

Article The Air and Sewage Pollutants from Biological Waste Treatment

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Abstract: The mechanical-biological waste treatment plants (MBTP), which include the municipal waste biogas plants, have an important role in sustainable urban development. Some plants are equipped with a sewage pre-treatment plant, which is then directed to the sewerage system and the treatment plant. Others, on the other hand, have only a non-drainage tank. The parameters of technological sewage (TS) or processing technology could reduce sewage contamination rates. In addition to the quality of sewage from waste treatment plants, the emission of odours is also an important problem, as evidenced by the results obtained over the sewage pumping station tank. The conducted statistical analysis shows a significant positive correlation between odour concentration (c_{od}) and volatile organic compounds (VOCs). Analysing the individual compounds, a high positive correlation was also found—the strongest being between H₂S, NH₃ and VOCs. In the case of sewage compounds, the insignificant correlation between P total and other parameters was found. For the rest of the compounds, the highest positive correlation was found between COD and BOD and N-NO₂ and N-NH₃ as well as COD and N-NO₂. The dilution of sewage is only an ad hoc solution to the problem. Further work should be aimed at reducing sewage pollution rates. The obtained results indicate large pollution of technological sewage and a high level of odour and odorants concentration. The novelty and scientific contribution presented in the paper are related to analyses of various factors on technological sewage parameters and odour and odorant emission from TS tank at biogas plant processing municipal waste, which may be an important source of knowledge on the management of TS, its disposal and minimisation of emitted compound emissions.

Keywords: biological treatment; chemical oxygen demand; odorant concentration; odour concentration; olfactometry; technological sewage

1. Introduction

The MBTP, which include the municipal waste biogas plants, an important element of sustainable management for future generations and a circular economy [1–4], are essential from the point of view of renewable energy, but also from minimising the odour nuisance of waste management facilities (the encapsulation of the first, most odorogenic phase of the biological process) [5]. The anaerobic digestion and composting are recommended for waste treatment processes, mainly for the biodegradable waste collected at the source. Both processes aim to convert waste into the least harmful form for the environment. The anaerobic digestion process is particularly proposed as an environmentally friendly and more cost-effective alternative to treating both household waste and waste activated sewage [6–12]. Nkoa [13] wrote that the digestate can cause, inter alia, nitrate leaching and ammonia emissions into the atmosphere. However, the inherent impact of waste treatment is the emission of the odorant compounds, but also of the production of technological sewage with a potentially high pollutant load [14,15]. The olfactory compounds characteristic of the waste management includes mainly VOCs (sulphur-containing VOCs, volatile fatty acids, phenolics and indolics), ammonia (NH₃) and hydrogen sulphide (H₂S) [16,17].

The TS is the leachate from individual waste treatment processes, e.g., treated at landfills, MBP plants and biogas plants, usually connected with rainwater. Technological



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(industrial) sewage is characterised by a high level of chemical oxygen demand (COD) as well as inorganic contaminants—Ca, Cu, Mg, Na, Ni, Zn and Ca, Fe and Mg which precipitate in the early phase of the process with the ammonium nitrogen [18]. Additionally, the storage process can emit greenhouse gases, i.e., methane and dinitrogen monoxide [19]. Unlike municipal wastewater, they usually contain certain types of pollutants, which makes their treatment process much more complex [20]. Nitrogen in wastewater is responsible for harmful gas emissions and nitric acid formation [21–25]. On the other hand, nitrogen is an important nutrient which allows the wastewater containing it to be used to improve the quality of soil or crops. The TS characterised by the high nitrogen concentration, discharged to sewerage systems, may contribute to the occurrence of the eutrophic conditions in the receiver [22,25].

At the end of 2015, eight municipal waste treatment plants equipped with biogas installation have operated in Poland. Only at one of them is the biodegradable waste collected being selectively is used, while in the remaining ones in the fermentation process, the waste fraction is separated mechanically from the mixed waste stream (with granulation of approx. 20–80 mm) [5]. In future, the amount of this type of biogas plants will probably increase, which is dictated by energy policy, as well as by changes in waste collection systems (the need for separate collection of biodegradable waste) [26,27]. Despite the many benefits of the plant, its operation is also associated with several technological problems, including the need to prepare the feedstock, the accumulation of volatile fatty acids, process instability, charge foaming, low buffer capacity, problematic wastewater production and high costs essential to waste transport and operation [7,26,28].

