



Nitrogen forms and total phosphorus in water courses: a study at Maringá stream, Paraná State

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ABSTRACT. This paper aimed to monitor the nitrogen compounds and total phosphorous in the Maringá Stream watershed in order to investigate the spatial and temporal variations in the water quality. For this, samplings were collected from seven sites during the period from October 2008 to September 2009. The results indicated the most critical stretches of water pollution with the inflow of the discharges from a sewage treatment plant of the city. Also it is important to highlight the influence of diffuse pollution coming from agricultural runoff and wastewater from fishing lakes, on the water quality.

Keywords: nitrogen, phosphorus, water pollution, watershed, eutrophication.

Formas nitrogenadas e fósforo total em cursos d'água: estudo de caso do ribeirão Maringá, Estado do Paraná

RESUMO. Este trabalho teve por objetivo o monitoramento dos compostos nitrogenados e fósforo total nas águas da bacia hidrográfica do ribeirão Maringá com o propósito de investigar a variação espaço-temporal da qualidade deste manancial. Para isso, foram coletadas amostras em sete pontos, durante outubro/2008 a setembro/2009. Os resultados obtidos mostraram trechos críticos de poluição hídrica com a entrada do efluente de uma das estações de tratamento de esgoto da cidade. Importante destacar também a influência da poluição difusa provinda do escoamento superficial do solo agrícola e dos despejos dos pesqueiros, intervindo, deste modo, na qualidade da água do ribeirão.

Palavras-chave: nitrogênio, fósforo, poluição hídrica, bacia hidrográfica, eutrofização.

Introduction

Studies on forms of nitrogen and phosphorus in groundwater and surface water have acquired importance mainly as for the degradation potential on the water quality. Although essential to biomass production, the excess of these nutrients can lead the water bodies to eutrophication and harmful consequences (FARIAS et al., 2007; OLIVEIRA et al., 2009; SILVA et al., 2010).

Among the published studies on the subject, stands out Cabral (2007) who analyzed the levels of nitrate and ammonium in waters from the Aquífero Barreiras in Belém – Pará State, and proved that human factors, such as the place of discharge of domestic effluents and the leakage of sewage pipes, have more influence on the changing of the levels of nitrate and ammonium in the waters than the seasonal factors.

Bollmann and Marques (2006) examined the variation between the carbonaceous organic matter, nitrogen and phosphorus in the waters of four small urban rivers. The results showed important

alterations in the relationships between the analyzed parameters, indicating that even small population densities are able to change the quality of waters.

Toledo and Nicoletta (2002) evaluated the water quality of a watershed for urban and rural use in Guaíra – São Paulo State, using a multivariate statistical technique. The authors concluded that, among the water quality parameters, it became evident the influence of high concentrations of total phosphorus in deteriorating the water quality, being the urban use the main causal agent.

Silva et al. (2010), when studying the water quality in the São Francisco Falso river, tributary of the Itaipu reservoir – Paraná State, considering the levels of nitrogen and phosphorus, found that the trophic state of the water ranged from oligo- to mesotrophic, being this latter status observed under the rainfall influence. Of the forms of nitrogen, the nitrite presented values above the recommended by the Canadian environmental agency (Canadian Council of Ministers of the Environment) – 0.06 mg L⁻¹, representing a risk to aquatic life.

In this respect, an important fact is verified in the Maringá stream watershed, located in the northern area of the Paraná State (Figure 1). At a given point of its course, the water receives the effluent from a sewage treatment plant (STP). Besides that, the major tributaries have the headwaters in the urban area and 63.70% of total area of the watershed is occupied by the agricultural activity (ALVES et al., 2008).

According to Oliveira et al. (2009), these particular characteristics make the watershed susceptible to factors of environmental degradation; since the impacts of these activities produce several changes in the aquatic systems.

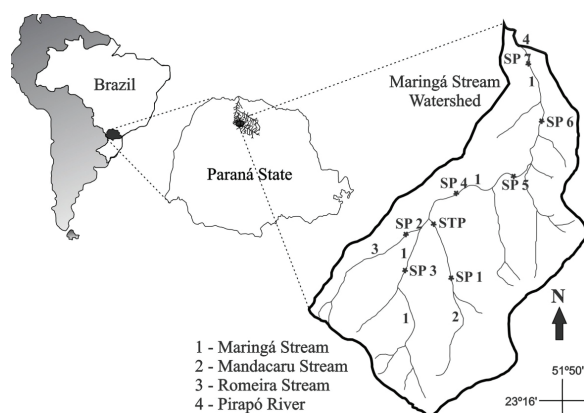


Figure 1. Maringá stream watershed. Highlight for location and distribution of sampling points.

