Rev. bras. oceanogr., 47(1):47-57, 1999

Seasonal variation of atmospheric and terrestrial nutrients and their influence on primary production in an oligotrophic coastal system-southeastern Brazil

Elisabete de Santis Braga
Instituto Oceanográfico da Universidade de São Paulo
(Caixa Postal 66149, 05315-970, São Paulo, SP, Brasil)

- ***Abstract:*** In an oligotrophic coastal zone, land drainage and atmospheric precipitation can temporarily modify the concentrations of specific dissolved compounds in local surface waters, mainly nutrient salts, setting up conditions for "new" primary production of phytoplankton. The Ubatuba region (23°30'S - 45°06'W) is considered an oligo-mesotrophic region subject to a high average annual precipitation (~ 2,000 mm). The small rivers flowing into Palmas' Inlet present outflow patterns linked to the precipitation cycle. Rain and river waters show nitrate, nitrite, ammonium, phosphate and silicate concentrations that are very variable often higher than in surface seawater. When one considers the total nutrient inventory of Palmas' Inlet (total volume) in each sampling period, the relative contribution of nutrients from rain water presents the following seasonal variations: DIN (0.1-21.0 %), nitrate (0.06 - 15.86 %), phosphate (0.01 - 2.75 %), silicate (0.01 - 0.50 %); and the contribution from river waters varies within the following limits: DIN (0.02 - 0.36 %); nitrate (0.01 - 0.88 %); phosphate (0.01 - 0.11 %); silicate (0.04 - 4.70 %). Primary production in this oligotrophic zone showed seasonal variations with up to 17.83 mgC m^{-3} h^{-1} in the winter of 1992. When fertilization caused by the South Atlantic Central Water (SACW, T-S characteristics ~14°C and S ~35.5 PSU) intrusion occurred in the spring of 1991, the average value (all depths) of primary production was significant (7.00 mgC m^{-3} h^{-1}). The atmospheric source of dissolved nitrogenous compounds is very important to this region on account of the high pluviosity and the fact that this input occurs directly into the surface seawater, and thus to the euphotic zone.

- ***Resumo:*** Em zonas costeiras oligotróficas, os aportes de compostos dissolvidos via drenagem continental e precipitação atmosférica podem modificar temporariamente as concentrações de certas espécies químicas na água do mar, principalmente os sais nutrientes, fornecendo condições para uma produção primária "nova" do fitoplâncton. A região de Ubatuba (23°30'S - 45°06'W) é considerada oligo-mesotrófica e possui uma precipitação anual média alta (~2.000 mm). Os pequenos rios que fluem para a Enseada das Palmas tem suas vazões refletindo os ciclos de precipitação local. As águas dos rios e das chuvas, possuem concentrações de nitrato, nitrito, amônio, fosfato e silicato variáveis, mas freqüentemente maiores que aquelas encontradas nas águas de superfície do mar. Quando consideramos o reservatório total de nutrientes na Enseada das Palmas (volume total), em cada período de amostragem, pode-se verificar que a contribuição relativa da água de chuva, apresentou variações sazonais dentro dos seguintes limites: NID (0,1-21,0 %), nitrato (0,06 - 15,86 %), fosfato (0,01 - 2,75%), silicato (0,04 - 4,70 %). A produção primária nesta zona oligotrófica mostra variações sazonais e o maior valor foi 17,83 mgC m^{-3} h^{-1}, na primavera de 1992. Enquanto que na primavera de 1991, ocorreu uma fertilização promovida pela intrusão de Água Central do Atlântico Sul (ACAS) verificada pelas características do diagrama T-S (T~14°C e S~35,50 USP), sendo que neste período, o valor médio da produção primária (considerando todas as profundidades) foi relativamente alto (7,00 mgC m^{-3} h^{-1}). A atmosfera como fonte de compostos nitrogenados dissolvidos é muito importante para esta região devido à alta pluviosidade e pelo fato deste aporte ser feito diretamente na superfície da água do mar, assim sendo, na zona eufótica.

- ***Descriptors:*** Nutrients; Atmospheric input; Terrestrial input; Nitrogenous compounds; Silicate; Phosphate; Primary production.

- ***Descritores:*** Nutrientes; Aportes atmosféricos; Aportes terrestres; Compostos nitrogenados; Silicato; Fosfato; Produção primária.

Contr. no. 824 do Inst. oceanogr. da Usp.

Introduction

In the oligotrophic coastal zone, the availability of dissolved nutrient salts in seawater is one of the most important factors for phytoplankton development. Several scientific studies have shown that primary production in oligotrophic oceans is mostly limited by nitrogen and nutrient elements of atmopheric origin may have significant influences on marine biological productivity (Paerl, 1985, 1995; Knap *et al.*, 1986; Willey & Cahoon, 1991). This control could also be at play in coastal oligotrophic areas where rainfall is high.

Surface water variability in nutrient concentrations may reflect differences in atmospheric inputs, physical forcing as well as in the biological processes of nitrate uptake and nitrification (Eppley *et al.*, 1991). Terrestrial inputs are important sources of nutrients in the coastal zone, especially where there is a significant river inflow. The contribution in nitrate, phosphate and silicate is high near the mouth of the large rivers, especially the polluted ones receiving domestic and agricultural effluents.

The Ubatuba region is referred to as an oligo-mesotrophic system, limited mainly by inorganic nitrogen sources (Teixeira, 1973, 1979; Teixeira & Tundisi, 1981; Braga, 1989). Phosphorus limitation is attenuated in relation to that of nitrogen (Teixeira & Tundisi, *op. cit.*). The absence of big rivers in this region together with high precipitation leads to atmospheric inputs being more significant than terrestrial inputs as a source of nutrients. Additional fertilization events may occur following intrusion of the SACW (South Atlantic Central Water) on the platform. When the SACW advances over the Brazilian continental shelf (Castro Filho *et al.*, 1987), it reaches in the Ubatuba region with high loads of nutrients (nitrate > 10 µmol dm^{-3}) originating from the upwelled waters (Braga, 1995). The advection of these water is from the nearby open sea (300-400 m depth) and they contain excess nitrate generated by oxidation of organic matter during transit over the shelf, where nitrification processes are verified by oxygen depletion (Braga, *op. cit.*, Braga & Muller, 1998). Incursions of the SACW into the shelf area are frequent at the end of spring and summer (Castro Filho. *et al.*, 1987; Braga, *op. cit.*).

The contribution of atmospheric inputs has been documented in the Yellow Sea (China) where atmospheric input is the major pathway for some elements (Zhang *et al.*, 1992). River inputs generally influence coastal areas but have only small effects offshore. Ubatuba has a high percentage of rainfall and it is characterized by the absence of big rivers. However, many small streams are present in this area which could potentially exert some limited influence on local fertilization processes.

