Net below canopy fluxes in Canarian laurel forest canopies

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Abstract

Bulk precipitation, stemflow and throughfall were collected in a Canarian laurel forest (North Tenerife), and chemically analysed to determine the net below canopy fluxes. Annual negative fluxes were found for H^+ , NO_3^- , SO_4^- and Cl^- and annual positive fluxes for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , HCO_3^- , PO_4^{3-} and DOC. Negative fluxes for most of these ions have been reported previously but this is the first time that they have all been measured at the same time in one forest.

The relative importance of atmospheric deposition and canopy leaching to net below canopy fluxes was evaluated using two approaches previously employed in this type of study. The first approach consisted of calculating total inputs, taking inputs as bulk precipitation or bulk precipitation plus the additional input from scavenging dry deposition by vegetation surfaces, corrected by the maximum and minimum leaching rate. The values obtained for inputs were very similar, possibly due to the minimum effect on scavenging particles by the canopy. In the second approach, linear regressions were developed for net below canopy fluxes and the variables related to dry deposition (antecedent dry period) and leaching (event quantity and duration, etc.); this showed that NO_3^- in net below canopy fluxes came from dry deposition, the rest of the elements from leaching, and SO_4^{2-} from both. Similar results were obtained using both approaches.

It was found that a simple linear regression model with event quantity as the independent variable can readily substitute the Lovett and Lindberg (1984) [J. Appl. Ecol. 21 (1984) 1013] model. The latter model was applied for separate internal and external sources in the case of SO_4^{2-} .

This forest differed greatly from other, previously studied forests. Large amounts of water were required for a positive flux (leaching), suggesting that the negative net below canopy fluxes of some elements were due to the low water regimes during the study year. Possible causes of this were the high value of the canopy saturation and the pattern of scattered rainfall, which led to extreme values of interception losses. The point at which the line representing the relationship between net below canopy fluxes and event quantity intersected the x axis varied depending on the leachable properties of the canopy ions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Canopy; Dry deposition; Nutrient balances; Net below canopy fluxes; Leaching

1. Introduction

One of the most interesting world wide ecosystems is the macaronesian laurel forest, an evergreen forest relict of the Tertiary Mediterranean flora which occupied southern Europe and northern Africa about

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20 million years ago and which today exists in the Canary Islands (Santos, 1990). However, until now no information on the nutrient balance of this forest has been reported in the literature.

There is general agreement that bulk precipitation chemistry can be altered considerably after passing through the forest canopy to the ground. The factors which control the hydrochemical balances in forest canopies are well known, although the relative importance of these factors are not clear. The results for nutrient balances depend on the forest type, and may reflect different patterns of behaviour in nutrients in different ecosystems.

There are marked differences in the hydrological functioning of laurel forests and other forest types (Aboal, 1998; Aboal et al., 1999a,b), attributable to both canopy (high canopy storage capacity) and climatic characteristics of the western Canary Islands (low mean evaporation rate during post-saturation rainfall and scattered rainfall events). This leads us to believe that the nutrient dynamics associated with these exceptional hydrological balances may also be inherently different in other biomes.

The main hydrochemical processes which differ among canopy forests are: (i) The capacity of canopy surfaces for scavenging atmospheric deposition (White and Turner, 1970; Eaton et al., 1973; Art et al., 1974; Bache, 1977; Lovett, 1987, 1994; Kazda and Glatzel, 1986)—they are more efficient as input collectors than as bulk precipitation collectors (such an increase in the bulk precipitation has a significant effect on some ecosystems); (ii) The leaching (of mineral elements from plant tissues, exudes and decomposition products) and ionic exchange reactions in the canopy (Lovett and Lindberg, 1984; MacDonald et al., 1993; Kozłowski and Pallardy, 1997); (iii) The capacity of the canopy to incorporate elements from bulk precipitation (Ulrich, 1983); and (iv) The capacity of the canopy to intercept elements from the bulk precipitation that will be washed by the rain.

Interpretation of the relative contributions of these different processes to the composition of net below canopy fluxes is still a matter of scientific debate (Ignatova, 1995). However, analysis of net below canopy fluxes provides a first approximation of the chemical transfer through different sectors of the vegetation, showing the ion input from dry deposition

and internal crown leaching and ion loss through absorption by the canopy.

The objectives of this study were to:

- Determine the changes that occur in the chemical composition of bulk precipitation while passing through the forest canopy, and the associated elemental fluxes.
- Determine forest inputs corrected by the differential factor of dry deposition wash off between canopies and standard bulk precipitation collectors.
- Determine the internal or external ion sources of net below canopy fluxes using different methods by evaluating factors such as antecedent dry period (ADP), event quantity, mean rainfall intensity, event duration and interception evaporation, for predicting net below canopy fluxes.

2. Materials and methods

2.1. Study site and species

The experimental plot was located in the Tenerife Agua García Mountains, in a protected area called 'Las Lagunetas' (UTM : $X = 362\,464$; $Y = 3\,148\,692$) at an altitude of 820–830 m and a slope of 8° to 12°, facing NNE. Soil in the plot, classified as Andisol, came from a bedrock that is a mixture of olivine basalt and volcanic ash. The plot was 3.3 km from the coast.

Trees with a stem diameter (DBH) greater than 0.06 m were found at a density of 1693 trees ha⁻¹. The six tree species (ranked in decreasing order of total basal area) were *Myrica faya* Ait., *Laurus azorica* (Seub.) Franco, *Persea indica* (L.) Spreng, *Erica arborea* L., *Ilex perado* ssp. *plathyphylla* Webb and Amarra, and *Ilex canariensis* Poivet (For further details see Morales et al., 1996a,b). Leaf area index (LAI) was 7.8 m² m⁻² (Morales et al., 1996a).

