

# Natural Waters in Amazonia

## VI - Soluble Calcium Properties <sup>(1)</sup>

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### ABSTRACT

The principle sources of the calcium found in the water of the tertiary Amazonian region near Manaus, are the water running over the tree trunks and the total forest water. The soluble calcium content must come from the rain washing the tree crowns, stems, and leaves, and to a certain point from the dissolution of metabolic products of macro and micro-organisms. Generally, only traces of calcium are found in rain water, soil, and river water. Therefore, calcium can be considered as an element circulating in a closed system. Altogether the calcium content in the natural water of the tertiary Amazon region is extremely low.

### INTRODUCTION

Because of the widespread occurrence of calcium in rocks, soils and plants the macronutrient calcium in dissolved form is present in nearly all natural waters. In rocks and soils of the Tertiary region of Central Amazonia, however, the calcium content is extremely low (IPEAN, 1969). Calcium bearing minerals such as calcium carbonates, dolomites, gypsum, anhydrites, etc. are completely lacking in the contact zone of cycling water. Unfortunately, the accumulation of calcium in plants and animal communities has not been quantitatively studied yet. Calcium is often immobilized in trees in the form of calcium oxalate, as calcium phosphate or forms salts with various organic acids. In natural waters, however, calcium deficit may be due to precipitation as calcium humate in presence of dissolved organics. Soluble calcium compounds are subject to leaching by rain, which totals about 2000 mm a year (Brinkmann & Nascimeto, 1972).

### MATERIAL AND METHODS

Soluble calcium properties were studied at 2 experimental sites along the Manaus-Itacoatiara Road (AM-10) in Central Amazônia (Fig. 1). Site descriptions are as follows:

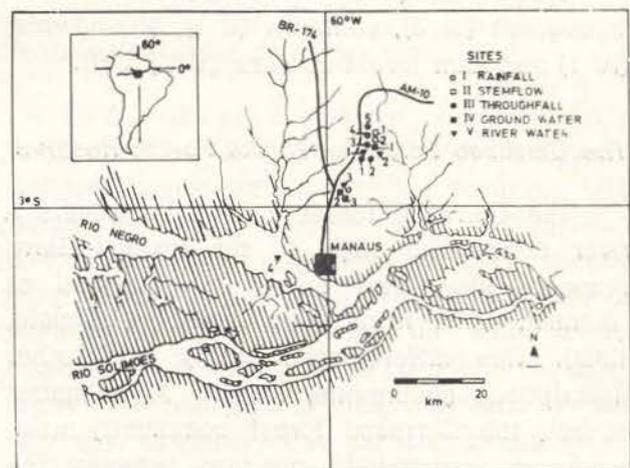


Fig. 1 — Sampling sites in Central Amazonia

### *The Riverine Forest at Ducke Forest Reserve*

This forest community is referred to as "Rain forest on the low terra firme" (Takeuchi, 1962). A 30 by 30 meter inventory yielded 57 trees (10 cm to 25 cm DBH), including some palms and 13 trees (above 25 cm DBH). The dominant tree species belong to families, as Leguminosae, Sapotaceae and Moraceae (Takeuchi, 1962). The canopy heights range from 25 m to 36 meters, are poorly defined, and the canopy area has many epiphytes, trailing lianas, Bromeliaceae and Orchidaceae.

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The dense ground cover consists of stemless palms, herbaceous plant communities and some seedlings and saplings. The herbaceous communities consists of Hymenophyllaceae, Polypodeaceae, Lycopodiaceae, Bromeliaceae, Maranthaceae, Rapateaceae, Araceae and Orchidaceae (Aubreville, 1961). Common palms are *Astrocaryum* sp, *Oenocarpus* spp, *Attalea* sp, and *Euterpe oleracea*.

The soils are of the sandy riverine complex with some humus accumulation in the upper 15 cm of the soils profile and a considerable litter layer. The groundwater level is quite high in all months of the year except for August to October. During, or shortly after heavy downpours, the forest floor is temporarily flooded by rain water surplus.

Water samples were collected from throughfall (III 3), stemflow (II 1), groundwater (IV 1) and Rain forest streams (V 1 / V 2).

