Technical note

Emissions of NO, TVOC, CO$_2$, and aerosols from a pilot-scale wastewater treatment plant with intermittent aeration

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Abstract

Atmospheric emissions from a pilot wastewater treatment plant performing aerobic and anoxic processes were investigated. The experiment was performed by sealing the whole aeration tank with an airtight cover of polyethylene in order to obtain a defined flow rate of the off-gas. By measuring concentrations in the known flux of the off-gas emission rates were determined. Due to the dimensions of the pilot plant and the air and water flows these emission rates represent upper limits. The emission rates were put into relation to CO$_2$ to obtain normalized data that can be used for emission inventories. Normalized emission rates (g component $\times$ g$^{-1}$ CO$_2$) were $8.9 \times 10^{-3}$ for TVOC, $6.6 \times 10^{-6}$ for non-methane hydrocarbons C$_2$–C$_7$ (NMHC), $2.1 \times 10^{-5}$ for NO and $3.0 \times 10^{-6}$ for particulate organic carbon (POC). Emission rates per capita equivalent per year accounted at the most for 244 g TVOC, 0.18 g C NMHC, 0.58 g NO and 0.08 g C POC on a basis of 27,400 g CO$_2$ per capita. The non-aeration periods also contributed to the production of NO and TVOC emissions of approximately one-third of the total emissions. From this, we conclude that the implementation of denitrification stages in European wastewater treatment plants according to the EU-directive 91/271/EEC will increase trace gas emissions in Europe. However, according to our estimates, emissions of trace gases and aerosols from wastewater treatment compared to anthropogenic sources will still remain very low.

Keywords: Denitrification; Methane; Aerobic treatment; Anoxic conditions; Hydrocarbons

1. Introduction

The study on the emissions of a wastewater treatment plant (WTP) produced during nitrification and denitrification periods was performed due to the following reasons: No emission rates concerning nitric oxides (NO, NO$_2$) and carbonaceous aerosols are available in literature (McInnes, 1996). Emissions of volatile organic compounds (VOC) from WTPs have been investigated, but emission rates ranged over several orders of magnitudes (Namkung and Rittmann, 1987; Bell et al., 1993; Zhu et al., 1999) and recent laws on solvent use in many states are expected to have an effect also on emissions of VOC from sewage treatment plants.

A new technology has to be accomplished in the European Union (CEC1, 1991) to allow the removal of more than 70% of total nitrogen from the wastewater. By adding the required anoxic denitrification stages to the current systems, the size of the plants must be approximately tripled with a considerable increase of the residence...
time of the anoxic phase. Consequently, it appears likely that trace gas emissions that are connected to the denitrification process (e.g. methane, NOx) will increase in the near future.

2. Experimental

2.1. Field site

Investigations were performed at the WTP of the University of Agricultural Sciences, in Vienna, Austria. The facility is an activated sludge pilot plant with a water capacity of 1.6 m$^3$. The aeration tank is a rectangular polyethylene basin fed with fresh wastewater out of the local municipal Viennese sewer line. A time-controlled feed produces an inlet rate of $1 \text{ m}^3 \text{ d}^{-1}$. Sludge is pumped back from the settling tank into the activated sludge system at a rate of about $1.7 \text{ m}^3 \text{ h}^{-1}$. Paddle mixers are used to stir the content of the aeration tank continuously. Aerobic digestion, nitrification and denitrification are all done in the same aeration tank. The aeration periods last 30 min at an air rate of $16 \text{ m}^3 \text{ h}^{-1}$ (STP based on $0^\circ \text{C}$ and 1013 mbar) followed by a non-aeration period of one hour. Rod-shaped diaphragm blowers (10 cm in diameter, Purator) are used for aeration. A schematic diagram of the plant and further descriptions are given in Fuerhacker et al. (2000).