The literature review has shown that there are few scientific studies on technological sewage from waste treatment processes and its odour emission. Wang et al. identified 49 odorants in the gas samples collected from the landfill leachate pipe. They were mainly hydrocarbons [29], sulphur compounds [15], halogenalkanes [2] and oxygenated hydrocarbons [3]. Among them, the key odorants were: mercaptans (odour contribution 45%), m-xylene (odour contribution 13%) and hydrogen sulphide (odour contribution 11%) [29]. According to the Fang et al., he main odorous substances emitted from landfill site were styrene, toluene, xylene, acetone, methanol, n-butanone, n-butylaldehyde, acetic acid, dimethyl sulphide, dimethyl disulphide and ammonia. Therefore, in the leachate-related area, relatively low concentrations of all those odorants were detected in leachate storage pool [30]. However, in the below-mentioned researches, the odour concentration was not measured.

2. Goal and Aim of the Study

The analysis carried out in this work may contribute to the search for effective solutions to problems related to sewage from the anaerobic digestion process. This paper presents the analysis of sewage and odour emitted from the biological waste treatment process carried out at two waste treatment plants located in Poland. This work aims to analyse the impact of physico-chemical parameters of technological sewage on odour emission. The results of the analysis may be significant from the point of view of control of the technological processes conducted.

3. Materials and Methods

3.1. Study Methodology

The research includes fourteen series of measurements of sewage from waste storage and stabilization site at two municipal waste biogas plants located in Poland. The scope of the research includes both physical and chemical parameters of technological wastewater and gases emitted from the tank into which sew-age flows. The odorant concentration: ammonia (resolution: 1.0 ppm), volatile organic compounds (resolution 10 ppb), hydrogen sulphide (resolution: 0.1 ppm) and methyl mercaptan (resolution: 0.1 ppm) were determined using the MultiRae Pro portable gas detector with build-in a pumping system in five repetitions at each measurement site [26]. Olfactometer Nasal Ranger is a lightweight, portable device with two replaceable filter cartridges with activated carbon for air purification. It includes a built-in channel system for mixing and sharing gas streams—deliberate targeting is known part of the inhaled air by bypassing filters. The control valve is used to adjust one of the eleven values of D/T (2, 4, 7, 15, 30, 60, 100, 200, 300, 400, 500) and to set the value of "blank", at which the researcher breathes by purified air stream [28,31].

Scentroid SM 100 is a field olfactometer, using compressed air from the cylinder under high pressure (31 MPa) to dilute the test sample. The apparatus consists of a dilution valve control. Its high accuracy is used to provide a constant flow of diluted air through the device which allows the user to select one of the 15 positions, which correspond to ratios of clean air to the dilution of the test air sample. The range of the device is between 2 and $30,000 \text{ ou/m}^3$, and the detection limit of the olfactometer is 3 ou/m^3 [32,33].

The TS parameters were determined using the following methods: pH: PN-EN ISO 10523:2012 [34], ammonium nitrogen (N-NH₃): PN-ISO 5664:2002 [35], total phosphorus (P_{tot}.): PN-EN 6878:2006 [36], COD: PN-ISO 6060: 2006 [37], solids: PN-EN 1899-1:2002 [38], nitrate-nitrogen (N-NO₂): PN-EN 26777:1999 [39], BOD: PN-EN 1899-1:2002 [40].

The independent samples *t*-tests—Student, Welch and Mann–Whitney—were used to assess whether the means of two populations are equal to each other. To check assumptions—normality and equality of variances—the Shapiro–Wilk's test and the Levene's test were made. To check correlations between examined variables, Pearson's r, Spearman's rho and Kendall Tau B coefficients were calculated. Furthermore, linear regression and Bayesian regression models were made. It contained four predictors with odour concentration as a dependent variable. Those regression analyses resulted in a hypothetical model of the relationship between the outcome and predictor variables. Bayesian linear regression model uses probability distributions rather than point estimates—its response is assumed from a probability distribution.

