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Relationship between the weathering of clay minerals and the nitrification rate: a rapid tree species effect

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Abstract We compared the properties of the clay mineral fraction and the composition of soil solutions in a *Fagus sylvatica* coppice (native forest) and four adjacent plantations of *Pseudotsuga menziesii*, *Pinus nigra*, *Picea abies* and *Quercus sessiliflora* planted in 1976. The results revealed changes of clay fraction properties due to tree species effect. Clay samples from Douglas fir and pine stands differ when compared to other species. Twenty-eight years after planting, we observed the following changes: a more pronounced swelling after citrate extraction and ethylene glycol solvation, a higher CEC and a smaller poorly crystallised aluminium content. All these changes affecting the clay fraction agreed well with soil solution analyses which revealed high NO_3^-, H^+ and Al concentrations under Douglas fir and pine. These changes were explained by a strong net nitrification under Douglas fir and pine stands when compared with other tree species. The higher NO_3^- concentrations in soil solutions should be linked to the presence, type and activity of ammonia-oxiding bacteria which are likely influenced by tree species. The production of NO_3^- in excess of biological demand leads to a net production of hydrogen ion and enhances the dissolution of poorly crystallised Al-minerals. Secondary Al-bearing minerals constituted the principal acid-consuming system in these soils. As a consequence, the depletion of interlayer spaces of hydroxyinterlayered minerals increases the number of sites for exchangeable cation fixation and increases CEC of the clay fraction. The dissolution of Al oxy-hydroxides explain the increase in Al concentrations of soil solutions under Douglas fir and pine stands when compared to other species. Nitrate and dissolved aluminium were conjointly leached in the soil solutions. A change in environmental conditions, like an introduction of tree species, enough modifies soil processes to induce significant changes in the soil mineralogical composition even over a period of time as short as some tens of years. Generally, mineral weathering has been considered to be very slow and unlikely to change over tens of years, resulting in few studies capable of detecting changes in mineralogy. This study appears to have detected changes in clay mineralogy during a period of 28 years after the planting of forest species. Our study represents a single location with a limited block design, but causes us to conclude that the observed changes could be widely representative. Where available, archived samples should be utilized and long-term experiments set up so that similar changes can be tested for and detected using more robust designs. The plausible hypothesis we present to explain apparent changes in

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clay mineralogy has strong relevance to the sustainable management of land.

Keywords Acid dissolution · Clay minerals · Nitrification · Smectitic layer · Tree species · Weathering

Abbrevations

BS	Base saturation
c	Citrate treatment
CEC	Cation exchange capacity
CwS	Coppice with standards
EA	Exchangeable acidity
EG	Ethylene glycol treatment
HIM	Hydroxy-interlayered mineral
HIS	Hydroxy-interlayered smectite
HIV	Hydroxy-interlayered vermiculite
ICP-AES	Inductively coupled plasma spectrometry-atomic emission spectrometry
XRD	X-ray diffraction

Introduction

Soil scientists and agronomists have long recognized the fundamental importance of biological effects on soil change and mineral weathering. Although the general principles governing how plants affect soil chemistry and mineral dissolution have been elucidated, little is known about the effects of tree species on the weathering of soil minerals. Moreover, for one species, the rates reported in the literature can differ considerably as a function of rock type, soil type, age of stand, climate and method of study (Berner et al. 2003). As highlighted by Binkley (1996), further studies are needed before more general conclusions can be drawn. Comparisons between tree species are particularly difficult because numerous factors must be taken into account (Augusto et al. 2002). In forest ecosystems, tree species can differ with regards to their effects on the soil through many mechanisms such as the quantity and quality of carbon compounds added to the soil (litter fall, exudation, production of different chelating organic acids), the biocycling of nutrients (uptake, return), mineralization and nitrification rates, atmospheric N fixation, atmospheric deposition, net primary production, biogenic mineral production (phytoliths), control of soil communities and hydrologic regime of the soil (Binkley and Giardina 1998; Augusto et al. 2002).

Most field studies are based on chemical analyses of soil and water draining from watersheds. Weathering rates are mainly calculated using the mass balance approach (input–output budget), the iso-element budget, soil mass balance determinations and isotopic methods. Weathering fluxes are very difficult to estimate in situ (Kolka et al. 1996) because the methods employed are based on hypotheses that are difficult to verify (soil age, erosion processes, homogeneity and composition of parent materials, linearity of phenomena). These methodologies have led to classic expectations that conifers (and especially Norway spruce) enhance mineral weathering when compared to hardwood species (Nys 1981; Sohet et al. 1988; Lelong et al. 1990; Fichter et al. 1998).

Results have also been generated by direct study of weathered minerals. Nordborg and Olsson (1999) found that, with respect to mixed deciduous forest, the clay fraction of topsoil beneath spruce stands had been depleted of all easily weatherable ferromagnesian minerals, and suggested abiotic and biotic causes for this phenomenon. Bouabid et al. (1995) reported that plagioclase exhibited more etch pitting under pine stands and oak basswood than under white cedar. Augusto et al. (2000) inserted weighed mineral samples (plagioclases) under different deciduous and coniferous stands and reported that subsequent dissolution was greater under conifers than under hardwoods. Many other studies have demonstrated that tree species influence mineral weathering (Spyridakis et al. 1967; Lelong et al. 1990; Quideau et al. 1996; Tice et al. 1996).

Chemical weathering of minerals in soils is a slow, but fundamental process, particularly for forested ecosystems (Ouimet 2008). Nevertheless, change in environmental conditions may have a rapid effect on soil and mineral transformations. Research on soil pedogenesis has mainly focused on the long-term soil formation and has most often neglected recent soil changes in response to human practices (Montagne et al. 2008). Such recent soil changes are however of considerable interest to study the timing of soil forming processes in response to changes in environmental conditions. In particular, the clay fraction exhibits a high specific surface area that may ensure its strong reactivity to environmental changes affecting the soil (Turpault et al. 2008). In line with this concept, the aim of the present research was to identify the direct effects of common European tree species on the mineralogical properties of the soil clay fraction.

This research was done at the Breuil-Chenue experimental forest site located in the Morvan mountains (France) which was set up specifically in 1976 to compare biogeochemical cycles among tree species. The stands were 28 years old when the soils were sampled in 2006.

This present work is trying to verify the following two hypotheses: (1) coniferous species enhanced mineral weathering when compared to hardwoods and (2) 28 years of stand growth is sufficient to create measurable differences in clay properties linked to tree species. Divergences affecting mineralogical changes are interpreted in the discussion section relative to the composition of soil solutions, in order to clarify the biogeochemical processes involved in the observed changes.

Despite the limited experimental design used in this study (two incomplete blocks), the conclusions revealed how mineralogical data can inform biogeochemical study.

Materials and methods

Study site

This research study was performed in the Breuil-Chenue experimental forest site located in the Morvan Mountains (47°18′ N, 4°5′ E, France) which was established in 1976 in order to compare the effects of tree species on environmental changes. The site contains two adjacent blocks with replicated stands. It lies at an altitude of 638 m, with a mean annual air temperature of 9 °C and annual precipitation averaging 1280 mm year^{-1}. The soil derived from “Pierre qui Vire” granite (Seddoh 1973) is acidic, well-drained, and classified as a Typic Dystrochrept (USDA 1999) with depths ranging from 120 to 140 cm. Table 1 shows that the bulk soil has a sandy-loam texture (55–60 % sand and less than 20 % clay) and is acidic (pH$_{\text{KCl}}$ 3.1–4.3). The cation exchange capacity (CEC) is low and the exchange sites are mainly occupied by Al (Table 1). Base saturation (BS) levels are below 10 %. The humus form is a moder (Brêthes et al. 1995) in the native forest and the carbon content reaches 7.4 % in the A1 horizon. The native forest was an old Coppice with Standards (CwS) dominated by beech (*Fagus sylvatica* L.) and oak (*Quercus sessiliflora* Smith). The initial forest was partially clear felled (one stand was conserved in each block) and replaced in 1976 by monospecific plantations distributed in 0.1 ha plots of different species. The species targeted during the study were the native forest, pine (*Pinus nigra* Arn. *ssp laricio*, var Corsicana), Douglas fir (*Pseudotsuga menziesii* Franco), oak (*Quercus sessiliflora* Smith) and spruce (*Picea abies* Karst), although oak and spruce were only studied in block 1.

