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L.M. Moreira-Nordemann
M.C. Forti
C.M. Espírito Santo

RESUMO - NOTAS / ABSTRACT - NOTES

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Results show a natural acidity in Amazonian environment, and lower ion concentration in rainwater above the canopy; an enrichment in all ion contents of the rainwater, falling through the vegetation, was observed except for NO_3^-. These ions seem not being lixiviated by draining water, but probably being recycled by the forest itself. The rainwater samples obtained in downtown Manaus show higher contents of NO_3^-, SO_4^{--} and Ca^{++}, compared to results obtained in the forest, probably due to anthropogenic contribution.

OBSERVAÇÕES/REMARKS

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RAINWATER CHEMISTRY OF CENTRAL AMAZÔNIA (DRY SEASON 1985)

L. M. Moreira Nordemann, M. C. Forti and C. M. Espírito Santo

Instituto de Pesquisas Espaciais - INPE
Ministério da Ciência e Tecnologia
C.P. 515 - São José dos Campos - 12201
SP - Brasil

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Results show a natural acidity in Amazonian environment, and lower ion concentration in rainwater above the canopy; an enrichment in all ion contents of the rainwater, falling through the vegetation, was observed except for NO_3^{-}. These ions seem not being lixiviated by draining water, but probably being recycled by the forest itself. The rainwater samples obtained in downtown Manaus show higher contents of NO_3^{-}, SO_4^{--} and Ca^{++}, compared to results obtained in the forest, probably due to anthropogenic contribution.

INTRODUCTION

The Amazonian region has been investigated more thoroughly during the last 15 years, by Brazilian and foreign scientists. These studies gave birth to a great number of publications in almost all branches of science. The main preoccupation of the scientific community is to quantify the changes induced by the human occupation of the region and its influence on the equilibrium of several biogeochemical cycles which exist today.

The chemical composition of the rain water of the Amazonian forest is not well known. However, this region is one of the few places in the world which offers the possibility of establishing reference standards for the composition of rain water without or almost without anthropogenic interference. Research groups have been studying the rainfall in the Amazonian area, whith the primary purpose of determining the hydrological cycle of the region. Franken & Leopoldo (1984), Santos et al. (1981), Salati et al. (1979), Stallard & Edmond (1981), Franken et al. (1982), are among the fewer works concerning the rainwater chemical composition.

The purpose of this work is to show the results obtained from the analyses of the samples taken during the July-August 85 campaign of the GTE/ABLE program. Details of this field experiment is given by Harris et al. (1986) in this issue.

Systematic sampling of rain water were collected in the city of Manaus and in the forest, under and above the canopy. Samples of water from the igarapé Barro Branco and samples of surface soils in the forest were also taken. The concentration of Na^+, K^+, Mg^{++}, Ca^{++}, NH_4^+, Cl^-, NO_3^- and SO_4^{--} were determined in these samples and results are presented in this report.

The analyses and discussion presented here are considerations about the most evident behaviour of these ions, with some speculations about their geochemical cycles. A more comprehensive data set is needed before conclusions about the origin, distribution and content of these ions and their role in the geochemical cycles involved are reached.

METHODS

During the period of 07/13/85 to 08/08/85, rain water samples were collected at three different places. One sampler was located on the roof of the Hotel Central, downtown Manaus; another one was placed at approximately 10m above the canopy of the forest, on the top of a 45m high meteorological tower erected in the Reserva Ducke, 26 km to the north-east of Manaus; the two others were placed under the canopy in the neighbourhood of the tower. These two samplers were not mantained in a fixed position but were moved randomly after each sampling, to assure the representativeness of these samples. Two types of samplers were used:

- a 52 cm diameter acrylic hemisphere protected with a nylon screen, linked to a 1 liter polyethylene bottle. It's sampling efficiency is about 75%;
- a 30cm diameter polyethylene funnel also protected with a nylon screen, with a 1 liter polyethylene bottle. It's sampling efficiency is about 20%.

Each sampling was made daily, by collecting individual rains; just two samples are accumulated rains. Special care was taken to avoid evaporation and contaminations. Being the dry season period, only few samples were obtained, but sampling were effectuated for all events.

In addition seven surface forest soil samples and two igarapé water samples were collected. The igarapé (typical amazonian natural channel of the surface water system) is also located in Ducke Reserve at approximately 1km from the tower.

In order to study the hydrochemical balance of the region, it is necessary to know the soil retention of the rain water ions. These water-soluble ions are removed from the soils by leaching.

