# IN SITU STUDY OF SOIL PROCESSES IN AN OXISOL-SPODOSOL SEQUENCE OF AMAZONIA (BRAZIL)

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We performed an in situ experiment with the aim of getting evidence for contemporary podzolization in a soil sequence near Manaus, Amazonia, Brazil. Samples of a test-mineral [high cation exchange capacity (CEC) vermiculite], as well as small bags of cation exchange or chelating resins, were inserted in soils (Oxisols, Ultisols, and Spodosols).

We based the study on the following principles: when placed in an acidic and complexing system (podzolization), the vermiculite undergoes a desaluminization process and its CEC saturates with Mg by relative accumulation. In a simply acidic system, aluminum accumulates in the interlayers, and rapid hydroxylation leads to the formation of an Al intergrade mineral easily detectable by X-ray diffraction.

The resins inserted in soils gave information about the chemistry of the soil solutions. We concluded that podzolization is a currently active process in the lower part of the sequence, even in soils where morphological podzolic features have not yet developed. This process would be active during the rainy season only.

The aim of this study was to get evidence for contemporary podzolization and seasonal variations of this process in a soil sequence including Oxisols, Ultisols, and Spodosols.

In the region north of Manaus (Amazonia, Brazil) the general landscape is a plateau with dissected valleys of various dimensions. In the largest valleys, Oxisols occupy the uplands (plateau remnants) and the upper parts of the valley slope, whereas Spodosols form the lowest members of the sequences. Changes in soil properties from Oxisols to Spodosols are always very gradual (Lucas et al. 1987), but important changes in the soil-forming processes are expected to occur. The formation of Oxisols is mainly ascribed to hydrolytic weathering, whereas genesis of Spodosols is largely governed by organic acids complexing with metals (Bravard and Righi 1989).

Previous studies of one of these sequences have essentially involved analysis of the solid phases (Chauvel et al. 1987; Bravard and Righi 1988). The data obtained with such studies reflect the cumulative effects of all forming processes active during the formation of the soils. As a consequence, some properties may be relict features of earlier stages of soil development.

In an attempt to define the present soil environment and weathering processes, we adopted a qualitative experimental method in which a standard pure test-mineral was inserted into the soil (Berthelin et al. 1983; Hatton et al. 1987). In addition, we completed the method by introducing chelating or exchange resin bags into the soil (Binkley and Matson 1983; Carlyle and Malcolm 1986). Results obtained from resin bags should give the same information as those obtained from lysimetry, but on a qualitative basis only.

## MATERIALS AND METHODS

### Site and soils information

The study area lies 60 km north of Manaus, Brazil (2°30'S, 60°W). In this region the climate is hot, with a mean annual temperature of 26.7°C and an average annual rainfall of about 2400 mm. A short but rather well-marked dry season occurs from July to October.

The soils have developed from Tertiary sediments known as "Barreiras." They consist of cross-bedded clayey and sandy layers with each layer a few decimeters thick. The sediments are mainly quartz and kaolinite, with feldspar, muscovite, and hematite as minor constituents (<5%). According to Soil Taxonomy (USDA 1975), soils with a high clay content on the plateau are Haplic Acrorthox. They have homogeneous profiles without clear horizon

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—boundaries within the first 150 cm. On the slope, soils contain less clay ($\approx$40%) and exhibit a textural change between the A and B horizons, with the A horizons being more sandy than the B horizons. This textural change becomes more evident down slope; soils grade from Ultic Haplorthox to Orthoxic Paleudult. At the foot of the slope Spodic Paleudult and Tropohumod occur, and both are sandy soils (<10% clay) (Fig. 1).

The gross composition of the soil profiles is rather similar except for the clay contents. All profiles are acid with a pH in water between 3.5 and 4.5. Cation exchange capacities (CECs) determined at pH 7 with $NH_4$—OAc range from 1 to 10 meq/100 g, and base saturation (S/T) ranges from 2 to 5%. Exchangeable Al ranges from 0.5 to 2.0 meq/100 g. Kaolinite dominates the clay fraction of all of the soils. The C/N ratio of organic matter increases from 12 (profile 1, A12) to 14 (profile 2, A11), 18 (profile 3, A1), and 42 (profile 4, A1/E).

