Ammonia removal in a deep reclaimed wastewater reservoir before agricultural reuse

S. Delgado[*], **S. Elmaleh**[**], **F. Díaz**[*], **J. Rodríguez-Sevilla**[*] **and M.C. Marrero**[*]

[*]Department of Chemical Engineering, Faculty of Chemistry, University of La Laguna, Avda. Astrofísico Fco. Sánchez S/N, 38200 La Laguna, Tenerife, Spain

[**]Groupe de Génie des Procédés. Université Montpellier II. CC024. Place E. Bataillon, 34095 Montpellier Cedex 5, France

Water Science and Technology **Vol 43 No10 pp 125–132** © IWA Publishing 2001

Abstract An experimental study has been carried out to determine the ammonia removal in a deep reclaimed wastewater reservoir of 50,000 m^3. The reservoir is part of the Reuse System of Reclaimed Wastewater of South Tenerife (Spain). The study has been conducted under batch mode operation, in three different periods (winter, spring-summer and winter-spring), with an average storage time of 85 days. Vertical profiles of temperature, dissolved oxygen and pH were determined together with NH_3-N, NO_2-N and NO_3-N concentrations at different points and different depths in the reservoir. Maximum removal efficiency was obtained during the winter periods, in absence of stratification and with good mixing conditions throughout the water column. During these periods, nitrification took place in some extension, favoring the ammonia removal. Average NH_3-N concentrations in the reservoir were calculated and apparent first-order rate constants were determined for different stratification conditions. Although ammonia nitrogen could be used as nutrient in the agricultural reuse, its removal from reclaimed wastewater could be useful in order to diminish the chlorine needs for disinfection.

Keywords Wastewater reuse; ammonia removal; thermal stratification; deep wastewater reservoir

Introduction

The reuse of urban wastewater is now required in places with such water shortage as the Canary Islands. They have a population of more than 1,600,000 inhabitants, and a dry subtropical climate tempered by the ocean, with an average annual temperature at sea level of 21°C. The water demand in the island of Tenerife (population, tourism, industry and agriculture) has far exceeded the island water resources. In order to make available more water than these provide, an ambitious project was started in 1993, to reuse reclaimed wastewater in crop irrigation on the south side of the island (specially banana plantation). Water is reused fairly far from the city of Santa Cruz. It is then necessary to transport water through a 61 km pipe and to store it in two deep reservoirs of 50,000 and 250,000 m^3, respectively.

Experimental data obtained in the first reservoir, under batch mode operation, were used to evaluate the effect of the storage time and the seasonal conditions on the ammonia removal. Ammonia nitrogen is considered as a pollutant, and normally a reduction in concentration is attempted before its release into the environment. However, when wastewater is destined for agricultural reuse, the nitrogen content can be useful as a nutrient for crops. Nevertheless, from the point of view of disinfection, the ammonia nitrogen increases the chlorine requirements for chlorination. Hence, the knowledge of ammonia removal kinetics during the storage is important because the process could diminish the chlorine needs for reclaimed wastewater disinfection before its agricultural reuse.

It is generally accepted that ammonia is removed in facultative wastewater stabilization ponds by the following three processes: gaseous ammonia stripping to the atmosphere, ammonia assimilation in algae and biological nitrification (Mara and Pearson, 1986).

Stripping and assimilation are usually the principal processes and some models have been proposed to correlate experimental data, mainly in low deep ponds. The models are based on first-order kinetics and perfectly mixed flow (Ferrara and Avci, 1982; Pano and Middlebrooks, 1982) or plug flow (Reed, 1985) and they show that ammonia removal depends mainly on temperature, pH and mean residence time.

Biological nitrification requires aerobic conditions and it can then occur in the pond surface layer, but needs long-lasting aerobic conditions to be significant (Diab *et al.*, 1993). Several factors can inhibit nitrification such as high solar radiation, toxic compounds, low mixing conditions and low temperatures (Abeliovich and Vonshak, 1993; Azov and Tregubova, 1995). Deep wastewater reservoirs are therefore unfavorable for intensive nitrification, although in some cases nitrification seems to be significant in winter and spring (Santos and Oliviera, 1987).

Thermal stratification in deep lagoons plays an important role in ammonia removal, i.e. high abatement is observed at the warm surface (epilimnion) but ammonia concentration increases near the cold bottom layers (hypolimnion) because of the anaerobic decomposition of organic matter (Llorens *et al.*, 1992).

