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Nitrogen removal kinetics in wastewater stabilization pond systems in Greece

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ABSTRACT

This paper refers to the dynamic of nitrogen removal in wastewater stabilization ponds (WSP) in Northern Greece. Three full-scale WSP systems treating municipal wastewater and consisting of one facultative pond, one or two maturation ponds and a rock filter before the final discharge were investigated. Systems were monitored during a year. The kinetic constants of TN, N-$NH_4^{\pm}$, N-NO_3^- removal were determined. For this aim the first-order model, the second-order model, the Kadlec and Knight model, the Stratton model and the Reed model were used. The models assessment, the accuracy and reliability of the results are evaluated by comparison with existing real data. The Kadlec and Knight model give the best adjustment. The biodegradation rate constant (K_T) of TN ranges from 0.0316 to 0.0416 md^{-1}, of N-$NH_4^{\pm}$ from 0.013 to 0.0415 md^{-1} and of N-NO_3^- from 0.00265 to 0.01005 md^{-1}. The constants K_T have a strong positive correlation with the organic input load and the dissolved oxygen (DO) concentration of WSPs. The study estimates these essential design parameters pertaining to local conditions to optimize the design considerations and sizing requirements. The estimated parameters can effectively be applied in sizing WSPs under Mediterranean or similar climatic conditions.

Keywords: Wastewater; Stabilization ponds; Nitrogen removal rate; Kinetic; Biodegradation rate constant

1. Introduction

Stabilization ponds have been used for wastewater treatment for a number of years. The first recorded construction of a wastewater stabilization pond (WSP) system was in 1901 in San Antonio, Texas, in the USA [1]. Nowadays, a large number of these systems are used worldwide for the treatment of municipal and industrial wastewater, under a wide range of weather conditions ranging from the tropics to the Arctic [2,3]. The main reasons for their popularity are the construction simplicity, the low cost and the low energy requirements [4]. However, although in many countries WSPs are a particularly popular treatment method, in Greece there are only a few active WSP systems, representing only 8% of municipal wastewater treatment plants in the country. These systems serve from 500 to 4,000 equivalent populations (e.p.) in rural areas exclusively [5]. Moreover, the research and the information about the WSPs operation in Greece are limited. Thereby, in this research, it was chosen to investigate three WSP systems in Northern Greece, treating municipal wastewater with the aim of estimating the reaction rate constants of specific pollutants TN, N-$NH_4^{\pm}$ and N-NO_3^- removal mechanisms.

The BOD and TSS removal WSPs capacity is fairly well documented and quite reliable. However, less attention has been given on the ability of nitrogen removal via WSPs and its impact on the system design, although there are worldwide a large number of literature studies for the conversion of nitrogen and its removal from aqueous systems and soil [6–12]. The different environmental and ecological conditions in the various ecosystems have the effect of different nitrogen conversion rates. Regarding the kinetics of nitrogen removal, there are a few reports in the literature. Most of them concern lab-scale researches about ANAMMOX systems [13–19]. Gholizadeh et al. in 2015 [20] give information about the nitrogen removal kinetics of a full-scale

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constructed wetlands system treating municipal wastewater in Iran. Concerning this issue, there is a lack of information about the WSP systems. One of the objective of this research was the determination of nitrate removal rates in facultative and maturation WSPs under Greek climate conditions and wastewater composition, since the nitrate removal is directly related to factors such as the temperature, pH, DO and the organic load [1,21]. Another objective was to determine the suitability and usefulness of different models, either available from the literature or newly developed. The models were compared by using statistic efficiency criteria, by which the lack of fit of the models was compared.

2. Materials and methods

2.1. Study area

All the three systems are situated in a lowland area in mainland of northern Greece in latitude ϕ: 41° up to 41°15′ N, longitude λ: 23°21′ up to 23°36′E and altitude from 14 to 52 m, in a Mediterranean climate. They treat only domestic wastewater and consist of one facultative pond, one (N. Skopos) or two (Vamvakofito, Charopo) maturation ponds and a limestone rock filter before the final discharge for algae filtration. The wastewater discharge becomes through an open channel of 0.75 m^2 vertical section. Every system has a different total hydraulic retention time (HRT). Skopos' HRT is 18.6 d, for Vamvakofito is 68.7 d and for Charopo 72.4 d.

The inflow is considered constant for each WSPs system and equal to the outflow. Each WSPs system has different design and functional features (Table 1).

2.2. Data

To determine the input and the output TN, $N\text{-}NH_4^{\pm}$, $N\text{-}NO_3^-$ loads for each system, instantaneous samples were taken from the inflow of the 1st pond and the outflow of the last pond, from October 2006 to September 2007, twice a month, at least [22]. During the months with the highest and lowest temperature, the sampling was done with a weekly frequency. The samples were collected approximately at the same morning period, while meteorological data were recorded. The samples were placed into 1,000 mL polyethylene bottles, and were transferred immediately to the wastewater laboratory of Serres City [23]. To enhance the range and accuracy of data, each of the samples was analyzed separately twice, with methods proposed by Simplified Laboratory Procedures for Wastewater Examination [24] and the averages were considered. The measurement of total nitrogen TN was done by a photometer UV-VIS, the $N\text{-}NH_4^{\pm}$ was measured by the volumetric turbidimetric method and $N\text{-}NO_3^-$ by Brucine method with a spectrophotometer. The pH measurement was performed in the field by potentiometric method with an equipment pH/Cond340i. Daily meteorological data were obtained from the National Meteorological Service (NMS), Serres office. The climate is classified as dry to semi-humid with excess of water in winter. The mean monthly air temperatures are from 4°C up to 29°C. The average annual temperature is 15.2°C and the average annual rainfall is 37.37 mm. The winds in the area are very weak and do not exceed 6 km h^{-1}. The water temperature was recorded locally in the days of sampling. The inflow and the outflow rates were measured with handheld electromagnetic flow meter, with the assumption that the wastewater supply was constant during the day.