The soils were sifted and two fractions with granules equal or smaller than 250 μm were obtained for each sample; 25g of this sifted soil were added to 250 ml of deionized water and the misture was stirred by 30 minutes in a magnetic stirring.Afterwards, the mixture obtained was spun in a centrifuge at a speed of 4,500 rpm (centrifuge spin limit) during 15 minutes. The resulting solid mass was separated, triturated, added to 250 ml of deionized water, stirred again with a magnetic stirring and spun in a centrifuge. This process was repeated producing for each soil sample three leaching water, containing the soluble soil ions in solution. The three soil leachings are for assuring that nearly all water-soluble ions were made soluble. This experiment was repeated for every sample in order to test the reproductibility of the results, which were found to be within 15% for all the elements measured.

The rain water and igarapé water samples were sealed and stored in a refrigerator at $4^{\circ}C$ until the analyses began. No acid or other product was added as preservative. The soil leaching solutions were analysed imediately after centrifugation.

The ions concentrations of rain water, igarapé and soils were obtained by potenciometry (Cl^-, NH_4^+) liquid cromatography (NO_3^-, SO_4^{--} and Cl^-) and atomic absorption (Na^+, K^+, Mg^{++}, Ca^{++}). The accuracy of the methods, is generally better than 10%, depending upon the concentration value (near detection limit). Concentrations of Cl^- were not reported here because the values obtained were under-estimated, and results determined by ion cromatography did not agree with the ones obtained by potenciometry.

Pluviometry - Manaus, as well as the entire Amazonian region, shows a rather high pluviometry all over the year. In spite of this, it can be said that there is a dry season and a rainy one. The former comprises the months of June until November, when approximately 30% of the total annual precipitation is recorded, while the latter comprises the months of December until March, when 300 mm montly mean are registered.

Taking into account the pluviometry of Manaus INEMET (Instituto Nacional de Meteorologia) and the Reserva Ducke INPA (Instituto Nacional de Pesquisas da Amazônia) stations, it is observed that, during the last years the rainfall in the Reserva Ducke (2500 mm/year) has been higher than in the city Manaus (2100 mm/year), the difference being not remarkable for the rainy season. However, the months of July and August show averages of 210 and 101 mm rainfall totals for the Reserva and Manaus respectively. From this point of view the sampling months of this experiment, were quite tipical with a 213.3 mm in the Reserva Ducke and 116.4 mm rainfall total in Manaus. Figure 1 shows the pluviometry of the Reserva Ducke (91.5 mm) and Manaus (84.5 mm) for the sampling period (July 13 - August 8). During the GTE/ABLE experiment meteorological parameters were measured by the NASA-INPE staff on site.

RESULTS

pH - A natural acidity in the environment may be noticed, after data showed in table I, for soils, river water and rain water samples, mainly above the canopy.

The distilled water in chemical balance with atmospherical carbon dioxide has a pH value equal to 5.65, this being taken generally as standard value for rainwaters. As it can be seen, the samples collected on the tower, above the canopy, are the ones that show lower pH. This acidity is attenuated by the incorporation of ions into the rainwater as it falls through the vegetation, and the pH values obtained under the canopy tend towards the standard value. It is interesting to note the stability of the values obtained, with a deviation of only ± 4% of the mean value.

Above the canopy, results agreed with those obtained for the same region by Brinkmann and Santos (1973), by Stallard and Edmond (1981) and with the value of 4.58 calculated by Talbot et al (1986, this issue)

Studies performed in the Amazonian region of Venezuela (Galloway et al, 1982; Ishizaki, et al. 1986) show that this environment is naturally acid. After these authors, this acidity is due to a misture of compounds, weak organic and strong inorganic acids, and is also due to the lack of neutralizing agents such as NH_3 and $CaCO_3$.

The rainwater pH in the city of Manaus appears to be more basic than the observed ones in the forest and tower rainwater, and these pH values obtained oscillates within ± 20% about the mean value. This tendency towards neutrality, as well as the large variation in the pH values, could be an indication of anthropic interference in Manaus, if the values obtained in the forest are considered normal.

IONS. The rain plays a fundamental role in washing the atmosphere, taking away practically all the soluble elements contained in it. In rain water, the concentrations of these natural or artificial elements are intimately linked to the frequency and the quantity of the rainfall, and ionic contents vary for element to element.

