

Appendix A ~ Wastewater flows

The influent wastewater BOD of the Esholt wastewater treatment works was found to vary considerably on a weekly basis and, as a result, it was decided to load the ponds weekly. It was of critical importance to the pond tracer studies that the hydraulic flow be kept as stable as possible, and the hydraulic regime was therefore kept as tightly controlled as possible. In order to change the influent BOD load to ensure the optimal pond loading for PFP's within the UK of 80 kg/ha d, the ratio of influent wastewater to freshwater was adjusted according to the BOD of the wastewater measured in the laboratory. The loading table presented in Table A.1 was prepared for the Green PFP, using the chosen theoretical hydraulic retention time of thirty days, where the total flow per day was calculated using equation A.1:

$$Q_T = \frac{V_{PFP}}{\theta_{theo}} \quad (\text{A.1})$$

where Q_T = total flow per day (m^3/d)

V_{PFP} = volume of primary facultative pond (which for the Green pond, was 51.3 m^3)

θ_{theo} = chosen theoretical hydraulic retention time (d)

This produced a total flow (Q_T) = $1.71 \text{ m}^3/\text{d}$ (1,188 ml/min).

The daily BOD loading in kg BOD/ $\text{m}^2 \text{ d}$ to produce an overall BOD loading of 80 kg/ha d was calculated using equation A.2:

$$L_1 = \frac{A_{PFP}}{10,000} \times \lambda_s \quad (\text{A.2})$$

where L_1 = influent BOD (kg BOD/ $\text{m}^2 \text{ d}$)

A_{PFP} = area of the PFP (for the Green pond, 33.6 m^2)

λ_s = BOD loading (kg/ha d)

This calculation produced a daily BOD loading of 0.2688 kg/m² d. The loading table, Table A.1, was prepared using the observed and calculated values to produce the required influent wastewater and freshwater flows in millilitres per minute, and these were altered according to the weekly BOD concentration obtained in the laboratory. The loading table was kept in the site log book, and proved to be a valuable and essential tool throughout the experiments.

Table A.1: Loading table for the Green pond with a theoretical hydraulic retention time of 30 d and a BOD loading of 80 kg/ha d.

BOD		Wastewater and freshwater inflow			
BOD mg/l	BOD load kg/m³/d	Q_{ww} (m³/d)	Q_{ww} (ml/min)	Q_{H2O} (ml/min)	Q_T (ml/min)
200	0.200	1.34	933	255	1188
225	0.225	1.19	830	358	1188
250	0.250	1.08	747	441	1188
275	0.275	0.98	679	509	1188
300	0.300	0.90	622	566	1188
325	0.325	0.83	574	614	1188
350	0.350	0.77	533	655	1188
375	0.375	0.72	498	690	1188
400	0.400	0.67	467	721	1188
425	0.425	0.63	439	749	1188
450	0.450	0.60	415	773	1188
475	0.475	0.57	393	795	1188
500	0.500	0.54	373	815	1188
525	0.525	0.51	356	832	1188
550	0.550	0.49	339	849	1188
575	0.575	0.47	325	863	1188
600	0.600	0.45	311	877	1188
625	0.625	0.43	299	889	1188
650	0.650	0.41	287	901	1188
675	0.675	0.40	277	911	1188
700	0.700	0.38	267	921	1188
725	0.725	0.37	257	931	1188
750	0.750	0.36	249	939	1188
775	0.775	0.35	241	947	1188
800	0.800	0.34	233	955	1188
825	0.825	0.33	226	962	1188
850	0.850	0.32	220	968	1188
875	0.875	0.31	213	975	1188
900	0.900	0.30	207	981	1188
925	0.925	0.29	202	986	1188
950	0.950	0.28	196	992	1188
975	0.975	0.28	191	997	1188
1000	1.000	0.27	187	1001	1188

In the same way, Table A.2 was prepared for the Blue pond, which was also operated with a BOD loading of 80 kg/ha d, and a theoretical hydraulic retention time of thirty days, using equations A.1 and A.2. The total flow for the Blue PFP operating under this loading regime was 1.96 m³/d (1,391 ml/min). The calculated BOD load (L_i), was 0.3248 kg/m² d

Table A.2: Loading table for the Blue pond with a theoretical hydraulic retention time of thirty days, and a BOD loading of 80 kg/ha d.

BOD		Wastewater and freshwater inflow			
BOD mg/l	BOD load kg/m³/d	Q_{ww} (m³/d)	Q_{ww} (ml/min)	Q_{H2O} (ml/min)	Q_T (ml/min)
200	0.200	1.62	1128	233	1361
225	0.225	1.44	1002	359	1361
250	0.250	1.30	902	459	1361
275	0.275	1.18	820	541	1361
300	0.300	1.08	752	609	1361
325	0.325	1.00	694	667	1361
350	0.350	0.93	644	717	1361
375	0.375	0.87	601	760	1361
400	0.400	0.81	564	797	1361
425	0.425	0.76	531	830	1361
450	0.450	0.72	501	860	1361
475	0.475	0.68	475	886	1361
500	0.500	0.65	451	910	1361
525	0.525	0.62	430	931	1361
550	0.550	0.59	410	951	1361
575	0.575	0.56	392	969	1361
600	0.600	0.54	376	985	1361
625	0.625	0.52	361	1000	1361
650	0.650	0.50	347	1014	1361
675	0.675	0.48	334	1027	1361
700	0.700	0.46	322	1039	1361
725	0.725	0.45	311	1050	1361
750	0.750	0.43	301	1060	1361
775	0.775	0.42	291	1070	1361
800	0.800	0.41	282	1079	1361
825	0.825	0.39	273	1088	1361
850	0.850	0.38	265	1096	1361
875	0.875	0.37	258	1103	1361
900	0.900	0.36	251	1110	1361
925	0.925	0.35	244	1117	1361
950	0.950	0.34	237	1124	1361
975	0.975	0.33	231	1130	1361
1000	1.000	0.32	226	1135	1361

However, in reality, loading the Green PFP was not a simple and straightforward task. The box fabricated better to control the freshwater influent flow, was indeed a better method of supplying water to the PFP's than the previous method, but this also was not without its problems. The box design did not prove wholly reliable and flows were therefore set as best they could be for that time. For varying reasons, the flows also dropped between site visits. The freshwater flow was altered by changes in the head pressure of the water tank, the tap valve working a little loose, or too much water feeding one of the other ponds. The wastewater flows dropped weekly because the hose tail filters (suspended in the main works inlet channel, and attached to the PFP influent feed pipes) accumulated debris in between cleaning periods, and the bore of the tubing gradually became coated in an ever thickening layer of biofilm, which reduced the cross-sectional area of the pipe and inhibited the flow.

