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The Impact of Technological Processes on Odorant Emissions at Municipal Waste Biogas Plants

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Abstract: Municipal waste treatment is inherently associated with odour emissions. The compounds characteristic of the processes used for this purpose, and at the same time causing a negative olfactory sensation, are organic and inorganic sulphur and nitrogen compounds. The tests were carried out at the waste management plant, which in the biological part, uses the methane fermentation process and is also equipped with an installation for the collection, treatment, and energetic use of biogas. The tests include measurements of the four odorant concentrations and emissions, i.e., volatile organic compounds (VOCs), ammonia (NH₃), hydrogen sulphide (H₂S), and methanethiol (CH₃SH). Measurements were made using a MultiRae Pro portable gas detector sensor. The tests were carried out in ten series for twenty measurement points in each series. The results show a significant impact of technological processes on odorant emissions. The types of waste going to the plant are also important in shaping this emission. On the one hand, it relates to the waste collection system and, on the other hand, the season of year. In addition, it has been proved that the detector used during the research is a valuable tool enabling the control of technological processes in municipal waste processing plants.

Keywords: ammonia; biogas plant; hydrogen sulphide; methanethiol; municipal waste treatment; VOCs

1. Introduction

The use of fossil fuels, as well as the impact of greenhouse gases on the environment, have helped to initiate research related to the production of alternative fuels. In Europe and the world, there is an increase in greenhouse gas emissions in the atmosphere, the main source of which is carbon dioxide (CO₂). Over 80% of global energy demand is covered by fossil fuels [1]. Biogas obtained as a result of biological treatment of biodegradable waste may play a key role in the energy industry in the future. Biogas as a renewable energy source can replace conventional fuels to produce heat and electricity and can also be used as gas fuel in the automotive industry. Research carried out so far indicates that biogas produced in the methane fermentation process provides significant benefits compared to other forms of bioenergy, because this technology is characterized by energy efficiency and environmental friendliness [2,3].

A modern waste management strategy should aim mainly at minimising waste generation (among others, by designing and manufacturing products that promote reuse and facilitate recycling and recovery), waste source separation and then reuse and recovery of energy and material resources from unavoidable waste [4]. The concept of “Zero Waste” is becoming more and more relevant by reducing the amount of waste, recycling, recovery, and minimisation of waste going to landfills [5,6]. However, literature data indicate that, still, unfortunately approximately 50% of municipal solid waste produced is sent to landfills [4]. Therefore, both the reduction of landfills volumes and the proper operation and reclamation of existing landfills are very important in terms of emission control (including
the minimisation of uncontrolled biogas emissions). In this context, the mechanical-biological waste treatment in both aerobic and anaerobic conditions (at biogas plants) has its full justification [7]. The biological process of methane fermentation is very complex and multiphase. In the last decade, devices for controlling individual process phases, as well as analytical tools, have been developed. These changes have contributed to increasing the energy efficiency of the process. The goal of the control system is to optimize the entire biogas production process and provide early warning to prevent failure of the entire process [8]. Thanks to the development of control and analysis systems, biogas plants can operate smoothly despite these extremely complex steps [9].

Until now, mainly biogas plants from agricultural, landfill, or sewage treatment plants were subjected to testing of odorous compounds [10–12]. Biogas plants processing municipal waste are not yet well understood in this respect and worldwide there are fewer of them compared to the previously mentioned installations [13]. However, due to energy (biogas energy production) and environmental (waste management) benefits, as well as publicly available source material, much more will probably be created in the future.

Odorants, chemical compounds that cause an olfactory effect, are probably one of the most demanding environmental challenges for the emerging environmental policy [14,15]. Odorants that cause a negative olfactory effect generally contain nitrogen or sulphur, i.e., amines, phenolic compounds, aldehydes, thiols, ketones, and alcohols. Each of these components is produced mainly as a result of the activity of microorganisms that break down complex organic compounds present in the organic matter [16–20].

One of the main odorants emitted during the decomposition of biodegradable waste are volatile organic compounds (VOCs) [15,21]. The World Health Organization (WHO) has recognized volatile organic compounds as the most significant indoor air pollution. So far, about 500 volatile compounds and those present in indoor air have been identified. Only a few were considered pathogenic. Nevertheless, it is believed that many of them contribute to such health problems as: allergies, headaches, loss of concentration, drying and irritation of the nasal mucosa, throat, and eyes, etc. [21–25].

