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Behavior simulation of nitrogen compounds in rivers with uncertainty analysis

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ABSTRACT

This study simulated nitrogen-compound concentration changes in rivers, taking into account uncertainty analysis carried out by the Monte Carlo Method. The study area is the final stretch of the Piracicaba River, located in Minas Gerais, Brazil, which is an important Doce River tributary. The uncertainty analysis took into account random generation of hydrodynamic variables, initial water quality conditions and kinetic constants. Different variation percentages for the organic nitrogen decay kinetic constants random generation did not influence considerably the ammonia or organic nitrogen maximum concentration extreme values. In the simulations, maximum organic nitrogen concentrations were most frequently between 0.20 $mg.L^{-1}$ and 0.22 $mg.L^{-1}$ (42%), maximum ammonia nitrogen between 0.28 $mg.L^{-1}$ and 0.30 $mg.L^{-1}$ (30%), maximum nitrite between 0.05 $mg.L^{-1}$ and 0.07 $mg.L^{-1}$ (49%) and maximum nitrate between 0.46 $mg.L^{-1}$ and 0.50 $mg.L^{-1}$ (37%). Estimated maximum concentrations for ammonia nitrogen, nitrite and nitrate did not exceed the environmental quality standards established by Brazilian CONAMA Resolution 357/2005 for Class 2 watercourses. Random generation of kinetic constants that regulate ammonia and nitrite decay produced significant ammonia nitrogen, nitrite, and nitrate peak concentrations value frequencies, histograms and forms changes, when considering variation percentages equal to or greater than 50%. Some simulation results showed more inhibition of oxidized nitrogen forms production.

Keywords: monte carlo method, stochastic modeling, uncertainty analysis, water quality.

Simulação comportamental de compostos nitrogenados em rios com análise de incerteza

RESUMO

O objetivo do presente estudo é simular transformações dos compostos de nitrogênio em rios com incorporação da análise de incerteza conduzida pelo Método de Monte Carlo. A área de estudo considerada foi o trecho final do Rio Piracicaba, importante afluente do Rio Doce no território mineiro. A análise de incerteza conduzida envolveu gerações aleatórias de variáveis hidrodinâmicas, condições

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iniciais de qualidade de água e constantes cinéticas. A adoção de diferentes coeficientes de variação nas gerações aleatórias das constantes cinéticas que regulam o decaimento do nitrogênio orgânico não influenciou de maneira significativa os valores extremos das concentrações máximas de nitrogênio orgânico ou nitrogênio amoniacal. Nas simulações conduzidas, concentrações máximas de nitrogênio orgânico que se situaram mais frequentemente entre 0,20 $mg.L^{-1}$ e 0,22 $mg.L^{-1}$ (42%), de nitrogênio amoniacal entre 0,28 $mg.L^{-1}$ e 0,30 $mg.L^{-1}$ (30%), de nitrito entre 0,05 $mg.L^{-1}$ e 0,07 $mg.L^{-1}$ (49%) e de nitrato entre 0,46 $mg.L^{-1}$ e 0,50 mg.L-1 (37%). As concentrações máximas estimadas para nitrogênio amoniacal, nitrito e nitrato não superaram os padrões de qualidade ambiental estabelecidos pela Resolução CONOMA nº 357/2005 para cursos d'água classe 2. Gerações aleatórias das constantes cinéticas que regularam o decaimento do nitrogênio amoniacal e do nitrito, considerando coeficientes de variação iguais ou superiores a 50%, produziram alterações relevantes nos valores e formas dos histogramas de frequência das concentrações máximas de nitrogênio amoniacal, nitrito e nitrato. Em determinadas simulações, foi observada, também, inibição da produção das formas mais oxidadas de nitrogênio.

Palavras-chave: método de monte carlo, modelagem estocástica, qualidade de água.

1. INTRODUCTION

Nitrogen compounds can be released into water bodies by natural sources or as the result of anthropogenic activities. Biological fixation, rainfall processes, runoff and rural drainage are some examples of natural nitrogen sources. Anthropogenic sources include several industrial activities, water surface runoff in urban areas, fertilizer use in rural areas, and feces and urine discharges into water bodies without proper treatment (Ferreti, 2005).

Nitrogen compounds (especially those in nitrate form), in their most different states of oxidation, in water bodies may cause human health problems. Nitrate is capable of producing methemoglobin, which is an element that reduces the transport of oxygen to tissues and in high concentrations in the human body is incompatible with life (Fernicola and Azevedo, 1981).

As observed by Reis and Mendonça (1998; 2009), other environmental problems associated with the nitrogen cycle in water courses deserve particular attention: a) ammonia is toxic to fish, particularly in the non-ionized form (with corresponding concentration and toxicity values depending on pH, temperature and salinity); and b) during the nitrification process (oxidation reactions) oxygen additions (or hydrogen removal) occur to the organic molecule. Thus, nitrification can deplete water body oxygen levels.

In this context, nitrogen cycle simulation with the aid of mathematical models of water quality, such as presented by Whitehead *et al.* (1998a; 1998b), Tong and Chen (2002), Ribarova *et al.* (2008), Gastaldini and Oppa (2011), Gomes and Simões (2014); Salla *et al.* (2014), Grizzetti *et al.* (2015), Li *et al.* (2017) and Ikenberry *et al.* (2017), becomes relevant for the adequate management of water bodies' nitrogenous compounds.

