USE OF TIME-DEPENDENT THROUGHFALL CHEMISTRY DATA TO CALCULATE THE DRY DEPOSITION FLUX

E-039

FINAL REPORT

to

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by

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ABSTRACT

Precipitation over a forested watershed is altered by a brief but significant interaction with plant surfaces, which act as a filtering mechanism for airborne gases and particles. This results in a major transfer to the forest floor of materials captured, washed, and leached from the forest canopy. Throughfall data collected at Woods Lake in the Adirondack Mountains of New York State under the Integrated Lake Watershed Acidification Study (ILWAS) showed major enrichment in acid anions and base cations similar to other reported studies. Hydrogen ion concentration was found to be dependent on tree species with coniferous canopies decreasing pH and deciduous canopy increasing pH of incident precipitation. However, controversy exists as to the net effect of the forest canopy, since leaching (foliar exudation) is the controlling mechanism rather than dry deposition for certain ions. Ionic enrichment of potassium for example, in throughfall is mainly due to exudation while sulfate enrichment results from deposition of particulate sulfate and gaseous SO_2. Sequential samples of wetfall and sequential samples of throughfall under deciduous and coniferous trees, were collected and chemically analyzed for major anions and cations. A simple washoff, mixing model was used to simulate throughfall chemistry and to decouple foliar exudation from dry deposition. The model was primarily based on the Leaf Area Index of each tree. Model results gave excellent predictions of the measured sequential throughfall using estimated values of dry deposition. The model can also be used to calculate dry deposition, if the sequential throughfall data and wetfall data are used as input variables.

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1. Introduction

Dry deposition of airborne gases and particles is a major atmospheric removal process estimated to be of similar magnitude with wet deposition. Trees and other vegetation act as natural filters in the environment by providing high surface area for dry deposition. Precipitation over a forested watershed is chemically altered as it cascades to the forest floor by a brief but significant interaction with plant surfaces. The result is a major transfer to the forest floor of chemicals captured, washed and leached from the forest canopy. The chemically altered precipitation is termed throughfall if it falls from the leaves and branches of the tree or stem flow if it runs down the tree trunk.

Event throughfall and stemflow data were collected at Woods Lake in the Adirondack Mountains of New York State during the Integrated Lake Watershed Acidification Study (ILWAS). Throughfall and stemflow showed major enrichment in acid anions and base cations similar to other reported studies (Eaton et al., 1973; Likens et al., 1977; Lindberg et al., 1979). Hydrogen ion concentration was found to be dependent on tree species with coniferous canopies decreasing pH and deciduous increasing pH (Johannes et al., 1985).

Chemical changes in throughfall can result from at least four major processes: washoff and dissolution of dry deposition, chemical reaction in the liquid phase, leaching from the vegetation, and chemical uptake by the vegetation. Controversy exists as to which mechanism is controlling and whether competing mechanisms exist for different chemical species.

Event throughfall data while providing information about net changes, masks details on the initial portion of an event where washoff of dry deposition is most likely to have the greatest effect. To study, the dynamics during an event, sequential samples of throughfall and wetfall were collected and chemically analyzed. The resulting data was studied using a simple mixing model.

2. Methods

Samples were collected in the Adirondack Mountains of New York State near Big Moose, NY (43° 49'N, 74°55'W) in September and early October 1981. A total of 9 events were sampled but events 6-9 were of limited value since the trees began to defoliate in early October.

Throughfall collectors were a modified version of the type used during ILWAS (Vasudevan et al, 1982). Each collector consisted of two 19 cm polyethylene funnels connected with tygon tubing to a 500 ml polyethylene collection bottle. A Whatman 500 filter was placed inside each funnel to remove any canopy debris prior to collection. Under each tree sampled and out in the open, a total event collector, sequential collector and rain gauge were located. Dryfall was collected between rain events using a white polyethylene bucket.

Samples were transported in the sealed collection bottles to the field laboratory and were processed as follows: sample volume, field pH, and conductivity were measured; the remainder of the sample was then filtered through a 0.4μm Nucleopore filter and stored in a clear polyethylene bottle. Samples were refrigerated at 3°C without preservatives until chemically analyzed. Dryfall samples were extracted with 250 ml of distilled-deionized water and processed in the same manner.

