

Rapid Clay Weathering in the Rhizosphere of Norway Spruce and Oak in an Acid Forest Ecosystem

Christophe Calvaruso

UR INRA 1138 "Biogéochimie des
Ecosystèmes Forestiers"
Centre INRA de Nancy
54280 Champenoux
France

currently at:

Université du Luxembourg "Physique des
Radiations"
Campus Limpersberg
L-1511 Luxembourg
Luxembourg

Louis Mareschal

Marie-Pierre Turpault*

UR INRA 1138 "Biogéochimie des
Ecosystèmes Forestiers"
Centre INRA de Nancy
54280 Champenoux
France

Elisabeth Leclerc

Andra
Direction Scientifique/Service Transferts
92298 Châtenay-Malabry
France

The mineralogy of bulk and rhizosphere soils was compared to assess the effect of roots on mineral weathering in a Typic Dystrachrept supporting Norway spruce (*Picea abies* [L.] Karst) and oak (*Quercus sessiliflora* Smith). In an experimental forest site (Breuil-Chenué, France), systematic soil sampling was performed in forty pits. The soil adhering to the roots was considered as rhizosphere soil. The remaining material was regarded as bulk soil. The mineralogy of the clay-sized particles of both fractions was determined by x-ray diffraction (XRD). Amorphous solid phases were estimated by extracting Fe and Al with hot Na-citrate and dithionite-citrate-bicarbonate. Total chemical analyzes were performed on the clay-sized particles via BaCl₂-saturation and an iso-zirconium weathering balance was calculated. The XRD demonstrated an increase of illite-like minerals in the rhizosphere of both species and the selective extractions revealed a decrease in the amorphous phases. The total chemical analyzes showed that the rhizosphere clay-sized fraction contained significantly more Si and K (for oak only) and less Fe and Al than the bulk soil. By way of the iso-zirconium weathering balance, these losses of Fe and Al in the rhizosphere were estimated at several tens of kilograms by hectare for the surface horizon (0–3 cm). This study demonstrates that, despite the short duration of the contact between the active part of a root and the solid mineral phase, the intensity of the processes occurring in the rhizosphere significantly increases mineral weathering.

Abbreviations: B, bulk soil; BS, base saturation; subscript c, hot Na-citrate treatment; CEC, cation exchange capacity; subscript d, dithionite-citrate-bicarbonate treatment; EA, exchangeable acidity; EG, ethylene glycol treatment; HIS, hydroxy-interlayered smectite; HIV, hydroxy-interlayered vermiculite; ICP-AES, inductively coupled plasma spectrometry-atomic emission spectrometry; ICP-MS, inductively coupled plasma spectrometry-mass spectrometry; R, rhizosphere; subscript [tot], total; XRD, x-ray diffraction.

The weathering of soil minerals is an important source of nutrients to the forest ecosystems which are, to a great majority, non-amended by humankind relative to farmlands (Ranger and Turpault, 1999; Gobran et al., 2005). This mineral weathering process results principally from meteoric water circulation and from biological activity in the soil and more particularly in the rhizosphere. The rhizosphere, defined as the volume of soil surrounding the roots which is affected by it (Darrah, 1993), constitutes the interface between the solid soil

phase, soil solution, and root system and is the zone where major processes take place. The characteristics of the rhizosphere may be drastically different from those of the bulk soil; that is the root-free soil material. Steep chemical, microbial, and physical gradients exist along the rhizosphere to bulk soil axis (Gobran et al., 1998; Hinsinger et al., 2005; Gregory, 2006).

Mineral grains in the rhizosphere are affected mechanically and chemically by invading plant roots and root-associated microorganisms such as fungi and bacteria (Robert and Berthelin, 1986; April and Keller, 1990; Barker et al., 1997; Angers and Caron, 1998; Kelly et al., 1998; Banfield et al., 1999; Landeweert et al., 2001; Gadd, 2007). The weathering rates of primary minerals were more than 10 times higher in sandboxes planted with red pine (*Pinus resinosa* Aiton) in comparison with the rates in the nonvegetated sandboxes, as demonstrated by Bormann et al. (1998) in an experimental ecosystem.

Because root growth is a highly dynamic process (Hinsinger et al., 2005), a portion of the bulk soil will become rhizospheric only for a short duration before becoming once again bulk soil. In consequence, the question we are faced with is the following: is the intensity of the processes occurring in the rhizosphere

Soil Sci. Soc. Am. J. 73:331-338

doi:10.2136/sssaj2007.0400

Received 19 Nov. 2007.

*Corresponding author (turpault@nancy.inra.fr).

