

Nutrient cycling disturbance in Atlantic Forest sites affected by air pollution coming from the industrial complex of Cubatão, Southeast Brazil

MARISA DOMINGOS^{1,2}, MÁRCIA INÊS MARTIN SILVEIRA LOPES¹
and YARA STRUFFALDI-DE VUONO¹

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Abstract - (Nutrient cycling disturbance in Atlantic Forest sites affected by air pollution coming from the industrial complex of Cubatão, Southeast Brazil). Several aspects of nutrient cycling were studied at two sites of Atlantic Forest, in São Paulo State, Southeast Brazil (23°46' S and 46°18' W), which exhibited different degrees of forest structure decline caused by the air pollution emitted by the industrial complex of Cubatão, here referred as the most and least affected sites (MAS and LAS, respectively). These investigations were developed during 1984-1986, a period in which the most severe negative effects of air pollution could be observed. Concentrations and amounts of N, P, K, Ca, Mg and S in four ecosystem compartments (leaves, litter layer, soil and roots) and in rainfall, throughfall and litterfall are briefly presented. At each site, the content of mineral elements generally decreased from leaves to litterfall and litter layer on the forest floor. Soil surface layer (0-5 cm) in both sites was the richest in mineral elements. Soil fertility was greater at LAS. In general, nutrient amounts remaining in the compartments and cycling through the ecosystem were greater at LAS as well, which could be due to the higher complexity of the forest structure at this site. Rainfall contributed more to soil inputs of K, Ca, Mg and S than litterfall at both sites. The nutrient residence times in the litter layer were higher and the index of nutrient use efficiency was lower at the most affected site. It was concluded that nutrient cycling was disturbed by air pollution at both sites, but to a greater extent at MAS. The main consequences of air pollution stress were detected in the flux of nutrients through litterfall and in the litter layer on the forest floor.

RESUMO - (Distúrbios na ciclagem de nutrientes em locais da Floresta Atlântica atingidos pela poluição aérea proveniente do complexo industrial de Cubatão, sudeste do Brasil). Foram estudados vários aspectos da ciclagem de nutrientes, em dois locais cobertos por Floresta Atlântica, no Estado de São Paulo, Sudeste do Brasil (23°46' S e 46°18' W). Esses locais exibiam diferentes graus de declínio da estrutura da floresta causado pela poluição aérea emitida pelo complexo industrial de Cubatão, sendo aqui referidos como locais mais e menos afetados (MAS e LAS, respectivamente). Os estudos foram desenvolvidos de 1984 a 1986, período em que eram observados os efeitos negativos mais graves da poluição aérea. São apresentados, de forma sintética, os valores médios das concentrações e das quantidades de N, P, K, Ca, Mg e S em quatro compartimentos do ecossistema (folhas, serapilheira acumulada sobre o solo, solo e raízes), na precipitação incidente, na água de gotejamento e na serapilheira produzida. Em cada local, os conteúdos dos elementos minerais foram decrescentes nas folhas, na serapilheira produzida e na acumulada sobre o solo. No local menos afetado (LAS), a camada superficial do solo (0-5 cm) foi mais rica em nutrientes; a fertilidade do solo e, em geral, as quantidades de nutrientes presentes nos compartimentos e as que ciclavam entre os mesmos também eram maiores, o que pode ser devido à maior complexidade da estrutura da floresta nesse local. Em ambos os locais, a precipitação geralmente contribuiu mais para a entrada de K, Ca, Mg e S no solo do que a serapilheira produzida. No local mais afetado pela poluição (MAS), o tempo de residência dos nutrientes na serapilheira acumulada sobre o solo foi maior e o índice de eficiência de uso desses nutrientes foi menor. O processo de ciclagem de nutrientes foi perturbado em ambos os locais, porém de forma mais intensa em MAS. As principais conseqüências do estresse causado pela poluição foram detectadas no fluxo de nutrientes através da queda de serapilheira e no compartimento da serapilheira acumulada sobre o solo.

