Biogas production, sludge accumulation and mass balance of carbon in anaerobic ponds

B. Picot*, J. Paing*, J.P. Sambuco**, R.H.R. Costa*** and A. Rambaud*

* Département Sciences de l’Environnement et Santé Publique, Université Montpellier I, BP 14491, 34093 Montpellier cedex 5, France  
(E-mail: Bernadette.Picot@pharma.univ-montp1.fr; jpaing@yahoo.fr)  
** Ceremher, Zone de Recherche du Lagunage, B.P. 118, 34140 Mèze, France  
(E-mail: jpsambuco@yahoo.fr)  
*** Departamento de Engenharia Sanitaria e Ambiental, Universidade Federal de Santa Catarina, Campus Universitario, Trinidade, 88010-970, Florianopolis, Santa Catarina, Brazil (E-mail: drejane@hotmail.com)

Abstract This work concerned the application of anaerobic ponds for the primary treatment of urban wastewater in a Mediterranean climate. It was carried out on anaerobic ponds at large scale in Mèze (France). The anaerobic ponds constitute a good primary treatment with the removal of 55% of SS and 30% of BOD5, with a small surface area. The accumulation rate of sludge was only 0.017 m3/capita.year, due to their intensive anaerobic degradation. The anaerobic digestion reached equilibrium after one year of operation. The accumulation of sludge then showed seasonal variations with a substantial accumulation in winter and the digestion of the stock in summer. This change can be related to the influence of the temperature on methanogenesis. The production of biogas (83% CH4) was measured by gas collectors especially developed for this study and was also strongly dependent on temperature. The mass balance of carbon showed that 74% of the removed organic carbon was converted into CH4, 13% into dissolved inorganic carbon and 15% was stored in sludge. However, the anaerobic ponds presented a risk of creating odor nuisances with the emission of H2S.

Keywords Anaerobic pond; biogas; mass balance of carbon; removal performance; sludge accumulation

Introduction
Anaerobic ponds are highly efficient at removing organic carbon from wastewater. The use of primary anaerobic ponds in waste stabilization pond systems allowed a significant reduction in the required surface area, without additional energy need. Unlike facultative and maturation ponds where a high proportion of organic carbon ends up as algal cells, anaerobic ponds convert organic carbon principally into methane and carbon dioxide. Conversion to biogas appears to be a more successful treatment mechanism, considering that the presence of algae reduces the quality of effluent (Green et al., 1995). The sludge production is also lower owing to the intensive anaerobic degradation.

Despite their advantages, anaerobic ponds have been rarely studied in temperate countries. Moreover, anaerobic digestion in sludge and gas production have rarely been studied, usually only their overall performances have been reported in the literature (Saqqar and Pescod, 1995a; Mara and Pearson, 1998). The principal treatment mechanisms are still the sedimentation of settleable solids and their subsequent anaerobic digestion in the resulting sludge layer. To study the sludge accumulation, the composition and the production rate of biogas is thus significant for the characterization of the treatment mechanisms. Knowing the characteristics and quantity of produced sludge is also essential for costing the operation of a process. The mass balance of carbon including accumulation in sludge and the emission to the atmosphere has never been quantified. However, knowing the fate of the purified carbon is important in evaluating the efficiency of a treatment process.

This work concerned the application of anaerobic ponds for the primary treatment of
urban wastewater under a Mediterranean climate (south of France). The objectives were to
determine the removal performances, the sludge accumulation and the production of biogas. The combined results will permit the quantification of the mass balance of carbon in anaerobic ponds.

Materials and methods
The experimental site was the large-scale research waste stabilization pond on the French Mediterranean coast (03°35‘06” E, 43°25‘10” N). This system, which treats the wastewater from the towns of Mèze and Loupian (population 13,800), had been enlarged in 1998 by the addition of two primary anaerobic ponds in parallel (mean characteristics: volume 5,000 m³, depth 3.1 m, retention time 4.6 days, mean volumetric loading 83 gBOD/m³.d). Anaerobic ponds received raw wastewater after it was passed through a fine screen to remove coarse material. These ponds have been investigated for a two year period from their start up (05/98). The mass balance of carbon has been studied for one complete year of operation (10/98–10/99), excluding the temporary period of start up (Paing et al., 2000). The climate of the area is temperate Mediterranean with an annual average temperature of 15°C during the period of study. The monthly averages varied from 6°C in January to 24°C in July.