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677 S. Segoe Rd. Madison WI 53711 USA

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sufficient to modify soil mineralogy? According to Hinsinger et al. (1992), the rhizosphere effect on mineral weathering can be very rapid. By way of pot experiments, these authors documented an impact within 3 d at a distance of 0.5 mm from a dense root mat of Italian ryegrass (*Lolium multiflorum* Lamb.). The release of 19% of the K contained in the phlogopite and the complete vermiculitization of the mineral at a distance of 0.5 mm of the root mat within 32 d were observed in a similar experiment by Hinsinger and Jaillard (1993). The conditions existing in these laboratory experiments are, however, very distant from those existing in natural ecosystems (White and Brantley, 2003), mainly because the devices used consist in limiting the ecosystem complexity (e.g., climatic conditions, solid mineral phase, soil solution, biological interactions...) and in maximizing the impact of the roots on the mineral by increasing the contact surface area between roots and minerals.

In consequence, the impact of the rhizosphere on soil mineralogy may be better assessed by in situ studies. However, since Spyridakis et al. (1967) observed transformation of biotite into kaolinite under the influence of coniferous and deciduous seedlings, little research has been done to relate the impact of roots on mineral characteristics in a forest ecosystem. For example, Courchesne and Gobran (1997) who compared the mineralogy of bulk and rhizosphere clay minerals in Swedish Podzols from XRD analyzes, demonstrated that the rhizosphere of Norway spruce soil contained lower amounts of easily weatherable minerals such as amphibole and expandable phyllosilicates than the bulk soil.

The objective of this study was to investigate, in a temperate forest ecosystem and by using different analytical methods, namely selective extractions, total chemistry, XRD analyzes, and an iso-zirconium chemical weathering balance, the effect of processes occurring at the root–soil interface on mineralogical composition of the clay-sized fraction. The study approach was to compare, in an acid forest soil supporting mature Norway spruce (*Picea abies* Karst) and oak (*Quercus sessiliflora* Smith), the properties of bulk and rhizosphere soils with emphasis on clay chemical and mineralogical changes.

MATERIALS AND METHODS

Study Site

The soil samples were collected at the Breuil-Chenué experimental forest site established in 1976 and located in the Morvan (47°18' N, 4°5' E, France). The forest is situated on a plateau at an altitude of 638 m, on a slight, northwest facing slope. Mean annual air temperature is 9°C and the annual precipitation averages 1280 mm yr⁻¹. The native forest was partially clear-felled and replaced in 1976 by monospecific plantations distributed in plots of 0.1 ha of different

species such as oak, beech (*Fagus sylvatica* L.), Norway spruce, and Douglas-fir (*Pseudotsuga menziesii* [Mirb.]Franco). The soil is classified as a Typic Dystrochrept (USDA, 1999), developed on the “Pierre qui Vire” granite (Seddoh, 1973). The bulk soil is sandy-loam textured (60% sands and < 20% clays) and acidic (Table 1). The cation exchange capacity (CEC) and the base saturation (BS) are low and decrease with depth (Table 1). The humus form is a moder (Brêthes et al., 1995) in the native forest.

Sample Collection and Soil Fractionation

The sampling of soil materials was performed in June under two adjacent stands of Norway spruce and oak. After removing the forest floor, systematic soil sampling was performed at three depths (0–3, 3–10, and 10–23 cm) in twenty pits each with a dimension of 80 by 35 cm, distributed throughout each plantation plot.

The separation of soil samples into bulk and rhizosphere fractions was conducted in the field. In each horizon, soil material was cut and extracted from the profile. Living roots with diameters < 2 mm were then carefully removed by hand and lightly shaken. Root-free soil fraction was collected and immediately air-dried in a steam-air dryer at 30°C to give the bulk soil sample (B). Roots with adhering soil aggregates < 1 cm in diameter were dried immediately in a steam-air dryer at 30°C. The soil fraction that came off spontaneously from the roots after drying was collected to give the rhizosphere soil sample (R).

Sample Preparation

Given the cost and time of preparation necessary for the mineralogical analyzes of each soil sample, a composite soil sample was made from the twenty individual samples (0–200 µm) for each species and compartment. Thus, 12 soil samples were treated: 2 species (Norway spruce and oak) × 2 compartments (B and R) × 3 depths (0–3, 3–10, and 10–23 cm).

Particle-Size Distribution

Particle-size distribution was done by pipette and wet-sieving methodologies (Krumbein and Pettijohn, 1938). Thirty grams of each composite soil sample were first treated to remove organic matter by 5% (v/v) H₂O₂, followed by deflocculation with NaCl (0.4 M) to avoid aggregate formation. Thereafter, the clay (<2 µm) and fine silt (2–20 µm) fractions of the 12 composite samples were separated by pipette method, based on the ‘Stokes’ sedimentation rates. The coarse silt (20–50 µm) and fine sand (50–200 µm) were subsequently isolated by wet sieving.

