# CHAPTER IV

# RESULTS AND DISCUSSION

The alternating biofilters were operated over a 10-month period and were fed with synthetic wastewater containing approximately 350 mg/L COD, 8 mg P/L of total phosphorus (TP) and 28 mg N/L of total nitrogen (TN). After 6 months of operation, E2 was added in the synthetic wastewater to study the removal of E2 in the alternating biofilters. The results of the study are summarized and presented below and are arranged according to the impact of cycle duration (CD), hydraulic retention time (HRT), air:water ratio, COD:N loading, COD:P loading, and an influent TP of 16 mg P/L.

## 4.1 Phosphorus Removal in Alternating Biofilters

### 4.1.1 Influence of CD and HRT

The overall removal efficiencies (through both anaerobic and aerobic biofilters) of TP, TN, and COD for various CDs and HRTs are presented in Table 4.1. The results of Table 4.1 are plotted as shown in Figures 1 and 2 where the impact of different CDs and for a given HRT are presented in Figure 4.1 while the same results showing the impact of different HRTs for a given CD are presented in Figure 4.2. As shown in Table 4.1, the overall percent removals of COD were above 87 % and fairly constant for all CDs and HRTs. The highest overall percent removal of COD was 97.7±2.2 % which was obtained for a CD of 6 hours and a HRT of 6 hours while the lowest overall percent removal of COD was 87.8±2.1 % which was obtained for a CD of 2 hours and a HRT of 2 hours. The overall percent removal of COD was found to increase slightly with longer HRT but was not impacted by different CDs for a given HRT.

**Table 4.1** Overall percent removals, percent removal in anaerobic and aerobic biofilters for TP, TN and COD for various CD and HRT

| | | Total Phosphorus Removal (%) | | | | Total Nitrogen Removal (%) | | | | Total COD Removal (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conditions | CD / HRT | 24 | 12 | 6 | 3 | 24 | 12 | 6 | 3 | 24 | 12 | 6 | 3 |
| Overall Removal | 6 | 87.5±0.2 | 79.8±1.0 | 78.0±4.2 | - | 67.1 | 46.1 | 68.0 | - | 91.3±2.6 | 94.5±2.3 | 97.7±2.2 | - |
| | 4 | 51.9±0.9 | 81.7±0.2 | 84.0±0.0 | - | 39.4 | 48.8 | 64.9 | - | 96.0±0.3 | 92.5±0.8 | 90.5±5.8 | - |
| | 3 | - | 20.5±1.8 | 72.8±2.7 | 85.6±0.9 | - | 26.3 | 63.3 | 72.1±0.6 | - | 95.7±0.9 | 97.2±4.0 | 95.9±1.5 |
| | 2 | - | 8.6±4.7 | - | 78.4±0.9 | - | 8.4 | - | 63.6±1.6 | - | 96.3±0.1 | - | 87.8±2.1 |
| | | | | | | | | | | | | | |
| Anaerobic Biofilter | 6 | -39.5±6.1 | -30.4±0.4 | -23.1±13.7 | - | 30.0 | 19.6 | 32.0 | - | 79.2±1.5 | 77.0±3.8 | 89.2±1.0 | - |
| | 4 | -19.2±1.2 | -29.0±1.0 | -39.8±0.3 | - | 13.8 | 24.0 | 24.1 | - | 51.4±10.2 | 79.0±4.7 | 75.8±7.5 | - |
| | 3 | - | -29.2±5.9 | -43.8±0.3 | -35.7±4.2 | - | 15.4 | 21.2 | 19.0±2.7 | - | 66.1±1.1 | 78.1±11.1 | 85.9±9.4 |
| | 2 | - | -34.5±0 | - | -36.0±1.1 | - | 10.0 | - | 13.9±1.6 | - | 66.1±1.9 | - | 61.7±2.9 |
| | | | | | | | | | | | | | |
| Aerobic Biofilter | 6 | 92.4±0.9 | 85.9±0.6 | 83.3±0.2 | - | 53.1 | 32.9 | 53.0 | - | 58.5±9.7 | 76.5±6.0 | 77.2±0.0 | - |
| | 4 | 61.1±1.3 | 86.9±0.2 | 90.3±0.0 | - | 36.5 | 32.6 | 53.7 | - | 91.7±1.2 | 63.8±4.1 | 62.6±12.4 | - |
| | 3 | - | 43.6±6.0 | 85.8±0.1 | 90.8±0.0 | - | 12.8 | 53.4 | 66.0±0.3 | - | 86.6±2.3 | 90.5±4.0 | 77.6±10.7 |
| | 2 | - | 40.1±3.0 | - | 86.2±0.3 | - | 4.6 | - | 57.6±4.0 | - | 89.0±0.8 | - | 68.2±2.9 |

