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An Empirical Model for the Variation in Concentration of Metal Ions during a Precipitation Event

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Abstract

The concentration of a pollutant in an air mass and the concentration of that pollutant in a series of rain water samples from a single event within that air mass, fluctuate during the course of the event. This the result of scavenging, diffusion, and advection processes. A simple mathematical model, containing only a scavenging term has had limited success in describing changes of concentration in rain water. To date, no attempt has been made to include diffusion or advection terms in the model. In this study, a two factor model was developed after determining that (1) the exponential scavenging term is dependent upon the amount of precipitation that has fallen rather than time elapsed and (2) that the magnitude of the diffusion/advection term is inversely proportional to the precipitation rate. Coefficients for the variables in the two terms [ψ_{av} and (bC_f) , respectively] were determined by the best fit of concentration curve derived from the model equation to experimental points. Time series from 24 rain events samples collected during 1987-88 and during the spring of 1998 were analyzed. The values of ψ_{av} were remarkably constant during both periods, but the two groups of ψ_{av} were different. The values of (bC_f) correlated moderately well with the concentrations of ions in the samples.

Introduction

The modeling of a time series of a single rain for the concentrations of solutes in rain water has proved to be a difficult problem because of the number of factors that determine those concentrations. Slinn (1977) developed a kinetic equation for the change in airborne particle concentration,

$$\partial X/\partial t = -(V \cdot \nabla)X + \nabla \cdot (K \cdot \nabla X) - \psi X + G + L \quad (1)$$

where X is the airborne concentration (mgL^{-1}) of particles or constituents of the particles in a polluted air mass, V is the wind velocity, and ψ is the rate constant for the scavenging of the species, X , from the air mass. The first term is the advection term, the second is the diffusion term, the third is the scavenging term, and the fourth and fifth represent other gains and losses, respectively.

Equation (1) was simplified and broken down (Slinn, 1975) to treat separately the particles attached to cloud water and the unattached (free) particles, $X_{\text{total}} = X_c + X_f$. Modifying slightly his equations, we arrive at

$$\partial X_f/\partial t = -\psi_f X_f + \nabla \cdot (K \cdot \nabla X_f) - a X_f \quad (2)$$

$$\partial X_c/\partial t = -\psi_c X_c + \nabla \cdot (K \cdot a \nabla X_f) + a X_f \quad (3)$$

where a is the rate of attachment of cloud particles to water

droplets.

A model was presented (Beverland and Crowther, 1991) which assumed that the scavenging term of equation (1) was the only significant factor early in a time series. Concentration data from within-event sampling of rain water provided information on the effect of scavenging and advective processes on the wet deposition of acidic species. High resolution sampling (every 0.5 mm of precipitation) was used to determine time series for nitrate and sulfate ion concentrations. Within events, falling concentrations were observed for the first 2 - 3 mm of rain, when scavenging processes are dominant. The scavenging term can be expressed as a simple first order term

$$X_c(r,t) = X_c(r,0) e^{-\psi(r)t} \quad (4)$$

where $X_c(r,0)$ is the concentration of particles of radius, r , within the initial rain sample of the time series, and $X(r,t)$ is the particle concentration at time, t , after the commencement of the time series. Since $\psi(r)$ varies slowly with r , it was approximated by ψ_{av} , the average scavenging efficiency for particles of all sizes. The varying particle, sulfate, and nitrate concentrations were modeled by a series of exponential terms dependent on t . The model simulation was restarted after any period of increased $X(t)$. It was assumed that these increases were due to an advection source. The period between the onset of an increase in concentration and the restart could not be modeled.

Modeling of sulfate and nitrate concentration time series curves is complicated by local sources of these ions. The oxidation of SO_x and NO_x during the event may be significant sources of these ions. The kinetic rate equations for these oxidations would have to be included in the model. The complication of a chemical reaction source can be avoided if analysis is limited to time series for the common metal ions: Mg²⁺, Ca²⁺, Na⁺, and K⁺.

The Beverland-Crowthier model was expanded by adding a term which incorporates the changes of ionic concentration in rain water due to the diffusion and minor advection of free particles in clouds. It was assumed that (1) ψ_{av} remained constant throughout the event, (2) diffusion and minor advection were sources or sinks of free ions which become attached to cloud water throughout the event, (3) diffusion of cloud water of concentration X(0) to the air column above the collection site was negligible compared to other sources, (4) metal ions were distributed uniformly in the cloud volume, (5) diffusion of cloud water was negligible, and (6) a major removal or supply of ions by advection was rare. The diffusion rate would depend on free particle concentration gradients which would be affected by the amount of precipitation, $\Delta\Pi$, that had left the cloud. Substituting the concentrations of any metal ion, j, in samples of cloud water (collected as rain water), $C_{c,j}$

$$\partial C_{c,j} = -\psi_{av} (C_{c,j}) \partial t + (bC_{f,j}) \partial t \quad (5)$$

where b is a combination of the operators in the first and second terms of equation (1). Solely for the sake of simplicity, $(bC_{f,j})$ was treated as a linear function of the total amount of precipitation which had been collected. An approximation for the integration of equation (5) over the time period Δt is possible for small values of Δt and by substituting equation (4) into equation (5)

$$C_{c,j}(t_2) = C_{c,j}(t_1) \exp(-\psi_{av} \Delta t) + (bC_{f,j}) \Delta t \quad (6)$$