The term VOCs refers to a wide group of chemical compounds whose vapour pressure is at least 0.01 kPa at 20 °C [26,27]. They are also characterized by low aqueous solubility. VOCs in the atmosphere participate in photochemical reactions, producing photochemical oxidants. According to Eitzer [28], who undertook pioneering research on the exhaustive characteristics of VOCs emitted at various stages of the biodegradation process, most VOCs in composting plants are emitted at early stages of the process. For example, Delgado-Rodriguez et al. [29] found that emissions of volatile compounds are closely related to the phases of the composting process: aldehydes, alcohols, carboxylic acids, esters, ketones, sulphides, and terpenes are emitted mainly in the initial acid phase, while in the thermophilic phase ketones, organosulfur compounds, terpenes, and ammonia dominate. In the cooling phase, the main volatile compounds emitted are sulphides, terpenes, and ammonia. These authors also studied the impact of process control parameters (humidity, aeration, and C/N ratio) on the emission of volatile compounds in municipal solid waste composting. The C/N ratio had the greatest impact on VOCs emission, followed by aeration and moisture content.

There are many odorous testing methods, which include sensory, sensor, and analytical methods. Table 1 shows examples of the uses of these methods.

Table 1. Methods of assessing odour and odorants concentration [29–32].

| Sensory Methods                        | Sensor Methods                        | Analytical Methods                        |
|----------------------------------------|---------------------------------------|-------------------------------------------|
| sensory evaluation method              | electronic nose (e-nose)              | gas chromatography (GC);                  |
| static olfactometry                    |                                       | gas chromatography coupled with mass spectrometry (GC–MS); |
| dynamic olfactometry, field olfactometry | portable detectors                   | gas chromatography coupled with olfactometry (GC-O) |
Sensory methods are used to determine the qualitative (method of sensory evaluation) or quantitative (olfactometry) smell. Using only sensory methods, it is not possible to obtain information on the types of compounds as well as their concentrations contained in the odorant mixture. For this purpose, analytical or sensor methods are used [33–35].

Portable detectors, classified as sensor methods, compared to most other methods, are characterized by uncomplicated service, as well as relatively low purchase costs [16]. The detectors use various types of sensors, which include:

- photoionization sensors—PID;
- nondispersive infrared sensors—NDIR;
- electrochemical sensors—EC;
- thermal sensors—PELLISTOR [36,37].

For the analysis of chemical compounds that cause an unpleasant olfactory effect, emitted during the treatment of municipal waste, photoionization and electrochemical sensors are most commonly used. In the case of the photoionization sensor, the operating principle is the ionization of neutral molecules of chemical compounds. When diffusing particles of VOCs encounter the UV lamp, they are ionized by photons. Then, the ions formed are directed between two polarized electrodes. The ions move towards the electrodes in the electric field generated by the electrometer. In this way, a current flow is generated, which is then converted into a voltage signal. This signal is proportional to the concentration of compounds subjected to ionization. Compounds having higher ionization energies than the maximum energies of the UV lamp photons are not detected. This type of sensor is most often used to measure the total concentration of VOCs [14,34,38–40].

The electrochemical sensor uses absorption of infrared radiation to identify the compounds. The principle of this type of sensor is to place the source of infrared radiation along the optical line with the detector. When the analysed gas appears in the measuring chamber, it absorbs radiation of a certain wavelength, and according to the Lambert–Beer law, there is a decrease in radiation reaching the detector which is converted into an electrical signal. This reduction in light intensity is proportional to the concentration of the gases or flammable vapours being detected [16,40].

This study undertakes intensive research aimed at analysing the impact of technological processes carried out at biogas plants (constituting waste treatment plants) on the emission of odorous compounds, using municipal waste as input material. So far, there have been few scientific studies related to the odour nuisance of this type of project or they have been carried out in a short period of time. Technological processes at municipal waste treatment plants are characterised by high variability and therefore require detailed analyses. The paper presents the results of almost a year-long research, which perfectly illustrates the complexity of the problem of odorant emissions, showing the relations between measured odorants and technological factors. The research results are potentially very valuable from the point of view of implementing new technologies in the field of both waste treatment and deodorization of process gases. Currently, there are in Poland eight biogas plants of this type but, in the future, it can be assumed that many more will be created due to the drive to obtain energy from raw materials available throughout the year.