In order to minimize the effect of the frequency and the quantity of the rain on the ion concentrations, these are weighted against the corresponding rainfall totals thus reaching mean weighted values. These calculations were effectuated for all the available rain samples and for all the analysed elements, which generated Table II, where the maximum, minimum values and the arithmetic means are given.

There were some difficulties in obtaining the pluviometry for collectors situated under the trees. Furthermore, as the samples were always collected in pairs for each event, the mean of the ionic concentrations were taken for both collectors, weighting them with 83% of the pluviometric value obtained on top of the tower which represents the quantity of precipitation non intercepted by the forest, according to the data obtained before (Molion, L.C.B., personnel communication, 1985; Shuttleworth et al., 1984).

Despite of having been collected in the dry period, the mean values of the Na^{+}, Ca^{++}, K^{+} and Mg^{++} concentrations obtained in the tower are relatively low, and much lower than the ones determined by Nortcliff and Thornes (1978) during the campaign effectuated at the same place, between March and May, 1977. Mean values obtained for Na^{+}, Mg^{++}, and SO_4^{--} concentrations are also slightly lower than the mean ones determined by Stallard and Edmond (1981) for the Amazon basin, but agree quite well with results obtained for terrestrial precipitation in the middle basin, by the same authors. Ca^{++} and K^{+} concentrations obtained in this study are similar to the ones determined by those authors and NO_3^{-} is slightly higher.

It can be verified in Table II, that there is great variability in the maximum and minimum values obtained, with the exception of K^{+}. It can be also noticed that there is an equilibrium between cations and anions and the ratio between them is one.

The ionic concentrations under the forest are higher than the ones determined at the tower top, which confirms the enrichment of the water in traversing the vegetation. This enrichment is greater in cations than in anions and the ratio between them is greater than 2. Among the cations the K^+ is the most enriched ion, while Ca^{++} is the one that presents less variation of concentration. In the case of the anions the greatest enrichment observed was in SO_4^{--}. The NO_3^- contents does not suffer any variation at all during the fall through the vegetation.

This enrichment is, certainly due to the washout, by the rainfall, of elements originating from the dry deposition, leaf exudation and transpiration and from the gases in the forest environment. These contributions were not measured separately; for this season the throughfall sample content represents the wet and the dry deposition altogether. However, Talbot et al. (1986 this issue) carried out aerosols measurements, during the same period, in the boundary layer, obtaining a concentration distribution which obeys to the following sequence: $NH_4^+ > K^+ \sim SO_4^{2-} > NO_3^-$ (for the fine particulate) and $NH_4^+ > K^+ \sim NO_3^- > SO_4^{2-}$ (for the coarse particulate). It can be seem, from Table II, that in the rainwater, over the canopy (tower), the sequence for the same ions was: $SO_4^{2-} > NH_4^+ \sim NO_3^- > K^+$. These results suggest that the prevailing ions are NH_4^+ and K^+ in the dry deposition and are SO_4^{2-} and NH_4^+ in the wet deposition this rough estimation points out the importance of these two components separately. Studies performed in decidous forest (Lindberg et al. 1986) have shown similar results; these authors have found predominant SO_4^{2-} and NH_4^+ in the wet deposition and K^+ dry deposition.

The water samples of the igarapé (Table III) were collected on August 5th and 8th. The first sample was collected after a 6-day dry period and the second one day after a 3.6 mm precipitation. Even so, the ionic contents found in both samples were practically the same, showing a surprising stability in the chemical composition of the water among the samples. The ionic contents obtained for the waters of the igarapé are very low, however, and agree with the results of Nortcliff and Thornes (1978), and Franken and Leopoldo (1984) except for SO_4^{--} determinations. These authors also stress the quick answer of the igarapé to the rainfall, what may explain the stability of the chemical composition verified. On the other hand, Franken and Leopoldo (1984) showed that precipitation lower than 3mm are not important for the igarapé discharge because these events do not increase the level of the river; although "small rains" (between 0 and 4.9 mm) represents 60% of all rainfall events, they yield only 27% of the total rainfall.

