### 4.0 Results and Discussion

### 4.1 Ammonia Volatilisation Results

Results showing the amount of ammonia volatilising from the ponds can be seen in Tables 4.1 and 4.2. The 'total ammonia lost' column represents the ammonia that was recorded volatilising from the surface of the pond in the investigation (assuming that the area of the on-pond chamber was a representative sample for the whole pond. The 'ammonia from the whole pond' column represents the amount of ammonia that was removed from the pond, from the influent to the effluent, irrespective of the method of removal. The '\% volatilised' column takes into account both of these parameters to calculate what percentage of the total ammonia removal from the pond can be accounted for by volatilisation.

### 4.1.1 Facultative Pond

Table 4.1 shows the results obtained in the facultative pond during the investigation.
Table 4.1 Results showing amount of ammonia volatilised as a percentage of total nitrogen removed from the facultative pond (2d.p)

|  | Total Ammonia Lost <br> g/d | Ammonia from whole pond <br> g/day | \% volatilised |
| :---: | :---: | :---: | :---: |
| Week 1 | 7.00 | 0.04 | 0.50 |
| Week 2 | 8.83 | 0.07 | 0.81 |
| Week 3 | 8.30 | 0.01 | 0.08 |
| Week 4 | 21.04 | 0.02 | 0.09 |
| Week 5 | 16.24 | 0.01 | 0.05 |
| Week 6 | 20.20 | 0.02 | 0.10 |
| Week 7\&8 | 16.91 | 0.01 | 0.05 |
| Week 9 | 22.95 | 0.01 | 0.03 |
| Week 10 | 18.51 | 0.01 | 0.08 |
| Week 11 | 18.51 | 0.01 | 0.05 |
| Week 12 | 9.15 | 0.02 | 0.17 |
| Week 13 | 4.20 | 0.01 | 0.25 |

The percentage of ammonia volatilised was calculated using the following equation:

$$
\begin{gathered}
\% \text { volatilised }=\frac{\left\{\left[\left(\left(\mathrm{A}_{1} \times \mathrm{V}_{1}\right) / 1000\right)+\left(\left(\mathrm{A}_{2} \times \mathrm{V}_{2}\right) / 1000\right)+\left(\left(\mathrm{A}_{3} \times \mathrm{V}_{3}\right) / 1000\right)\right] / \text { No\# days }\right\} \times(\mathrm{P} / \mathrm{B})}{\left(\mathrm{I} \times \mathrm{I}_{\mathrm{c}}\right)-\left(\mathrm{O} \times \mathrm{E}_{\mathrm{c}}\right)} \times 100
\end{gathered}
$$

where:
$\mathrm{A}_{1}=$ ammonia in jar 1 ( $\mathrm{mg} / \mathrm{l}$ )
$\mathrm{A}_{2}=$ ammonia in jar $2(\mathrm{mg} / \mathrm{l})$
$\mathrm{A}_{3}=$ ammonia in jar $3(\mathrm{mg} / \mathrm{l})$

NB. The ammonia levels in the jars represent the amount of ammonia volatilising off the top of the pond and dissolving in the boric acid samples (Figure 3.7)
$\mathrm{V}_{1}=$ volume of liquid in jar 1 (litres)
$\mathrm{V}_{2}=$ volume of liquid in jar 2 (litres)
$\mathrm{V}_{3}=$ volume of liquid in jar 3 (litres)
$\mathrm{P}=$ pond surface area $\left(\mathrm{m}^{2}\right)$
$B=$ box surface area $\left(\mathrm{m}^{2}\right)$
$\mathrm{I}=$ inflow ( $\mathrm{m}^{3} /$ day )
$\mathrm{I}_{\mathrm{c}}=$ mean influent concentration $\left(\mathrm{g} / \mathrm{m}^{3}\right)$
$\mathrm{O}=$ outflow ( $\mathrm{m}^{3} /$ day )
$E_{c}=$ effluent concentration $\left(\mathrm{g} / \mathrm{m}^{3}\right)$

It is apparent that the average percentage of ammonia volatilized from the facultative pond over the 13 weeks investigated was very small. The average was $0.19 \%$ which leaves $99.81 \%$ of the total nitrogen removed from the pond, due to other forms of removal such as nitrification/denitrification and algal sedimentation. However, if the results from the first two weeks are excluded, which were comparatively high and when the on-pond chamber design was not finalized, the average percentage volatilisation was only $0.095 \%$, with therefore $>99.9 \%$ of ammonia removal being due to other mechanisms.

