

Rainfall, throughfall and stream water chemistry data from two small catchments in São Paulo state Atlantic Forest (Brazil): urban and natural.

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#### ABSTRACT

This communication aims to disseminate a set of hydrochemical data obtained from two small catchments in the Atlantic Forest domain. Such data refers to the chemical composition of rainwater, throughfall water and river water from two catchments: one within an urban area, collected between 1999 and 2001, and the other within a forest area, collected between 2000 and 2004. The former is State Park of Fontes do Ipiranga (PEFI), a quadrangle delimited by parallels 23°40'20.4" S, 23°38'11" S, and meridians 46°36'38" W, 46°37'58" W. The latter is State Park of Serra do Mar, Núcleo Cunha-Indaiá (CUNHA) within parallels 23°13'28" and 23°16'10" S, and meridians 45°02'53" and 45°05'15" W. The datasets concerns the content of the main cations and anions ( $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cl^-$ ,  $NH_4^+$ ,  $NO_3^-$  and  $SO_4^{2-}$ ), as well as pH and alkalinity of rainfall, throughfall and stream water.

## 1. INTRODUCTION

This communication aims to disseminate a set of hydrochemical data obtained from two small catchments in the Atlantic Forest domain. Given the scarcity of this kind of environmental data, it is important that publicly funded research projects ensure not only the production of scientific articles, but also the availability of the subjacent data. The data presented herein refer to the chemical composition of rainwater, throughfall water and river water collected from two catchments: one within an urban area, collected between 1999 and 2001, and the other within a forest area, collected between 2000 and 2004. For a better understanding of the data, a brief description of the areas and references to the various studies conducted at these locations are offered.

Long-term data obtained from small catchments through an integrated approach are important in learning about hydrogeochemical functioning. Their relevance in understanding both the effects of long-term changes - such as those influenced by climate changes, soil use and occupation, and spurious atmospheric depositions – and the environmental impacts derived from such changes (Holko et al, 2015, Vose et al, 2014, Villarrubia et al, 1993) is clear. In addition, observational data are critical to the development and validation of models (Thomas et al, 2016).

High investments in human resources and materials are required in order to obtain this sort of data. In Brazil, investments are traditionally made through governmental grants to scientific foundations, research institutes and universities. Due to the public nature of this kind of funding, after a period of time the data should be made available, preventing that the knowledge associated with them is lost over time and allowing for them to be useful in research other than the originally proposed.

Integrated studies in small watersheds were implemented in the USA (Hubbard Brooks - <http://www.caryinstitute.org/newsroom/hubbard-brook-lessons-forest> consulted on May 05, 2017) and Europe/UK (Hornung et al, 1990) as early as in the 1950's. Their results generated great scientific progress, particularly in regard to the understanding of locally occurring processes. These integrated studies led to the formulation of several classes of models on the subject of soil-plant interactions, and a better understanding of the forest role in water resources conservation (quality and quantity, Neal, 2013, Vet et al., 2014; Cassiani et al, 2016), among other advancements. Time series analysis of this class of data, coupled with an increasing knowledge on

biogeochemical processes, has shown that it is possible to understand the mechanisms of observed changes and to distinguish between natural and anthropogenic causes (Moldan and Cerny, 1994, Kirchner, 2000).

Nevertheless, the number of studies focusing on that is very limited, particularly long-term ones. Data obtained by institutions as the Water National Agency (ANA - <http://www2.ana.gov.br/Paginas/default.aspx>), the National Institute of Meteorology (INMET - <http://www.inmet.gov.br/portal/>) and the Environmental Company of São Paulo State (CETESB - <http://www.cetesb.sp.gov.br>), whose mission is the monitoring of environmental parameters, are available mostly to a different class of scientific studies, in detriment of the ones referred to above.

