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Soil aggregation may be a relevant indicator of nutrient cation availability

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Abstract
• *Key message* Aggregation was studied in two acidic forest soils (NE France) to investigate the potential link between available Ca and Mg content and soil aggregate size distribution and properties. Clay content influenced the aggregation status while clay mineralogy influenced aggregate stability and dynamics. Aggregation status and reactivity of soil components contributed to the difference of exchangeable Ca and Mg content in topsoil between the two sites.
• *Context* Though nutrient fluxes are important to define forest soil chemical fertility, the quantification of nutrient reservoirs in the soils and their availability to tree uptake is essential. A thorough understanding of nutrient availability requires an investigation of nutrient location and distribution in the soil solid phase.
• *Aims* The general aim was to investigate the potential link between available Ca and Mg content and soil aggregate size distribution and their properties (chemical, physical, mineralogical).
• *Methods* Soil aggregates were separated according to three size classes (200–2000 μm; 50–200 μm; < 50 μm) in two forest soils of the Lorraine plateau (France), both classified as Luvisols ruptic. The physical, chemical, and mineralogical properties were measured for each aggregate class.
• *Results* We showed that the relative abundance of an intermediate aggregate class [200–50 μm] was relevant to explain the difference of exchangeable Ca and Mg between sites. These aggregates were the poorest in organic and reactive mineral components and were unstable, which may mitigate the retention of Ca and Mg by ion-exchange.
• *Conclusion* This study highlights the role of aggregation and reactivity of soil components as relevant determinants of cation availability to tree uptake in soils.

1 Introduction

Assessing the chemical fertility of soils and its role in the sustainability of forest ecosystems remains a challenge, in particular for forests developed on nutrient-poor acidic soils. The measurement of available and total nutrient reservoirs through ion-exchange and dissolution techniques is necessary, but nutrient fluxes and cycling are also relevant components of the chemical fertility of forest ecosystems (Legout et al. 2014). Understanding nutrient cation availability in the ecosystem and in the soil, in particular, is therefore of paramount interest.

The status of nutrient cations in soils (e.g. "free" in solutions, adsorbed on reactive solid surfaces, belonging to solid organic or mineral structures) determines their "potential" lability and their availability for uptake by plants. Their actual availability is, however, complex to assess and depends on many factors including soil structure. In soils, organic compounds, clay minerals, iron (Fe), and aluminum (Al) oxides form organo-mineral associations which cement soil particles

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of all sizes to form soil aggregates (Andreux et al. 1980; Bronick and Lal 2005). The bonding and arrangements (protection and coating) of soil particles determine the accessibility of nutrient cations sources and, therefore, their actual availability. The availability of an element adsorbed on reactive surfaces, but trapped in very stable aggregates, is for instance far lower than if it is situated on more accessible reactive surfaces (Girard et al. 2011).

Hence, the availability of nutrient cations in the soil is related to the stability of soil aggregates, which is thought to be proportional to their size (Balesdent et al. 2000; Oades and Waters 1991; Oades 1984; Schmidt et al. 2011) and related to soil organic matter (SOM) stability. SOM stability is inversely related to the size of aggregates where it is trapped: the carbon in the largest aggregates is the most labile, while carbon trapped in the finest aggregates is expected to be more stable (Andreux et al. 1980; Balesdent et al. 1998; Jolivet et al. 2003; Schmidt et al. 2011). The so-called humic substances are less represented in the macro-aggregates while they dominate the organic fraction of the micro-aggregates (Berthelin et al. 1999).

Different methods may be used to study the aggregation status of soils (i.e. the properties and abundance of different aggregate size classes). Studies which were mainly carried out on agricultural soils (Andreux et al. 1980; Balesdent 1996; Balesdent et al. 1998, 1991; Jolivet et al. 2003; Bronick and Lal 2005) used mechanical treatments to separate aggregate size classes in order to characterize their impact on carbon and nutrient availability. Usually, only the soil upper horizons from 0 to 20 cm were taken into account, and energetic treatments are required to separate the very stable fraction of aggregates in cultivated soils. Aggregate fractionation studies carried out on organo-mineral horizons [0–20 cm] have been mostly used for detailed SOM studies (Adesodun et al. 2007; Andreux et al. 1980; Balesdent et al. 1998; Britzke et al. 2012; Jolivet et al. 2003; Kuhn et al. 2012; Leguédois and Le Bissonnais 2004; Qin et al. 2010; Stemmer et al. 1998). Investigations on other components, especially minerals, remain scarce (Adesodun et al. 2007). To our knowledge, no such study has been carried out on whole soil profiles, and rarely on forest soils (Fernández-Ugalde et al. 2013). Unlike agricultural soils which are subjected to frequent disturbance through cultivation and inputs of fertilizers and lime, forest soils may remain undisturbed for many decades. Further research on aggregation status in forest ecosystems is thus required to assess its role on nutrient cation availability to tree uptake.

We believe that a better understanding of nutrient cation availability in soils could be achieved through a detailed investigation of their location and distribution in the different aggregate size classes. The specific objectives of this study were to (i) describe the aggregation status and characterize the different aggregate classes found and (ii) investigate the potential link between aggregation and nutrient cation (Ca, Mg) availability. For this purpose, two forest soils of the Lorraine plateau (France), both classified as Luvisols ruptic (WRB) but displaying different levels of exchangeable nutrient cation (Bedel et al. 2016), were studied, looking more particularly at soil aggregate size distribution and their properties (chemical, physical, mineralogical).

2 Material and methods

2.1 Study sites

This project was conducted at two experimental sites (5 ha each) set up in deciduous forests of the Lorraine plateau (North-Eastern France). The first site named CA is located in the "Grand Pays" state forest at Clermont-en-Argonne (49° 06′ 23″ N, 5° 04′ 18″ E) and the stand (mixed beech, oak, birch, and maple; 70 to 80 years old; dominant height 30.6 ± 5.9 m) is developed on a "gaize" bedrock (Gaize d'Argonne, Cenomanian). This siliceous sedimentary rock is usually permeable and poor in weatherable minerals, but can locally lead to a rather clayey saprolite. It is covered by a silty quaternary continental deposit (decarbonated), about 50 cm thick. The second site named AZ is located in the "Hauts-Bois" estate forest at Azerailles (48° 29′ 19″ N, 6° 41′ 43″ E) and the stand (mixed beech and oak; 70 to 80 years old; dominant height 33.3 ± 6.7 m) is developed on a clayey saprolite of Keuper marls which are covered by a quaternary alluvial silt deposit, also about 50 cm thick.

