

Linking nitrogen deposition patterns and land use change in tropical areas

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Land use changes in Brazil have driven a 2-3 fold increase in nitrogen deposition based on measurements made in industrialized regions of Brazil and in the Amazon region. Here we show that biomass burning emissions in Southern Brazil and the conversion of tropical rain forest into pasture in the Amazon basin drives a shift in the composition of N deposition from nitrate to ammonium. These large perturbations to the tropical atmospheric N cycle have important deleterious consequences for ecosystem functioning. Changes in net primary productivity, eutrophication problems, acidification of ecosystems, decreased biodiversity are all documented outcomes of enhanced nitrogen deposition in temperate systems, but the implications for the tropics with a much faster N cycle are less clear ¹.

In the past, natural biological N fixation dominated the reactive nitrogen inputs to the terrestrial biosphere. Nowadays, human activity has more than doubled the rate of formation of reactive nitrogen on the land surface of the Earth and the nitrogen cycle continues to accelerate ¹⁻⁴. The emitted N is deposited back to the Earth surface mainly

over the continents⁵. From the pre-industrial age to contemporary days, the pattern of N deposition has changed over the globe, from tropical to temperate latitude dominated N deposition with expanding industrialization over the last 200 years^{3,6}. Future tropical N deposition is predicted to equal or exceed current day N deposition rates for temperate regions due to expanding industrialization, urbanization, and deforestation^{2,7-9}. In spite of this prediction, most studies of N deposition, and its consequences, have focused on the temperate North Hemisphere¹.

Most of Brazil lies within tropical latitudes. It is a developing country, where “developed” areas with large urban centers, a large number of industries, and a high-technology agricultural system coexist with “developing” areas with low-technology and frontier-type agricultural systems¹⁰. The State of São Paulo is considered a typical “developed” region of Brazil, combining more than 90,000 industries with a high-technology agriculture based on cattle ranch, sugar cane and citrus production. As a consequence only 13% of its original vegetation remains. Almost 95% of the population of the State of São Paulo (37 million in 2000) lives concentrated in urban centers, with high population densities until almost 7,000 people per km². Northern Brazil, set entirely in the Amazon physiographic region, is the most remote region of the country. The entirely northern region of Brazil, approximately 3.9 million km², has a population density of only 3.4 inhabitants per km²¹¹, but has suffered extensive land use changes along the borders with other regions of Brazil^{12,13}. The last estimate of deforestation available (2001-2002) totaled approximately 25,500 km².yr⁻¹ of deforested area in the Brazilian Amazon region¹⁴.

We combined this understanding of continuing Brazilian land use change with measurements of N deposition and atmospheric composition. Nitrogen deposition in precipitation is a good measure of changing atmospheric chemistry and air quality because it samples the removal products (mainly ammonium and nitrate) of chemical

species that contribute to acid rain, nitric acid (HNO_3) concentration, surface O_3 pollution ($\text{NO}_x = \text{NO} + \text{NO}_2$), and the formation of aerosols, e.g. ammonium sulfate and ammonium nitrate particles, including those classified as $\text{PM}_{2.5}$ and PM_{10} . These compounds are important urban and industrial pollutants that can influence remote areas under some transport regimes. Analysis of NO_3^- , NH_4^+ and NO_2^- concentrations were performed on rainwater samples collected in remote and disturbed areas of the State of São Paulo and Amazon region. In the State of São Paulo, rainfall was sampled in the Piracicaba River basin near the cities of Bragança, Campinas, Piracicaba and Santa Maria and in the remote site of Intervales State Park. In Amazon Basin, rainwater was also sampled in Rondônia, a disturbed site near the city of Ji-Paraná, with one of the largest deforestation rates of the Amazon region, and in a remote site, Balbina (State of the Amazonas) (Table 1) (Figure 1).

