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REGULAR ARTICLE

Gross precipitation and throughfall chemistry in legume species planted in Northeastern México

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Abstract Plant cover modifies throughfall chemistry, and the solute concentration is dependent on the plant species at any given site. The chemistry of gross rainfall and throughfall of four endemic species planted in northeastern Mexico was evaluated from March 1996 to March 1997. Chemical solutes measured included Ca, K, Mg, Na, Fe, Mn, Cu, and Zn. Dry deposition and canopy leaching fluxes were estimated following the canopy budget model. Variance analyses tested the statistical dependence of the total and net fluxes on the species and seasons. Regression analysis tested the dependence of chemical concentrations on rainfall depth and lag time between rains. A total of 52 rainfall events were recorded during the study period summing 523 mm. Significant differences were noted on the total and net fluxes between the plant species. For total flux, average throughfall (37.8 kg ha^{-1} year^{-1}) almost doubled the flux of solutes compared to rainfall (24.1 kg ha^{-1} year^{-1}). *Pithecellobium ebano* (Berland.) C.H. Mull. (43.3 kg ha^{-1} year^{-1}), *Acacia berlandieri* Benth. (38.7 kg ha^{-1} year^{-1}), and *Pithecellobium pallens* (Bent.) Standl. (38.4 kg ha^{-1} year^{-1}) recorded the highest total flux of solutes, and *Acacia rigidula* Benth. (30.9 kg ha^{-1} year^{-1}) the smallest. Chemical solutes showed significant differences for total and net fluxes. Ca was the dominant cation with 48% and 52% of the total constituent flux for rainfall and throughfall, respectively. However, K, Mg and Cu approximately doubled in throughfall in contrast to gross rainfall. Species with the largest aboveground biomass had lower throughfall volumes (i.e., higher interception rates) but higher chemical solute inputs to the forest floor. Rainfall depth and lag time between rains explained part of the variation for most species, stressing the partial dependence of the washing effect and the amount of dry deposition on canopies. This research discusses the importance and the sources of incoming solutes on the studied plant species.

Keywords Gross rainfall · Native leguminous species · Throughfall chemistry

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Introduction

The role of gross precipitation as a major input of chemicals in ecosystems has been a cause of major concern in the last decades (Fahey et al. 1988; Gesper and Holowaychuk 1970; Parker 1983). In addition to rainfall, plants play a pivotal role in modifying the input of chemical solutes via throughfall (Gesper and Holowaychuk 1970) and stemflow (Parker 1983; Whitford et al. 1997). The chemistry of throughfall is made up of bulk deposition, dry deposition and canopy leaching, amongst other sources. Dry-fall collects on foliage, branches and stems of shrubs and is related to natural and anthropogenic emissions. The biological activity of micro-organisms in the canopies may also contribute to the availability of ions. Canopy leaching is another source of solute input in throughfall that may be important in several ecosystems. Other ion sources are likely explained by the different phenological phases, tissue exudation and decomposition, among other factors.

In arid and semi-arid landscapes, the architecture of trees, in addition to the typical sources of chemical solutes in canopies, generally increases ion concentrations in throughfall and stemflow, and consequently in the nutrient availability of soils, creating islands of soil moisture (Návar and Bryan 1990; Whitford et al. 1997) and fertility (Ambatzis et al. 2003; Breman and Kessler 1995; Jonsson et al. 1999; Schade and Hobbie 2005; Su et al. 2002; Whitford et al. 1997) relative to areas outside the canopy, which are characterized as arid, infertile soils (Schlesinger and Pilmanis 1998). Therefore, additional sources of several chemical solutes are of paramount importance in places where they are not readily available (Fahey et al. 1988) or where weathering processes are slow (Newman 1995).

In the islands of fertility of arid and semi-arid ecosystems, elements such as N, C and P are the most widely studied (Ambatzis et al. 2003; Breman and Kessler 1995; Whitford et al. 1997; Schade and Hobbie 2005; Wezel et al. 2000), although the elemental composition of plants has demonstrated that the most important 12 elements are C, H, O, N, S, P, Cl, Ca, Mg, K, Na and Fe (Mohr and Schopfer 1995). Therefore, studies dealing with the understanding of the concentrations and fluxes of cations such as Calcium (Ca), Magnesium (Mg), Potassium (K), Sodium (Na), Copper (Cu), Manganese (Mn), Zinc (Zn) and Iron (Fe) are required in order to understand plant nutrition in arid and semi-arid infertile soils, since most of the micro elements are important to plant nutrition and semi arid soils are deficient in these elements (Vlek 1985).

Moreover, studies dealing with the chemical concentration of throughfall are common in canopies of temperate and tropical vegetation (Filoso et al. 1999; Gauquelin et al. 1992; Germer et al. 2007; Parker 1983; Potter et al. 1991; Schreiber et al. 1990; Switzer et al. 1988; Tobón et al. 2004; Zimmermann et al. 2007). However, there is little research on the role that arid and semi-arid shrubs play on the net flux of the cations mentioned above into soils.

