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Sulphate, Chloride and Nitrogen Compound Concentration in Atmospheric Deposition and Effects on Nutrient Cycling in a Rubber Plantation Agroecosystem at Ikenne, SW Nigeria

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Abstract: Bulk precipitation, throughfall and stemflow solution chemistry beneath rubber (Hevea brasiliensis Willd) Muell-Arg. Euphorbiaecae plantation agroecosystem at Ikenne, SW Nigeria, was measured. Throughfall and stemflow chemistry from event-based sampling of 3 different age stands was compared with the chemistry of incident precipitation. Throughfall pH in 5 year old rubber (5.92), 15 year old (5.83) and 40 year old (5.70) canopies, respectively. These values were was significantly more acidic than gross precipitation (6.20). Stemflow pH ranged from 5.7 (5-year-old) to 6.0 (15-year-old). During the study period only Cl^- was significantly higher flux under the forest canopy relative to precipitation. About 50% of the inorganic nitrogen in precipitation was taken up by the canopy and there were significant differences in throughfall and stemflow chemistry among the 3 stands, perhaps due to differences in smoothness of the stem. Seasonal differences were important, with highest deposition in wet season. Multiple regression analysis of the throughfall patterns showed significant correlations of throughfall chemistry with the length of the antecedent dry period and rainfall quantity for all elements examined.

Key words: Atmospheric deposition, nitrate, chloride, sulphate, nutrient cycling, agroecosystem

INTRODUCTION

Acidic precipitation is largely caused by the inclusion of anthropogenic SOx, NOx and other acid precursors. Even so, neutralizing compounds like carbonates, bicarbonates and ammonia also influence the final acidity of atmospheric depositions (Kulshrestha *et al.,* 2003). Atmospheric depositions of sulphuric and nitric acids have increase in many parts of Nigeria since the expansion of industries and urban growth in the past three decade. Sulphuric and nitric acids, which are derived primarily from Sulphur dioxide (SO_2) and Nitrogen Oxide (NOx) gases created during fossil-fuel combustion. Several studies report that soil and surface water may be adversely affected by long-term exposure to acidic deposition (Unworth and Ormrod 1982; Likens and Bormann, 1995).

There has been increasing concern about the linkage between declining health of many forest ecosystems and atmospheric deposition. Several pathways by which atmospheric deposition can damage forests have been proposed: soil acidification, cation depletion and Al^{3+} toxicity (van Breemen *et al.*, 1982; Ulrich and Pankrath 1983; Likens *et al.*, 1996; Lawrence *et al.*, 1999); direct and indirect influence of pollutants on the physiological status of the trees (Unworth and Ormrod, 1982; DeHayes *et al.*, 1999) excess N deposition and subsequent soil acidification or physiological injury (Aber *et al.*, 1989, 1998; Nilsson and Wiklund, 1992).

Several researchers hypothesized that acid deposition could lead to soil cation depletion and subsequent soil acidification thereby affecting the health of forest ecosystems (Van Breemen *et al.*, 1982; Ulrich and Pankrath, 1983). Recently, using long-term data from temperate deciduous forests, Likens *et al.* (1996) and Lawrence *et al.* (1999) proposed that atmospheric deposition induced base cation depletion has a major detrimental effect on nutrient cycling and forest health.

Tree crops such as rubber, cocoa, kolanut and oil palm need adequate supplies of the essential nutrients for the synthesis of protoplasm, both for growth and repair and other materials that serve them as sources of metabolic energy. These elements are essential for both temperate and tropical woody species (Hobbs, 1944; Nwoboshi, 1982, 2000; Nwoboshi *et al.*, 1982, 1986, 1988).

Precipitation is a major source of input of nutrient into the tropical lowland rainforests are specifically characterized by high water input via rainfall including the frequent occurrence of rainstorm events. This environmental factor strongly influences the cycling of nutrients in tropical lowland rainforest ecosystems, because water is the major transport medium for nutrients and its movement is significantly influenced by topographic conditions (Likens and Bormann, 1995; Bonell, 1998).