Previous studies were carried out in the study area with the goal of diagnosis and monitoring the water quality in the presence of the sources of pollution identified until the moment, highlighting Alves et al. (2008) and Schneider et al. (2011). However, it has not yet been discussed the interference of nitrogen and phosphorus levels in the water, the spatial and temporal variations, the links between the sources of pollution, and the use and occupation of the watershed and consequences to the aquatic environment.

Oliveira et al. (2009) mentioned the importance of developing researches focused on the monitoring and the environmental diagnosis to strengthen the scientific basis in the area, allowing the exchange of mitigating measures of control and management of polluting sources.

Given the above, this study focused on the evaluation of the concentration dynamics of nitrogen and total phosphorus levels in the water of the Maringá stream watershed. The main goal was to investigate the spatial and temporal variations of the water quality after receiving the discharge of urban effluent, and also to evaluate the trophic state of the water, considering the agriculture as the main economic activity developed in the studied watershed.

Material and methods

To monitor the forms of nitrogen and phosphorus in the waters of the Maringá stream, it was performed punctual water sampling by the morning, with simple sampling at the central site of the section and in seven sampling points (SP) covering since its main springs until its mouth in the Pirapó river (Figure 1). After collecting, the samples were preserved by cooling and then acidified according to the literature (APHA, 1998).

The laboratory tests were carried out at the Laboratory of Management, Preservation and Environmental Control, Department of Chemical Engineering, State University of Maringá.

The ammonia nitrogen (N-NH_3) was determined by the Nessler Method. The nitrite (NO_2^- - mg L^{-1}) was obtained by the Diazotization Method. In order to determine the nitrate (NO_3^- - mg L^{-1}), it was used the Cadmium Reduction Method. All these methods are described by the equipment Portable Datalogging Spectrophotometer HACH DR/2010, following recommendations of APHA (1998).

The concentrations of total phosphorus (mg L^{-1}) were obtained through the ascorbic acid method after digestion with persulfate, according to the methodology contained in the Handbook of Physical and Chemical Analyses of Water for Supply and Wastewater (SILVA; OLIVEIRA, 2001).

In order to evaluate the trophic state of waters of the Maringá stream, the trophic state index (TSI_p) was calculated, which is based on total phosphorus (TP) for lotic environments, presented in Von Sperling (2007) and in the Equation 1.

$$\text{TSI}_p = 10 \cdot \left(6 - \left(\frac{0.42 - 0.36 \cdot (\ln \text{TP})}{\ln 2} \right) \right) - 20 \quad (1)$$

where:

TSI_p = Trophic state index based on total phosphorus;

TP = Concentration of total phosphorus ($\mu\text{g L}^{-1}$).

In the field were collected data of pH and temperature (T - $^{\circ}\text{C}$), through analytical equipments (DIGIMED®). The climatological data of the study period were furnished by the Climatological Station at the State University of Maringá. The study period covered the months between October, 2008 and September, 2009.

Results and discussion

The Figure 2 shows the rainfall levels in the area during the study period. In the city of Maringá predominates rainfall of low to moderate intensity during the dry season, which comprised the months of October and December, 2008, March, April, May and

August, 2009 and, rainfall from moderate to high intensity in the summer, months of November, 2008, January, February, June, July, September, 2009, that is, there is no well-defined dry season.

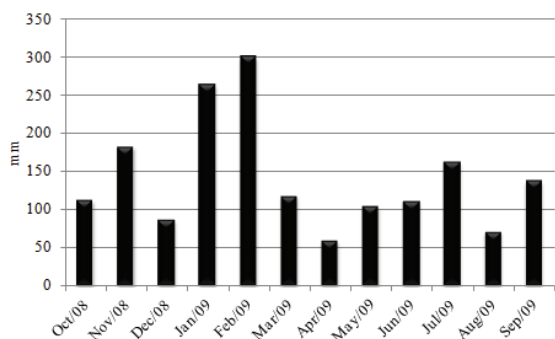


Figure 2. Monthly rainfall in the watershed during the study period.

The data obtained in the field and with the laboratory tests are listed in the Tables 1 to 4. The results are discussed based on the standards set for water courses by the Resolution number 357/2005 from CONAMA (BRASIL, 2005). In accordance with the SUREHMA Ordinance number 004 from March 21st, 1991, the water courses contained in the Maringá stream belong to the class 2, except for the Mandacaru stream, that belongs to the class 3 (PARANÁ, 1991).

In order to better visualize the results, the bold values show the parameters above the limit established by the legislation, in view of the suitability of the respective water courses.