## **2. DATA DESCRIPTION**

The data presented herein were generated as part of a study whose objective was to evaluate the rainwater-driven transfers of chemical species in soil-plant-atmosphere interfaces, and to relate them to the status of the local vegetation; the project received financial support from the São Paulo Research Foundation (FAPESP) Grant No 99/05204-4. For that purpose, an observation program was introduced in two small watersheds located in the Atlantic Forest, one of them in an urban area (polluted atmosphere - São Paulo/PEFI), and the other in a natural area (Núcleo Cunha-Indaiá/CUNHA). Samples from rainfall, throughfall and stream water were obtained during 27 months in the urban area and 17 months in the natural area, between May 1999 and September 2001 (Forti, 2003). The data concerns rainfall height, stream flow, the content of the main cations and anions (sodium, potassium, magnesium, calcium, ammonium, nitrate, sulfate, and chloride), pH and alkalinity. The most relevant results have been published in scientific journals (Fostier, et al, 2003; Bourotte et al, 2005; Forti, et al., 2005, Bourotte et al, 2006; Ranzini et al, 2007) and in book format (Bicudo et al 2002, Honda e Yamazoe, 2005). For both watersheds, a detailed soil description is offered elsewhere (Forti, 2003).

The small urban watershed is located in the biological reserve named Parque Estadual das Fontes do Ipiranga (PEFI) a quadrangle delimited by parallels 23°40'20.4" S, 23°38'11" S and meridians 46°36'38" W, 46°37'58" W with average altitude of 798 m (Oda, 1997). Relief and soil description can be found in Ab'Sáber

(1957), Ab'Saber (1956) and Almeida (1974). Details on the regional phytosociology and climate can be found in Santos and Funari (1976) and in Struffaldi -De-Vuono (1985); the region's normal precipitation is of the order of 1318 mm and mean temperatures in the coldest and warmest months are about 18°C and 22°C, respectively. A collection of studies about the PEFI was assembled by Bicudo et al (2002).

The small natural watershed is located in the State Reserve of Serra do Mar, Nucleo Cunha-Indaiá (CUNHA). It is also known as watershed B and belongs to the Laboratory of Hydrology "Dr. W Emmerich" of São Paulo state's Forestry Institute. CUNHA is in the northeast region of the state, in the Serra do Mar, at 2000 m mean altitude, in the headwaters of the Paraibuna River and on the right bank of the Paraíba River, between parallels 23°13'28" and 23°16'10" S and meridians 45°02'53" and 45°05'15" W, about 15 km from the coast. This watershed presents average temperatures between 26°C and 16°C with mean annual rainfall of 1500 mm, as described by Arcova et al. (1998) and Cicco (2009). Figure 1 shows the relative position of the areas.

