Characterization and prediction of odours from municipal sewage treatment plant
Weifang Li, Weihua Yang and Jiayin Li

ABSTRACT

One of the causes of public discomfort and complaint about odour in China is the nuisance odour, generated from the municipal sewage treatment plants. With the ability to be dispersed over a long distance, the odours can affect a large number of people. With the aim of identifying the compounds contributing the most to the overall odour emanating from municipal sewage treatment plant, and developing a prediction model for sensory odour concentration based on the compound odour activity value (OAV), odour samples from 2 days were collected at a municipal sewage treatment plant in Tianjin in the months of October and November 2013. Odour concentrations (OCs) were measured by the triangular odour bag method. Chemical components were quantified by gas chromatography–mass spectrometry. According to the analysis of odour emission characteristics, it was found that hydrogen sulfide and methyl mercaptan were the key odorants responsible for the overall odour. To understand the interrelationship of these two odorants, 10 groups of a binary mixture of hydrogen sulfide and methyl mercaptan, representing different levels of odour concentration and intensity, were prepared in the laboratory. OCs were regressed against OAV using multivariate linear regression. A statistically significant positive correlation was found between single-compound OAV and odour concentration (by both SPSS and Minitab software). Furthermore, the models were validated by field monitoring data, which showed the odour prediction concentration had a good fit to the measured concentration by using Minitab software. Lastly, the Austal 2000 model system was used for the simulation of the odour emission dispersion into the surrounding area. This study provides an effective way to predict the odour emission condition in municipal sewage treatment plant.

Key words | chemical characterization, interaction of binary odours, municipal sewage treatment plant, odour activity value (OAV), odour prediction model

INTRODUCTION

Odour emissions from wastewater treatment plants (WWTPs) induce impacts in the surrounding areas including devaluation of lands and reduction of life quality (Giuliani et al. 2015). Odorants can be perceived at low threshold levels, and complaints about offensive odour emitted from WWTPs have continued to rise (Zhang et al. 2015). As a result, odour problems have become a continuous environmental concern for urban communities, particularly those located closest to a WWTP (Muñoz et al. 2010; Pérez et al. 2013).

The odorants released from WWTPs vary depending on the raw wastewater entering the plant and the operation of the treatment processes. Jiang et al. (2017) summarized the odour production and emissions in wastewater systems, and concluded that hydrogen sulfide, organic sulfur compounds and aldehydes are the key odorants. Giuliani et al. (2015) studied the correlation in each treatment unit between the odour emission capacity of wastewater and the odour concentration measured by dynamic olfactometry according to EN13725:2003 in ambient air. The odour wheel for wastewater treatment processes, which makes sensory and chemical links between odour descriptors, was initially developed by Suffet et al. (2004). However, the characterization of odour emissions remains challenging even today. The principal odour measurement methods

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are classified into three categories (viz. analytical, sensorial and mixed) (Gostelow et al. 2001; Belgiorno et al. 2012; Naddeo et al. 2012; Godayol et al. 2014). Zarra et al. (2014) investigated the odour emissions from a WWTP and analysed the weaknesses and strengths of the different techniques.

Sensorial techniques use the human nose as a sensor and therefore give a good measurement of real perception of odours. This method requires a certain number of qualified panelists, as well as stringent test conditions. The testing procedure is normative, stringent, and conducive to quality control. But this approach is expensive in terms of time, sampling operation and transportation. In cases where sensory measurement is difficult to implement, another method has been applied as a substitution – converting the chemical concentrations into odour concentrations (OCs), and making a full use of the advantages of instrument analysis (Wu et al. 2015, 2016).

Furthermore, odour itself is a complicated subject (Rospars 2013). In wastewater treatment, the odour is a combination of several volatile organic compounds which are released from different treatment processes. Currently, there are two approaches of estimating the relationship between odour concentration and compound concentration. One approach equates the overall odour concentration to the sum of single-compound odour activity value (OAV), referred to as the aggregate model (Equation (1)):

\[ OC = \sum_{i=1}^{n} OAV_i \]  

where \( OC \) represents the odour concentration, \( OAV_i \) is the single-compound odour activity values, OAV is defined as the concentration of a single odorous compound divided by the odour threshold for that compound.

