

Direct Measurements of Odorous Volatile Organic Compounds Present in Biosolids Cakes by Proton Transfer Reaction – Mass Spectrometry Technique

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Abstract

This paper shows the results of investigation of concentration of odorous chemical compounds emitted upon ageing of anaerobically stabilised biosolids that could contribute to the overall odour character of nuisance emissions. Biosolids samples from wastewater treatment plant were collected in spring time. Concentrations of volatile organic compounds using a US EPA flux hood and Proton Transfer Reaction-Time of Flight-Mass Spectrometry technique were monitored during three weeks. The concentrations of identified odorants were estimated from 0.23 ppm to 2.93 ppm. Increasing concentrations of all identified compounds were observed after 10th day from the sampling days for two samples. It can be a consequence of biological process occurring in three week time in biosolids cakes.

1. Introduction

Wastewater treatment plants are one of the most important forms of human activity, which contributes to increasing amount of chemical compounds present in atmospheric air [1]. One of the potential sources of emission from the wastewater treatment plants can be biosolids cakes, which produces many odorous chemical compounds, mainly volatile organic compounds, volatile sulphur compounds, volatile nitrogenous compounds (trimethylamine), volatile aromatic compounds (toluene, ethyl benzene, *p*-cresol, indol, skatol) or others [2]. Presence of the odour compounds emitted from wastewater treatment plants to the air has disadvantageous effect on people, including headache, concentration problems,

dizziness or malaise. Their emission has a negative effect on the plant and animal ecosystem. The level of emission of these compounds into the environment, especially volatile organic compounds, is variable. It largely depends on many factors including rate of biological changes occurring in the collected sewage, technological solutions employed at the sewage treatment plants or sewage quality [3].

One of the instrumental solutions used to determination of volatile organic compounds present in various types of samples is Proton Transfer Reaction–Mass Spectrometry (PTR-MS). This technique is based on the conversion of the neutral molecules to the ionized form as a result of the proton transfer reaction between them and hydronium ions generated inside the device in an ion source by a hollow cathode discharge on water vapour [4, 5]. In 2009 the first instruments capable of switching between various reagent ions (besides H_3O^+ reagent ions can be O_2^+ , Kr^+ or NO^+) were presented [6, 7]. PTR-MS technique allows direct analysis in real time, without any sample preparation. Nowadays it is used in a wide range of scientific fields including: biotechnological application, atmospheric and environmental chemistry, medicine, food science or industrial process monitoring [7–13].

The objectives for this study are quantification and comparison of concentration of the volatile organic compounds associated with anaerobically stabilised two biosolids samples during three weeks. Differences between concentrations of odours chemical compounds with comparison to their odour descriptors can indicate which of these compounds can have the significant potential to contribute to nuisance emission from the biosolids at wastewater treatment plants.

2. Experimental

2.1 Reagents and chemicals

Approximately 10 L anaerobically stabilized dewatered biosolids samples were collected from the same location at the wastewater treatment plants “Gdańsk Wschód” located in Gdańsk, Poland in two consecutive day in spring time and transported in plastic bucket to the laboratory.

2.2 Instrumentation

Flux hood (designed according to US EPA) was used to produce emissions from the stored biosolids samples after purging (30 minutes) with a nitrogen flow of 5 L min^{-1} . After this time the biosolids samples were analysed using Proton Transfer Reaction–Time of Flight–Mass Spectrometry (PTR-TOF-MS, Ionicon Analytic, Austria). H_3O^+ ions, as the reagent ions, were produced from a pure water vapour flow in a hollow cathode discharge ion source. Volatile odours compounds from biosolids were introduced into the reaction drift tube via 1.5 m long heated



Table 1

Average concentration of odours chemical compounds present in first/second biosolids sample.

| Compound | Odour descriptors | Average concentration / ppm | | | | |
|------------------------|---|-----------------------------|-----------|-----------|-----------|-----------|
| | | 1st day | 7th day | 10th day | 14th day | 21st day |
| dimethyl sulfide | rubbish, seaweed, garlic, sulphur | 1.31/1.29 | 1.42/1.28 | 2.01/3.77 | 2.12/4.11 | 2.93/2.76 |
| diethyl disulfide | bad breath, garlic, sulphur | 0.43/0.29 | 1.11/1.05 | 1.49/1.44 | 1.49/1.46 | 1.51/1.53 |
| diethyl sulfide | sulphur, pungent garlic-like | 0.92/0.76 | 0.98/0.82 | 1.43/1.05 | 1.45/1.21 | 1.45/1.25 |
| dimethyl disulfide | garlic, sulphur, seaweed | 1.26/1.29 | 1.44/1.54 | 2.22/3.45 | 2.38/3.94 | 2.45/3.82 |
| toluene | solvent, gasoline, burning plastic | 0.23/0.27 | 0.29/0.31 | 0.69/0.75 | 0.99/0.86 | 0.97/0.91 |
| <i>m</i> -xylene | sweet, soybean sauce, cleaning product, roses, minty, solvent | 0.67/0.75 | 1.21/1.22 | 1.25/1.29 | 1.25/1.32 | 1.44/1.13 |
| α -pinene | yeast, soy sauce, sweet, pinene, floral, roses, | 0.45/0.49 | 0.56/0.76 | 0.96/0.94 | 0.92/0.93 | 0.89/0.84 |
| limonene | oranges, sweet, floral | 0.45/0.43 | 0.65/0.49 | 0.92/0.89 | 0.96/0.92 | 0.94/0.92 |
| 1,3,5-trimethylbenzene | geranium, herbaceous, pinene, grassy | 0.88/0.78 | 1.11/1.02 | 1.17/1.28 | 1.46/1.55 | 1.59/1.79 |
| ethyl benzene | aromatic, solvent | 0.75/0.72 | 0.94/0.79 | 0.99/0.88 | 1.45/1.49 | 1.55/1.42 |

