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Nitrogen removal during summer and winter in a primary facultative WSP pond: preliminary findings from ^{15}N -labelled ammonium tracking techniques.

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Abstract Nitrogen removal mechanisms and pathways within WSP have been the focus of much research over the last 30 years. Debates and theories postulated continue to refine our knowledge regarding the cycling and removal pathways for this important nutrient, but a succinct answer has yet to be provided for holistic nitrogen removal. In this study, two experimental runs using labelled ^{15}N as a stable isotope tracking technique were conducted on a pilot-scale primary facultative WSP in the UK; one in the summer of 2006, and the other in the winter of 2007. An ammonium chloride ($^{15}\text{NH}_4\text{Cl}$) spike was prepared as the slug for each experimental run, which also contained rhodamine WT to act as a dye tracer enabling the hydraulic characteristics of the pond to be mapped. Initial results from the study are reported here, and findings are compared and contrasted. Preliminary findings reveal that a greater proportion of ^{15}N is incorporated into the algal biomass by assimilation and subsequent release as soluble organic nitrogen in summer than in winter. ^{15}N ammonium passes out of the system much sooner and in a much higher proportion in the winter than in summer.

Keywords: ^{15}N ; nitrogen; primary facultative pond; removal; transformation

INTRODUCTION

The mechanisms and pathways by which total nitrogen is removed from WSP have been the subject of much debate and is continually being contested. Nitrogen reduction within wastewater effluents to fit with prescribed discharge consents is a major concern and an immensely important criterion which needs continual appraisal by wastewater treatment companies. It is a postulate too that more emphasis may be placed on the importance of one mechanism or pathway over another, as it may bear more significance and play a greater role in nitrogen removal for a WSP system within that locality. Research has been conducted which suggests that nitrogen removal mechanisms and pathways differ spatially and temporally on a global level. It is commonly known too that seasonality plays a significant role in nitrogen cycling within WSP - affecting ammoniacal nitrogen removal in particular. The principal and most widely accepted basis for ammonia removal within WSP has been attributed to the volatilization of ammonia (Pano and Middlebrooks 1982; Silva *et al.* 1995 and Soares *et al.* 1996), microbial uptake and assimilation (Senzia *et al.* 2002) and subsequent sedimentation and deposition into the sludge layer (Reed, 1985; Zimmo *et al.* 2003). Nitrification and denitrification are also observed mechanisms which have significantly contributed to the removal of nitrogen within WSP (Hodgson and Paspaliaris, 1996; Zimmo *et al.* 2003), but again, this mechanism is widely contested.

In order to contribute to the deeper understanding of which mechanisms and pathways of nitrogen removal predominate within WSP in the UK, this research comprised a detailed quantitative and qualitative study using ^{15}N -labeled ammonium on a primary facultative pond (PFP) which is part of an experimental pilot-scale WSP system at Esholt Wastewater Treatment Works, Bradford, West Yorkshire, UK. The first experimental run was undertaken between August and November 2006, and the second between February and May 2007.

MATERIALS AND METHODS

Field site and pilot scale pond

The PFP used for these studies was fed by screened wastewater which was pumped from the adjacent main inlet channel by a peristaltic Watson Marlow Washdown 604S/R pump. The pond volume, surface area, depth and length-to-breadth ratio were 58.8 m^3 , 40.6 m^2 , 1.5 m and 2.5:1 respectively. The pond was loaded at the optimum limit established for UK facultative WSP of 80 kg BOD/ha d (Abis 2002) with a total nitrogen loading of 11.7 kg N/ha d (of which 7.8 kg/ha d was applied as ammonium). The wastewater flow entering the pond was $0.79 \text{ m}^3/\text{d}$. Feeding the PFP solely by screened raw wastewater with its BOD_5 concentration would have produced a theoretical hydraulic retention time (θ) of $>80 \text{ d}$; therefore freshwater was added to the influent flow to dilute the influent wastewater and so reduce the hydraulic retention time as it was critical to confine the experimental runs to a particular season so the affects of seasonality could be observed. The resultant total flow (Q_T) entering the pond was $2 \text{ m}^3/\text{d}$, the theoretical hydraulic retention time was 30 d. The PFP had to be sampled for a period of 30 to ensure that nearly all of the $^{15}\text{NH}_4\text{Cl}$ and rhodamine WT were washed out from the system.