The CA and AZ sites have respectively an elevation of 270 and 300 m a.s.l., mean annual temperatures of 9.5 °C and 9 °C and mean annual rainfall (average over 30 years) close to 900 and 1000 mm (Kessler and Chambraud 1986). These sites were designed to study the impact of soil compaction on ecosystem functioning (Bottinelli et al. 2014; Capowiez et al. 2015; Goutal et al. 2016). However, all the observations, measurements and sampling for this study were carried out before the setting up of these experiments or on the control treatment of the experiments. Hence, the compacted treatments were not used in this study.

2.2 Soil description, sampling, preparation, and field measurements

Thirteen evenly distributed pits at CA and 17 at AZ were used for soil description and sampling. Soils of the two sites are Luvisols (ruptic) according to the World Reference Base for Soil Resources (WRB 2014) and Neoluvisols bilithique according to Référentiel Pédologique (Baize and Girard 2008), with an analogous physical organization dominated by silt in the upper 50 cm and a strong increase in their clay content in the deeper horizons. The strong clay enrichment at about

50 cm depth causes a temporary water table to invade the silt horizon during wet periods without leading to a typical hydromorphic soil. The sequence of horizons according to Référentiel Pédologique (Baize and Girard 2008) is as follows: A (0–10 cm), E (10–35 cm), BT(g) (40–60 cm), S (60–70), C (> 70 cm) at AZ and A (0–13 cm), E(g) (10–40 cm), BTg (40–75 cm), C (> 75 cm) at CA.

For the < 2-mm soil class (fine earth) characterization, soil samples were collected in each pit at systematic depths down to 75 cm (0–10; 10–20; 20–30; 30–45; 45–60; 60–75 cm) and in three pits per site below 75 cm depth (75–100, > 100 cm at AZ; 75–90, 90–110, >110 cm at CA). Soil samples were air-dried at the laboratory and sieved to separate coarse material from the < 2 mm class (fine earth); soil moisture was measured after oven-drying at 105 °C of all samples. The total number of samples processed was 104 at CA and 136 at AZ.

2.3 Characterization of the < 2 mm class (fine earth)

2.3.1 Properties of the < 2 mm class

Particle size distribution was measured after oxidation of organic matter by H2O2 (Kunze and Dixon 1986). Soil pH was measured in both 1 M KCl and in distilled water, with a soil to solution weight ratio of 1:2.5 (Mettler TSDL25 pH meter). Cation-exchange capacity (CEC) and exchangeable cation contents were measured by the colbaltihexamine (50 mmol + L^{-1}) extraction method with a soil to solution weight ratio of 1:20 (Ciesielski et al. 1997).

Total soil organic carbon (Corg) and nitrogen (Norg) contents were analyzed with a combustion system (Thermo Quest NCS 2500); total content of Al, Fe, Mg, Ca, K, Na, and Mn in the < 2 mm class (fine earth) were determined after HF digestion and ICP-AES measurements at the Inra-Soil Analysis Laboratory (LAS– Arras). Fe and Al oxides were quantified according to the method described in Mehra and Jackson (1960) using dithionite-citrate buffered with sodium bicarbonate with a soil to solution weight ratio of 1:75 (1960).

2.3.2 Mineralogy of the clay fraction

Clay mineralogy of the < 2 mm class (fine earth) was characterized for the soil samples collected at the central pit at each site (8 horizons per profile).

The clay fraction (< 2 μm) was extracted from the < 2-mm class (fine earth) according to Robert and Tessier (1974). The soil organic matter was digested using the daily addition of dilute hydrogen peroxide (20v) to fresh samples put on heating plates maintained at about 40 °C until total elimination of organic carbon. Samples were then introduced in bottles filled with distilled water to separate particle classes according to Stokes law of sedimentation for dilute systems. The clay and the fine silt (2–50 μm) fractions were separated by

siphoning until total disappearance (10 to 15 siphoning operations are usually necessary); then the coarser fractions (coarse silts, fine, and coarse sands) were quantified by sieving under distilled water.

The total analysis was performed on particle size fractions by the CNRS-CRPG rock and mineral analysis laboratory, using LiBO2 alkaline fusion and dissolution in 1 N HNO3. Concentrations were measured by ICP-OES for major element and by ICP-MS for trace elements (Carignan et al. 2001).

Clays were then saturated with barium (Ba), which is not abundant in soil, to measure the cation-exchange-capacity directly from the total analysis.

The fine clay fraction (< 0.1 μm) was separated from the total clay fraction by centrifugation according to (Hathaway 1958):

$$t = \frac{9}{2} \times \frac{\eta}{\omega^2 \phi^2 (\rho - \rho 0)} \times \ln\frac{Rmax}{Rmin}$$

where t (in s) is the centrifugation time; η is the water viscosity (g/cm s; ω is the angular velocity (rad sec^{-1}); ϕ is the maximum radius of particles (m); ρ is the specific gravity of water (g cm^{-3}); $\rho 0$ is the specific gravity of particles (g cm^{-3}); Rmax the minimal radius of the rotor (upper part of the sample) (m) and Rmin the maximum radius of the rotor (lower part of the sample) (m). Using the KR4I Jouan apparatus, it was necessary to centrifuge for 1 h 40 at 3000 rot min^{-1}, with Rmax = 28 cm and Rmin = 16 cm. The 0–2-μm clay fraction was dispersed using ultrasonic dispersion before centrifuging; the supernatant was collecting by siphoning. The dispersion/centrifugation/siphoning operation was repeated eight times to collect the largest part of the fine clay material.

After various saturations [e.g., barium (Ba), potassium (K), and ethylene glycol (EG)] under controlled air humidity and specific pre-treatments to specifically destabilize and quantify Fe cement (Mehra and Jackson 1960) or Al cement (Tamura 1958), oriented clay samples were deposited on glass slides and dried overnight at room temperature before diffraction measurements using a Siemens XRD Diffractometer D5000 (2 theta: 3–63, 0.035, 323.9 s, 25 °C). Tamura method was used to differentiate between primary chlorite and chlorite-like HIV (hydroxy-interlayered-vermiculite): this extraction is specific for interlayered-Al (abundant in acidic soils). Mehra Jackson method (dithionite-citrate-bicarbonate, DCB) was used more specifically to destabilize iron oxi-hydroxides. This strong redox reaction removes Fe, but also Al associated with Fe-Al mixed oxides; it is also known to cause some destabilization of primary structures (Jeanroy 1983).

The Hoffmann and Klemen test were used to determine the location of the negative charges within the dioctahedral smectite 2:1 layer (Greene-Kelly 1953; Hoffmann and Klemen 1950). The clay fraction (<2 μm) was Li-saturated using 1 N-LiCl (solid solution ratio 1:10), then rinsed several times

until Cl- was totally eliminated (AgNO3 test). An oriented preparation of the Li-clay fraction was heated at 300 °C for 5 h, then saturated with ethylene glycol before XRD analysis.

