Sugar cane nutrient requirements and the role of atmospheric deposition supplying supplementary fertilization in a Venezuelan sugar cane plantation

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RESUMEN

La región centro norte de Venezuela está caracterizada por lluvias de naturaleza ácida, cargadas de contaminantes que incluyen nutrientes, debido a la intensa actividad industrial y agrícola de la zona. Esta región presenta a su vez grandes extensiones de plantaciones de caña de azúcar. Una vez que la lluvia pasa por el dosel de bosques o de ecosistemas agrícolas, su composición química cambia, ya sea por absorción, lixiviación o lavado de iones depositados en el dosel. Este documento describe los cambios en la química de las aguas de lluvias después de pasar por el dosel de una plantación de caña de azúcar. En cuatro parcelas de 300 m^2 ubicadas en un área experimental de 4.5 ha, plantadas con *Saccharum officinarum*, se instalaron colectores de agua de lluvia y de escurrimiento foliar. El estudio corresponde al análisis de crecimiento de la tercera soca del cultivo. El pH del agua de lluvia se incrementa cuando pasa por el dosel. La magnitud de los cambios fue importante y se relacionó parcialmente con las cantidades significativas de cationes que se lavan del dosel. Las entradas de N en el agroecosistema fueron altas (25.25 kg ha^1 a^{-1}) como consecuencia de la fertilización y quema local de la caña antes de su cosecha y la actividad industrial (petroquímica y fertilizantes) desarrollada en la zona. Las precipitaciones (húmeda y seca) representan una importante fuente de entradas de nutrientes a la plantación. En el caso de los macronutrientes (N, P y K) las entradas fueron altas y suplen una significativa fracción de los requerimientos del cultivo, lo mismo ocurre en el caso del zinc y del cobre.

ABSTRACT

As a consequence of high industrial and agricultural activities, acidic rains loaded with pollutants—including nutrients—are characteristic of northern central Venezuela, a region dominated by sugar cane plantations. Canopies of forest and agricultural crops can modify the chemistry of rainfall through uptake, leaching and outwash of deposited ions. This paper describes the change in the chemistry of acid rains after passing through a sugar cane canopy. Four plots of 300 m^2 within a 4.5 ha experimental area, planted with *Saccharum officinarum* had rain and throughfall collectors installed. The study corresponds to the analysis of the growing season of the third ratoon. The pH of the rain in the agroecosystem increased after passing through the canopy. The magnitudes of the changes were important and partially related to the significant amount of cations leached from the leaves or washed out from dry deposition to the leaves. N inputs for wet and dry deposition in the agroecosystem were high (25.25 kg ha^{-1} yr^{-1}) as a consequence of the agricultural activity in the area, the local burning of sugar cane before cropping, and the location of the experimental area close

to petrochemical and fertilizer industries. Rainfall constitutes an important source of nutrient inputs to the sugar cane system. In the case of macronutrients (N, P and K) the inputs were high and supply an important fraction of plant nutrient needs, as occurs for zinc and copper.

Keywords: N-deposition, throughfall, foliar leaching, pollution, foliar fertilization.

1. Introduction

Acidic rains enriched with ammonium (NH_4), phosphorus (P) and sulphur (S) are characteristic of northern Venezuela (Morales *et al.,* 1998), a region currently supporting sugar cane plantations where significant agricultural and industrial activities take place generating significant revenue annually.

Nitrogen (N) inputs (NH_4^+ and nitrate NO_3^-) in precipitation are considered of great importance in the N economy of natural ecosystems (López-Hernández *et al.,* 2012), but in agroecosystems, those inputs are of lesser importance when compared with the N requirements for crop production (Stevenson, 1982; Thorburn *et al.,* 2005). N and other nutrients present in precipitation and dry deposition can originate from a variety of natural and anthropogenic sources, including air pollution (Rodrigo *et al.,* 2003). Emissions from anthropogenic pollution are beneficial, as some deposited elements are nutrients for forests and crops (López-Hernández *et al.*, 2012), but harmful as well under certain polluted environments, *e.g.* where trace metal deposition is important (Pritsch *et al.,* 2006).

Tree and agricultural crops canopies modify raindrop trajectories by partitioning the incident rainfall into throughfall and stemflow (Park and Cameron, 2008). A proportion of the incident rainfall is intercepted (I) by, and retained temporarily on leaf surface, branches and stems. Throughfall (TF) is the portion of rainfall (P) that reaches the soil by passing directly or by dripping from the canopies (forest or crop plantations). These components may be linked by the relationship:

$$I = P - TF$$

Concerning precipitation chemistry, canopies of forests and agricultural crops can modify the chemistry of rainfall in different ways: (1) uptake and retention by the canopy, (2) removal and leaching of ions from leaves, or (3) changes in the rain waters when passing through the canopy (throughfall) by the wash out of dry deposition (Tukey, 1970; Rodrigo *et al.,* 2003;

Perez-Marin and Menezes, 2008). The magnitude of the foliar leaching depends on a variety of factors: plant age, physiological state, plant composition and canopy morphology (Malek and Astel, 2007), but also on frequency, duration, intensity and chemical composition of the rainwater; moreover, in polluted areas the actual composition of the throughfall depends on the pollution source (Rodrigo *et al.,* 2003).