There has been an increased interest in assessing the regional extent of the phenomenon and subsequently to an interest in documenting the effects that deposition changes have on terrestrial ecosystems in different parts of the world. Although, the impact of acid deposition has not induced serious damage to tropical ecosystems compared to their temperate counterpart, there is the urgent need to assessing the current pattern of deposition of nutrient ions on the ecosystem to stem future problems of acidification.

The rainwater composition data are valuable for the validation of Global Chemistry Transport Models (GCTM) (Rodhe *et al.*, 1995) and help in determining global cycling of sulphur compound, oxidized and reduced nitrogen compounds (Rodhe *et al.*, 2002). In this study, effects of sulphate, chloride and nitrogen compounds concentrations in atmospheric deposition (rainfall, throughfall and stemflow) on nutrient cycling were examined in a rubber plantation agroecosystem.

MATERIALS AND METHODS

Study area: The study site is located in the Remo Rubber Plantation, Ikenne (Latitude 6°50' N and Longitude 3°40' E (Fig. 1). Precipitation averages 66 cm (36 in) annually, nearly all falling as rain in the wet season (April-October). The two site lies on the sedimentary rock (Abeokuta formation) of the southern part of Nigeria, which is underlain by the crystalline basement complex rocks of the Precambrian period (Kehinde-Phillips, 1992). The Abeokuta sedimentary rock formations most often have interaction of argillaceous sediments sometimes cemented by ferruginous, siliceous or carbonaceous substances. The relief is generally an undulating one, which is an extension of the coastal lowlands that starts from the southern part of the country and is a featureless plain with vast expanse of almost flat surfaces. Hardly does any area exceed 150 m above sea level. The mean diurnal and temperature ranges vary between 8-10°C during the dry season and between 3.5 and 5°C during the wet season.

The rainy climate has the temperature of the coolest month to be >18°C (68°F). The mean annual temperature is about 27°C with high relative humidity (80 %). This could be attributed to the prevalence of moisture laden tropical maritime air mass over the area for about nine months in the year). Periaswamy and Ashaye classified the soil of the area as Ultisols due to the annual rainfall that varies from 1,500-1,750 mm with base saturation often less than 50%. Base saturation by sum of cations of the argillic horizon generally decreases with depth and are below 35% at 1.8 m below the surface. The soils belong to the suborder Ustults with appreciable exchangeable Al characteristic of Ultisols (Soil Survey Staff, 1975). The higher base saturation in the upper horizons of these Ultisols is due to base cycling by vegetation. Trees species commonly found include Isotonia boonei, Anthocleista Vogeli, Cola gigantea Antiaris africana, Pentaclethra macrophylla and Elaeis guineensis (Gbadegesin, 1987).

Sample collection: Samples for the determination of atmospheric deposition chemistry were taken in three experimental plots, each representing the three stand ages (40, 15 and 5-year-old). Each plot was of the same size of 1000 m^2 (50×20 m). Throughfall samples were collected bi-weekly, in the morning, with a tolerance interval of 12 h to avoid the start of new precipitation or to allow an on-going event to end. On expiry of the tolerance period, the samples were collected in any case.

The collectors for throughfall measurement consist of sixteen-centimetre a diameter Nalgene (non-reactive) collection funnel, which was placed on a wooden pole at a height of 1.5 m above the ground. The funnel neck was attached to 75 cm Nalgene ½ I.D. tubing, which was half looped to minimize evaporation. The tubing ran into one-litre High-density polyethylene (HPDE) collection jars through a drilled cap. Each collector had an overflow bottle for measurement of total volume for large events. The overflows bottles were attached to the pole and attached to the one-litre collection bottles via ¼ I.D. Nalgene tubing folded at the top and drilled with two 1 mm holes, allowed venting of air pressure in the sample and overflow bottles. A De-Ionized water (DI) rinsed polywool plug was inserted into the neck of each funnel to exclude insect frass and plant litter from the collection bottle.