Table A.3 shows the mean influent and effluent flows for the Green PFP over the experimental period. The mean daily influent flow was simply calculated by equation A.3:

$$Q_{mean} = \frac{(Q_{initial} - Q_{end})}{2} \quad (A.3)$$

where Q_{mean} = the average daily flow (m³/d)

$Q_{initial}$ = the flow set, or reset at every site visit (m³/d)

Q_{end} = the flow measured upon each return to site (m³/d)

The net PFP effluent flows which were used both to calculate the theoretical hydraulic retention time (θ_0), and for various experimental calculations, incorporated a correction factor for net rainfall or net evaporation. Weekly data was collected using a Casella hook-gauge evaporimeter, which was located adjacent to the three PFP's. Net rainfall, or evaporation, for a set period, was then divided by the number of days within that period, and the net PFP effluent flow calculated according to equation A.4 (Abis, 2002):

$$Q_{effluent} = Q_{mean} \pm \{[(netE_v \text{ or } R_f) \times A_{PFP}] \times 10^{-3}\} \quad (A.4)$$

where $Q_{effluent}$ = net PFP effluent flow (m^3/d)

Q_{mean} = average daily influent flow (m^3/d)

$net E_v \text{ or } R_f$ = daily net evaporation or rainfall (mm/d)

Table A.3: Actual Green PFP influent and effluent flows for the winter 2006 experimental run.

DATE (Period flows measured from and to)		Influent flows			Net Rainfall (+) or Evaporation (-) (mm/d)	Effluent flows
From	To	Set flow (m^3/d)	End flow (m^3/d)	Mean flow (m^3/d)		Net flow (m^3/d)
20-Jan	24-Jan	1.66	1.30	1.48	0.55	1.50
24-Jan	31-Jan	1.66	1.70	1.68	0.08	1.68
31-Jan	03-Feb	1.66	1.38	1.52	-0.24	1.51
03-Feb	07-Feb	1.50	1.98	1.74	-1.90	1.68
07-Feb	14-Feb	1.67	1.99	1.83	0.99	1.86
14-Feb	17-Feb	1.76	1.14	1.45	3.41	1.56
17-Feb	21-Feb	1.79	1.81	1.80	1.83	1.86
21-Feb	24-Feb	1.81	1.57	1.69	2.43	1.77
24-Feb	28-Feb	1.81	1.72	1.77	0.62	1.79
28-Feb	03-Mar	1.81	1.61	1.71	0.62	1.73
03-Mar	07-Mar	1.81	1.61	1.71	0.62	1.73
07-Mar	10-Mar	1.83	1.64	1.74	0.62	1.76
10-Mar	14-Mar	1.64	2.36	2.00	3.11	2.10
14-Mar	17-Mar	1.92	1.76	1.84	3.11	1.94
17-Mar	21-Mar	1.70	1.99	1.85	-0.65	1.82
21-Mar	24-Mar	1.77	1.66	1.72	-0.65	1.69
24-Mar	28-Mar	1.79	1.79	1.79	5.50	1.97
28-Mar	31-Mar	1.77	1.71	1.74	5.50	1.92
31-Mar	04-Apr	1.73	1.76	1.75	1.71	1.80
04-Apr	07-Apr	1.76	1.76	1.76	1.71	1.82
07-Apr	11-Apr	1.76	1.44	1.60	1.23	1.64
11-Apr	17-Apr	1.79	1.70	1.75	0.62	1.77

Mean total influent flow = $1.72 m^3/d$

Mean total effluent flow = $1.77 m^3/d$

$\theta = 29.0 d$

Table A.4: Actual Blue PFP influent and effluent flows for the summer 2006 experimental run.

DATE (Period flows measured from and to)		Influent flows			Rainfall (+) or Evaporation (-) (mm/d)	Effluent flows
From	To	Set flow (m ³ /d)	End flow (m ³ /d)	Mean flow (m ³ /d)		Net flow (m ³ /d)
14-Aug	16-Aug	1.99	1.97	1.98	<i>No data</i>	1.98
16-Aug	22-Aug	1.83	2.00	1.92	<i>No data</i>	1.92
22-Aug	25-Aug	2.00	2.04	2.02	<i>No data</i>	2.02
25-Aug	29-Aug	1.96	1.94	1.95	8.08	2.28
29-Aug	04-Sep	1.94	1.93	1.94	2.21	2.02
04-Sep	12-Sep	1.93	2.06	2.00	-0.40	1.98
12-Sep	19-Sep	2.06	2.10	2.08	2.29	2.17
19-Sep	03-Oct	2.10	2.09	2.10	0.85	2.13
03-Oct	10-Oct	2.09	2.09	2.09	1.15	2.14
10-Oct	17-Oct	2.02	1.96	1.99	1.55	2.05
17-Oct	24-Oct	1.93	1.98	1.96	0.79	1.99
24-Oct	31-Oct	1.98	1.70	1.84	4.04	2.00
31-Oct	07-Nov	1.70	1.97	1.84	-0.79	1.80
07-Nov	12-Nov	1.97	1.97	1.97	0.89	2.01

Mean total influent flow = 1.98 m³/d

Mean total effluent flow = 2.04 m³/d

$\theta = 28.9$ d

Table A.5: Actual Blue PFP influent and effluent flows for the winter 2007 experimental run.

DATE (Period flows measured from and to)		Influent flows			Rainfall (+) or Evaporation (-) (mm/d)	Effluent flows
From	To	Set flow (m ³ /d)	End flow (m ³ /d)	Mean flow (m ³ /d)		Net flow (m ³ /d)
05-Feb	12-Feb	1.92	2.01	1.97	5.25	2.18
12-Feb	19-Feb	2.02	2.02	2.02	2.16	2.11
19-Feb	26-Feb	2.09	1.99	2.04	2.51	2.14
26-Feb	05-Mar	1.98	1.90	1.94	2.61	2.05
05-Mar	12-Mar	1.90	2.02	1.96	-1.20	1.91
12-Mar	14-Mar	1.97	1.97	1.97	0.49	1.99
14-Mar	19-Mar	1.97	1.96	1.97	0.49	1.98
19-Mar	26-Mar	1.97	1.86	1.92	1.39	1.97
26-Mar	02-Apr	1.92	1.97	1.95	1.39	2.00
02-Apr	16-Apr	2.00	2.00	2.00	-1.58	1.94
16-Apr	23-Apr	1.96	1.97	1.97	-1.20	1.92
23-Apr	30-Apr	1.94	2.17	2.06	2.08	2.14
30-Apr	08-May	2.17	1.96	2.07	1.14	2.11

Mean total influent flow = 1.99 m³/d

Mean total effluent flow = 2.03 m³/d

$\theta = 28.9$ d

Appendix B ~ Rhodamine WT and $^{15}\text{NH}_4\text{Cl}$ calculations

The Rhodamine WT spike preparation was based on the principle that the hydraulic regime of the PFP's was operating as a completely mixed reactor. The maximum detectable limit of the Rhodamine sonde probe was 200 $\mu\text{g}/\text{l}$, and therefore the in-pond concentration per litre of pond volume (assuming complete mixing) was calculated to be below this maximum threshold concentration.

