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Factors controlling throughfall chemistry in a balsam fir canopy: A modeling approach

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Abstract. This paper presents a model of water flux and throughfall concentrations of K^+ and NH_4^+ in a subalpine balsam fir forest. The model is based on a multi-layer submodel of hydrologic flow. Cloud water deposition and evaporation are incorporated as separate submodels. Chemical exchange is parameterized with diffusion resistances and internal foliar concentrations determined from leaching experiments on isolated canopy components. The model is tested against within-storm throughfall measurements and found to agree reasonably well in most instances. Some specific departures from observed data are noted, of which some can be explained. Differences between observed and modeled concentrations of K^+ early in the storm events suggest that pre-storm conditions, which were not modeled, are important in controlling the chemical exchange.

Responses of throughfall chemistry to changes in rain rate, rain concentration, and stand surface area index (SAI) were investigated by simulation with the model. Increasing rain rates increased leaching of K^+ and uptake of NH_4^+. Increasing concentrations of K^+ in rain decreased slightly the amount of K^+ leached, but increasing concentration of NH_4^+ in rain increased NH_4^+ uptake proportionately. Increasing canopy SAI increased the leaching of K^+ and the uptake of NH_4^+, with the pattern of the increase dependent on rain rate.

Introduction

The chemistry of precipitation that reaches the forest floor is influenced by the chemical and hydrologic characteristics of the incident precipitation, washoff of dry-deposited materials from canopy surfaces, washoff of material transported from within canopy tissues prior to the precipitation event, and absorption or release of substances by the plants and their associated microflora during the precipitation event. The nature of the resulting stemflow and throughfall has been investigated for many canopies and was recently reviewed by Parker (1983). However, our ability to separate the individual processes of depostion and chemical exchange, and thus predict the chemistry of throughfall and stemflow for a given forest stand, lags far behind our ability to quantify the net result of the chemical changes taking place.

It is with this in mind that we undertook a multifaceted project designed to elucidate how one forest canopy captures and alters atmospherically deposited material. The work has been performed in the subalpine balsam fir (*Abies balsamea* (L). Mill.) forest type of the northern Appalachian Mountains in the eastern U.S.A. (Reiners & Lang 1979). These forests have many significant advantages for such studies — they are generally short and even-sized, virtually monospecific, support considerable populations of chemically active, epiphytic lichens (Lang et al. 1980), and are exposed to a large amount of cloud water deposition as well as precipitation (Lovett et al. 1982).

Work in this system has included studies of the chemistry and deposition of throughfall and stemflow (Cronan 1980; Olson et al. 1981), experimental analysis of the uptake and release of ions by major canopy components, including lichens (Lang et al. 1976; Reiners & Olson 1984; Reiners et al. 1986); laboratory, field and modeling studies of cloud water deposition (Thorne et al. 1982; Lovett et al. 1982; Lovett 1984; Lovett & Reiners 1986), and analysis of within-event changes in throughfall and stemflow chemistry (Olson et al. 1985). A summary of work up to this point is presented by Reiners et al. (1987).

The goal of the modeling study described in this paper is to integrate and test our understanding of the biogeochemical processes that occur in these canopies. Thus the model takes into account rainfall, cloud water deposition, hydrologic flow within the canopy, and chemical exchanges between deposited solutions and canopy surfaces. Because our goal was a mechanistic understanding of the system, we developed a model based on simple principles, containing parameters that were biologically relevant and quantifiable independently of the model. The model is a formalization of our understanding of the system, and a statement of a complex hypothesis about how the system functions.

The specific system used in model development and testing was a balsam fir forest at 1220 m on Mt. Moosilauke, NH (77°50′W, 44°1′N). This forest is about 10 m tall, densely stocked (about 5300 trees/ha), and nearly monospecific. This is a remote area, with no strong local sources of air pollution. The climate is windy, cold, and wet, with a mean annual precipitation of around 180 cm, and low-lying clouds in contact with the canopy an estimated 40% of the time (Reiners & Lang 1979; Lovett et al. 1982). 'Storm events' in this zone frequently entail protracted periods of cloud immersion, punctuated by one or more rainstorms.

We chose to focus initially on K^+ and NH_4^+ for two reasons. First, these two ions exhibit opposite behaviors in contact with canopy surfaces, being the archetypes of the leached (K^+) and absorbed (NH_4^+) ions (Reiners & Olson 1984). Second, of all the major nutrients, these two are the least likely to exhibit an effect of interstorm dry (particle and gas) deposition, which we did not attempt to model. While NH_4^+ is abundant on atmospheric particles in the eastern U.S., the small size of these particles results in a small deposition rate, and a relatively minor contribution to total (wet plus dry) deposition (Lindberg et al. 1986). Dry deposition of K^+ may be comparable to wet deposition, but both are generally insignificant compared to efflux of K^+ from the foliage (Lindberg et al. 1986). While inclusion of dry deposition in the model would not be difficult, it would require air concentration data which were not available.

Model structure and parameter estimation

The model is composed of submodels describing cloud water deposition, evaporation from the canopy, and chemical exchange between canopy components and the solutions on their surfaces. These submodels are linked within the framework of a model of water percolation through the canopy (Fig. 1).

Canopy structure

The canopy structure information used by the model is derived from destructive sampling of trees near the target stand (Lovett 1981). By sampling the profile of foliage and branches on these trees, we were able to develop statistical descriptions of the vertical distributions of young (0–2 yr) and old (greater than 2 yr) foliage surface area in 1 m height layers in the target stand. Twig, branch and bole surface area were determined similarly but were not used in the model. Vertical profiles of lichen surface area index (SAI) were measured in a nearby, but somewhat taller, stand in a previous study (Lang et al. 1980). The height-normalized profiles of SAI of lichens on branches in that stand and branch SAI in our stand were nearly identical. Therefore, we determined the lichen SAI of each level of our canopy by multiplying the branch SAI of that level by the ratio (total branch lichen

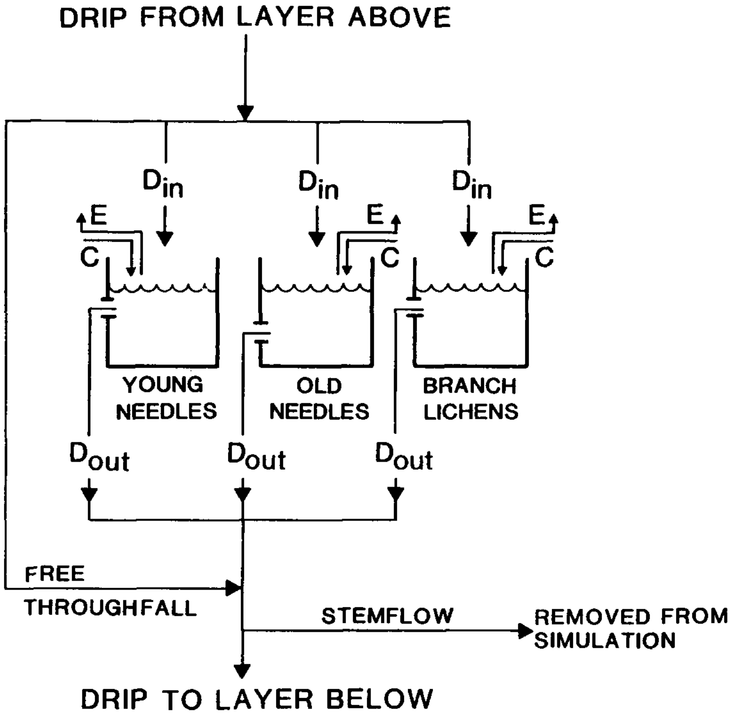

Fig. 1. Schematic diagram of the structure of the hydrologic model. E = evaporation, C = cloud water deposition, D_{in} = drip in, D_{out} = drip out.