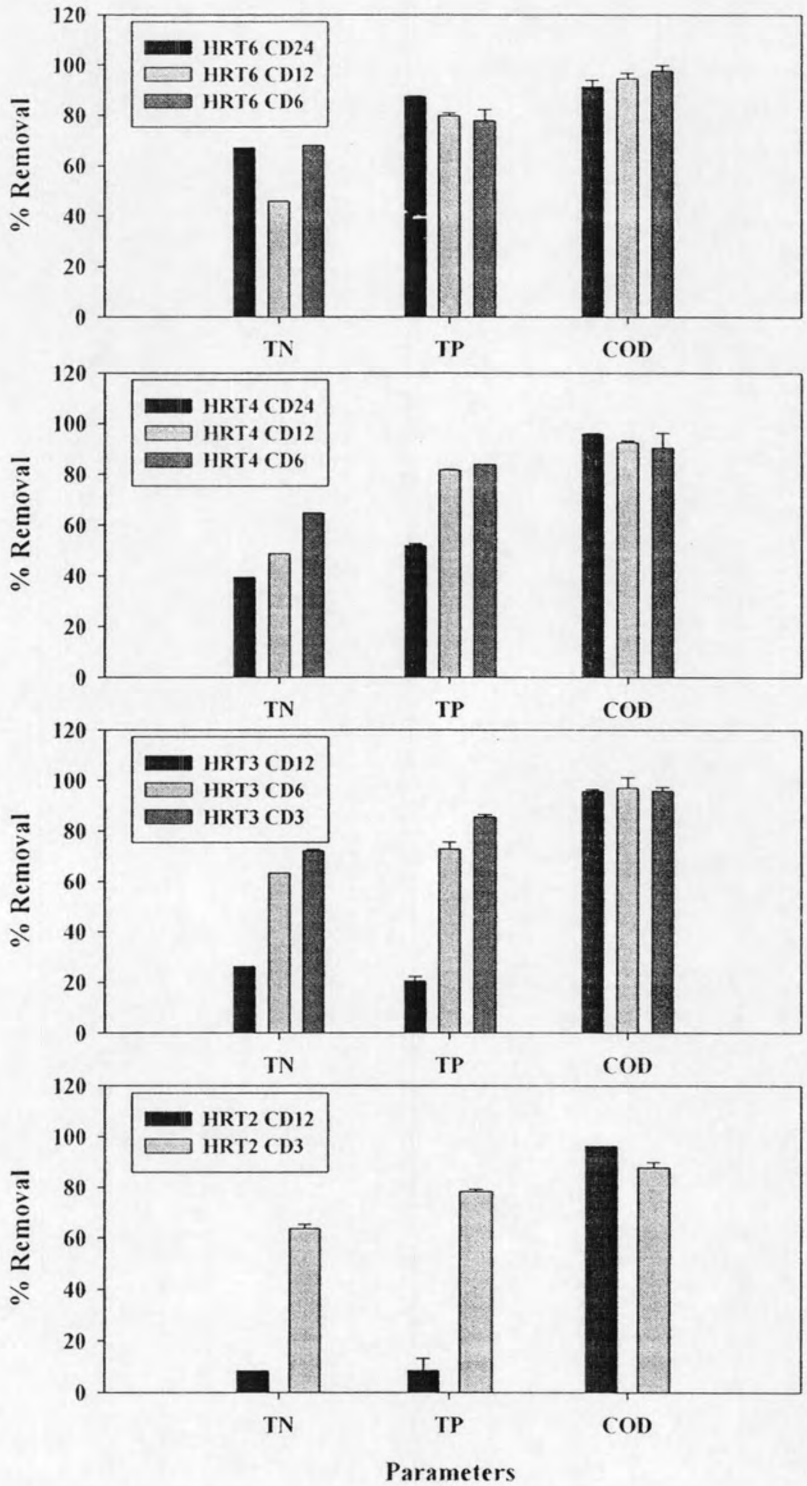


**Figure 4.1** Overall percent removal of TP, TN, and COD for a given HRT and various CDs

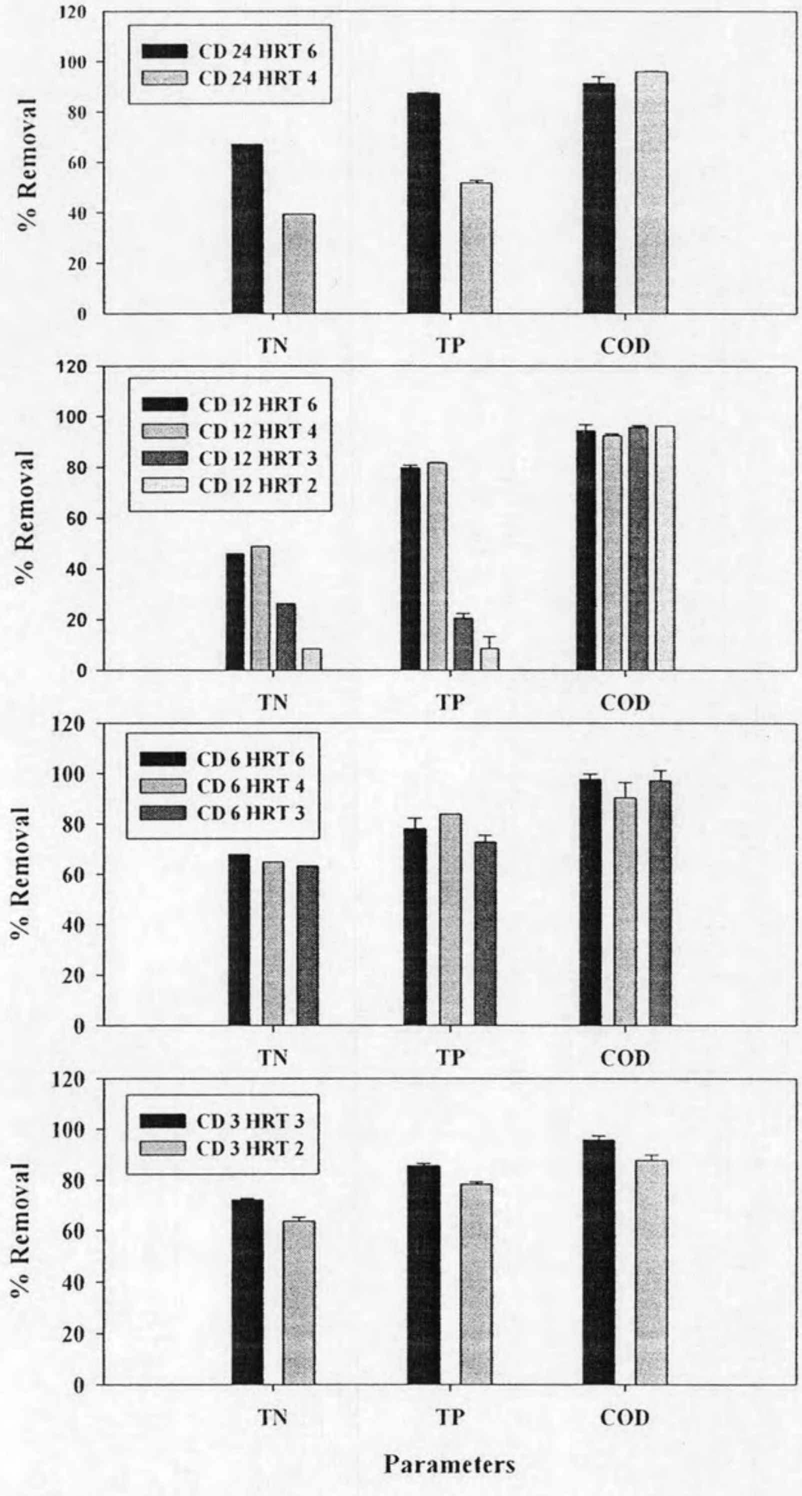


**Figure 4.2** Overall percent removals of TP, TN, and COD for a CDs and various HRTs

As shown in Table 4.1, the bulk of the influent COD was removed in the anaerobic biofilter while between 10 and 50% of the COD was removed in the aerobic biofilter. The highest percent removal of COD in the anaerobic reactor was 90.7±1.3%.

The highest overall percent removal of TP was 87.5±0.2 % for a CD of 24 hrs and a HRT of 6 hrs (see Table 4.1). For an HRT of 6 hours, a change in CD slightly decreased the overall percent removal of TP. In addition, Table 4.1 shows that the overall percent removal of TP decreased when the HRTs of the biofilters were reduced for a given CD. For a CD of 12 hours and HRTs of 3 and 2 hours, the overall percent removals of TP were decreased to 20.5±1.8 % and 8.6±4.7 %, respectively. Pak and Chang (2000) using a two biofilter system under alternating anaerobic/aerobic conditions found that the total phosphorus removal increased as the HRT increased which were in line with this experiment. Although this may be due to insufficient residence time, it is most likely due to early exhaustion of the PHAs in the aerobic biofilter before the CD was over. As one would expect short HRT affected TP removal, this trend, however, was not observed for CD of 6 and 3 hours. In fact, the percent removal of TP for a CD of 3 hours and a HRT of 3 hours was 85.6±0.9 % which was close to the percent removal of TP for a CD of 24 hours and HRT of 6 hours. This would imply that to obtain comparable percent removal of TP for a short HRT, a short CD would be required in order to regenerate or allow the PAOs to re-accumulate PHAs in their cells. This can be seen for a HRT of 3 hours where the overall percent removal of TP decreased with increasing CDs. This result is consistent with the results presented by Shanableh et al. (1997) where percent removal of phosphorus declined when CD increased.

To understand the relationship between CD and HRT on phosphorus removal, it can be seen from Table 4.1 that when the ratio of CD and HRT was less than 1 to 4, the overall percent removals of phosphorus were over 75%. Long CD seemed to be more effective for the operation with long HRT, whereas shorter CD require shorter HRTs to achieve comparable percent removal. The above results strongly suggest that the CD and HRT are coupled in the operations and had significant impact on the removal of phosphorus in alternating biofilter system.

Another interesting observation is that due to the high percent removal of COD in the anaerobic biofilter, the low COD concentrations entering the aerobic biofilter had minimum impact on TP removal. The results of the experiments were not in line with the study performed by Shanableh et al. (1997) where increased COD removal in the aerobic biofilter was accompanied with an increased phosphorus removal.

Percent removals of phosphorus within each biofilter as presented in Table 4.1 where for all CDs and HRTs, more than 40 % were removed in the aerobic biofilter. This is in line with the biological uptake of phosphorus under aerobic conditions. The small uptake of phosphorus in the anaerobic biofilter may be due to anoxic phosphorus uptake or due to the slight aerobic conditions at the top of the anaerobic biofilter which was open to air.

The highest percent removal of TN was 72.1±0.6 % for a CD of 3 hours and a HRT of 3 hours (Table 4.1). Similar trends as in phosphorus removal were observed where for a given HRT, an increase in CD resulted in a lower overall percent removal of TN whereas for a given CD, a shorter HRT resulted in a lower overall percent of TN. Table 4.1 also shows that less than 20% of the TN was removed in the anaerobic biofilter while about 40 – 50% of the TN was removed in the aerobic filter. The results implied that uptake of TN may be due to incorporation of nitrogen in the microbial cells rather than denitrification.

As in phosphorus removal, the overall percent removal of TN seemed to be related to the ratio of CD to HRT. CD of 6 and 3 hours with short HRTs of 3 and 2 hours achieved higher nitrogen removal than CD of 24 and 12 hrs. However, the impact of the ratio of CD to HRT for TN removal was not as significant as that for phosphorus removal.

The results showed that alternating attached growth biofilters operating in series under anaerobic and aerobic conditions can provide simultaneous phosphorus and nitrogen removal by varying the CD and HRT. An optimum operating procedure would be 6 hours of CD and 3 hours of HRT without causing excess changeover (CD) from anaerobic to aerobic and vice versa and minimizing the footprint of the biofilters without compromising performance.

**4.1.2 Concentration Changes within Media Depth**

The concentrations of various water quality parameters along the media depth for the anaerobic and aerobic biofilters for CDs of 24, 12, 6 and 3 hours are presented in Figures 4.3, 4.4, 4.5 and 4.6, respectively.

For all CDs and HRTs except for 6 hours CD and 6 hours HRT, there was an increase in TP concentrations by 4 to 8 mg TP/L in the anaerobic biofilter followed by a rapid uptake of TP in the aerobic biofilter reducing the TP concentrations to about 2 mg/L in most cases (see Figures 4.3, 4.4, 4.5 and 4.6). The changes in TP concentrations are evidence of enhanced biological phosphorus uptake. The highest release of TP of about 8 mg TP/L was for 12 hours CD and 6 hours HRT but the increase was accompanied by a decrease in phosphorous within the anaerobic biofilter indicating possible anoxic phosphorus uptake as shown by a corresponding decrease in nitrate.

To optimize biological phosphorus uptake, release of phosphorus under anaerobic conditions should be maximized. Several trends can be observed: (1) for 24 hours and 12 hours CD, the shorter the HRT the lower was the release of TP in the anaerobic biofilter followed by a corresponding lower uptake of TP in the aerobic filter, (2) for 6 hour and 3 hour CD, HRTs of 4 and 3 hours gave similar release of TP followed by a steep uptake of TP in the aerobic biofilters. The impact of CD and HRT on TP release and uptake may be explained by the PAOs consuming the stored PHA for the uptake of phosphorus within the few hours of a long CD of a short HRT resulting in lower TP removal efficiency. This tends to imply that if the system ran under short CD, higher removal rate can be reached even at low HRT.

Some ammonia oxidation was found in the anaerobic biofilter for all CDs and HRTs followed by a steep reduction in ammonia concentrations in the aerobic biofilter from 15 to 20 mg $NH_4$-N/L to 0.5 mg $NH_4$-N/L. Most of the ammonia in the aerobic biofilter was oxidized within the first 1/3 of the depth of the filter. A corresponding increase in nitrate in the aerobic biofilter was observed indicating nitrification. The impact of HRT for a given CD on ammonia oxidation was less apparent than phosphorus release and uptake. TN removal for all CDs and HRTs showed a steep decline in the aerobic biofilter indicating assimilation of nitrogen by carbonaceous bacteria for growth but the possibility of some denitrification in the anaerobic and aerobic biofilters may be possible. For all CDs and HRTs, the pH was observed to increase from about 7.0 to 8.3 providing evidence of the possibility of denitrification within the aerobic biofilter and the possibility of orthophosphate removal from the wastewater by the microorganism

