QUANTIFICATION AND COMPARISON OF METHANE EMISSIONS FROM ALGAE AND DUCKWEED-BASED WASTEWATER TREATMENT PONDS

Van der Steen, N. P.,* Ferrer, A. V. M.,** Samarasinghe, K. G.*** and Gijzen, H. J. *

* Unesco-IHE Institute for Water Education, PO Box 3015, 2601 DA, Delft, The Netherlands. Fax +31 (0)15 2122921.
e-mail: petervds@ihe.nl

** University of Baguio, General Luna Road, Baguio City 2600, Philippines.

*** Colombo Municipality, Sri Lanka

ABSTRACT
Natural systems for wastewater treatment may not only remove pollutants from the water phase, but also emit greenhouse gasses to the air. It is estimated that 8-11% of total global anthropogenic methane emissions originate from wastewater treatment. This research aimed at quantifying the methane emissions from algae and duckweed-based pond-reactors.

A laboratory set-up of an anaerobic pond-reactor (AN) from which the effluent was distributed over 4 pond reactors in parallel (2 algae-based (AP) and 2 duckweed-based (DP)) was fed with domestic sewage. The pond reactors consisted of columns of 97 cm effective height and 19 cm internal diameter. After 100 days of operation the emission of methane from the AN, AP and DP was measured by closing air-tight the headspace and monitoring the methane content. The methane content increased linearly with time. The emissions were on average 0.46 gCH$_4$/m$^2$/d and 0.20 gCH$_4$/m$^2$/d for the algae-based and duckweed-based reactors, respectively. Although the oxygen concentration in the AP fluctuated (< 1 mg/l early morning; > 10 mg/l late afternoon), the methane emissions from the AP seemed to be similar during the day and the night. This may indicate low activity of methane oxidisers in the AP’s. The methane emission from the DP was lower than from the AP, possibly due to the physical barrier provided by the duckweed cover or by microbiological methane oxidation. The reduction of methane emission by the duckweed cover resulted in higher dissolved methane values in the duckweed-based pond-reactor effluent. Duckweed covers may be applied to reduce methane emissions, but emission of methane from effluent after discharge should also be evaluated.

KEYWORDS
Duckweed, greenhouse gasses, lagoons, methane, wastewater.

INTRODUCTION
Removal of organic matter from wastewater in waste stabilisation ponds is partly or entirely due to conversion into methane. In cases where methane is not collected, this may be a typical example of transfer of an environmental problem from one phase to another phase, in this case from the water phase to the air. Estimates for the contribution of wastewater treatment systems to total global methane emissions are scarce. Some estimated that wastewater treatment accounts for about 5% of global emissions of methane, but a sound basis for this estimate is lacking (Czepiel et al., 1993).

The type of wastewater treatment technology also affects the amount of methane released per kg BOD treated. Data by Czepiel and co-workers indicated that, in the hypothetical case of all world citizens to be connected to an activated sludge system, wastewater treatment contributes only 0.08% of the total anthropogenic methane emission. Based on data by DeGarie and co-workers one can calculate that by connecting all world inhabitants to an anaerobic pond would increase wastewater treatment’s contribution to 1-4% (Van der Steen et al., in press)

The objective of this research is to quantify methane release from anaerobic, algae and duckweed pond-reactors by volatilisation, as well as to quantify the release in dissolved form in the effluent. This will enable to test the hypothesis that the duckweed cover is reducing the amount of methane volatilising from pond-reactors. The duckweed cover may then be a measure to reduce negative environmental impacts (greenhouse effect) of natural systems for wastewater treatment.
MATERIALS AND METHODS
A laboratory set-up of pond-reactors (Figure 1) was continuously fed with domestic wastewater. The set-up consisted of an anaerobic pond-reactor for pre-treatment followed by four pond-reactors in parallel, of which two were covered with a layer of duckweed (*Lemna gibba*). The pond-reactors were cylindrical transparent Plexiglas containers of 1 meter depth and 19 cm internal diameter (Figure 2). The side walls of the pond-reactors were totally covered with black plastic, except the upper half of the pond-reactors without duckweed cover. A 5 centimetre thick layer of sediment collected from a ditch just outside Delft was added to each reactor at the start of system operation (October 2001). Illumination of the system was artificially by 400 Watt HQI-BS lamps. Light intensity on the water surfaces of the pond-reactors was between 120 and 170 µEm²s⁻¹. The entire set-up was placed in a dark room in order to control day and night such that night-measurements could be carried out conveniently.