Nitrogen removal is shown to increase with retention time, pH and temperature up until $20^{\circ} \mathrm{C}$ (Pano \& Middlebrooks, 1982). After $20^{\circ} \mathrm{C}$ thermal stratification and poor mixing conditions are thought to occur in the ponds, which may inhibit ammonia release. From Table 4.1 it can be seen that in weeks 12 and 13 the temperature exceeded $20^{\circ} \mathrm{C}$, but looking at the percentage of ammonia volatilising in these weeks, there was no decrease; in fact there was a small increase compared to the other weeks. This suggests that any stratification that may have occurred in the facultative pond did not have any significant effect on volatilisation during these weeks.

The greatest amount of volatilisation was seen during weeks $1,2,12$ and 13. During weeks 1 and 2 , the on-pond chamber design was not finalised, making these results less accurate. These higher readings may also be accounted for by the presence of Daphnia (Figure 4.1), particularly in weeks 12 and 13 when large Daphnia blooms were seen. The ponds were occasionally susceptible to Daphnia infestations. Daphnia are small crustaceans more commonly known as water fleas. They inhabit lakes and ponds and are important in food chains as they feed on algae, passing their energy further up the food chain. However,
this is detrimental in terms of wastewater treatment. The algae are essential in raising the pH and creating optimal conditions for nitrogen removal and wastewater treatment. The Daphnia reproduce prolifically and thrive on algae, so when they are present the algae diminish significantly to leave little or no photosynthesis occurring in the ponds.


Figure 4.1 Photograph of a Daphnia
Daphnia blooms were recorded in the facultative ponds during weeks 3, 12 and 13. In all other weeks the ponds were clear of Daphnia. The apparent increase in ammonia volatilisation in weeks $1,2,12$, and 13 may actually be due to the relatively low ammonia removal in the ponds due to the presence of Daphnia in these weeks. Looking at the total ammonia lost in these weeks (Table 4.1), it is roughly half of the total ammonia lost in the other weeks, whereas the amount volatilising from the surface of the pond is roughly the same. This would account for the apparent increase in volatilisation.

### 4.1.2 Maturation Pond

Table 4.2 shows these results for the maturation pond during the investigation.
Table 4.2 Results showing amount of ammonia volatilised as a percentage of total nitrogen removed from the maturation pond (2d.p \& 3d.p)

|  | Total Ammonia Lost <br> g/d | Ammonia from whole pond <br> g/day | \% volatilised |
| :---: | :---: | :---: | :---: |
| Week 1 | 2.68 | 0.004 | 0.16 |
| Week 2 | 2.34 | 0.005 | 0.23 |
| Week 3 | 2.68 | 0.006 | 0.21 |
| Week 4 | 2.26 | 0.005 | 0.23 |
| Week 5 | 2.66 | 0.004 | 0.15 |
| Week 6 | 2.55 | 0.003 | 0.12 |
| Week 7 | 2.39 | 0.004 | 0.17 |
| Week 8 | 2.24 | 0.004 | 0.17 |

NB. Equations for calculations are the same as section 4.1.1

From Table 4.2 it is evident that the ammonia volatilisation percentage from the maturation pond is not very significant. The average amount of ammonia volatilisation from the maturation pond was $0.18 \%$, leaving $99.82 \%$ of the nitrogen removal to other forms such as nitrification/denitrification and sedimentation.

Although the percentage of ammonia volatilisation is still small in comparison to the total amount of ammonia removal, it is nevertheless roughly twice the amount of ammonia volatilisation from the facultative pond (using the figures that exclude the facultative pond results obtained in the first two weeks). This would be expected, due to the higher pH levels both anticipated and seen in the maturation pond (Tables 4.3 and 4.4). A higher pH is expected in the maturation pond due to its shallower depth. The sunlight can penetrate the pond further so even algae at the bottom of the pond are able to access sunlight and photosynthesize, so causing a dissociation of the carbonate and bicarbonate ions, thus raising the pH .

The ammonia volatilisation percentage in the maturation pond does not vary greatly from week to week unlike that in the facultative pond. Daphnia were seen in weeks 1 and 3 in the maturation pond, but this did not seem to affect the maturation pond as adversely. This may be due to the Daphnia bloom: the Daphnia blooms in the facultative pond were more intense. This may have been due to the age of the ponds as the maturation pond was newly commissioned. It had been running for approximately a month before the investigation started, so the algal population may not have had a chance to establish itself as well as in the facultative pond. With fewer algae to feed on, the Daphnia blooms would be less intense in the maturation pond.

### 4.2 Sonde Probe Readings

The sonde probe was placed at the surface of the ponds for the duration of the investigations. Readings were taken every three hours to give a representative value of the average pH and temperature over this time. It also enabled the fluctuations in patterns to be observed diurnally.

### 4.2.1 Facultative Pond

In Table 4.3 the average pH and temperature of the facultative pond are shown, along with the highest and lowest values to give a more accurate representation of the conditions within the pond.