Moreover, it is necessary that the parameters describing the modeled system be obtained in an appropriate way for a water quality mathematical model to produce satisfactory responses. However, there are uncertainties in the determinations of the main factors influencing quality parameters in rivers. Establishing these factors reliably is a complex task, and depends on data collection, laboratory testing and field measurements, which can be sources of inaccuracies and uncertainties. As a consequence, model simulated values may present different degrees of uncertainty. In addition, parameters determined at one time may not be representative of the process that occurs over a long period of time (Salas and Shin, 1999). In this context, the behavior of input data and models water quality coefficients can be treated as a stochastic process, subject to uncertainty analysis, due to the variability, randomness and uncertainties associated with the use of mathematical models.

Several uncertainty analysis methods have been developed and applied in water resource

engineering. Among the most widely used methods is the Monte Carlo Method (Salas and Shin, 1999), as illustrated by Whitehead and Young (1979), Beck (1987), Pastres and Ciavatta (2005), Lindenschmidt *et al.* (2007), Mannina and Viviani (2010), Dotto *et al.* (2012), Jiang *et al.* Holguin-Gonzalez *et al.* (2013) and Shojaei *et al.* (2015), Abokifa *et al.* (2016), Sparkman *et al.* (2017) and Sharior *et al.* (2019).

In the Monte Carlo method, different input variables are randomly considered in pre-established inputs, simulating the corresponding output values (Clemen and Reilly, 2013). By this technique, all uncertainties about input factors can be considered simultaneously or individually (Saisana *et al.*, 2005). The generated responses are then analyzed statistically for quantification of uncertainties.

The main objective of this research is to simulate the transformation of nitrogen compounds in the final stretch of the Piracicaba River, incorporating uncertainty analysis carried out by the Monte Carlo Method. The Piracicaba River is an important tributary of the Doce River (Minas Gerais State, Brazil). The approach allowed the nitrogen cycle transformations to be treated stochastically, thus avoiding the analysis of single profiles for the different nitrogen compounds, which is the usual procedure adopted in the deterministic approach for water quality mathematical simulation. Due to the uncertainties associated with the kinetic constants that regulate the nitrogen cycle, the variation percentages for the random generation influence of these constants was also investigated.

2. STUDY AREA

There were considered hydrological and water quality data for the Piracicaba River final stretch, between Coronel Fabriciano city and its mouth, corresponding to a total length of 60 km. The Piracicaba River watershed (Figure 1) is a Doce River sub basin located in Minas Gerais State east center region. In particular, the Piracicaba River mainspring is located in Espinhaço mountain range, near Ouro Preto city, at an altitude 1,680 m, and flows into Doce River at an altitude 210 m, close to Ipatinga city. Piracicaba River is 241 km long (Mourão Júnior, 2010).

The population of the municipalities that are totally or partially located in the Piracicaba watershed is 761,356 inhabitants (IBGE, 2010). Ipatinga, the largest and most important municipality in the region, presents 239,468 inhabitants. It is followed by Coronel Fabriciano municipality, that presents103,694 inhabitants. Known nationally as an industrial pole, the city of Ipatinga has a dense commerce and services network.

According to Normative Resolution No. 09, issued on April 19, 1994 by Minas Gerais State Environmental Policy State Council (COPAM), the Piracicaba River was classified, in the simulated stretch, as a Class 2 watercourse.

The Piracicaba River receives large nitrogenous compound contributions from industrial and municipal effluents. Hence, domestic and industrial pollution is one of the main environmental watershed problems.

3. METHODOLOGY

3.1. Hydrological and Water Quality Information

Critical conditions concerning surface water source pollution occur more frequently in drought periods. Thus, in this research, water quality simulations were carried out by assuming an average seven-day low flow which occurs once in ten years (i.e.$_7Q_{10}$).

The Piracicaba River $_7Q_{10}$ flow rate value, 23.68 $m^3 s^{-1}$, was estimated by Mourão Junior (2010) based on data from the ACESITA fluviometric station (station installed and operated by the Brazilian National Water Agency).