Key words - Air pollution effects, nutrient cycling, Atlantic Forest, Cubatão

Introduction

Emissions of air pollutants due to the disorganized industrial development in the tropics and subtropics during the last few decades have caused severe effects on natural ecosystems. In Southeast Brazil, for example, the Atlantic Forest decline in the

1. Seção de Ecologia, Instituto de Botânica, Caixa Postal 4005, 01061-970 São Paulo, SP, Brasil.
2. Corresponding author: mdomingos@sntp-gw.ibot.sp.gov.br

neighborhood of the industrial complex of the Cubatão is known world wide. There are more than 20 major industries within such area, including chemical/petrochemical, fertilizer, cement and steel industries (Alonso & Godinho 1992). According to these authors, only in 1984, about 114,000 tons of particulate materials, 28,500 of sulfur dioxide, 22,200 of nitrogen oxides, 3,100 of ammonium and 950 of fluorides were released to the atmosphere by the industries. Predominant air currents at daytime transport this complex mixture of air pollutants from the sea level, where they are produced, through narrow valleys up to the forested slopes of the Serra do Mar mountains, where they are deposited (Fiedler & Massambani 1997). In Cubatão, this situation is exacerbated by climatic conditions, characterized by high temperature, rainfall and humidity, and by local geography. The forest decline is particularly evident on the most exposed slopes, from the sea level to above 800 m of altitude. In many areas, the upper tree stratum experiences intense injury and high mortality rates, causing a reduction in species diversity and disturbance in its ecological functions (Secretaria do Meio Ambiente 1990, Gutberlet 1996). As a consequence, the frequency of large-scale landslides increased, reaching a maximum in 1985 (Ab'Saber 1987, Secretaria do Meio Ambiente 1990, Leitão-Filho et al. 1993, Gutberlet 1996, Domingos et al. 1998).

Several studies in temperate regions have demonstrated that ecosystem vitality, especially nutrient cycling, can be affected by air pollution stress (Smith 1981, Liljelund & Nihlgard 1988, Delitti 1995). These functional changes are more intense in forests whose physiognomy and structure were also

affected (Smith 1981). According to this author, air pollutants may influence nutrient dynamics at different points in the cycle, providing additional nutrients via meteorological inputs, altering decomposition, leaching, and weathering rates and interfering with symbiotic microorganisms. Similar effects, with differing intensities depending on the extension of forest structure alterations, were hypothesized to happen in tropical regions, where negative effects might be more severe since forest ecosystems rely heavily upon the efficient cycling of mineral nutrients (Vitousek 1982, 1984).

In order to evaluate the extension in which disturbances on the structure and physiognomy of Atlantic Forest observed at the Serra do Mar mountains were followed by functional changes, some aspects of nutrient cycling were studied in two sites, differentially affected by air pollutants from the industrial complex of Cubatão. The investigation was performed during 1984-1986, a period in which the negative effects of air pollution were at the maximum.

Material and methods

The study area - The study area is located in São Paulo State, Southeast Brazil (23°46'S and 46°18'W), on the plateau of the Serra do Mar mountains and belongs to the Biological Reserve of Paranapiacaba, which was created in 1909 (Hoehne 1925) and preserved since then. The vegetation is classified as Tropical Submontane Rain Forest, typical Atlantic Forest from that region, and it was characterized by high species diversity in the past (Coutinho 1962). General characteristics of the area are described in table 1. Due to its location facing the Mogi river valley, the reserve has been affected by air pollution

Table 1. General characteristics of the Biological Reserve of Paranapiacaba (23°46'S and 46°18'W), Southeast Brazil.

Altitude	750-890 m
Soil	Alic Red Yellow Latosol + Dystrophic Cambisol
Climate - Koeppen	Cfb
- Thornthwaite	Mesothermic, super humid
Mean annual temperature	17.9 °C (mean of 52 years: 1870 to 1922)
Mean annual rainfall	3381 mm (mean of 23 years: 1945 to 1968)
Dry season	absent
Relative humidity	frequently about 100%
Predominant vegetation	Tropical Submontane Rain Forest (regionally known as Atlantic Forest)

emitted by the industrial complex of Cubatão (Gutberlet 1996, Klumpp et al. 1996, Domingos et al. 1998), installed at sea level at the other end of the valley. Pollutants are transported by wind through this narrow and deep valley (Fiedler & Massambani 1997), reaching mainly the most exposed portions of the forest, located at the extreme East of the Biological Reserve. The greatest effects of air pollution on the ecosystem were those caused by gaseous compounds of fluorine, nitrogen and sulfur, observed during the sixties to eighties, when tree mortality was peaked and a simplification of forest structure occurred in those portions (Secretaria do Meio Ambiente 1990). At the present time, the above gaseous emissions are better controlled (Alonso & Godinho 1992) and the forest is mainly affected by phytotoxic concentrations of secondary compounds such as ozone (Klumpp et al. 1994).