2. Materials and Methods

2.1. Characteristic of the Analysed Plant

The plant, being the subject of research, is located in the southern part of Poland. The plant is equipped with installations for mechanical and biological treatment of municipal waste. The input material for the fermentation process is the biodegradable fraction mechanically separated from the mixed waste stream. The fermentation process is carried out in two separate chambers. Each of them is equipped with four mixers and a digestate dewatering line. The fermentation process is carried out in semi-dry, mesophilic conditions. A flow-chart of processes at the mechanical-biological waste treatment installation is shown in Figure 1.
2. Materials and Methods

2.1. Characteristic of the Analysed Plant

The plant being the subject of research is located in the southern part of Poland. The plant is equipped with installations for mechanical and biological treatment of municipal waste and is equipped with four mixers and a digestate dewatering line. The fermentation process is carried out in two closed fermentation chambers. The system is equipped with a system of screens and separators connected by conveyors. The biodegradable fraction is transported to two buffers, located in a closed feedstock preparation hall for the fermentation process. The fermentation process itself takes place in two closed fermentation chambers. After the fermentation process is completed, the input material is subjected to a dewatering process (via a press and a centrifuge) in a closed dewatering hall. Dehydrated digestate is directed to special tunnels, located in a closed hall for the first stage of oxygen stabilisation (28 days) and then to the open field for the second stage of oxygen stabilization (14 days).

2.2. Study Methodology

The study reported here includes the determination of levels of ammonia, hydrogen sulphide, methanethiol, and VOCs at twenty measurement points identified during inventory and pilot tests as sources of emissions of odorous compounds (Table 2) [41]. The tests were carried out in ten measurement series, from July to December 2019 (Table 3). The sensor method was used to determine the indicated compounds—the MultiRae Pro portable multi-gas gas detector (RAE Systems, Inc.; San Jose, CA, USA). Measurements were made with five one-minute replicates at each point, and the obtained results were averaged. The characteristics of individual sensors that the detector is equipped with are presented in Table 4. At the same time, measurements (T) and relative humidity (RH) of air at a height of 1.5 m were carried out using a portable Kestrel 4500 NV weather meter. The minimum, average, and maximum values of measurements during each of the series are presented in Figure 2a,b. Emission levels were calculated according to the methodology presented in reference [42].

Figure 1. Process flowchart of mechanical-biological treatment of waste at the analysed plant.

Waste storage is conducted in a closed hall. The hall is equipped with three ventilators which intakes are located: above the mixed waste and above the conveyors transporting waste to the machining hall. The processes of waste screening and sorting (mechanical treatment) are carried out in a hall equipped with a system of screens and separators connected by conveyors. The biodegradable fraction is transported to two buffers, located in a closed feedstock preparation hall for the fermentation process. The fermentation process itself takes place in two closed fermentation chambers. After the fermentation process is completed, the input material is subjected to a dewatering process (via a press and a centrifuge) in a closed dewatering hall. Dehydrated digestate is directed to special tunnels, located in a closed hall for the first stage of oxygen stabilisation (28 days) and then to the open field for the second stage of oxygen stabilization (14 days).

Figure 2. Cont.
Table 4. Characteristics of the gas detector sensors.

| Kind of Sensor | Type of Sensor | Resolution | Range | Accuracy | Average |
|---------------|---------------|------------|-------|----------|---------|
| ammonia (NH₃) | Electrochemical (EC) | 1 ppm | 0–100 ppm | ±10% | 250 cm³/min |
| hydrogen sulphide (H₂S) | 0.1 ppm | 0–100 ppm |
| methanethiol (CH₃SH) | 0.1 ppm | 0–10 ppm |
| volatile organic compounds (VOCs) | Photoionisation (PID) | 0.01 ppm | 0–100,000 ppm |

Figure 2. Minimum, average, and maximum temperature (T) (a) and relative humidity (RH); (b) at individual measurement series.

