

## **Water Chemistry of the Nilambe Oya, a Tributary in the Central Mahaweli Valley of Sri Lanka 2. Phosphorus, Nitrate and Nitrite Concentrations**

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### **Abstract**

Concentrations of phosphorus (total and dissolved), nitrate and nitrite of the Nilambe Oya were determined monthly from June 1994 to May 1995 for ten randomly selected sites employing standard sampling and analytical methods. Results were analyzed using one-way ANOVA to examine spatial and temporal variations in relation to seasonal rainfall and land use patterns of the watershed. Concentrations of total and dissolved phosphorus are within the range reported for tropical streams and rivers but the levels of nitrate were relatively higher than the reported values for tropical regions. Concentrations of both total phosphorus and nitrate increased during the rainy season from October to December. However, phosphorus concentration (total and dissolved) did not show significant seasonal variability. Seasonal variability in nitrate and nitrite concentrations was statistically highly significant. In contrast, concentrations of phosphorus (total and dissolved) and nitrogen species (nitrate and nitrite) showed statistically significant inter-site variability.

### **Introduction**

Distribution of phosphorus (P) and nitrogen (N) compounds in the hydrosphere is a function of their behavior in magmatic weathering, and sedimentary and biological processes. Anionic forms of both P and N are essential plant nutrients. Phosphorus is also used to manufacture industrial products, mainly detergents. Anionic forms of P and N may be adsorbed to soil particles (organic or inorganic) or leached out and transported to water courses in particulate and dissolved forms by mean of runoff from agricultural and forested lands. P and N effluents are also discharged into water ways in urbanized areas from industries. Groundwater discharge and atmospheric deposition also contribute to P and N loading. Enrichment of standing water bodies with P and N species has resulted in eutrophication which ultimately lead to hyper-eutrophication or algal blooming. Many lakes and reservoirs in the world today are either eutrophic or hypertrophic (Shapiro 1988). The cycles of P and N in the ecosystems differ from each other and N has a much faster cycle (Wetzel 1983). In the case of P, it takes millions of years to complete the cycle (Wetzel 1983). Therefore, increasing consumption of P will certainly result in serious problems in modern agriculture and other human activities.

Considerable concern has been focused on the possible pathogenic effects of nitrate (Tannenbaum et al. 1977). When water containing high nitrate levels is used to prepare baby food, the nitrate can cause meta-haemoglobinaemia, the "blue baby syndrome" in neo-natal infants (WHO 1984). Nitrate is also suspected to be associated with gastric cancer (Tannenbaum et al. 1977). Therefore, pollution of natural waters with P and N compounds has become a significant environmental problem throughout the world. This situation has been more aggravated in the tropics due the application of enormous amounts of fertilizer and lack of facilities for pre-treatment of N and P compounds from effluents (Viner 1982). The concentrations of N and P species in streams and rivers are presumed to be unacceptable when they drain watersheds which are subjected to intensive and variable land use. However, information on spatial and temporal distributions of N and P species in tropical surface waters is scarce. In Sri Lanka, except for a little data on concentrations (Geisler 1967; Weninger 1972; Dissanayake 1985; De Alwis 1991), spatial and temporal patterns of micro-nutrients in lotic ecosystems are unknown. In this paper, an attempt is made to examine the site-specific and time-bound concentrations of phosphorus (total and dissolved), nitrate and nitrite in the Nilambe Oya draining a sub-watershed of the Mahaweli basin which has been subjected to intensive and variable land use.

### Materials and Methods

Geographic location and land use pattern of the Nilambe Oya where this study was carried out are described by Silva (1998). Water samples were collected monthly from 10 sampling (Silva, 1998) sites from June 1994 to May 1995, in cleaned pre-washed Nalgene bottles and delivered to the laboratory within 3 hours. In the laboratory, water samples were filtered through pre-washed Sartorius membrane filter papers (47 mm diameter) using a Millipore filtration manifold. Sub-samples from the filtrate were processed within 24 hours to determine dissolved phosphorus content by reacting with molybdate to form molybdophosphoric acid which in turn is reduced to a molybdenum blue complex. This reaction was performed with a freshly prepared mixed reagent (Makereth et al. 1978) and the color intensity was subsequently compared spectrophotometrically with a standard series at 880 nm. The same procedure was followed to determine the total phosphorus but unfiltered samples were used and digested with ammonium persulphate to convert colloidal and particulate phosphorus into orthophosphate.

