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Chemical composition of rainwater and anthropogenic influences in the Piracicaba River Basin, Southeast Brazil

L.B.L.S. Lara^a, P. Artaxo^b, L.A. Martinelli^a, R.L. Victoria, P.B. Camargo, A. Krusche, G.P. Ayers^c, E.S.B. Ferraz, M.V. Ballester

^aCentro de Energia Nuclear na Agricultura, Universidade de São Paulo, Av. Centenário 303, 13416-000 São Paulo, Brazil

^bInstituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R, 187, CEP 05508-900 São Paulo, S.P., Brazil

^cCSIRO, Division of Atmospheric Research, Aspendale 3195, Australia

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Abstract

The influences of different kinds of anthropogenic activities on rainwater chemistry in a tropical area were studied during one uninterrupted year at Piracicaba River Basin (Southeast Brazil). A total of 272 rainwater samples collected continuously from August 1997 to July 1998 at four different sites were analyzed for F^- , CH_3COO^- , $HCOO^-$, MSA, Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} , $C_2O_4^{2-}$, PO_4^{3-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , DOC (dissolved organic carbon), DIC (dissolved inorganic carbon), pH and conductivity. The most abundant ion was H^+ and rain acidity was significant at all sampling sites (average pH of 4.4–4.5). The sources of this free acidity differ among sites and appear to be correlated to the different land-uses. The composition of rainwater appeared to be controlled mostly by three sources: soil dust, sugar cane burning and industrial emissions. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Land-use and industrial activities are considered the most important driving forces in the ongoing process of atmospheric chemistry alteration. Most of these anthropogenic influences in the atmospheric chemistry are due to emissions of N, ammonia, and sulfur (Munger and Eisenreich, 1983; Galloway et al., 1995; Puxbaum et al., 1998). The oxidation of these chemicals and subsequent scavenging by precipitation has caused, mainly in northern Europe and northeastern United States, widespread acidification of precipitation and an extra input of N to terrestrial and aquatic systems, with several deleterious consequences to the environment, such as decline of forests and crop productivity, increase of lake and soil acidification, and loss of biodiversity (Zhang,

1994; Wilson and Skeffington, 1994; Vitousek et al., 1997; Furiness et al., 1998; Kuylenstierna et al., 1998; Torseth and Semb, 1998). However increasing development and industrialization worldwide has been the problem of acidic deposition extend in recent times to other areas, such as East Asia (WMO, 1997).

Numerous studies on atmospheric chemistry have been published for the Northern Hemisphere (Keene et al., 1983; Munger and Eisenreich, 1983; Puxbaum et al., 1998; Sequeira and Lai, 1998). In contrast, there are few studies on the rainwater chemistry of tropical countries (Moreira-Nordemann, 1988; Ayers et al., 2000; Gillett et al., 2000), and many of these have been concentrated in more pristine areas, such as the Amazon Basin (Stallard and Edmond, 1981; Lesack and Melack, 1991; Williams et al., 1997). Relatively little information is available for developing regions of tropical and subtropical areas, where land-use changes are intense and followed by rapid urbanization, associated with a large industrial expansion (Moreira-Nodermann et al., 1988).

*Corresponding author.

E-mail addresses: zebu@cena.usp.br (L.B.L.S. Lara), artaxo@if.usp.br (P. Artaxo).