Considering the absence of information on the role of atmospheric and terrestrial inputs in this coastal region, this work sets out to study their relative contributions to the marine environment and the resulting effects on the primary production in the Ubatuba region.

Study area, sampling and analytical methods

Palmas' Inlet is a small bay located on the north side of Anchieta Island, which lies in the Ubatuba region, i. e. in the southwestern sector of the South Atlantic (23°30'S - 45°06'W). The volume of this Inlet is approximately 14.5 x 10^6 m^3 and the area is about 2.9 x 10^6 m^2 . Seawater, rain water and river water were sampled (see Table 2) during four seasonal periods in 1991 and 1992. Precipitation acidity measuremnts were performed at the North Base of the Oceanographic Institute of São Paulo University (IOUSP). Each sampling included four rivers (A, B, C, D) of Anchieta Island and the seawater samples. River flows were measured concomitantly to calculate input rates. Rain water was sampled whenever the precipitation event coincided with a sampling period. Sampling positions are shown in Figure 1.

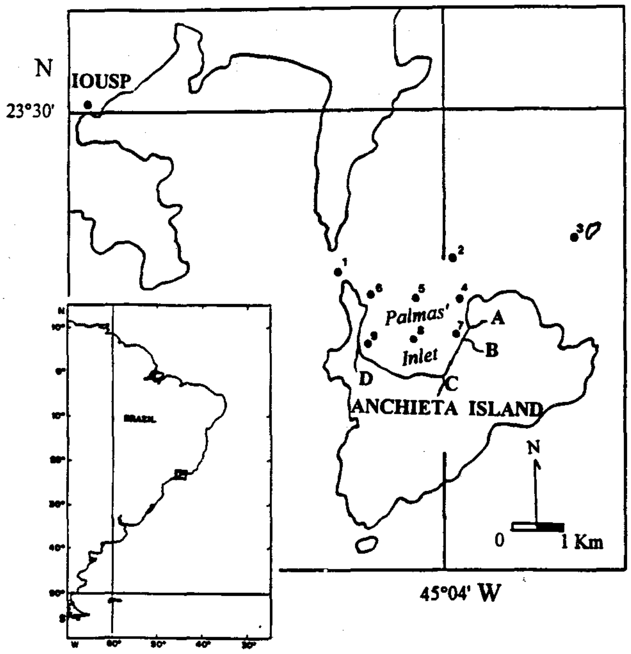

Fig. 1. Location of sampling stations in relation to the rivers A, B, C, D and the IOUSP Base.

The seawater nutrient samples were taken by means of Nansen bottles on board of the R/V "Veliger II". The river waters were sampled directly from the rivers in clean flasks and rain water was collected utilizing a sampling collector and then put into clean flasks. Samples which were permissible, were stored frozen whenever the analyses could not be done immediately.

The methods for automated analysis of nitrate and nitrite followed the recommendations of Tréguer & Le Corre (1975), utililizing a Technicon AutoAnalyzer II® system. Ammonium concentrations were determined by the traditional colorimetric method described in Tréguer & Le Corre (*op. cit.*). Phosphate and silicate were determined colorimetrically as recommended by Grasshoff *et al.*, 1983. Dissolved inorganic nitrogen (DIN) is the sum of ammonium, nitrate and nitrite.

The measurement of pH were carried out immediately after sampling (at IOUSP Base Laboratory) with a Micronal pH-meter, model 375, and primary production was measured by C^{14} method proposed by Steemann-Nielsen (1952) with modifications proposed by Teixeira (1973).

Results and discussion

Annual precipitations ware 1,920 mm in 1991 and 2,013 mm in 1992. The monthly distribution of precipitation in the dry period (winter) was different in 1991 from 1992. During the winter period in 1991, monthly precipitation was fairly uniform around 100 mm. In 1992 there was an unusually high rainfall in July and a very rainy spring (Fig. 2). In fact, considerable differences may be observed in monthly from one year to the next.

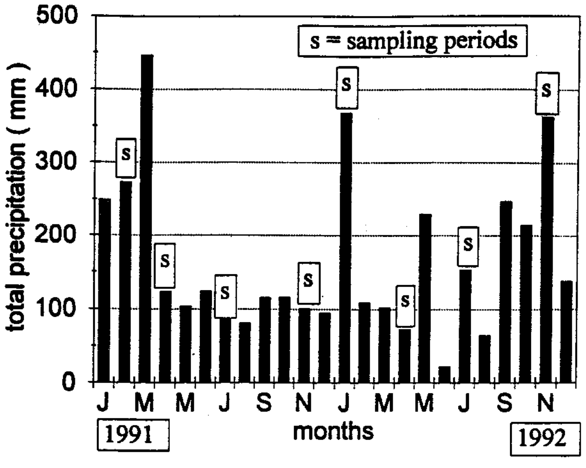

Fig. 2. Total monthly precipitation in the Ubatuba region in 1991 and 1992.

The pH values in the individual samples of rain water ranged from 4.4 to 7.8 (see Fig. 3), the smallest value (4.4) was recorded in the winter of 1992 and the highest (7.8) in autumn of 1992. Some studies (Cogbill & Likens, 1974; Pratt *et al.*, 1983; Savoie *et al.*, 1987; Moreira-Nordemann, 1985) have reported extensive changes in the atmospheric chemical composition in several cities due to anthropogenic inputs. The region studied does not have heavy industrial or agricultural activities. There, a pH near 8 seems high, but it is reasonable because of the influence of marine aerosol. The pH under 8 can be explained by the presence of weak acids (organic acids) such as acetic acid liberated by the forest bordering the Atlantic coastline or by aerosol brought from a more distant polluted source.

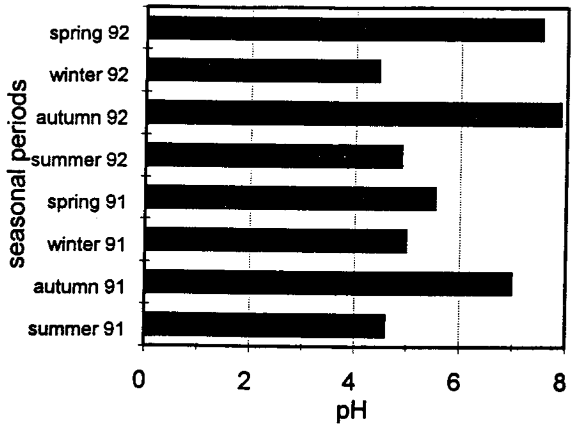

Fig. 3. pH values of rain water in the seasonal periods in 1991 and 1992.