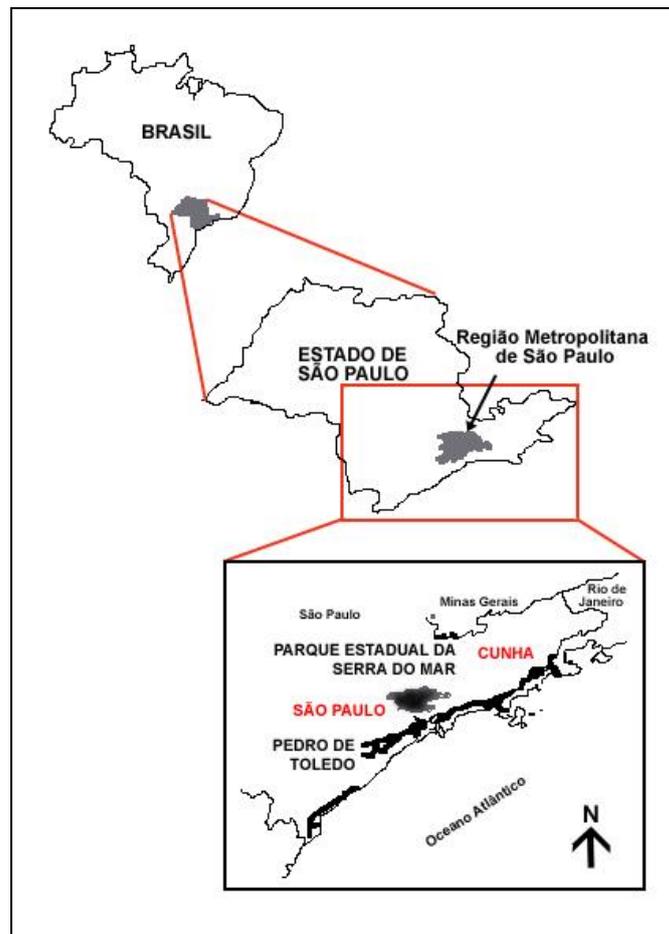


Figure 1 - Relative position of PEFI and CUNHA (extracted from Bicudo et al, 2002a).

### 3. DATA ACQUISITION

The hydrological data were provided by the collaborating institutions involved in the project and cover the whole of its duration. In the case of the CUNHA watershed, these data are a subset extract from the full dataset that has been continuously compiled since 1989 (Honda e Yamazoe, 2005). At this site, rainfall height was measured using tipping bucket pluviograph (0.5 mm/bucket) and fluviometric heights were recorded by float lines installed in fluviometric stations (Arcova et al, 1998). For the PEFI watershed, rainfall data were obtained from the meteorological station of University of São Paulo's Astronomical and Geophysical Institute. Flow data were obtained from the weekly reading of a scale installed in a weir (Pereira Filho et al, 2002).

If enough rain had fallen, the sampling bottles of rain and throughfall water would be collected every 7 days, constituting accumulated samples for the period. In order to minimize dry deposition, all sampling bottles would be replaced with fresh ones after 15 days in case there had been no rain. At both sites, samples were collected in bulk samplers (5 L polyethylene bottle attached to a funnel with a diameter of 167.45 cm<sup>2</sup> protected with a nylon screen), as well as in wet-only samplers (Figures 1a and 1b).



Figure 1a – Picture of the bulk collector installed next to the catchment B weir at CUNHA (Forti, 2000).



Figure 1b – Photo of wet-only collector (brand MTX - Italy) installed atop of the water tank at PEFI (Forti, 2000).

Each throughfall sample was a combination of 10 individual samples proportionally mixed to each sampled volume collected in a plot of 25 by 25 m. As described previously, the individual samples were collected in bulk collectors placed on 10 of the 36 spots of the plot, each separated from the others by 5 m. At each spot, a wooden stake (approximately 1.5 m high) was plunged into the soil and numbered from 1 to 36 before having a bulk rainfall collector fit to the free extremity. In order to maximize the probability of sampling the throughfall over the entire plot area, the 10 different positions were randomly moved at the end of each collection period. Their new positions were determined through the generation of 10 random numbers from 1 to 36. Figure 2 shows a CUNHA throughfall plot where there are two stakes. One of them has a collector fit to its upper end (foreground) and the other does not (background). For each rainfall or throughfall sample collected, the sampled volume was gravimetrically determined. As mentioned above, after determining the volume in each collector, throughfall samples were proportionally mixed to compose one single blended sample.



Figure 2 – Photo of the throughfall plot installed at CUNHA (Forti, 2000).

The stream water samples were collected every 7 days, about 10 m upstream from the backwater area of the weir. That was done by plunging the bottle into the middle of the stream, rinsing it at full volume and filling it up again to obtain the sample. For the PEFI, the scale was read simultaneously with the stream sampling. Figures 3a and 3b show pictures of the PEFI and CUNHA weirs, respectively.



Figure 3a. Weir installed at the PEFI stream basin (Forti, 2000).



Figure 3b. Weir installed at the CUNHA stream B watershed (Forti, 2000).

In order to obtain the soluble fraction and sterilize the sample, all samples were vacuum filtered using pre-washed 0.22  $\mu\text{m}$  pore membrane filters. After proper preservation (Apello & Postma, 1996), all samples were stored in a refrigerator at 4° C until the analysis.