Experimental sites - In the extreme East of the study area, two experimental sites (one ha each) were selected for conducting parallel studies of nutrient cycling. The criterion employed to select the sites was the degree of detectable decline in the forest structure, in order to select a more and a less affected site by air pollution, hereafter referred as MAS and LAS, respectively. Both sites are at about the same altitude (750-790 m), on a flat local relief. The distance from each other is only approximately 500 m, but the MAS is nearer to the entrance of the Mogi valley than the LAS, and, consequently, it was more severely reached by the air pollutants. Table 2 summarizes the state of both sites during 1984-1986, when the studies reported here were conducted. Taking into account that all this part of the Biological Reserve of Paranapiacaba, including both sites, had a similar physiognomy until the sixties (Coutinho 1962) and that no other natural or anthropogenic phenomena was registered at that time (Struffaldi-De Vuono & Domingos 1990), differences in functional processes observed between sites are attributed to the higher forest decline caused by air pollution at MAS. This site also presented structural changes, including greater number of gaps and standing dead trees in the forest canopy.

Nutrient cycling studies - These studies were based on the compartment and flux model proposed by Eriksson (1971).

In both experimental sites, the compartments analyzed were leaves, litter layer, soil and roots, while the fluxes were rainfall, throughfall and litterfall. The concentrations ($\text{mg} \cdot 100 \text{ g}^{-1}$ dry mass) of N, P, K, Ca, Mg and S were determined in all fractions. The standing stocks ($\text{kg} \cdot \text{ha}^{-1}$) and fluxes ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{y}^{-1}$) of these mineral elements were also estimated, except for the leaf compartment, whose biomass could not be estimated through destructive or non-destructive methods.

Samples were taken from points randomly selected inside each experimental site. In winter (August/1985) and summer (February/1986), five mixed samples of fully expanded leaves of all trees living around five sampling points were obtained. Thirty samples of litter layer were collected from 10 sampling points, after summer and winter seasons (March and September/1985, respectively), using a 0.25 m^2 plot (Lopes et al. 1990). During the same periods and in the same points, 30 soil samples at 0-5, 5-10 and 10-60 cm depths were taken, using one-liter cylindrical gauge, in order to analyze soil chemical and physical properties. Thirty soil samples at 0-60 cm depth were additionally taken, in the same periods and sampling points and using the same gauge, from which all roots were extracted through decanting soil particles and manual separation from the remnant organic material (Struffaldi-De Vuono et al. 1989b). Over a period of one year (October/1984 to September/1985), two samples of rainfall and 10 of throughfall were taken biweekly from polyethylene pluviometers, with 165 cm^2 funnels (Domingos et al. 1995). During the same period, litterfall was monthly sampled, using 25 traps with 0.25 m^2 each (Domingos et al. 1990). Pluviometers and litter traps were grouped around the same five sampling points where the leaves were taken. More details about the sampling methods employed are described in the literature above cited.

Chemical analysis - Plant samples were oven-dried (70°C), ground and digested. N was determined by spectrophotometry, P by colorimetry, K, Ca and Mg by atomic absorption spectrophotometry, and S by a turbidimetric method (Zagatto et al. 1981).

Soil samples were air and oven-dried (80°C), ground and sieved. Total N was determined by macro-Kjeldahl, extractable PO_4^{3-} and K using 0.05 N sulfuric acid by colorimeter and flame photometer respectively, and exchangeable Ca and Mg in 1 N potassium chloride by titration, and water soluble SO_4^{2-} , precipitated as barium sulfate, using a gravimetric method (EMBRAPA 1979, Raij & Quaggio 1983).

Rain samples were filtered and frozen, and NH_4^+ and NO_3^- contents were analyzed. Filtered and acidified (with concentrated nitric acid 1:1000) rain samples were used for determining PO_4^{3-} , K, Ca, Mg and SO_4^{2-} . The analytical methods were the same as those the plant material analyses.

Results of the concentrations and standing stocks of nutrients obtained in both sites are expressed as annual means, while the fluxes of mineral elements are presented as sum of amounts per year.

Results

At both sites, the concentrations of each mineral element in the forest compartments decreased from leaves to litterfall and litter layer on forest floor, except for Ca, whose concentrations were similar in leaves and litterfall. These results show the effects of nutrient translocation before leaf fall or leaching

from leaf surfaces or both, as well as the release of nutrients during the decomposition process, as currently described. Except for K, the analyzed nutrients were less concentrated in roots than in other plant compartments and in litterfall (table 3).