The history of the Breuil-Chenue forest is well known from archives dating back to 1800 which show that the native forest has always been a coppice with standards. The coppice has not been harvesting since the second half of the last century.

When the plantations were established in 1976, no difference in soil properties between the two blocks

Table 1 Soil properties of the original old Coppice with Standards (CwS) from the central profile of the stand (Mareschal 2008)

Depth (cm)	pH (KCl)	C (g kg^{-1})	N (g kg^{-1})	Clay (%)	Silt (%)	Sand (%)	Ca (cmolc kg^{-1})	Mg (cmolc kg^{-1})	K (cmolc kg^{-1})	Al (cmolc kg^{-1})	CEC[†] (cmolc kg^{-1})
0–5	3.1	73.4	3.9	17.1	25.2	57.7	0.15	0.27	0.39	7.3	9.2
5–10	3.7	37.9	2.0	18.4	26.6	55.0	0.05	0.12	0.21	6.7	6.9
10–15	4.1	31.6	1.7	16.2	23.8	60.0	0.02	0.06	0.12	4.8	5.2
15–25	4.3	19.1	1.0	18.8	25.2	56.0	ld	0.03	0.09	3.3	3.4
25–40	4.3	13.2	0.7	19.6	26.9	53.5	0.02	0.02	0.08	2.5	2.7
40–55	4.3	ND	ND	17.7	23.1	59.2	0.02	0.02	0.08	2.6	2.7
55–70	4.3	ND	ND	19.0	24.0	57.0	0.02	0.02	0.08	2.4	2.7

[†] Cation exchange capacity (CEC) = ($Mg^{2+} + Ca^{2+} + K^{+} + Na^{+} + Fe^{3+} + Mn^{2+} + H^{+} + Al$)

was observed (analysis of 10 profiles randomly distributed though the site). The analysis performed were pH, cation exchange capacity, exchangeable elements, C and N concentrations particle size distribution. In 2004, a precise cartography of the site was realised using geostatistical tools and variogram maps were generated (Forêt 2004). The variables used were mainly percentage of stone and fine earth, particle size distribution and total analysis of fine earth. This study led to the conclusion that the soil was homogeneous within the experimental site. However, Mareschal (2008) reported some minor variations in mineralogical properties between the two blocks, likely linked to rock grain size. Because of these variations, for the purposes of this study it was necessary to study tree species effects in each block separately. The similarity of the effects in the two blocks was then used to validate the impact of tree species on mineral weathering. This example clearly demonstrates the difficulty of performing studies of tree species effects on soil, as the satisfactory integration of environmental heterogeneity is essential.

Sampling and sample preparation

Mineral soil samples were collected at the four corners of a 8 × 8 m square localised in the center of each stand giving us eight profiles for each species in the two blocks. Forest floor material was removed prior to sampling. Volumetric soil sampling was performed at three depths (0–5, 5–10 and 10–15 cm) using a cylindrical corer with a diameter of 10 cm. Three adjacent samples (10 cm far) were sampled at each corner of the square and then composited. Approximately one kg of soil was collected for each sample. The soils were sieved to 2 mm to remove any roots and coarse materials. Fifty grams of each soil sample were first treated to remove organic matter using dilute H_2O_2 (5 %), followed by Na saturation (NaCl, 0.4 N) and dispersion with NaOH to prevent aggregate formation (Robert and Tessier 1974). The clay particles were separated by repeated sedimentation in a sedimentation cylinder. Immediately prior to size fractionation, each cylinder was shaken for 2 min to fully disperse the mineral soil. Following a predetermined settling time, the topmost suspension was removed using a siphon according to the Stockes law (Robert and Tessier 1974). Each cylinder was then topped up with distilled water and the operation repeated until the suspension withdrawn became clear, indicating that complete removal of clay fraction had been achieved.

Solid analyzes

Chemical analyses

The exchange capacity of clay samples was determined by performing a total analysis after Ba^{2+} saturation (Turpault et al. 1996). The saturation was realised with a 1 M $BaCl_2$ solution (solid/solution ratio: 1/100; duration: 10 h; one solution renewal; 20 °C). The barium content enabled determination of the CEC because levels of this trace element were very low in the soil (within the range 120–180 ppm) with respect to Ba-saturated clay (within the range 13,000–27,000 ppm). After saturation, barium assays were performed at the Centre de Recherches Pétrographiques et Géochimiques (CNRS-CRPG) in Nancy (France). The samples were fused with $LiBO_2$ and dissolved in 1 N HNO_3. The barium cation content was determined by ICP-AES (Thermo Electron IRIS Advantage). The error of this analysis was estimated to be less than 2 % with respect to concentrations in the samples.

Tricitrate treatment (c) (Tamura 1958) was used to extract amorphous phases and interlayer aluminium hydroxides of vermiculite and smectite. For this, 0.05 g of clay was treated at 100 °C for 3 h in a thermostatic water-bath with 1 M Na tricitrate solution (Normapur) adjusted to pH 7.3. The extracting solution was renewed every hour and the solid:solution ratio was 1:600. Solutions were filtered through Whatmann 42 filter paper and analyzed for Al (Alc), Si (Sic), and Mg (Mgc) using ICP-AES with an uncertainty of less than 5 %. Standard solutions and blanks were matrix-matched to the extractive solution.

The Student-Fisher test was then used to establish significant differences among tree species ($\alpha = 0.05$) for Sic, Alc, Mgc and CEC. The software used was SPSS version 13 (SPSS Inc, IBM company, Chicago).

X-ray diffraction

X-ray diffraction method allows one to distinguish the different major clay mineral phases present with precision and to follow the changes which occur under different environmental conditions. Especially,

Table 2 Influence of the analytical treatment of mineralogical clay (saturation with Ca or K, swelling by ethylene glycol, dissolution of interlayered Al by tricitrate treatment or heating) on the location of its main peak (nm) on the X-ray chart

Saturation	Air-dried	Ethylene glycol		Air-dried		Heated (550 °C)
	Mg	Mg		K		K
Tricitrate	Without	Before	After	Before	After	Without
Chlorite	1.4	−1.4		1.4		**1.4**
Vermiculite				**1.0**		1.0
HIV				1.4	**1.0**	
Smectite		**1.6–1.7**	**1.6–1.7**		1.0–1.4	
HIS		1.4	**1.6–1.7**			
Kaolinite	0.715					(-)

The shift of the main peak enables the differentiation and the identification of mineralogical clay. Bold and underlined numbers correspond to key steps in the identification (from Barnhisel and Bertsch 1989)

(-): peak disappearance, *HIV* Hydroxy-interlayered vermiculite, *HIS* Hydroxy-interlayered smectite, *Tricitrate* chemical treatment (Tamura 1958) used to extract amorphous phases and interlayer aluminium hydroxides of vermiculite

this technique allows characterization of the interlayer space of expandable 2:1 phyllosilicates and its occupancy by polymerized aluminium which significantly affects the physicochemical properties of the original minerals. In particular, the cation exchange capacity, the ability to fix potassium and to swell and collapse are modified (Mareschal et al. 2009). Clay minerals were identified according to Table 2. Briefly, Tricitrate extraction was used to remove the aluminium precipitated in the interlayer spaces of hydroxy-interlayered minerals (HIM). Once the hydroxyl-Al interlayers are removed, the clay minerals tend to exhibit physico-chemical properties of either vermiculite or smectite with the corresponding X-ray properties (Barnhisel and Bertsch 1989). Ethylene glycol (EG) was used to expand swelling layers (smectite), K saturation to collapse interlayer spaces of vermiculite and heatings served both to collapse interlayer spaces of HIM and to identified kaolinite and gibbsite (peaks disappearance at 550 and 330 °C respectively).