For 10 months in 1977, Sequeira (1981) observed that weak organic acids controlled the pH of rain in American Samoa. Weak organic acids were responsible for about 60% of free acidity in precipitation during the 1981-1982 wet season in Katherine, Australia (Keene *et al.*, 1983). In the Ubatuba region, marine aerosols in winter could have originated from a more distant source, such as the city of Cubatão, located southwest of Ubatuba, which is an industrial centre notorious for its air pollution. There is a paucity of data on the chemical properties of rain in these regions. It is difficult to explain these values without knowledge of the chemical compounds responsible for the rainfall acidity. To determine the contribution of various atmospheric processes considering the overall chemical composition of the rain, several authors have pointed out the importance of collecting the sample over a short period within a single precipitation event (Baker *et al.*, 1981; Raynor and Hayes, 1981). The composition of rain changes during a single event from the begning to the end in such manner to reflect the different washout ratios of each of the constituents. For this reason, the value of each chemical parameter varies within a rain event. In this work, no attempt was made to assess the compositional variations with time so the reported parameters relate to the total rain event.

The chemical composition of the rain and river waters (Figs 4 and 5) showed wider variations in nitrate, ammonium, nitrite, phosphate and silicate concentrations than were observed in the surface waters of the Inlet (Table 1), which are normally near zero at some points. The nutrient concentrations were often higher in the rain and the river water than in the surface seawater. The DIN:DIP ratios show a local defficient inventory of inorganic nitrogenous compounds in relation to the inorganic phosphorus verified by the constant values below 15 (i.e. Redfield ratio), putting in evidence the nitrogen limitation for the primary production as cited by some authors. The nutrient concentrations at this site are determined largely by natural sources, the anthropogenic influence being minimal.

The discharge of small rivers showed intra specific differences in response to climatological conditions. The river inflow into the Palmas' Inlet is minor, ranging between 10 and 67.10^{-3} m^3/s (Fig. 6). It was found that total river discharge over a 24 h period accounted for less than 0.05% of the total water volume of the Inlet.

The integrated values of nitrogenous compound concentrations (DIN) in the Palmas' Inlet (Fig. 7) were below 2.0 µmol dm^{-2}, nitrate being the dominant form. If we consider nutrient concentrations to be constant in both river and rain waters and also in the Inlet during each sampling period, we can compare the observed nutrient concentrations in the Palmas' Inlet with these in the freshwater end-members. The total input by rain water in each event is represented in Figure 8. The associated rain nutrient inputs into Palmas' Inlet varied seasonally within the following limits: DIN (0.1 - 21.0 %), nitrate (0.06 - 15.86 %), ammonium (0.01-23.0 %), phosphate (0.01 - 2.75 %) and silicate (0.01 - 0.50 %). This was calculated considering the

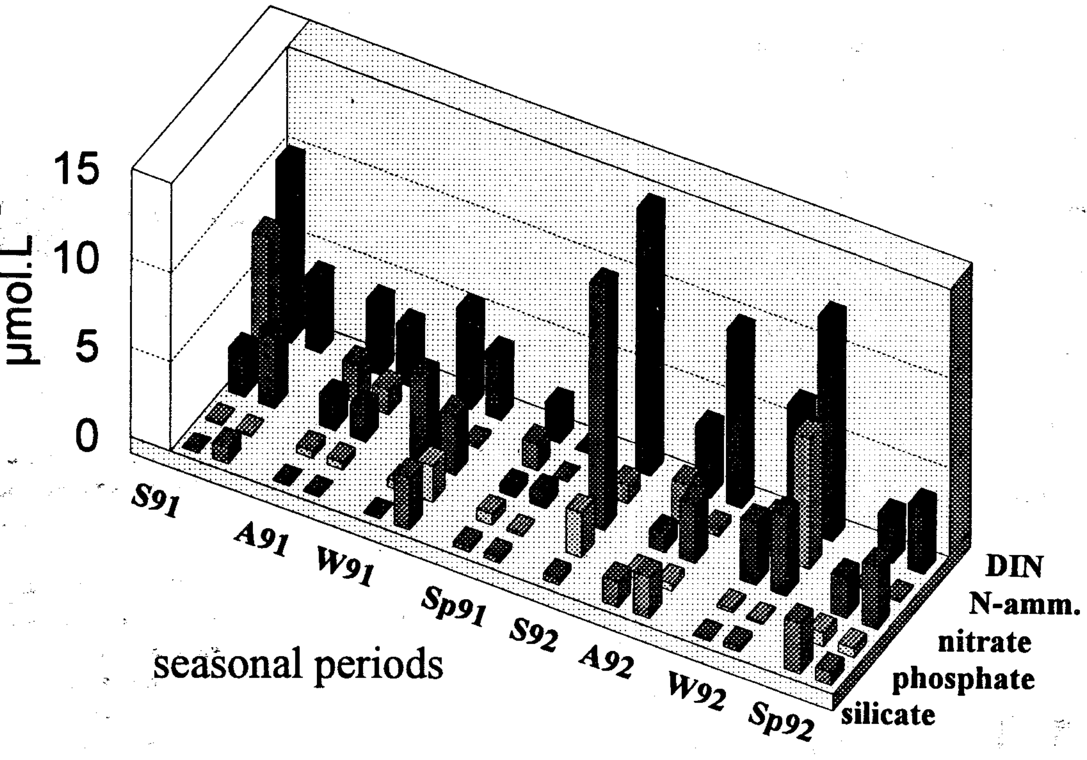

Fig. 4. Nutrient concentrations (where dissolved inorganic nitrogen = DIN and Ammonium = N-amm.) in the rain waters during 1991 and 1992.

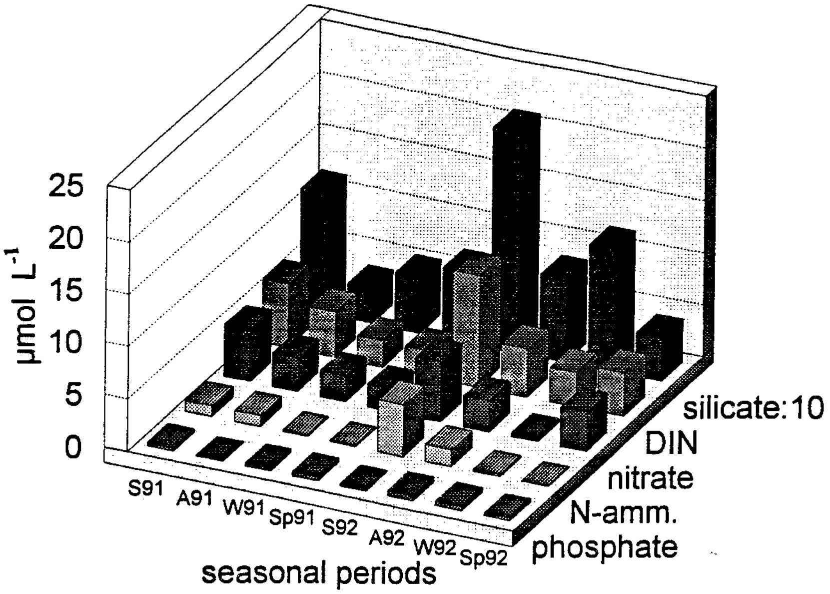

Fig. 5. Nutrient concentrations (where dissolved inorganic nitrogen = DIN and Ammonium = N-amm.) in the river waters during 1991 and 1992.

total contribution of rain water during a 24 h period compared to the inventory of nutrients in the total volume of the Inlet, the latter being constant, see Figure 9. Nitrate and ammonium are frequently the main nutrient forms brought in by rain water.

