Emission of H$_2$S and mass balance of sulfur in anaerobic ponds

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Abstract Anaerobic ponds are highly efficient at removing BOD from wastewater with a reduced land area requirement. However, their use is often limited because of the problem of odor release, primarily due to the emission of hydrogen sulfide (H$_2$S). The experiments were conducted on full scale anaerobic ponds used for the primary treatment of urban wastewater under Mediterranean climatic conditions (south of France). A model was developed to estimate the emission of H$_2$S from water characteristics (temperature, pH and sulfides concentration). The emission rate from anaerobic ponds varied between 20 and 576 mg-S/m$^2$.d, leading to concentrations of H$_2$S in the surrounding atmosphere between 0.2 and 5.2 ppm. These concentrations risked creating odor nuisances for nearby inhabitants. The whole of the results and the analysis of sulfur species in sludge permitted the production of a complete mass balance for sulfur. Methods of reducing the emission of odorous compounds were tested on a large scale. The recirculation of secondary effluent and the use of impermeable or permeable covers appeared to be the most interesting solutions.

Keywords Anaerobic pond; emission; hydrogen sulfide; odor control; odor nuisance

Introduction
Anaerobic ponds are a cost-effective and practical way to treat domestic, agricultural and industrial wastewater. They are so efficient at removing BOD that their inclusion substantially reduces the land area required by a waste stabilization pond system. However, the use of anaerobic ponds with open surfaces is often limited due to the release of malodorous gas creating nuisances to neighbors. Those odors are primarily due to the emission of hydrogen sulfide H$_2$S, which has a very low odor detection threshold, between 0.001 and 0.1 ppm amongst different authors (Parsons et al., 2000). In anaerobic treatments, the presence of sulfide is principally due to the dissimilatory reduction of sulfate by sulfate-reducing bacteria such as Desulfovibrio (Pescod, 1996).

According to Mara and Pearson (1998), odor problems in anaerobic ponds can be avoided if the recommended design loadings are not exceeded (100 gBOD/m$^3$.d at 10°C and 350 gBOD/m$^3$.d at 20°C) and if the sulfate concentration in the raw wastewater is less than 300 mgSO$_4$/l. However, the H$_2$S emission rate from anaerobic ponds has never been determined, only the concentration of sulfides in pond water was sometimes reported.

The first aim of this study was to measure the H$_2$S emission rate and the resulting concentration of H$_2$S in the atmosphere. With these measures, a predictive model to estimate the emission of H$_2$S from the characteristics of wastewater was defined. The second aim was to use this model to discuss the recommendations for avoiding odor problems and the solutions for reducing the odor emission. This work was performed on anaerobic ponds used for the primary treatment of urban wastewater under a Mediterranean climate (south of France).
**Materials and methods**

The experimental site was the large-scale research waste stabilization pond of Mèze on the French Mediterranean coast (03°35’06” E, 43°25’10” N), shown in Figure 1. This system 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, organic loading 83 gBOD/m³.d, population 13,800) and of 4 facultative ponds with step-feeding and recirculation (Sambuco *et al*., 2002). Those ponds have been investigated for a two year period from their start up (05/98). The mass balance of sulfur has been carried out for one complete year of operation (10/98–10/99).

The characteristics of the influent and effluent were determined with twice monthly composite 24 h samples for the influent and individual samples for the effluent. The following parameters were measured according to *Standard Methods* (APHA, 1995): suspended solids (SS), chemical oxygen demand (COD), dissolved COD, sulfides by the iodometric method ($S_{\text{II}}$), sulfate by the turbidimetric method (650 nm). Bicarbonate and volatile fatty acids (expressed as acetic acid) were determined by an alkalimetric method.

The accumulation of sludge was measured according to a protocol described in Picot *et al*. (2003). Different forms of sulfur present in the peat were analyzed with methods commonly used in the analysis of sediments (described in Picot *et al*., 2001): FeS (ferrous monosulfide), FeS₂ (pyrite), $SO_4^{2-}$, org-S (organic sulfur) and total sulfur. These analyses were performed on 9 sludge samples.

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. The daily biogas production rate ($E_{\text{biogas}}$ in l/m².d) was measured weekly and the biogas was sampled in a *Tedlar bag* and analyzed rapidly. $H_2S$ concentration ($[H_2S]_{\text{biogas}}$) was measured by bubbling the biogas into a solution of 0.1M zinc acetate and then analyzing the precipitated sulfides.

The concentration of $H_2S$ in the atmosphere surrounding the anaerobic ponds ($[H_2S]_{\text{atm}}$) was measured using a method adapted from LeCloirec *et al*. (1988), with a detection limit of 0.02 ppm. Air was pumped for 5 hours at a flow rate of approximately 60 l/h and bubbled into 100 ml of 0.1 M zinc acetate solution. Eight bubbling chambers were positioned all around the anaerobic ponds once a week, on the banks at 1 m from the water, in order to measure a mean concentration of $H_2S$. Nine bubbling chambers were also positioned according to Figure 1, in order to determine the principal sources of odors in this treatment plant.