Table 1
WSPs design and functional features

WSPs system	Vamva-kofito	N. Skopos	Charopo
Inflow ($m^3\,d^{-1}$)	121	152	137
HRT (d)	68.7	18.6	72.4
Total surface (m^2)	6,016	2,112	7,415
Total volume (m^3)	8,311	2,827	9,921
depth (m)	F: 1.00–2.40	F: 0.75–2.40	F: 0.80–2.40
	M: 0.75–1.50	M: 0.70–1.50	M: 0.70–1.50
m^3 /e.p.	8.9	2.4	9.4
m^2 /e.p.	6.5	1.8	7.0
m^2 facultative pond's /e.p	2.65	0.67	1.77
m^2 maturation pond's /e.p.	3.86	0.67	5.23

Note: F – Facultative pond, M – Maturation pond, e.p. – equivalent population.

Table 2 presents data for BOD_5, COD, DO, TN, $N\text{-}NH_4^{\pm}$ and $N\text{-}NO_3^-$ inflow and outflow concentrations and systems' removal efficiency. The outflows, regarding nitrogen and COD concentrations, are within the limits laid down by the Greek legislation (125 mg L^{-1} and 15 mg L^{-1}, respectively). However, it is not true in the case of BOD_5; the limit is 25 mg L^{-1}.

The WSPs as open natural systems, subject to the laws of nature and are influenced by local weather conditions. Thus, their operation and performance are affected. So, the outflow data have been corrected by mass balance method, to eliminate errors from atmospheric precipitation and evapotranspiration, as many researchers believe that the mass balance is the most authoritative method to approach mechanisms and parameters that determine the performance of natural systems and the changes occurring in these [25–27]. The mass balance described by the general expression [28]; mass accumulation is equal to mass input minus the mass output ± mass generation or mass consumption. The water balance estimation described by the Eq. (1), uses the principles of conservation of mass in a closed system:

$$Q_{out} = Q_{in} + I - \text{PET} \tag{1}$$

where Q_{out} is the wastewater outflow quantity [$m^3\,d^{-1}$], Q_{in} is the wastewater inflow quantity [$m^3\,d^{-1}$], I is the water quantity which enters in the system via precipitation [$m^3\,d^{-1}$] and PET is the water quantity which is lost from the system via evapotranspiration [$m^3\,d^{-1}$].

The height of precipitation H_{rain} obtained by Hellenic Meteo Service, Bureau of Serres, and the height of evapotranspiration H_{PET} has calculated with customizing Thornthwaite method due to the small number of required data for its implementation, compared with the model of

Table 2
Systems' inflow and outflow concentrations data and systems' removal efficiency

Parameter	WSPs system	Influents (mg L^{-1}) concentration	Effluents (mg L^{-1}) concentration	Mean removal efficiency %
BOD_5	V[a]	212.51 (110–420)	68.08 (38–95.0)	64.95
	N.S	105.03 (56–204)	53.15 (33–79.0)	43.37
	Ch	155.20 (102–201)	77.80 (49–105.4)	49.66
COD	V	299.57 (132–621)	78.57 (48.0–99)	69.89
	N.S	112.00 (58–216)	59.83 (35.6–83)	40.81
	Ch	177.83 (108–245)	88.11 (52.8–121)	49.99
DO	V	1.11 (0.3–2.5)	4.01 (2.2–6.0)	
	N.S	0.74 (0.4–2.1)	3.65 (2.8–5.5)	
	Ch	0.81 (0.5–1.3)	3.72 (2.9–5.5)	
TN	V	24.7 (12.6–38.3)	2.95 (1.1–4.7)	88.13
	N.S	22.5 (20.6–24.3)	14.1 (13.9–14.3)	35.25
	Ch	23.2 (22.9–23.5)	10.3 (10.2–10.4)	54.21
$N\text{-}NH_4^{\pm}$	V	19.5 (9.7–30.0)	2.0 (0.6–3.3)	90.02
	N.S	17.7 (16.2–19.2)	10.7 (10.6–10.8)	35.57
	Ch	18.1 (17.9–18.2)	8.0 (7.9–8.1)	55.27
$N\text{-}NO_3^{-}$	V	0.4 (0.1–1.0)	0.3 (0.1–0.9)	15.53
	N.S	0.4 (0.2–0.7)	0.4 (0.2–0.6)	14.36
	Ch	0.3 (0.2–0.3)	0.2 (0.2–0.3)	19.48

[a]V – Vamvakofito, N.S – N. Skopos, Ch – Charopo.

Perman–Monteith, which is considered more reliable [29]. The Thornthwaite model, in accordance with other researchers, gives a very good estimation of the water balance for the purposes of this research [30].