The magnitude of total N deposition increased along the gradient of land use change and industrialization. Total N deposition measurements in most industrialized regions of the Piracicaba Basin (Bragança, Campinas and Piracicaba) were almost 2 times greater than the measurements made at remote sites (Intervales State Park - São Paulo State, and Balbina - State of Amazonas, $P < 0.01$) (Table 2). Nitrogen deposition at Santa Maria site (Piracicaba Basin) with a lower population density and less intense industrialization and agriculture⁸ was intermediate between that measured at the most disturbed sites at the Piracicaba Basin (Bragança, Campinas, and Piracicaba) and at the remote sites (Intervales and Balbina). The results are consistent with other studies that showed higher N wet deposition in the Southeast region of Brazil ($5.5 \text{ kg.N.ha}^{-1}.\text{yr}^{-1}$) compared to the Central Amazon region ($2.9 \text{ kgN.ha}^{-1}.\text{yr}^{-1}$)^{8, 15}.

Not only the magnitude of N deposition is changing, but also the composition of the N deposition is changing along the gradient of land use change. The change in magnitude for ammonium annual deposition exceeded the change in magnitude of

nitrate annual deposition (Table 2). Nitrate annual deposition dominated in the more remote areas (Intervales and Balbina) switching to ammonium domination in disturbed areas (Piracicaba Basin) (Table 2). During the dry season, ammonium accounted for approximately 64% of the total N wet deposition at the disturbed sites (Piracicaba basin) compared to 40% of the total N wet deposition at undisturbed sites (Intervales and Balbina). During the wet season, ammonium accounted for approximately half of the total N wet deposition at the disturbed sites, compared to 34% at undisturbed sites (Table 2)

At all sites sampled, except for the NH_4^+ -N deposition in the Piracicaba and NO_3^- -N deposition in the Rondônia sampling sites, where was not found seasonal differences in the fluxes, deposition of N follows the pattern of precipitation, wet season fluxes are greater than dry season fluxes. By contrast, the volume weighted mean concentration of all N species is higher in the dry season than in the wet season at all sites (Table 2). Nitrate concentrations dominated N either in the dry and wet seasons for the Balbina and Intervales sites, the only areas with native forest as main land cover (Table 2). For the areas undergoing urbanization, industrialization, and land use change, with few exceptions in the wet season, ammonium concentrations exceeded nitrate and nitric oxide concentrations (Table 2).

Both nitrogen oxides and ammonia are emitted by biomass burning and by chemical and biological processes in soils following biomass burning^{8,16-19}. In Rondônia, for the first time it was possible to link seasonal pattern of biomass burning to N deposition and concentration (Figure 2). We found a strong positive correlation ($P < 0.01$) of NH_4^+ -N ($r^2 = 0.98$) and NO_3^- -N ($r^2 = 0.83$) deposition and the number of hot pixels¹⁴. Therefore, in these unmatched results it has been established a causal link between land use change (biomass burning) and increasing N deposition. Consequently, we are able to say that biomass burning is associated with increased N deposition, and

this increase will likely be accompanied by the shift towards ammonium dominated deposition. As biomass burning in the State of São Paulo and in the Amazon region is coincident with the dry season, the ambient chemical environment is much more polluted during this season than the wet season. The contrast is driven by extensive biomass burning during the dry season^{8,17}, and an atmosphere that is cleansed less often by rain, allowing the accumulation of biomass burning pollutants.

While oxidized species generated from fossil fuel combustion dominate the N deposition in North Hemisphere and reduced species derived from farming or animal waste dominate the Western Europe^{3,6}. In Brazil, most due to biomass burning, ammonium is becoming the dominant form of nitrogen deposition. As the oxidation state of the nitrogen is quite distinct between these two compounds, we anticipate that important changes may occur in the atmosphere chemistry and in terrestrial and aquatic ecosystems^{1,20-22}. In the atmosphere ammonia plays an important role in the indirect effects of aerosols on radiative forcing and thus on global climate change²³. Additionally, the formation of ammonium affects the atmospheric transport of SO₂ and NO_x emissions²⁰. Once deposited, ammonium releases acidity since the nitrogen is either accumulated in organic nitrogen form or nitrified and leached as nitrate. In many areas, soil acidification from nitrification of ammonium deposited from the atmosphere is comparable to that from the deposition of nitric acid²¹. Deposition of N as ammonium can produce furthest acidity per molecule than deposition by nitrate^{1, 20}. As many of the soils in these studied areas are acidic, highly weathered^{24,25}, additions of anthropogenic N may increase that acidity, leading to the increased losses of cations and decreased availability of phosphorous and other limiting nutrients, ultimately reducing plant production and altering other ecosystem functions¹. Our results pointed out that increase in N deposition indeed appears to be happening and as a result most of the consequences cited above and other already discussed predictions¹ become more than conjecture and speculation.