The aim of this work is to study the effect of the storage time and the seasonal conditions on the ammonia removal efficiency in a deep wastewater reservoir. The paper is focused on establishing hints about the importance of the thermal stratification on the process kinetics.

Material and methods

Description of the system

The deep reservoir where the study was carried out is part of the Reuse System of Reclaimed Wastewater of South Tenerife (Spain), it has a maximum depth of 10 m and a maximum capacity of 50,000 m^3 (Figure 1). Experimental was carried out over a 1-year period in three runs with different seasonal conditions –winter, spring/summer and winter/spring – (Table 1). During each run the reservoir was operated in batch mode, following a cycle of loading, storage and unloading. There were no significant inflows and outflows.

During each load of the reservoir, the average characteristics of the incoming water were determined by daily sampling of the water inlet and measuring the inlet volumes (Table 2). Once the reservoir was fully filled, weekly *in situ* measurements at different depths were performed with a multiparametric probe (Hydrolab H20®) to determine the vertical pro-

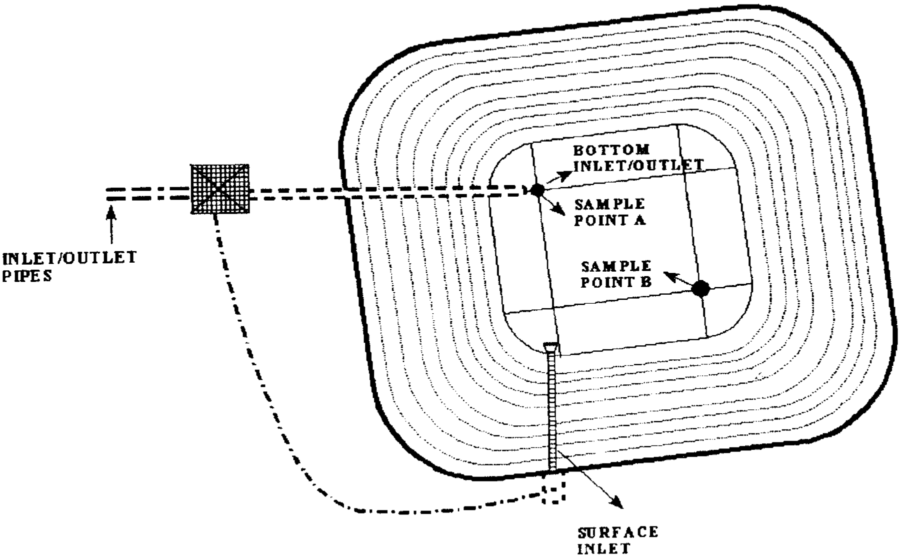


Figure 1 Layout of the deep wastewater reservoir showing the sampling points

files of temperature, dissolved oxygen, electrical conductivity and pH. According to the temperature profile, four samples were collected along the water column, two from the epilimnion and two from the hypolimnion. Sampling was carried out between 15 and 17 p.m., when approximately middle values of temperature, oxygen and pH were reached on the daily cycle. During run 1, two different points of the reservoir were studied (A and B); since no significant differences were evidenced in the analyzed parameters, only point A was sampled in the other runs. The collected samples were cooled during transportation and analyzed in the laboratory. The samples were characterized by measuring suspended solids (SS), chemical oxygen demand (COD), N-NH_3, N-NO_2, N-NO_3, PO_4^{3-}, SO_4^{2-}, S^{2-}, chlorophyll-a and fecal coliforms. All the parameters were determined according to Standard Methods (APHA, 1998).

Results and discussion

In situ measurements

Figure 2 shows selected vertical profiles of temperature, dissolved oxygen and pH during the three experimental runs (Marrero,1998). The distribution in time and space were typical conditions met in deep stabilization ponds (Llorens *et al.*, 1992).