Table 2. Measurement points at the examined biogas plants.

| Mark of Odour Source | Name of Odour Source | Name of the Measurement Point |
|----------------------|----------------------|-------------------------------|
| a                    | waste storage plant  | inside the hall-centre        |
| b                    | mixed waste *        |                               |
| c                    | selectively collected waste * |       |
| d                    | mechanical treatment plant | in front of the hall entering |
| e                    | in the hall—1.5 m    |                               |
| f                    | in the hall—4.0 m    |                               |
| g                    | storage shelter      | shredded preRDF fraction (pre refuse derived fuel) * |
| h                    | fermentation preparation plant | inside the hall-centre |
| i                    | digestate dewatering plant | inside the hall-centre |
| j                    | over the wastewater tank (after the press) |       |
| k                    | over the wastewater tank (after the centrifuge) |       |
| l                    | oxygen stabilisation plant (1. stage) | inside the hall- waste subjected to an oxygen stabilization process * |
| m                    | the technological wastewater pumping station | over the wastewater tank |
| n                    | oxygen stabilisation shelter (2. stage) | waste subjected to an oxygen stabilization process * |
| o                    | roof ventilators from waste storage plant | ventilator 1—process gases captured from over-mixed waste |
| p                    | roof ventilators from digestate dewatering plant | ventilator 4-inside the hall |
| q                    | roof ventilators from digestate dewatering plant | ventilator 5 |

* surface sources for which the gas sample was taken from under cover.
Table 3. Dates of measurement series at a biogas plant.

| Series | Date       | Series | Date            |
|--------|------------|--------|-----------------|
| 1      | 11 July 2019 | 6      | 03 October 2019 |
| 2      | 25 July 2019 | 7      | 17 October 2019 |
| 3      | 08 August 2019 | 8      | 07 November 2019 |
| 4      | 22 August 2019 | 9      | 21 November 2019 |
| 5      | 05 September 2019 | 10     | 30 December 2019 |

Table 4. Characteristics of the gas detector sensors.

| Kind of Sensor       | Type of Sensor | Resolution | Range          | Accuracy | Average Flow Rate |
|----------------------|----------------|------------|----------------|----------|-------------------|
| ammonia (NH$_3$)     | Electrochemical (EC) | 1 ppm | 0–100 ppm    | ±10%     | 250 cm$^3$/min    |
| hydrogen sulphide (H$_2$S) |               | 0.1 ppm | 0–100 ppm    |          |                   |
| methanethiol (CH$_3$SH) |             | 0.1 ppm | 0–10 ppm     |          |                   |
| volatile organic compounds (VOCs) | Photoionisation (PID) | 0.01 ppm | 0–100,000 ppm |          |                   |

3. Results and Discussion

The distribution of concentrations of tested odorants for the waste storage plant in individual measurement series is presented in Figure 3a,b, while the distribution of emission levels from exhaust ventilators, which are at the waste storage plant, is presented in Figure 4a–c.

The highest level of VOCs emissions was recorded from the roof ventilator, which has its air intake located above the mixed waste stored a. This is consistent with the high concentrations of VOCs observed at the place where mixed municipal waste was stored b. Increased VOCs emissions were also recorded in the gases discharged from the ventilators, which have their air intakes located inside the hall r and above the selectively collected waste storage (10 measurement series). Periodically increased VOCs concentrations were also recorded at other measurement points—in the place of selectively collected waste storage c—measurement series 7, inside the hall a—measurement series 2. The highest levels of NH$_3$ (ammonia) emissions were also recorded from roof ventilators discharging air from waste storage plant p and r. A similar relationship was also observed for hydrogen sulphide and methanethiol. The presence of these compounds was only noted in the gases discharging from the waste storage plant through roof ventilators p, r, and s.
Figure 2. Minimum, average, and maximum temperature (T) (a) and relative humidity (RH); (b) at individual measurement series.

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The distribution of concentrations of tested odours for the waste storage plant in individual measurement series is presented in Figure 3a,b, while the distribution of emission levels from exhaust ventilators, which are at the waste storage plant, is presented in Figure 4a–c.

Figure 3. Distributions of volatile organic compounds (VOCs) (a) and ammonia (NH₃) concentration; (b) at the waste storage plant in particular measurement series (a-inside the hall; b-mixed waste; c-selectively collected waste).

Figure 4. Cont.
The analysis of Figure 3a shows that, in the case of a mixed waste storage site, the largest increase in VOCs concentration, to a level of about 20 ppm, was observed during measurement series 6. During the same series, a significant increase in ammonia emissions from roof ventilators was also observed, the air intake of which is located inside the hall, above the conveyor transporting waste \( r \) and above the selectively collected waste storage \( c \)–Figure 4b. During the tests, an odour similar to the solvent smell was perceptible in the hall. The sensing substance was probably the source of the increased VOCs emissions compared to the results obtained in the other series. In the case of waste collected selectively, increased VOCs concentration was observed only during measurement series 7–at the place of storage of this waste \( c \) (Figure 3a), and during measurement series 10–increased level of emissions–in the air discharged by the ventilator from the selectively collected waste \( s \) (Figure 4a). This probably resulted from improper and ineffective separate waste collection.