A 20% Rhodamine WT stock solution was used to prepare the dye tracer slug, the exact concentrations of which are presented in Table 4.3. The slug was prepared to ensure a chosen in-pond concentration of 110 $\mu\text{g}/\text{l}$. The calculations were made according to equation B.1:

$$W_{Rho} = \left[\frac{(110 \mu\text{g}/\text{l} \times V_{PFP})}{1,000,000} \right] \times 5 \quad (\text{B.1})$$

where W_{Rho} = weight of rhodamine WT (20%) needed for slug (g)
 V_{PFP} = volume of PFP (m^3).

The stable isotope compound of $^{15}\text{NH}_4\text{Cl}$ had a purity of 98%, and the concentration needed for the spike slug was determined by using equations B.2, B.3, and B.4. Firstly, the theoretical amount of ^{15}N incorporated within the pond water column, or influent wastewater was calculated by equation B.2:

$$C_{PFP} = C \times \frac{0.36(\text{mg } ^{15}\text{N})}{100(\text{mgTotal} - \text{N})} \quad (\text{B.2})$$

where C_{PFP} = concentration (mg $^{15}\text{N}/\text{l}$) within PFP water column or wastewater influent.

C = concentration (mg NH_3/l) of ammonium-nitrogen with which to calculate the required amount of $^{15}\text{N}/\text{l}$ within either the pond water column or the wastewater influent (i.e., an in-pond average concentration of 13 mg NH_4^+/l was used for the Green pond winter 2006 spike; the average influent wastewater

concentration of 40 mg NH_4^+ /l was used for both the summer 2006 and the winter 2007 Blue PFP spikes).

The value of 0.36 mg ^{15}N in the top line of equation B.2 is the natural abundance of ^{15}N in the atmosphere.

The C_{PFP} concentration of ^{15}N within the pond column or wastewater sample (calculated in equation B.2), was used in conjunction with the PFP volume to obtain the concentration of ^{15}N per litre of pond volume using equation B.3:

$$C^{15}\text{N} = C_{PFP} \times V_{PFP} \quad (\text{B.3})$$

where $C^{15}\text{N}$ = the calculated concentration of ^{15}N (mg/l) needed per litre of pond water.

The quantity of labelled ammonium chloride used to spike the PFP's was calculated using equation B.4:

$$^{15}\text{NH}_4\text{Cl}_{PFP} = \frac{\left[C^{15}\text{N} \times \left(\frac{54.5}{15} \right) \right] \times \left[\frac{100}{98} \right]}{1,000} \quad (\text{B.4})$$

where $^{15}\text{NH}_4\text{Cl}_{PFP}$ = the quantity of $^{15}\text{NH}_4\text{Cl}$ (g) used in each spike.

The value 54.5 is the relative atomic mass of $^{15}\text{NH}_4\text{Cl}$.

Appendix C ~ Dionex data

As detailed in section 4.5.3, the high chloride concentration contained in the effluent spiked samples caused numerous problems in ion chromatographic analysis. Analysis was conducted by coupling an absorbance detector upstream of the electrochemical conductivity cell. Figures C.1 and C.2 show correlation scatter plots obtained by the two different detection methods from spiked effluent samples, and weekly pond monitoring samples respectively.

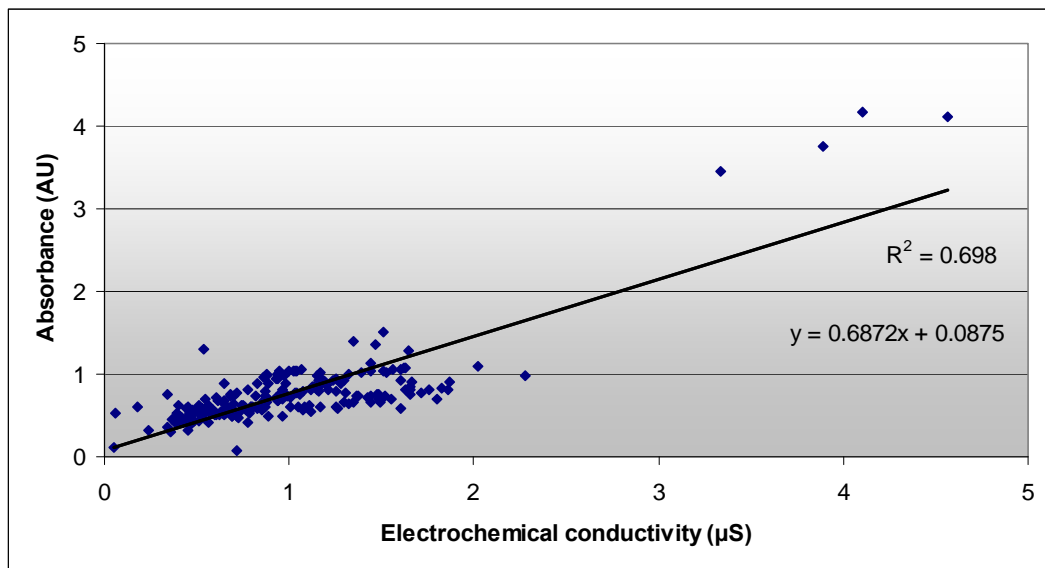


Figure C.1: Correlated data for nitrate analysis from experimentally spiked effluent samples.

The high chloride concentrations in the spiked effluent samples affected the base line stability and anion peak heights so badly in the electrochemical conductivity cell that the chromatogram output revealed that these results could not be reliably used. A paired t -test ($\alpha = 0.05$) revealed that there was a significant difference ($t(216) = 10.097$; $p = 0.000$) between the two methods, and the electrochemical data were disregarded. The absorbance detector performed much better upon analysis of individual chromatograms, the cell being seemingly unaffected by the high chloride concentrations. This data set was corrected for nitrate concentrations (by subtracting the internal standard from the obtained output), and the results used in the calculation of ^{15}N concentrations and to determine the total nitrogen mass balances.

