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Original article

Element analysis of tree rings in pedunculate oak heartwood: an indicator of historical trends in the soil chemistry, related to atmospheric deposition

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Summary — When investigating historical alterations of the soil chemistry, it could be interesting to determine the mineral content of the successive annual tree rings. The study reported here aimed at verifying this assumption. Oak heartwood was selected in order to minimize the disturbance due to element translocations in the wood. This study was carried out in a forest included in a floristic and edaphic survey performed earlier throughout northeast France. Xylem cores were extracted from the boles of five over 60-year-old pedunculate oaks in each of 68 plots. The analysis showed on average an increase in nitrogen and aluminum, a decrease in phosphorus, potassium and magnesium, and no change for calcium, in the rings corresponding to the last 30 years of the heartwood (1938–1967). These results are consistent with those of the floristic and edaphic survey, which had shown an increase in nitrogen and a trend towards acidification in most of the soils between 1970 and 1990, mainly due to atmospheric deposition (Thimonier et al, 1992). Thus, these changes in the soil chemistry had probably already affected the forest studied between 1938 and 1967. Finally, tree-ring analysis of oak heartwood appeared to be an effective approach to reveal historical changes in forest soil chemistry.

tree ring / pedunculate oak / heartwood / soil chemistry / atmospheric deposition

Résumé — Analyse minérale des cernes annuels du bois de cœur de chêne pédonculé ; un outil de détection de changements intervenus dans les propriétés du sol, en relation avec les dépôts atmosphériques. *L'étude porte sur l'intérêt potentiel de l'analyse des cernes successifs du bois pour appréhender l'évolution dans le temps des propriétés du sol. Le choix du bois de cœur de chêne pédonculé pour cette étude devrait permettre de minimiser les effets perturbateurs des translocations d'éléments à l'intérieur du bois. L'étude a été réalisée dans une forêt incluse dans une enquête floristique et édaphique réalisée précédemment dans le nord-est de la France (Thimonier et al, 1992). Des «carottes» de bois ont été extraites du tronc de cinq chênes pédonculés âgés de plus de 60 ans dans chacun des 68 placeaux retenus. L'analyse a montré en moyenne une augmentation de l'azote et de l'aluminium, une diminution du phosphore, du potassium et du magnésium, et aucune tendance pour le calcium, dans les cernes correspondant aux 30 dernières années du bois de cœur (de 1938 à 1967). Ces résultats sont cohérents avec ceux de l'étude floristique et édaphique, qui avait montré que* *la plupart des sols concernés avaient subi entre 1970 et 1990 un enrichissement en azote et une tendance vers l'acidification, essentiellement à la suite de dépôts d'origine atmosphérique. Il est donc probable que cette évolution des propriétés du sol ait déjà affecté la forêt étudiée entre 1938 et 1967. Il apparaît ainsi que l'analyse des cernes annuels de bois de cœur de chêne pédonculé pourrait constituer une approche intéressante pour révéler des changements intervenus dans le passé au niveau des propriétés chimiques du sol.*

cerne annuel / chêne pédonculé / bois de cœur / chimie du sol / dépôt atmosphérique