Having estimated, by Thornthwaite method, the height of evapotranspiration H_{PET} and knowing the amount of H_{rain} precipitation, the change of ponds water level ΔH [cm] can be calculated. Multiplying ΔH by the surface of each system, changes in volume ΔV [m^3] are estimated. Dividing ΔV by the number of each month days, the term ΔV d^{-1} [m^3 d^{-1}] is resulting, that is, the daily change of the ponds volume for each month. The term ΔV d^{-1} is subtracted from the initial daily flow Q and thus resulting a new term Q′. Multiplying the new daily flow Q′ [m^3 d^{-1}] by the mean of the concentrations [mg L^{-1}] and by the number of days, elapsed between sampling (d), the output mass $Mass_{out}$ [kg] is estimated – with appropriate conversion of units. In the same way, the input mass system $Mass_{in}$ [kg] is estimated too. The difference $Mass_{in} - Mass_{out}$ determines the variation of mass throughout the study period.

2.3. Kinetic models

The corrected measurement fed into mathematical models in order to calculate the kinetic constants k_T. In the literature, many mathematical models listed on the kinetics of biomass change processes have been presented. The models used in this research are the most common models describing the TN, $N\text{-}NH_4^{\pm}$, $N\text{-}NO_3^{-}$ kinetic. They are (1) the first-order kinetic model, (2) the second-order kinetic model, (3) Kadlec and Knight model, (4) Straton model and (5) the Reed model.

2.3.1. First-order kinetic model

Assuming that the WSPs system has a complete mix flow and first-order kinetic, the rate of the pollutant concentration changes could be expressed as follows:

$$-\frac{dC}{dt} = \frac{QC_{in}}{V} - \frac{QC_{out}}{V} - k_1 C_{out} \quad (2)$$

Under false-steady conditions, at the rate of substrate changes, the $-\frac{dC}{dt}$ concentration is considered unimportant. Therefore, the Eq. (2) can be modified as follows [31]:

$$\frac{C_{in} - C_{out}}{\mathrm{HRT}} = k_1\, C_{out} \quad (3)$$

where C_{in} and C_{out} are the inflow and outflow pollutant concentration (mg L^{-1}), respectively, HRT of pollutant in the WSPs, k_1 the first-order constant of pollutant removal rate d^{-1}.

2.3.2. Second-order kinetic model

It is usually used to describe the kinetic of activated sludge. The general equation describing the second-order kinetic is the following [32]:

$$\frac{dC}{dt} = k_2 x \left(\frac{C_{out}}{C_{in}}\right)^2 \quad (4)$$

After the integral of Eq. (4) and then its linearization the formula [31] results:

$$\frac{C_{in}\mathrm{HRT}}{C_{in} - C_{out}} = \mathrm{HRT} + \frac{C_{in}}{k_2 x} \tag{5}$$

where x is the average concentration of biomass in the WSPs system (mg L^{-1}), and k_2 is the second-order constant of the substrate removal rate d^{-1}.

2.3.3. Kadlec and Knight model

Kadlec and Knight [32] developed a model, for wetlands, that is a combination of the basic equation of the plug flow model and the aqueous mass balance. This model is known as K-C* model. It is a reversible first-order reaction equation and includes a non-zero substrate concentration. It describes better the removal of pollutants, as they cannot be reduced to zero in wetlands or in the ponds, due to the subsequent release of pollutants from the ponds into the treated water. The non-zero background concentration represents in more realistic way the pollutants resulting from transformation processes within the sediments and from the interactions between the sediments and the wastewater. The main reason of these processes is the production of organics from the decomposition of organic materials and the endogenous autotrophic processes [33,34]. The substrate utilization rate was directly related to the specific growth rate of heterotrophic bacteria in the stabilization ponds, as also was shown by Panikov in 2000 [35] and Kayombo et al. in 2003 [36]. As the examined stabilization pond systems have characteristics similar with wetlands – no sludge removal throughout the years of operation and simultaneously a significant growth of self-sown reeds at the banks of the ponds (Fig. 1) – it was assumed that this model can be used. The K-C* model is written as in the Eq. (6) [32]:

$$k_3 = \frac{Q}{A}\mathrm{In}\left(\frac{C_{in} - C^*}{C_{out} - C^*}\right) \tag{6}$$

where k_3 is the first-order kinetic constant md^{-1} and C* is non-zero background [mg L^{-1}]. Q is the input flowrate [m^3 d^{-1}], A is the pond's surface [m^2]. The value of C^* for wetlands, according to Kadlec and Knight [32], is equal to 1.5, 0, 0 for TN, N-$NH_4^{\pm}$, N-NO_3^- respectively. In this research, the value of C^* was examined in the range of 0 to 1.5.

2.3.4. The Straton Model (1968)

It gives the first-order kinetic constant of the ammonia nitrogen removal in stabilization ponds with the Eq. (7) [37]:

$$\frac{C_{out}}{C_{in}} = e^{(-k_4 t)},\ d^{-1} \tag{7}$$

where t is the retention time [d], C_{in}, C_{out} are the WSPs inflow and outflow TN concentration [mg L^{-1}], respectively. This model is proposed by Reed et al. [38]. According to Archer and O'Brien [39] and Picot et al. [40] it approaches the real facts of ammonia nitrogen removing better. According to Archer and O'Brien [39] the nitrification-denitrification mechanism has a more important role in the ammonia nitrogen removal than the volatility of ammonia. Ammonia volatility could be regarded as the main mechanism of the ammonia nitrogen removal, when the pH values are higher than 8.5. However, in WSPs water very low ammonia evaporation rates are expected as pH was less than 8.5. Zimmo et al. [41] reported that only the 1.5% of nitrogen removal is due to ammonia volatility.

The Reed Model [42–44] is stated in nitrogen removal for plug flow's WSPs. The model is described with the Eq. (8):

$$\frac{C_{out}}{C_{in}} = e^{-k_5[t + 60.6(pH - 6.6)]} \tag{8}$$

where t is the retention time [d], C_{in}, C_{out} are the WSPs inflow and outflow TN concentration [mg L^{-1}], respectively.