Annually 7,500 to 8,600 Tg of dry material is emitted to the atmosphere around the world by burning¹⁷ which represent an important global source of particles and gases to the atmosphere. About 43% of this dry material is derived from savannah burning, 23% from the burning of agricultural waste, 18% from rainforest burning and 16% from wood burning used to produce fuel¹⁷. Therefore, if the kind of changes in the atmosphere composition detected in Brazil are also taking place in other tropical areas of the world, where most of the biomass burning occur, in a few decades significant regional nitrogen cycle changes can be expected with possible global nitrogen cycle consequences.

Methods

The rainwater samples have been continuously collected with a wet only sampler in five sites in São Paulo State: four in disturbed areas and one in remote area (Figure 1). In the four disturbed areas; Bragança (22°54'S, 46°25'W), Campinas (22°53'S, 47°05'W), Piracicaba (22°42'S, 47°38'W) and Santa Maria (22°32'S, 47°55'W), the rainwater was sampled from July 1997 through March 1999. In the remote area (Intervales State Park, 24°16'S, 48°24'W) the rainwater was sampled from June 2002 through April 2003. In Amazon Basin, rainwater was sampled in two different sites: one in remote area, Balbina (1°55'S, 59°24'W) located approximately 100 km north of the city of Manaus in Central Amazon from March, 2000 through December, 2001, and a second one, Rondônia, in a pasture site called "Fazenda Nossa Senhora Aparecida" (10°45'S, 62°21'W), closed to the city of Ji-Paraná in the State of Rondônia, the most disturbed site, where the accelerated land-changes, most of that by the use of biomass burning could be altering the atmospheric chemistry. In this site, the samples were collected in two periods: first one from March 1998 through July 1998 and the second from September 2002 through November 2002, during the SMOCC campaign (Smoke aerosols, clouds, rainfall and climate-aerosols from biomass burning

perturb global and regional climate). Using ion chromatography, NO_3^- , NH_4^+ , NO_2^- were determined in the rainwater samples collected in all sites, the only exception was the first period sampled in Rondônia, from March 1998 through July 1998 (wet season), when only NO_3^- was analyzed. The sites studied here are part of the projects BIOTA/FAPESP (State of São Paulo) and LBA (Large-Scale Biosphere-Atmosphere Experiment in Amazon). The burning season of sugar cane in São Paulo State occurs from May through October coincident with the dry season. In the Amazon basin the dry season extends from June through November.

To calculate the differences between the concentrations in dry and wet seasons it was applied Tukey Honest Significant difference test ($P < 0.01$). In order to correlate the N deposition with biomass burning in Rondônia (Rondônia) it was done a linear regression between the deposition of NH_4^+ -N and NO_3^- -N for each precipitation event with the number of hot pixels in the State of Rondônia from the last three days before the precipitation event. "Pixel" stands for "picture element", corresponding to the "grain" (spatial resolution) of the image, which in the case of the AVHRR varies from 1.1 km at the center of the image up to about 5 km at the lateral edges. However, due to the strong thermal energy emitted by the vegetation fires, even a fire front with about 30 m by 0.5 m will be detected. Therefore, a fire pixel may correspond to a small vegetation fire, to many and close small fires, or to a single large fire with 1 km².