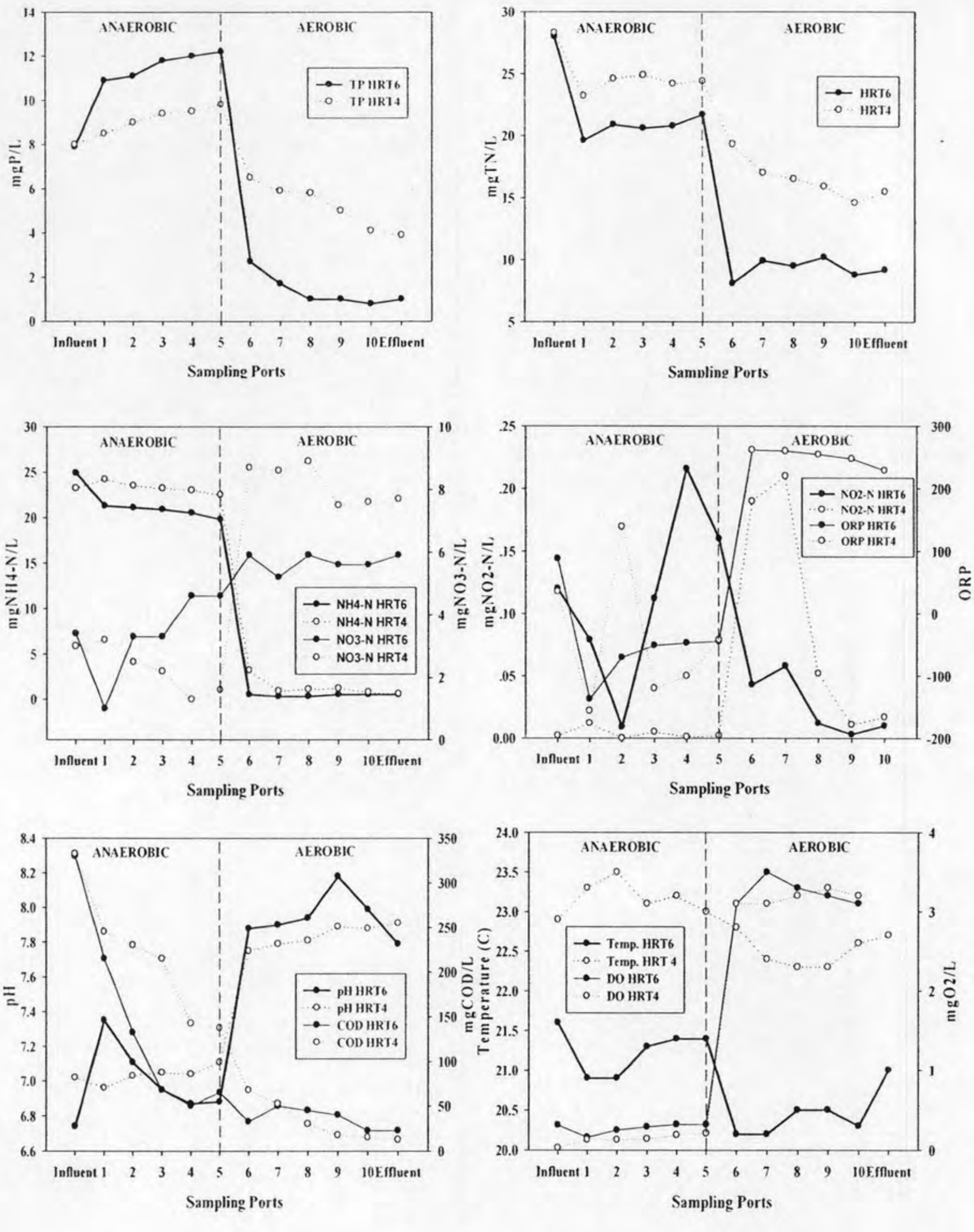


**Figure 4.3** Effect of CD of 24 hrs under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

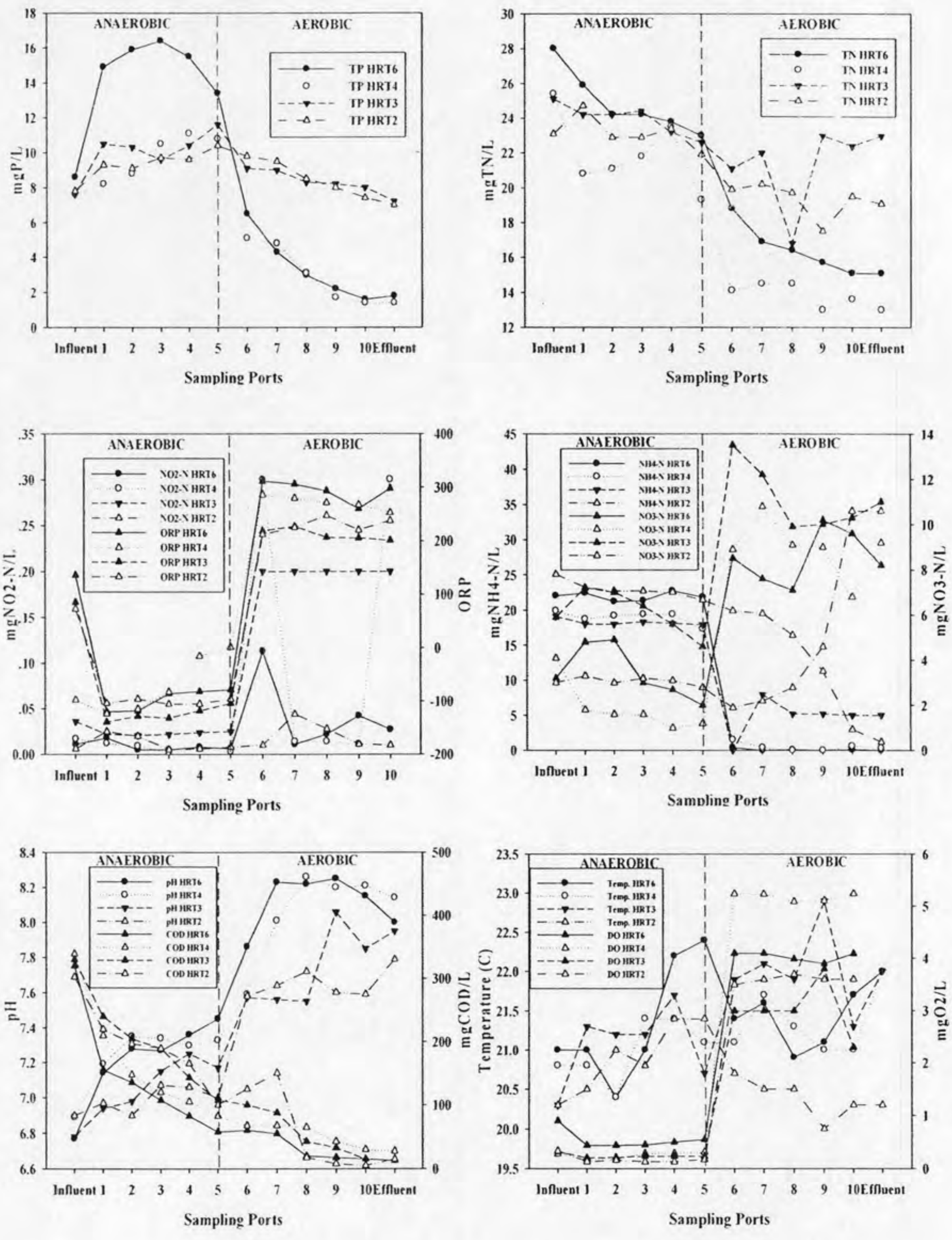


**Figure 4.4** Effect of CD of 12 hrs under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

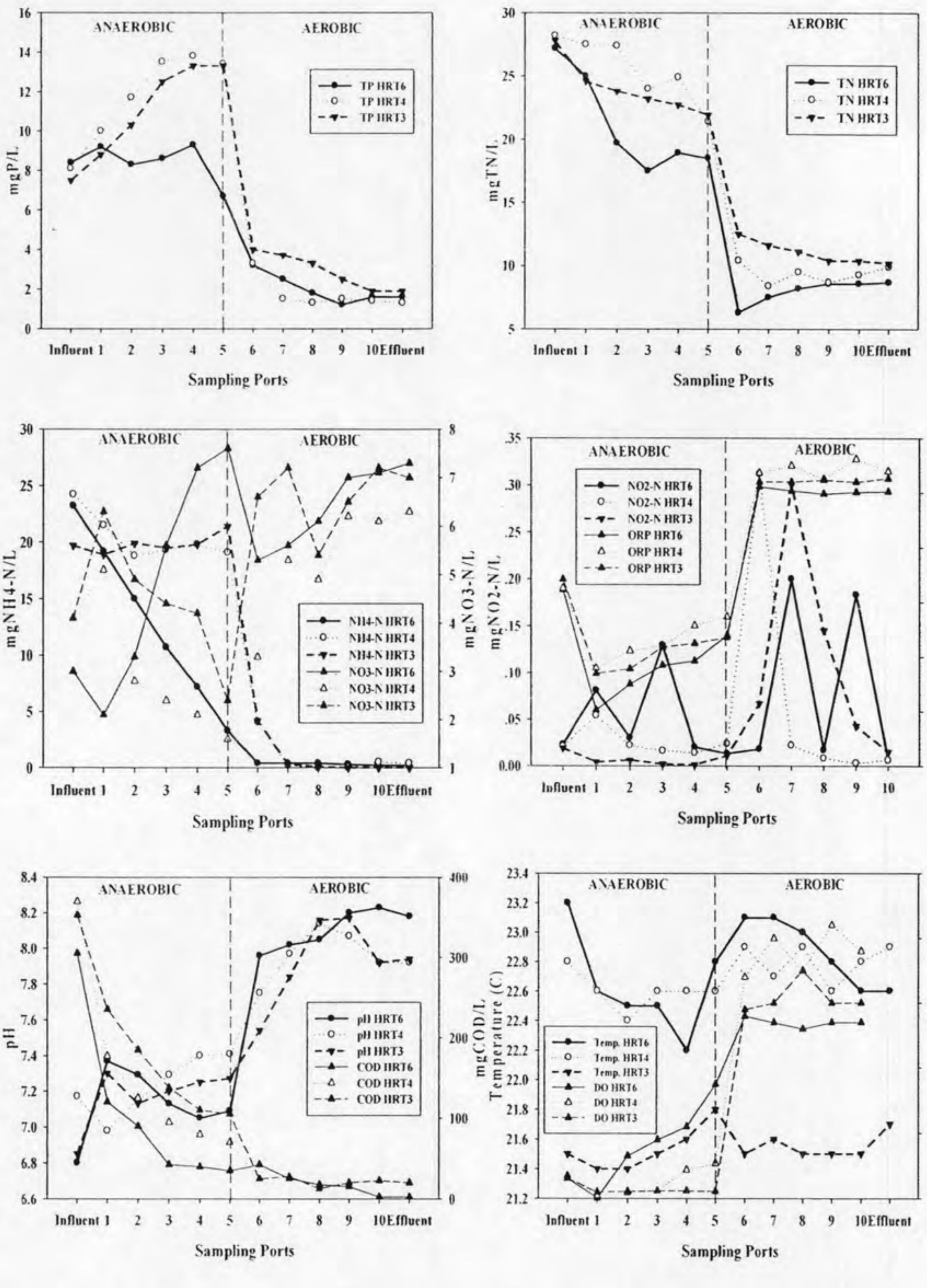


**Figure 4.5** Effect of CD of 6 hrs under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

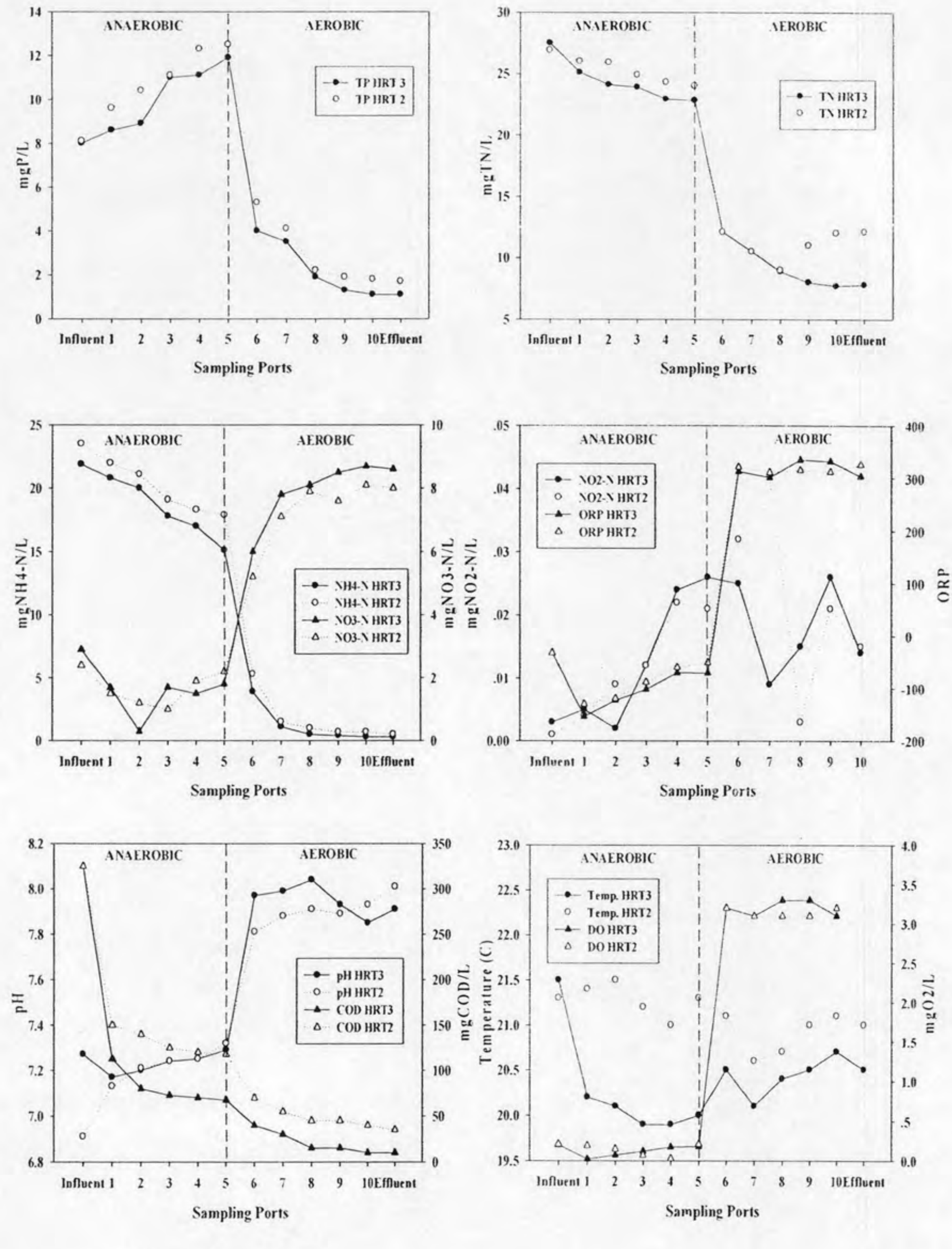


**Figure 4.6** Effect of CD of 3 hrs under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

under aerobic conditions for poly-P synthesis which may result in a pH increase (Converti et al., 1995). In addition, a slight decrease in the nitrate concentrations in the anaerobic filters may indicate nitrification in the later half of the anaerobic biofilter or the possibility of phosphorus uptake by denitrifying PAOs (dPAOs) (Zeng et al., 2003b). In practice, the capability of dPAOs can achieve phosphorus removal and denitrification at the same time. But using the stored polyphosphates as the energy source under denitrifying conditions by dPAOs will lower the EBPR performance and will be less efficient than phosphorus uptake by PAOs (Hu et al., 2002).

When TP and TN removal for all CDs and HRTs were compared, the operating condition of CD 3 hours and HRT 3 hours was probably the most effective condition for simultaneous phosphorus and nitrogen removal. This operating condition was used for the subsequent experiments to test the impact of air:water ratio, COD:N loading, COD:P loading, and with an influent TP concentration of 16 mg P/L.