2.4. Models evaluation

The evaluation of the models, the accuracy and reliability of their results, were assessed by comparing the real observed values Cout of WSPs collected data with the predicted by the models' equations values F(Cout). To evaluate model performance, efficiency criteria are defined as mathematical measures of how well the model simulation fits the available observations [44]. For each WSPs system, the "k" values were obtained after the predicted values function optimization. The predicted values were generated from the applied models.

Vamvakofito WSPs system   Charopo WSPs system

Fig. 1. General view of WSP systems where be apparent the plants growth.

The used efficiency criteria, in this study, was (1) the coefficient of determination R^2, defined as the squared value of the coefficient of correlation according to Bravais–Pearson. It provides a measure of how well observed outcomes are replicated by the model, as the proportion of total variation of outcomes explained by the model. The range of R^2 lies between 0 (no correlation) and 1.0 (the dispersion of the prediction is equal to that of observation). The fact that only the dispersion is quantified is one of the major drawbacks of R^2 if it is considered alone, it is advisable to take into account additional information which can cope with that problem. (2) The Nash-Sutclife efficiency E. The range of E lies between 1.0 (perfect fit) and $-\infty$. An efficiency of 0 ($E = 0$) indicates that the model predictions are as accurate as the mean of the observed data, whereas an efficiency less than zero ($E < 0$) occurs when the observed mean is a better predictor than the model or, in other words, when the residual variance (described by the numerator in the expression above), is larger than the data variance (described by the denominator). Essentially, the closer the model efficiency is to 1, the more accurate the model is. (3) The unitized risk or coefficient of variation CV that is defined as the ratio of the standard deviation σ to the mean μ. It shows the extent of variability in relation to the mean of the population. CV measures are often used as quality controls for quantitative laboratory assays. The closer the CV value to zero, better the fit is. The combination of the above criteria gives more information about the efficiency of used equations. For the statistical and mathematical data analysis, the Microsoft Office EXCEL 2007 was used.

3. Results and discussion

The WSPs water temperature ranged from 5°C to 30°C and the pH value from 6.76 to 8.2 (Table 3). Gerardi, in 2006 [45], reports that for pH between 7.3 and 8.0, the nitrification rate is stable and optimal pH value for nitrification ranges from 8.1 to 8.5. Bitton [46] indicates that the optimum pH value for Nitrosomonas and Nitobacter bacteria is ranging between 7.5 and 8.5. The dissolved oxygen (DO) values were higher than 2.2 mg L^{-1}, in all the three systems (Table 3). The input and output loads vary from system to system and their performance in nitrate removal too [47]. In Table 3, the qualitative characteristics of the three WSP systems are presented.

The obtained values of "k_{TN}", after the mathematical and statistical processing of the collected data, according to the described above models, are presented as following in Tables 4–6.

Taking into account all the evaluation criteria (R^2, E, CV) for the three WSP systems, the simple Kadlec and Knight model gives the best results for "k_{TN}". Each WSPs system, as an independent ecological system, operates with different nitrogen removal rate. So, for the Vamvakofyto, the k_{TN} proposed value is 0.0416 md^{-1}. For N. Skopos WSPs system, the proposed value is 0.0316 md^{-1} and for the Charopo one is 0.013 md^{-1}. The differentiation of the C^* value does not alter the k, but the value C^* equal to 0 gives better coefficient of variation CV. A good adaptation of Kadlec and Knight model shows that this model can be applied for WSPs design with C^* equal to 0. Gholizadeh et al. using the first-order kinetic

Table 4
Vamvakofito – TN biodegradation rate constant (m.r.e. 87.5%)[a]

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.888	0.6676	0.0416	–	0.034
R^2	0.229	0.136	0.720	–	0.268
E	0.672	0.581	0.975	–	0.704
CV	0.582	1.389	0.003	–	0.294

[a]m.r.e.: mean removal efficiency adjusted by water balance.

Table 5
N.Skopos – TN biodegradation rate constant $H_4^{\pm}$ (m.r.e. 33.8%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0506	0.085	0.0316	–	0.077
R^2	0.731	0.774	0.877	–	0.052
E	0.932	0.891	0.993	–	0.339
CV	0.586	0.760	0.029	–	0.559

Table 6
Charopo – TN biodegradation rate constant $H_4^{\pm}$ (m.r.e. 50.4%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0984	0.0492	0.013	–	0.012
R^2	0.226	0.016	0.472	–	0.006
E	0.885	0.772	0.986	–	0.947
CV	0.494	0.779	0.006	–	0.292

Table 3
The qualitative characteristics of the three WSP systems

WSPs	Input loads (mg L^{-1})			WSPs qualitative characteristics		
	TN	N-$NH_4^{\pm}$	N-NO_3^{-}	pH	DO mg L^{-1}	T°C
V	24.65 ± 6.20	19.45 ± 4.96	0.47 ± 0.22	7.63 ± 0.30	4.01 ± 0.91	16.4 ± 9.6
N.S.	24.47 ± 5.73	19.28 ± 4.50	0.41 ± 0.20	7.05 ± 0.32	3.65 ± 0.75	16.3 ± 9.7
Ch	23.17 ± 2.73	18.44 ± 2.39	0.42 ± 0.19	7.39 ± 0.24	3.72 ± 0.77	16.3 ± 9.7

Note: V – Vamvakofito, N.S. – N. Skopos, Ch – Charopo.

model for a full-scale constructed wetland found the value 0.138. This value cannot be proposed since the coefficient of determination R^2 was equal to –0.15. The Stover–Kincannon model gave optima results with R^2 equal to 0.859.