SAI)/(total branch SAI) for the whole plot. All types of lichens occurring on branches were grouped together in this model and in the chemical parameterization experiments described below.

Cloud water deposition and evaporation

The submodels describing cloud water deposition and evaporation have been described in detail elsewhere (Lovett 1984). Using the same base of canopy structure information, these submodels calculate droplet deposition (via impaction and sedimentation) and evaporation for each component in each height level. The rates of droplet and vapor transfer are modeled using aerodynamic and boundary-layer resistances. The aerodynamic resistance is computed from canopy structure information and the above-canopy wind speed (Lovett 1984), and the boundary-layer resistances are derived from wind tunnel studies on individual branches (Thorne et al. 1982 for droplet deposition, and Landsberg and Thom 1971 for evaporation). These models have been tested independently in our target stand (Lovett 1984).

Hydrologic model

Each canopy component in each level is treated independently in the hydrologic model (Fig. 1). A water retention threshold, defined as the volume of water per unit surface area able to be held without dripping, was determined for each component type in the laboratory (Lovett 1981). Inputs of water to each component in each level included drip from above (D_{in}) (or rainfall, in the case of the top level) and cloud deposition (C). Outputs included evaporation (E) and drip to the level below (D_{out}). Thus, the conservation equation for water on each component can be written as:

$$\frac{dS_e}{dt} = D_{in} + C - E - D_{out} \tag{1}$$

where S_e is the external water storage on the component surfaces (expressed in cm) and D_{in}, D_{out}, C and E are water flux rates expressed in cm min^{-1}. In a manner similar to the whole-canopy hydrologic model of Rutter et al. (1971), the drip rate off the component is modeled as a function of S_e and the water retention threshold of the component. The functional relationship is such that if S_e is less than the water retention threshold, no drip occurs. If S_e exceeds the threshold, the drip rate (D_{out}) is proportional to S_e. Thus the system operates like a leaky cup, where the rate of leakage depends on the depth of the water above the level of the leak (Fig. 1).

Incoming drip is apportioned between the canopy components in a given height level proportionately to their projected surface areas. Open space at each level receives it proportional share of the drip, called free throughfall in Fig. 1. Drip from each component is summed and free throughfall is added at each level, and a portion is diverted to stemflow (see below). The resulting drip is apportioned to the components in the level below, and so forth through the stand. Drip plus free throughfall from the lowest level is the throughfall for the time interval. The water balance (eq. 1) is solved analytically for each time interval during a storm event. The length of the time interval is 15 min at low rain rates, but is decreased as rain rates increase to avoid mathematical instabilities.

Although we had originally intended to simulate stemflow as well as throughfall, this made the modeling task much more difficult because the focusing of large amounts of water onto the relatively small surface area of the boles magnified the instability problems. Nonetheless, diverting some water to stemflow was necessary in order to simulate the correct volume of throughfall. Measurements for 2 storms in 1981 indicate that stemflow accounts for 10–13% of the total below-canopy precipitation in this stand.

This is an underestimate of the amount of water diverted from throughfall, because some water is retained on bark and, especially, bole lichens. Therefore, we assumed that 15% of the potential drip was diverted to stemflow in each time interval, but we did not model the percolation of water down the stem.

Chemical exchange

To characterize the chemical behavior of individual components, we used the results of experiments reported by Reiners & Olson (1984), in which artificial rainstorms were applied to individual canopy components of balsam fir, and chemical exchange was measured as a function of time. Rather than simply describing the influx or efflux rates with regression equations and using those equations in the model, we chose to use the leaching experiments to determine crucial parameters of the chemical exchange and then incorporate those parameters into a more general model.

Potassium

The time course of K^+ efflux from canopy components as determined by Reiners and Olson (1984) showed a strong decline in efflux rate during the initial part of the experimental storms, followed by a leveling off as the storm continued. This suggested an exponential depletion of foliar K^+. We assumed that K^+ efflux was a process of diffusion from an internal pool in the foliar apoplasm to an external pool in the water on the foliar surface. This concept of foliar chemical exchange is similar to that used by McFarlane and Berry (1974), Luxmoore et al. (1978), Hamilton et al. (1982), and Olson et al. (1985) and can be described mathematically as:

$$F_K = \frac{([K_i] - [K_e])}{R_K} \qquad (2)$$

where F_K is the flux of potassium across the surface (μeq cm^{-2} min^{-1}), $[K_i]$ and $[K_e]$ are the internal and external concentrations (μeq mL^{-1}), respectively, R_K is a diffusion resistance (cm min^{-1}), and positive values indicate efflux from the leaf. Here efflux is described as the quotient of the concentration gradient between external and apoplastic solutions, and a resistance term which should be related to the physical and chemical properties of canopy component surfaces that control ion movement (Price 1982).

Equation 2 can be the basis for incorporation of K^+ exchange into the hydrologic model if the concentration gradient and the resistance can be determined. For the artificial rainstorms generated by Reiners and Olson,

$[K_i]$ and R_K are unknown, but F_K was measured and $[K_e]$ can be assumed to be the concentration of K^+ in their artificial rain. If we assume that F is the only flux affecting the internal pool of K (K_i, expressed as μeq cm^{-2}) and express the internal concentration ($[K_i]$) as K_i/S_i, where S_i is the volume of water available to ions diffusing within the leaf (probably the apoplastic water or some fraction of it), then we can write eq. 2 as:

$$F_K = \frac{dK_i}{dt} = \frac{K_i}{S_i R_K} - \frac{[K_e]}{R_K} \qquad (3)$$

Integrating eq. 3 yields K_{it}, the size of the internal pool of K at time t:

$$K_{it} = [K_e]\, S_i\, (1 - e^{-t/S_i R_K}) + K_{io}\, e^{-t/S_i R_K} \qquad (4)$$

and substituting back into eq. 3 yields F_K at time t:

$$F_{Kt} = \frac{K_{it}}{S_i R_K} - \frac{[K_e]}{R_K} = \left(\frac{K_{io}}{S_i R_K} - \frac{[K_e]}{R_K}\right) e^{-t/S_i R_K} \qquad (5)$$

where K_{io} is the internal pool at time 0 and $[K_e]$ is constant. This equation describes the artificial storm results in terms of three unknown parameters, K_{io}, R_K, and S_i. The product $S_i R_K$ can be called the 'leaching time constant'; it is expressed in units of time and can be interpreted as the amount of time it takes for an apoplastic pool of K^+ to be reduced to 1/e of its original value when exposed to a constant external concentration of 0. This is a very important term in the model, because when the external concentration $[K_e]$ is very small relative to the internal concentration K_i/S_i, which is usually the case, the right hand side of eq. 5 reduces to $(K_{io}/S_i R_K)\, e^{-t/S_i R_K}$, and the parameter $S_i R_K$ completely controls the pattern of K efflux.

Taking the logarithm of both sides of eq. 5 yields

$$\ln(F_{Kt}) = \ln\left(\frac{K_{io}}{S_i R_K} - \frac{[K_e]}{R_K}\right) - \frac{t}{S_i R_K} \qquad (6)$$

This indicates that if the artificial storm data of Reiners and Olson (1984) are plotted as ln (F_{Kt}) *vs.* t, the slope is $-1/S_i R_K$ and the intercept is

$$\ln\left(\frac{K_{io}}{S_i R_K} - \frac{[K_e]}{R_K}\right)$$

Thus, the leaching time constant can be calculated directly as the negative inverse of the slope of this plot, and if $[K_e]$ is assumed to be the concen-

Table 1. Parameters of the chemical exchange models for K^+ and NH_4^+.