2.2. Field site: environmental conditions

The climate is humid Mediterranean with an annual mean temperature of 14.0 °C, an absolute maximum of 39.0 °C and an absolute minimum of 0.2 °C. Annual mean relative humidity is 80%, mean

annual precipitation 733 mm, mean annual number of rainy days 94, and absolute maximum daily rainfall 121 mm. During the study period (27th December 1994–31st December 1995), total precipitation was 626 mm, absolute maximum daily rainfall 31 mm, and absolute maximum weekly rainfall 131 mm. There were 29 weeks with less than 5 mm of rain.

Throughfall was 323.4 mm and stemflow was 42.9 mm (Aboal et al., 1999a); subtracting both from the gross precipitation gave an interception which was 259.7 mm or 41.48% of the incident rainfall (Aboal et al., 1999b).

2.3. Field instrumentation and sample collection

An automatic rain gauge (model Skye, Int. Llandrindod, UK), and a standard rain gauge were fixed 2 m above the top of the canopy, on a 17 m high wooden tower. Meteorological data were recorded as 30 min totals with a data logger (Delta-T Devices Ltd., Cambridge, UK).

During the period from 27th December 1994 to 31st December 1995, two gauges (17 cm diameter funnels, a 5 l polyethylene collection bottles) for collecting bulk precipitation were placed on the top of the tower. The wind did not introduce significant error in rainfall data (Aboal et al., 1999a). A composite sample was made by combining samples from the two gauges. Filters of fine mesh plastic gauze were placed on the funnels in order to prevent contamination by plant debris or insects and were removed weekly for washing. Algae growth was never observed. The gauges were cleaned with double-distilled and deionised water after each sampling period. We collected bulk precipitation because atmospheric deposition is frequently measured in biogeochemical studies as the material collected by a continuous open funnel or bucket (a 'bulk' deposition collector). Bulk collections are used because of the simplicity and economy of the method (Lovett, 1994). Unfortunately, other sources of error exist; during dry periods bulk samplers collect aerosols and particles as well as other anomalous material, including some material of local origin not considered to be ecosystem input, such as bird droppings, pollen, insects, local dust on the funnel that washed into the sampling bottle with the next rain (Matzner and Meiwes, 1994; Lovett, 1994). Nevertheless, inputs to the forest are usually

underestimated by standard open field polyethylene collectors, because of the effect of canopy surfaces in scavenging atmospheric particles. As a result, bulk collectors tend to overestimate wet deposition and underestimate total deposition in many areas (Lovett, 1994).

To measure throughfall, 40 gauges were randomly placed at fixed positions and samples combined proportionally to make a composite sample. The throughfall collectors were identical to those used for bulk precipitation, as were maintenance and sampling procedures. The collecting surfaces were at a height of 1 m to avoid splash contamination. To measure stemflow, we selected 30 trunks (five of each species in the plot), according to Aboal et al. (1999a). Stemflow was then measured by the standard method of rubber collars around trunks, with polypropylene tubes to transfer the collected water to 36 l polyethylene storage bags. Bulk precipitation, throughfall and stemflow were measured at weekly intervals, except after high-intensity rainfall events, after which they were measured immediately (two or three times a week). For analyses that required single events (assigning values to antecedent period and rainfall amount) we used the following procedure, considering three types of periods. Firstly, periods when there had only been one day of rain were not problematical, because the measured throughfall and stemflow for that period corresponded to that day of rain. Secondly, for periods in which two or more rainfall events had occurred, each separated by less than 3 h, throughfall and stemflow on each day/days of rain were taken to be the corresponding totals. Thirdly, periods (usually weeks) when rainfall events separated by more than 3 h had occurred, were excluded from the analysis. Nevertheless, periods of the third type were used in the estimation of total amounts of precipitation. All samples were transported to the laboratory, stored at -10°C , and analysed the following week.

2.4. Chemical analysis

For analysis, the volume of sample required was 250 ml. Water chemical analyses were carried out following the methods of the American Public Health Association (1992), after filtration. Subsamples of 200 ml were filtered through $0.45\text{ }\mu\text{m}$ filters (Millipore). Unfiltered subsamples (50 ml) were used to

Table 1
Annual hydrological fluxes (mm) and annual chemical fluxes ($\text{kg ha}^{-1} \text{ yr}^{-1}$) in bulk precipitation (1), throughfall (2) stemflow (3), below canopy fluxes ($\text{BCF} = 2 + 3$) and net below canopy fluxes ($\text{NBCF} = (2) + (3) - (1)$)