Collections were postponed until the rain stopped if it was raining during the routine collection. The volume of all throughfall and precipitation samples was measured in the field and a 500 mL subsample collected. The remainder of each sample was used to clean the collectors, tubing and storage bucket. When bulk samples were collected, the collecting bottles were changed, even when there was no precipitation, to avoid any accumulation of dust and detritus in the bulk collectors. After each collection, collectors were washed with deionized water until the conductivity of the rinse water was less than 6 mmhos/cm.

Open field depositions (bulk precipitation) were sampled using the same continuously exposed collectors used for the throughfall using 5 collectors randomly distributed and placed above the ground adjacent to the three rubber stand ages in order to obtain a measurement representative for the study area. This was to ensure that any samples, which were clearly polluted, could be discarded without the loss of the whole sample for the sampling period (Slanina *et al*., 1990; Mosello *et al*., 2002) is that any samples, which were clearly polluted, could be discarded without the loss of the whole sample for the sampling period.

In this study, stemflow samples were collected based on representative trees in each stand taking into account tree age, class, diameter and height (Brechtel, 1989). Stemflow was collected with collars consisting of vinyl tubing, cut longitudinally and attached to each tree trunk in an upward spiral using galvanized nails. Silicone sealant was applied to seal the collar to the trunk and to plug nail heads. The uncut section of each stemflow collar was connected to an 80 L capacity collection bin lined with a chemically inert sampling bag.

Only 10 replicate trees were sampled in each stand age for stemflow collection because high numbers of collectors are not feasible in this study for financial reasons. The choice of fewer stemflow collectors was based on the recommendation of the ICP Forest manual (Programme Coordinating Centre, 1994) that gives a guideline number of 5-10 stemflow gauges especially for homogenous, even-aged stands.

Laboratory analysis: Conductivity and pH were measured on all samples within 3 h of collection. Volume measurements were performed in the field, the throughfall samples were pooled and the sample aliquots were transported to the IAR and T laboratory in Ibadan for chemical analysis. Prior to analysis samples were stored at 4°C. Ionic concentrations were analyzed on filtered samples (Gelman Science GN-6 grid 0.45 mm sterilized filter paper) using ion chromatography (Lin *et al*., 1997) (Table 1). Sulphate SO_4-S) sulphur was determined by Inductively Coupled Plasma Atomic Emission Spectrum (ICP-AES, IRIS ER, Thermo Jarrel Ash Corporation, USA). Total N was obtained by Kjeldahl digestion followed by analyses of NH_4^+ -ions (micro-Kjeldahl distillation and titration with 0.001 NHCI). NO_3^- - N was determined after reduction to NO_2^--N by colorimetric method (Sulphhanilmide/N-I-napthyethylene-diamnie dihydrochloride, Institute of Soil Academic. Trend analyses were performed on volume weighted monthly averages.

Data analysis: Differences in ion concentrations and fluxes between precipitation and throughfall and among the three rubber plots were examined using one-way analysis of variance (ANOVA). Differences were considered statistically significant at p (0.05) unless otherwise stated using the student t-test. A correlation analysis was also performed between the ionic bi-weekly concentrations measured for the throughfall and the bulk samples at the study site. The statistical analyses were performed using the SPSS for windows Version 11.0.

Table 1: Analytical methods used

Variables	Method	References
pH	Potentiometric	
Conductivity	Potentiometric	
Sulphate	Turbidimetric	ICP-AES
	Ion cromatography	
Nitrate	colorimetric	Institute of Soil Academic (1978)
	Ion chromatography	Lin *et al.* (1997)
Chloride	Titration with Ag nitrate (after known Cl addition)	A.P.H.A. (1971)
	Ion chromatography	Lin *et al.* (1997)
Ammonium	Spectrophotometric	Wagner (1969)

RESULTS AND DISCUSSION

Hydrological fluxes: Canopy interception in the different rubber stand was characterized by a distinct seasonal pattern, a low capacity for water storage and was greatly influenced by the total rainfall and rainfall intensity. The amount of incident rainfall intercepted by the canopies in the rubber plantation varied among the different stand ages. It ranged from 13% of precipitation in the 15-year-old rubber stand to 18.9% in the 40-year-old rubber stand (Table 2). The seasonal patterns of precipitation amount are similar among the different wet months and much lower volumes during dry months. Because of the strong seasonality in precipitation depositional fluxes of major ions are much higher in wet season than in dry season. Canopy interception in the 5-year-old rubber stand is 16% of incident rainfall. Monthly interception ranged from 6.2-19.4% in the rainy season and 18.5-70.3% in the dry season.