INTRODUCTION

It is generally accepted that the mineral content of a tree stemwood partly depends on the chemical composition of xylem sap (Bondietti and Shortle, 1990). The element concentration of each tree ring may therefore, to a certain extent, reflect the properties which characterized the soil during the year when this ring was formed (Bondietti and McLaughlin, 1992). That is the reason why tree-ring analysis has been used for several years to investigate historical changes which occurred in soil chemistry. This approach could be of great interest as other methods like soil analyses or floristic surveys do not generally enable us to go back very far in the past. Soil analyses would require repeated sampling at exactly the same place at a pace of several decades and exactly the same analytical procedures to be used. Tree-ring analysis proved to be more or less in accordance with historical events involving the soil, including: i) contamination of the environment by different elements, in particular Cu, Pb, Zn, Mn, Al, Fe, B, Ni, Cd, generally coming from industrial areas, coal-burning power generators or vehicle exhaust fumes. Species involved were conifers (Robitaille, 1981; Baes and McLaughlin, 1984; Guyette and McGinnes, 1987; Guyette et al, 1991; Zayed et al, 1992) as well as broadleaved species (Vroblesky and Yanosky, 1990; Stewart et al, 1991) including oaks (Herrmann et al, 1978; Kardell and Larsson, 1978; Queirolo et al, 1990; Yanosky and Vroblesky, 1992); ii) fertilization (McClenahen et al, 1989; Kashuba, 1992); iii) acidification of the soil, generally ascribed to atmospheric deposition (Meisch et al, 1986; Arp and Manasc, 1988; Ragsdale and Berish, 1988; Scherbatskoy and Matusiewicz, 1988; Bondietti et al, 1989; Bondietti and McLaughlin, 1992).

However, results of the different studies were not always clear nor consistent with one another, and interpreting tree-ring analysis often proved to be a complicated task. The main reason is the widespread occurrence of radial and vertical translocation of elements, which alters the mineral content of annual rings to varying degrees. Some elements are more susceptible to translocation than others (McClenahen et al, 1989; Kairiukstis and Kocharov, 1990), including in some cases redistributions associated with the transformation of sapwood to heartwood (Okada et al, 1988; Frelich et al, 1989; De Visser, 1992). Some macronutrients are often partly remobilized from older annual rings and transferred towards younger and more active parts of the wood (Ogner and Bjor, 1988; Häsänen and Huttunen, 1989; Peterson and Anderson, 1990; Chun and Hui-yi, 1992; De Visser, 1992). Translocation mainly affects the sapwood, and therefore the mineral content of a given ring is likely to vary with time as long as it is part of the sapwood. Translocation may also concern the heartwood (Wardell and Hart, 1973), but generally on a much smaller scale, except for some elements absorbed in excess in contaminated areas that may be transferred to the heartwood through a detoxication process (Trüby, 1988; Long and Davis, 1989; Kairiukstis and Kocharov, 1990; Vroblesky et al, 1992). Translocation may also depend on the species under study (Guyette et al, 1992). In particular, each ring is used for sap transport during a variable number of years: so, the initial mineral content of a given ring may be altered over a long period after its formation, by cation exchange processes with the xylem sap (Arp, 1988; Arp and Manasc, 1988; Bondietti et al, 1989; Bondietti and Shortle, 1990; Bondietti et al, 1990; Bondietti and McLaughlin, 1992; McClenahen and Vimmerstedt, 1993). For those reasons, it could be interesting, in particular when investigating macronutrients, i) to pay special attention to the mineral content of the rings in the heartwood; ii) to work on oaks, which are ring-porous species in which sap is mainly transported in the current year or last 2- or 3-year-old vessels (Hinckley and Lassoie, 1981; Hagemeyer et al, 1992; Granier et al, 1994), even though the wood structure of broadleaved species is more likely to allow lateral transfer than that of conifers (Zayed et al, 1992). We therefore carried out a study to test tree-ring analysis on the heartwood of pedunculate oak as an indicator of temporal trends in some chemical properties of the soil.

We worked in a forest included in a floristic survey performed earlier in forest ecosystems located throughout northeast France. This survey, completed with soil analyses in some of the forests studied, showed a widespread enrichment of the soils in nitrogen between 1970 and 1990 (Thimonier, 1994); in addition, it revealed a trend towards a more acidic state for a large number of the soils during the same period. We examined the two approaches – tree-ring analysis and floristic survey – to see if the results were consistent with each other, and to test the interest of tree-ring analysis.