The high primary production (*ca.* 60-100 ton ha^{-1} yr^{-1}), and the particular plant architecture of the canopy of the sugar cane allow an important leaf interception of the income precipitation. Rainfall arriving sugar cane systems, in turn, might have a change in its chemical composition mainly due to throughfall processes, before it reaches the soil. However, few studies have tried to understand the changes in the chemistry of the atmospheric deposition through canopy interactions in a sugar cane agroecosystem during its development.

This paper describes the changes in the chemistry of acid tropical rainwater after passing through a sugar cane canopy along the development of their third ratoon. Particular emphasis is given to the quantification of the inputs of macronutrients (N, K, P) and micronutrients (Fe, Mn, Zn, and Cu) in the agroecosystem. Therefore, we studied whether the element deposition (particularly for the macronutrients N, P, K) constituted a relevant proportion of the nutrients retained in the sugar cane canopy.

2. Material and methods

2.1 Study site

The study was located in a sugar cane farm near San Felipe, Yaracuy state, central Venezuela (10º 29'44'' N and 68º 31' 44'' W). The experimental site corresponds to a tropical humid climate region (1400-1700 mm of precipitation) affected by marine aerosols.

Four plots of 300 m^2 within an experimental area of 4.5 ha planted with *Saccharum officinarum* were selected for the installation of rain and throughfall collectors. Study corresponds to the analysis of the growing period of two sugar cane varieties (Puerto Rico 1028 [PR] and Venezuela 58-4 [V]). The soil is

a Mollisols, Haplaquoll (fine loam, isohiperthermic, muscovite, montmorillonitic, kaolinitic) with a pH of 7.4, moderate to high effective cation exchange capacity (ECEC), moderate to high available and total P contents, and moderate N content.

2.2 Collection of rain and throughfall waters and analysis

Collection of rain and throughfall waters was weekly conducted during three consecutive years; however information here presented corresponds to the year of the third ratoon.

Bulk depositions (*i.e.*, wet plus dry) were collected with plastic funnels of 18.5 cm internal diameter (PVC polyvinyl chloride) attached 4.5 m above soil surface and above the sugar cane canopies. The funnels were permanently open to the atmosphere; therefore, precipitation thus collected corresponds to bulk deposition as named by Eriksson (1953) and comprises the wet deposition flux and the dry deposition flux of gravitory sedimentation (Rodrigo *et al.,* 2003). The funnels were connected to 2 L polyethylene terephtalate (PET) bottles, which were first acid-washed (HCl 50%) and then rinsed with demineralized water. Bulk deposition (BD) for chemical analysis was sampled during one year from five gauges located in the plots.

Throughfall waters were collected in PVC funnels attached 0.30 m above soil surface within the canopies connected to PET bottle collectors. In this study, due to the usual high variability of the throughfall measures, a total of twenty collectors were installed for regular sampling instead of the five installed for bulk collection. Nylon meshes were placed in the funnel necks, and at the end of tube and bottle connections to prevent insects or vegetal debris from falling inside the sampling collectors.

Net throughfall for a particular element (*NTFe*) corresponds to the modification of precipitation chemistry as water enters the system and is defined as *NTFe = TFe – BDe*, where *TFe* and *BDe* correspond to the amount of the element in throughfall and bulk deposition, respectively. More details of the methodology are presented in Infante *et al.* (1993) and López-Hernández *et al.* (2005).

2.3 Chemical analysis

After one day of collection, the samples were taken to the laboratory where pH was measured with a glass electrode. Water samples were then filtered through 0.45 µm pore size Millipore filters, and phenyl mercury acetate (1 ml L^{-1}) was added as preservative. Samples were rejected when contaminated by debris. Two aliquots of each sample (one acidified with 1 ml L^{-1} pure HNO$_3$ bidistilled with a quartz distiller) were kept for further analysis.

In the non-acidified samples, NO$_3$ and NH$_4$ in the waters were analyzed in a Technicon Auto Analyzer II (Technicon Industrial Systems, 1974) whereas P (PO$_4^{-3}$) was determined with the colorimetric method of Murphy and Riley (1962). Cations (Na, K, Ca and Mg) were analyzed by atomic absorption in a Varian Techtron AA6.

Aliquot samples acidified with HNO$_3$ (in order to avoid adsorption of micronutrients in the recipient walls) were kept at 4 ºC until the micronutrient analysis was performed. Micronutrients (Fe, Mn, Zn and Cu) in precipitation and throughfall waters were analyzed by flameless absorption spectroscopy, but without preconcentration; an HGA 2100 heated graphite atomizer (Perkin-Elmer) was employed.

