



A comparative study of the soil solution chemistry of two Amazonian forest soils (Central Amazonia, Brazil)

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Abstract

Analyses of the chemical composition of rapidly percolating soil water were used to study the genesis of a shallow podzol in a Campinarana forest and a clayey ferralsol from a typical rainforest located in North Manaus (Amazonia, Brazil). The samples were collected in lysimeters and analysed for Ca^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Fe, Si, and Al. A large percentage of the nutrients was recycled in the upper 40 centimetres of both soils. The soil water concentrations in nutrients were very similar for both environments but levels of Si, Fe and Al were higher in the podzol than in the ferralsol. In the podzolic environment, the waters were enriched in Si, Fe and Al when passing through the organic layer and the top 10 cm of the soil. The concentrations decreased between 10 and 40 cm depth due to variations in mineralogy of this soil. In the ferralsol, the Si concentrations increased considerably on reaching the soil top-horizons while small increases occurred for Al and Fe. Thermodynamic equilibrium calculations indicate that most of the dissolved Al and Fe in both soil environments were in the form of organo-metallic complexes and that the waters were under-saturated in respect to kaolinite and gibbsite.

Introduction

As a result of an intense leaching environment, tropical soils are generally highly weathered and, consequently, very poor in plant nutrients (Anonymous, 1972; Herrera *et al.*, 1978; Nortcliff and Thornes, 1978; Jordan *et al.*, 1980; Herrera, 1985; Forti and Moreira-Nordemann, 1991). This nutrient deficiency is one factor contributing to the failure of many agricultural management experiments in the Amazon forest. Yet, several studies have shown that forests are very efficient in recycling major nutrients. Other elements, such as Si, Fe and Al, are also recycled by the forest, and this can play a major role in soil genesis (Lucas *et al.*, 1993; Rose *et al.*, 1993); this is supported by the observations of Benedetti *et al.* (1994) who showed that vegetation increases rock weathering rates.

Many tropical ferralsols have kaolinite horizons overlying horizons richer in gibbsite (Goldman, 1955; Leneuf, 1959; Delvigne, 1965; Sieffermann, 1969; Novikoff, 1974; Dennen and Norton, 1977; Kobilsek and Lucas, 1988; Lucas *et al.*, 1986, 1989). The stability and formation of such profiles is not consistent with thermodynamic model predictions, which conclude that the succession should be

reversed. Such profiles are thus often considered as resulting from a sedimentary succession. However, recent studies (Lecomte, 1988; Lucas *et al.*, 1986; Colin and Vieillard, 1991; Butt, 1992; Boulet *et al.*, 1993; Giral 1994) have shown that many of these soil profiles were formed in situ; Si recycling has been proposed as an answer to the apparent contradiction between thermodynamic models and field observations (Lucas *et al.*, 1993).

Ferralsols, characterised by the accumulation of secondary kaolinite and oxi-hydroxides, are often associated with podzols, containing quartz grains and lacking secondary mineral phases. This has been observed, for example, in French Guyana (Turenne, 1977) and in Manaus (Brabant, 1987). Ferralsols and podzols may develop in the same landscape environment from the same parent material (Lucas, 1989). The aim of this study was to understand the kaolinite stability in the upper horizons of the ferralsol and the mechanisms leading to differentiation of two different soil types developed from the same parent material. The principal information used was the chemical composition of soil solutions collected using free-flow lysimeters at 2 sites, one representative of a forest on ferralsol and the other of a forest on podzol.

Study area

Two Amazonian forests located North of Manaus, central Amazonia were examined. These forests developed on a Cretaceous-Eocene sedimentary formation (Alter do Chão), composed principally of kaolinite and quartz (Daemon, 1975). The region has a moist tropical climate, characterised by high precipitation (annual mean of 2,100 mm) and high temperature (annual mean of 26 °C). The wet season occurs between December and May, (average rainfall = 1550 mm), and the drier season between June and November, (average rainfall = 550 mm) (Nimer, 1989, Salati, 1985). Annual evapotranspiration ranges from 1000 to 1900 mm according to different studies (Jordan and Heuvelodop, 1981; Salati, 1985; Leopoldo *et al.*, 1987).

The regional topography is characterised by low plateaux separated by flat bottom shallow valleys. Typical rainforest vegetal cover, characterized by high species diversity of around 250 species (Higuchi *et al.*, 1985; Guillaumet, 1987) and a canopy height around 30 m (Guillaumet, 1987), is found on the plateaux and upper slopes. This forest developed on clayey, deeply weathered ferralsols. The lower slopes are covered with a scleromorphic forest called 'Campinarana', characterised by small trees (mean height of 8 m), reduced biodiversity (60% of the tree cover comprises only 3 species) and a high endemism level (Anderson, 1978). This forest develops on sandy, shallow podzols. Table 1 gives a comparative description of the surface soil horizons of the two ecosystems studied.

The two study sites are part of INPA reserves (National Institute of Amazonian Research) located North of Manaus: 'bacia 3' for the rainforest, Campina reserve for the Campinarana forest (Fig. 1).

Experimental design

FIELD EXPERIMENT

Free-flow lysimeters were used in this study because they allow measurement of both the quality and quantity of percolating soil waters (Joffe, 1932; Jordan, 1968) and are particularly well adapted for use in well structured soils with high clay contents (White, 1985; Barbee and Brown, 1986).