Table 4.3 Table showing the average, lowest and highest pH and temperature levels of the facultative pond

|  | Ave pH | Highest pH | Lowest pH | Ave Temp $\left({ }^{\circ} \mathrm{C}\right)$ | Highest Temp $\left({ }^{\circ} \mathrm{C}\right)$ | Lowest Temp $\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week 2 | 6.22 | 6.51 | 5.4 | 10.95 | 14.99 | 8.75 |
| Week 3 | 6.63 | 7.23 | 5.82 | 13.46 | 19.33 | 9.95 |
| Week 4 | 8.3 | 10.02 | 6.52 | 18.25 | 25.65 | 13.13 |
| Week 5 | 7.01 | 8.94 | 6.25 | 16.9 | 23.23 | 13.38 |
| Week 6 | 7.49 | 9.82 | 6.01 | 17.2 | 23.69 | 14.18 |
| Week 7\&8 | 8.78 | 10.45 | 7.2 | 20.44 | 27.45 | 14.53 |
| Week 9 | 7.84 | 9.41 | 6.34 | 17.11 | 24.31 | 13.6 |
| Week 10 | 8.74 | 10.18 | 7.13 | 17.85 | 24.91 | 13.93 |
| Week 11 | 8.72 | 9.79 | 6.89 | 18.6 | 23.28 | 15.36 |
| Week 12 | 6.91 | 7.17 | 6.64 | 21.41 | 25.37 | 17.6 |
| Week 13 | 7.04 | 7.25 | 6.9 | 22.12 | 27.08 | 18.64 |

With the exception of the first two weeks, both the temperatures and pH levels were very high in the facultative pond as the majority of the investigation in this pond took place during the summer months. The temperatures fluctuated from a minimum of 13 or $14^{\circ} \mathrm{C}$ to $24^{\circ} \mathrm{C}$ each week. The pH levels fluctuated from about 6 to 9 , each week. These fluctuations would be due to the diurnal and nocturnal variations.

Over the weeks the average pH and temperature levels did not vary greatly. Usually there was only a variation of a couple of degrees in the temperature, and a unit in the pH .

Figure 4.2 shows the relationship between the average pH and temperature in the facultative pond during the investigation. By looking at this figure, the fluctuations can be observed and any corresponding patterns can be analysed.


Figure 4.2 Graph showing the fluctuations in pH and temperature over the weeks in the facultative pond

From Figure 4.2 it can be seen that the pH levels and temperature generally correlate with each other, the only exception being weeks 12 and 13 , all the other weeks peaked and lowered in the same fashion.

Daphnia, one of the major inhibiting factors involved with this experiment would explain the low pH values seen in weeks 12 and 13 when there were high temperatures. These results correspond with the patterns we found in Figure 4.2. The Daphnia blooms in weeks 12 and 13 would explain why there was a low pH even when the temperature was high and algal growth should have been at an optimum.

Another way of judging the degree of Daphnia infestation would be to look at the chlorophyll $a$ content of the pond as has been done in Figure 4.3. The amount of chlorophyll $a$ present is a direct representation of the amount of algae in the pond. If there is less chlorophyll $a$ then there is less algae, which would result from a Daphnia bloom feeding on the algae. Therefore chlorophyll $a$ is adversely affected by the presence of Daphnia. With the lack of algal photosynthesis, it also means that the pH would decrease, showing that the chlorophyll $a$ content is directly proportional to the pH .


Figure 4.3 Amount of chlorophyll $a(\mu \mathrm{~g} / \mathrm{l})$ recorded in the facultative pond over the testing period

Figure 4.3 provides further evidence of the effect of the Daphnia blooms on the conditions in the pond. This graph shows the chlorophyll $a$ content found in the effluent and a column sample. The column sample takes a sample of the pond water through a column; including the surface, middle and bottom of the pond to give an accurate, overall representation. In this graph it can be seen that on the 21 July (week 12) there was a large decline in the amount of chlorophyll $a$, which continued through week 13 . This corresponded with the Daphnia bloom in the facultative pond and the decline in pH .

As well as observing the average pH and temperatures in the ponds, it was important to observe the diurnal patterns of the pH and temperatures in the ponds. Any fluctuations between the daytime and night-time could have significant and profound effects on the nitrogen removal methods. Two examples of the typical weeks observed during the investigation in the facultative pond are shown in Figures 4.4 and 4.5


Figure 4.4 Example graph showing the fluctuations in pH and temp during continuous readings in week4

From Figure 4.4 it can be seen that there are clear fluctuations at different times of the day. The temperature and pH readings correlate with each other. Peaks for both factors occurred between 6 pm and 9 pm everyday; this would be due to the fact that there had been several hours of sunlight to raise the temperature, which in turn, would increase the photosynthetic activity of the algae. By the evening most carbonate and bicarbonate ions would have dissociated causing the highest pH readings for that 24 -hour period. Equally the lowest readings were found between 4 am and 9 am . This would be due to the lack of sunshine causing a lower air temperature and reduced photosynthetic activity during the night.