Considering the variation in water temperature (Figure 3), the maximum value, 26.0°C, was registered in February, and the minimum, 15.0°C, in July. This result is strictly related to the seasonal factors than to any other interference of pollution by heat. The pH values remained between 6.8 and 8.5 (Figure 4), therefore, within the neutral-alkaline range established by the legislation.

The results for ammonia nitrogen (Table 1) showed that the stretches downstream of the discharge from the sewage treatment plant presented the highest concentrations of this nitrogen form in the water.

In the stretch associated with the site SP4, the result was expected due to proximity to the discharge of the sewage treatment plant, given that the ammonia nitrogen is a by-product of organic matter degradation. The study of Santos et al. (2008) obtained similar results for the influence of ammonia nitrogen after the release of effluents from domestic sewage treatment plants on changing the water quality of Vieira runlet – Rio Grande do Sul State.

Due to the sedimentation and degradation of this nitrogen form, the concentration is reduced along the

stream (Maringá stream) course. However, on the stretches associated with the sites SP6 and SP7, the concentration of ammonia nitrogen increases again. This can be justified by the inflow of waters from a stream that probably receives urban wastewater, upstream of the stretch of the site SP6.

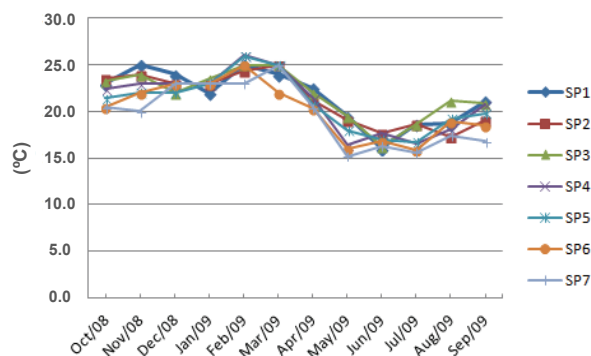


Figure 3. Temperature variation (°C).

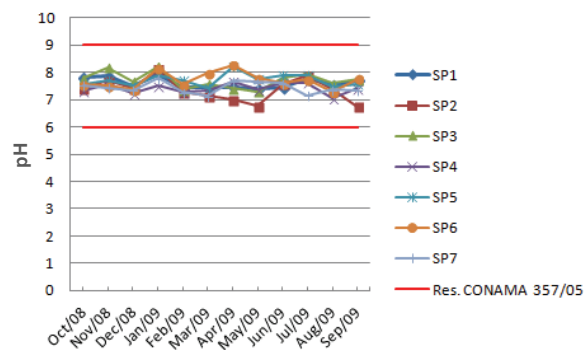


Figure 4. pH variation. The line Res. 357 refers to the Resolution no. 357/2005 from CONAMA indicating the range of variation allowed (6 – 9).

Table 1. Variation in ammonia nitrogen concentration (mg L⁻¹).

Date	SP1	SP2	SP3	SP4	SP5	SP6	SP7
Oct. 2008	0.37	0.05	0.05	8.48	3.12	4.62	5.00
Nov.	0.00	0.00	0.02	9.13	1.60	2.13	2.13
Dec.	0.07	0.08	0.00	5.68	2.36	3.40	4.07
Jan. 2009	0.07	0.10	0.10	3.00	1.43	2.17	2.74
Feb.	0.15	0.12	0.05	10.03	1.70	1.74	2.19
Mar.	0.07	0.04	0.03	7.85	1.96	2.98	3.68
Apr.	0.06	0.11	0.24	13.40	2.32	3.56	4.74
May	0.01	0.02	0.01	6.20	1.37	2.75	2.58
Jun.	0.01	0.08	0.68	9.13	1.48	1.97	2.39
Jul.	0.08	0.02	0.19	7.75	1.85	2.13	2.41
Aug.	0.08	0.10	0.27	9.30	2.70	3.68	4.65
Sep. 2009	0.05	0.08	0.11	9.08	1.60	2.44	2.98

Another possibility may be related to the presence of fishing lakes in the region, where there is a continuous water circulation in the ponds, and such waters are usually discharged into the water body. These effluents, according to Simões et al. (2008), have the feature of enriching the water body with ammonia, organic matter, phosphorus and other nutrients.

With regard to the nitrite concentration (Table 2), during the sampling period, it was also observed values higher than established by the law (1.0 mg L^{-1}).

Table 2. Variation in nitrite concentration (mg L^{-1}).