It is just as likely that $\Delta C_{c,j}$ due to scavenging is a function of the amount of precipitation fallen, $\Delta\Pi$, during time Δt . Equation (6) may be rewritten

$$C_{c,j}(t_2) = C_{c,j}(t_1) \exp(-\psi_{av} \Delta\Pi) + (bC_{f,j}) \Delta t \quad (6)$$

where Δt is the time elapsed during the fall of $\Delta\Pi$ mm of rain. In this expression Δt is also understood to be $\Delta t/\Delta\Pi = 1/P$ (the inverse of the precipitation rate).

As either equation (6) or equation (7) could be used to construct the model time series curve for the events analyzed in this study, regression analysis was used to determine whether Δt or $\Delta\Pi$ was the better predictor for $C_{j,c}(t_2)$ or π_2 during the time early in the rain event when the scavenging factor is predominant.

Regression fits of the first three to five samples in the

time series of seven rain events indicated that either Δt or $\Delta\Pi$ was an adequate predictor in the exponential portion of the concentration curves. The R² for both predictors were the same for five samples. The R² for Δt was greater in one and in the other (with a highly variable precipitation rate), R² for $\Delta\Pi$ was greater. It is obvious from the later portion of Figure 1 that the diffusion/minor advection factor, more important at that time, varies with the inverse of the precipitation rate which appears in disguise in equation (7) as Δt , the time elapsed during a segment of precipitation $\Delta\Pi$ (or $\Delta t/\Delta\Pi = 1/P$). We chose to use equation (7) to model the concentrations of the metal ions.

Methods

Sample Collection and Analysis.--The sampling site for the 1987-88 samples was an area near downtown Jonesboro, AR and, for the 1998 samples, an area of the Arkansas State University campus in eastern Jonesboro. Both sites were free of overhead obstructions. The collectors consisted of polycarbonate funnels of 15 and 25 cm diameters. Samples of 1 - 5 mm of rainfall were collected in 1987- 88 and of 0.30 - 1.31 mm in 1998 and fed into polycarbonate receivers. The samples were immediately transferred to polycarbonate bottles, filtered through 0.45 μ m micropore filters, and either analyzed within 24 h of collection or frozen to await analysis by atomic absorption or atomic emission spectroscopy.

Empirical Fitting of Model Concentrations to Experimental Data.--For each metal ion, model $C(j,c,\Pi)$ values were calculated for every 0.1 mm of rainfall for 1987-88 samples and for every 0.05 mm for 1998 samples. The actual concentrations of the first rain water sample was used as the model's $C(j,c,\pi_1)$. The coefficients, (bC_f) and ψ_{av} , in equation (7) were determined by a trial and error assignment of values until the deviation of calculated points from experimental points (s) was minimized by the following method.

- 1 A first estimate of ψ_{av} was made from the slope of the first 3 - 5 points in the time series in a plot of the concentrations against amount of rain fallen, so that numerical integration of the 0.1 mm segments along the model curve for each sample should yield
$$\int_{\pi_1}^{\pi_2} C_{model} \partial\Pi = C_{sample} \Delta\Pi$$
- 2 The initial and final values for (bC_f) were estimated from the values necessary to bring the exponential curve up to the experimental concentrations. The intermediate values of this parameter, $(bC_f)_i$, are calculated from $[(bC_f)_{initial} (\Pi_i - \Pi_{initial}) + (bC_f)_{final} (\Pi_{final} - \Pi_i)] / (\Pi_{final} - \Pi_{initial})$.
- 3 $\Delta t/\Delta\Pi$ for each model segment of the calculated time series was estimated from interpolating between the samples' average inverse rainfall rate,

$(\Delta t/\Delta \Pi)_k$ (see Figure 1). The uncertainty of the estimate is small if the sample sizes are small and/or if the rainfall rate is constant.

- The values of the three parameters [ψ_{av} , $(bC_f)_{initial}$, and $(bC_f)_{final}$] were adjusted until Σs was minimized and the following constraints are met as closely as possible.

The final fit must satisfy several constraints.