Precipitation chemistry: Statistical difference in throughfall ionic composition was found among the three plots ($p>0.05$). The annual precipitation amount recorded at the study site, from 2005-2007 ranged between 1420 and 1575 mm, with a mean value of 1504.3 mm. Acidic deposition is lower than in major sites of North America and Europe because of the relatively low level of pollution presently in the area. The concentrations of the substances analysed in atmospheric depositions bi-weekly samples are reported as annual averages for the study period in Table 3. The values show no significant differences between among the rubber plots. The values for ammonium and chloride registered at the site suggest

Table 2: Precipitation (P) partitioning into throughfall, stemflow and interception loss in the 40, 15 and 5-year-old rubber stands at the Remo Rubber Plantation, Ikenne (2005-2006)

	40-year-old		15-year-old		5-year-old	
	mm y^{-1}	% of P	mm y^{-1}	% of P	mm y^{-1}	% of P
Throughfall	990.1	64.3	1036.6	67.3	1075.0	70
Stemflow	258.9	16.8	303.4	19.7	210.2	14
Interception	291.3	18.9	200.3	13	255.1	16
Precipitation	1540.3	100.0	1540.3	100.0	1540.3	100.0

Table 3: Seasonal and annual input of nutrients via bulk precipitation and throughfall (All Stands) in rubber (Hevea brasiliensis) plantation agroecosystem at Remo Rubber Plantation, Ikenne, SW Nigeria in dry season (n = 6) and wet season (n = 11)

Items	Season	SO_4	NO_3	NH_4	Cl^-
		kg ha year $^{-1}$			
Bulk	Dry	0.01	<0.001	<0.001	0.29
Precipitation	Wet	0.05	<0.001	<0.001	5.64
	Total	0.06	<0.001	<0.00	15.93
40-year-old	Dry	0.02	<0.001	<0.001	0.32
Throughfall	Wet	0.09	<0.001	<0.001	15.82
	Total	0.11	<0.001	<0.001	16.14
15-year-old	Dry	0.01	<0.001	<0.001	0.66
Throughfall	Wet	0.06	<0.001	<0.001	18.5
	Total	0.07	<0.001	<0.001	19.2
5-year-old	Dry	0.01	<0.001	<0.001	0.16
Throughfall	Wet	0.03	<0.001	<0.001	9.18
	Total	0.04	<0.001	<0.001	10.24

no significant local disturbance. The median pH value of throughfall and bulk precipitation ranged from 2005 to 2007 between 5.80 and 6.30. These values show that the precipitation in the region has low acidity in comparison with the pH median values recorded in Europe for instance in Canton Ticino, Switzerland where they ranged from slightly above 4.0-4.3-4.4.

Throughfall and stemflow chemistry: Within the rubber plantation, the amount of stemflow comprised only 17% of the annual rainfall on the average. The stemflow is significantly increased in the 15-year-old rubber stand (19.7% of total incident rainfall). Stemflow (SF) amount range from 16.7-23% of the net throughfall (TF+SF) in 40-5-year-old rubber stands. Since, stemflow water and nutrient inputs are controlled in part by branching angle tree species with larger proportion of erectophile branches may have higher stemflow leachate inputs than those with gently sloping branches.

Rubber trees have steep sloping leaves and therefore produce considerable high amount and nutrient inputs. SF amount was 258.9 mm (16.8%) of gross precipitation in the 40-year-old rubber stand, while it was 303.4 mm (19.7%) and 210.2 (14%) of gross precipitation for the 15 and 5-year-old stands, respectively.