In the case of the roof ventilator \( p \), which has its air intake located above the mixed waste, during each of the measurement series the levels of volatile compounds emission were similar; while the levels of ammonia emission increased significantly in measurement series 4–9. Analysing the results of the levels of hydrogen sulphide and methanethiol emissions in Figure 4c, a significant increase in hydrogen sulphide emissions can be observed during series 6 and 9 (\( p \) ventilator). Figure 4c shows the results only from ventilators \( p \), \( r \) and \( s \) because, at the waste storage plant, the values of H\(_2\)S (hydrogen sulphide) and CH\(_3\)SH (methanethiol) concentrations were greater than 0.1 ppm only at these measurement points (the threshold level of determination of the device for the measured chemical compounds). In each of the measurement series, high levels of emissions of both hydrogen sulphide and ammonia from \( p \) and \( r \) ventilators were observed. The composition of mixed waste and storage time probably had a significant impact on the results obtained. The long storage time of waste containing biodegradable fractions contributes to their compaction and uncontrolled anaerobic processes.

Figure 5a,b shows the results of VOCs concentration and ammonia concentration for the mechanical treatment plant, storage shelter for the shredded preRDF fraction (pre refuse derived fuel), and the fermentation preparation plant.
hydrogen sulphide emissions can be observed during series 6 and 9 (p-ventilator). Figure 4c shows the results only from ventilators p, r, and s because, at the waste storage plant, the values of H₂S (hydrogen sulphide) and CH₃SH (methanethiol) concentrations were greater than 0.1 ppm only at these measurement points (the threshold level of determination of the device for the measured chemical compounds). In each of the measurement series, high levels of emissions of both hydrogen sulphide and ammonia from p and r ventilators were observed. The composition of mixed waste and storage time probably had a significant impact on the results obtained. The long storage time of waste containing biodegradable fractions contributes to their compaction and uncontrolled anaerobic processes.

Figure 5a,b shows the results of VOCs concentration and ammonia concentration for the mechanical treatment plant, storage shelter for the shredded preRDF fraction (pre refuse derived fuel), and the fermentation preparation plant. (a)

Figure 5. Distribution of VOCs (a) and NH₃; (b) concentration at measurement points related to mechanical treatment of waste and fermentation preparation in particular measurement series (d—in hall front entrance; e—inside the hall, at 1.5 m; f—inside the hall, at 4.0 m; g—shredded preRDF fraction (pre refuse derived fuel); h—inside the fermentation preparation hall).

In individual measurement series, the highest VOCs concentration accompanied the storage of fuel from preRDF g waste and mechanical waste treatment operations—inside mechanical treatment plant f and inside the fermentation preparation plant h. The preRDF fraction mechanically separated from the mixed waste stream and stored under a covered shelter was also the source of the largest ammonia emission. The results obtained at point g are characterized by a large variation in the concentration of volatile organic compounds and a relatively constant level of ammonia (2–5 ppm), not including the result obtained during series 9 (35 ppm).

Figure 6a–c shows the distribution of measuring odorant concentrations for the digestate dewatering plant, while Figure 7a,b presents the distribution of emission levels in individual measurement series from roof ventilators, which are at the digestate dewatering plant.
In individual measurement series, the highest VOCs concentration accompanied the storage of fuel from preRDF waste and mechanical waste treatment operations—inside mechanical treatment plant and inside the fermentation preparation plant. The preRDF fraction mechanically separated from the mixed waste stream and stored under a covered shelter was also the source of the largest ammonia emission. The results obtained at point are characterized by a large variation in the concentration of volatile organic compounds and a relatively constant level of ammonia (2–5 ppm), not including the result obtained during series 9 (35 ppm).

Figure 6a–c shows the distribution of measuring odorant concentrations for the digestate dewatering plant, while Figure 7a,b presents the distribution of emission levels in individual measurement series from roof ventilators, which are at the digestate dewatering plant.