The objectives of this research were: i) to evaluate the concentration of eight chemical solutes (Ca, Mg, K, Na, Cu, Mn, Zn and Fe) in gross rainfall and throughfall of each of four species: *Acacia rigidula* Benth., *Acacia berlandieri* Benth., *Pithecellobium ebano* (Berland.) C.H. Mull. and *Pithecellobium pallens* (Bent.) Standl., and ii) to estimate total and net fluxes, and iii) to investigate whether there are significant differences in throughfall chemistry among plant species and to discuss the potential sources of throughfall chemistry variation. The hypotheses tested were that constituent inputs (total and net) are similar between: a) the species and b) the chemical solutes.

Materials and methods

An experimental site was placed at the Faculty of Forest Sciences of the University of Nuevo Leon, FCF-UANL (24°47′ N, 99°32′ W, at an elevation of 350 m above sea level, masl). The FCF-UANL is located 8 km south of Linares, Nuevo Leon, Mexico. The region is within the physiographic province of the northern coastal plains of the Gulf of Mexico and is characterized by a semi-arid, sub-tropical climate. Mean annual temperature and precipitation are 21°C and 760 mm, respectively. The standard deviation of annual rainfall is 260 mm. Approximately 80% of the annual precipitation is delivered between May and October. Potential annual evapotranspiration, estimated using the Thornthwaite method, is 1,150 mm (Návar et al. 1994). Deep Vertisols (0.30–1.00 m), which shrink and swell noticeably in response to soil moisture content, dominate the lowlands of the plains (Woerner 1991).

The study was conducted on shrubs planted during 1984. Plantings with the species *A. rigidula*, *A. berlandieri*, *P. pallens* and *P. ebano* were conducted on a randomized block design. The plant species are distributed widely from the Tamaulipan thornscrub of the plains to the Submontane Matorral in the Eastern Sierra Madre mountain range. They are commercially important for forage and fuelwood. Each block contains 16 shrubs, with three blocks per species. Four plants of each of four species were selected to measure gross rainfall and throughfall chemistry and depth. The dasometric characteristics of the studied plant species are described in Table 1. The top height and basal diameter of leguminous tree species are similar to the average values reported for the Tamaulipan thornscrub plant community evaluated in a similar physiographic region. Romero (1999) reported mean figures for the Tamaulipan thornscrub similar to those reported for the studied shrubs.

Gross rainfall (Pg) was measured using 4-liter cylindrical collectors with polyethylene funnels, 20 cm in diameter, on top of the collector to facilitate rainfall entrance and avoid splashing and evaporation. Rainfall collectors were placed on a wooden box with a height of 42 cm to impede rain splashing into the collectors. In total, four gross rainfall collectors were placed in openings, each one next to each forest plantation monitored for throughfall. Throughfall (Pe) was measured below the canopies of each of four shrubs per each species in a similar manner used to collect gross rainfall. Throughfall collectors were placed below the canopy at an average distance of 45 cm from the main stem. Polyethylene mesh (screen, 2.5 mm in size) was placed on top of the funnels to isolate throughfall from leaves, branches, and other potential sources of contamination. After rainfall events, collectors were emptied while recording total volume and depth, and throughfall samples were collected for chemical analysis. Gross rainfall and throughfall were collected within 12 h after each rainfall event to prevent evaporation from collectors and chemical reactions with potential sources of contamination. Collectors were washed with hydrochloric acid and deionized water after the collection of gross rainfall and throughfall, and they were randomly relocated within the canopy radius described above in order to understand the full throughfall depth and the spatial variation of the throughfall chemistry.

In the laboratory, collected samples of gross rainfall and throughfall were filtered and frozen until chemical analysis was conducted. The concentrations of Ca, K, Mg, Na, Fe, Mn, Cu and Zn were estimated with an atomic absorption spectrophotometer (Perkin Elmer AA3000). The detection limits in parts per million were: Ca (0.09), K (0.04), Na (0.03), Mg (0.01), Mn (0.0001), Fe (0.0001), Zn (0.0001) and Cu (0.0001). The relative standard deviation on repeated measures of internal quality control never surpassed 5% for each chemical constituent. Each precipitation event for each collector under each shrub was independently analyzed. In total we analyzed 1,040 samples (52 rainfall events, four plant species plus the gross rainfall and four replicates).

Plant biomass was calculated from the non-linear equation developed by Návar et al. (2004) for Tamaulipan thornscrub species (i.e. $bt=0.059*Db^{2.43}*No\ S$; where: bt = total aboveground biomass (kg per shrub)), Db = basal diameter, No S = number of stems and the total constituent flux, tcf, (Kg ha^{-1}) was regressed to constituent fluxes in throughfall and throughfall amount.