Such information is relevant, since recent estimates show that in a near future more than half of N inputs related to energy consumption in the Earth will take place in tropical and subtropical regions (Galloway et al., 1994). In addition, tropical, terrestrial and aquatic systems appear to function differently from temperate systems, where N limitation is more severe than in the tropics (Martinelli et al., 1999a). Therefore, conclusions based only in studies conducted in temperate regions may not be valid for tropical and sub-tropical regions. A typical example of these highly developed areas in the tropics is the Piracicaba River Basin, a meso-scale basin located in the southeast region of Brazil (São Paulo State). This basin has almost 3 million people and more than 7000 industries. Alone this region is responsible for 10% of the gross internal product of Brazil. Approximately 85% of the basin are covered with croplands and 5% is occupied with urban centers. Only 9% of the area covered by original forests, removed more than three decades ago, are left. Sugar cane is the main crop in the basin, covering an area of approximately 4000 km². The majority of this large area is burned every year from May to October. Annually approximately 20 tons ha⁻¹ of leaves are burned ha⁻¹. Considering the total area cropped with sugar cane, this amount corresponds to an input of approximately 100,000 tons of organic matter, or 50,000 tons of carbon, to the atmosphere. Besides carbon, biomass burning is also an important source of organic acids, nitrate, and sulfate to the atmosphere (Levine et al., 1995; Andrea et al., 1987). Under this scenario, which combines industrial emissions with biomass burning, changes in the atmospheric composition can be considerable and similar to those experienced by other non-investigated developed regions of tropical and sub-tropical areas. In this study, we investigated the effects of different kinds of anthropogenic activities and their emissions on the chemical composition of rainwater in samples collected during one uninterrupted year at four different sites of the Piracicaba River Basin.

2. Study area

Piracicaba River Basin is a developed meso-scale basin (12,400 km²) located in the southeast Brazil (São Paulo State). The basin encompasses 61 counties, with a population of almost 3 millions inhabitants. The headwaters of this basin are situated less than 30 km from the São Paulo metropolitan area, in which more than 15 million people live. There are more than 7000 industries in the basin. Both population and industries are concentrated in the central to western parts of the basin. Approximately 60% of the entire population live in only eight counties, and 70% of the total industrial energy consumption occurs in these counties. Sugar cane covers

approximately 31% of the basin, and it is cropped mainly in central and western regions of the basin with use of agrochemicals and fertilizers. The sugar cane burning season extends from May to October, with very high aerosol concentrations for most of the basin. More than 100 kg of N is annually applied in sugar cane fields. Pasture fields and silviculture, mainly present in the eastern region, are also important in the basin, occupying, respectively, an area equivalent to 47% and 10% of the basin.

The climate is classified as sub-tropical C, and average temperatures range from 19°C in the winter to 24°C in the summer. The dry season lasts from April to September and wet season from October to March. Eighty percent of the total annual rainfall of 1200–1500 mm occurs in the wet season, with monthly storm size ranging from less than 20 mm during the dry season to more than 300 mm during the wet season (Pellegrino et al., 2000). Soils are mainly acidic, infertile, tropical ultissols and oxissols. Only a few areas are dominated by shallow soils or fertile alfissols.

3. Methods

3.1. Sampling

From August 1997 to July 1998 precipitation was continuously collected in the Piracicaba River Basin at four different sites. From east to west: Bragança, Campinas, Piracicaba and Santa Maria (Fig. 1). The locations of the sampling sites were chosen in order to encompass different sources of anthropogenic activities (Table 1). The sampling site called Bragança was installed in the headwaters of the Piracicaba River Basin, near the city of Bragança Paulista. This region has a population density similar to Piracicaba, but fewer industries than Piracicaba and Campinas, although it is located around 50 km from the large São Paulo metropolitan area, which is the most industrialized area in the country. The main land-use in this area is pasture, and this is the area with the largest cover of trees (natural forest + silviculture = 20%, Table 1). The site Campinas was located in a suburb area near the city of Campinas, which is the most urbanized and industrialized area of the basin (Table 1). The site Piracicaba is located in the vicinity of the city of Piracicaba. This area is the second most urbanized and industrialized in the basin (Table 1). The main land-use in both sites is sugar cane, with a cover of approximately 60% in Campinas and almost 80% in Piracicaba. Both sites had the smallest area covered by trees (Table 1). Finally, a fourth collector was installed in the western side of the basin, near the city of Santa Maria da Serra (Santa Maria). In this area there are very few industries and one of the smallest population densities in the basin (Table 1).