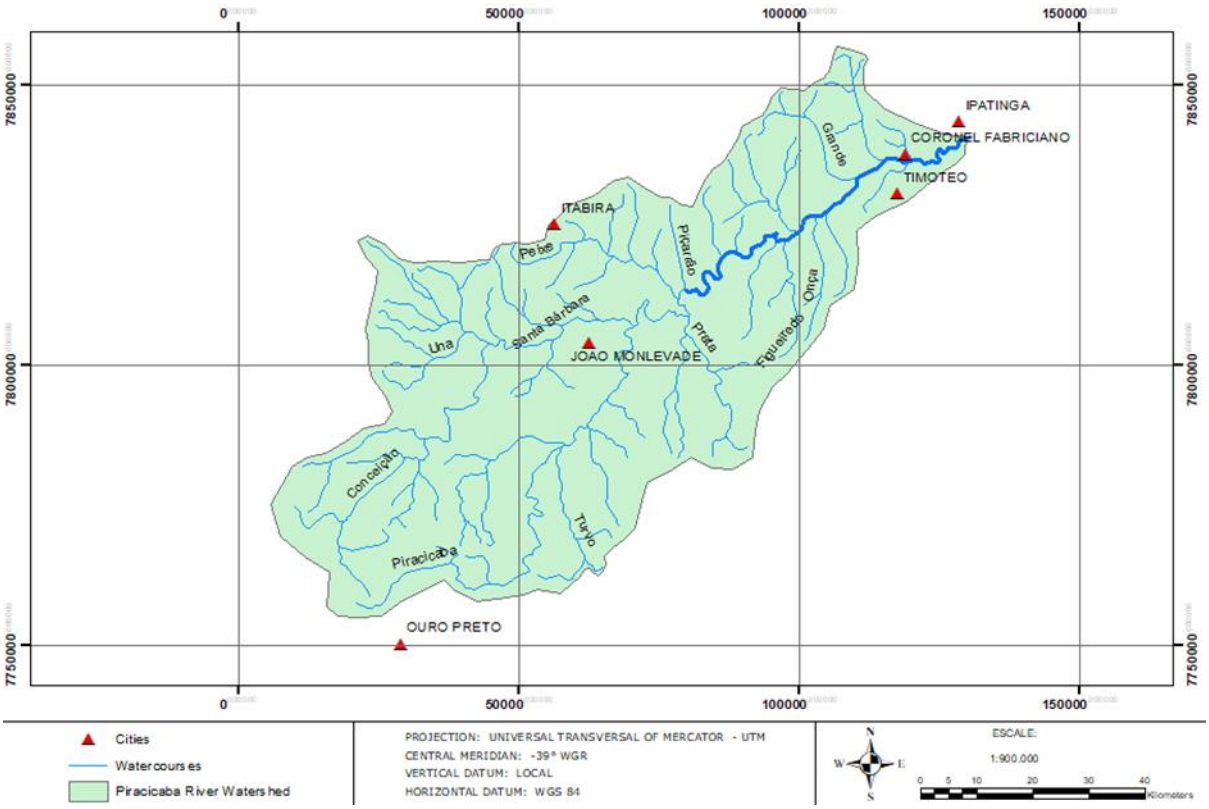

Figure 1. Piracicaba River watershed.

In the computational simulations, the nitrogen compound concentrations presented in Table 1 were assumed for the simulated upstream boundary condition, reproducing the quality conditions observed by Mourão Júnior (2010) when conducting Piracicaba River lower stretch water-quality monitoring studies.

Table 1. Nitrogen concentrations in the Piracicaba River upstream boundary condition.

Organic Nitrogen ($mg.L^{-1}$)	Ammoniacal Nitrogen ($mg.L^{-1}$)	Nitrite ($mg.L^{-1}$)	Nitrate($mg.L^{-1}$)
0.00	0.00	1.0	1.0

In the different simulations, raw sewage disposal was assumed at the beginning of the simulated stretch, 03 (three) km downstream the simulated river stretch. A 0.175 m^3s^{-1} flow rate was assumed for this disposal, corresponding to Coronel Fabriciano city average sewage production, considering a water per capita consumption 180 $L.hab^{-1}.day^{-1}$ and return coefficient 80%. Diffuse inputs were not considered in the simulations. The assumed per capita water consumption corresponds to the center of the values range suggested by Von Sperling (2006) for medium-sized cities (cities presenting population between 50,000 and 250,000 inhabitants). The return coefficient, in turn, was established based on those indicated by NBR 9649/1986 Brazilian Standard.

For the domestic sewage load point, values corresponding to the upper limits of the parameters variation ranges suggested by Von Sperling (2006) were considered. Thus, the raw sewage discharge organic and ammoniacal nitrogen concentrations considered in the simulations were 30 and 40 $mg.L^{-1}$, respectively. Raw sewage nitrite and nitrate concentrations were considered null in all simulations.

3.2. Mathematical Modeling of the Nitrogen Cycle

The equations utilized to represent the watercourse nitrogen cycle transformations

reproduced those assumed by Von Sperling (2007) during QUAL-UFMG model development.

Equation 1 was used to estimate organic nitrogen variation in the watercourse by means of transformation into ammoniacal nitrogen by ammonification process and organic nitrogen loss by sedimentation.

$$\frac{dNorg}{dt} = -K_{oa}.N_{org} - K_{sed}.N_{org} \quad (1)$$

Where:

- N_{org}: Organic nitrogen concentration (mg-N.L^{-1});
- K_{oa}: Organic nitrogen to ammonia conversion coefficient (per day);
- K_{sed}: Organic nitrogen removal by sedimentation coefficient (per day).

Ammoniacal nitrogen accumulation occurs through organic nitrogen transformation and eventual introduction by the bottom sediment. The transformation of ammoniacal nitrogen into nitrite by nitrification causes loss of a portion of this accumulation, thus closing the mass ammonia compounds Equation 2.

$$\frac{dNamom}{dt} = K_{oa}.N_{org} - K_{an}.N_{amon} + \frac{SN_{amon}}{H} \quad (2)$$

Where:

- N_{amon}: Ammonia concentration (mg-N.L^{-1});
- K_{an}: Ammonia to nitrite conversion coefficient (per day);
- SN_{amon}: Coefficient of ammonia release from the bottom sediment ($gO_2.m^{-2}.day^{-1}$);
- H: watercourse depth (m).

Nitrite concentration variation in the watercourse was simulated by using Equation 3. This equation represents the formation of nitrite from ammoniacal nitrogen and nitrite decay for nitrate formation. Nitrite accumulation is an intermediate phase between ammoniacal nitrogen and nitrate.

$$\frac{dNnitri}{dt} = K_{an}.N_{amon} - K_{nn}.N_{nitri} \quad (3)$$

Where:

- N_{nitri}: Nitrite Concentration of (mg-N.L-1);
- K_{nn}: Nitrite to nitrate conversion coefficient (per day).