The weighted monthly pH values (5.8-7) for precipitation are close to neutrality. Acidity (pH) of throughfall solutions decreased as total rainfall increased, with obviously lower pH values in throughfall solutions showing more H+ leaching. Within the sampling periods, the average electrical conductivity was 19.5 μScm^{-1} and throughfall was observed to be significantly ($p<0.05$) different as compared to rainfall and there was a positive relationship in pH values between rainfall and throughfall. The pH value of stemflow was considerably lower than that of precipitation and throughfall and ranging between pH values of 5.2 and 6.1. Seasonal variation of pH in precipitation revealed maximum pH values in the rainy season and maximum values in the dry season.

Correlations between the ionic bi-weekly concentrations measured for the throughfall and the bulk samples at the study site show a good agreement for ammonium (r = 0.67), nitrate (r = 0.76) and sulphate (r = 0.59), proving the low contribution of these ions through atmospheric deposition. Higher values of pH were measured for most bulk samples than for throughfall samples, with differences generally up to 0.1 unit and a correlation coefficient between bulk and throughfall. H+ concentrations equal to 0.32.

The three main factors influencing precipitation chemistry are anthropogenic air pollution, mineral dust and sea spray. The low concentrations of nitrate and sulphate both with a median concentration in the wet samples around 3 $\mu mol\ L^{-1}$, show the low level of pollution from fertilizer usage. However, alkaline dust, transported by air masses from the Sahara, is relatively frequent in the atmospheric precipitation of the area and influences mostly the calcium concentrations exerting a buffering action on the acidity of depositions H^+, $SO_4^{=}$ and NO_3^-.

The low concentration of chloride in the study site (Table 3) and precipitation (Table 4) shows that the

Table 4: Seasonal and annual input of nutrients stemflow (All Stands) in rubber (Hevea brasiliensis) plantation agroecosystem at Remo Rubber Plantation, Ikenne, SW Nigeria in dry season (n = 6) and wet season (n = 11)

Items	Season	NO_3	NH_4	Cl^-	SO_4
		---kg ha year $^{-1}$---			
40-year-old	Dry	0.01	<0.001	<0.001	0.02
Stemflow	Wet	0.03	<0.001	<0.001	0.12
	Total	0.04	<0.001	<0.001	0.14
15-year-old	Dry	0.01	<0.001	<0.001	0.06
Stemflow	Wet	0.06	<0.001	<0.001	0.10
	Total	0.07	<0.001	<0.001	0.16
5-year-old	Dry	0.01	<0.001	<0.001	0.01
Stemflow	Wet	0.01	<0.001	<0.001	0.08
	Total	0.02	<0.001	<0.001	0.09

Different letter between solution composition in the columns indicate significant differences at the 95% level of confidence