At the start time of the experiment (i.e., at $t=0$), the $^{15}\text{NH}_4\text{Cl}$ and rhodamine WT solution was introduced into the pond in the influent stream as a single pulse through a small funnel connected to influent tubing.

Sampling and sample analysis

^{15}N has a natural abundance in the environment of 0.36% (Hoefs, 1987), therefore in order to increase this isotopic fraction so it would be detectable in the pond effluent, the fraction was doubled from its background level in the influent by the addition of the $^{15}\text{NH}_4\text{Cl}$ slug. The primary facultative pond was spiked with 31.392 g of 98% purity $^{15}\text{NH}_4\text{Cl}$ in summer 2006, and 31.399g in winter 2007. The pond was simultaneously spiked with a 20% rhodamine WT standard to obtain the hydraulic characteristics of the pond. The summer and winter spikes each contained 32.357 g of rhodamine WT, which, assuming a complete mix model for the pond, would provide an in-pond concentration of $110 \mu\text{g}$ rhodamine/l of pond volume. The rhodamine WT was measured in real time by a YSI 6820 sonde which was fixed in the effluent outflow point of the pond. Real time DO, ORP, temperature and pH were also logged hourly by the sonde. Weekly pond profile measurements were obtained for these parameters at 20-cm depth intervals from the pond surface. An autosampler (Aquamatic Aquacell P2-Multiform) was used to sample 200 ml of pond effluent every hour. To prevent chemical species undergoing transformations because of microbiological activity and to preserve the samples, 1 ml of 3M HCl containing 1 g of CuCl_2 per 100 ml of sample to be collected, was added to the autosampler bottler

before the sampling program was reset prior to each sampling run. These samples were collected and transported to the laboratory and combined to produce a 1-litre 24 hour composite sample. Ammonia volatilization was measured from the pond surface by a Perspex chamber, where the air inside the chamber was removed from the chamber by a Dymax 30 diaphragm vacuum pump pumping at 3 l/min. Prior to the spike introduction, five buckets were placed at designated intervals linearly from the inlet to outlet to measure sludge deposition and composition over the 30 experimental period.

The daily composite samples were frozen and analysed at a later date; samples were analysed for total TKN, filtered TKN, (both fractions by method 4500 - Norg C; APHA, 1998), NH_4^+ (4500 - NH_3 B) and suspended solids (2540 D). Samples were then partitioned and the soluble organic nitrogen removed by complete filtration of the samples through C18 Isolute resins, and then ammonium and subsequent nitrite and nitrate were removed and from the samples utilising the ammonium diffusion method adapted from research by Holmes *et al.*, (1998). Suspended organic nitrogen, soluble organic nitrogen and ammonium samples were then analysed for $^{15}\text{N}:^{14}\text{N}$ ratios by continuous flow isotope ratio mass spectrometry within the School of Earth and Environment, University of Leeds. The $\delta^{15}\text{N}$ values (given as parts per thousand, ‰) obtained from mass spectrometry analysis were converted into actual ^{15}N concentrations per sample analysed ($\mu\text{g } ^{15}\text{N/l}$) by the equation devised by Camargo Valero (2008).