2.4 Characterization of aggregation

At both sites, fresh samples were collected in one additional pit for aggregate characterization. Four soil layers characterizing four contrasted conditions were sampled: the surface organic layer (0–10 cm), the silty and low C content layer (10–20 cm), a medium depth layer (30–45 cm) intermediate between the loamy and the clayed units and a deep clayey layer (from 50 to 120 cm). Four replicates (one per pit face) were collected at each depth and pooled in the field. The deep layer was sampled but only bulk soil was studied at a 100–120-cm depth because it was impossible to separate aggregates in such a clayey material. Samples were stored at 4 °C until aggregate separation.

2.4.1 Soil aggregate size fractionation

The soil aggregate separation method used in this study is based on the methods used to study carbon turnover rates and the different protection of SOM according to aggregate stability (Billings 2006; Jiménez et al. 2011; Moni et al. 2010, 2012). After some preliminary tests, it appeared that the method used by Andreux et al. (1980) or Balesdent et al. (1998) to separate aggregates in agriculture soils would lead to complete soil disaggregation in the loamy layers due to the acidic pH of the studied soils and the low stability of soil aggregates. We then adapted the method used by Balesdent et al. (1998) or Clark et al. (2010), eliminating the mechanical shaking phase: 200 g of dry soil were slowly water saturated by imbibition with ultra-pure distilled water. Using 2000-, 200- and 50-μm mesh sieves allowed to separate the coarse aggregates [2000–200 μm], the intermediate aggregates [200–50 μm] and the fine aggregates [< 50 μm] through gentle sieving. The first two classes contain only aggregates while the [< 50 μm] class contains both micro-aggregates and individual particles. Two origins were supposed for these particles: either real free particles in the soil or particles produced by disaggregation of fragile aggregates during the sieving operation.

After separation, all aggregate classes were first oven dried at 65 °C (in order to eliminate the water excess) then at 35 °C, avoiding a total drying of the solid phase. The walls of the beakers were daily cleaned using a glass stick with a Teflon tip, to avoid fine particles loss.

The abundance of aggregates in the different classes (2000–200 μm, 200–50 μm; < 50 μm) was computed for each horizon and site.

2.4.2 Granulometry, clay mineralogy, and chemical analysis of aggregates

For each horizon and site, a first aliquot of the aggregate classes was dedicated to particle size distribution measurements and clay mineralogy. The methods used are similar to those used for the fine earth. A second aliquot of each aggregate class was fully dissolved using concentrated acid for total analysis (1 ml of HF and 6 ml of HNO3 added to 1-g dry aggregates at 130 °C; the solution was then evaporated and the residue was dissolved with 7 M HCl to measure the major element concentrations using ICP-OES (Agilent Technologies – 700 Series). A third aliquot was used for the extraction of exchangeable cations using 1 M NH4OAc at pH 7. This reagent was preferred to colbaltihexamine in this part of the study to be able to later carry out Mg and Ca isotopic ratio analysis: 40 ml of solution were added to 4 g of dry aggregates (solid solution ratio 1:10). Two successive extractions were carried out 24 h + 1 h. Major element concentrations were measured by ICP-OES (Agilent Technologies – 700 Series).

2.5 Statistical analyses

Elementary statistics were used on the general soil properties at the two sites to characterize the mean values and standard deviations from replicate measurements. Variance analysis (using all replicated pits) followed by Tukey's tests at the 95% level were performed at each site on the fine earth dataset down to 75-cm depth in order to identify a depth effect. Student's t tests (using all replicated pits) were also performed for each soil layer down to 75-cm depth to identify a site effect. The statistical dependence between variables was assessed using the Pearson's correlation coefficient, as linear relationships were observed. Lastly, a principal component analysis (PCA, XLSTAT 2013.3.04) was performed to identify the main variables discriminating sites. Several PCA based on different combinations of available variables collected on the aggregate classes were tested.

2.6 Validity of the approach

In order to evaluate the coherence between the < 2 mm class (fine earth) analysis and the aggregate class analysis, we recalculated total < 2 mm class (fine earth) concentrations from the concentrations measured in the different aggregate size classes. First, we calculated the weighted mean cation saturation for a layer from the proportion of each aggregate class (same elements were measured in both cases, except H which represents about 10% of the saturating cations). Then, we calculated the CEC of the soil layer using the base saturation rate, assuming that the methodology used for the extraction of exchangeable cations (e.g., cobaltihexamine for

total soil and NH4+-acetate at pH 7 for fractions) did not change this rate.

3 Results

3.1 Characteristics of the fine earth

3.1.1 Texture

Both soils were loamy textured in the upper layers and clayey textured below 50-cm depth (Table 1). Clay eluviation occurred in the silt cover, leading to a significant increase in clay content below 30-cm and 45-cm depth respectively at CA and AZ. Nevertheless, significant differences were observed between the soils of the two sites (Table 1), with lower clay content at CA than at AZ in the soil layers down to 75-cm depth.

3.1.2 Clay mineralogy

At the CA site, the clays in the deep layers consisted of an admixture of kaolinite, illite, and smectite (Supplementary File 1, Supplementary File 2). The Hoffmann-Klemen test indicated a tetrahedral charge deficit for the smectite, characteristic of the Beidellite group. In the upper soil layers, kaolinite, illite, and a 1.4-nm phase dominated; the beidellite content strongly decreased in both pure and interstratified phases (changes occurred at about 45-cm depth).

At the AZ site, the mineralogy of the clay fraction of the deeper soil layers was rather simple, with a dominant illite mineral associated with traces of kaolinite (Supplementary File 1, Supplementary File 2). In the upper soil layers, three phases occurred: kaolinite, illite, and a 1.4-nm phase composed of chlorite and of vermiculite more or less interstratified (Supplementary File 1).

3.1.3 Soil chemistry

Soil chemistry at both sites is summarized in Table 1. The pH water of the soil layers down to 30-cm depth was significantly higher at AZ compared to CA and a significant increase was observed at both sites from the surface to depth. Organic carbon and nitrogen contents were significantly higher at AZ than at CA. The total soil cationic exchange capacity (CEC) was similar between sites except in the 0- to 20 cm layers and significantly increased with depth at both sites (from 3.5 to 4.5 cmol + kg^{-1} in the surface layers to 12 to 18 cmol + kg^{-1} in depth). The Ca and Mg contents were significantly higher in the 0–10-cm and 0–20-cm layers at AZ than at CA, respectively. The Al content in the 0-10-cm layer was significantly lower at AZ compared to CA and base cation saturation (BS) was significantly higher in the 0-10-cm layer at AZ than at CA.