#### *The Carrasco Forest at Ducke Forest Reserve*

The Carrasco forest community covers a river terrace-like slope of the Igarapé Barro Branco valley. The forest is described as "inclined terra firme Rain forest" (Takeuchi, 1962). This differs considerably from other descriptions (Aubreville, 1961). As a matter of fact, the Carrasco forest community maintains an intermediate position between the Riverine forest and the terra firme Rain forest.

The canopy heights range from 22 m to 32 meters, including some emergent trees (*Hymenolobium excelsum* Ducke). Although the forest community is quite heterogeneous, *Protium* spp and *Eschweilera* spp are more frequent than other tree species. A 30 m by 30 meter inventory recorded 35 trees (10 cm to 25 cm DBH) and 20 trees (above 25 cm DBH) respectively (Takeuchi, 1962). Epiphytes, Bromeliaceae and Orchidaceae are less abundant than in the Riverine forest community. The understory consists of numerous seedlings and saplings, some herbaceous plants and small palms. The soils are of the latosolic complex, but contain a considerable amount of sand at least in the upper part of the soil profile.

Water samples were collected from throughfall (III 4) and stemflow (II 2).

#### *The Terra Firme Rain Forest at Ducke Forest Reserve*

The terra firme Rain forest community is typical for the Tertiary formations of Central Amazonia, which are never flooded by river waters during flood season.

The climax forest along the Manaus-Itacoatiara Road was preliminary inventorized in 1965 (Rodrigues, 1967). Dominant tree species of the heterogeneous terra firme climax forest are *Eschweilera* spp (6.5 trees/ha), *Steronema micranthum* Ducke (3.4 trees/ha), *Corythopora aita* Knuth (2.9 trees/ha) and *Nyagala spuvia* (Ducke) Aubr. (2.2 trees/ha). The forest inventory contains all trees with stem diameters above 25 cm DBH. More than 40% of all trees above 10 cm in diameter (DBH) belong to the families Leguminosae, Letythidaceae and Sapotaceae (Takeuchi, 1962). The total number of trees counted in a 1600 m<sup>2</sup> inventory at Ducke Forest Preserve was at 123 trees (above 25 cm DBH). Canopy heights range from 25 m to 35 meters and canopy strata are relatively well defined. Epiphytes, Bromeliaceae and Orchidaceae are less frequent than in the Riverine forest community but more abundant than in the Carrasco forest. Trailing lianas, however, are quite common. Palms, as *Astrocaryum munbaca*, *Syagrus inajai* and *Bactris* sp form the shrubstratum. Seedlings, stemless palms as *Oenocarpus* spp, *Scheelea* sp, *Orbygnia spectabilis*, and a few herbs (Cyperaceae, Maranthaceae and Orchidaceae) represent the ground stratum.

About 85% of the "chapada" soils belong to the latosolic group. These latosols are low in soils pH (range: pH 3.6 to pH 4.1), very low in extractable calcium, magnesium and potassium and extremely low in phosphorus (Brinkmann & Nascimento, 1972; IPEAN, 1969).

Water samples were collected from throughfall (III 1/III 2/III 5) at 3 terra firme Rain forest sites slightly different in their floristic composition.

### *The Clearing at Km 18 of the Manaus-Itacoatiara Road*

The climax forest of this site, similar in composition to the above described Carrasco forest, was slashed and burned in 1966. During the first year some rice and manioc was harvested. But in 1968 the clearing was abandoned. During the period of investigation the clearing was increasingly covered with *Cecropia* spp and *Solanum* spp and also some stemless palms. Oil palms were planted in 1969 but did not grow well.

The area is covered with deep white sand layers, which are extremely low in plant nutrients (Brinkmann & Nascimento, 1972; IPEAN, 1969; Klinge, 1967). Water samples were collected from rainwater (I), ground water (IV 2/IV 3) and Rain forest stream water (V 3).