	Component type		
	Young foliage	Old foliage	Lichens
K^+			
R^2 of regression*	0.88	0.62	0.91
n	14	8	10
S_iR_K (min)	192	104	141
R_K (min cm^{-1})**	3840	2080	2820
K_{io} (ueq m^{-2})**	70	161	1730
NH_4^+			
R_N (min cm^{-1})	1567	2000	177

* Regression equation: $\ln(F_{Kt}) = a\,t + b$, data from Reiners & Olson (1984).
**Calculated assuming $S_i = 0.5\,L\,m^{-2}$

tration in the artificial rain, and S_i is specified independently, then R_k and K_{io} can be calculated also.

To determine these parameters, we performed regression analysis on the new foliage, old foliage and branch lichen data from Reiners & Olson (1984). The data consisted of efflux rates corresponding to different times during the artificial storms, with each point in time being the mean of 15 replicate determinations. The regressions explained between 62 and 91% of the variance in the data, using 8 to 14 points in time (Table 1). The leaching time constant S_iR_K was calculated from the inverse of the regression slope. We estimated S_i to be $0.5\,L\,m^{-2}$, based on typical apoplastic water fractions reported for conifers by Tyree & Jarvis (1982), and then calculated R_K as S_iR_K/S_i. We calculated K_{io} from the intercept of the regression, assuming $[K_e]$ to be the concentration of K^+ in the artificial rain ($3\,\mu eq/L$). The values of K_{io} and R_K thus calculated are shown in Table 1. The choice of apoplastic water volume S_i is not of great consequence; if we reduce S_i by a factor of 10 (to $0.05\,L\,m^{-2}$), the calculated resistance increases by a factor of 10, but the crucial parameter S_iR_K does not change and K_{io} decreases by only 2%. As long as the same value of S_i is used both in this calculation and in the model, its magnitude has little effect on the simulated throughfall.

We used these parameters to calculate K^+ efflux from the whole canopy in the model. It was assumed that the values in Table 1 applied to all height levels of the stand, and initial internal K^+ pools were set at K_{io} times the SAI of the component. The chemical flux model simultaneously keeps track of changes in the internal and external K^+ pools for each component in each height level over time. The conservation equation for the internal pool is eq. 3, and for the external pool

$$\frac{dK_e}{dt} = I_K - \frac{K_e}{S_e} \cdot D_{out} + \frac{dK_i}{dt} \tag{7}$$

Here, I_K represents the input rate of K^+ via drip and cloud water, S_e is the amount of water stored on the component surface, and D_{out} is the drip rate of water off the component.

In the model, the cloud deposition, evaporation, and hydrologic submodels are run to determine I_K, S_e, and D_{out}, then equations 3 and 7 are solved numerically using a Runge-Kutta algorithm. In each level, the K^+ in drip from each component is added to the K^+ in free throughfall, and these are assumed to mix thoroughly before dripping to the next level. As with water, 15% of the K^+ in the potential throughfall is diverted to stemflow.

In using Reiner's and Olson's experimental data to parameterize this model (both for K^+ and for NH_4^+, described below), we are making several simplifying assumptions that are open to question. First, we are assuming that the parameters derived from application of rain with a single external concentration of K^+ and NH_4^+ will adequately describe canopy exchange in the variable-concentration conditions imposed by different storms and multiple layers in the canopy. Second, we are assuming that all branches in the canopy have the same parameter values. Third, we assume that the exchangeable pool of K^+ is recharged rapidly afer a rain event, so that the initial internal concentrations are the same for every event.

Ammonium

In Reiners & Olson's (1984) experiments, NH_4^+ exhibited a behavior fundamentally different from that of K^+. First, the net flux was into the canopy components, rather than out of them. Second, increasing rain rates resulted in significant increases in influx, except in the case of old foliage. Third, for a given rain rate, the influx rates were constant over the course of a rain event. These characteristics suggest an ammonium uptake potential that is less than, but is influenced by, the rate of supply of NH_4^+ to the leaf surfaces by the artificial rain. This can happen if uptake rates are sufficient to draw down NH_4^+ concentrations on the leaf surface, thus feeding back to decrease subsequent uptake rates. Faster supply rates would minimize the drawdown and act to maintain high uptake rates. One way to describe this mathematically, consistent with our concept of K^+ exchange, is as diffusion from an external pool to an internal pool which has an ammonium concentration constantly held to zero by cellular uptake (i.e., a perfect sink). In anology to eq. 2, this can be expressed as:

$$F_N = \frac{[N_i] - [N_e]}{R_N} \tag{8}$$

where F_N is the flux of NH_4^+ across the leaf surface, $[N_i]$ and $[N_e]$ are the internal and external concentrations of NH_4^+, and R_N is the resistance. If $[N_i]$ is always 0, then

$$F_N = -\frac{[N_e]}{R_N} = -\frac{N_e}{S_e R_N} \tag{9}$$

where N_e is the external pool of NH_4^+ and S_e is the water storage on the component surface. The result is a negative number, indicating influx. The dynamics of the external pool of NH_4^+ also involve an input rate (I_N) from drip and cloud water, and the output which is drip off the surface. The conservation equation is thus:

$$\frac{dN_e}{dt} = I_N - \frac{N_e}{S_e} \cdot D_{out} - \frac{N_e}{S_e R_N} \tag{10}$$

where D_{out} is the drip rate of water from the surface. Integrating equation 9 yields

$$N_{et} = \frac{I_N}{b}(e^{bt-1}) + N_{eo}e^{bt} \tag{11}$$

where

$$b = \frac{D_{out}}{S_e} - \frac{1}{S_e R_N} \tag{12}$$

To model NH_4^+ influx, it is necessary to know the resistance R_N, which can be determined from the Reiners and Olson (1984) experiments, in which artificial rain was applied to isolated canopy components at a variety of rain rates. If equation 9 describes the influx rates in their artificial storm experiments, then the measured influx rates (F_N) and the concentration in their artificial rain (94 μeq/L) can be used to calculate R_N. For this calculation we must assume that the concentration in the artificial rain was equal to the concentration on the component surfaces ($[N_e]$). In these experiments, the influx rates for new needles and lichens decreased with decreasing supply (i.e., rain) rate, indicating that at the low supply rates the influx rates were sufficient to drawn down $[N_e]$ to a concentration below that in the artificial rain. Thus, the assumption that $[N_e]$ equals the artificial rain concentration is probably true only for the highest rain rates used by Reiners and Olson, so we used the influx data from the highest rain rates to calculate R_N. In the case of old needles, for which influx rates were not significantly different between rain rates, we used the mean influx rate to calculate R_N. The calculated values of R_N are shown in Table 1.

In the model, the cloud water, evaporation, and hydrologic submodels are run to determine I_N, D_{out} and S_e for each interval, then equation 11 is solved to determine N_e at the end of the interval. As with K^+, drip from each component is homogenized with free throughfall and 15% is diverted to stemflow before becoming input to the level below.

Comparison with other models

Several other attempts to model throughfall have been reported in the literature. The hydrologic model of Rutter et al. (1971) successfully calculates the water balance of a single-layer forest canopy. Their formulation, elaborated to include multiple layers and multiple canopy components, is the basis of the hydrologic model used here.

Chen et al. (1983) simulated annual average throughfall chemistry for a northern hardwood forest using an unstated, but presumably monthly, time step. A single-layer canopy was used, and dry deposition was included between rain events. The leaching behavior of the leaves was modeled as a linear function of the total foliar content of each element. Two leaching parameters and a dry deposition collection efficiency were determined by 'calibration,' i.e., matching model output to observed data. It is unclear if the model was tested against an independent data set. Uptake of NH_4^+ was not permitted in this model; instead NH_4^+ was assumed to leach from the leaves and then to nitrify in the canopy to produce NO_3^- in throughfall.