The lysimeter trays (37 cm × 45 cm) were installed at different depths within the soil profiles according to the horizon differentiation described in Tab. 1: below the organic horizon (reduced to the litter in the ferralsol case), and at depths of 10, 20 and 40 cm. Each tray was connected to a 1 litre bottle by a polyurethane tube. Because of the spatial homogeneity of these soils and large sample volumes generated, only a single lysimeter was used per sampling depth.

Ten through-fall collectors were also located in each site. Because through-fall is spatially heterogeneous in quantity and quality, only data from the collectors located adjacent to the lysimeters at each site were used to quantify the chemical input to the soil surface above the lysimeters. These collectors were made from a 15 cm diameter funnel, located about 1.5 m above the soil and connected to a 5-litre bottle by tubing. A 0.5 mm nylon mesh filter in the funnel kept fine litter from entering the collector. All the material was white polyurethane plastic to avoid metal contamination. Soil water and through-fall were collected for each rain event during two sampling periods: May 1993, at the end of the rainy season (3 and 6 rain events in Campinarana and rainforest respectively) and April 1994, at the peak of the rainy season (5 rain events in both forests).

Table 1. Soil profile characteristics at the lysimeter locations in both study environments.

Lysimeter depth	Ferralsol horizons	Podzol horizons
0 cm	A _{oo} , 3–0 cm : Thin litter of unbroken leaves	A _{oo} and Ah, 10 to 20 cm thick organic layer composed of fresh unbroken leaves, broken leaves and fine black organic material. Roots very abundant.
10 cm	0–10 cm : brownish coloured (10 YR 5/3) A horizon, rich in organic matter, mainly kaolinite (70%) with a small amount of gibbsite, goethite and quartz, aggregated structure, with abundant roots	0–5 cm : E horizon, 5 to 10 cm of an irregular grey to white sandy quartz horizon, very poor in kaolinite, gibbsite and goethite.
20 cm	10–30 cm: yellow (10 YR 7/5) AB horizon. Progressive decrease of organic matter content and root abundance.	5–20 cm : B _h horizon : sandy soil becoming darker due to a richer amount of organic carbon.
40 cm	30–40 cm: yellow (10 YR 7/5) B1 horizon, very poor in nutrient, with a very fine porosity.	with larger amount of organic carbon, kaolinite, goethite and gibbsite.