Nitrate accumulation was simulated as a function of nitrite transformation, through nitration, according to Equation 4.

$$\frac{dN_{nitra}}{dt} = K_{nn}.N_{nitri} \quad (4)$$

In Equation 4 N_{nitra} represents the nitrate concentration (mg-N.L^{-1}). Total nitrogen accumulation (N_{total} in mg-N.L^{-1}) was obtained by a simple sum of the different nitrogen compounds, as indicated by Equation 5. The total nitrogen concentration in the watercourse will be constant whenever the denitrification process is not considered, the approach assumed in the present study.

$$N_{total} = N_{org} + N_{amon} + N_{Nitri} + N_{nitra} \quad (5)$$

The different equations related to nitrogen cycle description were numerically solved with the aid of the Euler method (Campos Filho, 2001), in the Microsoft Excel spreadsheet computational environment. Hydraulically, it was assumed that the watercourse could be represented as a sequence of full-mix reactors in series, reproducing QUAL-UFMG model functional and computational structures.

3.3. Kinetic constants

The values of the kinetic constants that regulate the nitrogen cycle used in this research were obtained from Mourão Júnior (2010), a study that calibrated and applied the QUAL-UFMG model for the Piracicaba River water quality simulations. The values of cited kinetic constants are presented in Table 2.

Table2. Kinetic constants used in computational simulations.

K_{so} (per day)	K_{oa} (per day)	K_{an} (per day)	K_{nn} (per day)
0.05	0.20	0.20	0.75

Note: Ksed - Organic nitrogen removal by sedimentation coefficient; Koa - Organic nitrogen to ammonia conversion coefficient; Kan - Ammonia to nitrite conversion coefficient; Knn - Nitrite to nitrate conversion coefficient.

3.4. Monte Carlo Method

The Monte Carlo Method was applied for uncertainty analysis of the different variables and coefficients associated with mathematical simulation of nitrogen-compound transformations in the Piracicaba River. The method application involved many simulations, generating, for each simulation, different water quality model input variables and kinetic coefficients values.

The random numbers needed for the Monte Carlo Method application were generated by using the Microsoft Excel Random Number Generation tool, assuming Normal Probability Distribution. Input data and kinetic coefficients random generation was carried out by using Equation 6.

$$\text{Value} = \text{Average.}\,(1 + \text{Random.}\,\eta) \quad (6)$$

Where:

- Value: new value for the input data or model coefficient, to be used in each new simulation;
- Random: random number generated according to the Normal distribution;
- η: variation percentage.

For the random generation of kinetic constants (variables presenting greater uncertainties), a 20% variation percentage was assumed. As indicated by Silva (2007), the adoption of a 20% perturbation represents more adequately all model parameters and input data coefficient variations. For other input data (river and effluent nitrogen compounds concentrations, river and effluent flows and river velocity) generations, a 5% variation percentage was considered, as suggested by Von Sperling (2007).

From Normal Distribution application, 1,000 (thousand) concentration profiles were generated for the different nitrogen compounds. From the concentration profiles, box-plot graphs were used to indicate the median and extreme values of nitrogen compounds for three different river sections located downstream of the final effluent disposal (Sections 3 km, 15 km

and 30 km downstream the discharge point). Additionally, the frequency distributions of organic nitrogen, total ammonia, nitrite and nitrate maximum concentrations were established. The maximum concentration frequency diagrams of the Nitrogen compounds were established considering eight (8) class intervals, defined from the highest and lowest maximum concentrations values. In those situations where class intervals would require the adoption of concentrations less than 0.01 $mg.L^{-1}$, frequency diagrams were constructed with less class intervals.

Additional simulations were carried out to evaluate the kinetic constant random generation influence on nitrogen compound concentration variations. Thus, in addition to the 20% variation percentage, 10%, 50% and 90% percentages were assumed in K_{so}, K_{oa}, K_{an} and K_{nn} coefficients of random generations. To evaluate the effects of each assumed value for the variation percentage, one thousand (1000) simulations were performed per coefficient, forming twelve thousand (12,000) additional simulations.

Also at this stage of the research, frequency distributions were established for organic nitrogen, total ammonia, nitrite and nitrate maximum concentrations, for each group of simulations.

The maximum concentration values, summarized by the frequency histograms, were compared with the environmental quality standards established for ammonia nitrogen, nitrite and nitrate by Resolution No. 357, issued on March 18, 2005 by the Brazilian National Environmental Council (CONAMA, 2005).

4. RESULTS AND DISCUSSION

4.1. Maximum Concentrations of Nitrogen Compounds

Figure 2 presents box-plot graphs that indicate organic nitrogen, ammonia nitrogen, nitrite and nitrate median and extreme concentrations for the set of one thousand (1,000) simulations, for the three fluviometric sections (3km, 15 km and 30 km downstream of the final effluent disposal point) where the transformations were most evident. In these simulations, a 20% variation percentage was assumed for kinetic constant random generation and a 5% variation percentage for the other input data generations. Figure 3, in turn, presents nitrogen compound maximum concentration frequency distributions for the same set of simulations.