#### SAMPLING AND ANALYTICAL PROCEDURES

In 1969/70 water samples were collected from rainwater (I), stemflow (II 1/ II 2), throughfall (III 1 - III 5), ground water (IV - 1 IV 3) and Rain forest stream water (V 1 - V 3). Rainfall, throughfall and stemflow were collected per event (at least 2 liters of water per samples), while ground water and Rain forest stream water were sampled weekly.

Calcium was determined titrimetrically using Komplexon III (Merck) and HHSNN-Indicator (Merck). Interferences did not occur. Calcium concentrations below 20 ug/1 Ca<sup>++</sup> were presented unorganized as follows from the detection limit of the analytical procedures.

#### THE WATER SOLUBLE CALCIUM CYCLE

The annual cycle of plant nutrients or nonessential elements in a tropical Rain forest system and on man-made openings was studied for the first time by the authors (Brinkmann & Santos, 1970a; 1970b; 1971; 1972a; 1972b), as far as water cycle bound components are concerned. The pathways of soluble calcium compounds were investigated as follows from the simplified model below:

#### *Man-made openings*

rainwater  
soil/ground water  
stream water

#### *Tropical Wet Forest sites*

rainwater/throughfall/stemflow  
soil/ground water  
stream water

Soluble calcium concentrations are given for all waters sampled as dry season (June-October), wet season (November-May) and yearly averages in ug/1 Ca<sup>++</sup> (tab. 1) and as frequency distribution (%) of Ca<sup>++</sup> concentrations grouped by 300 ug/1 Ca<sup>++</sup> intervals (tab. 2).

#### SOLUBLE CALCIUM IN RAINWATER

Rainwater of 51 storm samples (bulk samples from 3 collectors) was analyzed. Calcium concentration in all samples was below 20 ug/1 Ca<sup>++</sup>. The hydrogen-ion concentration in rainwater samples ranged from pH 4.2 to pH 5.5, while about 75% of samples analyzed showed up with a pH between pH 4.3 and pH 4.9. Particle sampling under the canopy of the Carrasco forest recorded extremely low particle counts in air samples (mean 500 particles/cm<sup>3</sup>) and neither marine nor land-borne calcium particles were present (Sheesley et alii, 1972). Particle counts in the open, however, are also low. At Rio Tarumã the daily average particle counts were about 300 cn/cm<sup>3</sup> on April 17th, 1970 and also 300 cn/cm<sup>3</sup> on September 29th, 1970 respectively. The daily average particle count at Rio Solimões was at about 200 cn/cm<sup>3</sup> on October 1st, 1970. As a matter of fact, the calcium input involving rainout and dry fallout is an insignificant source of supply in the calcium budget of central Amazonian Rain forest. Recently published data on rainwater analyses at Ducke Forest Preserve (4 samples) including calcium determinations are far to high if compared with the results obtained during our investigations (Anan., 1972).

## SOLUBLE CALCIUM IN STEMFLOW

Stemflow was sampled in the Riverine forest (bulk samples of 12 collectors) and the Carrasco forest (bulk samples of 18 collectors). 98 storm samples were analyzed in 1969/70. The soluble calcium concentrations in stemflow of the Riverine forest were about twice as high as in the Carrasco forest referring to seasonal and yearly averages. As described above, the canopy area of the Riverine forest has many with epiphytes, Bromeliaceae, Orchidaceae, etc. Stems, branches and twigs are usually coated with mosses, lichen, algae, fungi and other stem area communities. The leaching of calcium from these stem area communities is the principle calcium source in stemflow. Occasionally the leached excreta of non-photosynthetic macro-and microorganisms may also play a part. The hydrogen-ion concentration in stemflow ranges from pH 4.3 to pH 7.3. About 75% of all samples recorded pH values between pH 5.2 and pH 6.7. Compared with rainwater pH, a significant pH shift to neutral conditions is evident. The leaching of calcium is favored by heavy bacterial and mainly fungal decomposition. The latter will play a dominant part in the canopy areas as follows from the acid environment. The release of calcium is slightly higher in the dry season. This is due to accumulation of decomposition products between the rains, which occur in greater intervals than during the wet season (tab. 1). The calcium concentrations in the stemflow of the Riverine forest and the Carrasco forest, however, show distinctive differences in their distribution pattern. About 60% of stemflow samples in the first forest community (II 1) report calcium concentrations below 1200  $\mu\text{g/l Ca}^{++}$ , while the latter stand (II 2) registers about 90% (tab. 2). This is due to significant differences in composition and density of the stem area communities of both stands. The high calcium release (about 38% of all samples analyzed are found to be between 1200 and 2100  $\mu\text{g/l Ca}^{++}$ ) in the Riverine forest is due to a greater density of stem coating biomass which provides a higher yield

of decomposition products between rains, a fact, which renders more soluble calcium compounds mainly in the dry season.