METHODS

We selected the Amance State Forest, about 1 000 ha, in the Lorraine plain, 15 km northeast of Nancy, in the northeast of France. This forest is subjected to a semicontinental climate, with an average annual rainfall of 700 mm. It stands on different formations of the Lias. The substrate frequently consists of marl, in some places limestone, but rarely of sandstone, and it is generally covered with a variable thickness of silt of eolian origin. The full range of soil types in the Amance Forest is fairly large, but many of the soils are mottled leached brown, fairly rich in nutrients, with a mesotrophic mull and a pH in A1 (measured in water) often close to 5.0. They frequently display a temporary water table which, however, may rise to the soil surface only in a very few places. Table I gives the chemical analysis of one of these mottled leached brown soils, in which properties are roughly intermediate between those of the poorest and the richest soils present in this forest (Morel, 1973). Almost all the stands are composed mainly of pedunculate (*Quercus robur* L) and sessile (*Quercus petraea* (Matt) Liebl) oaks, often mixed. From the 19th century, the stands

Table I. Chemical properties of a mottled leached brown soil from Amance Forest.

Mean depth (cm)	*Horizon*	*pH* [a]	Ca^{2+} [b]	K^{+} [b]	Mg^{2+} [b]	Al^{3+} [b]	*CEC* [bc]
–10	A1	4.85	29.4	4.4	7.3	6.8	125
–30	A2g	4.35	10.7	0.9	4.1	28.0	84
–50	A2g/Bg	4.60	34.2	2.8	17.1	58.7	134
–80	Bg	5.05	51.7	3.7	35.6	57.5	193
–110	Cg	5.40	93.0	3.4	43.5	43.6	210

[a] In water; [b] in mmol kg^{-1}; [c] CEC: cation exchange capacity.

have been changing from coppice with standards to high forest; this conversion was more or less completed, depending on the plots.

Five pedunculate oaks over 60 years old were selected in the dominant or codominant classes from each of 68 plots representative of the environmental variability in this forest. Early in 1988, one xylem core was extracted at 2.80 m above the ground from the southern side of each tree bole, with a 5-mm diameter teflon-coated increment borer. The cores were stored in a refrigerator in closed plastic tubes. The different increments of each core were dated according to a procedure described by Becker et al (1994), using a moving graphic program after the progressive detection of so-called pointer years. The surface of each core was decontaminated by sticking a piece of adhesive tape onto it, and then removing it. The glue of this tape, when analyzed in our laboratory, was free of the elements to be determined. The different annual increments of each core were separated, under a magnifying glass, with a ZrO_2 ceramic blade in order to avoid any mineral contamination. Most authors investigating tree-ring analysis use several-year increments; in order to collect more detailed data, we worked on annual increments, some of them as narrow as 0.8 mm. The last annual increment (1987) was removed, because it might have been contaminated by the bark, whose mineral content is often much higher than that of the xylem. All the increments formed a given year in all 68 plots were combined. Thus, we obtained 49 annual samples, from 1938 to 1986, which were oven-dried at 65 °C for 24 h. Each of these samples was weighed. One part (about 1.5 g) was oven-ashed at 500 °C; ashes were processed according to the method described by Pinta (1973), then analyzed for the macronutrients P, K, Ca, Mg and for Al, an element which is linked to acidity in the soil, by inductively coupled plasma spectrometry (ICP-AES), and an ultrasonic nebulisor when elemental concentrations were particularly low (Clément et al, 1994). Another part (about 0.5 g) of each sample was analyzed for N by a segmented continuous flow analyser at 630 nm, after Kjeldahl digestion in the presence of a K_2SO_4 and Se catalyzer.

Temporal trends of the stemwood mineral contents were analyzed by considering the significance of the linear correlation coefficients, which were virtually always higher than the nonlinear ones.

RESULTS

A visual examination of the cores showed that the sapwood–heartwood boundary was located on average between the 1967 and 1968 increments.

The mineral content of the sapwood

In addition to fluctuations from one year to the next, the overall variation of the element concentration across the sapwood (ie, from 1968 to 1986) showed different patterns (fig 1). Potassium was the only element in which variation was nonlinear (polynomial function). The linear correlation coefficients were positive and significant at the 1‰ level for the other macronutrients, but not for aluminum.

