

Estimation of Rate Constants for Nutrient Transformations



Najamussahar H Mulla, J Mohammed Nayaz Baig, B. M. Krishna, B. Manoj Kumar, Mudassira Tahneet B. Lahori

Abstract: Non-point source pollution of surface water is a major impediment to meet water quality objectives. Managing such pollution sources in a sustainable way is a key success factor in maintaining high water quality and to prevent eutrophication. Mathematical models are widely used to simulate ecological and water quality interactions in surface waters. Simulation errors may arise due to uncertainties of the structure, input data and the model parameters. In this study, an attempt has been made to estimate the rate constants for nutrient transformations in Kabini River located in Southern part of Karnataka state in India. The experimental results demonstrated both ammonia and nitrite oxidation. In the river water, DO concentration was 5.2 mg/L. After addition of pollutants it reduced to 3.9 mg/L. EC changed from 370 to 550 $\mu\text{S/cm}$. pH remained almost the same. At 32°C, the rate constants for phosphate, nitrate, nitrite, potassium and ammonia were found to be 0.165, 0.21, 0.077, 0.0777 and 0.078/hr respectively. The results obtained clearly specify that the rate constants are concentration and temperature dependent.

Index Terms: Nutrient Transformations, Rate Constants, Surface Water, Water Quality Modelling.

I. INTRODUCTION

Non-point source pollution of surface water is a major impediment to meet water quality objectives. Managing such pollution sources in a sustainable way is a key success factor in maintaining high water quality and to prevent eutrophication. The phenomenon of over fertilization of lakes, streams and estuaries is generally referred to as eutrophication. The first step in this process involves the inorganic nutrients. Inorganic nutrients such as phosphorus, nitrogen are the essential elements which provide chemical

building blocks for life in aquatic systems. Agricultural and urban runoff, sediments from improperly managed construction sites, crop and forest lands and atmospheric deposition and hydro modification are some typical nonpoint sources to aquatic ecosystem [1], [2].

Nutrients are present in dissolved organic, dissolved inorganic, particulate organic, sediment and in biotic forms. Each of these undergo continuous recycling as shown in Figure 1 [3].

The problems associated with eutrophication include; overgrowth of floating plants which decrease the water clarity and formation of unsightly scums. Overgrowth of rooted plants can hinder navigation and recreation activities. Plant growth and respiration can impact pH balance of such water system. Decomposition of nuisance plants cause fish kills due to oxygen shortage. Certain algal blooms cause taste and odor problems in drinking water, and form tri-halo methane during water chlorination process in water treatment plants. Further, certain blooms can kill livestock and may pose a serious health hazard to humans. It can cause anoxia of the bottom waters of thermally stratified systems. It can act as a major factor in the loss of aquatic biodiversity [1], [2].

The United States Environmental Protection Agency (USEPA) reported that the routine agricultural activities are responsible for more than 60 percent of surface water pollution. In India high consumption of nitrogen containing chemical fertilizers and the resulting 30-50 percent losses of nitrogen has also been reported to contaminate surface and ground water systems [4], [5].

In order to understand and resolve the problems caused by nonpoint source pollution, and to evaluate the effectiveness of various control measures suitable water quantity-quality models can be used [6].

Mathematical models are widely used to simulate ecological and water quality interactions in surface water over the past few decades. Simulation techniques can offer an integrated and sound course for evaluating wasteload abatement alternatives if the physical mechanisms involved are represented accurately. Furthermore, even if the model successfully describes the physical mechanisms, poor results may be obtained because of insufficient data available to estimate rate constants and coefficients [3].

Models are generally based on region specific values for rate constants which limit their applicability to other regions. They can however be applied to other regions by incorporating several statistical tools for calibration, validation, sensitivity and uncertainty analysis. Simulation errors arise due to uncertainties of the structure, input data and the model parameters [7].