X-Ray diffraction (XRD) was performed using a Siemens D5000 diffractometer equipped with a graphite monochromator set to select Cu Kα radiation (30 mA/40 kV). Diffractograms were recorded using a Daco-MP recorder combined with a microcomputer using Diffracplus software, 2006 (Socabim). The measurement range was 1.5° to 31°2″, with a step size of 0.02° and a 4 s counting time.

To achieve oriented deposits on glass slides, clay samples before and after citrate extraction were cation exchanged with a 1 M saturated solution of either CaCl$_2$ or KCl. K saturated samples were heated to 110, 330 and 550 °C for 4 h. The solvation of Ca saturated samples was ensured using EG. To achieve this, the Ca-samples oriented glass slides were exposed to EG vapour for 12 h.

Soil solutions: sampling and analysis

Soil solutions were collected from block 1 under all the stands studied in this work. Forest floor solutions were collected at the base of the forest floor layer by 3 sets of 3 thin tensionless polypropylene lysimeters (40 × 2.5 cm). These were designed to disturb the continuity between the forest floor and the mineral soil as little as possible. Mineral soil solutions were collected using five replicates of tension lysimeters (ceramic cups Oïkos, Germany) introduced into the soil at depths of 15, 30 and 60 cm under constant suction (½y½40 kPa). The lysimetric protocol was set up in the summer of 2001 and solutions were collected monthly from December 2001 to December 2006. All soil solutions were filtered at 0.45 µm, stored at 4 °C before analysis.

Total cations were measured by ICP-AES (Jobin & Yvon 180). Error was dependent on the concentration of each element, but was lower than 5 % for all elements. Nitrate was analysed using ionic chromatography on a Dionex X320 apparatus. The pH of the solution was measured at room temperature on an aliquot of solution using a Mettler Toledo DL70 ES titrator with an AgCl-KCl combination electrode.

The Student-Fisher test was used to establish significant differences between tree species at 5 % levels for Al, NO_3^- and H^+.

Results

Mineralogy of the clay fraction

The major if not exclusive method to identify clay mineral in complex soil assemblages is by X-Ray diffraction methods using oriented particle samples (Barré et al. 2007). Simplified identification procedure for phyllosilicates is described in the “Materials and methods” section (Table 2). The XRD patterns of oriented Ca-saturated samples (Fig. 1) exhibited peaks of primary minerals: quartz (0.426 and 0.333 nm), micas (1.0, 0.5, and 0.333 nm) and traces of K feldspar (0.324 nm). The secondary minerals were kaolinite (0.715 and 0.356 nm), gibbsite (0.483 nm; the disappearance of this peak after heating at 330 °C was observed but is not shown) and a peak at 1.4 nm which corresponded to different minerals (Table 2). The samples contained a mixed-layered phase producing this peak, part of which expanded toward small angles following treatment with EG (Fig. 1). This expansion behaviour revealed smectitic layers only at the first level. After K saturation, vermiculite layers were identified at all depths by partial collapse of the 1.4 nm peak to 1.0 nm (not shown). The samples contained secondary 1.4 nm minerals, which gradually collapsed to 1.0 nm on heating, suggesting interlayering with some hydroxyaluminium (not shown). Indeed, after citrate extraction (removal of Al precipitated in interlayer position), the collapse at 1.0 nm after K saturation increased, and expansibility after EG solvation was more marked at the −5 cm level (Fig. 1) but also appeared at −10 cm and −15 cm, suggesting the occurrence of both hydroxy-interlayered vermiculite (HIV) and hydroxy-interlayered-smectite (HIS).

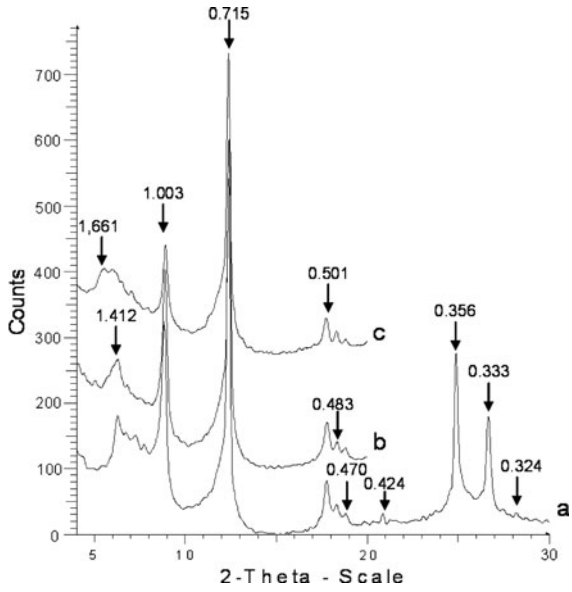


Fig. 1 Selected X-Ray diffraction patterns (Cu Kα-radiation) of the clay fraction from the 0–5 cm level under native forest in block 1. **a**: Ca-saturated clay sample, **b** Ca-saturated and ethylene glycol-solvated clay sample and **c** Ca-saturated and ethylene glycol-solvated clay sample following citrate extraction. Reflections are noted in nanometres (nm). The expansion of the 1.412 nm peak toward little angles (**c**) after citrate treatment (removal of polymerized Al in interlayer position) and EG solvation reveals the presence of HIS layers in the sample

Chlorite was identified by persistence of a 1.4 nm peak of low intensity after heating at 550 °C (not shown). Clay fraction samples from all soil profiles in blocks 1 and 2 had a similar mineralogical composition. All these minerals identified using XRD method were currently observed in Typic Dystrochrept derived from granite (Righi and Meunier 1991; Meunier 2003).

Homogeneity of the clay mineralogy

The integration of spatial variability was crucial to comparing the effects of tree species on soil. To achieve this, all replicates for the same tree species and depth were compared. The X-ray diffraction patterns for one species and one level were superimposed in order to evaluate their homogeneity. These verifications revealed that the mineralogical composition of the clay fraction was identical in replicates from each stand, as shown by the superimposition of XRD tracings of clay from all tree species (Fig. 2) in the two blocks taken separately. Moreover, variations between the stands were limited, as shown in Fig. 2. After verifications of homogeneity, and in view of this strong intra-stand uniformity, only one representative profile per stand was used to produce the XRD tracings presented here to illustrate how clay mineralogy was affected by tree species.

