

6. RESULTS AND DISCUSSION: AMMONIA VOLATILISATION IN MATURATION PONDS

Ammonia volatilisation has been reported as the main nitrogen removal mechanism in WSP during periods of high temperature and pH (Pano and Middlebrooks, 1982; Reed, 1985; Silva *et al.*, 1995; Soares *et al.*, 1996; Rockne and Brezonik, 2006). Studies using models based on first-order kinetics and depending on variables such as pH, temperature and hydraulic retention time concluded that ammonia volatilisation could be the predominant pathway for nitrogen and ammonia removal in WSP (Pano and Middlebrooks, 1982; Reed, 1985). However, none of these models had been calibrated or validated by means of direct measurements of ex-pond ammonia volatilisation rates. Results given in this chapter were obtained from a method developed to measure ammonia volatilisation rates in WSP, including an apparatus to collect ammonia in situ.

That method was developed under controlled conditions in the laboratory and then applied on site to measure ammonia volatilisation rates from maturation ponds and thus determine the relative importance of ammonia volatilisation in nitrogen removal in WSP. On-site experiments were conducted both under summer and winter conditions.

6.1 Laboratory experiments

The results related to the design and development of an apparatus to measure ammonia volatilisation rates, under controlled conditions in the laboratory are given in this section. That apparatus comprises a capture chamber and an ammonia absorption system. Laboratory experiments included testing three absorption systems and two capture chambers.

6.1.1 Ammonia absorption system

Three ammonia absorption systems (AS1, AS2 and AS3) were tested in triplicate as described previously in section 3.4.1. Ammonia was volatilized from the controlled capture system at an average rate of 2,517 g NH₃-N/ha d; mean water temperature and pH figures inside the closed capture chamber were 17.1°C and 10.1, respectively. Absorption systems AS1 and AS2 recovered on average 54 and 60 percent of the volatilized ammonia, respectively (Figure 6.1). However, the ammonium concentration

values in the final conical flask for both absorption systems were higher than in the blank which means that tested absorption systems were not able to trap all volatilized ammonia gas.

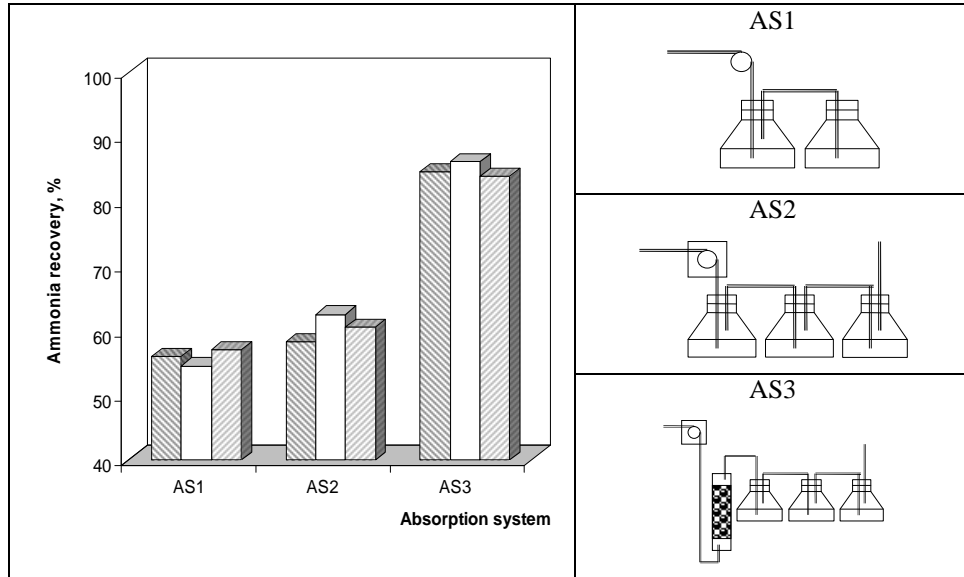


Figure 6.1 Results for ammonia recovery from absorption systems AS1, AS2 and AS3



Packed Column
(height 40 cm; diameter 100 mm)

