

Nitrogen removal in maturation ponds: tracer experiments with ^{15}N -labelled ammonia

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Abstract A primary maturation pond (M1) was spiked with labelled ammonium chloride ($^{15}\text{NH}_4\text{Cl}$) to track ammonium transformations associated with algal uptake and subsequent sedimentation. Conventional sampling based on grab samples collected from M1 influent, water column and effluent, and processed for unfiltered and filtered TKN, ammonium, nitrite and nitrate, found low total nitrogen removal (8%) and high ammonium nitrogen removal (90%). Stable isotope analysis of ^{15}N from suspended organic and ammonium nitrogen fractions in M1 effluent revealed that labelled ammonium was mainly found in the organic fraction (69% of the ^{15}N recovered), rather than the inorganic fraction (5%). Algal uptake was the predominant pathway for ammonia removal, even though conditions were favourable for ammonia volatilization ($8.9 < \text{pH} < 10.1$ units, $15.2 < \text{temperature} < 18.8^\circ\text{C}$). Total nitrogen was removed by ammonia volatilization at 15 g N/ha d (3%), organic nitrogen sedimentation at 105 g N/ha d (20%), and in-pond accumulation due to algal uptake at 377 g N/ha d (71%). Algal uptake of ammonium and subsequent sedimentation and retention in the benthic sludge, after partial ammonification of the algal organic nitrogen, is thus likely to be the dominant mechanism for permanent nitrogen removal in maturation ponds during warm summer months in England.

Keywords ^{15}N -ammonium; maturation pond; nitrogen; removal

Introduction

Feasible mechanisms and pathways by which nitrogen in its various forms can be transformed in and removed from waste stabilization ponds (WSP) have been proposed and supported by research carried out in many parts of the world. However, there is still much debate regarding the relative importance of the various mechanisms by which, and pathways through which, nitrogen is removed in WSP. In general, after organic nitrogen is hydrolyzed to ammonium, ammonia volatilization has generally been reported as (or assumed to be) the main nitrogen removal mechanism in WSP; this hypothesis is based on two observations: (a) in-pond pH values can reach high values (>9 , even >10), so increasing the proportion of the total ammonia present as the un-ionized form (NH_3), and (b) in-pond temperatures can also be high, so improving the mass transfer rate of NH_3 to the atmosphere (Pano and Middlebrooks, 1982; Silva *et al.*, 1995; Soares *et al.*, 1996; Rocknie and Brezonik, 2006). However, algal uptake of ammonium and subsequent sedimentation into, and then partial retention in, the pond sludge have also been proposed as an alternative mechanism for permanent nitrogen removal (Ferrara and Avci, 1982; Reed, 1985; Pearson *et al.*, 1988). Maynard *et al.* (1999) suggested that ammonia volatilization may dominate nitrogen removal during warm periods of the year (summer), while nitrogen removal via biological uptake and further sedimentation could be the dominant removal mechanism in winter.

The research that we report on in this paper was undertaken to elucidate the important mechanism(s) and pathway(s) involved in nitrogen removal and transformations occurring in WSP. In order to determine the fate of the ammonium-N entering a primary maturation

pond in summer in England, the influent was spiked with labelled ammonium chloride ($^{15}\text{NH}_4\text{Cl}$) and the resulting levels of ^{15}N in the suspended organic N and ammonium-N fractions in pond effluent samples determined.

Methods and materials

Pilot-scale maturation pond

The pilot-scale WSP system located at Esholt Sewage Treatment Works, Bradford, West Yorkshire, UK, comprises one primary facultative pond (PFP) [coded Blue in a previous work by [Abis and Mara \(2003\)](#)], which is fed with screened wastewater; and two maturation ponds in series as described by [Camargo Valero and Mara \(2005\)](#). The PFP was loaded at 80 kg BOD/ha d and 8 kg N/ha d and had a mean hydraulic retention time of 60 d; the primary maturation pond (M1) received the Blue pond effluent at an average rate of 0.6 m³/d; the loading rates were 9.3 kg BOD/ha d and 6.0 kg N/ha d and the mean hydraulic retention time (θ_{M1}) 17.5.

Sampling and sample analysis

M1 was spiked in summer 2005 with 0.6812 g of $^{15}\text{NH}_4\text{Cl}$ (98% ^{15}N ; Cambridge Isotope Laboratories, Cambridge); this quantity was chosen as it increased the background level of ^{15}N in the pond by a factor of two to 18 $\mu\text{g } ^{15}\text{NH}_4\text{-N/L}$ [assuming complete mixing – i.e. $C * \text{sensu Levenspiel (1998)} = 9 \mu\text{g } ^{15}\text{NH}_4\text{-N/L}$]. M1 was sampled for a total time of $3 \times \theta_{\text{M1}}$ (19 July – 09 September 2005) and 1-day composite samples were collected in an autosampler (Aquamatic, model Aquacell P2-Multiform). Samples were preserved by the addition of 4.5 mL of 6 mol L⁻¹ HCl solution containing 2 g CuCl₂/L and they were processed for ammonium (method 4500-NH₃ B; [APHA, 1998](#)), suspended solids (2540 D), unfiltered and filtered TKN (4500-Norg C) and nitrite and nitrate (Dionex DX500 ion analyzer). The samples were also partitioned to extract two nitrogen species separately: suspended organic nitrogen by filtration on fibre glass filters (Whatman GF/C), and ammonium nitrogen by a diffusion method ([Holmes *et al.*, 1998](#)). Each fraction was analyzed by continuous flow-isotope ratio mass spectrometry in the School of Earth and Environment, University of Leeds, to determine $^{15}\text{N}/^{14}\text{N}$ ratios. A YSI model 6820 sonde was used to measure in real time the dissolved oxygen (DO) concentration, temperature and pH in the effluent of M1.