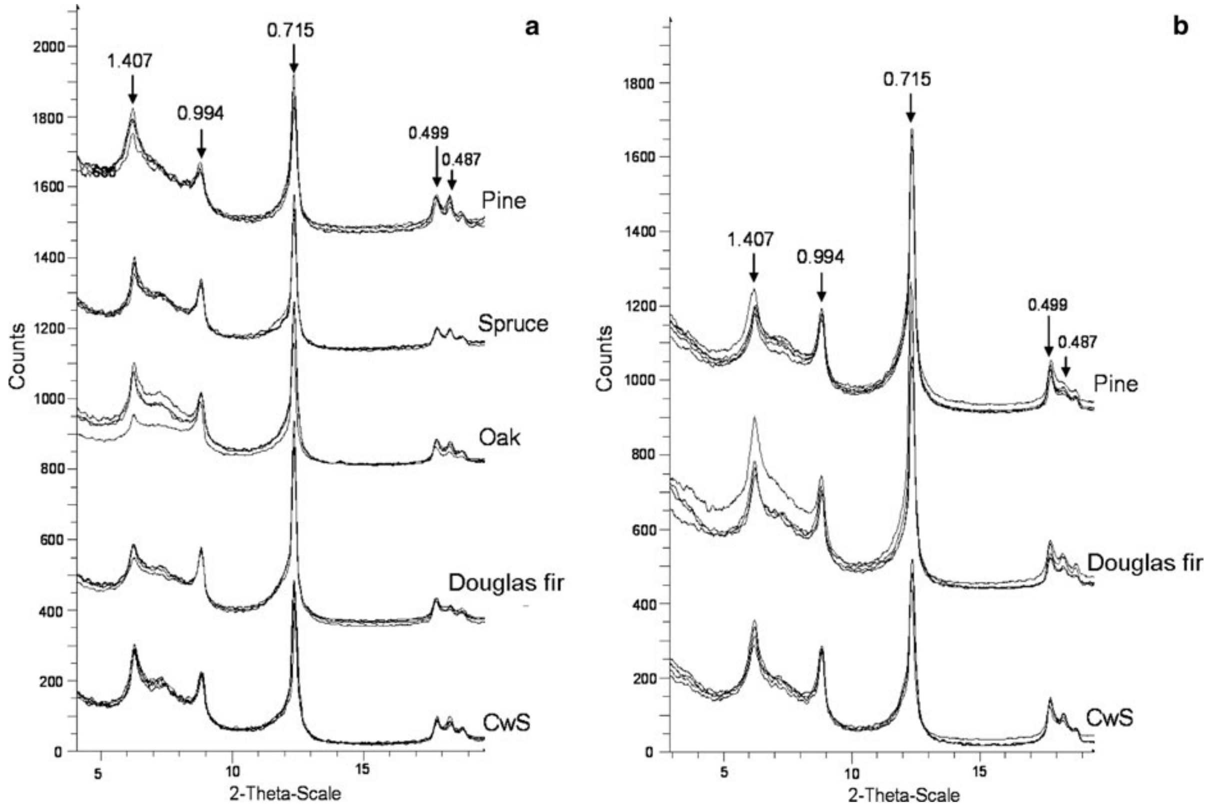


Fig. 2 X-ray diffraction patterns (Cu Kα-radiation) obtained from oriented deposits after the Ca-saturation of clay samples under all species in the two blocks (block 1: **a**; block 2: **b**) at 0–15 cm. The Figure illustrates the good homogeneity of the four replications per stand. Reflections are noted in nanometres (nm)

Effect of tree species on clay mineralogy

Citrate extraction

Tree species could have an effect on the dissolution of Al from soil mineral and Al mobility toward deeper soil layer (Dijkstra and Fitzhugh 2003). To measure the difference in Al compound of the clay fraction among tree species, citrate extractions were performed.

In block 1, the Alc content extracted from the clay fraction ranged from 6.3 to 15.5 g kg^{-1}, depending on stand and depth (Fig. 3a). Lower values within the range 4.2–10.4 g kg^{-1} were measured in block 2 (Fig. 3c). Whereas the Alc content increased with depth, the Sic content decreased (Fig. 3b, d). A comparison of tree species showed that Alc and Sic contents were quite similar at the 0–5 cm depth in all stands of each block. The Alc content was significantly lower under pine and Douglas fir stands than under other stands in block 1, at the 5–10 and 10–15 levels. Indeed, the difference reached 44 and 42 % under Douglas fir versus native forest stands at 5–10 and 10–15 cm, respectively. The differences between pine and native forest stands were smaller, reaching 33 and 32 % at the same depths. Inversely, the citrate-extractable Si content was higher under these two species than under others. Oak and spruce did not display any significant variations in Alc and Sic contents when compared with native forest at the three depths.

The same pattern was observed in block 2, but only at the depth of 10–15 cm. At this depth, Alc was found to be 13.5 and 18.5 % lower under the Douglas fir and pine stands respectively when compared with native forest (Fig. 3c).

Previous studies have already reported modifications of Al and Fe contents and speciation in soil resulting from vegetation over relatively short periods (Cornu et al. 2008; Calvaruso et al. 2009), but there is

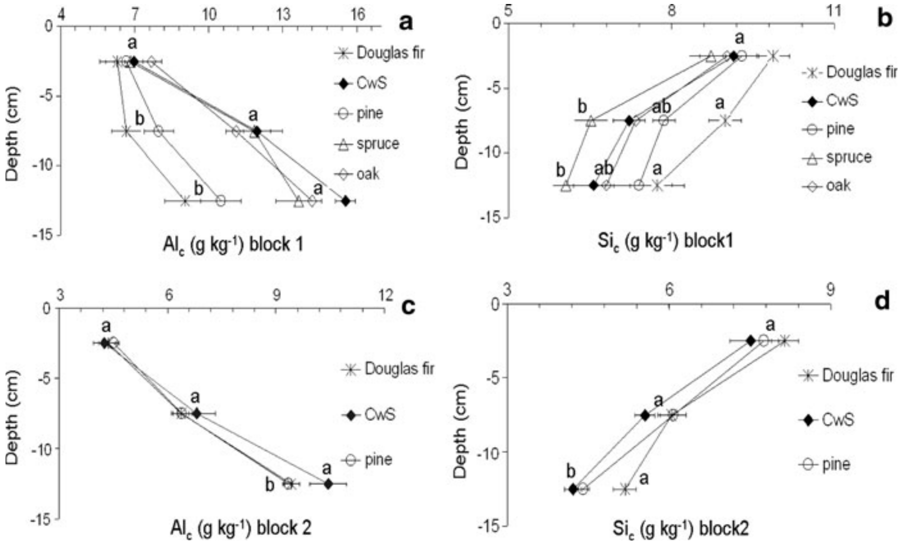


Fig. 3 Mean of Al (**a**, **c**) and Si (**b**, **d**) concentrations extracted from the clay fraction using the citrate method in all stands (block 1 and 2) at the three depths. *Letters in lower case* represent significant differences at the 5 % level, and *horizontal bars* represent the standard error

still a lack of study concerning the effect of a change to tree species on the clay fraction.

XRD analyses

XRD analysis was used to highlight tree species effect on clay mineralogy and particularly on expandable phyllosilicates because their interlayer spaces were susceptible to record changes linked to the soil environment (Barnhisel and Bertsch 1989; Turpault et al. 2008; Egli et al. 2001).

The X-ray diffraction patterns of Ca-saturated samples highlighted any variations between tree species in the two blocks (Fig. 2). In the same way, after EG solvation, no changes were observed amongst the different tree species. The expansibility of smectitic layers (revealed using EG solvation) between depths of 0 and 5 cm was identical, and no effect of tree species was discernable. Swelling was minor in all stands and decreased identically with depth.

