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## Abstract

Soil organic-N dynamics, its controlling factors and its relationships with stand quality were studied in the 0-15 cm soil layer of 24 pinewoods with contrasting age, productivity and parent material (granite; acid schists), searching for N variables useful to predict stand growth and site quality. No significant differences were found between young and old stands for any of the N variables considered, nor two- or three-order interactions among stand age, site quality and parent material. The soil total-N content, which was correlated positively with the Al oxides content [a soil organic matter (SOM) stabilizing agent], did not vary significantly according to parent material, but it was lower ( $P \leq 0.02$ ) in stands with high than with low site index ( $2.68 \pm 1.11$  and  $3.97 \pm 1.13$  g N kg<sup>-1</sup> soil, respectively). The soil  $\delta^{15}\text{N}$  ranged from +3.5 to +6.5 ‰, without significant differences among stand groups, and it was negatively correlated with water holding capacity, exchangeable bases, Al oxides and N content, suggesting that: i) N losses by  $\text{NO}_3^-$  leaching are the most important controlling factor of  $\delta^{15}\text{N}$  in these temperate humid region soils; and ii) soil N richness is related with limited N losses, which discriminate against  $^{15}\text{N}$ . At any incubation time, no significant differences were found in soil inorganic-N content among stand groups ( $7.78 \pm 4.57$ ,  $39.33 \pm 16.20$  and  $67.80 \pm 26.50$  mg N kg<sup>-1</sup> soil at 0, 42 and 84 d, respectively). During the incubation, the relative importance of the ammonification decreased and that of the nitrification increased. The net N mineralization rate (NNMR, in % of organic N) was significantly higher in granite than in schists soils at both 42 d ( $1.24 \pm 0.34$  and  $0.75 \pm 0.37\%$ , respectively) and 84 d ( $2.18 \pm 0.56$  and  $1.53 \pm 0.66\%$ , respectively). In high quality pinewoods, the NNMR at 42 d and 84 d ( $1.16 \pm 0.45$  and  $2.12 \pm 0.79\%$ , respectively) were significantly higher than in low quality stands ( $0.83 \pm 0.35$  and  $1.59 \pm 0.45\%$ , respectively). This result, together with those on soil total-N and inorganic-N supply, suggests that soil N dynamics in low and high quality stands is different: in the former there is a bigger N pool with a slower turnover, whereas in the latter there is a smaller N pool with a faster turnover, both factors being nearly compensated, making similar the soil available N supply. After 42 and 84 d of incubation, the NNMR and the nitrification rate were higher in the coarse textured soils, likely due to the low physical and chemical protection of their SOM; both rates were positively correlated with available P, exchangeable  $\text{K}^+$  and CEC base saturation, suggesting strong relationships among the availabilities of the main plant nutrients, and they increased with SOM quality (low C-to-N ratio). The strong negative correlation of site index with soil total-N ( $r = -0.707$ ;  $P \leq 0.005$ ), and its positive correlations with NNMR after 42 and 84 d of incubation, suggested that site quality and potential productivity are closely related to soil organic-N dynamics. Half of the site index variation in the stands studied could be predicted with a cheap and easy analysis of soil N content, the prediction being slightly improved if soil  $\delta^{15}\text{N}$  is included and, more significantly, by including N mineralization measurements.

**Keywords:** Delta  $^{15}\text{N}$ ; Forest productivity; N mineralization; Pinewoods; Soil quality.

## 1. Introduction

Nitrogen fertility is so closely associated with soil organic N dynamics that organic matter and organic matter-dependent properties are considered the key to the long-term sustainability and productivity of soils (Peoples et al., 1995), and the most promising indicators for soil quality assessment to be used in management decisions (Schoenholtz et al., 2000; Wander and Drinkwater, 2000). Likewise, several variables of soil N status and dynamics, such as N content, potentially mineralizable N and nitrification, have been proposed as basic soil quality indicators (Karlen et al., 1994; Lal, 1997; McCarty and Meisinger, 1997; Knoepp et al., 2000).

Most of the nutrient cycling models to predict long-term forest growth and sustainability focus primarily on the role of N dynamics on stand growth (Schoenholtz et al., 2000). Moreover, Reich et al. (1997) showed that across a wide climatic and soils gradient, and across both hardwood and softwood species, wood production increased linearly with net N-mineralization, which explained 50% of the variation in wood production. Consequently, Morris and Boerner (1998) strongly advocate developing forest health indicators based on key ecosystem processes, such as N mineralization and nitrification, even if its study consume more time and effort than that of chemical variables.

On the other hand, site index (i.e. the height of dominant trees at a specific age) is the most widely accepted index of site quality and potential productivity (Carmean, 1975; Richardson et al., 1999) and the standard for both direct and indirect methods of estimating site quality (Carmean, 1975). But accurate site index measurements cannot be made before a minimum of years of stand growth (20-25 y for *Pinus radiata*) and, thus, site quality for forest production could not be well known prior to stand establishment. Therefore, it is necessary to know the relationships between productivity and key soil indicators that relate to processes controlling forest health and productivity (Richardson et al., 1999). This line of research, usually based on multiple regression analysis to relate soil and climatic variables to some measure of forest productivity, commonly site index (see Burger and Kelting, 1999), should take into account that soil quality will change with plantation age (Kelting et al., 1999).

Accordingly, our objectives were: i) to study soil organic N dynamics and its controlling factors in soils under *P. radiata* stands; and ii) to analyse the relationship between soil organic N dynamics and stand quality, searching for N variables useful to predict stand growth and site quality.

## 2. Material and methods

### 2.1. Sites and field sampling

Twenty-four soils under stands of *Pinus radiata* D. Don were selected according to parent material (granite and acid schists), stand age (young: 11 to 18 y; old: 22 to 34 y) and site index (low: 14.1 to 20.3 m; high: 22.4 to 25.5 m); three soils were sampled for each parent material, stand age and site index combination. The stand sites have soil depths from 33 to 120 cm, slopes from 4 to 30%, all kinds of sun exposure and altitudes from 315 to 790 m a.s.l.; the stands are located between 42°01' and 43°19' N, and between 7°18' and 8°51' W. The soils were under the first rotation of *P. radiata* and site preparation prior to the plantation was generally slight, or limited to a subsoil ploughing with a ripper along the plantation lines. Climate is characterised by a total rainfall of 800-1200 mm y<sup>-1</sup> (1500 mm y<sup>-1</sup> at one site), distributed as follows: 200-400 mm in winter, 200-300 mm in spring, 100-200 mm in summer and 300-400 mm in fall. The average annual air temperature is 12-14 °C, with 8-10 °C in winter, 12-14 °C in spring, 18-20 °C in summer and 10-12 °C in fall. These soils were chosen to represent those with *P. radiata* plantations in the temperate-humid zone of Spain. Soil samples were taken in spring from the A horizon (0-15 cm depth) with a stainless steel probe (3.5 cm dia). Fifteen sub-samples were taken at random from the whole area of each plot, mixed and thoroughly homogenized after sieving (4 mm). Air-dried soil samples were used to assess the main soil variables listed in Table 1. Biological mineralization assays were carried out using samples kept frozen.

