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Detection of active oxalate–carbonate pathway ecosystems in the Amazon Basin: Global implications of a natural potential C sink

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ABSTRACT

The oxalate–carbonate pathway (OCP) is a biogeochemical process, which has been described in *Milicia excelsa* tree ecosystems of Africa. This pathway involves biological and geological parameters at different scales: oxalate, as a by-product of photosynthesis, is oxidized by oxalotrophic bacteria leading to a local pH increase, and eventually to carbonate accumulation through time in previously acidic and carbonate-free tropical soils. Former studies have shown that this pedogenic process can potentially lead to the formation of an atmospheric carbon sink. Considering that 80% of plant species are known to produce oxalate, it is reasonable to assume that *M. excelsa* is not the only tree that can support OCP ecosystems.

The search for similar conditions on another continent led us to South America, in an Amazon forest ecosystem (Alto Beni, Bolivia). This area was chosen because of the absence of local inherited carbonate in the bedrock, as well as its expected acidic soil conditions. Eleven tree species and associated soils were tested positive for the presence of carbonate with a more alkaline soil pH close to the tree than at a distance from it. A detailed study of *Pentaplaris davidsmithii* and *Ceiba speciosa* trees showed that oxalotrophy impacted soil pH in a similar way to at African sites (at least with 1 pH unit increasing). African and South American sites display similar characteristics regarding the mineralogical assemblage associated with the OCP, except for the absence of weddellite. The amount of carbonate accumulated is 3 to 4 times lower than the values measured in African sites related to *M. excelsa* ecosystems. Still, these secondary carbonates remain critical for the continental carbon cycle, as they are unexpected in the acidic context of Amazonian soils. Therefore, the present study demonstrates the existence of an active OCP in South America. The three critical components of an operating OCP are the presence of: i) local alkalinization, ii) carbonate accumulations, and iii) oxalotrophic bacteria, which were identified associated to the oxalogenic tree *C. speciosa*.

If the question of a potential carbon sink related to oxalotrophic–oxalogenic ecosystems in the Amazon Basin is still pending, this study highlights the implication of OCP ecosystems on carbon and calcium biogeochemical coupled cycles. As previously mentioned for *M. excelsa* tree ecosystems in Africa, carbonate accumulations observed in the Bolivian tropical forest could be extrapolated to part or the whole Amazon Basin and might constitute an important reservoir that must be taken into account in the global carbon balance of the Tropics.

1. Introduction

At the turn of the last century, tropical forest lumberjacks discovered unexpected “stones” in tissues of iroko trees (*Milicia excelsa*). These mineral inclusions were identified as calcium carbonate ($CaCO_3$; Campbell and Fisher, 1932). A few decades later, calcite-cemented sandstones were described in wounds on trunks, as well as associated with the rhizosphere of a *M. excelsa* tree in Ivory Coast (Carozzi, 1967). This $CaCO_3$ accumulation is totally unexpected as the soils in these tropical areas are acidic, with pH values varying between 4.3 and 6.0 (Leneuf, 1959). Investigations in the domains of microbiology and geology have recently been conducted in order to understand how such a biomineralization process can occur. These studies aimed at testing the hypothesis that a specific pathway, the oxalate–carbonate pathway (OCP), is at the origin of such pedogenic carbonate accumulations (e.g. Bravo et al., 2011; Cailleau et al., 2011; Martin et al., 2012). This pathway was first proposed as a model, based on chemical equilibrium between oxalate and carbonate species, in the context of chalk weathering (Verrecchia, 1990; Verrecchia and Dumont, 1996). Historically, this model is linked to the isolation of oxalate-oxidizing bacteria in soils, as well as to the demonstration that this bacterial metabolism

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leads to an increase in pH and a concomitant release of carbon dioxide in the aqueous medium (Jayasuriya, 1955). Indeed, studies based on *M. excelsa* trees in Ivory Coast and Cameroon clearly demonstrated that pedogenic carbonates, accumulated in the *M. excelsa* rhizosphere, constitute the final product of the oxalate consumption by soil oxalotrophic bacteria (Braissant et al., 2002, 2004; Cailleau et al., 2005).

Under appropriate geological settings, the OCP acts as an atmospheric C sink. This is the case when calcium-sequestering carbon (C) as pedogenic $CaCO_3$ originates from a different source than an inherited $CaCO_3$ according to Elbersen et al. (2000). An amount of 8 tons of $CaCO_3$ (around 1 ton of pure carbon) was quantified in a soil associated with a 170 year-old *M. excelsa*, constituting an important C sink (Cailleau et al., 2004, 2011). Considering the geographical distribution of *M. excelsa* in Africa and their potential of C trapping through the OCP, it is reasonable to consider that this type of C sink should not be ignored in the global C cycle of the Tropics. Results obtained in the past few years have allowed temporal (Cailleau et al., 2011) and theoretical models (Verrecchia et al., 2006) of the processes involved in the *M. excelsa* ecosystem to be developed.

All the studies carried out so far have only focused on the *M. excelsa* tree (Braissant et al., 2004; Bravo et al., 2013; Cailleau et al., 2004, 2005, 2011). However, oxalate is a common photosynthetic by-product in the Plant Kingdom (Khan, 1995; Pobeguin, 1943). It can be assumed that oxalotrophic ecosystems associated with other oxalogenic trees must exist elsewhere on Earth. In order to identify an active oxalogenic–oxalotrophic system, several parameters must be considered: i) alkalinization of the soil close to the studied oxalogenic plant, which is the first consequence of the OCP; ii) the presence of carbonate, the ultimate result of OCP, if the local environmental or micro-environmental conditions reach the stability pH for calcite; and, iii) the presence of the biological agents as well as the initial products (i.e. oxalotrophic bacteria and oxalate-producing organisms). All these elements support a site with an effective OCP. As a consequence, two specific initial conditions should exist in the field. First, the investigated area must present acidic soils on which the alkalinization due to oxalotrophy can be identified. Secondly, the absence of inherited carbonate in the soil and the basement is fundamental to accurately determine the final consequence of an active OCP ecosystem, i.e. the presence of $CaCO_3$.

The aim of the present study is twofold: i) to make an inventory of trees in the Amazon Basin presenting some of the characteristics associated to an active OCP, such as the presence of unexpected alkaline soil conditions among acidic tropical soils and the presence of $CaCO_3$ on the tree and/or in the soil; and ii) to validate a field methodology for the screening and characterization of OCP systems that can be applied worldwide.

2. Material and methods

2.1. Site settings

During this study, an important exploration phase was carried out in the Alto Beni province of Bolivia (Fig. 1) in order to find oxalogenic trees. As part of the Tertiary Andean intracratonic range, this area constitutes the western boundary of the sub-Andean zone, located between the Brazilian shield and the Hercynian range of the Eastern Cordillera. The valley of the river Río Alto, where the exploration phase was carried out, has its southwestern flank aligned with a reverse fault oriented SE–NW. This fault divides the southwestern flank of the valley, composed of Palaeozoic formations of the Eastern Cordillera, from the northeastern Cretaceous deposits. The studied sites, mainly northwards of the Sapecho village, are located on late Cretaceous to early Cenozoic formations, mainly composed of sandstones, considered as carbonate-free deposits according to Elbers (1995). The only soil map of the area describes three types of soils with the exception of soils developed on young terraces of river Río Alto Beni (Elbers, 1995). According to the WRB classification (IUSS, 2006), Cambisol, Lixisol, and Acrisol are present in the studied area. Following Köppen's climate classification, Sapecho corresponds to an Aw type, i.e. a tropical wet and dry or savannah climate. The climate becomes of type Af, i.e. a tropical rainforest climate as at Entre Ríos, at altitudes higher than 550 m. At Sapecho, precipitations range from 1300 to 1600 mm/yr.