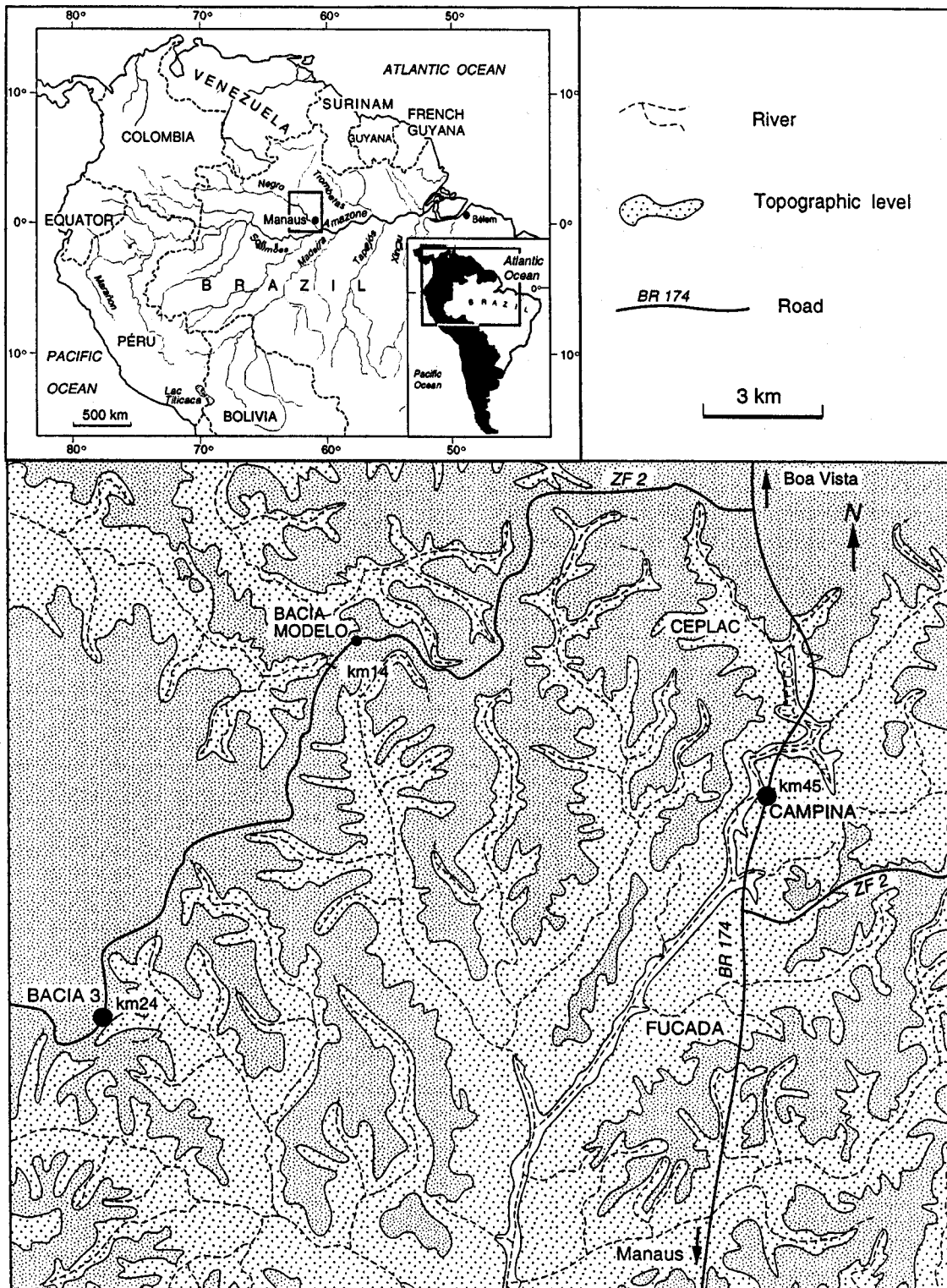


Fig. 1 Location of the areas of study

ANALYTICAL METHOD

pH was measured within a few hours of sampling. The samples were filtered through pre-washed 0.22 m cellulose acetate filter (Millipore, type GFWP). The following analyses were performed :

- SO_4^{2-} , NO_2^- , NO_3^- , K^+ , Ca^{2+} , Na^+ by capillary electrophoresis (Waters CIA analyser);
- Fe and Al by ICP-AES (Jobin Yvon 38 Type 3) and AAS graphite furnace (Hitachi Z-8200);
- Si and NH_4^+ by colorimetry, using the respective procedures of Govett (1961) and Anderson and Ingram (1993);
- DOC by photochemical oxidation Dohrmann (DC 80) apparatus.

THERMODYNAMIC EQUILIBRIUM MODELLING

A thermodynamic equilibrium model (MINTEQA, 1993) was used to calculate soil solution speciation of Si, Fe and Al, and the state of saturation of the dominant minerals (kaolinite, gibbsite, quartz). Thermodynamic constants for the water-mineral equilibrium (Gibbsite $\log K = -8.205$; Kaolinite $\log K = -7.410$; Quartz $\log K = 3.999$) were selected from Trolard and Tardy (1987, 1989) and Ambrosi (1990). The only Al-bearing minerals considered were kaolinite and gibbsite; the Al contained in substitution in goethite (Lucas, 1989) was neglected. The possibility of Fe and Al complexation by dissolved organic matter (OM) was taken into account by assigning identical $\log K$ of -5 to these two equilibria in accordance with Stevenson and Vance (1989) and Eyrolle (1994). The temperature was considered equal to 28°C . The OM site densities required by MINTEQA were assumed to range from 6 to 12 meq per gram of carbon for the dissolved organic substances (Buffle, 1988) and 8 meq per gram of carbon for stream water from Manaus region (Eyrolle, 1994).

Results

pH VALUES

While the through-fall pH was approximately 5.5 for both forest environments, the soil water pH varied with depth depending on the nature of the soil (Table 2). In Campinarana, the pH decreased within the litter and reached values around 3.5. In the ferralsol, the waters are less acidic with values around 4.5 in the mineral horizons.

The pH decrease in both cases is due to the release of organic acids in the soil solution. In Campinarana, the water passing through the litter became black and enriched in organic particles. Water in the ferralsol, on the other hand, remained clear reflecting the fact that smaller quantities of organic compounds are released. These organic compounds are more highly decomposed than in the podzol (Leenheer, 1980). In the rainforest environment, the pH decreased.

Table 2. Mean pH values (\pm sd) of the soil water and throughfall in Campinarana and rainforest

Depth	Campinarana	Rainforest
Through-fall	5.9 ± 0.5	5.5 ± 0.2
Litter	3.4 ± 0.2	5.3 ± 0.2
10 cm	3.6 ± 0.2	4.3 ± 0.3
20 cm	3.6 ± 0.2	4.6 ± 0.1
40 cm	4.2 ± 0.4	4.5 ± 0.2

NUTRIENT CONCENTRATIONS

Nutrient concentrations were highly variable over time, but are generally of the same order of magnitude as those found in other studies for the same region (Chauvel, 1978; Nortcliff and Thornes, 1978; Brinkmann, 1989; Forti, 1989). Concentrations of NO_3^- , SO_4^{2-} , Na^+ , Ca^{2+} , K^+ and NH_4^+ (Fig. 2, Table 3, 4) were similar in both forest environments. At the 40 cm depth, concentrations were lower than those at other depths and were often similar to those in the corresponding through-fall samples.

In both ecosystems, Ca^{2+} , Na^+ , and DOC concentrations were higher during the second sampling period in all samples (Table 3, 4 and Fig. 2, 3). This may be due to release of elements by the vegetation during the rainy season when the leaves begin to decompose before falling (dos Santos *et al.*, 1981). The soil water concentrations of NO_3^- , K^+ and SO_4^{2-} for Campinarana and of NH_4^+ for the rainforest were highly variable over the first sampling period. Over this period, rain events were scarce in Campinarana (Fig. 4), resulting in a highly variable soil moisture which affects bacterial activity (Luizão and Schubart, 1987), with resulting repercussions on NO_3^- , NH_4^+ , and SO_4^{2-} concentrations.

SI, FE, AL AND DOC CONCENTRATIONS

Changes with depth

Si, Fe and Al concentrations in the podzol (Fig. 3, Table 3) were positively inter-correlated (Table 5). Concentrations in the through-fall were low, followed by element enrichment as the water passes through the litter and the upper 10 to 20 cm of the soil; under 20 cm the concentrations decreased. The Si:Al ratio (Fig. 3) was almost always less than 1.