### 2.2. Chemical properties of soils

The dry matter content of soils was assessed by oven-drying fresh material at 110 °C for 5 h. Soil water-holding capacity was determined in a Richards membrane-plate extractor at a pressure of 10 kPa. The texture was determined in air dried and sieved ( $\leq 2$  mm) samples by the international mechanical analysis method. The methods described by Guitián Ojea and Carballas (1976) were used to determine the following variables in air dried and sieved ( $\leq 4$  mm) samples: pH in H<sub>2</sub>O, pH in KCl and pH in *p*-nitrophenol (soil: solution, 1:2.5); buffering index; CEC and exchangeable cations by extraction with 1 M ammonium acetate at pH 7 (Ca, Mg, Na and K) and with triethanolamine-barium chloride at pH 8.2 (H and Al); Fe and Al free oxides by extraction with a mixture of sodium hydrosulphite and oxalic acid-ammonium oxalate. Soil labile P was extracted by shaking 4 g of soil for 30 min with 120 ml of 0.5 M NaHCO<sub>3</sub> at pH 8.5. The H ions were measured by potentiometry, Na and K by atomic emission spectrophotometry and Ca, Mg, Fe and Al by atomic absorption spectrophotometry, whereas P was measured by the colorimetric method of Murphy and Riley (1962). The C and N contents of soils and their

$\delta^{15}\text{N}$  isotopic signatures were measured on finely ground samples ( $\leq 125$   $\mu\text{m}$ ) with an elemental analyser (CHNS 1108, Carlo Erba, Milano, Italy) coupled on-line with an isotopic ratio mass spectrometer (Finnigan Mat, delta C, Bremen, Germany).

Table 1. Main characteristics of the soils studied.

Variable	Min.	Max.	Mean	Standard deviation
pH (H <sub>2</sub> O)	4.43	5.21	4.86	0.23
pH (KCl)	3.50	4.28	3.89	0.23
pH ( <i>p</i> -nitrophenol)	5.11	5.77	5.43	0.19
Buffering index	3.70	6.30	5.06	0.60
Total C (g kg <sup>-1</sup> )	20.70	85.90	53.05	18.76
Total N (g kg <sup>-1</sup> )	1.53	5.75	3.33	1.28
Delta <sup>15</sup> N	3.41	6.41	4.89	0.87
C-to-N ratio	11.25	24.51	16.44	3.90
Available P (mg kg <sup>-1</sup> )	0.70	251.30	42.15	62.18
Exchangeable Na <sup>+</sup> (cmol kg <sup>-1</sup> )	0.03	0.12	0.07	0.02
Exchangeable K <sup>+</sup> (cmol kg <sup>-1</sup> )	0.00	0.13	0.03	0.03
Exchangeable Mg <sup>+2</sup> (cmol kg <sup>-1</sup> )	0.12	0.47	0.24	0.10
Exchangeable Ca <sup>+2</sup> (cmol kg <sup>-1</sup> )	0.30	1.60	0.69	0.31
Exchangeable H <sup>+</sup> (cmol kg <sup>-1</sup> )	13.15	41.60	27.69	7.84
Exchangeable Al <sup>+3</sup> (cmol kg <sup>-1</sup> )	3.39	9.56	6.14	1.56
Base saturation of CEC (%)	0.48	2.59	0.94	0.46
Non-crystalline Al oxides (g kg <sup>-1</sup> )	9.12	50.77	16.61	8.60
Non-crystalline Fe oxides (g kg <sup>-1</sup> )	1.00	9.00	3.38	2.74
Fine sand (g kg <sup>-1</sup> )	203.9	893.6	390.3	155.1
Gross sand (g kg <sup>-1</sup> )	44.2	545.0	320.8	161.7
Silt (g kg <sup>-1</sup> )	81.6	316.9	159.6	66.5
Clay (g kg <sup>-1</sup> )	112.6	214.8	154.4	27.7
Bulk density (g cm <sup>-3</sup> )	0.82	1.19	1.01	0.11
Water holding capacity (g kg <sup>-1</sup> )	344.0	769.3	522.9	127.2

For the inorganic N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) analysis, 20 g soil samples were shaken with 100 ml of 2 M KCl for 1 h and the extracts were filtered through glass microfibre filters (Whatman GF/A, 125 mm diameter). The inorganic-N forms were converted to NH<sub>3</sub> by adding MgO (NH<sub>4</sub><sup>+</sup>) or MgO and Devarda alloy (NO<sub>3</sub><sup>-</sup>) and the resulting ammonia was steam distilled, collected into 10 ml of 0.01 N H<sub>2</sub>SO<sub>4</sub> and measured by back titration of the excess of H<sub>2</sub>SO<sub>4</sub> with 0.01 N NaOH. For each form of N two distillates were performed and titrated.

The N mineralization capacity was determined by aerobic incubation in an hermetic glass system with intermittent aeration with a flow of air previously humidified by bubbling it through a water column. Six replicate 50 g samples of each soil were placed in 500 ml Erlenmeyer flasks and incubated in a thermostat bath at 28 °C and at 75% of sieved soil field capacity for 84 d. After both 42 and 84 d of incubation three replicates were withdrawn and the inorganic N was analysed by the methods described above. The net N ammonification, nitrification and mineralization for a given period were calculated as the difference between the final and the initial concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and inorganic N, respectively.

### 2.3. Data analysis

Data on N mineralization were statistically analysed by three-way ANOVA and honestly significant differences were established at  $P \leq 0.05$  using the Tukey's test. The relationships among the N mineralization indices, as dependent variables, and the main soil characteristics, as independent variables, were established by multiple linear regression analyses; the same was made with site index as dependent variable and the soil N variables (total N,  $\delta^{15}\text{N}$ , N mineralization indices) as independent variables. The most discriminating variables were determined using the all-possible regressions procedure, wherein the "best" models were selected based on the criteria of maximizing the adjusted  $R^2$  and minimizing the mean square error. Multilinear regression on standardized (normal 0, 1) data were used to ascertain the relative importance of the variables included in the best models. To prevent problems of multicollinearity among the soil properties used as independent variables in the multiple regression analyses, the models selected included only variables with a tolerance higher than 0.66, i.e., with at least two-thirds of their variances not explained by other variables already included in the equation.