The heartwood mineral content

Figure 2 shows the variations in the elements analyzed from the heartwood between 1938 and 1967 (30 years). All long-term variations were linear. Three patterns may be distinguished: an increase in nitrogen and aluminum; no trend for calcium; and a decrease in phosphorus, potassium and magnesium. The correlation coefficients were significant at the 5% level for nitrogen and at the 1‰ level for aluminum, phosphorus, potassium and magnesium.

DISCUSSION AND CONCLUSION

There were large fluctuations in the concentration from one annual ring to the next, both in sapwood and heartwood, for all the elements analyzed. These fluctuations were probably directly related to interannual changes of climatic conditions and/or of ring

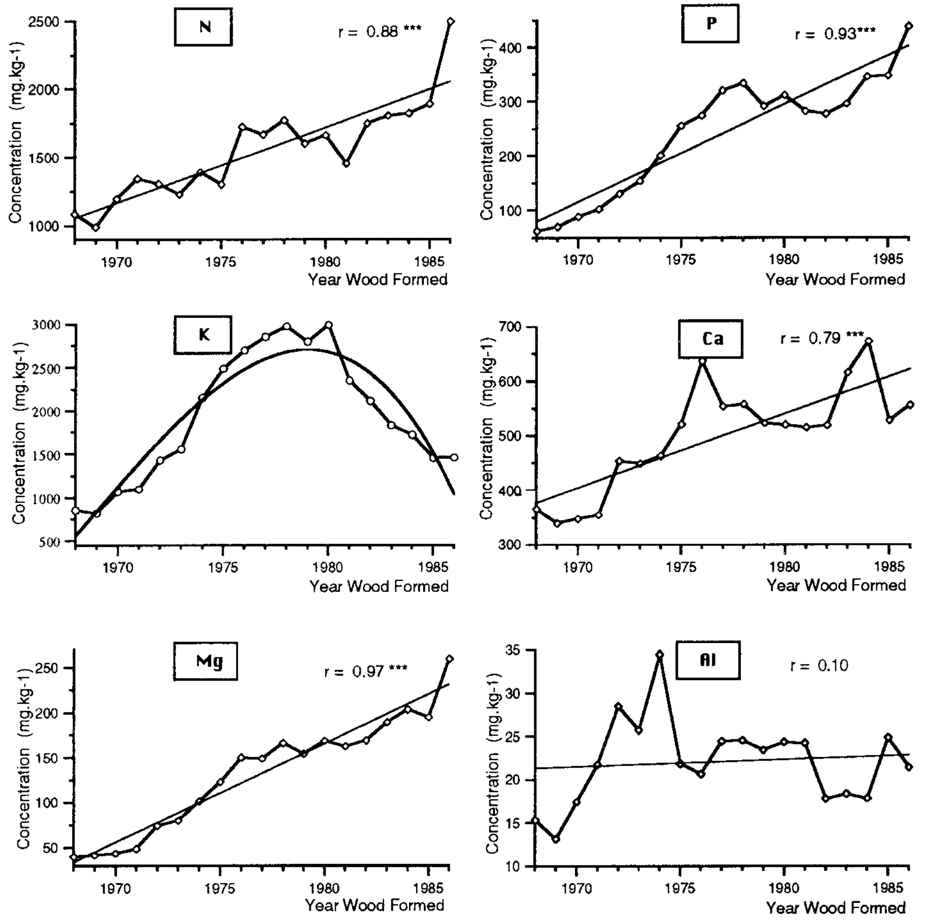

Fig 1. Elemental concentrations in the annual rings of pedunculate oak sapwood (Amance Forest, northeast France). *** Significant at the 1‰ level.

width, the latter change altering the relative proportions of earlywood and latewood in oak. We are not able to go further with this for the moment.