Data analysis The major sources of variation of the solute fluxes were statistically determined by variance analysis. That is, the experiment fitted well a randomized block design with two major sources of variation: species including the control (5) and chemical solutes (8) with four replicates. Mean throughfall solute concentrations and net fluxes were tested for differences between species and chemicals with Tukey`s honest

Table 1 The mean dasometric characteristics (confidence intervals, α=0.05) of four legume species planted inside the Tamaulipan thornscrub in northeastern Mexico

Plant species	Average		No. of stems/Plant	Vertical projection of canopy (m^2)
	Height (m)	Diameter (cm)		
Acacia rigidula	2.50±(0.68)	1.40±(0.24)	18.2±(3.54)	3.89±(1.26)
Acacia berlandieri	2.63±(0.87)	1.85±(0.38)	9.8±(4.58)	4.80±(0.95)
Pithecellobium ebano	3.01±(0.46)	6.35±(0.26)	1.0±(1.85)	3.18±(1.37)
Pithecellobium pallens	3.80±(0.49)	2.78±(0.49)	6.6±(2.36)	5.26±(1.12)

Vertical projection of the canopy was measured as the area the canopy shades on the ground significant difference (HSD) mean separation test. For the species, to compare mean fluxes we used the contrast statistic, since the experimental design is set to test for differences between the control and the species and between the species themselves (i.e. two *Acacia spp* and two *Pithecellobium spp*), with a probability of $\alpha=0.05$. The ANOVA was conducted on the total and net fluxes. The element concentration (mg L^{-1}) was also analyzed by variance analysis with two major sources of variation: seasons (4) and the species, including the control (5). Seasons were determined following the calendar year, i.e., spring from March 21st to June 20th.

Linear regression and non-linear regression equations were fitted to either the concentration or net flux of each constituent and gross rainfall depth and lag time between rainfall events. The latter statistical technique tested the dependence of chemical concentration or net flux on the rainfall depth and lag time between rainfalls, and gives information on the intercept and slope of these relationships which could have some meaningful interpretation. In order to fit the mathematical functions, first the solute (mg L^{-1}) or the net flux (Kg ha^{-1} y^{-1}) of the constituent and rainfall depth (mm) or lag time between rainfalls (days) were graphed. Following, the SAS statistical software v. 8.0 was used to carry out the ANOVA and regression analysis (SAS 2000). Throughfall depth was regressed against aboveground biomass and an equation is developed to understand how plant biomass controls interception loss. Aboveground biomass partially controls total and net fluxes; therefore these constituent fluxes were regressed against total estimated aboveground biomass.

Results

A total of 52 gross rainfall events were recorded during the period of March, 1996–March, 1997. In all 52 rainfall events, the total recorded rainfall depth was 522.8 mm, with an average and standard deviation of 10.5 mm and 16.6 mm, respectively. Deep convection by mid-latitude disturbances and cyclone activity from the Gulf of Mexico promoted most rainfall in the region. The hurricanes "Dolly" and "Hernan" produced two major storms with electrical activity. Of all the rainfall events, 60% had a depth of less than 5 mm, 20% between 5 mm and 10 mm and 5% between 50 mm and 70 mm in depth. Seventy percent of rainfall events had antecedent periods of 1–5 days and 30% had 5–40 days. 63% of gross rainfall depth was recorded between June and October of 1996.

The species showed significant differences in throughfall percentages (throughfall depth/rainfall depth *100) with mean values of 94.0%^{A}, 81.3% ^{B}, 92.4% ^{A} and 86.7% ^{AB} for *A. rigidula, P. pallens, A. berlandieri* and *P. ebano,* respectively. Percentages with the same letter are statistically different ($p=0.0001$). That is, *P. pallens* had the smallest throughfall percentages. The significant differences could be associated with total aboveground biomass, since throughfall and total aboveground biomass, bt, fitted well with a negative linear relationship (i.e. throughfall (%)=101.24–3.38 bt; $r^2=0.71$; $P=0.0001$; $n=16$). That is, shrubs with large aboveground biomass had small throughfall values and vice versa. Biomass components (foliage, branches and boles) provide surfaces to wet and to evaporate intercepted rainfall. A positive linear relationship with high statistical significance (with all r^2 values above 90%) was found between gross rainfall and throughfall depth for all four plant species (Fig. 1).

Fluxes of chemical solutes

The chemical fluxes in gross rainfall showed the following trend: Ca>Na>K>Mg>Fe>Zn>Mn>Cu (Table 2). Therefore, Ca dominated the total flux contribution of the species (49%), followed by Na (37%) and K (12%), while Cu contributed a negligible total flux (0.03%). The ANOVA showed significant differences in total fluxes between chemical solutes ($P=0.0001$), unlike the plant species including the control ($P=0.11$). According to the mean comparisons of Tukey, the chemical solutes had a significan different contribution, following the pattern described below in total element flux (kg ha^{-1} $year^{-1}$): Ca (18.3^{A}), Na (9.2^{B}), K (6.0^{B}), Mg (1.4^{C}), Fe (0.09^{C}), Zn (0.04^{C}), Mn (0.03^{C}), and Cu (0.026^{C}). Although the ANOVA showed that the plant species contributed in a similar way to chemical flux; the contrast statistic showed that the *Acacias* (*A. rigidula* and *A. berlandieri*) had smaller total element fluxes than *Pithecellobiums* (*P. pallens* and *P. ebano*) ($p=0.017$). In general, the former species recorded smaller total aboveground biomass estimates. A regression equation (Total Deposition=2.7B+27.7; $r^2=0.59$; $p=0.0001$; $n=16$) indicated that total aboveground biomass (B) partially explains the total flux contribution of the