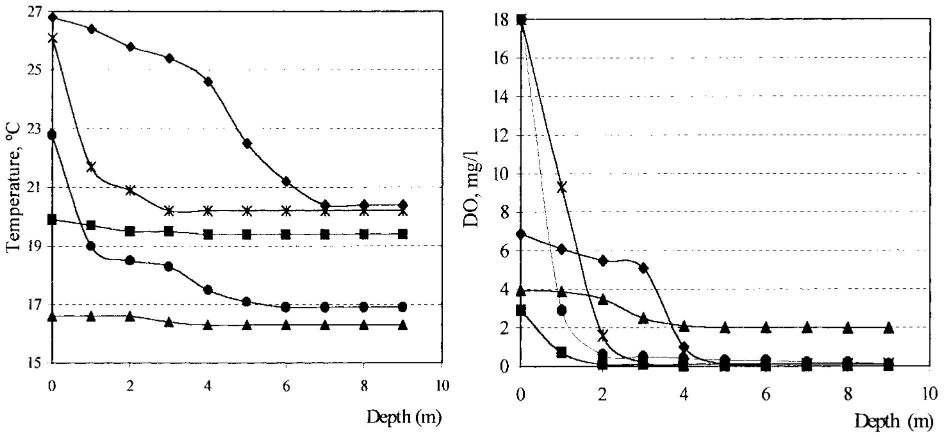
Temperature (Figure 2a). The temperature profiles show homothermicity in run 1 (winter), a marked stratification in run 2 (spring–summer) and transition from homothermicity to stratification in run 3 (winter–spring). Minimum and maximum surface temperatures, at the time of sampling, were around 16ºC in February and 27ºC in June, respectively. Run 2 showed initially a sharp thermocline, located between 0.5 and 2 m deep, that became deeper and wider – between 1 and 6 m deep – at the end of the period.

Table 1 Reservoir operational characteristics

	Run 1	Run 2	Run 3
Date	12/07/95–02/29/96	05/28/96–07/18/96	01/22/97–04/24/97
Season	Winter	Spring–Summer	Winter–Spring
Loading time (days)	10	5	7
Storage time (days)	87	75	92
Average volume (m^3)	47,700	38,300	46,600
Average surface area (m^2)	7,790	7,050	7,730
Average depth (m)	9.7	8.5	9.6
Monthly average ambient temperature (ºC)	December: 19.1 January: 18.3 February: 17.4	May: 21.8 June: 22.2 July: 23.6	January: 18.1 February: 19.8 March: 20.5 April: 19.8

Table 2 Average composition of the incoming water

Parameter	Run 1	Run 2	Run 3
pH	7.74	7.98	7.91
EC (µS/cm)	1288	1659	1585
SS (mg/l)	8	5	11
Total COD (mg/l)	48	59	52
N-NH_3 (mg/l)	26.3	42.3	23.5
N-NO_2 (mg/l)	0.04	0.02	0.03
N-NO_3 (mg/l)	0.06	0.46	0.31
PO_4^{3-} (mg/l)	27	41	30
SO_4^{2-} (mg/l)	–	119	91
S (II) (mg/l)	2.71	4.0	2.1
Fecal Col., log	4.1	4.2	4.1



(a) Temperature

(b) Dissolved oxygen

(c) pH

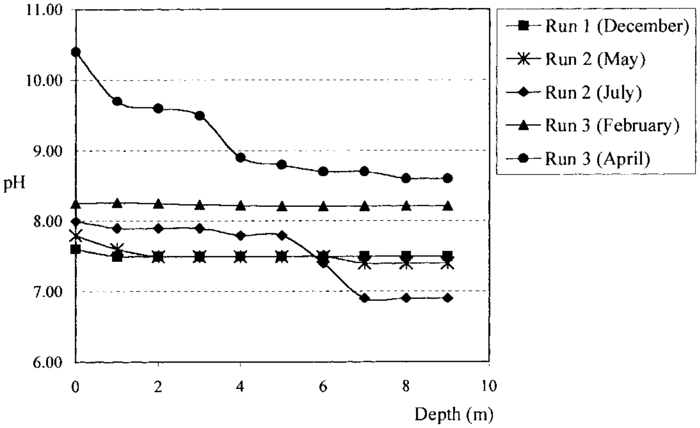


Figure 2 Vertical profiles of temperature, dissolved oxygen and pH

Dissolved Oxygen (Figure 2b). In facultative ponds, most of the oxygen is generated by the photosynthetic activity of algae. The oxygen profiles put into evidence oversaturation resulting from the algae bloom. In winter, excluding these oxygen oversaturation days, the oxygenation of the surface layer was poor but in occasions included the whole water column. It may be due to the absence of thermal stratification, that favored the mixing in the reservoir. During the periods of thermal stratification, the surface layer was highly oxygenated but the bottom remained, most of time, under anoxic conditions. The width of the aerobic layer was closely related with the location of the thermocline.

pH (Figure 2c). The biological and chemical processes which mainly can influence the pH values in a deep wastewater reservoir are:

- increasing pH: algal photosynthesis, denitrification and methanogenic step of the anaerobic digestion of organic matter;
- reducing pH: algal respiration, nitrification and acidogenic step of the anaerobic digestion of organic matter.

