Atmospheric deposition to a rural tropical site

Analysis of the relationship between amount of precipitation and chemical composition

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Abstract. Chemical analysis of Na, K, Ca and Mg in bulk deposition, using 230 events, showed that variations in atmospheric deposition are explained better by measured concentration than by precipitation amount. In addition, measured concentration is related to precipitation by a significant power function with the exponent near −1. These observations led us to propose an inverse linear model which makes it possible to calculate two parameters: one of them is indicative of the mean composition of "cloud rain" and is assumed to be typical for the study area; the other parameter is representative of particulates, aerosols and gases that are washed out from the atmosphere in the initial phases of precipitation, including dry deposition. This initial component represents an average of 64% of the bulk deposition for the cations studied. The functions that explain the relations between atmospheric deposition and measured concentration are, within statistical limits, equal for the four cations.

Abbreviations: D — Atmospheric deposition (g/ha) on an event basis, P — Precipitation amount (mm) on an event basis, C— Measured concentration (mg/l) on an event basis, i — Sampling replicates

Introduction

Bulk deposition sampling is the simplest and most inexpensive way to estimate the contribution of atmospheric input to geochemical fluxes. Owing to a mixture of dry and wet deposition in the samples, the use of bulk deposition is discouraged in studies of rain chemistry, but it has been considered adequate and even mandatory (Galloway & Likens 1978) to evaluate transport to ecosystems and to measure patterns of nutrient inputs of significance to plants (Kellman et al. 1982).

Our work aims to maximize the information from bulk deposition data. Although bulk deposition has been used extensively in the Northern Hemisphere, in many tropical countries there are few representative data of precipitation amount and its chemistry on regional and temporal scales. In Brazil, methods of fractionated collection have only recently been introduced (Mello et al. 1987; Forti & Moreira-Nordemann 1989), but they usually require sophisticated techniques and expensive equipment.

When collectors are kept open to both wet and dry deposition, the chemistry of the water sampled at the end of an event is a result of:

— the removal as precipitation of particles that have nucleated water condensation and grown into cloud droplets, and eventually into raindrops;
— the removal of dry particles and gases by already formed raindrops that capture them below the cloud base either by inertial collection, by diffusion, or by phoretic forces, depending on the aerosol size; and
— the washing of particles deposited in the collector surface during the dry period by the processes of sedimentation, impaction, or adsorption (Twomey 1977).

The atmospheric deposition D (mass per unit area) is calculated by multiplying a concentration C (mass per unit volume) measured in the rainwater by an amount of precipitation P (volume per unit area) on an event basis. Our hypothesis is that the concentration measured in the water retrieved from the collectors as bulk deposition can be disaggregated into two components, which, on the average represent:

— smaller aerosols originating within the cloud by diffusion to a cloud droplet that later becomes part of a raindrop (rainout process), and
— the component originating below the cloud base by washout and by sedimentation or impaction during dry periods (Iribarne & Cho 1980).

We also discuss the relationship between atmospheric deposition D and its two factors, C and P, answering the questions:

— are P and C independent of each other? and
— are P and C equally important in bulk deposition?

Methods

We analyzed samples of 230 rainfall events collected as bulk deposition

from October 1983 to March 1986 to evaluate atmospheric inputs of Na, K, Ca and Mg to an experimental agricultural field designed to test soil water erosion. The study area is near Rio de Janeiro (22° 45′ S, 41° 43′ W), Brazil, 33 m above sea level and 22 km from the Atlantic coast. The weather is Aw, after Köppen, with humid summers and dry winters. The mean maximum temperature is 32.5 °C in February and the minimum is 15.0 °C in July. Based on a recurrence interval of 45 years, 1984 was the driest year on record (700 mm), and the precipitation amount (1520 mm) in 1985 was above the average annual rainfall (1250 mm) (Carvalho 1987). Neverthless, comparing the two years, the differences in precipitation amount are due to a few showers greater than 30 mm, a pattern of tropical rainfall also reported by many authors (Franken & Leopoldo 1984; Coelho Netto 1985).