Four profiles were selected to support the experimentation in situ: profile 1 )Haplic Acrorthox), profile 2 (Orthoxic Paleudult), profile 3 (Spodic Paleudult), and profile 4 (Tropohumod). The location of the profiles in the sequence are shown in Fig. 1. More detailed soil descriptions and data on the geochemistry and clay mineralogy were given by Bravard and Righi (1988, 1989).

### In situ experimental procedure

Small bags (5 × 10 cm) of 20-$\mu$m mesh polyamide containing either 3-g samples of the test-mineral or 6 g (wet) of a cation exchange resin (Amberlite IRN 77) or chelating resin (Chelex 100) were carefully introduced in the main horizons of the soils. These bags were put in from the front of a pit that was then refilled, retaining the original horizonation.

The test-mineral is a high CEC (160 meq/100



FIG. 1. Diagram of the soil sequence and location of the experimental sites. 1, 2, 3 and 4: profile numbers.

g) vermiculite from Spain (Santa Olalla). Before the experiment we cleaned the mineral with distilled water, sieved it to retain the 200- to 500-$\mu$m particles only, and then saturated it with $Na^+$. Achieving a complete exchange with $Na^+$ was not possible, so we saturated the vermiculite introduced in soils with both 130 meq $Na^+$ and 30 meq $Mg^{2+}$ per 100 g.

The cation exchange resin was $Na^+$-saturated too; the chelating resin was $Na^+$ (90% of the CEC) and $H^+$ (10%) saturated. The pH of the chelating resin was then adjusted to 6.

The bags were removed from the soils after 6 months, beginning November 15, 1986, to May 15, 1987 (i.e., during the rainy season—rainfall: 1600 mm this year) and from May 15, 1987, to November, 1987 (i.e., the dry season—rainfall: 620 mm this year). A series of vermiculite bags stayed in the soils over 1 year. We experimented with the resin bags during the rainy season only.

After removal from the soils, we analyzed the test-mineral for exchangeable cations ($Na^+$, $Mg^{2+}$, $Ca^{2+}$, and $K^+$:N, $NH_4Cl$ extraction), exchangeable Al (N, KCl extraction), CEC, and Na-citrate-extractable Fe and Al (Tamura 1958). Tamura reagent was expected to extract both exchangeable Al and more or less polymerized hydroxy-Al polycations located in the vermiculite interlayers. All samples were analyzed by X-ray diffraction (XRD) (1) after K saturation followed by a progressive heating from 20°C (room temperature) to 550°C and (2) after the Na-citrate treatment and K saturation.

Cations (K, Ca, Mg, Fe, and Al) retained from soil solutions by the exchange resin and Fe and Al on the chelating resin were desorbed and analyzed by atomic absorption spectroscopy.

We deduced the basis for interpretation of the results from the experimental work of Robert et al. (1979): in an acid and complexing medium (podzolization), vermiculite undergoes a desaluminization process and its exchange sites are progressively saturated with Mg by relative accumulation. In an acid but not complexing medium, aluminum accumulates in the interlayers, causing the formation of an Al-interlayered intergrade mineral easily identified by XRD.

We expected that the comparison of Al and Fe retained by either the cation exchange resin or the chelating resin would distinguish between cationic species of Al or Fe (retained by both of the two resins) and organocomplexes of Al or Fe (retained by the chelating resin only).
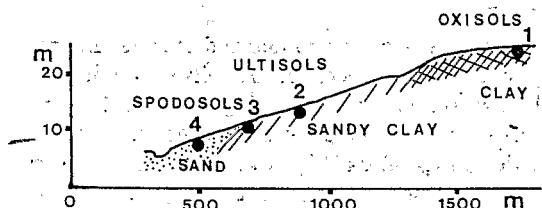
## RESULTS

### Nature and amounts of elements sorbed on the resins

Very small amounts of $K^+$, $Ca^{2+}$, or $Mg^{2+}$ were sorbed on the cation exchange resin (maximum, 17 meq/g; 60°C dry resin basis). The greatest amounts were obtained from the resin bags inserted within the upper layers of the soils (5, 25, or 35 cm) (Table 1).