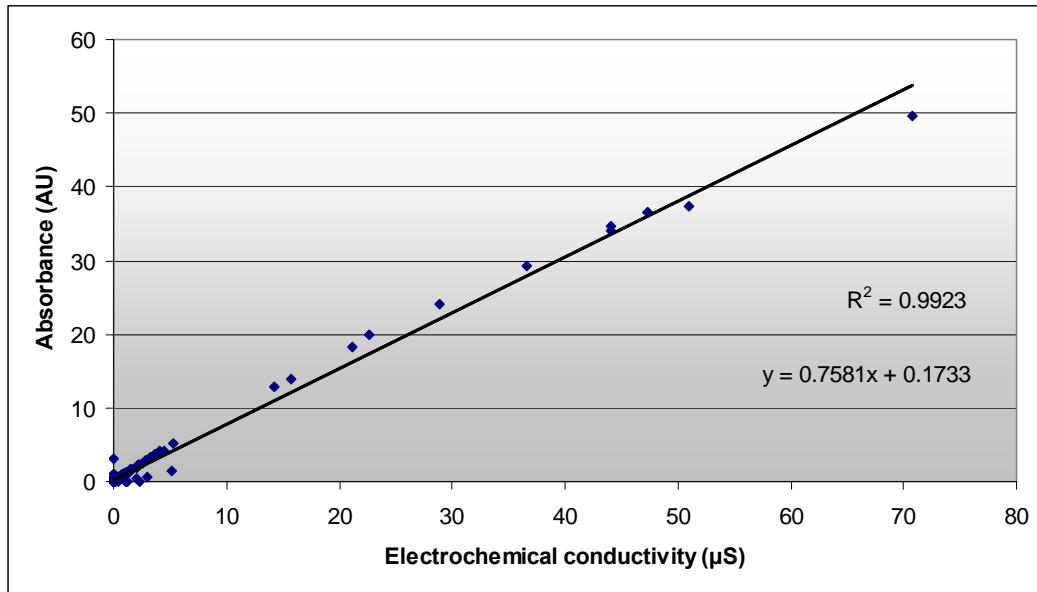


Figure C.2: Correlated data for nitrate analysis from weekly pond monitoring samples.

The weekly PFP monitoring samples were also analysed by the two different methods of electrochemical conductivity and absorbance detection. The results of the raw data set between the two methods did differ significantly (paired samples *t*-test, $t(290) = 2.782$; $p = 0.006$), although there was very high correlation ($R^2 = 0.9923$) between the two data sets. Nine data points were removed from the data set which were known to have been incorrect through introduced error in analytical procedures, and the data were reanalysed. The new *t*-test value revealed that there was no significant difference between the two analytical methods ($t(281) = 1.349$; $p = 0.178$). The recorded values between the two data sets did differ slightly, sometimes the electrochemical method showing very slightly higher concentrations than the absorbance method, and vice versa. When these differences arose, the higher concentration value was used in the calculation of mass balances.

Appendix D ~ Mass spectrometer data conversion

In 2008, Camargo Valero derived an equation, as yet unpublished, which converted the $\delta^{15}\text{N}$ (‰) fraction per sample into actual ^{15}N concentration data for that sample ($\mu\text{g/l}$). Firstly, it was necessary to obtain the average concentration for each nitrogen fraction from the chemical data from all of the spiked samples, analysed in the laboratory. The average value had to be used in the calculation as the data in each data set (Figures D.1 – D.12) was highly variable.

However, initial analysis of the data revealed some interesting, but problematical, differences in some of the samples. Of the 49 spiked samples used in the analysis of the winter 2006 spike, only 80% (39/49) of samples could be used to determine the average concentrations of suspended organic-nitrogen, soluble organic-nitrogen, and ammonium-nitrogen. In the same way, only 80% (48/60), and 82% (49/60) of summer 2006 and winter 2007 samples respectively, could be used for the calculation of average values of the same three nitrogen fractions. This was because the values obtained for each fraction did not work out as they should have done for these omitted samples. Typically, results for suspended and soluble organic-nitrogen returned negative values when ammonium was deducted from raw and filtered TKN concentrations, meaning that ammonium concentrations were larger than the TKN concentrations. This could have happened for a few reasons.

All of the samples on site were preserved with the addition of 1 ml 3M HC per 100 ml sample. This had a coagulating effect on the colloidal and suspended solid fraction of the PFP sample; thus, when samples were collected from the autosampler, the autosampler bottler had to be swilled a couple of times to re-suspend the thickish layer of organic material which had settled out in the bottom. The effect that freezing had on the samples made this problem worse. In both the winter 2006 and winter 2007 experimental runs, the samples within the autosampler underwent continual freezing and thawing. Frequently, during site visits throughout each of these periods, the samples in the autosampler bottler would be completely or partly frozen. This caused the formation of large flocs of solid organic material, which partitioned the organic and inorganic fractions

within each sample further. Upon return to the laboratory, the samples were appropriately combined to produce 24-hour composite samples. These samples were frozen for analysis at a later date, and this too contributed to the partitioning of solid organic, and soluble inorganic nitrogen fractions within the sample. When analysing the samples for ^{15}N , the samples were processed in batches. Each sample was shaken vigorously to re-suspend and fragment the solid organic fraction within each sample bottle, in order to obtain a representative raw TKN concentration. However, the analysis of TKN samples was a rate-limiting factor in the overall processing flow chain; therefore the samples were stored with Kjeldahl catalyst and 10 ml 18M H_2SO_4 in 100-ml Nalgene HDPE sample bottles and stored at 4°C . Samples were processed as quickly as they could be, but this lag time could well have induced changes between each nitrogen fraction comprising the total nitrogen pool. Time was a limiting factor, and, as the analysis was a highly laborious task and took place over many months, these discrepancies were not noticed until all of the nitrogen fractions for each sample has been analysed and their concentrations calculated.

It was decided to use all of the samples in each experimental run to obtain the average nitrate values for the calculation of ^{15}N concentrations, as each sample contained very low levels of nitrate.

Figured D.1 – D.12 show the concentrations for each of the four nitrogen fractions determined from chemical data obtained from each sample processed in the laboratory. As mentioned above, the samples which produced invalid results were not incorporated into the analysis.