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Table 1: Description of the sampling sites in São Paulo State and Amazon

Basin. The Bragança, Campinas, Piracicaba, and Santa Maria sampling sites are located near the cities of same name in the Piracicaba Basin in the State of São Paulo. Intervales site is located in a protected State Park of almost 50,000ha, in one of the few remaining primary Atlantic Forests in the State of São Paulo. Rondônia sampling site is located near the city of Ji-Paraná. In this region, forests have been replaced extensively to pastures, by burning the forest. In Central Amazon region, samples were near the hydroelectric power plant of Balbina (Figure 1), which is far less disturbed than the sampling area located in the State of Rondônia.

Sampling site	Land use	Population density (inhabitants/km ²)	Rate of deforestation (2000-2001) (km ² /yr)	Sampling period
State of São Paulo	Piracicaba Basin ⁸	350		July 1997 to March 1999
	50% pasture			
	32% sugar cane			
	9% forest			
	5% urban			
	Intervales State Park	Uninhabited		June 2002 to April 2003
Amazon Basin	Rondônia (State of Rondônia)	5.79	2,700	March 1998 to July 1998 September to November 2002
	75% forest			
	20% pasture			
	Balbina (State of Amazonas)	0.78	600	March 2000 to December 2001
	Most Terra-Firme rainforest			

Table 2: Volume weighted mean concentrations ($\mu\text{mol.L}^{-1}$) of NH_4^+ , NO_3^- , and NO_2^- in precipitation and associated N wet deposition (kg.N.ha^{-1}). The concentrations and depositions ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) values are showed during dry and wet seasons as well as N annual wet deposition rate ($\text{kg.N.ha}^{-1}.\text{yr}^{-1}$).

	Season	Bragança	Campinas	Piracicaba	S. Maria	Intervales	Balbina	Rondônia
NH_4^+	Dry	28.8*	24.4*	28.2*	23.3*	9.9*	6.2*	18.5
	Wet	17.2*	14.3*	11.6*	12.7*	4.5*	2.2*	
NO_3^-	Dry	17.1	18.6	20.6	18.3	16.4	7.5	17.1
	Wet	14.5	17.9	13.8	12.3	9.7	5.9	5.1
NO_2^-	Dry	0.1		0.2	0.3	0.1	0.1	2.9
	Wet			0.1	0.2	0.1		
$\text{NH}_4^+\text{-N}$	Dry	0.9	1.1	1.4	1.3	0.5	0.4	1.4
	Wet	2.3	2.0	1.4	1.4	0.6	0.6	
	Annual	3.1	3.1	2.8	2.7	1.1	1.0	
$\text{NO}_3^-\text{-N}$	Dry	0.6	0.7	0.8	0.8	0.8	0.5	1.2
	Wet	1.9	2.5	1.7	1.3	1.3	1.4	1.2
	Annual	2.5	3.2	2.7	2.1	2.1	1.9	2.4
Total N	Annual	5.6	6.3	5.5	4.8	3.2	2.9	

(*) These values indicate significant differences ($P < 0.01$) between wet and dry seasons.

Figure 1: Map of Brazil with divisions of the States showing the sampling sites. Underlines are the names of the States. The Piracicaba basin has a population density of almost 350 inhabitant per km² and more than 7,000 industries ²⁶. The leaves of sugar cane which is the main crop of the basin are burning every year during the dry season in order to facilitate harvesting ^{8,22}. The conversion of primary forest to croplands or pasture is the predominant land cover in Rondônia ²⁷.

Figure 2: Relationship between N wet deposition (kg.N.ha⁻¹.mo⁻¹) from ammonium (black circles) and nitrate (open circles) and hot pixels for Rondônia. Linear regression was done between the calculated deposition of NH₄⁺-N and NO₃⁻-N for each precipitation event (n=22 samples) with the number of hot pixels in the State of Rondônia from the last three days before the precipitation event ¹⁴. More than 60,000 km² of the State of Rondônia has been deforested at an average rate of 2,500 km².yr⁻¹ for the period 1978-2000 ¹⁴, correspondent to an area equivalent to 25% of the total area of the State.

Lara_fig1



Lara_fig2