Mineralogical Analyses

The abundance of amorphous secondary solid phases was estimated in the bulk and rhizosphere clay-sized fractions. The Al and Fe were extracted with Na-citrate at 100°C (Tamura, 1958) and by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960). The Al and Fe extracted by hot Na-citrate (Al₂O_{3(c)} and Fe₂O_{3(c)}) and by dithionite-citrate-bicarbonate (Al₂O_{3(d)} and Fe₂O_{3(d)}) were analyzed by inductively coupled plasma spectrometry-atomic emission spectrometry (ICP–AES; JY180 ULTRACE).

The mineralogical composition of the clay-sized fraction of both bulk and rhizo-

Table 1. Particle-size distribution, pH, organic C, and exchangeable cations of the soil profile at the experimental site (Breuil, France).

Depth cm	pH†	Clay %	Silt %	Sand %	Organic C g kg ⁻¹	Ca cmol _c kg ⁻¹	Mg cmol _c kg ⁻¹	K cmol _c kg ⁻¹	CEC‡	BSS§ %
0–8	4.3	16.0	15.0	69.0	7.9	0	0.5	0.3	12.2	7.7
10–18	4.6	13.0	26.0	61.0	1.2	0	0.3	0.2	10.5	5
20–28	4.7	14.0	24.0	62.0	0.9	0	0.2	0.1	8.9	3.5

† Soil pH was measured in H₂O with a soil to solution ratio of 1:2.

‡ Cation exchange capacity: CEC = Mg²⁺ + Ca²⁺ + Na⁺ + Fe³⁺ + Mn²⁺ + Ba²⁺ + H⁺ + Al.

§ Base saturation: BS = (Mg²⁺ + Ca²⁺ + Na⁺ + Fe³⁺ + Mn²⁺ + Ba²⁺)/CEC.

sphere soil samples was determined by XRD using a Siemens D5000 diffractometer (Siemens Corp., New York, NY), equipped with a graphite monochromator and a Cu tube (Cu-K α radiation) operated at 30 mA and 40 kV. Subsamples of the clay-sized fractions, before and after hot Na-citrate and dithionite-citrate-bicarbonate treatments, were saturated with Ca, Ca-ethylene glycol (EG), or K; and then mounted in preferential orientation on glass slide. The K-saturated samples were analyzed when air-dry and also after heating to 110, 220, 330, 440, and 550°C. Diffractograms were recorded using a DACO-MP recorder associated with a microcomputer using Diffrac AT software (Socabim, Champs-Sur Marne, France). In all, 288 diffractograms were analyzed after background removal. The integrated intensity of each mineral was normalized relative to the intensity of the (100) peak ($d = 0.426$ nm) of quartz to compare diffractograms. The 1.0- to 1.4-nm peak intensity ratios were calculated for the different clay samples saturated with Ca.

Chemical Analyses

The pH of the soil samples was measured in H₂O with a soil to solution ratio of 1:2 (pHmeter Mettler TSDL25). Total organic C in soil fractions was estimated using a TOC analyzer (Shimadzu 5050). Exchangeable cations in soil samples were extracted in either 1 M KCl (Mg²⁺, Ca²⁺, Na⁺, Fe³⁺, Mn²⁺, and Ba²⁺) or 1 M NH₄Cl (K⁺), according to Espiau and Peyronel (1976), and determined by ICP-AES (JY180 ULTRACE). The 1 M KCl soil extract was also titrated on an automatic titrimeter (Mettler TS2DL25) to assess exchangeable H⁺ and Al (Rouiller et al., 1980). Exchangeable acidity (EA) was calculated by taking the sum of H⁺ and Al. Cation-exchange capacity (CEC) was calculated by taking the sum of both extracted exchangeable base cations (Mg²⁺, Ca²⁺, Na⁺, Fe³⁺, Mn²⁺, and Ba²⁺) and exchangeable acidity (H⁺, Al). Base saturation (BS) is the percentage of exchangeable base cations in the CEC: $BS = (Mg^{2+}, Ca^{2+}, Na^+, Fe^{3+}, Mn^{2+}, \text{ and } Ba^{2+})/CEC$.