Bulk deposition and throughfall waters were analyzed individually from several samples collected during a given month and averaged for monthly inputs as the product of bulk deposition and throughfall volumes, and monthly weighted average concentration of the element. The annual inputs of elements in incident rainfall (BDe) and throughfall (TFe) to the sugar cane plantation were expressed per unit area (ha).

2.4 Statistical analyses

Analyses were carried out with *t*-tests (Student *t*-test, $p < 0.05$) for paired samples on the difference between monthly concentration of elements in precipitation and throughfall waters.

3. Results

3.1 Developing of the sugar cane canopy and rain interception

The monthly percentage of canopy interception increased sharply with the age of the plantation during the first five months (third ratoon, Fig. 1) until a maximum of 60.3%, and then it fluctuated around that maximum (38.3-59.9%). During the study period, the total precipitation measured was 1752 mm, whereas the water volume estimated from the throughfall was 1124 mm, which corresponds to 64% of the total precipitation.
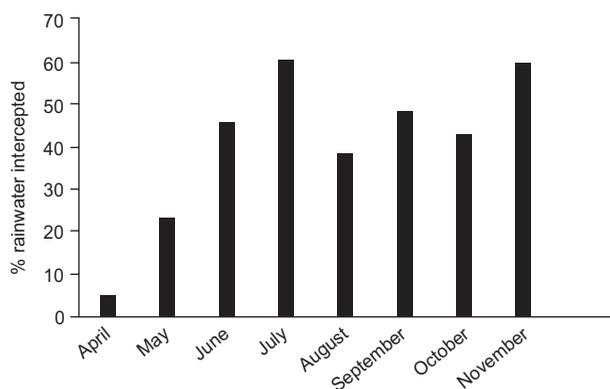
Fig. 1. Percentage of rainwater intercepted by the canopy in a sugarcane agroecosystem.

3.2 The pH and base cation concentrations in rainwater

The pH of bulk deposition in the sugar cane agroecosystem increased by 0.93 to 1.64 pH units as it passed through the canopy (Table I). Those results may reflect the significant amount of cations leached from the leaves or washed out from materials deposited on the leaves and cane stems (Table I). Thus, throughfall waters were enriched in bases compared with bulk deposition, particularly after June (peak of the rainy season) when the sum of bases in the throughfall waters surpassed the values of the bulk deposition (Table I, Fig. 2).

The average monthly values for cations (Fig. 2) followed the order $Na > K > Mg > Ca$. The dominance of Na in precipitation reflects the deposition of marine aerosols in the studied area. Na and K in the precipitation water at the sugar cane agroecosystem (Fig. 2) showed an annual mean concentration of 1.87

and 1.41 mg L^{-1}, respectively. Mg presented an intermediate concentration (0.24 mg L^{-1}) whereas the Ca average concentration was the lowest (0.12 mg L^{-1}).

3.3 Net throughfall of cations

There was a net positive throughfall of Mg from the canopy (more than twice the bulk deposition) and to a lesser extent for Ca. In contrast, the Na concentration showed a net negative throughfall that was significantly different (*t*-test, $p < 0.05$) between deposition and throughfall from April to October (Fig. 2, Table II), whereas for K there was a small net negative throughfall (Table II); however, the canopy losses were high in the months of August to October (Fig. 2).

3.4 Nitrogen and phosphorus concentrations in rain waters

NH_4 was the predominant N form in the precipitation water with a mean value of 1.29 mg L^{-1} (Fig. 3), but nitrate-N was not detectable in the majority of months (Fig. 3). P (PO_4^{-3}) concentrations in rainwater ranged from 0.10 to 1.64 mg L^{-1} (Fig. 3). After passing through the sugar cane canopy there was a strong enrichment in nitrates in the throughfall compared with the bulk deposition (28.67), whereas in the case of NH_4 and orthophosphate the annual concentrations of the bulk deposition decreased in a significant form due to canopy absorption (Table III).

3.5 Net throughfall of nitrogen and phosphorus

There was an important N fertilization (net negative throughfall) of the canopy through NH_4 absorption. In contrast, the net positive throughfall of NO_3

Table I. Monthly average pH and sum of cation concentrations (µeq L^{-1}) in bulk deposition and throughfall in a sugarcane agroecosystem located in central northern Venezuela. Bulk deposition included wet and dry deposition collected above the sugarcane canopy.

Month	BD pH	TF pH	Sum of BD cations	Sum of TF cations	Sum of TF/BD cations
April	4.52	5.50	227	138	0.61
May	3.70	5.26	177	105	0.60
June	3.97	4.99	209	271	1.30
July	3.97	4.90	156	145	0.93
August	4.22	5.45	83	134	1.61
September	3.67	5.20	113	225	1.99
October	3.54	4.50	66	198	3.00
November	4.12	5.76	126	210	1.67
December	4.20	5.29	103	251	2.44