### 4.1.3 Influence of Air:Water Ratio

Figure 4.7 shows the impact of air:water ratio of 0.072, 0.048, and 0.024 on TP, TN, and COD removal. The biofilters were found to be impacted by the air:water ratios where the percent removals of TP, TN, and COD declined when air:water ratio was decreased. Ammonia oxidation was not impacted by the air:water ratio but nitrate concentrations in the effluent for an air:water ratio of 0.072 was found to be lower than the nitrate concentrations for an air:water ratio of 0.024.

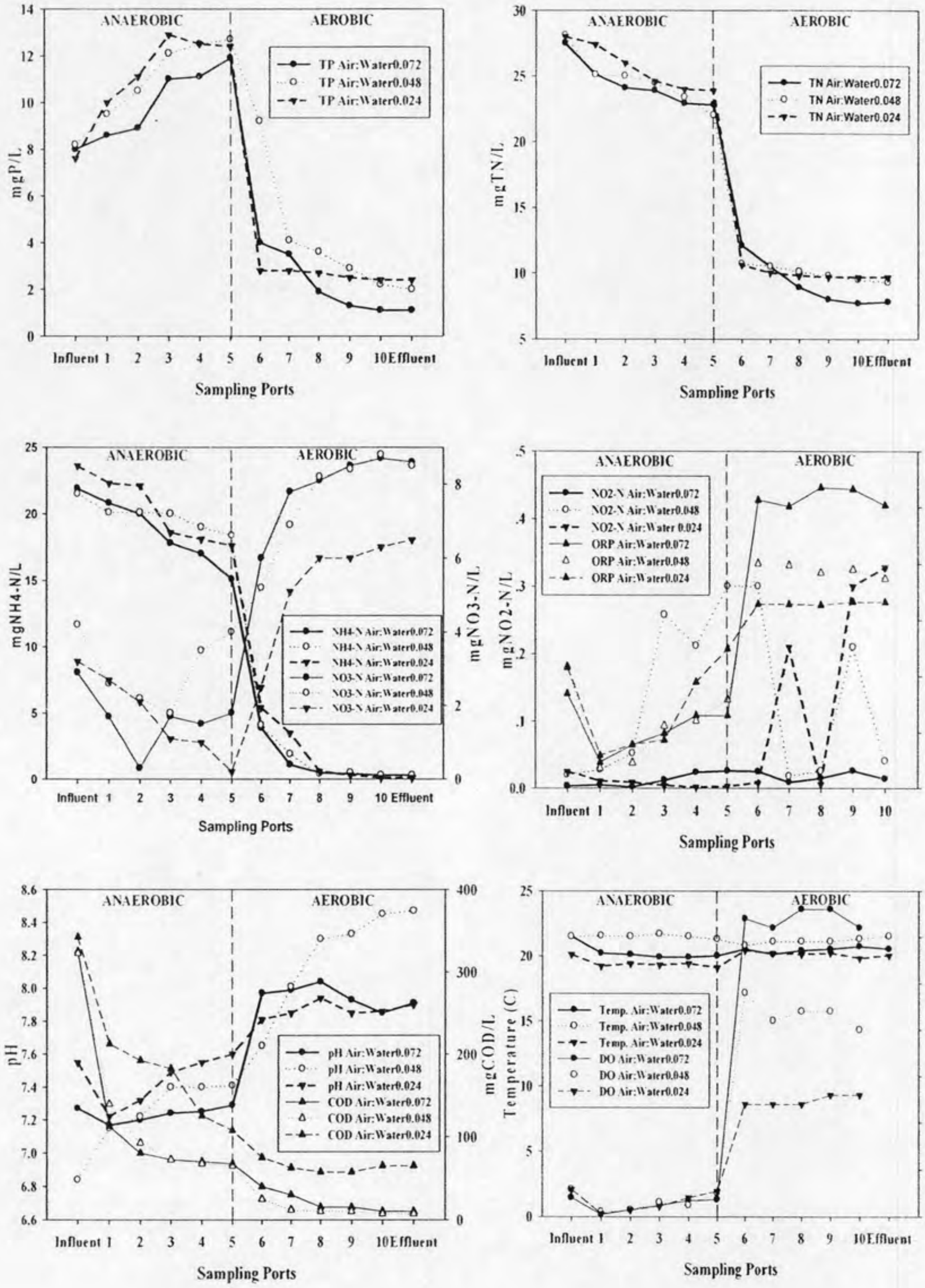


**Figure 4.7** Effect of air:water under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

### 4.1.4 Influence of COD:N Ratio

According to Figure 4.8, nitrification was not affected by the COD:N ratios with effluent ammonia concentrations of less than 1 mg/L. TN and nitrate concentrations in the effluent changed proportionally with the COD:N ratios. TP removal was impacted by a higher COD:N ratio (16). TP removal at COD:N ratios of 12 and 8 were similar. When the condition of the biofilter was switched over from aerobic to anaerobic condition, the remaining nitrate in the aerobic biofilter which was now anaerobic can affect microbial phosphorus release (Wentel and Ekama, 1997). Figure 4.8 shows that the presence of nitrate in the anaerobic biofilter did not negatively affect the phosphorus removal.