3.2. Characteristic of Analysed Plants

Both MWTP, which are the subject of the research, are mechanical-biological treatment installations of municipal waste which are equipped with biogas installation and methane fermentation in the biological part. The feedstock for the fermentation chambers at A plant is a fraction of biodegradable waste separated mechanically from the mixed waste stream and at plant B it is biodegradable waste selectively collected. The fermentation process is carried out under dry mesophilic conditions at both plants. The input material in the design assumption should be anaerobically treated for 21 days. At plant A, after this period, the digestate should be stabilised under aerobic conditions in an aeration chamber for 14 days and then subjected to a second-stage aerobic stabilisation at the ripening site for four weeks. Due to the limitations of the area of the technological yard on the premises of the plant, as well as a large amount of delivered waste, the plant periodically operates in "emergency mode". During these periods, the digestate is not always subjected to first and/or second-degree aerobic stabilisation after the end of the fermentation process but is sent to landfill. The measurements were carried out in the tank where flow sewage from stored, stabilized and composted waste and rainwater. This tank is a non-drainage tank, requiring periodic emptying and transport to the drainage station.

At plant B, after the first stage of the biological process (21 days), the digestate is directed to the processing site and there it undergoes oxygen stabilisation (approx. 28 days). The TS from the technological yard is directed by gravity to the collective sewage system (together with rainwater and domestic wastewater) and then is directed to a sewage treatment plant.

Sewage parameters were determined under laboratory conditions after earlier sampling directly from sewage tanks. The parameters of emitted gases were determined in field conditions using direct measurements. The measurements were taken from the sewage tanks.

4. Results and Discussion

Table 1 contains the results of technological wastewater and air compounds determinations at both plants (A and B).

Table 1. Results of technological wastewater and air compounds determinations in biogas plants A and B.

		Technological Sewage						Air					
Date	Plant	pН	COD	Solids	BOD	N-NO ₂	N-NH ₃	P _{tot} .	c _{od}	\mathbf{NH}_{3}	VOC	H_2S	CH ₃ SH
Date	1 14111	-			mg	/dm ³			ou/m ³	5	ppm		
19.01.2018		6.9	13,865	4204	7600	2.14	1352	49.1	678	55	20.34	35.1	10
19.02.2018		6.8	21,575	1393	15,000	2.67	1283	77.4	721	75	24.56	52.6	10
14.05.2018		6.7	31,876	1764	16,500	2.82	1184	42.4	3600	100	30.74	100	10
21.06.2018		7.3	2615	276	2151	0.642	210	5.45	31	4	2.50	0.1	0.1
26.09.2018		7.2	2740	2142	976	0.799	311	12.3	22	6	1.95	0.1	0.1
31.01.2019		7.2	7642	3218	3227	1.64	901	32.5	78	15	5.46	10.1	8.4
27.02.2019	٨	7.3	28,515	2168	15,750	2.8	1457	22.2	3600	100	20.1	100	100
28.03.2019	А	7.0	11,547	3515	6717	2.24	1051	30.7	656	42	4.57	32.4	10
08.04.2019		8.0	12,890	3896	4200	2.74	2816	57.1	678	54	6.14	42.3	10
29.05.2019		6.9	2114	228	915	0.523	205	22.2	22	4	1.56	1.4	3.2
25.06.2019		6,8	2574	192	880	0.633	65.8	35.0	31	5	1.40	1.6	3.5
25.07.2019		7.6	5902	598	2550	1.51	953	39.4	187	14	2.64	0.1	0.3
21.08.2019		7.3	5788	396	2250	1.11	546	748	187	13	2.52	0.2	0.4
26.09.2019		8.6	8115	760	2226	2.6	1706	43.4	246	25	2.42	0.6	0.6
18.07.2019		7.8	2050	250	790	0.1	138	12.0	2050	1	1	0	0
01.08.2019		7.8	2110	205	750	0.11	140	12	2110	1	1.3	0	0
19.09.2019		7.8	2150	203	720	0.12	138	13.0	2150	1	1	0	0
10.10.2019	D	7.8	2100	200	790	0.13	140	12	2100	1	0.9	0	0
27.11.2019	D	7.8	6390	511	3120	0.27	310	31.9	6390	1	0.3	0.5	3
05.12.2019		7.8	2180	203	800	0.13	142	13.0	2180	1	0.3	0.2	0.3
11.12.2019		7.8	3050	643	1260	0.062	150	16.6	3050	1	0.3	1	1.5
16.01.2020		7.8	2170	203	750	0.13	145	13.0	2170	0	0.19	0	0

4.1. Air Compounds

Table 2 contains independent sample *T*-test results of air compounds determinations, while Table 3—its assumption checks.