Winter 2006

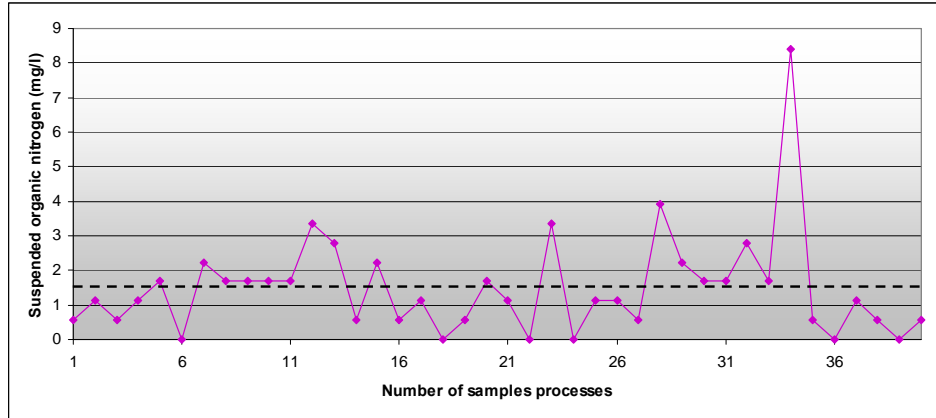


Figure D.1: Samples processed for winter 2006 suspended organic-nitrogen content. The number of samples processed was 39, and the average concentration was 1.5 mg suspended organic-nitrogen/l.

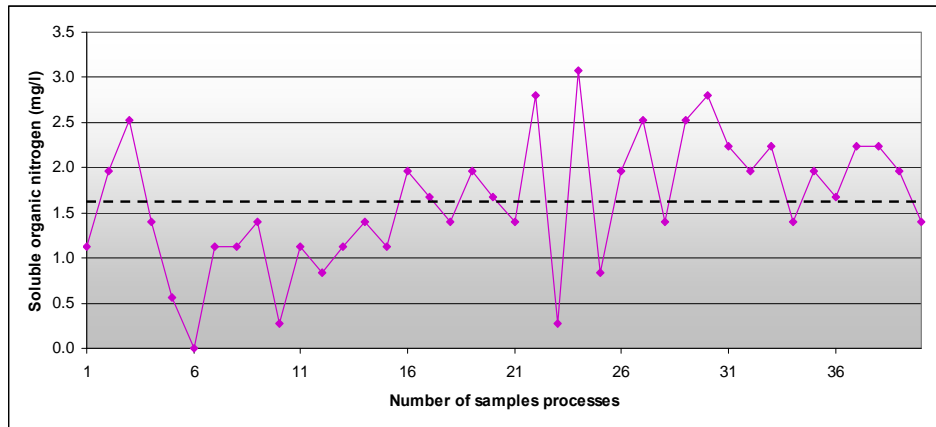


Figure D.2: Samples processed for winter 2006 soluble organic-nitrogen content. The number of samples processed was 39, and the average concentration was 1.6 mg soluble organic-nitrogen/l.

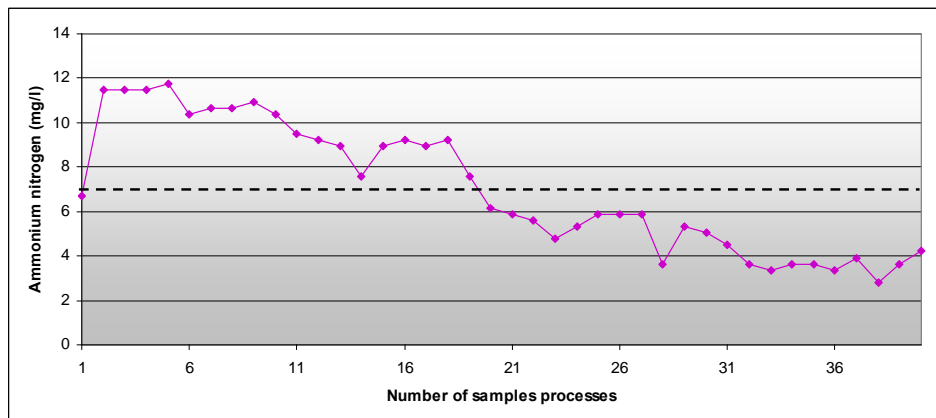


Figure D.3: Samples processed for winter 2006 ammonium-nitrogen content. The number of samples processed was 39, and the average concentration was 7 mg ammonium-nitrogen/l.

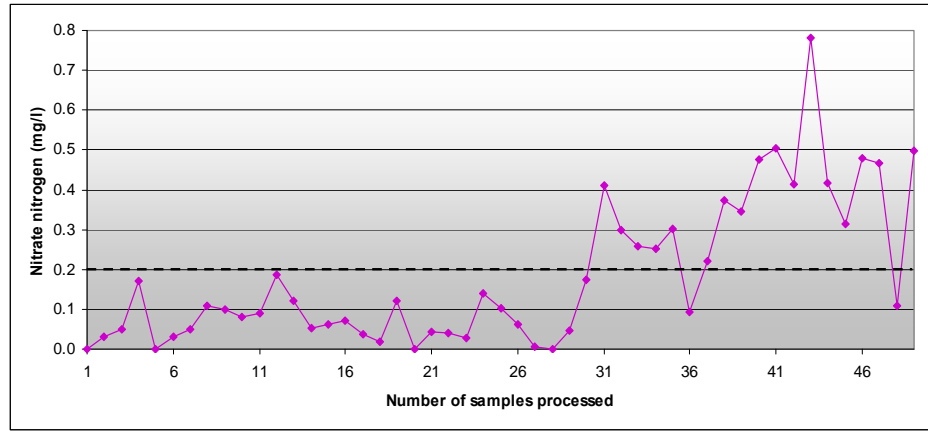


Figure D.4: Samples processed for winter 2006 nitrate-nitrogen content. The number of samples processed was 49, and the average concentration was 0.2 mg nitrate-nitrogen/l.

Summer 2006

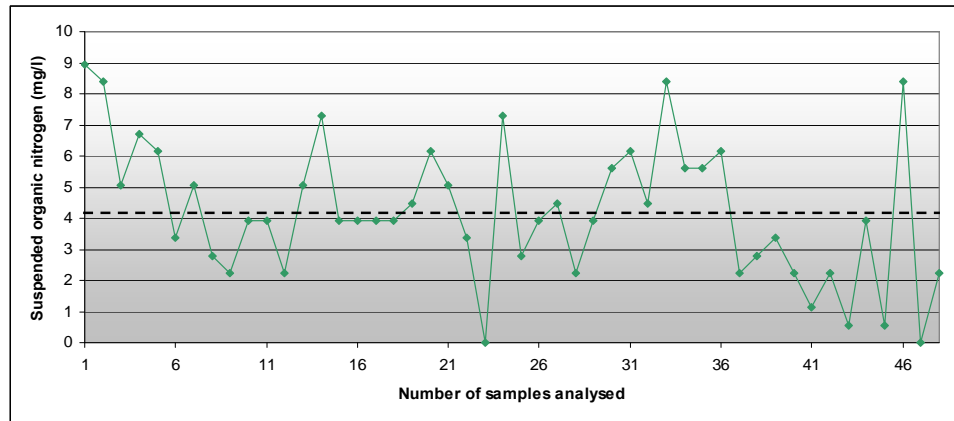


Figure D.5: Samples processed for summer 2006 suspended organic-nitrogen content. The number of samples processed was 48, and the average concentration was 4.2 mg suspended organic-nitrogen/l.