Dissolved nitrite in filtered water samples was reacted with sulphanilamide in the presence of ammonium chloride buffer (pH = 10.25). The resulting diazonium salt was coupled with N-1 naphthylenediamine dihydrochloride to form the red azo-dye of which color intensity was determined spectrophotometrically at 543 nm. The same technique was used to determine the concentration of nitrate after reducing nitrate to nitrite and passing it through a Cu/Cd reduction column (APHA 1988). The concentration of nitrate was computed as the difference between the total nitrite concentration after the reduction procedure and the initial concentration of nitrite. Monthly rainfall of the watershed recorded at sites 1, 7 and 10 were obtained from the Mahaweli Authority and from Levolen and Deltota Groups. Data were subjected to one-way ANOVA coupled with Duncan Multiple Range Test (DMRT) to determine inter-site and inter-month variability.

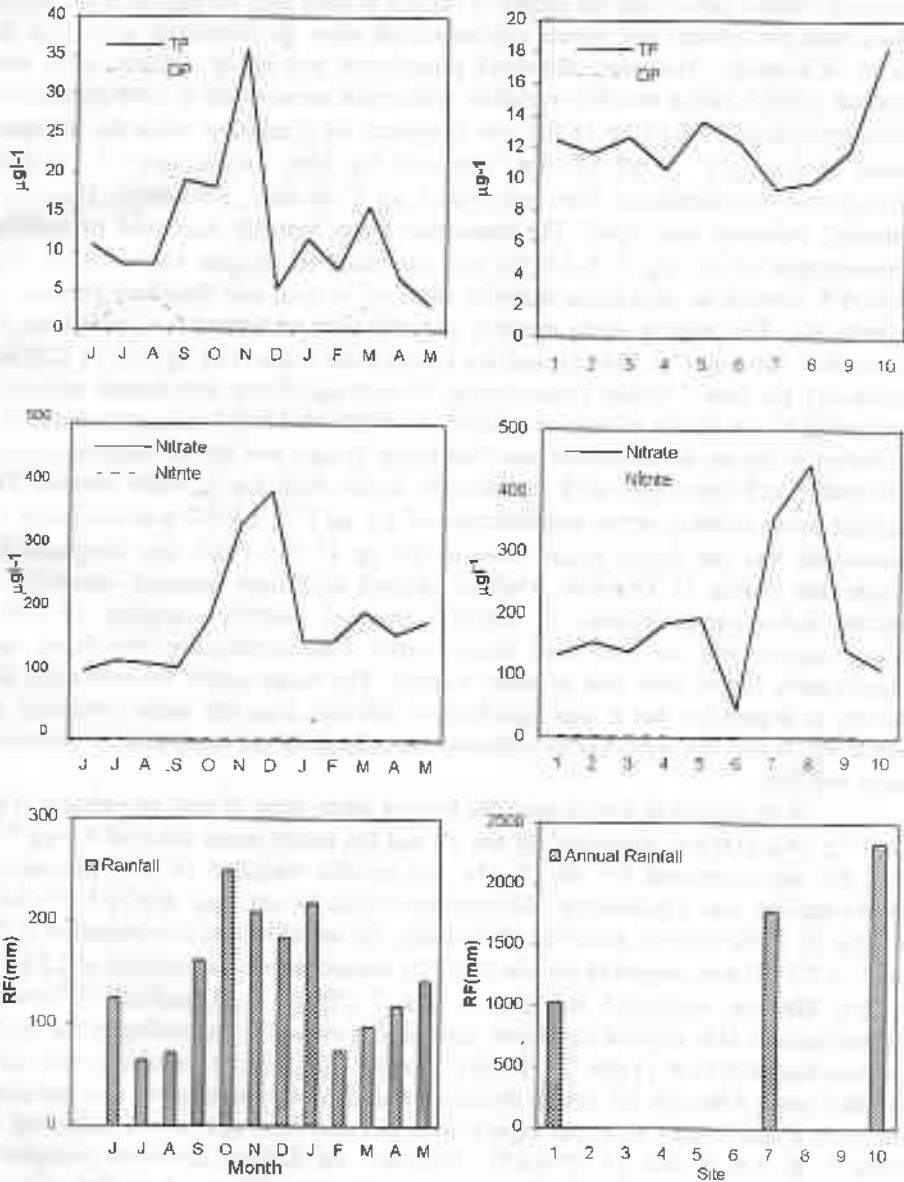


Fig. 1 Monthly and annual mean values of total and dissolved phosphorous and nitrate and nitrite for each site and each month.