Manuscript published on 30 September 2019

* Correspondence Author

Najamussahar H Mulla*, Ph.D. Scholar, Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka, India. Email: sahasrabeer1413@gmail.com

J Mohammed Nayaz Baig, M.Tech. Scholar, Department of Health Science and Water Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka, India. Email: ziya.nay@gmail.com

Dr. B. M. Krishna, Associate Professor, Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka, India. Email: bmkrishna_71@yahoo.com

Dr. B. Manoj Kumar, Professor, Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka, India. Email: bmanoj@sjce.ac.in

Mudassira Tahneet B. Lahori, Software Developer, REOTRIX Technologies, Pune, Maharashtra, India. mudassiratahneet@gmail.com

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an [open access](https://creativecommons.org/licenses/by-nc-nd/4.0/) article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

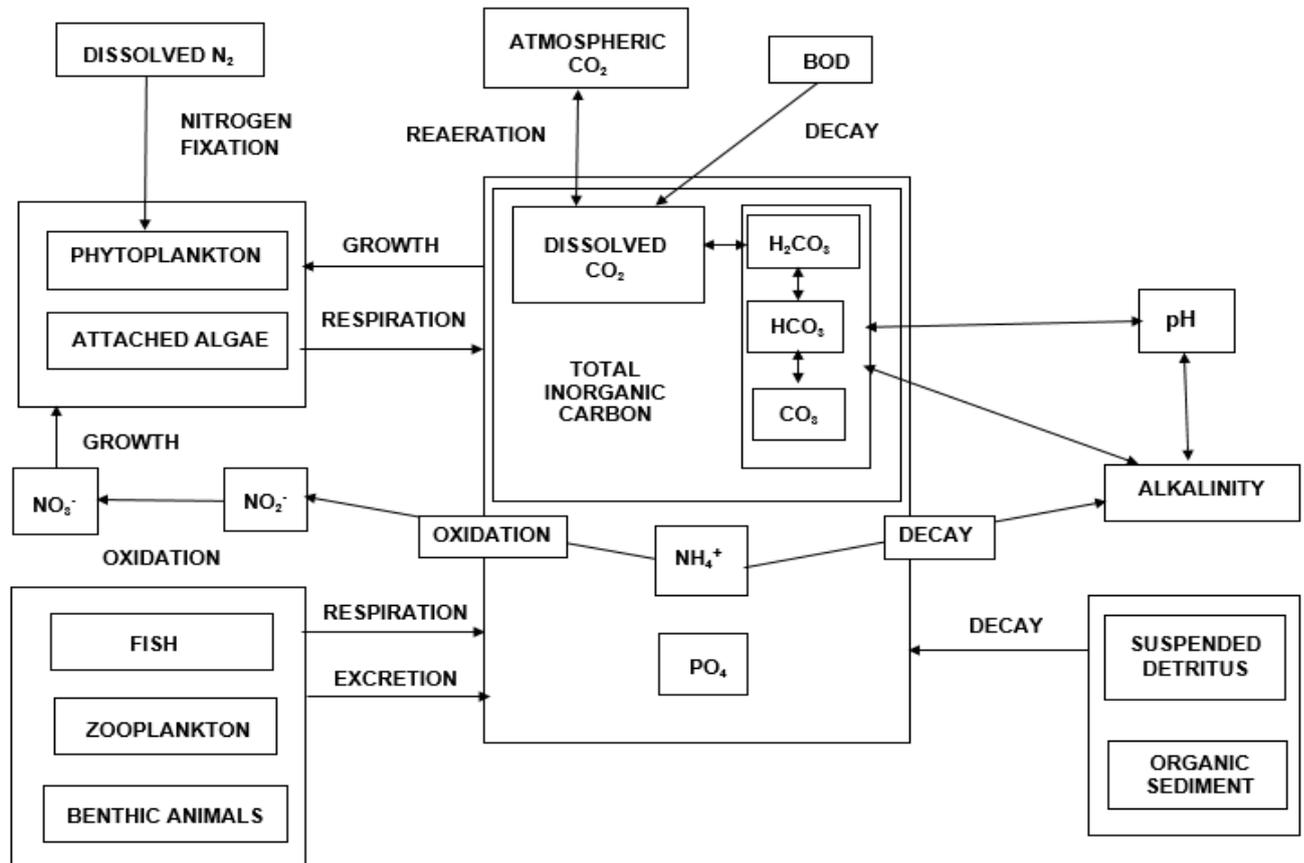


Fig. 1. Carbon, Nitrogen and Phosphorus transformations (Source: G. L. Bowie, et al.)

