

## 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 of atmospheric deposition is a complex task. It is necessary to

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 ( $22^{\circ} 45' S$ ,  $41^{\circ} 43' W$ ), 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  $32.5^{\circ}C$  in February and 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  $\text{Na}^+$  and  $\text{K}^+$  (emission photometry) and  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  (atomic absorption spectrophotometry) without the addition of

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

		P	Na		K		Ca		Mg	
			C	D	C	D	C	D	C	D
P		1								
Na	C	-0.45	1							
	D	0.20	0.78	1						
K	C	-0.41	0.60	0.37	1					
	D	0.29	0.30	0.53	0.75	1				
Ca	C	-0.52	0.64	0.34	0.66	0.31	1			
	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	
	D	0.26	0.34	0.55	0.40	0.61	0.69	0.69	0.41	1

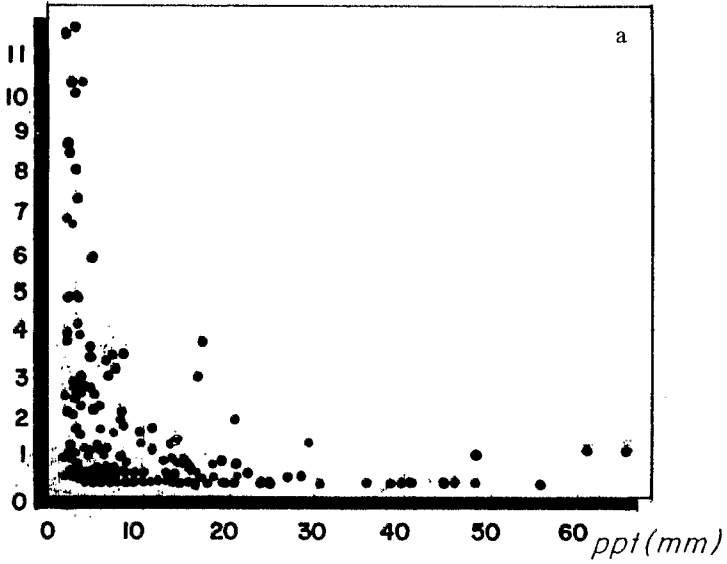
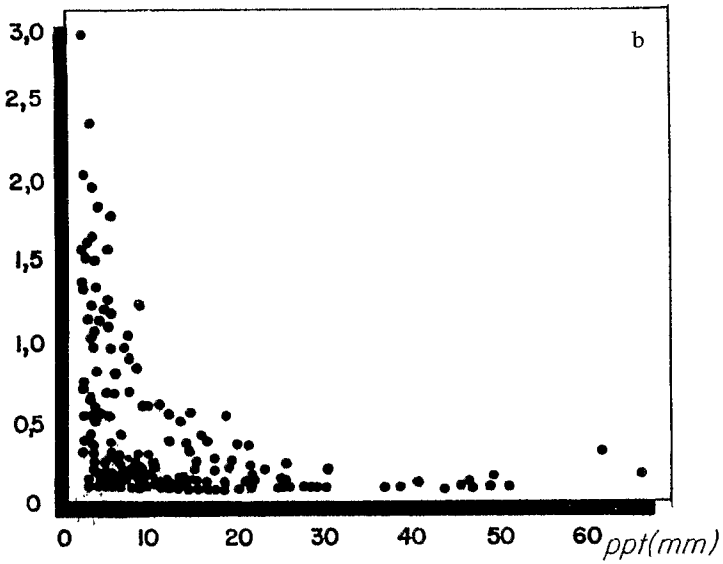
$Na (mg/l)$  $Ca (mg/l)$ 

Fig. 1. Relation between precipitation (ppt-mm) and: (a) sodium concentration (Na-mg/l)  $n=203$ , (b) calcium concentration (Ca-mg/l)  $n=205$ .