	Prec. (mm)	H^+	Ca^{+2}	Mg^{+2}	Na^+	K^+	CO_3H^- ($\text{kg ha}^{-1} \text{ yr}^{-1}$)	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	DOC
(1) Bulk precipitation	625.2	7.5×10^{-3}	7.5	5.6	51.0	7.2	91.7	94.7	26.7	9.6	4.4	75.6
(2) Throughfall	323.6	1.8×10^{-3}	8.8	6.8	47.6	39.4	107.0	84.0	21.8	5.8	4.9	183.4
(3) Stemflow	42.9	3.6×10^{-3}	0.9	0.6	4.4	4.2	8.9	9.0	3.0	0.7	0.3	18.2
$\text{BCF} (2) + (3)$		5.5×10^{-3}	9.7	7.3	51.9	43.6	115.9	93.1	24.9	6.5	5.2	201.5
$\text{NBCF} (2) + (3) - (1)$		-2.0×10^{-3}	2.2	1.8	0.9	36.4	24.3	-1.7	-1.8	-3.1	0.8	125.9
Estimated leaching rate % (Min.)			38.0	34.0	0.0	83.0		2.0	22.0			
Estimated leaching rate % (Max.)			47.0	52.0	12.0	90.0		12.0	38.0			
(4) Add. inputs collec. by canopy (Min.)			1.2	0.8	0.8	3.6						
(5) Add. inputs collec. by canopy (Max.)			1.4	1.2	0.9	6.2						
(6) Total inputs (TI) = (4) + (1) (Min.)			8.7	6.4	51.8	10.8						
(7) Total inputs (TI) = (5) + (1) (Max.)			8.9	6.7	51.9	13.4						

Minimum and maximum leaching rates (Domingo et al., 1994), except for CO_3H^- , NO_3^- and PO_4^{3-} , for which no leaching rate data was available. Additional inputs collected by the canopy, (minimum and maximum, (4) and (5)), and total input (minimum and maximum, (6) and (7)).

determine dissolved organic carbon (DOC). The pH was determined using a pH-meter (Crison digit 501), with a combined selective electrode (Ingold-V5402). Electric conductivity was determined with continuous shaking and temperature correction, using a conductivity-meter (WTW LF 537), with an electrode (WTW Tetralon 36). Cations were determined as follows: Na and K by Flame Emission Photometry (Perkin Elmer AA Spectrometer 3100); Ca, Mg, Al, Si and Fe by Atomic Absorption Spectrophotometry (Perkin Elmer AA Spectrometer 3100). Anions were determined as follows: alkalinity (TA and TAC) by automatic titration with HCl (auto-analyser Mettler DL25 Titrator); NO_3^- by colorimetry by the Brucine method; SO_4^{2-} by the turbidimetric method; Cl by potentiometric titration with silver nitrate solution and combined silver–silver chlorate electrode (DM-141) (automatic analyser Mettler DL25 Titrator) and PO_4^{3-} by direct colorimetry by the ascorbic acid method. Finally, DOC was determined by oxidation with permanganate by the method of Barlett and Ross (1988).

2.5. Data analysis

Net below canopy fluxes were calculated for each chemical species as follows: $\text{NBCF} = \text{BCF} - \text{BPF}$, where NBCF is the net below canopy flux; BPF is the bulk precipitation flux; and BCF is the below canopy flux, throughfall plus stemflow.

To estimate the percentage of material leached from the vegetation in throughfall (leaching fraction) leaching coefficients were used. Ranges of leaching percentages previously reported for an ecosystems (Domingo et al., 1994; Ferm and Hultberg 1995a), and which included many different types of forests, were as follows: for sodium (0–12%), potassium (83–90%), calcium (38–47%), magnesium (34–54%), sulphate (22–38%) and chloride (2–12%). The leaching percentages depend on many factors such as plant species, the environmental characteristics of the systems studied and the method of measurements employed (Domingo et al., 1994). The maximum and minimum value of canopy internal leaching were then determined for each ion. By subtracting the leaching value (obtained multiplying the leaching percentages by the net below canopy fluxes) from the net below canopy fluxes, dry deposits collected by the canopy

were determined. Finally, the total input to the ecosystem was calculated as the bulk precipitation input plus dry deposits collected by the canopy (Domingo et al., 1994).

To analyse the quantitative relationships among factors that control the canopy modification processes we used a regression technique to distinguish between external (dry deposition) and internal (canopy leaching) sources of each element independently in the net below canopy fluxes (Lovett and Lindberg, 1984).

3. Results

3.1. Net below canopy fluxes

Net below canopy fluxes contained a smaller amount of the major ions (except K^+) than bulk precipitation, Table 1. During the hydrological year studied, DOC accounted for 67.8% of the total net below canopy fluxes, followed to a lesser extent by K^+ (19.6%), HCO_3^- (13.1%), and Ca^{2+} , Mg^{2+} , Na^+ and PO_4^{3-} (all about 1%).

Some ions showed negative net below canopy fluxes. The H^+ net below canopy fluxes were negative for the year studied, but both uptake and release occurred; release only occurred when rainfall pH was high, ranging between pH 6.04–7.98. We also found negative NBCF for NO_3^- , SO_4^{2-} and the Cl^- . The net below canopy fluxes for the remainder of the ions analysed were positive.

Ion balances for bulk precipitation and throughfall were calculated ($Bi = (S^- - S^+)/ (S^- + S^+)$; where S^- and S^+ are, respectively, the sum of the anions and cations) with values of 0.25 and 0.07, respectively, and with mean values of EC ($\mu S/cm$) of 68.5 and 210.0. Ion balances for stemflow were calculated for each species with the following results: -0.01 *E. arborea*, 0.10 *I. canariensis*, 0.04 *I. perado*, 0.14 *L. azorica*, 0.03 *M. faya* and 0.16 *P. indica*; the mean values of EC ($\mu S/cm$) were 261.5, 193.5, 297.5, 187.5, 313.5 and 146.5. In accordance with Custodio and Llamas (1976) the lower the values of EC, the greater the error (e.g. bulk precipitation error of 25%, $68.5 \mu S/cm$) and the greater the value of EC the smaller the error (e.g. *M. faya* error of 3%, $313.5 \mu S/cm$), although all the values of Bi considered as errors would be within the permitted limits (Custodio and

Llamas, 1976). All values (except stemflow of *E. arborea*) showed an imbalance of charges in favour of anions, which can be attributed to: (i) non inclusion of ammonium ion, (ii) overestimation of bicarbonate, considering the level of DOC and alkaline particles in the bulk precipitation, throughfall and stemflow. Nevertheless we confirm that anions were taken up by the canopy while water passed through it.