Table 1 General characteristics of the soils at the two sites. Mean and standard deviation values were computed down to 75-cm depth from 13 pits at CA and 17 at AZ, and below 75-cm depth from 3 pits per site. At each site, significant difference between depths (Depth) down to 75 cm is indicated by different letters (ANOVA and Tukey test at the 95% level). At each depth, significant difference between sites (Site) down to 75 cm are mentioned (*5‰; **1‰; ***1‰, Student's *t* test). CEC = cationic-exchange capacity; exch = exchangeable; DCB = dithionite-citrate buffered with sodium bicarbonate (Mehra and Jackson 1960)

	Depth cm	pH H₂O Mean	pH H₂O S.D.	pH Site	C org g·kg⁻¹ Mean	C org S.D.	C org Site	N org g·kg⁻¹ Mean	N org S.D.	N org Site	Clay g·kg⁻¹ Mean	Clay S.D.	Clay Site	Fine Silt g·kg⁻¹ Mean	Fine Silt S.D.	Coarse Silt g·kg⁻¹ Mean	Coarse Silt S.D.	Coarse Silt Site	Fine Sands g·kg⁻¹ Mean	Fine Sands S.D.	Fine Sands Site	Coarse Sands g·kg⁻¹ Mean	Coarse Sands S.D.	Coarse Sands Site	CEC cmol+·kg⁻¹ Mean	CEC S.D.	CEC Site	Ca exch cmol·kg⁻¹ Mean	Ca exch S.D.	Ca exch Site	Mg exch cmol+·kg⁻¹ Mean	Mg exch S.D.	Mg exch Site	Al exch cmol+·kg⁻¹ Mean	Al exch S.D.	Al exch Site	Base cation saturation % Mean	Base cation saturation % S.D.	Base cation saturation % Site	Fe DCB % Mean	Fe DCB % S.D.	Fe DCB % Site	Al DCB % Mean	Al DCB % S.D.	Al DCB % Site
Aserailles (AZ)	0-10	4.8	0.3	ab ***	26.7	5.6	a	1.8	0.4	a	222	41	b	356	41	201	32	a ***	58	49	a ***	165	49	a ***	5.7	1.6	bc **	2.2	1.7	bc *	0.5	0.3	c	1.9	0.9	c ***	63	0.2	a ***	1.8	0.2	bc ***	0.3	0	b ***
	10-20	4.6	0.2	b *	15.0	3.8	b ***	1.0	0.2	b ***	216	47	b ***	363	38	208	32	a ***	59	53	a ***	154	53	a ***	4.3	0.9	c	0.5	0.5	c	0.1	0.1	c	2.9	0.8	bc	24	0.1	c	0.5	bc	0.3	0	b
	20-30	4.6	0.2	b ***	10.8	2.9	c ***	0.8	0.1	c ***	235	5.8	b	363	41	204	37	a	59	12	a	140	44	a ***	4.5	1.3	c	0.5	0.6	c	0.1	0.1	c	3.1	1.2	bc	24	0.1	c	1.5	0.9	c	0.3	0.1	b
	30-45	4.6	0.4	ab ***	5.5	1.1	d ***	0.5	0.1	c	323	124	b ***	328	61	ab	173	60	ab ***	47	13	a	129	54	ab ***	7.0	3	b	0.5	0.3	c	0.7	0.3	c	4.6	2.6	ab	29	0.2	bc *	2.2	0.4	ab ***	0.4	0.1	a ***
	45-60	4.7	0.5	ab	3.6	0.8	d **	0.4	0.1	c	455	136	a	289	58	139	66	b ***	33	11	b	84	33	bc *	12.0	3.7	a	3.4	3.3	ab	1.3	0.7	b	6.5	2.5	a	43	0.2	ab	2.7	0.6	a	0.5	0.1	a
	60-75	4.9	0.5	a	2.0	0.2	d	0.3	0	c	501	135	a	273	48	137	61	b	30	7	b	58	13	c	15.3	2.1	a *	4.1	2.7	a	1.9	0.5	a	5.9	2.3	a	47	0.2	a	2.3	0.3	a	0.5	0	a
	75-100	5.2	0.2		1.5	0.0		0.3	0.0		590	150		233	54	93	68		26	13		59	17		14.2	3.7		6.0	2.4		2.7	0.4		7.5	2.7		70	0.4		2.4	0.4		0.4	0.0	
	>100	5.1	0.2		1.5	0.2		0.3	0.0		631	162		240	58	77	62		17	17		35	25		17.9	3.1		5.6	2.3		3.4	0.2		6.8	1.1		54	0.0		2.5	0.8		0.4	0.0	
Clermont en Argonne (CA)	0-10	4.4	0.2	c	26.1	4.2	a	1.4	0.2	a	128	11	d	357	18	365	18	a	140	37	a	10	8	a	4.3	0.34	d	0.7	0.4	c	0.1	0	c	4.3	0.3	c	29	0.1	b	0.6	0.2	d	0.2	0	d
	10-20	4.5	0.1	c	9.6	2.4	b	0.5	0.1	b	128	10	d	357	14	362	15	a	141	35	a	13	12	a	3.4	0.41	d	0.2	0.2	c	0.1	0.1	c	2.6	0.3	c	16	0.2	d	0.6	0.2	d	0.2	0	c
	20-30	4.5	0.1	c	4.5	1.7	c	0.3	0.1	c	155	51	c	345	22	ab	348	25	ab	134	39	a	18	17	a	4.5	1.5	d	0.2	0.2	c	0.1	0.1	c	3.8	1.6	c	12	0.1	c	0.8	0.3	cd	0.2	0	bc
	30-45	4.6	0.1	c	2.6	0.7	c	0.3	0.1	c	212	57	c	328	25	bc	321	39	b	124	43	a	15	14	a	7.3	2.94	c	0.4	0.4	c	0.2	0.2	c	6.6	2.6	b	12	0	c	1.0	0.1	b	0.3	0	ab
	45-60	4.8	0.2	b	10.6	5.8	b	0.3	0	c	285	47	b	305	32	cd	284	40	c	113	42	a	13	13	a	12.7	3.28	b	1.7	1	b	1.2	0.7	b	9.1	2.5	a	26	0.1	b	1.0	0.1	ab	0.3	0	a
	60-75	5.0	0.1	a	13.4	6.9	b	0.2	0	c	380	17	a	277	32	d	251	39	c	124	46	a	18	35	a	16.7	11.47	a	4.0	11	a	2.5	0.6	a	9.4	1.9	a	42	0.1	a	1.0	0.1	ab	0.3	0	a
	75-90	5.0	0.2		1.4	0.2		0.3	0.0		386	32		297	21	241	40		120	2		6	4		16.9	3.5		5.4	2.2		3.1	1.0		8.2	1.2		53	0.2		1.0	0.1		0.3	0.0	
	90-110	5.1	0.2		1.2	0.2		0.2	0.0		334	12		281	2	287	30		89	21		10	5		17.8	2.9		6.3	2.3		3.2	0.9		7.0	1.1		55	0.1		1.0	0.1		0.3	0.0	
	>110	5.1	0.2		1.2	0.2		0.2	0.0		329	7		264	20	246	23		137	16		24	10		19.5	1.1		7.8	1.8		3.4	0.5		6.8	1.8		60	0.1		1.0	0.1		0.2	0.0	