- The first order (concentration independent) scavenging rates of the four metal ions should be the same:

$$\psi_{av}(\text{Mg}) \sim \psi_{av}(\text{Ca}) \sim \psi_{av}(\text{K}) \sim \psi_{av}(\text{Na})$$

- The concentration of an ion, j , in the rain water samples should be proportional to the concentration of that ion attached to cloud water at the time of collection:

$$b_j C_{f,j} \propto C_{c,j} \quad \pi_2 \quad \text{and} \quad b_1 C_{f,1}/b_2 C_{f,2} = C_{c,1}/C_{c,2}$$

- For all points, $\int_{\pi_1} C_{\text{model}} \partial \Pi = C_{\text{sample}} \Delta \Pi$

Results

A good fit was obtained for model equation concentrations with experimental data for Mg^{2+} and Ca^{2+} in 24 of the 26 time series rain events. The fits for the Na^+ and K^+ occasionally proved less satisfactory, so discussion will concentrate on the former two species. All constraints listed above were well met for the fits, but the correlation coefficients for (bC_f) with C_c were somewhat disappointing, 0.5 and 0.6 for Mg^{2+} and Ca^{2+} , respectively.

Figures 1 and 2 present the fit for a complex event of 1988 and for two simple events from 1998, respectively. Table 1 lists the mean ψ_{av} , the median of the initial values of (bC_f) , and median values for (bC_f) , the change in (bC_f) between two consecutive model points for both the 1987-88 and 1998 samples. If three outliers are removed from the list of 1987-88 values of ψ_{av} , the average value becomes 0.35 ± 0.08 .

Table 1: Empirical Values of Constants in Equation (7)

Year	ψ_{av}	Median $(bC_f)_0$		Median $\Delta(bC_f)$	
		Mg	Ca	Mg	Ca
1987-88	0.41 ± 0.018	0.020	0.059	$+2.0 \times 10^{-6}$	$+1.4 \times 10^{-5}$
1998	1.4 ± 0.1	0.12	0.40	-4.7×10^{-5}	0.0×10^{-5}

Discussion

In most cases, it was possible to derive a good fit from a model that considers scavenging and diffusion/minor advection as factors in determining the concentration of Mg^{2+} and Ca^{2+} in a time series of rain water samples. The assumption of a linear change in (bC_f) with time elapsed during the event appears to be valid. The magnitude of the diffusion effect should decrease as the concentration gradient is reduced as free ions leave the cloud during the rain event, i.e. diffusion should yield negative values of (bC_f) . Since half of the (bC_f) are positive and half negative, this factor is probably a combination of diffusion and continuous small magnitude advection terms.

Increases in sample ionic concentrations during an event are usually caused by diffusion and small magnitude advection that outweigh the scavenging effect later in the time series during periods of low precipitation rate. Sudden, large magnitude additions of ions were observed in only 2 events (see Figure 2) and sudden drops in ionic concentration were not observed at all. Thus it can be assumed that

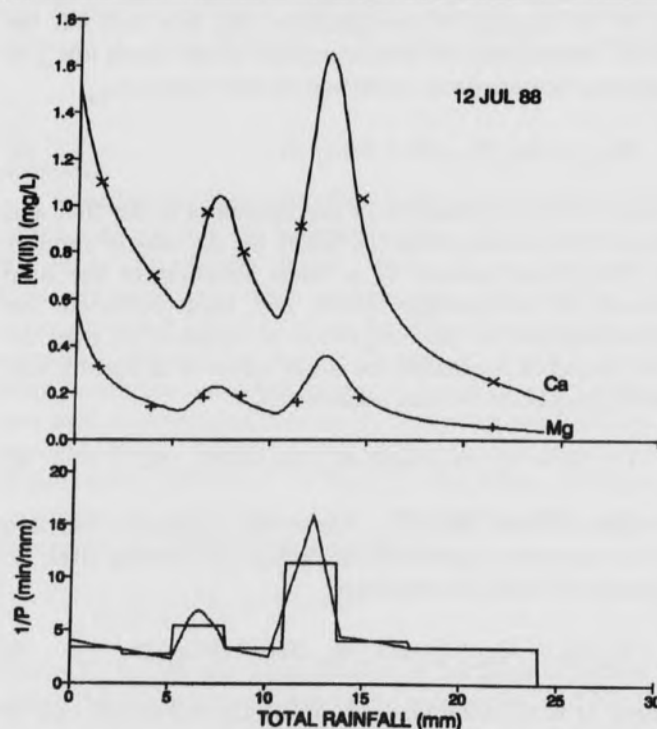


Fig. 1. Variation of concentration with amount of precipitation fallen and the rate of precipitation in a complex event. Upper plot: Fit of model concentration of Mg^{2+} and Ca^{2+} (line) to data points (x and +, respectively) Lower plot: Estimation of $(\Delta t \Delta \Pi)_i$ (curved line) from the amount of rain water collected in individual samples (bar chart).

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major advective additions are rare.