The sharp overall increase of most of the macronutrients (N, P, Ca, Mg) across the sapwood from 1968 to 1986 could be explained in two different ways: it might reflect an increase in these elements in the soil from 1968 to 1986, or it might be a consequence of their translocation in the tree. The first assumption is not in accordance with Thimonier (1994), who detected a slight decrease in nutrients in the soil from 1970 to 1990 throughout northeast France, except for N. On the other hand, many authors have shown that macronutrients are often transferred from older rings of the sapwood to younger and more active parts of the tree (see *Introduction*). Thus, the second assumption is likely to be right, and successive annual losses of elements through

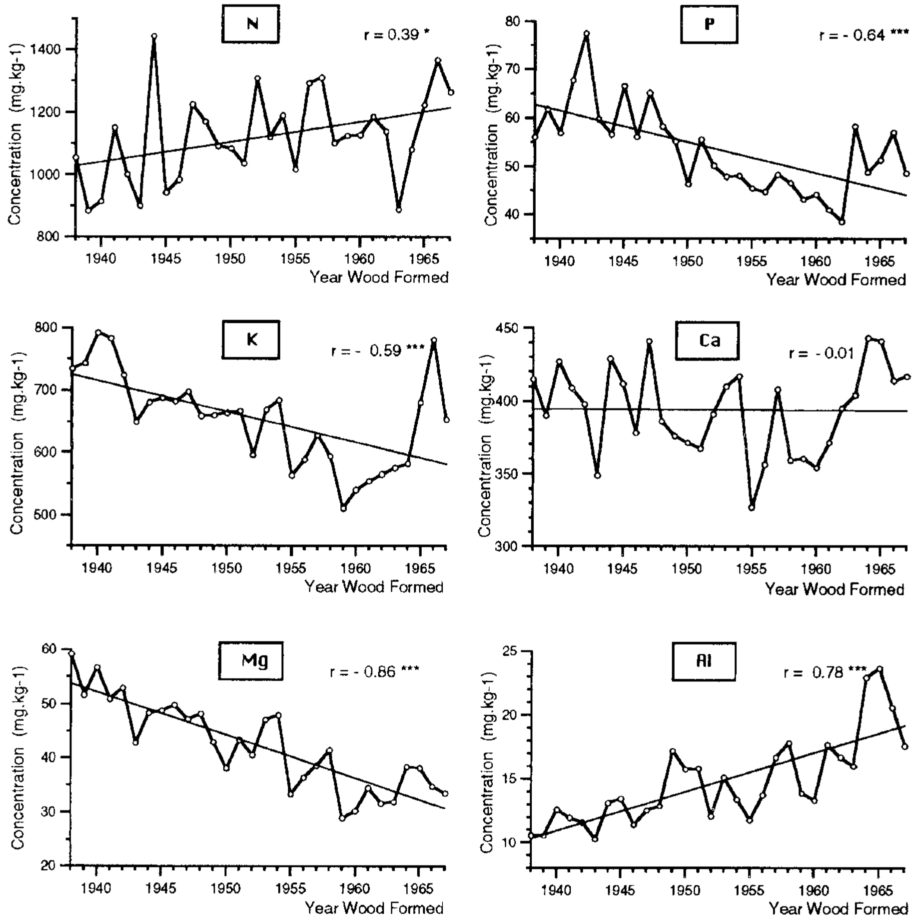

Fig 2. Elemental concentrations in the last 30 annual rings of pedunculate oak heartwood (Amance Forest, northeast France). *** Significant at the 1‰ level; * significant at the 5% level; no * not significant.

translocations inside the tree would probably conceal the effects on the ring mineral content of possible temporal decrease of their concentration in the soil. Even if the mineral content of the last ring depends on the soil properties the year it was formed, variations in the concentration of macronutrients across the sapwood could probably not be used as an indicator of temporal changes in their availability in the soil.