The overall anaerobic digestion occurs at maximum rate in the pH range 6–8 and its overall result is a small reduction of pH value.

The pH profiles are the result of the combined effect of some of the above processes together with thermal stratification. During the periods of homothermicity, pH values remained almost constant, between 7.5 and 8.5, along the water column, except when oxygen oversaturation in the surface layer was observed. During the periods with thermal stratification, marked variations with depth were detected, with values in the well oxygenated surface layer higher than in the anoxic bottom. Significant differences in the pH range between bottom and surface were found for the stratified periods in runs 2 and 3 (6.5–8 and 8.5–10, respectively). The differences in the bottom may be related with the strict anaerobic conditions in run 2, without NO_2-NO_3 present, as contrasted with the only anoxic conditions, with NO_2-NO_3 present, observed in run 3. So anaerobic degradation would take place in the first case and a denitrification would take place in the second case, which would favor the pH increase.

Ammonia nitrogen removal

Figure 3 shows the evolution of the NH_3-N and (NO_2+NO_3)-N concentrations with the storage time for the three experimental runs. During run 1, in absence of thermal stratification, the nitrogen concentration values were almost constant throughout the water column and the behavior of the reservoir can be regarded, approximately, as complete mixing. Under that condition, average concentration values were numerically calculated according to:

$$C_{av} = \frac{1}{L}\int_0^L C dl \qquad [1]$$

where L is the depth of the reservoir.

As shown in Figure 3(a), the average NH_3-N concentration decreased in the reservoir with the storage time, producing a NH_3-N removal of approximately 60% in the first 40 days. At the same time, an increase of the average (NO_2+NO_3)-N concentration was observed, indicating that a partial nitrification process, mainly nitritation, took place in the reservoir.

During run 2, when thermal stratification existed, the ammonia removal occurred only in the epilimnion, as it is shown in Figure 5(b). At hypolimnion, NH_3-N concentration firstly remained constant and afterwards increased until to reach a maximum, probably due to the ammonia liberation by anaerobic digestion; the decrease after the maximum could be caused either by ammonia diffusion towards the surface or its assimilation by algae. The values of (NO_2+NO_3)-N concentration were very low throughout the water column and the nitrification was negligible.

Run 3 shared characteristics of the previous ones and the behaviour was mainly marked by the thermal stratification. During the first half of the period, temperature and nitrogen concentrations were almost constant throughout the water column, NH_3-N decreased and a partial nitrification took place. During the second half, a thermocline was developed, the NH_3-N concentration continued decreasing at epilimnion but it remained constant at hypolimnion. At the same time, (NO_2+NO_3)-N concentration was depleted, mainly at hypolimnion, probably by denitrification due to the anoxic conditions that existed in the bottom of the reservoir. In this last step, the high values of pH (> 9.5) at the epilimnion could help the stripping of gaseous ammonia to the atmosphere.

In order to evaluate the overall ammonia removal in the reservoir, average NH_3-N concentrations were calculated, throughout the water column, according to Eq. (1) for all the experimental runs. With the object of discussing the results, the run 3 was divided in two periods: a homothermic one (1st half of the run) and a stratified one (2nd half of the run). Table 3 shows the overall removal efficiencies, after 40 days of storage, together with average values of temperature and pH, calculated by similar equations to (1). Data suggest that thermal stratification, and therefore mixing throughout the water column, was the main fac-