The difference between the groups is statistically significant at the 0.05 level for NH_3 and VOCs. Cohen's d was used as an effect size statistic for a paired *t*-test. It is calculated as the difference between the means of each group, all divided by the standard deviation of the data. The effect size was medium for c_{od} and CH_3SH and large for the rest of the effects. The assumption checks were statistically significant in most cases, except the normality test of VOCs in plant B and the test of variances equality for CH_3SH . For that last parameter, we consider the Welch version of the *t*-test, because the Welch version does not assume that the variances in the two groups are equal. Therefore, *p* values calculated by both *t*-test versions were more than 0.05.

Furthermore, the equivalence independent samples *t*-test was made, which allows one to test the null hypothesis that the population means of two independent groups fall inside a by the user-defined interval. This procedure follows the two-one-sided tests (TOST). Only when both the upper bound and the lower bound statistic are rejected, the initial non-equivalence hypothesis is rejected—in the present study, that situation was only in one case—CH₃SH. In the rest cases, *p*-value for the lower bound test was <0.05, so the effect was smaller than or equal to the lower bound.

Figure 1 contains the correlation plot of air components, with Pearson's r, Spearman's rho and Kendall Tau B coefficients.

	Test	Statistic	df	р	VS-MPR *	Effect Size
Cod	Student Walch	1.489 1.966	20.000	0.152	1.284	0.660
cou	Mann–Whitney	91.500	13.942	0.017	5.409	0.634
NH ₃	Student Welch Mann-Whitney	2.855 3.817 112.000	20.000 13.005	0.010 0.002 <0.001	8.127 28.018 346.388	1.265 1.443 1.000
VOC	Student Welch Mann-Whitney	2.317 3.095 112.000	20.000 13.083	0.031 0.008 <0.001	3.400 9.096 280.835	1.027 1.170 1.000
H ₂ S	Student Welch Mann–Whitney	2.077 2.776 99.500	20.000 13.005	0.051 0.016 0.003	2.426 5.634 20.489	0.920 1.049 0.777
CH ₃ SH	Student Welch Mann–Whitney	1.228 1.640 99.500	20.000 13.083	0.234 0.125 0.003	1.083 1.417 21.255	0.544 0.620 0.777

Table 2. Results of independent sample T-test for air compounds determinations.

Note. For the Student *t*-test and Welch *t*-test, the effect size is given by Cohen's d. For the Mann–Whitney test, the effect size is given by the rank biserial correlation. * Vovk–Sellke Maximum *p*-Ratio: Based on a two-sided *p*-value, the maximum possible odds in favor of H₁ over H₀ equals $1/(-e p \log(p))$ for $p \le 0.37$ (Sellke, Bayarri, and Berger, 2001).

Table 3. Assumptions checks for independent sample *T*-test results of air compounds determinations—the test of normality (Shapiro–Wilk test) and test of equality of variances (Levene test).

		Normality		Equality of Variances			
	Plant	W	р	F	df	р	
Cod	A B	0.609 0.689	<0.001 0.002	4.41	1	0.049	
NH ₃	A B	0.841 0.418	0.017 <0.001	23.5	1	<0.001	
VOC	A B	0.740 0.842	<0.001 0.079	20.5	1	<0.001	
H ₂ S	A B	0.757 0.686	0.002 0.002	15.6	1	<0.001	
CH ₃ SH	A B	0.441 0.648	<0.001 <0.001	2.20	1	0.153	

The Pearson correlation coefficient is used to assess the linear relationship between the two variables. Kendall Tau B measures the monotonic relationship. While Kendall's Tau B is to be interpreted in terms of probability, Spearman's rho is to be interpreted in terms of the percentage of the variance of the rank of one variable explained by the other. For this reason, all three coefficients have been considered in these analyses. Almost all correlations are significant at alpha = 0.001 level except the correlation between CH_3SH and VOCs, which is significant at alpha = 0.05 level. Therefore, all of them are significant.



Figure 1. Correlation plot of air components, with Pearson's r, Spearman's rho and Kendall Tau B coefficients.

Considering values of Pearson's r, Spearman's rho and Kendall Tau B coefficients, correlation between odour concentrations and main odorants is high, between 0.7 and 0.9 (Pearson's r), 0.8 and 0.9 (Spearman's rho) as well as 0.7 and 0.8 (Kendall's Tau B). Correlation between odour concentration and VOCs is lower, but still high or moderate: 0.8 (Pearson's r), 0.7 (Spearman's rho) and 0.6 (Kendall's Tau B). Furthermore, considering Pearson's r, there is a very high correlation between H₂S and NH₃ and VOCs—coefficients are 0.9. Furthermore, correlation coefficient values are more than 0.9 in case of NH₃ and VOCs. Considering Spearman's rho coefficient, correlations are moderate or high in all cases. The highest—more than 0.9 values of the correlation coefficient are for CH₃SH and H₂S as well as NH₃ and VOCs. In the case of Kendall's Tau B coefficient, its value is more than 0.9 for H₂S and CH₃SH. In rest cases, correlation is from moderate to high—the lowest (0.5) is for VOCs and c_{od} , H₂S and CH₃SH. All of *p*-values of the Shapiro–Wilk test for bivariate normality were <0.001.