From a simple inspection of Figures 2 and 3, the following observations are relevant:

- Considering the use of kinetic constants that regulate the decay of organic nitrogen to ammonia (K_{oa}) and ammonia to nitrite (K_{an}) presented in Table 2 (Koa = Kan = 0.20 per day), the maximum ammoniacal nitrogen concentrations occurred invariably in the river-effluent mixture section (located 3 km downstream of the simulated stretch). However, whenever kinetic constant random generation led to K_{oa} values greater than K_{an}, (organic nitrogen decaying faster to ammonia than ammonia to nitrite), the maximum ammonia nitrogen concentrations were estimated for sections located downstream of the mixing point;
- Since the nitrite to nitrate decay coefficient average value (K_{nn} = 0.75 per day, as in Table 2) is substantially higher than the average value of the coefficient regulating the conversion of ammonia to nitrite (K_{an} = 0.20 per day), the nitrite concentrations are substantially lower than other nitrogen compounds concentrations for all carried out computational simulations. In the simulations where the coefficients were generated randomly, although variations were allowed in the coefficients' average values surroundings, K_{nn} values remained invariably greater than K_{an}. According to the graph that describes the nitrite variation (Figure 2C), the maximum values and these maximum occurrence sections were variable along the simulated stretch, depending exclusively on the relative values between K_{an} and K_{nn};
- Since the denitrification process was not considered in the simulations, nitrate concentrations invariably increased along the river stretch subject to water quality simulations. However, in those simulations where kinetic constants were generated randomly, favoring

intermediate nitrogen compound forms accumulation, the nitrification process was not carried out in the simulated section;

● The frequency histogram associated with organic nitrogen (Figure 3A) shows that the estimated maximum concentrations for this constituent in the analyzed watercourse ranged from 0.16 mg.L^{-1} to 0.27 mg.L^{-1}. In addition, it is relevant to note that approximately 42% of the maximum organic nitrogen values were in the range from 0.20 mg.L^{-1} to 0.22 mg.L^{-1} and the probability that the organic nitrogen maximum concentrations are less than 0.19 mg.L^{-1} or greater than 0.25 mg.L^{-1} did not exceed 13%;

● Maximum ammoniacal nitrogen concentrations, according to Figure 3B, presented a 78% probability of being between 0.26 mg.L^{-1} and 0.32 mg.L^{-1}, with approximately 30% of the maximum concentrations in the range 0.28 mg.L^{-1} to 0.30 mg.L^{-1}. The frequency of ammoniacal nitrogen maximum concentrations below 0.26 mg.L^{-1} was around 8%. In only 138 simulations (13.8%) the ammonia maximum concentrations exceeded 0.32 mg.L^{-1};

● In approximately half of the performed simulations (48.9%), the maximum nitrite concentrations were in the range from 0.05 mg.L^{-1} to 0.07 mg.L^{-1}. The frequency that the maximum concentrations were above 0.11 mg.L^{-1} or below 0.04 mg.L^{-1} did not exceed 5%;

● In more than four hundred simulations, the maximum nitrate concentrations were in the range from 0.45 mg.L^{-1} to 0.49 mg.L^{-}1. Maximum concentrations lower than 0.37 mg.L^{-1} occurred in only 7 (seven) simulations (0.7%). Concentrations above 0.57 mg.L^{-1} were observed only in approximately 0.3% of the simulations.

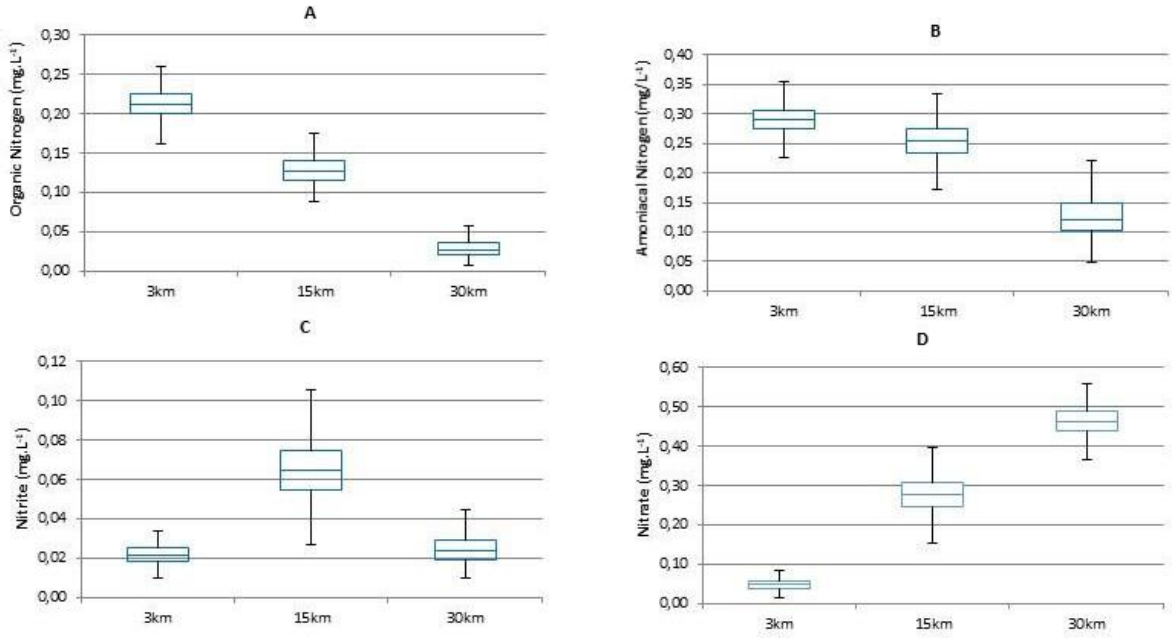

Figure 2. Organic nitrogen (A), ammoniacal nitrogen (B), nitrite (C) nitrate (D) concentration profiles for a set of computational simulations with kinetic constants, hydrodynamic variables and initial quality conditions random generation.