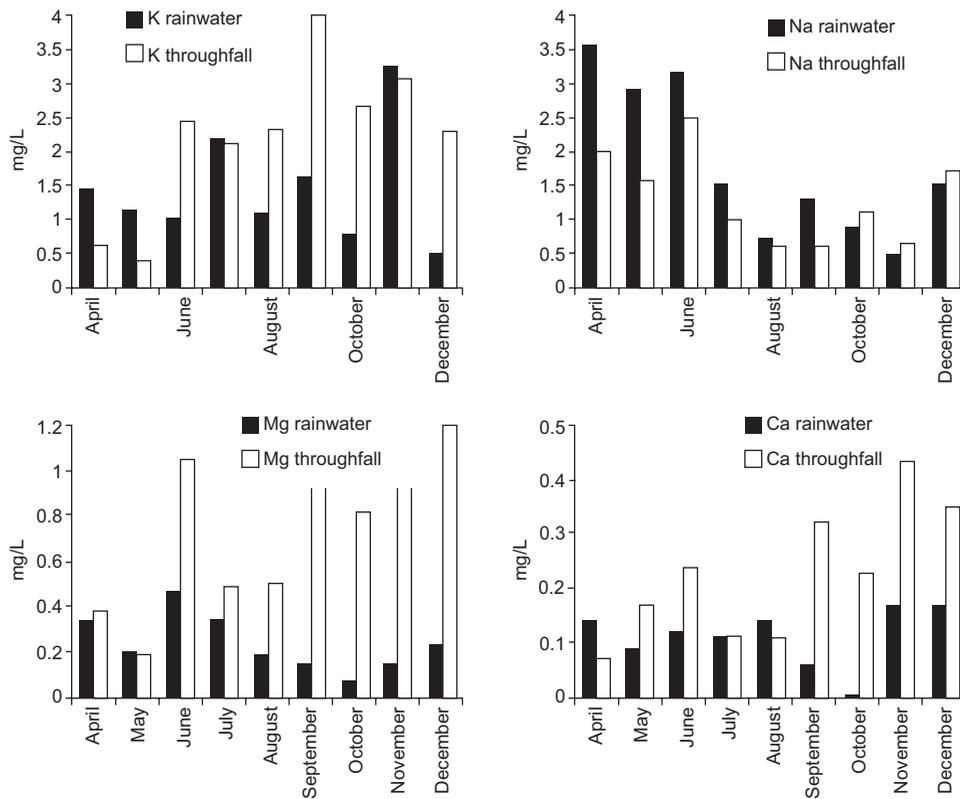BD: bulk deposition; TF: throughfall.

Fig. 2. Monthly weighted average concentrations of cations (mg L^{-1}) in rain and throughfall waters.

indicates that NO_3 was leached from the canopy (leaves and stem) in throughfall waters (Table II, Fig. 3), particularly in the months when NO_3 was not detectable in bulk deposition. The important

Table II. Annual fluxes (kg ha^{-1} yr^{-1}) of nutrients in bulk deposition and throughfall, and net throughfall in a sugarcane agroecosystem located in central northern Venezuela. Significant differences (*t*-test, P < 0.05) between bulk deposition and throughfall are shown in bold in the column "net throughfall".

Element	Bulk deposition	Throughfall	Net throughfall
Na	24.92	14.34	**−10.58**
K	22.54	21.54	−1.00
Mg	3.34	7.89	**4.55**
Ca	1.93	2.45	0.52
N-NO$_3$	0.06	4.14	**4.08**
N-NH$_4$	25.19	9.30	**−15.89**
P-(H$_2$PO$_4^{-3}$)	14.71	4.84	**−9.87**
Zn	0.633	0.269	**−0.364**
Cu	0.104	0.098	−0.006
Mn	0.131	0.062	**−0.069**
Fe	0.263	0.201	−0.062

amounts of P (PO$_4^{-3}$) entering the sugar cane system in the incident precipitation were retained in the canopy of the agroecosystem; therefore a negative annual throughfall of 9.87 kg P ha^{-1} yr^{-1} was found (Table II).

3.6 Trace metals concentrations in rainwater

Figure 4 presents the weighted average concentrations of the trace metals analyzed (Fe, Mn, Zn and

Table III. Annual weighted average of macronutrients (mg L^{-1}) and heavy metals (μg L^{-1}) in bulk deposition and throughfall in a sugarcane agroecosystem located in central northern Venezuela.

Element	BD	TF	TF/BD
N-NO$_3$	0.015	0.43	28.67
N-NH$_4$	1.88	1.00	0.53
P-(H$_2$PO$_4^{-3}$)	0.76	0.43	0.57
Zn	40.1	25.3	0.63
Cu	6.2	8.9	1.43
Mn	8.9	6.0	0.67
Fe	15.6	19.5	1.25