Flow rate measurement was carried out with a flow meter (Mag 3100W Danhoff) situated at the inlet. The characteristics of the influent and effluent were determined twice a month. Composite 24 h samples for the influent and individual samples for the effluent were taken to the laboratory and analyzed daily. The following parameters were measured according to Standard Methods (APHA, 1995): suspended solids (SS), total chemical oxygen demand (COD), dissolved COD (Whatman GF/C filters), sulfide (by the iodometric method), kjeldahl nitrogen, ammonium, total phosphorus and orthophosphate. Biological oxygen demand (BOD₅) was measured with a special apparatus Oxytop WTW. A turbidimetric method was used for determining sulfate concentration with a Beckman spectrophotometer (650 nm). Bicarbonate (HCO₃⁻) and volatile fatty acids (VFA, expressed as acetic acid) were determined by an alkalimetric method using a two stage sequential titration (Anderson and Yang, 1992). Total organic carbon (TOC or organic C) was measured in some of the samples with an analyzer TOC-5000A Shimatsu. The ratio COD/TOC was equal to 2.8 (r² = 0.8236, n = 17). Inorganic carbon (inorganic C) corresponded to the sum of HCO₃⁻ + H₂CO₃, with H₂CO₃ calculated from the concentration of HCO₃⁻ and the pH.

The accumulation of sludge was measured monthly at 4 sampling points, and half-yearly at 40 sampling points (spaced 5 m apart). Sludge depth was measured using a pH electrode fixed on a graduated pole (Paing et al., 2000). Sludge was sampled in triplicate with a manual peristaltic pump. Bicarbonate and volatile fatty acids were measured after centrifugation (15 minutes, 2,460 g) with the same method used for wastewater. Dry solids (DS) were determined after drying at 105°C and volatile solids (VS) after ignition at 550°C during 2 hours. Total organic carbon (TOC or organic C) was measured in some of the samples with an analyzer TOC-5000A Shimatsu, combined with a special unity for solid samples SSM-5000A. A linear relationship was obtained between the TOC (in mg/g dry weight) and the percentage of volatile solids (in % DS): TOC = 5.3485 × VS (r² = 0.8204, n = 20).

The production of biogas was measured with 4 gas collectors specially developed for this study. They were made with a circular plexiglass cap with a bottom area of 0.3848 m² (Figure 1). They were supported at the surface with floats and anchored with lines to the banks. This prevented disturbance of the sludge layer and the biogas production as happened with collectors anchored to the bottom or positioned just above the sludge layer (Iwema et al., 1987; Toprak, 1995). The volume of the gas collected was measured weekly, directly with a graduated scale, 24 h after the collector was purged of air, to calculate the
daily biogas production rate \( E_{\text{biogas}} \) in l/m\(^2\).d. With these collectors, composite 24 h samples were collected and the mean daily rate of gas production was measured, taking into account the important daily variations underlined by Toprak (1995). The collectors were opaque in order to stop UV penetration and prevent algal growth within the system. Problems such as the increase of \( O_2 \) concentrations were thus eliminated. Moreover, as opposed to other surface gas collectors, these collectors were well stabilized by the floats and lines and not disturbed by high winds or heavy rains. During the biogas collection, the temperature of the pond water was recorded hourly by an internal sonde recorder (Bioblock Scientific) positioned 1m under the water surface.

The biogas collected was sampled, weekly, in a Tedlar bag and transported rapidly to the laboratory for analysis. The \( CH_4 \) and \( CO_2 \) concentrations were measured with a gas chromatograph (Girdel 30) fitted with a thermal conductivity detector. Two stainless steel columns (2 m \( \times \) 3.175 mm) in parallel were used for separation, one packed with 60/80 Porapak Q and a molecular sieve column 5A (60–80 mesh). The oven, detector and injection temperatures were 50°C, 70°C and 90°C respectively. The filament intensity of the detector was 90 mA. Nitrogen was used as carrier gas at a flow rate of 25 ml/min. \( H_2S \) concentration was measured by bubbling the biogas into a solution of 0.1 M zinc acetate and then analyzing the precipitated sulfide according to Standard Methods (APHA, 1995).