The other model relates the overall odour concentration to the maximum compound OAV, referred to as the maximum model (Equation (2)):

\[ OC = \max OAV \]  

They both are simplified models, ignoring the interaction between each compound, such as multiplication and cancellation. And hence, the application of the above two models is limited. The emission characteristics of various odour sources are different. Considering the complicated interactions among varieties of odorants, further investigation and scientific experiments should be conducted before establishing the forecast model of odour pollution for a specific emission.

This paper aims to present: (a) the interaction between the key odorants; (b) models to predict OC using multilinear regressions based on compound concentration and OAV; and (c) the odour impact of the municipal sewage treatment plant (MSTP).

**METHODS**

**Description of the situation**

The selected MSTP for the study is one of the largest in Tianjin, China, treating effluents of 1,110,000 citizens and 730 industrial plants that are connected to the municipal sewer system. The design value of the daily effluent intake of the sewage treatment plant was 400,000 m³/day on average during the period of 2013, and the process is based on the biological-chemical treatment method.

Field sampling was carried out on 2 days in October and November 2013. Weather conditions on the sampling days are listed in Table 1. Sampling sites (P1–P4) were set at coarse bar screen, fine bar screen, grit removal, and sludge thickening, as shown in Figure 1. In order to ensure the representativeness of the air sample, gases sampling was conducted at approximately 1.2 m from above the open surface of different treatment units. For sensorial analysis, gas samples were collected in 8 L polyester bags using odour pollution source samplers (Sinodour Co., Ltd, Tianjin). For compound analysis, gases were collected into stainless steel SUMMA canisters (Entech Instruments Inc., USA). Three parallel samples were collected at each point on selected days. The samples were analysed within 24 hours.

**Experimental method**

Compound analyses were performed in accordance with the standard methods TO-14 and TO-15 (US EPA 1999a, 1999b).

**Table 1 | Main climatic factors in Tianjin during the sampling period**

<table>
<thead>
<tr>
<th>Date</th>
<th>Wind speed (m/s)</th>
<th>Stability class</th>
<th>Temperature (°C)</th>
<th>Prevailing wind direction</th>
<th>Relative air humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21/10/2013</td>
<td>0.8</td>
<td>E</td>
<td>20.4</td>
<td>SW</td>
<td>35.9</td>
</tr>
<tr>
<td>14/11/2013</td>
<td>1.3</td>
<td>D</td>
<td>17.8</td>
<td>NW</td>
<td>23.0</td>
</tr>
</tbody>
</table>
The gas samples were pre-concentrated with a three-stage cold trap concentrator (Entench 7100, USA) and then analysed by gas chromatography mass spectrometry (GC–MS). The GC system (Agilent 7890A, USA) and MS system (Agilent 5975C, USA) were equipped with a DB-5MS column (60 m × 0.32 mm × 1.0 mm), with helium as the carrier gas and a temperature program of three ranges (35–150 °C with a step rate of 5 °C/min, 150–220 °C with a step rate of 15 °C/min and then 220 °C for 7 min). In addition to the volatile organic chemicals included in the US EPA TO-14 and TO-15, sulfur compounds and terpenes were also analysed. Compound concentrations were quantified by the internal standard method. The standard curve for each chemical compound was established prior to the analyses using a single standard substance or mixed standard substances (Han et al. 2015).

Odour concentration was measured by the triangular odor bag method (GB/T 14675-1993).

**Date analysis**

The single-compound odour threshold (COT) is the lowest concentration of a single compound in air that can be detected by the human olfactory sense when compared to a non-odourous sample (Sironi et al. 2015). The COT data in this paper used that published in Japan (Nagata 2003).

OAV is widely used for assessing the relative importance of an individual compound in a complex odour mixture (Sivret et al. 2016). The OAV of each compound was calculated by Equation (3):

\[ \text{OAV} = \frac{C}{SC_{OT}} \]

where \( C \) is the concentration of the compound (μg/m³), and \( SC_{OT} \) is the odour detection threshold for the single compound (μg/m³).

Japanese researchers believed that the odour index can reflect the human olfactory sensation better than odour concentration (Iwasaki et al. 1978). Odour index can be calculated by Equation (4):

\[ N = 10 \cdot \log OC \]

where \( N \) is the predicted odour concentration index, \( OC \) is the predicted odour concentration.