2.2. Field screening

Four sites in the area around Sapecho and along the Río Quendeque in Bolivia (Fig. 1; sites A, B, C, and D) were included in the sampling strategy during the exploration phase in order to find mineralizing trees. In this first step, a systematic screening for the presence of the OCP was conducted around large trees found in the studied area. A simple set of tests was carried out, consisting of an acid test with 10% HCl on bark, top-, and 10 cm-deep soil samples in order to detect the presence of carbonates, as well as the measurement of the topsoil pH using a pH determination kit (Hellige pH meter) for soils, near and at distance from the tree trunk. The second test was used to determine if an unexpected alkaline pH was present near a tree compared to the distant soil, where the pH should be acidic, considering the type of soil normally occurring in this area (tropical oxisols).

Plant tissue samples collected during this first phase were air-dried in order to prevent any decay process. An ajipa tree (*Pentaplaris davidsmithii*) was selected at site A (approximately 15°33′00.00″S; 67°20′28.00″W). It had a diameter at breast height (i.e. DBH) of 1.20 m and the tree itself was about 30 m high. It was growing on a slope of roughly 20° and two soil profiles were dug, one close to the trunk (A1) and the other 13 m away (A2), on the same isohypse (contour line). At site B (approximately 15°33′15.00″S; 67°20′00.00″W), a flor de mayo tree (*Ceiba speciosa*) was selected (DBH 1.30 m, height about 30 m). The tree was located on a roughly 5 to 10° slope. Two soil profiles were investigated, one near the trunk (B1) and the other 15 m away (B2), at approximately the same altitude. Samples were collected in each identified soil horizon. In addition, rock samples were collected at site C, a spot called *Cumbre de Marimonos*, in order to determine the nature of the bedrock. Various plant samples were harvested during the exploration phase at site D, near the confluence of Río Quendeque and Río Alto Beni to build a non-exhaustive database of plant mineralogical content.

2.3. Soil analyses

Approximately 500 g of soil were collected from each soil horizon, air-dried in the field, and sieved to 2 mm for further laboratory analyses. When needed, soil samples were powdered using a mortar grinder RM 100 (Retsch). All plant samples were air-dried in the field and powdered using a rotor mill pulverisette 14 (Fritsch).

Preliminary analyses focused on confirming the presence or absence of OCP in Bolivia. One of the major changes induced by the OCP is an increase in pH of upper soil horizons: consequently, pH_{H2O} was measured using a Metrohm 827 pH lab. In addition, carbonate content was evaluated using a back titration method. Briefly, 0.5 N H_2SO_4 was added to 1 g of a 2 mm sieved soil sample and 0.5 N NaOH was used to back-titrate the resulting solution until a pH of 7. Carbonate content is expressed in percentage of dry weight.

The oxalate content was determined using an enzymatic method for plant and soil samples (adapted from Certini et al., 2000). Twenty-five milliliters of HCl 1 N were added to 10 g of dried powdered sample for an overnight reaction. Then, pH was adjusted to 2 with a 6 N HCl solution. The resulting solution was filtered to 2 μm with a Nalgene syringe. The filtrate was analyzed using an oxalate determination kit (Sigma). This test works with the coupled action of an oxalate oxydase and a peroxydase in order to obtain a colorimetric measurement of the oxalate concentration. Measurements were carried out using a spectrophotometer (Perkin-Elmer) at 590 nm. Final results are expressed in mg of oxalate per kg of soil.

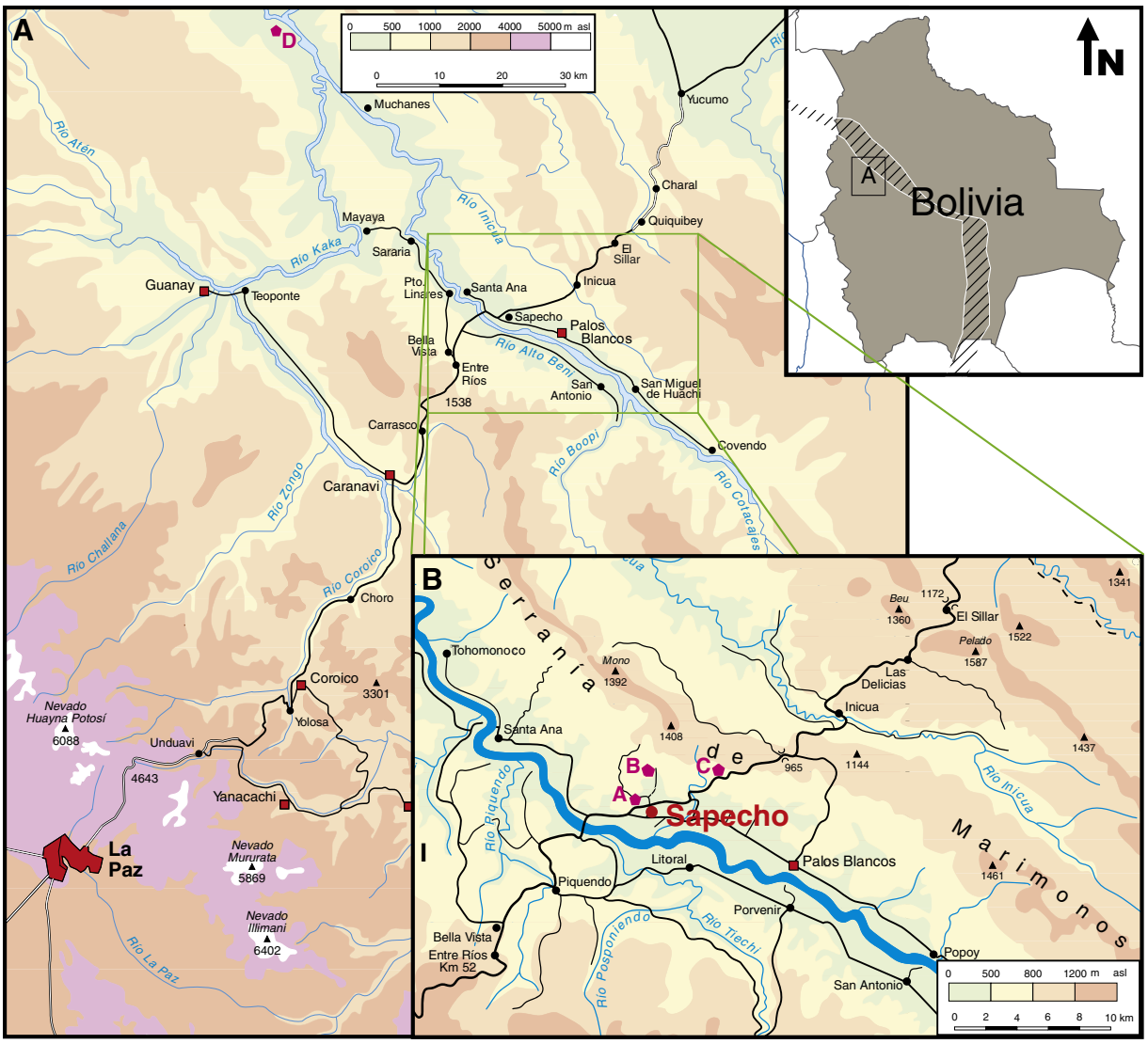

Fig. 1. Location map of the four sites (A, B, C, and D) investigated in the Alto Beni (Bolivia). The hatched area identifies the Subandean zone. A: general location including Quendeque (site D at the top of the map). B: close-up map of the Sapecho area where A, B, and C sites are located.
Modified after Elbers (1995) and Espurt et al. (2011).