The total chemical analyzes of the clay-sized fraction of both bulk and rhizosphere soil samples were performed after Ba-saturation by ICP-AES (JY180 ULTRACE) for major elements (SiO_{2tot} \pm 1%, Al₂O_{3tot} \pm 1%, Fe₂O_{3tot} \pm 2%, MgO_{tot} \pm 5%, K₂O_{tot} \pm 5%....) and inductively coupled plasma spectrometry-mass spectrometry (ICP-MS; PerkinElmer Elan 6000, Perkin Elmer, Waltham, MA) for trace elements (Zr_{tot} \pm 8%....), after using LiBO₂ and dissolution by HNO₃. These total chemical analyzes were recalculated to consider the residual organic matter remaining in the soil samples after organic matter destruction. Organic matter was determined from C concentrations measured using CHN analyzer (Thermoquest NCS2500, Thermo Quest, Milan, Italy). To assess the effect of the rhizosphere on the chemical composition of the clay-sized fraction, the difference of concentrations of one element E in the rhizosphere (R) and in the bulk soil (B), called $\Delta_{(R-B)} [E]$, was calculated for each element and for each species according to the following formula:

$$\Delta_{(R-B)} [E] = \frac{([E]_{R(0-3cm)} - [E]_{B(0-3cm)}) + ([E]_{R(3-10cm)} - [E]_{B(3-10cm)}) + ([E]_{R(10-23cm)} - [E]_{B(10-23cm)})}{3}$$

Furthermore, to more accurately evaluate mineral weathering and root-induced losses of elements, an iso-zirconium assessment method (Sohet et al., 1988) has been applied to the surface horizon (0–3 cm). This method consists of determining quantitative losses or gains of an element by normalizing its concentration to that of an invariant element such as Zr contained in zircon silicate minerals, considered

to be unaffected by weathering processes. Usually the weathering balance with the iso-zirconium method is used at the profile scale and allows one to compare a soil horizon with its reference (i.e., parent material). In our case, the clay-sized fraction of the bulk soil was used as the reference and this concept was applied to the estimation of the weathering intensity for the rhizosphere clay-sized fraction.

The calculation of the element losses in the rhizosphere in comparison to the bulk soil, for a soil surface area of 1 ha and a soil thickness of 3 cm (0–3 cm) is in accordance with the following formula:

$$[X_b - X_r \times (Z_r/Z_b)] \times Rc$$

where X_r is the concentration of the element of interest in the rhizosphere, X_b is the concentration of that element in the bulk soil, Z_r is the concentration of the index element (Zr) in the rhizosphere, Z_b is the concentration of that element in the bulk soil, and Rc is the amount of rhizospheric clay-sized fraction for 1 ha of soil and a soil thickness of 3 cm (0–3 cm).

Statistical Analyses

Because the datasets were normally distributed, the effect of the rhizosphere on the particle-size distribution and soil pH was determined using analysis of variance (ANOVA) at the threshold level of $p = 0.05$ and the Bonferroni-Dunn test. The Superanova software (Abacus Concepts, Inc., Berkeley, CA) was used for all these analyzes. The Student-Fischer test was performed to establish significant differences between soil compartments (bulk soil and rhizosphere) at levels of $p = 0.10$ (*) and $p = 0.05$ (**), for Si, Al, Fe, Mg, K, Al_c, and Fe_d.

RESULTS

Particle-Size Distribution and Soil pH

The proportion of clay-sized fraction in the rhizosphere of the 0- to 23-cm soil horizon was not different from that of the bulk soil for Norway spruce and oak (data not shown). This result allows us to compare the rhizosphere and the bulk soils for each species.

The pH was significantly lower in the rhizosphere of Norway spruce (pH = 4.0) compared with that of the bulk soil (pH = 4.3) whereas there was no difference for the oak (pH = 4.3). The pH was significantly lower in the Norway spruce rhizosphere compared with that of the oak whereas there was no difference between the two species as regards to the pH of the bulk soil.

X-Ray Diffraction Analyses

Identification of the Different Clay Fraction Minerals

From XRD patterns, similar clay minerals were identified in the rhizosphere and the bulk soil under Norway spruce and oak.

The XRD patterns of oriented Ca-saturated samples exhibited peaks of mica (1.0, 0.5, and 0.333 nm), kaolinite (0.715 and 0.350 nm; the disappearance of the 0.715-nm peak after heating at 440°C was observed but not shown), gibbsite (0.484 nm; the disappearance of this peak after heating at 330°C was observed but not shown), K-feldspar (0.323 nm), and quartz (0.426 and 0.333 nm) (Fig. 1).

The 1.4-nm peak corresponded to different minerals:

- chlorite was identified by the persistence of the 1.4-nm peak after heating at 550°C (data not shown).