**Results and discussion**

**Wastewater characteristics and removal performances**

The raw wastewater was principally from domestic sources, except for some winery wastewater (in particular in September), which produced severe increases of COD and decreases of pH (Table 1). The anaerobic ponds have a good buffer capacity to regulate the pH and the severe increases of organic load. The change in the parameters between the influent and effluent showed the anaerobic activity of the pond with a reduction of pH, an increase in the volatile fatty acids, an increase in the bicarbonates due to the solubilization of \( CO_2 \) (Toprak, 1995), and an increase in sulfides resulting from the reduction of sulfate by sulfate-reducing bacteria.

The mean annual removal performances were 55% for SS, 22% for COD and 30% for \( BOD_5 \). Those performances were relatively constant throughout the year except for punctual decreases in summer due to the sludge feedback when the biogas production increased. The removal of particulate COD was 39% whereas the removal of dissolved COD was only 7%. Indeed, the removal of particulate COD results principally from the
sedimentation and from the anaerobic digestion of sludge whereas the removal of dissolved COD results from anaerobic degradation in the water column. However, the metabolic activity is more significant in the sludge layer because the development of methanogenic bacteria is favored by the long residence times and by the presence of a solid surface. The removal of dissolved COD was thus low, especially as degradation in the water column was counterbalanced by the feedback of intermediate products from the degradation of sludge (Saqqar and Pescod, 1995a). With these climatic conditions, the removal performances were thus principally due to the sedimentation of particulate organic matter.

**Sludge accumulation**

The temporal variations of sludge volume are shown in Figure 2. These variations could be related to the anaerobic degradation of sludge which increased with the pond maturation and with high temperatures. The measures of sludge characteristics showed that the complete stabilization of anaerobic digestion was reached after one year of operation. Indeed, the start-up of methanogenesis resulted in the progressive decrease of the VFA concentration in sludge, until it reached low values that indicated an equilibrium between acidogenesis and methanogenesis (Figure 2). After the start-up period, the accumulation of sludge exhibited seasonal variations with a significant increase in winter and the digestion of the stock in summer.

At the end of summer, when the sludge volume was at a minimum, the mean dry solids content was 81g/l with 49% of volatile solids. With those values, the mean annual rate of sludge accumulation could be calculated to be 26 kgDS/d, equivalent to 0.017 m³/capita.year or 10 cm/year. This rate was less than the value of 0.04 m³/capita.year commonly used for anaerobic ponds at 20°C (Mara and Pearson, 1998). However, this rate was close to the 0.02 m³/capita.year measured by Gomes de Sousa (1988) in Portugal. Gonçalves (2000) reported values between 0.03 and 0.15 m³/capita.year in a literature review. With the model developed by Saqqar and Pescod (1995b), the coefficient Kₘ could be calculated to be 0.3, indicating that the biodegradability rate of the sludge was elevated. The rate of sludge accumulation could also be compared to those of facultative ponds, estimated at 0.085 m³/capita.year on average by Picot *et al.* (2001). In anaerobic ponds, the rate was lower (considering the ratio of sludge production/removal performances for BOD) due to the efficiency of the degradation of sludge but also to the low internal biomass production in anaerobic processes.

Knowledge of the rate of sludge accumulation is essential when planning the desludging