The effects of tree species were pronounced following citrate extraction. Clay samples from the pine and Douglas fir stands revealed more swelling after Ca saturation and EG solvation when compared with native forest in block 2, and native forest, oak and spruce in block 1. This effect was observed at depths of both 5–10 cm and 10–15 cm (Figs. 4, 5). Swelling are more pronounced under Douglas fir and pine which indicate that interlayer material of expandable 2:1 phyllosilicates was less stable when compared with other tree species. This lower stability, likely due to partial removal of interlayer material, allowed a more pronounced swelling after EG solvation. Interlayer material removal or precipitation has already been observed as a function of environmental changes in the rhizosphere of tree species (Turpault et al. 2008) or in bulk soil (Egli et al. 2001). For other minerals such as kaolinite, micas and vermiculite, no clear tree species effects were noted.

CEC of the clay fraction

CEC was a relevant parameter for clay minerals with respect to soil functioning and availability and dynamics of plant nutrients. Modification of biogeochemical soil environment impacts clays properties especially CEC of 2:1 expandable phyllosilicates which influences part of the element flux (Barnhisel and Bertsch 1989), notably potassium in soils (Mareschal et al. 2009).

CEC values of the clay fraction ranged from 23.5 to 29.8 cmolc kg^{-1} in block 1 and 19.2–29.6 cmolc kg^{-1} in block 2 (Fig. 6). CEC values were markedly lower at the 10–15 cm level in block 2, but remained almost stable with depth in block 1. Tree species effects were similar in the two blocks at depths of 10–15 cm. Indeed, CEC values were significantly higher under Douglas fir and pine than under native forest at this depth. Differences of 20 and 14 % were observed between the Douglas fir stand and native forest at depths of 5–10 and 10–15 cm, respectively, in block 1, and 17 % in block 2 at the depth of 10–15 cm.

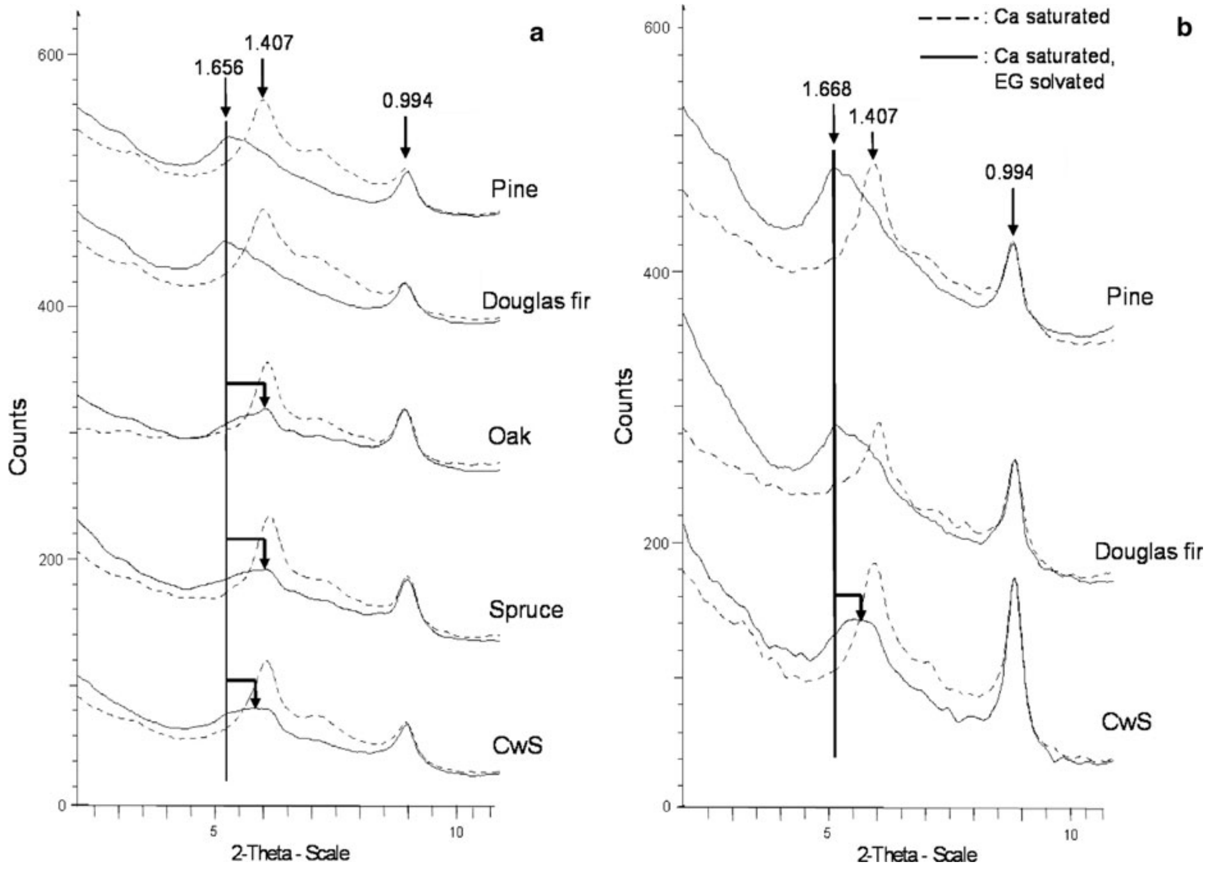


Fig. 4 X-ray diffractograms (Cu K-radiation) of clay samples from the different stands (block 1: **a**, block 2: **b**) at 5–10 cm depth after citrate treatment and Ca saturation plus EG solvation. Reflections are noted in nanometres (nm). *Arrows* indicate the less pronounced swelling after ethylene glycol solvation for oak, spruce and native forest samples when compared with Douglas fir and pine samples. The more pronounced swelling of Douglas fir and pine clay samples indicates an enhanced removal of polymerized Al in interlayer position when compared to other species

Between the pine stand and native forest the differences were smaller, reaching 12 and 11 % in block 1 at 5–10 and 10–15 cm respectively and 13 % in block 2 at the depth of 10–15 cm.

The CEC values reported here were within the range commonly observed for temperate forest soils (Turpault et al. 1996). However previous studies did not report changes in CEC of clay fraction resulting from vegetation over periods of decades. CEC change function of tree species have been reported only with the method of vermiculite test mineral (Augusto et al. 2001) incubated in the soil for a period of 3 years.

Soil solution

Soil solutions fill an important place in the functioning of biogeochemical cycles of forest ecosystems as they are the main interface between vegetation, microflora, minerals and organic matter of soil (Marschner 1991). Due to their central role that the study of soil solutions gives information on the nutrient level available for the vegetation or the current level of soil acidification (Boudot et al. 1994b). Potentially, tree species could modify the chemical composition of soil solution (Augusto et al. 2001; Dijkstra and Fitzhugh 2003).

In this work, aluminium concentrations found in the forest floor solutions were high when compared to those in soil solutions (Fig. 7). These important quantities of Al collected under forest floor did not originate from rainfall (which contained very low levels, at 1.73 mg L^{-1}, the mean of 6 years) on this site (Jaffrain 2006). At greater depth, Al concentrations evolved were different by tree species. A marked increase was observed under the Douglas fir and pine