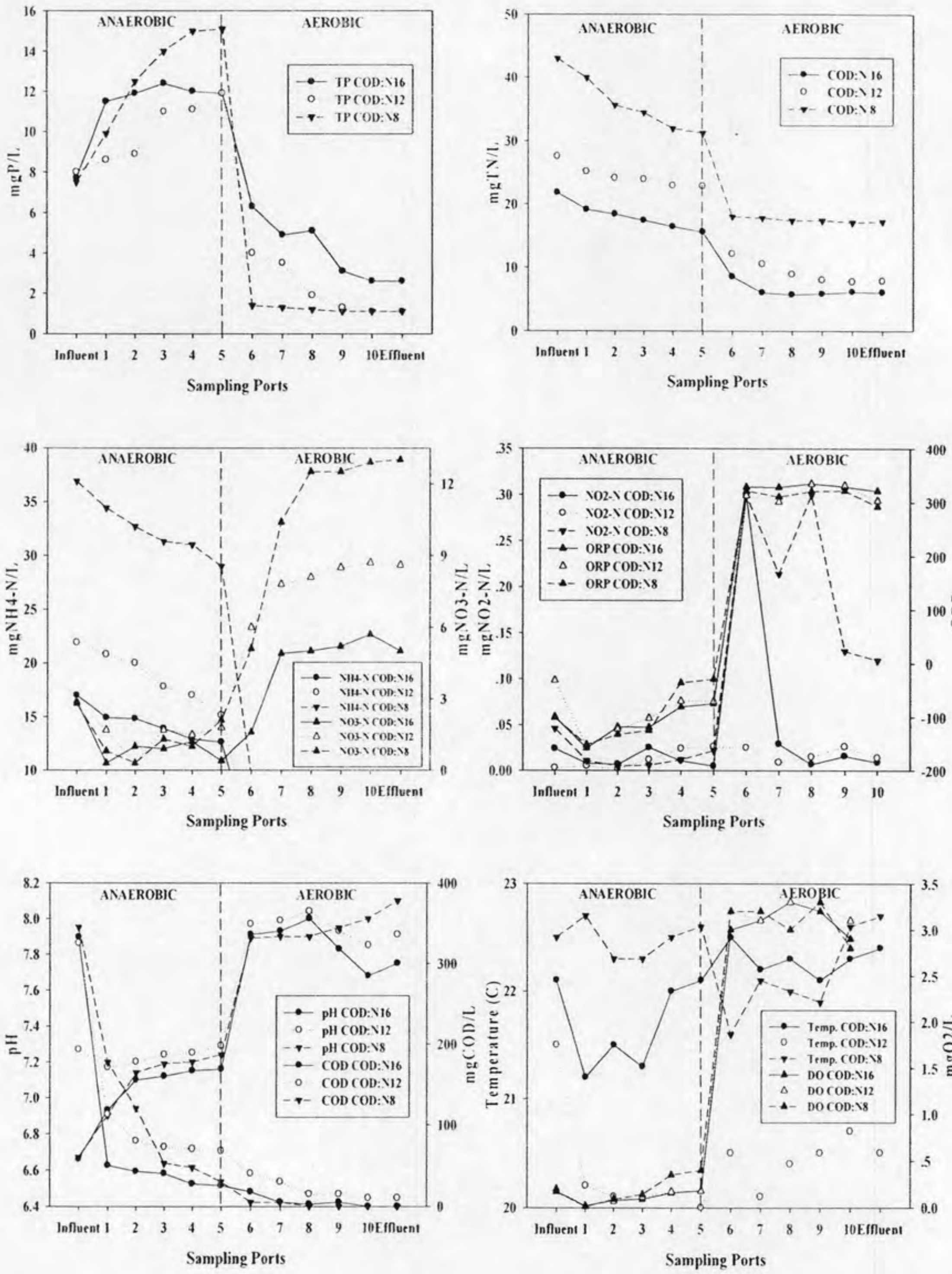


**Figure 4.8** Effect of COD:N under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

### 4.1.5 Influence of COD:P Ratio

To study the influence of COD:P on the TP removal, TP concentration was fixed at 8 mg P/L and the COD concentration varied from 230 to 470 mg COD/L by changing the concentration of organic substrate, sodium citrate, in the synthetic wastewater. The results showed that TP removal were not similar (see Figure 4.9) at 96.6%, 92.5, % and 86.2% for COD:P ratios of 30, 60, and 45, respectively. High COD:P loading tends to reduce the microbial phosphorus uptake by inhibiting the microbial phosphorus release and uptake in the system. TN removal was found to be affected by the COD:P ratio where lower TN removal was obtained for lower COD:P ratios. COD removals were similar for all three COD:P ratios.

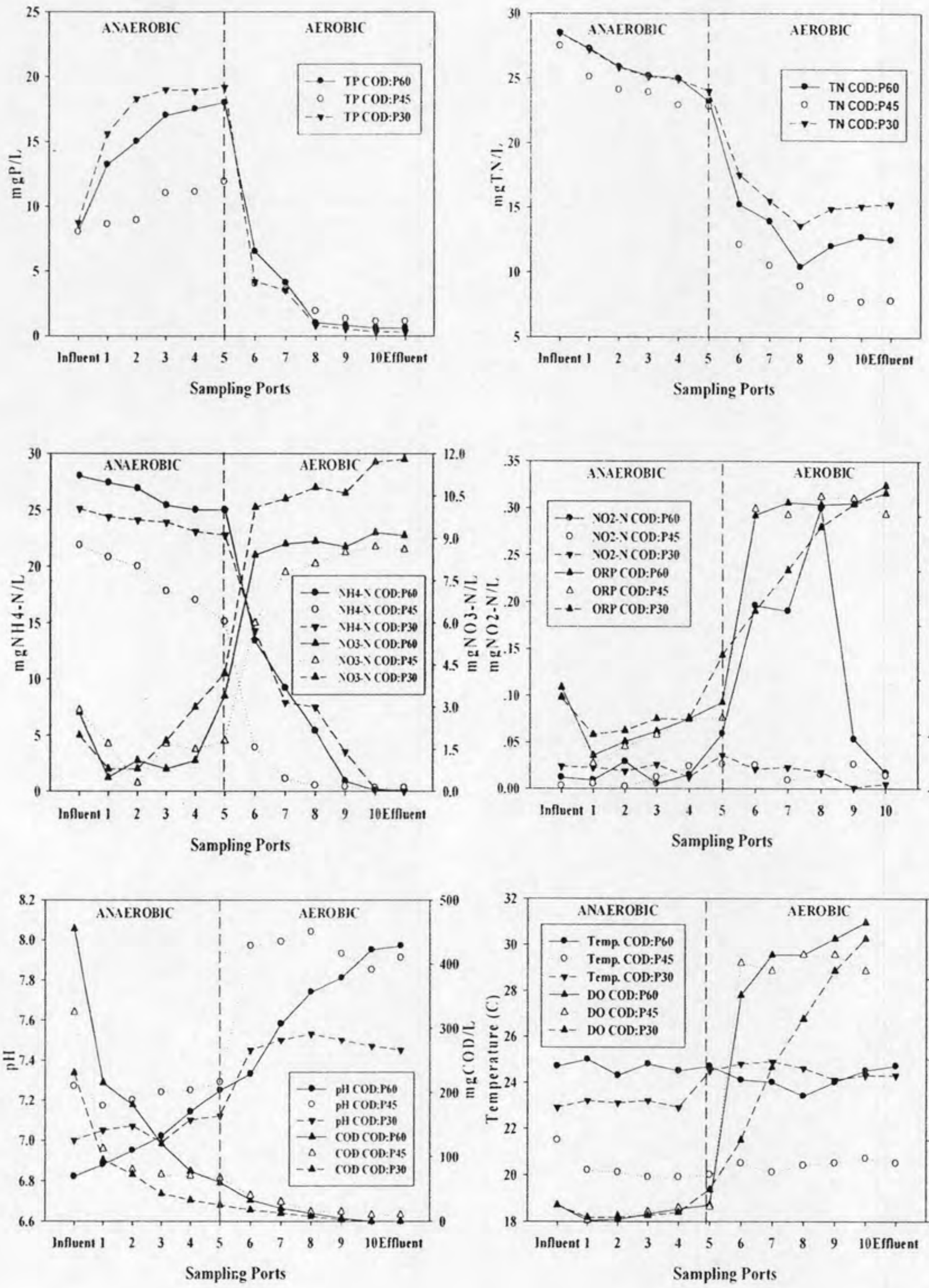


**Figure 4.9** Effect of COD:P under different HRTs on (a) phosphorus release and uptake, (b) TN removal, (c) changes in ammonia and nitrate concentrations, (d) nitrate and ORP changes, (e) pH changes and COD removal, and (f) changes in temperature and DO with media depth

### 4.1.6 Influence of TP at 16 mg/L

As shown in Figure 4.10, more than 85% and 95% TP were removed with influent TP concentrations of approximately 8 and 16 mg P/L, respectively. The results showed that the biofilters can remove TP at about twice the typical TP concentrations in municipal wastewater.

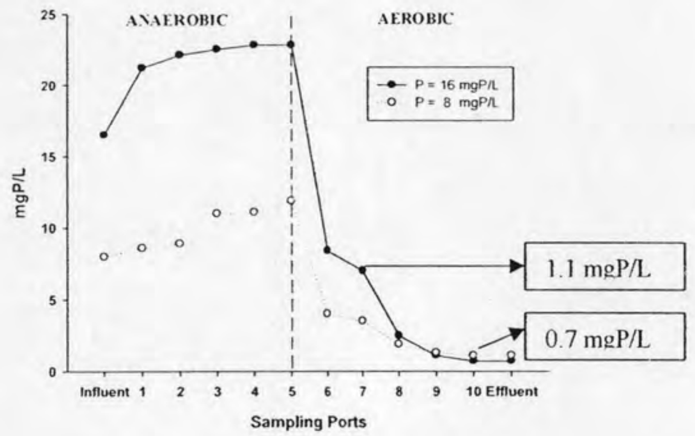


**Figure 4.10** TP removal with influent P concentrations of 8 and 16 mg P/L

### 4.1.7 Recirculation of Effluent to Enhance TN Removal

The nitrate in the effluent can be reduced by recirculating the effluent back into the anaerobic biofilter. In this case, the effluent was recirculated back at about halfway of the media depth (Port number 3). This created an initial anaerobic zone followed by an anoxic zone. A total of 100% of the effluent was recirculated back into the anaerobic biofilter and the biofilters were operated at 6 hours CD and 4 hours HRT. Table 4.2 presents the results of the study. TN and TP removal were the same with and without recirculation while there was COD removal was better for recirculation. A probable reason for the lack of nitrogen removal is that the time for denitrification (upper half of the anaerobic biofilter) may be too short (2 hours only).

**Table 4.2** Percent removal of TN and TP with and without recirculation

| Conditions | % Removal | | |
|---|---|---|---|
| | TN | TP | COD |
| CD 6 hrs HRT 4 hrs | 64.9 | 84±0.0 | 90.5±5.8 |
| CD 6 hrs HRT 4 hrs (recirculation) | 64.1±0.2 | 75.6±0.4 | 98.6±0.0 |

### 4.1.8 Phosphorus Content in Biomass

The amount of phosphorus incorporated in the sludge of conventional activated sludge process is approximately 0.03 mg P/mg SS. The percentage of phosphorus content in biomass for this study for different CDs and HRTs are summarized in Table 4.3. The percent of phosphorus in the biomass of the aerobic biofilters were all larger than 0.03 mg P/mg SS. The phosphorus content was as high as 0.05 mg P/mg SS (5%) for a CD of 3 hrs and HRT of 3 hrs which was the optimum CD and HRT found in the experiment. The percent of phosphorus in the anaerobic biomass were less than 0.03 mg P/mg SS indicating that phosphorus were released from the biomass. The percents of phosphorus in the biomass provided evidence that the removal of phosphorus was due to biological phosphorus uptake. Table 4.4 provides the total phosphorus for conventional activated sludge and various EBPR processes.