The collection of precipitation was made on two pairs of white polyethylene funnels (diameter $= 21$ cm) positioned 40 m apart, placed 1.5 m above the grassy ground and linked by plastic tubes to 5 l capacity plastic bottles (Brown et al. 1989). To prevent evaporation, the bottles were protected from sunlight in an underground hole, and the entrance and air exhaust tubes were coiled to trap water vapor. The collectors were kept open all the time, even during dry periods. After each sampling, all of the equipment was washed with deionized water. It was washed monthly with 6 N HCl to reduce algal growth. There was no sample preservation, since the natural measured pH is considered to be self-preserving for Na, K, Ca and Mg analysis (Galloway & Likens 1976).

Sampling of bulk deposition suffers from many types of interference, mainly in rural sites (Swank & Henderson 1976; Hendry & Brezonik 1980; Molitor & Raynal 1982; Wolff et al. 1983; Colin et al. 1990). In agricultural fields, interference can be strongly influenced by crop management cycles and/or meteorological conditions. To minimize intrusion of flying insects and birds (Graustein 1981), we covered the lower part of the funnels with a 1-mm mesh nylon screen (Brown et al. 1989). Smaller particles of various sizes may be recycled either by resuspension of dust by the wind (Colin et al. 1990; Prospero et al. 1981), by pollen production (Lewis & Grant 1978), by release from the plant surfaces (Beauford et al. 1977) or by fertilizer inputs. Although these aerosols can enter the lowest atmosphere and become available for dry deposition, depending on settling velocities and/or residence times (Kritz & Rancher 1980; Stewart et al. 1990), their immediately settling onto the collectors was attenuated by washing the funnels twice weekly during dry periods, in an attempt to minimize the influence of this dry deposition in this study. In addition, Vaugham (1976) (in Lewis & Grant 1978) has reported that leaves collect dry deposition more efficiently than the

smooth funnel surfaces do. Thus any overestimation of the dry fallout to the ecosystem should have been prevented.

At the end of each rainfall event the precipitation volume was measured with calibrated cylinders, 100 ml aliquots were sampled for chemical analysis of Na^+ and K^+ (emission photometry) and Ca^{++} and Mg^{++} (atomic absorption spectrophotometry), without the addition of any interference suppressor (APHA 1984). The four replicates were not pooled; they were used to offer protection against systematic errors (Lewis & Grant 1978) and to evaluate analytical, sampling, and spatial variability (Galloway & Likens 1978).

The atmospheric deposition D for each cation in each rainfall event was calculated as

$$D = \left(\sum_{i=1}^{4} Ci \times Pi \right) \bigg/ \sum_{i=1}^{4} i,$$

where i are the sampling replicates. Rainfall amount, its chemical concentration, and atmospheric deposition have log-normal distributions (Chi-square, $p \gg 0.05$). Pearson's coefficient was used to indicate the correlation between the log-transformed variables. Least-square linear regression, with sensitivity analysis for outliers, was used to find the best function fit between these variables (Snedecor & Cochran 1980).

Results and discussion

All of the correlations between log-transformed variables, excluding values near the detection limit of measured concentrations (Table 1), are significantly different from zero ($p < 0.01$). We wish to stress three main points:

— precipitation is inversely correlated with the measured concentrations of the four cations;
— correlations between C and D are higher than between P and D; and
— correlations between C and D are equal for the four cations (Chi-square, $p \gg 0.05$).

The relations between P and C of Na, K, Ca and Mg (Fig. 1a—d) show that when P is large C tends to an asymptotic 'non-zero' value, independent of P (an outlier not shown in the graphs has a precipitation of 190 mm and confirms this behavior of C). At small P, C is very variable, with high and sharply decreasing values for precipitation events below 10 mm. The coefficients of potential functions (Table 2) are the

Table 1. Pearson's coefficients matrix of log-transformed variables.*

		P	Na C	Na D	K C	K D	Ca C	Ca D	Mg C	Mg D
P		1								
Na	C	−0.45	1							
Na	D	0.20	0.78	1						
K	C	−0.41	0.60	0.37	1					
K	D	0.29	0.30	0.53	0.75	1				
Ca	C	−0.52	0.64	0.34	0.66	0.31	1			
Ca	D	0.26	0.34	0.55	0.40	0.61	0.69	1		
Mg	C	−0.52	0.84	0.56	0.77	0.43	0.76	0.41	1	
Mg	D	0.29	0.55	0.80	0.50	0.74	0.39	0.69	0.66	1

* ($n = 152$; $r > 0.21 \Rightarrow p < 0.01$). P = precipitation amount (mm); C = concentration (mg/l); D = atmospheric deposition (g/ha).

best fit between these variables, chosen from linear, exponential and polynomial fits. A general tendency like this was found by Lindberg (1982), who fitted some exponential equations to sulfate and transition metal data, also inverse with respect to P, and with independent coefficients related to asymptotic concentrations. Hendry & Brezonik (1980) showed for individual storms that the specific conductance decreased rapidly and reached a steady-state value near 10 μmho/cm within 20 min, a dilution behavior which resembles that of our event data set. Furthermore, Swank & Henderson (1976) stressed that the quantity of ions such as Ca, Mg and K which enter bulk precipitation primarily as dry fallout, is independent of precipitation amount.