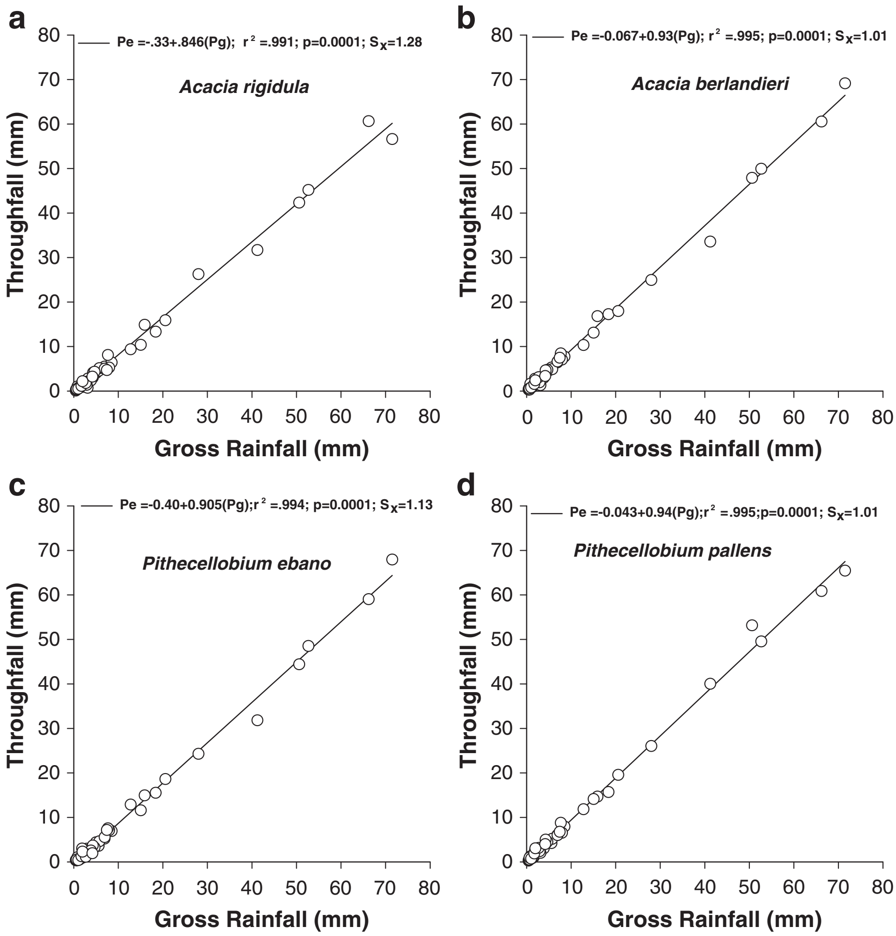

Fig. 1 The relationship between throughfall and gross rainfall for tour leguminous shrub species planted in northeastern Mexico

Table 2 The mean (confidence intervals, α=0.05) fluxes for several chemical solutes (kg ha^{-1} $year^{-1}$) in gross rainfall and throughfall for four species planted in northeastern Mexico

Element	Flux	Rainfall (Pg)	Throughfall (Pe)			
		Control	*A. rigidula*	*A. berlandieri*	*P. ebano*	*P. pallens*
Ca	Total	11.74±(2.53)	14.17±(4.71)	20.62±(6.98)	24.53±(8.54)	20.39±(6.097)
	Net		2.43±(0.52)	8.88±(3.56)	12.79±(7.6)	8.64±(6.3)
K	Total	2.83±(0.72)	7.09±(1.84)	6.80±(1.69)	7.57±(1.63)	5.72±(1.16)
	Net		4.26±(1.08)	3.97±(2.58)	4.74±(2.8)	2.89±(1.7)
Mg	Total	0.56±(0.18)	0.94±(0.46)	1.62±(1.56)	1.95±(0.73)	1.69±(0.78)
	Net		0.38±(0.12)	1.06±(0.87)	1.39±(3.8)	1.13±(1.5)
Na	Total	8.81±(3.01)	8.51±(4.76)	9.39±(5.59)	9.01±(4.07)	10.42±(4.45)
	Net		−0.30±(0.10)	0.58±(0.32)	0.20±(0.13)	1.61±(0.75)
Cu	Total	0.008±(0.0056)	0.026±(0.018)	0.037±(0.011)	0.031±(0.013)	0.026±(0.016)
	Net		0.02±(0.01)	0.03±(0.06)	0.02±(0.03)	0.02±(0.03)
Fe	Total	0.075±(0.055)	0.110±(0.31)	0.101±(0.29)	0.109±(0.30)	0.091±(0.034)
	Net		0.04±(0.02)	0.03±(0.10)	0.03±(0.13)	0.02±(0.06)
Mn	Total	0.025±(0.020)	0.031±(0.016)	0.040±(0.012)	0.038±(0.015)	0.033±(0.017)
	Net		0.01±(0.005)	0.02±(0.01)	0.01±(0.01)	0.01±(0.01)
Zn	Total	0.044±(0.013)	0.040±(0.085)	0.036±(0.098)	0.037±(0.077)	0.039±(0.012)
	Net		0.00±(0.001)	−0.01±(0.01)	−0.01±(0.02)	−0.01±(0.01)

species. That is, shrubs with the largest aboveground biomass produce the largest total constituent fluxes in throughfall, mainly stressing the effect of aerial biomass on dry deposition and canopy exchange.