In the soil, the highest concentrations of mineral elements at both sites (table 3) were found in the

Table 2. Characteristics of the most affected site (MAS) and the least affected site (LAS) by air pollution, in the Biological Reserve of Paranapiacaba, Southeast Brazil (data from the period 1984-1986).

Characteristics	MAS	LAS
Forest structure (trees with D.B.H. \geq 5 cm) ^a		
Total density (ind.ha ⁻¹)	1453	2114
Number of families	20	30
Number of species	37	63
Soil ^a		
Surface chemistry (0-5 cm)		
pH in H ₂ O	3.5-3.7	3.4-3.6
Potential acidity (H ⁺ +Al ³⁺ / meq.100 cm ⁻³)	12.0-16.5	16.6-18.4
Sum of bases (meq.100 cm ⁻³)	2.0-3.1	2.4-3.6
CEC at pH 7.0 (meq.100 cm ⁻³)	14.0-19.6	20.3-20.9
Base saturation (%)	14.5-15.9	11.6-18.0
Aluminum saturation (%)	27.9-41.7	32.6-47.9
Organic matter (%)	15.1-20.9	21.9-22.4
Granulometry (0-20 cm)	sandy silt	sandy silt
Sand (%)	70.6	68.1
Silt (%)	21.4	21.9
Clay (%)	8.0	10.0
Litterfall (kg.ha ⁻¹ .y ⁻¹) ^b	1803	3810
Standing stock (kg.ha ⁻¹) ^c	8174	8989
Decomposition rate (loss of dry weight - %.y ⁻¹) ^d	48	53
Roots (0-60 cm) ^a		
Total biomass (kg.ha ⁻¹)	6771	9288
Rain precipitation ^e		
Rainfall (mm)	3112	3153
Throughfall (mm)	3027	2032
Mean annual interception (%)	2.7	35.6
pH of rainfall water	4.4-6.3	4.6-5.8
pH of throughfall water	4.4-5.5	5.0-5.6

^a Struffaldi-De Vuono et al. (1989b); ^b Domingos et al. (1990); ^c Lopes et al. (1990); ^d Struffaldi-De Vuono et al. (1989a);

^e Domingos et al. (1995).

surface layer (0-5 cm), with a distinct decrease in concentrations associated with increasing depth. Soil chemical status at LAS was higher than at MAS, which may be a result of the greater complexity of the forest structure, the higher amount of litter produced and accumulated on soil, as well as the higher decomposition rates and rain interception at LAS (table 2).

Comparing the two sites, LAS had, in general, higher amounts of nutrients retained in the compartments and cycling through the ecosystem (table 4). Although not estimated, leaf biomass at LAS probably contained higher contents of nutrients than at MAS, considering the most complex forest structure in this site, which could be evidenced through litterfall and rain interception (table 2). The root compartment at both sites was small and stored low amounts of nutrients (table 4), when compared to data reported for other tropical and subtropical forests (Vitousek & Sanford Jr. 1986, Vogt et al. 1986, Medina & Cuevas 1989).

The stocks of N, Ca and Mg were greater in the upper soil compartment (0-5 cm) than in the litter layer+roots; however, the amounts of the other nutrients were similar both in soil and litter layer+roots (table 4).

The input of K, Ca, Mg and S through rainfall at both sites was far greater than the contribution of litterfall (table 4), while the opposite was observed

in relation to the input of N and, in a less extent, of P. The figures for net throughfall demonstrate the higher complexity of forest structure in the LAS.

Discussion

Results obtained in the present study confirm that plant communities display an important role in the nutrient cycling, contributing for the mineral enrichment of soil, which can be considered as shallow, sandy, acid and infertile, such as other soils under Atlantic Forest of Southeast Brazil (Rossi & Pfeifer 1991) and from other tropical forests (Jordan & Herrera 1981, Vitousek 1984, Vitousek & Sanford Jr. 1986, Medina & Cuevas 1989, Delitti 1995).

Litterfall is considered one of the most important ways of nutrient transfer to soil in undisturbed forests (Vitousek & Sanford Jr. 1986). In the present study, even at LAS, the input of some nutrients via litterfall (for example Ca, Mg and S) was lower or comparable to the input via throughfall (table 4). This could be explained by changes in the forest structure and consequent very low litterfall, as previously emphasized (Domingos et al. 1990).