The physical–chemical properties of the wastewater were determined according to the DIN-German Industrial Standards (DEV, 1998). Average values obtained for the influent were 198 mg l$^{-1}$ total organic carbon (TOC), 437 mg l$^{-1}$ chemical oxygen demand (COD), 207 mg l$^{-1}$ biological oxygen demand (BOD$_5$), 4.3 mg l$^{-1}$ phosphate (PO$_4$–P), 6 mg l$^{-1}$ total phosphorus (P$_{\text{total}}$), 150 mg l$^{-1}$ suspended solids (SS), and 36 mg l$^{-1}$ ammonia–nitrogen (NH$_4$–N). Effluent values were 6 mg l$^{-1}$ TOC, 0.5 mg l$^{-1}$ P$_{\text{total}}$, 1 mg l$^{-1}$ ammonia–nitrogen (NH$_4$–N), and 4 mg l$^{-1}$ nitrate–nitrogen (NO$_3$–N). Average pH was 7.1 and dissolved oxygen 1.3 mg l$^{-1}$.

2.2. Methods

The special feature of this study was that the whole aeration tank was completely sealed with a polyethylene cover. A slight overpressure in the chamber was maintained. Additional air at a flow rate of 5.5 m$^3$ h$^{-1}$ (STP) was pumped continuously into the cover to form a chamber volume of 2 m$^3$. A glass manifold was connected to the chamber at a distance of 0.5 m above the water level of the aeration tank. All samples were collected from the outlet of the manifold, which was heated to 25$^\circ \text{C}$ to avoid condensation. In addition, intake air used for aeration was checked several times a day. Concentrations of CO$_2$ were determined with a non-dispersive infrared (NDIR) gas analyzer (Maihak UNOR 6N), NO and NO$_2$ with a Nitrogen Oxides Analyzer Model 8840 (Monitor Labs Inc.), and TVOC with a Hydrocarbon-Analyzer Model VE 5 with a Flame-Ionization Detector (FID; Messer, Austria). The FID was calibrated with propane. Methane was included in the results for TVOC, which are given in mg C m$^{-3}$. Data were collected every 20 s. An average of every minute was calculated and used to determine daily minima (lowest values) and maxima (highest values) as well as arithmetic averages of the gaseous components over the aeration and non-aeration periods for the selected time intervals. Samples of NMHC were collected on adsorption tubes filled with Carbosieve SII (60/80 Mesh size, Supelco) and Molecular Sieve 5 Å (60/80 Mesh size, Chrompack) adsorbens. The analysis was carried out on a Gas Chromatograph with FID (HP-5890 Series II). Details are described in Sree et al. (2000).

Aerosols were collected on quartz-fiber filters (TISSUQUARTZ 2500QAT-UP, Pallflex, USA) placed in polycarbonate filter stacks (NILU – Norwegian Institute for Air Research). Sampling rate was about 2 m$^3$ h$^{-1}$ (STP). Total carbon was determined by burning an aliquot of the filter at 1000$^\circ \text{C}$ in oxygen. The evolved CO$_2$ was measured using an NDIR analyzer (Maihak UNOR 6N). The set up of the above combustion method is described elsewhere (Puxbaum and Rendl, 1983).

Data used to determine the emission rates were taken from the 9 February 1998 until the 13 February 1998. During this period, the plant was controlled intensively. The wastewater temperature was 18–19$^\circ \text{C}$.

3. Results and discussion

Table 1 contains the concentration data of the determined components. To calculate the daily emission rates ($E$) the following equation is used:

$$E = (c_{ae} t_{ae} F_{ae}) + (c_{nae} t_{nae} F_{nae}),$$

where $c_{ae}$ stands for the average concentration of a component minus the concentration of this component in the intake air during the aeration phase, and $c_{nae}$ is the average concentration of the component during the non-aeration phase minus the concentration of this component in the additional air that was pumped into the cover (Table 1). $t_{ae}$ stands for the duration of the aeration phase ($8 \text{ h} d^{-1}$), respectively, $t_{nae}$ for the duration of the non-aeration phase ($16 \text{ h} d^{-1}$), $F$ represents the gas flow, which was 21.5 m$^3$ h$^{-1}$ STP ($F_{ae}$) in the aeration phase and 5.5 m$^3$ h$^{-1}$ STP ($F_{nae}$) in the non-aeration phase. The concentrations and mixing ratios in the intake air are 2.1 ppb NO, 1.3 mg C m$^{-3}$ TVOC and 0.04 vol% CO$_2$. The mixing ratios are converted into concentrations by the conversion factors 1.34 for NO (µg m$^{-3}$) and 19.6 for CO$_2$ (gm$^{-3}$). For POC, which is completely removed
The concentration of NO, TVOC, CO₂, and POC in the off-gas emitted by the aeration tank of the pilot wastewater treatment plant in Vienna, estimates of aeration and non-aeration phase contributions; lowest (min) and highest (max) minute means on the respective day and daily averages.