In relation to the net element flux, the ANOVA showed significant differences between chemical solutes (p=0.0001) and the plant species (p=0.05). For chemical solutes, the following pattern emerged from the mean comparisons of Tukey: Cu (2.75^{A}), Mg (1.76^{B}), K (1.40^{BC}), Ca (0.70^{CD}), Mn (0.42^{D}), Fe (0.37^{D}), Na (0.06^{D}) and Zn (−0.14^{D}) (Table 2). That is, throughfall increased fluxes, in contrast to gross rainfall, on average, Cu (275%), Mg (176%), and K (140%). The remaining solutes although increased by more than 37% but less than 74%, they were not significant different. Negative net fluxes were recorded for Zn, which was reduced (14%) by the plant species compared to gross rainfall, however, this element was not significantly different to Na, Fe, Mn, and Ca, which presented positive net fluxes in throughfall. Total aboveground biomass also explained partially the net flux variability, with the following regression equation: Net Flux = 0.51B+5.4; r^2=0.18; p=0.0028; n=16.

For the plant species, the contrast statistic showed that *A. berlandieri* (p=0.026) and *P. ebano* (p=0.078) had the largest net constituent flux input into the soil compared to the rest of the semi arid species studied. The total average net flux contribution for all plant species for all solutes was 57% of the total flux measured in gross rainfall. At the plant species level, the contribution varied from 60% to 80% in *A. berlandieri* and *P. ebano*, respectively, and from 29% to 59% in *A. rigidula* and *P. pallens*, respectively, of the total flux recorded in gross rainfall.

Concentration of chemical solutes

Calcium was the dominant constituent concentration in both gross rainfall and throughfall. Ca concentration increased two to three orders of magnitude in throughfall compared to the concentration of gross rainfall for all seasons with the exception of the summer and fall (p=0.05) (Fig. 2). Between the plant species, there were no significant differences in Ca concentrations for all seasons. However, *P. ebano* recorded the highest concentrations and *P. pallens* recorded the lowest (Fig. 2).

Plant cover significantly modified Mg concentrations for all seasons compared to the concentration in gross rainfall (p=0.05) (Fig. 2). There were significant differences between the species only for the summer season. At this time, *P. ebano* recorded the largest Mg concentrations and *A. berlandieri* and *P. pallens* recorded the smallest (p=0.05).

The concentration of K was greater in throughfall than in rainfall for all seasons except the fall. Between the plant species, there were statistical differences only during the summer. Again, *P. ebano* recorded the largest K concentrations and *A. berlandieri* and *P. pallens* recorded the smallest. On an annual basis, *A. rigidula* and *A. berlandieri* contributed to the largest K fluxes. Sodium concentrations in Pe and Pg were statistically similar for all seasons; although *A. rigidula* recorded the highest and *A. berlandieri* recorded the lowest concentrations (Fig. 2). The concentrations of sodium were significantly different in Pe and Pg, but only for the summer. The species recorded similar concentrations of Na for all seasons.

The concentration of Cu was larger in Pe than in Pg for all seasons with the exception of fall. However, Cu concentrations were statistically similar for all of the studied plant species. Mn concentrations increased in Pe compared to the Mn concentration in Pg during the spring and summer (p=0.05). During the fall and winter, the Mn concentrations were similar in Pe and Pg (Fig. 3). The concentrations of Zn were statistically different in Pe and Pg only for the summer, although the species recorded similar concentrations for all seasons. Fe concentrations were larger only during the spring and summer, and only for the species *A. rigidula*, *P. ebano* and *A. berlandieri*, which was a contrast to the Fe concentrations in Pg (p=0.05).

Regression analysis

The positive effect of Pg depth was statistically observed for several chemical solutes for several plant species. A positive relationship was observed between the net flux of Ca, Cu, Fe, Na, and K (Kg ha^{-1} year^{-1}) and rainfall depth for some individual species. However, a negative relationship was observed between the net flux of Mn, Zn, and Mg and rainfall depth, but only for *A. rigidula*.

The relationships between the mean concentration for most solutes (K, Mg, Na, Fe, Mn, and Cu) and rainfall depth fitted well with the negative reciprocal—power functions with negative slopes (Table 3). These mathematical functions explain that the concentration