Aluminum was the major sorbed cation. The depth function trends for aluminum sorbed either on the cation exchange resin or the chelating resin were similar (Fig. 2). Amounts of Al sorbed regularly decrease from the upper to the lower layers with one exception: in profile 3 the largest amount of Al sorbed on the cation exchange resin was for the bag inserted at a 35-cm depth (Bh horizon). For the bags in the most superficial layers, these amounts decrease from profile 1 to profile 4, but the amounts on the chelating resin were larger than those on the cation exchange resin. The reverse was observed for the samples from the deeper layers.

In all samples the amounts of iron sorbed on the cation exchange resin were very low. The same was true in profile 1 for the chelating resin,

but far larger amounts were found on the samples from profiles 2 and 3. A maximum of sorbed iron was found for the chelating resin sample inserted in the Bh horizon of profile 3 (Fig. 3).

### Evolution of the test-mineral

#### CEC-exchangeable $Na^+$ and $Mg^{2+}$

After 1 year in the soils a significant decrease of the CEC of the test-mineral had occurred. That decrease was more pronounced for the samples inserted in the upper horizons, and the depth function of that decrease was not the same in every soil; it was restricted to the first 35 cm in profile 2 but affected deeper horizons in the other soils (Table 2).

The decrease in the amount of exchangeable Na has the same pattern as the CEC decrease (Fig. 4). Compared to the initial mineral, the amounts of exchangeable $Mg^{2+}$ increased in the surface horizons of all profiles. That increase occurred during the rainy season essentially (Fig. 5).

#### Na citrate-extractable Al (Tamura)

There was no Tamura-extractable Al in the initial mineral, but significant amounts of this Al form were analyzed in the samples removed from the soils. The greatest amounts were in the samples from the most superficial horizons (Fig. 6). These amounts were decreasing from profile 1 to 4, and the formation of a Tamura-extractable Al fraction mainly occurred during the dry season.

#### Mineralogical transformations (XRD)

Compared to that of the initial mineral, the XRD diagrams of samples that remained in soils during the rainy season were only slightly changed (Fig. 7): a more or less intense peak at 1.4 nm appeared on the K-saturated sample diagrams. This peak readily moved toward the large angles when the samples were heated to 110°C.

These were more pronounced changes in the samples that had been in the soils either during the dry season or for a full year. The 1.4-nm peak intensity was greater but decreased from profile 1 to profile 4. Moreover, this 1.4-nm peak was still present after heating in 110°C. Heating to 250°C was required to make this peak move toward the large angles. After the Tamura treatment the 1.4-nm peak disappeared.

### TABLE 1

Amounts of $K^+$, $Ca^{2+}$, and $Mg^{2+}$ sorbed on the cation exchange resin (meq/g 60°C dry resin) (resin CEC = 4250 µg/g 60°C dry resin)

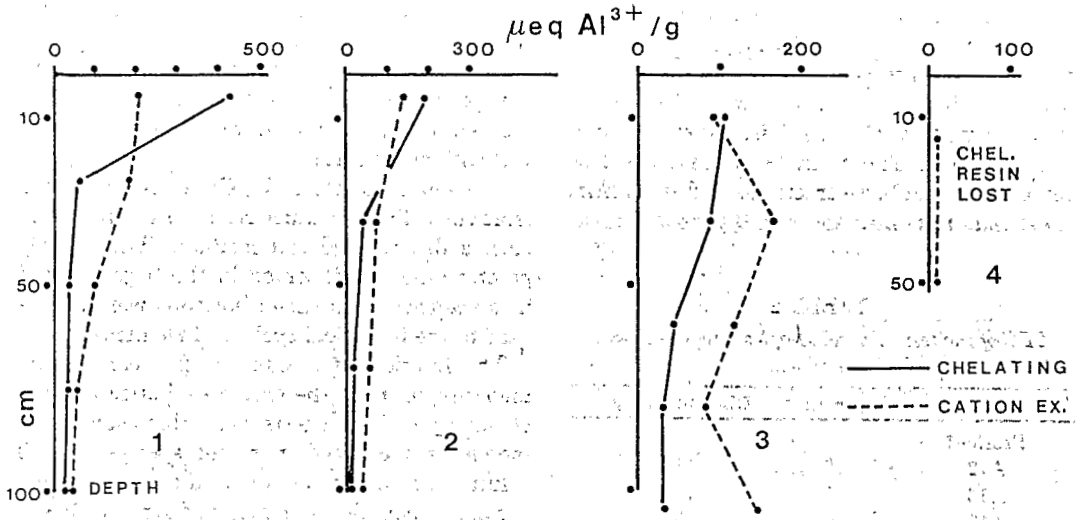| Horizon | depth, cm | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---------|-----------|-------|-----------|-----------|
|         |           | (meq/g) | | |
| **Profile 1** | | | | |
| A12 | 5 | 9 | 7 | 12 |
| A13 | 25 | 12 | 7 | 14 |
| A13 | 50 | 5 | 3 | 6 |
| B11 | 75 | 7 | 4 | 7 |
| B11 | 100 | 5 | 5 | 2 |
| **Profile 2** | | | | |
| A11 | 5 | 6 | 3 | 4 |
| A13 | 35 | 13 | 5 | 4 |
| B11 | 70 | 5 | 4 | 4 |
| B12 | 100 | 4 | 3 | 4 |
| **Profile 3** | | | | |
| A1 | 10 | 7 | 6 | 5 |
| Bh | 35 | 5 | 5 | 6 |
| B21 | 60 | 5 | 4 | 3 |
| B22 | 80 | 4 | 4 | 3 |
| B23 | 110 | 5 | 5 | 2 |
| **Profile 4** | | | | |
| A1/E | 15 | 17 | 9 | 14 |
| E | 50 | 13 | 8 | 12 |