In Table II, it can be noticed that Na^{+}, Mg^{++} and NO_3^{-} concentrations determined for igarapé water are approximately equal to the weighted means obtained in rain water, above the canopy (tower). NH_4^{+} and K^{+} contents in igarapé are slight higher, and SO_4^{--} and Ca^{++} concentrations are lower than the weighted average of the tower rainwater. However, Franken and Leopoldo (1984) determined that discharge of the igarapé Barro Branco corresponds to only 21% of the total precipitation that falls into the basin. Also Molion (1976) and Salati et al. (1978) show that about 50% of the rainfall returned to the atmosphere through evapotranspiration. During the 1985 dry period (Molion, 1986), this value was higher and reached 75%. Taking into account these results, and also the ionic enrichment of rain water falling through the vegetation, it would be expected to obtain higher ion concentrations in Barro Branco igarapé water! The increase in ionic contents found in the throughfall water was not detected in the igarapé water samples. The forest probably is recycling these ions. Also, it seems that the input of elements by rainwater above the canopy is equal to the output determined in the river for Na^{+}, Mg^{++} and NO_3^{-}. This output were slightly higher for K^{+} and NH_4^{+} and lower than the input for Ca^{++} and SO_4^{--}.

The NH_4^{+} and NO_3^{-} quantities that enter the forest through the rain are equivalent; however, there seems to be slightly higher NH_4^{+} than NO_3^{-} quantities in the water of the river. These results do not agree entirely with the ones obtained before (Salati et al., 1982), where N - NH_4^{+} values 5 to 10 times higher than the N - NO_3^{-} ones, in the rains as well as in the rivers of the region were observed.

Table IV presents the ionic contents determined in the lixiviation water of the soils. As can be seen, these contents vary widely from sample to sample although the mean for Na^{+}, K^{+} and Mg^{++} are equivalent. The Ca^{++} content however is the lowest among the cations. Taking into account the current results and the low Ca^{++} content obtained in the igarapé, it leads to the conclusion that Ca^{++} is not being lixiviated, nor accumulated in the soils. This element might be retained in the litter and in the vegetation, confirming results observed for other tropical forest (Golley et al.

1978). The Ca^{++} ion belongs to the structural matter of trees, mainly associated to the leaves and to the stems, bound to insoluble organic salts and strongly adsorbed by proteins.

The estimated budget shows that Mg^{++}, Na^{+} and NO_3^- ions are in equilibrium, suggesting that their ionic contents found in the soils are the participating fraction of the forest cycle itself. Probably Mg^{++} and Na^{+} came from the soils itself meanwhile, NO_3^- can originates from biological activity.

The lixivation waters show high Cl^- and NH_4^+ contents, and SO_4^{--} in smaller quantities. Lindberg et al (1986) have shown that the precipitation plus the washed-off dry deposition filled 96% of the annual below-canopy flux, suggesting little or no leaching of SO_4^{--} from the internal parts of the plant. These results corroborates with the hypothesis that SO_4^{--} may be retained by the soil through biologic activity in the soil surface-litter interface. This fact explains the low SO_4^{--} concentration found in the river. Unfortunately results of Cl^- concentrations in rain and river waters were not consistent, but it is possible to reason that the input by rain water, and the output of Cl^- in river water, must be equivalent, and that Cl^- content in soils are also being recycled by the forest.

The high NH_4^+ content found in the lixiviation waters of the soils, may be related to the high biologic acitivity exiting in the forest soils of the region.

A more complete soil study in the region will be carried out in the next campaing, and this experience in lixiviation of soils was just a first attempt to understand the ionic absorption by soils.

Rainwater in Manaus: A comparison between mean ionic concentrations obtained in the samples of the rainwater in Manaus (Table II) and the ones at the top of the tower, show an enrichment in all the contents obtained in Manaus, specially Ca^{++}, K^{+}, Mg^{++}, SO_4^{--} and NO_3^{-}. The great number of civil constructions in the city, with the intense use of concrete, may well be responsible for the enrichment in Ca^{++}, K^{+} and Mg^{++} in the rainwaters, as this material is essentially rich in CaO, as well as, in smaller proportions, in MgO and K_2O. This excess of Ca^{++} in the rainwaters was also observed in other brazilian cities (Tavares et al. 1983; Ferreira and Moreira-Nordemann, 1985; Moreira-Nordemann et al., 1985).

The contents of nitrate in the city rain may be due to the vehicles engines, which produce nitrogen oxides in large quantities (specially NO_2) and several hydrocarbons. A fraction of the nitrite formed, is oxidized in the atmosphere, forming nitrate (Junge, 1963). NO_3^{-} contents are higher in Manaus rainwater than in the samples obtained under the forest canopy.

The sulphate is easily produced by the oxidization of SO_2 present in the atmosphere. This is mainly produced by the combustion of fossil fuels and wood. This combustion is quite generalized in Manaus, mainly by the abundance of wood and by the oil driven thermoelectric power plant. This fact may explain the SO_4^{--} contents in rainwater of Manaus city.