- PVC spheres (diameter, 20mm)
- Silicon rings (length, 15mm; diameter, 5mm)
- glass rings (length, 8mm; diameter, 6mm)

Figure 6.2 Packed column for the ammonia absorption system AS3

Absorption system AS3 achieved an average ammonia recovery of 85 percent, with the packed column (Figure 6.2) absorbing most of the volatilized ammonia (90–99% of the total ammonia collected) whilst the conical flasks absorbed the remaining ammonia gas.

The ammonium concentration was below the detection limit (0.3 mg N/l) in the final flask in this system; therefore, AS3 was chosen as the best absorption system.

6.1.2 Ammonia gas capture chamber

Capture chambers CC1 and CC2 were tested with the AS3 absorption system and the best performance in terms of volatilized ammonia recovery (57%) was achieved with the baffled perspex box (CC2) and an air flow of 2.6 l/min. CC1 chamber did not perform well and ammonia was recovered in average at 41 percent only. Further trials with higher air flow rates (3.0, 3.5 and 4.0 l/min) were carried out to improve the ammonia recovery in the CC2-AS3 system (Figure 6.3). It was found that the net ammonia volatilisation rate was not affected by increasing the air flow, but that ammonia absorption was; a higher air flow rate reduced ammonia accumulation and short-circuiting in the head space in CC2 and improved ammonia absorption in the packed column.

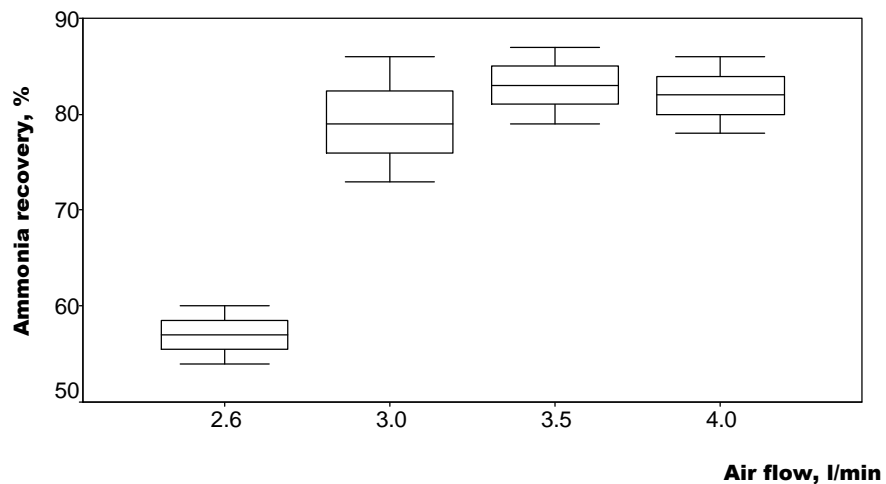


Figure 6.3 Box-plots for the CC2-AS3 system tested at different air flow rates

The selected air flow was 3.0 l/min (79% ammonia recovery) as there was no clear difference in terms of net ammonia recovered in comparison with higher air flows (83% at 3.5 l/min and 82% at 4.0 l/min). Moreover, when the air flow was higher than 3.0 l/min, the boric acid solution in the last conical flask was blown out of the system. CC2 capture chamber, AS3 absorption system and an air flow of 3.0 l/min were chosen as the best arrangement to be used for ammonia volatilisation experiments on site. Ammonia volatilisation rates measured under these optimal laboratory conditions should be corrected by an absorption efficiency factor of 1.27.

6.2 On-site Experiments

A set of experiments were carried out to assess nitrogen removal by ammonia volatilisation in M1 maturation pond under summer and winter conditions. Figure 6.4 shows the experimental set up placed on site. The ammonia gas capture and absorption system (CC2-AS3) was operated with an air flow of 3.0 l/min.