FIG. 2. Amounts of Al sorbed on the cationic or chelating resin. 1, 2, 3 and 4: profile numbers.
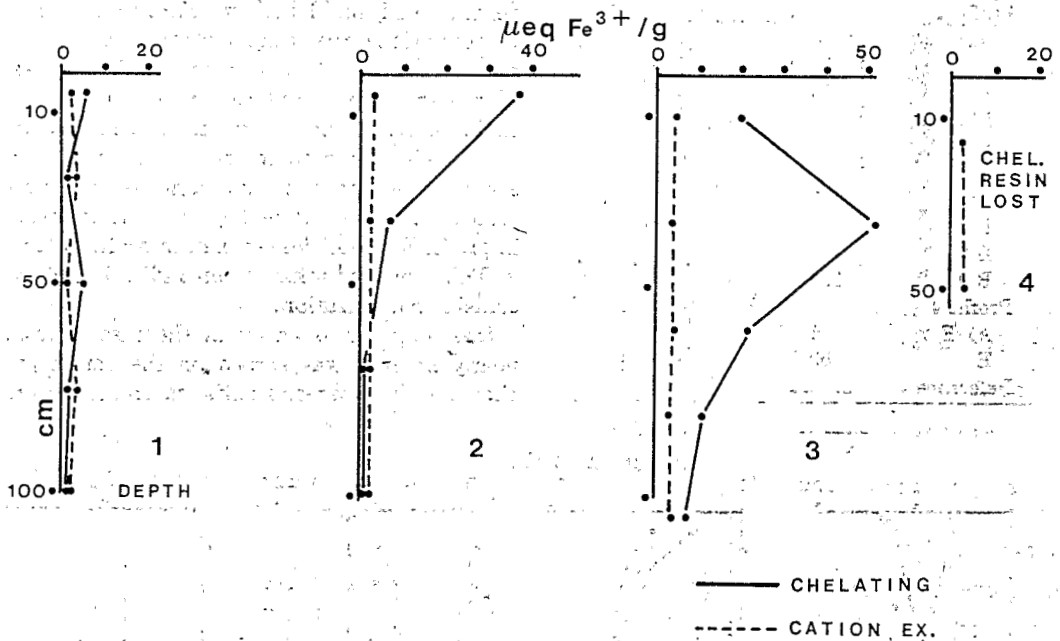


FIG. 3. Amounts of Fe sorbed on the cationic or the chelating resin. 1, 2, 3 and 4: profile numbers.

## DISCUSSION

The mass and nature of elements leached through the soil must be known to describe accurately the current soil-forming processes. Lysimetry and the removal of soil solution with suction extractors are the most common methods for getting these data. Lysimeters give both the concentration and quantity of the solution leached, but their installation and maintenance are costly and time-consuming. The collection of soil solutions with suction extractors also provides qualitative information; being done at discrete points in time, however, the representivity of the collected samples is always questionable (Ugolini et al. 1988).

