, the different horizons forming a soil profile showing generally contrasting isotope compositions (Åberg *et al.*, 1989, Blum & Erel, 1997; Kennedy *et al.*, 2002; Poszwa *et al.*, 2003; Drouet *et al.*, 2005; Bullen & Bailey, 2005). Forest aging (Hamburg *et al.*, 2003) or limitations of nutrient availability in specific soil horizons in response to modifications of environmental factors – e.g. drought stress (Poszwa *et al.*, 2003) or acid deposition inducing aluminum toxicity (Ulrich 1989; Poszwa *et al.*, 2003; Bullen & Bailey, 2005) – have been hypothesized to explain a deepening or a shallowing of the effective depth of root uptake over the forest growth period. But forest stand development implying change in soil rooting depths or difference in organic acid production enhancing as suggested by Hamburg *et al.* (2003) may, however, be ruled out in the forest stands of High Belgium in view of an increasing isotope ratio from young trees and/or plantlets to mature trees of *Fagus sylvatica* in the POUR and SMD sites (Table 2). Such an increase of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio with tree growth goes against the observed temporal trend. On the other hand, an extensive study of beech and oak growth curves in High Belgium (Penninckx, 2001) has not shown increased drought stress contemporary to the change in tree-ring Sr isotope composition, suggesting that the isotopic pattern is not related to climatic factors. The third hypothesis, the ‘aluminum toxicity’ hypothesis, which was specially developed by Bullen & Bailey (2005) to explain the decreasing temporal trend in the stemwood Sr isotopic ratio of a north-American red spruce forest by progressive shallowing of the effective depth of alkaline earth elements uptake by fine roots during the past 130 years, is open to discussion. Using  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ba ratios of spruce tissues and soil fractions together in a multi-tracer approach, Bullen and Bailey hypothesized that the preferential growth and expansion of the fine root network in the upper forest floor is a consequence of acid deposition and a response to Ca depletion and/or mobilization of ‘monomeric Al’, which induces aluminum toxicity in the lower forest floor and the upper mineral soil horizons. Hence, the nutrient uptake by roots is transferred from soil horizons with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (characteristic of mineral weathering) to the uppermost and organic soil horizons with lower isotopic ratios. A nearly similar scenario was proposed by Ulrich (1989) to explain an increasing sensitivity of forest to drought: low concentrations of basic cations and high levels of exchangeable Al in mineral horizons, resulting from soil acidification, could promote the development of

Table 2 Physical and chemical properties of soil profiles in the forest stands studied