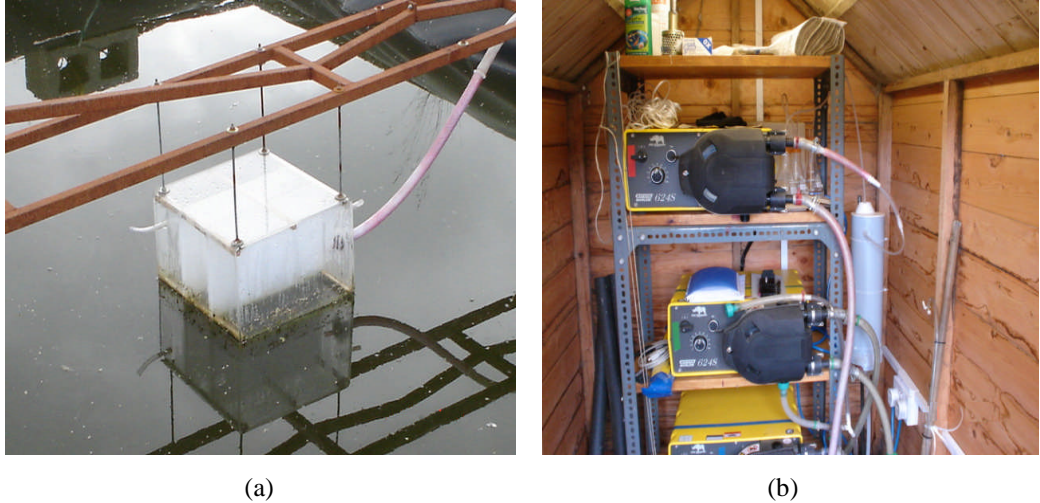


Figure 6.4 Capture chamber (a) and absorption system (b) on site

6.2.1 Ammonia volatilisation under summer conditions

Experiments to estimate ammonia volatilisation rates from M1 were carried out from 19 July to 9 September 2005. Results for summer 2005 experiments (Table 6.1) reported that on-site ammonia volatilisation rates over 72 hours were in the range $1\text{--}27\text{ g N/ha d}$ (mean rate = 15 g N/ha d), which was very low considering that during the experimental timeframe ammonium was removed from M1 at $3,747\text{g N/ha d}$.

In order to explain how ammonium was removed from M1 in summer 2005, results from the ammonia volatilisation and organic nitrogen sedimentation tests were used, in conjunction with laboratory analyses of nitrogen fractions from M1 influent and effluent, to produce a net nitrogen mass balance (Appendix C). Nitrogen fractions were defined as suspended organic nitrogen (TKN – filtered TKN), soluble organic nitrogen (filtered TKN – ammonium), ammonium nitrogen, nitrate and nitrite. Mean values of each fraction are reported in Figure 6.5; nitrite concentration was negligible both in M1 influent and effluent.

If the nitrogen fractions are compared, ammonium nitrogen was removed to a much greater degree (90%) than total nitrogen (8%), whilst in-pond suspended organic nitrogen

concentration increased from 10.70 to 13.50 mg/l, as well as the same fraction increased from 3.47 mg-N/l in M1 influent to 13.60 mg-N/l in M1 effluent. That would suggest that ammonium nitrogen was mainly transformed into suspended organic nitrogen (biomass) rather than removed from the maturation pond.