![Flow scheme of experimental set-up for treatment of domestic wastewater in pond-reactors](image1.png)

**Figure 1.** Flow scheme of experimental set-up for treatment of domestic wastewater in pond-reactors. D=duckweed pond-reactor, A=algae pond reactor and AN=anaerobic pond-reactor

![Cross section of pond-reactors with (left) and without (right) duckweed layer](image2.png)

**Figure 2.** Cross section of pond-reactors with (left) and without (right) duckweed layer
The influent wastewater was domestic wastewater collected at the treatment plant of Hoek van Holland (The Netherlands). Because of the diluted nature of this wastewater, BOD was added in the form of a mixture of neutralised acetic and propionic acid (Table 1). Other process conditions are presented in Table 2.

Table 1. Influent composition during experiment (day 365-460**8)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD (mg/l)</td>
<td>645 ± 67 (n=5)</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>901 ± 193 (n =9)</td>
</tr>
<tr>
<td>Ammonia (mgN/l)</td>
<td>22.4 ± 6.7 (n = 6)</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Table 2. Process conditions in pond reactors during experiment A and experiment B

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Anaerobic pond-reactor</th>
<th>Duckweed and algae pond reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT(days)</td>
<td>2.42</td>
<td>10.1-11.0</td>
</tr>
<tr>
<td>Light intensity(µEm-2s-1)</td>
<td>150-170</td>
<td>150-170</td>
</tr>
<tr>
<td>Light regime</td>
<td>12 hrs light</td>
<td>12 hrs light</td>
</tr>
<tr>
<td>Duckweed wet density(g/m2)</td>
<td>-</td>
<td>1600-1800</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>20± 2</td>
<td>20± 2</td>
</tr>
<tr>
<td>Volume of reactor(litres)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Harvesting frequency</td>
<td>-</td>
<td>Once a week</td>
</tr>
</tbody>
</table>

Monitoring and analytical methods

Grab samples were collected from the influent, AN, DP and AP effluents and analysed for biological oxygen demand (BOD₅), chemical oxygen demand (COD), total suspended solids (TSS), ammonium nitrogen (NH₄⁺-N), nitrate nitrogen (NO₃⁻-N) and nitrite nitrogen (NO₂⁻-N) according to Standard Methods (APHA, 1992). Process parameters such as flow rate, pH, temperature, dissolved oxygen (DO) and light intensity were also measured. pH measurements were carried out using the standard WTW microprocessor pH meter 323. DO was measured using the standard WTW microprocessor oxi-meter 330 with electrode 096 at five different depths. The DO measurements were taken just below the water surface as well as at various depths to study the variation of DO due to diurnal variations in the ponds.

Measurement of methane emissions

To measure methane emissions each reactor was covered with a transparent PVC sheet for gas collection. A rubber ring gasket was placed in between the top of the column and the PVC sheet and was fastened with nuts and bolts at the rim of the column symmetrically in order to maintain airtight conditions. Headspace air samples were collected with a gas tight Hamilton micro litre syringe 1710N through a septum in the PVC cover. The samples were injected in a Chrompack CP 9000-type gas chromatograph, coupled to an integrator. In order to quantify methane emission rates reactors were covered for several hours/days and gas samples were injected in the GC. Calibration curves were prepared by injecting known volumes of pure methane in the GC.

The anaerobic reactor was tested for leaks by pumping air for a few seconds through an opening in the headspace while the reactor was covered. In order to observe any leak a liquid-leak-detector was applied around the septum and the rim of the reactor under the cover. The pressure of the air in the headspace was monitored by a manometer, which indicated 15cm water head. No leaks were observed during this test.
RESULTS

The performance of the anaerobic pond-reactor was slightly better than usually observed for anaerobic ponds treating domestic sewage (COD removal was 70% and BOD removal was 84%), probably due to the high biodegradability of the influent (acetic and propionic acids). Additional removal of BOD in the DP’s and AP’s was around 90%, resulting in effluent BOD values of 7-13 mg/l. The AP’s functioned as typical facultative ponds. The pH and DO varied during the day as well as with the depth below the water surface. The anaerobic effluent had pH values in the range of 7.4-7.8 and this did not change very much during treatment in the DP’s (7.6 – 8.0). The pH in the AP’s changed from typically 8.0 before ‘sunrise’ to about 9.0 just before ‘sunset’. The DO in the duckweed pond-reactors was stable and around 0.1 mg/l. In the AP’s the DO varied from close to 0 before ‘sunrise’ to about 10 mg/l at ‘sunset’.