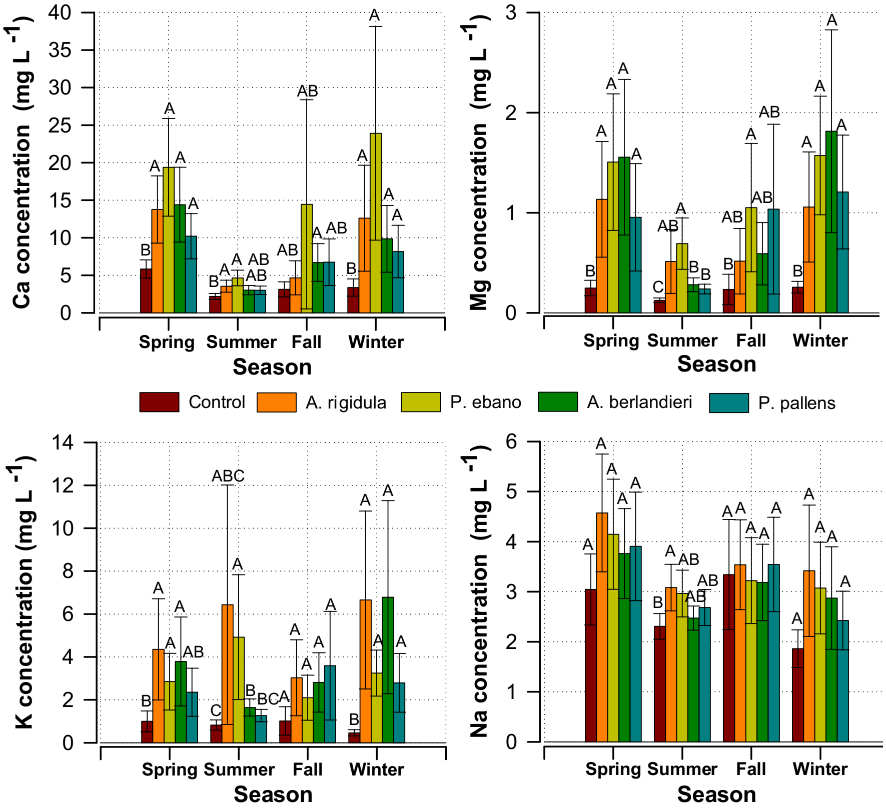

Fig. 2 Average seasonal concentrations and confidence intervals (α=0.05) of Ca, Mg, K and Na in gross rainfall and throughfall of four planted species of northeastern Mexico (means with different letter are statistically significant)

of most solutes decays quickly with small increments in rainfall depth indicating that rainfall depth washes most of the chemical solutes from the canopies with small rainfall depths. Further rainfall depth increments reduce constituent concentrations probably by dilution.

The relationship between the concentration (mg L^{-1}) of several chemical solutes and lag time between rainfall events was positive for Na, Fe, Zn, Mn, Cu, Ca, and K for several plant species and negative for Mn (*A. berlandieri, P. ebano and P. pallens*). In fact, the mean concentration of Ca, Mg and Na and lag time between rainfalls (days) fitted well with positive linear relationships (Table 3). That is, the solute concentration increases with the lag time between rainfalls.

Discussion

Total rainfall for the study period from March 1996 to March 1997 was 523 mm, and it is considered to be a dry year since mean annual rainfall depth for the region is 760 mm with a standard deviation of 260 mm (Návar et al. 1999). That is, assuming that the annual rainfall distributes normally, there is only an 18% probability of occurrence of a year with less than 523 mm of rainfall depth. Regardless of the small rainfall depth, similar observations on interception loss were reported at the individual species level (Návar and Bryan 1990; 1994) as well as at the plant community scale (Návar et al. 1999) for the Tamaulipan thornscrub, which included the plant species observed in this research. At the species level, differences were observed and partially associated with total aboveground biomass. Shrubs with large surface areas of foliage and branches serve to intercept and redistribute rainfall below the canopies. Schroth et al. (2001) also observed statistical differences in throughfall among semi-arid plant species in tree-based land use systems and spontaneous tree vegetation in Central Amazonia and Breman and Kessler (1995) did so in the semi-arid plants of agro-ecosystems in the Sahelian countries.