Horizon	Sampling depth (cm)	Soil texture*	Stoniness OM (wt%)	C/N	pH-H <sub>2</sub> O	CaCO <sub>3</sub> (%)	Exchangeable cations <sup>†</sup>				Effective base saturation (BS <sub>e</sub> ) (%)	Al <sup>3+</sup> saturation (%)	Ca <sup>2+</sup> saturation (%)			
							Exchangeable acidity <sup>†</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	Ca <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	Mg <sup>2+</sup>	K <sup>+</sup>				Exchangeable Al <sup>3+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )		
<b>Central Belgium</b>																
<i>MES site acid-leached soil (Dystric Podzoluvisol), Soignes Regional Forest</i>																
A <sub>h</sub>	0-5	Loam	0	21.3	18.3	3.7	0.0	3.28	0.73	0.29	0.29	0.29	2.69	28.5	58.6	15.9
E	5-25	Loam	0	2.2	4.0	0.0	2.59	0.14	0.14	0.06	0.06	0.09	2.59	10.1	89.9	4.9
B <sub>1t</sub>	25-35	Loam	0	1.8	4.1	0.0	2.98	0.14	0.14	0.06	0.13	0.13	2.98	10.0	90.3	4.2
B <sub>21t</sub>	55-75	Clay loam	0	0.2	4.2	0.0	3.05	0.55	0.55	0.18	0.15	0.15	3.05	22.4	77.8	14.0
B <sub>22t</sub>	80-90	Clay loam	0	0.1	4.4	0.0	2.26	1.97	1.97	0.93	0.21	0.21	2.26	57.9	42.1	36.7
B <sub>3t</sub>	175-200	Clay loam	0	0	4.9	0.0	1.29	4.19	4.19	1.35	0.22	0.22	1.29	81.7	18.3	59.4
C	230-240	Loam	0	5.3	5.3	0.0	0.00	10.32	10.32	2.80	0.18	0.18	0.00	100.00	0.0	77.6
C <sub>k</sub>	300-320	Loam	0	7.4	7.4	15.1	0.00									
<i>CTE site, acid-leached soil (Dystric Podzoluvisol), Soignes Regional Forest</i>																
A <sub>h</sub>	0-5	Loam	0	32.4	22.2	3.4	0.0	6.35	0.67	0.83	0.50	0.50	4.35	25.1	52.1	8.0
E	5-25	Loam	0	4.5	4.5	0.0	2.75	0.04	0.04	0.03	0.05	0.05	2.44	5.3	85.1	1.2
B <sub>21t</sub>	55-75	Clay loam	0	1.32	4.9	0.0	0.36	1.32	1.32	0.87	0.18	0.18	0.14	87.1	4.9	48.2
B <sub>3t</sub>	175-200	Clay loam	0	0.73	5.2	0.0	0.73	3.69	3.69	1.80	0.73	0.73	0.61	88.6	9.5	57.8
C	260-270	Loam	0	5.2	5.2	0.0	0.23	4.59	4.59	1.33	0.10	0.10	0.14	96.4	2.3	73.5
C <sub>k</sub>	295-305	Loam	0	7.5	7.5	13.2	0.00									
<i>ODE site, acid-leached soil limed in 1972 (Dystric Podzoluvisol), Soignes Regional Forest<sup>‡</sup></i>																
A <sub>h</sub>	0-5	Loam	0	17.3	14.7	4.9 ± 1.2	nd	1.78 ± 1.89	15.2 ± 19.3	0.75 ± 0.57	0.31 ± 0.16	0.31 ± 0.16	1.60 ± 1.59	78 ± 23	20 ± 20	70 ± 24
E	5-25	Loam	0	4.7 ± 0.9	nd	4.7 ± 0.9	nd	1.53 ± 1.22	2.20 ± 2.11	0.13 ± 0.03	0.09 ± 0.03	0.09 ± 0.03	1.53 ± 1.22	59 ± 34	41 ± 34	52 ± 33
B <sub>1t</sub>	25-35	Loam	0	4.3 ± 0.1	nd	4.3 ± 0.1	nd	3.88 ± 0.74	0.74 ± 0.42	0.10 ± 0.07	0.13 ± 0.04	0.13 ± 0.04	3.88 ± 0.74	19 ± 6	81 ± 6	15 ± 6
B <sub>21t</sub>	60-70	Clay loam	0	4.2	4.2	4.2	0.0	5.83	0.80	2.69	0.09	0.09	5.83	38.0	62.0	8.5
B <sub>22t</sub>	100-120	Clay loam	0	4.8	4.8	4.8	0.0	1.62	4.99	2.88	0.13	0.13	1.62	83.2	16.8	51.9
<b>High Belgium</b>																
<i>POUR site, Ochreous brown earth (Dystric Cambisol), Herbennont State Forest</i>																
A <sub>h</sub>	0-3	Silty clay	28.5	29.8	19.9	3.7	0.0	8.41	0.69	0.48	0.33	0.33	6.75	15.1	68.1	7.0
A <sub>h</sub> /B	3-10	Silty clay	39.5	13.7	22.7	3.9	0.0	6.94	0.14	0.19	0.18	0.18	5.75	6.8	77.2	1.9
B <sub>1w</sub>	10-25	Sandy clay loam	46.6	6.4	4.5	0.0	3.37	0.05	0.05	0.05	0.07	0.07	2.99	4.8	84.5	1.4
B <sub>2w</sub>	30-40	Sandy clay loam	59.2	4.7	4.4	0.0	2.44	0.05	0.05	0.03	0.06	0.06	2.27	5.4	88.0	1.9
B <sub>2w</sub> /C	45-55	Sandy clay loam	77.2	2.5	4.5	0.0	1.74	0.03	0.03	0.02	0.05	0.05	1.66	5.4	90.2	1.6
C	70-85	Sandy clay loam	75.9	0.6	4.4	0.0	2.68	0.04	0.04	0.02	0.06	0.06	2.53	4.2	90.4	1.4
<i>SMD site, Ochreous brown earth (Dystric Cambisol), Smuid wood</i>																
A <sub>h</sub>	0-3	Silty clay	nd	22.0	14.1	3.7	0.0	4.98	0.82	0.36	0.65	0.65	4.14	28.1	59.8	12.0
A <sub>h</sub> /B	3-10	Silty clay	nd	7.6	15.3	4.0	0.0	4.46	0.09	0.09	0.18	0.18	3.82	9.2	77.8	2.0
B <sub>1w</sub>	10-25	Sandy clay loam	nd	4.5	4.4	0.0	2.36	0.05	0.05	0.03	0.07	0.07	2.13	9.2	82.0	2.2
B <sub>2w</sub>	25-40	Sandy clay loam	nd	1.3	4.4	0.0	1.71	0.04	0.04	0.02	0.06	0.06	1.57	11.6	81.2	2.3
B <sub>2w</sub> /C	40-50	Sandy clay loam	nd	0.5	4.5	0.0	3.94	0.03	0.03	0.03	0.09	0.09	3.73	5.8	89.2	0.7
C	60-70	Sandy clay loam	nd	0.4	4.5	0.0	2.78	0.03	0.03	0.04	0.08	0.08	2.57	8.4	84.6	1.2