Table 1

<table>
<thead>
<tr>
<th>Date</th>
<th>NO (ppb)</th>
<th>TVOC (mg m⁻³)</th>
<th>CO₂ (vol%)</th>
<th>POC (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Average</td>
<td>Min</td>
</tr>
<tr>
<td><strong>Aeration phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Feb</td>
<td>—</td>
<td>405</td>
<td>64.0</td>
<td>16.0</td>
</tr>
<tr>
<td>11 Feb</td>
<td>—</td>
<td>40.5</td>
<td>65.4</td>
<td>12.8</td>
</tr>
<tr>
<td>12 Feb</td>
<td>32.7</td>
<td>65.4</td>
<td>48.6</td>
<td>18.2</td>
</tr>
<tr>
<td>13 Feb</td>
<td>10.5</td>
<td>44.4</td>
<td>38.4</td>
<td>—</td>
</tr>
<tr>
<td>c_{ae} (10–13 Feb)</td>
<td>47.7 ± 18.1</td>
<td>—</td>
<td></td>
<td>29.7 ± 8.0</td>
</tr>
<tr>
<td><strong>Non-aeration phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Feb</td>
<td>—</td>
<td>38.6</td>
<td>69.8</td>
<td>15.7</td>
</tr>
<tr>
<td>11 Feb</td>
<td>38.6</td>
<td>89.8</td>
<td>55.9</td>
<td>12.7</td>
</tr>
<tr>
<td>12 Feb</td>
<td>29.8</td>
<td>68.9</td>
<td>49.3</td>
<td>18.0</td>
</tr>
<tr>
<td>13 Feb</td>
<td>27.3</td>
<td>44.4</td>
<td>35.8</td>
<td>—</td>
</tr>
<tr>
<td>c_{nac} (10–13 Feb)</td>
<td>47.0 ± 17.9</td>
<td>—</td>
<td></td>
<td>23.0 ± 3.6</td>
</tr>
</tbody>
</table>

Fig. 1 gives the average curve of the measured trace gas concentrations in contrast to the dilution curves, which were obtained by Eq. (2). This figure also clearly illustrates the increase of NO and TVOC concentrations during the non-aeration period, while concentrations of CO₂ decreased during the non-aeration period and increased during the aeration phase of the plant. The contribution of the different periods to the total emissions (Table 2) was calculated by the amount of the component produced during the aeration phase and measured during the aeration phase (A_{a} F_{ac}), and the amount of the component produced during the aeration phase but due to the carry-over of the gases measured during the non-aeration phase (A_{n} F_{nac}) minus the amount of the component that originates from the last non-aeration phase (A_{n} F_{nac}) minus the intake air (Eq. (3)). The calculation was performed in the same way for the non-aeration period (Eq. (4)).

E_{ae} = A_{a} F_{ac} + A_{n} F_{nac} - A_{f} F_{ac}, (3)

E_{nac} = A_{f} F_{ac} + A_{f} F_{nac} - A_{n} F_{nac}. (4)

A_{f} and A_{n} were calculated by the integration of Eq. (2) and A_{v} by Eq. (5) with n = 30 for A_{h} and n = 60 for A_{v}.