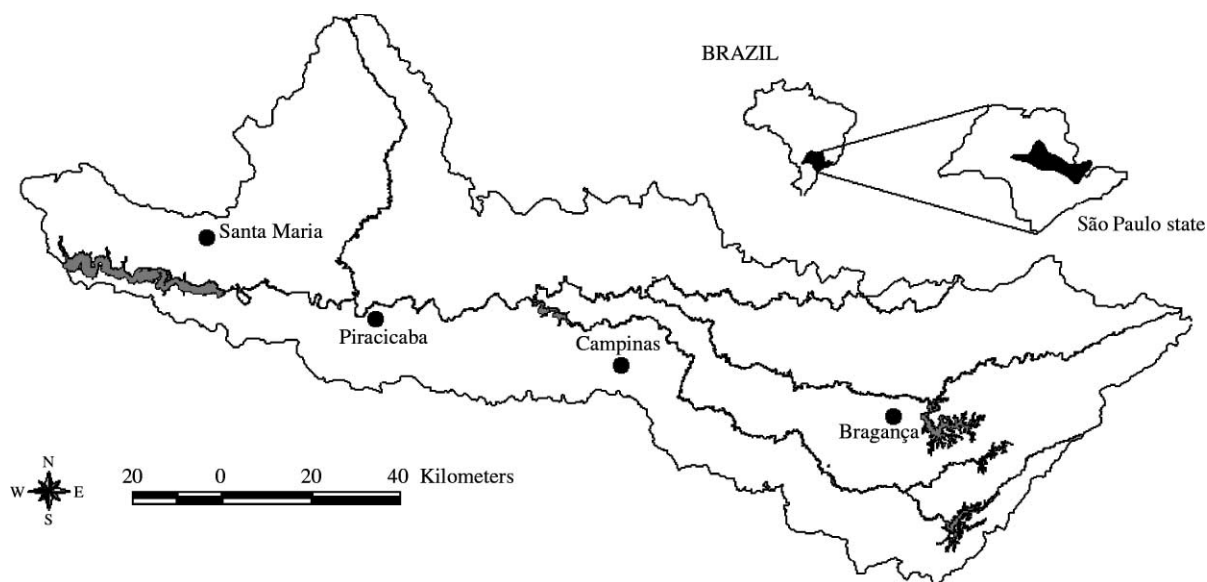


Fig. 1. Location of Piracicaba River Basin and sampling sites.

Table 1

Number of industries, populational density (inhab km⁻²) and land-uses (%) in an area encompassed by a circumference centered by each sampling point and with a radius of 20 km (area of approximately 1200 km²)

	Bragança	Campinas	Piracicaba	Santa Maria
Industries	623	1899	1088	79
Pop. density	212	1061	207	17
Urban	3.8	19.0	5.5	0.0
Forest	10.9	1.5	3.3	6.8
Sugar cane	0.0	61.1	79.4	63.0
Pasture	69.7	13.6	11.1	19.4
Silviculture	8.7	1.0	0.2	0.3
Annual crops	3.2	1.9	0.0	0.0
Water	2.5	1.6	0.5	10.6
Others	1.1	0.5	0.0	0.0

Land-use in the vicinity of this site is also dominated by sugar cane plantations. A total of 58 daily-precipitation samples in Bragança, 85 in Campinas, 64 in Piracicaba and 65 in Santa Maria were collected.

Rainwater samples were collected using a wet-only rainwater collector (Aerochem Metrics) on an event basis, integrated for 24 h. 100% of events of rain storms larger than 2 mm were collected. After each sampling event, the collectors were cleaned with deionized water (DIW). The polyethylene sample bottles were cleaned with 10% HCl and rinsed seven times with DIW. Since acid washing is a source of chloride contamination, conductivity was measured for every three bottles, and DIW washing was continued until conductivity measurements reached 0.85 $\mu\text{S cm}^{-1}$. The rainwater samples were separated into several aliquots, according to the analytical technique to be applied. For the aliquots to be

analyzed by ion chromatography, Thymol was used as a preservative. For the analysis of dissolved organic carbon (DOC), preservation was done with H₃PO₄ immediately added after collection. Additionally, samples were stored in the dark at 4°C (Gillet and Ayers, 1991; Kaplan, 1994).