Some authors, including Gosz et al. (1976), Vitousek (1982, 1984) and Bridgham et al. (1995), proposed indices to evaluate how efficient is the nutrient use in many tropical ecosystems, which normally show very different nutritional status of

Table 3. Annual concentrations (mg.100 g⁻¹ dry mass) of mineral elements in the vegetation-litter-soil system in the most affected site (MAS) and the least affected site (LAS) by air pollution, in the Biological Reserve of Paranapiacaba, Southeast Brazil, in the period 1984-1986. Values are the means of concentrations measured during winter and summer seasons (leaves, litter layer, roots and soil) or during one year (litterfall).

Vegetation-litter-soil system	N		P		K		Ca		Mg		S	
	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS
Leaves	2650	2320	180	140	1040	1020	1220	1060	280	250	450	390
Litterfall ^a	2620	2190	120	90	350	270	1240	1020	170	140	390	350
Litter layer ^b	1730	1710	80	70	90	90	670	620	70	80	330	320
Roots ^c	1340	1130	60	60	110	110	190	420	50	60	180	180
Soil ^c 0-5 cm	810	990	1.5	2.2	4.1	5.5	33	38	9.2	11	5.4	10
5-10 cm	250	310	0.83	0.83	2.0	2.1	16	18	5.5	6.2	2.3	11
10-60 cm	160	210	0.83	0.59	1.7	1.5	12	12	4.1	5.0	2.2	3.4

Nutrients in soil: Total N, extractable PO₄³⁻-P and K, exchangeable Ca and Mg, and water soluble SO₄²⁻-S. ^aDomingos et al. (1990); ^bLopes et al. (1990); ^cStruffaldi-De Vuono et al. (1989b).

Table 4. Standing stocks (means of amounts estimated in winter and summer seasons) and fluxes (sum of amounts per year) of mineral elements in different compartments in the most affected site (MAS) and least affected site (LAS) by air pollution, in the Biological Reserve of Paranapiacaba, Southeast Brazil, in the period 1984-1986.

Standing stocks/Fluxes	N		P		K		Ca		Mg		S	
	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS
Standing stocks (kg.ha ⁻¹) ^{a, b}												
Litter layer	138	155	7	7	7	8	55	54	6	7	27	29
Roots (0-60 cm)	91	106	4	6	7	10	13	39	3	6	12	17
Soil 0-5 cm	4041	4957	8	11	20	27	165	192	46	54	27	52
5-10 cm	1255	1542	4	4	10	11	83	90	28	31	12	57
10-60 cm	8095	10684	41	31	87	72	587	621	205	252	112	172
Organic reservoir (kg.ha ⁻¹)												
Litter layer+roots	229	261	11	13	14	18	68	93	9	13	39	46
Fluxes (kg.ha ⁻¹ .y ⁻¹) ^{c, d}												
Rainfall	17	17	1	1	6	8	19	13	3	4	26*	43*
Throughfall	17	17	2	3	18	35	41	35	6	7	44*	47*
Net throughfall	0	0	1	2	12	27	22	22	3	3	18*	4*
Litterfall	46	82	2	3	6	10	21	38	3	5	7	13

N in rain water estimated through NO₃-N + NH₄-N; P and S in rain water and soil estimated through PO₄-P and SO₄-S respectively; *Results from 10 months. ^a Lopes et al. (1990); ^b Struffaldi-De Vuono et al. (1989b); ^c Domingos et al. (1995); ^d Domingos et al. (1990).

soil. Data from several ecosystems, including plantations and forests at different successional stages, were utilized to test those models. According to Vitousek (1982), it should be possible to find sites where N is adequately available, but some factor, such as drought stress, strongly limits production. In this case, the pattern predicted in his model will not be reached. Based on this statement, the indices proposed by Gosz et al. (1976), Vitousek (1982, 1984) and Bridgman et al. (1995) were estimated, using data obtained in both sites of the present study (table 5), aiming at better understanding the extent of air pollution influence in the nutrient cycling in the Atlantic Forest.

Very low litterfall (Domingos et al. 1990) and high litter accumulation on the soil surface (Lopes et al. 1990) resulted in greater nutrient residence times (*sensu* Gosz et al. 1976) in the litter layer at MAS than at LAS (T1 - table 5). Vogt et al. (1986) reported mean residence times between 0.2 and 2.9 years for N and between 0.9 and 2.3 years for P, in tropical and subtropical broadleaf forests. Estimated resi-

dence times for both nutrients at MAS were longer than those limits and close to the upper limit of the range at LAS. Vogt et al. (1986) hypothesized that one of the causes of such variations is the dissimilar use of nutrients by microflora during the decomposition process. In forests disturbed by air pollution, the microbial community is affected itself, resulting in decomposition rates lower than expected (Smith 1981, Fritze et al. 1992), which may have happened in the sites here studied, causing increases in the nutrient residence times in the litter layer.