This pattern of fluctuations was observed for weeks 4 until 11. However during weeks 2, 3, 12 and 13 the temperature fluctuated but the pH stayed relatively stable (Figure 4.5; see A.3.1 for the other weeks' graphs).


Figure 4.5 Example graph showing fluctuating temperature but stable pH during week 12

This graph is an example of the conditions in the pond when Daphnia were present. As you can see from the graph, the pH was relatively low compared to the high temperatures seen in the pond. The fact that there are no fluctuations also shows that the pH is not affected by diurnal patterns. This reinforces the Daphnia theory: if there are no algae present in the pond, the presence or absence of sunlight is unable to affect the in-pond pH .

### 4.2.2 Maturation Pond

In Table 4.4 the average pH and temperature of the facultative pond are shown, along with the highest and lowest values to give a more accurate representation of the conditions of the pond.

Table 4.4 Table showing the average, lowest and highest pH and temperature levels of the maturation pond

|  | Average pH | Highest pH | Lowest pH | Average Temp | Highest Temp | Lowest Temp |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Week 1 | 8.82 | 9.44 | 7.83 | 20.98 | 22.99 | 18.97 |
| Week 2 | 7.06 | 8.62 | 5.72 | 17.44 | 21.92 | 14.99 |
| Week 3 | 8.42 | 9.57 | 5.57 | 17.59 | 21.89 | 14.52 |
| Week 4 | 9.81 | 10.53 | 8.77 | 18.65 | 26.05 | 15.29 |
| Week 5 | 9.55 | 10.41 | 8.64 | 16.72 | 23.35 | 12.76 |
| Week 6 | 9.87 | 10.91 | 8.99 | 14.47 | 19.19 | 11.36 |
| Week 7 | 9.62 | 10.44 | 8.77 | 13.03 | 16.05 | 10.51 |
| Week 8 | 9.37 | 10.46 | 8.44 | 13.4 | 16.05 | 10.39 |

Figure 4.6 shows the relationship between the average pH and temperature in the maturation pond during the investigation. By looking at this figure, the fluctuations can be observed and any corresponding patterns can be analysed.


Figure 4.6 Graph showing the fluctuations in pH and temperature over the weeks in the facultative pond

Like the facultative pond, the pH and temperature of the maturation pond generally correlated with each other. In Figure 4.6 it can be seen that when the temperature rose and fell so did the pH levels. The last three weeks are a slight exception. In weeks 6,7 and 8 it can be seen that the pH was higher than the other weeks, whereas the temperature was decreasing.

Daphnia were seen in the maturation pond in weeks 1 and 3. By looking at Figure 4.6 we can see that the same pattern seen during the Daphnia blooms in the facultative pond occured in the maturation pond. During weeks 1 and 3, week 1 in particular, there was a low pH , even though the temperatures were relatively high.

An example of a typical week observed during the investigation of the maturation pond is shown in Figure 4.7.


Figure 4.7 Example graph showing the fluctuations in pH and temperature during continuous reading in week 8

However, in contrast to the facultative pond, all the weeks had fluctuating temperatures and pH levels, as shown in Figure 4.7 (and in A.3.2). In weeks 1 and 4 the pH fluctuations were not as dramatic as the example but did vary slightly. This may suggest that although there were not large amounts of algae present to cause an increase in the overall pH , there may have been enough to cause slight fluctuations diurnally. Some of the anomalies in the readings may also have been due to the relatively young age of the pond and the irregularities of the pond settling down.

### 4.2.3 Comparison of maturation pond and facultative pond readings

Over the investigation period, the facultative pond had an average pH of 7.61 and an average temperature of $17.7^{\circ} \mathrm{C}$, whereas the maturation pond had an average pH of 9.07 and an average temperature of $16.5^{\circ} \mathrm{C}$. This shows that the pH in the maturation pond, on average, was much closer to the optimal pH levels for ammonia volatilisation to occur than the facultative pond, even though the temperatures worked out at roughly the same. So in theory there should have been more ammonia volatilising from the maturation pond than
from the facultative pond. The higher pH in the maturation pond is due to the depth of the ponds. The maturation pond is shallower than the facultative pond, being only 1 m deep. This allows more sunlight penetration through the pond creating greater algal photosynthesis through the entire pond, rather than just the top as in the facultative pond. The shallow depth of the maturation pond would also mean that, in theory, there is more dissolved oxygen due to mixing by the wind. This increase in oxygen through algal photosynthesis and wind mixing would cause a greater mass transfer coefficient for the ammonia.