3.2 Chemical composition of particle size fractions

Total analysis of the different particle size fractions (clays, fine silts, coarse silts, fine sands, and coarse sands) are presented in Table 2. When comparing the two sites, significant content differences were observed for SiO2 in fine sands, Al2O3 in fine silts and fine sands, Fe2O3 in sands, and MnO in coarse sands (Table 2). The geological origin of the material easily explained these differences between sites, with the occurrence of Fe rich glauconite in the sand fraction at CA (Albian/Cenomanian substratum). Within a site and for a given soil particle size class, the total chemical composition of soil particles was not significantly different between aggregate size classes and soil horizons (data not shown).

3.3 Abundance of aggregate size classes

In the AZ soil, the abundance of coarse aggregates [200–2000 μm] decreased with depth, from 45% in the [0–10 cm] layer to 24% in the [30–45 cm] layer (Fig. 1a). The less represented class was the intermediate class, which represented about 20% of the < 2 mm class (fine earth) in the surface layers [0–20 cm] and slightly increased to reach 28% in the [30–45 cm] layer. The fine aggregates represented 31% in the [0–10 cm] layer, reaching 50% at [20–45 cm] depth. In the surface layer [0–10 cm], coarse aggregates dominated while the finest ones [< 50 μm] dominated in the deeper layers.

At CA, coarse aggregates [200–2000 μm] always represented less than 25% of the < 2 mm class (fine earth), reaching a minimum of 11% in the [10–20 cm] layer (Fig. 1b). The intermediate class [50–200 μm] represented more than 50% of the < 2 mm class (fine earth) in the [0–20 cm] layer. This intermediate class decreased with soil depth but still represented more than 40% in the [30–45 cm] layer. In this layer, the finest aggregate class [< 50 μm] increased to reach 40.5%, so their abundance is equivalent to that of the intermediate class.

3.4 Major element contents of the aggregate size classes

At CA, the highest concentrations of C and N were found in the finest class [< 50 μm] and the lower ones in the intermediate class [50–200 μm] (Supplementary File 3). The C:N ratio was the highest in the coarse aggregate class [200–2000 μm]. At AZ, the same tendency was observed below 10 cm depth, but in the soil surface layer, the concentrations of C decreased with the size of aggregates.

Total and exchangeable Ca and Mg concentrations were always lower at CA than at AZ (except for total Mg at [100–120 cm] depth) (Supplementary File 3). Changes in total Ca concentration according to the aggregate size did not show any clear trend at CA, whereas in AZ intermediate aggregate size class tended to be the most concentrated for each depth.

Table 2 Total analysis (%) of particle size fractions in the < 2 mm class (fine earth) for the soil samples collected at the central pit at the two sites (AZ = Azerailles, CA = Clermont-en-Argonne). Mean and standard deviation values were computed for the whole soil profile (8 horizons per site). Significant differences between sites are mentioned (*5‰; **1‰; ***1‰, Student's t test)

Site—particle size	SiO2%		Al2O3%		Fe2O3%		MnO%		MgO%		CaO%		Na2O%		K2O%		TiO2%		P2O5%		LOI%	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
AZ—clay	47.3	2.1	21.4	0.6	9.9	1.3	0.1	0.1	1.6	0.4	0.0	0.0	0.2	0.0	3.0	0.9	1.2	0.2	0.3	0.1	12.5	1.2
CA—clay	51.5	3.3	17.2	1.4	8.2	0.8	0.0	0.0	1.3	0.3	0.0	0.0	0.3	0.1	2.3	0.2	1.3	0.3	0.1	0.0	13.6	1.5
AZ—fine silt	84.1	3.6	7.1*	1.6	2.0	1.3	0.0	0.0	0.4	0.1	0.2	0.0	1.0	0.3	2.4	1.0	1.1	0.1	0.1	0.0	2.0	0.7
CA—fine silt	86.8	2.4	5.4*	1.0	1.1	0.6	0.0	0.0	0.3	0.2	0.2	0.1	0.9	0.2	1.6	0.2	1.1	0.2	0.1	0.0	1.9	1.2
AZ—coarse silt	88.6	2.7	4.8	0.7	1.4	1.4	0.0	0.0	0.2	0.1	0.3	0.1	0.9	0.2	1.6	0.1	0.8	0.1	0.1	0.1	0.8	0.4
CA—coarse silt	92.0	2.0	3.4	0.4	0.7	0.4	0.0	0.0	0.1	0.1	0.2	0.1	0.7	0.1	1.2	0.1	0.9	0.1	0.0	–	0.8	0.6
AZ—fine sand	86.0*	6.6	4.8**	1.3	3.4***	3.2	0.1	0.1	0.2	0.2	0.1	0.0	0.5	0.2	1.8	0.3	0.3	0.1	0.1	0.1	1.5	1.0
CA—fine sand	94.8*	2.8	1.6**	0.7	0.8***	0.8	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.1	0.6	0.2	0.4	0.0	0.0	–	1.1	0.7
AZ—coarse sand	90.9	0.8	2.0	0.3	3.4*	0.4	0.1**	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.6	0.2	0.1	0.1	0.1	0.0	1.5	0.1
CA—Coarse sand	75.3	11.2	5.1	0.6	9.8*	7.4	0.5***	0.4	0.5	0.1	0.1	0.0	0.3	0.1	1.0	0.1	0.6	0.1	0.3	0.0	3.0	0.0

Exchangeable Ca distribution was different from total Ca in aggregate classes, but exchangeable Ca contents had similar relative trends at both sites: the highest concentrations were measured in the finest aggregates and the lowest one in the intermediate class (Fig. 2), whatever the horizon. At CA, the lowest concentrations of total Mg were found in the intermediate aggregate size class while at AZ no clear trend was observed between total Mg and aggregate size class. At both sites, the highest total Mg concentrations were observed in the finest aggregate size class of the topsoil (0–20 cm). At both sites, the distribution of exchangeable Mg was the same as exchangeable Ca, with the highest concentrations observed in the finest aggregates and the lowest in the intermediate ones (Fig. 2).