Ammonia losses by volatilization were estimated following the procedure described by [Camargo Valero and Mara \(2006\)](#), and nitrogen removal by sedimentation was determined from sludge samples collected in 10-L metal buckets which were strategically placed on the bottom of M1 at the beginning of the experiment. Sediment samples were processed for TKN (method 4500-Norg C; [APHA, 1998](#)), solids (2540 B, 2540 D, 2540 F) and moisture (at 103 – 105 °C). The samples were filtered and the filtered solids were analyzed to determine their 14N/15N ratios. Additionally, grab samples were collected weekly from the M1 influent, water column and analyzed for chlorophyll *a* ([Pearson *et al.*, 1987](#)) and suspended solids, unfiltered and filtered TKN, ammonia, and nitrite and nitrate, as described above.

Results and discussion

Laboratory results from the weekly M1 grab samples provided essential information for the contextual analysis of the ^{15}N results, see [Figure 1](#). Total nitrogen was poorly removed (8%) at 531 g N/ha d, but ammonium removal reached 90% (3,747 g N/ha d). This indicates that the transformations of nitrogen fractions inside M1 were led by biochemical processes leading to ammonia removal, rather than any net nitrogen removal pathway. The nitrogen fraction results (suspended organic nitrogen, soluble organic

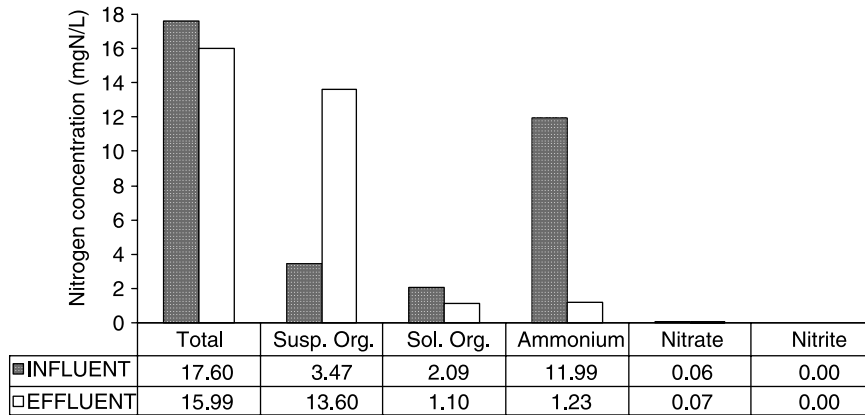


Figure 1 Mean nitrogen fraction concentrations in M1 influent and effluent

nitrogen, ammonium nitrogen, nitrate and nitrite) showed that the predominant nitrogen fraction in the influent to M1 was ammonium nitrogen (68%), while in the effluent it was the suspended organic nitrogen fraction (85%). Nitrate and nitrite concentrations from M1 influent and effluent were both very low and their contribution to the net nitrogen mass balance was negligible, showing that nitrification should not be considered as a feasible mechanism for ammonium removal.

Results from the ammonia volatilization and organic nitrogen sedimentation tests were used, in conjunction with laboratory analyses of the nitrogen fractions, to produce a net nitrogen mass balance. Total nitrogen removal was achieved by ammonia volatilization at 15 g N/ha d (3%), organic nitrogen sedimentation at 105 g N/ha (20%), and in-pond accumulation due to biological uptake at 377 g N/ha d (71%). These results demonstrate that biological uptake and subsequent sedimentation of the biologically incorporated organic nitrogen were the principal mechanisms for nitrogen transformation and removal in M1.

The results for ^{15}N in the suspended organic and ammonium nitrogen fractions in M1 effluent are initially reported as delta values in parts per thousand ($\delta^{15}\text{N}$, ‰) (Figure 2). Delta values are not concentrations of the isotope but differences between $^{15}\text{N}/^{14}\text{N}$ ratios from the sample and air; they are one of the most widely used natural abundance standards in ^{15}N studies. The ammonium nitrogen fraction was found to be richer in ^{15}N than the suspended organic nitrogen fraction at the beginning of the experiment as expected, but after five days the $^{15}\text{N}/^{14}\text{N}$ ratio in the organic fraction was consistently higher.