### 4.3 Nitrate/Nitrite Results

During the investigation, results of the nitrate and nitrite concentrations in the influent and effluent samples were recorded. This showed a view of the different forms of nitrogen in the ponds, allowing more evidence to speculate on the methods of nitrogen removal in the ponds.

These results were originally in nitrate and nitrite form ( $\mathrm{mg} / \mathrm{l}$ ) but they were converted to Nitrate-N and Nitrite- N for comparable reasons. By multiplying the original results by the conversion factors ( $14 / 62$ for nitrate and $14 / 46$ for nitrite) this takes into account the atomic and molecular weights of the nitrogen forms and makes them more comparable with ammonia and so more accurate.

### 4.3.1 Facultative Pond

Samples were taken on alternative weeks in the facultative pond. The levels of Nitrate-N and Nitrite-N were recorded for both the influent and effluent samples. This gave an idea of their occurrence and patterns in the facultative pond. These results can be seen in Table 4.5.

Table 4.5 Dionex results showing Nitrate-N/Nitrite-N levels ( $\mathrm{mg} / \mathrm{l}$ ) of influent and effluent samples of the facultative pond

|  | Sample Type | Nitrate-N | Nitrite-N |
| :---: | :---: | :---: | :---: |
| Week 3 | Influent | 0.059 | 0 |
| Week 3 | Effluent | 0.05 | 0 |
| Week 4 | Influent | 0 | 0 |
| Week 4 | Effluent | 0.068 | 0 |
| Week 6 | Influent | 0 | 0 |
| Week 6 | Effluent | 0 | 0 |
| Week 7\&8 | Influent | 0 | 0 |
| Week 7\&8 | Effluent | 0 | 0 |
| Week 10 | Influent | 0 | 0 |
| Week 10 | Effluent | 0 | 0 |
| Week 11 | Influent | 0.032 | 0 |
| Week 11 | Effluent | 0 | 0 |
| Week 12 | Influent | 0.061 | 0 |
| Week 12 | Effluent | 0.027 | 0 |

The Nitrate-N and Nitrite-N results have more significant implications if the dissolved oxygen (DO) content of the pond is analysed as well. These DO results were recorded by the sonde probe every three hours. The average dissolved oxygen content of the facultative pond is shown in Figure 4.8.


Figure 4.8 Graph showing the pattern of the average $\mathrm{DO} \%$ during the facultative pond investigation

When looking at the results in Table 4.5 it is apparent that the levels of nitrate-N and nitrite-N are either very small or non-existent, over all the weeks of the investigation. This
has to be taken into consideration when analysing the results as these small levels could be due to other factors and not necessarily due to any nitrogen removal pathways.

However, assuming they are reflective of the nitrogen processes in the pond, the only week in which nitrification occurred was week 4 . In this week there was an increase in the amount of nitrate in the pond from zero to $0.068 \mathrm{mg} / \mathrm{l}$. Looking at the dissolved oxygen content measured during this week there was an average of $168.9 \%$. This was a high DO content at the surface, which suggests that anoxic conditions at the bottom of the pond were unlikely, which would explain why denitrification may not have occurred. Figure 4.8 shows that it is one of the highest DO concentrations of all the weeks investigated.

During the weeks that nitrate- N and nitrite-N were not detected, it should not be assumed that nitrification did not occur. Pano and Middlebrooks (1982) justified their focus on ammonia volatilisation as the main nitrogen removal pathway due to the absence of nitrate in their samples. However Hurse and Connor (1999) argued that, just because there was no nitrate present in the samples, it did not necessarily mean there was no nitrification. They maintained that the lack of nitrate in their samples was due to the fact that the nitrate was rapidly denitrified to nitrogen gas. So a lack of nitrate in the ponds does not prove that nitrification has not occurred. When analysing the nitrate and nitrite results it is important to remember that a lack of nitrate in the pond does not prove either way that nitrification did or did not occur.

Daphnia blooms were present in weeks 3, 12 and 13. During these weeks the DO contents at the surface were $25.0 \%, 9.0 \%$ and $12.7 \%$ respectively. This is very low for the surface of the pond, so would suggest that anoxic conditions may be present in the bottom layer of the facultative pond, allowing denitrification to take place. From Figure 4.8 it is clear that the Daphnia had a significant effect on the DO content of the pond.

The pattern of fluctuations in the DO content in the facultative pond is important when considering the possibility of nitrification and denitrification. These fluctuations are shown in Figure 4.9.