The linear regression model—which contains four predictors with c_{od} as the dependent variable—was made. The model coefficients are in Table 4.

Model		Unstandardized	Standard Error	Standardized	t	p	Tolerance	VIF
H ₀	(Intercept)	527.455	218.842		2.410	0.025		
H_1	(Intercept)	122.349	95.979		1.275	0.220		
	NH ₃	-20.877	10.359	-0.664	-2.015	0.060	0.042	23.645
	VOC	1.044	22.957	0.009	0.045	0.964	0.114	8.803
	H_2S	49.632	10.580	1.509	4.691	< 0.001	0.044	22.503
	CH ₃ SH	4.864	5.459	0.100	0.891	0.385	0.368	2.717

Table 4. Model coefficients with collinearity statistics.

Note: Tolerance and VIF are collinearity statistics.

The R² factor, 0.92, is high and the adjusted R², 0.90, drops only a little, showing robust model (probably not very high overfitting). The test of the fit of the model was also prepared. The explained variance of the model is statistically highly significant (p < 0.001). Therefore, the variance inflation factor is more than 10 for NH₃ (24.6) and H₂S (22.5), so the multicollinearity in an ordinary least square is high. Furthermore, a Bayesian Linear Regression was made (Table 5).

Table 5. The Bayesian linear regression model.

Predictors Contained in the Model	P(M)	P(M Data)	BF _M	BF ₁₀	\mathbf{R}^2
$NH_3 + H_2S$	0.033	0.336	14.671	1.000	0.917
H ₂ S	0.050	0.318	8.875	0.632	0.888
$NH_3 + H_2S + CH_3SH$	0.050	0.094	1.977	0.187	0.922
$NH_3 + VOC + H_2S$	0.050	0.065	1.310	0.128	0.918
$VOC + H_2S$	0.033	0.063	1.956	0.188	0.900
$H_2S + CH_3SH$	0.033	0.054	1.670	0.162	0.899
$NH_3 + VOC + H_2S + CH_3SH$	0.200	0.052	0.221	0.026	0.922
$VOC + H_2S + CH_3SH$	0.050	0.016	0.307	0.032	0.903
NH ₃	0.050	$3.177 imes 10^{-4}$	0.006	$6.305 imes10^{-4}$	0.764
$NH_3 + CH_3SH$	0.033	$2.885 imes 10^{-4}$	0.008	$8.587 imes10^{-4}$	0.815

Note: P(M): Prior model probabilities. P(M | data): Posterior probabilities of the models considered. BF_M : Posterior model odds. BF_{10} : Bayes factor. R^2 : Explained variance.

The posterior model probabilities express the probability of a model after seeing the data. The Bayes factor quantifies the data-induced change from prior model odds to posterior model odds. The prior probability of the respective models was between 0.033 and 0.200—the highest coefficient was in case of all four covariates. The maximum posterior model probabilities and the Bayes factor for the model were, respectively, 0.336 and 14.7—for NH₃ + H₂S variant. Maximum R² coefficient was calculated for the sum of all four factors (R² = 0.922).

4.2. Technological Sewage Compounds

Table 6 contains independent sample *T*-test results of air compounds determinations, while Table 7—its assumption checks.

The difference between the groups is statistically significant at the 0.05 level for all of compounds, except P total. The effect size statistic for a paired *t*-test was medium for P total and large for the rest of effects. The assumption checks were statistically significant in most cases, except test of normality of solids and N-NH₃ at plant A and test of variances equality for P total at plant B. Therefore, for that last parameter, we consider the Welch version of the *t*-test. According to the results of independent samples *t*-test for sewage results, reject initial non-equivalence hypothesis was rejected in two cases: P total and c_{od}. In the rest cases, the effect was smaller than or equal to the lower bound.