(at 60°C) PEEK tubing with a flow rate of about 60ml min⁻¹. The key operating parameters were held at: drift tube pressure 2.0 mbar, drift voltage 600 V, temperature 60 °C and E/N ratio of about 130 Td (where E is electric field strength, N is gas number density, 1 Td = 10–17 V cm²). PTR-MS measurements were conducted in a three-week period in May and June 2017 (at 1st, 7th, 10th, 14th and 21st days after sampling days, for both analysed biosolids samples). For each measurement temperature of the cakes surface was recorded. 

3. Results and discussion

Table 1 shows average concentration of some odorous volatile organic compounds emitted from the two biosolids samples for each measurement day. It can be observed that the highest concentrations were recorded for dimethyl sulfide and dimethyl disulfide. Other compounds emitted from the biosolids cakes revealed similar concentration at the same day. For each compound, it can be observed that the highest concentration of n compound was between 10 and 21 days from the day of sampling of the biosolids cakes. It can be a result of biodegradation process related to microbial activity. At the 14th day from the sampling day



Table 2Odour detection thresholds (*ODT*) and odour activity values (*OAV*) for identified compounds in cakes 1.

| Compound | <i>ODT</i> ^a / ppm | <i>OAV</i> | | | | |
|-----------------------------|-------------------------------|------------|---------|----------|----------|----------|
| | | 1st day | 7th day | 10th day | 14th day | 21st day |
| dimethyl sulfide | 0.0030 | 436.7 | 473.3 | 670.0 | 706.7 | 976.7 |
| diethyl disulfide | 0.0020 | 215.0 | 555.0 | 745.0 | 745.0 | 755.0 |
| diethyl sulfide | 0.0033 | 278.8 | 297.0 | 433.3 | 439.4 | 439.4 |
| dimethyl disulfide | 0.0022 | 572.7 | 654.5 | 1009.1 | 1081.8 | 1113.6 |
| toluene | 0.3300 | 0.7 | 0.9 | 2.1 | 3.0 | 2.9 |
| <i>m</i> -xylene | 0.0410 | 16.3 | 29.5 | 30.5 | 30.5 | 35.1 |
| α -pinene | 0.0180 | 25.0 | 31.1 | 53.3 | 51.1 | 49.4 |
| limonene | 0.0380 | 11.8 | 17.1 | 24.2 | 25.3 | 24.7 |
| 1,3,5-trimethyl- benzene | 0.1700 | 5.2 | 6.5 | 6.9 | 8.6 | 10.5 |
| ethyl benzene | 0.1700 | 4.4 | 5.5 | 5.8 | 8.5 | 9.1 |

^a From ref. [14, 15].

of both cakes samples, the odour became more intensive and during last week of the measurement they were very similar. Biological process occurring in the cakes samples can have significant impact on odour type during the measurements. Commonalities between the cakes were the similar concentrations identified by PTR-TOF-MS as the cakes were aged, with a slight decline being noted at the finish of three weeks of time.

In order to determine which from the identified compounds significantly contributing to odour emissions from the biosolids cakes, odour activity value (*OAV*) was calculated, according to the following equation

$$OAV = c / c_{od} \quad (1)$$

where *c* is chemical concentration [ppm] and *c*_{od} is odour detection threshold [ppm]. Detection threshold data and calculated odour activity values are shown in Table 2.

Determination of odour activity values showed that sulphur compounds are dominated groups of identified compounds, contributing to odour emission from biosolids cakes. This fact can be related to relative small values of odour detection threshold for volatile organic compounds compared to other compounds identified in analysis samples. Chemical compounds characterized by highest values of odour activity values can be considered as potential markers of odour emission from wastewater treatment plants.



4. Conclusions

The application of PTR-TOF-MS facilitated quantification of volatile organic compounds emission from biosolids samples during three weeks and monitored their concentration during this time. Some of volatile organic compounds can be responsible for malodour. Based on the measurement with PTR-TOF-MS and calculated odour activity values, it can be observed that sulphur compounds: dimethyl sulfide, diethyl disulfide, diethyl sulfide and dimethyl disulfide can have significant impact on a summary odour character. Their exhibit varying degree of impact on odour nuisance, since they are characterised by different odour properties: odour intensity, hedonic quality or type of smell of malodorous substances. It is very important to know about properties of main odour compounds emitted from biosolids samples to elaborate effective deodorization methods.

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