3.2. Chemical analysis

The pH of each sample was measured using an Orion pH meter (model EA940) with a glass electrode using low ionic strength buffer solutions (Orion application solution). For calibration, two standard solutions with pH 4.01 and 7.00 were used. The resolution of the measurement was 0.01 pH units. Conductivity was measured with a Digital Conductivity Meter (Amber Science Inc., Model 2052).

Anion and cation concentrations were determined at the Division of Atmospheric Research, CSIRO (Australia) with a Dionex DX500 ion chromatograph composed of a gradient pump (GP40), electrochemical (ED40) and conductivity detectors (CD20) for anions and cations, respectively, a Dionex IonPac AS-11 and CS-12 with pre-columns Dionex AG-11 and CG-12. The eluents were NaOH and MSA for anions and cations, respectively. International standards (Ultra-Science) were used for calibration. Detection limits were 0.1 μM for all determined anions and cations. It was possible to determine concentrations of F^- , CH_3COO^- , HCOO^- , MSA, Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} and Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} . In this paper only the concentrations of Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} will be discussed. Dissolved inorganic carbon (DIC) and DOC were determined with a Shimadzu TOC-5000A instrument.

Quality control of the analytical data was performed by balancing cations and anions of the individual samples. The high significant correlation ($R^2 = 0.92$) between anions and cations shows that the main ions were determined for these samples, and that a good ionic balance was achieved. Only 4% of the samples had to be eliminated due to the ion balance quality control criteria, based on the US EPA methodology (EPA, 1984).

3.3. Data analyses

Storm size influences the chemical composition of the rainwater, where larger storms tend to be more dilute.

This dependence on storm size requires the use of volume weighted mean (VWM) in the calculations of seasonal and annual concentration averages.

3.4. Statistical analysis

In order to analyze differences between sampling sites and seasonal differences in rainwater composition for each site, ANOVA was used. Relationships between concentrations of different ions were investigated with factor analyses, which allows the identification of a small number of factors that could explain most of the original data variability (Hopke, 1985). A few factors are more easily interpreted than all the original variables with the inherent interrelationships between them.

4. Results

The VWM concentrations of measured components from each of the four sampling sites, divided into dry and wet seasons, are shown in Table 2. The most abundant ion was H^+ , followed in descending order by $\text{NH}_4^+ > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+}$. The average acidity (pH 4.4–4.5) in the precipitation at Piracicaba Basin was significant, with the hydrogen ion concentration varying from 29.7 to 39.7 $\mu\text{eq l}^{-1}$. In general VWM concentrations were not statistically distinct among sampling sites. Conversely, VWM concentrations were statistically higher during the dry season in relation to the wet season. A notable exception was

Table 2

Average volume weighted mean ionic concentrations in the rainwater for the four sampling sites. Values are expressed in $\mu\text{eq l}^{-1}$, with the exception of DOC, expressed in $\mu\text{M l}^{-1}$

	Bragana			Campinas			Piracicaba			Santa Maria		
	Dry	Wet	Ann	Dry	Wet	Ann	Dry	Wet	Ann	Dry	Wet	Ann
PH	4.6	4.4	4.4	4.6	4.5	4.5	4.8	4.5	4.5	4.4	4.3	4.4
H^+	22.5	39.2	36.3	26.1	31.1	29.7	17.4	34.0	33.0	35.9	40.6	39.7
Na^+	2.2	2.3	2.3	3.1	2.7	2.7	4.2	2.1	2.7	5.6	4.2	4.5
NH_4^+	23.8	17.2	18.6	19.9	14.3	15.4	26.0	11.6	17.1	21.3	12.7	14.5
K^+	2.6	2.5	2.5	2.7	1.6	3.4	4.5	2.1	2.9	3.2	2.5	3.5
Mg^{2+}	1.3	1.2	1.2	1.6	1.2	1.3	3.1	1.9	2.3	2.7	2.3	2.3
Ca^{2+}	3.6	3.4	2.3	3.9	3.6	3.7	7.8	4.3	5.3	10.3	7.0	7.7
Cl^-	3.5	5.2	4.9	5.1	6.3	6.0	8.4	6.0	7.0	11.1	8.0	8.8
NO_3^-	17.0	14.5	15.0	18.6	17.9	18.0	20.6	13.8	16.6	18.3	12.3	13.5
SO_4^{2-}	15.1	17.3	17.0	19.6	19.9	19.7	27.4	14.8	18.7	15.3	11.5	12.3
HCO_3^-	0.4	0.3	0.3	0.3	0.3	0.3	0.9	0.3	0.4	0.9	0.4	1.2
DOC	84.9	51.7	58.8	80.4	47.1	50.8	134.5	78.8	94.4	100.5	43.9	76.6
DIC	55.7	48.4	50.0	23.7	33.5	30.7	34.2	43.5	43.9	81.8	62.4	67.8
Cationic sum	56.0	65.7	64.2	57.3	54.5	56.1	62.9	56.1	63.2	79.0	69.3	72.3
Anion sum	36.6	38.0	37.7	45.3	47.5	46.6	60.2	36.4	44.7	45.1	34.0	38.0
Total sum	92.5	103.7	101.9	102.6	102.0	102.7	123.1	92.5	107.7	24.1	109.2	113.5
DEF ^a	19.4	27.7	26.6	12.1	7.0	9.5	2.7	19.7	18.3	33.9	35.4	34.3