Immediately after collection and preparation, the pH of all samples was measured, as was the alkalinity of the stream samples, the latter using the Gran titration method. Determination of chemical species was carried out by means of liquid ion chromatography technique, using Dionex DX-500 equipment. For the basic cations and ammonium, a CS12 analytical column and sulfuric acid were used as eluent; for the anions, an AS4A analytical column and sodium carbonate / bicarbonate were used as eluent with an electrochemical detector. The accuracy and precision obtained for this data set are presented in Table 1. Accuracy values were calculated using synthetic rain reference samples 409 for the main cations and anions produced by Environmental Canada and primary standards provided by the Center for Ecology and Hydrology of the Natural Environmental Research Council - United Kingdom.

Table 1 – Precision and accuracy (PR: Precision; AC: Accuracy), as determined by liquid ion chromatography, for the chemicals, in %

	$Na^+$	$K^+$	$Mg^{2+}$	$Ca^{2+}$	$NH_4^+$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$
PR %	3	3	8	8	10	3	3.5	8
AC %	7	9	11	9	11	8	10	8

#### 4. DATASETS AVAILIABILITY

The available data were edited and submitted to the critical analysis of project participants using statistical tools. Datasets and their metadata are available as follow:

Type of Collect	Reserve name	Dataset and Metadata available at:
Bulk	State Park of Fontes do Ipiranga - PEFI	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q76U6L">http://urlib.net/rep/8JMKD3MGP3W34P/3Q76U6L</a>
Wet-only	State Park of Fontes do Ipiranga - PEFI	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q77A3L">http://urlib.net/rep/8JMKD3MGP3W34P/3Q77A3L</a>
Manual Bottle	State Park of Fontes do Ipiranga - PEFI	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q77AK8">http://urlib.net/rep/8JMKD3MGP3W34P/3Q77AK8</a>
Troughfall Bulk	State Park of Fontes do Ipiranga - PEFI	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q77B5H">http://urlib.net/rep/8JMKD3MGP3W34P/3Q77B5H</a>
Bulk	State Park of Serra do Mar Núcleo Cunha - CN	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q73ELH">http://urlib.net/rep/8JMKD3MGP3W34P/3Q73ELH</a>
Wet-only	State Park of Serra do Mar Núcleo Cunha - CN	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q76HME">http://urlib.net/rep/8JMKD3MGP3W34P/3Q76HME</a>
Manual Bottle	State Park of Serra do Mar Núcleo Cunha - CN	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q76JM5">http://urlib.net/rep/8JMKD3MGP3W34P/3Q76JM5</a>
Troughfall Bulk	State Park of Serra do Mar Núcleo Cunha - CN	<a href="http://urlib.net/rep/8JMKD3MGP3W34P/3Q76L4S">http://urlib.net/rep/8JMKD3MGP3W34P/3Q76L4S</a>

Rainfall - The dataset obtained for the PEFI (May-99 to September-01) includes three rainy and two dry periods. In CUNHA the dataset was obtained during 17 months covering 1 period of rain and 2 dry periods. For these samples, a statistical comparison was made between the data from the bulk and the wet-only collectors. For CUNHA, no statistically significant differences were found between the two sample sets for any chemical species. For PEFI, it was observed that, for  $Na^+$ ,  $K^+$  and  $Cl^-$ , the differences between the two types of collectors were significant, and the mean concentration values for the bulk collectors were larger than for the wet-only type. It leads to the conclusion that for periods of exposure of up to 15 days, bulk collectors can be used in natural regions or in regions where anthropogenic chemicals concentration in the atmosphere is low therefore, the bulk concentration values can be considered as wet-only deposition. Table 2 presents statistics for the content of the different chemical species in the rainwater at both sites.