In the ferralsol, Si, Fe and Al concentrations were lower than in the podzol (Fig. 3, Table 4) and were not inter-correlated (Table 5). The Si and Al concentrations increased within the mineral horizons and the Si:Al ratios were greater than 1 (Fig. 3). This ratio is higher during the second sampling period than during the first. The concentrations in Si and Fe were lower at 40 cm than in the rest of the mineral horizons (Fig. 3).

Table 3. Volume weighted mean concentrations (mmol.L⁻¹) of the throughfall and soil waters in elements for each sampling period (May 1993 and April 1994) in Campinarana

	SO ₄ ²⁻	NO ₃ ⁻	K ⁺	Ca ²⁺	Na ⁺	NH ₄ ⁺	Fe	Al	Si	DOC
May 1993										
Through-fall	0.001	0.001	0.005	0.004	0.024	0.000	0.001	0.001	0.001	0.36
Litter	0.010	0.315	0.054	0.009	0.213	0.102	0.003	0.035	0.029	6.97
10 cm	0.049	1.374	0.032	0.009	0.224	0.000	0.005	0.161	0.059	3.48
20 cm	0.080	1.357	0.029	0.004	0.147	0.000	0.005	0.194	0.147	4.92
April 1994										
Through-fall	0.001	0.000	0.018	0.101	0.449	0.004	0.002	0.004	0.001	15.22
Litter	0.004	0.175	0.018	0.087	0.594	0.008	0.004	0.023	0.013	13.77
10 cm	0.004	0.069	0.017	0.083	0.526	0.006	0.009	0.092	0.045	11.20
20 cm	0.004	0.204	0.015	0.072	0.477	0.008	0.006	0.073	0.038	11.75
40 cm	0.020	0.039	0.012	0.064	0.455	0.003	0.003	0.036	0.025	9.28

The DOC concentrations increased within the litter horizon in both environments, but were higher in the podzol than in the ferralsol (Fig. 3). They decreased with depth in the podzol, while remaining constant in the ferralsol. The DOC concentrations in the podzol were, however, still higher than in the ferralsol.

There is no correlation between DOC concentrations and concentrations in Fe, Si or Al in either environment.

Al and Fe speciation

MINTEQ calculations indicated that more than 90% of Al and Fe are present in the water samples as organic complexes, and that Al-sulphate complexes were insignificant (due to the very low SO₄²⁻ concentrations). The effect of

varying of K values for the OM-complex reaction on model results was tested; it was found to have little effect because of the high DOC concentrations and the rather acidic pH values of the waters. DOC is therefore the dominant factor determining Al and Fe speciation of these soils, as is generally the case in forested soils (Stevenson and Vance, 1989).

MINERAL STABILITY

The values of pH of the waters were quite acidic (<5); the main form of predicted inorganic Al was, therefore, Al³⁺. The calculated Al³⁺ concentrations were introduced into the thermodynamic diagrams (Fig. 5 a, b); these show that

Table 4 : Volume weighted mean concentrations (mmol.L⁻¹) of the through-fall and soil waters in elements for each sampling period (May 1993 and April 1994) in the rain-forest

	SO ₄ ²⁻	NO ₃ ⁻	K ⁺	Ca ²⁺	Na ⁺	NH ₄ ⁺	Fe	Al	Si	DOC
May 1993										
Through-fall	0.010	0.158	0.031	0.022	0.183	0.005	0.002	0.006	0.001	0.65
10 cm	0.015	0.268	0.033	0.006	0.084	0.019	0.002	0.025	0.025	0.51
20 cm	0.030	0.321	0.034	0.002	0.050	0.108	0.001	0.005	0.011	0.72
40 cm	0.007	0.144	0.026	0.017	0.058	0.011	0.003	0.013	0.024	0.37
Litter	0.109	0.355	0.128	0.040	0.078	0.015	0.006	0.042	0.031	4.84
April 1994										
Through-fall	0.006	0.451	0.036	0.070	0.322	0.004	0.002	0.003	0.002	8.82
Litter	0.008	0.070	0.031	0.080	0.424	0.027	0.003	0.003	0.002	12.71
10 cm	0.013	0.111	0.027	0.088	0.532	0.002	0.003	0.005	0.030	10.78
20 cm	0.016	0.158	0.033	0.099	0.542	0.002	0.002	0.004	0.028	8.33
40 cm	0.013	0.087	0.024	0.080	0.475	0.002	0.002	0.004	0.021	10.19