Our results indicate an effect of linear dilution of precipitation amount on the initial conditions of the atmosphere and collecting system. The asymptotic values of C with large P suggest that the composition of rain after the lower atmosphere is cleansed may be related to the composition of the water available for precipitation from the clouds.

If the above assumptions are correct, then observed values should obey an equation of the type

$$C = R + I / P,$$

with a high degree of correlation. Here C is the concentration and P is the rainfall amount measured on an event basis; R is a parameter indicative of a mean concentration in the clouds, representing a typically regional value; I is indicative of the mean initial atmospheric conditions below the clouds and of the dry deposition on the collectors.
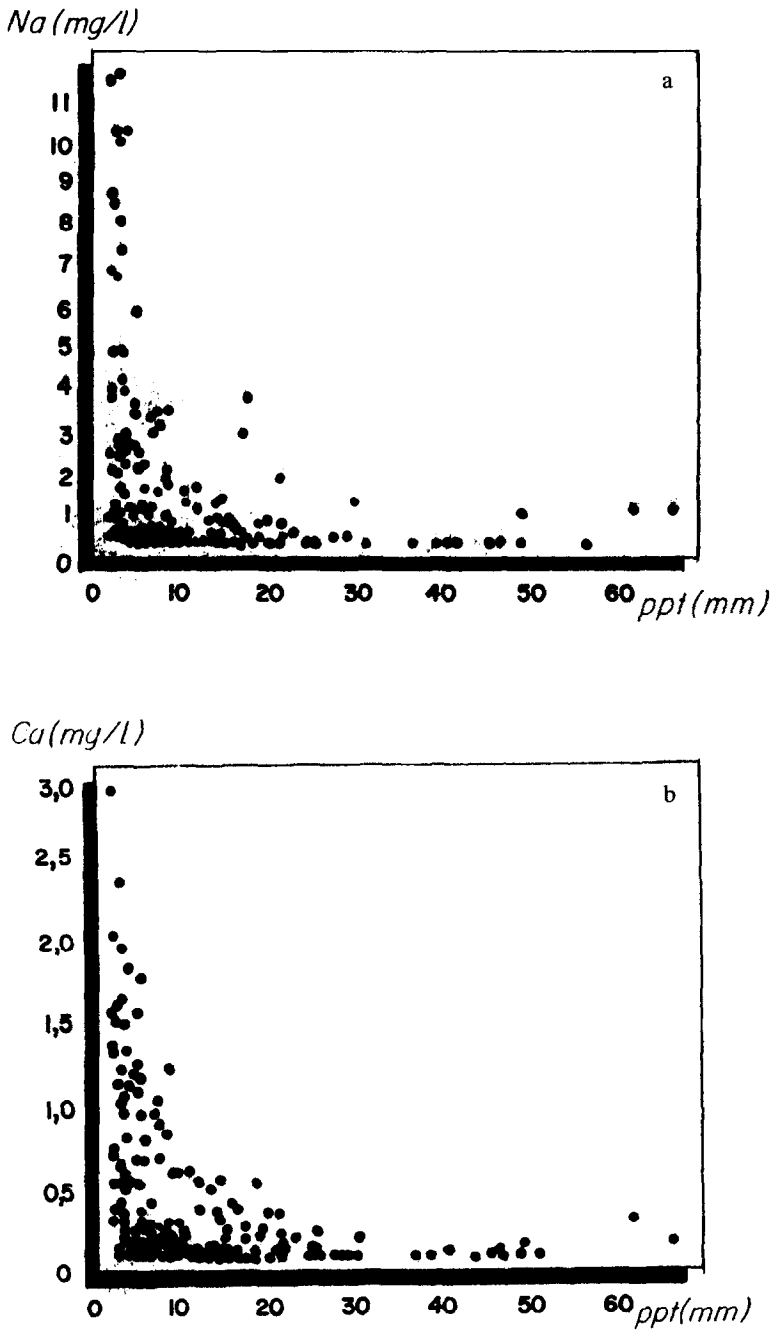
Fig. 1. Relation between precipitation (ppt-mm) and: (*a*) sodium concentration (Na mg/l) *n* =203, (*b*) calcium concentration (Ca-mg/l) *n* =205.
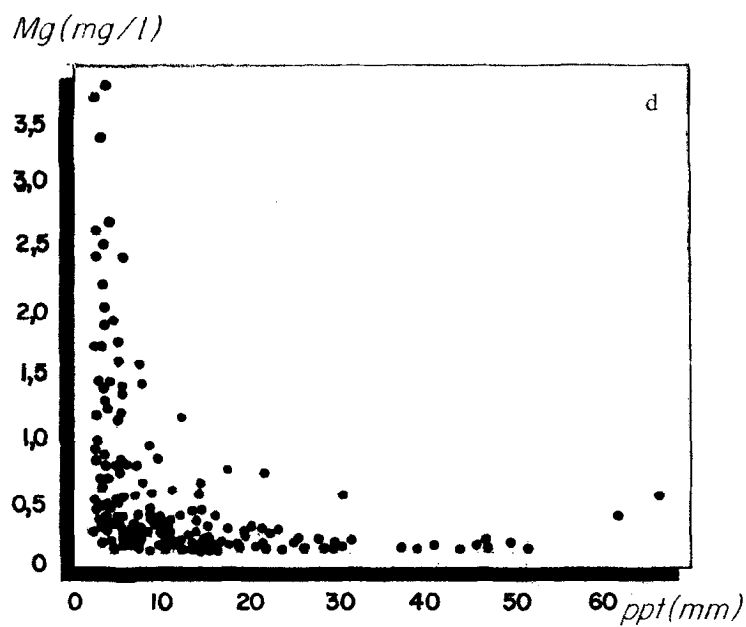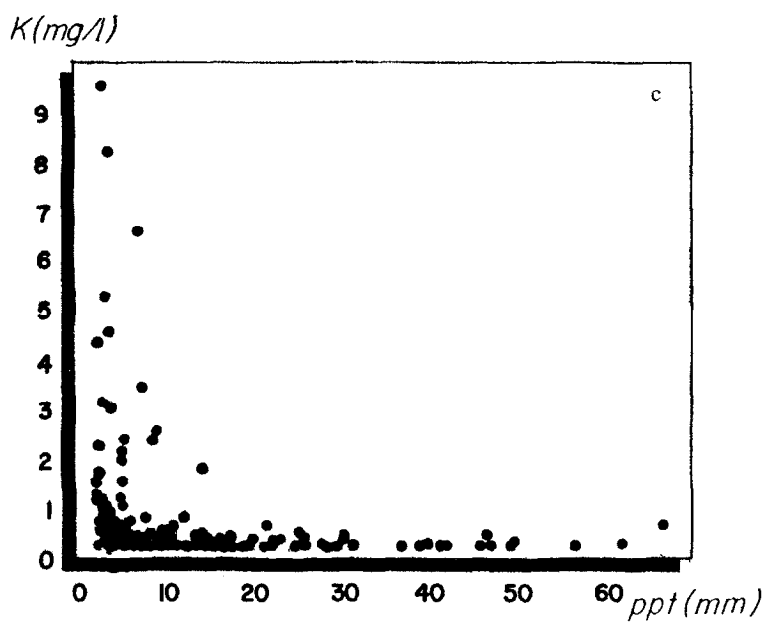
Fig. 1. Relation between precipitation (ppt-mm) and: (c) potassium concentration (K mg/l) $n = 196$, (d) magnesium concentration (Mg-mg/l) $n = 211$.

Table 2. Potential function of best fit between the precipitation amount (P-mm) and its measured concentration (C-mg/l).

Equation		Coefficients		
$C = a \cdot P^b$	n	a	b	$r*$
Sodium	203	2.80	−1.08	0.58
Potassium	196	0.70	−0.75	0.51
Calcium	205	0.85	−0.93	0.59
Magnesium	211	1.07	−0.92	0.61

* All $r \neq 0$; $p \lll 0.01$.