Table 6.1 Ammonia volatilisation rates from M1 pond

Experiment	Ammonia volatilisation rate*, g N/ha d
1	22
2	17
3	27
4	<1
5	9
6	19
7	22
8	20
9	18
10	17
11	16
12	8
13	8
14	<1

*Including an absorption efficiency recovery factor of 1.27 (section 6.1.2)

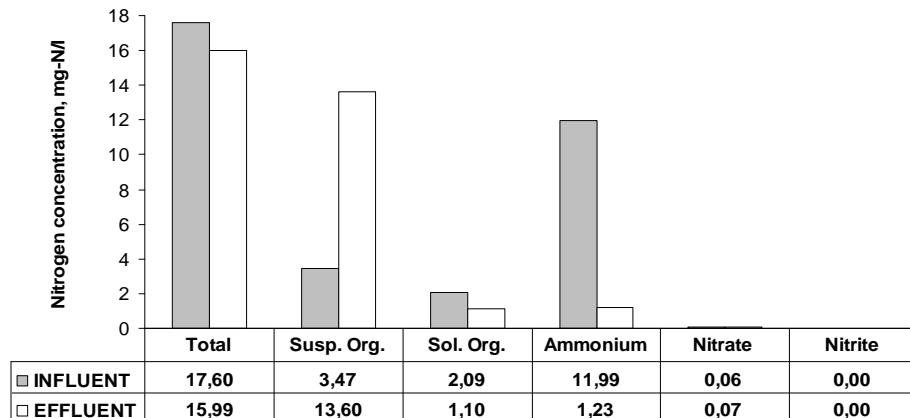


Figure 6.5 Mean nitrogen fractions concentration from M1 influent and effluent

The net nitrogen mass balance shows that M1 was loaded at 6,116 g N/ha d and that the average nitrogen removal rate during summer 2005 was 531 g N/ha d. Total nitrogen removal was achieved mainly by organic nitrogen sedimentation (20%) and in-pond nitrogen accumulation due to biological uptake (71%), and a minimum contribution of ammonia volatilisation (3%). Biological nitrogen uptake was carried out mainly by algae as in-pond average chlorophyll *a* was 1022 µg/l. These results demonstrate that

ammonium nitrogen was mainly removed by biological uptake in summer, despite the occurrence of favourable conditions for ammonia volatilisation ($8.9 < \text{pH} < 10.2$; $15.2 < T < 18.2^\circ\text{C}$).

Theoretical ammonia volatilisation rates were calculated from an equilibrium-based mass transfer equation (equation 6.1), assuming that the ammonia concentration in the air above the pond surface was negligible and that the mass transfer coefficient did not depend on wind speed:

$$\lambda_{\text{NH}_3} = \frac{K_l \times [\text{NH}_3] \times V}{A} \quad (6.1)$$

where λ_{NH_3} is the ammonia volatilisation rate (g N/ha d); K_l is the mass transfer coefficient in the liquid phase (d^{-1}); $[\text{NH}_3]$ is the free ammonia concentration (g N/ m^3); V is the pond volume (m^3); and A is the pond surface area (ha). Values for the parameters in equation 6.1 were obtained by using the equations reported in Table 2.2 and average figures for in-pond total ammonium concentration, pH and temperature. The total ammonium concentration in the water column sample (mean value = 3.3 mg N/l) and 24-hour pH and temperature readings were used to calculate theoretical ammonia volatilisation rates (Figure 6.6).