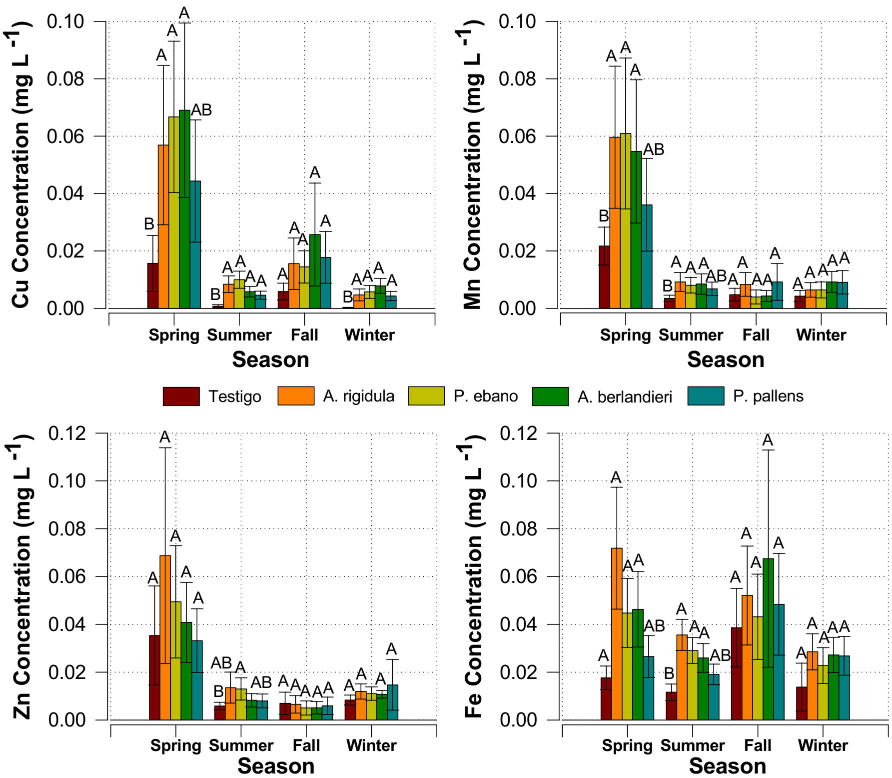

Fig. 3 The average seasonal concentrations and confidence intervals (α=0.05) of Cu, Mn, Fe and Zn in gross rainfall and throughfall of four planted species of northeastern Mexico (means with different letter are statistically significant)

The species from semi-arid region played an important role in chemically enriching throughfall, as this has also been found in other ecosystems (Borken et al. 2004; Rothe et al. 2002). Shrubs have foliage and branches exposed to wind that serve as traps for dust and natural particle emissions; the sticky exudates from some species may enhance their capacity to collect dust. Other sources of chemicals in

Table 3 The mathematical functions to predict the mean concentration (mg L^{-1}) of several solutes as a function of rainfall depth and lag time between rainfalls

Constituent concentration	Mathematical function	R^2	Probability $p = 1 - \int_{F=0}^{F=F} f(F)\partial F$
Ca	$\frac{1}{0.090\left(\frac{1}{RD}\right)^{-0.43}}$	0.34	0.0001
K	$\frac{1}{0.259\left(\frac{1}{RD}\right)^{-0.48}}$	0.29	0.0018
Mg	$\frac{1}{0.807\left(\frac{1}{RD}\right)^{-0.65}}$	0.44	0.0001
Na	$0.15 - 0.138 Ln \frac{1}{RD}$	0.54	0.0001
Fe	$\frac{1}{24.68\left(\frac{1}{RD}\right)^{-0.44}}$	0.27	0.0025
Cu	$\frac{1}{50.53\left(\frac{1}{RD}\right)^{-0.02}}$	0.31	0.0001
Zn	$\frac{1}{68.19\left(\frac{1}{RD}\right)^{-0.41}}$	0.16	0.021
Ca	$4.99 + 0.46LT$	0.25	0.0032
Mg	$0.53 + 0.035LT$	0.13	0.046
Na	$2.58 + 0.065LT$	0.16	0.039

Where: RD = Rainfall depth (mm); LT = Lag time (days), f(F) is the mathematical function for the F-Fisher probability density function throughfall include canopy exchange, which appeared to control throughfall input of solutes. Canopy leaching fluxes have also dominated solute input in contrast to dry deposition in other forest ecosystems (Devlaeminck et al. 2005; Zhang et al. 2006). Henceforth, the chemical interaction among rainfall, dry deposition, sticky exudations and canopy leaching is probably the main cause of throughfall enrichment with most solutes for most seasons.

In this study, coarse estimates indicate that canopy leaching contributed with 83% of the total net throughfall solute input. In places where canopy exchange dominates solute input, the enrichment of throughfall has been described by numerous processes. For example, increased Cu solutes in throughfall have been explained by the internal leaching of this element (Marschner 1986; Mengel and Kirkby 1982). Several investigators (Parker 1983; Poszwa et al. 2000; Santa Regina et al. 1997; Tukey 1970) suggest that the mobility of Ca, Mg, and K inside leaf tissue may explain the high concentrations measured in throughfall compared to gross precipitation. Indeed, foliar analysis indicated that the leaves of *P. ebano* had the highest Ca concentrations (Pérez 1997), stressing that the chemical interaction of rainfall with leaves could be another potential throughfall source, via the chemical exchange between plant tissue and gross rainfall. Pérez (1997) also observed high Mg concentrations in the leaves of *P. ebano*. Csikkel and Kiss (1997) concluded that the high Mg concentrations in the leaves of *Pinus sylvestris* were the result of the increased autophosphorylation of the Kinase protein. Calcium appears to be the dominant cation flux in throughfall in other ecosystems as well (Crockford et al. 1996; Knops et al. 1996), and it is specifically important in acidic and calcareous soils where a preferential translocation of Ca from roots to leaves occurs (Poszwa et al. 2000). On the other hand, Potter et al. (1991) suggested that the chemical reaction between anions may explain the increased concentrations of Ca below the canopies.

Dry deposition has been found to also be an important source of several solutes in other ecosystems (Ignatova 1995). Several investigators have proposed that dry fallout between storms dominates the chemical input in throughfall (Fenn and Bytnerowicz 1997; Fenn et al. 2000). Air concentrations are related (amongst other things) to dust emissions associated with traffic on unpaved roads or agricultural tillage, and natural particle emissions. Therefore surface area and form of the canopy are prime factors influencing throughfall chemistry that may explain the largest net flux contribution of *P. ebano* and *A. berlandieri*. In general, shrubs with the largest aboveground biomass components produced the largest total annual fluxes for all chemicals measured in this study.