The coefficients of the inverse linear equation above, fitted to each of the four cation sets, are shown in Table 3. Although the Pearson's coefficients only have an illustrative meaning, they are far from zero, emphasizing the affinity of our proposed model to the observed conditions. The value of I for sodium may be associated with the proximity of the sea, 22 km to the south.

As a first approximation, testing the model validity, data from 1984 and 1985 were selected from the whole set. Table 4 shows the percentage variation between calculated and measured atmospheric annual deposition, expressed as the percent difference from the mean. It also shows the annual contribution of I, and emphasizes that 1984, having more frequent and longer dry periods, had higher contributions of I than 1985.

The spatial variability of these particulates in the atmosphere was evaluated by comparing four different regions, including two rural sites and two near-shore sites. Although this variability among elements (Table 5) has shown that the results are site-specific, our data are within

Table 3. Inverse linear function between the precipitation amount (P-mm) and its measured concentration (C-mg/l).

Equation		Coefficients		
$C = R + I / P$	n	R	I	$r*$
Sodium	204	0.11	5.06	0.53
Potassium	196	0.15	1.66	0.31
Calcium	205	0.05	1.42	0.62
Magnesium	212	0.08	1.65	0.56

* All r illustrative; $r \neq 0$; $p \lll 0.01$.

Table 4. Inverse linear model test, using 1984 and 1985 data set.

Characteristics *	Na		K		Ca		Mg	
	1984	1985	1984	1985	1984	1985	1984	1985
n	73	88	70	88	77	87	74	88
P	697	1519	697	1519	697	1519	697	1519
Dc	4.5	6.1	2.2	3.7	1.4	2.0	1.8	2.7
Dm	4.8	5.6	1.5	3.8	1.2	1.5	1.9	2.5
(Dm −Dc)/(Dm +Dc) (%)	3	4	18	1	7	14	3	3
I/Dc (%)	83	73	53	39	76	62	69	54
I (g/m^2)	0.37	0.44	0.11	0.14	0.11	0.12	0.12	0.14

* Dm = measured atmospheric deposition (kg/ha); Dc = calculated atmospheric deposition (kg/ha); P = precipitation amount (mm); I = initial amounts removable by rainfall.

Table 5. Particulates in the atmosphere.

Deposition	Na	K	Ca	Mg	References
g/m^2.yr	0.46	0.07	0.48	0.08	Hendry & Brezonik 1980
dry/(dry +wet) (%)	46	22	49	36	
g/m^2.yr	1.03	1.90	5.82	1.24	Swank & Henderson 1976
dry/(dry +wet) (%)	28	64	38	46	
g/m^2.yr	0.27	0.12	0.15	0.09	Forti & Moreira-Nordemann 1989
dry/(dry +wet) (%)	85	57	33	56	
g/m^2.ano	0.88	0.27	0.53	0.17	Mello et al. 1987

these ranges, as shown by the I (g/m^2.yr) values for 1984 and 1985 in Table 4. Our data also confirm that the composition of the soil-like aerosols at individual sites resembles the composition of the resuspended soil at the same site (Cahill et al. 1981).

The inverse linear model seems to be a helpful tool to maximize the information given by the bulk deposition samples. Considering the actual characteristics of the atmosphere, and owing to the emphasis it puts on initial conditions, we suppose that the model can be improved by intro-

ducing a variable indicative of the antecedent conditions. Lindberg (1982) found poor correlation between concentration and an antecedent period, measured as the number of days without rain. Carvalho (in prep.) used an antecedent precipitation index, measured in mm-rainfall, that explains well the antecedent soil moisture and can further be tested as an indication of the amount of aerosols available to washout during rainfall.

Among the best fitted functions between P and D (Table 6) the only one different from the linear equation is the potential equation that explains potassium, but its coefficient b is near zero, which could mean an input independent of precipitation. These linear coefficients may be regarded as a reinforcement of linear dilution: indeed, the b coefficient in the linear equation at Table 6 has the same physical meaning as R in Table 3, and the values are similar, especially for Ca and Mg. The poor correlations between D and P are indicative of the great influence of initial conditions I, which are independent of P, which in turn are related to the episodic pattern of D (Brown et al. 1989). Table 7 shows that 1% of the chemical deposition occurs through about 30% of the cumulative rainfall, distributed in at least 45 events, all with a mean precipitation amount greater than the total mean. Similarly, 10% of the total deposition occurs in almost 50% of the precipitation amount and events. Finally, 50% of D occurs in only 30 events, corresponding to no more than 30% of the total precipitation.