The formation of nitrate in the atmosphere occurs through a number of mechanisms. It has been shown that nitrite reacts with ozone in the presence of hygroscopic aerosols, such as NaCl, to produce nitrate (Cox, 1974). The enrichment of nitrate of atmospheric origin in the rain results in a positive action of the washout process and the easy nitrate remotion from the atmosphere below the clouds. This fact is in accordance with the results cited by Naik *et al*, 1994.

The river input calculations were made by the same procedure cited above as for rain water in a 24 h period (Fig. 6) and the contribution to Palmas' Inlet, varied between: DIN (0.02 - 0.36 %), nitrate (0.01 - 0.88 %), phosphate (0.01 - 0.11 %) and silicate (0.04 - 4.70 %), as a percentage of the total nutrient concentrations (Fig. 10). There were some differences in the individual nutrient river concentrations and a remarkable flux of nitrogenous compounds, phosphate and silicate were introduced by A, B and C rivers, in the western part of the Inlet, near stations 7 and 8, where the primary production was high in most of the seasonal periods.

The depth-average nutrient concentrations in the seawater are invariably higher than the ones measured at the surface, the latter being close to the detection limit, thus nutrient inputs to the sea surface are likely to be very important in maintaining the biological activity in the region.

Seasonal primary production in surface waters and at some points of the Inlet (Table 2), as well as, surface average primary production in several seasons (Fig. 11) present high values associated with the terrestrial and atmospheric inputs, especially at stations 7 and 8. In the Spring of 1991, the high average value of primary production was probably more influenced by the oceanic input brought by SACW upwelling in the region, as corroborated by the T-S characteristics of the shallow stations (S ~ 35.5 PSU and T° ~ 14°C , Fig. 12) and a high nitrate concentration (> 10.00 µmol dm^3), produced by intensive nitrification processes occurred along the trajectory over the platform (Braga & Muller, 1998; Braga, 1995).

The intensive rainfall which occurred in the winter of 1992 (July) is an important source of nutrients to support the primary production as the average of nitrogenous nutrients in the Inlet water was low in this period. In the case of the spring of 1992, the nutrient rain inputs were not the only remarkable source of nutrients for the biological process, but it was associated with a relatively high concentration of nutrients in river and seawaters. It is necessary to take into account that intensive rainfall events causes turbulences, mixing and reduction of the penetration of light in the water columns causing a momentary negative effect on primary production processes. In relation to the solar radiation, the values of total solar radiation during sampling periods of primary production experiments is present in Figure 13, except for the Spring of 91. Lower values were present in the autumm and winter of 1992.

Table 1. Nutrient concentrations in the surface water of Palmas' Inlet.

St. X; SD	NH_4^+ *	NO_2^- *	NO_3^- *	PO_4^{3-} *	$Si(OH)_4$ *	DIN:DIP	St.	NH_4^+ *	NO_2^- *	NO_3^- *	PO_4^{3-} *	$Si(OH)_4$ *	DIN:DIP
	Summer 1991							**Summer 1992**					
1	1.25	0.12	0.28	0.06	0.3	27.5	1	0.41	0.12	0.18	0.16	1.7	4.4
2	0.25	0.06	0.44	0.07	0.4	10.7	2	0.00	0.01	0.02	0.18	4.1	0.9
3	0.26	0.07	0.43	0.11	0.4	6.9	3	0.29	0.15	0.05	0.16	1.6	3.1
4	0.36	0.07	0.43	0.07	0.9	12.3	4	0.62	0.17	0.43	0.18	3.9	6.8
5	0.46	0.08	0.52	0.07	1.0	14.7	5	0.09	0.11	0.49	0.19	3.2	3.6
6	0.31	0.08	0.12	0.12	1.0	2.3	6	0.23	0.12	0.08	0.17	3.3	2.5
7	0.55	0.07	0.23	0.15	2.8	5.7	7	0.24	0.12	0.08	0.16	5.1	2.8
8	0.31	0.08	0.22	0.10	0.5	6.1	8	0.45	0.11	0.09	0.14	6.1	4.6
9	0.34	0.08	0.00	0.00	0.7	5.3	9	0.42	0.14	0.06	0.23	4.3	2.7
$\bar{X}$	0.45	0.08	0.30	0.08	0.9	10.2	$\bar{X}$	0.31	0.12	0.16	0.17	3.7	3.5
SD	0.31	0.02	0.17	0.04	0.8	7.6	SD	0.19	0.04	0.17	0.03	1.5	1.7
	Autumn 1991							**Autumn 1992**					
1	0.53	0.32	1.58	0.21	3.0	11.6	1	0.96	0.05	0.61	0.34	9.4	4.8
2	0.58	0.20	0.65	0.32	2.0	4.5	2	0.76	0.05	0.45	0.14	3.5	9.0
3	0.38	0.22	1.62	0.17	1.8	13.1	3	0.95	0.07	0.73	0.31	6.2	5.7
4	0.43	0.16	0.26	0.14	1.7	6.1	4	0.19	0.08	0.52	0.72	4.5	1.1
5	0.53	0.16	0.30	0.10	1.5	9.9	5	0.17	0.06	0.52	0.26	4.7	2.9
6	0.46	0.18	0.35	0.16	1.0	6.2	6	0.23	0.12	0.08	0.17	3.3	2.5
7	0.50	0.32	1.48	0.27	3.6	8.5	7	0.24	0,12	0.08	0.16	5.1	2.8
8	0.43	0.28	2.03	0.16	2.0	17.1	8	0.45	0.11	0.09	0.14	6.1	4.6
9	0.41	0.21	2.00	0.10	2.5	26.2	9	0.42	0.14	0.06	0.23	4.3	2.7
$\bar{X}$	0.47	0.23	1.14	0.18	2.1	11.5	$\bar{X}$	0.49	0.09	0.35	0.27	5.2	4.0
SD	0.07	0.06	0.74	0.07	0.8	6.8	SD	0.32	0.03	0.27	0.18	1.9	2.3
	Winter 1991							**Winter 1992**					
1	0.01	0.09	0.09	0.13	4.1	1.5	1	0.36	0.35	0.60	0.23	7.6	5.7
2	0.00	0.03	0.20	0.23	1.9	1.0	2	0.80	1.04	1.29	0.45	10.4	7.0
3	0.05	0.03	0.26	0.15	3.6	2.3	3	0.56	0.20	0.65	0.28	6.0	5.0
4	0.04	0.00	0.49	0.15	3.9	3.5	4	1.01	0.40	0.89	0.37	8.0	6.2
5	0.01	0.00	0.06	0.11	3.6	0.6	5	0.42	0.27	0.50	0.31	11.7	3.8
6	0.03	0.04	0.48	0.16	3.7	3.4	6	0.71	0.41	0.53	0.49	6.9	3.4
7	0.00	0.04	0.37	0.17	2.3	2.4	7	0.87	0.25	0.95	0.39	6.7	3.0
8	0.00	0.08	0.00	0.19	4.7	0.4	8	0.87	0.23	0.74	0.45	10.1	4.1
9	0.00	0.04	0.00	0.17	3.4	0.2	9	0.47	0.14	0.22	0.31	6.5	2.7
$\bar{X}$	0.02	0.04	0.22	0.16	3.5	1.7	$\bar{X}$	0.67	0.37	0.71	0.36	8.2	4.5
SD	0.02	0.03	0.20	0.03	0.9	1.3	SD	0.23	0.27	0.31	0.09	2.0	1.5
	Spring 1991							**Spring 1992**					
1	0.00	0.17	0.00	0.17	3.4	1.0	1	0.15	0.10	0.11	0.38	3.8	1.0
2	0.07	0.21	1.07	0.29	4	4.7	2	0.19	0.09	0.26	0.34	1.0	1.6
3	0.02	0.22	0.03	0.16	3	1.7	3	0.11	0.07	0.31	0.24	6.0	2.0
4	0.02	0.17	0.03	0.24	3.6	0.9	4	0.17	0.11	0.79	0.35	1.8	3.0
5	0.03	0.24	0.01	0.18	4.7	1.6	5	0.00	0.07	0.43	0.28	2.0	1.8
6	0.06	0.17	0.00	0.24	3.4	1.0	6	0.00	0.10	0.28	0.32	1.9	1.2
7	0.07	0.15	0.00	0.28	3.5	0.8	7	0.04	0.07	0.14	0.20	3.1	1.3
8	0.03	0.15	0.00	0.26	12.6	0.7	8	0.06	0.09	0.31	0.52	3.7	0.9
9	0.00	0.00	0.40	0.29	3.7	1.4	9	0.04	0.12	0.26	0.34	2.1	1.2
$\bar{X}$	0.03	0.16	0.17	0.23	4.66	1.5	$\bar{X}$	0.08	0.09	0.32	0.33	2.8	1.6
SD	0.03	0.07	0.36	0.05	3.02	1.2	SD	0.07	0.02	0.20	0.09	1.5	0.7