Table 2 - Statistics for the ionic content in rainwater collected at PEFI and CUNHA (between 1999 and 2001), with 3 significant figures. Concentrations in  $\mu Eq.L^{-1}$ , precipitation in mm. P: precipitation during the period, N: number of samples, MAX: maximum value, MIN: minimum value and VWM: volume-weighted mean

	PEFI				CUNHA			
	Prec	2713 mm			Prec	2312 mm		
	N	VWM	Max	Min	N	VWM	Max	Min
		$\mu Eq.L^{-1}$				$\mu Eq.L^{-1}$		
$H^+$	58	54.0	427	0.01	53	2.65	20.4	0.05
$Na^+$	60	15.5	231	0.00	50	8.06	80.5	0.00
$K^+$	60	12.1	155	0.59	50	5.30	65.2	0.00
$Mg^{2+}$	60	8.93	180	1.06	50	2.81	19.4	0.00
$Ca^{2+}$	60	30.0	464	0.58	50	1.82	18.3	0.00
$NH_4^+$	60	70.0	490	4.90	50	27.9	955	0.00
$Cl^-$	60	27.0	341	0.00	50	17.0	204	1.91
$NO_3^-$	60	70.0	424	0.00	50	4.78	106	0.00
$SO_4^{2-}$	60	46.0	388	0.34	50	6.99	77.3	0.00

Throughfall - Throughfall is defined as the precipitation that crosses the canopy and called “internal precipitation” by some authors. Leaves surfaces are active in response to several atmospheric components, exchanging chemicals in different states (solid, liquid and gaseous). Thus, when a rainy episode occurs, rainwater interacts with the canopy generating throughfall, which is the result of the change in rainwater composition resulting from its interaction with the vegetation. Several active processes take place – namely, the washing of soluble species such as  $Na^+$  and  $Cl^-$  deposited over its parts, the leaching of soluble chemical species in leaf tissue as  $K^+$  or on plant structures in decomposition such as  $Ca^{2+}$ , and the absorption of other species such as  $NH_4^+$  and  $NO_3^-$ . In regions like PEFI, where atmospheric chemical species input is highly anthropic derived, the natural interaction processes are altered by the excess of these species (Forti et al, 2005). Table 3 presents statistics for the content of the different chemical species in the throughfall water at both sites during the study period.

Table 3 - Statistics for the ionic content of throughfall water collected at PEFI and CUNHA (between 1999 and 2001), with 3 significant figures (TR). Concentrations in  $\mu Eq.L^{-1}$ , precipitation in mm and interception in %. PTR: height of throughfall during the period, Interc: interception; N: number of samples, MAX: maximum value, MIN: minimum value and VWM: volume-weighted mean.

	PEFI				Cunha			
	PTR	2330 mm	INTERC.	14 %	PTR	1804 mm	INTERC.	20 %
	N	VWM	MAX	MIN	N	VWM	MAX	MIN
	$\mu Eq.L^{-1}$				$\mu Eq.L^{-1}$			
$H^+$	60	6.0	100	0.04	53	0.410	234	0.02
$Na^+$	62	36.5	170	1.21	50	39.2	147	18.5
$K^+$	62	143	741	3.15	50	216	882	72.6
$Mg^{2+}$	62	44.0	231	6.30	50	28.6	180	10.4
$Ca^{2+}$	62	80.6	515	12.0	50	31.9	291	7.16
$NH_4^+$	62	77.9	1821	0.33	50	16.3	1374	0.00
$Cl^-$	62	79.9	400	5.33	50	131	534	37.3
$NO_3^-$	62	63.0	293	0.00	50	5.17	51.7	0.00
$SO_4^{2-}$	62	115	590	0.00	50	47.4	332	11.8

The throughfall pH is higher in CUNHA (pH around 6) than in PEFI (pH around 5). Throughfall water in PEFI is slightly acidic indicating that the bases, normally leached from the vegetation or solubilized from the dry deposition, are not enough to neutralize the acidity introduced by the precipitation.