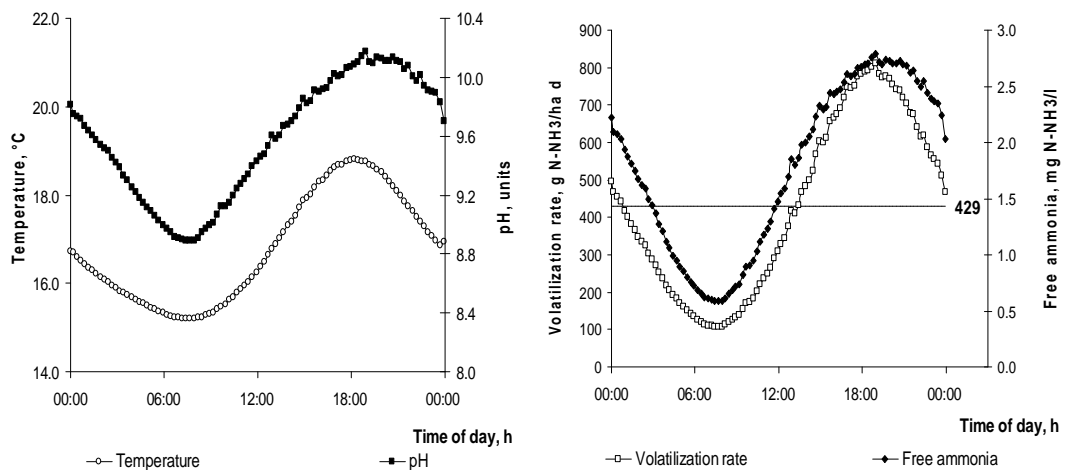


Figure 6.6 Theoretical ammonia volatilisation rates in M1 under summer conditions

The M1 ammonia volatilisation rates measured on site (0–27 g N/ha d) were much lower than the calculated theoretical values (107–812 g N/ha d) and even lower than (a) the annual value of 828 g N/ha d reported by Rockne and Brezonik (2006) who used an equilibrium-based model with wind speed adjustment for the WSP system at Harris, Minnesota (i.e., in a cold region with a long ice-cover season); (b) the values of 105–223

g N/ha d measured in situ by Zimmo *et al.* (2003) from an algal WSP located in Ginebra, southwest Colombia; and (c) the values of 198–811 g N/ha d calculated by Zimmo *et al.* (2003) using the Stratton's equation (Ferrara and Avci, 1982). Considering that the prediction of ammonia mass transfer coefficients based on the chemical equilibrium of ammonium-ammonia for the ideal water–ammonia–air system (e.g., Stratton's equation; Ferrara and Avci, 1982) does not include the influence of strong interferences on free ammonia concentration (e.g., biological activity), it is only to be expected that theoretical models for ammonia volatilisation rates would not be able to predict ammonia removal in maturation ponds.

On the other hand, if Pano and Middlebrooks' model for ammonia removal (equation 2.34) and Reed's model for total nitrogen removal (equation 2.35) are applied to M1, the predicted figures (97% and 68%, respectively) are much higher than the actual values found for both ammonia removal (90%) and total nitrogen removal (8%) in M1 in summer 2005. Even though feasible pathways have been identified for total nitrogen and ammonia removal in WSP, both the Reed and the Pano and Middlebrooks models derive final equations which depend on variables which do not define any particular mechanism involved in total nitrogen and/or ammonia transformation and removal. Therefore, any agreement found between results predicted by these models and actual field results does not confirm the validity of the mechanism(s) for ammonia removal in WSP assumed in their development.

6.2.2 Ammonia volatilisation under winter conditions

A complementary set of experiments for ammonia volatilisation was carried out in winter from 20 December 2006 to 28 February 2007. It was assumed that, because in-pond water temperatures and pH values are lower in winter than in summer, the ammonia volatilisation rates would be lower in winter as well; for that reason, each experiment was carried out for 7 days. However, the results for ammonia volatilisation rates in winter (0–2 g N/ha d) were even lower than expected and there was no a clear difference with blanks; therefore, ammonia volatilisation in M1 under winter condition was negligible.

Based on the results reported in this chapter, it seems that ammonia volatilisation was not the most important mechanism involved in either total nitrogen or ammonia removal processes in M1. Ammonia and total nitrogen may be mainly removed by biological algal uptake under summer conditions. Ammonia removal in maturation ponds cannot be predicted with models based on mass transfer equations for ammonia volatilisation as this is only a minor pathway for ammonia removal in maturation ponds.

6.3 Related Publications

This research work was partially published as part of the conference proceedings of the 7th IWA Specialist Conference on Waste Stabilization Ponds held at the Asian Institute of Technology in Bangkok, 25–27 September 2006. The corresponding paper was selected for publication in *Water Science and Technology* as follows:

Camargo Valero, M. A. and Mara D. D. (2007). Nitrogen removal via ammonia volatilization in maturation ponds. *Water Science and Technology*, **55**(11), 87-92.