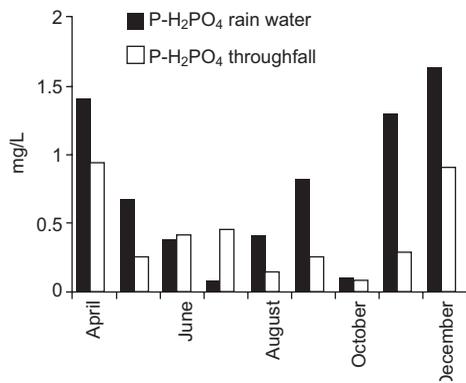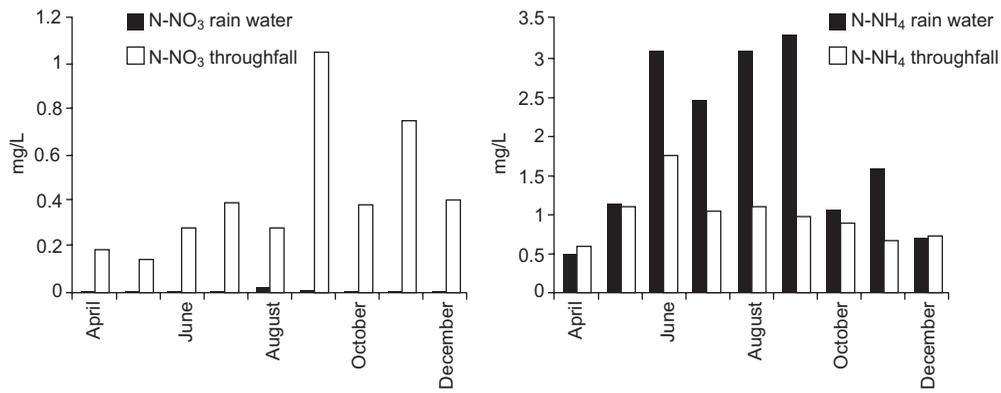BD: bulk deposition; TF: throughfall.

Fig. 3. Monthly weighted average concentrations of N (N-ammonium and N-nitrate) and P (P-H$_2$PO$_4$) in bulk deposition and throughfall in a sugar cane agrosystem.
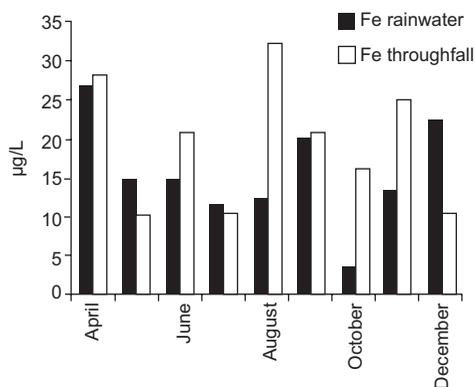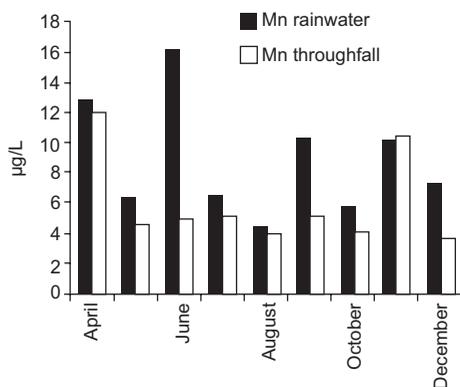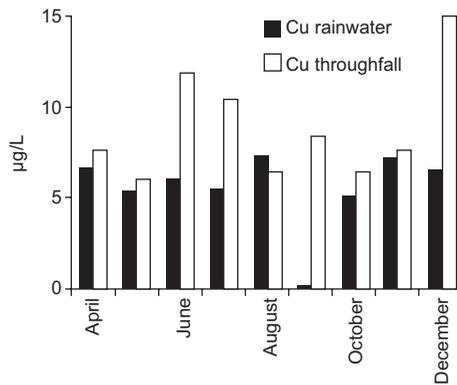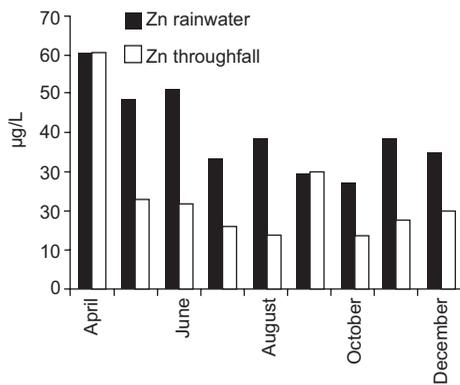

Fig. 4. Monthly weighted average concentrations of heavy metals in bulk deposition and throughfall in a sugar cane agroecosystem.

Cu) in the precipitation waters. Zn had the highest concentration followed by Fe, while Cu and Mn presented similar values (Fig. 4). Throughfall waters were enriched in Cu and Fe compared with bulk deposition (Table III); on the contrary, the annual concentrations of bulk deposition decreased significantly in the case of Zn and Mn due to active canopy absorption (Table III).

3.7 Net throughfall of trace metals

Net throughfall deposition was negative for Zn, Mn and Fe (Fig. 4, Table II), whereas in the case of Cu, rain and throughfall depositions were almost similar. Net throughfall of Mn and Fe were moderately negative (62-69 g ha^{-1} yr^{-1}), whereas for Zn it was strongly negative accounting for a significant foliar absorption (364 g ha^{-1} yr^{-1}).