Samples were analyzed for pH, SO_4^{-2}, NO_3^-, Cl^-, NH_4^+, Ca^{+2}, Mg^{+2}, Na^+ and K^+. The cations (except NH_4^+) were measured using a Perkin Elmer Model 403 Atomic Adsorption Spectrophotometer. Anions and NH_4^+ were analyzed using

Technicon Auto Analyzers. Specific details of the chemical analyses are reported elsewhere (Johannes et al. 1981).

To determine differences between deciduous and coniferous throughfall chemistry, collectors were located under an American Beech tree (deciduous) and a Red Spruce tree (coniferous) of similar diameter. Leaf surface area and leaf area index were calculated for each tree using regression equations and the diameter at breast height (Whittaker et al., 1974). Calculated leaf area index for the American Beech and Red Spruce was 2.7 and 5.9 respectively.

Sequential samples were collected approximately every 60 ml. The time and volume were carefully recorded for each sample. During the later part of low intensity, protracted events, collection frequency dropped to hourly intervals. Complete details on sampling and physical characteristics of the trees are given by Dackson, (1983).

3. Results and Models

Typical sequential data showed highest ion concentrations during the initial portion of an event and decreased during the event. For most ions (except NH_4+) the coniferous tree gave much higher concentrations than the deciduous tree. Deciduous throughfall in the latter portion of an event had anion concentrations which were similar to wetfall. Cation concentrations in throughfall were one or two orders of magnitude higher than wetfall. Although most cation concentrations decreased during an event, the later concentrations for both deciduous and coniferous throughfall remained much higher than wetfall. Organic acids were not measured during the study, but since most of the samples were slightly colored (yellow or brown) and total anion to cation ratios were less than unity, organic acids were defintely present.

The cascade of water through a tree follows many different flow paths depending on leaf and branch structure. Contact time on each leaf surface is rather short and is dependent on many variables. In this preliminary model, the tree was conceptualized as a series of stages or levels where dissolution, leaching and mixing occurs. The number of stages for each tree was based on total leaf surface area. Since the model attempts to link dry deposition with throughfall, this area was divided by the projected area of the tree to put it on the same basis as the dryfall collector. The result is leaf area index and this value rounded to the next higher integer was used to determine the number of stages per tree. Dry deposition was assumed to be present on each stage at the start of an event. Estimates of dry deposition during these initial simulations were based on dry bucket measurements.

The relationship between wetfall and throughfall volume under American Beech was obtained by linear regression. Throughfall volume was found to be a linear function of wetfall volume (Figure 1). A least squares fit of the sequential data yielded the following regression equation for the American Beech (volume in liters).

$$[\text{Throughfall Volume}] = 0.711\ [\text{Wetfall Volume}] - 0.028.$$

An interpretation of this equation is that a tree has a unique storage capacity (generally termed interception or holdup) which must be exceeded before any throughfall is observed. A holdup parameter may be derived from the preceeding equation by setting the throughfall volume equal to zero and solving for the wetfall volume required (or 0.0392 L in this case). A similar linear regression was calculated for stemflow since stemflow was not measured but was required for the water, mass balance.

The model calculates throughfall volume and ion concentrations from one stage to the next with respect to time. Initially, a compartment is assumed to contain only dry deposition. The incoming throughfall (or wet deposition in the first stage) enters a stage and completely mixes with any water already present. Stages must be completely filled before any stemflow or overflow to the next compartment occurs. Calculations of concentrations were done on a basis of one minute, reflecting the accuracy of the experimental data.

Leaching parameters were determined by calibration. A linear regression between ion concentrations in throughfall and wetfall was calculated for each event and the slopes are listed in Table 1. Positive values indicate enrichment while negative values indicate removal. Ions were grouped using Duncan's test. Two groupings were indicated with several overlap ions. Group one was comprised of Na^+, Ca^{2+}, Mg^{2+} and K^+. Group two was comprised of NO_3^-, NH_4^+, Cl^- and possibly SO_4^{2-}. Overlap ions included Cl^-, Mg^{2+} and Na^+. Maximum estimates based on wetfall concentrations and on dryfall, factored by the leaf area index, showed that group one ion concentrations had to result from foliar exudation rather than dry deposition. No evidence was found for the group two ions and SO_4^{2-} to support enrichment by exudation.