## SOLUBLE CALCIUM IN THROUGHFALL

Throughfall was sampled in the Riverine forest, the Carrasco forest and at 3 different sites of the terra firme Rain forest (210 storm samples — bulk samples of 10 collectors at each site). Although the yearly averages of soluble calcium compounds very considerably from site to site the dry season averages are much higher than the corresponding wet season averages of soluble calcium at all 5 forest sites (tab. 1). This holds partly for a storage effect of decomposition products in the canopy area between rains, which are less frequent in the dry season. A principle source of soluble calcium in throughfall is pre-fall decomposition of leaves. As leaf-fall occurs mainly in the dry season (Araujo, 1970; Klinge & Rodrigues, 1968), and old leaves are known to accumulate a considerable amount of calcium, the higher dry season concentration of soluble calcium in throughfall is quite real. It was observed in many cases that leaves were demineralized in the canopies to such an extent that only leaf veins remained. Another main source of soluble calcium compounds in throughfall is the leaching of epiphylls (microflora on leaf surfaces), which are abundant on leaves in the canopy area as well as in the shrubstratum and ground stratum communities. Algal and fungal epiphylls are considered to have a high absorption capacity. Decomposition taking place in such leaf surface communities will release a considerable amount of soluble calcium. Finally, up to some extent the leaching of metabolites from leaves also play a part. Throughfall pH ranged from pH 4.6 to pH 7.3 with about 80% of all determinations between pH 5.5 and pH 6.4. Compared with rainwater pH, a slight shift to neutral conditions is obvious. About 87% to 96% of throughfall samples analyzed report soluble calcium concentrations below 1200  $\mu\text{g/l Ca}^{++}$ . But actually, concentration levels in throughfall are also remarkably high and similar to soluble

calcium compounds determined in stemflow, except for sampling site II 1, where stem surface communities render an extremely high release of soluble calcium.

#### SOLUBLE CALCIUM IN GROUND WATER

Ground waters were sampled in 3 wells. The first well was dug into the sandy soils of the Riverine forest (IV 1), while the latter 2 wells were located at the clearing at Km 18 of the Manaus-Itacoatiara Road. Well IV 2 was dug into the white sands of a slight slope of a "chapada" of the Tertiary uplands. Well IV 3 was located about 30 meters from a Rain forest stream (V 3) at the bottom of a valley. The aquifer thickness was in the order of 180 cm having an impermeable barrier below.

Ground waters were sampled weekly. 144 water samples were collected from the 3 well, but 12 times the wells were exhausted during the dry season. Calcium concentration in ground water of the Riverine forest well (IV 1) was below 20  $\mu\text{g/l Ca}^{++}$  for all samples analyzed. The calcium retention by calcium return to the standing crop mainly by roots and mycorrhiza, the absorption and uptake by photosynthetic and non-photosynthetic organisms in the litter layer and the upper 50 cm layer of the soil profiles is such that only traces of soluble calcium are lost to streams. Keeping in mind the considerable amount of soluble calcium supplied by stemflow and throughfall (tab. 1) and a calcium return of about 17 Kg/ha/year in total litter (Klinge & Rodrigues, 1968), the partly immediate recycling of some of the calcium into the photosynthetic and non-photosynthetic standing crop is real. This holds the more as calcium accumulation and fixation in the mineral soil did not occur (IPEAN, 1969). The ground water pH ranged from pH 4.3 to pH 5.2 with about 85% of pH determinations between pH 4.3 and pH 4.9. As a matter of fact, ground water pH in the Riverine forest is about the same as rainwater pH.