4. Discussion

4.1 Development of the sugar cane canopy and rain interception

Information corroborates the effect of crop development in rainwater interception. There is an initial increase of interception as the canopy develops, and then it stabilizes around 40% of interception when the canopy is fully developed (Fig. 1). After the fifth month of crop development, when the maximum interception is achieved, a high variability in interception measures is found (38.3-59.9%) that is related to plant senescence. Thus, the incremental accumulation of dead materials (leaves and stems) relative to the living parts strongly affected rainwater interception (Dunne and Leopold, 1978). Rutter (1963) and Grimm and Fassbender (1981) have pointed out that successive and copious rain events contribute to saturation or overflooding of the canopy surface, consequently decreasing its interception capacity.

Although the information for canopy interception is copious in temperate and tropical forests, fewer studies of rainfall interception in grasslands have been done (Friesen *et al.*, 2012). Leopoldo *et al.* (1981) reported 57% of precipitation interception in domestic sugar cane, a similar value to the one presented here, whereas in a recent publication Friesen *et al.* (2012), comparing rainfall interception in tropical hardwood trees and wild sugar cane *Saccharum venosum,* found interception values of 56.1% for the wild grass.

The interception value at maximum crop development reported here is lower than the values presented by Dezzeo and Chacón (2006) for tropical forests (77-80%) and Rodrigo *et al.,* (2003) in holm oak (*Quercus ilex* L.) Mediterranean forests (72-85%); however, our value corresponds to the lower limit (62.1-94.5%) of the range presented by Galoux *et al.,* (1981) for different tropical forests and was higher compared with other gramineous plants (Ward, 1967). The interception values of the sugar cane agroecosystem are related with the architecture of the sugar cane canopy at the end of the growing season, which is characterized by abundant foliage with a receptacle formed between the stem and the basis of the foliage that helps to hold and therefore intercept rainwater within the canopy.

4.2 The pH and base cation concentrations of rainwater

Precipitation pHs in the studied plantation ranged from 3.54 to 4.52 (Table I), a common situation in northern central Venezuela as a consequence of high industrial (petrochemical and fertilizer production plants) and agricultural (crop fertilization and cattle raising) activities (Lewis and Weibezahn; 1981, Sequera *et al.,* 1991; López-Hernández et al., 2012). In the rest of Venezuela, even in the absence of anthropogenic influence, precipitation is fairly acid (5.1-5.8) (Montes *et al.,* 1987, López-Hernández 2008).

Concentrations of Na and K were higher than the values presented by Steinhardt and Fassbender (1979) in a cloud forest located in San Eusebio, Venezuela, and by López-Hernández *et al.* (1994) in a flooded savanna ecosystem in Mantecal, Venezuela located far from the ocean and in a more pristine environment. On the contrary, Steinhardt and Fassbender (1979) in a forest site at San Eusebio, Venezuela and López-Hernández *et al.* (1994) at Mantecal, Venezuela reported higher annual averages for Ca and Mg. In a pristine forest ecosystem at the Canaima National Park, located in Gran Sabana, southeastern Venezuela, Dezzeo and Chacón (2006) reported very low mean concentration of cations (0.04 and 0.11 mg L^{-1} for Ca and K, respectively) in incident waters.

4.3 Changes in pH and bases in the throughfall waters

The pH of bulk deposition in the sugar cane agroecosystem increased as it passed through the canopy

(Table I). These results may reflect the significant amount of cations leached from the leaves or washed out from materials deposited on the leaves and cane stems from terrestrial dust (Table I), though we cannot separate both effects based on the information obtained. Throughfall waters were enriched in bases compared with bulk deposition, particularly after June (peak of the rainy season) when the sum of bases in the throughfall waters surpassed the values of the bulk deposition (Table I, Fig. 2). Similar information is presented by Rodrigo *et al.* (2003) for Mediterranean forests that receive African red rains, which were responsible for most of the inputs of alkalinity and base cations inputs from bulk deposition. However, the precipitations in the Mediterranean environment were more enriched in Ca and Mg compared with this tropical site.

4.4 Net throughfall of cations
Net throughfall differs among cations, thus there was a net positive throughfall of Mg from the canopy and to a lesser extent for Ca. In contrast, Na concentration showed a net negative throughfall that was significantly different (*t*-test, $p < 0.05$) between deposition and throughfall from April to October (Fig. 2, Table II), whereas for K there was a small net negative throughfall (Table II). However, canopy losses were high in the months of August to October (Fig. 2).

In two polluted forest sites in the México City air basin, Pérez-Suárez *et al.* (2008) reported a net positive throughfall deposition of Ca, Mg and K. Pérez-Marín and Menezes (2008) reported important K inputs to the soil from the throughfall waters in an agroforestry system with *Gliricidia sepium* in the semi-arid northeastern Brazil. Moreover, Dezzeo and Chacón (2006) reported that the low mean concentration of cations in precipitation waters was significantly higher (positive throughfall) after the passage through the forest canopy in a pristine forest ecosystem in the Canaima National Park, Gran Sabana, southeastern Venezuela.