* $\mu mol\ L^{-1}$

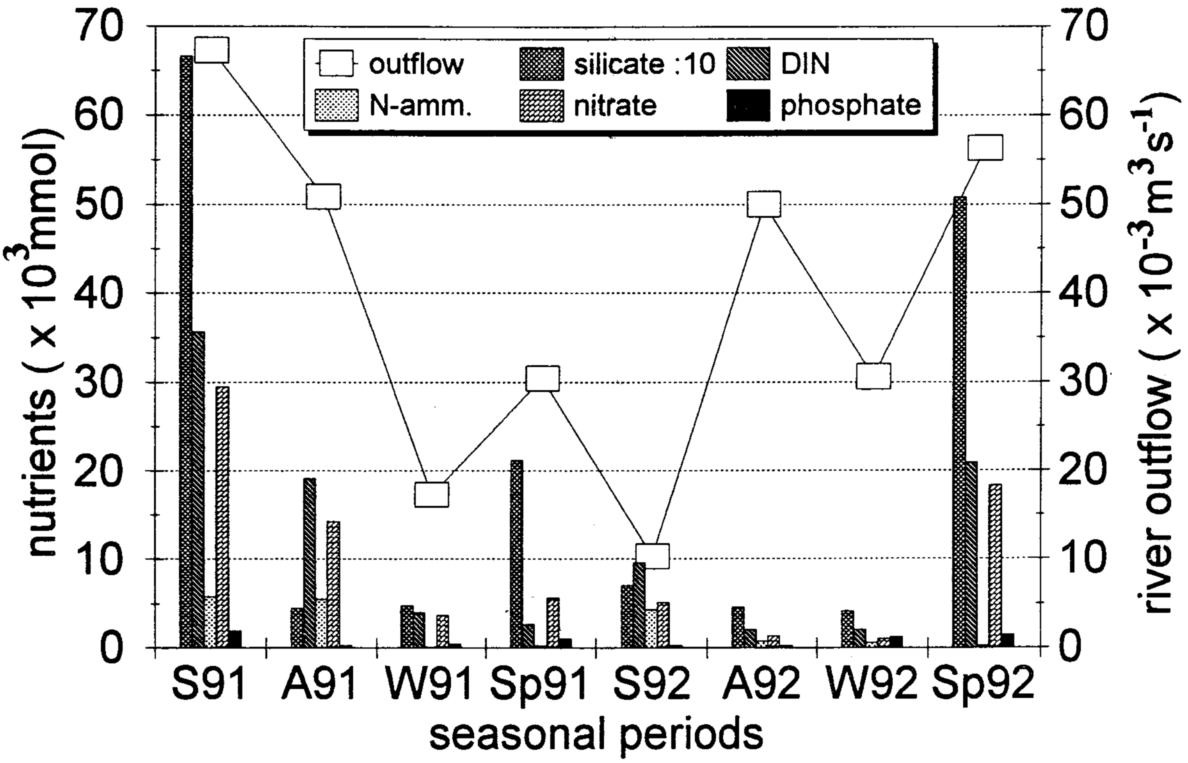

Fig. 6. River outflows and nutrient river discharge in 24 h period in some seasonal periods.