At both sites, the lowest exchangeable to total ratios for both Ca and Mg were found in the intermediate aggregate class [50–200 μm] (Supplementary File 3). The highest Caexch:CaTot and Mgexch:MgTot ratios were not observed in the same aggregate class at CA and AZ on the surface horizon: at CA, these ratios were the highest for the finest aggregate class [< 50 μm], while at AZ it was in the coarser class [200–2000 μm].

3.5 Particle size distribution of the aggregate size classes

The results presented in Supplementary File 4 indicated that the distribution of individual particle size in the three aggregate classes was more specific of the aggregate class considered, than of the site. Clays represent 20 to 40% of the finest aggregate size class [< 50 μm] while the lowest (< 10%) was found in the intermediate class [50–200 μm]. Fine silts dominated the fine class [< 50 μm] of both soils; the lowest abundances were observed in the intermediate aggregate size class [50–200 μm] at CA but not at AZ where their abundances increased with the aggregate size. Coarse silts represent 40 to 50% of the intermediate aggregate size class at CA and 25 to 35% at AZ; the lowest abundances were

found in the finest aggregate size class in CA and in the largest class in AZ. Fine sands were more abundant in the intermediate aggregate size class [50–200 μm] than in the other classes. Lastly, coarse sands can only be found in the larger size class, but their proportion in the coarse aggregates was strongly related to the site (less than 2% in the surface horizons of CA vs 43 to 55% at AZ).

3.6 Clay mineralogy of the aggregate size classes

At CA, very weak differences appeared after normalization of the diagrams of the clay fraction by the illite intensity peak (Supplementary File 5). This normalization was carried out after the EG treatment and/or after [Tamura + K + 550 °C] treatments, for the [< 50 μm] and [50–200 μm] aggregate classes. Some complex interstratified mineral belonging to the beidellite-illite type would vary according to aggregate class. The fine clay fraction (< 0.1 μm) XR traces showed that swelling clays present in the fine and coarse aggregates were not detected in the intermediate class [50–200 μm] (data not shown).

At AZ, some small differences appeared after normalization of the diagrams on the treatment [Tamura + K + heating at 550 °C] of the clays from the [<50 μm] class, which would refer to chlorite stability (Supplementary File 5). The fine clay fraction (< 0.1) revealed the occurrence of some swelling particles in the fine and coarse aggregate classes, but not in the intermediate size class [50–200 μm] (data not shown).

3.7 Multivariate analysis

A multivariate analysis which summarized the physical and chemical properties of the two soils is presented in Fig. 3. The F1 and F2 axis explained 87% of the total variance and discriminated satisfactorily the two soils and their respective horizons. CA soil upper horizons were related to the coarse silt fraction characteristic while the coarse sand fraction discriminated the AZ soil upper layer. Organic C opposed to clay on
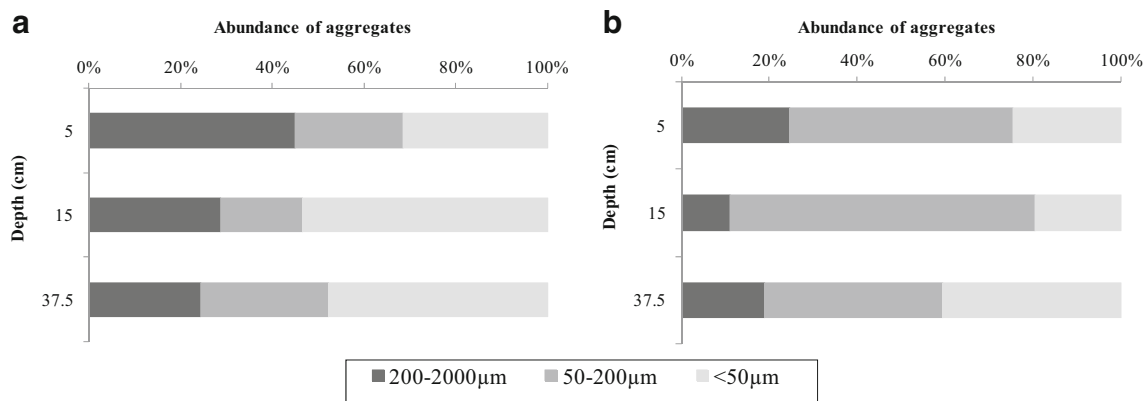

Fig. 1 Abundance of aggregate classes (200–2000 μm; 50–200 μm; < 50 μm) at the three sampled depths (0–10 cm, 10–20 cm, and 30–45 cm) at Azerailles (A) and Clermont-en-Argonne (B). Samples were collected in one pit per site; four replicates (one per pit face) were collected at each depth and pooled in the field
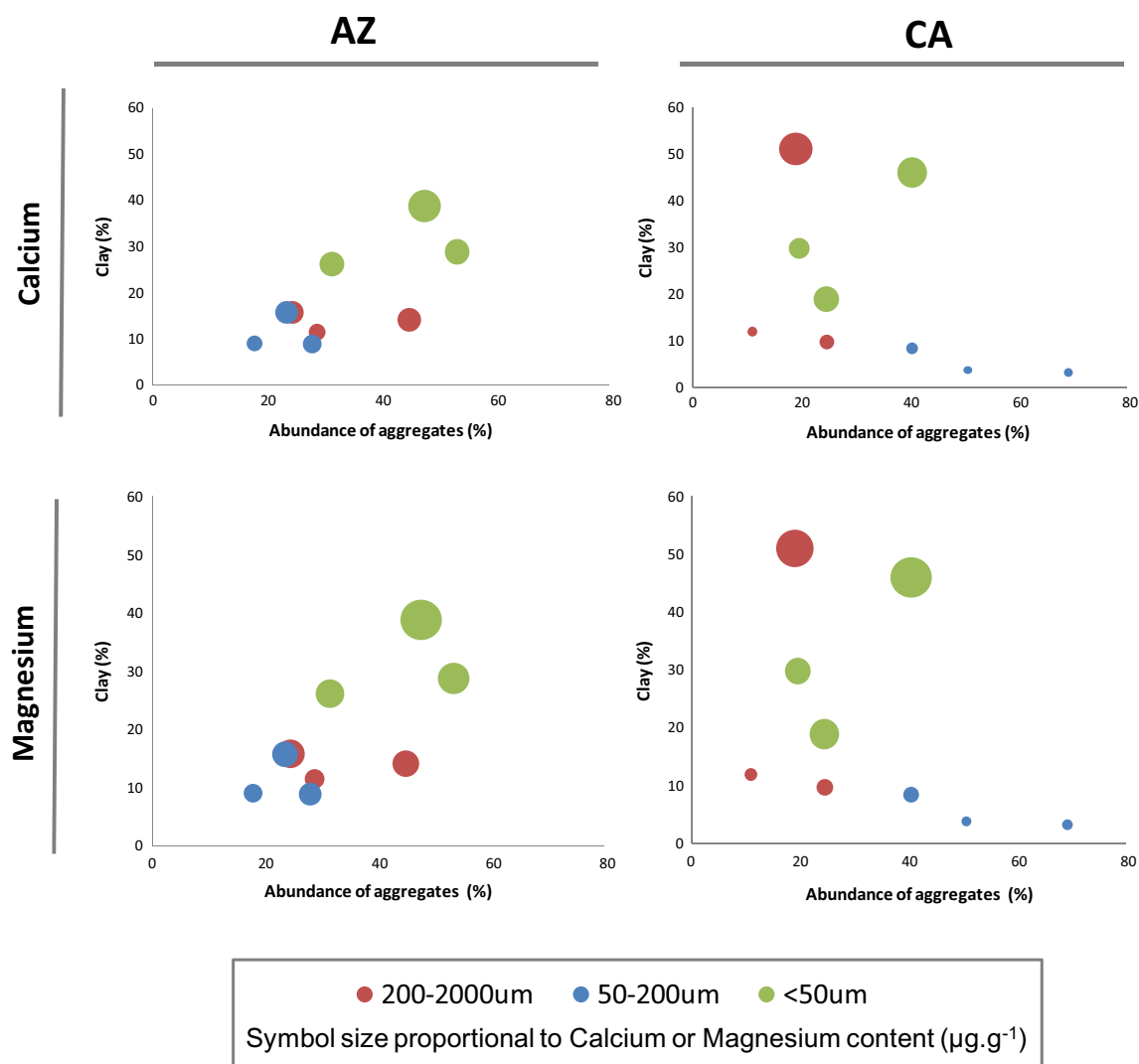
Fig. 2 Relationships between the clay content of an aggregate class, the abundance of the class and its concentration in exchangeable calcium or magnesium at the two sites. AZ = Azerailles; CA = Clermont-en-