The model was run first in a calibration mode with no leaching or dry deposition. The calculated water balance (Figure 2) showed excellent agreement with the measured values. Predicted SO_4^{2-} and K^+ concentrations (Figure 3 and 4) gave low values, as expected, with little correlation for K^+ with measured values. Inclusion of dry deposition in the model did not significantly change the K^+ concentrations but gave significantly better sulfate concentrations (Figure 5). Leaching coefficients based on mean concentrations were than introduced into the model. Potassium ion concentrations (Figure 6) increased significantly and gave reasonable dynamics.

The model was then rerun using a new and untested event with the leaching factors derived by calibration. Water balance, Sulfate concentrations (Figure 7) and potassium concentrations (Figure 8), showed excellent agreement with the measured results. Similar agreement was found for the other anions and cations with the exception of NH_4^+.

4. Conclusions

Ionoic species were found to be grouped into 3 sets: Washoff controlled (SO_4^{2-}, NO_3^- and Cl^-,); leaching controlled (K^+, Ca^{2+}, Na^+ and Mg^{2+}); and washoff-leaching competitive (NH_4^+). For the leaching controlled ions, dry deposition was of only minor importance, and then only in the very early stages of an event. Although leaching coefficients were emphirically fitted to the data during calibration, excellent agreement was found during comparison. In this preliminary study, the mass residue left on the leaves at the end of an event was not taken into account and resulted in somewhat lower concentrations during the initial portion of the event. In spite of these deficiencies, the model yields reasonable predictions of throughfall concentrations.

Table [illegible]

Black Box Res[illegible]

Event	H	SO4	NO3	Cl	NH4	Ca	Mg	Na	K
1	-.41272	-.24986	-.14884	-.05679	[illegible]	.02370	.02140	[illegible]	.05983
3	-.40984	-.56538	.02794	.02024	[illegible]	[illegible]	.01775	-.00282	.19982
5	-.19506	-.03989	-.04488	.02979	[illegible]	[illegible]	.02381	.00312	.09246
MEAN	-.37262	-.26974	-.09819	-.02700	[illegible]	[illegible]	.02112	.03662	.09122
SDEV	.08568	.16557	.07197	.04039	[illegible]	[illegible]	[illegible]	[illegible]	.05389

Groupings of averages ranked from high to low

H	SO4	NO3	NH4	Cl	Mg	Na	Ca	K
		A	A	A				
				B	B	B		
				C	C			
					D	[illegible]	[illegible]	[illegible]

5. SUMMARY

The proposed project was originally divided into three phases based on the sophistication of the models developed in each stage. In phase one, a very simple micro-mixing model was used to simulate throughfall chemistry based on an initial estimate of dry deposition. If the dynamics of the simulation did not match experimental values, a new estimate of dry deposition, was used and the simulation was repeated. Phase I was completely successful and estimates of dry deposition were reasonable based on literature values.

Phase two of the project which required complex backwards simulations in time has not been fully finished. This phase involves mainly software development to avoid trial and error solutions and has been conceptualized but not yet implemented.

Phase three of the project which involves an entirely different simulation, model and approach has recently been initiated. Results to this point are very preliminary and still conceptual in nature. Additional work is required.