If the input of nutrients via throughfall is also considered (Gosz et al. 1976), residence times (T2 - table 5) decrease considerably, mainly for MAS, showing again the greater importance of rain water to the nutrient cycle at this site (ΔT - table 5). However, part of this input may have been lost before being taken up by the plants, due to high rainfall, low interception and low capacity of buffering rain water acidity along the year (Domingos et al. 1995).

Table 5. Nutrient residence times (T1 and T2; in years) in the litter layer, according to Gosz et al. (1976), and index of nutrient-use efficiency (NUE), according to Vitousek (1982), in the most affected site (MAS) and least affected site (LAS) by air pollution, in the Biological Reserve of Paranapiacaba, Southeast Brazil. Values were obtained after estimation for 1984-1986.

Nutrient	T1		T2		ΔT		NUE	
	MAS	LAS	MAS	LAS	MAS	LAS	MAS	LAS
N	3.0	1.9	2.2	1.5	0.8	0.5	39	46
P	3.3	2.0	1.5	1.1	1.8	0.9	901	1089
K	1.2	0.8	0.3	0.2	0.9	0.6	300	385
Ca	2.5	1.4	0.9	0.7	1.6	0.7	84	99
Mg	2.1	1.4	0.7	0.6	1.4	0.8	622	733
S*	3.9	2.2	0.5	0.5	3.4	1.7	258	289

*Results from 10 months in throughfall. $T1 = L/Lf$; $T2 = L/(Lf+T)$; $\Delta T = T1-T2$; $NUE = LF/Lf$. Where: L = amount of nutrients in the litter layer; Lf = amount in litterfall; T = amount in throughfall; LF = litterfall mass.

The index of nutrient use efficiency (Vitousek 1982, 1984) was lower at MAS than at LAS (NUE - table 5), which was a consequence of higher concentrations of all nutrients in the litterfall at the first site (table 3). Thus, the forest at MAS seemed to have a lower capacity for nutrient conservation and was not able to produce as much organic matter per unit of mineral taken up as the forest at LAS (*sensu* Vitousek 1982), probably resulting in higher nutrient concentrations in the leaf and litter compartments (table 3).

The vegetation at MAS presented a very low index of N and P-use efficiency, according to the model created by Bridgham et al. (1995) based on the approach of Vitousek (1982, 1984), and was completely out of the range predicted by the model. Nutrient-use efficiency was low at LAS, but closer to that predicted by the model. According to Bridgham et al. (1995), litterfall increases asymptotically with P and N returns in it, predicting a litterfall rate of about 6,000 to 7,000 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ for a N return of 45.6 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ and a P return of 2.0 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ (nutrient amounts obtained in MAS - table 4), while the litterfall value was only 1,803 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ at this site (table 2). At LAS, a litterfall rate between 7,000 and 8,000 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ was predicted, considering a N return of 82.3 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ and P return of 3.5 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$, but only 3,810 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ of litterfall were obtained (table 2).

The index of N use-efficiency found in another site of the Reserve of Paranapiacaba, not affected by air pollution (Domingos et al. 1997) was 44 (*sensu* Vitousek 1982); the litterfall was estimated as 7,000 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ and N return as 159 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$. Such figures fit very well with the model proposed by Bridgham et al. (1995). Similarly, close fit was observed by Moraes et al. (1999), investigating litter production in another well preserved area covered by Atlantic Forest, in Southeast Brazil. The index of N use-efficiency in that site was 62, litter production was 6,300 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$, and N return was 102 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$.

The results proved that functional changes caused by air pollution in the ecosystem, observed in temperate forests, also happen in the tropics. In the studied period, nutrient cycling was disturbed in both sites, but to a greater extent at MAS, where the simplification of the vegetation structure was visible. The main consequences of the disturbance were detected in the litter layer and in the nutrient fluxes via litterfall.