Soil organic matter content was determined by loss on ignition (LOI). Approximately 10 g of 105 °C oven dried soil was precisely weighted in a crucible and put into an oven at 450 °C for 4 h. After cooling, the crucible was weighed in order to determine the weight loss.

2.4. Mineralogical analyses

Rock samples from site C were crushed using an agate mortar. Leaves and wood samples were collected on living trees using axes and then air-dried to prevent fungal development. The same procedure was used for wood samples collected on the ground.

Mineralogical determination of rock, soil, and plant samples was performed using a XRD 2000 powder diffractometer (Scintag). Diffractograms were analyzed using the Macdiff software (Petschick, 2010). Grain size distribution was carried out as follows: 20 g of sample were first decarbonated with 10% HCl in a water bath at 80 °C. Caution was taken to maintain the obtained pH above 2–3 to avoid clay denaturation (a 0.1 N NaOH solution was used to adjust pH). Samples were washed several times using deionized water. Organic matter was removed using H_2O_2 in a warm water bath and the pH kept to 8–8.5 in order to catalyze the organic matter oxidation. Samples were washed several times using deionized water. Dispersion of the samples was carried out by addition of 20 mL of 40 g/L $(NaPO_3)_6$. Samples were agitated for 17 h. Finally, samples were sieved at 1 mm, 500 μm, 250 μm, 125 μm, and 63 μm. Smaller fractions were kept for grain size laser analysis using a CIS-1 particle analyser (Galai). Data were then compiled between the three following grain size classes: clay (<2 μm), silt (2 μm < × < 63 μm), and sand (>63 μm).

2.5. Microbiological analysis

Seven soil samples were collected at the *C. speciosa* site (site B) in order to assess the numbers of total cultivable bacteria, as well as total cultivable oxalotrophic bacteria: six samples from soil profile B1 (S6, S5, S4, S3, S2, and S1 at 2, 30, 50, 60, 100, and 130 cm deep, respectively) and one sample from soil profile B2 (S7 at 2 cm deep). Soil samples for microbiological purposes were collected using sterile tubes during the last day of the sampling mission. They were maintained at room temperature and then kept at 4 °C upon the arrival to the laboratory and prior to the analyses. Two grams of wet soil were mixed with 20 mL of 1% $(NaPO_3)_6$ and homogenized using an Ultra thurrax (IKA) at 19,000 rpm for 1 min. Resulting soil suspensions were then diluted in a 0.9% saline solution down to 10^{-6} in triplicate. 10^{-3} to 10^{-6} diluted suspensions were plated on two different media: i) TSA 1/10 + cycloheximide 50 ppm to

assess the number of total cultivable bacteria, and ii) bi-layered Schlegel AB (Aragno and Schlegel, 1992) + CaC_2O_4 7 g/L to assess numbers of total cultivable oxalotrophic bacteria. Plates were incubated between 3 and 10 days at 30 °C and the number of colony forming units (CFU) was then counted. Furthermore, in order to evaluate the impact of oxalotrophic bacteria on pH, soil suspensions were also incubated in serial dilutions (down to 10^{-9}) for 20 days at 30 °C in microplates with Ca-oxalate (Caox), as the sole C source, and a pH indicator (liquid Schlegel AB + CaC_2O_4 7 g/L + 3% of universal pH indicator).

3. Results

3.1. Soil description

3.1.1. Site A

Soil and humus forms have been described using guidelines from the WRB (IUSS, 2006) and Jabiol et al. (2013), respectively. Soil profile A1 is located close to the trunk of a *P. davidsmithii* tree and is 300 cm deep (Fig. 2A1). Because of the presence of large roots of the *P. davidsmithii* tree, some parts of the upper soil could not be sampled. The litter layer of this soil is characterized by both an OL and a discontinuous OH horizons. The A horizon does not reach 10 cm in depth, and another A horizon (of juxtaposition) is observed from 25 to 30 cm deep in cambic horizons (absence of clay illuviation). Texture is silty to silty–loamy (Fig. 3). This soil profile is characterized by an important presence of fine roots in the upper 30 cm. The pH is relatively stable all along the profile and ranges from 7.2 to 8 (Fig. 2A1), the topsoil being more alkaline. Carbonate content varies from 1.7 to 6% (Fig. 2A1). The lowest values occur between 40 cm and 150 cm deep. Highest values are observed in the deepest part of the profile, below 210 cm. In the topsoil, high values can reach up to 5%. Present in an area described as dominated by Lixisol and chromic Cambisol (Elbers, 1995), the presence of carbonate, the absence of clay accumulations, as well as the soil's yellowish color, surprisingly define this soil as a Cambisol (Calcaric) (IUSS, 2006).

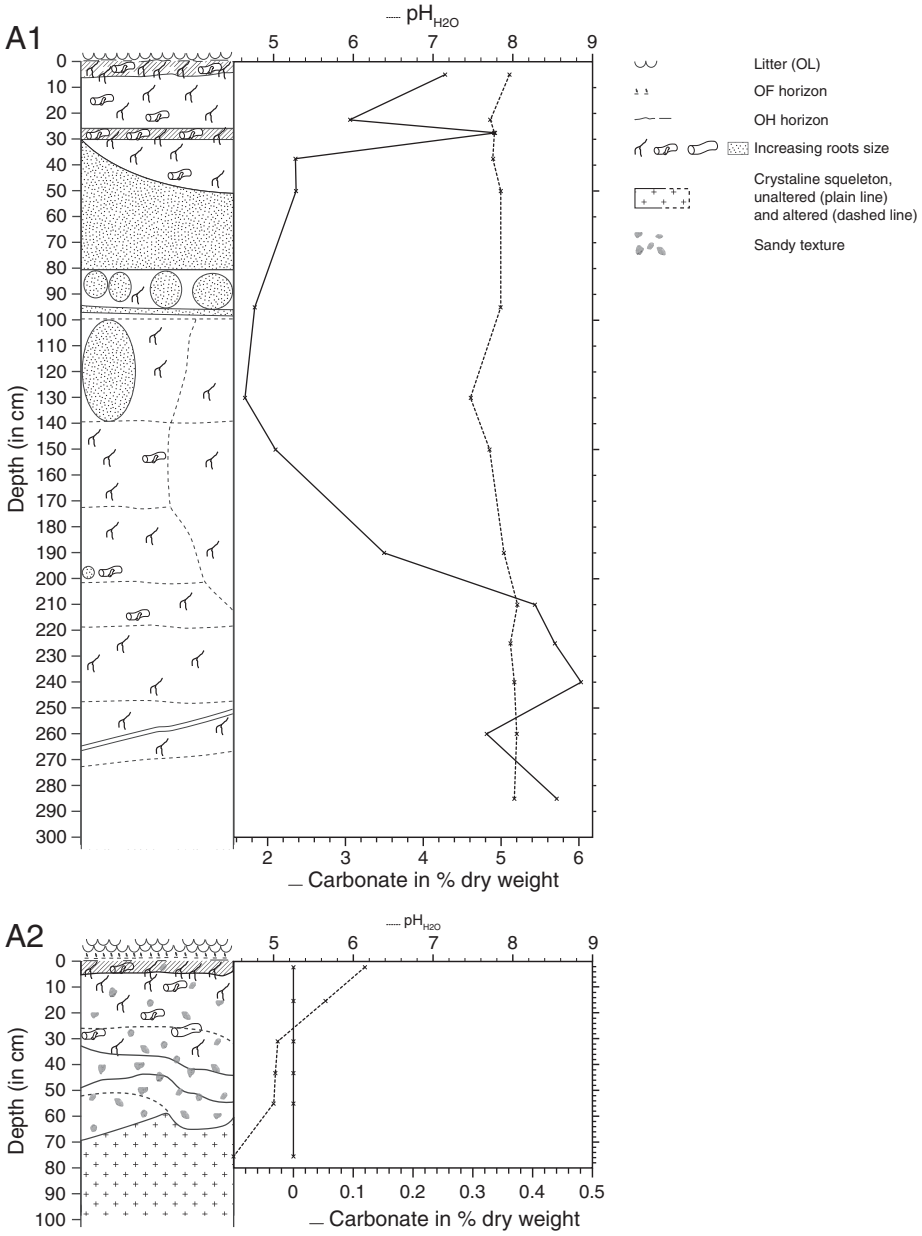

Fig. 2. Sketches of A1 and A2 soil profiles at the *Pentaplaris davidsmithii* tree station. pH_{H2O} variations along the two soil profiles are represented by the continuous line while the carbonate content in % dry weight is represented by the dashed line.