4.5 Nitrogen and phosphorus in rainwaters
NH_4 was the predominant N form (mean value 1.29 mg L^{-1}) in the precipitation water, but nitrate-N was not detectable in the majority of months (Fig. 3). Steinhardt and Fassbender (1979) in the cloud forest of San Eusebio, Venezuela, located about 300 km from the experimental site, and also affected by petrochemical activity, reported a lower N concentration (0.64 mg L^{-1}, mostly NH_4). In Venezuelan more pristine environments at Gran Sabana, very much lower N concentration in incident waters (0.04 mg L^{-1}) has been reported (Dezzeo and Chacón, 2006).

The P (PO_4^{-3}) concentrations in rainwater ranged from 0.10 to 1.64 mg L^{-1} (Fig. 3). The values exceeded the information generally presented in the literature, which are about 0.05 mg L^{-1}. Concentrations of P (PO_4^{-3}) in rainfall are much affected by ash deposition, since the higher concentrations correspond to the period from November to March (Fig. 3), when the sugar cane plantations are burned in the areas located in the neighborhood of the experimental plot (Sequera *et al.,* 1991).

4.6 Changes in nitrogen and phosphorus contents in the throughfall waters
There was an important N fertilization (net negative throughfall) of the canopy through NH_4 absorption. In contrast, the net positive throughfall of NO_3 indicates that NO_3 was leached from the canopy (leaves and stem) in throughfall waters (Table II, Fig. 3), particularly in the months when NO_3 was no detectable in bulk deposition. In two polluted forest sites in the México city air basin, Pérez-Suárez *et al.* (2008) reported also a negative throughfall deposition of NH_4 under fir and pine canopies, whereas Rodrigo *et al.* (2003) reported a relative low negative annual throughfall of 1.64 and 1.61 kg ha^{-1} yr^{-1} of NO_3 and NH_4, respectively, for Mediterranean forests. The important amounts of P entering the sugar cane system in the incident precipitation were retained in the canopy of the sugar cane agroecosystem; therefore a negative annual throughfall of 9.87 kg P ha^{-1} yr^{-1} was found (Table II).

4.7 Trace metals in rainwaters
The weighted average Zn concentration in precipitation (40.1 μg L^{-1}) was higher in the sugar cane agroecosystem than the values presented in tropical environments by Steinhardt and Fassbender (1979) in a cloud forest (2.4 μg L^{-1}), López-Hernández (2008) in a seasonally flooded Venezuelan savanna (28.6 μg L^{-1}), and McColl (1981) in a temperate eucalypt forest (16.1 μg L^{-1}), but lower than Zn concentration reported by Golley *et al.* (1975) in a Panamanian rain tropical forest (44 μg L^{-1}), and by

Liu *et al.* (2005) in the southern Yellow sea, China (60-150 µg L^{-1}). In pristine environments, the weighted average Zn concentration in precipitation greatly surpasses the Cu concentrations (Driscoll *et al.,* 1994; Liu *et al.,* 2005; Muezzinoglu and Cukurluoglu, 2006).

The weighted average Cu concentration in rainwater (about 8.3 µg L^{-1}) is higher than the values presented by Steinhardt and Fassbender (1979) in San Eusebio, Venezuela (2.79 µg L^{-1}) and lower than the information given by Golley *et al.* (1975) for the Panamaniam forest ecosystem (24.0 µg L^{-1}) and by Muezzinoglu and Cukurluoglu (2006) in Izmir, Turkey (19.7 µg L^{-1}). Cu mean concentration is however about the values presented by López-Hernández (2008) in a flooded savanna (12.1 µg L^{-1}) and Liu *et al.* (2005) in a coastal region in the southern Yellow sea, China (3-15 µg L^{-1}). Fe and Mn concentrations were much lower than values reported by Steinhardt and Fassbender (1979) in San Eusebio, Venezuela.

4.8 Element inputs at the sugar cane agroecosystem
The study site is near the sea; therefore, the cation concentrations in rainwater are affected by marine aerosols, although terrestrial dusts can also affect rainwater composition. Na and K inputs were high (24.92 and 22.54 kg ha^{-1} yr^{-1}, respectively, Table II) when compared with other Venezuelan ecosystems, whereas in the cases of Mg and Ca the rain inputs (3.34 and 1.93 kg ha^{-1} yr^{-1}, respectively) were lower and not much different than other Venezuelan sites.

Although nitrates were leached in throughfall waters (Fig. 3, Table II), N balance revealed significant N fertilization of the leave canopy (leaves and stem) through NH_4^+ absorption (Table II). Nitrogen inputs (25.25 kg ha^{-1} yr^{-1}) for wet and dry deposition, mostly in the NH_4^+ form (25.19 kg NH_4^+ ha^{-1} yr^{-1}, Table II), were high compared with other ecosystems. This is, no doubt, due to the high agricultural (fertilization, cattle raising and burning before cropping of the plantation) and industrial (petrochemical and fertilizer production plants) activities near the experimental area. In Venezuelan savannas distant from urban activities, mineral nitrogen inputs by precipitation, on the contrary, ranged from 2.2 to 6.2 kg N ha^{-1} yr^{-1} (López-Hernández *et al.,* 2012).