A comparison of figures 1 and 2 reveals a contrast between the sapwood and heartwood in the temporal trend of the macronutrients, except for nitrogen. The lowest mean concentrations of these elements are located close to this boundary. This is likely to confirm that the macronutrients remaining in a heartwood ring probably made up the fraction the most strongly bound to the wood in the year when the

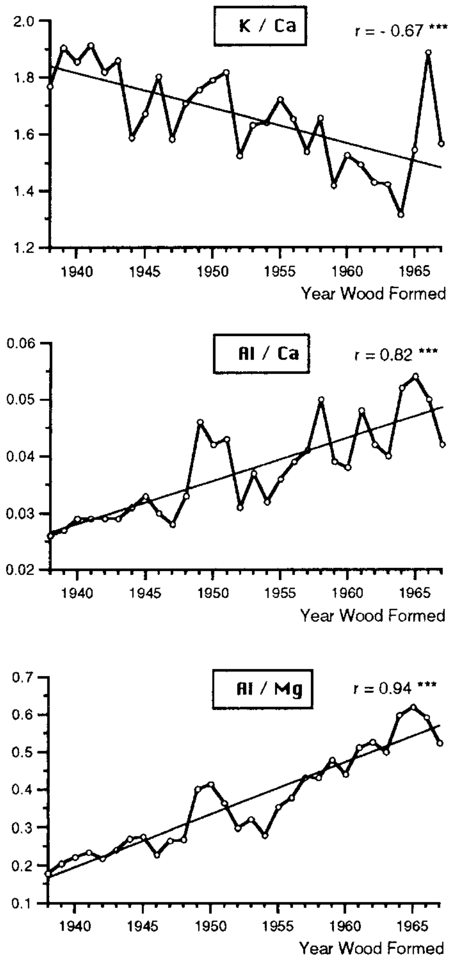

Fig 3. Elemental ratios in the last 30 annual rings of pedunculate oak heartwood (Amance Forest, northeast France). *** Significant at the 1‰ level.

ring was formed, and that translocation towards younger parts of the tree did not significantly affect a ring from the time it became part of the heartwood. Therefore, the macronutrient concentration in each ring of the heartwood may be directly related to the chemical properties of the soil the year when the ring was formed, and long-term changes in the macronutrient concentration across the heartwood may be related to temporal trends of these elements in the soil.

The increase in nitrogen in the heartwood rings from 1938 to 1967 is consistent with the floristic survey carried out in Amance Forest, which showed an enrichment of nitrogen in the soil between 1970 and 1990, probably due to atmospheric deposition (Thimonier et al, 1992, 1994; Thimonier, 1994). Indeed, Amance Forest is subjected to nitrogen deposition, mainly on account of the proximity of this forest not only to agricultural land, but also to the Nancy area and the Moselle Valley with its steel industry and road traffic, in addition to pollutants coming from longer distances. Annual nitrogen inputs in this forest by rainwater were assessed to be 20–30 kg ha^{-1} $year^{-1}$ early in the 1970s (Aussenac et al, 1972). In 1991, they had decreased to 14–20 kg ha^{-1} $year^{-1}$ (8–12 kg under canopy), depending on the location in the forest, probably in relation to the collapse of the steel industry (Thimonier, 1994). Over 60% was in the form of NH_4^+; however, these nitrogen inputs in 1991 were probably underestimated because of the rainfall deficit (22% under the "normal" figures). The increase in the frequency of nitrogen-demanding species between 1970 and 1990, revealed by the floristic survey, is particularly marked on the edges of the forest exposed to the prevailing winds, coming from the Nancy area, which is consistent with the N-deposition hypothesis (Thimonier et al, 1992). The tree-ring analysis study suggests that nitrogen deposition and the increase in nitrogen in the soil probably began much earlier than 1970. This assumption is consistent with the fact that there has been a marked increase in road traffic since 1960 and in the use of nitrogenous fertilizers since the early 1970s in the farmlands near Amance Forest, but also in emissions of NH_3 by livestock and of NOx generated by the steel industry from 1938 to 1967 (Thimonier, 1994).