## 3. Results

### 3.1. Young and old stands compared

The three-way ANOVA of the data showed no significant differences between young and old stands for any of the soil N variables considered, nor two- or three-order interactions among stand age, site quality and parent material. Therefore, henceforwards young and old stands were grouped into a single pool.

### 3.2. Soil N and $\delta^{15}\text{N}$

The total N content was significantly lower ( $P \leq 0.02$ ) in the soils from stands with high site index ( $2.68 \pm 1.11$  g N  $\text{kg}^{-1}$ ; mean  $\pm$  standard deviation) than in those with low site index ( $3.97 \pm 1.13$  g N  $\text{kg}^{-1}$ ), whereas no significant differences were found between stands over granite or acid schists (Fig. 1A). The extreme value of the LEO-1 plot for total N content (see Fig. 1A) strongly influenced the relationships between this variable and the main soil properties and, therefore, this plot was discarded for the correlation and multiple regression analyses. The soil N content correlated positively with the water holding capacity (WHC), C, total-CEC and  $\text{H}^+$ -CEC ( $P \leq 0.001$ ) and with  $\text{Mg}^{2+}$ -CEC, buffering index and Al oxides ( $P \leq 0.05$ ), whereas it only correlated negatively with soil  $\delta^{15}\text{N}$  ( $P \leq 0.005$ ). Almost all the variation of the total N content was jointly explained by the C content and the C-to-N ratio (Table 2).

The soil  $\delta^{15}\text{N}$  ranged from + 3.5 to + 6.5 ‰, without significant differences among stands with different site quality or parent material (Fig. 1B). The soil  $\delta^{15}\text{N}$  correlated positively only with the available P ( $P \leq 0.02$ ) and negatively with WHC ( $P \leq 0.001$ ), soil-N ( $P \leq 0.005$ ),  $\text{Na}^+$ -CEC and  $\text{Mg}^{2+}$ -CEC ( $P \leq 0.01$ ) and Al oxides ( $P \leq 0.05$ ). Two-thirds of the variation of the soil  $\delta^{15}\text{N}$  isotopic signature were jointly explained by C-to-N ratio, available P,  $\text{Mg}^{2+}$ -CEC and  $\text{Na}^+$ -CEC (Table 2).

### 3.3. Ammonification

During the first 42 d of incubation, the soil  $\text{NH}_4^+$ -N content increased from the mean initial values of  $7.37 \pm 4.48$  mg  $\text{kg}^{-1}$  to  $29.05 \pm 18.13$  mg  $\text{kg}^{-1}$  (Fig. 2A), without significant differences between the soils grouped according to their parent material or site index. From 42 to 84 d, the amount of  $\text{NH}_4^+$ -N still increased in the soils over granite but not in those over schists and the differences in the  $\text{NH}_4^+$ -N content between both group of soils ( $38.85 \pm 21.60$  and  $18.06 \pm 14.09$  mg  $\text{kg}^{-1}$ , respectively; Fig. 2A) became significant at 84 d ( $P \leq 0.05$ ).

In parallel with these results, the net N ammonification rate (NNAR) after 42 d (Fig. 2B) did not differ among the soil groups ( $0.61 \pm 0.52$  and  $0.69 \pm 0.38\%$  of organic N in the granite and the schists soils, respectively), but at 84 d it was significantly higher ( $P \leq 0.02$ ) in the former ( $0.98 \pm 0.51\%$  of organic N) than in the latter ( $0.41 \pm 0.55\%$  of organic N). The percentage of soil inorganic N as  $\text{NH}_4^+$ -N decreased from 42 (73.97%) to 84 d (44.97%).

**Table 2.** Best multiple regression models obtained for the soil N variables and the site index.

<b>Dependent variable</b>	<b>Adjusted R<sup>2</sup></b>	<b>Independent variables (beta standardized)</b>	<b>Tolerance</b>
Soil N content	0.953	Soil C (0.940); C-to-N ratio (-0.528).	> 0.956
Soil $\delta^{15}\text{N}$	0.660	Available P (0.566); C-to-N ratio (0.430); exchange. $\text{Mg}^{2+}$ (-0.289); exchange. $\text{Na}^+$ (-0.275).	> 0.809
$\text{NH}_4^+$ -N content at 42 d	0.629	WHC (0.636); C-to-N ratio (0.398); exchange. $\text{Na}^+$ (0.390).	> 0.861
Net N ammonification rate at 42 d	0.549	C-to-N ratio (0.511); exchange. $\text{Na}^+$ (0.414); exchange. $\text{Ca}^{2+}$ (-0.410); non-crystalline Fe oxides (0.260).	> 0.900
$\text{NH}_4^+$ -N content at 84 d	0.649	Non-crystalline Fe oxides (0.633); available P (-0.586); silt (-0.481); exchange. $\text{Na}^+$ (0.297).	> 0.705
Net N ammonification rate at 84 d	0.519	Silt (-0.510); non-crystalline Fe oxides (0.390); C-to-N ratio (0.381).	> 0.889
$\text{NO}_3^-$ -N content at 42 d	0.714	C-to-N ratio (-0.956); soil $\delta^{15}\text{N}$ (0.432); non-crystalline Al oxides (-0.339).	> 0.742
Net N nitrification rate at 42 d	0.747	Fine sand (-0.441); available P (0.353); CEC (-0.355).	> 0.735
$\text{NO}_3^-$ -N content at 84 d	0.667	C-to-N ratio (-0.568); silt (0.460); total N (0.220).	> 0.821
Net N nitrification rate at 84 d	0.626	C-to-N ratio (-0.605); silt (0.534); WHC (-0.448); exchange. $\text{K}^+$ (0.286).	> 0.751
Inorganic N content at 42 d	0.524	WHC (0.373); non-crystalline Fe oxides (0.352); exchange. $\text{Na}^+$ (0.252); buffering index (0.251).	> 0.688
Net N mineralization rate at 42 d	0.501	Gross sand fraction (0.398); buffering index (0.398); exchange. $\text{K}^+$ (0.394); total N (-0.336).	> 0.783
Inorganic N content at 84 d	0.512	Total N (0.580); sum of exchange. bases (0.239); buffering index (0.318).	> 0.690
Net N mineralization rate at 84 d	0.574	Base saturation (0.609); buffering index (0.336); fine sand (-0.272); non-crystalline Al oxides (-0.252).	> 0.673
Site index	0.653	Total N (-0.792); net N mineralization rate at 84 d (0.378); soil $\delta^{15}\text{N}$ (-0.255).	> 0.658
	0.631	Total N (-0.839); soil $\delta^{15}\text{N}$ (-0.360); net N mineralization rate at 42 d (0.355).	> 0.670
	0.519	Total N (-0.878); soil $\delta^{15}\text{N}$ (-0.304).	> 0.682