6. References

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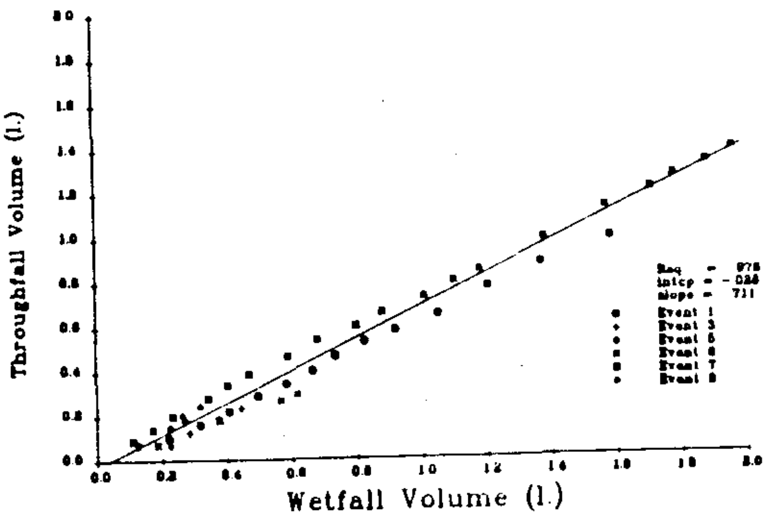

Figure 1 : Throughfall vs. Wetfall Volumes

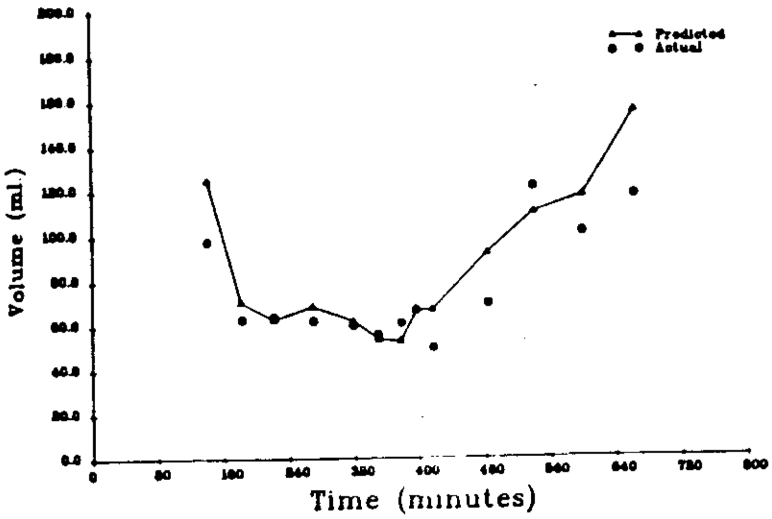

Figure 2 : Predicted Volume, Calibration Phase

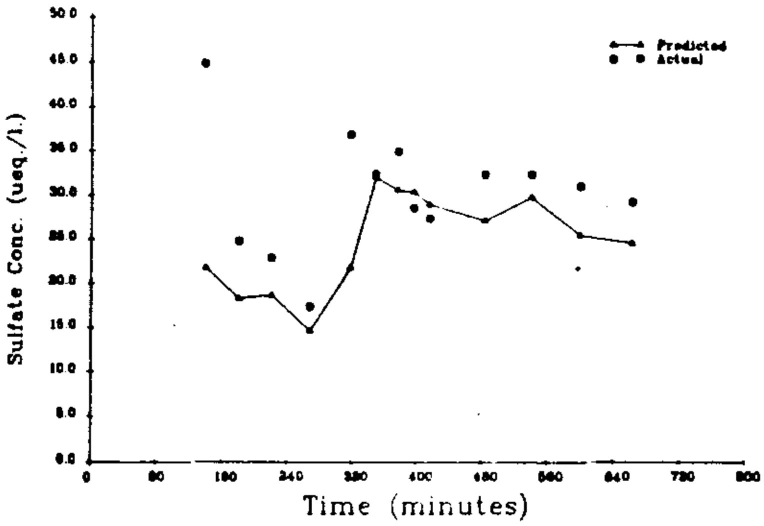

Figure 3 : Predicted Sulfate Concentration (no leaching or dry deposition)