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**Figure 1** Schematic of the waste stabilization pond system of Mèze (France)
Results and discussion
As soon as the anaerobic ponds were started up, a number of complaints about odors occurred from residences surrounding the treatment works (the first houses were 200 m East of the ponds). These odors were emitted principally by the two anaerobic ponds, as shown by the analysis of the H$_2$S concentration in Figure 2. An analysis by gas chromatography of the biogas produced by these ponds revealed that hydrogen sulfide was the principal odorous compound, at a concentration of 2,400 mg/m$^3$. Methylmercaptan was also detected but only at 4.8 mg/m$^3$. Amines and organic acids were not detectable. Those results showed that investigations of odor emissions could thus be limited to the study of H$_2$S emission from the anaerobic ponds, related to the production of sulfides.

Wastewater characteristics
The raw wastewater was principally from domestic sources, except for some winery wastewater (Table 1). 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 bicarbonate, and an increase in sulfides resulting from the reduction of sulfate by sulfate-reducing bacteria. It should be noted that the raw wastewater was already anoxic, as shown by the presence of sulfides and volatile fatty acids. The sulfides concentration (3.8 mgS/l) was considered as “moderate” by the classification of Hvitved-Jacobsen and Nielsen (2000). Sulfides created problems in the network (concrete corrosion, odor emissions), so that control measures had been installed in 2001 by the municipality (ferrous salts addition).

Sulfide production
The presence of sulfides in anaerobic ponds is principally due to the dissimilatory reduction of sulfate, but also to the anaerobic degradation of organic sulfur and to the presence of sulfides in the raw wastewater. In the anaerobic ponds of Mèze, the mean rate of the sulfate reduction was 63%. The quantity of the removed sulfate (monthly mean expressed in

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**Figure 2** H$_2$S concentration at different sampling points in the waste stabilization pond system

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw wastewater</th>
<th>Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean min. max.</td>
<td>mean min. max.</td>
</tr>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>18.6 12.2 25.3</td>
<td>17.3 8.1 25.8</td>
</tr>
<tr>
<td>pH</td>
<td>7.4 6.1 8.4</td>
<td>7.1 6.7 7.4</td>
</tr>
<tr>
<td>Suspended solids (mg/l)</td>
<td>256 151 404</td>
<td>114 60 217</td>
</tr>
<tr>
<td>Total COD (mgO$_2$/l)</td>
<td>589 356 960</td>
<td>462 278 614</td>
</tr>
<tr>
<td>Dissolved COD (mgO$_2$/l)</td>
<td>321 121 477</td>
<td>302 158 456</td>
</tr>
<tr>
<td>Bicarbonate (mgCaCO$_3$/l)</td>
<td>321 121 477</td>
<td>380 214 487</td>
</tr>
<tr>
<td>Volatile fatty acids (mg ac.ac./l)</td>
<td>41 14 115</td>
<td>75 33 111</td>
</tr>
<tr>
<td>Sulfides (mgS/l)</td>
<td>3.8 0.0 8.8</td>
<td>19.2 3.2 36.4</td>
</tr>
<tr>
<td>Sulfate (mgSO$_4$/l)</td>
<td>165 96 222</td>
<td>57 3 123</td>
</tr>
</tbody>
</table>
kgS/d) was dependent on temperature with a linear relationship ($R_{SO4} = 2.091T + 2.532$, $r^2 = 0.7045$, $n = 12$). However, the quantity of produced sulfides was not obviously dependent on temperature. Their concentration seemed to be controlled by other mechanisms and influenced by several parameters such as pH, organic loading and retention time. In this study, the mean ratio between the sulfides concentration in anaerobic ponds and the sulfate concentration in the raw wastewater ($S_{\text{II}}/S_{\text{SO4}}$) was 0.35, in accordance with the ratio of 0.28 calculated by Toprak (1997) with a similar anaerobic pond. Almasi and Pescod (1996) found ratios of 0.4 (10°C) and 0.6 (25°C) at pilot scale.

**Model for the H$_2$S emission**

The principal mechanisms governing the emission of volatile compounds in the atmosphere are volatilization at the surface and gas stripping. In the case of anaerobic ponds, the production of biogas, which is released by bubbling to the atmosphere, is a major mechanism. Stating the hypothesis that the surface volatilization is less important than the emission by bubbling with the biogas, the H$_2$S emission rate can be calculated from the H$_2$S concentration in the biogas ($[H_2S]_{\text{biogas}}$) and the biogas emission rate ($E_{\text{biogas}}$). A model was developed to calculate those parameters from data measured in the pond water: temperature, pH and sulfides concentration (Figure 3).