**Table 4.3** Percent phosphorus contents in biomass for different CDs and HRTs.

| CD (Hrs) | 24 | | 12 | | | | 6 | | | 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HRT (Hrs) | 6 | 4 | 6 | 4 | 3 | 2 | 6 | 4 | 3 | 3 | 2 |
| Anaerobic | 2.02 | 2.00 | 1.8 | 2.1 | 2.26 | 2 | 2.3 | 2.5 | 2.5 | 3.33 | 2.1 |
| Aerobic | 3.34 | 2.9 | 3.3 | 3.9 | 2.5 | 2.3 | 3.9 | 4.1 | 3.9 | 5 | 3.9 |

**Table 4.4** Comparison of percent phosphorus contents in biomass in different processes.

| Processes | g P/g SS |
|---|---|
| Conventional activated sludge | 0.03 |
| Bardenpho | 0.04-0.07 |
| A/O | 0.05-0.08 |
| Phostrip | 0.04-0.07 |
| This work (aerobic) | 0.03-0.05 |

## 4.2 E2 Removal

### 4.2.1 Batch Adsorption Experiments

#### 4.2.1.1 Sorption Kinetics

Results of the sorption kinetics of E2 to establish the time for steady state sorption conditions are presented in Figure 4.11. Steady state conditions were observed to be reached after 16 hrs. However, after 24 hours, there was an increase in the aqueous concentrations of E2 indicating the possibility of some E2 desorption into the aqueous phase. This observation may be due to an increase in dissolved organic matter in water phase from the biomass used as suggested by Gao et al. (1998) where total concentration of hydrophobic pesticides in the pore water increased due to the bounding of pesticides to dissolved organic carbon. The time used for the sorption experiments was set at 16 hrs to reflect maximum E2 sorption.

#### 4.2.1.2 Sorption Isotherms

Results of sorption of E2 onto the biofilter backwashed biomass using batch sorption experiments are presented in Figure 4.12. The sorption of E2 onto the biofilter backwashed biomass was nonlinear. The data was fitted with a Freundlich model as shown in Figure 4.12. The $R^2$ for the Freundlich model was 0.9327 giving a sorption coefficient, $K_F$, of 8.43 ($\mu g^{1-1/n}.L^{1/n}.g^{-1}$) and a 1/n value of 0.664. The Freundlich parameters found were different and lower than that of Ren et al. (2007) where they found a $K_F$ value of 12.46 ($\mu g^{1-1/n}.L^{1/n}.g^{-1}$) and a 1/n value of 0.79 using activated sludge. Lai et al. (2000) found that the $K_F$ and 1/n for sorption of E2 onto sediment were 36.31 ($\mu g^{1-1/n}.L^{1/n}.g^{-1}$) and 0.67, respectively. However, the $K_F$ and 1/n values found by Andersen et al. (2005) using activated sludge was 2 orders of magnitude larger for $K_F$ with a value of 1106±627 ($\mu g^{1-1/n}.L^{1/n}.g^{-1}$) while 1/n was 0.770±0.093. Work done by Clara et al. (2004) using activated sludge showed linear sorption with a $K_F$ value of 622 ($\mu g^{1-1/n}.L^{1/n}.g^{-1}$) and a 1/n value of 0.8999. The differences in the $K_F$ values may be due to the different biomass used. Parallel control experiments for the sorption experiments gave recoveries exceeding 75% (data not shown).

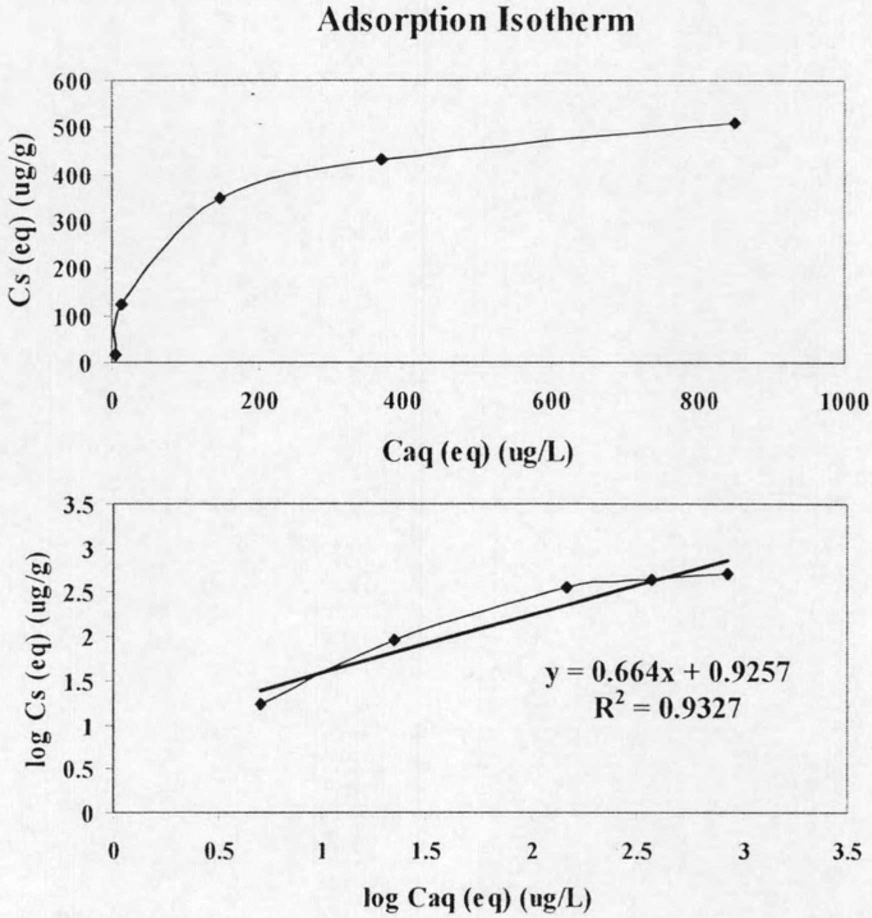


**Figure 4.11** (a) Sorption of E2 onto biofilter backwashed biomass with Freundlich isotherm (b) normalized Freundlich isotherm

### 4.2.2 Influence of HRT

With an influent concentration of approximately 100 μg/L, the overall removal of E2 through the anaerobic and aerobic biofilters were 94.9, 96.9, and 95.6 % for an HRT of 6, 4 and 3 hours, respectively for a CD of 6 hours (see Figure 4.12). The results showed that the biofilters operating in series were effective in removing E2 from the synthetic wastewater. Note that very low concentrations of E1 in μg/L range were detected in the effluent of the aerobic biofilter. Figure 4.12 also presented removal of E2 through each biofilter. The percent removal of E2 in anaerobic column was found to be dependent on the HRT with percent removal decreasing from 94.6 % for 6 hours HRT to 51.2 % for 3 hours HRT. In contrast, percent removals of E2 in the aerobic biofilter were similar at approximately 89.9 % and 90.9 % for 4 hours and 3 hours HRT, respectively. The low percent removal for 6 hours HRT in the aerobic biofilter may be an artifact due to the low influent concentrations of E2 (approximately 5 μg/L) due to the almost complete removal of E2 by the anaerobic biofilter. It appeared that removal of E2 was not as dependent on HRT as that of anaerobic biofilter. This result seemed to be in line with that of Joss et al. (2004) who concluded that the HRT of anoxic/aerobic fixed bed reactor may have little impact on estrogen removal as shown by the high E2 removal (≥ 90%) for short HRTs as low as 35 minutes in their studies.

E2 was found to decrease along the depth of media as shown in Figure 4.13 even within the anaerobic biofilter with a steeper decrease for a longer HRT. Interestingly, E1 was found to be formed and were at concentration comparable to that E2 in the anaerobic biofilter and then decreased to concentrations similar to that of E2 at the effluent of the aerobic biofilter. This indicates that E2 was converted to E1 within the biofilter even under anaerobic conditions followed by the degradation of E1 in anaerobic and aerobic conditions as shown in Figure 4.13. It appeared that E1 was rapidly degraded in the aerobic biofilter even for 3 hours HRT. This results are consistent with other studies (Joss et al., 2004; Lee and Liu, 2002; Ternes et al., 1999b; Vader et al., 2000; Shi et al., 2004).