3.2. Estimated total inputs and sea salt input

Different total inputs can be calculated by considering the inputs as the bulk precipitation alone, or bulk precipitation plus the effect of the canopies scavenging dry particles. The usual approach, not corrected, is based on bulk precipitation measurement. An additional method was applied (Domingo et al., 1994) correcting the total inputs by the additional inputs (dry deposits collected by the canopy). Additional inputs were only calculated when the net nutrient flux was positive. Results of all total inputs (bulk precipitation, Max. and Min.) were similar for all of the elements (Table 1).

Knowing the concentration of Na and the amount of rainfall, the sea salt deposition values were calculated in the conventional manner ($kg\ ha^{-1}$) from: $D = [(Na) \times R] / 10 \times (100/30.5)$; where $[Na]$ is the seasonal weighted mean concentration of sodium ($mg\ ml^{-1}$), R the seasonal cumulative rainfall (cm) and 30.5, the percentage of sodium in sea salt. The sea salt deposition value obtained was $167.0\ kg\ ha^{-1}\ year^{-1}$ of sea salt. An excess of Na^+ can be calculated using Cl^- as the sea salt tracer element; this calculation requires the selection of a conservative component, for which Cl^- is suitable since it shows little fractionation (Dewalle and Swistock, 1994). The equivalent ratio of Na^+/Cl^- in sea water is multiplied by the Cl^- concentration in the sampled bulk precipitation, and then subtracted from the concentration of Na^+ in the sampled bulk precipitation (Dewalle and Swistock, 1994; Appelo et al., 1993). Using Cl^- as tracer the excess of Na^+ (mequ) was -0.036 , this sodium deficit value is consistent with the ratio of these ions in sea salt, as expected from a previous report that Na^+/Cl^- ratios remain similar to sea water in coastal areas of different sites of the world (Appelo et al., 1993).

Fig. 1. Single regressions ($n = 25$) for net below canopy fluxes ($kg\ ha^{-1}$) against event quantity (EQ) (mm), with the regression coefficients for each of the studied ions.

3.3. Regressions

We attempted to separate the external and internal contributions, of each element independently, to the net below canopy fluxes, using the method proposed by Lovett and Lindberg (1984). This method consists of a regression model that treats canopy exchange as a statistically explainable phenomenon, estimating total dry deposition—including both gases and particles—and canopy leaching on net below canopy fluxes. Following the method of Capellato and Peters (1995), before assessing with a multiple regression model (Lovett and Lindberg, 1984), a simple regression was performed to examine whether individual indepen-

dent variables could account for the variability in net below canopy fluxes and whether the variables used in this model ADP and event quantity, were the best subset of those tested (Figs. 1 and 2).

ADP, event quantity, and other variables such as event duration, mean rainfall intensity, and interception evaporation were also examined (Table 2). Interpretations of results are based on the relative importance of canopy leaching and dry deposition to net below canopy fluxes. The best fit linear relationship was chosen based on the r^2 values, showing the absence of an irregular removal of dry deposition from canopy surfaces or a non-linear internal leaching.

Fig. 2. Single regressions ($n = 25$) for net below canopy fluxes (kg ha^{-1}) against ADP (days), with the regression coefficients for each of the studied ions.

The dry deposition accumulated prior to a storm and washed off by a subsequent rainfall event (Lovett and Lindberg, 1984) was assumed to be proportional to the ADP. The ADP was only significant for N-NO₃ and S-SO₄. Because canopy leaching occurs primarily by exchange and diffusion of constituents from a leaf (Lovett and Lindberg, 1984), and is lost from the free space or apoplast due to rainfall (Lovett and Lindberg, 1984; Kozłowski and Pallardy, 1997), variables related to the hydrological fluxes (event quantity, event duration, mean rainfall intensity and interception evaporation) were assumed to be proportional to canopy leaching (Lovett and Lindberg, 1984; Veneklass, 1990; Capellato and Peters, 1995).

We found a clear positive correlation between net below canopy flux and event quantity, for most ions, with the exception of H⁺, PO₄³⁻ and NO₃⁻. We obtained poor significant correlations of net below canopy fluxes with the mean rainfall intensity for Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻ and DOC and the correlation coefficient values were always less than that obtained for event quantity. Results of the correlation between interception evaporation and net below canopy fluxes were similar to those obtained between event quantity and net below canopy fluxes. For all ions for which there was a correlation between event quantity and net below canopy fluxes, no correlation was found between event duration and

Table 2
Statistics of simple regression for net below canopy fluxes NBCF ($\text{kg ha}^{-1} \text{yr}^{-1}$) against different variables: ADP (days), event quantity (EQ) (mm), interception evaporation (I) (mm), event duration (ED) (in h), and mean rainfall intensity (MRI) (mm h^{-1})