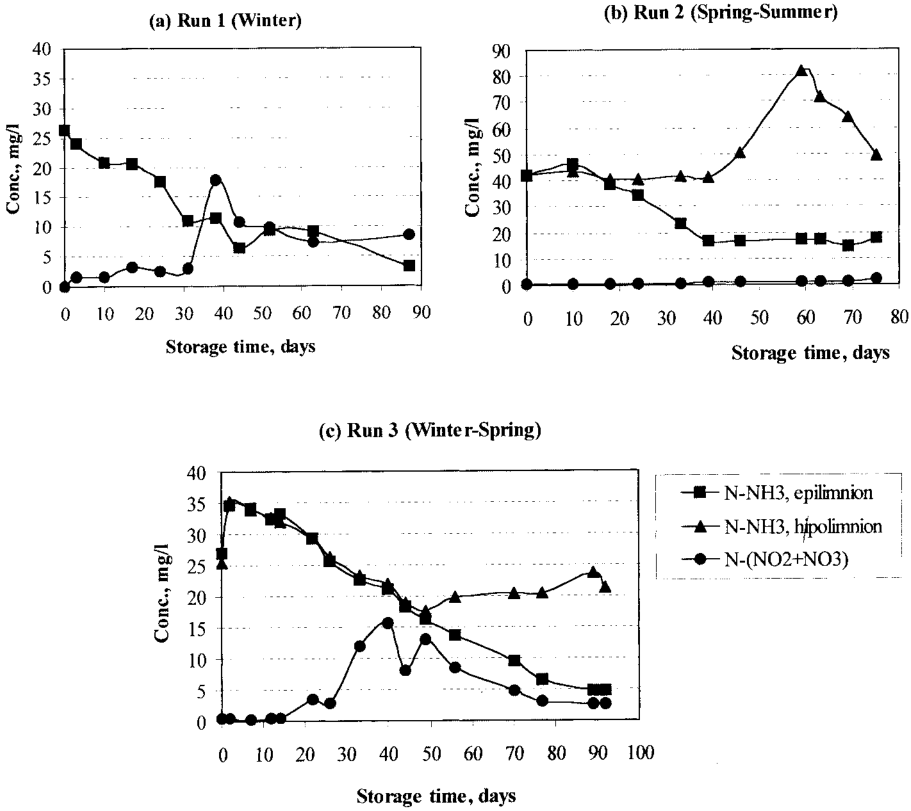


Figure 3 Evolution of the nitrogen concentrations in the reservoir with the storage time

Table 3 Average characteristics of the reservoir behavior

	Run 1	Run 2	Run 3 (1st half)	Run 3 (2nd half)
Thermal stratification	No	Yes	No	Yes
Storage time, days	87	75	44	48
Average temperature in the reservoir, °C	17.5	22.0	17.2	18.2
Average pH in the reservoir	7.7	7.5	8.2	9.1
Overall ammonia removal efficiency after 40 days, %	57	26	47	19
First-order rate constant (*k*), days^{-1}:				
– This work	0.023	0.0068	0.012	0.0037
– Pano and Middlebrooks (1982), eq. [3]	0.0074	0.0075	0.018	0.103

tor that affected the overall ammonia removal in the reservoir. As it can be observed, maximum removal efficiencies were obtained in absence of stratification, in spite of the differences in temperature and pH.

Most of the literature proposes a first-order kinetics to model the ammonia removal in ponds. If the reservoir is regarded as a homogeneous batch reactor of constant volume, the following equation is obtained:

$$-\ln(C_{av}/C_{av'o}) = k.t \qquad [2]$$

where C_{av} is the average NH_3-N concentration at time t (mg/l); $C_{av'o}$, the initial average NH_3-N concentration (mg/l); k, the first-order rate constant (days^{-1}) and t, the time (days).

Figure 4 shows the plot of $-\ln(C_{av}/C_{av'o})$ versus time. The k values obtained for each experimental run are shown in Table 3. However, since the system is full scale and temperature and pH varied during the runs, the experimental data may be considered acceptably well distributed along only two straight lines, according to the stratification conditions of the reservoir. Apparent first-order kinetic constants were determined from the slopes of these lines, resulting in the following values:

$k = 0.021$ days^{-1} ($r^2 = 0.853$) for no stratified reservoir;
$k = 0.0062$ days^{-1} ($r^2 = 0.756$) for stratified reservoir.