Johannes et al. (1986) briefly described a model that is outwardly similar to the one described in this paper. Both are multi-layer models intended to predict within-event patterns in throughfall chemistry. Johannes et al. modeled hydrologic percolation as a simple cascade, in which a storage capacity in one level is filled and then any excess water drips to the next level. They determined leaching coefficients for test trees by regression analysis of ion concentrations in throughfall and wetfall. Particulate deposits were assumed to exist on leaf surfaces before the storm, and the amount of these deposits was calculated from particulate dryfall collections made with open buckets. The model was calibrated and tested on data from two throughfall collectors, one under a conifer and one under a deciduous tree. Test data were shown for SO_4^{2-} and K^+ concentrations in throughfall during only one storm.

Model testing

We compared the output of our model to throughfall data from the research site. The data used for testing were independent of any throughfall data used to parametierize the model. In 1980, five storm events were samples manually using variable time intervals of collection during each storm. Throughfall collections were made in the 10 × 10 m plot using 15 polyethylene funnels (each 19.5 cm diameter) draining into polyethylene bottles. Incident precipitation was sampled in a nearby clearing using a standard, alter-shielded rain guage for precipitation amount and three replicate funnel-bottle collectors for chemistry. Descriptions of field, laboratory and analytical methods can be found in Reiners & Olson (1984) and Olson et al. (1985).

In running the model for these events, we used measured precipitation rates and chemical concentrations for the collection periods, which were of variable length. We divided the amount of rain collected during the period by the length of the collection period to determine the average rain rate, which was used as the precipitation input in the model. In some cases, we were absent from the site during part of long collection periods (e.g., overnight), so the average precipitation rate for these periods is a very rough approximation of what may actually have occurred (e.g., a 0.05 cm/h average rain rate might have included 1 cm of rain in an hour plus 19 hours of no rain).

We estimated the total cloud water deposition for each event as the amount of throughfall plus stemflow (TF + SF) collected in excess of rainfall for the entire event. We then scaled the output of the cloud water deposition submodel to match this excess deposition, and distributed the deposition evenly during the event. The cloud water deposition submodel also permits us to specify the spatial distribution of these inputs among canopy components and height levels. If TF + SF was less than rainfall amount, cloud deposition was assumed to be 0 and the cloud deposition submodel was not used. Thus, we 'measured' cloud water inputs as we did rainfall, so these simulations do not test the cloud water deposition submodel. Independent tests of this submodel are reported by Lovett (1984). We note that our means of estimating cloud water deposition will usually result in a slight underestimate because interception loss from the canopy is not considered in the calculation of cloud water deposition as (TF + SF) minus rainfall. Cloud water deposition was very small compared to rainfall in most of these events.

To measure the chemical concentrations in cloud water, we used a harp-like device in which wind-driven cloud droplets impacted on thin, vertical strands of nylon line and then dripped into a collection bottle. The collections were made above the canopy from a meteorological tower. For storms in which these collections were not available, we used the mean measured chemical concentrations of K^+ (10 ueq L^{-1}) and NH_4^+ (108 ueq L^{-1}) in cloud water reported for this site by Lovett et al. (1982). The implications of the lack of complete meteorological and cloud chemistry data will be discussed below.

Figures 2–6 show the observed data and model output for 5 storm events sampled in 1980. In each figure, panel 'A' shows the hydrologic fluxes — rain

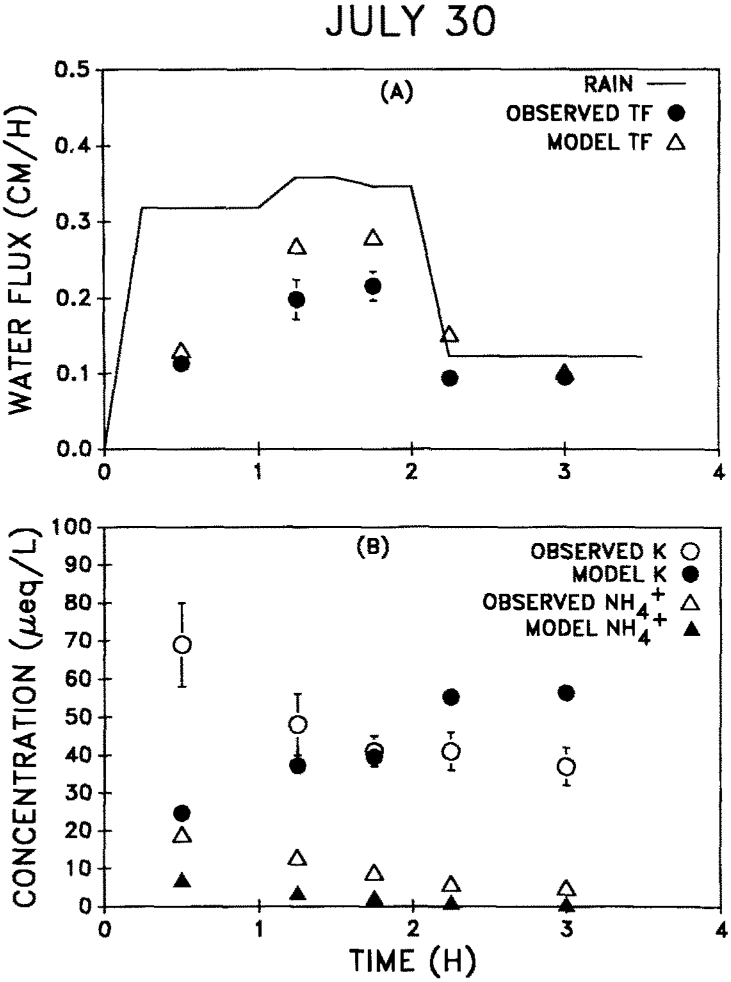

Fig. 2. Simulation of July 30, 1980 storm event. (*A*) Hydrologic fluxes. (*B*) Throughfall concentrations. Error bars (standard error) are included on all 'observed' data in A and B; if error bars do not show they are smaller than the width of the plotted point.

or cloud water deposition and modeled and observed throughfall amounts. Panel 'B' shows the observed and modeled concentrations of K^+ and NH_4^+ in throughfall. In Fig. 4, A and B are combined.

The sampled storms include a variety of storm types, ranging from the brief, moderate rainfall of July 30 to the protracted cloud/rain event of August 13 and the cloud-only event of September 5. In each case, time zero of the graphs is the time at which the throughfall collectors were manually