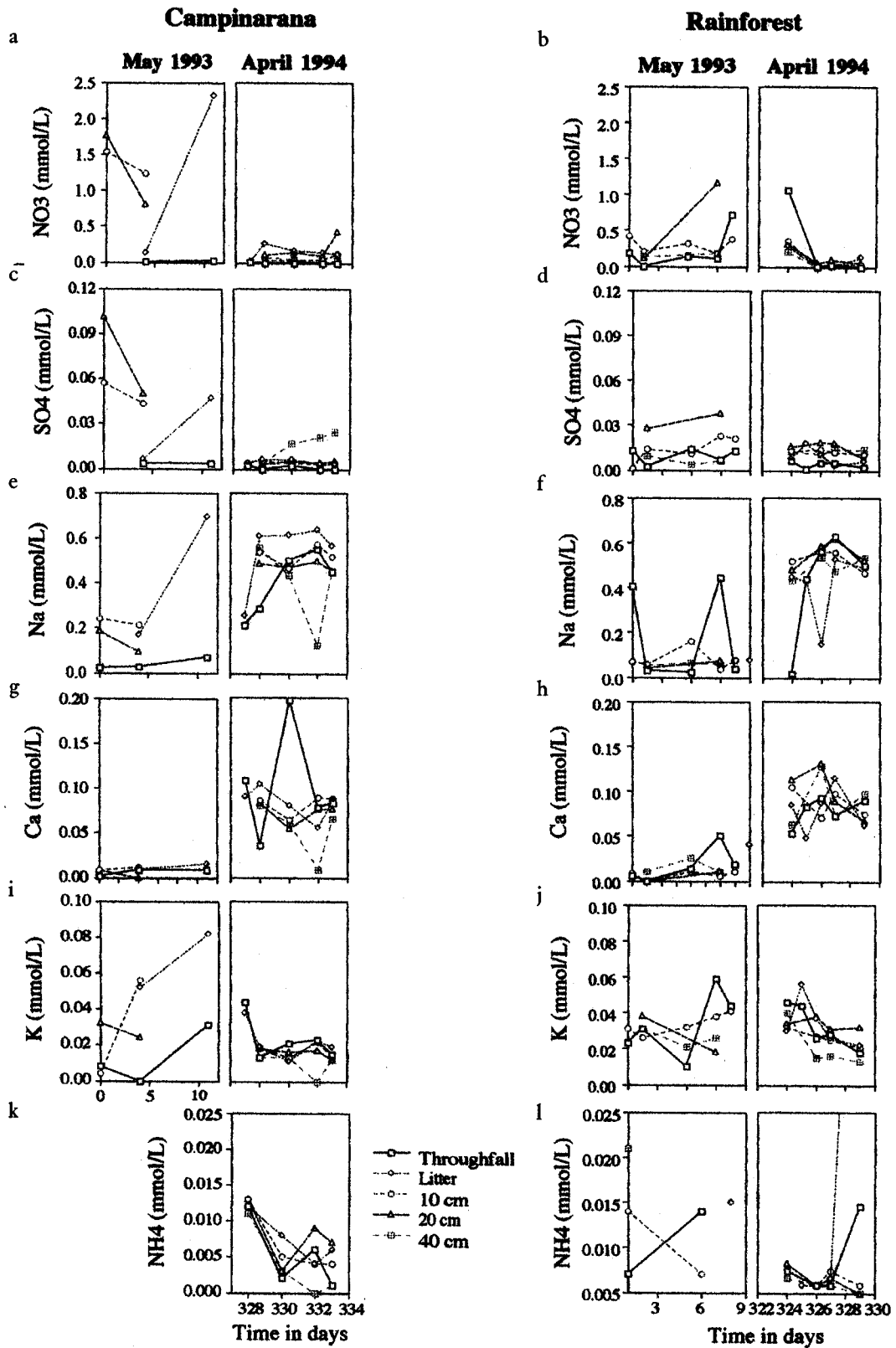


Fig. 2 Temporal variation in nutrients concentration: (a) NO_3^- in Campinarana, (b) NO_3^- in the rainforest, (c) SO_4^{2-} in Campinarana, (d) SO_4^{2-} in the rainforest, (e) Na^+ in Campinarana, (f) Na^+ in the rainforest, (g) Ca^{2+} in Campinarana, (h) Ca^{2+} in the rainforest, (i) K^+ in Campinarana, (j) K^+ in the rainforest, (k) NH_4^+ in Campinarana, (l) NH_4^+ in the rainforest.