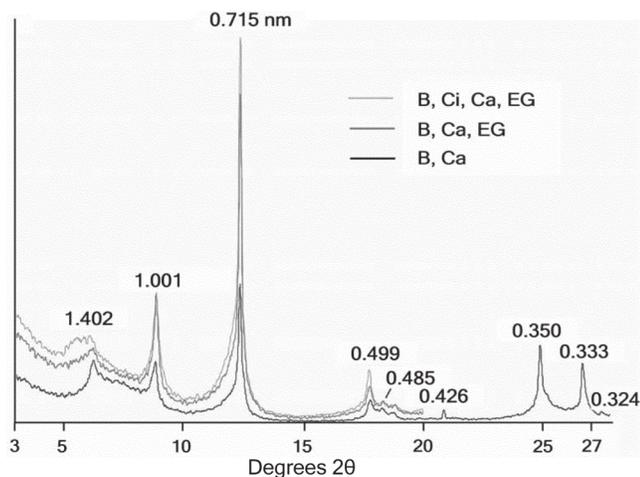


Fig. 1. Selected x-ray diffraction patterns of Ca-saturated bulk soil clay fraction (B) in the 0- to 3-cm soil horizon: (i) without pretreatment (B, Ca), (ii) ethylene glycol-solvated (B, Ca, EG), and (iii) ethylene glycol-solvated and pretreated with citrate (B, Ci, Ca, EG).

- smectite layers were identified by swelling after Ca-saturation and EG-solvation (Fig. 1).
- vermiculite was identified by the partial collapse of the 1.4- to 1.0-nm peak after K-saturation without heating (data not shown).
- hydroxy-interlayered phyllosilicate occurrence was shown by progressive collapse as temperatures increased (data not shown). The hydroxy-interlayered-smectite (HIS) was identified because swelling increased after Ca-saturation, citrate pretreatment and EG-solvation (Fig. 1). The hydroxy-interlayered-vermiculite (HIV) was identified by an increase in the intensity ratio of 1.0- and 1.4-nm peaks after citrate pretreatment and K-saturation (data not shown).

The different treatments of the clay fraction demonstrated the presence of complex interstratified minerals (with micas, vermiculite, smectite, HIS and HIV layers) in the 6 to 8 2θ scale region which were not studied in details in this paper.

Rhizosphere Effect on Clay Fraction

The diffractograms of the clay-sized fraction treated with Ca-saturation revealed an increase of the 1.0- to 1.4-nm peak intensity ratios in the rhizosphere in comparison with that of the bulk soil, except for the 10- to 23-cm depth oak sample (Table 2). This increase revealed the presence of a higher proportion of mica-like minerals in the rhizosphere.

The diffractograms of the clay-sized fraction treated with Ca-saturation and EG-solvation showed greater swelling near the 1.4-nm peak for the Norway spruce (Fig. 2). This swell-

Table 2. Ratios of the 1.0- to 1.4-nm peak intensity from the x-ray diffraction for the bulk soil and rhizosphere clay fractions saturated with Ca.

Depth cm	Norway spruce		Oak	
	Bulk soil	Rhizosphere	Bulk soil	Rhizosphere
	Peak intensity ratio			
0-3	1.33	1.65	1.19	1.54
3-10	1.95	2.19	1.31	1.75
10-23	0.65	0.88	0.78	0.77

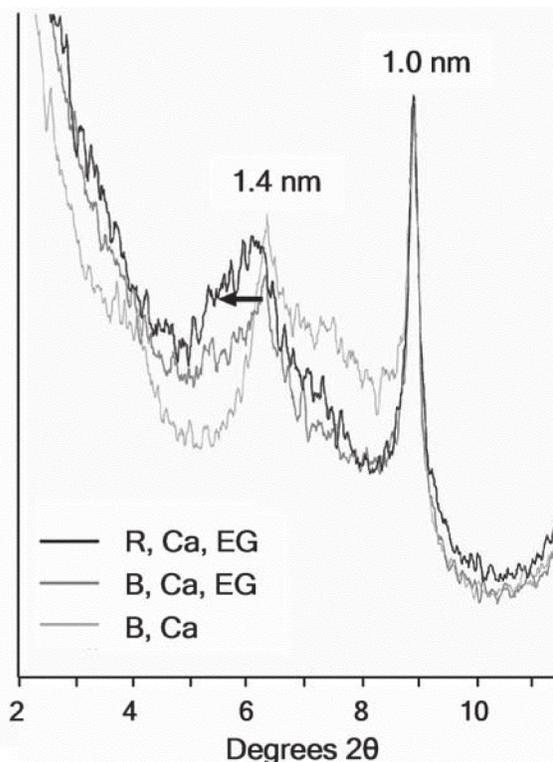


Fig. 2. Selected x-ray diffraction patterns of Ca-saturated clay fraction in the 0- to 3-cm soil horizon from Norway spruce bulk soil: (i) without treatment (B, Ca) and (ii) ethylene glycol-solvated (B, Ca, EG) and from Norway spruce rhizosphere: (iii) ethylene glycol-solvated (R, Ca, EG).

ing revealed a destabilization of the interlayer polymers in the rhizosphere of Norway spruce.