Finally, the effect of burning biomass was noticed during the experiment in air and aerosol composition, but the results obtained for rainwater do not show clearly such an influence. For the last rainwater sample collected it was noticed the increase of ionic concentrations in the three sampling locals due to the lack of rainfall during ten days before the event.

CONCLUSIONS

A natural acidity was found in the Amazonian environment, it was observed lower pH values in rainwater, river water and soils of this region .

In spite of being collected in the dry season, the ionic concentrations determined in the rains of the Amazon forest above the canopy are low, lower than the ones obtained before by other authors. There is a balance between the total cation and anion quantities, and the ratio between them is equal to one.

The rainwaters undergo and enrichment in the contents of all ions, specially in K^+ and SO_4^{--} during the fall through the vegetation, with the exception of NO_3^- which had its value unaltered.

Although the number of samples collected is very reduced, it was found that the waters of the igarapé have very low ionic concentrations, thus confirming results obtained before. A great quantity of Cl^- is being retained by the soils, through adsorption, and in much lower proportions, SO_4^{--}. The great biologic activity of this environment may be responsible for the high NH_4^+ content absorbed in the soils.

Apparently, Ca^{++} is neither being accumulated in the soils nor lixiviated by draining waters.

The increase in ionic concentrations obtained by rainwater during the fall through the vegetation, does not seem to be released into the river, staying in the forest and probably being recycled in it. But any conclusion on geochemical balance drawn from these results must be considered preliminary. A new campaign will be carried out during the wet season, and might being evidence the variation of the geochemical cycle in function of the meteorological factors of the region. Attempts will be made to obtain samples during a longer period, so as to determine a better and representative geochemical balance picture of the ecossystem of the Amazon forest.

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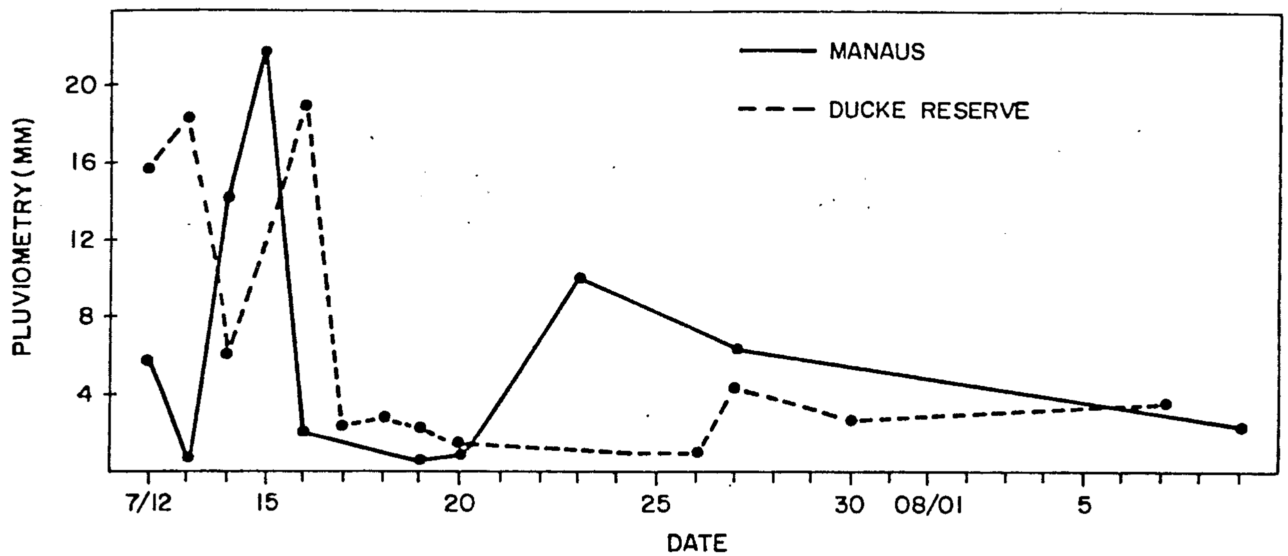

Fig. 1 - Manaus and Ducke reserve pluviometry for the sampling period.

TABLE I - pH values of the rainwater samples under and above the canopy, downtown Manaus, river water and soils.