RESULTS AND DISCUSSION

The rhodamine tracer curves are depicted in Figures 1 and 2. The summer curve (Figure 1) reveals that the rhodamine passed out of the pond at a much lower and more gradual rate, with a peak rhodamine concentration of 45.77 $\mu\text{g/l}$ occurring on the 15th day of the experimental run; whereas in winter, a maximum peak rhodamine concentration of 109.55 $\mu\text{g/l}$ occurred after only five hours of the spike injection into the pond. The dispersion number (D/uL) in summer 2006 was 0.2358, and for winter 2007 it was 0.3421. Both dispersion numbers reveal large deviations from both plug flow and complete mixing, and therefore in both summer and winter, the hydraulic characteristics of the ponds best approximate the dispersed flow model.

The results shown in Figures 3 and 4 reveal the marked changes that the labelled ammonium underwent in summer and winter seasons. Figure 3 portrays the $\delta^{15}\text{N}$ data - i.e., the $^{15}\text{N}:^{14}\text{N}$ ratios. The passage of ammonium leaving the system at the effluent point as an unchanged ^{15}N fraction from the $^{15}\text{NH}_4\text{Cl}$ (Figures 3e and 3f) corroborates very well with the rhodamine distribution curves in Figures 1 and 2 for summer and winter, respectively. The maximum peak concentrations of $\delta^{15}\text{N}$ (‰), the actual ^{15}N concentration within each sample, and the elapsed time in which these peaks occurred are given in Table 1. In both the summer and winter experimental runs, the peak of ammonium leaving the system occurred exactly two days after the rhodamine peak passed out (summer 2006: rhodamine peak at 15 d, $^{15}\text{NH}_4$ peak at 17 d; and winter 2007: rhodamine peak within first 5 h, $^{15}\text{NH}_4$ peak at 2 d).

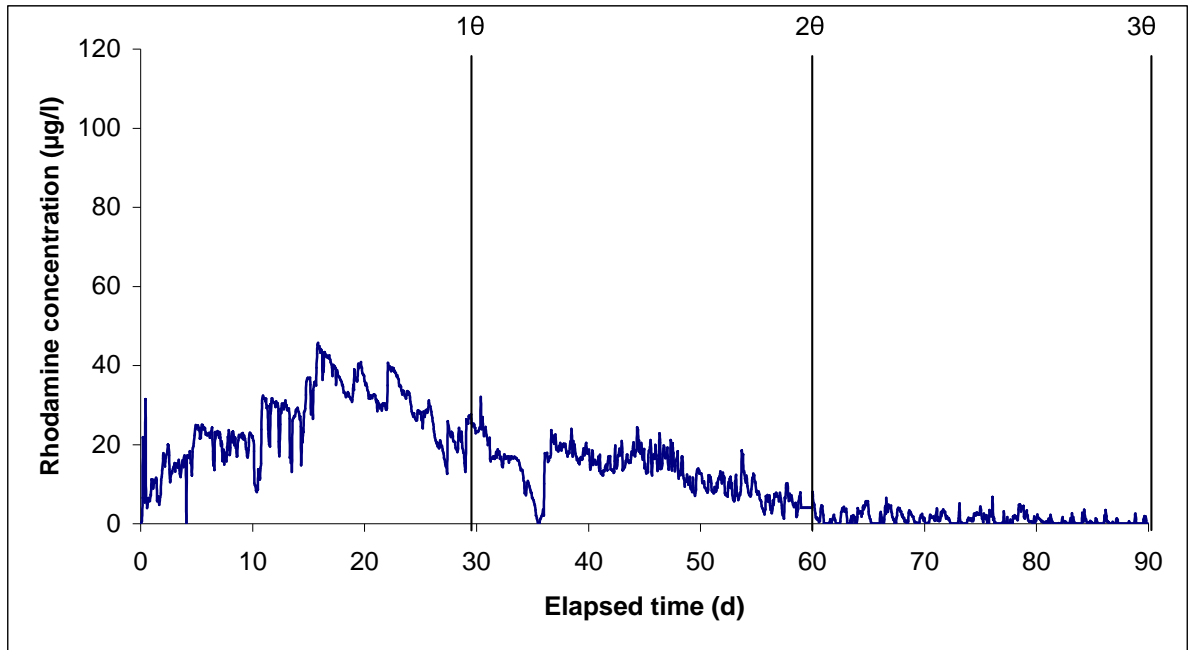


Figure 1: Rhodamine dispersion curve measured in real time for the summer 2006.