Figure 1. Methane accumulation in the headspace as a function of time elapsed of algae pond reactor 2

Figure 2. The emission of methane from the anaerobic pond-reactor during the experimental periods
Methane accumulated linearly with time in the headspace of all three type of pond-reactors when the headspace was closed airtight. Figure 1 shows typical results for AP reactor 1. Figure 2 and 3 show the methane emissions for AN, DP’s and AP’s with time. The emissions do not show a particular trend, but significant fluctuations were observed. The average emission from the AP’s for the entire experimental period was 0.46 g/m²/d (n = 14; sd = 0.19). For the DP’s this value was 0.20 g/m²/d (n = 10; sd = 0.18). Statistical analysis (T-test; paired) showed the difference to be significant (p< 0.05).

Figure 3. The emission of methane from the AP’s and DP’s during the experimental periods

The methane emission from AP’s was measured during a period of 54 hours, both during day and night (Figure 4). The accumulation rate during daytime was not different from the accumulation rate during the night. Figure 5 shows the methane released from the AP’s and DP’s by volatilisation to the headspace as well as the release in the dissolved form with the effluent. The total release by these two mechanisms was very similar in AP1, AP2 and DW2, but significantly lower in DW1. The amount of methane in the effluent seemed to be higher in the DP’s effluent.

Figure 4. Methane measurements at half an hour interval to study diurnal variations in emissions from algae pond reactors
Figure 5. Total average methane release from pond reactors via volatilisation and dissolved in the effluent (headspace methane in algae ponds n = 4, in duckweed ponds n=2 and dissolved methane n = 4)

**DISCUSSION**

Methane volatilisation from the anaerobic pond-reactor (0.17 kg CH₄ / kg BOD_{loaded}) was higher than observed by DeGarie and co-workers (2000) who reported the generation (and emission to the air) of 0.043-0.105 kg CH₄/kgBOD_{loaded} for anaerobic ponds fed with municipal sewage. The higher values observed in this research may be explained by the higher anaerobic biodegradability of the influent, as compared to typical municipal sewage. This may also explain the higher per capita (assuming 100 g COD/capita/d) methane emissions observed in this research (8.4 m³/capita/year) as compared to the values reported by Picot et al. (2002) for real scale ponds (3.3 m³/capita/year).

The volatilisation of methane from the AP's was much lower (0.05 kg CH₄ / kg BOD_{loaded}) than the volatilisation from the anaerobic pond reactor, showing that most of the BOD-load was removed aerobically. The low methane emission may also be the result of oxidation of methane by methanotrophs, taking place in the aerobic part of the water column, i.e. the top layer. Since the oxygen concentration during the night decreased to almost negligible values, it was expected that methanotropic activity would come to a halt during the night also. However, the methane volatilisation during the night appeared to be very similar as the volatilisation during the day. If methanotrophs in AP’s could effectively reduce methane emission, one would expect no or very low emissions during daytime. The results of Figure 4 suggest that methanotropic activity in the AP’s was not significant under the experimental conditions applied.

The methane volatilisation from the DP’s was significantly lower than the volatilisation from the AP’s. At first sight this seems unexpected, since more BOD will be degraded anaerobically in DP’s as compared to AP’s. Although this may indeed be the case, other mechanisms apparently prevented methane emissions from the DP’s. This may be because the duckweed layer forms a physical barrier to volatilisation, but it may also be due to methanotrophs attached to the duckweed fronds and roots. Microscopic investigation of the duckweed roots indicated the presence of aerobic filamentous sulfur bacteria, which proofs the presence of aerobic micro-sites in the duckweed layer. Whether methanotrophs significantly contribute to the prevention of methane emission cannot be assessed from this research. Measurement of the dissolved methane in the DP’s effluent showed that at least part of the methane that is prevented from volatilising ends up in the DP’s effluent. The methane content of the DP’s effluent was higher than the content in the AP’s (limited data did not allow statistical tests). It seems that the duckweed layer reduces methane volatilisation, but increases the dissolved methane content of the effluent. The fate of methane in subsequent
treatment steps or after final discharge needs to be taken into account also for a full environmental impact analysis of these natural treatment systems.

CONCLUSIONS
Methane volatilisation from facultative pond-reactors, expressed in kg CH₄/kg BODₗoaded was significantly less than the volatilisation observed for anaerobic pond-reactors. Although this may be explained by methanotrophic activity in the facultative pond-reactors, this could not be confirmed by studies on diurnal patterns for methane volatilisation. Methane volatilisation during daytime was not less than during nighttime.

The presence of a duckweed cover on wastewater stabilisation pond-reactors decreases the volatilisation of methane. The cover probably is a physical barrier to volatilisation, which results in higher dissolved methane values in the effluent of a duckweed covered pond-reactor.

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REFERENCES