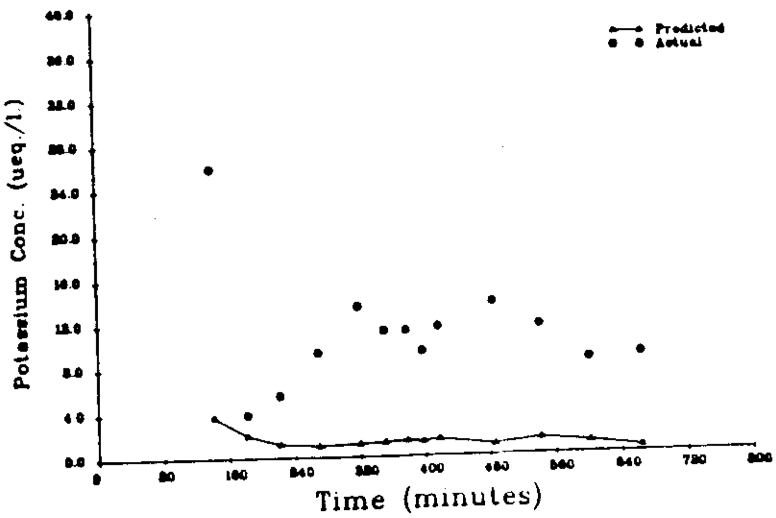

Figure 4 : Predicted Potassium Concentration (no leaching or dry deposition)

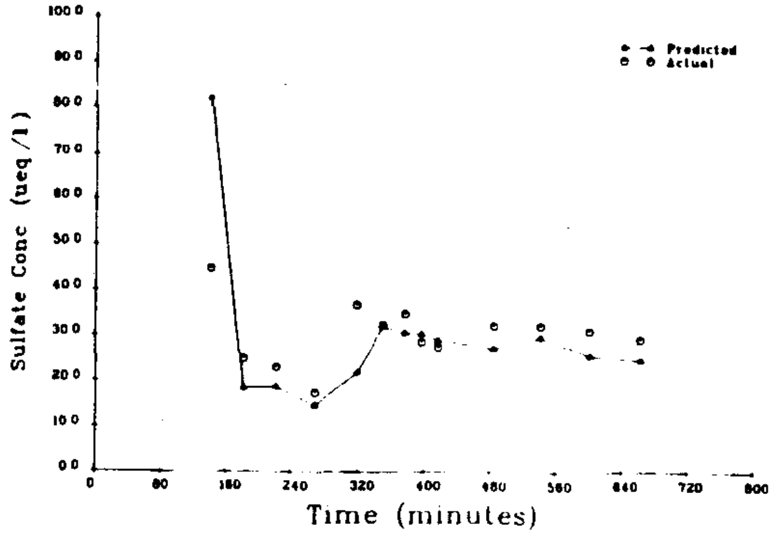

Figure 5 : Predicted Sulfate Concentration (dry deposition only)

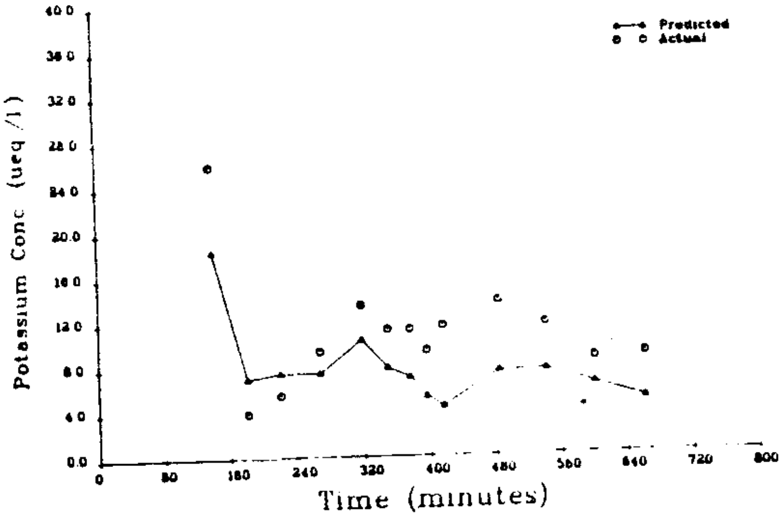

Figure 6 : Predicted Potassium Concentration (leaching and dry deposition)