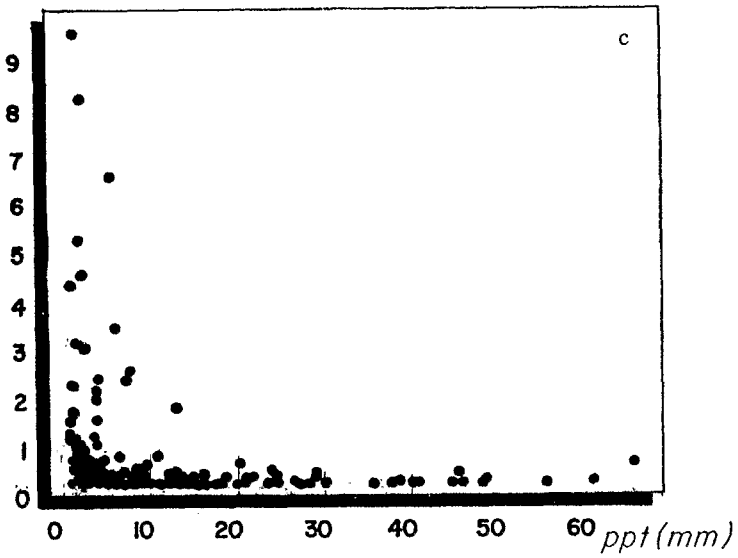
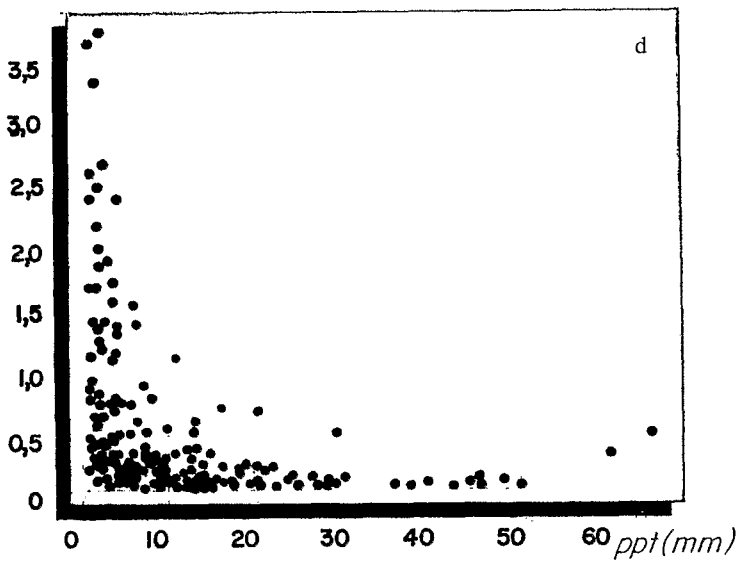
$K(mg/l)$  $Mg(mg/l)$ 

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	<i>n</i>	Coefficients		
		<i>a</i>	<i>b</i>	<i>r</i> *
$C = a \cdot P^b$				
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



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

these ranges, as shown by the I (g/m<sup>2</sup>.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

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

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	<i>n</i>		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	<i>n</i>		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	<i>n</i>		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	<i>n</i>		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  $I_{\text{at}}(C_{\text{at}})$  and the atmospheric deposition ( $D_{\text{at}}$ ) and  $I_{\text{at}}(C_{\text{at}})$

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.