Abbreviations: base saturation, base saturation of CEC; CEC, complex of exchangeable cations; exchange., exchangeable; WHC, water holding capacity;

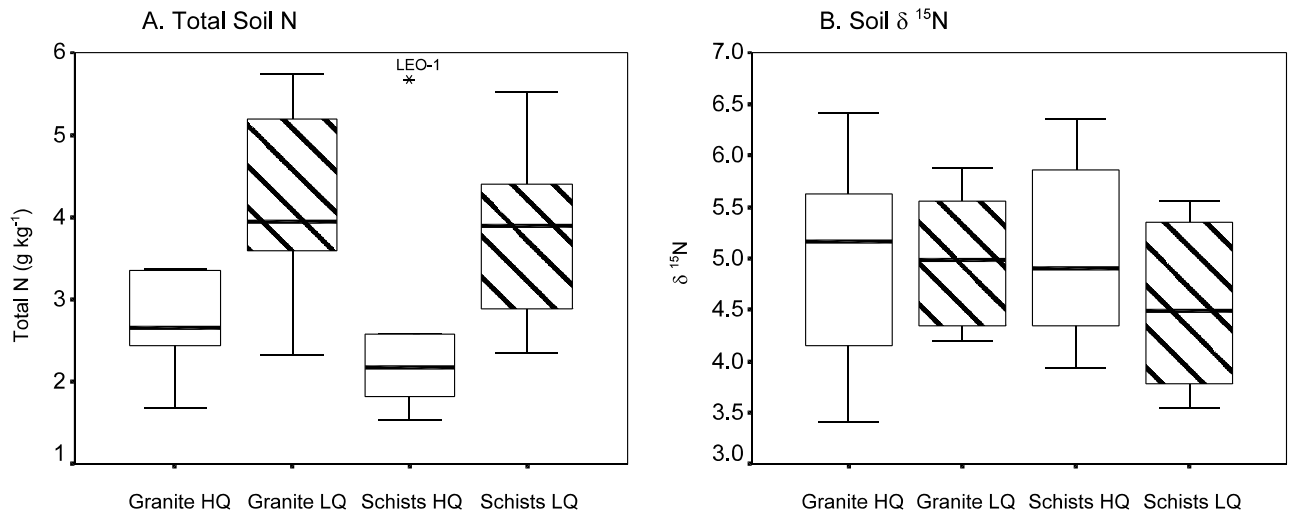


Fig. 1. Box-and-whiskers plots for the soil total N (A) and  $\delta^{15}\text{N}$  (B) in the soils grouped according to parent material and site index (HQ, high quality; LQ, low quality). The upper and lower boundaries of the boxes are the upper and lower quartiles, i.e., the box contains the middle 50 % of values in a group; the horizontal line inside the box identifies the group median. The lines emanating from each box (the whiskers) extend to the smallest and largest values in a group that are not outliers. The outlier values (at 1.5-3 times the interquartile length from the box upper or lower boundary) are marked with a small circumference. The extreme values (at > 3 times the interquartile length from the box upper or lower boundary) are marked with an asterisk.

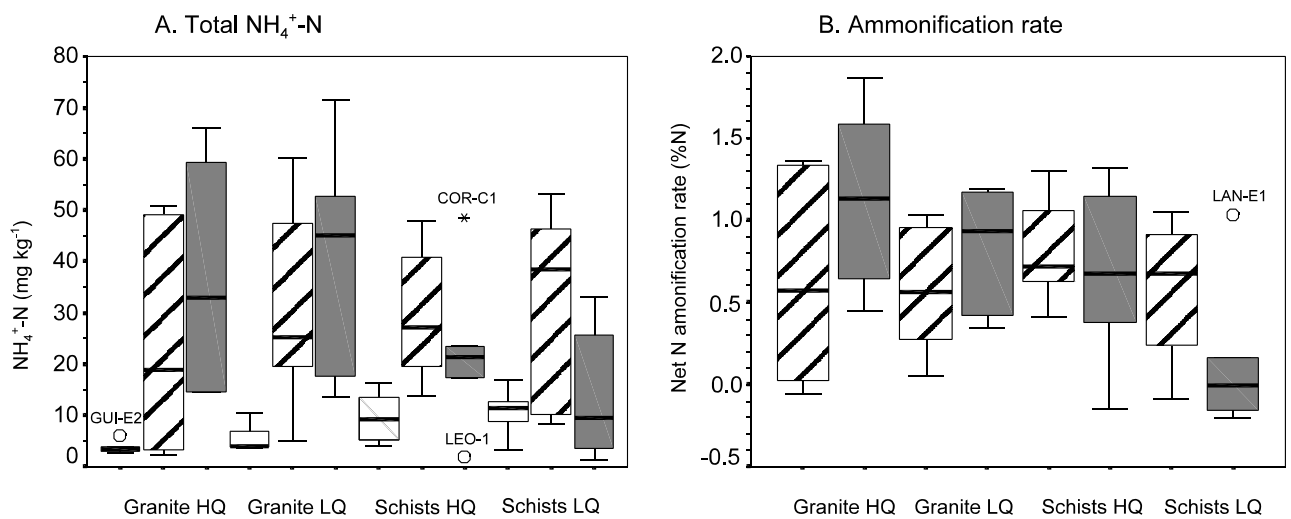


Fig. 2. Box-and-whiskers plots for the absolute  $\text{NH}_4^+\text{-N}$  content (A) and the net N ammonification rate (B) at 0, 42 and 84 d of incubation (blank, striped and grey rectangles, respectively), in the soils grouped according to parent material and site index (HQ, high quality; LQ, low quality). For the explanation of the figure see Fig. 1.

The amount of soil  $\text{NH}_4^+\text{-N}$  after 42 d was positively correlated with the variables related to the high soil organic matter (SOM) content (WHC,  $P \leq 0.001$ ; C, CEC and  $\text{H}^+\text{-CEC}$ ,  $P \leq 0.005$ ; N and buffering index,  $P \leq 0.05$ ), as well as with  $\text{Na}^+\text{-CEC}$  ( $P \leq 0.05$ ), and negatively ( $P \leq 0.05$ ) with  $\text{Ca}^{2+}\text{-CEC}$ , P content and soil  $\delta^{15}\text{N}$ . Around two-thirds of the variation in the soil  $\text{NH}_4^+\text{-N}$  content at 42 d was explained by WHC, C-to-N ratio and  $\text{Na}^+\text{-CEC}$  (Table 2).