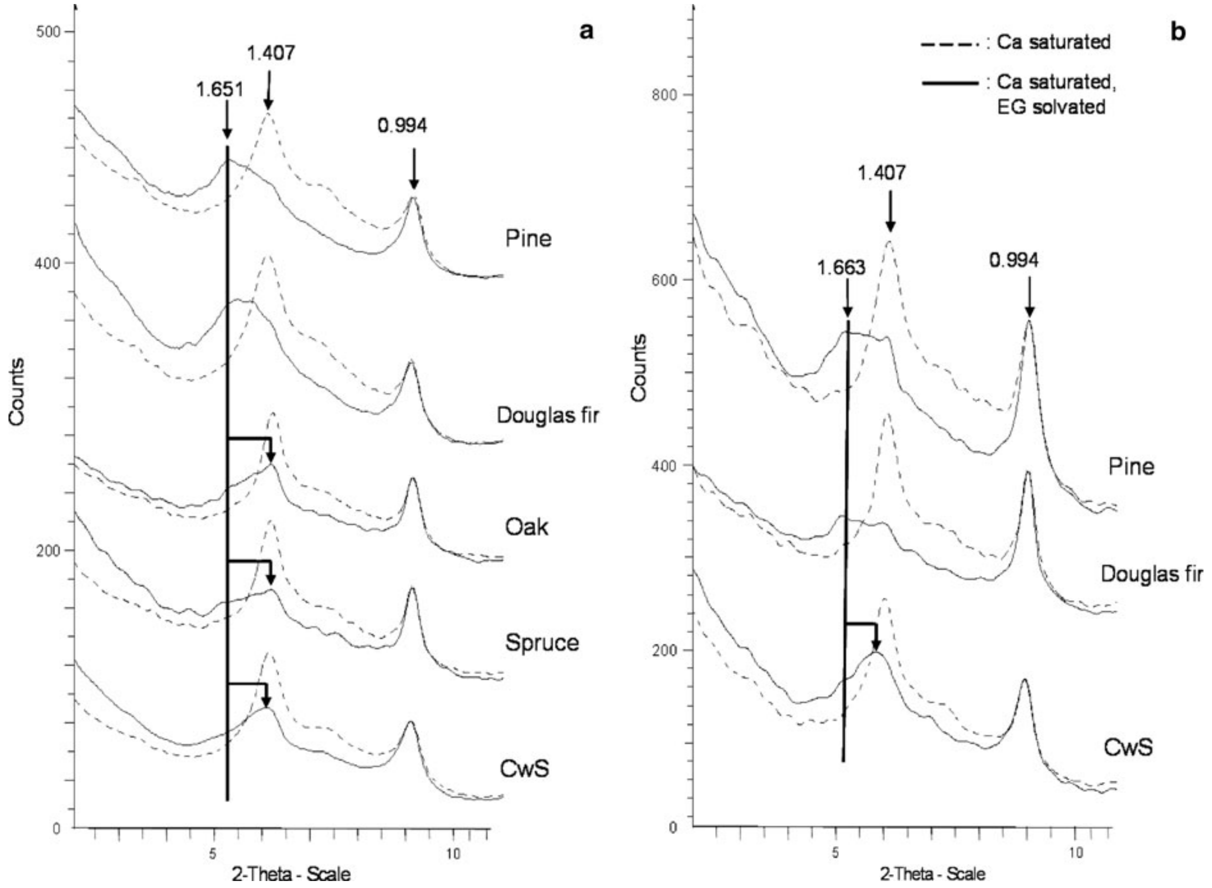
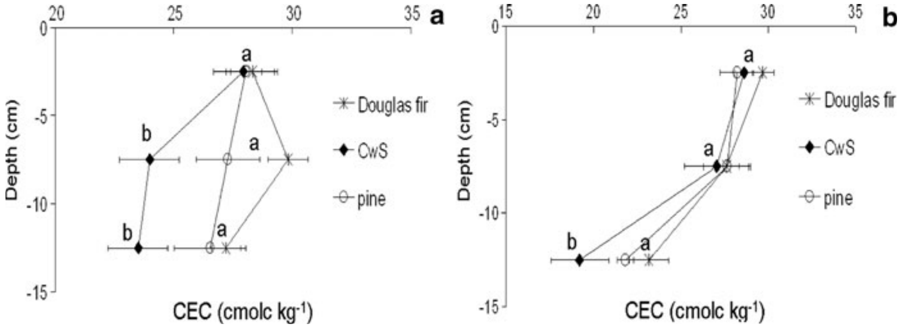


Fig. 5 X-ray diffractograms (Cu K-radiation) of clay samples from the different stands (block 1: **a**, block 2: **b**) at 10–15 cm depth after citrate treatment and Ca saturation plus EG solvation. Reflections are noted in nanometres (nm). *Arrows* indicate the less pronounced swelling after ethylene glycol solvation for oak, spruce and native forest samples when compared with Douglas fir and pine samples. The more pronounced swelling of Douglas fir and pine clay samples indicates an enhanced removal of polymerized Al in interlayer position when compared to other species

Fig. 6 Cation exchange capacity of the clay fraction measured by total analysis after Ba^{2+} saturation in block 1 (**a**) and block 2 (**b**). *Letters in lower case* represent significant differences at the 5 % level



stands, a smaller increase under oak and stable concentrations under native forest and spruce stands. The difference in Al concentrations in soil solutions at the15 cm depth and the litter solution was clearly positive for Douglas fir and pine (and to a lesser extent for oak), but no increase was noted in the CwS stand. Nitrate levels exhibited the same pattern as Al as a function of tree species. Nitrate was well correlated with Al ($r^2449 = 0.93$; $p < 0.01$). Moreover, nitrates and protons also showed positive correlations

($r^2$450 = 0.76; $p < 0.01$) (Fig. 8). Higher acidity was observed under Douglas fir and pine stands than under other species. Aluminium, nitrate and proton concentrations were strongly dependent on tree species.

The acidification of the ecosystem by some tree species was significant with the respect to the pH of soil solutions. Such modification of the pH of soil solutions could have an impact on the biogeochemical processes of forest ecosystems like mineral weathering (Augusto et al. 2002).

Discussion

Mineralogical transformations

The effect of trees on soil weathering has been recognized for a long time but few studies have presented direct observations on the clay fraction. In this work, the results of investigations of the clay mineralogy have shown that the main mineral affected was hydroxy-interlayered mineral. Properties of HIM are well known and have been widely described in acid soils (Rich 1968; Aurousseau et al. 1983; Ji-Quan 1983; Karathanasis et al. 1983; Barnhisel and Bertsch 1989; Pai et al. 2004; Meunier 2007) that allow us to

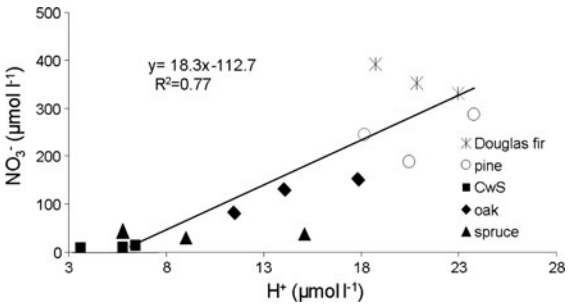


Fig. 8 Relationship between mean nitrate and proton concentrations measured in soil solution. The Figure shows the position of tree species in this relationship. Soil solutions were collected monthly over a 6-year period at three depths per stand