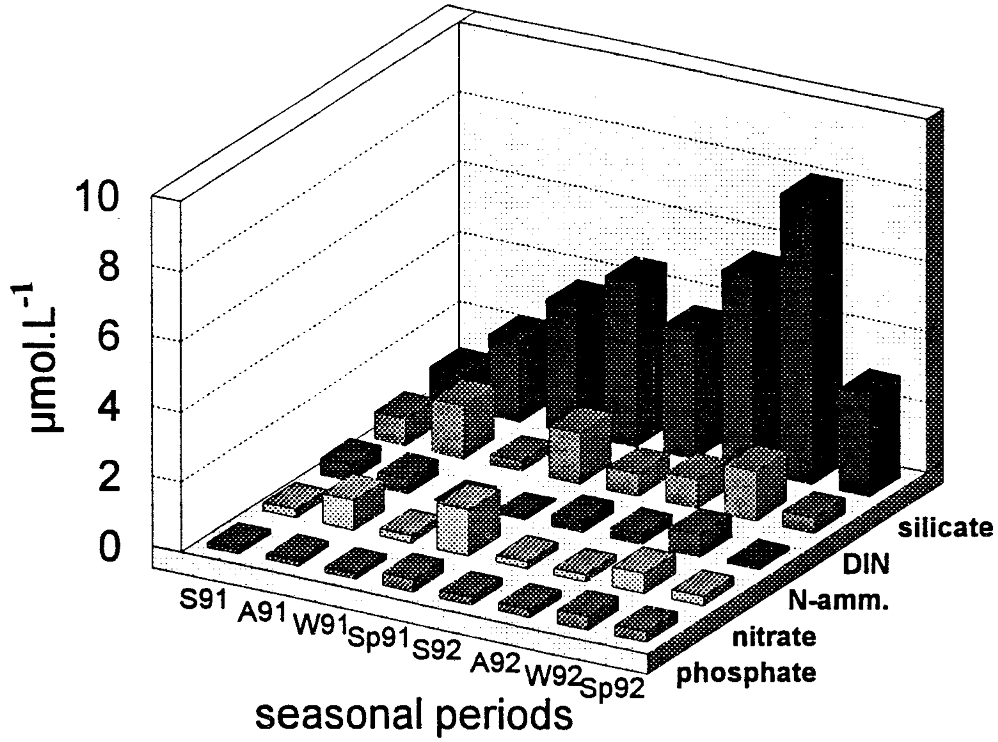

Fig. 7. Seasonal variations of integrated values of nutrient concentrations in Palmas' Inlet.

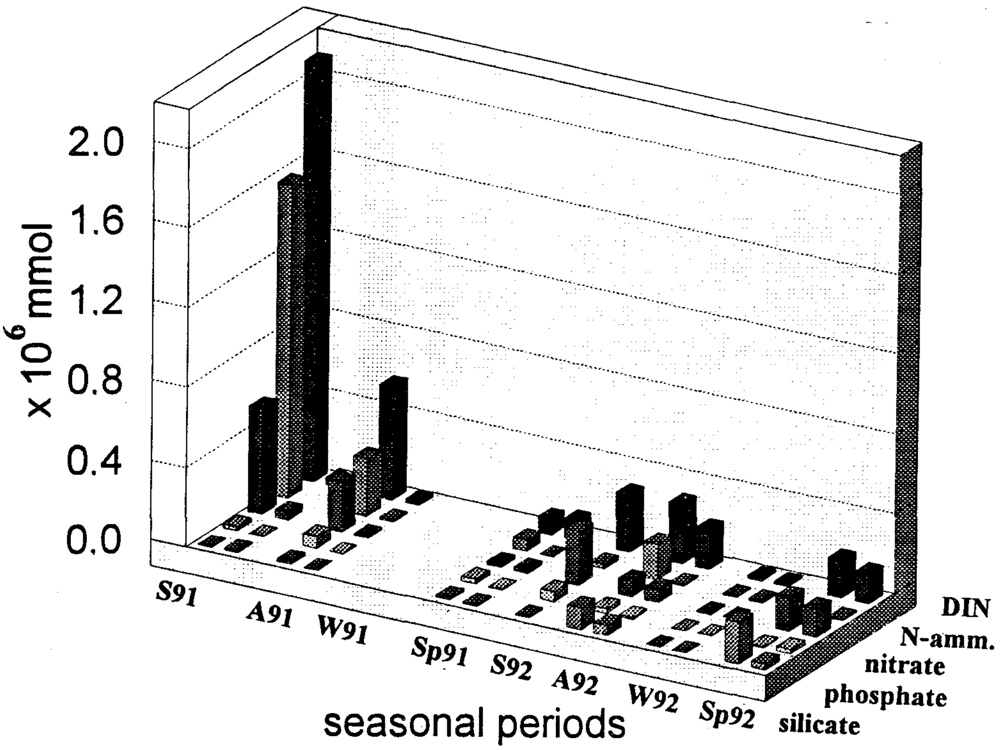

Fig. 8. Rain waters: total nutrient input in each rain event during 1991 and 1992.

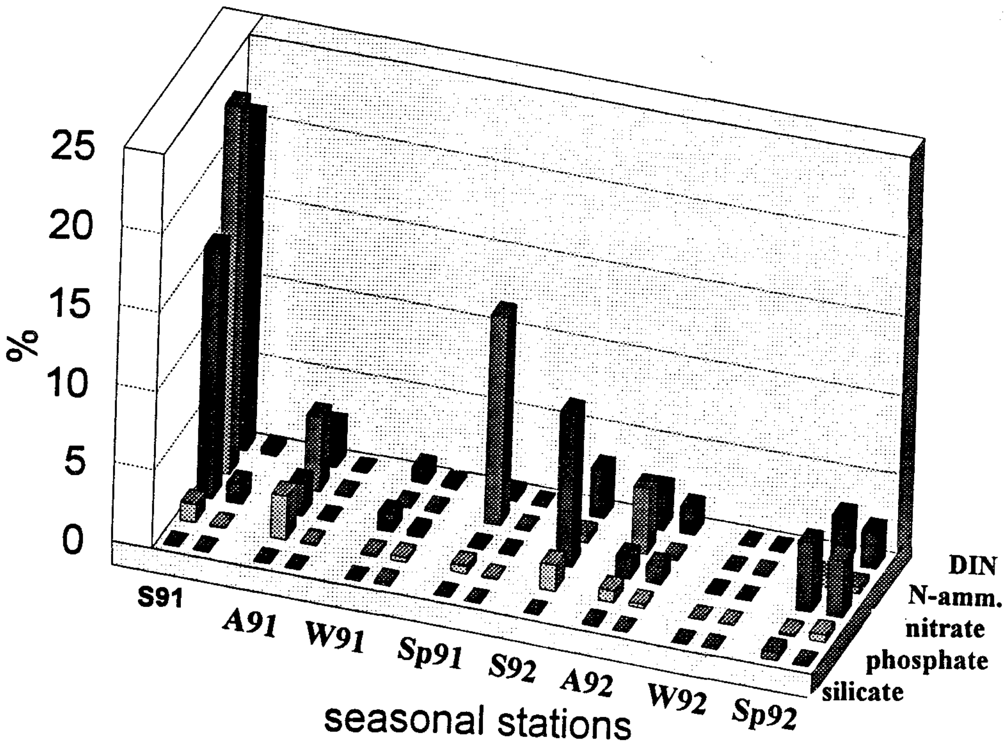

Fig. 9. Percentage of nutrient inputs to Palmas' Inlet by rain waters.