The C-to-N ratio was the only variable positively correlated ( $P \leq 0.05$ ) with the NNAR at 42 d, which had negative relationships ( $P \leq 0.05$ ) with the amount of available P and  $\text{Ca}^{2+}$ -CEC. More than a half of the variation of the NNAR at 42 d was explained by the C-to-N ratio and the contents of  $\text{Na}^+$ -CEC,  $\text{Ca}^{2+}$ -CEC and non-crystalline Fe compounds (Table 2).

After 84 d, the soil  $\text{NH}_4^+$ -N content was no longer correlated with any of the variables found for  $\text{NH}_4^+$ -N at 42 d and it was significantly correlated ( $P \leq 0.05$ ) only with the concentration of Fe oxides (positively) and the silt fraction (negatively). Around two-thirds of the variation in the soil  $\text{NH}_4^+$ -N content at 84 d was explained by the contents in Fe oxides, available P, silt and  $\text{Na}^+$ -CEC (Table 2).

Like the absolute amount of  $\text{NH}_4^+$ -N, the NNAR at 84 d was no longer correlated with any of the variables found for the NNAR at 42 d but it was correlated positively with the coarse sand fraction and the Fe oxides content ( $P \leq 0.05$ ), and negatively with the silt content ( $P \leq 0.005$ ). The soil content in silt and Fe oxides and the C-to-N ratio explained a half of the variation of the NNAR at 84 d (Table 2).

### 3.4. Nitrification

In all the soils, the concentrations of  $\text{NO}_3^-$ -N were very low at d 0 ( $0.41 \pm 0.60 \text{ mg kg}^{-1}$ ; Fig. 3A) and increased during the incubation. Nitrification was initially faster in the soils over granite, which mean  $\text{NO}_3^-$ -N content at 42 d ( $18.12 \pm 14.55 \text{ mg kg}^{-1}$ ) was significantly higher ( $P \leq 0.005$ ) than that of the schists soils ( $2.44 \pm 3.55 \text{ mg kg}^{-1}$ ), but these differences disappeared by the end of the incubation, when the  $\text{NO}_3^-$ -N content of granite soils ( $36.71 \pm 18.87 \text{ mg kg}^{-1}$ ) was even slightly surpassed by that of the schists soils ( $41.99 \pm 32.12 \text{ mg kg}^{-1}$ ). These results were reflected in the net N nitrification rate (NNNR; Fig. 3B) which was significantly higher ( $P \leq 0.01$ ) in the granite than in the schists soils at 42 d ( $0.63 \pm 0.63\%$  and  $0.05 \pm 0.09\%$  of organic N, respectively), whereas no significant differences were found at 84 d ( $1.20 \pm 0.79$  and  $1.23 \pm 0.68\%$  of organic N, respectively). The relative importance of the  $\text{NO}_3^-$ -N as a fraction of the soil inorganic N pool increased from d 42 to 84 (26.03% and 55.03% of the inorganic-N, respectively).

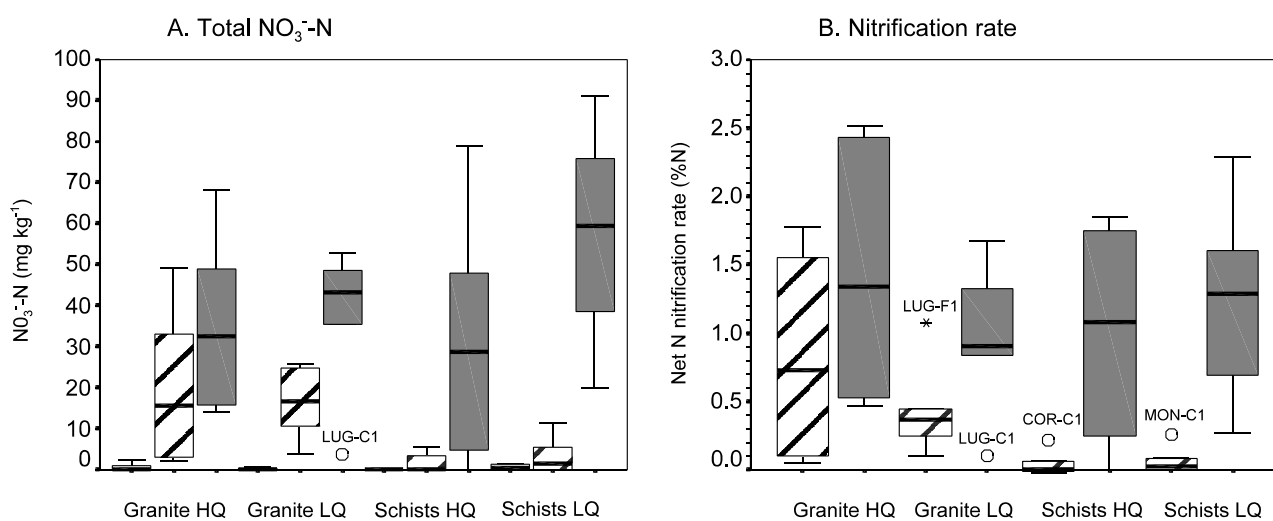


Fig. 3. Box-and-whiskers plots for the absolute  $\text{NO}_3^-$ -N content (A) and the net N nitrification rate (B) at 0, 42 and 84 d of incubation (blank, stripped and grey rectangles, respectively), in the soils grouped according to parent material and site index (HQ, high quality; LQ, low quality). For the explanation of the figure see Fig. 1.

After 42 d of incubation, the amount of soil  $\text{NO}_3^-$ -N correlated positively with coarse textures (coarse sand,  $P \leq 0.005$ ) and nutrient richness (available P and CEC-base saturation,  $P \leq 0.005$ ;  $\text{K}^+$ -CEC,  $P \leq 0.05$ ), and negatively ( $P \leq 0.05$ ) with fine sand, C-to-N ratio and  $\text{H}^+$ -CEC. Around three-quarters of the variation in the soil  $\text{NO}_3^-$ -N content at 42 d was explained by the C-to-N ratio, soil  $\delta^{15}\text{N}$  and the concentration of non-crystalline Al oxides (Table 2).

As the absolute amount of  $\text{NO}_3^-$ -N, the NNNR at d 42 was positively correlated with coarse textures (coarse sand,  $P \leq 0.005$ ) and nutrient content (available P,  $\text{K}^+$ -CEC and CEC-base saturation,  $P \leq 0.005$ ;  $\text{Ca}^{2+}$ -CEC,  $P \leq 0.05$ ). Also as the absolute amount of  $\text{NO}_3^-$ -N, the NNNR at d 42 correlated negatively with the fine sand fraction ( $P \leq 0.001$ ) and with the variables related to high unhumified SOM content and base desaturation of CEC ( $\text{H}^+$ -CEC,  $\text{Al}^{3+}$ -CEC, CEC, C, C-to-N ratio,  $P \leq 0.05$  to  $P \leq 0.005$ ). The best multiple regression model obtained for the NNNR at 42 d, explaining around three-quarters of its variation among soils, included as independent variables the fine sand and available P contents and the CEC (Table 2).