**Figure 6.** Distribution of VOCs (a), NH$_3$; (b) and H$_2$S and CH$_3$SH; (c) concentration at digestate dewatering plant in particular measurement series (i-inside the hall; j-over wastewater tank (after the press); k-over wastewater tank (after the centrifuge)).
The concentration of hydrogen sulphide and methanethiol at the measurement points related to the oxygen stabilization process are technological wastewater from this plant. On the other hand, significantly lower concentrations of VOCs and NH₃ in all measurement series accompanying the 2nd phase of aerobic processing testify to a properly conducted oxygen stabilization process. In the case of digestate subject to stabilization, the concentration of both volatile organic compounds and ammonia occur above the process wastewater tank after the press. This indicates the different quality of digestate sent to the tank after its cleaning. The tanks are subjected to weekly cleaning, and the results of odorant concentrations above the tank after its cleaning are at a low level, compared to the results obtained before cleaning.

Analysis of the results obtained for the digestate dewatering plant shows that the highest concentrations of both volatile organic compounds and ammonia occur above the process wastewater tanks after the press j and after the centrifuge k, except for series 1 and 10, where the VOCs concentration was at a similar level in all measurement points related to digestate dewatering. Figure 7b shows that, in series 6, there was a clear increase in ammonia emissions from roof exhaust ventilators, whose air intakes are located at the digestate dewatering plant. The increase in ammonia emissions was due to the failure of one of the technological lines intended for digestate dewatering. In the case of tanks (points j and k), the odorant concentration is associated to the greatest extent with operations carried out in relation to these tanks, including the maintenance of their filling levels and cleaning. The tanks are subjected to weekly cleaning, and the results of odorant concentrations above the tank after its cleaning are at a low level, compared to the results obtained before cleaning.

The concentration of hydrogen sulphide and methanethiol at the measurement points related to digestate dewatering varied during individual measurement series, reaching maximum values of 19.4 ppm (in series 9) and 10 ppm (in series 5, 9 and 10), respectively.

Analysing Figures 8 and 9, it can be observed that the sources of the largest emission of the tested odorants in relation to the oxygen stabilization process are technological wastewater from this...
process, which is directed to the tank of the pumping station \( n \) and wastes subjected to the first-degree oxygen stabilization process. In the case of digestate subject to stabilization, the concentration levels of both VOCs and ammonia are variable, although the measurements were carried out on the same day of the technological process. This indicates the different quality of digestate sent to the oxygen stabilization process, which is most likely the result of different compliance with the technological regime during digestate drainage or the quality differentiation of waste going to the plant. On the other hand, significantly lower concentrations of VOCs and \( \text{NH}_3 \) in all measurement series accompanying the 2nd phase of aerobic processing testify to a properly conducted oxygen stabilization process of the 1st degree.

![Diagram](image)

**Figure 8.** Distribution of VOCs (a) and \( \text{NH}_3 \); (b) concentration at measurement points related to oxygen stabilisation of digestate in particular measurement series (l—inside the hall; m—waste subjected to an oxygen stabilization process (1st stage); n—over the wastewater tank; o—waste subjected to an oxygen stabilization process (2nd stage).
Figure 9. Distribution of hydrogen sulphide and methanethiol related to wastewater storage from oxygen stabilisation of digestate (point n) in particular measurement series.

Figure 10a,b shows the distribution of concentrations of VOCs and ammonia for all measurement points in the ten measurement series.

Figure 10. Values of minimum, average, median, and maximum results of VOCs; (a) and NH$_3$; (b) concentration at particular measurement points during all measurement series.
The above analysis indicates which places in the technological sequence are most exposed to the variability of odorant emissions as a result of changes in the quality of processed waste and implemented technological processes. The largest differences in VOCs and NH\textsubscript{3} concentrations occur at measurement points related to the storage of mixed municipal waste (a, b, p) and preRDF (g), with the collection of process wastewater—both from the digestate dewatering process and its oxygen stabilization (j, k, n) and with waste directed to the aerobic treatment process (m, o). It is at these points in the technological sequence that the type of processed waste and the type of technological and operational measures taken have the greatest impact on odorant emissions.

Figure 11 shows the correlation matrices for the odorants tested. Along the diagonal of the matrices, there are histograms representing the distribution of values of each variable. Table 5 shows the correlation coefficients based on Figure 11.

Figure 11. Correlation matrices for the tested compounds corresponding to all measurements.