The high amounts of P entering the sugar cane system as bulk deposition (Table II) account for a high P input (14.71 kg ha^{-1} yr^{-1}), most of it (11.01 kg ha^{-1} yr^{-1}) in months when active burning of sugar cane plantations is taking place (November to April, Fig. 3); therefore, dry deposition of phosphate salts might be occurring in the area.

Zn input at sugar cane agroecosystem (633 g ha^{-1} yr^{-1}) was similar to the value presented for Mantecal´s savannas (595 g ha^{-1} yr^{-1}) by López-Hernández (2008), much higher than the value (30 g ha^{-1} yr^{-1}) reported by Steinhardt and Fassbender (1979) for a cloud forest located at San Eusebio, Venezuela, and similar to the value presented by Liu *et al.* (2005) in a coastal region of the southern Yellow sea (428 g ha^{-1} yr^{-1}). However, Zn input at the agroecosystem was very much lower than the value presented by Heinrichs and Mayer (1977) in an industrialized Central European forest ecosystem (3900 g ha^{-1} yr^{-1}). Copper input in the sugar cane plantation (97.8 g ha^{-1} yr^{-1}) also exceeded the 45 g ha^{-1} yr^{-1} presented for San Eusebio, Venezuela (Steinhardt and Fassbender 1979) and was under the values presented by Heinrich and Mayer (1977) in a heavy industrialized European forest ecosystem (224 g ha^{-1} yr^{-1}) and by López-Hernández (2008) in the savannas of Mantecal, Venezuela (227 g ha^{-1} yr^{-1}). Annual deposition of iron (263 g ha^{-1} yr^{-1}) is much lower than the reported Steinhardt and Fassbender (1979) at San Eusebio, Venezuela. Manganese (Mn) input in precipitation water (131 g ha^{-1} yr $^{-1}$) was lower than values reported in other tropical areas (Steinhardt and Fassbender, 1979).

4.9 Nutrient inputs in relation to sugar cane nutrient requirements
Bulk deposition of polluted areas might be an important source of nutrient inputs to plants, which helps to cope with their nutrient needs. By using information already published concerning the macro- and micronutrient requirements (*e.g.*, amount of the element contained in stems, green leaves and roots at the peak of maximum development) of the sugar cane varieties examined in this study (López-Hernández *et al.,* 1993; Vallejo-Torres, 1988) we have found that in the case of the micronutrients, all the Zn absorbed from bulk precipitation would be in excess (217%) of sugar cane requirements (Table IV). Cu demand by the crop is also well covered (48.7%) by this mechanism; however, much less of the Mn, K and Fe (9.9, 5.0 and 1.7%, respectively) required by the sugar cane can be obtained by bulk precipitation.

Table IV. Nutrient inputs in bulk deposition and nutrient requirements in a sugarcane agroecosystem located in central northern Venezuela. The N and P requirements were taken from López-Hernández *et al.* (1993) and micronutrient requirements from Vallejo-Torres (1988).

Element	Precipitation input (kg ha^{-1})	Requirement (kg ha^{-1})	Percent of requirement from bulk deposition
Zn	0.666	0.306	217
Cu	0.098	0.201	48.7
Mn	0.178	1.791	9.9
Fe	0.440	25.637	1.7
N	25.3	228.0	11.1
P-($H_2PO_4^{-3}$)	15.0	62.0	24.2
K	22.5	453.0	5.0

The N input of rain water (25.25 kg ha^{-1} yr^{-1}) represents around 11% of the N requirements (228 kg ha^{-1} yr^{-1}) for biomass production of the sugar cane plantation while in the case of P the input as bulk deposition (15 kg ha^{-1} yr^{-1}) represents 24% of the P requirements (62 kg ha^{-1} yr^{-1}) of the varieties studied.

5. Conclusions

Incident rainfall constitutes an important source of nutrient inputs to the sugar cane system studied. In the case of macronutrients (N and P) the inputs were considerable when compared with other tropical regions and supply an important fraction of plant nutrient requirements; a similar situation was recorded in the case of the micronutrients analyzed particularly for zinc and copper. Although the input of K was important, the high demand of the sugar cane for this element makes the contribution marginal. We did not register Na uptake, however a significant proportion of the Na coming with the bulk deposition was retained in the canopy (Table II). About 10% of the Mn needs can be covered by rainfall input, whereas in the case of iron, the precipitation supply is negligible compared with the plant's needs. In the agroecosystem, Mg and K concentrations increased considerably during the passage of rainwater through the canopy, suggesting that these elements tend to be leached from plant tissues and were mobile, particularly at the end of the growing season.

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