Several authors did not observe clear trends in the concentrations of macronutrients across the heartwood apart from changes related to the environmental conditions. DeWalle et al (1991) noted relatively constant concentrations of P, K, Ca, Mg in the inner zone, including most, if not all, of the heartwood of two broadleaved species, of which one was an oak (*Quercus rubra* L); however, these element concentrations increased sharply in the outer zone as the cambium was approached. According to this pattern, therefore, a decrease in nutrients such as Mg, Ca or K from the pith towards the youngest rings of the heartwood would not result from a biological process, but could be interpreted as a reduction in the content or availability of these elements in the soil. This may be an indication of acidification of the soil. Acidification in a soil, whatever its causes, is the consequence of an increase in the number of protons, which results in a gradual decline of the soil acid neutralizing capacity (Van Breemen et al, 1984) and in most cases leads to a decrease in available Mg^{2+}, Ca^{2+} and K^+, an increase in Al^{3+} and often, but not always if the soil buffer action is high, a decrease in pH. Phosphorus uptake may also be reduced. This is why our results may suggest a gradual acidification of the soil between 1938 and 1967, although a decline in Ca concentrations was not observed. Ca^{2+} is more strongly adsorbed on the soil complex than Mg^{2+} and K^+, and Blanpied and Oberly (1978) did not notice such a decline in spite of acid rainfall. However, according to some authors, variations in Mg, Ca or K across the heartwood cannot be a valid indicator of soil acidification in some situations. A review of these cases is given here.

First, declines in Ca and Mg concentrations from the pith to the youngest hartwood rings have often, but not always, been reported in conifers (Arp and Manasc, 1988; Bondietti et al, 1989; Helmisaari and Siltala, 1989; Momoshima and Bondietti, 1990; Peterson and Anderson, 1990) in relation to a decrease in the availability of the wood exchange sites for divalent cations with increasing radial distance from the pith (Bondietti et al, 1989, 1990; Momoshima and Bondietti, 1990). In contrast, K concentration rose or remained constant, and therefore the K/Ca ratio increased from the older to younger heartwood (Momoshima and Bondietti, 1990). This pattern is unlikely to concern broadleaved species, whose xylem structure is quite different from that of conifers. In particular, it cannot explain the trends observed between 1938 and 1967 in the Amance Forest, where, although the Mg radial decrease (fig 2) is in accordance with the pattern, the decline of K (fig 2) and K/Ca (fig 3) is not.

Second, according to some authors (Bondietti et al, 1989), the absolute values of Ca and Mg concentrations may remain constant or even increase in the wood in some situations, while there is a trend towards acidification in the soil. Indeed, at the beginning of acid deposition on poor soils, exchangeable bases may be mobilized from the raw humus, which may result in an enhanced growth of the trees (Raunemaa et al, 1982; Bondietti et al, 1989; Bondietti and Shortle, 1990; Bondietti and McLaughlin, 1992). An inversion of these trends occurs later, with an impoverishment of nutrients in the soil and a decrease in growth. Therefore, in order to detect a trend towards acidification, these authors prefer to examine changes in the wood of the Al/Ca and Al/Mg ratios, which reflect the relative activity of the cations concerned in the soil solution: when the pool of protons increases in the soil, the Al activity rises more than that of Ca or Mg due to the difference in charges of these cations. Although the soils are not poor and their Al^{3+} content is likely to be often fairly low in the Amance Forest, we have represented the temporal trend in these ratios in figure 3. The trends observed reinforce the assumption of a gradual acidification of the soils in the Amance Forest between 1938 and 1967 stated after the observations of the absolute values of the nutrients (see earlier).

Thirdly, Starck et al (1984) observed that concentrations of metabolically important macronutrients in the xylem sap of Douglas fir tended to be higher in young trees than in older ones. Could that explain the temporal trends of Mg, K and P concentrations in Amance Forest oak heartwood?