Chemical Analyses

A significant increase in the proportions of Si was observed in the rhizosphere clay fraction compared with those of the bulk soil for both species (Fig. 3). This increase represented 4.2 g kg^{-1} of dry clay fraction for the Norway spruce and 2.1 g kg^{-1} of dry clay fraction for the oak. A significant increase in the proportions of K was also observed in the rhizosphere clay fraction but only for the oak. This increase represented 0.8 g kg^{-1} of dry clay. In contrast, significant decreases in the proportions of Al, Fe, Al_c , and Fe_d were observed in the rhizosphere clay fraction compared with those of the bulk soil for both species. The concentrations of Mg did not vary between the rhizosphere and the bulk soil for both species.

The iso-zirconium chemical weathering balance method underlined a loss of Al, Fe, Mg, Al_c , and Fe_d in the rhizosphere of the two species (Fig. 4). This element loss was three to five times higher in the rhizosphere of Norway spruce in comparison with that of the oak.

DISCUSSION

The mineral assemblages of the rhizosphere and the bulk soil were comparable for the Norway spruce as well as for the oak in the Breuil-Chenu forest. They consisted of quartz, mica, kaolinite, gibbsite, K-feldspar, chlorite, smectite, vermiculite, HIS, HIV, and complex interstratified minerals. The total chemical analyzes revealed, however, that the rhizosphere clay-sized fraction contained significantly more Si and less Fe

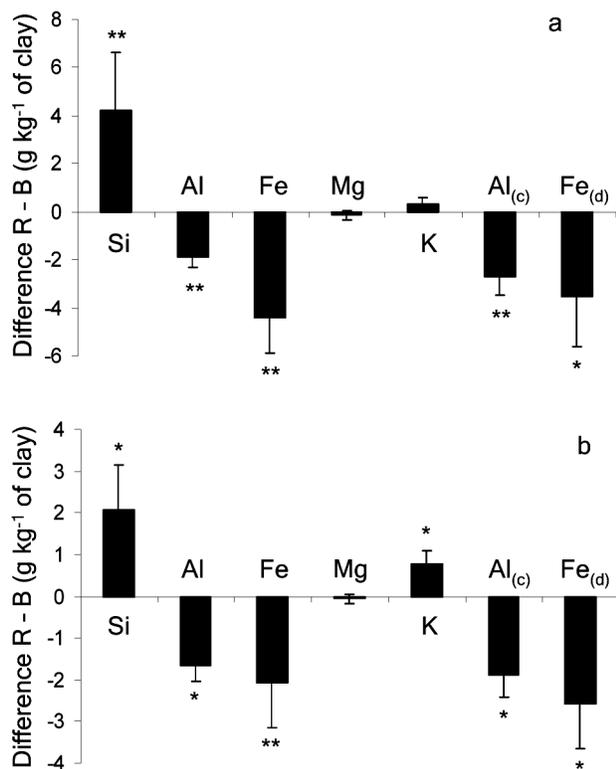


Fig. 3. Differences between the concentration of an element in the rhizosphere clay fraction (*R*) and that of the bulk soil clay fraction (*B*) in the experimental site (Breuil, France), for Norway spruce (a) and oak (b). Histograms represent the mean value of three replicates. Bars represent standard deviations. Values are significantly different according to a Student-Fischer analysis, respectively $p = 0.05$ (**) and $p = 0.10$ (*). Al_c = Al extracted by Na-citrate at 100°C, Fe_d = Fe extracted by dithionite-citrate-bicarbonate.

and Al than the bulk soil, indicating that there had been dissolution of the minerals containing Fe and Al. Likewise, the results of selective extractions and the diffractogram observations demonstrated a decrease in the amorphous phases (Fe and Al hydroxides) in the rhizosphere. The iso-zirconium chemical weathering balance performed on the surface horizon (0–3 cm) even showed that the activity of Norway spruce and oak roots generated element losses reaching several tens of kilograms by hectare according to the element. All these results are concordant and reveal a more intense dissolution of the clay-sized fraction minerals in the vicinity of Norway spruce and oak roots. This observation is in accordance with the studies performed in other forest ecosystems by April and Keller (1990) in Eastern American soils, Courchesne and Gobran (1997) in Swedish podzols and Séguin et al. (2005) in Canadian luvisols. Their results indicated that easily weathered minerals such as amphibole and expandable phyllosilicates were depleted in the rhizosphere as compared with the bulk soil. Eich-Greatorex and Strand (2006), which compared in Northern Norway woodland the soil chemical properties in the vicinity of pores with and without tree roots, also observed preferential dissolution of biotite close to root surfaces. This increase of mineral weathering in the rhizosphere results from physical and chemical processes linked to the activity of roots and root-associated microorganisms (Robert and Berthelin, 1986; Barker et al., 1997; Banfield et al., 1999; Van Breemen et al., 2000; Berner et al., 2005; Gadd, 2007).