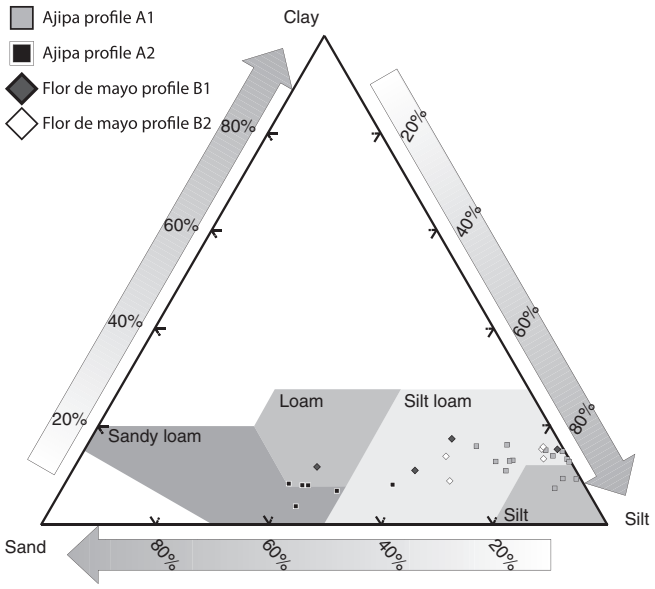

Fig. 3. Ternary diagram of grain size distribution observed in the four soil profiles.

Soil profile A2 is located at 14 m from soil profile A1 and is 100 cm deep (Fig. 2A2). The litter layer is characterized by well developed OLn, OLv, and OF as well as discontinuous OH horizons. The A horizon is observed in the top 5 cm of the soil profile. Fine roots are present in the top 40 cm, but are more developed in the A horizon. The texture was slightly coarser throughout the soil profile compared to A1 (sandy–loamy to silty–loamy; Fig. 3). The pH is acidic in all horizons (from 4.5 to 6.2; Fig. 2A2). Carbonate is absent throughout the soil profile. These characteristics are typical of a cambic diagnostic horizon, which defines this soil as a Cambisol.

3.1.2. Site B

Soil profile B1 is located near the trunk of a *C. speciosa* tree and is 130 cm deep (Fig. 4B1). Tree roots are locally present, directly overlying the red sandstone soil parent rock. Only a discontinuous OL horizon is observed. The limit of the A horizon varies between 10 and 30 cm in depth. Roots are mostly observed in the upper layer of the soil profile (up to 50 cm deep), even if large roots are still present down to 100 cm of depth. The soil texture is loamy to silty–loamy (Fig. 3). This profile has a relatively stable pH and ranges from 7.4 to 7.7 (Fig. 4B1). Carbonates are present all along the soil profile (1.4 to 3.6% weight), but in higher amounts in the upper third (Fig. 4B1). The red sandstone does not react to HCl. This soil is identified as a Cambisol (Calcaric) (IUSS, 2006).

Soil profile B2 is located 15 m from the *C. speciosa* tree and is 100 cm deep (Fig. 4B2). This soil displays a well developed OL and discontinuous OF and OH horizons. The A horizon is 15 cm thick, the upper 5 cm containing more organic matter (OM) than the remaining 10 cm. Roots, mainly small ones (millimeter size), are present in the upper half of the soil profile. The texture is silty–loamy (Fig. 3). The soil pH is neutral at the topsoil (up to 6.5) and more acidic in the deepest part (down to 5.1). Carbonates were not detected in the four deepest samples (from 10 to 85 cm deep), while the topsoil sample (2 cm deep) is characterized by a very low concentration of 1.4% of dry mass (Fig. 4B2). Due to its reddish color, and in agreement with Elbers (1995), this soil is defined as a Cambisol (Chromic) (IUSS, 2006).

3.2. Soil oxalate content

X-ray diffraction analyses did not allow the presence of oxalate (Fig. 5) to be detected. Thus, a more sensitive approach using enzymatic kits was used. Results for the four soil profiles are given in Table 1. In soil profile A1, the oxalate content ranged from 0.2 to 26.8 mg/kg of soil. Highest values were observed in the topsoil and the lowest ones in the deepest horizons. The trend is the same in soil profile A2 with values

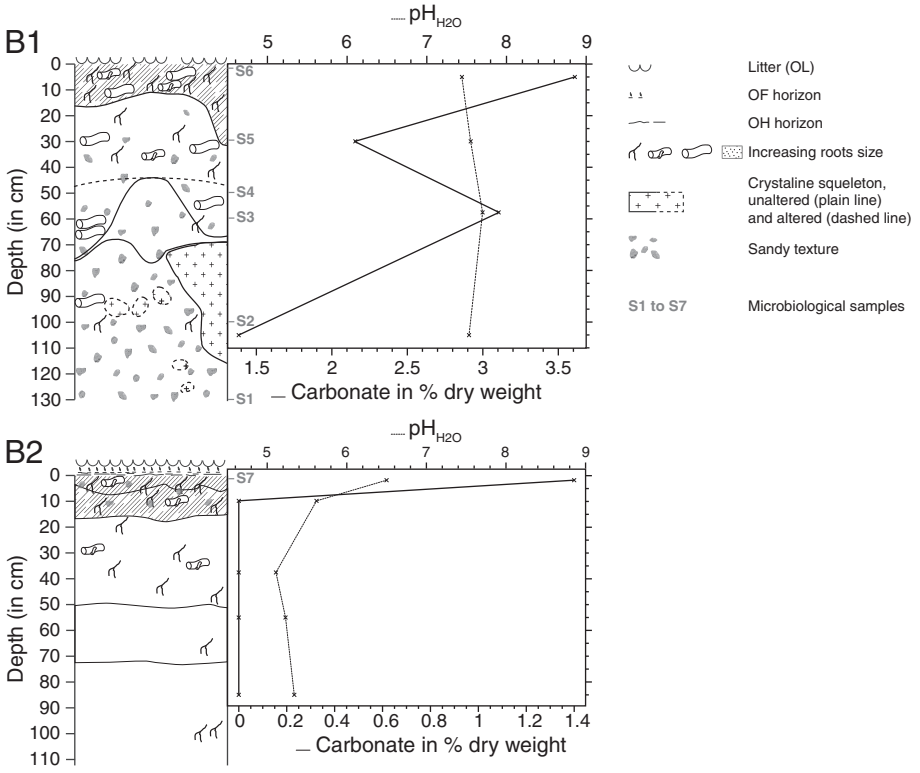

Fig. 4. Sketches of B1 and B2 soil profiles at the *Ceiba speciosa* tree station. pH_{H2O} variation along the two soil profiles is represented by the continuous line, while the carbonate content in % dry weight is represented by the dashed line.