These results can be compared with the first-order rate constant derived from the correlation of Pano and Middlebrooks (1982), for temperatures up to 20°C. They assumed an ammonia-stripping model and complete mixing in the ponds; the following equation can be obtained for batch-mode operation:

$$k = (A/V)\,(0.0038 + 0.000134.T)\,.\exp\,[(1.041 + 0.0044.T)(\mathrm{pH} - 6.6)] \qquad [3]$$

where A is the pond surface area (m^2); V is the pond volume (m^3) and T is the temperature (°C). The k values obtained by Eq. (3), for the conditions of our experimental runs, are shown in Table 3. As it can be observed, in our case those values generally overestimate the pH influence on the ammonia removal and they do not take into account the effect of the thermal stratification. However, it must be pointed out that the above equation was obtained for low deep ponds (1.22–1.52 m depth) and Pano and Middlebrooks (1982) also noted that, above 20°C, the ammonia removal dropped slightly, possibly due to thermal stratification and poor mixing conditions.

Conclusions

- Nitrogen-ammonia removal took place in the reclaimed wastewater reservoir in all the study periods, under batch mode operation and different seasonal conditions. This result could be useful in order to diminish the chlorine needs for reclaimed wastewater disinfection before its agricultural reuse.
- Thermal stratification, and therefore mixing throughout the water column, was the main factor that affected the overall ammonia removal in the reservoir. Maximum efficiencies were obtained under vertical homothermicity and good mixing conditions, when nitrification took place in some extension.

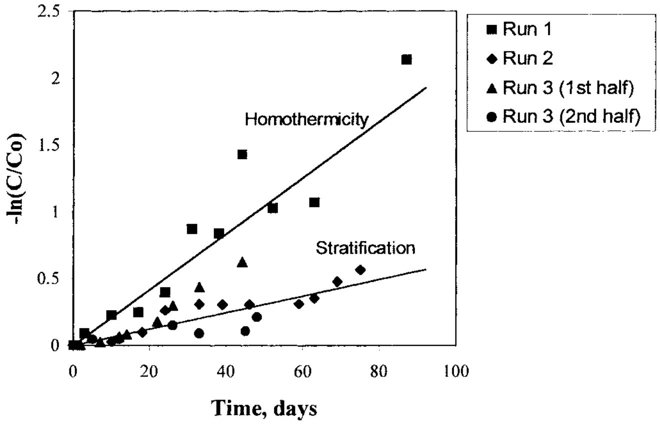


Figure 4 Effect of time on the average NH_3-N concentration in the reservoir (solid lines indicate first-order kinetics)

- In order to characterized the effect of the storage time, apparent first-order rate constants were determined, in the observed range of temperature and pH, for different stratification conditions.

Acknowledgements

This work was financially supported by a cooperative agreement between Balsas de Tenerife (BALTEN) and the Department of Chemical Engineering of the University of La Laguna.

References

APHA (1989). *Standard Methods for the Examination of Water and Wastewater*, 17th edition. American Public Health Association, Washington D.C.

Abeliovich, A. and Vonshak, A. (1993). Factors inhibiting nitrification of ammonia in deep wastewater reservoirs. *Wat. Res.*, **27**, 1585–1590.

Azov, Y. And Tregubova, T. (1995). Nitrification processes in stabilization reservoirs. *Wat. Sci. Tech.*, **31**(12), 313–319.

Diab, S., Kochba, M. and Avnimelech, Y. (1993). Nitrification patterns in a fluctuating anaerobic-aerobic pond environment. *Wat. Res.*, **27**, 1469–1475.

Ferrara, R.A. and Avci, C.B. (1982). Nitrogen dynamics in waste stabilization ponds. *Journal WPCF*, **54**, 361–369.

Llorens, M., Saenz, J. and Soler, A. (1992). Influence of thermal stratification on the behavior of a deep wastewater stabilization pond. *Wat. Res.*, **26**, 569–577.

Mara, D.D. and Pearson, H.W. (1987). Artificial Freshwater Environment: Waste Stabilization Ponds. In *Biotechnology* (Rehm, H.J. and Reed, G., editors), 177 – 206.

Marrero, M.C. (1998). *Evolución de Aguas Residuales Depuradas Almacenadas en Balsas*. Tesis Doctoral, Universidad de La Laguna, España.

Pano, A. and Middlebrooks, E.J. (1982). Ammonia nitrogen removal in facultative wastewater stabilization ponds. *Journal WPCF*, **54**, 344–351.

Reed, S.C. (1985). Nitrogen removal in wastewater stabilization ponds. *Journal WPCF*, **57**, 39–45.

Santos, M.C.R. and Oliveira, J.F.S. (1987): Nitrogen transformations and removal in waste stabilization ponds in Portugal: seasonal variations. *Wat. Sci. Tech.*, **19**(12), 123–130.