	TOWER	FOREST-A	FOREST-B	MANAUS	SOIL	RIVER WATER
MIN.VALUE	4.57	5.13	5.18	4.91	3.4	5.04
MAX.VALUE	4.97	5.63	5.72	7.17	3.9	5.09
MEAN VALUE	4.84 ±0.16	5.34 ±0.17	5.52 ±0.20	5.89 ±0.90	3.8 ±0.8	-

TABLE II - Maximum and minimum values arithmetic (A. Mean) and volume weighted (W.Mean) means in μeq/l of the analysed ions in Manaus, tower and forest rainwater samples, and in river water (igarapé).

		Na^+	K^+	Mg^{++}	Ca^{++}	NH_4^+	SO_4^{--}	NO_3^-
MANAUS	MAX.V.	73.9	56.4	139	740	51.7	116	89.8
	MIN.V.	0.26	1.8	1.7	6.0	1.9	14.3	0.6
	A.MEAN	14.4	13.9	29.2	161	10.9	40.0	20.6
	STANDARD DEVIATION	29.1	21.0	51.7	228	18.3	38.3	34.0
	W.MEAN	5.2	5.1	10.8	56	5.8	23.7	9.7
TOWER	MAX.V.	20.9	1.8	11.7	8.5	6.4	11.1	19.5
	MIN.V.	0.87	0.9	0.8	0.5	2.2	3.4	1.3
	A.MEAN	5.2	1.0	3.3	3.5	3.9	5.8	6.3
	STANDARD DEVIATION	6.5	0.3	4.2	3.0	1.6	2.9	5.7
	W.MEAN	3.0	0.9	1.9	2.7	4.9	5.2	4.8
FOREST	MAX.V.	131.3	84.4	67.5	65.5	20.3	58.0	10.2
	MIN.V.	9.1	7.4	9.2	4.5	2.8	10.2	1.5
	A.MEAN	45.7	22.8	22.5	16.5	10.0	24.6	4.5
	STANDARD DEVIATION	39.6	25.4	19.2	20.0	6.7	15.6	3.2
	W.MEAN	34.4	17.2	16.7	11.0	7.2	21.5	5.0
IGARAPÉ 1		3.0	1.8	1.7	0.3	7.7	1.6	4.6
IGARAPÉ 2		3.0	1.8	2.5	0.3	6.7	2.0	5.0

TABLE III - Igarapé Barro Branco ion concentrations determined by different authors (mg/l).

Na^{+}	Ca^{++}	K^{+}	Mg^{++}	NH_4^{+}	SO_4^{--}	AUTHORS	SAMPLING PERIOD
0.19	0.01	0.06	0.03	-	-	Nortcliff and Thornes (1978)	May 1977
0.22	-	0.10	-	0.05	3.79	Franken and Leopoldo	1976 - 1977
0.07	0.01	0.07	0.03	0.14	0.08	This study	August/5 1985
0.07	0.01	0.07	0.02	0.12	0.10	This study	August/8 1985

TABLE IV - Maximum, minimum and arithmetic mean (A. MEAN) values concentration (μeq/g) of the analysed ions in soil samples for three leaching. The sum of these mean values are also shown.

		Na^+	K^+	Mg^{++}	Ca^{++}	NH_4^+	Cl^-	NO_3^-	SO_4^{--}
1st leach.	MAX.V.	2.3	1.23	1.24	0.68	4.95	13.03	0.60	11.5
	MIN.V.	0.41	0.55	0.68	0.25	3.51	4.84	0.14	1.8
	A.MEAN	0.98	0.86	0.93	0.44	4.53	9.91	0.40	4.1
	STANDARD DEVIATION	0.60	0.22	0.18	0.18	0.47	3.31	0.19	3.4
2nd leach.	MAX.V.	0.36	0.40	0.58	0.41	1.84	0.73		
	MIN.V.	0.08	0.13	0.30	0.15	0.99	0.31		
	A.MEAN	0.18	0.29	0.46	0.26	1.45	0.51		
	STANDARD DEVIATION	0.10	0.10	0.12	0.09	0.26	0.14		
3rd leach.	MAX.V.	0.09	0.16	0.27	0.20	1.00	0.14		
	MIN.V.	0.03	0.07	0.20	0.12	0.44	0.06		
	A.MEAN	0.05	0.12	0.23	0.17	0.77	0.11		
	STANDARD DEVIATION	0.02	0.03	0.03	0.04	0.17	0.03		
	SUM	1.21	1.27	1.62	0.87	6.75	10.53		

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AUTOR(ES):
L. M. Moreira - Nordemann
M. C. Forti
C. M. Espirito Santo

ORIENTADOR:

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