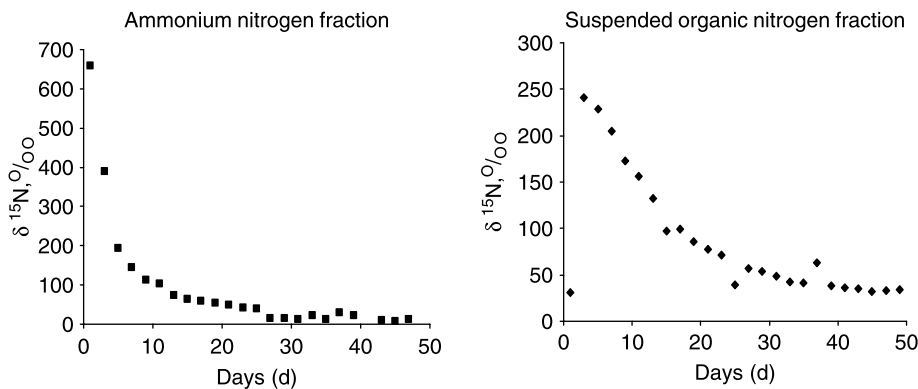


Figure 2 Delta- ^{15}N values for ammonium and suspended organic nitrogen fractions in M1 effluent

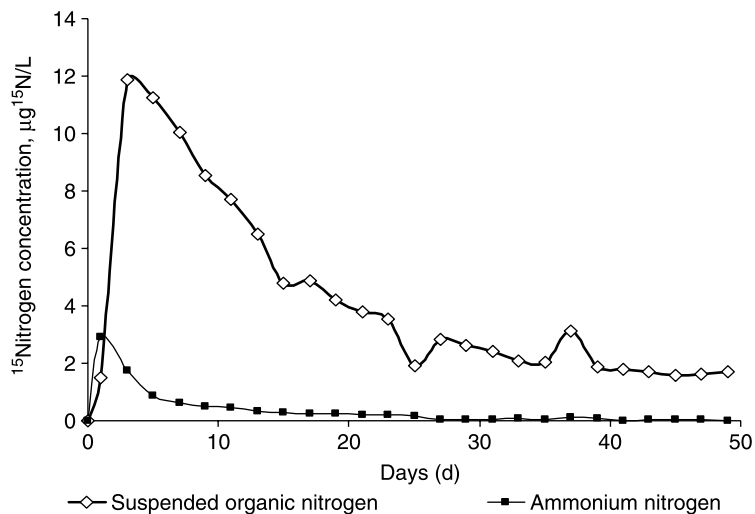


Figure 3 ^{15}N concentrations for ammonium and suspended organic fractions of nitrogen in M1 effluent

suggests that ^{15}N was transformed from inorganic nitrogen to organic nitrogen into suspended solids in the pond.

Delta- ^{15}N readings from M1 effluent were converted to ^{15}N concentrations (Figure 3) and the biological uptake of ammonium nitrogen was found to be very important as the ^{15}N concentration in the organic N fraction reached a peak nearly five times higher than that of the inorganic fraction. After three nominal (i.e. V/Q) retention times, 69% of the ^{15}N spike was recovered from the suspended organic fraction and only 5% was recovered as ammonium; therefore, algal uptake can be considered the predominant pathway for ammonium-N removal due to the high photosynthetic activity found during the study period, which was confirmed by the high mean values for photosynthesis-associated parameters such as chlorophyll *a* (1141 $\mu\text{g/L}$), pH (8.9–10.1 units) and dissolved oxygen (11.0 mg/L).

Ammonium removal by volatilization can be discounted as a predominant pathway for ammonium nitrogen removal as models based on mass transfer coefficients for the ideal water–ammonia–air system ignore the fact that the water in a WSP is a very complex matrix, and high pH and temperature values should not necessarily favour ammonia volatilization over alternative mechanisms like algal uptake which is clearly identified in this work as the major mechanism for ammonium removal during warm summer months when pH and temperatures reach their annual maxima. Ammonium removal predicted for M1 under summer conditions by the model proposed by Pano and Middlebrooks (1982) is 97%, which is higher than the value found (90%). Their model assumed that ammonia volatilization is the major ammonia removal mechanism and it is based on pH, water temperature and hydraulic loading rate (retention time); but their resulting equation is actually a simple first-order equation for a completely mixed reactor with the rate constant being a function of pH, temperature and mean hydraulic retention time. However, agreement of field results with values predicted by their equation does not provide any information on the nature of the N removal mechanisms involved. It is only by tracking ^{15}N spikes, as reported herein, that these removal mechanisms can be elucidated.

Conclusions

- Under summer conditions in England the most likely sequence for ammonia removal is the uptake of ammonia by pond algal biomass, followed by assimilation into

organic nitrogen, and then sedimentation of this organic N into the pond benthos and partial retention therein.

- Ammonia volatilization can be discounted as a significant mechanism for ammonia removal, even when the pH and temperature are favourable for its occurrence.

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