The total OAV (OAVsum) for a mixture sample was calculated by summing the OAV of individual components (Equation (5)):

\[ \text{OAVsum} = \text{OAV}_1 + \text{OAV}_2 + \ldots + \text{OAV}_n \]

where \( \text{OAV}_1 \) through \( \text{OAV}_n \) are the calculated OAV of the \( n \) individual compounds. OCs were regressed against OAVsum using linear regression (Equation (6)):

\[ OC = B_0 + B_1(\text{OAVsum}) \]

where \( B_0 \) and \( B_1 \) are regression coefficients. Substituting Equations (5) and (6) into Equation (4) allows \( N \) to be expressed as (Equation (7)):

\[ N = A_0 + A_1 \log (\text{OAV}_1 + \text{OAV}_2 + \ldots + \text{OAV}_n) \]

where \( A_0 \) and \( A_1 \) are regression coefficients.

It should be noted that the calculation of OC using Equations (6) and (7) places equal weight on all individual OAVs. However, it is known that compounds do not all contribute equally to the odour mixture (Lee et al. 2013).
To overcome the equal weighting shortcomings of Equations (6) and (7), prediction equations were also developed using multilinear regression techniques (Equation (8)):

\[ N = C_0 + C_1\log OAV_1 + C_2\log OAV_2 + \ldots + C_n\log OAV_n \]  

(8)

where \( C_0, C_1 \ldots C_n \) are regression coefficients (i.e., weights applied to the OAV values) determined in the multilinear regression analyses.

**Dispersion model**

The Austal 2000 model system was used for the simulation of the odour emission dispersion into the surrounding area. Austal 2000 is an atmospheric dispersion model for simulating the dispersion of air pollutants in the ambient atmosphere and a three-dimensional Lagrangian particle dispersion model. It is set up and verified in conformance with the German guideline VDI 3945/3 as a mesoscale model to be used for assessment/licensing procedures or local and regional air quality studies.

**RESULTS AND DISCUSSION**

**Chemical characterization of the municipal sewage treatment plant**

The total average mass concentration of the four sampling points was 191.99 mg/m³ and 183.58 mg/m³ in the first and second sampling time, respectively. For the first detection time, the average mass concentration of the sludge thickening workshop (P4) was highest, which accounted for 66.52% of the total mass concentration, while for the second detection time, the highest mass concentration was in grit removal (P3), accounting for 58.69% of the total mass concentration. The average detected concentration in each point was \( P_4 \) (87.38 mg/m³) > \( P_3 \) (62.31 mg/m³) > \( P_2 \) (31.52 mg/m³) > \( P_1 \) (6.57 mg/m³). It is seen that \( P_4 \) and \( P_3 \) were the most seriously polluted units in the MSTP (see Figure 2).

A total of 59 compounds were detected in the MSTP, including 10 alkane compounds, four alkene compounds, 11 arene compounds, 16 halohydrocarbon compounds, 13 oxygenated organic compounds, three organic sulfides and two inorganic gases. The highest number of different substances was detected at \( P_3 \), followed by \( P_2 \) and \( P_4 \).

For complicated odour samples, it is an important concern to determine the contribution of individual compounds and then find the most significant odorants. So far, the most commonly used method is based on OAV which reflects the combined effect of compound concentration and its olfactory threshold. The larger the OAV, the more likely the compounds contribute to the overall odour (Genthner 2014). The top five compounds with rather higher OAVs and their mass concentration are provided in Table 2.

From Table 2, it can be seen that hydrogen sulfide ranked the highest in both mass concentration and OAV at all sampling points, at least one order of magnitude higher than other compounds, demonstrating that hydrogen sulfide was the most prevalent contaminant in MSTP. Although the concentration of methyl mercaptan was much lower than other compounds, its OAV ranked second due to its much lower olfactory threshold. As for the other compounds, their proportions of both concentrations and OAVs were much smaller. Therefore, hydrogen sulfide and methyl mercaptan were selected as the representative odorants of the MSTP.

**Odour concentration prediction model**

To develop a prediction model of odour concentration, we need to understand the interaction between hydrogen sulfide and methyl mercaptan. We first conducted laboratory studies and prepared 10 groups of hydrogen sulfide and methyl mercaptan samples with various concentration levels, as shown in Table 3. The concentration levels of the two compounds were determined by diluting its standard gas to a certain proportion, and the composite OCs were measured by the triangular odour bag method.
From Table 3, it can be found that six groups (1, 2, 4, 5, 6, 9) of odour concentration increased significantly after mixing hydrogen sulfide and methyl mercaptan, reflecting their mutual promoting role, whereas the OCs among the remaining four groups of samples were decreases, which was the result of their mutual inhibition effect. Therefore, the interaction among them was very complicated.