\*Belgian soil classification (all soil are silt loam after the FAO classification, except the silty E horizons).

<sup>†</sup>1M KCl extraction.

<sup>‡</sup>1M CH<sub>3</sub>COONH<sub>4</sub> pH 7 extraction.

<sup>§</sup>Mean values ± standard deviation show the heterogeneity of some chemical data caused by the liming in the upper horizons.

MES, *Mésanges*; CTE, *Comte de Flandre*; ODE, *Odeur*; POUR, *Poursumont*; SMD, *Smuid*; nd, not determined.

**Table 3** Isotopic compositions, Sr, Ca, Ba concentrations and Sr/Ca, Sr/Ba ratios of the atmospheric and the weathering endmembers and of the soil exchangeable fraction in the Belgian studied stands

Atmospheric precipitation		Sampling date	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma \times 10^{-6}$	Sr ( $\mu\text{g L}^{-1}$ )	Ca ( $\mu\text{g L}^{-1}$ )	Sr/Ca ( $\text{g g}^{-1}$ )
Central Belgium*		28-XI-2001	$0.709026 \pm 10$	1.3	250	0.0052
Central Belgium*		29-XII-2002	$0.709175 \pm 7$	1.4	292	0.0048
High Belgium*		23-I-2003	$0.709238 \pm 7$	2.4	1112	0.0021
Central Belgium mean bulk precipitation ( $n = 17$ ; mean $\pm$ SD)				$1.6 \pm 1.3$	$510 \pm 465$	$0.0032 \pm 0.0008$
High Belgium mean precipitation (Offagne, $n = 36$ ; mean $\pm$ SD)				$3.2 \pm 1.7$	$1490 \pm 1250$	$0.0024 \pm 0.0006$
Soil	Soil horizon	Sampling depth (cm)	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma \times 10^{-6}$	Sr ( $\text{mg kg}^{-1}$ )	Ca ( $\text{mg kg}^{-1}$ )	Sr/Ca ( $\text{g g}^{-1}$ )
<i>Weathering endmember (0.1 M HCl leaching)</i>						
POUR site	$A_h$	0–3	$0.714070 \pm 6$	0.71	69	0.0104
	$A_h/B$	3–10	$0.716204 \pm 6$	0.42	37	0.0116
	$B_{1w}$	10–25	$0.717617 \pm 6$	0.46	35	0.0132
	$B_{2w}/C$	45–55	$0.717027 \pm 5$	0.48	35	0.0137
SMD site	$A_h$	0–3	–	–	–	–
	$A_h/B$	3–10	–	0.25	26	0.0097
	$B_{1w}$	10–25	$0.717099 \pm 6$	0.22	20	0.0110
	$B_{2w}$	45–55	–	0.11	10	0.0114
MES site	$A_h$	0–5	$0.713643 \pm 7$	0.37	32	0.0117
	$E$	10–25	$0.713114 \pm 6$	0.14	8	0.0179
	$B_{21t}$	55–75	$0.712067 \pm 7$	0.39	15	0.0257
<i>Exchangeable fraction (1 M <math>\text{CH}_3\text{COONH}_4</math> extract)</i>						
POUR site	$A_h$	0–3	$0.714509 \pm 9$	0.69	135	0.0051
	$A_h/B$	3–10	$0.715634 \pm 9$	0.12	12	0.0098
	$B_{1w}$	10–25	$0.715427 \pm 13$	0.05	5	0.0101
	$B_{2w}/C$	45–55	$0.717020 \pm 5$	0.03	4	0.0075
SMD site	$A_h$	0–3	$0.714809 \pm 5$	0.75	164	0.0046
	$A_h/B$	3–10	$0.715857 \pm 7$	0.12	19	0.0061
	$B_{1w}$	10–25	$0.716250 \pm 5$	0.06	11	0.0054
	$B_{2w}$	45–55	$0.714920 \pm 17$	0.05	9	0.0055
MES site	$A_h$	0–5	$0.712138 \pm 6$	0.89	190	0.0047
	$E$	10–25	$0.712888 \pm 7$	0.12	19	0.0062
	$B_{21t}$	55–75	$0.715291 \pm 6$	0.48	66	0.0073