The k values for the $N\text{-}NH_4^{\pm}$ biodegradation rate are presented in Tables 7–9 and the k values concerning on the $N\text{-}NO_3^-$ biodegradation rate are presented in Tables 10–12.

Based on all the evaluation criteria for the three WSP systems, the Kadlec and Knight model gives the best results for $N\text{-}NH_4^{\pm}$ biodegradation rate constant too. For the Vamvakofyto system, the k proposed value for $N\text{-}NH_4^{\pm}$ is 0.045 md^{-1}. For N. Skopos WSPs system, the proposed value is 0.0314 md^{-1} and for the Charopo one is 0.013 md^{-1}. It is observed that the $N\text{-}NH_4^{\pm}$ removal rate values are similar to those of the TN removal rate in all the three systems. The biodegradation rate constant of TN and $N\text{-}NH_4^{\pm}$ of Vamvakofito and N. Skopos WSP systems are within the limits described by the literature: from 0.1095 to 0.0137 and from 0.11 to 0.027 md^{-1}, respectively [32].

The nitrate nitrogen removal rate values were much lower than those of the total nitrogen and ammoniacal nitrogen in all the three systems. The Kadlec and Knight model gives in this case also the best results based on the evaluation criteria. For the Vamvakofito WSPs system, the k value of $N\text{-}NO_3^-$ biodegradation rate is equal to 0.0027 md^{-1}. For the N. Skopos system, the corresponding k value is 0.0093 md^{-1} and for the Charopo one 0.010 md^{-1}. The plug flow Reed model gave good results too for the Vamvakofito WSPs system. The k value is for the TN biodegradation rate 0.034 d^{-1}, for the $N\text{-}NH_4^{\pm}$ is 0.038 d^{-1} and for $N\text{-}NO_3^-$ is 0.0017 d^{-1}, proving that is a plug flow system. The type of flow is also confirmed by a research of Gratziou et al., referred to the hydrodynamic characteristics of the Vamvakofyto WSPs. In the N. Skopos and Charopo WSP systems of the first-order kinetic model that refers to complete mix flow is better adapted for TN and $N\text{-}NH_4^{\pm}$ removal. The k values for N. Skopos system are 0.0506 d^{-1} και 0.0504 d^{-1}, respectively, and for the Charopo system the k value is equal 0.0984 d^{-1} both TN, $N\text{-}NH_4^{\pm}$.

Table 7
Vamvakofito- biodegradation rate constant of $N\text{-}NH_4^{\pm}$ (m.r.e. 89.5%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.9873	0.6724	0.0450	0.311	0.0381
R^2	0.196	0.0705	0.681	0.055	0.248
E	0.826	0.5408	0.970	0.430	0.669
CV	0.558	1.409	0.003	0.564	0.289

Table 8
N. Skopos – biodegradation rate constant of $N\text{-}NH_4^{\pm}$ (m.r.e. 34.1%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0504	0.0671	0.0314	0.369	0.0104
R^2	0.726	0.779	0.892	0.698	0.635
E	0.976	0.900	0.994	0.908	0.969
CV	0.567	0.724	0.027	0.557	0.381

Table 9
Charopo – biodegradation rate constant of $N\text{-}NH_4^{\pm}$ (m.r.e. 50.4%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0984	0.0392	0.013	0.062	0.0158
R^2	0.258	0.031	0.529	0.181	0.007
E	0.885	0.775	0.986	0.901	0.902
CV	0.494	0.774	0.006	0.476	0.293

Table 10
Vamvakofito- biodegradation rate constant of $N\text{-}NH_4^{\pm}$ (m.r.e.11.2%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0108	0.00004	0.00265	0.0087	0.00167
R^2	0.937	0.934	0.950	0.931	0.942
E	0.974	0.977	0.991	0.985	0.989
CV	1.114	1.582	0.032	1.151	0.893

Table 11
N. Skopos- biodegradation rate constant of $N\text{-}NO_3^-$ (m.r.e.12.5%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0108	0.0003	0.0093	0.0098	0.0035
R^2	0.984	0.987	0.997	0.984	0.993
E	0.993	0.988	0.999	0.993	0.998
CV	0.579	0.779	0.033	0.566	0.338

Table 12
Charopo – biodegradation rate constant of $N\text{-}NO_3^-$ (M.A. 13%)

Kinetic model	1st order d^{-1}	2nd order d^{-1}	Kadlec and Knight md^{-1}	Straton d^{-1}	Reed d^{-1}
k_{TN}	0.0111	0.00007	0.01005	0.0026	0.081
R^2	0.929	0.908	0.928	0.941	0.056
E	0.977	0.953	0.988	0.990	0.019
CV	0.967	1.251	0.964	0.027	0.768

It is not appropriate to compare the above values with the results of other researches mentioned in the introduction paragraph, since those researches are referred to systems with lab-scale different treatment process. Furthermore, the most of those studies did not concern municipal wastewater.

The input concentrations of TN, N-NH_4^+, N-NO_3^- and their biodegradation rates "k" have a significant correlation with a coefficient of determination R^2 higher than 0.92 (Fig. 2).

The correlation of DO concentration versus the biodegradation rates "k" of TN, N-NH_4^+, N-NO_3^- has R^2 values higher than 0.76, 0.83, 0.99, respectively (Fig. 3).