To further explore the effect of OAV (H₂S + CH₃SH) on odour concentration, regression analyses were conducted in the following study. As the odour index can reflect the human olfactive sensation better when compared with the odour concentration, the data were log-transformed by Equation (4). The calculated results are shown in Table 4.

### Relationship between odour concentration and OAV_sum

As shown in Figure 3, OCs were positively correlated with OAV_sum (H₂S + CH₃SH) for MSTP. The R² value (0.67) demonstrated that a maximum 67% of the variation in OCs could be predicted by using total gas concentrations (H₂S + CH₃SH). Ideally, the slope in Figure 3 would be equal to 1.0, and the y-intercepts would be zero. The actual slope was 0.88, indicating that OAV_sum (H₂S + CH₃SH) can account for two-thirds of the odour concentration. Plausible causes could include: (a) the existence of synergistic effects among compounds, (b) actual OCs were overestimated. From this result, we conclude that OAV_sum (H₂S + CH₃SH) is a useful tool for assessing general trends in odour concentration at a MSTP, but it cannot be used with a high degree of accuracy for predicting OC.

### Relationship between odour concentration and single compound

With OAV index of hydrogen sulfide and methyl mercaptan as the independent variable and odour concentration index as the dependent variable, multilinear regressions were analysed by using the SPSS and Minitab software, respectively.

### Table 2 | The top five OAVs of the compounds in each point

<table>
<thead>
<tr>
<th>Substances</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_max (mg/m³)</td>
<td>OAV</td>
<td>C_max (mg/m³)</td>
<td>OAV</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>6.996</td>
<td>11,216</td>
<td>38.154</td>
<td>61,172</td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>0.059</td>
<td>393.99</td>
<td>0.337</td>
<td>2,238</td>
</tr>
<tr>
<td>Hexanal</td>
<td>0.146</td>
<td>49.48</td>
<td>0.169</td>
<td>57.21</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.244</td>
<td>27.03</td>
<td>0.267</td>
<td>29.64</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.231</td>
<td>1.42</td>
<td>2.014</td>
<td>12.38</td>
</tr>
</tbody>
</table>

### Table 3 | Ten groups of hydrogen sulfide and methyl mercaptan samples prepared in the laboratory

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>50.00</td>
<td>121.67</td>
<td>185.00</td>
<td>233.33</td>
<td>541.67</td>
<td>42.75</td>
<td>71.50</td>
<td>98.33</td>
<td>176.67</td>
<td>207.75</td>
</tr>
<tr>
<td>CH₃SH</td>
<td>104.48</td>
<td>323.88</td>
<td>1,313.4</td>
<td>577.61</td>
<td>1,925.3</td>
<td>68.66</td>
<td>155.22</td>
<td>208.96</td>
<td>746.27</td>
<td>404.48</td>
</tr>
<tr>
<td>Odour</td>
<td>741</td>
<td>3,090</td>
<td>13,193</td>
<td>2,344</td>
<td>7,413</td>
<td>1,318</td>
<td>1,738</td>
<td>977</td>
<td>17,378</td>
<td>3,090</td>
</tr>
</tbody>
</table>

*The OAV of hydrogen sulfide; \(^b\)the OAV of methyl mercaptan; \(^c\)odour concentration.

### Table 4 | The log-transformed calculated results of odour by Equation (4)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>16.99</td>
<td>20.85</td>
<td>22.67</td>
<td>23.68</td>
<td>27.34</td>
<td>16.31</td>
<td>18.54</td>
<td>19.93</td>
<td>22.47</td>
<td>23.18</td>
</tr>
<tr>
<td>Odour</td>
<td>28.70</td>
<td>34.89</td>
<td>41.20</td>
<td>33.69</td>
<td>38.70</td>
<td>31.20</td>
<td>32.40</td>
<td>29.90</td>
<td>42.40</td>
<td>34.90</td>
</tr>
</tbody>
</table>