Date	SP1	SP2	SP3	SP4	SP5	SP6	SP7
Oct. 2008	1.0	0.0	1.0	1.0	2.0	1.0	0.0
Nov.	2.0	1.0	2.0	2.5	3.0	3.0	3.0
Dec.	2.0	0.5	2.0	1.0	3.0	2.5	2.0
Jan. 2009	1.0	4.0	4.0	4.0	5.5	7.0	14.0
Feb.	3.0	1.0	2.0	1.4	2.0	2.5	0.0
Mar.	2.0	1.0	2.0	1.0	2.5	2.5	2.0
Apr.	2.0	1.0	0.0	0.0	2.5	2.0	0.0
May	0.0	2.0	3.5	0.0	6.0	3.5	4.0
June	1.0	1.5	2.0	2.0	1.0	1.0	1.0
July	0.0	0.0	0.0	1.0	2.5	1.0	1.0
Aug.	2.0	0.0	0.0	1.0	2.0	2.0	0.0
Sep. 2009	1.0	4.4	1.0	1.0	2.0	2.0	4.0

High nitrite levels in the water indicate the presence of domestic and industrial wastewater (BARD, 2002; ESTEVES, 1998). Indeed, the Mandacaru Stream (SP1) receives frequent discharges of sewage, and the Maringá stream is not different, as highlighted by Alves et al. (2008) and Schneider et al. (2011).

In the stretches related to the sites SP2 and SP3, within an agricultural area, the variations can be associated with the use of fertilizers and/or nitrogen-based compounds in the crops which are washed into to the water courses by the rainfall action. The studies of Silva et al. (2001, 2010) showed the relationship between the use of fertilizers and the concentration of nitrogen forms in surface waters.

Regarding the nitrate concentration (Table 3) no concentrations were detected above the allowed by legislation (10.0 mg L^{-1}).

Table 3. Variation in nitrate concentration (mg L^{-1}).

Date	SP1	SP2	SP3	SP4	SP5	SP6	SP7
Oct. 2008	3.4	1.7	4.0	2.5	3.7	4.4	4.1
Nov.	6.4	0.8	5.8	2.4	3.3	3.5	2.8
Dec.	6.0	0.4	5.5	2.9	4.0	3.9	1.0
Jan. 2009	3.3	1.0	4.5	3.8	3.3	2.6	1.0
Feb.	3.5	0.9	4.8	2.3	3.3	4.1	3.3
Mar.	4.2	2.1	4.9	3.1	3.9	2.5	2.0
Apr.	4.9	2.5	2.7	1.9	5.5	3.8	4.7
May	3.9	1.6	2.9	3.1	3.7	3.9	2.9
June	3.6	2.4	3.9	2.9	3.4	2.9	3.3
July	3.5	2.6	3.1	0.0	0.7	0.0	0.5
Aug.	4.1	2.6	4.3	2.9	4.9	2.6	4.3
Sep. 2009	4.0	2.5	7.5	1.9	4.0	3.7	4.5

Even in disagreement with the law, quantitatively, it was obtained considerable concentrations of this compound in the water. These results added to the results for ammonia nitrogen, nitrite, temperature and pH, indicated that the nitrogen cycling occurs rapidly in the studied water bodies.

Brandeiro et al. (2010) monitored the nitrogen compounds in the Meia Ponte river – Goiás State, and verified that, during the hot and rainy summer

months, the lower concentrations were due to the highest flow of the water course. This trend cannot be clearly observed in the Maringá stream because in this part of the year, the surface runoff of the agricultural soil operates as a source of diffuse pollution for the water of this watershed.

For the total phosphorus, high concentration values were registered in the Maringá stream basin throughout the study months. As observed in the Table 4, the values were higher than established by the law, i.e. 0.10 mg L^{-1} for rivers class 2, and 0.15 mg L^{-1} for rivers class 3, in almost every monitoring site during the study period. Rare exceptions were found in the monitoring sites SP1, SP2 and SP3, mainly in November, 2008, February and April, 2009, probably due to the rainfall a few days before the samplings.

Table 4. Variation in total phosphorus concentration (mg L^{-1}).