^a DEF express the deficit of anions ($\text{DEF} = \Sigma\text{Cations} - \Sigma\text{Anions}$) in $\mu\text{eq l}^{-1}$.

H^+ , which had higher concentrations during the wet season (Table 2).

Typically it was observed an anion deficit varying from 11 to 25 $\mu\text{eq l}^{-1}$ (Table 1), which is within the range observed for other areas (Galloway et al., 1982; Lesack and Melack, 1991). In 70% of the samples an unidentified peak appeared in the anion chromatographic run and which could not be identified after several tests with different standards. The identification of such unknown peak is difficult because there are only very little rainwater composition studies in South America. Most of rainwater studies have been made elsewhere. In the North America, nitrate, sulfate and ammonium are the main ions responsible for the rainwater acidity (Munger and Eisenreich, 1983; Furi-ness et al., 1998), which is also the case in Malaysia and Indonesia (Ayers et al., 2000; Gillett et al., 2000), while in Africa, soil derived particles, provided by wind erosion, are the dominant source (Galy-Lacaux and Modi, 1998). In tropical and sub-tropical South America there are several unidentified organic compounds (Lesack and Melack, 1991; Willians, 1997), which could be interacting and be responsible for the unknown anion.

In order to identify possible associations between measured species, principal component analysis (PCA) was performed. Table 3 shows the factor analysis results with the VARIMAX rotated factor-loading matrix for each of the sampling sites. The communality for each variable, which represents the fraction of each variable that is, explained by the retained factors. In this analysis, communalities are typically higher than 70%. The last line on Table 3 express the percentage of variance explained by each factor. Qualitative sources, suggested by PCA results were: (1) influence of soil dust associated with Ca^{2+} and Mg^{2+} ; (2) biomass burning, more specifically sugar cane burning, which is associated with K^+ and Cl^- (3) industrial emissions, referred to as H^+ with significant correlations with SO_4^{2-} and NO_3^- ; (4) organic acidity factor, with DOC correlated with H^+ . The same structure has been observed in other rainwater and aerosol studies (Galy-Lacaux and Modi, 1998). For the Campinas site, a factor comprising industrial and soil dust related species explains the largest amount of data variability. This factor has high loadings for SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} , NH_4^+ and H^+ . The second factor is loaded with the organic components (DOC and DIC), and the third factor is associated with biomass burning emissions with high loadings for K and Cl. The communalities are high for most of the variables, except for DOC. For the Piracicaba site, sugar cane burning dominates data variability, followed by soil dust. The third factor with the presence of DOC and DIC surprisingly is also associated with acidity, indicating that acidity is dominated by organic acids, and not by SO_4^{2-} or NO_3^- . The last factor in Piracicaba is associated

with NO_3^- and acidity. For the Santa Maria a similar pattern to that of Piracicaba was observed, with large dominance of sugar cane burning, but also important sources in soil dust. A third component is present with acidity and DIC, but the nature of this component is unclear to us. For the Braganca site soil dominates the variability, followed by organic acidity. This picture is similar to the one observed in Campinas.