Considering soluble calcium compounds in well waters of thick white sand layers (IV 2) covered with secondary growth, the situation is quite different. The yearly average of soluble

calcium of this particular ground water is extremely low. Ground water analyses during the dry season proved that the dislocation of calcium was insignificant due to lack of leaching water. The transport of soluble calcium occurred mainly during the wet season, although the total amount of dislocated calcium was low also. The principle source of soluble calcium in ground water at this particular site is the leaching of the remainders of slash and burn agriculture applied to the area in the past. As a great part of liberated calcium from the burned biomass is lost after some months (Brinkmann & Nascimento, 1972), the availability of calcium at this site is minimized for a while, as calcium is badly needed by the secondary growth. This holds the more, as the primary calcium source is limited and exhaustible. The ground water pH ranged from pH 4.3 to pH 5.5 with about 80% of all pH determinations between pH 4.3 and pH 4.9. Compared with rainwater pH, the data in both waters are quite equal.

The concentration pattern of soluble calcium in the ground water sampled from well IV 3 at the bottom of a valley is completely different from all other ground waters analyzed (tab. 1). Seasonal variations are insignificant if referred to dry season and wet season averages of soluble calcium. The high amount of soluble calcium and the lack of seasonal variations is due to an accumulative effect as follows from very low flow rates in the aquifer. Additionally, a relatively dense secondary growth community contributes some calcium in the form of decomposed litter. The calcium supply through calcium transfer from the clearing (well IV 2) certainly plays a minor part as well. As a matter of fact, the soluble calcium concentrations analyzed in well IV 3 area not representative for a greater area while limited to specific eco-conditions.

#### SOLUBLE CALCIUM IN RAIN FOREST STREAM WATERS

The amount of soluble calcium in Rain forest stream waters (V 1-V 3) was below 20  $\mu\text{g/l Ca}^{++}$  in all samples analyzed, inde-

pendently from season and extension of the catchment area. The low amount of available calcium in the waters of Rain forest streams of the central Amazonian Tertiary formations proves the rapid recycling of the macronutrient. Although primary productivity in the Rain forest stream waters analyzed is low, a rapid calcium uptake by aquatic organisms and floating root systems was expected. In the presence of dissolved organics a calcium fixation, as calcium-humate, in the sediments may occur, but has not yet been proved.

#### CONCLUSIONS

The principle source of soluble calcium in cycling water of a Riverine forest, a Carrasco forest and 3 terra firme Rain forest communities was the forest vegetation itself. Calcium input by rainwater was below 20 ug/1 Ca<sup>++</sup> in all samples analyzed. High calcium concentrations were determined in stemflow and throughfall. The principal sources of soluble calcium in stemflow were: 1) release of calcium from photosynthetic stem, branch and twig coating communities favored by heavy bacterial but mostly fungal decomposition processes, 2) the solubilization and leaching of epiphytal communities and their humus packs and 3) leaching of excreta of non-photosynthetic macro-and microorganisms. The main sources of soluble calcium in throughfall were: 1) solubilization processes on leaves and epiphylls, 2) calcium release during heavy pre-fall decomposition of leaves and 3) sporadic leaching of excreta of non-photosynthetic macro-and microorganisms from leaf surfaces. The amount of soluble calcium analyzed in ground water of the Riverine forest was below 20 ug/1 Ca<sup>++</sup>. The soluble calcium, however, apparently liberated from the forest by stemflow, throughfall and litter was rapidly removed by the forest communities before entering the ground water and streams. Hence this is evidence for extremely rapid uptake by plants, photosynthetic and non-photosynthetic organisms in the main root-zone thus maintaining a tightly closed cycle.

The principle calcium source of the bleached white sand layers at Km 18 of the Manaus-Itacoatiara Road was the leaching of remaining slash. As this source is limited and exhaustible, a serious calcium stress for the secondary growth has to be expected. As a matter of fact, the climax forest of the Tertiary formations of Central Amazonia has to be handled with care during silvicultural and agricultural efforts to avoid serious harms to the tropical environment. The climax forest on tropical podzol soils should be conserved as soils will be exhausted after several years, if used for slash and burn agriculture.