On the one hand, the measured values of $[H_2S]_{\text{biogas}}$ were compared to theoretical values of the H$_2$S concentration ($[H_2S]_{\text{biogas,eq}}$), calculated at equilibrium from Henry’s law and the H$_2$S concentration in the aqueous phase ($[H_2S]_{\text{aq}}$). A linear relationship was obtained, indicating the biogas was over-saturated in H$_2$S. On the other hand, the biogas emission rate was found to be strongly dependent with temperature with a non-linear relationship (Picot et al., 2001). All these theoretical and statistical equations allowed the calculation of the H$_2$S emission rate. Finally, the atmospheric concentration of H$_2$S around the anaerobic ponds ([H$_2$S]$_{\text{atm}}$) measured with bubbling chambers was compared to the H$_2$S emission rate. A linear relationship was obtained indicating that the H$_2$S emission rate explained 73.3% of the variation in [H$_2$S]$_{\text{atm}}$. Indeed, this parameter could also be influenced by other factors like wind speed and meteorological conditions. In summary, this model showed that the H$_2$S emission rate was principally dependent on temperature which influenced the biogas production and the transfer of H$_2$S in the gaseous phase. The pH and the sulfide concentration were also important factors.

![Predictive model for the emission of H2S (S-II and [H2S]aq in mgS/l; [H2S]biogas and [H2S]atm in mgS/m3; $E_{\text{biogas}}$ in l/m2.d; H2S emission rate in mgS/m2.d)](https://iwaponline.com/wst/article-pdf/48/2/227/423153/227.pdf)

* measured at 1 m from the water

**Figure 3** Predictive model for the emission of H$_2$S (S-II and [H$_2$S]$_{\text{aq}}$ in mgS/l; [H$_2$S]$_{\text{biogas}}$ and [H$_2$S]$_{\text{atm}}$ in mgS/m$^3$; $E_{\text{biogas}}$ in l/m$^2$.d; H$_2$S emission rate in mgS/m$^2$.d)
Seasonal variations

Figure 4a shows the annual variations for the sulfides concentration measured in pond water and for the calculated emission rate of biogas. Figure 4b shows that the concentration \([H_2S]_{\text{atm}}\) calculated with the model exhibited high values in summer, between June and September, when water temperatures were greater than 20°C. In winter, even if the concentration of sulfides was high, the \(H_2S\) emission rate was limited because the production of biogas was low.

Table 2 shows the mean annual values of the measured and calculated parameters. The mean concentration of \(H_2S\) in the biogas was 3,390 mg-S/m³ and the mean emission rate of \(H_2S\) was 172 mgS/m².d. The concentration of \(H_2S\) around the anaerobic ponds varied between 0.2 and 6.9 mgS/m³, equivalent to 0.2 and 5.2 ppm. \([H_2S]_{\text{atm}}\) was then always greater than the odor detection threshold equal to 0.005 ppm according to Parsons et al. (2000). The limit of 5 ppm (6.6 mgS/m³) considered unsafe for working with 8 hours exposure, seemed to have been reached occasionally.

Mass balance of sulfur

For a complete mass balance of sulfur, the different forms of sulfur were analyzed in the sludge. The concentration of total sulfur was 9,890 µgS/g dry weight. Organic sulfur was predominant, accounting for 70%, due to the large amount of organic matter. The forms of reduced inorganic sulfur \(FeS\) and \(FeS_2\) accounted respectively for 16 and 13%. The amount of sulfate was not significant. The presence of \(FeS\) could result from the precipitation of \(Fe^{2+}\) with sulfides.

All of the results together allowed the complete mass balance of sulfur shown in Figure 5 to be carried out. The concentration of organic sulfur in the wastewater was estimated to be 5 mgS/l (Parker, 1979). The annual emission of \(H_2S\) was calculated to be 0.28 kgS/d for a surface emission of 1,615 m². The accumulation in sludge was estimated to be 0.26 kgS/d, with a rate of sludge accumulation equal to 0.017 m³/capita.year or 26 kgDS/d (Picot et al., 2002). The loss of \(H_2S\) in the atmosphere and the accumulation in sludge were thus very low compared to the flow arriving with the influent. It should be noted that this mass

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**Table 2** Mean annual characteristics of anaerobic pond AP1 (n = 22)