\*Data from Drouet *et al.* (2005).MES, *Mésanges*; CTE, *Comte de Flandre*; ODE, *Odeur*; POUR, *Poursumont*; SMD, *Smuid*.

roots in the organic layers. A shallowing of the effective depth of element uptake under the influence of acid deposition could also be put forward in the forest stands of High Belgium (POUR and SMD sites) and could explain the outward decreasing trend of the Sr isotopic ratio observed in beech and oak tree-rings: the soil Sr isotopic ratios increase with depth and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are measured in the humic layers (Table 3). However, in addition to the fact that an alternative explanation can be formulated, it must be

emphasized that the whole of our set of data does not totally agree with this hypothesis. Firstly, it is surprising that in the forest stands of Central Belgium (MES and CTE sites) the isotopic signal recorded in beech tree-rings is stable over time, while: (1) the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the soil exchangeable fraction decreases in the uppermost, organic-rich forest floor, in the same way as in the High Belgium sites; and (2) the gradient with depth of the soil chemical parameters are also favorable to a shallowing of the effective depth of base cation

uptake by tree roots (i.e., a strong Ca depletion and very high aluminum saturation rates in the upper mineral soil horizons, in contrast with the overlying humic layer) (Table 2). Secondly, the 'shallowing hypothesis' is not confirmed in all our studied forest stands when, as suggested by Bullen & Bailey (2005), the Sr/Ba ratio is used as a complementary tracer. These authors have shown that in the Cone Pond red spruce forest, the Sr/Ba ratio of stemwood samples tends on average toward values that are characteristic of the 'plant available' fraction of the uppermost forest floor. By contrast, in all our studied forest sites, the radial evolution of the Sr/Ba ratio in growth rings of both beech and oak shows no marked trend.

#### *Changes of atmospheric vs. weathering source ratio in tree nutrition*

If the Sr isotopic composition of neither the atmospheric nor the weathering source has changed with time, only a temporal change in their respective mass contributions to tree nutrition can explain the decreasing trends of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in growth rings observed in long-term chronologies of both beech and oak trees of the High Belgium forest stands and, generally speaking, the similar decreasing trend detected in different tree species of Scandinavia (Åberg, 1995) and North America (Bullen & Bailey, 2005). The use of a two-member mixing equation (Eqn. (2)) allows to calculate the proportion of Ca atmospheric input for each stand in the course of time, assuming that Sr is a proxy for Ca and that the vegetation cation pool is a mixture of Sr derived from mineral weathering (weathering endmember) and from atmospheric input (atmospheric endmember) (respective Sr/Ca and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are given in Table 3). The atmospheric endmember was measured in bulk precipitation samples, and the weathering endmember was determined by dissolution of soil samples from different soil horizons using 0.1 M HCl (Table 3). Between 1850 and 2000, atmospheric contributions increased from ~21% to ~56% in the SMD beech stand, and from ~45% to ~66% for beech and from ~44% to ~70% for oak trees in the POUR stand (Fig. 1). So, in both stands and whatever the tree species, the contribution of the weathering source has decreased by around 30% during a 150-year time interval. How can this decrease be explained? The supply of available Ca for a forest stand depends mainly on the soil exchangeable reserve. The Sr isotopic composition of this cation pool is controlled by weathering processes and by the input of Sr from atmospheric deposition and organic restitutions. In the High Belgium forest sites, calculation (based on Eqn. (2)) indicates that around 65% of the soil