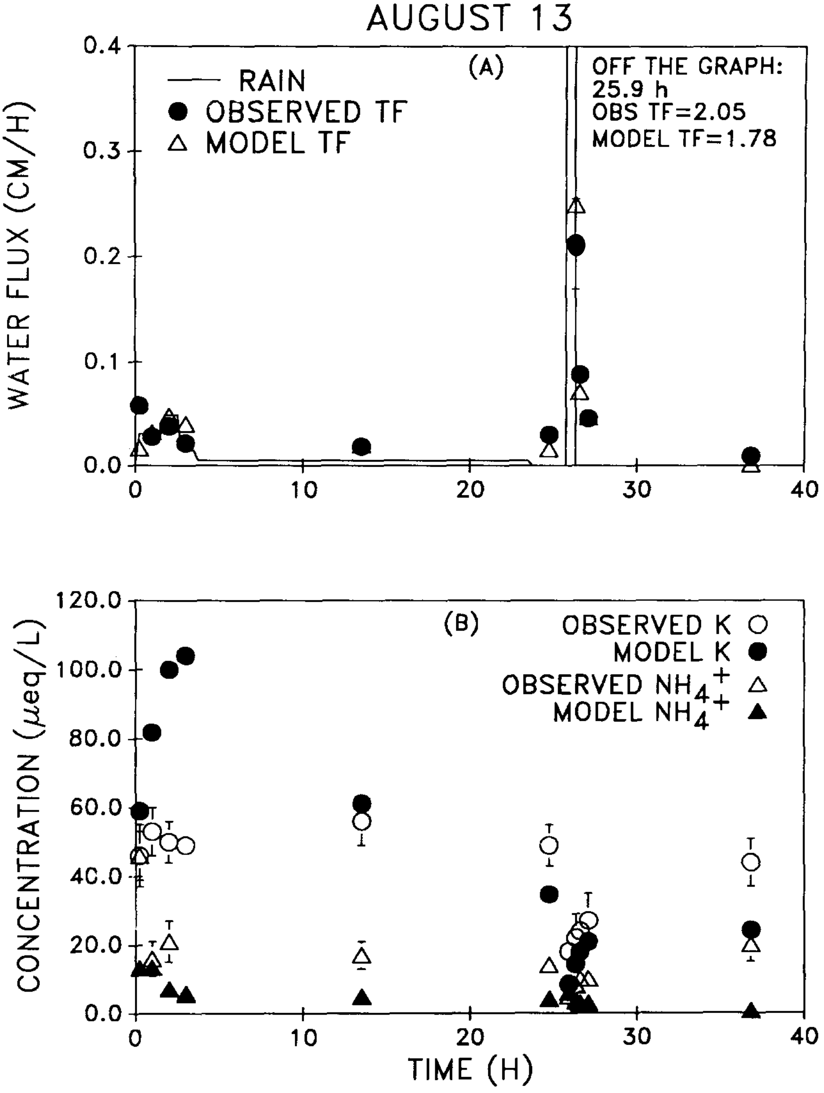

Fig. 3. Simulation of August 13, 1980 event. (Caption as in Fig. 2).

opened to begin sampling. Frequently there was cloud water input to the site prior to this time; in these cases the simulations included an appropriate period of cloud water deposition prior to time 0 which is not shown in Figs. 2–6. All data in these figures are plotted at the midpoints of the collection intervals.

The model simulations of throughfall amount are slight underestimates in some cases and overestimates in others, but they faithfully track the pattern of the observed data in general. This agreement happens in spite of our lack of information on the temporal distribution of cloud water deposition because most of the water delivered to the canopy during these events was from rain, not cloud. The exception to this is the September 5 cloud-only event (Fig. 4). Because we estimated cloud deposition rates based on the observed TF + SF data, the September 5 event is not an independent test of the cloud water deposition submodel. However, this does provide an important test of the chemical exchange submodels under cloud deposition conditions. While rain far exceeds cloud deposition during most rain events, inputs of chemicals and water via cloud deposition can be significant over the year because of the relatively long periods of cloud immersion relative to periods of rainfall (Lovett et al. 1982).

The performance of the K^+ chemical exchange model was variable. In general, predicted and observed concentrations were in the same range, but in some cases (most notably July 30), significant patterns in the observed

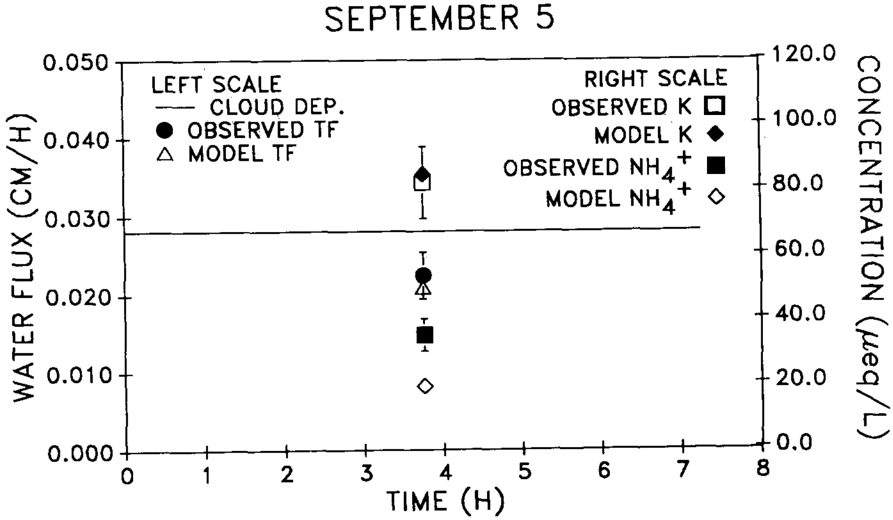

Fig. 4. Simulation of September 5, 1980 cloud-only event. (Caption as in Fig. 2). Horizontal line represents cloud deposition rate.

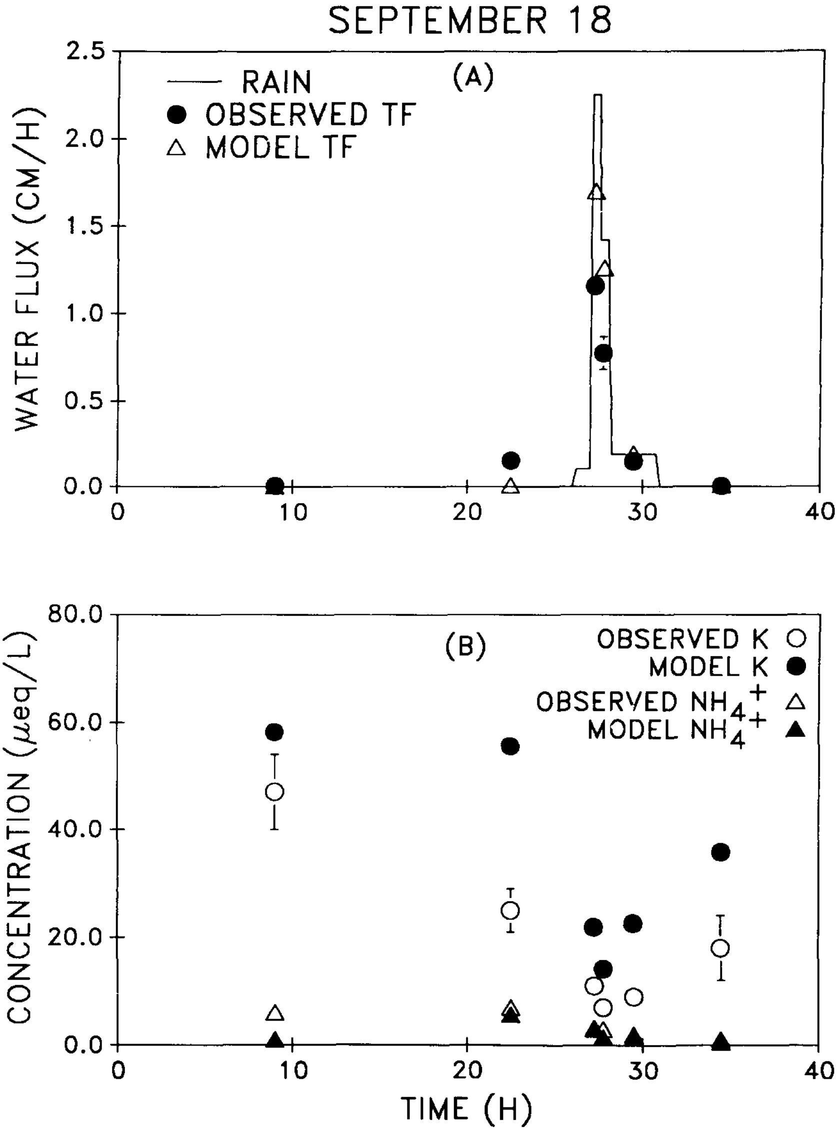

Fig. 5. Simulation of September 18, 1980 event. (Caption as in Fig. 2).