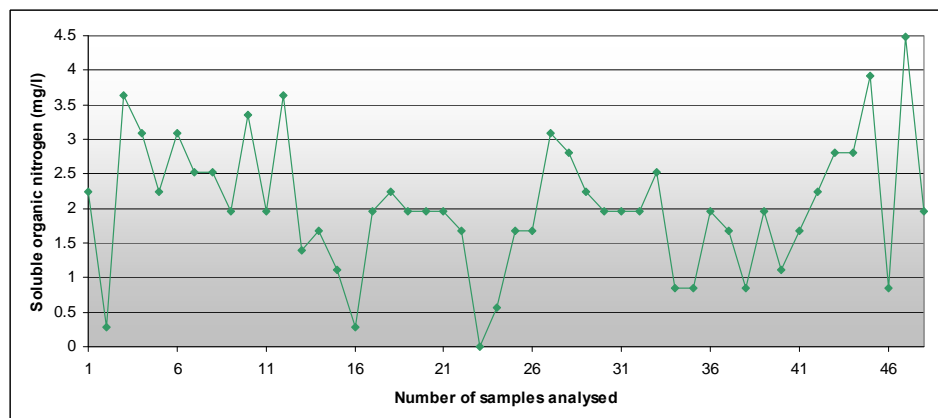


Figure D.6: Samples processed for summer 2006 soluble organic-nitrogen content. The number of samples processed was 48, and the average concentration was 2 mg soluble organic-nitrogen/l.

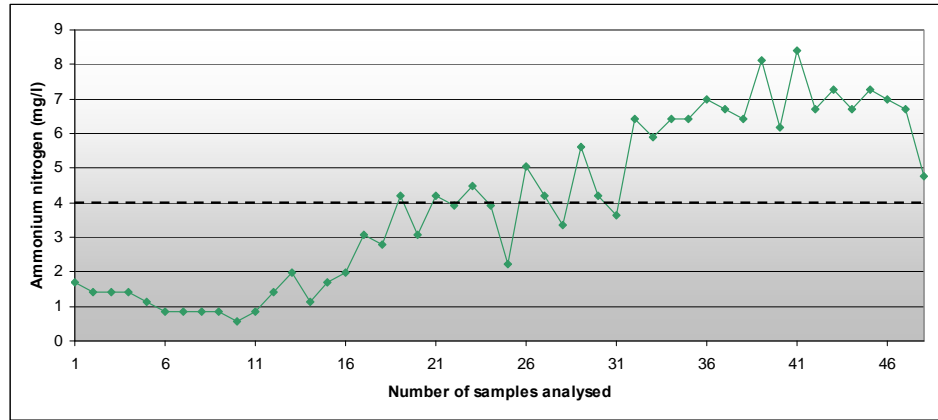


Figure D.7: Samples processed for summer 2006 ammonium-nitrogen content. The number of samples processed was 48, and the average concentration was 4 mg ammonium-nitrogen/l.

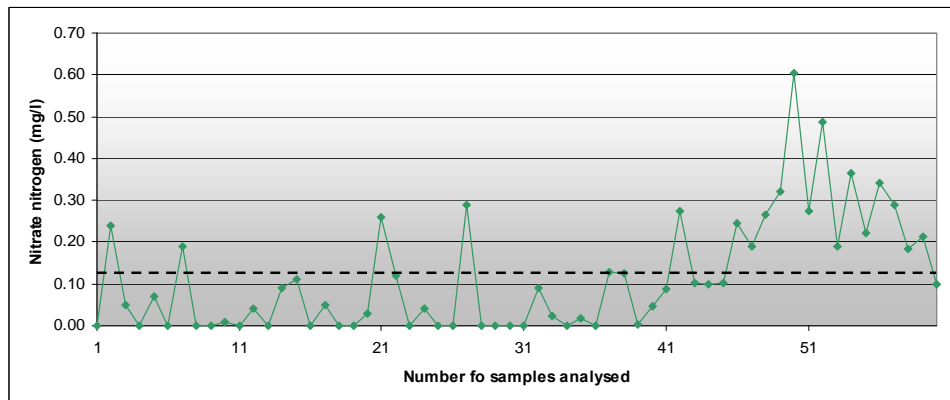


Figure D.8: Samples processed for summer 2006 nitrate-nitrogen content. The number of samples processed was 60, and the average concentration was 0.12 mg nitrate-nitrogen/l.

Winter 2007

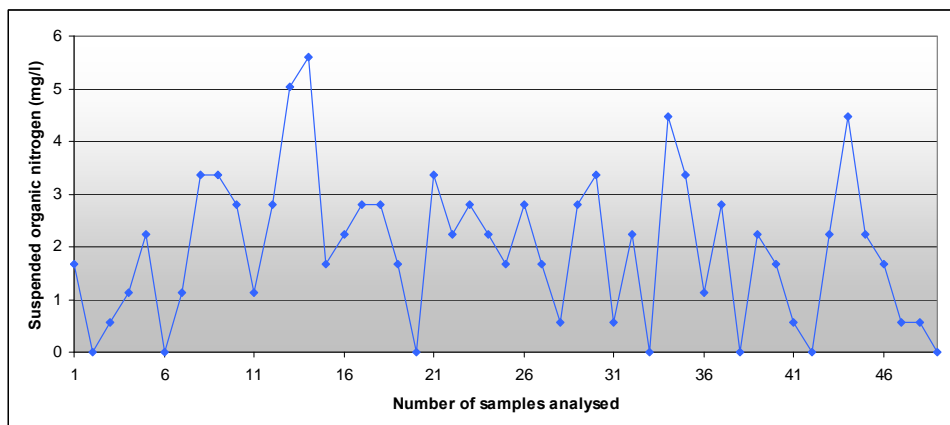


Figure D.9: Samples processed for winter 2007 suspended organic-nitrogen content. The number of samples processed was 49, and the average concentration was 1.9 mg suspended organic-nitrogen/l.