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References

- AB'SABER, A.N. 1987. A Serra do Mar na região de Cubatão: Avalanches de janeiro de 1985. A ruptura do equilíbrio ecológico na Serra de Paranapiacaba e a poluição industrial. In Anais do simpósio sobre ecossistemas da costa sul e sudeste brasileira - síntese de conhecimentos (ACIESP, ed.). Publicação ACIESP 54 (II), p.74-116.
- ALONSO, C.D. & GODINHO, R. 1992. A evolução do ar em Cubatão. *Química Nova* 15:126-136.
- BRIDGHAM, S.D., PASTOR, J., MCCLAUGHERTY, C.A. & RICHARDSON, C.J. 1995. Nutrient-use efficiency: a litterfall index, a model, and a test along a nutrient-availability gradient in North Carolina Peatlands. *American Naturalist* 145:1-21.
- COUTINHO, L.M. 1962. Contribuição ao conhecimento da ecologia da mata pluvial tropical. *Boletim da Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo* 257, *Botânica* 18:11-219.
- DELITTI, W.B.C. 1995. Estudos de ciclagem de nutrientes: instrumentos para a análise funcional de ecossistemas terrestres. *Oecologia Brasiliensis* 1:469-486.
- DOMINGOS, M., POGGIANI, F., STRUFFALDI-DE VUONO, Y. & LOPES, M.I.M.S. 1990. Produção de serapilheira na floresta da Reserva Biológica de Paranapiacaba, sujeita aos poluentes atmosféricos de Cubatão, SP. *Hoehnea* 17:47-58.
- DOMINGOS, M., POGGIANI, F., STRUFFALDI-DE VUONO, Y. & LOPES, M.I.M.S. 1995. Precipitação pluvial e fluxo de nutrientes na floresta da Reserva Biológica de Paranapiacaba, sujeita aos poluentes atmosféricos de Cubatão, SP. *Revista Brasileira de Botânica* 18:119-131.
- DOMINGOS, M., KLUMPP, A. & KLUMPP, G. 1998. Air pollution impact on the atlantic forest in the Cubatão region, SP, Brazil. *Ciência e Cultura* 50:230-236.
- DOMINGOS, M., MORAES, R.M., STRUFFALDI-DE VUONO, Y. & ANSELMO, C.E. 1997. Produção de serapilheira e retorno de nutrientes em um trecho de Mata Atlântica secundária, na Reserva Biológica de Paranapiacaba, SP. *Revista Brasileira de Botânica* 20:91-96.
- EMBRAPA - EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA. 1979. Manual de métodos de análise de solo. Serviço Nacional de Levantamento e Conservação de Solos, Rio de Janeiro, v.1.
- ERIKSSON, E. 1971. Compartment models and the reservoir theory. *Annual Review of Ecology and Systematics* 2:67-83.
- FIEDLER, F. & MASSAMBANI, O. 1997. Circulation and mass transport module. In *Air pollution and vegetation damage in the tropics - the Serra do Mar as an example - Final Report 1990-1996* (D. Klockow, H.T. Targa & W. Vautz, eds.). German/Brazilian Cooperation in Environmental Research and Technology, SHIFT (Studies on Human Impact on Forests and Floodplains in the Tropics) Programme. GKSS - Forschungszentrum Geesthacht GmbH, Geesthacht, p.II.1-II.45.
- FRITZE, H., KIKKILA, O., PASANEN, J. & PIETIKAINEN, J. 1992. Reaction of forest soil microflora to environmental stress along a moderate pollution gradient next to an oil refinery. *Plant and Soil* 140:175-182.
- GOSZ, J.R., LIKENS, G.E. & BORMANN, F.H. 1976. Organic matter and nutrient dynamics of the forest and forest floor in the Hubbard Brook forest. *Oecologia* 22:305-320.
- GUTBERLET, J. 1996. Cubatão: desenvolvimento, exclusão social, degradação ambiental. Editora Universidade de São Paulo, São Paulo.
- HOEHNE, F.C. 1925. *Album da Secção Botanica do Museu Paulista e suas dependencias, etc.* Imprensa Methodista, São Paulo.
- JORDAN, C.F. & HERRERA, R. 1981. Tropical rain forests: are nutrients really critical? *American Naturalist* 117:167-180.
- KLUMPP, A., KLUMPP, G. & DOMINGOS, M. 1994. Active biomonitoring at the Serra do Mar near the industrial complex of Cubatão, Brazil. *Environmental Pollution* 85:109-116.
- KLUMPP, A., KLUMPP, G., DOMINGOS, M. & SILVA, M.D. 1996. Fluoride impact on native tree species of the Atlantic Forest near Cubatão, Brazil. *Water, Air and Soil Pollution* 87:57-71.
- LEITÃO-FILHO, H.F., PAGANO, S.N., CESAR, O., TILMONI, J.L. & RUEDA, J.J. 1993. *Ecologia da Mata Atlântica*. Editora UNESP/Editora UNICAMP, Campinas.
- LILJELUND, L.E. & NIHLGARD, B. 1988. Nutrient balance in forests by air pollution. In *Liming as a measure to improve soil and tree condition in areas affected by air pollution - results and experiences of an enjoying research program* (F. Anderson & T. Persson, eds.). National Swedish Environmental Protection Board, Report 3518, Solna, p.93-15.