Data	SP1	SP2	SP3	SP4	SP5	SP6	SP7
Oct. 2008	0.489	0.003	0.128	7.977	3.176	4.649	4.727
Nov.	0.047	0.067	0.074	1.597	0.376	0.514	0.604
Dec.	0.209	0.069	0.084	0.981	0.981	0.686	0.762
Jan. 2009	0.148	0.185	0.144	0.509	0.375	0.495	0.597
Feb.	0.053	0.032	0.055	1.404	0.286	0.307	0.337
Mar.	0.264	0.197	0.244	2.265	0.890	1.106	1.239
Apr.	0.000	0.072	0.043	0.991	0.458	0.630	0.815
May	0.497	0.449	0.491	1.384	0.871	1.063	1.181
June	0.325	0.319	0.415	1.477	0.644	0.773	0.836
July	0.494	0.383	0.564	3.801	1.360	1.471	1.627
Aug.	0.337	0.304	0.345	1.502	0.705	0.901	1.145
Sep. 2009	0.306	0.279	0.346	3.289	0.555	0.674	0.999

Similarly to the results obtained for the nitrogen forms, the stretch associated with SP4, had the highest levels of phosphorus. According to Esteves (1998), the discharge of domestic sewage is a potential source for the presence of phosphorus compounds in lotic environments. In this way, the Maringá stream, by receiving effluents of domestic origin, either treated or not, gets a very significant load of pollutants.

In general, the spatial and temporal variations of total phosphorus were similar to those of the nitrogen compounds: its concentration decreased along the water body, but in the stretches associated with the sites SP6 and SP7, increased again. In fact, this variation was influenced by the same reasons previously mentioned, indicating a strong relationship between the parameters nitrogen-phosphorus regarding the pollution sources.

What is of concern in the case of the total phosphorus is the concentration in the water, which reached extremely high values and, in some periods, the concentration exceeded the allowed by the Guideline number 357/2005 of CONAMA on dozens of times. In the Table 5 it was possible to verify the trophic state indices, estimated by the Equation 1, for each site during each sampling.

Table 5. Trophic state index based on total phosphorus for the Maringá stream.

Date	SP1	IET _p	SP2	IET _p	SP3	IET _p	SP4	IET _p	SP5	IET _p	SP6	IET _p	SP7	IET _p
Oct. 2008	54.45	b	47.98	b	58.67	c	72.48	f	65.79	e	68.61	f	68.95	f
Nov.	66.10	d	39.82	a	59.12	d	80.60	f	75.82	f	77.80	f	77.88	f
Dec.	53.95	b	55.79	c	56.27	c	72.25	f	64.73	e	66.36	e	67.20	f
Jan. 2009	61.69	d	55.92	c	56.93	c	69.72	f	69.72	f	67.86	f	68.41	f
Feb.	59.90	d	61.06	d	59.74	d	66.31	f	64.72	e	66.17	e	67.14	f
Mar.	54.52	c	51.89	b	54.78	c	71.58	f	63.31	e	63.68	e	64.17	e
Apr.	62.90	d	61.37	d	62.50	d	74.06	f	69.21	f	70.34	f	70.93	f
May	45.90	b	56.17	c	53.45	c	69.77	f	65.77	e	67.42	f	68.75	f
June	66.18	e	65.66	e	66.12	e	71.51	f	69.10	f	70.13	f	70.68	f
July	63.97	e	63.88	e	65.25	e	71.84	f	67.53	f	68.48	f	68.89	f
Aug.	66.16	e	64.83	e	66.84	e	76.75	f	71.41	f	71.82	f	72.35	f
Sep. 2009	64.16	e	63.64	e	64.30	e	71.93	f	68.00	f	69.28	f	70.52	f

Note: a – ultraoligotrophic; b – oligotrophic; c – mesotrophic; d – eutrophic; e – supereutrophic; f – hypereutrophic.

From the data, it was verified that the aquatic system is compromised as for the quality of its waters. The high trophic level of the water ranged from a eutrophic state, upstream of the discharge from the STP, to a hypereutrophic state, downstream of this. In this respect, it is noticed again the strong activity of diffuse sources on the watershed, by changing the water quality even upstream of the release of effluents from the sewage treatment plant. Furthermore the eutrophication process, formed by the excess of nutrients in the waters, has not been clearly evidenced owing to the low depth of the stream bed and the high water flow, as observed in the field.

Conclusion

The results obtained for the Maringá stream allowed verifying that the most critical stretches occurred with the inflow of effluents from the sewage treatment plant. However, it is important to highlight the influence of the soil runoff during rainfall events and of dumps from the fishing ponds.

The results of ammonia nitrogen, nitrite, nitrate, temperature and pH indicated that the nitrogen cycling occurs rapidly.

As for the total phosphorus, the trophic state index showed favorable to the biomass development, but the eutrophication had not been visually established due to the hydraulic characteristics of the water courses.

Acknowledgements

The authors thank to CAPES and CNPq/CTHidro, for the financial support, and the Laboratory of Management, Preservation and Environmental Control (LGPCA), where all the laboratory analyses were carried out, and to all the employees of the DEQ/UEM.

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Received on July 15, 2011.

Accepted on March 13, 2012.

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