CANOPY ION EXCHANGE MECHANISMS
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ABSTRACT

Field studies have been conducted to identify mechanisms involved in the regulation of foliar leaching and throughfall chemistry in sugar maple (*Acer saccharum* Marsh.). In 1991 field and laboratory experiments were initiated to determine the relative importance of foliage *vs* stems in canopy ion exchange. This was accomplished by comparing the foliar leachate chemistry of normal sugar maple branches (leaves and stems) with that of artificially-defoliated branches (stems only). Please see the 1991 VMC Annual Report for details of this study and results. A second study designed to examine the contribution of leaf surface deposits to canopy ion exchange was performed in 1992. Leachate chemistry was examined for 30 sugar maple branches treated with an acidic solution, or a deionized water rinse, or left unwashed and then sequentially misted with an artificial precipitation solution at pH 3.8 or 5.3. Treated and untreated (control) branches were collected for tissue ion analysis to examine the relationship between ion concentrations in leachate and foliage. Ion inputs from surface deposits ranged from 0% of the Na to 50% of the Mg (an amount equal to that leached from sugar maple foliage over a 2 hour misting event). Contributions of ions from surface deposits were also relatively large for Ca, K, and NO_3, exceeding 40% of the total amount released. Ions removed from surface exchange sites accounted for 20% and 16%, respectively of the Ca and Na leached and smaller percentages of the Mg, K, and NO_3. Acidity of misting treatments affected the leaching of most ions except NO_3 which was unaffected. In general, more ions were removed from foliage misted with artificial precipitation solution of lower pH. Statistical analyses and interpretation of data from this study will continue in 1994.

INTRODUCTION

Integrated field and laboratory experiments were conducted with sugar maple (*Acer saccharum* Marsh.) during two growing seasons. In 1991, the objective was to identify the relative importance of foliage *vs* stems in canopy ion exchange. This was done by comparing the chemistry of foliar leachate from normal and artificially-defoliated branches, and evaluating the kinetics of ion exchange in each. Please see the 1991 VMC Annual Report for details of methods and significant findings from this portion of the study. Also in 1991, laboratory studies examined the ion transport properties of isolated leaf cuticles from the field foliage in order to calculate ion permeability rates. These data will be used to compare ion flux between cuticle and branch levels. In 1992, a second experiment designed to evaluate the contribution of leaf surface deposits to canopy ion exchange was performed. Because of an unexpected and rather lengthy delay caused by an equipment breakdown, we did not receive laboratory results until 1993. This report will cover progress made during 1993 in analyses and interpretation of data from the 1992 field experiment.

Objectives:

The broad goal of this work is to better understand mechanisms controlling foliar ion exchange (foliar leaching and uptake) in forest canopies. This is important in order to properly assess effects of changing atmospheric chemistry and climate on nutrient cycling processes in forests. Specific objectives of this project include:

1. characterizing the ion exchange rates in sugar maple foliage during artificial precipitation events,

2. identifying the relative importance of possible sources and sinks for exchanging ions,

3. relating tissue ion concentrations to ion exchange rates, and

4. developing a mechanistic model predicting canopy ion exchange rates.

METHODS:

In early August 1992, an experiment designed to evaluate the contribution of leaf surface deposits to canopy ion exchange was conducted. This was done by comparing the chemistry of leachate collected sequentially from sugar maple foliage previously washed with either an acidic solution at pH 3.3 (deionized water adjusted to pH 3.3 with HCl), deionized water, or left unwashed. Foliage receiving the acidic solution or deionized water prewashes were briefly rinsed with deionized water and allowed to dry for 0.5 hr prior to misting. All foliage was subsequently misted for two hours with an artificial precipitation solution at either pH 3.8 or 5.3. These treatments were applied in a randomized complete block design to 30 sugar maple branches chosen from four open-grown trees at the Proctor Maple Research Center (400 m elevation). A total of six treatment combinations (3 prewashes x 2 acid mists) were used and the experiment was replicated five times for a total of 30 branches treated. Treatment solutions were applied as a mist to small branches contained in polyethylene branch chambers (1 x 0.3 x 0.3 m). This was the same branch misting chamber design and collection method used in 1991.

Leachate samples were collected sequentially from each branch chamber over 15 min intervals during the first hour and over 30 min intervals during the second hour for a total of six leachate samples per chamber per replicate. All prewash and rinse solutions were also collected and saved for chemical analysis. Following misting, all treated branches, as well as untreated (control) branches from each tree, were collected for leaf and stem surface area determination and analysis of tissue ion concentrations. Relationships between ion concentrations in the leachate and foliage tissues will be examined. Leaf cuticles were also collected from treated foliaged for further ion permeability measurements. Leachate samples were analyzed for major ions at the Institute of Ecosystem Studies in Millbrook, NY and foliage samples were analyzed at the UVM Agriculture Testing Laboratory.