Annual deposition of total N was high, varying from 4.3 to 6.0 g m^{-2} . Hydrogen annual deposition was also high (38–44 meq m^{-2}), and sulfate annual deposition was smaller and varied from 13 to 25 meq m^{-2} (Table 4). Na^+ , K^+ , Mg^{2+} and Ca^{2+} deposition values are between values observed in remote and polluted areas of the Northern Hemisphere.

5. Discussion

In most studies of precipitation chemistry, an excess of cations relative to anions was generally found (e.g., Galloway et al., 1982; Keene et al., 1983). The precipitation chemistry in the Piracicaba River Basin also showed an anion deficit, which was comparable to the ones found in other tropical areas (Willians et al., 1997; Filoso et al., 1999). The unaccounted free acidity is normally attributed to organic acids (Keene et al., 1983; Keene and Galloway, 1984), which were measured but were close to the detection limit. The rainfall solute concentrations obtained in this work can be compared with some values for relatively pristine tropical areas (Table 5). The values obtained in this work were, in general, higher than the ones found in Manaus, except for K^+ , Mg^{2+} , and DOC (Willians et al., 1997; Filoso et al., 1999).

Three single factors appear to control the chemical composition of the rainfall in the Piracicaba Basin. The most important is soil dust related ions, such as Ca^{2+} and Mg^{2+} , since soil dust was the dominant source of variability in Braganca, and, was also present in the remainder sampling sites. Sugar cane burning is the second most important factor controlling the precipitation chemistry in the basin. The fact that agricultural related factors, such as soil dust and sugar cane burning, have strong influence on the atmospheric chemistry it is not surprising. Since 85% of the basin is cropland, and sugar cane plantations alone cover almost 31% of the basin area. Sugar cane is burned every year from May to October, emitting annually to the atmosphere approximately 100,000 tons of organic matter. In addition, each 5–6 yr plants are removed and replaced by new ones. Consequently, exposure of bare soil during the year, and a high erosion potential risk (Cerri et al., 2000) are a common fact in this basin. Besides the atmospheric chemistry effects, sugar cane burning emissions are also responsible for severe health effects in the area (Saldiva

Table 3
Component loading of component principal analysis for rainwater samples in the sampling cites

	Braganca soil	Braganca organic acidity	Braganca inorganic carbon	Braganca sugar cane	Braganca cummunal	Campinas inorganic acid./soil	Campinas organic acidity	Campinas sugar cane	Campinas cummunal
H ⁺	—	0.85	—	—	77	0.51	0.66	—	72
Na ⁺	0.78	0.32	0.68	—	70	—	0.80	—	68
NH ₄ ⁺	0.78	—	0.38	—	80	0.72	0.35	—	65
K ⁺	—	—	—	0.80	67	—	—	0.98	96
Mg ²⁺	0.81	0.34	—	0.22	81	0.87	0.20	—	79
Ca ²⁺	0.81	0.42	—	—	86	0.89	—	—	80
Cl ⁻	—	—	—	0.82	71	—	—	0.98	98
NO ₃ ⁻	0.85	—	—	—	83	0.79	—	—	63
SO ₄ ²⁻	0.85	—	—	—	76	0.64	0.33	0.39	66
DOC	—	0.70	—	—	56	—	0.63	—	43
DIC	—	—	0.92	—	86	—	0.76	—	60
% Var.	32.8	15.1	13.9	13.9		31.1	21.3	19.5	
	Piracic. sugar cane	Piracic. soil	Piracic. organic acidity	Piracic. inorganic acidity	Piracic. cummunal.	S. Maria sugar cane	S. Maria soil	S. Maria inorganic acidity	S. Maria cummunal.
H ⁺	—	—	0.79	0.5	88	—	—	0.90	72
Na ⁺	0.82	0.38	—	—	84	0.78	0.30	0.42	68
NH ₄ ⁺	0.81	0.27	—	—	74	0.39	0.67	—	65
K ⁺	0.61	0.53	—	—	54	0.72	0.29	—	96
Mg ²⁺	0.23	0.94	—	—	95	—	0.88	—	79
Ca ²⁺	0.28	0.91	—	—	93	0.27	0.90	—	80
Cl ⁻	0.69	0.23	0.27	—	67	0.74	0.45	0.37	98
NO ₃ ⁻	—	—	—	0.96	93	—	0.91	—	63
SO ₄ ²⁻	0.37	0.81	—	—	84	0.87	0.29	0.21	66
DOC	—	—	0.85	—	77	0.91	—	0.22	63
DIC	0.53	—	0.53	—	56	0.67	—	0.61	60
% Var.	26.3	25.2	15.1	10.5		36.5	30.9	15.6	