Each rate constant used in a model should not be considered as an “afterthought”, but should be considered as an integral part of the modeling process. In this study, an attempt has been made to estimate the rate constants for nutrient transformations in Kabini River located in Southern part of Karnataka state in India.

To apply a model in predictive form, the scientific and technical literature can provide necessary information to choose or estimate the proper coefficients [8]. Temperature is one of the most important physical characteristics of surface waters and a crucial factor in water quality modelling. It affects the solubility of gases and solids. All nutrient transformation rates are temperature dependent. Almost all models use the exponential Van’t Hoff Arrhenius relationship to describe these effects. At a reference temperature of 20°C, the resulting equation is:

$$K_T = K_{20} * \Theta^{(T-20)} \quad (1)$$

Where, K_T = rate coefficient at temperature T, 1/time, K_{20} = rate coefficient at 20°C, 1/time, T = temperature, °C and Θ = temperature adjustment coefficient [3].

This expression depends on an empirical dimensionless factor Θ , specific for each reaction considered. A few models use different temperature adjustment formulations. For example, logistic equation.

Table I presents rate coefficients for nutrient transformations along with the corresponding temperature adjustment factors [3, 8].

Table- I: Rate coefficients for nutrient transformations

Sl.No.	Description	* K_T		Θ
		Min	Max	
1	Transformation rate of organic nitrogen into ammonia	0.02	0.4	1.047
2	Transformation rate of ammonia into nitrate	0.1	1.0	1.083
3	Transformation rate of ammonia into nitrite	0.1	0.5	1.047
4	Transformation rate of nitrite into nitrate	0.2	2.0	1.047
5	Rate of organic phosphorus decay	0.01	0.7	1.047

II. MATERIALS AND METHODS

A. Materials

The study was carried out in summer, low flow conditions. In April 2019, Surface water and bottom sediments were collected from Kabini River, Nanjangudu Taluk, Mysuru, Karnataka. Water sample was collected in a 20 L plastic can and the bottom sediment sample was collected in an air tight bag. Few parameters such as pH, temperature, DO, TDS and electrical conductivity were measured in situ using digital meters.



The initial characteristics of the river water are presented in Table II.

Table- II: Initial characteristics of the river water

Parameter	Value
Temperature (°C)	28.1
pH	8.0
Electrical Conductivity (µS/cm)	370
Total Dissolved Solids (mg/L)	178
DO (mg/L)	5.2
BOD (mg/L)	3.4
COD (mg/L)	19.2
Phosphates (mg/L)	0.873
Nitrate (mg/L)	0.21
Nitrite (mg/L)	0.015
Ammonia (µg/L)	26.0
Potassium (mg/L)	3.0

B. Experimental Setup

The experiment was conducted in a 35 L capacity round plastic tub with the dimensions of 10 x 20 inches as shown in Figure 2. It was kept in open space under the sunlight and filled with 20 L water sample. In a beaker, 5g cow dung and 200g bottom sediments were weighed and 200ml water from the tub was used to prepare the slurry. In another beaker, fertilizers in 1:1:1 ratio were weighed and dissolved in water drawn from the tub. Then, the contents of the beakers were transferred to the tub. At this point of time, a gentle stir was given using a glass rod.

The experiment was started at 11.00 in the morning and 200 ml sample was collected every hour from time zero to seven hour. Concentrations were measured every hour to develop data for time and concentration.