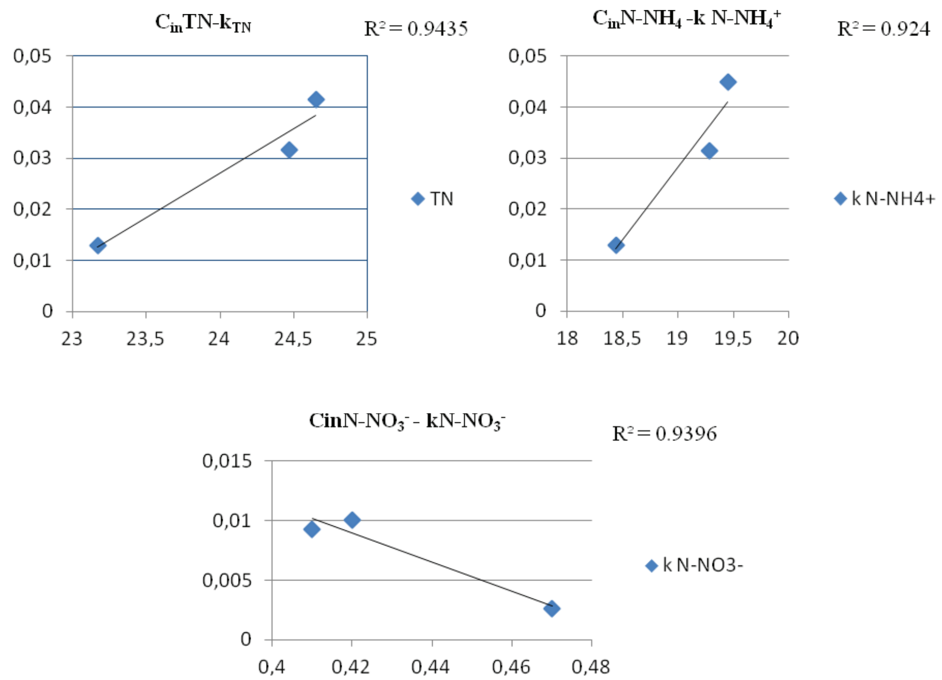

Fig. 2. Correlations of TN, N-NH_4^+, N-NO_3^- input concentrations Vs their biodegradation rates constants "k".

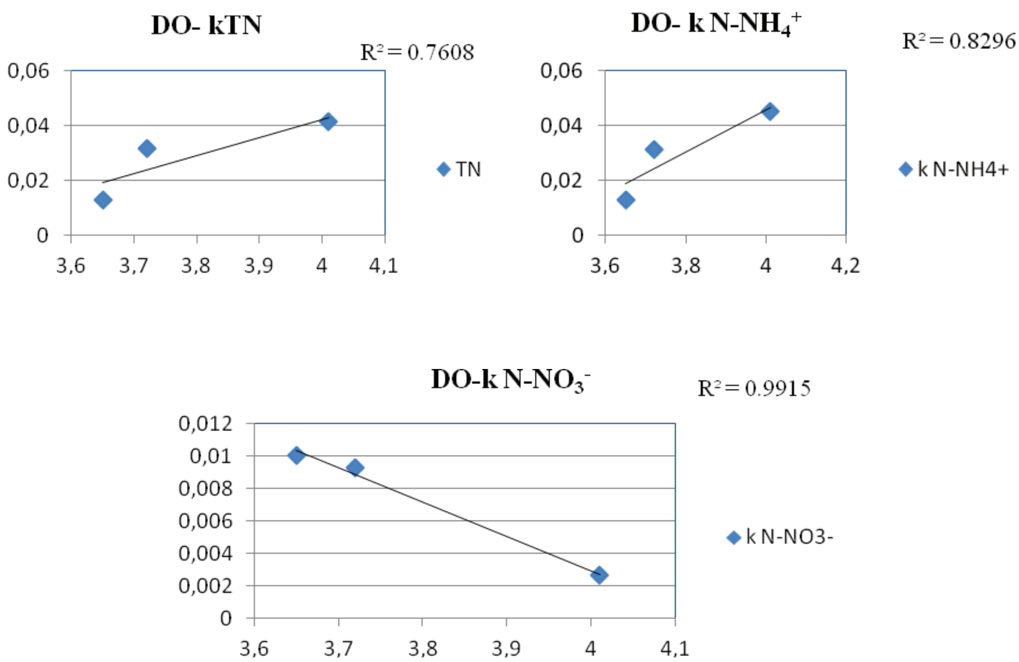

Fig. 3. Correlations of DO Vs biodegradation rates constants "k".

4. Conclusions

Even though the climatic and hydrological conditions and terms are the same, each WSP systems have different characteristics and behavior, due to multi parameter factors of their complex ecosystem.

To determine the kinetic rate of nitrogen removal by WSPs, the Kadlec and Knight model gave the best results compared with the first- and second-order kinetic models and with the models proposed by Reed and Straton. The proposed value of C^* is zero.

The biodegradation rate constants values, k_T, of the three WSPs in Northern Greece region, range for TN from 0.0316 to 0.0416 md^{-1} ($0.72 \le R^2 \le 0.877$), for N-NH$^{\pm}_4$ from 0.013 to 0.0415 md^{-1} ($0.68 \le R^2 \le 0.892$), and for N-NO$^-_3$ from 0.00265 to 0.01005 md^{-1} ($0.928 \le R^2 \le 0.997$). These values are within the limits described by the literature.