exchangeable Ca of the  $B_{1w}$  horizon (10–25 cm depth) originates from atmospheric inputs. The steep decrease of the Sr isotope ratio in tree-rings can therefore be related to: (1) a fall of the soil base saturation (BS) and of the Ca saturation rate; (2) a modification of the Sr isotopic composition of this exchange pool because of an increasing contribution of cations originating from the atmospheric source. Both soil BS decrease and Ca depletion from the soil exchange pool originating from the weathering source lead to a decrease of the plant-available elements what display mainly the Sr isotopic signature of the weathering endmember and, accordingly, a significant increase of the atmospheric contribution. A decrease of the soil BS during different periods of the last century has been highlighted in Europe and North America by several methods (e.g. soil resampling) (Falkengren-Grerup *et al.*, 1987; Thimonier *et al.*, 2000) and long-term site observations (Likens *et al.*, 1998; Blake *et al.*, 1999). As early as 1995, in order to see whether the decrease over time of the Sr ratio in growth rings of two Scandinavian trees was a general feature, Åberg looked for another independent system and used the freshwater pearl mussel *Margaritifera* that grows in Central Swedish rivers. The results show that there is a distinct decrease in Sr isotope ratio in the *Margaritifera* shells over the studied time interval (1901 to 1990) and that the trend is the same as those recorded in tree-rings in the same region; this also suggests an ongoing acidification of the environment and a leaching of exchangeable base cations because of acid deposition (Åberg, 1995; Åberg *et al.*, 1995).

#### *Historic timing of the temporal trend of long-term chronologies and causal mechanisms*

The similar isotopic patterns, which are observed for different tree species with contrasting wood structure in different world countries (from North America to North and Western Europe) (Fig. 1), could arguably point to a common environmental effect.

The decrease of the Sr isotope ratio in trees of sensitive sites occurs in a very narrow period of time (Fig. 1), from ca. 1870 to 1890, with a major impact on the Ca sources available for root uptake. Interestingly, there is a striking parallelism between the beginning of the  $^{87}\text{Sr}/^{86}\text{Sr}$  decrease and the beginning of the increase of sulfur emission because of industrial activities at the end of the 19th century. This is highlighted by  $\text{SO}_4^{2-}$  deposition estimations (Ulrich, 1987) and by a record of nonmarine  $\text{SO}_4^{2-}$  deposition in an ice core from South-Central Greenland (Mayewski *et al.* 1990) (Fig. 1g and h). A similar interpretation was already proposed by Åberg *et al.*, (1995) and, recently, by Bullen & Bailey (2005). The latter concluded that the timing of den-

drochemical changes, which suggest a response to soil acidification in red spruce stemwood, is consistent with the established history of inorganic acid deposition in northeastern North America. Deposition of sulfates is known to increase the loss of basic cations from the rooting zone by leaching (Reuss, 1983). This soil acidification process leads to the mobilization of cationic Al competing with Ca, eventually reducing Ca availability for root uptake (Lawrence *et al.*, 1995; Tomlinson, 2003). As a result, the Sr isotope composition of the soil water taken up by trees moves toward that of the atmospheric source. The regular decrease of the Sr isotopic signal in tree-rings (Fig. 1a and 1c), from ca. 1870 to 1890, could be interpreted as a gradual effect of acid deposition over this time period. However, it must be kept in mind that this trend is influenced by a radial reequilibration process in beech rings, which implies that ring activity can last about 50 years after the ring formation. It may therefore be expected that the effect of acid deposition has not occurred gradually from 1870 to 1920, but more abruptly around the 1920s. Our opinion is that the steep decrease of the Sr isotope ratio in tree-rings is a consequence of a broken equilibrium caused by the change of the dominant acid in soil (Wesselink *et al.*, 1995). In the not highly acidic context of a preindustrial forest ecosystems, the dominant anion was either bicarbonate ( $\text{HCO}_3^-$ ) or organic. In the 1870s, the combustion of fossil fuel caused the substitution of the dominant carbonic acid by sulfuric acid, which has a higher dissociation constant (Tomlinson, 2003). The result is a substantial increase in nutrient cations transferred from the exchangeable pool to the soil solution. This explanation reconciles the rapidity of the phenomenon with a subsequent slower evolution, when a new Ca weathering–leaching–uptake equilibrium has been reached. After 1920, the Sr isotopic signal of the tree-rings reaches a more or less constant value (except in the case of oak trees in the High Belgium POUR stand and in the New Hampshire spruce forest studied by Bullen & Bailey (2005) corresponding to a maximum change in the Ca source contributions of 12%, despite a continuous increase of acid deposition until the beginning of the 1980s (the amounts of acid loads in 1980 are two times higher than those around 1920). Atmospheric contribution of Ca continues to grow from 45% to 70% in only one oak time series of High Belgium until the 1980s (Fig. 1).