Fig. 2. Experimental setup

C. Experimental Methods and Analysis

Water sample was collected, transported and analyzed following standard methods (APHA, 2005). The test of physical parameters such as temperature, pH, DO and EC were measured using portable sensors. Ammonia nitrogen,

nitrite nitrogen, nitrate nitrogen and phosphate concentrations were determined by spectrophotometric method. Potassium concentration was determined by Flame Photometer.

D. Analysis of Rate Data by Integral Method

The kinetics or rate of the reaction is expressed by the law of mass action. For a single reactant, it is represented as:

$$dc/dt = -kc^n \tag{2}$$

Where, c = the concentration of the single reactant, k = rate constant and n = the order. The integral method consists of guessing n and integrating Eq. 2 to obtain a function, c (t). As all the nutrient transformations follow first- order kinetics, n = 1 is chosen. Graphical method is then employed to determine the rate constants.

III. RESULTS AND DISCUSSION

The experimental results for the samples collected from zero to seven hour are presented in Table III.

Figures 3-7 show the graphs to evaluate the rate constants of nutrient transformations.

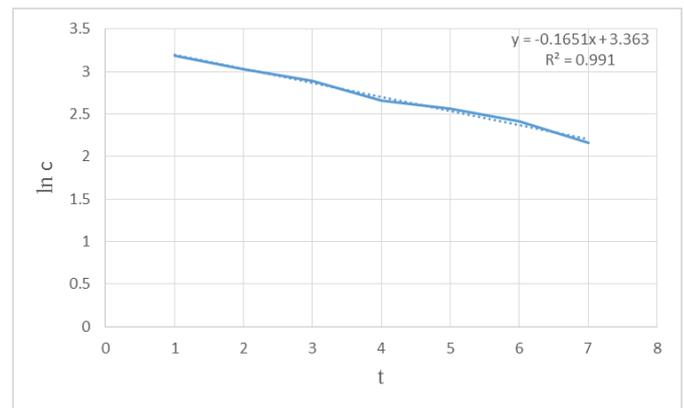


Fig. 3. Rate constant for phosphate transformation

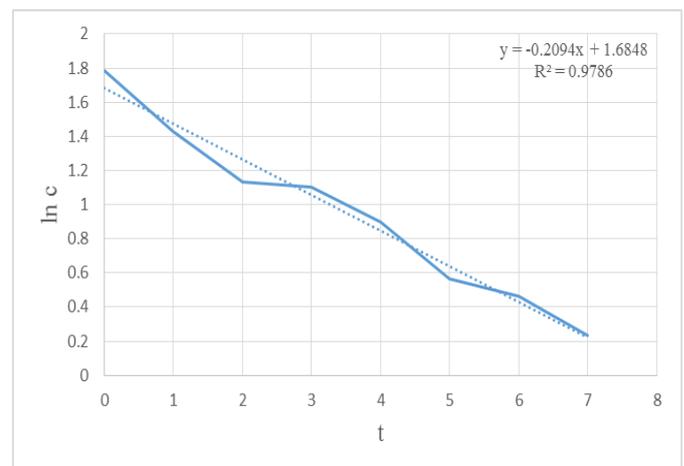


Fig. 4. Rate constant for nitrate transformation

Estimation of Rate Constants for Nutrient Transformations

t (h)	T (°C)	pH	EC (μS/cm)	TDS (mg/L)	DO (mg/L)	PO ₄ (mg/L)	Nitrate (mg/L)	Nitrite (μg/L)	Ammonia (μg/L)	Potassium (mg/L)
0	28.3	7.7	525	252	3.9	54.49	5.95	158.33	106	33.2
1	31.3	7.8	540	259	4.0	24.27	4.18	110.51	100	32.6
2	33.4	7.7	540	259	3.7	20.68	3.11	96.45	93	32
3	34.2	7.7	558	262	3.3	18.05	3.01	92.88	90	31.3
4	33.0	7.9	554	262	3.1	14.27	2.46	84.35	81	28.7
5	32.8	7.8	547	252	2.9	13.04	1.76	77.87	70	24.8
6	32.0	8.1	550	269	2.4	11.17	1.59	74.68	-	20
7	31.2	7.9	547	265	2.0	8.731	1.27	81.25	-	20