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>(S_{\text{at}}) (mgS/l)</th>
<th>([H_2S]_{\text{atm}}) (mgS/l)</th>
<th>([H_2S]_{\text{biogas}}) (mgS/m³)</th>
<th>Biogas emission rate (l/m².d)</th>
<th>(H_2S) emission rate (mgS/m².d)</th>
<th>([H_2S]_{\text{atm}}) (mgS/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>17.3</td>
<td>7.1</td>
<td>19.2</td>
<td>9.5</td>
<td>3,390</td>
<td>49</td>
<td>172</td>
<td>2.0</td>
</tr>
<tr>
<td>min.</td>
<td>8.1</td>
<td>6.7</td>
<td>3.2</td>
<td>1.2</td>
<td>510</td>
<td>13</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>max.</td>
<td>25.8</td>
<td>7.4</td>
<td>36.4</td>
<td>22.4</td>
<td>8,640</td>
<td>108</td>
<td>576</td>
<td>6.9</td>
</tr>
<tr>
<td>σ</td>
<td>5.7</td>
<td>0.2</td>
<td>8.3</td>
<td>5.1</td>
<td>1,960</td>
<td>32</td>
<td>172</td>
<td>2.0</td>
</tr>
</tbody>
</table>
balance was not equilibrated with 67 kgS/d entering the anaerobic pond and 47.6 kgS/d “outgoing”. This could be explained by the under-estimation of the \( \text{H}_2\text{S} \) emission rate or by errors in the estimation of sulfur species in wastewater.

Solutions to reduce odor emission

In the case of the waste stabilization pond system of Mèze, the \( \text{H}_2\text{S} \) emission from anaerobic ponds involved a risk of odor nuisances all the year for neighboring inhabitants. Indeed, \([\text{H}_2\text{S}]_{\text{atm}}\) measured around the anaerobic ponds could be interpreted like a maximum concentration that risked being smelt by close inhabitants because the effects of dilution and dispersion could be insignificant with particular meteorological conditions. The limit for nuisances could be fixed at 0.05 ppm of \( \text{H}_2\text{S} \) (10 odor units/m\(^3\) according to Parsons et al., 2000) and was then always exceeded. The odor nuisances appeared, despite the recommendations of Mara and Pearson (1998) which were followed with an organic loading less than 100 gBOD/m\(^3\).d and a mean sulfate concentration in the raw wastewater less than 300 mgSO\(_4^{2-}\)/l. These limit values were then not sufficient in the case of very close residences (200 m in this study).

In that case, measures to reduce the odor emissions should be undertaken. Possible solutions are listed in Table 3. Addition of FeCl\(_3\) should not be attempted because of the toxicity risk for algal biomass in secondary ponds. Liming, surface aeration and recirculation were tested at full scale on the anaerobic pond A1, A2 served as reference. Liming was efficient with a reduction of \( \text{H}_2\text{S} \) emission rate of 66% for a pH increase from 7.0 to 7.7 (addition of lime: 200 kg/d for 5,000 m\(^3\)). The efficiency should be greater with a higher pH (92% for pH 8.5), but it could be toxic for anaerobic bacteria and other odorous compounds like ammonia or amines could appear. The surface aeration was not efficient because of the impossibility of obtaining a stratification of the pond water and the aeration power installed \((4 \times 0.35\text{kW})\) was not sufficient to aerate the whole pond. The recirculation of the effluent from the facultative pond L2 with ratios \( \text{R/Q} = 1 \) and \( \text{R/Q} = 2 \) reduced \( \text{H}_2\text{S} \) emission rate by 80%. The efficiency was due to the dilution effect and to the production of oxidizing conditions from photosynthetic activity. Indeed, chlorophyll \( a \) and bacteriochlorophyll \( a \) were detected, the latter represented photosynthetic sulfur bacteria like Chromatium and Thiocapsa (Almasi and Pescod, 1996). However, the effect on removal performances in the long term was not determined.

The installation of an impermeable cover like a geomembrane is very efficient for odors and allows the reuse of the biogas to produce energy. However, this radical solution is relatively expensive and needs additional maintenance. Finally, the use of a synthetic or biological permeable cover was recently developed and showed a good efficiency with
lower costs. The use of a biological cover consisting of a floating peat bed with plants was tested at laboratory scale and showed an excellent efficiency with a 96% reduction of H₂S emission rate (Picot et al., 2001).

Conclusion
This work permitted the development of a predictive model for the estimation of H₂S emission from anaerobic ponds from water characteristics (temperature, pH and sulfides concentration). In the case of this study, the H₂S emission rate varied between 20 and 576 mgS/m².d, leading to a concentration between 0.2 and 5.2 ppm of H₂S in the surrounding atmosphere. These concentrations risked creating odor nuisances for nearby houses. The use of dispersion models with the H₂S emission rate could indicate the minimum distance between anaerobic ponds and habitations to avoid odor problems. Solutions to reduce the emission of odorous compounds could also be envisaged. The impermeable cover for gas collection and treatment is the more radical solution but its installation and maintenance is relatively expensive. This solution allows the reuse of the biogas to produce energy. The recirculation of a secondary effluent rich in oxygen and algae is efficient and less expensive but the long term effect on removal performances should be further determined. The use of synthetic or biological permeable covers seemed also to offer interesting possibilities.

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