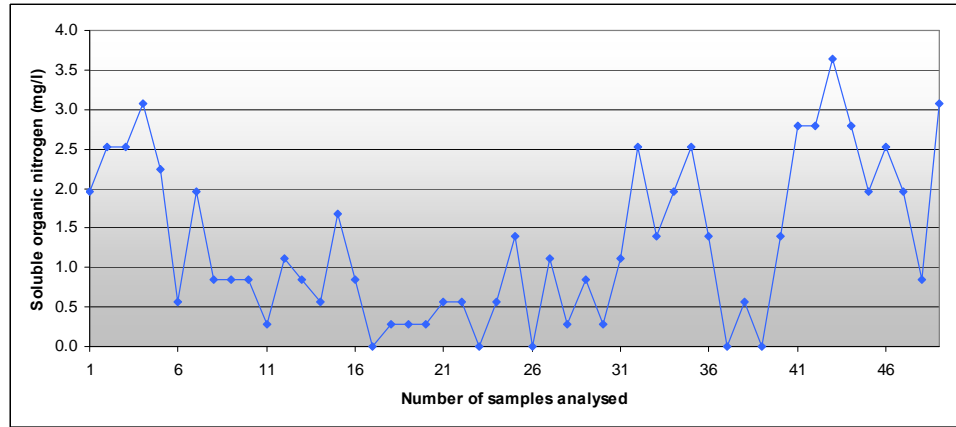


Figure D.10: Samples processed for winter 2007 soluble organic-nitrogen content. The number of samples processed was 49, and the average concentration was 1.2 mg soluble organic-nitrogen/l.

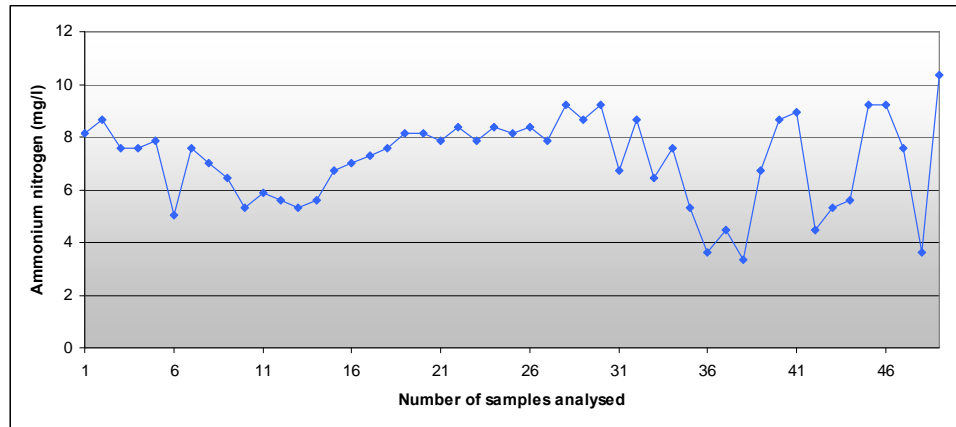


Figure D.11: Samples processed for winter 2007 ammonium-nitrogen content. The number of samples processed was 49, and the average concentration was 7 mg ammonium-nitrogen/l.

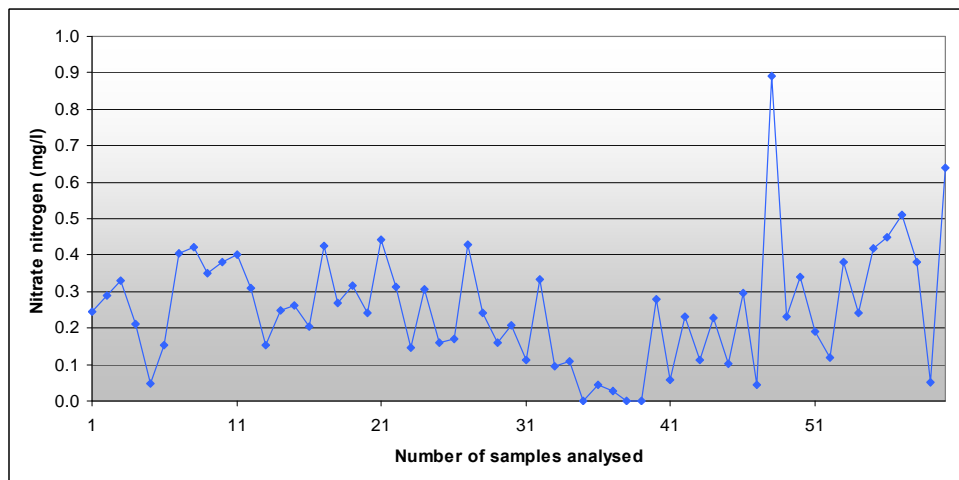


Figure D.12: Samples processed for winter 2007 nitrate-nitrogen content. The number of samples processed was 60, and the average concentration was 0.25 mg nitrate-nitrogen/l.

The calculation used to convert $\delta^{15}\text{N}$ (‰) into actual concentrations of ^{15}N within samples ($\mu\text{g/l}$) was devised by Camargo Valero in 2008, and is shown in equation D.1. The average concentration of each nitrogen fraction measured in the laboratory (as shown in Figures D.1 – D.12) was multiplied by the natural abundance of $^{15}\text{N}/^{14}\text{N}$ ratio (0.0036765) in the atmosphere, and divided by a factor of 1,000 to obtain the results in $\mu\text{g } ^{15}\text{N/l}$ of sample.

Concentrations of sample ^{15}N were also obtained from composite samples made right up until the point of spike introduction. These samples inevitably contained some fraction of ^{15}N ; thus all of the spiked samples processed were corrected for ^{15}N content by subtracting the background ^{15}N content from the actual ^{15}N content obtained from equation D.1.

$$^{15}\text{N}_{\text{sample}} = \frac{\text{Average } N_{\text{fraction}} \times \left\{ 0.0036765 \times \left[\left(\frac{\delta^{15}\text{N}_{\text{sample}}}{1,000} \right) + 1 \right] \right\}}{\left\{ 1 + 0.0036765 \times \left[\left(\frac{\delta^{15}\text{N}_{\text{sample}}}{1,000} \right) + 1 \right] \right\}} \times 1,000 \quad (\text{D.1})$$

The rate, and quantity of ammonia volatilized from the PFP's was calculated aerielly, using the total amount of ammonia absorbed in the boric acid, the surface area of the ammonia volatilization capture chamber, and the surface area of the PFP.

The quantity of nitrogen added to the sludge via sedimentation (measured in kg N/ha d) was determined by equation D.2:

$$\text{kg } N_{\text{sed.}} / \text{ha.d} = \frac{gTKN \times 10^{-3}}{(A_{\text{bucket}} \times 10^{-4}) \times t} \quad (\text{D.2})$$

where $gTKN$ = the average concentration of TKN, in grams

A_{bucket} = the surface area of a bucket (m^2)

t = the number of days over which the sludge was collected.