*Why an unvarying tree-ring Sr isotopic composition over time in the forest sites of Central Belgium ?*

The lack of a decrease of the Sr isotopic ratio in the tree-rings of beech in the Central Belgium sites (MES and

CTE sites: Fig. 1i and j) is a very instructive cases to complete the explanation of the above-discussed process. Even if the difference of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between the two endmembers (0.709 and 0.713) in these sites is 1.5 times lower than in the High Belgium stands, they are well separated and not overlapping. The conditions for applying the isotopic method are then well respected (Capo *et al.*, 1998). We have calculated that an increase of 3% and 9% of the Ca atmospheric contribution in Central Belgium should be detectable at a significant to highly significant level, respectively (paired *t*-test). So, a change in the Ca sources proportion of 20–30%, as in the High Belgium stands, would have been detectable.

The stability of the Sr isotopic signature in the beech wood of Central Belgium could be explained by a soil-effective base saturation  $\text{BS}_e$ , on average higher than the critical value of 20% (or a Ca saturation higher than 15%) in the upper meter (Table 2). Above these values, the soil solution is considered to be buffered mainly by release of base cations from the exchange complex (Reuss, 1983).

Moreover, the acid-leached soils developed on loess of Central Belgium (MES and CTE sites) contain 12 times more total Ca and 30 times more exchangeable Ca in their upper meter than the ochreous brown earths on Devonian shales of High Belgium (POUR and SMD sites) (Table 2). Even if only the upper 50 cm of the soil is taken into account (i.e. the depth mainly prospected by beech roots), the Ca contents are still clearly distinct: the loessial soils contain seven times more total Ca and 15 times more exchangeable Ca than the soils of High Belgium. In other words, the Central Belgium forest stands are growing on soils that can be considered as slightly sensitive to acid deposition.

## Conclusions

Our results show that long-term records of strontium isotopic composition in tree-rings are an exceptional historic-timing record of chemical changes in the soil environment. An accurate interpretation of the tree-ring records however, needs, to take into account the influence of the lateral reequilibration of base cation in the tree-rings. The opportunity to verify the reliability of the tree-ring recorder was provided by a well-controlled nutritional perturbation in the context of a limed forest stand induced 30 years ago by addition of crushed limestones with a known Sr isotopic signature. In the 'sensitive' forest sites of High Belgium (i.e. forest stands growing on very acid soils with low Ca reserve), the dendrochemical curves show a decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in growth rings from inner to outer wood, for both beech and oak, suggesting

that these forest ecosystems were abruptly affected by atmospheric inputs of strong acids around the 1920s. By contrast, the forest sites of Central Belgium, growing on Ca-richer soils, are slightly sensitive to acid deposition and, consequently, show a stability of the Sr isotopic signature. The steep decrease of the Sr isotope ratio in tree-rings is thought to be a consequence of a broken equilibrium induced by the massive input of SO<sub>4</sub> through atmospheric pollution. The nearly similar radial patterns of decreasing Sr isotope ratio recorded in long-term chronologies of *F. sylvatica* and *Q. pedunculata* in High Belgium, of *Q. pedunculata* and *P. sylvestris* in Scandinavia (Åberg, 1995), and of *P. rubens* in North America (Bullen & Bailey, 2005), associated with a clear evidence of a similar historic timing, reveal a general trend on a large geographic scale in sensitive forest ecosystems affected by acidic deposition.

### Acknowledgements

This research was financially supported by the 'Fonds pour la Recherche Fondamentale et Collective' FRFC (Belgium) to J. Herbauts and D. Demaiffe. Th. Drouet is a fellow of the FRIA (Fonds de Formation pour la Recherche dans l'Industrie et l'Agriculture). We gratefully acknowledge Wolf Gruber for assistance in the laboratory. Patricia Hermand is warmly thanked for the maintenance of the mass spectrometer and supervision of the isotopic measurements. Th. D. is grateful to Prof. Göran Åberg for constructive correspondence. The authors are extremely grateful to the two anonymous reviewers for their critical comments on the manuscript. Thanks are because of Springer Science and to Nature for their permission to reproduce some figures.

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