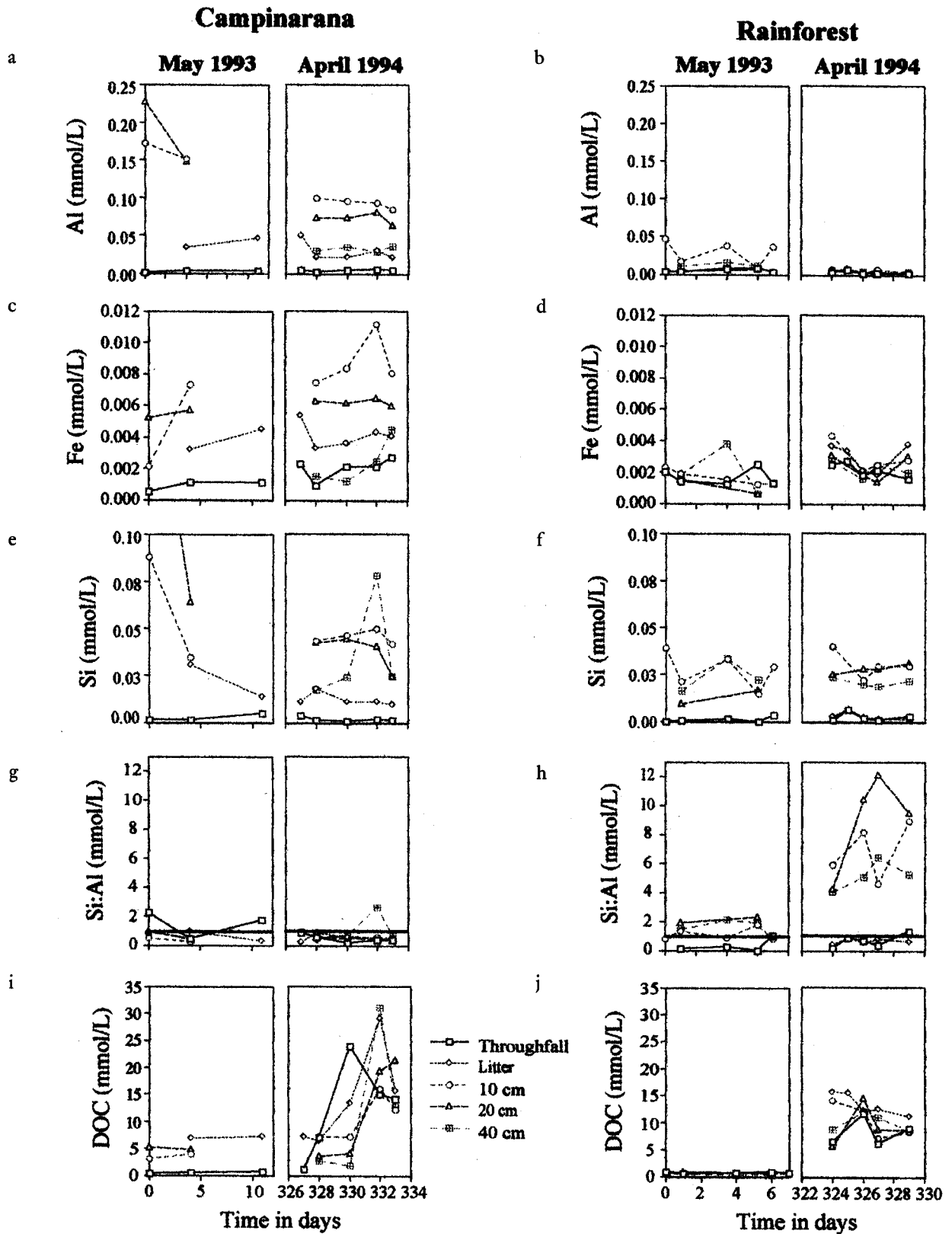


Fig. 3 Temporal variation in Si, Fe, Al and DOC concentration: (a) Al in Campinarana, (b) Al in the rainforest, (c) Fe in Campinarana, (d) Fe in the rainforest, (e) Si in Campinarana, (f) Si in the rainforest, (g) Si:Al in Campinarana, (h) Si:Al in the rainforest, (i) DOC in Campinarana, (j) DOC in the rainforest.

Table 5. Correlation coefficient of Si, Fe, Al concentration in both environments

	Campinarana	Rainforest
	n = 66	n = 66
Fe-Al	0.87	0.1
Fe-Si	0.65	0.06
Si-Al	0.72	0.29

through-fall at both sites is apparently at saturation, or over-saturated, with respect to gibbsite. The water going through the organic soil layer, under-saturated with respect to all mineral phases in the podzol, was close to equilibrium with respect to gibbsite in the ferralsol. In both cases, the waters become under-saturated with respect to all Al and Si bearing minerals upon reaching the mineral horizons. However, some samples from the podzol at the 10 and 40 cm depths showed high Si concentrations exceeding quartz saturation.

Cornu *et al.* (1995) showed that crystalline kaolinite and synthetic gibbsite were weathered after 6 months in the topsoil for both soil types. The thermodynamic modelling is in good agreement with these field experiment results.

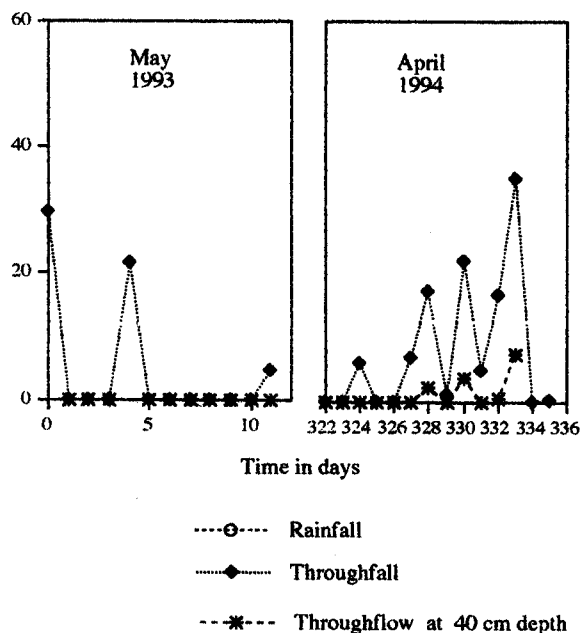
Fig. 6 presents the pH values of the water versus ($\log Al_{tot} + \log Si_{tot}$), where Al_{tot} and Si_{tot} are the dissolved concentrations of Al and Si respectively in the water samples from the rainforest environment. The 10 and 20 cm samples give linear relationships with a slope of about 0.3 (Fig. 6). Grimaldi (pers. com.) found the same relationship for Manaus ferralsol water collected from the upper hill slopes. This relation can be interpreted as kaolinite controlling Si and Al concentrations as a function of pH in the soil solution at the 10 and 20 cm depths. Si and Al concentrations of the waters passing through the litter are, on the other hand, not linked to pH.