The resin and test-mineral bag method seems

to be adequate to study soil solutions over extended time sequences. Although the resin or test-mineral bags can be placed with minimal soil disturbance, the continuity of their hydraulic contact with the soil is, however, a practical problem. The resin beads and the test-mineral are sand-size fractions, and implanting these materials into soil would probably intro-

#### TABLE 2
*CEC of the test-mineral samples after the 1-year experiment*

| Horizon | depth, cm | CEC, meq/100 g |
|---|---|---|
| Profile 1 | | |
| A12 | 5 | 118 |
| A13 | 25 | 133 |
| A13 | 50 | 138 |
| B11 | 75 | 152 |
| B11 | 100 | 163 |
| Profile 2 | | |
| A11 | 5 | 108 |
| A13 | 35 | 146 |
| B11 | 70 | 159 |
| B12 | 100 | 161 |
| Profile 3 | | |
| A1 | 10 | 108 |
| Bh | 35 | 146 |
| B21 | 60 | 159 |
| B22 | 80 | 161 |
| B23 | 110 | 166 |
| Profile 4 | | |
| A1/E | 15 | 140 |
| E | 50 | 135 |
| Reference | | 160 |

duce a textural discontinuity and alter water flow patterns. As a consequence only gravity waters are expected to go through and react with the resins or the test-mineral. Using finer grained resins would probably improve the contact with soil materials.

The low amounts of K, Ca, or Mg obtained from the cation exchange resin were expected in such a desaturated soil medium. The slightly greater amounts observed in the bags inserted into the most superficial horizons were attributed to the biological cycling of elements.

The fixation of aluminum, in nearly equal amounts, on both the cation exchange and the chelating resin suggests that this element is mobile as a charged inorganic species. In soil solutions, however, weakly and strongly bound organo-Al complexes (David and Driscoll 1984), as well as low- and high-molecular-weight complexing organic acids, may be present simultaneously (Vedy and Bruckert 1979). According to Hodges (1987), the cation exchange resin could break down weakly bound organic complexes. Moreover, large complexes are excluded from chelating resins that retain only low-molecular-weight Al-organic complexes. Thus, giving an accurate speciation of aluminum would be hazardous, but Al as retained by the chelating resin in profile 3 moved deeper than in profiles 1 and 2. This could be taken as an indication of increasing podzolization.

Interpretation is easier in the case of iron: nearly no iron was sorbed on the cation exchange resin, whereas significant amounts were
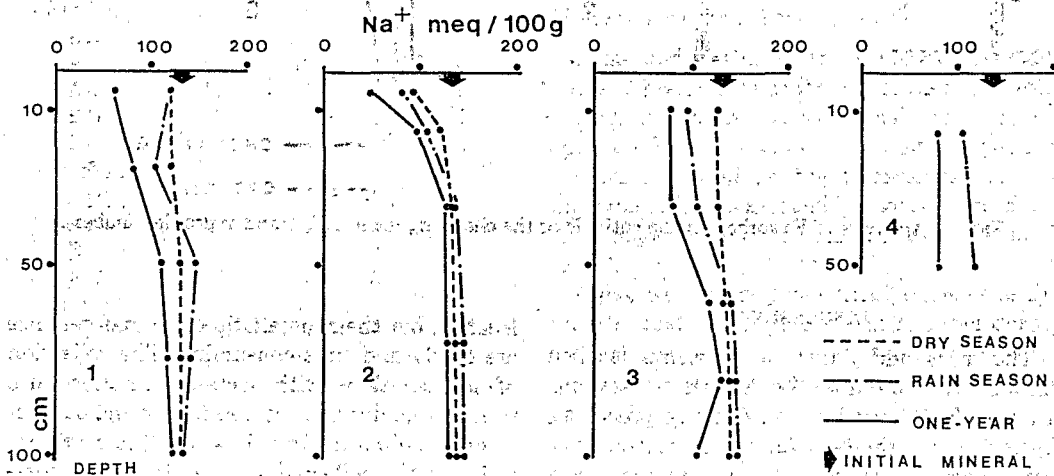