- LOPES, M.I.M.S., STRUFFALDI-DE VUONO, Y. & DOMINGOS, M. 1990. Serapilheira acumulada na floresta da Reserva Biológica de Paranapiacaba, sujeita aos poluentes atmosféricos de Cubatão, SP. *Hoehnea* 17:59-70.
- MEDINA, E. & CUEVAS, E. 1989. Patterns of nutrient accumulation and release in Amazonian forests of the upper Rio Negro basin. In *Mineral nutrients in tropical forest and savanna ecosystems* (J. Proctor, ed.). Blackwell Scientific Publications, Oxford.
- MORAES, R.M., DELITTI, W.B.C. & STRUFFALDI-DE VUONO, Y. 1999. Litterfall and nutrient return in two Brazilian tropical forests. *Revista Brasileira de Botânica* 22:9-16.
- RAIJ, B.V. & QUAGGIO, J.A. 1983. Métodos de análise de solo para fins de fertilidade. *Boletim Técnico do Instituto Agrônomo de Campinas* 81:1-31.
- ROSSI, M. & PFEIFER, R.M. 1991. Pedologia do Parque Estadual da Serra do Mar. I. Levantamento de reconhecimento dos solos. *Revista do Instituto Florestal de São Paulo* 3:1-44.
- SECRETARIA DO MEIO AMBIENTE. 1990. The rain forest of the Serra do Mar: degradation and reconstitution. Document series, São Paulo, Brazil.
- SMITH, W.H. 1981. Air pollution and forests - interactions between air contaminants and forest ecosystems. Springer-Verlag, New York.
- STRUFFALDI-DE VUONO, Y., DOMINGOS, M. & LOPES, M.I.M.S. 1989a. Decomposição da serapilheira e liberação de nutrientes na floresta da Reserva Biológica de Paranapiacaba, sujeita aos poluentes atmosféricos de Cubatão, São Paulo, Brasil. *Hoehnea* 16:179-193.
- STRUFFALDI-DE VUONO, Y., LOPES, M.I.M.S. & DOMINGOS, M. 1989b. Air pollution and effects on soil and vegetation of Serra do Mar near Cubatão, São Paulo, Brazil. In *Proceedings of the 15th international meeting for specialists in air pollution effects on forest ecosystems - air pollution and forest decline* (J.B. Bucher & I. Bucher-Wallin, eds). Eidgenössische Anstalt für das forstliche Versuchswesen (EAFV), v.II, p.396-398.
- STRUFFALDI-DE VUONO, Y. & DOMINGOS, M. 1990. The Biological Reserve of Paranapiacaba (São Paulo-SP) as a preservation, education and research unit in "Mata Atlântica". In *Anais do II simpósio de ecossistemas da costa sul e sudeste brasileira - estrutura, função e manejo* (ACIESP, ed.). Publicação ACIESP 71 (II), p.296-301.
- VITOUSEK, P.M. 1982. Nutrient cycling and nutrient use efficiency. *American Naturalist* 119:53-72.
- VITOUSEK, P.M. 1984. Litterfall, nutrient cycling, and nutrient limitation in tropical forests. *Ecology* 65:285-298.
- VITOUSEK, P.M. & SANFORD JR., R.L. 1986. Nutrient cycling in moist tropical forest. *Annual Review of Ecology and Systematics* 17:137-167.
- VOGT, K.A., GRIER, C.C. & VOGT, D.J. 1986. Production, turnover, and nutrient dynamics of above and below ground detritus of world forests. *Advances in Ecological Research* 15:303-377.
- ZAGATTO, E.A.G., JACINTHO, A.O., REIS, B.F., KRUG, F.J., BERGAMIN FILHO, H., PESSENDA, L.C.R., MORATTI, J. & GINE, M.F. 1981. Manual de análise de plantas e águas empregando sistemas de injeção em fluxo. CENA/Universidade de São Paulo, Piracicaba.