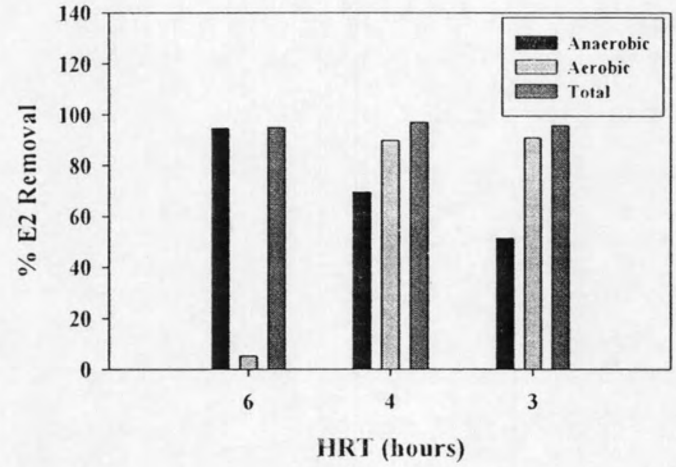


**Figure 4.12** Anaerobic, aerobic, and total removal of E2 under different HRTs.

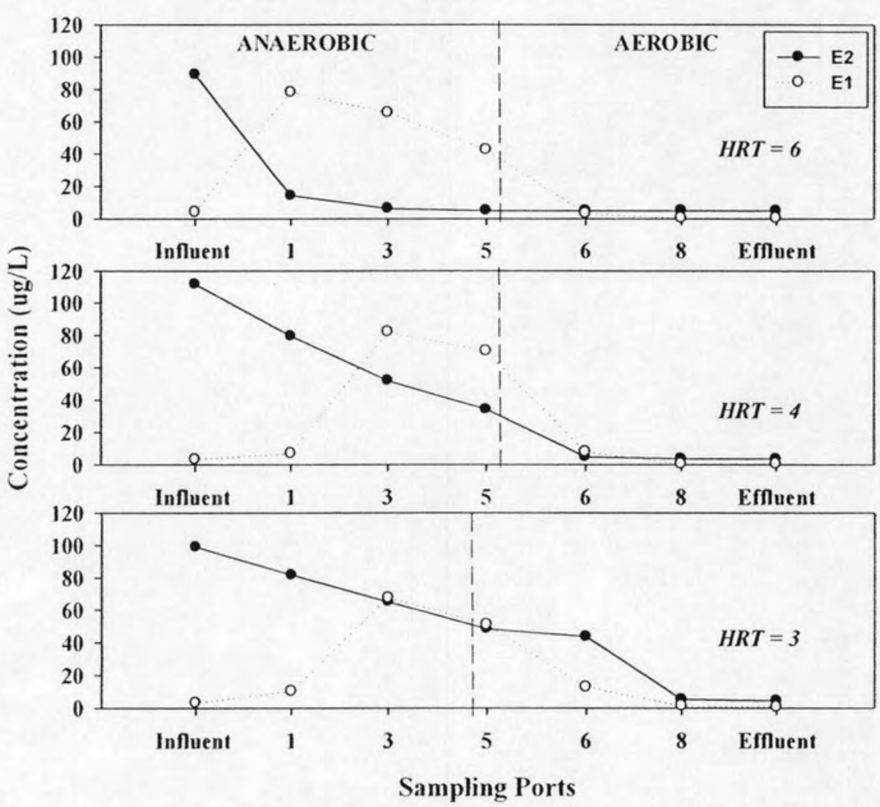


**Figure 4.13** E2 removals under different HRTs under anaerobic and aerobic conditions by media depth

### 4.2.3 Influence of Air:Water Ratio

E2 and E1 concentrations in the influent of anaerobic biofilter, effluent of anaerobic biofilter and effluent of the aerobic biofilters along with the percent removals of E2 and E1 for each biofilter and air:water ratio (air flow rate: water flow rate) are given in Table 4.5. The biofilters were operated with a 3 hour CD and 3 hour HRT. The changes in E2 and E1 concentrations along the media for various air:water ratio are presented in Figure 4.14. As expected, E2 percent removals were similar in the anaerobic biofilter (approximately 70 %) but E2 percent removal was found to decrease with a decrease in air:water ratio in the aerobic biofilter (see Table 4.5). For a lower air:water ratio, E1 was not completely degraded at the end of the aerobic biofilter (see Table 4.5). The experimental results showed that an increase in E2 removal (90.2, 82.2, and 81.6 % for air:water ratio of 0.072, 0.048, and 0.024) in the aerobic biofilter was correlated to an increase in nitrification (8.6, 7.9, and 6.5 mg NO3-N/L for air :water ratio of 0.072, 0.048, and 0.024, respectively). This may partially support the observation by others where the nitrifying biomass was found to remove estrogens (Shi et al., 2004; Vader et al., 2000). Higher air flow rates and low COD tend to promote nitrification and autotrophic nitrifers in the aerobic biofilter.

**Table 4.5** Concentrations and percent removals of E2 and E1 for different air:water ratios

| | E2 (µg/L) | | | | | E1 (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Air: water Ratio** | Ana. Infl. | Ana. Effl. | Aer. Effl. | % Removal Ana. | % Removal Aer. | Ana. Infl. | Ana. Effl. | Aer. Effl. | % Removal Ana. | % Removal Aer. |
| **0.072** | 121.1 | 27.5 | 2.7 | 77.3 | 97.8 | 3.9 | 33.0 | 0.6 | -748.6 | 98.3 |
| **0.048** | 80.2 | 23.2 | 4.2 | 71.0 | 82.2 | 5.1 | 35.3 | 2.8 | -591.2 | 92.2 |
| **0.024** | 91.4 | 21.8 | 4.0 | 76.1 | 81.6 | 4.0 | 27.9 | 12.0 | -593.5 | 56.9 |

Ana. - Anaerobic; Aer. – Aerobic

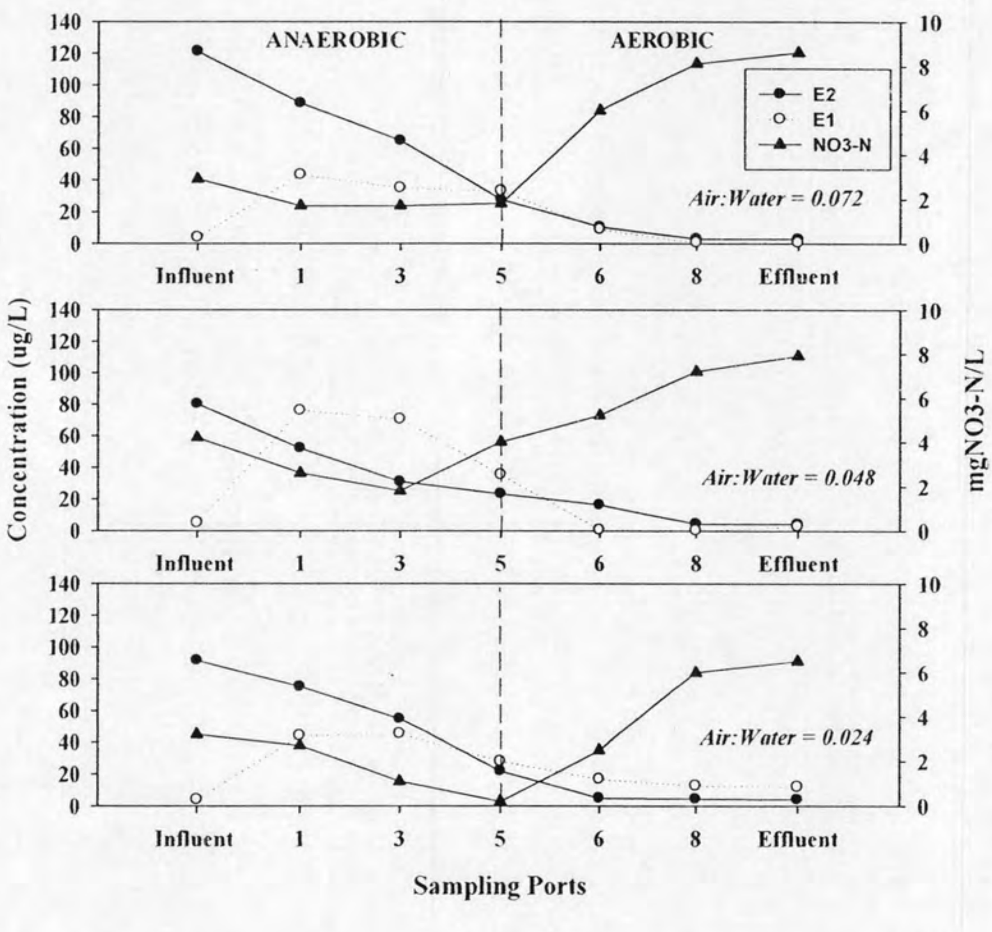


**Figure 4.14** Impact of air:water ratio on E2 removal under anaerobic and aerobic conditions.

### 4.2.4 Influence of COD:N Ratio

E2 and E1 concentrations in the influent of anaerobic biofilter, effluent of anaerobic biofilter and effluent of the aerobic biofilters along with the percent removals of E2 and E1 for each biofilter and COD:N ratios are given in Table 4.6. The biofilters were operated with a 3 hour CD and 3 hour HRT. The changes in E2 and E1 concentrations along the media for various COD:N ratios are presented in Figure 4.15. According to Figure 4.15, E2 removal efficiencies increased as the COD:N ratios decreased (96.7, 97.8, and 98.5 % for COD:N ratio of 16, 12, and 8). Of the three operating conditions, COD:N ratio of 8 gave the highest E2 removal. On the other hand, the percent E2 removal corresponded to the air:water ratio. (90.2, 82.2, and 81.6 % for air:water ratio of 0.072, 0.048, and 0.024). The potential impact on nitrifiers tends to became less and less when the carbon concentration became sufficiently high. This trend confirms the concept that nitrification will be inhibited by heterotrophic processes, as heterotrophs become more dominant when organic carbon is available. This result was similar to the previous work of Zhu and Chen (2001). Their results stated that low nitrification tends to be corresponded to high organic loading in fixed film reactor.

**Table 4.6** Concentrations and percent removals of E2 and E1 for different COD:N ratios

| | E2 (ug/L) | | | | | E1 (ug/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **COD:N** | Ana. Infl. | Ana. Effl. | Aer. Effl. | % Removal Ana. | % Removal Aer. | Ana. Infl. | Ana. Effl. | Aer. Effl. | % Removal Ana. | % Removal Aer. |
| **16** | 104.5 | 22.3 | 3.48 | 78.6 | 84.4 | 9.8 | 48.8 | 0.5 | -396.1 | 99.0 |
| **12** | 121.1 | 27.5 | 2.7 | 77.3 | 90.2 | 3.9 | 33.0 | 0.6 | -749.6 | 98.3 |
| **8** | 110.5 | 10.6 | 1.6 | 90.4 | 84.6 | 2.93 | 45.1 | 0.1 | -1437.9 | 99.7 |