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#### RESUMO

As principais fontes do cálcio encontrado na água na região terciária Amazônica próxima a Manaus, são a água escorrendo sobre os troncos e a água total da floresta. O teor em cálcio solúvel deve ser proveniente da lavagem, pela chuva, da copa, dos caules, folhas e, até um certo ponto, da dissolução de produtos metabólicos de macro e microorganismos.

Na água da chuva, nas águas do solo e dos rios geralmente só foram encontrados traços de cálcio. Portanto, o cálcio pode ser encarado como elemento circulante num sistema fechado. De um modo geral, os teores de cálcio das águas naturais da região terciária Amazônica são extremamente baixos.

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in ug Ca<sup>++</sup>/l

RAIN	STEMFLOW		THROUGHFALL					GROUND WATER			STREAM WATER				
	I	II <sub>1</sub>	II <sub>2</sub>	III <sub>1</sub>	III <sub>2</sub>	III <sub>3</sub>	III <sub>4</sub>	III <sub>5</sub>	IV <sub>1</sub>	IV <sub>2</sub>	IV <sub>3</sub>	V <sub>1</sub>	V <sub>2</sub>		V <sub>3</sub>
<20.0	1179.0	553.0		493.0	273.0	611.0	756.0	496.0	< 20.0	< 20.0	237.0	< 20.0	< 20.0	< 20.0	dry season
<20.0	1128.0	477.0		159.0	111.0	273.0	217.0	382.0	< 20.0	65.0	243.0	< 20.0	< 20.0	< 20.0	wet season
<20.0	1152.0	530.0		533.0	203.0	448.0	531.0	439.0	< 20.0	28.0	240.0	< 20.0	< 20.0	< 20.0	year

Table 1 Yearly and seasonal calcium averages of natural waters in the Amazonian Tertiary region near Manaus. — **Rainfall**: averages of 51 storm samples (bulk samples from 3 collectors) — **Stemflow**: averages of 98 storm samples (bulk samples of 12 collectors in the Riverine forest and 18 collectors in the Carrasco forest) — **Throughfall**: averages of 210 storm samples (bulk samples of 10 collectors at each site) — **Ground water**: averages of 144 well samples collected in weekly intervals 12 times the well were without water) — **Stream water**: averages of 156 samples collected in weekly intervals.

GROUPS	RAIN	STEMFLOW		THROUGHFALL					GROUND WATER			STREAM WATER			
	in ug Ca <sup>++</sup> /l	I	II <sub>1</sub>	II <sub>2</sub>	III <sub>1</sub>	III <sub>2</sub>	III <sub>3</sub>	III <sub>4</sub>	III <sub>5</sub>	IV <sub>1</sub>	IV <sub>2</sub>	IV <sub>3</sub>	V <sub>1</sub>	V <sub>2</sub>	V <sub>3</sub>
0 <sub>1</sub> - 300	100.0	—	45.7		51.7	75.0	48.3	37.5	50.0	100.0	100.0	66.0	100.0	100.0	100.0
300 <sub>1</sub> - 600	—	20.6	17.1		17.2	7.1	13.8	16.6	12.5	—	—	22.2	—	—	—
600 <sub>1</sub> - 900	—	26.5	14.3		10.3	10.7	20.7	25.0	20.8	—	—	7.4	—	—	—
900 <sub>1</sub> - 1200	—	14.7	14.3		10.3	3.6	6.9	8.3	8.3	—	—	—	—	—	—
1200 <sub>1</sub> - 1500	—	11.8	2.8		—	3.6	6.9	8.3	8.3	—	—	—	—	—	—
1500 <sub>1</sub> - 1800	—	5.9	2.8		3.4	—	3.4	4.1	—	—	—	3.7	—	—	—
1800 <sub>1</sub> - 2100	—	20.6	2.8		6.9	—	—	—	—	—	—	—	—	—	—

Table 2 Frequency distribution (%) of soluble calcium compounds in natural waters of Central Amazonia grouped in intervals of 300 ug/l Ca<sup>++</sup>.