At 84 d, the soil  $\text{NO}_3^-$ -N content was positively correlated with WHC ( $P \leq 0.05$ ), silt ( $P \leq 0.05$ ) and soil N ( $P \leq 0.01$ ), and negatively with soil  $\delta^{15}\text{N}$  ( $P \leq 0.05$ ) and, like the  $\text{NO}_3^-$ -N at 42 d, with the C-to-N ratio ( $P \leq 0.001$ ). Two-thirds of the variation of the  $\text{NO}_3^-$ -N content at 84 d was explained by the C-to-N ratio, silt and soil N (Table 2).

As at 42 d, at 84 d the NNNR was correlated positively with  $\text{K}^+$ -CEC ( $P \leq 0.05$ ) and CEC-base saturation ( $P \leq 0.01$ ), and negatively with the C-to-N ratio ( $P \leq 0.005$ ),  $\text{Al}^{3+}$ -CEC and total CEC ( $P \leq 0.05$ ), but at 84 d the nitrification was no longer significantly correlated with coarse and fine sand fractions, total C and available P. The soil variables included in the best multiple regression model for the NNNR at 84 d were C-to-N ratio, silt, WHC and  $\text{K}^+$ -CEC (Table 2).

### 3.5. N mineralization

During the incubation, the inorganic-N content increased continuously in all soils from the mean initial values of  $7.78 \pm 4.57 \text{ mg kg}^{-1}$  to  $39.33 \pm 16.20 \text{ mg kg}^{-1}$  at 42 d and to  $67.80 \pm 26.50 \text{ mg kg}^{-1}$  at 84 d (Fig. 4A). At no time were significant differences found for the inorganic N content between the soils grouped according to parent material or site index, but the net N mineralization rate (NNMR) in the granite soils was significantly higher ( $P \leq 0.005$ ) than that in the schists soils after 42 d ( $1.24 \pm 0.34$  and  $0.75 \pm 0.37\%$  of organic N, respectively), and the same was true ( $P \leq 0.02$ ) at 84 d ( $2.18 \pm 0.56$  and  $1.53 \pm 0.66\%$  of organic N, respectively; Fig. 4B). In the stands of high site index, the NNMR at both 42 d ( $1.16 \pm 0.45\%$  of organic N) and 84 d ( $2.12 \pm 0.79\%$  of organic N) was significantly higher ( $P \leq 0.05$ ) than that in the low quality stands at both times of incubation ( $0.83 \pm 0.35$  and  $1.59 \pm 0.45\%$  of organic N, respectively).

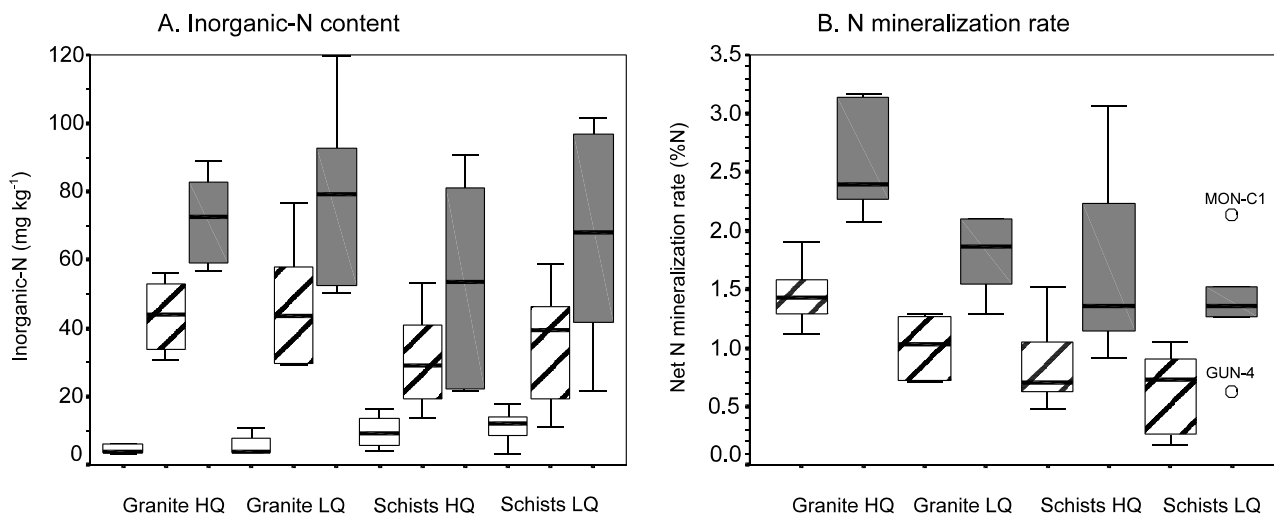


Fig. 4. Box-and-whiskers plots for the absolute inorganic-N content (A) and the net N mineralization rate (B) at 0, 42 and 84 d of incubation (blank, stripped and grey rectangles, respectively), in the soils grouped according to parent material and site index (HQ, high quality; LQ, low quality). For the explanation of the figure see Fig. 1.

The inorganic N content of the soils after 42 d correlated positively ( $P \leq 0.005$ ) with soil-N and WHC, which were also highly correlated between them ( $r = 0.903$ ;  $P \leq 0.0001$ ), and with the buffering index of the soils and their contents in non-crystalline Fe compounds and  $\text{Na}^+$ -CEC ( $P \leq 0.05$ ). No significant



negative correlations were found between the inorganic N content at 42 d and any of the soil variables considered. Half of the variation in the soil inorganic N content at 42 d was explained by WHC, buffering index, non-crystalline Fe oxides and Na<sup>+</sup>-CEC (Table 2).

Like the NNNR, the NNMR at 42 d was positively correlated with coarse textures (coarse sand,  $P \leq 0.005$ ) and nutrient richness (CEC-base saturation,  $P \leq 0.005$ ; K<sup>+</sup>-CEC,  $P \leq 0.01$ ; available P,  $P \leq 0.05$ ). The NNMR at 42 d was also correlated positively with the content in amorphous Fe compounds ( $P \leq 0.01$ ) and negatively with the fine sand ( $P \leq 0.005$ ) and the Al<sup>3+</sup>-CEC ( $P \leq 0.05$ ). The best multiple regression model explained around a half of the variation of NNMR and was constructed with gross sand, buffering index, K<sup>+</sup>-CEC and soil-N as independent variables (Table 2).