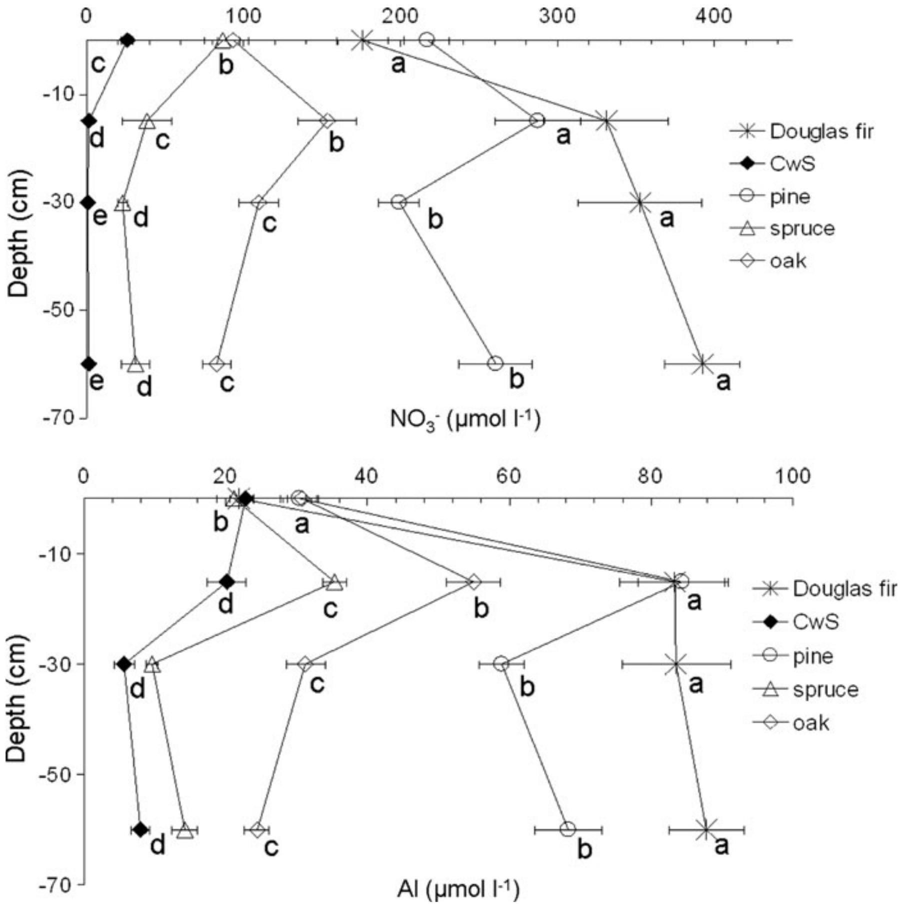


Fig. 7 Total aluminium and nitrate levels (µmol l^{-1}) measured in forest floor leachates (zero tension lysimeters) and soil solutions (tension lysimeters) from 0 to 60 cm depths in block 1. *Letters in lower case* represent significant differences at the 5 % level

well interpret the results. HIS are unaffected by ethylene glycol solvation because Al polymers prevent the swelling. During our study, swelling only occurred after citrate extraction (citrate extraction allowed Al polymers removal, see “Materials and methods” section), as shown by X-ray diffraction patterns for the 5–10 cm and 10–15 cm levels (Figs. 4, 5). Occupancy of the interlayer space of smectite layers significantly modifies the physico-chemical properties of the original minerals. The most important changes concern a reduction in cation exchange capacity and a tendency towards less swelling (Barnhisel and Bertsch 1989). Our results showed that the Alc content was lower in the Douglas fir and pine stands than in other stands, and this feature was reproducible in both blocks. The dissolution of poorly crystalline Al compounds was enhanced under these species, and notably hydroxy-interlayered material in expansible phyllosilicates, because both the increases in CEC under Douglas fir and pine stands (Fig. 6), and swelling after EG solvation (Figs. 4, 5), were more pronounced than under native forest following citrate treatment. Indeed, citrate extraction was more efficient in removing interlayer material under Douglas fir and pine stands, and allowed HIS to swell more than under other species. Without sodium citrate extraction, swelling was identical in all tree species. It is likely that residual interlayered material may have prevented greater swelling under the Douglas fir and pine stands. It has been shown elsewhere that sodium citrate treatment is unable to completely extract polymerized interlayer aluminium (Tamura 1958; Mareschal et al. 2009). Hence we suggest that interlayer material was more markedly destabilised under Douglas fir and pine species in the natural environment than with other species. This process allowed citrate extraction to dissolve interlayered Al compounds more completely. This is consistent with the smaller quantities of Alc extracted and the more pronounced swelling under these species. This process are consistent with the results of Egli et al. (2001) which report the removal hydroxyl-Al interlayers of soil HIS in a time span of 24 years favoured by a high load of acids (pollution by F and biodegradation of organic matter).

CEC was negatively correlated with Al extracted by sodium citrate in both blocks (Fig. 9). This feature revealed that Al compounds were fixed on cation-exchangeable sites and caused lower CEC values (Barnhisel and Bertsch 1989; Augusto et al. 2001; Meunier 2007). Under Douglas fir and pine the density of exchangeable sites increased through the dissolution of adsorbed or interlayered Al hydroxides. Figure 9 shows the translation (represented by arrows) of Douglas fir and pine samples toward higher CEC values and lower Alc concentrations. This feature, visible in both blocks, could be discussed in terms of soil fertility. In the short term, the depolymerisation of interlayered compounds corresponds to an increase in soil fertility (increase in the number of sites free for exchangeable base cation fixation) but the increase of Al in solution may lead to toxicity and competition for nutrient uptake, by instance Al for Ca (Rengel and Zhang 2003; Nygaard and de Wit 2004; van Scholl et al. 2005). However, in the longer term, the minerals dissolution process could cause a reduction in soil fertility and enhance dissolution of nutrient bearing mineral. The potential productivity of soil under pine and Douglas fir stands should be affected and the soil impoverished due to acidification.

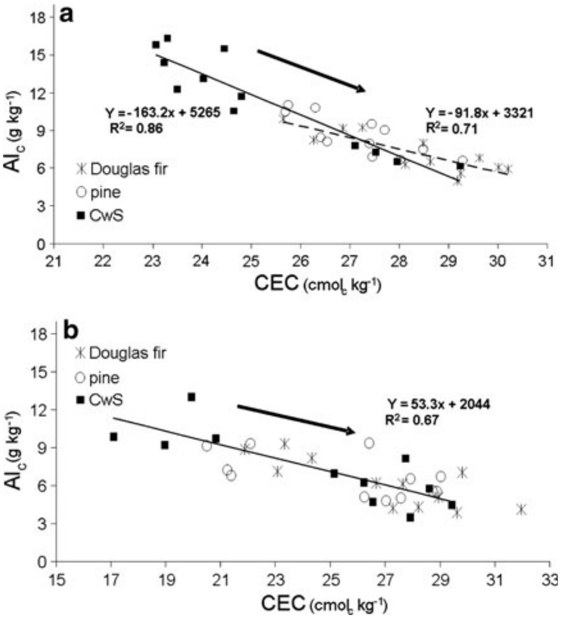


Fig. 9 Relationship between Al extracted by the citrate method and CEC values measured by total analysis after Ba^{2+} saturation on the clay fraction in block 1 (**a**) and block 2 (**b**). *Arrows* indicate the translation of Douglas fir and pine sample positions by comparison with native forest toward higher CEC values and lower Al_c values

The changes in soil mineralogy are rarely documented in the literature because this requires a soil sampling over a long period of time (Egli et al. 2001).

Some studies have demonstrated a reduction in Al bound to oxy-hydroxides linked to silvicultural practices. The recent work on this subject published by Cornu et al. (2008) concerned modifications to Al and Fe contents and speciation in an acid soil after the reforestation (beech) of grassland. The authors showed that reforestation induced soil podzolization 60 years after planting. The processes that could explain this rapid change were mainly linked to a lower pH and the stronger complexing activity of organic matter derived from beech.