Figure 4.9 Example of fluctuations seen in DO content at the surface of the facultative pond

Figure 4.9 shows that there was a definite pattern in the concentration of DO. During the night, the \% DO dropped dramatically to zero. This also provides strong evidence that anoxic conditions could be present in the bottom layer during the night, allowing denitrification to take place. Likewise during the day, high levels of oxygen were seen which would have provided ideal conditions for nitrification to take place at the surface during the day.

### 4.3.2 Maturation Pond

Samples were taken every week for the first five weeks during the investigation in the maturation pond, this was due to the shorter investigation period. The levels of nitrate- N and nitrite- N were recorded for both the influent and effluent samples. The results obtained are given in Table 4.6.

Table 4.6 Dionex results showing nitrate-N and nitrite-N levels of influent and effluent samples of the maturation pond

|  | Sample Type | Nitrate-N | Nitrite-N |
| :---: | :---: | :---: | :---: |
| Week 1 | Influent | 0 | 0 |
| Week 1 | Effluent | 0 | 0 |
| Week 2 | Influent | 0 | 0 |
| Week 2 | Effluent | 0 | 0 |
| Week 3 | Influent | 0.088 | 0 |
| Week 3 | Effluent | 0.038 | 0 |
| Week 4 | Influent | 0.056 | 0 |
| Week 4 | Effluent | 0.02 | 0 |
| Week 5 | Influent | 0.149 | 0.265 |
| Week 5 | Effluent | 0.02 | 0 |

The occurrence of denitrification is less likely in the maturation pond than the facultative pond. This is due to the depth of the pond. The maturation pond is shallower which enables increased wind mixing, this means that there is more oxygen in the pond and so anoxic conditions required for denitrification is less probable at the bottom of the pond.

Like the facultative pond, the DO content of the maturation pond is also very important when speculating on the importance and relevance of the nitrate-N and nitrite-N concentrations. The average DO contents of the maturation pond are shown in Figure 4.10.


Figure 4.10 Graph showing the pattern of the average $\mathrm{DO} \%$ during the maturation pond investigation

If we compare the DO concentrations seen in Figures 4.8 and 4.10, it is clear that the DO\% was much higher in the maturation pond than the facultative. The maturation ponds DO content never fell below $76.35 \%$ during the investigation. These high DO concentrations indicate that an anoxic layer in the maturation pond would have been unlikely, especially considering the depth of the pond. Therefore denitrification was less likely to have occurred under these conditions.

Daphnia were present in the maturation pond in weeks 1 and 3, so these blooms may account for the lower DO content in the first three weeks of the investigation, particularly the dip seen in week 2 . In the aftermath of the Daphnia bloom the algae were growing rapidly; this could explain the reduction in nitrate and nitrite seen in weeks 3, 4 and 5. Fitzgerald \& Rohlich (1964) (as cited by Lai \& Lam, 1997) stated that when the preferred ammonium source is at low concentrations algae directly uptake nitrate and nitrite as an alternative source. This could account for the reduction in nitrate in these ponds; this was also seen in the investigation by Lai \& Lam (1997).

During nitrification, ammonia is converted into nitrite initially before its final form of nitrate. In the influent of week 5 there was a small amount of nitrite present. The influent sample for the maturation pond comes from the facultative pond (effluent). Therefore the presence of nitrate in this sample may suggest that nitrification is taking place in the facultative pond, and this nitrite, given more oxygen, would be converted into nitrate.

The pattern of fluctuations in the DO content in the maturation pond is shown in Figure 4.11.


Figure 4.11 Example of fluctuations seen in DO content at the surface of the maturation pond

Like the facultative pond, diurnal fluctuations in the DO content occurred in the maturation pond. During the night the DO content was also dramatically reduced but, contrary to the facultative pond, this was not at a $0 \%$ level. The DO content was relatively higher in the maturation pond at all times of the day. In week 5 (Figure 4.11), the DO content decreased to a minimum of just below $100 \%$ at night (still a high value for the surface) and, considering the depth of the pond, the bottom layer would probably no
t have been anoxic, although this cannot be known for sure. There was however, plenty of oxygen present for nitrification to take place.

### 4.4 Total nitrogen

Having investigated the results for all forms of nitrogen going in and out of the pond, it is possible to work out the total nitrogen removed from the pond each week, and hence work out an average daily removal rate. This can then be compared to the amount of ammonia volatilised during these weeks to give a more accurate representation of the nitrogen removal.

TKN is made up of ammonia nitrogen and organic nitrogen. It does not include nitrates and nitrites, so when calculating the total nitrogen removal, the TKN results were combined with the nitrate and nitrite results.

In Table 4.7 the amount of total nitrogen removed from the facultative pond is compared to the amount of ammonia volatilising from the surface of the pond.