Conversely to the NH<sub>4</sub><sup>+</sup>- and the NO<sub>3</sub><sup>-</sup>-N contents, the total inorganic N content at 84 d was still correlated with the same soil variables as at 42 d, but at 84 d the correlations were higher. Moreover, some variables almost significantly correlated with the inorganic N at 42 d reached significant levels at 84 d (positive correlations with Na<sup>+</sup>-CEC, Mg<sup>2+</sup>-CEC and the sum of bases; negative correlations with C-to-N ratio and soil  $\delta^{15}\text{N}$ ). More than 60% of the variation in the soil inorganic N content at 84 d was explained by the total N content, the sum of exchangeable bases and the soil buffering index (Table 2).

Like the absolute amount of inorganic N, the NNMR at 84 d was also correlated with the same soil characteristics than at 42 d; moreover, some additional variables reached significant levels of correlation ( $P \leq 0.05$ ), positive (sum of exchangeable bases) or negative (CEC, C-to-N ratio, H<sup>+</sup>-CEC), with the NNMR at the end of the incubation. The best multiple regression model obtained includes the CEC-base saturation, the soil buffering index, the fine sand and the Al oxides content (Table 2).

### 3.6. Site index and N dynamics

The site index was strongly correlated with soil N ( $r = -0.707$ ;  $P \leq 0.005$ ) and, of the N mineralization variables considered, was only correlated positively with the NNMR at both 42 and 84 d ( $P \leq 0.05$  and  $P \leq 0.02$ , respectively). Almost two-thirds of the variation in the site index was explained by the best multiple regression model using N variables (soil N, NNMR at 84 d and soil  $\delta^{15}\text{N}$ ). The substitution of the NNMR at 84 d for that at 42 d gave an only slightly worse model. Finally, a model constructed with only soil N and soil  $\delta^{15}\text{N}$  still explained more than a half of the variation in the site index (Table 2).

## 4. Discussion

### 4.1. Soil N and $\delta^{15}\text{N}$

The total soil N contents in the *P. radiata* stands studied were within the ranges previously reported for *Pinus* spp. stands ( $4.73 \pm 2.73$  g kg<sup>-1</sup>; mean  $\pm$  standard deviation) and deciduous forests ( $3.65 \pm 1.61$  g kg<sup>-1</sup>) from the same area (González-Prieto et al., 1992, 1996), but they were slightly higher than in *P. radiata* stands ( $2.3 \pm 0.1$  g kg<sup>-1</sup>) in northern Spain (Merino and Edeso, 1999). In addition to the strong relationships between the N content and the variables associated with high SOM content (C content, WHC, buffering index and H<sup>+</sup>-CEC), the total soil N content appeared positively correlated with the Al oxides content, a well-known SOM stabilizing agent (Carballas et al., 1979; Stevenson, 1982; González-Prieto et al., 1992, 1996). The strong negative correlation between the soil N content and its  $\delta^{15}\text{N}$  isotopic signature agrees with the results of Kerley and Jarvis (1997) and suggests that soil N richness is related with limited N losses, which discriminate against the heavy isotope <sup>15</sup>N (Högberg et al., 1995), and, therefore, with "closed" N cycling (Chang and Handley, 2000; Eshetu and Högberg, 2000).

The  $\delta^{15}\text{N}$  isotopic signature of soil N under the studied pine stands fell within the range of -1 to +8 ‰ normally found in both forest and culture soils, fertilized or not (Cheng et al., 1964; Binkley et al., 1985; Mordelet et al., 1996; Handley and Scrimgeour, 1997; Koba et al., 1998). The negative correlations between soil  $\delta^{15}\text{N}$  and WHC, exchangeable bases and Al oxides suggest that N losses by NO<sub>3</sub><sup>-</sup> leaching are the most important controlling factor of soil  $\delta^{15}\text{N}$  in this temperate humid region. High WHC reduce water percolation, or delay it giving time to NO<sub>3</sub><sup>-</sup> assimilation by plants or microorganisms. High concentrations of exchangeable bases (mainly Na<sup>+</sup> and Mg<sup>2+</sup>) may indicate reduced leaching of bases and NO<sub>3</sub><sup>-</sup>. High contents in Al oxides, which have positive charges, are related to important anion exchange capacities and, therefore, to the capacity to retain the NO<sub>3</sub><sup>-</sup>-N within the soil profile. In the same way, the

positive correlation of  $\delta^{15}\text{N}$  and available P could be indirectly explained by the negative relationship between the contents in available P and Al oxides. These results are in agreement with the high positive correlation found by Högberg and Johansson (1993) between the  $^{15}\text{N}$  abundance in *P. sylvestris* forests and the losses of N.

#### 4.2. Soil supply of plant available N

After 42 d, the amount of  $\text{NH}_4^+$ -N accumulated in the soils studied ( $29.0 \pm 18.1 \text{ mg kg}^{-1}$ ) was about half that found in similar incubations by González-Prieto et al. (1996) in soils under *Pinus* spp. from the same region. Nevertheless, the mean NNAR ( $0.65 \pm 0.45\%$ ) was only 20% lower than that reported by these authors, indicating that this difference is mainly due to the lower N content of the soils we studied. Conversely, the mean values for the amount of  $\text{NO}_3^-$ -N accumulated ( $10.3 \pm 13.0 \text{ mg kg}^{-1}$ ) and NNNR ( $0.34 \pm 0.53\%$ ) at 42 d were 45% and 3 times higher, respectively, than those found by González-Prieto et al. (1996). As a consequence of these results, the amount of inorganic N available after 42 d ( $39.3 \pm 16.2 \text{ mg kg}^{-1}$ ) was 43% lower than that reported by González-Prieto et al. (1996) whereas the NNMR ( $0.99 \pm 0.43\%$ ) was almost equal.

The daily NNMR for the entire 84 d incubation ( $0.81 \pm 0.47 \text{ mg kg}^{-1} \text{ d}^{-1}$ ) was within the range of  $0.39$ - $1.01 \text{ mg kg}^{-1} \text{ d}^{-1}$  found by Carlyle et al. (1998) and Scott et al. (1998) in medium- to long-term laboratory incubations of *P. radiata* soils, with similar N contents, from Australia and New Zealand. Moreover, expressed in a per area basis (taking into account the bulk density), the amount of available N at the end of the incubation in the 0-10 cm layer was equivalent to approx.  $68 \pm 25 \text{ kg ha}^{-1}$ , a figure close to the N mineralization of  $70$ - $74 \text{ kg}^{-1} \text{ ha}^{-1} \text{ y}^{-1}$  found by Carlyle et al. (1998) in field experiments at the two sites with similar soil N content as those we studied.