Table 4
Annual deposition rates of ions ($\text{meq m}^{-2} \text{yr}^{-1}$) for each sampling site

	Brag.	Camp.	Pirac.	S. Maria	NE-USA ^a	Jakarta ^b	Remote ^c
H ⁺	43.8	38.4	34.4	41.6	70.0	34.0	12.0
Na ⁺	2.8	3.5	3.0	4.9	20.0	—	—
NH ₄ ⁺	22.4	19.8	7.7	16.0	15.0	77.0	5.0
K ⁺	3.0	2.3	3.2	2.9	2.0	—	—
Mg ²⁺	1.4	1.6	2.6	2.5	5.0	—	—
Ca ²⁺	4.1	4.7	6.0	8.3	15.0	—	2.0
Cl ⁻	5.8	7.8	7.7	8.2	25.0	—	—
NO ₃ ⁻	18.1	23.0	17.9	14.8	30.0	49.0	5.0
SO ₄ ⁻	20.5	25.3	20.8	13.3	65.0	68.0	15.0

^aNortheastern US (Munger and Eisenreich, 1983).

^bJakarta (Gillett et al., 2000).

^cRemote area: NW Europe (Galloway et al., 1982).

Table 5
Comparison of VWM for selected solutes at four sampling sites and Manaus (Amazon)^a. All concentrations are expressed in $\mu\text{eq l}^{-1}$, except DOC in $\mu\text{M l}^{-1}$

	Bragança	Campin.	Piracic.	Santa Maria	Manaus (Amazon) ^a
H ⁺	36.3	29.7	33.0	39.7	17.0
PH	4.4	4.5	4.5	4.4	4.7
NH ₄ ⁺	18.6	15.4	17.1	14.5	3.0
Na ⁺	2.3	2.7	2.7	4.5	2.4
K ⁺	2.5	1.3	2.9	3.5	8.0
Ca ²⁺	2.3	3.4	5.3	7.7	2.4
Mg ²⁺	1.2	3.7	2.3	2.3	9.0
Cl ⁻	4.9	6.0	7.0	8.8	4.6
NO ₃ ⁻	15.0	18.0	16.6	13.5	2.0
SO ₄ ⁻	17.0	19.7	18.7	12.3	4.2
DOC	58.8	50.8	94.4	76.6	159

^aData from Willians et al. (1997).

et al., 1994). The third most important factor is industrial emissions, mainly in Campinas and Piracicaba sites, where the number of industries is much higher in comparison with Bragança and Santa Maria (Table 1).

As a consequence of these activities significant rainfall acidity was detected in the basin, which, in turn, was similar to values found in the most developed regions of the globe, where it is associated with strong anthropogenic activities (Levine et al., 1995; Chung et al., 1996; Granat et al., 1996; Mosello and Marchetto, 1996). Although rain acidity was found in all four sampling sites, the origin of this acidity appears to be different in each site. The association of DOC and H⁺ found in Bragança sampling site, in conjunction with the fact that most of the remainder original forests in the basin and extensive areas of silviculture are the dominant land-use in this part of the basin (Table 1), suggests that biogenic emissions, which could be oxidized to organic acids in

atmosphere (Andrea et al., 1987) could be a significant source of acidity in this region. However, further studies must be performed in this area to support the role of biogenic emissions. On the other hand, the high correlation between H⁺ and SO₄²⁻ and NO₃⁻ observed in Campinas, which is the most industrialized and urbanized area in the basin, suggests that sulfur and N play an important role in rain acidification in this part of the basin. Finally, sugar cane burning appears to exert the main control on atmospheric chemistry of sampling sites Piracicaba and Santa Maria. Biomass burning emissions include a significant amount of NO_x, which, converted to NO₃⁻, could be responsible for the acidity in the precipitation at Piracicaba and Santa Maria sampling sites. This hypothesis is supported by the association of K⁺ and Cl⁻ that can be released by biomass combustion in the form of KCl (Sequeira and Lai, 1998).