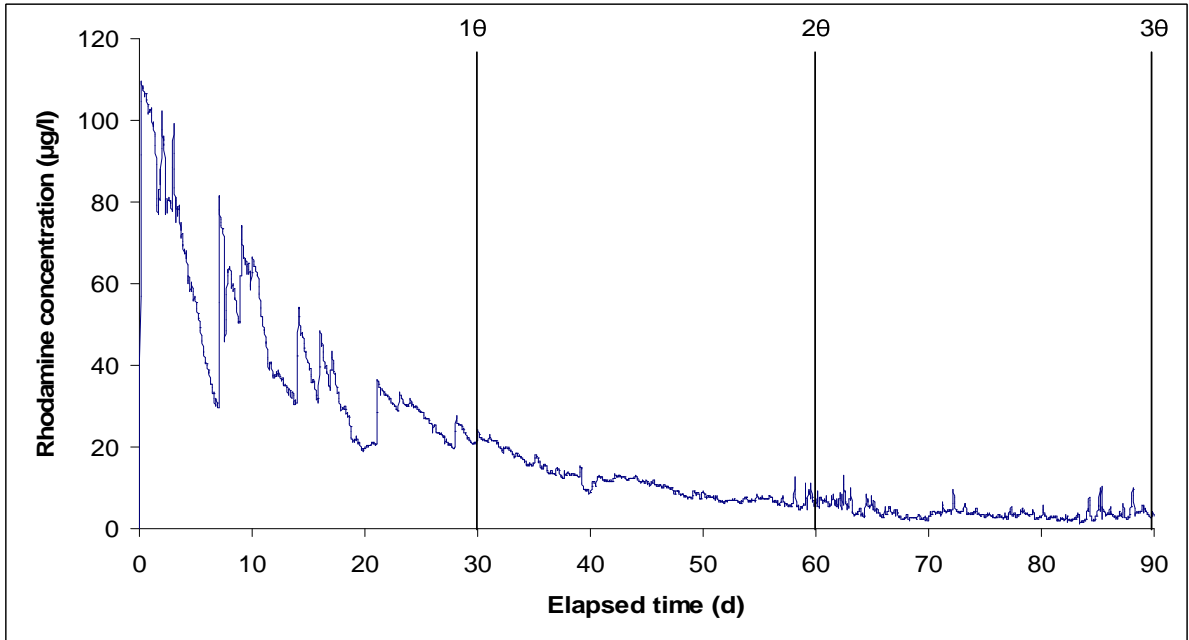


Figure 2: Rhodamine dispersion curve measured in real time for the winter 2007.