Table 4.7 Comparison of total nitrogen removal and ammonia volatilised in the facultative pond ( $2 \mathrm{dp} \& 5 \mathrm{dp}$ )

|  | Total N load removed/day | Amm. volatilised/day |
| :---: | :---: | :---: |
|  | g/day | g/day |
| Week 4 | 1.52 | 0.00006 |
| Week 6 | 0.92 | 0.00007 |
| Week 7\&8 | 2.05 | 0.00003 |
| Week 10 | 8.55 | 0.00005 |
| Week 12 | 0 | 0.00005 |

Looking at Table 4.7, it can be seen that the amount of ammonia volatilising from the facultative pond is a very small fraction of the total nitrogen being removed in the pond. It is also apparent that the amount of ammonia volatilising from the pond does not vary greatly with a large variation in the nitrogen removal. Looking at the difference between week $7 \& 8$
and week 10, the nitrogen removal increased greatly, almost quadrupled, whereas the increase in the ammonia volatilisation was very slight ( $0.00002 \mathrm{~g} / \mathrm{day}$ ).

In Table 4.8 the amount of total nitrogen removed from the maturation pond is compared to the amount of ammonia volatilising from the surface of the pond.

Table 4.8 Comparison of total nitrogen removal and ammonia volatilised in the maturation pond ( $2 \mathrm{dp} \& 5 \mathrm{dp}$ )

|  | Total N load removed/day | Amm. volatilised/day |
| :---: | :---: | :---: |
|  | g/day | g/day |
| Week 1 | 0.34 | 0.00003 |
| Week 2 | 0.21 | 0.00003 |
| Week 3 | 0.25 | 0.00004 |
| Week 4 | 0.35 | 0.00003 |
| Week 5 | 0.38 | 0.00003 |

The nitrogen removal in the maturation pond did not fluctuate as much as the facultative pond: both the total nitrogen removal and the ammonia volatilisation were steady over the weeks. Comparing the difference in the amount volatilising between the two ponds, it can be seen that, although there was significantly less total nitrogen removal in the maturation pond, the difference in volatilisation between the ponds was not as dramatic. As stated in the previous section, the volatilisation in the maturation pond was comparatively higher than the facultative pond, when taking into account the total nitrogen removal rate.

The total nitrogen load removed per day was calculated using the following equation:

Total N load removed $(\mathrm{g} /$ day $\left.)=\left[\left(\mathrm{TKN}_{\mathrm{i}}+\mathrm{Na}_{\mathrm{i}}+\mathrm{Ni}_{\mathrm{i}}\right) \times \mathrm{I}\right]-\left[\left(\mathrm{TKN}_{\mathrm{o}}+\mathrm{Na}_{\mathrm{o}}+\mathrm{Ni}_{\mathrm{o}}\right) \times \mathrm{O}\right)\right] /[\mathrm{N}]$
where:
$\mathrm{TKN}_{\mathrm{i}}=$ Total Kjeldahl nitrogen in (mg/l)
$\mathrm{TKN}_{\mathrm{o}}=$ Total Kjeldahl nitrogen out (mg/l)
$\mathrm{Na}_{\mathrm{i}}=$ Nitrate -N in $(\mathrm{mg} / \mathrm{l})$
$\mathrm{Na}_{\mathrm{o}}=$ Nitate -N out $(\mathrm{mg} / \mathrm{l})$
$\mathrm{Ni}_{\mathrm{i}}=$ Nitrite- N in (mg/l)
$\mathrm{Ni}_{\mathrm{o}}=$ Nitrite -N out $(\mathrm{mg} / \mathrm{l})$
$\mathrm{I}=$ inflow ( $\mathrm{m}^{3} /$ day )
$\mathrm{O}=$ outflow ( $\mathrm{m}^{3} /$ day )
$\mathrm{N}=$ number of days of observation

### 4.5 Ammonia Stripping Model

This mathematical model, developed by Pano \& Middlebrooks (1982) considers theoretically the amount of ammonia being removed from wastewater ponds, given a number of key factors on which ammonia volatilisation is dependent.

By introducing the variable values of average pH , average temperature and hydraulic loading rates measured during the different weeks of the investigation, this model can be used to assess and determine the reliability of the results obtained during this study.

### 4.5.1 Results of ammonia stripping model vs. actual results

In Table 4.9 the actual amount of ammonia present in the effluent of the facultative pond was compared to the theoretical amount of ammonia in the effluent calculated using Pano \& Middlebrooks (1982) ammonia stripping model.