The best fit of C and D shown in Table 8 is a significant power equation. On this account, relative variations between the two variables are equal to the b coefficient, meaning that variations of 100% in C cause variations of about 60% in D for the four cations. Another result in Table 8 is that the b coefficients in all the functions are equal to each other ($p = 0.05$), and the a coefficients are equal ($p = 0.05$) in K, Ca and Mg; the Na coefficient is in the same confidence interval of the three

Table 6. The best fit equation between atmospheric deposition (D-g/ha) and precipitation amount (P-mm).

Equation	Cation	n	a	b	$r*$
$D = a + b \cdot P$	Na	203	37.8	2.15	0.26
$D = a \cdot P^b$	K	197	13.5	−0.07	0.39
$D = a + b \cdot P$	Ca	205	14.1	0.40	0.22
$D = a + b \cdot P$	Mg	211	13.7	0.84	0.30

* r illustrative: $r \neq 0$; $p \lll 0.01$.

Table 7. Characteristics of the rainfall events needed to reach the indicated atmospheric deposition.*

Cation	Rain	D%	1%	2%	5%	10%	25%	50%	100%
Na	*n*		71	88	115	140	177	207	228
	P%		40	45	54	62	73	81	100
	mean P		17	16	14	14	13	12	13
K	*n*		56	71	100	130	180	207	220
	P%		29	33	42	53	73	87	100
	mean P		15	14	13	12	12	12	13
Ca	*n*		56	70	96	126	179	197	229
	P%		27	35	46	55	76	83	100
	mean P		15	15	15	13	13	13	13
Mg	*n*		45	60	95	115	161	200	228
	P%		27	32	45	49	65	70	100
	mean P		18	16	14	13	12	11	13

* D% — cumulative deposition /total deposition (%).
n   — number of events needed to reach D %.
P% — cumulative rainfall needed to reach D%/Total rainfall amount (%).
mean P — arithmetic mean precipitation amount of the events needed to reach D%.

Table 8. Potential function of best fit between the atmospheric deposition (D-g/ha) and its measured concentration (C-mg/l).

Equation		Coefficients		
$D = a \cdot C^b$	*n*	a	b	r*
Sodium	204	50.1	0.68	0.83
Potassium	198	37.8	0.65	0.74
Calcium	206	32.8	0.62	0.77
Magnesium	212	34.8	0.60	0.74

* All $r \neq 0$; $p \lll 0.01$.

other cations if we accept $p = 0.01$. If these cations behave so similarly we might suppose that they have the same origin. Since our Mg^{++}/Na^{+} ratio is greater than the seawater ratio we assumed that our mean concentration of sodium can be used as a reference species of sea-salt origin. We determined that 90% of the potassium and calcium and 70% of the magnesium have terrestrial origin. Although these calculations are

only approximate, because they used mean observations and were not obtained by regression on specific pairs (Keene et al. 1986), the percentage values are so high that we can interpret them as being influenced by the crustal dust, vegetation exudates and biomass burning typical of agricultural fields.

Conclusions

The following are the most important conclusions:

— Variations in atmospheric deposition, calculated as the product of precipitation and measured concentration, depend primarily on concentration.
— Measured concentrations depend significantly on precipitation by a power function with the exponent near −1.
— These two conclusions led us to associate parameters of an inverse linear model to important physical characteristics of the precipitation process. According to this model, by collecting just the bulk deposition we could fractionate the measured concentration into two components:
  • a parameter that represents the mean concentration of rainwater in the clouds, a value considered to have regional meaning, and
  • another parameter that represents an amount of materials present in the beginning of the rainfall process, within the atmosphere and in the collector. This is the amount available for dilution by the rainfall.
— The relation of atmospheric deposition to measured concentration is identical for the four cations. Would it be possible to save time and money measuring only one of them and inferring the others?

Although the inverse linear model can be regarded as a first approximation, it works well for our test conditions. Further research is needed on the initial conditions represented by the component I. This could be accomplished by introducing a variable related to the precedent conditions of the atmosphere available to scavenging by washout. To regionalize and validate these observations it would be useful to analyze simultaneous collections of bulk and dry deposition at other sites to investigate differences. In countries lacking economic resources, our method may be considered as an acceptable approximation to total ion deposition, especially considering its small cost.

Acknowledgements

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