In the simulations, the environmental quality standards established by CONAMA Resolution 357/2005 for nitrite (1.0 mg.L^{-1}) and nitrate (10.0 mg.L^{-1}) in Class 2 rivers were not exceeded. It is relevant to note that the boundary conditions imposed null values for these nitrogen compounds in the effluent and that the percentage of variation employed for the random generation of new concentrations was 5%. The environmental quality standard set for ammonia nitrogen, dependent on watercourse pH, was also not exceeded in the water quality simulations in the present study. This standard is stricter for waters with higher pH values, ranging in Class 2 between 1.0 mg.L^{-1} (for waters with pH> 8.5) and 13.3 mg.L^{-1} (pH <7.5). It

should be noted that the percentage of variation employed for the random generation of new ammonia nitrogen concentrations was also only 5% and that the boundary conditions assumed zero ammonia concentrations for the watercourse.

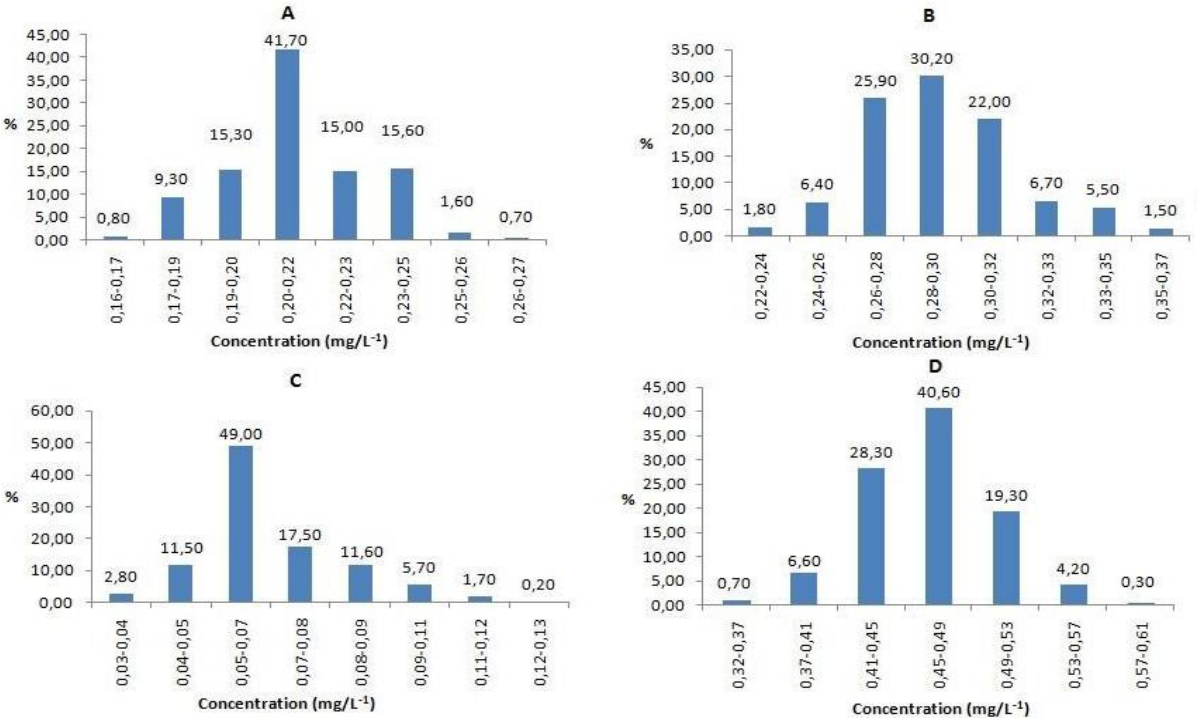

Figure 3. Organic nitrogen (A), ammoniacal nitrogen (B), nitrite (C) and nitrate (D) compounds maximum concentrations frequency distributions - Kinetic constants random generations for a 20% variation percentage and, for the other input variables, 5% variation percentage.

4.2. Extreme Values of Kinetic Constants

The maximum extreme values concentrations for the different nitrogen compounds, considering K_{so}, K_{oa}, K_{an} and K_{nn} coefficient random generations for different variation percentages are presented in Tables 3, 4, 5 and 6.

Table 3. Nitrogen compound maximum concentration extreme values ($mg.L^{-1}$) considering generated K_{so} values for different variation percentages.

Parameter	Extreme Value	Variation percentages (%)			
		10	20	50	90
Organic Nitrogen	Minimum	0.16	0.16	0.16	0.16
	Maximum	0.27	0.27	0.27	0.27
Ammoniacal Nitrogen	Minimum	0.22	0.22	0.22	0.22
	Maximum	0.37	0.37	0.37	0.37

Table 4. Nitrogen compound maximum concentration extreme values ($mg.L^{-1}$) considering generated K_{oa} values generated, for different variation percentages.