The constants k_T have a strong positive correlation with the input load concentration ($R^2 \ge 0.924$), as well as with DO system concentration, notably the N-NO$^-_3$ constant removal rate ($R^2 > 0.99$). As alternative, the prices k_T in d^{-1} for TN $k = 0.05$ d^{-1} ($R^2 > 0.73$), for N-NH$^{\pm}_4$ $k = 0.0504$ d^{-1} ($R^2 > 0.72$) and for N-NO$^-_3$ $k = 0.0035$ d^{-1} ($R^2 > 0.99$) are proposed.

The kinetic research is an essential tool for the investigation of the model and the pollutant removal mechanisms as well as a great assistance in the design. The estimated parameters can effectively be applied in WSPs sizing under Mediterranean or similar climatic conditions.

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References

[1] M.A. Camargo Valero, D.D. Mara, Ammonia volatilization in WSP: a cascade of misinterpretations, Water Sci. Technol., 61 (2010) 555–561.
[2] M. von Sperling, C.A. Lemos Chernicharo, Biological Wastewater Treatment in Warm Climate Regions, Vol. 1, IWA Publishing, London, 2005.
[3] R. Maassarani, The Effects of Climate on Microalgae Growth in Arctic Wastewater Stabilization Ponds: A Thesis Submitted to the Department of Civil Engineering, Queen's University Kingston, Ontario, Canada, 2015.
[4] M.P. Varon, D.D. Mara, Waste Stabilization Ponds: International Water and Sanitation Centre, Delft, 2004.
[5] M. Gratziou, M. Chalatsi, M. Tsalkatidou, N. Kotsovinos, Natural Systems for Wastewater Treatment in Northern Greece, Hydrogea, Aristotle University of Thessaloniki, Thessaloniki, 2009, pp. 365–376.
[6] J.F. Fritz, A.C. Middleton, D.D. Meredith, Dynamic process modelling of wastewater stabilization ponds, J. Water Pollut. Contr. Fed., 51 (1979) 2724–2743.
[7] K.R. Reddy, Nitrogen and phosphorus interchange between sediments and overlying water of a wastewater retention pond, Hydrobiologia, 98 (1983) 237–243.
[8] M.A. Senzia, A.W. Mayo, T.S.A. Mbwette, J.H.Y. Katima, S.E. Jorgensen, Modelling nitrogen transformation and removal in primary facultative ponds, Ecol. Model., 154 (2002) 207–215.
[9] J. Vymazal, Removal of nutrients in various types of constructed wetlands, Sci. Total Environ., 380 (2007) 48–65.
[10] A.W. Mayo, E.E. Hanai, Dynamics of nitrogen transformation and removal in a pilot high rate pond, J. Water Resour. Protect., 6 (2014) 433–445.
[11] A.W. Mayo, M. Abbas, Removal mechanisms of nitrogen in waste stabilization ponds, Phys. Chem. Earth, 72–75 (2014) 77–82.
[12] A.W. Mayo, Nitrogen mass balance in waste stabilization ponds at the University of Dares Salaam, Tanzania, Afr. J. Environ. Sci. Technol., 7 (2013) 836–845.
[13] R.C. Jin, P. Zheng, Kinetics of nitrogen removal in high rate anammox upflow filter, J. Hazard. Mater, 170 (2009) 652–656.
[14] S.Q. Ni, P.H. Lee, S. Sung, The kinetics of nitrogen removal and biogas production in an anammox non-woven membrane reactor, Bioresour. Technol., 101 (2010) 5767–5773.
[15] S.Q. Ni, S. Sung, Q.Y. Yu, B.Y. Gao, Substrate removal evaluation of granular anammox process in a pilot-scale uplow anaerobic sludge blanket reactor, Ecol. Eng. 38 (2012) 30–36.
[16] N. Alavi, R. Azadi, N. Jaafarzadeh, A.A. Babaei, Kinetics of nitrogen removal in an anammox upflow anaerobicbio reactor for treating petrochemical industries wastewater, Asian J. Chem., 23 (2011) 5250–5224.
[17] A.A. Babaei, R. Azadi, N. Jaafarzadeh, N. Alavi, Application and kinetic evaluation of upflow anaerobic biofilm reactor for nitrogen removal wastewater by Anammox process, Iranian J. Environ. Health Sci. Eng., 10 (2013) 20.
[18] G. Abbas, L. Wang, W. Li, M. Zhang, P. Zheng Ghulam Abbas, L. Wang, W. Li, M. Zhang, P. Zheng, Kinetics of nitrogen removal in pilot-scale internal-loop airlift bioparticle reactor for simultaneous partial nitrification and anaerobic ammonia oxidation, Ecol. Eng., 74 (2015) 356–363.
[19] S. Tomar, S.K. Gupta, Investigating the process kinetics and nitrogen gas production in Anammox Hybrid Reactor with special emphasis on the role of filter media, Int. J. Environ. Chem. Ecol. Geol. Geoph. Eng., 9 (2015) 1053–1059.
[20] A. Gholizadeh, M. Gholami, R. Davoudi, A. Rastegar, M. Miri, Efficiency and kinetic modeling of removal of nutrients and organic matter from a full-scale constructed wetland in Qasre-Shirin, Iran, Environ. Health Eng. Manag. J., 2 (2015) 107–116.
[21] E.J. Middlebrooks, S.C. Reed, A. Pano, V.D. Adams, Nitrogen Removal in Wastewater Stabilization Lagoons. Sixth National Drinking Water and Wastewater Treatment Technology Transfer Workshop, Kansas City, Missouri 64105, 1999, Available at: http://agrienvarchive.ca/bioenergy/download/nitrem3final.pdf
[22] M. Chalatsi, Wastewater Stabilization Ponds Qualitative and Hydrodynamic Characteristic, N. Greece, PhD Thesis Submitted to the Department of Civil Engineering, Democritus University of Thrace, Greece, 2014.
[23] A.D. Eaton, Standar Methods for the Examination of Water and Wastewater, 21st ed., APHA-AWWA-WEF, American Public Health Association, Washington, DC, 2005.
[24] F.D. Heliotis, C.B. DeWitt, A conceptual model of nutrient cycling in wetlands used for wastewater treatment: a literature analysis, Wetlands, 3 (1983) 134–152.
[25] P.F. Breen, A mass balance method for assessing the potential of artificial wetlands for wastewater treatment, Water Res., 24 (1990) 689–697.
[26] E.A. Korkusuz, M. Beklioglu, G.N. Demirer, Comparison of the treatment performances of blast furnace slag-based and gravel-based vertical flow wetlands operated identically for domestic wastewater treatment in Turkey, Ecol. Eng., 24 (2005) 185–198.
[27] J. Kuo, Practical Design Calculations for Groundwater and Soil Remediation, 2nd ed., Chapter 4: Mass-Balance Concept and Reactor Design, 2nd ed., Taylor & Francis Group, New York, 2014, pp. 113–150.
[28] R.C. Ward, Mark Robinson, Principles of Hydrology, Published by McGraw-Hill Higher Education, U.S.A, 2000.
[29] D. Chen, G. Gao, C.Y. Xu, J. Guo, G. Ren, Comparison of the thornthwaite method and pan data with the standard Penman-Monteith estimates of reference evapotranspiration in China, Clim. Res., 28 (2005) 123–132.