concentrations were not reproduced by the model. In general, the modeled concentrations tracked the observed changes during the events, especially during the latter part of the events and during high-rainfall periods. We suspect that the poor performance at the start of some events (July 30, August 13, October 11) resulted from our inability to specify accurately the initial, internal pool (K_{io}). In all our simulations, the initial internal pool was

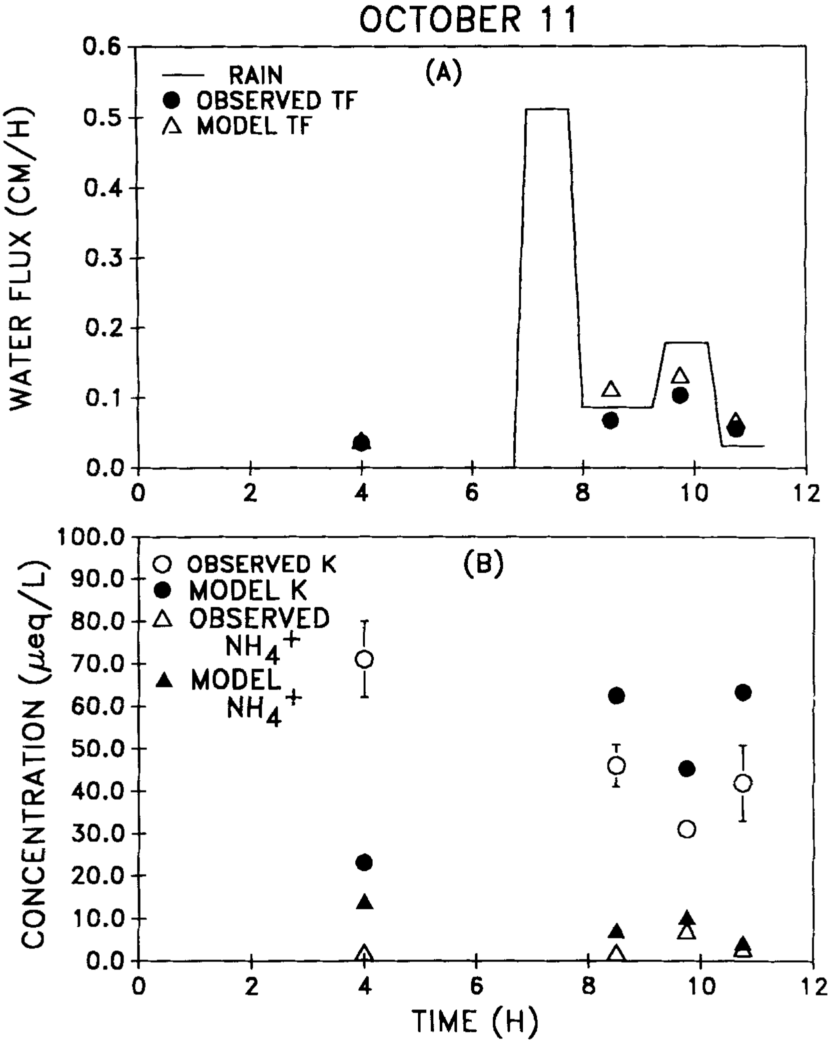

Fig. 6. Simulation of October 11, 1980 event. (Caption as in Fig. 2).

calculated as K_{io} for each component (Table 1) multiplied by the SAI of that component. In nature this pool probably varies from storm to storm, depending on the extent of depletion of the pool during the previous rain even and the recharge since that event (Reiners and Olson 1984). We note that in some cases the model predictions for the beginning of the event were low (July 30, October 11) while in others they were high (August 13, September 18) suggesting that the problem is not a systematic bias in the model. Other aspects of the stand's initial conditions which may account for these errors are possible loadings of dry deposits on the leaves or residual salts left over from the evaporation of the previous rain event. Exudation of K^+ from the needles between rain events is probably not important (Reiners et al. 1986). Inaccuracies in predictions later in the events may result from not accounting for within-event recharge of the internal pool. Least-squares regression of observed vs. predicted K^+ concentrations for all time periods in all events yielded a slope of 0.72 (SE = 0.24) and an R^2 of 0.27, indicating that the model explained 27% of the observed variance and that the model predictions were, in general, slightly lower than the observed concentrations. If we omit collections of the first mm of throughfall in each event, the R^2 improves to 0.42 and the slope to 1.02 (SE = 0.28). Although there is still a substantial amount of variance unexplained by the model, there is little bias in the predictions.

In the case of NH_4^+, the model results were satisfactory. Predicted concentrations approximated the observed data in magnitude and pattern. There appears to be a slight bias towards low predictions in all storms except October 11. Unlike K^+, for which the throughfall concentrations are controlled principally by the amount leached and the input fluxes have little effect (see below), the inputs of NH_4^+ have a large effect on the concentrations in throughfall. Therefore we expect errors in specifying those inputs to be a significant source of variation between model predictions and observed data. Cloud water deposition is the most uncertain input. The concentration of NH_4^+ in cloud water was measured only for the September

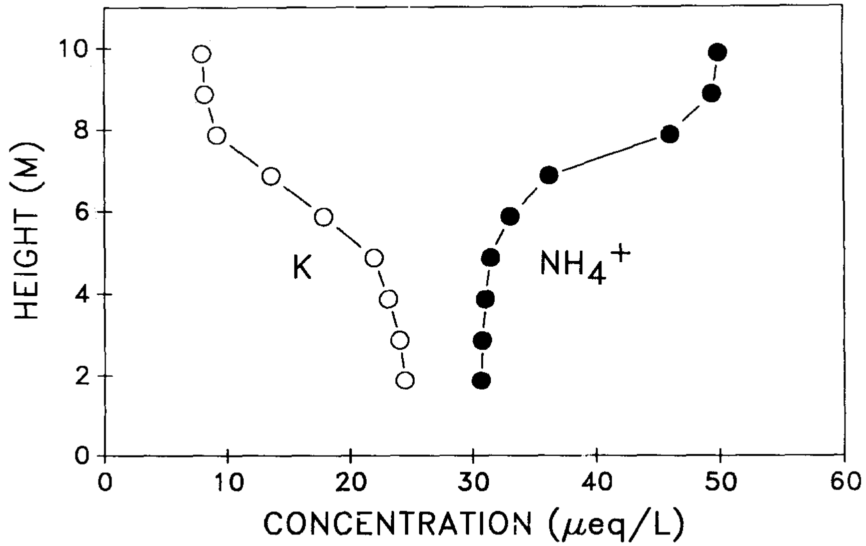

Fig. 7. Canopy profiles of throughfall concentrations (μeq/L) after 3 hr rain event at 0.5 cm/h. Concentrations in rain: K^+, 8 μeq/L; NH_4^+, 50 μeq/L.

18 and October 11 events, and those storms seem to show the best agreement between modeled and observed data. For the other simulations, the NH_4^+ concentration in cloud water was set at 108 ueq L^{-1}, the mean concentration measured in cloud water at this site during 1980 and 1981 (Lovett et al. 1982). Considering this, the two-fold difference between modeled and observed NH_4^+ concentration for the September 5 cloud only event is understandable.

We note also that comparing predicted and observed throughfall concentrations is a rather severe test of the model. The arithmetic mean NH_4^+ concentration observed in throughfall was 11 μeq L^{-1}, while the mean predicted value was 5.4 μeq L^{-1}. In contrast, the mean NH_4^+ concentrations in rain and cloud were 22 and 97 μeq/L, respectively, for these simulations. Thus the difference of 5.6 μeq/L between predicted and observed throughfall concentrations, although large in comparison to the observed values, is small in comparison to the predicted uptake of NH_4^+ in the canopy.