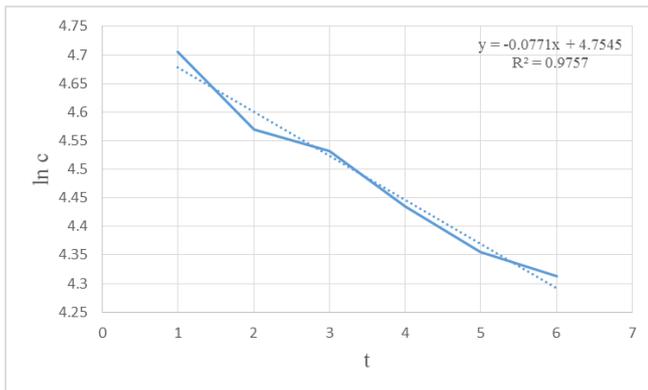


Fig. 5. Rate constant for nitrite transformation

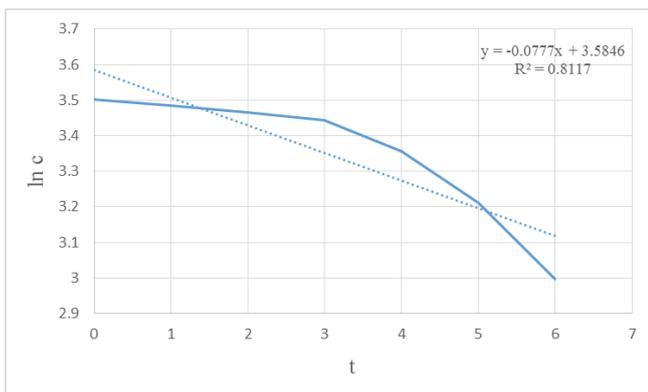


Fig. 6. Rate constant for potassium transformation

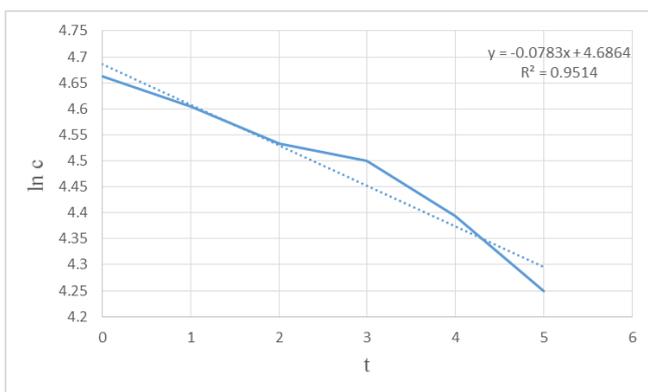


Fig. 7. Rate constant for ammonia transformation

The experimental results demonstrate both ammonia and nitrite oxidation. In the river water, DO concentration was 5.2 mg/L. After addition of pollutants it reduced to 3.9 mg/L. EC changed from 370 to 550 μS/cm. pH remained almost the same. At 32°C, the rate constants for phosphate, nitrate, nitrite, potassium and ammonia were found to be 0.16, 0.21, 0.077, 0.0777 and 0.078/hr respectively. It is comprehensive

from the results that all nutrient transformation rates found in this study fall within the decay rates reported in the literature except the nitrate transformation rate. It is clear that all the transformations request for large amount of oxygen. The amount of nitrite nitrogen increases due to the oxidation of ammonia and decreases due to its transformation into nitrate.