Variable	Element	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3H^-	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	DOC
ADP	Significance	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	*	**	n.s.	n.s.
	R	-0.039	-0.335	-0.382	-0.346	0.021	-0.053	-0.383	-0.450	-0.515	0.262	-0.353
EQ	Significance	n.s.	***	**	**	***	***	***	**	n.s.	n.s.	***
	R	-0.198	0.816	0.610	0.512	0.781	0.701	0.617	0.614	0.031	0.215	0.776
	a	-	0.016	0.007	0.043	0.059	0.149	0.095	0.003	-	-	0.265
	b	-	-0.358	-0.107	-1.181	-0.015	-3.412	-2.77	-0.121	-	-	-1.820
I	Significance	n.s.	***	**	*	***	***	**	**	n.s.	n.s.	***
	R	-0.182	0.782	0.558	0.459	0.780	0.688	0.561	0.574	-0.031	0.251	0.697
ED	Significance	***	n.s.	n.s.	n.s.	*	n.s.	n.s.	n.s.	n.s.	*	n.s.
	R	0.655	0.120	-0.360	-0.280	0.538	-0.161	-0.050	-0.064	-0.306	-0.443	0.237
MRI	Significance	n.s.	*	**	*	*	n.s.	*	n.s.	n.s.	n.s.	**
	R	0.171	0.405	0.561	0.500	0.437	0.054	0.417	0.355	0.313	0.198	0.555

Regression coefficients a and b . Significance of the regression coefficients: *** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$ and n.s. not significant.

net below canopy fluxes, except for K^+ . P-PO_4 and H^+ , which had no correlation with other tested variables, had correlation with event duration and net below canopy fluxes.

Results from a stepwise multiple regression analysis using net below canopy fluxes (kg ha^{-1}), and five independent variables namely: ADP, event quantity, mean rainfall intensity, interception evaporation and event duration, indicate that ADP and event quantity were the best two-variable predictors for SO_4^{2-} . Only the results for SO_4^{2-} support the use of Lovett and Lindberg's (1984) multiple regression, as follows: $\text{NBCF} = a\text{EQ} + b\text{ADP} + c$ where NBCF is net below canopy fluxes, EQ is event quantity (mm) in a period of time (weeks in our case) and an ADP, antecedent dry period (days in our case). We obtained the following relationship: $\text{NBCF}(\text{SO}_4^{2-}) = 2.57 \times 10^{-2}\text{EQ} - 3.14 \times 10^{-2}\text{ADP} - 6.47 \times 10^{-1}$, regression coefficients significant at $a P \leq 0.01$ and $b P \leq 0.05$; the adjusted correlation coefficient for the regression was $r^2 = 0.58$. Regression coefficient a represents the crown leaching rate (kilograms per hectare per millimetre of precipitation) and b represents the dry deposition rate (kilograms per hectare per millimetre). Because of the difficulty in interpreting results obtained by this method (Lovett and Lindberg, 1984) it was only used for qualitative (and not quantitative) assessment of those elements which have more importance in dry deposition.

4. Discussion

The net below canopy fluxes were lower than those found in other forests (Aboal, 1998). This indicates that both scavenging dry deposition and canopy leaching were small and had minimal effects in the forest studied. Such a large number of constituents with negative fluxes has not previously been reported. There have been previous reports of negative net below canopy fluxes in an annual cycle for NO_3^- (Steinhardt, 1979; Lindberg et al., 1986; Foster and Nicholson, 1988; Shephard et al., 1989; Veneklass, 1990; Neary and Gizyn, 1994; Shibata and Sakuma, 1996), for H^+ (MacDonald et al., 1993; Matzner and Meiwes, 1994; Neary and Gizyn, 1994; Capellato and Peters, 1995; Shibata and Sakuma, 1996), and for Cl^-

(Shibata et al., 1995). There are also previous reports of negative values for SO_4^{2-} (Capellato and Peters, 1995; Johnson and Lindberg, 1991). Interpretation of these negative fluxes varies among different authors. These ions can be retained by the canopy surfaces, and possibly washed off by a subsequent strong precipitation event (Neary and Gizyn, 1994) or absorbed by leaves, twigs (Kozłowski and Pallardy, 1997) and stems (Katz et al., 1989; Mitterhuber et al., 1989; Cape, 1993).

The remaining elements had positive fluxes. Special attention must be paid to Na^+ , an element considered to be inert with respect to the canopy (Ferm and Hultberg, 1995a,b), and since the net below canopy fluxes for Na^+ were very low, this confirms the minimum effect of canopy scavenging dry particles.

The net below canopy fluxes values of K^+ and HCO_3^- were high (the latter probably because the analytical method, for HCO_3^- includes organic compounds, borate, phosphate, silica and other basic compounds). The negative net below canopy fluxes for H^+ was possibly due to the ability of the forest cover to neutralise acidic inputs, through surface cation exchange (Reiners and Olson, 1984; Lovett et al., 1989), the latter which explains cation leaching and positive net below canopy fluxes. Surface ionic exchange occurs especially with monovalent cations, such as K^+ as in the present study, which is readily leached and is the most mobile element in the canopy. The divalent cations (e.g. Ca^{2+} , Mg^{2+}) (Cape, 1993), are more strongly bound (Kozłowski and Pallardy, 1997). The sign of the H^+ fluxes will thus depend on the pH value, as demonstrated by our results.

The low net below canopy fluxes (except for K^+) were responsible for the small number of differences among total inputs corrected by the additional inputs (calculated on the leaching factor basis), which again could be interpreted as the reduced effect of canopy surfaces on scavenging atmospheric deposition.

Results of the regressions showed a positive correlation between net below canopy fluxes and ADP for NO_3^- and for SO_4^{2-} , similar findings have previously been reported for the latter ion (Eaton et al., 1978; Lovett and Lindberg, 1984; Lindberg and Lovett, 1992). Both are usually primary constituents of dry deposition. This leads to believe that the effect of dry deposition on net below canopy fluxes for these

substances is due to the differential effect of forest canopy scavenging processes. The lack of significant results for the ADP again confirms the reduced effect of canopy surfaces in scavenging atmospheric deposition of these chemicals in this forest ecosystem.