A = \sum_{i=1}^{n} c_{t_{i-1}} (\tau_{i} - \tau_{i-1}). (5)

The results of the above calculations are included in Table 2. The relative contributions of NO, TVOC and CO₂ emitted during the non-aeration periods are 38, 34, and 17%, respectively. Yearly emissions of TVOC, NMHC, NO and POC per capita equivalent and the emission rates normalized to CO₂ are also given in Table 2. The yearly trace gas emissions were calculated from the normalized emission rates and on a basis of 27,400 g CO₂ per capita equivalent (accounts for wastewater from inhabitants and other sources). This basis is obtained from McInnes (1996).

3.1. Nitrogen oxides

Emission rates of NO obtained by the current study are approximately 0.58 g per capita equivalent per year (Table 2). Assuming that the operating conditions have the most important influence on the amount of NO emissions the variation of the emission rates with
different operating conditions was investigated. During a measuring period in January 1998 the WTP was operated under different working conditions (Fuerhacker et al., 2000). To compare the results of the different stages the emissions were put into relation to the inlet by dividing the NO emissions (mg NO d$^{-1}$) by the amount of TOC in the inlet (g TOC d$^{-1}$). The average NO emissions over the four different stages were 0.086 mg NO g$^{-1}$ TOC. Slightly higher emissions of 0.131 mg NO g$^{-1}$ TOC were obtained for stage I with low load and high aeration (aeration period: 2 h). Stage III operating under overloaded working conditions gave smaller emissions (0.053 mg NO g$^{-1}$ TOC). The results of the current study (0.081 mg NO g$^{-1}$ TOC) fit well to the emissions of stage II with balanced feed and aeration (0.078 mg NO g$^{-1}$ TOC). With a standard deviation of 0.033 a coefficient of variation of 38% is obtained. Even under very different operating conditions of the WTP the NO emissions are of the same order of magnitude 0.1 mg NO g$^{-1}$ TOC and an emission rate of 0.58 ± 0.22 g NO per capita equivalent per year is obtained. A remarkable amount of this emission (38%) was produced during the non-aeration periods. This indicates a considerable outgassing during the non-aeration period, simultaneously with methane (Table 2).

3.2. Volatile organic compounds

Emissions of TVOC are 244 gC TVOC per capita equivalent per year (Table 2) or $8.9 \times 10^{-3}$ gC TVOC g$^{-1}$ CO$_2$. Tentative results showed that methane contributed more than 97% of the TVOCs. These results were obtained by removing the NMVOCs in the off-gas by adsorption on activated charcoal and detecting the remaining methane. Approximately, 66% of the TVOC emissions are produced during the aeration periods (Table 2). The increased emission (34%) during the non-aeration period in relation to CO$_2$ indicates that active outgassing of TVOC (presumably methane) proceeds during non-aeration.

The emission rate obtained in the present study (approximately 237 g methane per capita per year) corresponds well with the emission factors for emissions to air from WTPs of 300 g methane per capita equivalent (McInnes, 1996). This is in contrast to 39 g per person per year as determined by Czepiel et al. (1993) for a primary and secondary activated sludge treatment process.

Individual non-polar NMHC (C$_2$-C$_7$) were determined by GC–FID and accounted for 0.1% of emissions of TVOC. Polar organic compounds and higher hydrocarbons, which are supposed to contribute to the TVOC emissions, could not be determined with the applied technique. Converting the NMHC data (Sree et al., 2000) to the units used in Table 2, the WTP in the current study emits 0.18 gC NMHC per capita equivalent per year or $6.6 \times 10^{-6}$ gC NMHC g$^{-1}$ CO$_2$ (or 0.005 g NMHC m$^{-3}$ wastewater). Emissions of aromatic HC, halocarbons and other VOC reported in the literature were much higher. Namkung and Rittmann (1987) estimated emissions of 11 aromatic HC and halocarbons of 0.032–0.036 g m$^{-3}$ wastewater, Bell et al. (1993) reported stripping rates of aromatic and halogenated VOCs in the same range (0.036–0.050 g m$^{-3}$ wastewater). Zhu et al. (1999) observed even emissions of eight VOCs of 40–100 g m$^{-3}$, which consisted to 75% of acetone. The relatively low NMHC emissions in the present study...
Table 2
Normalized emission rates, emissions per capita equivalent per year and contribution of the non-aeration period to the total emissions of the pilot wastewater treatment plant in Vienna