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## References

- APHA (1984) Standard Methods for the Examination of Water and Wastewater, 15th edition. American Public Health Association, New York
- Beauford W, Barber J & Barringer AR (1977) Release of particles containing metals from vegetation into the atmosphere. *Science* 195: 571–573
- Brown IF, Silva Filho EV & Ovalle ARC (1985) The use of binary state analysis for estimating element fluxes in a subtropical premontane wet forest, Rio de Janeiro, Brazil. In: *Proceedings of the Workshop on Biogeochemistry of Tropical Rain Forests*. CENA/USP, Piracicaba, Brazil
- Brown IF, Silva Filho EV, de Paula FC & Ovalle ARC (1989) Measurement of atmospheric deposition at the canopy level in a subtropical premontane wet forest, Rio de Janeiro, Brazil. *Biotropica* 21(1): 15–19
- Cahill TA, Ashbaugh LL, Eldred RA, Feeney PJ, Kusko BH & Flocchini RG (1981) Comparisons between size-segregated resuspended soil samples and ambient aerosols in the Western United States. In: Macias ES & Hopke PK (Eds) *Atmospheric Aerosol-source/Air Quality Relationship* (pp 269–285). American Chemical Society, Washington
- Carvalho CN (1987) Entradas atmosféricas de potássio em um agrossistema experimental. *Congresso Brasileiro de Geoquímica*, 1. Anais: 233–242
- Carvalho CN (in prep.) Fluxo geoquímico de elementos em função do uso agrícola. PhD thesis, Universidade Federal do Rio de Janeiro, Brazil
- Coelho Netto AL (1985) Surface hydrology and soil erosion in a tropical mountainous rainforest drainage basin, Rio de Janeiro. PhD thesis, University of Leuven, Belgium
- Colin JL, Jafrezo JL & Gros JM (1990) Solubility of major species in precipitation: factors of variation. *Atmospheric Environment* 24A(33): 537–544
- Forti MC & Moreira-Nordemann LM (1989) Estudo da interação chuva/particulado atmosférico em São José dos Campos, SP. *Ciência e Cultura* 41(6): 583–590
- Franken W & Leopoldo PR (1984) Hidrology of catchment areas of Central-Amazon forest streams. In: Sioli H (Ed) *The Amazon, Limnology and Landscape Ecology of a Mighty Tropical River and Its Basin* (pp 501–519). W. Junk, Publ. The Hague
- Gatz DF, Stensland GJ, Miller MV & Leslie ACD (1981) Sources of airborne calcium in rural central Illinois. In: Macias ES & Hopke PK (Eds) *Atmospheric Aerosol-source/Air Quality Relationship* (pp. 303–325). American Chemical Society, Washington
- Galloway JN & Likens GE (1976) Calibration of collection procedures for the determination of precipitation chemistry. *Water, Air and Soil Pollution* 6: 241–258
- Galloway JN & Likens GE (1978) The collection of precipitation for chemical analysis. *Tellus* 30(1): 71–82
- Graustein WC (1981) The effects of forest vegetation on solute acquisition and chemical

- weathering, a study of the Tesuque watersheds near Santa Fe, New Mexico. PhD thesis, Yale University
- Hendry CD & Brezonik PL (1980) Chemistry of precipitation at Gainesville, Florida. *Environ. Sci. and Technol.* 14(7): 843–849
- Iribarne JV & Cho HR (1980) Atmospheric Physics. D. Reidel Publ. Co. Dordrecht
- Keene WC, Pszenny JN, Galloway JN & Hawley ME (1986) Sea-salt corrections and interpretation of constituents ratios in marine precipitation. *Journal of Geophysical Research* 91(D6): 6647–6658
- Kellmann M, Hudson J & Sanmugas K (1982) Temporal variability in atmospheric nutrient influx to a tropical ecosystem. *Biotropica* 14(1): 1–9
- Kritz MA & Rancher J (1980) Circulation of Na, Cl and Br in the tropical marine atmosphere. *Journal of Geophysical Research* 85(C3): 1633–1639
- Lewis WM, Jr & Grant MC (1978) Sampling and chemical interpretation of precipitation for mass balance studies. *Water Resources Research* 14(6): 1098–1104
- Lindberg SE (1982) Factors influencing trace metal, sulfate and hydrogen ion concentrations in rain. *Atmospheric Environment* 16(7): 1701–1709
- Mello WZ, Souza MP & Motta JST (1987) Medidas de fluxos de deposição seca em Niterói, RJ — nota preliminar. *Ciência e Cultura* 39(11): 1075–1078
- Mollitor AV & Raynal DJ (1982) Acid precipitation and ionic movement in Adirondack Forest soils. *Soil Sci. Soc. Am. J* 46: 137–141
- Prospero JM, Glaccum RA & Nees RT (1981) Atmospheric transport of soil dust from Africa to South America. *Nature* 289(12): 570–572
- Snedecor G & Cochran WG (1980) *Statistical Methods*, 7th edition. Iowa University Press, Ames
- Stewart RW, Thompson AM & Owens MA (1990) Atmospheric residence times for