Stream waters - Water infiltrated into the soil emerges at points along the riverbed. These are natural areas of groundwater discharge, as are water sources and infiltration regions. In discharge zones, ion exchange reactions must occur within the root zone, preserving the ionic balance with the relatively saline groundwater. Therefore, stream water chemistry results from interaction processes that take place from the moment rainfall drops reach the catchment until water emerges on the streambed. Table 4 presents statistics for the stream waters of the PEFI and CUNHA catchments for the period considered.

Table 4 - Statistics for the stream waters ionic content sampled at PEFI and CUNHA B catchments. Concentrations in  $\mu\text{Eq.L}^{-1}$ , Dis: Discharge in mm during the period, N: number of samples, MAX: maximum value, MIN: minimum value and DWM: discharge weighted mean.

	PEFI				CUNHA			
	Dis.	327.95 mm			Dis	1331 mm		
	N	DWM	Max.	Min.	N	DWM	Max.	Min.
		$\mu\text{Eq.L}^{-1}$				$\mu\text{Eq.L}^{-1}$		
$H^+$	97	14.4	81.3	1.10	65	0.23	0.72	0.03
$Na^+$	97	67.5	1823	4.49	65	70.0	202	38.0
$K^+$	97	16.2	112	3.08	65	15.7	111	0.11
$Mg^{2+}$	97	39.4	213	2.06	65	28.4	62.1	6.12
$Ca^{2+}$	97	25.4	78.3	0.00	65	19.9	36.0	0.00
$NH_4^+$	97	7.32	72.8	0.00	65	10.9	27.9	0.00
$Cl^-$	98	72.1	318	19.9	65	32.5	129	2.72
$NO_3^-$	98	31.3	363	0.14	61	11.2	76.8	0.22
$SO_4^{2-}$	98	35.7	68.7	5.94	65	8.77	95.9	1.16

## 5. MAIN CONCLUSION AND RECOMMENDATION

As an urban forest, PEFI is under the influence of high deposition of pollutants and contaminants, a condition that is reflected by the species deposited through rainfall. On the other side, far from urban centers, CUNHA presents comparatively low deposition values (Bourotte, 2002). The netflow of chemicals in the case of throughfall waters show significant differences in the nutritional status of the vegetation, which can be attributed to the difference in the action of pollutants between the two sites.

A sensible hypothesis would be that CUNHA's nutrient cycle remains preserved, rendering the area a reference for future small catchment studies.

Chemical fluxes through the catchment compartment are significantly higher in PEFI, mainly due to the large amount of pollutants present in the atmosphere, especially  $NO_3^-$  and  $SO_4^{2-}$ . Additionally, observed throughfall transfer patterns bring forward an altered nutritional status of the vegetation due to both soil and atmospheric transfers of excess nutrients. It is likely that PEFI stream waters are acidified either due to the closeness of sulfate adsorption capacity or already reached it. As expected for tropical forests the chemical transfers to the stream river waters are low, for both catchments, as a result of the internal recycling of nutrients and poor soils.

It must be emphasized that this study has not been followed by others, hindering the consolidation of knowledge for example, on the Nitrogen cycle as well as on the improvement of biogeochemical models applied to tropical regions. It is necessary to intensify and multiply integrated studies in different ecosystems, improve data quality and increase the number of comparative studies, leading to a deeper understanding of processes in soil-plant-atmosphere interaction. Such actions allow for the development and implementation of conceptual and mathematical models that could be useful as an additional tool in understanding the functioning of different biomes.

Finally, when seeking to integrate regions with different biomes and areas under anthropic pressure into a global network, much benefit could be attained by the expansion of integrated-approach (soil-plant-atmosphere, mediated by water) studies, particularly to tropical areas. The relative lack of such studies in South America places us far behind other countries in the advancement of our knowledge on how tropical regions - as natural forests, planted forests, crops and other agroecosystems - function, leaving us unable to define conservation and sustainability parameters.

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