The ψ_{av} values were unexpectedly constant during the 11 months of sampling in 1987-88 and for the 5 samples taken in Spring 1998. However the values for the two groups are very different.

This study shows that the concentration of metal ions in a same series for a single rainfall can be modeled by a kinetic equation of two terms. The first term is the well-known first order exponential term. The second, a term describing the effects of diffusion and constant low-magnitude advection, is probably a complex combination of terms but it can be effectively approximated by assuming a simple linear change in the term with time from the onset of the event.

The major disadvantage of this model is that it is not possible to assign a physical interpretation to the individual values of ψ_{av} . Perhaps a study of the meteorological condi-

tions during rain events will lead to such a physical interpretation.

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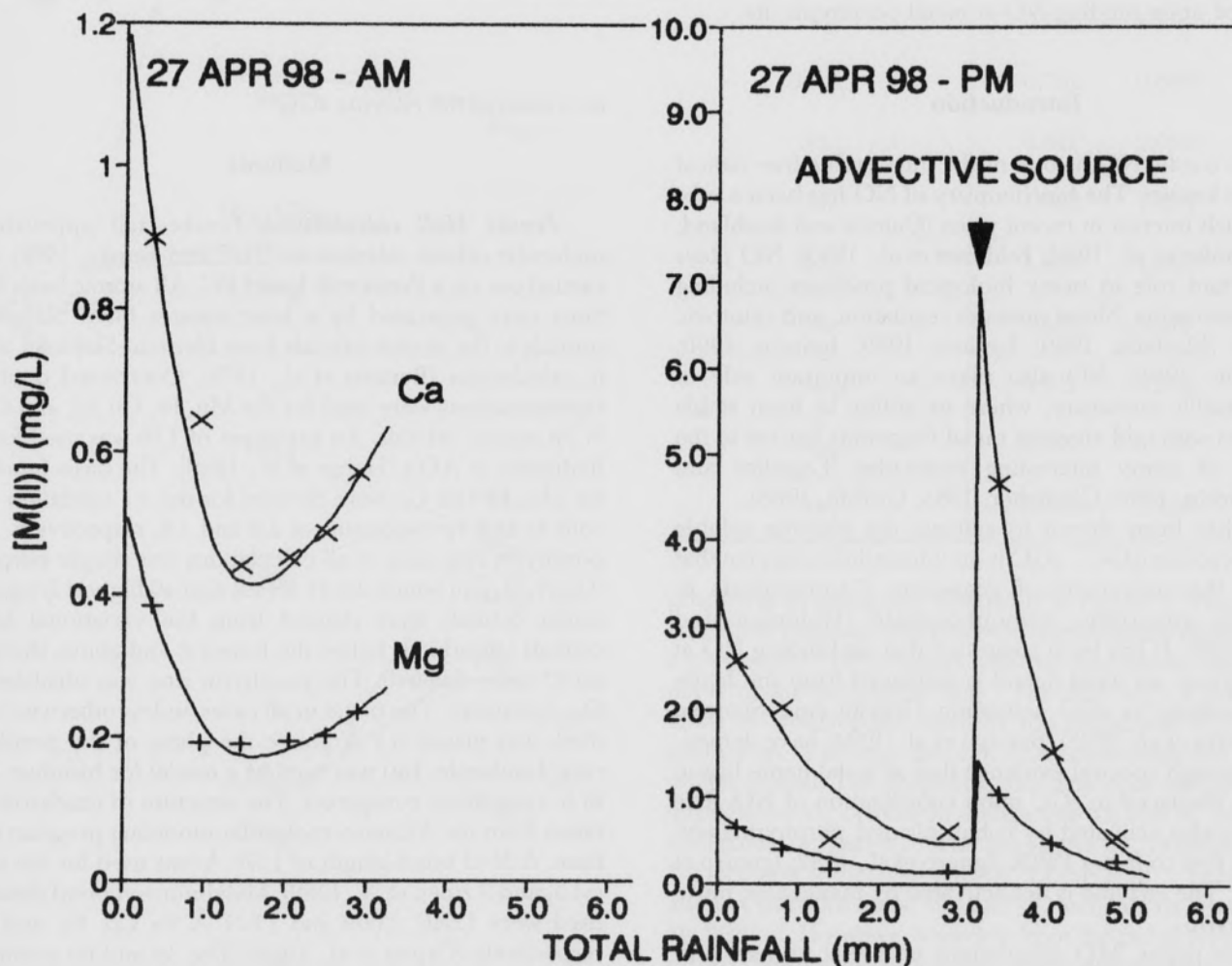


Fig. 2. Fit of model concentration of Mg^{2+} and Ca^{2+} (line) to data points (x and +, respectively). Left plot: Scavenging controls concentration early and diffusion/minor advection control late. Right plot: Scavenging controls concentration at all times except for a sudden advective addition of ions.