## Results

Figure 1 shows the monthly mean values of total and dissolved phosphorus and nitrate and nitrite concentrations for each site and each month together with the monthly rainfall pattern and the ranges of rainfall at three sites during the study period. Both total phosphorus and nitrate concentrations show an increasing trend with the onset of rainfall. However, dissolved phosphorus and nitrite did not show such marked rainfall bound monthly variation. Maximum mean monthly total phosphorus concentration of  $35 \mu\text{g l}^{-1} \pm 16 \text{ SD}$  was computed for December while the minimum mean of  $3.1 \mu\text{g l}^{-1} \pm 0.8 \text{ SD}$  was computed for May. In the case of dissolved phosphorus, concentrations were less than  $1 \mu\text{g l}^{-1}$  in June, September, December, January, February and April. The maximum mean monthly dissolved phosphorus concentration of  $4.1 \mu\text{g l}^{-1} \pm 1.9 \text{ SD}$  was computed for August 1995 and one-way ANOVA showed no significant monthly variation in total and dissolved phosphorus (Table 1). The highest mean monthly concentration of nitrate was computed for December ( $393 \mu\text{g l}^{-1} \pm 224 \text{ SD}$ ) and the lowest mean value ( $108 \mu\text{g l}^{-1} \pm 72 \text{ SD}$ ) was computed for June. Nitrate concentration showed significant time-bound variability according to the results of one-way ANOVA (Table 1). DMRT categorized monthly variation in nitrate concentration into two major groups and nitrate concentration in November and December were significantly higher than that of other months. The highest mean monthly nitrite concentration of  $4.5 \mu\text{g l}^{-1} \pm 2.3 \text{ SD}$  was computed for November and the lowest mean value of  $0.6 \mu\text{g l}^{-1} \pm 1.1 \text{ SD}$  was computed for September (Table 1). One-way ANOVA showed significant seasonal variability in nitrate concentration (Table 1). DMRT grouped monthly variation of nitrite concentration into six sets and mean nitrite concentration in November was significantly higher than that of other months. The mean nitrite concentration was lowest in September but it was significantly different from the value computed for April which was not significantly different from those values computed for February, June and July.

With respect to stream sites, the highest mean value of total phosphorus ( $18.3 \mu\text{g l}^{-1} \pm 14.6 \text{ SD}$ ) was computed for site 10 and the lowest mean value of  $9.4 \mu\text{g l}^{-1} \pm 8.1 \text{ SD}$  was computed for site 7. The site-specific variation in total phosphorus concentration was significantly different according to one-way ANOVA ( $P < 0.05$ ) (Table 2). In the case of dissolved phosphorus, the highest mean concentration of  $2.4 \mu\text{g l}^{-1} \pm 2.5 \text{ SD}$  was computed for site 1 and the lowest mean concentration of  $1.2 \mu\text{g l}^{-1} \pm 0.6 \text{ SD}$  was computed for sites 6 and 7 (Table 2). Dissolved phosphorus concentrations also showed significant site-specific variability according to the results of one-way ANOVA (Table 2). DMRT grouped site-specific variability into three distinct sets. Although the lowest dissolved phosphorus concentration was computed for sites 6 and 7, they were not significantly different from the values computed for sites 3, 4, 5, 8, 9 and 10 ( $P > 0.05$ ). Similarly, the highest dissolved phosphorus concentration computed for site 1 was not significantly different from that of site 2 which was also not significantly different from sites 3, 4, 5, 8 and 10 ( $P > 0.05$ ).

*Water chemistry of a Sri Lankan river*Table 1. Mean values  $\pm$  SD of total and dissolved phosphorus, nitrate and nitrite concentrations ( $\mu\text{g l}^{-1}$ ) and the results of the one-way ANOVA for monthly variation.