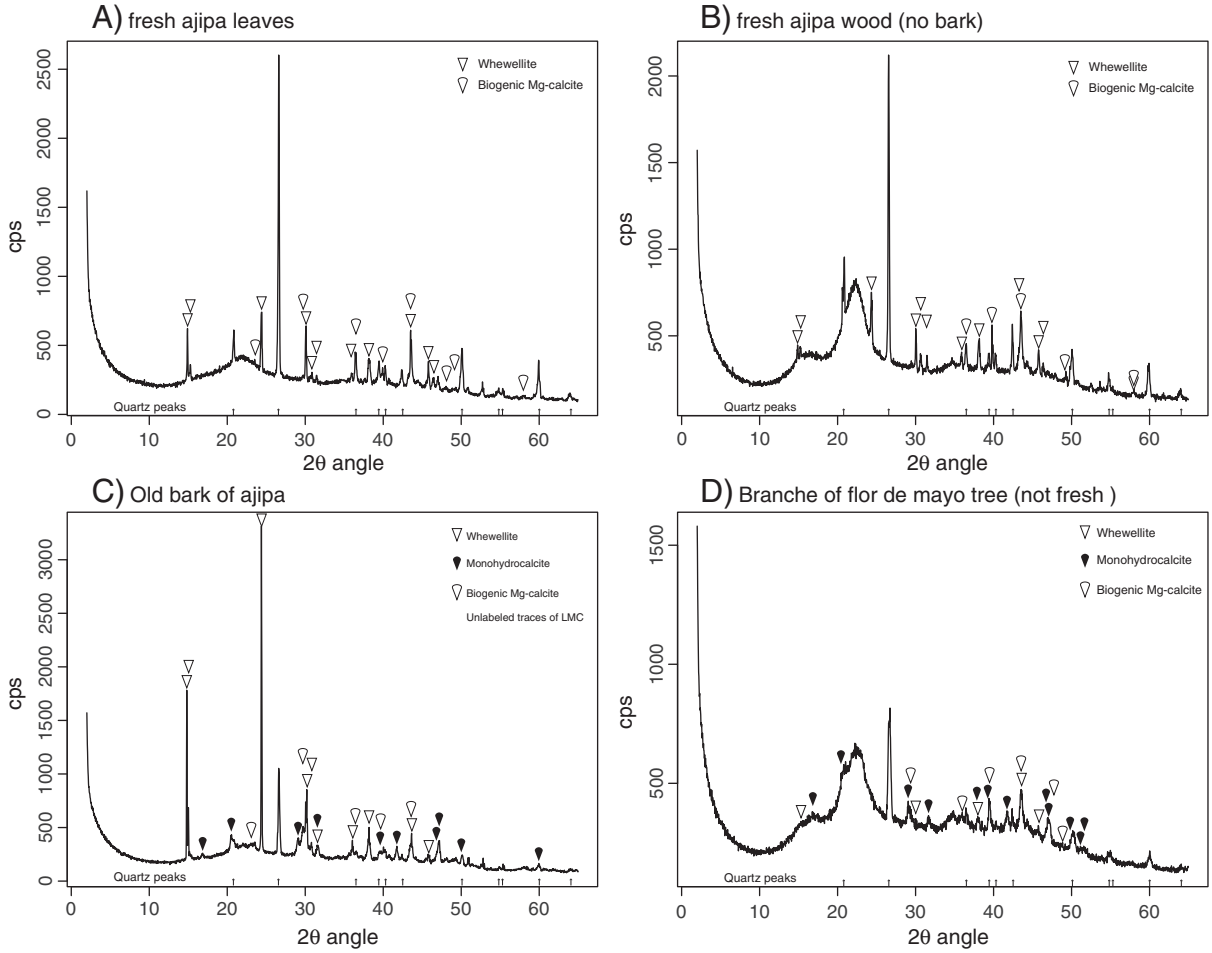

Fig. 5. X-ray diffractograms of organic tissues originating from trees. A and B: wood tissues of a *Pentaplaris davidsmithii* tree, both leaves and wood (*sensus stricto*) contain whewellite and LMC (biogenic Mg-calcite). C: *Pentaplaris davidsmithii* bark sample collected on the trunk. The fragment is old enough to have been subject to transformation of its initial mineral content. In addition to whewellite and LMC, monohydrocalcite, as well as traces of LMC, are detected. D: Mineral content in a branch of a *Ceiba speciosa* tree, collected on the forest ground. In this sample, whewellite, monohydrocalcite, and LMC are detected. Quartz peaks are noted by small marks on the x axis.

ranging from 0 to 6.6 mg/kg with highest values within the topsoil and lowest ones in deepest horizons. Most of the values in soil profile A1 are higher than those from soil profile A2. At B site, the oxalate content is between 1.6 and 27.8 mg/kg in soil profile B1. The highest value (27.8 mg/kg) is observed in the topsoil whereas deeper samples are below 2.5 mg/kg. In soil profile B2, except for the topsoil sample (25.39 mg/kg), values are either zero or not exceeding 0.2 mg/kg.

3.3. Loss on ignition (LOI)

Results from the four soil profiles are given in Table 1. In soil profile A1, the OM content ranges from 1.6 to 7.0% of dry-weight. A marked decreasing trend from the topsoil to the deeper horizons characterizes this soil profile. The same trend is observed in soil profile A2, with values ranging from 0.7 to 4.5% of dry-weight, the highest values measured being in the topsoil. At B site, soil profile B1 shows a similar trend with highest values in the upper horizons, whereas the lowest values are observed in the deepest samples. Values range from 2.1 to 8.7% of dry weight. In soil profile B2, values range from 2.0 to 9.0% of dry weight with highest values at the topsoil and an obvious decrease towards the deepest horizons.

3.4. Mineralogy

X-ray diffraction analyses were performed on samples of various tree tissues. Results are presented in Table 2. Whewellite, the monohydrate form of Caox, is always present in samples, independent of the origin. Fresh leaves of *P. davidsmithii* (Fig. 5A) and verdolago (colorado — *Terminalia amazonia* and amarillo — *Terminalia oblonga*) trees contain whewellite, as well as calcium carbonate species (biogenic Low Mg-Calcite — LMC and High Mg-Calcite — HMC >4% $MgCO_3$). Fresh leaves of other tree species, such as *C. speciosa* or *quina quina* (*Myroxylon balsamum*), contain only whewellite. Regarding fresh wood tissues of *P. davidsmithii*, *C. speciosa*, *M. balsamum*, and *T. oblonga* trees, all contain whewellite and biogenic HMC (Fig. 5B). Tree tissues, which cannot be considered as only composed of fresh OM due to evidences of rotting (i.e., old bark of *P. davidsmithii* collected 1 m from the ground), contain biogenic HMC and traces of biogenic LMC, as well as monohydrocalcite — $CaCO_3 \cdot H_2O$ (Fig. 5C). A tree branch of *C. speciosa* (also considered as not being composed of fresh OM) was collected from the ground where it was partially attacked by termites. This sample is characterized by the presence of biogenic HMC, traces of biogenic LMC, and monohydrocalcite (Fig. 5D).

White sandstones, with a small amount of phyllosilicates and microcline, constitute rock samples from the C site. Three other sampled clayey rocks are composed of quartz, mica, kaolinite, calcic and sodic plagioclases, and microcline. Soil mineralogy is dominated by quartz and phyllosilicates (illite, mica, kaolinite, chlorite, and montmorillonite), found in high amounts. Other minerals, such as microcline or calcic and sodic plagioclases, are present in much lower amounts, with some traces of iron oxides (goethite and hematite). Various forms of carbonate, such as LMC and HMC were detected in soils under the influence

Table 1
Oxalic acid content, pH_{H2O}, carbonate content, and loss on ignition in a selection of samples from the two study sites.