Table 5. Correlation table of examined parameters.

| Odorant | VOCs | NH\textsubscript{3} | H\textsubscript{2}S | CH\textsubscript{3}SH |
|---------|------|---------------------|-------------------|-------------------|
| VOCs    | 1.00 | 0.54                | 0.34              | 0.39              |
| NH\textsubscript{3}| 0.54 | 1.00                | 0.60              | 0.73              |
| H\textsubscript{2}S| 0.34 | 0.60                | 1.00              | 0.76              |
| CH\textsubscript{3}SH| 0.39 | 0.73                | 0.76              | 1.00              |

Analysis of the correlations between the tested odorants (Figure 11 and Table 5) indicates the largest relationship between hydrogen sulphide and methanethiol at 0.76 and between ammonia and methanethiol at 0.73. Larger relations between the above odorants were observed at measurement points related to waste storage (a, b, c, p, r, s) and digestate dewatering (i, j, k, t, u)—at the level of 0.76–0.81. The smallest correlation was observed between hydrogen sulphide and volatile organic compounds.

Analysis of the correlation between points of subsequent stages in the technological processes showed relationships at a similar level. The differences were observed for points related to mechanical treatment and fermentation preparation—for these correlation points they were lower.

4. Conclusions

In this study, the results of several months of research conducted at a biogas plant processing municipal waste in Poland have been presented. They show the relations between particular measured odorants and between odorants and technological factors. The novelty and scientific contribution
presented in this work are related to the impact of technological aspects on odorant emissions at the municipal waste biogas plant. The literature review shows that, so far, such analyses have been conducted mainly at agricultural biogas plants, biogas plants on landfills or biogas plants related to sewage treatment. The impact of technological factors was identified by measuring odorant concentration (volatile organic compounds, ammonia, hydrogen sulphide, and methanethiol) and observing their changes between individual measurement series. The main conclusions and contributions of this research can be summarised as follows:

1. Odorant sources can be divided into the following five categories related to technological processes conducted at analysed biogas plant: waste storage, preRDF storage, waste mechanical treatment and fermentation preparation, digestate dewatering, and oxygen stabilization.

2. The biggest odorant concentrations accompany such unit operations as: storage of mixed municipal waste, digestate dewatering, digestate oxygen stabilization of the 1st-degree, and technological wastewater storage (both from digestate dewatering and its oxygen stabilization). The largest organized emissions are related to the evacuation of gases by means of roof ventilators.

3. The biggest VOCs concentrations are associated with mixed-waste storage (19.79 ppm) and aerobic stabilization of 1st-degree digestate (23.56 ppm). In turn, the highest NH$_3$ concentrations accompany such technological processes as digestate dewatering (technological wastewater storage: 100 ppm) and 1st-stage oxygen digestate stabilization (100 ppm). The highest CH$_3$SH concentrations also accompany the storage of mixed municipal waste, as well as digestate dewatering and 1st-stage oxygen stabilization (10 ppm). The biggest concentration of hydrogen sulphide is associated with the storage of wastewater from the digestate aerobic stabilization process (40 ppm), which indicates too long storage time and is the result of operational irregularities.

4. The highest emissions of odorants tested—to 0.42 kg/h (VOCs), 0.44 kg/h (NH$_3$), 0.41 kg/h (CH$_3$SH), and to 0.25 kg/h (H$_2$S)–are emissions from a roof ventilator which has its air intake located above the mixed-waste storage.

5. The following factors affect the concentration of the odorants tested, and thus the volume of emissions:
   
   - a municipal waste collection system in the service area (clearly higher odorant concentrations accompany storage and mechanical treatment of mixed municipal waste in relation to selectively collected waste);
   - trouble-free and continuous work of the technological line in the waste processing plant (the sources of uncontrolled and increased odorant emissions are periodically occurring technological line failures);
   - technological operations related to the unloading of transported waste and internal transport of waste in the processing plant (especially with loaders and conveyors);
   - keeping equipment and storage places clean at the waste treatment plant;
   - compliance with the technological regime and operational correctness.

6. The largest differences in VOCs and NH$_3$ concentrations occur at measurement points related to the storage of mixed waste and preRDF, with the collection of technological wastewater (both from digestate dewatering and its oxygen stabilization) and waste directed to the aerobic process. In this case, the type of waste processed and the type of technological and operational measures taken are of fundamental importance.

7. The odour nuisance of waste management plants, including municipal waste biogas plants, should be minimised by adapting the processes carried out to the best available techniques BAT conclusions [43].

8. The detector used during the research is a valuable tool enabling control of technological processes in such facilities.
Further research should combine olfactometric and meteorological tests in addition to odorants.

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