The amount of nitrogen in the PFP influent (total-N entering the pond), and leaving the pond in the pond effluent (in suspended and soluble organic-N fractions, and in inorganic nitrogen fractions as ammonium and nitrate) was calculated in kg N/ha d by equation D.3:

$$kgN_{in/out} / ha.d = \left(\frac{Q \times C_o}{A_{PFP}} \right) \times 10 \quad (D.3)$$

where Q = the influent flow to, or effluent flow from, the PFP, in m³/d

C_o = concentration of nitrogen, in whichever fraction (mg/l)

A_{PFP} = the surface area of the PFP (m²)

Appendix E ~ Ammonia volatilization data

The ammonia volatilization data for mass spectrometry analysis is presented in Table E.1. The results for both summer and winter data sets were not corrected for background concentration as, in each case, only one week's worth of data was collected prior to the commencement of the experimental runs. The winter 2006 background value cannot be accurately used as there was a problem in the processing of the sample within the mass spectrometer (observed by the excessively long retention time of the sample within the column, and also the very large peak height value).

Table E.1: Mass spectrometry ammonia volatilization data.

Sample Name	RT (Sec)	Height (nA)	delta N15	$\delta^{15}N$ air	$\delta^{15}N$ ($\mu\text{g/l}$)
winter 2006, background	39650.95	121.6	3.3	3.81	7.10
winter 2006, end week 4	125.00	3.36	-2.3	-17.3	6.95
winter 2006, end week 5	124.60	2.44	-20.1	-35.0	6.82
winter 2006, end week 6	124.90	7.80	-23.5	-38.4	6.80
winter 2006, end week 7	123.00	8.74	-22.4	-37.2	6.81
winter 2006, end week 8	121.30	6.90	-16.2	-31.1	6.85
winter 2006, end week 9	121.80	9.05	-12.9	-27.9	6.87
winter 2006, end week 10	121.80	2.46	-15.3	-30.3	6.86
winter 2006, end week 11	121.60	13.33	11.4	-3.8	7.04
summer 2006, background	117.00	21.82	0.7	-14.3	3.03
summer 2006, end week 1	116.00	0.39	18.08	2.9	3.09
summer 2006, end week 2	121.80	0.37	11.2	-4.0	3.06
summer 2006, end week 3	122.40	1.51	-12.2	-27.2	2.99
summer 2006, end week 4	116.60	7.49	-20.0	-34.7	2.97
summer 2006, end week 5	115.70	2.63	-13.8	-28.5	2.99
summer 2006, end week 6	121.90	8.15	-18.2	-33.1	2.98
summer 2006, end week 7	122.60	1.27	-2.5	-17.6	3.02
summer 2006, end week 8	122.30	0.87	0.6	-14.5	3.03
summer 2006, end week 9	122.50	5.75	-16.5	-31.4	2.98
summer 2006, end week 10	122.40	8.72	-26.1	-41.0	2.95
summer 2006, end week 11	122.80	3.82	-18.2	-33.1	2.98
summer 2006, end week 12	122.00	0.24	-6.6	-21.6	3.01
summer 2006, end week 13	122.70	4.52	-17.2	-32.1	2.98

Tables E.2 and E.3 present the total amount of ammonia volatilized and the rates of ammonia volatilization for the experimental run of winter 2006 and summer 2006, respectively.

Table E.2: Ammonia volatilization data for the winter 2006 experimental run.

Ammonia Volatilization - WINTER 2006 (start date Friday 20th January; end date Monday 17th April)

DATE	Total volatilized (mg/l)	volatilization rate (mg/m²/week)	volatilization rate (mg/m²/day)	volatilization rate (g/m²/d)	volatilization rate (mg/ha/day)	volatilization rate (g/ha/day)	Total pond area (mg/week)	Total rate/day for whole pond (mg/day)
20/01/2006	2.80	24.96	3.57	0.0036	35651	36	838.50	119.79
31/01/2006
10/02/2006
17/02/2006
24/02/2006	0.84	7.49	1.07	0.0011	10695	11	251.55	35.94
03/03/2006	2.52	22.46	3.21	0.0032	32086	32	754.65	107.81
10/03/2006	0.84	7.49	1.07	0.0011	10695	11	251.55	35.94
17/03/2006	1.96	17.47	2.50	0.0025	24955	25	586.95	83.85
24/03/2006	3.36	29.95	4.28	0.0043	42781	43	1006.20	143.74
31/03/2006	2.80	24.96	3.57	0.0036	35651	36	838.50	119.79
07/04/2006	1.40	12.48	1.78	0.0018	17825	18	419.25	59.89
14/04/2006	1.68	14.97	2.14	0.0021	21390	21	503.10	71.87
TOTAL	15.40	137.25	19.61	0.0196	196078	196	4611.76	658.82
AVERAGE	1.93	17.16	2.45	0.0025	24510	25	576.47	82.35

Table E.3: Ammonia volatilization data for the summer 2006 experimental run.

Ammonia Volatilization - SUMMER 2006 (start date Monday 14th August; end date Sunday 12th November)

DATE	Total volatilized (mg/l)	volatilization rate (mg/m²/week)	volatilization rate (mg/m²/day)	volatilization rate (g/m²/d)	volatilization rate (mg/ha/day)	volatilization rate (g/ha/day)	Total pond area (mg/week)	Total rate/day for whole pond (mg/day)
14/08/2006	0.56	4.99	0.71	0.0007	7130	7	202.64	28.95
22/08/2006	1.96	17.47	2.50	0.0025	24955	25	709.23	101.32
29/08/2006	0.28	2.50	0.36	0.0004	3565	4	101.32	14.47
05/09/2006	1.40	12.48	1.78	0.0018	17825	18	506.60	72.37
12/09/2006	0.56	4.99	0.71	0.0007	7130	7	202.64	28.95
19/09/2006	0.00	0.00	0.00	0.0000	0	0	0.00	0.00
26/09/2006	1.40	12.48	1.78	0.0018	17825	18	506.60	72.37
03/10/2006	0.84	7.49	1.07	0.0011	10695	11	303.96	43.42
10/10/2006	0.84	7.49	1.07	0.0011	10695	11	303.96	43.42
17/10/2006	2.24	19.96	2.85	0.0029	28520	29	810.55	115.79
24/10/2006	0.28	2.50	0.36	0.0004	3565	4	101.32	14.47
31/10/2006	0.56	4.99	0.71	0.0007	7130	7	202.64	28.95
07/11/2006	0.00	0.00	0.00	0.0000	0	0	0.00	0.00
13/11/2006	0.56	4.99	0.71	0.0007	7130	7	202.64	28.95
TOTAL	10.92	97.33	13.90	0.0139	139037	139	3951.44	564.49
AVERAGE	0.84	7.49	1.07	0.0011	10695	11	303.96	43.42

Hierdie werk is voltooi in die naam van Jesus Christus ons Here