#### 4.3. Relationships of N mineralization with site and soil characteristics

The lack of significant differences between soils from low and high site index in their capacities to supply plant available N contrasts with the clear differences found between them in NNMR and total N content. This suggests that soil N dynamics in low and high quality stands is different: in the former there is a bigger N pool with a slower turnover, whereas in the latter there is a smaller N pool with a faster turnover, both factors being more or less compensated making the soil available N supply similar. This finding agrees with the fact that higher total N contents do not necessarily supply higher amounts of available N as reported Williams (1983) and González-Prieto et al. (1992, 1996). Moreover, our result also agrees with the inverse relationship found by Côté et al. (2000) between total pool sizes and organic matter quality that cancels the effects of soil organic matter quality on N and C fluxes.

The shift during the incubation of the relationships among some of the main soil characteristics and the net production of  $\text{NH}_4^+$ - and  $\text{NO}_3^-$ -N contrasts with the lack of changes in their relationships with the net production of inorganic-N. This result can be explained from a global point of view because during the incubation there was also a shift in the relative importance of net ammonification and net nitrification: the former decreased and the latter increased, net mineralization integrating both tendencies. In the same way, three out the ten soil characteristics correlated with the  $\text{NH}_4^+$ -N content at 42 d, but not at 84 d, are three out the five soil variables most correlated with  $\text{NO}_3^-$ -N content at 84 d, but not at 42 d, and also with the total inorganic N content at both 42 and 84 d. In all these cases, the total N content and the soil WHC were positively correlated with both N mineralization and its predominant process (ammonification or nitrification), whereas the  $\delta^{15}\text{N}$  was negatively correlated with them.

After 42 and 84 d of incubation, most of the main soil characteristics significantly correlated with the NNMR also showed similar correlations with the NNNR. Both N mineralization rates were higher in the coarse textured than in the fine textured soils, as reported by González-Prieto et al. (1992, 1996) and Côté et al. (2000), likely due to the higher physical and chemical protection of soil N in the latter (Adu and Oades, 1978; Sorensen, 1981; Stevenson, 1982). NNNR and NNMR increased in the soils rich in available P, as also found Côté et al. (2000),  $\text{K}^+$ -CEC and base saturation of the CEC, in agreement with the results of González-Prieto et al. (1992) but in contrast with those of González-Prieto et al. (1996) and Côté et al. (2000); these positive correlations indicate that there are strong relationships between the biological availability of the main macronutrients that limit plant growth (N, P, K). Finally, NNNR and NNMR also increased with SOM quality (low C-to-N ratio) as reported by Robertson (1982), Duchaufour (1984), Niklinska et al. (1999) and Côté et al. (2000).

Nine of the 25 main soil characteristics considered were often included as independent variables in the 12 best models obtained by multiple regression analyses for the N mineralization indices, at both short and medium-term incubation periods. The variables most useful to predict N mineralization were the C-to-N ratio and the Fe oxides content, which were included, respectively, in 6 and 4 of the multiple regression models. The C-to-N ratio was an important factor on N mineralization at both 42 and 84 d of incubation, influencing positively the ammonification and negatively the nitrification processes; its importance, highlighted by its condition of independent variable with the highest standardized coefficient in 4 of the models, agrees with the results of many authors (Robertson, 1982; Niklinska et al., 1999; Côté et al., 2000; Schoenholtz et al., 2000). The Fe oxides content was included, with positive coefficients, in the multiple regression models for absolute and relative ammonification at 42 and 84 d of incubation; the positive effect of Fe oxides on ammonification could be explained by the results of Andreux (1981) who reported that iron increases the biodegradability of organic compounds. The other soil characteristics often included as independent variables in the multiple regression models were the exchangeable  $\text{Na}^+$ , the silt fraction and the buffering index (4 models), and soil N content and soil WHC (3 models). The influence of soil texture and N content on N mineralization is well known (Adu and Oades, 1978; Sorensen, 1981; Stevenson, 1982; Williams, 1983; González-Prieto et al., 1992, 1996; Niklinska et al., 1999; Côté et al., 2000); the inclusion in the models of the buffering index and soil WHC is likely due to the strong relationships of the former with the C and N content and of the latter with soil texture and SOM content.

The strong negative correlation of site index with the total soil N content, and its positive correlations with NNMR after 42 and 84 d of incubation, clearly suggested that site quality and potential productivity are closely related to soil organic N dynamics and availability which, as previously discussed, are strongly associated with the availability of other main nutrients (P, K). These results agree with the fact that N is the most common limiting nutrient for forest production (Nilsson et al., 1995; Schoenholtz et al., 2000) and also with the proposition of soil N content and potentially mineralizable N as basic soil quality indicators (Karlen et al., 1994; Lal, 1997; McCarty and Meisinger, 1997; Knoepp et al., 2000). The correlation that we found between NNMR and site index also agrees with the results of Keeney (1980) and Reich et al. (1997), but not with those of Grigal and Homann (1994). Finally, from an applied point of view it is important to highlight that the multiple regression models obtained indicates that half of the site index variation in the pine stands studied could be predicted with a cheap and easy analysis of soil N content; the prediction for site index improves slightly if  $\delta^{15}\text{N}$  of soil N was included and, more significantly, with short- or medium-term N mineralization measurements.

#### 4.4. Conclusions

Our results suggested that: i) soil N richness is related with limited N losses and, therefore, with "closed" N cycling; ii) N losses by  $\text{NO}_3^-$  leaching are the most important controlling factor of  $\delta^{15}\text{N}$  in these temperate humid region soils; iii) in low quality stands there is a big soil N pool with a slow turnover, whereas in high quality stands there is a small N pool with a fast turnover, both factors being nearly compensated, making similar the soil available N supply; iv) the nitrification and mineralization rates increased with coarse textures, soil organic matter quality (low C-to-N ratio), available P,  $\text{K}^+$ -CEC and CEC-base saturation; v) the variables most useful to predict N mineralization were the C-to-N ratio and the Fe oxides content, followed by  $\text{Na}^+$ -CEC, silt fraction, buffering index, and the contents in N and fine sand, the sum of bases or CEC-base saturation and the soil water holding capacity; vi) site quality and potential productivity are closely related to soil organic N dynamics and availability, which are strongly associated with the availability of other main nutrients (P, K); and vii) half of the site index variation in the pine stands studied could be predicted with an analysis of soil N, the prediction being improved slightly if soil  $\delta^{15}\text{N}$  is included and, more noticeably, with N mineralization measurements.

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