FIG. 4. Amounts of exchangeable $Na^+$ (meq/100 g) in the test-mineral samples. 1, 2, 3, and 4: profile numbers.
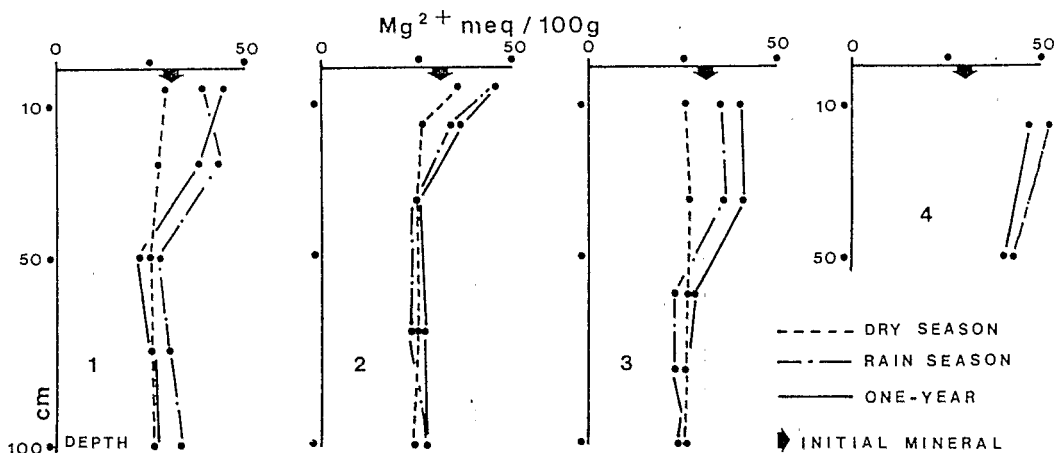
FIG. 5. Amounts of exchangeable $Mg^{2+}$ (meq/100 g) in the test-mineral samples. 1, 2, 3, and 4: profile numbers.
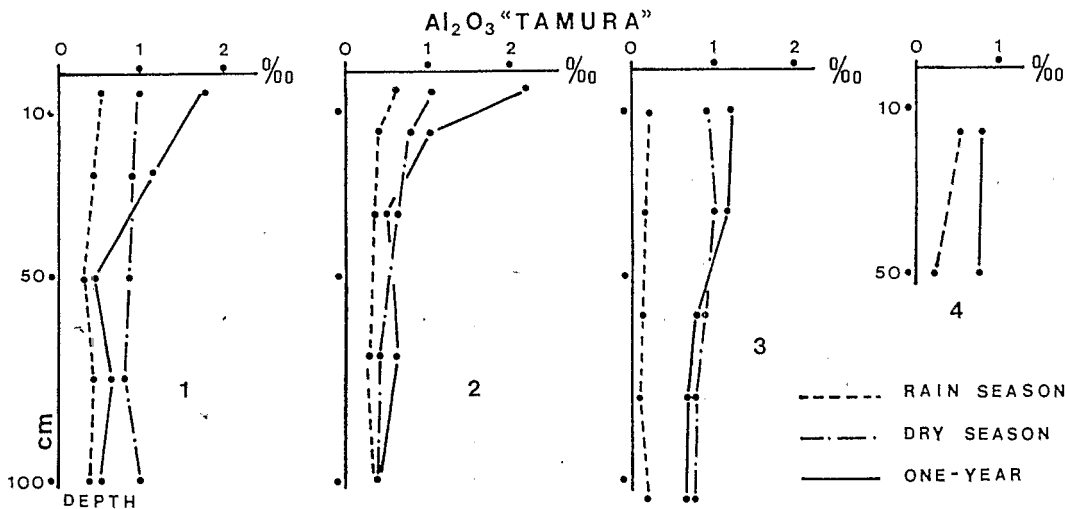


FIG. 6. Amounts of aluminum extracted from the test-mineral samples by Tamura treatment (expressed as $Al_2O_3$ per 1000 of 105°C dry samples). 1, 2, 3, and 4: profile numbers.

sorbed on the chelating resin. This is clear evidence that, in soil solutions, iron is present essentially as an organic complex. As for aluminum, translocation of iron as an organic complex is a typical process for podzolization. Thus, the podzolization process (as revealed by the formation of organo-Fe complexes) would not be active in profile 1 (Haplic Acrorthox) but would be active in the A horizon of profile 2 (Orthoxic Paleudult), with the most clear evidence of activity being in profile 3 (Spodic Paleudult).