Clear positive correlations between net below canopy fluxes of most elements and the hydrological variables suggest that the leaching process is dominant in most cases. event quantity was a statistically significant predictor, implying higher leaching amounts in periods with abundant precipitation (Table 2). However, a resultant spurious correlation is possible because the regression of event quantity with the net below canopy fluxes was carried out on the basis of the same event quantity (which is used to calculate net below canopy fluxes). Furthermore, these correlations depend on there being precipitation events of more than 100 mm; without these, even though the slope and the intersection with the x -axis are similar, statistical significance is lost. It therefore appears that these large events favour the leaching process, confirming the conjecture that there is higher leaching in periods of abundant precipitation. Other ions showed no significant relationships (H^+ , PO_4^{3-} and NO_3^-), a finding also described by Neary and Gizyn (1994). The probable reason for the close agreement between the correlations of net below canopy fluxes vs event quantity and net below canopy fluxes vs Interception, was the typical direct relation occurring between both variables: interception and event quantity. The influence of mean rainfall intensity on net below canopy fluxes has also been described previously (Potter et al., 1991; Lovett and Schaefer, 1992; Crockford et al., 1996). Assuming that event duration is also related to canopy leaching, the behaviour of P-PO_4 and H^+ net below canopy fluxes (take up or release through the canopy) can also be explained on this basis.

Absence of a significant correlation of between the ADP and the net below canopy flux hydrological variables may be due to different factors: (i) canopy absorption which confuses these relationships (Crockford, 1996); (ii) canopy structure; (iii) the effect of pools of water forming on the leaves; or (iv) the variation in composition and amount of atmospheric deposition.

Both the leaching rates and the effect of canopy surfaces in scavenging atmospheric deposition are

dependent on the vegetation type and density, and increase with canopy surface area and with the degree of forest development (Striegel et al., 1994; Crockford et al., 1996; Schaeffler and Jacobson, 1996). In the present study, the forest was characterised by a very homogeneous tree height, high LAI value, no gaps, by the leaves being big and positioned almost parallel to the floor. This means that a small canopy surface area (similar to a bulk precipitation collector), can influence the reduction effect of canopy surfaces in scavenging atmospheric deposition. The capacity of nutrient losses by foliar leaching also varies among species. Leaves with a thick waxy surface are wetted and leached with difficulty (Kozłowski and Pallardy, 1997). The laurel forest tree leaves have highly developed thick cuticles, a factor that explains the small net below canopy fluxes found in the present study. There were also relatively small nutrient losses by leaching from healthy leaves, similar to those of other forests studied (Kozłowski and Pallardy, 1997).

The effect of forming pools, with retention of some elements, creates a time lapse between the arrival of the dry or wet deposition and the entry as net below canopy fluxes. These pools can only be removed only during heavy storms, therefore a critical amount of water is required to remove dry deposition completely (Neary and Gizyn, 1994). The ADP not only provides for the deposition of dry particles and gas, but also for the replenishment of the canopy nutrient pool (Lovett and Schaefer, 1992; Capellato and Peters, 1995). Thus, the net ion flux depends on the amount of material left on the canopy from a previous event relative to the amount remaining on the canopy after an event (Neary and Gizyn, 1994).

An interesting implication of the linear relationships between event quantity and net below canopy fluxes was the regression line intercepts. In contrast with those of other canopies, where line intercepts did not differ significantly from zero (Veneklass, 1990; Capellato and Peters, 1995), all the ions in the Canarian laurel forest differed significantly from zero. This may be explained by the retention of some elements, such as Ca^{2+} or Na^+ not largely involved in the plant biomass, suggesting some mineral immobilisation by precipitation in temporary pools, which would be removed only during heavy storms (Domingo et al., 1994). These elements (and others) required large volumes of water for their

removal (e.g. Ca^{2+} and Na^+ required 22.2 and 27.5 mm, respectively, to be leached ($y = 0$) (Table 2)). If we consider Na^+ as an inert ion with respect to the canopy, this can only be explained by the formation of these pools. However, it may also be due to evaporation process, where some water inevitably remains on the canopy after the event, and as it evaporates leaves the associated ions (Neary and Gizyn, 1994). The high value of the canopy saturation (S) 2.45 mm (Aboal et al., 1999b), the scattered rainfall pattern and the extreme value of the interception losses (41.5%) of this forest may magnify the latter factor. For other elements such as K^+ and DOC, the pattern was different due to their easily leachable property. This pattern was consistent with those described by Veneklass (1990) and Ferm and Hultberg (1995a,b). This finding allows for a high internal circulation of K^+ in trees, hence no conclusions can be made concerning the dry deposition trends of base cations with respect to K^+ .

Finally, we know of the existence of terrestrial sources of dry deposition in bulk precipitation (excess of elements) in this ecosystem, mainly caused by dust and particles coming from the Sahara desert (Aboal, 1998); we also know that canopy surfaces affect scavenging atmospheric deposition in dusty atmospheres, such as that of the studied site (Domingo et al., 1994). Therefore the small effect of the canopy scavenging dry deposition was due to canopy structure or canopy absorption.

5. Conclusions

Net below canopy fluxes were found to have annual negative fluxes for H^+ , NO_3^- , SO_4^{2-} and Cl^- , most of which have been reported previously, but not all together for a single forest.