[30] R.-C. Jin, P. Zheng, Kinetics of nitrogen removal in high rate anammox upflow filter, J. Hazard. Mater, 170 (2009) 652–656.
[31] P. Grau, M. Dohanyas, J. Chudoba, Kinetics of multicomponent substrate removal by activated sludge, Water Recour., 9 (1975) 337–342.
[32] R.H. Kadlec, R.L. Knight, Treatment Wetlands, Lewis Publishers, CRC Press, Boca Raton, Florida, 1996.
[33] IWA, Constructed Wetlands for Pollution Control: Processes, Performance, Design and Operation, Scientific and Technical Report No.8', IWA Publishing, London, UK, 2000.
[34] A.D. Ronnie Frazer-Williams, A review of the influence of design parameters on the performance of constructed wetlands, J. Chem. Eng., 25 (2010) 29–42.
[35] N.S. Panikov, Microbial Growth Kinetics, 2nd ed., Chapman & Hall, London, 2000.
[36] S. Kayombo, T.S.A. Mbwette, J.H.Y. Katima, S.E. Jørgensen, Effects of substrate concentrations on the growth of heterotrophic bacteria and algae in secondary facultative ponds, Water Res., 37 (2003) 2937–2943.
[37] F.E. Stratton, Ammonia nitrogen losses from streams, Journal of the Sanitary Engineering Division–ASCE, December, SA6 (1968) 1085–1092.
[38] S.C. Reed, R.W. Crites, E.J. Middlebrooks, Natural Systems for Waste Management and Treatment, 2nd ed., McGraw-Hill, Inc., New York, NY, 1995.
[39] H.E. Archer, B.M. O'Brien, Improving nitrogen reduction in waste stabilisation ponds, Water Sci. Technol., 51 (2004) 133–138.
[40] B. Picot, T. Andrianarison, J.P. Gosselin, F. Brissaud, Twenty years monitoring of Meze stabilisation ponds – removal of organic matter and nutrients, Water Sci. Technol., 51 (2004) 23–31.
[41] O.R. Zimmo, N.P. van der Steen, H.I. Gijzen, Comparison of ammonia volatilisation rates in algae and duckweed-based waste stabilisation ponds treating domestic wastewater, Water Res., 37 (2003) 4587–4594.
[42] S.C. Reed, Nitrogen Removal in Wastewater Ponds, CRREL Report 84–13, USA CRREL, Hanover, NH, 1984.
[43] S.C. Reed, Nitrogen removal in wastewater stabilization ponds, J. Water Pollut. Cont. Fed., 57 (1985) 39–45.
[44] P. Krause, D.P. Boyle, F. Bäse, Comparison of different efficiency criteria for hydrological model assessment, Adv. Geosci., 5 (2005) 89–97.
[45] M. Gerardi, Wastewater Bacteria,John Wiley & Sons, Inc. Publishing, New Jersey, 2006, available at http://ssu.ac.ir/cms/fileadmin/user_upload/Daneshkadaha/dbehdasht/markaz_tahghighat_olom_va_fanavarihaye_zist_mohiti/e_book/Wastewater_Bacteria.pdf
[46] G. Bitton, Wastewater Microbiology, 3rd ed., Wiley-Liss, Department of Environmental Engineering Sciences, University of Florida, Gainesville, Florida, John Wiley & Sons, Inc., Florida 2005.
[47] M. Gratziou, M. Chalatsi, Nitrogen Removal from Domestic Wastewater by Stabilization Ponds Treatment Under Mediterranean Conditions, Proc. Fifth International Conference on Environmental Management, Engineering, Planning and Economics, A. Kungolos, K. Aravosis, C. Laspidou, P. Samaras, K.-W. Schramn (Eds.), Mykonos Island, Greece, 2015.