Table 4.9 Comparison of actual ammonia effluent concentration and model concentrations in the facultative pond (2dp)

|  | Model Effluent Ammonia (mg/l) | Actual Effluent Ammonia (mg/l) |
| :---: | :---: | :---: |
| Week 2 | 11.06 | 4.50 |
| Week 3 | 6.35 | 4.79 |
| Week 4 | 3.34 | 3.63 |
| Week 5 | 13.37 | 5.62 |
| Week 6 | 5.76 | 3.98 |
| Week 7\&8 | 5.17 | 3.39 |
| Week 9 | 2.32 | 1.23 |
| Week 10 | 6.53 | 2.82 |
| Week 11 | 6.61 | 2.82 |
| Week 12 | 5.19 | 6.17 |
| Week 13 | 4.72 | 7.94 |

The ammonia stripping model was calculated using this equation:
$\mathrm{C}_{\mathrm{e}}=\underline{\mathrm{C}}_{\underline{i}} /\left\{1+\left[(\mathrm{A} / \mathrm{Q})\left(0.0038+0.000134^{\mathrm{T}}\right) \times \exp \left(\left(1.041+0.044^{\mathrm{T}}\right)(\mathrm{pH}-6.6)\right)\right]\right\}$
where:
$\mathrm{C}_{\mathrm{e}}=\mathrm{NH}_{3}-\mathrm{N}$ concentration for effluent ( $\mathrm{mg} / \mathrm{l}$ )
$\mathrm{C}_{\mathrm{i}}=\mathrm{NH}_{3}-\mathrm{N}$ concentration for influent (mg/l)

A = pond surface area $\left(\mathrm{m}^{2}\right)$
$\mathrm{Q}=$ flow ( $\mathrm{m}^{3} /$ day )
$\mathrm{T}=$ temperature $\left({ }^{\circ} \mathrm{C}\right)$

The majority of the results obtained in this study were below the values predicted by the Pano and Middlebrooks model, with the exception of three weeks. These exceptions were all affected by Daphnia blooms; in week 4 the actual result was only slightly higher, and in weeks 12 and 13 the actual results were $0.98 \mathrm{mg} / \mathrm{l}$ and $3.2 \mathrm{mg} / \mathrm{l}$ higher, respectively. This shows that during these weeks less ammonia removal was actually being removed from the pond than was expected. This can be accounted for by the Daphnia infestations having had adverse affects on the ammonia removal rate.

By comparing the actual results against the model results on a graph, a clearer picture of the correlation can be seen. This graph can be seen in Figure 4.12 for the facultative pond.


Figure 4.12 Comparison of the Pano \& Middlebrooks model and the actual results from the facultative pond

Figure 4.12 shows that the actual results do not correlate well with the predicted results of the model. The $\mathrm{R}^{2}$ value is very low( 0.0844 ), so this shows that there is not a strong correlation. For there to be a significant correlation between the actual results and the
predicted model results, the $\mathrm{R}^{2}$ value need to be 0.8 or above. The $45^{\circ}$ line represents the line that would be the perfect correlation between the two results. It can be seen that the line of best fit between or results does not correlate with the $45^{\circ}$ line in angle or position.

In Table 4.10 the actual amount of ammonia present in the effluent of the maturation pond was compared to the theoretical amount of ammonia in the effluent calculated using Pano \& Middlebrooks (1982) ammonia stripping model.

Table 4.10 Comparison of actual ammonia effluent concentration and model concentrations in the maturation pond (2dp)

|  | Model Effluent Ammonia (mg/l) | Actual Effluent Ammonia (mg/l) |
| :---: | :---: | :---: |
| Week 1 | 0.68 | 1.23 |
| Week 2 | 3.78 | 1.78 |
| Week 3 | 2.32 | 1.23 |
| Week 4 | 2.07 | 1.91 |
| Week 5 | 2.53 | 1.26 |
| Week 6 | 1.53 | 1.45 |
| Week 7 | 1.48 | 1.70 |
| Week 8 | 1.77 | 1.95 |

Like the facultative pond, the majority of the actual results were below the predicted results, again with the exception of three weeks. These weeks were weeks 1,7 and 8 . Week 1 experienced Daphnia, so like the facultative pond this may have accounted for a reduction in ammonia removal. The difference between the actual results and predicted results of weeks 7 and 8 are not as great as the difference in week 1.

The correlation between the results in the maturation pond can be seen in Figure 4.13.


Figure 4.13 Comparison of the Pano \& Middlebrooks model and the actual results from the maturation pond

Like the facultative pond, there is not a strong correlation between the actual results and the predicted model results, as seen in Figure 4.13. The $\mathrm{R}^{2}$ value is 0.0591 , showing that there was not a significant correlation. The $\mathrm{R}^{2}$ value of the maturation pond is also slightly smaller than the facultative pond, which shows that the actual results of the maturation pond is slightly less significant than the actual results of the facultative pond. As with the facultative pond, the line of best fit between the results does not correlate with the $45^{\circ}$ line in angle or position.