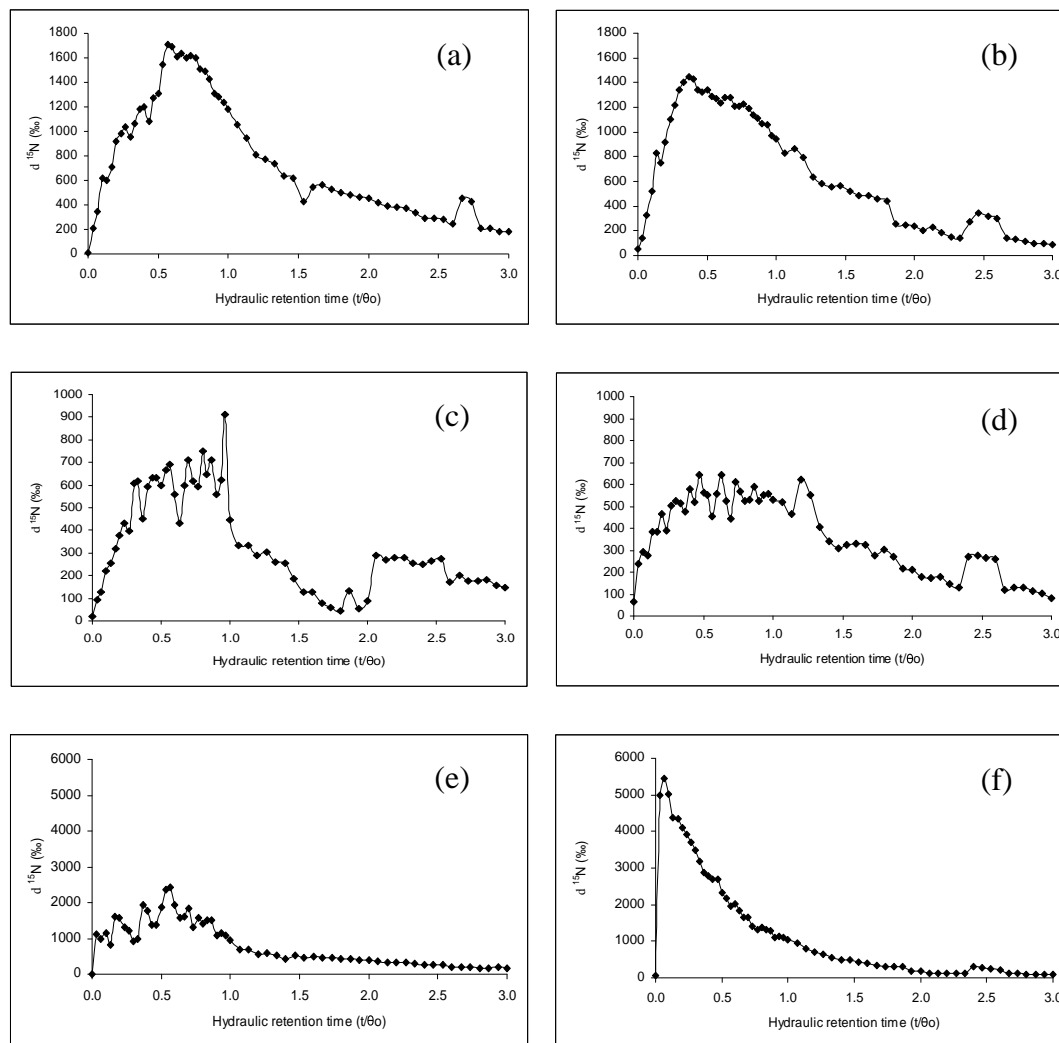


Figure 3: (a) $d^{15}\text{N}$ values for suspended organic nitrogen fractions in summer 2006; (b) $d^{15}\text{N}$ values for suspended organic nitrogen fractions in winter 2007; (c) $d^{15}\text{N}$ values for soluble organic nitrogen fractions in summer 2006; (d) $d^{15}\text{N}$ values for soluble organic nitrogen fractions in winter 2007; (e) $d^{15}\text{N}$ values for ammonium nitrogen fractions in summer 2006; and (f) $d^{15}\text{N}$ values for ammonium nitrogen fractions in winter 2007.

When the $d^{15}\text{N}$ ammonium values were converted into actual ^{15}N concentrations (Figures 4e and 4f), the peak concentration measured $54.80 \mu\text{g/l}$ in summer 2007 and $141 \mu\text{g/l}$ in winter 2007 - i.e., almost three times as much leaving the pond unchanged compared to the summer.

Interestingly, the suspended organic nitrogen $d^{15}\text{N}$ values for summer and winter show similar trends. The $d^{15}\text{N}$ peak value for summer 2006 occurred at 17 d, and measured 1709.6‰ . The ^{15}N peak value for winter 2007 was not much lower, measuring 1443.8‰ , but occurred at 11 days. However, when the actual ^{15}N concentrations for these peaks are compared, the ^{15}N incorporated into the maximum summer 2006 value measured $29.71 \mu\text{g/l}$ compared with a maximum concentration of $13.67 \mu\text{g/l}$ for winter 2007 - more than double.