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**Table 1** Annual mean characteristics for the influent and effluent of the anaerobic pond. Mean, minimum, maximum and standard deviation σ (n=22)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw wastewater mean</th>
<th>Raw wastewater min.</th>
<th>Raw wastewater max.</th>
<th>Effluent mean</th>
<th>Effluent min.</th>
<th>Effluent max.</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>18.6</td>
<td>12.2</td>
<td>25.3</td>
<td>17.3</td>
<td>8.1</td>
<td>25.8</td>
<td>5.7</td>
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<tr>
<td>pH</td>
<td>7.4</td>
<td>6.1</td>
<td>8.4</td>
<td>7.1</td>
<td>6.7</td>
<td>7.4</td>
<td>0.2</td>
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<tr>
<td>Suspended solid (mg/l)</td>
<td>256</td>
<td>151</td>
<td>404</td>
<td>114</td>
<td>60</td>
<td>217</td>
<td>39</td>
</tr>
<tr>
<td>Total COD (mgO₂/l)</td>
<td>589</td>
<td>356</td>
<td>960</td>
<td>462</td>
<td>278</td>
<td>614</td>
<td>85</td>
</tr>
<tr>
<td>Dissolved COD (mg O₂/l)</td>
<td>332</td>
<td>160</td>
<td>641</td>
<td>302</td>
<td>158</td>
<td>456</td>
<td>58</td>
</tr>
<tr>
<td>Bicarbonate (mg CaCO₃/l)</td>
<td>321</td>
<td>121</td>
<td>477</td>
<td>380</td>
<td>214</td>
<td>487</td>
<td>61</td>
</tr>
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<td>Volatile fatty acids (mg ac.ac./l)</td>
<td>41</td>
<td>14</td>
<td>115</td>
<td>75</td>
<td>33</td>
<td>111</td>
<td>24</td>
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<tr>
<td>Sulfides (mgS/l)</td>
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<td>8.8</td>
<td>19.2</td>
<td>3.2</td>
<td>36.4</td>
<td>8.3</td>
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<td>Sulfate (mgSO₄/l)</td>
<td>165</td>
<td>96</td>
<td>222</td>
<td>57</td>
<td>3</td>
<td>123</td>
<td>33</td>
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<td>Kjeldahl nitrogen (mgN/l)</td>
<td>59</td>
<td>25</td>
<td>92</td>
<td>59</td>
<td>30</td>
<td>83</td>
<td>17</td>
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<tr>
<td>Ammonium (mgN/l)</td>
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<td>63</td>
<td>51</td>
<td>26</td>
<td>68</td>
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<tr>
<td>Total phosphorus (mgP/l)</td>
<td>10.4</td>
<td>5.0</td>
<td>13.4</td>
<td>9.5</td>
<td>4.0</td>
<td>11.1</td>
<td>1.9</td>
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<tr>
<td>Orthophosphate (mgP/l)</td>
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<td>2.2</td>
<td>8.5</td>
<td>7.1</td>
<td>3.1</td>
<td>8.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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by guest
intervals. Anaerobic ponds require desludging when they are around one third full of sludge (Mara and Pearson, 1998). For the anaerobic ponds of Mèze, it should be performed after 13 years of operation. Owing to the seasonal variations in sludge accumulation, desludging will have to be achieved at the end of summer, when the winter stock has been metabolized.

**Biogas production**

The composition of the biogas collected at the surface of the pond was relatively constant in time and homogeneous over the entire surface. CH$_4$ was the major component and accounted on average for 83%. As observed by Oswald et al. (1963) and Green et al. (1995), the percentage of CO$_2$ was very low (<4%), in contrast with the concentration of the biogas produced by anaerobic digestion, which is typically 25–30% (Metcalf and Eddy, 1992). This difference was due to the dissolution of CO$_2$, which was converted to bicarbonate alkalinity when the biogas, produced at the pond bottom, bubbled through the water column. The mean concentration of H$_2$S was less than 1% (from 75 to 4,770 ppm) but was the cause of important odor nuisances (Paing et al., 2002). Indeed, the odor threshold of H$_2$S is very low, estimated between 0.001 and 0.1 ppm amongst different authors. The residual 14% of the gas was probably nitrogen (N$_2$), resulting from the molecular diffusion of nitrogen dissolved in water (Iwema et al., 1987).

Measurements of the biogas production rate ($E_{\text{biogas}}$ in l/m$^2$.d) were related to the pond temperature (T in °C). Figure 3 shows that an exponential relation was obtained, as found by Toprak (1995).

$$E_{\text{biogas}} = 4.8451 \times e^{0.1203T} \quad (r^2 = 0.9200, n = 16) \quad (1)$$

This relation results from the sensitivity of methanogenic bacteria whose activity decreases at low temperatures. Indeed, sludge contained principally mesophilic species with a maximum activity between 30 and 35°C. This was demonstrated by a series of batch tests to determine the methanogenic activity of sludge at different temperatures (method developed in Paing et al., 2000). Even if the microorganisms are exposed to psychrophilic conditions in the anaerobic pond (between 8 and 26°C), they retained an optimum temperature between 30 and 35°C, as observed by Rebac et al. (1995) in an expanded granular sludge bed. The existence of a specific psychrophilic population in anaerobic digestion remained unclear and has been rarely observed. It should also be noted that methanogenesis was still active at 6°C and that even when the temperature decreased rapidly, there was no

![Figure 2](https://iwaponline.com/wst/article-pdf/48/2/243/423259/243.pdf)
accumulation of volatile fatty acids (Figure 2). In some cases, the digestion process could become unbalanced as the various metabolic groups of bacteria respond in different manners to the change of temperature (Cha and Noike, 1997).