RESULTS:

Chemical analyses of leachate and foliage samples have been completed. Preliminary analysis of leachate data are summarized here, providing information about the relative contribution of foliage surface deposits to canopy ion exchange. Foliage surface deposits can be considered to be of two types based on their affinity for leaf and stem ion exchange sites. One category includes ions and other substances loosely held on foliage and stem surfaces; these can be easily washed off the surface with water. Alternatively, ions and ionic compounds can be tightly held to cation exchange sites on and within surface materials; these are released through ion exchange, especially with more acidic solutions. The acidic and deionized water (DI) prewashes were designed to elucidate these different mechanisms.

The following table summarizes the proportions of each ion removed from branches by the two prewash treatments, relative to the total removed (prewash + rinse + 2 hr misting). The proportion leached by the DI prewash is assumed to be mainly surface deposits, while that leached by the acid prewash is assumed to include more tightly held ionic substances. The difference, therefore, represents additional ions released under acidic conditions from foliar cation exchange sites.

TABLE 1. RELATIVE CONTRIBUTION OF PREWASH TREATMENT SOLUTIONS TO THE TOTAL AMOUNT OF IONS LEACHED

Prewash:	Ca %	Mg %	K %	Na %	NO_3 %	SO_4 %	Cl %
DI water	44	50	45	0	44	--	29
Acid sol.	64	61	51	16	46	44	
difference	20	11	6	16			

Results from the DI water prewash show that surface deposits, depending on the specific ion, can account for 0% (Na) to an amount equal to that leached from tissues over a 2 hour misting event (Mg). Contributions of ions from surface deposits were generally large for Ca, K, and NO_3, exceeding 40% of the total amount of each ion released. These are overall results, averaged across both acid mist treatments. The difference between the quantity of ions removed by the acid prewash solution and those removed by the DI water prewash represents the percentage of ions tightly attached to surface exchange sites. For example, 20% of the total Ca leached was removed from these exchange sites.

A substantial proportion of these ions were removed from the foliage simply by deionized water, suggesting they are relatively loosely held to leaf and branch surfaces. For some ions, however, such as Ca and Na, a substantial proportion of the ions available for leaching appear to be located on ion exchange sites. This source is presumably particularly important under acidic precipitation conditions. It is notable that the removal of K, which is quantitatively important in throughfall, is affected very little by the acidic prewash.

The pH of acid mist treatments did significantly affect the leaching of Ca and Mg. The relative amounts of ions leached from sugar maple leaf and stem tissues at pH 3.8, compared to pH 5.3, are shown in the following table.

'ABLE 2. RATIO OF IONS LEACHED AT pH 3.8 RELATIVE TO pH 5.3

Ca	Mg	K	Na	NO_3	SO_4
2.37	2.75	.20	1.22	1.00	1.16

More than twice the quantity of Ca and Mg was leached from sugar maple foliage misted with pH 3.8. Similar results were found for sugar maple by Lovett and Hubbell (1991). Under the pH 3.8 mist, significantly more K was leached during the first hour, but differences due to pH were no longer evident following a second hour of misting.

As was found in 1991, NH_4 was consistently taken up by sugar maple foliage (leaves and stems). Although NH_4 was released during misting of defoliated stems in the 1991 study, any NH_4 leaching from stems during this experiment was apparently masked by the uptake by leaves, presumably due to the large amount of leaf surface area compared to stem surface area.

DISCUSSION

Over much of the world forest canopies provide the dominant receptor surface for pollutants deposited to the earth from the atmosphere. As global environmental change occurs, it becomes increasingly important to understand the biological and chemical factors controlling rates of canopy nutrient exchange. It has been hypothesized that acidic deposition or other environmental stresses may affect foliar exchange mechanisms and possibly disrupt forest nutrient cycling processes. The concern is that these stresses might affect the flux of ions between the leaf apoplast and precipitation. This study will provide information about important sources, sinks, and pathways for ion exchange during precipitation. Knowledge of ion exchange rates and direction and mechanisms of transport at the leaf and branch levels are necessary first steps toward understanding nutrient/chemical cycling processes in plants and ecosystems.

Preliminary analysis of the data from these two field experiments indicate that our experimental approach was successful in teasing apart foliar leaching processes, including the relative importance of leaves and stems (1991 experiment) and the effects of acidity and prewashing (1992 experiment). In the first experiment, we showed that branch stems make a disproportionately large contribution (for their surface area) to foliar leaching. In both studies we saw that most of the flux of ions occurs during the first 15 minutes of a precipitation event. In the second experiment, we have obtained information about the sources of leached ions and the relative effect of pH on leaching.

FUTURE PLANS:

Work remaining includes completion of all statistical analyses, determination of relationships between leachate chemistry and canopy tissue ion concentrations, completion of cuticle structure and ionic permeability work, and development of a mechanistic model. The purpose of the model is to predict canopy exchange rates from information on the distribution of leaves and stems, deposition chemistry, and cuticle permeability. In 1994, we will also begin working on a manuscript describing this work and results.

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LITERATURE CITED:

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