Passages of the soluble organic nitrogen fraction between summer and winter data sets also showed broadly similar patterns. The $\delta^{15}\text{N}$ peak height of summer 2006 (910.8 ‰) is questionable: it is possibly an anomaly from the main data set. The second highest value is 749.8 ‰, which occurred 24 days after spike injection. The maximum $\delta^{15}\text{N}$ value for winter 2007 was 644.1 ‰, this occurred 19 days after spike injection. The trends for summer and winter soluble organic nitrogen fractions (observable in Figures 3c and 3d) also corroborate well; the bulk of the peak area occurring in 0 - 1 θ , with very similar peak values. However, once $\delta^{15}\text{N}$ values are converted into actual ^{15}N concentrations (Figures 4c and 4d), it can be observed that almost five times more ^{15}N was incorporated into soluble organic nitrogen in the summer than in the winter (14.39 $\mu\text{g/l}$ and 3.15 $\mu\text{g/l}$ in summer and winter respectively).

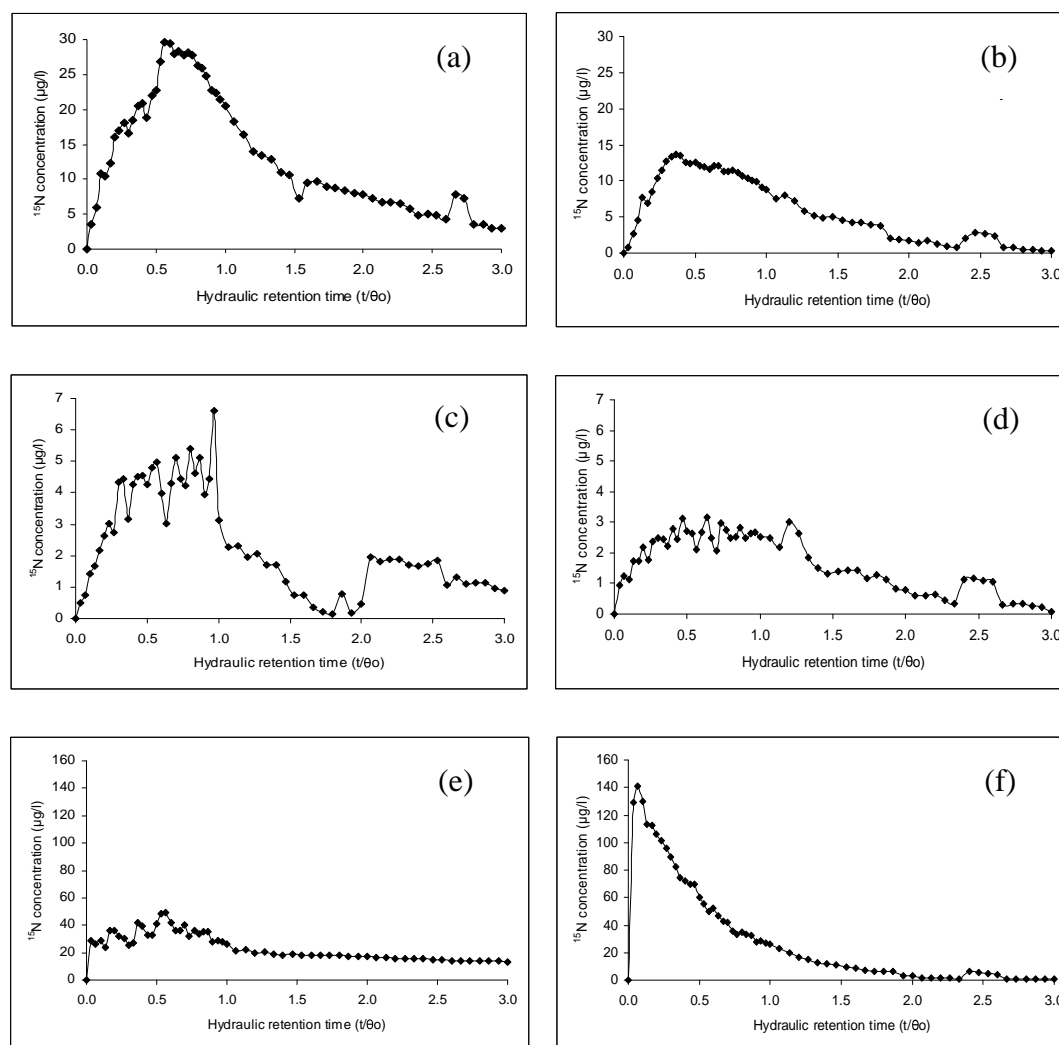


Figure 4: (a) ^{15}N concentrations for suspended organic nitrogen fractions in summer 2006; (b) ^{15}N concentrations for suspended organic nitrogen fractions in winter 2007; (c) ^{15}N concentrations for soluble organic nitrogen fractions in summer 2006; (d) ^{15}N concentrations for soluble organic nitrogen fractions in winter 2007; (e) ^{15}N concentrations for ammonium nitrogen fractions in summer 2006; and (f) ^{15}N concentrations for ammonium nitrogen fractions in winter 2007.

Table 1: Summary of the maximum $\delta^{15}\text{N}$ values, corresponding ^{15}N concentrations per nitrogen fraction, and the elapsed time at which these peaks occurred in summer and winter.

Nitrogen fraction	Summer 2006			Winter 2007		
	$\delta^{15}\text{N}$ (‰)	^{15}N ($\mu\text{g/l}$)	Elapsed time of peak height (d)	$\delta^{15}\text{N}$ (‰)	^{15}N ($\mu\text{g/l}$)	Elapsed time of peak height (d)
Suspended organic nitrogen	1709.6	29.71	17	1443.8	13.67	11
Soluble organic nitrogen	910.8	14.39	29	644.1	3.15	19