IV. CONCLUSION

Many researchers have determined the typical rates of water quality kinetics for various parameters in different parts of the world by using laboratory and field studies. However, typical rates of water quality kinetics are available in the developed countries, whereas not much is known about the water quality kinetics of the remaining part of the world, where the climate, environment and nature of pollution is different. Hence, the main objective of this study was to find out the rate constants for the nutrient transformations. The experimental results demonstrated both ammonia and nitrite oxidation. The results obtained clearly specify that the rate constants are concentration and temperature dependent. Values of many constants and coefficients are dependent upon the way they are used in modelling formulations. Another simple approach to perform this experiment would be to introduce some of the pollutant into a series of bottles filled with the river water.

REFERENCES

1. A. Mishra, R. Singh and V. Singh, "Evaluation of nonpoint source N and P loads in a small mixed land use land cover watershed," *Journal Water Resource and Protection*, vol. 2, 2010, pp. 362-372.
2. D. Sharma, and A. Kansal, "Assessment of river quality models: A review," *Rev Environ Sci Biotechnol*, vol. 12, 2013, pp. 285-311.
3. G. L. Bowie, et al. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling, USEPA, Georgia, 1985.
4. H. Li, J. Lee and M. Cai, "Nutrient load estimation methods for rivers," *International Journal of Sediment Research*, vol. 18, No.4, 2003, pp. 346-351.
5. M. Benedini and G. Tsakiris, *Water Quality Modelling for Rivers and Streams*, New York: Springer-Dordrecht Heidelberg, 2013.
6. S. C. Chapra, *Surface Water-Quality Modeling*, Illinois: Waveland Press, 2008.
7. S. R. Carpenter, et al. "Nonpoint pollution of surface waters with phosphorus and nitrogen," *Ecological Applications*, vol. 8, No. 3, 1998, pp. 559-568.
8. USEPA, "Guidance specifying management measures for sources of non-point pollution in coastal waters," USEPA, Washington, D.C., 1993.

AUTHORS PROFILE



Najamussahar H Mulla received her Bachelor of Engineering in Chemical Engineering from Shri Dharmasthala Manjunatheshwara College of Engineering and Technology (SDMCET), Dharwad, Karnataka. Master of Technology in Environmental Engineering from JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka. She is pursuing Ph.D. in the Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru. Her current research includes river water quality modelling.



J Mohammed Nayaz Baig received his Bachelor in Engineering in Civil Engineering from HKBK College of Engineering, Bengaluru. He is currently pursuing his Master in Technology in Health Science and Water Engineering from JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka. His areas of interest are Water and Wastewater Management and Treatment Technologies.



Dr. B. M. Krishna is an Associate Professor in the Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka. He received his Bachelor in Engineering in Civil Engineering and Master of Technology in Environmental Engineering from P.E.S. College of Engineering, University of Mysore, Mandya, Karnataka. Earned his Ph.D. from Bangalore University, Bengaluru in 2012. His primary areas of expertise include advanced water and wastewater treatment systems as well in monitoring & modelling of environmental systems.



Dr. B. Manoj Kumar is a Professor in the Department of Environmental Engineering, JSS Science and Technology University (Formerly SJCE), Mysuru, Karnataka. He received his Bachelor in Engineering in Civil Engineering and Master of Technology in Environmental Engineering from University of Mysore, Mysuru, Karnataka. Earned his Ph.D. from Centre for Environmental Science and Engineering, Indian Institute of Technology, Bombay in 2006. His primary areas of expertise include advanced water and wastewater treatment systems as well in monitoring & modelling of environmental systems.



Mudassira Tahneet B. Lahori received her Bachelor of Engineering in CSE from REVA Institute of Technology, Bengaluru (affiliated to VTU, Belagavi) and Masters of Technology in CSE from NMAMIT, Nitte (Autonomous), VTU, Belagavi. She has researched and published papers in Major Journals and Conferences. She is a member of various professional bodies and associations. She has worked as an Assistant Professor in Department of Computer Science and Engineering at Beary's Institute of Technology, Mangaluru. Currently she is working as a software developer in REOTRIX Technologies, Pune. Her research interest is Machine Learning.