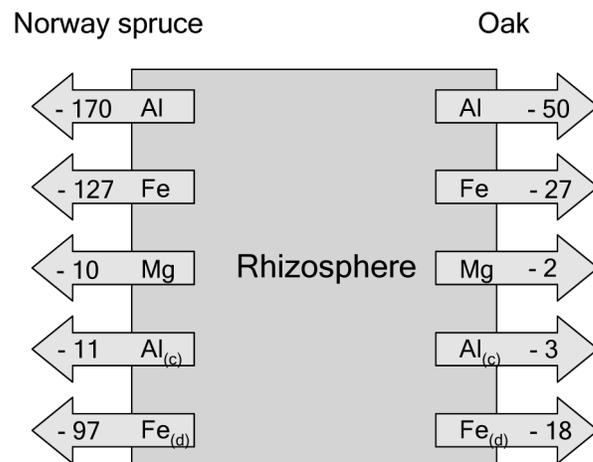


Fig. 4. Schematic representation of the amounts of elements (in kg ha⁻¹) lost in the rhizosphere of Norway spruce and oak as compared with the bulk soil for a surface area of one hectare and for the surface horizon (0–3 cm) in the experimental site (Breuil, France). These values are obtained from the chemical analyzes and by using the iso-zirconium weathering balance method. Al_c = Al extracted by Na-citrate at 100°C, Fe_d = Fe extracted by dithionite-citrate-bicarbonate.

Growing roots fracture mineral grains (April and Keller, 1990). Furthermore, due to their very weak diameter (some micrometers), hyphae can penetrate inside the rocks, minerals or even between phyllosilicate layer packs, generating segregation and microdivision of the minerals (Robert and Berthelin, 1986; Jongmans et al., 1997). Mechanical forces exerted by roots can also affect the orientation of mineral grains (April and Keller, 1990). These authors observed the alignment of the long axis of phyllosilicate grains tangential to the root surface in scanning electron microscope analysis. These mechanical effects of the root and hyphae on adjacent mineral grains increase the surface of fresh mineral material exposed to the weathering regime (April and Keller, 1990). Radial pressure exerted by the growing roots compress the soil in their vicinity (Dexter, 1987) resulting in a decrease of the porosity in that zone (Bruand et al., 1996). Soil structure is influenced by soil water content and its variation with plant growth can strongly influence the magnitude and frequency of wetting and drying cycles (Doussan et al., 2003). Finally, the production of mucilage by roots and microorganisms has been shown to affect viscosity, surface tension properties of the soil, and thereby soil–water relationships in the rhizosphere (Read and Gregory, 1997). The production of exudates by plant roots and microorganisms in the rhizosphere, together with soil fragmentation and intense wetting and drying cycles due to evapotranspiration, contribute to soil particle aggregation (Amellal et al., 1998; Czarnes et al., 2000; Denef et al., 2002; Whalley et al., 2005; Rillig and Mummey, 2006). This change in soil structure and the capacity of roots to bind fine particles improve soil water retention, thus increasing contact time between root, soil solution, and mineral, hence favoring mineral weathering (Drever, 1994).

Through the uptake of water and nutrients, which is the major function of roots, the plants modify the nutrient concentrations in the rhizosphere and generate depletion or accumulation of nutrients in the soil solution (Barber, 1995). The nature and the intensity of the changes in ionic concentrations depend on the correspondence of the plant requirements and

the supply by the soil (Hinsinger, 1998). When the plant requirements exceed the supply by the soil, the soil solution is progressively depleted in that element by root uptake. The interaction between the liquid and the solid phases requires then a transfer of these elements from the soil minerals, thus accelerating the weathering of minerals. Owing to the weak plant requirement of Fe and Al in comparison with the supply by our soil (Jaffrain, 2006), the depletion of these elements from the soil solution by root uptake is most likely not the process responsible for the Fe and Al losses observed in the rhizosphere clay-sized fraction.