Ana - Anaerobic; Aer. – Aerobic

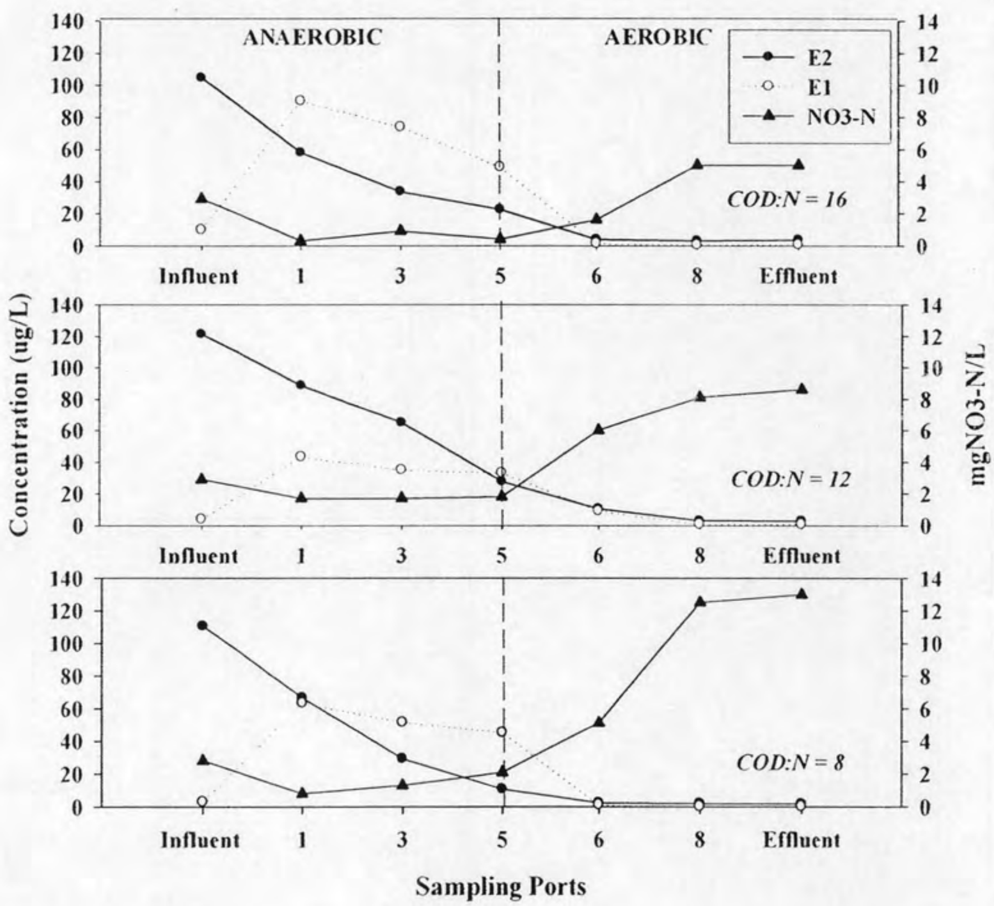


**Figure 4.15** Impact of COD:N ratio on E2 removal under anaerobic and aerobic conditions.

**4.2.5 Performance of Aeration Condition on E2 Removal**

Aerobic conditions tend to have better E2 removal than anaerobic conditions as shown in Figure 4.16. Since the aerobic biofilter came after the anaerobic biofilter, the concentrations of E2 were usually reduced to low concentrations before it entered into the aerobic biofilter (see Figures 4.14 to 4.15). In a separate experiment to assess removal of E2 at concentrations of about 100 µg/L, the intermediate tank was supplemented with E2 to obtain the influent concentration to the aerobic biofilter at about 100 µg/L. In this test, E2 was almost observed to be completely removed within the first third of the biofilter for HRTs of 6 and 4 hours (see Table 4.7 and Figure 4.16). For a HRT of 3 hours, complete removal was observed about two thirds into the media depth of the biofilter. Work done by Furuichi et al. (2006) showed that degradation of estrogens under anaerobic conditions was significantly lower than under aerobic process. It should be noted that at HRTs of 6 and 4 hours, E1 formation was found to be low indicating that there was sufficient residence time for the degradation of E1. However, for a HRT of 3 hours, there was an increase in E1 concentration along the media depth indicating insufficient residence time although most of the E1 formed were degraded in the effluent of the aerobic biofilter.

**Table 4.7** Concentrations and percent removals of E2 and E1 in aerobic biofilter for different HRTs

| HRT | E2 (ug/L) | | | E1 (ug/L) | | |
|---|---|---|---|---|---|---|
| | Aer. Infl. | Aer. Effl. | % Removal Aer. | Aer. Infl. | Aer. Effl. | % Removal Aer. |
| **6** | 91.6 | 2.9 | 96.8 | 3.2 | 0.4 | 88.0 |
| **4** | 105.3 | 4.0 | 96.2 | 3.2 | 0.3 | 91.3 |
| **3** | 103.1 | 4.4 | 95.8 | 4.0 | 0.3 | 92.5 |

Ana - Anaerobic; Aer. – Aerobic

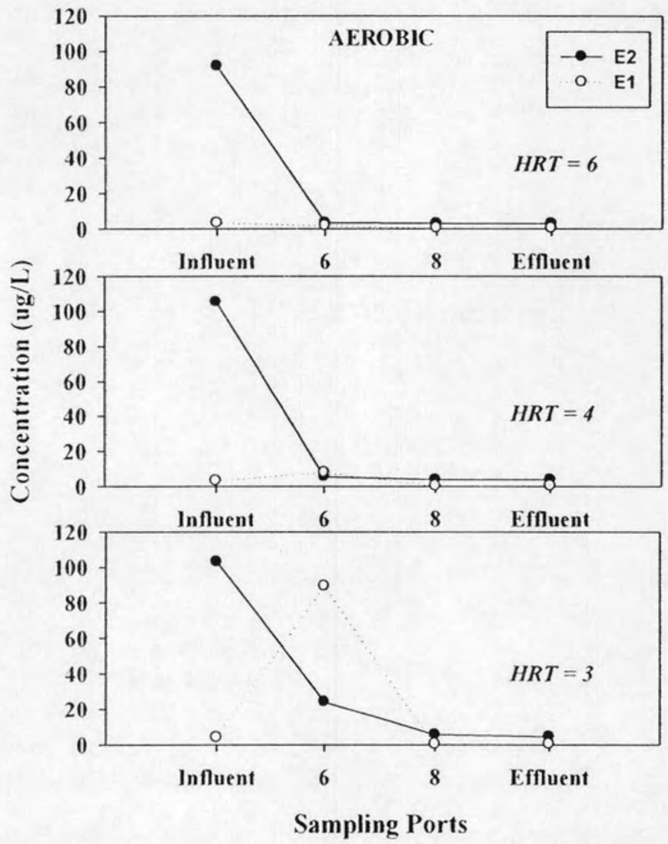


**Figure 4.16** E2 removals in aerobic biofilter with media depth.

### 4.2.6 Mass-balance of E2

To determine the main removal processes of E2, the alternating biofilters were operated over a 3-day period with CD of 3 hrs and a HRT of 3 hrs. The system was backwashed before the start of the 3-day period and at the end of the 3-day period. Samples were taken at the end of the last cycle of the 3-day period.

The mass balances are shown in Section 3.8 and are repeated here in Figure 4.17

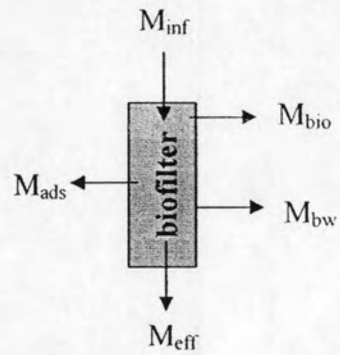


**Figure 4.17** Mass balance of E2

The total mass in put in to the biofilters

$$M_{inf} = M_{eff} + M_{bw} + M_{ads} + M_{bio}$$

The following equation was calculated by assuming newly growth of biofilm was scoured out during backwashing step ($m_{biofilm} = m_{biomass,bw}$).

$$= \overbrace{[M_{ss\,eff} + M_{aq,eff}]}^{M_{eff}} + \overbrace{[(M_{aq,bw})]}^{M_{bw}} + M_{ads} + M_{bio}$$

$$t_{cycle}.Q_{inf}.C_{inf} = \overbrace{[(t_{cycle}.Q_{eff}.SS_{eff}.C_{sorbed}) + (t_{cycle}.Q_{eff}.C_{eff})]}^{M_{eff}} +$$

$$\overbrace{[(t_{bw}.Q_{bw}.C_{aq,bw})]}^{M_{bw}} + \overbrace{[(t_{bw}.Q_{bw}.C_{sorbed,bw}.SS_{bw})]}^{M_{ads}} + [M_{bio}]$$

**Table 4.8** Input data for mass balance.

| General | Values | Units | Anaerobic | Values | Units | Aerobic | Values | Units |
|---|---|---|---|---|---|---|---|---|
| $t_{cycle}$ | 1.5 | days | $C_{inf}$ | 107.14 | ug/L | $C_{inf}$ | 27.53 | ug/L |
| $Q_{inf}$ | 41.66 | mL/min | $SS_{eff}$ | 8 | mg/L | $SS_{eff}$ | 4 | mg/L |
| $Q_{eff}$ | 41.66 | mL/min | $C_{sorbed}$ | 240.44 | ug/g | $C_{sorbed}$ | 5.75 | ug/g |
| $t_{bw}$ | 15 | min | $C_{eff}$ | 27.53 | ug/L | $C_{eff}$ | 3.7 | ug/L |
| $Q_{bw}$ | 0.8 | L/min | $C_{aq.bw}$ | 5.32 | ug/L | $C_{aq,bw}$ | 4.01 | ug/L |
| $K_F$ | 8.43 | $\mu g^{1-1/n}.L^{1/n}.g^{-1}$ | $C_{sorbed,bw}$ | 958.03 | ug/g | $C_{sorbed,bw}$ | 30 | ug/g |
| 1/n | 0.064 | - | $SS_{,bw}$ | 138 | mg/L | $SS_{,bw}$ | 306 | mg/L |
| $M_{biomass,total}$ | 1933.28 | g | | | | | | |

**Table 4.9** Estimated masses for various components.

| Reactor 1 and 2 | $M_{inf}$ (ug) | $M_{eff}$ (ug) | $M_{bw}$ (ug) | $M_{ads}$ (ug) | $M_{bio}$ (ug) |
|---|---|---|---|---|---|
| Anaerobic 1.5 days | 9641.06 | 2650.39 | 63.84 | 1586.50 | 5340.33 |
| Aerobic 1.5 days | 2477.30 | 335.02 | 48.12 | 110.16 | 1984.01 |
| Total | 12118.36 | 2985.41 | 111.96 | 1696.66 | 7324.33 |

**Total mass input** = **12118.36 µg**

**Total mass removal by adsorption** = **1696.66 µg**

= **14.00 %**

**Total mass removal by biodegradation** = **7324.33 µg**

= **60.44 %**

It can be seen that removal of E2 sorbed onto biomass was not quantitatively important as an ultimate fate of E2 compared to biodegradation. The main removal process during both anaerobic and aerobic conditions were most likely due to biodegradation. Adsorption caused an average loss of 13.09 and 0.91 % of the E2 in anaerobic and aerobic biofilters, respectively. This finding was inconsistent with Ren et al. (2007) where they found that natural estrogen compounds were mainly removed from the aqueous phase by adsorption onto associated solid phases. Andersen et al. (2005) however in his study using activated sludge system estimated that 66±13% of E2 were sorbed.