The changes in the test-mineral are linked to the volume of water percolating through the

bags. These changes were more pronounced in the upper than in the lower soil horizons. Thus, according to the reaction of the test-mineral, the percolation of gravity waters would be restricted to the first 35 cm of profile 3 (Spodic Paleudult). That can be explained by the presence of a more clayey and less permeable horizon at that depth. Consequently, a lateral circulation of drainage waters above this horizon can be expected in that part of the sequence. Part of the Al or Fe organic complexes is then exposed to lateral leaching and might have accumulated lower on the slope.

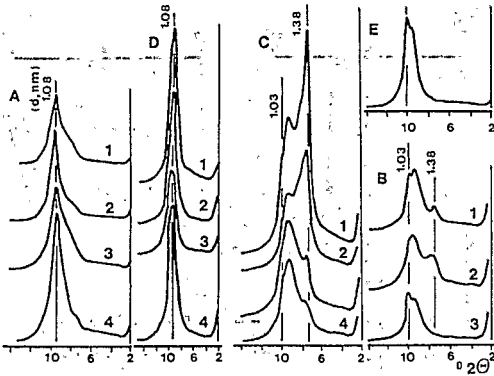In the test vermiculite, exchangeable Mg in-

FIG. 7. X-ray diffraction diagrams of the test-mineral samples inserted in the superficial horizon of the profiles under study. A: samples from the rainy season experiment (K-saturated and heated to 110°C). B: samples from the dry season experiment (K-saturated and heated to 110°C). C: samples from the 1-year experiment (K-saturated and heated to 110°C). D: Same samples as C but after TAMURA treatment (K-saturated). E: Reference mineral (K-saturated and heated to 110°C). 1, 2, 3, and 4: profile numbers.

creased during the rainy season. As indicated by the cation exchange resin, there were only very low amounts of Mg in the soil solutions during this period. Thus, exchangeable Mg is likely to come from the mineral itself. This is indicative of a *complexing medium* (*podzolization*): being less complexable than Al, Mg tends to accumulate in the interlayers (Robert et al. 1979).

In an acidic, but *noncomplexing* medium an interlayered hydroxy-Al sheet would form. Identification of these Al-interlayered minerals is based on the XRD diagram pattern. They collapse less readily than vermiculite but more readily than chlorite. Such behavior was evidenced by the test-mineral samples that had been in the soils either during the dry season or for a full year.

Another indicator of an interlayer-Al sheet was the formation of a Tamura-extractable Al fraction: The more resistant to collapse was the test-mineral, the more Al was extracted. Moreover, after treatment the test-mineral XRD diagram regained its initial pattern.

So, during the dry season, the soil medium was acidic but noncomplexing and caused the aluminization of the vermiculite interlayers. That aluminization became less pronounced when going from profile 1 to profile 4, which indicates that organic complexation is effective in the lower part of the sequence, even during

the dry season. This more active organic complexation is linked to changes in the humification processes at either end of the sequence, as was established by a study of organic compounds (Bravard and Righi 1987). In a quite similar environment (French Guyane), Turenne (1975) demonstrated that large quantities of low-molecular-weight fulvic acids were dissolved in soil solutions at the beginning of the rainy season.

## CONCLUSIONS

This in situ experiment clearly reveals differences in the physicochemical conditions of pedogenesis at either end of the sequence. Oxisols on the plateau are characterized mainly by a simply acidic system, whereas Spodosols on the slope are more affected by organic complexation. Thus, we identified a currently active podzolization process in the lower part of the sequence. This process has already started in soils where morphological features of podzolization have not yet developed (profile 2). Another aim of this experiment was to note seasonal changes in the soil-forming process; podzolization was active mainly during the rainy season. Seasonal podzolization during the winter only was observed by Dambrine (1987) in the French northern Alps. In this area, soils are strongly leached during winter, drainage is restricted during summer, and high temperatures favor fast biodegradation of organic acids.

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