This influence of temperature involves important seasonal variations of the biogas production which can be related to those of sludge accumulation described previously. Indeed, the biogas comes essentially from the degradation of sludge and not from the reactions in the water column. The production of biogas was not directly related to the removal performances. The mean annual rate of biogas production could be calculated as 49 l/m².d with Eq. (1), varying from 13 l/m².d in winter to 108 l/m².d in summer. This rate was in accordance with Toprak (1995) and Driouache et al. (1997), who measured respectively 29–83 and 35 l/m².d. With a total surface of 1,615 m², the mean annual production of biogas was 79 m³/d, equivalent to a ratio of 3.3 m³CH₄/capita.year.

Mass balance of carbon

The whole of the results obtained for the removal performances, sludge accumulation and production of biogas permit the complete mass balance of carbon to be calculated (Figure 4):

- 257 kg-C/d (210 organic C + 47 inorganic C) entered with raw wastewater
- 216 kg-C/d (163 organic C + 53 inorganic C) went out with the effluent
- 35 kg-C/d were emitted in the atmosphere (CH₄)
- 7 kg-C/d were stored in sludge (organic C).

The mass balance is well equilibrated with 257 kgC/d entering and 258 kgC/d “outgoing” (216 + 35 + 7). It is also important to know the fate of the organic carbon eliminated from the effluent (47 kgC/d with 80% particulate and 20% dissolved):

- 74% are converted into CH₄ emitted in the atmosphere
- 13% are converted into inorganic carbon dissolved in the effluent
- 15% are stored in sludge.

In anaerobic ponds, the eliminated organic carbon was thus essentially converted into CH₄. The biogas could be used to produce energy but the equipment could be expensive. CH₄ represented 2.8 kWh/m³ according to data from DeGarie et al. (2000). The emission of CH₄ (recognized as a greenhouse gas) into the atmosphere from anaerobic ponds could be considered as insignificant owing to the wide variety of natural and anthropogenic sources of CH₄, estimated by Minami and Takata (1997). The annual accumulation of carbon in sludge was very low, in particular because of the efficiency of the anaerobic degradation of sludge, particularly active in summer. The low production of sludge was also explained by the low internal production of biomass. In aerobic ponds, the algal growth involves an additional production of biomass which can be found in sludge. In contrast to the mass balance of the carbon carried out in aerobic ponds (Green et al., 1995), this
mass balance did not show an input of atmospheric CO₂. In aerobic ponds, CO₂ is used by
the algae for the production of their cells.

Conclusions
The application of anaerobic ponds for primary treatment of urban wastewater under a
Mediterranean climate is thus satisfactory considering the removal performances. With a
removal of 55% for SS, 30% for BOD₅ and 22% for COD with a small surface area,
aerobic ponds allow significant reductions in the surface area necessary for the waste
stabilization pond system. They allow a good preparation of the effluent for the secondary
stages of purification with the elimination of the settleable particulate organic matter and
also the predigestion of the dissolved organic matter. They have also a good capacity to
control peaks of pollution or sudden changes of pH, thus protecting the sensitive algal
population of the secondary ponds. The sludge production was very low because of its
anaerobic digestion which allows the conversion of the organic matter into biogas
(principally CH₄ emitted to the atmosphere and CO₂ dissolved in the effluent). The strong
dependence of methane fermentation with temperature involved a seasonal variation of the
volume of accumulated sludge. This variation should be taken into account when
estimating desludging intervals, a process that should be carried out at the end of the sum-
mer, when the anaerobic fermentation of sludge is complete. However, the risk of odor
nuisances caused by the emission of H₂S with the biogas, limits the application of this
process close to habitations (Paing et al., 2002). In that case, arrangements for the control of
the odor emissions have to be undertaken (recirculation, impermeable or permeable cover).

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