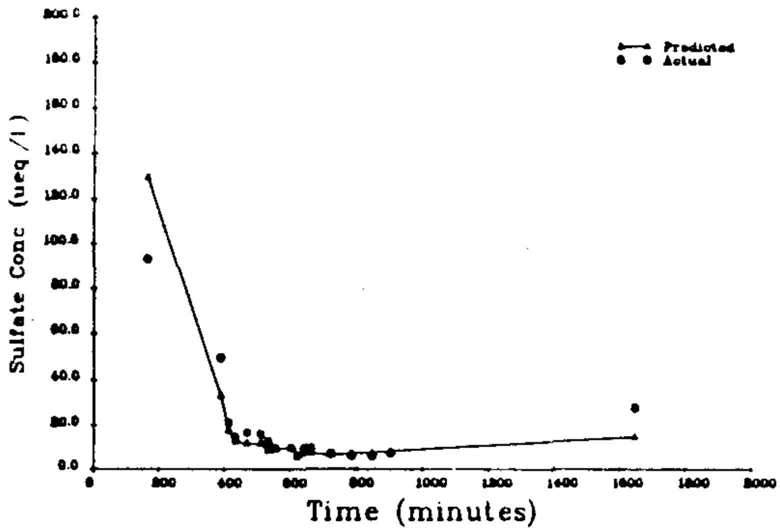

Figure 7 Sulfate Concentration vs. Time, Comparison Phase

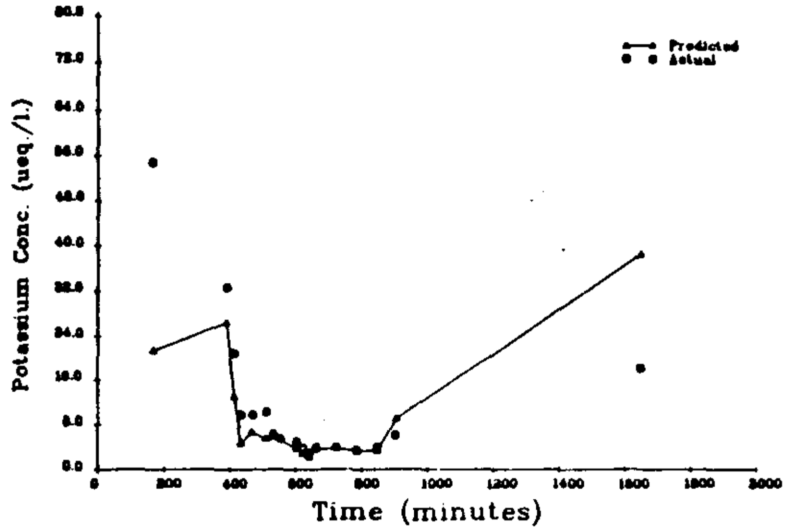

Figure 9 : Potassium Concentration vs. Time, Comparison Phase

7. CONTRACTUAL INFORMATION

Proposals-Submitted:

"Determination of Base Cation Flux to Surface Waters as Affected by Acidic Deposition, Decoupling of Atmospheric Deposition and Canopy-Soil Recycle" by Dr. Arland H. Johannes.

Submitted to the United States Environmental Protection Agency, $107,390/12 months. Rejected.

Proposals-In Preparation:

"Use of Time-Dependent Throughfall Chemistry Data to Calculate the Dry Deposition Flux," by Dr. Arland H. Johannes, National Science Foundation.

Publications:

"Modeling of Throughfall Chemistry and Indirect Measurement of Dry Deposition," Submitted to the Journal of Water, Air and Soil Pollution.

Presentations:

"Measurement of Dry Deposition Using Sequential Throughfall Chemistry Data," Paper No. 32e, presented at the Annual Meeting of the American Institute of Chemical Engineers, Chicago, Ill., November (1985).

"Modeling of Throughfall Chemistry and Indirect Measurement of Dry Deposition," Paper No. A-1(31), presented at the International Symposium on Acidic Precipitation, Muskoka, Canada, September (1985).

Theses and Dissertations:

"Modeling of Throughfall Chemistry and Indirect Measurement of Dry Deposition," Ph.D. thesis (in progress), Y. L. Chen, Oklahoma State University.

Other Graduate Students Partially Supported:

S. J. Chern (Ph.D. Student)

S. Siddiqui (Masters Students)