Discussion

NUTRIENT RECYCLING

The water volumes (Cornu, 1995) and concentrations of most of the nutrients studied were greatest in the through-fall and decreased progressively with soil depth in both environments (Fig. 4). The nutrients were therefore retained strongly in the upper 40 cm of the soil, which is, on the other hand, also very poor in most nutrients. This implies that nutrients are being recycled actively by the vegetation, as observed by Stark and Jordan (1978). This nutrient recycling is clearer in Campinarana than in the rainforest where the concentration variability with time was higher, probably due to the greater availability of nutrients in the latter environment as compared to the former.

Campinarana



Rainforest

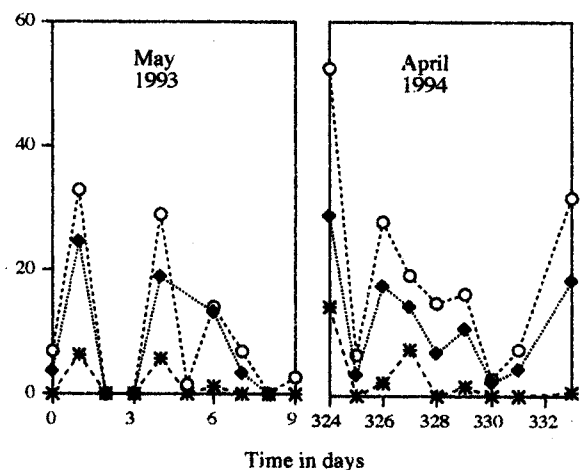


Fig. 4 Volume of throughfall, rainfall and leachate at 40 cm depth in Campinarana and in the rainforest.

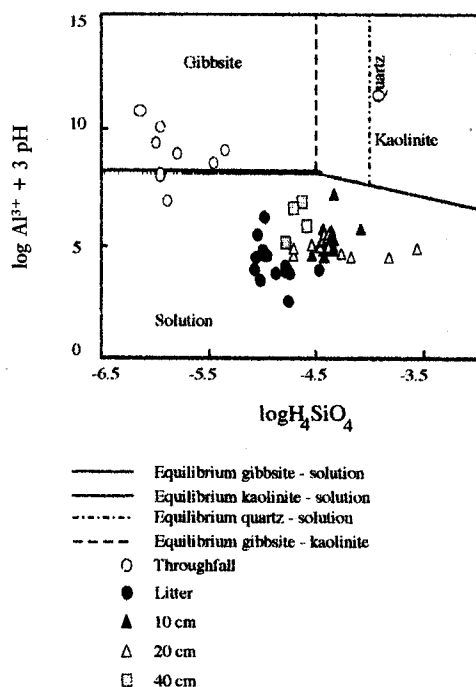
SI, FE, AL CONCENTRATION CHANGE WITH DEPTH

Campinarana podzol

Free-flow lysimeters allow sampling of water contained in pores larger than 15 μm in equivalent diameter. In the Campinarana soil, these pores make up 80% of the total porosity (Cornu, 1995).

The Si, Fe, and Al concentrations increased as soil water percolated through the litter. In Campinarana, the litter

a : Campinarana



b : Rainforest

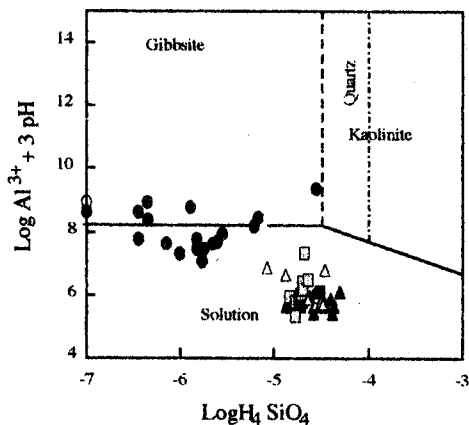


Fig. 5 Thermodynamic equilibrium of the waters with respect to the main Al and Si bearing mineral phases of the Campinarana podzol (a) and of the rainforest ferralsol (b).

comprised a 10 to 20 cm thick root mat composed of organic fragments. The retention time of the water in the organic layer was also quite high. The water was enriched in Si, Fe and Al, probably released by the decomposing organic fragments, which contain these elements. The Si:Al ratio in water was, however, less than 1 (kaolinite Si:Al ratio = 1) in the throughfall and organic layer waters in both environments. The litter Si:Al ratio is very high (around 16). This implies that most of the Si contained in the litter is not released in a dissolved form but, rather,

either remains in the topsoil or is transported out of the system in the form of phytoliths (Alexandre *et al.*, 1994).

Leached Fe and Al are observed in the shallow eluvial horizon located beneath the litter layer, (Cornu, 1995). Soil water passing through this horizon is enriched in Si, Fe and Al, probably due to mineral dissolution. The Si:Al ratio in solution was always less than 1. This indicates that the Si and Al contained in the $< 0.22 \mu m$ fraction were due not to small kaolinite particles, but rather to dissolved Si and Al-organic matter complexes. Iron was also in the form of OM complexes. The Si probably originated from dissolution of trace amounts of soil kaolinite and quartz, the main constituent of the horizon. Since neither gibbsite, nor any other pure Al mineral phases, were found in the 10 first cm of that soil (Cornu, 1995), Al must be released by organic matter decomposition or kaolinite dissolution. Goethite was also probably undergoing dissolution. This is consistent with the fact that thermodynamic calculations indicate that these waters were unsaturated with respect to these minerals. Since this horizon is predominantly made up of quartz, it also has a very low sorption capacity, facilitating downward leaching of Al and Fe released by mineral dissolution.