The effects of acid rain on ecosystems are acidification of soils and aquatic systems. Soils of the Piracicaba Basin are typically weathered tropical soils with natural low pH, variable charges and a low cation exchange capacity (see: www.cena.usp.br/piracena). Although other factors, such as soil texture and organic matter content, have to be taken into account, these soils have the basic conditions to be acidified by the high acidity observed in the Piracicaba River Basin (Rodhe et al., 1988). Surface water acidification is another potential problem in the basin, since levels of alkalinity in rivers, streams and reservoirs of the less polluted headwater regions are generally low (Martinelli et al., 1999b).

The sulfate concentration and deposition were lower than in other industrialized regions in Europe (Puxbaum et al., 1998) and North America (Munger and Eisenreich, 1983; Furiness et al., 1998). The annual deposition of total N in the basin (5.4 g m^{-2}) was similar to polluted regions of North America ($6.3\text{--}7.1 \text{ g m}^{-2}$) (Munger and Eisenreich, 1983; Furiness et al., 1998) and higher than deposition values (3.1 g m^{-2}) found in Asia (Granat et al., 1996). This high rate of N deposition was mainly in the form of ammonium. The high concentrations of ammonium can be attributed to sugar cane burning itself, volatilization of N from fertilizers, and biologically from sugar cane leaves, are also important sources of N to the atmosphere. It was estimated that from a total of approximately 36,000 tons of N annually applied in the field, approximately 75% of the available N is lost to the atmosphere (Filoso et al., 2001, submitted for publication). Considering the whole basin, the total annual N deposition would be equal to approximately $6300 \text{ tons yr}^{-1}$. Similar amounts of N is added annually to the rivers of the basin as urban sewage ($8400 \text{ tons yr}^{-1}$) and as industrial wastes ($5500 \text{ tons yr}^{-1}$) (Filoso et al., 2001, submitted for publication). Excess N availability has innumerable effects both on terrestrial and aquatic systems (Galloway et al., 1995; Vitousek et al., 1997). In temperate forests, depending on amount available, excess N may increase the terrestrial biomass primary productivity (Townsend et al., 1996), or may lead to “N saturation”, with deleterious consequences to the environment. On the contrary, in terrestrial tropical ecosystems, the excess of available N appears to reduce carbon uptake by vegetation through several mechanisms (Vitousek et al., 1997). In aquatic ecosystems, excess N can cause further acidification, and eutrophication. Although the Piracicaba River Basin as a whole is not accumulating N, but rather transferring N to higher order streams and exporting N to other areas, there are reaches of Piracicaba Basin rivers that had their N natural cycle severely disrupted by addition of anthropogenic N (Filoso et al., 2001, submitted for publication). Atmospheric N deposition in the basin is actively contributing to aggravate such scenario.

6. Conclusions

More than 10 years ago, the southeast region of Brazil was considered as a potentially problematic area regarding acidification problems (Moreira-Nodermann et al., 1988; Rodhe et al., 1988). The results of this study clearly showed that acid rain, followed by high deposition rates of N are already taking place in the Piracicaba River Basin. Land-use factors, such as intensive soil cultivation and sugar cane burning, together with industrial emissions, are the main causes of such environmental problems. Several other basins in the southeast region of Brazil are facing a similar type of “development”, with few concerns about the consequences of such changes on the environment. The few original patches of forest were replaced by croplands, followed by an increase in the number of industries and, consequently, people. Therefore, changes in the atmospheric composition in such basins can be considerable and similar to those experienced in the Piracicaba River Basin.

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