Total and net fluxes are a function of total biomass. Therefore, statistical relationships were noted between chemical fluxes and total aboveground biomass. Wang and Klinka (1997) observed that K concentrations in leaves were statistically correlated in a positive manner with tree top height and diameter at breast height, partially explaining the importance of biomass interception of dry deposition and canopy leaching.

The relationships between solute concentration and rainfall depth and lag time between storms resulted in reciprocal and linear relationships, respectively. The former equations indicate that most chemical solutes are washed off the canopies with little rainfall depth and that eventually the concentration levels off. The steady state appears to be controlled by the chemical solute concentration in bulk rainfall and probably by the canopy leaching processes. The positive relationships between the chemical solute concentration and lag time between rainfall events explain the amount of intercepted emissions and probably exudates from plant tissue. This relationship has been explained in terms of the time canopies have to intercept dust from biomass components (Wedding et al. 1976). In this process, the exudation of several chemicals from leaves to intercept dust emissions and to chemically interact with rainfall must not be ruled out. Several researchers have proposed to use the statistical parameters of these relationships to explain the sources of net flux (Lovett and Lindberg 1984; Neary and Gizyn 1994; Puckett 1990). Lovett et al. (1996) and Schreiber et al. (1990) have suggested that in addition to rainfall depth and lag time between rains, H^+ concentrations in rainfall play an important role in increasing throughfall concentrations of most solutes.

Sources of chemicals in throughfall by dry deposition are explained by the air masses dominating the landscapes of northeastern Mexico. In the region of Linares, air masses called ‘huastecos’ and ‘nortes’ dominate during most of the year and sporadically during the winter-spring season, respectively. Warm, wet air masses, called 'huastecos' originating in the Atlantic Ocean and Gulf of Mexico and transported by easterlies, appear to explain the large K, Na, Cu, and Fe concentrations in gross rainfall and throughfall during the summer. This has also been reported in other ecosystems dominated by similar air masses by Brown and Lles (1991), Crockford et al. (1996) and Waring and Schlesinger (1985). Sodium e.g., is commonly dissolved in precipitation which falls along ocean coasts, (Linares is just 300 km away from the coast of the northern Gulf of Mexico) or chemicals may adhere to dust particles which become temporarily suspended in the atmosphere and return to the soil as dry fallout between storms.

The 'nortes' may also explain the high concentration of most cations in gross rainfall and throughfall which were recorded during the spring and winter seasons. At this time, the concentrations of most solutes are high due to a combination of rainfall with small depths and the amount of dry deposition. It is likely that rainfall depth is limiting when considered to wash most dry deposition from branches and stems. This is noted mainly in the concentrations of Cu, Mn and Zn during spring. During winter and spring, the cold, high-pressure air masses coming from the north may bring dust from the Metropolitan Area of Monterrey and farther places up north since Domingos et al. (1995) observed that several solutes were more abundant in areas of high air contamination. Specifically, the solutes Ca (spring and winter), Mg (spring and winter), K (winter), Na (spring), Cu (spring), Mn (spring), and Zn (spring) increased concentrations in rainfall and throughfall in contrast to the rest of the seasons.

The semi arid, sub tropical soils are generally deficient of microelements such as Zn, Mn, Fe, Cu, and Mo (Vlek 1985). The addition of micronutrients as fertilizers increases crop productivity in arid and semi arid soils (Rashid and Ryan 2004). In the northeast of Mexico, shifting cultivation is a common land use with duration between rotations of 10–20 years. Loss of fertility is the main cause of land abandonment and peasants call this practice 'to let the land rest for a while'. Shrubs studied in this research are pioneer plant species that colonize first abandoned lands and their contribution to increase micronutrients in throughfall in contrast to rainfall was noted by the net flux equation. The net flux of Cu, Fe, and Mn was from one to close to three orders of magnitude in throughfall in contrast to the net flux in gross rainfall. After plant establishes, soil nutrient recovers and the land is cleared again for crop production. Therefore, this research stresses the importance of native plant cover to increase micronutrient input, via throughfall, and mainly through canopy leaching processes, which is the largest flux in contrast to dry deposition.

Conclusions

Rainfall is an important source of chemical solute input (Ca, Na, Mg, K, Mn, Fe, Zn, and Cu), contributing with a total flux of 24.11 Kg ha^{-1} y^{-1}. However, the canopies of plant species also contributed with an average net flux of 13.72 Kg ha^{-1} y^{-1}. Chemicals and specific differences in throughfall chemistry stressed the differential contributions of air masses on the total and net fluxes of plant species. Although Ca, Na and K dominated total flux, the net flux was controlled by Cu, Mg, and K. *P. ebano* recorded the highest and *A. rigidula* the smallest total and net fluxes. Total aboveground biomass partially explained the total and net fluxes stressing the effect of interception of dust and natural particle emissions and the intensity of canopy exchange processes. Rainfall depth and lag time between rainfall events explained part of the additional variation, stressing the importance of local and external sources of chemical solutes in throughfall of these semi-arid, subtropical species.

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