Month	Total Phosphorous	Dissolved Phosphorous	Nitrate	Nitrite
Jun 94	10.8 $\pm$ 3.3	0.1 $\pm$ 0.0	108 $\pm$ 72	0.3 $\pm$ 0.9
Jul	8.3 $\pm$ 2.2	3.7 $\pm$ 1.9	124 $\pm$ 86	2.5 $\pm$ 1.0
Aug	8.4 $\pm$ 4.8	4.1 $\pm$ 1.9	120 $\pm$ 90	0.2 $\pm$ 1.2
Sep	19.1 $\pm$ 7.8	1.0 $\pm$ 0.0	114 $\pm$ 83	0.6 $\pm$ 1.1
Oct	18.2 $\pm$ 5.1	1.2 $\pm$ 0.6	192 $\pm$ 62	3.0 $\pm$ 1.8
Nov	35.7 $\pm$ 16.1	1.2 $\pm$ 0.4	340 $\pm$ 312	4.5 $\pm$ 2.3
Dec	5.3 $\pm$ 4.1	1.0 $\pm$ 0.0	393 $\pm$ 224	3.2 $\pm$ 1.4
Jan 95	11.6 $\pm$ 5.8	1.0 $\pm$ 0.0	156 $\pm$ 92	1.7 $\pm$ 1.9
Feb	7.8 $\pm$ 4.3	1.0 $\pm$ 0.0	156 $\pm$ 175	1.7 $\pm$ 0.9
Mar	15.8 $\pm$ 8.5	3.0 $\pm$ 2.1	202 $\pm$ 144	3.1 $\pm$ 1.1
Apr	6.7 $\pm$ 2.6	1.0 $\pm$ 0.0	167 $\pm$ 108	1.4 $\pm$ 1.2
May	3.1 $\pm$ 0.8	1.2 $\pm$ 0.6	187 $\pm$ 142	2.7 $\pm$ 0.9
F-value	2.13	2.54	8.81	8.82
F-prob	0.337	0.114	0.0001	0.0001

In the case of nitrate, the highest mean concentration of 444  $\mu\text{g l}^{-1} \pm 249$  SD was computed for site 8 while the minimum mean concentration of 45  $\mu\text{g l}^{-1} \pm 32$  SD was computed for site 6 (Table 2). One-way ANOVA showed highly significant site-specific variability in nitrite concentration (Table 2). DMRT grouped inter-site variability into four distinct categories. Mean concentrations of nitrate at site 8 and 7 were significantly different from each other and were also significantly higher than that of other sites. There was no significant site-specific difference between sites 6 and 10 although these values were significantly lower than that of other sites. However, the mean nitrate concentration at site 10 was not significantly different from that of sites 1, 2, 3, 4, 5 and 9. The highest mean concentration of nitrite (3.8  $\mu\text{g l}^{-1} \pm 2.3$  SD) was computed for site 10 and the lowest mean value of 1.0  $\mu\text{g l}^{-1} \pm 0.9$  SD was computed for site 6 (Table 2). One-way ANOVA showed statistically highly significant inter-site variability in mean nitrite concentration (Table 2). DMRT grouped inter-site variability into five distinct sets and mean nitrite concentrations at sites 3, 1 and 10 were not significantly different from each other. Mean concentration at site 10 was also not significantly different from sites 5, 9, 2 and 8. Similarly, there was no significant difference in mean concentration of nitrite between site 6 and 7. However, the mean nitrite concentration at site 7 was not significantly different from that of sites 2, 8 and 4.

### Discussion

Hynes (1963) and Ross (1963) discussed land water interactions as fundamental properties determining the structure and functioning of lotic ecosystems. Streams and rivers are efficient at retention of sediment and organic materials near their source of origin (Young et al. 1978; Speaker et al. 1984). However, the relationship between nutrient loading and land use is poorly understood in tropical

Table 2. Mean values  $\pm$  SD of total and dissolved phosphorus and nitrate and nitrite concentrations ( $\mu\text{g l}^{-1}$ ) and the results of the one way ANOVA for site-specific variability.

Site	Total phosphorous	Dissolved phosphorous	Nitrate	Nitrite
1	12.4 $\pm$ 6.6	2.4 $\pm$ 2.5	133 $\pm$ 107	3.3 $\pm$ 1.2
2	11.6 $\pm$ 7.1	2.3 $\pm$ 2.3	154 $\pm$ 97	2.4 $\pm$ 1.4
3	12.6 $\pm$ 7.2	1.7 $\pm$ 1.3	138 $\pm$ 65	3.7 $\pm$ 1.7
4	10.6 $\pm$ 3.3	1.6 $\pm$ 1.2	184 $\pm$ 91	2.0 $\pm$ 1.3
5	13.6 $\pm$ 11.7	2.0 $\pm$ 1.3	194 $\pm$ 80	2.6 $\pm$ 1.2
6	12.3 $\pm$ 12.7	1.2 $\pm$ 0.6	45 $\pm$ 32	1.0 $\pm$ 0.9
7	9.4 $\pm$ 10.5	1.2 $\pm$ 0.6	357 $\pm$ 174	1.5 $\pm$ 1.0
8	9.8 $\pm$ 8.1	1.5 $\pm$ 1.2	444 $\pm$ 249	2.3 $\pm$ 0.9
9	11.8 $\pm$ 8.5	1.3 $\pm$ 1.8	143 $\pm$ 109	2.6 $\pm$ 1.7
10	18.3 $\pm$ 14.6	1.8 $\pm$ 1.8	111 $\pm$ 68	3.8 $\pm$ 2.3
F-value	2.13	2.54	17.96	7.02
F-crit.	0.0337	0.0114	0.0001	0.0001