It has also been demonstrated that roots and root-associated microorganisms produce a great variety of acid compounds such as protons, organic acids, and complexing organic acids (Jones, 1998; Kelly et al., 1998; Welch et al., 1999; Landeweert et al., 2001; Liermann et al., 2000) which are important factors controlling mineral weathering (Drever and Stillings, 1997) notably in low-nutrient environments such as forest ecosystems (Marschner, 1995; Grayston et al., 1996; Dakora and Phillips, 2002). These molecules can directly attack mineral surfaces and/or chelate elements in solution which generates disequilibrium between the solid phase and the soil solution. These acidic root secretions were attributed to carbonic and organic acids produced by roots and rhizosphere microflora through respiration and exudation and to proton release by the roots to compensate for an unbalanced cation–anion uptake at the soil–root interface (Hinsinger et al., 2003). According to Haynes (1990), the pH of the rhizosphere differs from that of the bulk soil mainly because of the predominant form of N taken up by the roots; that is NH_4^+ or NO_3^- . Recent studies of Colin-Belgrand et al. (2003) and Zeller et al. (2007) have demonstrated that most of the N present in the Norway spruce soil in the Breuil-Chenue site is the NH_4^+ form (82%), suggesting that the Norway spruce mainly consumed NH_4^+ . To compensate for this principal uptake of positive charges in their root cells, the Norway spruce roots release protons in the surrounding soil. This abundant exudation of acid compounds by Norway spruce roots, confirmed by our soil pH measurements [$|\text{pH}(\text{R}-\text{B})| = 0.3$], could thus explain the significant increase of mineral dissolution in the rhizosphere of this species.

To explain mineralogical differences between rhizospheric and non-rhizospheric soils in Canadian Podzols supporting corn, Kodama et al. (1994) also evoked precipitation from suspension which went through root channels. However, this hypothesis is not conceivable in our study since, contrary to these authors, we observed a decrease of Al and Fe amorphous phases in the rhizosphere clay-sized fraction of both species. Moreover, the downward movement of the soil solution in a Typic Dystrochrept is much weaker than that of a Podzol which is characterized by important leaching. In the same study and by way of transmission electron microscope, Kodama et al. (1994) observed that clay-sized fraction particles were trapped in areas where mucilage produced by corn roots had accumulated. The morphology of these particles revealed that they appeared to be tiny particles of certain phyllosilicates. This observation could indicate that certain clay-sized fraction particles strongly adhere to the roots, while others are less likely to adhere. Up-to-now, however, no study has demonstrated this hypothesis.

The XRD analyzes of the clay-sized fraction revealed, for 80% of the samples, an increase of the 1.0- to 1.4-nm peak intensity ratio in the rhizosphere with respect to the bulk soil. These results underlined an upper concentration of illite-like minerals in the rhizosphere clay-sized fraction. Moreover, the K content increased in this fraction. This last observation can be interpreted as a consequence of illite-like mineral enrichment in the rhizosphere. This increase of illite-like minerals in the rhizosphere can be explained according to the interpretation of Barré et al. (2007) who defined the amount of illite-like minerals in temperate soils as a function of K status. According to these authors, the increase of exchangeable K (e.g., after fertilization or litter mineralization) in the top soil was correlated with an increase of illite-like minerals in the clay-sized fraction. A reversed trend was observed after decrease of K content (e.g., after intensive agricultural practice without fertilization). The same process was applied to the rhizosphere clay-sized fraction since many authors have observed an enrichment of exchangeable K in the rhizosphere soil and solution of different mature tree species such as Norway spruce, trembling aspen (*Populus tremuloides* Michx), and Douglas fir (Clegg and Gobran, 1997; Dieffenbach and Matzner, 2000; Yanai et al., 2003; Séguin et al., 2004; Turpault et al., 2005). This increase in K concentrations could be due to positive differences between element input fluxes, principally by mass flow, mineral weathering and organic matter mineralization, and element output fluxes, principally by plant uptake in the rhizosphere. Consequently, the K, present in large amounts in the rhizosphere solution due to a positive transfer budget, and possessing a strong affinity for the high charge expandable phyllosilicate like vermiculite, becomes fixed in the interlayer space to form mica-like minerals (Nettleton et al., 1973; Tice et al., 1996; Turpault et al., 2005). The formation of mica-like minerals in the rhizosphere could thus be explained by a two-step mechanism when the initial mineral was HIV. First, the acid and complexing compounds produced in the rhizosphere release the interlayer Al of the HIV and generate vermiculite which is characterized by an expandable interlayer space. Second, the K enters the interlayer space, collapsing the structure to form a mineral with a mica-like spacing.

The results taken as a whole reveal more intense mineral weathering in the rhizosphere of Norway spruce and oak as compared with 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. This study also suggests that the rhizosphere of Norway spruce increases the weathering of soil minerals through the exudation of important amounts of acid compounds, mainly to compensate NH_4^+ absorption.

ACKNOWLEDGMENTS

We thank J. Ranger for critical review of the manuscript, G. Nourrisson, P. Bonnaud and J. Marchand for their technical help and the analysis, A. Nys and K. Bateman for review of the English language. This work was supported by the Andra (Agence Nationale pour la Gestion des Déchets Radioactifs), the Ministry of French Research (ACI quantitative ecology project), the “Lorraine” Region, and the Luxemburg Ministry of Culture, Superior Teaching, and Research.

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