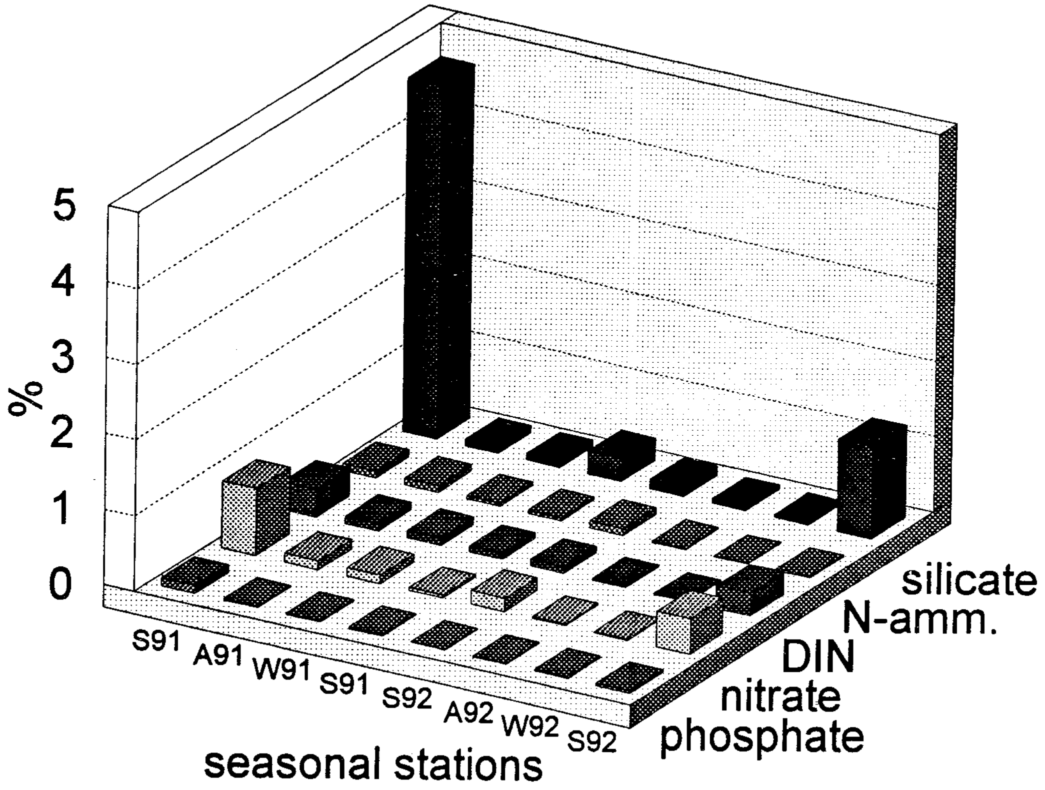

Fig. 10. Percentage of nutrient inputs to Palmas' Inlet by river waters.

Table 2. Primary production in the seasonal periods at some surface points in Palmas' Inlet.

	1991		1992	
Seasonal periods	Stations	PP*	Stations	PP*
Summer	1	5.63	1	8.44
	7	4.76	7	11.18
	8	4.13	8	12.96
	9	4.68	9	1.74
Autumn	1	5.65	1	4.00
	3	-	3	1.26
	7	11.34	7	14.16
	8	11.09	8	6.05
	9	7.09	9	9.92
Winter	1	3.40	1	14.96
	3	10.93	-	-
	7	2.58	7	15.41
	8	2.66	8	17.83
	9	3.77	9	14.39
Spring	1	7.11	1	12.15
	3	5.28	3	5.91
	7	7.82	7	16.19
	8	9.10	8	16.27
	9	5.69	9	9.11

PP* = Primary Production mgC m^{-3} h^{-1}

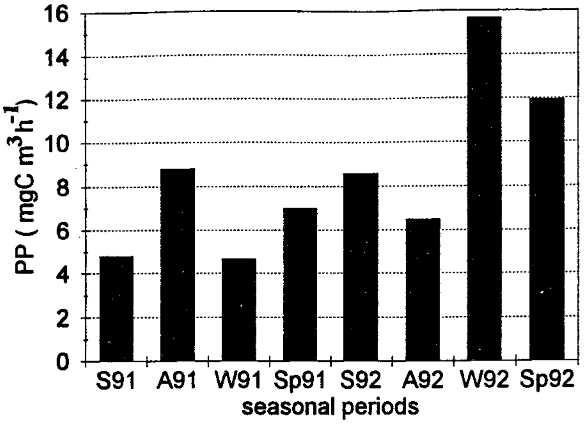

Fig. 11. Primary production average in surface water of Palmas' Inlet.

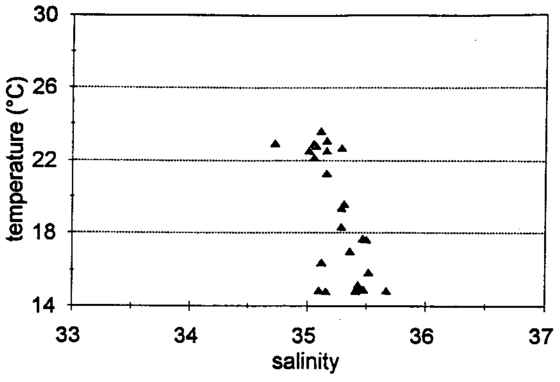

Fig. 12. T-S diagram in Spring 1991.

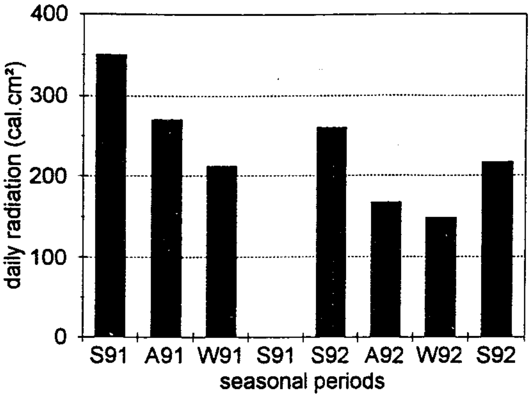

Fig. 13. Daily solar radiation during the primary production experiment.

It is difficult to work with average data due to the time variations that occur in the chemical composition of the river waters and due to the variations in the chemical composition of the rain water from the beginning to the end of each event. It is clear that the atmospheric and terrestrial inputs have a high concentration of nutrients in relation to the surface waters of the oligo-mesotrophic systems and their influence on the biological processes is associated to other factors like climatological conditions, winds, turbulence, the pluviometric index, solar radiation, kinds of biological populations and others.

Conclusions

The Ubatuba region is representative of oligo-mesotrophic conditions in that primary production is regulated by atmospheric and terrestrial inputs of nitrogenous nutrients most of the time, while occasional blooms of phytoplankton may take place at times of penetration of the South Atlantic Central Water (SACW) over the continental shelf. This work has highlighted the significance of atmospheric inputs in the nitrogenous nutrient mass balance of this coastal oligotrophic system.