watersheds. Further, tropical stream ecosystem studies suffer from a lack of both long term perspectives and a range of spatial scales.

Most of the tropical streams and rivers have an annual cycle, which is determined by the pattern of rainfall (Payne 1986). Since many tropical areas have distinct rainy seasons, when the annual precipitation occurs there tend to be a seasonal cycle in the discharge rate of the rivers and streams. Such fluctuations in discharge rate can cause marked variation in water chemistry and suspended materials. Usually the concentration of ions in the water is at a maximum during the dry season when the influence of ground water is greatest. The rains tend to have a dilution effect. However, during the dry season, mineralization of organic matter in the soils of the basin proceeds, so that when the first rains arrive there is a flushing effect resulting in high concentration of ions (Payne 1986). This effect may be particularly significant with respect to nitrate, since alternate wetting and drying of soil enhance the mobilization of nitrate ions.

Results of this study clearly show that there is no marked monthly variation in the concentration of phosphorus both dissolved and total. However, monthly variations in nitrate and nitrite concentrations are highly significant. In the case of phosphorus, mobilization is determined by absorption and adsorption mechanisms. Forelich (1988) has shown that adsorption of phosphorous onto inorganic particles has fast kinetics while solid state diffusion of adsorbed phosphate from the surface into the interior of particles has slow kinetics. Naturally, clay particles have a high capacity of adsorbing phosphate and maintaining a low phosphate concentration equilibrium in solution. This may be the reason for the relatively low concentration of phosphate found in the stream water of the Nilambe Oya. However, it has been assumed that a relatively high concentration of phosphorus is present in streams that are draining watersheds subjected to intensive agriculture based land use. Concentrations of phosphorus in the Nilambe Oya were within the range reported for tropical streams and rivers (Visser 1974; Viner 1975, 1982). Mtada (1985) reported extremely low concentrations of  $\text{PO}_4$

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-P for an undisturbed stream in Sierra Leone. Low concentrations of phosphorus have been reported also from streams in Sri Lanka (Geisler 1967; Weninger 1972). Monthly variation of nitrate/nitrite concentration in the Nilambe Oya has a strong relationship with the monthly rainfall pattern in the watershed. The nitrate concentration of the Nilambe Oya was extremely high compared to the values reported for other tropical streams and rivers (Visser 1974; Viner 1982; Mtada 1985). Weninger (1972) reported relatively higher concentrations of nitrate from streams in Sri Lanka. Although it has been reported that the major source of nitrate in streams is rain water (Payne 1986), the results of this study indicates that application of nitrogenous fertilizer in tea plantations appear to play a significant role in enhancing nitrate concentration in stream water. Neill (1989) has shown an increased nitrate concentration in Irish rivers in relation to the application of nitrogenous fertilizer. Nitrate loading into stream ecosystems changes in relation to variation in annual and seasonal run-off regimes (Hill 1986). Increased nitrate concentration in stream water has also been attributed to organic pollution resulting from human waste (Weninger 1972).

Significant inter-site variability in the phosphorus (total and dissolved) and nitrogen (nitrate and nitrite) concentrations in the Nilambe Oya may be attributed to intensive and variable land use even though the watershed is fairly small. The highest phosphorus concentration was found at the site located in the Galaha area where the population density is relatively high. The sites 7 and 8 had the lowest phosphorus concentrations. These sites receive water draining from tea plantations. Similarly, significant inter-site variability in nitrate and nitrite concentrations may also be attributed to land use changes. However, in contrast to phosphorus concentration, the highest nitrate concentrations were found at sites 7 and 8. This reflects that the nitrogenous fertilizer application to tea plantations has a significant impact on nitrate concentration in stream water. The lowest nitrate concentration was found at a site draining an undisturbed land.

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