Parameter	Extreme Value	Variation percentages (%)			
		10	20	50	90
Organic Nitrogen	Minimum	0.16	0.16	0.16	0.15
	Maximum	0.27	0.27	0.27	0.28
Ammoniacal Nitrogen	Minimum	0.22	0.22	0.22	0.22
	Maximum	0.37	0.37	0.38	0.41

Table 5. Nitrogen compound maximum concentration extreme values ($mg.L^{-1}$) considering generated K_{an} values, for different variation percentages.

Parameter	Extreme Value	Variation percentages (%)			
		10	20	50	90
Organic Nitrogen	Minimum	0.23	0.22	0.22	0.22
	Maximum	0.39	0.37	0.54	0.55
Ammoniacal Nitrogen	Minimum	0.03	0.03	0.00	0.00
	Maximum	0.15	0.13	0.14	0.17

Table 6. Nitrogen compound maximum concentration extreme values ($mg.L^{-1}$) considering generated K_{nn} values, for different variation percentages.

Parameter	Extreme Value	Variation percentages (%)			
		10	20	50	90
Organic Nitrogen	Minimum	0.03	0.03	0.02	0.02
	Maximum	0.10	0.13	0.54	0.59
Ammoniacal Nitrogen	Minimum	0.32	0.31	0.00	0.00
	Maximum	0.61	0.61	0.61	0.87

Figure 4 shows maximum frequency distributions for ammoniacal nitrogen and nitrite concentrations associated with the random generations related to the coefficient K_{an}. Similar graphs were produced for the different nitrogen compounds through the random generations associated with the other kinetic coefficients (K_{so}, K_{oa} and K_{nn}).

Simple inspection of Tables 3 to 6 and Figure 4 (and similar tables and figures produced for the other kinetic coefficients), shows that the following considerations are relevant:

- The coefficient K_{so} is substantially lower (order of magnitude one) than the other coefficients that regulate the transformations associated to the nitrogen cycle.

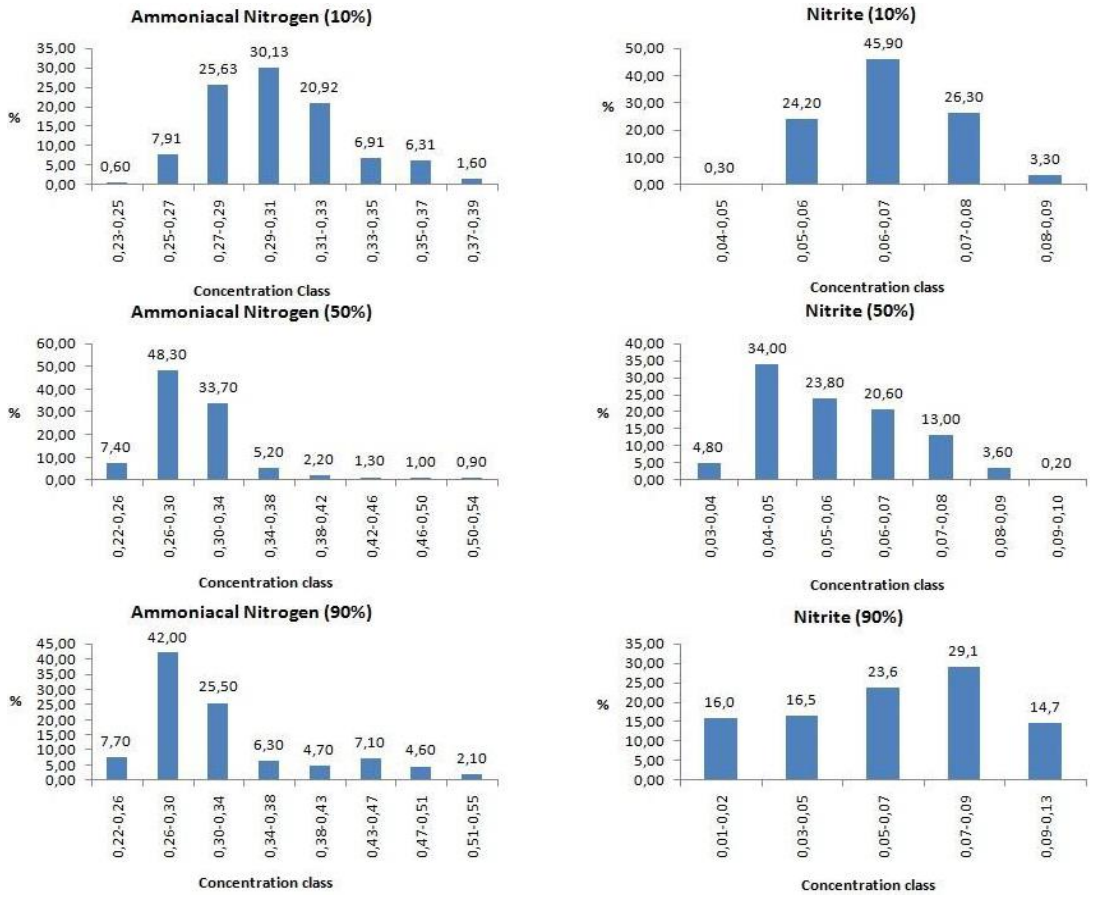

Figure 4. Maximum ammoniacal nitrogen and nitrite concentration frequency distributions - results associated with random generations relative to the coefficient $K_{an.}$