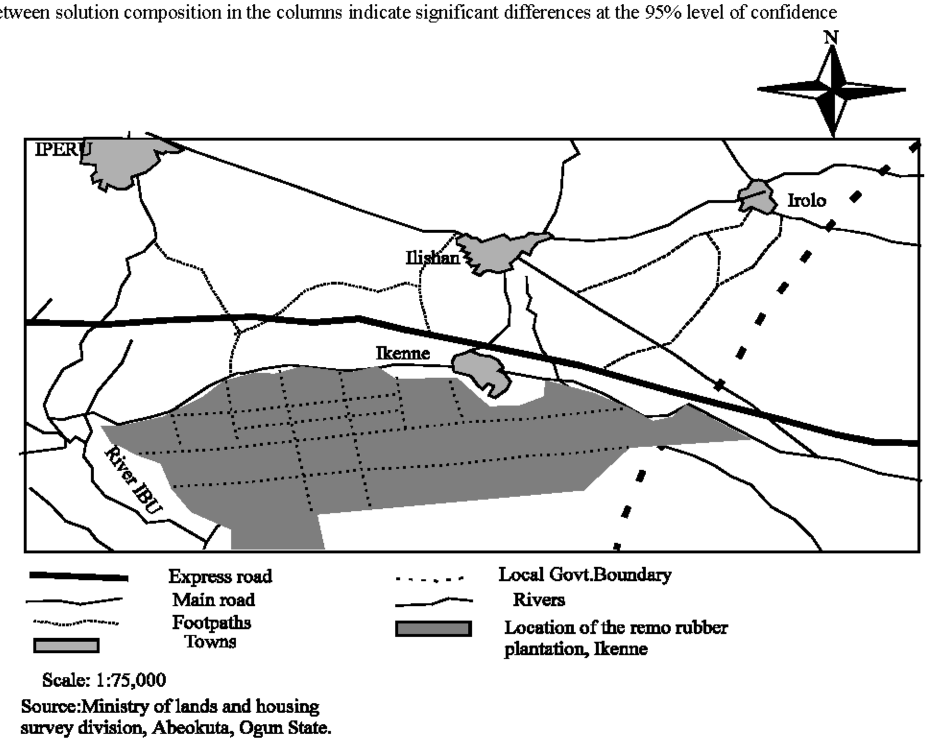

Fig. 1: Map of Remo Rubber Plantation, Ikenne, Southwestern Nigeria

influences of sea spray is negligible. It is interesting to note however, that throughfall concentrations are over 70% of the precipitation average, while a higher value would be expected because of evapotranspiration. Data for the full year for 2006 were collected and presented in Table 5.

Weighted average for sulphate is presently at 50-70 µeq l-1 higher for Milchsee and lower for Langsee. This value is about twice as high as the recent average concentration in atmospheric precipitation (30 µeq l-1). The sulphate/chloride ratio, which is distinctly higher in the lakes than in precipitation, shows that evapotranspiration, cannot be made responsible for the sulphate accumulation and that the lakes must be influenced by some sulphur minerals present in the watershed. Results from an extensive survey made on high altitude lakes in the province showed that this is true for most lakes. The same survey also showed that alkalinity and pH are lower in lakes where the percentage of acidic rocks within the watershed is high and higher where a high percentage of alpine prairies within the watershed is present. On the contrary, nitrate concentrations were higher in lakes with a watershed mainly composed of acidic rocks and lower in lakes with a high percentage of alpine prairies indicating nitrate uptake by the terrestrial vegetation. Nitrate is used also by aquatic microorganisms (in-lake uptake). As a result nitrate concentrations were lower in the lakes than in precipitation.

The proportional amount of throughfall in the different rubber Hevea brasiliensis stands at the Remo Rubber plantation, lies in the lower range of values recorded for some montane and lowland forests. In a natural Lithocarpus/Castanopsis forest at Xujiaba, Ailao

Table 5: Monthly mean values of precipitation amount, conductivity and ion concentrations in bulk and wet precipitation at Remo Rubber Plantation (2006) and significance of the monthly Variations (ANOVA)

	Prec. mm	H^+ μeq l^{-1}	Cond. μS cm^-	NH_4^+ μeq l^{-1}	NO_3^- μeq l^{-1}	$SO_4^=$ μeq l^{-1}	Cl^- μeq l^{-1}
Jan	24.7	16	10.4	8	18	22	7
Feb	25.6	36	30.7	15	30	27	8
Mar	30.9	26	31.0	48	72	52	14
Apr	77.7	16	21.7	43	45	48	10
May	112.4	13	17.0	46	37	47	12
Jun	161.9	8	14.1	50	31	36	9
Jul	140.7	10	15.2	46	32	47	10
Aug	135.0	9	13.8	44	35	42	11
Sep	87.6	16	16.1	39	32	45	8
Oct	85.7	12	18.3	20	25	26	8
Nov	52.1	19	14.0	18	29	26	11
Dec	32.9	16	11.5	8	16	16	6
	p<0.0001	p<0.0086	p<0.01618	p<0.0001	p<0.0001	p<0.0001	p<0.0225

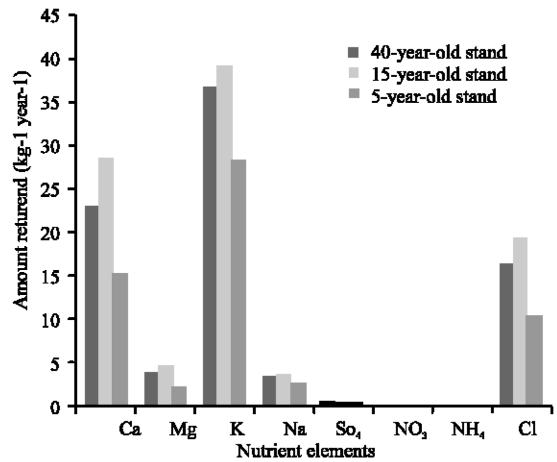

Fig. 2: Nutrient return via throughfall (All Stands) in rubber (Hevea brasiliensis) plantation agroecosystem at Remo Rubber Plantation, Ikenne, SW Nigeria