Sample name	Profile	Depth (cm)	Oxalic acid (mg/kg)	^{pH}H20	Carbonate (weight %)	Loss on ignition (weight %)
8956 A1P1 12	A1	5	16.33	8.0	4.3	6.36
8957 A1P1 11	A1	22.5	5.71	7.7	3.1	4.67
8958 A1P1 9	A1	27.5	26.86	7.8	4.9	7.00
8959 A1P1 10	A1	37.5	2.45	7.8	2.4	4.08
8960A1P1 8	A1	50	3.13	7.9	2.4	4.39
8961A1P1 7	A1	95	5.01	7.9	1.8	3.28
8962A1P1 6	A1	130	9.34	7.5	1.7	3.35
8963A1P1 5	A1	150	3.23	7.7	2.1	2.76
8964A1P1 3	A1	190	NaN	7.9	3.5	2.13
8965A1P1 2	A1	210	2.84	8.1	5.4	1.81
8966A1P1 1	A1	225	NaN	8.0	5.7	1.88
8967 A1P1 13	A1	240	2.73	8.0	6.0	1.60
8968 A1P1 14	A1	260	NaN	8.1	4.8	1.73
8969 A1P1 15	A1	285	0.20	8.0	5.7	2.09
8970 A1P2 1	A2	2.25	6.62	6.1	0.6	4.48
8971A1P22	A2	14.75	2.13	5.7	0.0	1.73
8972A1P2 3	A2	31	0.79	5.0	0.3	1.55
8973 A1P2 4-5	A2	43	2.17	5.0	0.8	1.38
8974A1P26	A2	55	0.00	5.0	0.0	1.21
8975 A1P2 7	A2	75.5	0.20	4.5	0.5	0.74
8976 FM1P1 A	B1	5	27.84	7.4	3.6	8.74
8977 FM1P1 S1/AS	B1	30	1.62	7.6	2.2	3.76
8978 FM1P1 S2	B1	57.5	2.43	7.7	3.1	2.90
8979 FM1P1 S3	B1	105	2.44	7.5	1.4	2.13
8980 FM1P2 A	B2	1.75	25.39	6.5	1.4	9.04
8981 FM1P2 AS	B2	9.75	0.00	5.6	NaN	3.18
8982 FM1P2 S1	B2	37.5	0.00	5.1	0.9	3.00
8983 FM1P2 S2	B2	55	0.00	5.2	NaN	2.13
8984 FM1P2 S3	B2	85	0.20	5.3	0.8	1.97

of oxalogenic trees. No oxalate was detected in the investigated soil samples using XRD.

3.5. Microbiology

Oxalotrophic bacteria were isolated from all the samples. Surface samples (S6 and S7) show the highest number of total cultivable bacteria, as well as oxalotrophic cultivable bacteria. Both categories decrease with depth, with samples S2 and S1 showing the smallest numbers (Fig. 6). The incubation of the soil suspensions with Caox as the sole C source had the consequence to increase pH up to 9 in all samples. However, this result is also dependent on the dilution factor of soil suspensions. In samples containing the highest number of cultivable oxalotrophic bacteria, as assessed by plate counting, pH increasing is observed in solutions down to a 10^{-9} dilution (typical for surface samples S6 and S7). To contrast, a pH increase was not observed at higher dilutions of deeper samples (e.g. S1).

4. Discussion

The main objective of this study was to determine if the OCP is a process only occurring in a few African areas, such as the *M. excelsa* tree surroundings, or if it can be considered as a more common and widespread phenomenon. The *M. excelsa* ecosystem has been thoroughly described by various authors (Braissant et al., 2004; Cailleau et al., 2005, 2011) and is used as a reference in order to estimate the potentially similar behavior of South American trees. Indeed, the methodical screening of mature trees in the Alto Beni area was successful, delivering

Table 2
Mineralogy of crystals observed in various tissue samples; freshness and plant families are given. Note the omnipresence of whewellite (WW) and some carbonate species, such as Low Magnesium Calcite (LMC), High Magnesium Calcite (HMC), and monohydrocalcite.

Scientific name	Vernacular name	Family	Fresh leaves	Fresh wood	Other samples (mixture, decaying,…)
Apuleia leiocarpa	K'ara k'ara	Fabaceae	WW, HMC	–	–
Caesalpinia pluviosa	Momoqui	Fabaceae	WW	–	–
Cariniana estrellensis	Colomero	Lecythidaceae	WW	–	–
Ceiba speciosa	Flor de Mayo	Malvaceae	WW	WW, LMC[a], HMC	WW[b], LMC[b], HMC[b], monohydrocalcite[b]
Centrolobium ochroxylum	Huasicucho	Fabaceae	–	WW	–
Clarisia racemosa	Mascajo amarillo (Murure)	Moraceae	WW	WW, HMC	–
Erythrina crista-galli	Ceibo	Fabaceae	WW	–	–
Ficus coerulescens	Bibosi colorado	Moraceae	–	–	WW[c], LMC[c], HMC[c]
Hymenaea courbaril	Paqulo	Fabaceae	–	WW, HMC	–
Myroxylon balsamum	Quina Quina	Fabaceae	WW	WW, HMC	–
Ormosia sp.	Huayruro	Fabaceae	WW	WW, HMC	–
Pentaplaris davidsmithii	Ajipa	Malvaceae	WW, HMC	WW, HMC	WW[d], LMC[ad], HMC[d], monohydrocalcite[d]
Pouteria sp.	Lujma	Sapotaceae	–	WW, HMC	–
Terminalia amazonia	Verdolago colorado	Combretaceae	WW, HMC	WW, LMC	–
Terminalia oblonga	Verdolago amarillo	Combretaceae	WW, LMC	WW	–

[a] Traces.
[b] Branch of flor de mayo tree (not fresh).
[c] Bark.
[d] Old bark sampled at 1–1.5 m from the ground.

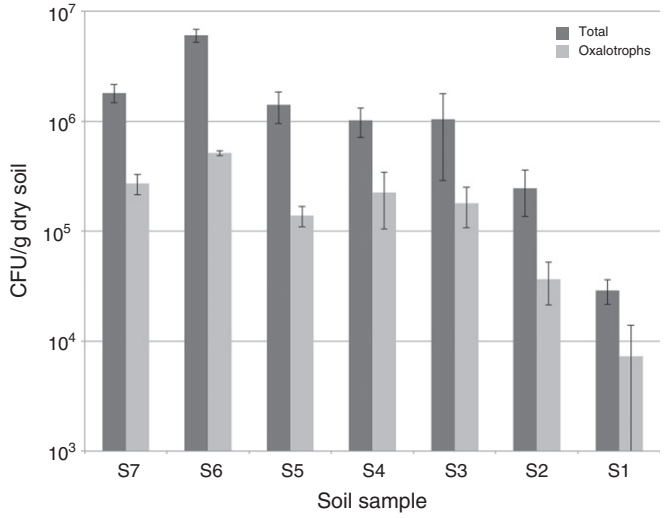

Fig. 6. Barplot showing the numbers of total cultivable bacteria (dark gray) and total cultivable oxalotrophic bacteria (light gray) for S7 surface sample from soil profile B2 and for each sampling depth from soil profile B1 (S6 at 2 cm in depth to S1 at 130 cm in depth).

15 species for which soil alkalinization and carbonate presence were observed (Table 2).