The relative importance of atmospheric deposition and canopy leaching on net below canopy fluxes were evaluated using different approaches, with similar results. Therefore the effect on scavenging particles by canopy was minimal. The NO_3^- in net below canopy fluxes came from dry deposition, the remaining elements from leaching, and SO_4^{2-} from both.

Results of analyses which aimed to separate internal and external sources, were optimal; we found that a simple linear regression model with

event quantity as the independent variable can readily substitute the Lovett and Lindberg's (1984) model. This model was applied for separate internal and external sources in the case of SO_4^{2-} .

This forest differed greatly from other previously studied forests. Large amounts of water were required for a positive flux (leaching), suggesting that the negative net below canopy fluxes of some elements were due to the low water regimes during the study year. Possible causes of this behaviour were the high value of the canopy saturation and the pattern of scattered rainfall, which leads to extreme values of interception losses. The intercept with the x axis for the relationship between net below canopy fluxes and event quantity, varied depending on the leachable properties of the canopy ions (i.e. Ca^{2+} and Na^+).

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References

- Aboal, J.R., 1998. Los flujos netos hidrológicos y químicos asociados en un Bosque de Laurisilva en Tenerife. PhD Thesis, Universidad de La Laguna, Spain.
- Aboal, J.R., Morales, D., Hernández, J.M., Jiménez, M.S., 1999a. The measurement and modelling of the variation of stemflow in a laurel forest in Tenerife, Canary Islands. *Journal of Hydrology* 221 (3–4), 161–175.
- Aboal, J.R., Jiménez, M.S., Morales, D., Hernández, J.M., 1999b. Rainfall Interception in laurel forest in the Canary Islands. *Agricultural and Forest Meteorology* 97, 73–86.
- American Public Health Association, 1992. Standard Methods for the Examination of Water and Waste Water, APHA–AWWA–WPCF, Washington.
- Appelo, C.A.J., Postma, D., Balkema, A.A., 1993. *Geochemistry, Groundwater and Pollution*, Bookfield, Rotterdam, Netherlands.
- Art, H.W., Bormann, F.H., Voigt, G.K., Woodwell, G.M., 1974. Barrier island forest ecosystems: role of meteorological nutrient input. *Science* 184, 40–60.
- Bache, D.H., 1977. Sulphur dioxide uptake and leaching of sulphates from a pine forest. *Journal of Applied Ecology* 14, 881–895.
- Barlett, R.J., Ross, D.S., 1988. Colorimetric determination of oxidizable carbon in acid soil solutions. *Soil Science Society American Journal* 52, 1191–1192.
- Cape, J.N., 1993. Direct damage to vegetation caused by acid rain and polluted cloud: definition of critical levels for forest trees. *Environmental Pollution* 82, 167–180.
- Capellato, R., Peters, N.E., 1995. Dry deposition and canopy leaching rates in deciduous and coniferous forest of the Georgia Piedmont: an assessment regression model. *Journal of Hydrology* 169, 131–150.
- Crockford, R.H., Richardson, D.P., Sageman, R., 1996. Chemistry of rainfall, throughfall and stemflow in a eucalypt forest and a pine plantation in southeastern Australia: 3. Stemflow and total inputs. *Hydrological Processes* 10, 25–42.
- Custodio, E., Llamas, R., 1976. *Hidrología subterránea*. Omega, Barcelona.
- Dewalle, D.R., Swistock, B.R., 1994. Differences in oxygen-18 content of throughfall and rainfall in hardwood and coniferous forest. *Hydrological Processes* 8, 75–82.
- Domingo, F., Puigdefabregas, J., Moro, M.J., Bellot, J., 1994. Role of the vegetation in biogeochemical balances of a small afforested catchment in southern Spain. *Journal of Hydrology* 159, 275–289.
- Eaton, J.S., Likens, G.E., Bormann, F.H., 1973. Throughfall and stemflow chemistry in a northern hardwood forest. *Journal of Ecology* 61 (2), 495–508.
- Eaton, J.S., Likens, G.E., Borman, F.H., 1978. The input of gaseous and particulate sulphur to a forest ecosystem. *Tellus* 30, 239–251.
- Ferm, M., Hultberg, H., 1995a. Method to estimate atmospheric deposition of base cations in coniferous throughfall. *Water Air and Soil Pollution* 85, 2229–2234.
- Ferm, M., Hultberg, H., 1995b. Method to estimate atmospheric deposition and internal circulation of base cations to a forested catchment area. *Water Air Soil and Pollution* 85, 2235–2240.
- Foster, N.W., Nicholson, J.A., 1988. Acid deposition and nutrient leaching from deciduous vegetation and potzolic soils at the Turkey Lakes Watershed. *Canadian Journal of Fisheries Aquatic Sciences* 45, 96–100.
- Ignatova, N., 1995. Changes in crown leaching composition induced by a sudden increase in atmospheric deposition. A case study in South-western Bulgaria. *Plant and Soil* 168–169, 373–382.
- Johnson, D.W., Lindberg, S.E., 1989. Acidic deposition on Walker Branch Watershed. In: Adriano, D.C., Havas, M. (Eds.), *Acidic precipitation. Case studies*, vol. 1. Springer, New York, pp. 1–38.
- Katz, C., Oren, R., Schulze, E.D., Milburn, J.A., 1989. Uptake of water and solutes through twigs of *Picea abies* (L.) Karst. *Trees* 3, 33–37.
- Kazda, M., Glatzel, G., 1986. Dry deposition, retention and wash-off processes of heavy metals in beech crowns: analysis of