Analysis and discussion of the model

We believe that the model reproduces the basic behavior of NH_4^+ and K^+ concentrations in throughfall in this stand for most events, using a very simple formulation of exchange between the leaf and incident water. The parameterization was based on the behavior of individual canopy components, and the results were 'scaled up' to the whole canopy by incorporation into our models of canopy architecture and water flow. In this process, we assumed that all components throughout the canopy had the same resistances and initial pool sizes as those which were used to parameterize the model. However, we could not have scaled up the experimental data simply by multiplying the individual-component influx or efflux rates by the surface area index of that component for the whole canopy. Examination of the model output shows that the chemistry of the throughfall water changes substantially with height in the canopy (Fig. 7), indicating that components at different levels are exposed to different concentration gradients. This has been shown experimentally by Schaefer et al. (1988). The canopy components at the top of the canopy deplete the solution of NH_4^+ and enrich it in K^+, thus reducing the NH_4^+ influx and K^+ efflux from the components in lower levels. Thus it is the interaction between components, in addition to the properties of the components themselves, which determines the chemical behavior of the whole canopy.

It is difficult to test the response of real canopies to possible controlling variables like rain rate, rain concentration, and canopy SAI because during real rain storms several factors are usually changing simultaneously. The model permits us to investigate whole-canopy response to changes in particular input variables while holding the other factors constant.

Figures 8–10 show model responses to changes in rain rate, concentration, and SAI. In each figure, panel 'A' shows the amount of K^+ leached or NH_4^+ taken up during the entire simulated storm, and panel 'B' shows the event-average throughfall concentrations of the two ions. We chose reference

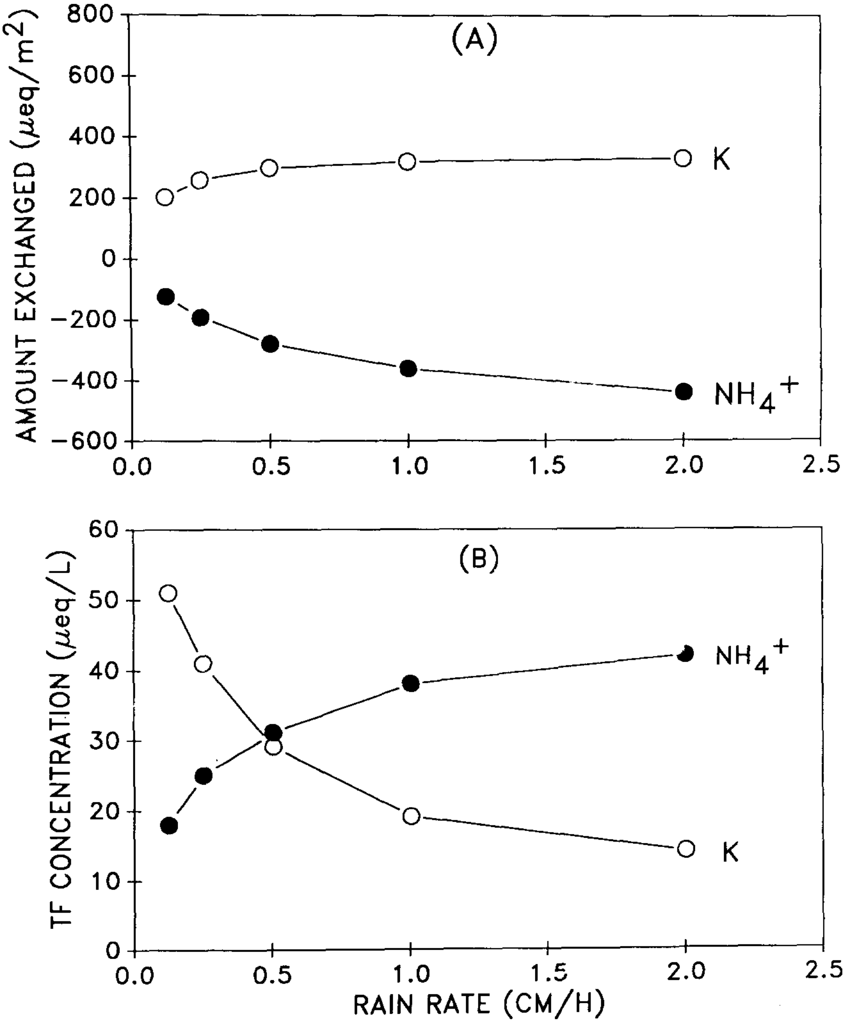

Fig. 8. Effect of rain rate on (*A*) canopy exchange, and (*B*) throughfall concentrations of K^+ and NH_4^+ for reference conditions.

conditions of: rain rate, 0.5 cm/h; SAI, 6.7; rain [K^+], 8 μeq/L; rain [NH_4^+], 50 μeq/L; no cloud water deposition; and length of storm, 3 hours. For each simulation shown in Figs. 8–10, all reference conditions were held constant except the one specified on the X axis, which was changed to 0.25, 0.5, 1, 2, and 4 times its reference value. In interpreting these graphs, recall that negative canopy exchange values indicate influx to the canopy.

Figure 8A shows that increases in rain rate result in increased efflux of K^+ and influx of NH_4^+, but both responses asymptote at higher rain rates. This occurs because faster rain rates cause faster turnover of water on component surfaces, resulting in less time for equilibration between internal and external concentrations (Olson et al. 1985). The response of K^+ efflux is much less than that of NH_4^+ influx, probably because the gradient is much larger for K^+, so changes in the external concentration cause only minor changes in the gradient. As rain rate increases, the concentration of K^+ in throughfall decreases, showing a dilution effect (Fig. 8B). However, the NH_4^+ concentration increases, indicating that the canopy is able to take up a smaller fraction of the total NH_4^+ delivered by the higher rain rates. This is simply a matter of kinetics — diffusion through the cuticle to the presumed site of uptake is just not fast enough to keep pace with the increased deposition of NH_4^+. The actual fraction of deposited NH_4^+ taken up varies from 65% at 0.125 cm/h to 15% at 2 cm/h.

Efflux of K^+ and influx of NH_4^+ are linearly related to concentrations of these ions in rain (Fig. 9A). For these simulations, the concentrations of the ions were varied together, and the scale on the X axis ('concentration ratio') represents the concentration used for the simulation divided by the reference concentration (8 μeq/L K^+, 50 μeq/L NH_4^+). Increased K^+ concentrations in rain caused only slight changes in K^+ efflux, reflecting the fact that the large gradient between internal and external concentrations is only slightly affected by a 16-fold change in the small external concentration. For NH_4^+, however, the influx is proportional to the concentration in rain, with a 16-fold increase in concentration (12.5 to 200 μeq/L) causing a 16-fold increase in influx. For both ions, increased concentrations in rain cause increased concentrations in throughfall (Fig. 9B), however, the response for NH_4^+ is much larger.