4.1. Laboratory evidence for Amazon OCP ecosystems

The determination of the mineralogical content of plant tissues showed that the field screening was relevant. First of all, whewellite is always detected in fresh samples, which is similar to the case of the *M. excelsa* tree (Braissant et al., 2004; Cailleau et al., 2005). The presence of oxalate, whatever its nature (i.e. as monohydrate, dihydrate, or a complex combination), is demonstrated for all the trees selected during the field screening. On the other hand, a typical mineral association is often observed when samples were in an obvious state of decay (Fig. 5D) or suspected to be old enough to be exposed to agents able to modify their mineralogical nature (Fig. 5C), such as termites (Cailleau et al., 2011). Indeed, in addition to whewellite-LMC-HMC, monohydrocalcite is often detected in samples collected on the ground (e.g. branches of *C. speciosa* tree attacked by termites), as well as in old bark of the *P. davidsmithii* trees. This mineral has already been found in various contexts such as decaying cacti (Garvie, 2003) or partially decayed and mineralized wood found inside the soil (Cailleau et al., 2005). Monohydrocalcite is assumed to be a precursor of magnesium-enriched calcite (Skinner et al., 1977; Taylor, 1975), which, in the case of the Bolivian samples, makes sense as HMC is also found. However, the absence of weddellite in the XRD spectra is unexpected, as this mineral has been formerly considered as an indicator of fungal involvement in the breakdown of organic matter (Braissant et al., 2004). As the absence of ligninolytic fungi is unlikely in such environments, it is possible that different fungal strains and/or guilds are active in the OCP detected at the investigated sites, compared to those in Africa. Different environmental conditions could also affect the type of oxalate produced by fungi. Further work is needed to better understand the complex relationships between OCP, fungi, and environmental parameters. To conclude at this point, African and South American OCP systems appear to be very similar in terms of mineralogical features, except for the absence of weddellite in Amazonian sites.

The expected consequences of an active OCP have been found in the studied plant tissues and/or soils. However, the agents of oxalotrophy must also be present to attest to the existence of oxalotrophic–oxalogenic ecosystems. Oxalotrophic bacteria have been identified in the soil profile under the oxalogenic tree *C. speciosa*, as well as at the surface of a distant soil profile. While they are more abundant in surface samples, where Caox concentration is high, bacteria are still present at depth, but with large variations between replicates. This high variability in deeper soil horizons could result from lower quantities of available oxalate. As a matter of fact, it can be expected that in surface horizons where Caox is present in high quantity, its distribution is more homogeneous. To the contrary, in deeper soil horizons the fact that Caox is present in lower quantities most likely leads to a more heterogeneous substrate distribution. This irregular supply reduces substrate access for oxalotrophic bacteria leading to their patchy distribution. In all samples, an increase in pH was observed upon incubation of soil suspensions with Caox as the sole C source, meaning that the oxidation of Caox likely led to this rise in pH. Therefore, all these results indicate that oxalotrophic bacteria are present in the soil nearby the *C. speciosa* tree and that their oxalotrophic metabolism can efficiently lead to a pH increasing in the soil. To conclude, the presence of the OCP is established in South America based on all the above outcomes, i.e. chemical, mineralogical, as well as microbiological results.

4.2. Further comparisons between South American and African OCP ecosystems

Four soil variables can describe an OCP ecosystem: pH, carbonate and oxalate contents, and LOI. In this context, soil pH is known to be strongly influenced by oxalotrophy (Braissant et al., 2004). If an OCP is active for a sufficiently long time span, it will eventually favor carbonate accumulation as an end-product. The oxalate is obviously considered as the limiting-substrate for an active OCP. Finally, LOI appears to be a good proxy for the flux of organic matter entering the soil, as well as for the influence of soil biota. Both are related to soil Caox pools, as oxalate can be provided by both plants and saprophytic fungi. To emphasize these conclusions, the Pearson correlation matrix was calculated using these variables from the two soil profiles under the influence of *P. davidsmithii* and *C. speciosa* trees (i.e. A1 and B1 given in Table 3).

At the *P. davidsmithii* tree site, soil profile A1 is clearly alkaline (from 7.2 to 8; Fig. 3A1). In contrast, the distant soil pH (soil profile A2) is acidic (from 4.5 to 6.2) and the difference between both soils is greater than 1.5 pH units, which is significant in such environments. Therefore, an alkalinization is clearly occurring close to the *P. davidsmithii* tree. At the *C. speciosa* site, there is a sharp difference in soil pH between soil profile close to the tree (B1; between 7.4 and 7.7) and at a distance from the tree (B2; from 5.1 to 6.5, the highest pH being in the topsoil). These results present similar trends between the soil close to the tree and the distant soil compared to those obtained in *M. excelsa* tree studies from Africa, where soil pH can increase up to 4 units (e.g. Cailleau et al., 2005).

The carbonate content is low, never exceeding 6% around both studied trees (*P. davidsmithii* and *C. speciosa*). This is rather low compared to what has been observed around African *M. excelsa* trees, which can accumulate up to 16.5% of carbonate in soft soil samples (Cailleau et al., 2004) and form large carbonate blocks (composed of up to 96% of carbonate).

Only LOI and oxalate content were correlated ($r = 0.89$, $n = 15$, p-value $= 0.0108$). This is in agreement with the presumption that the oxalate is provided by both an autotrophic source (i.e. the trees) and presumably by a heterotrophic source, partly represented by saprophytic fungi known to produce oxalate during ligninolysis for instance (Gadd, 1999). LOI and oxalate do not correlate with soil pH and carbonate content, which is not surprising, as both are consequences of the degradation of oxalate in a dynamic flux relationship. A correlation between the "consequence and by-product" of oxalotrophy (i.e. soil pH and carbonate content) can be expected despite the fact that this was not observed in Ivory Coast (Cailleau et al., 2005). In the present study a correlation is observed ($r = 0.68$, $n = 18$, p-value $= 0.001964$). This relationship is not very strong. The reason could be that the alkaline conditions found close to the trees represent more the direct result of oxalotrophic activity than the carbonate buffering. The soil pH is close to the stability pH for calcite ($\approx$8.4 in these environmental conditions

Table 3
Pearson's correlation coefficients calculated between oxalate content, soil pH_{H2O}, carbonate content, and LOI parameters from soils under the influence of OCP (i.e. A1 and B1 soil profiles). Correlations between oxalate content and other variables are calculated with n = 15 observations, while other correlations are calculated on n = 18 observations. p-value given for 95% confidence intervals.

	Oxalate content (mg/kg)	^{Soil} $P^{H}H2O$	Carbonate content (% weight)	LOI
Oxalate content (mg/kg)	1	−0.29	0.19	0.89
Soil $P^{h}_{H2}o$	p-value = 0.3008	1	0.68	−0.44
Carbonate content (% weight)	p-value = 0.4818	p-value = 0.001964	1	−0.13
LOI	p-value = 0.0108	p-value = 0.06896	p-value = 0.605	1

of temperature and pressure) but clearly not sufficient to allow important carbonate accumulations. One can expect that the soil pH is only high enough in microenvironments to allow carbonate to precipitate. As a consequence, it can be hypothesized that the OCP associated to these two Amazonian trees has not been working efficiently enough, or not for long enough, to shift from initial acidic to permanent alkaline conditions able to support carbonate accumulations. In the absence of further data on the growth rate of trees, the time frame for OCP to act upon this soil remains unknown. Additionally, climatic parameters could also play a potential role in OCP production, parameters such as the water balance or the length of the dry season. But this point has not been documented yet.