In contrast, these authors found that Al concentrations in the xylem sap were independent of tree age. Moreover, aluminum in tree rings is widely considered as a valid bioindicator of its availability in the soil because it is not subjected to great translocation in conifers (Baes and McLaughlin, 1984, 1986; Guyette and McGinnes, 1987; Elling et al, 1989) as well as in broadleaved species (McClenahen et al, 1989), including oaks (Chun and Hui-yi, 1992; De Visser, 1992). The relationship between the chemical composition of any ring and that of the soil during the year when this ring was formed is probably closest for Al than for the macronutrients. An increase in the absolute concentration in aluminum from older to younger rings, as observed in our study, was therefore interpreted by many authors as a temporal trend towards acidification of the soil, generally as a consequence of acid deposition (Baes et al, 1983; Meisch et al, 1986; Scherbatskoy and Matusiewicz, 1988; McClenahen et al, 1989; Ward and Homer, 1989; Zayed et al, 1991; Bondietti and McLaughlin, 1992). All these observations enhance the assumption of a gradual acidification of the soil in the Amance Forest between 1938 and 1967. Therefore, at least part of the decline of Mg, K and P concentrations in oak heartwood probably also results from this process.

These assumptions are consistent with the results of the floristic and edaphic survey performed in stands located throughout the northeast of France (Thimonier, 1994). Indeed, in addition to an enrichment of nitrogen in the soils, this study showed a small (except on the more acidic soils), but widespread trend towards acidification between 1970 and 1990. This acidification was manifested by a decrease in K, Mg and Ca on the absorption complex in the A1 horizon and sometimes in deeper horizons, but only in the A1 horizon was this accompanied by a slight decrease in the pH value (–0.1 unit on average). This acidification was probably due to both natural forest aging (Tamm and Hallbäcken, 1988) and atmospheric deposition, in particular of nitric acid and ammonium dissolved in rain. Indeed, nitrification or direct root uptake of this ammonium are a source of protons for the soil, as well as nitric acid (Bonneau et al, 1987; De Visser, 1992); but ammonium may also have an antagonistic effect on other nutrients, in particular magnesium.

This trend towards acidification probably involved the whole of northeast France. However, the floristic survey performed in the Amance Forest (Thimonier et al, 1992) revealed a (slight) acidification of the soil from 1970 to 1990 in only some areas of the forest. The authors suggest, however, that acidification could have been hidden elsewhere in this forest, as indicator values of the species in the sample did not always allow a clear discrimination between an increase in nitrogen and acidification. Thus, the results of the tree-ring analysis are consistent with those of the floristic survey, although taking a different period of time into account.

We finally assume that a gradual, although probably slight, acidification of the soil occurred in the Amance Forest between 1938 and 1967. Among the causes of this acidification, we may mention aging of the stands and deposition of some nitrogenous compounds, as in the later period, but also a deposition of SOx, which then decreased everywhere in France during the 1980s.

According to Becker et al (1994), the mean growth of pedunculate oak probably increased between 1938 and 1986 in the Amance Forest. This was ascribed to a combination of gradual climatic variations and increasing atmospheric CO_2 concentration. An effect of the increasing amounts of available nitrogen in the soil is also possible. Thus, the probable but not very marked acidification of the soil during this period did not affect tree growth clearly. This was predictable on soils such as those of the Amance Forest.

Finally, it appears that tree-ring analysis on pedunculate oak heartwood could be an interesting approach to reveal historical trends in some chemical properties of the soil whatever their causes, in particular changes in the nitrogen content or an acidification process even for soils which are not very acid or poor. However, it cannot provide quantitative values of these alterations; it is only an indicator, but seemingly quite a sensitive one. In most cases, this method should allow one to investigate earlier periods than is possible using other approaches, such as soil analyses or floristic survey.

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