Some others studies have demonstrated rapid and faster soil transformation in various pedological contexts. Frank and Gebhart (1989) have observed a significant dissolution of muscovite and alkali-feldspar occurring within 20 years. This change is explained by the high load of acids. In an Alocrisol, Calvaruso et al. (2009) showed mineralogical transformations and increasing mineral dissolution in the rhizosphere of a spruce stand when compared to the bulk soil. This study demonstrates that, despite the short duration of the contact between the active part of a root and a mineral, the intensity of the processes occurring at the soil-root interface significantly affects mineral weathering and can influence pedogenesis. In a chronosequence of podzolic soils, Burt and Alexander (1996) demonstrated the formation of a subsoil organic horizon (Bh) in 38 years and the boundary between E and Bhs horizon was macromorphologically identified within 70 years. Montagne (2006) showed a change in the soil mineral composition due to modification of eluviation and redox potential after 16 years of subsurface drainage in a Albeluvisol. This work suggests that the soil minerals and particularly the clay fraction are precise markers of the spatial and temporal variability of the biogeochemical soil environment. In this study, significant transformations occurring over 28 years have been shown. Clay minerals develop a large surface area, they have a considerable capacity to react with the other soil phases and record, in space and time, the subtle chemical changes occurring during these interactions.

Nitrification and weathering

The effect of tree species on nitrification was studied on the Breuil Chenue experimental site by Zeller et al. (2007). The results showed that gross nitrification was higher in the Douglas fir and pine stands than in the native forest, oak and spruce stands. These results agreed well with the high NO_3^- concentrations measured in soil solutions under Douglas fir and pine.

The nitrification in excess of biological demand under Douglas fir and pine stands was not explained by a lower requirement for N with respect to other species because N storage per hectare in the aerial biomass of Douglas fir and pine was higher or comparable to the other trees (Sicard et al. 2006). It was well documented that the type of tree species may induce variation in N transformations across forest soils (Finzi et al. 1998; Priha and Smolander 1999; Chen and Stark 2000; Menyailo et al. 2003; Lovett et al. 2004) and experiments into N net nitrification rates indicated that these were linked strongly to the species growing in the soil (Nugroho et al. 2006). The presence, type and activity of ammonia-oxidising bacteria are likely to be influenced by tree species (Nugroho et al. 2006) resulting in an increase of NO_3^- produced that is on excess of biological demand.

Under anaerobic conditions, significant loss of NO_3^- does occur as a consequence of denitrification. The soil of the Breuil site was sandy and well drained. The process may also occur in anaerobic microenvironment of well drained soils, such as in small pores and in the vicinity of roots or decomposing residues. Because NO_3^- concentrations are rate limiting and oxygen is needed to sustain denitrification through nitrification (Öquist et al. 2007) this process could be enhanced in anaerobic microenvironment under Douglas fir and pine stands.

Excessive nitrification occurs when produced nitrates were not entirely absorbed by vegetation or immobilized by micro-organisms. This leads to a net production of hydrogen ion (Breemen et al. 1983; Reuss and Johnson 1986; Vries et al. 1987; Kirikae et al. 2001), as shown in Fig. 8. Some nitrogen fertilisers can also increase soil acidity but the extent depends on the amount of $NH4^+$, urea, or biologically fixed N that are lost from the soil, e.g., in drainage waters or farm products (Bolan et al. 1991). Acidity enhances mineral dissolution and particularly that of Al bound to oxy-hydroxides. This explains the stronger concentration of Al in soil solution under Douglas fir and pine and the lower concentration of Alc of the solid phase. Several authors have reported that the dissolution of Al-hydroxide layer of 2:1 clay minerals is a source of soil Al (Hem et al. 1973, Johnson et al. 1981; Dahlgren et al. 1989). Acidification processes result in increasing solubility of aluminium, releasing Al^{3+} ions into solution (Berdén et al. 1997; Habs 1997).

A low pH induces weathering of soil minerals with a high release of Al^{3+} (Beyer et al. 1993) and mobilisation increases drastically when soil solution pH decreases to <4.5 (Falkengrengrerup and Bergkvist 1995). Among the most damaging effects of acidification is the release of potentially toxic aluminium species into the soil solution and surface water (Driscoll et al. 1980; Haug 1984; Fernadez-Sanjurjo et al. 1998).

Nitrate concentrations in soil solutions were well correlated with the level of dissolved Al ($R^2 = 0.93$) because nitrate was the dominant ion associated with aluminium. These two elements are leached jointly in such well-drained, acid soil. This may indicate that an increase in Al concentrations in soil solution originates from Al-bearing minerals under these trees species. This hypothesis agreed well with the results we obtained regarding solid phases which exhibited a reduction in poorly crystalline Al compounds under Douglas fir and pine. Moreover, the dissolution of Al interlayer material was attested by XRD patterns which showed a more enhanced swelling under these two species. The acid consuming system was principally poorly crystalline Al-bearing minerals which controlled the Al concentration in the liquid phase. With a reduction in the pH, the dissolution of secondary Al compounds would become more important to the pH buffering system than the weathering of primary silicate (Skeffington and Brown 1986). According to Robert et al. (1979), non-complexing acid conditions induce the Al interlayering of expansible phyllosilicates and hence transformation of the mineral into HIM, whereas under complexing acid conditions, aluminium is not involved in interlayering but is complexed by the acid compound, which results in podzolisation. According to this theory, maintenance of the d001 reflection of smectites at 1.4 nm after EG solvation would indicate Al interlayering and hence non-complexing acid conditions. During the present study, we showed that the acid dissolution process, coupled with the considerable production of non-adsorbed anions such as NO_3^-, destabilised interlayer Al hydroxyl compounds and caused the marked lixiviation of aluminium. In the long term, and without complexation, it was possible that the interlayer spaces of HIS could be depleted of Al hydroxides under Douglas fir and pine stands. With respect to the solid phase of near surface horizons, the divergence between complexation and acid dissolution process (H^+) was due (among other factors) to the mobility and transfer of aluminium. And unlike podzosols where complexation occurs, no agent of Al transfer was generally present at high concentrations in non-podzolic acid soils. The excessive production of nitrates thus enabled both the strong transfer of aluminium in pine and Douglas fir soil solutions and after 28 years, would facilitate swelling of smectitic layers after EG solvation.

Conclusions

Despite limited experimental design (two blocks in a single location), the comparison of the clay minerals and chemistry of soil solutions among tree species suggests that during 28 years of tree species growth significant difference occurs in soil properties. The processes affecting soil under Douglas and pine could be as follows:

Poorly crystalline Al minerals were affected by a net production of hydrogen ion because of excessive nitrification under Douglas fir and pine stands when compared with native forest, oak and spruce stands. Secondary Al-bearing minerals and Al-hydroxyl interlayered material constituted the main acid consuming-system under Douglas fir and pine stands. The consequences of the strong dissolution of poorly crystalline Al minerals led to both an increase in the CEC of the clay fraction and swelling of expandable minerals under Douglas fir and pine stands when compared with other tree species. The results were convergent with respect to XRD diffraction, CEC measurements and Alc content in the solid phase and nitrates and aluminium concentrations in the liquid phase.

Because of limited replication, the hypothesis of this work and the processes described above should be confirmed in further studies using a more robust design and particularly those where achieved soil samples were available.

If these processes are verified in others experimental sites, it would be necessary to conduct studies of stream water chemistry at the catchment scale planted with Douglas in view to the important nitrate and aluminium lixiviation.

Secondly it would be interesting to verify if the general features of the excessive nitrification observed in this study is reproducible under pine and Douglas in the same and others ecological conditions.

Norway spruce, which is usually considered as an 'aggressive species' that enhances mineral weathering when compared to hardwoods, provoked no visible effects on the mineral phases in this soil. Conversely, the results seemed to reveal an effect of Douglas fir and pine on clay weathering 28 years after planting. We hypothesised that soil mineral change may occur within rather short period of time. This change was rapid when set against the classically accepted soil transformation periods considered in pedogenesis. Indeed, soil changes and mineralogical transformations are classically considered as slow processes but some recent studies reveal that rapid changes, the most often linked to human practises, are of considerable interest to study the timing of soil forming process.

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