Figure 10 shows the results of changing the surface area index (SAI) of the canopy. For these simulations, surface area of all canopy components was changed equally, and the vertical profile of relative surface area was unchanged. Open space at each level was decreased in correspondence to the increased SAI. As expected, efflux of K^+ and influx of NH_4^+ both increased with increasing SAI. There is evidence of a decreasing slope of the responses

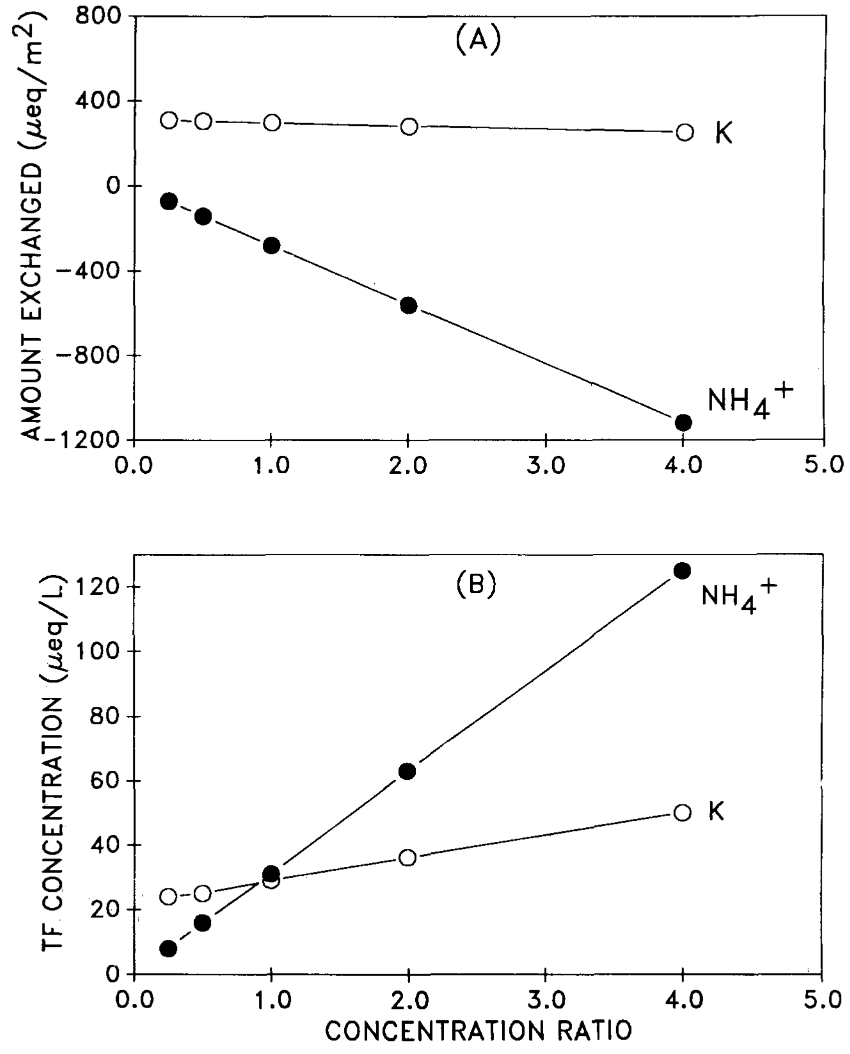

Fig. 9. Effect of concentration in rain on (*A*) canopy exchange, and (*B*) throughfall concentrations. Abscissa is concentration in simulated event divided by reference concentrations (K^+ = 8 μeq/L, NH_4^+ = 50 μeq/L.

for both ions at high SAI. Because only the top of the canopy is exposed to high concentration gradients, increases in SAI produce diminishing returns in the influx or efflux of ions. This effect is more pronounced at lower rain rates and less pronounced at higher rain rates in accordance with the changes in within-canopy concentration gradients. Results for 3 rain rates are shown in Fig. 10A. The increased efflux of K^+ at higher SAI produces

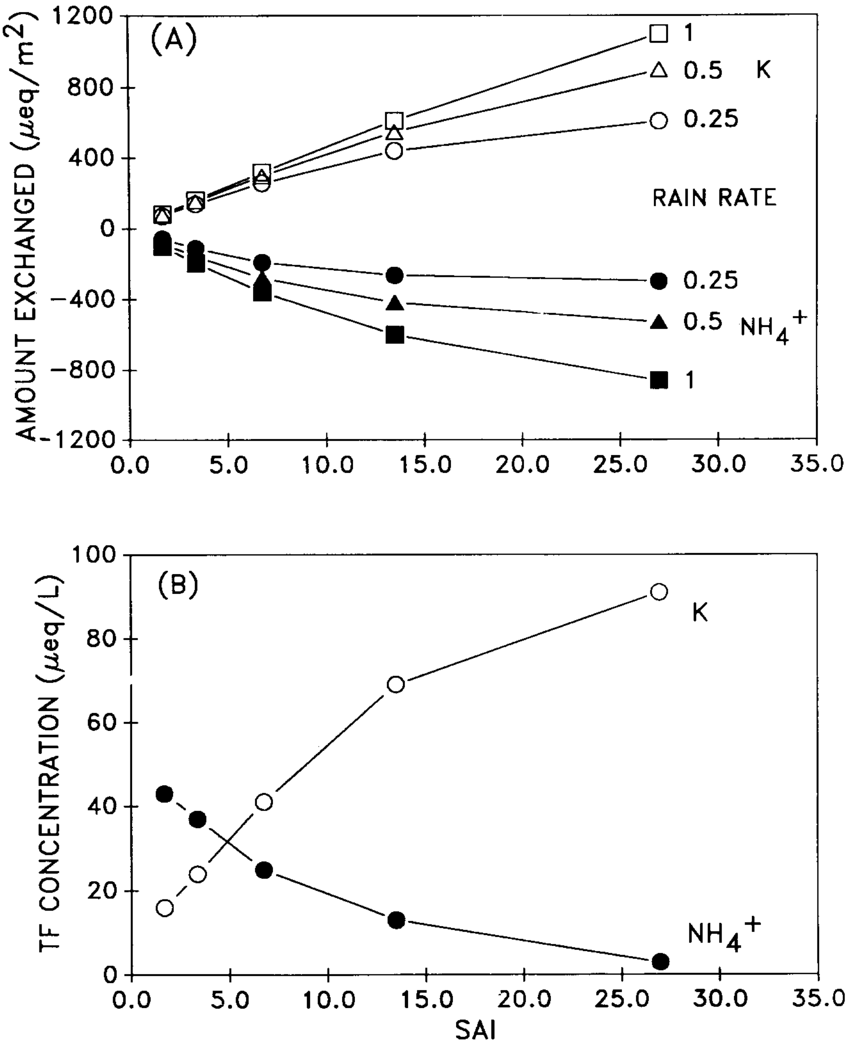

Fig. 10. Effect of changes in canopy surface area index (SAI) on (*A*) canopy exchange (illustrated for 3 rain rates), and (*B*) throughfall concentrations (at 0.25 cm/h).

increased concentration of K^+ in TF (Fig. 10B). Likewise, increased influx of NH_4^+ at high SAI produces decreased concentrations in TF.

Summary and conclusions

The model presented in this paper links the chemical behavior of canopy components with a multi-layer model of hydrologic flow to simulate chemical fluxes from the whole canopy. The chemical submodel is based on physically identifiable properties of canopy components, such as resistance to flux and apoplastic ion concentrations, which can be independently measured. Thus the basic structure of the model is general, and should be applicable to other forest canopies for which the parameterization data can be obtained.

This model is probably most useful as an heuristic tool, allowing easy examination of the ramifications of particular assumptions about the nature of canopy exchange, or testing of the effects of differing storm or canopy conditions. It will be more useful, we feel, for qualitative rather than quantitative predictions, because the number of interacting variables that must be specified make it difficult to achieve quantitative accuracy. The heuristic and qualitative uses are very valuable, however, and could benefit even more from addition of factors which have been ignored in this version. For instance, the role of pre-storm dry deposition may be important for some ions and could easily be incorporated with a submodel very similar to the cloud deposition submodel used here. The effects of acid rain and pollutant gases on foliar leaching of ions should be incorporated if those effects can be described mechanistically. Also, some aspects of the physiological state of the trees prior to and during the event certainly affect the leaching and uptake of ions, and those factors should be elucidated and incorporated into the model. Clearly, much research needs to be done before many of these processes are understood well enough to model. This type of model can incorporate the results of such studies and provide a framework within which to integrate the many biogeochemical processes interacting in forest canopies.

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