Argonne. Samples were collected in one pit per site; four replicates (one per pit face) were collected at each depth and pooled in the field. Symbol size is proportional to calcium or magnesium content

the F2 axis contributed to discriminate the horizon depths. The CA soil was related to the intermediate aggregates while the AZ soil was related to the coarse and fine aggregates.

3.8 Relationship between measured and estimated CEC

The results presented in Supplementary File 6 showed satisfactory agreement between the CEC measured on the fine earth and the CEC estimated from the aggregate class. The difference in sampling and method used could explain the limited discrepancy and tended to validate our approach. Nevertheless, the two outliers, corresponding to the AZ sub-surface samples ([10–20 cm] and [30–45 cm] layer), suggested that in some cases, soil analysis of the total < 2 mm class (fine earth) or separate aggregate classes does not lead to

the same result. We may hypothesize that the geometry of the efficient ion-exchanger (i.e., accessibility of surfaces) changed between aggregates and fine earth.

4 Discussion

In the framework of this study, we developed a soil aggregate separation method adapted to forest soils and acidic soils in particular. Due to the lengthy aspect of this separation method, we were unable to apply it to multiple replicates of soil samples for each investigated depth (0–10, 10–20, and 30–45 cm). However, to our knowledge, few studies have investigated and measured soil aggregate classes in forest soils making this dataset, which combines different approaches, rather unique and original. The study of the fine earth shows that the Ca

Fig. 3 Results of the principal component analysis on aggregate characteristics summarizing the discrimination between the two soils. The *x* and the *y* axis represent respectively the first and second factor of the principal component analysis. The percentage of explained variance for each principal component is indicated in brackets. The contributing variables are colored in red. AZ = Azerailles; CA = Clermont-en-Argonne; CEC = cationic-exchange capacity; DCB = dithionite-citrate buffered with sodium bicarbonate (Mehra and Jackson 1960); Exch = exchangeable. Abundance of aggregate classes (200–2000 μm; 50–200 μm; < 50 μm) are supplementary variables
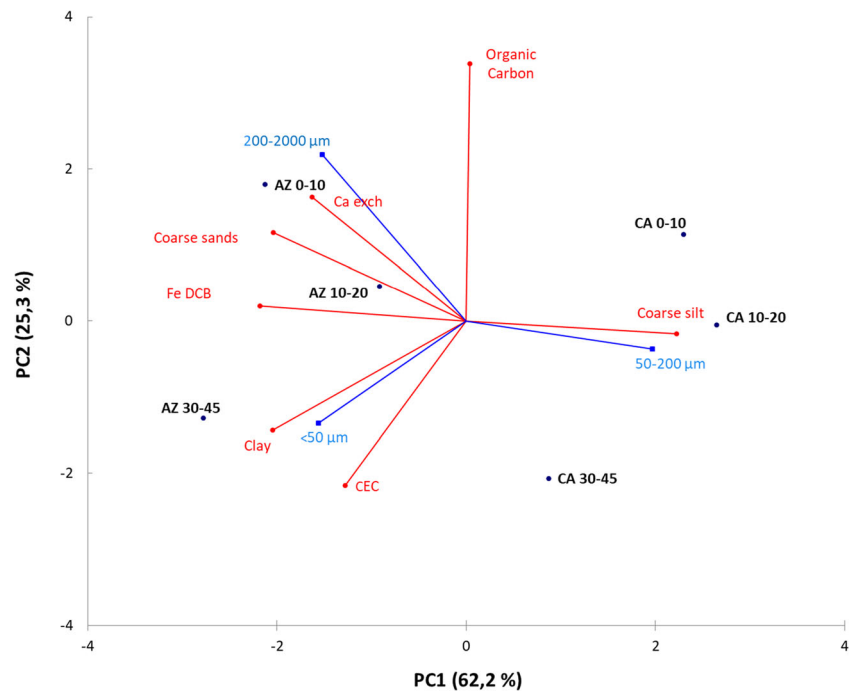
and Mg availability in the upper soil layers assessed through ion exchange were significantly different between sites. Although no statistical tests could be performed to support the observed differences in soil aggregation between both studied sites, these differences were large and enable to discuss the potential relations between soil aggregation and nutrient cation availability to tree uptake at these two sites.

4.1 Differences in the soil aggregation status between the two soils

The gentle method used in this study for separating aggregates allowed us to observe differences in terms of aggregation, between the two soils. The intermediate class [50–200 μm] dominated at CA while the coarse and fine aggregate classes were dominant at AZ. Several parameters detailed below may contribute to explaining these differences.

Firstly, the low clay content at CA may limit the cement effect of clays (Horn 1990) and the occurrence of a low, but significant amount of swelling clays in coarse and fine aggregate classes at CA may decrease aggregate stability. Singer (1994) and Stern et al. (1991) observed similar patterns: a low rate of smectite associated with kaolinite and illite decreased the aggregate stability. The relatively low content of Fe and Al oxides and the lower soil C content and organic matter quality (C:N) at CA compared with AZ could also limit the efficiency of cementation.