This aspect conforms to the fact that the variations resulting from organic nitrogen removal by sedimentation were considerably smaller than the variations associated with organic nitrogen to ammoniacal nitrogen conversion;

- The results showed that changes in the variation percentage due to the small influence of K_{so} on organic nitrogen concentrations did not significantly influence either the nitrogen compound concentration extreme values, the form of the maximum concentration frequency diagram, or the maximum concentration occurrence probability in the different concentration classes. Regardless of the permissible fluctuation of the K_{so} values around their mean value, the maximum organic nitrogen concentrations occurred predominantly between 0.20 $mg.L^{-1}$ and 0.22 $mg.L^{-1}$. The ammoniacal nitrogen extreme values varied between 0.16 $mg.L^{-1}$ and 0.27 $mg.L^{-1}$.
- Simulation results associated with random generation of the coefficient values that represent the organic nitrogen to ammonia transformations (K_{oa}) indicated that changes in the variation percentages between 10% and 50% did not modify organic nitrogen and ammoniacal nitrogen maximum concentrations extreme values.
- The maximum organic nitrogen concentrations varied from 0.16 $mg.L^{-1}$ to 0.27 $mg.L^{-1}$ for variation percentages between 10% and 50%. The maximum ammoniacal nitrogen concentrations, in turn, varied between 0.22 $mg.L^{-1}$ and 0.38 $mg.L^{-1}$.
- The adoption of the variation percentage 90% for K_{oa} coefficients values random generation produced relevant modifications in maximum ammoniacal nitrogen concentration profiles and frequency diagrams. Maximum ammoniacal nitrogen concentrations varied between 0.29 $mg.L^{-1}$ and 0.32 $mg.L^{-1}$, a range that concentrated approximately 37% of the maximum ammonia concentration values;

- Frequency histograms associated with K_{an} coefficient random generation showed that ammoniacal nitrogen maximum concentrations varied from 0.23 mg.L^{-1} to 0.39 mg.L^{-1} when variation percentage 10% was adopted. Considering more than 400 (four hundred) simulation results, for K_{an} values random generation, ammoniacal nitrogen maximum concentrations varied from 0.26 mg.L^{-1} to 0.30 mg .L^{-1}, for variation percentages 50% and 90%;
- Adoption of a 10% variation percentage for K_{nn} coefficient values random generation produced maximum nitrite concentrations ranging from 0.03 mg.L^{-1} to 0.10 mg.L^{-1}, with approximately 80% (79.2%) of the maximum concentrations concentrated in the range 0.05 mg.L^{-1} to 0.08 mg.L^{-1}. The adoption of 50% or 90% variation percentages caused deformation in frequency histograms, since it produced substantially higher maximum nitrite concentrations. The use of a 50% variation percentage produced maximum nitrite concentration 0.54 mg.L^{-1}. The adoption of 90%, in turn, produced a maximum concentration 0.59 mg.L^{-1}.
- K_{nn} coefficient values random generations produced an inverse effect to that produced on nitrite and nitrate concentrations. The adoption of a 10% variation percentage produced maximum nitrate concentrations in the range 0.32 mg.L^{-1} to 0.61 mg.L^{-1}, with approximately 67% of the maximum concentrations in the range 0.43 mg. L^{-1} to 0.50 mg.L^{-1}. However, the adoption of 50% and 90% variation percentages established the possibility of nitrite accumulation without eventual nitrate generation. Considering a 50% variation percentage, for 31 of the 1,000 simulations, the maximum nitrate concentrations were in the range between zero and 0.07 mg.L^{-1}. The 90% variation percentage produced, for 143 of the 1,000 simulations, maximum concentrations between zero and 0.11 mg.L^{-1}.

5. CONCLUSIONS

The simulation of the spatial variation of nitrogen compounds, with the incorporation of uncertainty analysis, allowed the indication of concentration ranges in which organic nitrogen, ammoniacal nitrogen, nitrite and nitrate maximum concentrations most likely could be. Kinetic constants random generation with 20% variation percentage and hydrodynamic and water quality variables with 5% variation percentage produced, for the study area, maximum concentrations that were most frequently between 0.20 mg.L^{-1} and 0.22 mg.L^{-1} (42%)for organic nitrogen,between 0.28 mg.L^{-1} and 0.30 mg.L^{-1} (30%) for ammoniacal nitrogen, between 0.05 mg.L^{-1} and 0.07 mg.L^{-1} (49%) for nitrite and from 0.46 mg.L^{-1} to 0.50 mg.L^{-1} (37%) for nitrate.

Estimated maximum concentrations for ammonia nitrogen, nitrite and nitrate did not exceed the environmental quality standards established by CONAMA Resolution 357/2005 for Class 2 watercourses.

The adoption of different variation percentages in the random generations of kinetic constants that regulate organic nitrogen decay did not influence significantly the organic nitrogen and ammoniacal nitrogen maximum concentrations extreme values.The adoption of higher variation percentage values (50% and 90%) for the random generation of the kinetic constants that regulate the ammoniacal nitrogen and nitrite decay caused significant changes in the maximum ammoniacal nitrogen, nitrite and nitrate concentration values and frequency histogram forms. In some simulations, production of the most oxidized forms of nitrogen was not observed.

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