The input of dissolved nitrogenous compounds by rain water into Palmas' Inlet is considerable, mainly due to high annual rainfall and high concentrations of nitrogenous nutrients. Rivers have a significant influence on the dissolved silicate input whereas their influence on nitrogen and phosphorus inputs are minor and observed in the proximity of the mouths of the rivers.

The following conclusions were made: 1) The atmosphere is an important pathway for some nutrients mainly nitrate to the surface waters of the Ubatuba region. 2) Sometimes, the SACW upwells and fertilizes the surface waters. 3) The river input is limited to the coastal areas and has little effect on the region due to the small discharges of river waters.

Acknowledgements

The author would like to thank Dr Teixeira, C. for his help during this project and Dr Tundisi, J. G. for the incentive to produce this paper. I also thank Mr Philip Barsanti for this collaboration. This work was carried out as part of the research programme NITAM (Nutrients: terrestrial, atmospheric and marine interactions) which was supported by FAPESP, process number 90/3375-1.

References

Baker, M. B.; Caniparoli, D. & Harrison, H. 1981. An analysis of the first year of MAP3S rain chemistry measurements. Atmos. Environ., 15(1):43-55.

Braga, E. S. 1989. Estudo dos nutrientes dissolvidos nas águas da Enseada das Palmas, Ilha Anchieta (Ubatuba, SP) com ênfase as formas nitrogenadas e contribuição por aportes terrestres e atmosféricos. Dissertação de mestrado. Universidade de São Paulo, Instituto Oceanográfico. 207p.

Braga, E. S. 1995. Nutrientes dissolvidos e produção primária do fitoplâncton em dois sistemas costeiros do Estado de São Paulo. Tese de doutorado. Universidade de São Paulo, Instituto Oceanográfico. 2 v.

Braga, E. S. & Muller, T. 1998. Observation of regeneration of nitrate, phosphate and silicate during upwelling off Ubatuba, Brazil. Cont. Shelf Res., 18(8):915-922.

Castro Filho, B. M. de; Miranda, L. B. de & Miyao, S. Y. 1987. Condições hidrográficas na plataforma continental ao largo de Ubatuba: variações sazonais e em média escala. Bolm Inst. oceanogr., S Paulo, 35(2):135-151.

Cogbill C. V. & Likens, G. E. 1974. Acid precipitation in the Northeastern United States. Water Resour. Res., 10(6):1133-1137.

Cox, R. A. 1974. Particle formation from homogeneous reactions of sulphur dioxide and nitrogen dioxide. Tellus, 26(1-2):235-240.

Eppley, R. W.; Garside, C.; Renger, E. H. & Orellana, E. 1991. Variability of nitrate concentration in nitrogen-depleted subtropical surface waters. Mar. Biol., 107(1):53-60.

Grasshoff, K.; Ehrhardt, M. & Kremling, K. 1983. Methods of seawater analysis. 2nd ed. Weinnhein, Verlag Chemie. 419 p.

Keene, W. C.; Galloway, J. N. & Holden Jr., J. D. 1983. Measurement of weak organic acidity in precipitation from remote areas of the world. J. Geophys. Res., 88(C9):5122-5130.

Knap, A. H.; Jickells, T.; Pszenny, A. & Galloway, J. N. 1986. Significance of atmospheric derived nitrogen on producitivity of Sargasso Sea. Nature, 320(6058):158-160.

Moreira-Nodermann, L. M.; Forti, M. C.; Andrade, M. J. & Orsini, C. Q. 1985. Composição iônicadas chuvas da cidade de S. Paulo. In: SIMPÓSIO BRASILEIRO DE HIDROLOGIA E RECURSOS HÍDRICOS, 6. São Paulo, 1985. Anais. São Paulo, ABRH. p.419-424.

Naik, M. S.; Khemani, G. A.; Momin, P. S.; Rao, A.; Pillai, A. G. & Safai, P. D. 1994. Variation in the ionic composition in convective showers in Pune, India. Tellus, 46B:68-75.

Paerl, H. W. 1985. Enhancement of marine primary production by nitrogen-enriched acid rain. Nature, 315(6022):747-749.

Paerl, H. W. 1995. Coastal eutrophication in relation to atmospheric nitrogen deposition: current perspectives. Ophelia, 41:237-259.

Pratt, G. C.; Coscio, M.; Gardner, D. W.; Chevone, B. I. & Krupa, S. V. 1983. An analysis of the chemical properties of rain in Minnesota. Atmos. Environ., 17(2):347-355.

Raynor, G. S. & Hayes, J. V. 1981. Acidity and conductivity of precipitation on central Long-Island, New York in relation to meteorological variables. Water Air Soil Pollut., 15(2):229-245.

Savoie, D. L.; Prospero, J. M. & Ness, R. T. 1987. Washout ratios of nitrate, non sea-salt surface and sea-salt on Virginia Key, Florida and on American-Samoa. Atmos. Environ., 21(1):103-112.

Sequeira, R.. 1981. Acid rain: Some preliminary results from global data analysis. Geophys. Res. Lett., 8(2):147-150.

Steemann-Nielsen, E. 1952. The use of radio-active carbon (C^{14}) for measuring organic production in the sea. J. Cons. int. Explor. Mer, 18:117-140.

Teixeira, C. 1973. Preliminary studies of primary production in the Ubatuba region (Lat. 23°30'S – Long. 45°06'W), Brazil. Bolm Inst. oceanogr., S Paulo, 22:49-58.

Teixeira, C. 1979. Produção primária e algumas considerações ecológicas da região de Ubatuba (Lat. 23°30'S - 45°06'W), Brasil. Bolm Inst. oceanogr., S Paulo, 28 (2):23-28.

Teixeira, C. & Tundisi, J. G. 1981. The effects of nitrogen and phosphorus enrichments on phytoplankton in the region of Ubatuba (Lat. 23°30'S – Long. 45°06'W) Brazil. Bolm Inst. oceanogr., S Paulo, 30(1):77-86.

Tréguer, P. & Le Corre, P. 1975. Manuel d'analysis des sels nutritifs and l'eau de mer. 2ème éd. Brest, Université de Bretagne Occidentale. 110 p.

Willey, J. D. & Cahoon, L. B. 1991. Enhancement of chlorophyll-a production in Gulf Stream surface seawater by rainwater nitrate. Mar. Chem., 34(1/2):63-75.

Zhang, J.; Huang, W. W.; Liu, S. M.; Liu, M. G.; Yu, Q. & Wang, J. H. 1992. Transport of particulate heavy metals towards the China Sea: a preliminary study and comparison. Mar. Chem., 40(3-4):161-178.

(Manuscript received 03 June 1998; revised 06 December 1998; accepted 28 June 1998)