SHORT CONTRIBUTION

Soluble organic nitrogen in Venezuelan rains

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(Manuscript received 2 June 2003; in final form 1 April 2004)

ABSTRACT

We present data which show that soluble organic nitrogen (SON) is an important component of tropical continental rains, especially in remote unpolluted sites where it represents up to 90% of the total soluble nitrogen. The inclusion of SON wet deposition in the N budget significantly increases the N nutrient input to the soil vegetation reservoir of Venezuelan ecosystems.

1. Introduction

Nitrogen is one of the major limiting factors that controls the dynamics, biodiversity and functioning of most ecosystems. Fixed N also affects the growth and dynamics of the herbivore population and their predators. In general, low deposition rates of soluble inorganic nitrogen (SIN) are found in Venezuelan ecosystems (Sanhueza et al., 1992; Sanhueza and Crutzen, 1998). Recently significant amounts of soluble organic nitrogen (SON) have been found in rainwater at various sites in the world (e.g. Cornell et al., 2001), a major fraction of which is bioavailable (e.g. Seitzinger and Sanders, 1999). We report the content of SON in rains collected at urban, suburban, rural and remote sites in Venezuela. Results indicate that SON makes a significant contribution to the regional deposition of soluble nitrogen.

2. Field measurements

Only wet rain samples were collected at two main cities (Caracas and Valencia), at the top of a cloud forest (Altos de Pipe) near Caracas, a rural site (Calabozo) and a remote site (Parupa). Site locations are indicated in the map in Fig. 1. The major features of the sites were given in a recent publication (Holzinger et al., 2001).

Rain samples were collected immediately after each event, preserved with chloroform and stored at 4 °C. Samples were not filtered prior to analysis, since insoluble particulate ON in rainwater is not a significant component of nitrogen (Cornell et al.,

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2003); therefore our SON concentrations may include some minor amounts of insoluble particulate nitrogen. SON was determined by subtracting the inorganic fraction from the total soluble nitrogen (TSN). NH_4^+ and NO_3^- were determined directly in rain samples using a selective electrode and ion chromatography, respectively. TSN was analysed as nitrate, after wet chemical oxidation with persulfate (Solórzano and Sharp, 1980), using the cadmium reduction method. Recoveries of N following persulfate oxidation of standard urea solutions were >80%. Therefore, results reported in this study could underestimate SON concentrations.

3. Results and discussion

Volume-weighted concentrations of SON, NH_4^+ and NO_3^- are summarized in Table 1. Urban concentrations of NH_4^+ and $NO_3^$ are ~ 10 times larger than the concentration observed at the remote site, whereas the difference in SON is less than three times. Assuming that these precipitation subsets are representative, the results suggest that, compared with the inorganic fraction, anthropogenic activities produce a lower impact on SON levels. We are unaware of previous SON reports for urban rains. On the other hand, SON concentrations found at our non-urban sites (A de Pipe 31 μ M N, Calabozo 24 μ M N, Parupa 24 μ M N) agree well with the levels reported in the literature (see Table 2). According to the review of Cornell et al. (2001), the SON interquartile range in continental (rural) rains is $13-34 \,\mu$ MN, with a mean value of 23 μ M N. Coastal and oceanic rains have lower concentrations compared with continental rains, suggesting a land source for organic nitrogen or of its precursors.

In concordance with this work (see Table 1), low levels of NH_4^+ and NO_3^- in rain have also been previously measured in

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Table 1. Volume-weighted concentrations as N of SON, NH_4^+ and NO_3^- at various sites in Venezuela

Site	Rain (mm yr ⁻¹)	n*	NH_4^+ ($\mu\mathrm{M}$)	NO ₃ ⁻ (μM)	SON (µM)
Valencia (urban)	1087	30	29	8.7	57
Caracas (urban)	901	9	24	11.9	58
Altos de Pipe (suburban)	1100	14	5.0	2.9	31
Calabozo (rural)	1300	17	3.0	4.2	24
Parupa (remote)	1350	24	1.2	0.8	24

*Number of rain events.

the Venezuelan savannah region (Sanhueza et al., 1992). These concentrations are much lower than those recorded in rural areas of Europe and North America. As is shown in Table 2, these low levels of inorganic components produce a very high contribution of SON to the TSN. Therefore, compared with other parts of the world (see Table 2), deposition of SON plays a major role in the nitrogen budget in Venezuelan "natural" ecosystems.

Table 2. Soluble organic nitrogen in Venezuelan rains, compared with literature data reviewed by Cornell et al. (2001)

	SON (μM)	$100 \times \text{SON/TSN}$
This work:		
Caracas (urban)	57 ^a	61
Valencia (urban)	58 ^a	62
Altos de Pipe (sub urban)	31 ^a	79
Calabozo (rural)	24 ^a	76
Parupa (remote)	24 ^a	92
Cornell et al. (2001):	IQR (mean) ^b	
Continental (rural)	13-34 (23)	29 ^c
Coastal	6-11 (9)	26
Oceanic	2-8 (7)	62

^aVolume-weighted average.

^bHere IQR is the interquartile range (the range covered by the middle 50% of data).

^cThe mean value of the published averages.

Fig 1. Partial map of Venezuela indicating the monitoring sites.

The results of Cornell et al. (2001) indicate that inorganic nitrogen is associated with coarse particles, whereas most of the organic nitrogen is found in fine particle aerosols. This is in agreement with the general finding that organic compounds are the second most abundant component of fine particles after sulfates (Jacobson et al., 2000). Therefore, it is likely that organic nitrogen is scavenged less efficiently than inorganic nitrogen. This would provide an explanation for the greater relative concentration of organic nitrogen in remote oceanic regions (Cornell et al., 1995). It would be in agreement with the results obtained in this work, where the highest contribution of SON (89%) is observed at the Parupa remote site. It is worth mentioning that stream chemistry data from unpolluted forests in temperate South America indicate that SON is responsible for the majority of N losses (61-97% of total N) from these forests (Perakis and Hedin, 2002).

In conclusion, it is clear that SON is an important component of tropical rains, especially in remote unpolluted sites, where it represents up to 90% of the TSN. Therefore, in order to have an adequate understanding of the cycling of atmospheric nitrogen, information about other components of the cycle (i.e. SON emission fluxes to the atmosphere from the soil vegetation reservoir, SON production by chemical reaction in the atmosphere, SON dry deposition) is needed. At present, our laboratory is measuring SON concentrations in Venezuelan airborne particles.

4. Acknowledgments

These studies on biogeochemical cycles in tropical ecosystems were supported by the Venezuelan National Science Council (FONACIT) through grant No G-98001124.

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