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Normalized emission</th>
<th>Emissions per capita equivalent</th>
<th>Emitted in non-aeration period (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1 g CO₂ g CO₂⁻¹</td>
<td>27400 g CO₂</td>
<td>17</td>
</tr>
<tr>
<td>TVOC</td>
<td>8.9 x 10⁻³ g TVOC g CO₂⁻¹</td>
<td>244 gC</td>
<td>34</td>
</tr>
<tr>
<td>C₂–C₇ NMHC</td>
<td>6.6 x 10⁻⁶ g NMHC g CO₂⁻¹</td>
<td>0.18 gC</td>
<td>n.d.</td>
</tr>
<tr>
<td>NO</td>
<td>2.1 x 10⁻⁵ g NO g CO₂⁻¹</td>
<td>0.58 g NO</td>
<td>38</td>
</tr>
<tr>
<td>POC</td>
<td>3.0 x 10⁻⁶ gC g CO₂⁻¹</td>
<td>0.08 gC</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*McInnes (1996); TVOC: total gaseous organic carbon determined with FID. C₂–C₇ NMHC: individual C₂–C₇ hydrocarbons. n.d.: not determined.

might be explained by the fact that solvent discharge to wastewater is strictly regulated in Austria. Therefore, the NMHC emissions did not contain halogenated hydrocarbons (they were all below the detection limit of the method) and compared to the above studies low emissions of aromatic HC were obtained. More detailed results of the NMHC data of the current project are described elsewhere (Sree et al., 2000).

3.3. Particulate organic carbon

Due to the heavy aeration of activated sludge units and the aerosol formation caused by bursting bubbles (Woodcock, 1955), it was expected that sewage treatment plants are an important source of aerosol emissions. Surprisingly, emission rates of POC determined by the present study are quite low below 0.1 gC per capita equivalent per year (Table 2).

4. Conclusions

For the calculation of the emission rates it is assumed that mass transfer of the trace gases and aerosols of the pilot plant is comparable to a full-scale WTP. Nevertheless, the air-to-water ratio is much higher in the pilot plant and the surface area is larger and the reactor is more intensively mixed than a standard anoxic zone in a full-scale WTP. Taking these points into consideration would lead to rather smaller emission rates. Therefore, the emission rates determined in the present study (Table 2) have to be taken rather as upper limits for emissions from WTPs.

Applying a dilution model it was found that emissions of NO and TVOC are also produced during the non-aeration periods at approximately one-third of the total emissions. Since denitrification stages in European WTPs will be implemented until 2005 it can be predicted that trace emissions of NO and TVOC will increase in the next years. Until now no emission rates of NOₓ and carbonaceous aerosols produced by WTPs are available in literature.

However, the contribution of emissions from WTPs to continental emissions, even in combination with denitrification stages, is expected to be very low. In Vienna (1.6 million population) total NOₓ-N emissions in 1995 were approximately 5000 t N (Umweltbundesamt Wien, 1995). The Vienna Main WTP processes an average daily wastewater load (including industry) corresponding to a capita equivalent of 3.4 million (Kainz and Hofstetter, 1996). The NOₓ-N emission from WTPs in Vienna including the denitrification stages is thus estimated to be not more than 0.9 ± 0.3 t N yr⁻¹, which is < 0.02% of the total NOₓ-N emission.

Emissions of POC in Vienna are estimated to be less than 1 t yr⁻¹, which is a very small contribution to the estimated emissions of particulate matter in Vienna of more than 10,000 t yr⁻¹ (Pucher and Rüdiger, 1997). Emissions of methane produced by WTPs in Vienna are estimated to be not more than 800 ± 300 t C yr⁻¹. In Vienna total yearly emissions of methane are 51,200 t (Umweltbundesamt Wien, 1995) resulting in a maximum of 2% emitted by WTPs. Even after the implementation of denitrification stages in European treatment plants emissions of wastewater treatment plants will remain very low.

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