- sequentially sampled stemflow. In: Georgii, H., (Ed.), *Atmospheric Pollutants in Forested Areas*, D. Reidel, Dordrecht, pp. 215–222.
- Kozlowski, T.T., Pallardy, S.G., 1997. *Physiology of Woody Plants*, Academic Press, San Diego.
- Lindberg, S.E., Lovett, G.M., 1992. Deposition and forest canopy interactions of airborne sulphur: results from the integrated forest study. *Atmospheric Environment* 26a, 1477–1492.
- Lindberg, S.E., Lovett, G.M., Richter, D.D., Jhonson, D.W., 1986. Atmospheric deposition and canopy interactions of major ions in a forest. *Science* 231, 141–145.
- Lovett, G.M., 1987. Atmospheric deposition: process and measurement methods. *Proceedings of California Forest Response Program Planning Conference*, Pacific Grove, CA, pp. 117–121.
- Lovett, G.M., 1994. Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective. *Ecological Applications* 4 (4), 629–650.
- Lovett, G.M., Lindberg, S.E., 1984. Dry deposition and canopy exchange in a mixed forest as determined by analysis of throughfall. *Journal of Applied Ecology* 21, 1013–1027.
- Lovett, G.M., Reiners, W.A., Olson, R.K., 1989. Factors controlling throughfall chemistry in a balsam fir canopy: a modelling approach. *Biogeochemistry* 8, 239–264.
- Lovett, G.M., Schaefer, D.A., 1992. Canopy interactions of Ca, Mg and K. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Ecological Studies, Atmospheric Deposition and Forest Nutrient Cycling*, vol. 91. Springer, New York, pp. 253–275.
- MacDonald, N.W., Witter, J.A., Burton, A.J., Pregitzer, K.S., Richter, D.D., 1993. Relationship among atmospheric deposition, throughfall, and soil properties in oak forest ecosystems. *Canadian Journal of Forest Research* 23, 2348–2357.
- Matzner, E., Meiwes, K.J., 1994. Long-term development of element fluxes with bulk precipitation and throughfall in two German Forests. *Journal of Environmental Quality* 23, 162–166.
- Mitterhuber, E., Pfanz, H., Kaiser, W.M., 1989. Leaching of solutes by the action of acidic rain: a comparison of efflux from twigs and single needles of *Picea abies* (L. Karst). *Plant and Cell Environment* 12, 93–100.
- Morales, D., Jiménez, M.S., Gonzalez-Rodriguez, A.M., Cermak, J., 1996a. Laurel forests in Tenerife, Canary Islands: I. The site, stand structure and stand leaf area distribution. *Trees* 11, 34–40.
- Morales, D., Jiménez, M.S., Gonzalez-Rodriguez, A.M., Cermak, J., 1996b. Laurel forests in Tenerife, Canary Islands: II. Leaf distribution patterns in individual trees. *Trees* 11, 41–46.
- Neary, A.J., Gizyn, W.I., 1994. Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario. *Canadian Journal of Forest Research* 24, 1089–1100.
- Potter, C.S., Harvey, L., Ragsdale, H.L., Swank, W.T., 1991. Atmospheric deposition and foliar leaching from three deciduous forest canopies. *Canadian Journal of Forest Research* 15, 1055–1060.
- Reiners, A.R., Olson, R.K., 1984. Effect of canopy components on throughfall chemistry; an experimental analysis. *Oecologia* 63, 320–330.
- Santos, A., 1990. *Evergreen Forest in Macaronesian Region*, Council of Europe, Strasbourg.
- Schaeffler, M., Jacobson, G.L. Jr., Pugh, A.L. IV, Norton, S.A., 1996. Influence of vegetation structure on capture of salt and nutrient aerosols in a marine peatland. *Ecological Applications* 6 (1), 263–268.
- Shephard, J.P., Mitchell, M.J., Scott, T.J., Zhang, Y.M., Raynal, D.J., 1989. Measurements of wet and dry deposition in a northern hardwood forest. *Water Air and Soil Pollution* 48, 225–238.
- Shibata, H., Satoh, F., Tanaka, Y., Sakuma, T., 1995. The role of organic horizons and canopy to modify the chemistry of acidic deposition in some forest ecosystems. *Water Air and Soil Pollution* 85, 1119–1124.
- Shibata, H., Sakuma, T., 1996. Canopy modification of precipitation chemistry in deciduous and coniferous forest affected by acidic deposition. *Soil Science Plant Nutrition* 42 (1), 1–10.
- Steinhardt, U., 1979. Untersuchungen über den Wasser- und Nährstoffhaushalt eines andinen Wolkenwaldes in Venezuela. *Göttinger Bodenkundliche Berichte* 56, 1–185.
- Striegel, G., Ruhiyat, D., Prayitno, D., Sarmina, S., 1994. Nutrient input by rainfall into secondary forests in East Kalimantan, Indonesia. *Journal of Tropical Ecology* 10, 285–288.
- Ulrich, B., 1983. Interaction of forest canopies with atmospheric constituents: SO₂, alkali and earth alkali cations and chloride. In: Ulrich, B., Pankrath, J. (Eds.), *Effects of Accumulation of air Pollutants in Forest Ecosystems*, D. Reidel, Dordrecht, pp. 33–45.
- Veneklass, E.J., 1990. Nutrient fluxes in bulk precipitation and throughfall in two Montane Tropical rain forest, Colombia. *Journal of Ecology* 78, 974–992.
- White, E.J., Turner, F., 1970. A method of estimating income of nutrients in a catch of airborne particles by a woodland canopy. *Journal of Applied Ecology* 7, 441–461.