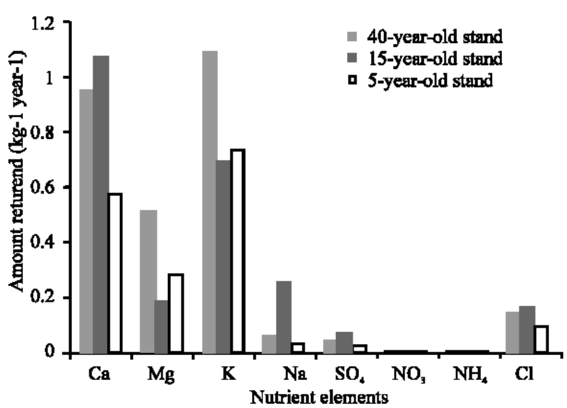

Fig. 3: Nutrient return via stemflow (All Stands) in rubber (Hevea brasiliensis) plantation agroecosystem at Remo Rubber Plantation, Ikenne, SW Nigeria

SW China, Liu *et al*. (2002) recorded annual throughfall of 1886 mm (87.1% of total rainfall), whereas in Ghanaian lowland forest, Nye accounts throughfall as 84% of rainfall (1850 mm).

The result of the one-way analysis of variance among solutions (bulk precipitation, throughfall and stemflow) among all the rubber stands showed that the amount returned to the soil varied significantly ($p<0.05$, $F = 628$, $R^2 = 0.975$). These variations were also noted within stands. In the 40-year-old stand the result of the one-way analysis of variance showed that there were significantly difference ($p<0.05$, $F = 956$, $R^2 = 0.984$), while the values were ($p<0.05$, $F = 614$, $R^2 = 0.975$) and ($p<0.05$, $F = 2230$, $R^2 = 0.993$), for the 15 and 5-year-old stands respectively. Analysis of variance of the flux of nutrients in the plantation also revealed significant variations between and within rubber stands. For instance in the 15-year-old stand, the ANOVA results were ($p<0.05$, $F = 14.9$, $R^2 = 0.383$) (Fig. 2 and 3).

The rainfall composition of the study area ranks it as a pristine area and the pristine status can be attributed to low sulphur and nitrogen concentration; neutral pH values (range 6.2-7.0) of rainfall water and no significant difference between rainy and dry season pH values.

Differences detected in pH values and sulphur concentrations between rainfall and throughfall or stemflow were also low for the rubber plantation in all the stands. The acidifying effect of sulphur dioxide in precipitation is not a threat in the area compared to many European and North American forests (Parker, 1983; Aerts, 1997; Levia and Frost, 2006).

CONCLUSION

The amount of interception loss by the rubber canopies is higher in the 40 year-old rubber stand (291.3 mm or 18.9%) compared to 200.3 mm (13%) and 255.1 mm (16%) in the 15 and 5-yer-old other rubber stand respectively. High throughfall in the 5-year-old rubber stands may be attributed to the high rainfall during the study period and also due to the fact that there are many gaps within the stands. Parker (1983) and Liu point out that the amount of precipitation controls the magnitude of throughfall. The study also showed that interception increases with decreased rainfall and rainfall intensity especially during the dry seasons. There are no significant variations in NH_4^+ -N, $NO3^-$ - N and SO_4^{2-} probably due to their extremely lower fluxes. The quantification of nutrient fluxes is an important step in the development of sustainable land use systems, especially on low-fertility soils of the humid tropics. These results can help to devise measurement programs for nutrient cycling in tree-dominated land use systems and spontaneous vegetation in the humid tropics. Possible effects of concentrated nutrient solutions on microbial processes in soil and litter merit further investigation.

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