*The index of hydrogen sulfide’s OAV; \(^b\)the index of methyl mercaptan’s OAV; \(^c\)odour index.
Both software packages enter all independent variables into the model; for the SPSS software, the independent variable with the largest p-value ($P > 0.1$) is removed, and the regression is re-calculated. If this weakens the model significantly, the variable is re-entered; otherwise it is deleted. However, for Minitab software, all independent variables are shown in the result. The fitting results by these two software packages are shown in Table 5. All correlations were statistically significant. A statistically significant positive correlation (0.80) was found between the single-compound OAV and odour concentration by using Minitab software, but it was lower (0.67) by using SPSS software. Based on the regression analyses, the two conversion methods are entirely different. However, there is no doubt that H$_2$S is the highest contributor to odour.

We used the odour data obtained from an MSTP to verify the predictability of the two conversion methods. Figure 4 shows the measured odour concentration as a function of the predicted odour concentration by SPSS (Figure 4(a)) and Minitab (Figure 4(b)). All correlations were statistically significant by using these two software programs ($P < 0.05$); they accounted for 24% of the variation in the odour concentration. The correlation coefficient ($R^2$) between measured and predicted odour concentration was 0.24 by SPSS model, while the relationship $\log_{10}OC_{\text{pre}} - \log_{10}OC_{\text{mea}}$ presents a much stronger linear correlation factor with $R^2 = 0.77$ by Minitab model. Despite the variability in odour measurements and measurement errors, the developed Minitab model shows that it is possible to explain 77% of the variation in the odour concentration based on odorants’ OAV. Therefore, the preliminary modelling approach for odour prediction is feasible.

### Odour impact assessment

It is difficult to simulate all the processing units; the main three odour sources ($P_1$, $P_2$, $P_3$), which were placed outdoors, were used to predict the influences on the surrounding environment. The ground meteorological climate data of October and November in 2013 were provided by the Tianjin weather station; the main parameters included hourly wind direction, wind speed, dry bulb temperature, relative humidity, total cloud cover and low cloud cover. The Austal model system was used to quantify the odour impacts around the monitored MSTP, as shown in Figure 5. It is seen that the

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**Table 5** | Prediction models by using the SPSS and Minitab software

<table>
<thead>
<tr>
<th></th>
<th>SPSS</th>
<th>Minitab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$N = 0.831X_1$</td>
<td>$N = 1.675X_1 - 0.890X_2$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.67</td>
<td>0.80</td>
</tr>
<tr>
<td>$P$</td>
<td>0.002</td>
<td>0.004</td>
</tr>
</tbody>
</table>

$N$ is the predicted odour concentration index; $X_1$ is the OAV index of hydrogen sulfide; $X_2$ is the OAV index of methyl mercaptan.
occurrence frequency of odour pollution in the area of 300 m × 300 m was highest, reaching 100%, and was mainly due to the relatively concentrated position and the higher odour concentration at these three units. The maximum distance of odour dispersion from the MSTP, calculated according to the German guidelines, was at 1,500 m in the north direction. The affected area was up to 1,500 m × 900 m, far beyond the scope of a MSTP.

CONCLUSIONS

The following conclusions were drawn from this research.

The highest odorous compound concentrations were determined in the sludge thickening unit as well as in grit removal, and these two units were the most seriously polluted units in the MSTP.

The most significant compounds which contributed most to the overall odour were hydrogen sulfide and methyl mercaptan compounds in each point.

A maximum 67% of the variation in OCs could be predicted by using OAV\textsubscript{sum} (H\textsubscript{2}S + CH\textsubscript{3}SH). It was concluded that OAV\textsubscript{sum} (H\textsubscript{2}S + CH\textsubscript{3}SH) can account for two-thirds of the odour concentration in the MSTP.

Statistically significant positive correlations were found between single-compound OAV and odour concentration. After verification, the sensory prediction model was \( N = 1.675X_1 - 0.890X_2 \) (\( X_1 \) is the OAV index of hydrogen sulfide, \( X_2 \) is the OAV index of methyl mercaptan) (\( R^2 = 0.80, p < 0.005 \)).

The result of the odour dispersion simulation showed that the affected area of the MSTP reached to 1,500 m × 900 m.

The research here shows the preliminary ways to convert the OAV of key odorants to predict the overall odour concentration of an MSTP. However, further studies would be needed to prove the validity of the model.

ACKNOWLEDGEMENT

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