Horizons richer in kaolinite, gibbsite, goethite and organic matter are found at the 20 and 40 cm depths, and the corresponding percolating solutions show decreased DOC, Si, Fe and Al concentrations. DOC and organic bound Al and Fe are removed from the soil solution and retained on the soil matrix. The Si:Al ratio at the 40 cm depth remains constant, and Si and Al are retained in a 1:1 ratio perhaps because of kaolinite generation. The chemistry of water percolating rapidly through the podzol explains the soil horizon formation of the podzol.

Rainforest ferralsol

In the ferralsol, 85% of the pore volume is represented by pores smaller than $15 \mu m$ in equivalent diameter. This means that the lysimeters sampled water passing through roughly only 15 % of the soil porosity, the remainder of the water having a much longer residence in the soil (Cornu, 1995). The Si and Al concentrations in the rapidly percolating water increased within the first 10 cm of the soil. A Si:Al ratio higher than 1 indicates that Si release rate exceeds that of Al. This Si release could be due to (a) quartz dissolution, (b) release by organic matter which has a Si:Al ratio of 16, or (c) kaolinite dissolution. Quartz dissolution kinetics are very low compared to kaolinite dissolution. Large quantities of biological silica (phytoliths) were observed in the upper part of these soils (Alexandre *et al.*, 1994). A steady state system where phytolith input equals phytolith dissolution would not explain a net dissolved Si output. Since the Si:Al ratio in the water remained higher than 1, and kaolinite dissolution releases Al and Si in equal amounts to the soil solution, some Al must be trapped as gibbsite or adsorbed on exchange surfaces if this hypothesis is to hold.

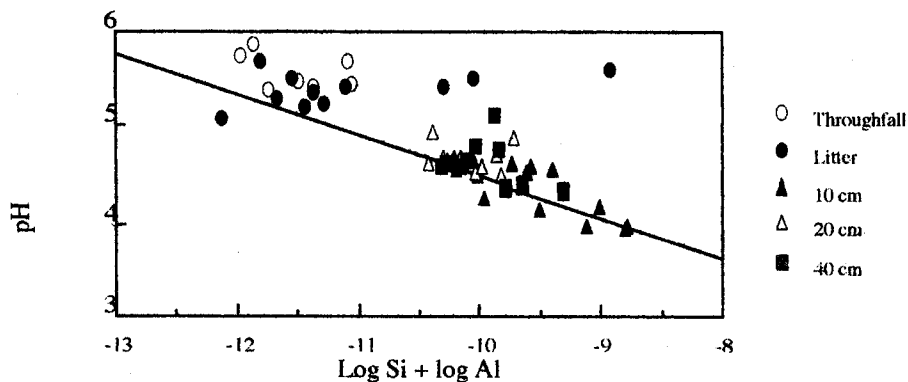


Fig. 6 Kaolinite influence on the water chemistry in the ferralsol.

The Si:Al ratio of the water samples percolating through the mineral horizon is higher during the second sampling period than during the first, indicating preferential Si release during the second period. This may be due to a greater organic matter decomposition, or a greater mineral dissolution due to the higher organic acid concentrations. The DOC content is, in fact, higher during the second period.

Water samples were under-saturated with respect to all minerals, so gibbsite precipitation was unlikely. Since Al accumulation was not observed in the top horizon, Al was likely to be fixed temporarily on the soil matrix, then released between the rain events and transferred to the slowly percolating water. In the ferralsol, the study of the rapidly percolating water did not suggest an explanation for kaolinite formation in the upper part of the profile. Other transfers, possibly in the slowly percolating water or in particle form must be studied to understand the processes of formation of this soil.

Conclusion

Studies of the soil water collected with free flow lysimeters in two different Amazonian soils show that the concentrations of nutrients were of the same order of magnitude in both environments and that nutrients were highly recycled on the 40 upper cm of the soils. The soil water concentrations in Si, Fe and Al are higher in the podzol water, even though these elements were less abundant in the podzol than in the ferralsol.

In both environments, dissolved Al and Fe are complexed principally with organic compounds. The waters were under-saturated with respect to kaolinite, gibbsite and quartz.

In the podzol, the variations of solute concentrations with depth are in agreement with the standard podzolisation theory.

In the ferralsol, the Si, Fe and Al concentrations increased in the soil, probably as a result of release from organic matter and kaolinite dissolution.

Previous studies of this ferralsol (Lucas, 1989; Giral, 1994) have shown that this soil profile is in a steady state, and that the kaolinite of the upper horizons was formed in situ. This implies that Si is maintained in the topsoil. Lucas *et al.* (1993) showed that the release of Si and Al contained in the litter within the water percolating annually through this soil would lead to soil solutions in equilibrium with respect to kaolinite. The present study confirms that the large amounts of Si and Al brought to the topsoil by forest element cycling is released slowly into soil solutions. The processes are, however, more complex than assumed previously. Indeed, Al and Fe are not present in the soil solution as free ionic elements, but form organo-metallic complexes. This leads to under-saturation of rapidly percolating waters with respect to all minerals. In the ferralsols studied, the composition of rapidly percolating soil waters does not support kaolinite generation, mainly due to the presence of Al-OM complexes in the water. To investigate kaolinite formation in the soil surface horizons, other transfers such as slowly percolating water contained in the fine pores have to be studied.

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