Moreover, the two sites lie on a slope (20° and 5° to 10° for the *P. davidsmithii* and *C. speciosa* sites, respectively), which was not the case at African sites (Cailleau et al., 2005). In addition, soil profiles A1 and A2 have a fine texture, which is different from the coarser soil texture of the African sites. Whatever the soil texture, the topography will allow material to migrate downslope on the forest floor, as well as within the soil, "diluting" the local impact of oxalotrophy. On the other hand, fine soil texture will prevent *per descensum* diffusion in the soil, favoring spreading. This point is in agreement with the observation of a migrating carbonate plume along a slope (about 20°) observed in the same area of the Alto Beni valley, which was observed on the site but was not subjected to a specific study.

Another aspect to keep in mind is the efficiency of the tree itself to produce oxalate in important quantities in order to induce a sufficient flux to the soil. This aspect points to a possible difference between species. In addition, calcium bio-availability should also be considered, as it is well known to influence oxalate production in plants (Franceschi and Nakata, 2005). In typical acidic soils of the inter-tropical belt, calcium is easily leached and exported to streams, and as a result, soils are highly depleted in Ca. Consequently, the phytomass constitutes the mineral reservoir, which puts back nutrients and other elements for use by the biomass during organic matter turnover (Nykvist, 1998). Consequently, the impact of the type of forest on such turnovers (i.e. evergreen or deciduous) must be considered. Finally, an ultimate difference between American and African sites is the presence of termites infesting *M. excelsa* (Cailleau et al., 2011). Their absence in the studied *P. davidsmithii* and *C. speciosa* trees could also have an impact on the OCP efficiency. Indeed, regarding the *M. excelsa*, termites are at the origin of an additional and very local flux (however, interpreted as important) of oxalate-bearing OM to the soil, which enhances the rate of alkalinization.

4.3. A ubiquitous process?

The presence of OCP associated with trees of different species highlights its potentially wide distribution in tropical ecosystems. Even if, in the present study, the carbonate content remains smaller than in the African *M. excelsa* ecosystem (Cailleau et al., 2004), the potential C reservoir over the Amazon Basin could represent an important figure, not yet taken into account in the global terrestrial C cycle. Until now the OCP has been considered somehow as an interesting but limited process related to the *M. excelsa* tree and maybe some cacti (Garvie, 2003). The present study highlights the ubiquitous nature of this process. As oxalogenesis is a widespread process among the Plant Kingdom (and not only as it is well known that saprophytic fungi produce oxalate for different reasons, e.g. during the organic matter breakdown on the forest ground, mineral weathering, or metal detoxification; Gadd, 1999), it is not so surprising to find OCP in natural environments where oxalate is produced. Moreover, oxalotrophy is a metabolic pathway that a large number of phylogenetically diverse bacteria are able to perform. Until now, all but one known oxalotrophic bacteria are facultative oxalotrophs (Sahin, 2003), meaning that their presence does not rely on the occurrence of oxalate in space and time at a given location. Consequently, the presence of oxalotrophs is expected independently of the environmental conditions and geographic areas (Cromack et al., 1977; Dutton and Evans, 1996). Obvious, or suspected, systems matching an oxalate-oxalotrophy ecosystem and OCP can be found in the literature. In arid environments, OCP is strongly suspected to be active since studies in Galilee, Israel (Verrecchia et al., 1993) and the Sonoran desert, Arizona (Garvie, 2003). At these two sites, OCP can only be suspected (even if extremely likely), as no investigation on the presence of oxalotrophs has been performed. Additionally, OCP has been detected in the Tabernas desert near Almería, Spain (Braissant, 2005). In forest environments, active OCP has also been demonstrated in various locations and climates, from Douglas-fir temperate forests (Oregon, US; Cromack et al., 1977) to tropical forests of Africa (Braissant et al., 2004; Cailleau et al., 2005). OCP is also strongly suspected to be involved in carbonate accumulations inside termite mounds (Liu et al., 2007; Mujinya et al., 2011), even if the presence of oxalotrophs has not been yet confirmed.

4.4. A potential C sink

It still remains to be proven if the accumulations of carbonate related to the observed OCP constitute a C sink. A C sink is effective only if the calcium sequestering C as pedogenic $CaCO_3$ does not originate from an inherited $CaCO_3$ source (Elbersen et al., 2000). At the investigated sites, no carbonate has been detected in the deepest horizons of the two distant soils. This suggests, as Elbers (1995) demonstrated, that no carbonate is present in the substratum during soil development. As a consequence, the calcium should be provided by the only pertinent input remaining, the atmosphere. Atmospheric calcium inputs over the Alto Beni area can have two origins. First, the 200 hPa winds (high troposphere) blowing eastward during half of the year (from April to September) can transport calcium-rich carbonate-free ash from eruptive products of volcanoes from the Andies Cordillera. The presence of laumonite in some soil samples can originate from weathered andesite, which could support the hypothesis of a volcanic Ca supply. A second atmospheric input can come from the 850 hPa winds (low troposphere) blowing south-westward (May to August) to south-south-eastward (September to April). These winds could blow some carbonate materials over the Alto Beni area from the Amazon Basin known to include some carbonate formations, though scarce. As a consequence, a fraction of the calcium present in the carbonate accumulated through OCP could originate from a non-carbonate-free source. In conclusion, the definition of tropical bio-induced carbonates as a C sink is highly suspected but has still to be further investigated in terms of calcium sources and balances.

5. Conclusions

The importance of OCP as a strong pedological agent has been demonstrated in Africa using *M. excelsa* tree ecosystems, in which important and unexpected secondary carbonate deposits have accumulated through time. Considering that 80% of plant species are known to have oxalate crystals in their tissues, it is reasonable to assume that *M. excelsa* is not the only tree that can induce soil carbonate accumulations. Consequently, investigations were conducted in the Amazon forest in South America to search for other candidates presenting an active OCP.

During a first screening period in the Alto Beni forest (Bolivia), several tree species (11 trees; Table 2) were tested positive for having carbonate on their trunk as well as in the surrounding soil, and for presenting more alkaline soil pH close to the tree than at a distance from it. The absence of local inherited carbonate in the local basement as well as the presence of "expected" acidic conditions clearly made these soils good candidates for OCP in the presence of oxalogenic trees. The present study demonstrates the existence of an active OCP in South America as local alkalinization, carbonate accumulations, and oxalotrophic bacteria were found in the soil under these trees. OCP provides positive feedback to the ecosystem such as soil alkalinization, able to theoretically prevent leaching of calcium and base cations, which in turn, could enhance calcium oxalate production by plants, feeding the system.

A detailed study of *P. davidsmithii* and *C. speciosa* trees showed that soil pH close to the trunk is higher than in the distant soil. The difference is at least of 1 pH unit, but can reach 1.8 units (site A). This is similar to African sites. Regarding the mineralogy, whewellite is always present as the only detected oxalate species, whatever the type of tissue. Carbonate (as LMC, HMC, and monohydrocalcite) is present in most of tissues as well. Carbonates were also detected in surrounding soils and in the following proportions, 3.6 and 6% for the *C. speciosa* and *P. davidsmithii*, respectively. These amounts are 3 to 4 times lower than those measured at African sites (Cailleau et al., 2004) but remain significant, as they are unexpected considering the acidic context of Amazonian soils.

If the question of a potential C sink related to the oxalotrophic–oxalogenic ecosystems in the Amazon Basin is still pending, this study highlights the implication of such an ecosystem in biogeochemical cycling involving C and Ca. Carbonate accumulations observed in tropical ecosystems of Bolivia could constitute an important reservoir that must be taken into account in the C balance, as previously reported by Cailleau et al. (2004, 2011) for the *M. excelsa* tree ecosystems in Africa. As a consequence, further work is needed in order to answer this question and to assess the global magnitude of the OCP on the terrestrial C cycle.

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