Secondly, the pH and base cation saturation were slightly lower in the upper soil layer at CA compared to AZ. This small difference was nevertheless important for soil biogeochemistry: soil pH at CA was below the first pK of the Al hydrolysis

reactions. The stability of the Al-monomeric chemical form strongly increases below pH 4.5 (Zelazny and Jardine 1989) impacting both geochemical (CEC saturation) (Julien et al. 2007) and biological processes (earthworms, microbial activity) (Hobbie et al. 2006). Both Al and Ca cations are flocculating agents; however, depending on clay mineralogy, their different hydrolysis constants could lead to changes in the flocculation process (Zelazny and Jardine 1989; Haynes and Naidu 1998). The greater abundance of exchangeable Al at CA (Al:Ca ratio was twofold higher at CA) could thus induce differences in terms of aggregation.

Lastly, the soil acidity at CA led to the disappearance of anecic earthworms (Bottinelli et al. 2014) known to act as engineers of the soil structure. Roots and fungi were then the only biological agents contributing to aggregation, essentially during the growing season. Conversely, at AZ, the higher soil pH and exchangeable Ca and Mg pools allowed the occurrence of a higher biological activity (e.g., anecic earthworms were observed Bottinelli et al. 2014 and Capowiez et al. 2015).

4.2 Assessing the dynamic of soil aggregation

Previous studies on soil aggregate dynamics suggest that the fine and intermediate aggregate classes are formed from the collapsing of macro-aggregates (Piccolo et al. 1997; Bronick and Lal 2005; Reichert et al. 2009). At CA, the C:N ratios of fine aggregates do not suggest the presence of organic cement resulting from biological activity (von Lützow et al. 2007). Moreover, the intermediate aggregate class had low Corg content, with C:N values between those of coarse and fine classes,

and a low clay content, without any very fine clays. These findings agree with the hypothesis that intermediate aggregates at CA originated from the collapsing of macro-aggregates. The soil resistance to penetration was measured at both sites (data not shown). The soil mechanical properties estimated from this method are in agreement with a collapsing structure at CA (data not shown).

n the AZ soil, our results concurred with the concept of Christensen (1992): the fine aggregates are expected to be enriched in evolved and protected organic matter (Balesdent et al. 2000; Oades and Waters 1991; Schmidt et al. 2011; Six et al. 2004) and in reactive clay particles. The fine aggregates at AZ had the highest clay content, and the lowest C:N value, without nevertheless having the highest Corg content. The coarse aggregates are expected to be enriched in organic matter belonging to the active pool because the fresh detritus are rapidly decomposed by microbes (Oades 1984), with none or few reactive minerals (sand or silt material with low surface area and low bonding affinities with organic material) (von Lützow et al. 2007). This is consistent with our results: the coarse aggregates at AZ had the highest Corg content and lower CEC than fine aggregates.

Though the dynamics of aggregation-desegregation were difficult to assess with our dataset, the physical and chemical properties of the different aggregate classes suggest that soil aggregation was more stable at AZ than at CA. Interestingly, clay content and mineralogy appeared to be key elements for aggregate formation and stability at our study sites. However, the present data are insufficient to conclude on this hypothesis and further investigations would be necessary.

4.3 Consequences for nutrient cation retention

Clay content and mineralogy, as well as organic matter content and quality, are key parameters that contribute to the CEC and consequently to the nutrient cation retention in soils. At both sites, there was no evidence of a relation between aggregate size and clay mineralogy: contrarily to what was observed by Fernández-Ugalde et al. (2013), our results suggested that neither the clay type nor specific clay properties were associated with aggregate size classes. However, clay content clearly appeared as a driver for nutrient cation retention in the different aggregate classes of the loamy upper soil horizons: correlation coefficient values between clay and nutrient cations were always significant at CA and AZ and greater than 0.85 (data not shown). Paradoxically, there was only a limited effect of Corg on the retention of nutrient cations (correlation coefficient values between Corg and nutrient cations for AZ and CA, were all nonsignificant and close to 0).

The composition of the soil cationic exchangeable pool which depends on the nature (organic/mineral) of the cationic exchanger, varied between the soil aggregate classes and sites.

Soil aggregate data agree with the hypothesis that Mg and Ca are more efficiently retained in the surface soil layers at AZ compared to CA. At AZ, fine aggregates [0–50 μ] rich in clay and Corg dominated in these soil layers and soil aggregates were likely to be more stable than at CA. At CA, the clay content was lower than at AZ and clay minerals at CA may be less reactive (presence of clays of the Fe-beidellite type, poorly reactive according to Robin et al. 2015). Although Ca and Mg cycled in the ecosystem through atmospheric deposition and litterfall were of the same magnitude as at AZ (Bedel et al. 2016) the [50–200 μm] aggregates dominating at CA did not seem to efficiently retain the nutrient cations. In acid forest ecosystems, biological cycling is often of paramount importance as it allows to maintain nutrients in the topsoil. However, the nutrient recycling efficiency depends among other things on the nutrient retention capacity of soils: at CA, this capacity seems to be low in the topsoil and linked to the aggregation status. In our soils, we may thus consider that the study of soil aggregation helped to understand the nutrient cation availability to tree uptake. However, the reduced number of study sites does not allow to conclude on this hypothesis and further studies need to be done to gain insight on the link between soil aggregation and chemical fertility in forest ecosystems.

5 Conclusion

The investigation on soil aggregation was relevant to clarify the biogeochemical functioning of the two studied soils, which are described as the same soil type, but which nevertheless have different nutrient cation availability in the upper soil layers.

Our results highlighted that clay content in the < 2 mm class (fine earth) may be used as an indicator of soil aggregation status while clay mineralogy is helpful for understanding their stability. We showed that fine aggregates [0–50 μ] rich in clay and Corg dominated at AZ while the intermediate aggregate class [200–50 μm] poor in clay and in Corg dominated at CA. Lastly, our findings suggested that soil aggregation is more stable at AZ than at CA.

Even with the same atmospheric deposition rates and the same fluxes of nutrient cations in litterfall, the two compared ecosystems behaved very differently in terms of nutrient cation retention: when compared to AZ, the CA soil seems unable to fix nutrient cations. We suggested that the dominant aggregate class [200–50 μm] at CA, less stable and poor in reactive minerals and organic components, may mitigate the retention of nutrient cations by ion-exchange.

Though the results of this local case study do not enable to conclude at large scale, they agree with the hypothesis that soil aggregation plays an important role in nutrient cation availability to tree uptake.

Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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