Ammonium nitrogen	2415.3	54.80	17	5454.4	141.00	2

CONCLUSIONS

This research has shown that ammonium nitrogen is rapidly taken up by the pond biomass (mainly algae) and assimilated into cell material, thus undergoing transformation from inorganic nitrogen to an organic fraction. This is subsequently released as soluble organic nitrogen as a by-product of cell metabolism, but it is mainly released through the degradation of cells through algal die-off. More than double the amount of ^{15}N was taken up in the suspended organic nitrogen fraction in summer compared to that in winter, and just under five times as much ^{15}N appeared as soluble organic nitrogen in the summer than in winter. As temperatures and insolation are higher in the summer than winter and thus cell synthesis and metabolic functions occur faster, it is natural that a high proportion of the influent $^{15}\text{NH}_4\text{Cl}$ should be uptaken very quickly by the components of the pond biomass that use inorganic substrates as their nutrient source. This is reflected by both the higher $\delta^{15}\text{N}$ and ^{15}N concentration values for suspended organic nitrogen apparent in the summer data set. Preliminary findings for the summer experiment therefore show that a large proportion of the $^{15}\text{NH}_4\text{Cl}$ leaves the pond unchanged, but that pond biomass does play a very important role in the uptake of influent ammonium nitrogen within the system. The $\delta^{15}\text{N}$ and ^{15}N concentrations of suspended organic nitrogen and soluble organic nitrogen were much lower in comparison to the summer data, demonstrating that uptake and assimilation rates are much less in winter than in summer; by far the largest proportion of ^{15}N left the pond in its unchanged $^{15}\text{NH}_4\text{Cl}$ fraction as a result of lower temperatures and insolation amongst other influencing variables affecting pond operability and performance.

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