	Test	Statistic	df	р	VS-MPR *	Effect Size
	Student	2.431	20.000	0.025	4.041	1.078
COD	Welch	3.206	14.057	0.006	11.492	1.222
	Mann–Whitney	99.000		0.002	27.639	0.768
	Student	2.814	20.000	0.011	7.567	1.247
solids	Welch	3.730	13.645	0.002	26.027	1.417
	Mann–Whitney	96.000		0.007	10.647	0.714
	Student	2.250	20.000	0.036	3.080	0.997
BOD	Welch	2.971	13.917	0.010	7.886	1.131
	Mann–Whitney	102.000		0.002	31.060	0.821
	Student	5.105	20.000	< 0.001	692.871	2.262
N-NO ₂	Welch	6.807	13.204	< 0.001	2805.832	2.577
	Mann–Whitney	112.000		< 0.001	279.760	1.000
	Student	3.183	20.000	0.005	14.667	1.411
N-NH ₃	Welch	4.239	13.296	< 0.001	57.110	1.606
	Mann–Whitney	102.000		0.002	31.060	0.821
	Student	1.047	20.000	0.308	1.014	0.464
P _{tot} .	Welch	1.398	13.058	0.185	1.177	0.529
	Mann–Whitney	96.000		0.007	10.745	0.714

Table 6. Results of independent sample T-test for technological sewage compounds determinations.

Note. For the Student *t*-test and Welch *t*-test, effect size is given by Cohen's d. For the Mann–Whitney test, the effect size is given by the rank biserial correlation. * Vovk–Sellke Maximum p-Ratio: Based on a two-sided p-value, the maximum possible odds in favour of H₁ over H₀ equals $1/(-e p \log(p))$ for $p \le 0.37$ (Sellke, Bayarr and Berger, 2001).

Table 7. Assumptions checks for independent sample *T*-test results of technological sewage compounds determinations—test of normality (Shapiro–Wilk test) and test of equality of variances (Levene test).

	Normality			Equality of Variances		
	Plant	W	p	F	р	
COD	A B	0.845 0.551	0.019 <0.001	9.869	0.005	
solids	A B	0.888 0.659	0.075 <0.001	13.399	0.002	
BOD	A B	0.773 0.551	0.002 <0.001	9.159	0.007	
N-NO ₂	A B	0.870 0.759	0.042 0.010	9.869	0.005	
N-NH ₃	A B	0.921 0.477	0.224 <0.001	13.399	0.002	
P _{tot.}	A B	0.384 0.574	<0.001 <0.001	9.159 2.356	0.007 0.140	

Figure 2 contains the correlation plot of technological sewage components, with Pearson's r, Spearman's rho and Kendall Tau B coefficients. P total was excluded from analysis since correlation coefficients were between -0.013 and 0.075. All correlations of analysed components are significant at alpha <0.05 level (most of them <0.001 level). The highest correlation is between COD and BOD—Pearson's r correlation coefficient is 0.98. There is also a very high correlation between N-NO₂ and N-NH₃ (Pearson's rho 0.89) as well as COD and N-NO₂ (0.84). Therefore, Pearson's r correlation between solids and COD as well as N-NH₃ and COD is, respectively, 0.51 and 0.54, while Spearman's rho is, in the above cases, 0.82 and 0.89. Generally, Spearman's rho correlation values are bigger than Pearson's r and Kendall's tau—they are between 0.72 and 0.95 while Pearson's r and



Kendall's tau values are, 0.45–0.97 and 0.50–0.84, respectively. Almost all of *p* values of Shapiro–Wilk test for bivariate normality were <0.001, except BOD-N-NO₂ (p = 0.002).

Figure 2. Correlation plot of technological wastewater components, with Pearson's r, Spearman's rho and Kendall Tau B coefficients.

The linear regression model—which contains seven predictors with c_{od} as the dependent variable—was made. Model coefficients there are in Table 8.

Model		Unstandardized	Standard Error	Standardized	t	р	Tolerance	VIF
H_0	(Intercept)	527.455	218.842		2.410	0.025		
H_1	(Intercept)	-866.332	1620.863		-0.534	0.601		
	pH	75.096	211.913	0.036	0.354	0.728	0.312	3.205
	COD	0.311	0.042	2.654	7.428	< 0.001	0.025	40.031
	solids	-0.009	0.078	-0.012	-0.117	0.909	0.301	3.324
	BOD	-0.277	0.070	-1.380	-3.971	0.001	0.026	37.879
	N-NO ₂	-151.692	215.553	-0.159	-0.704	0.493	0.062	16.032
	N-NH ₃	-0.524	0.310	-0.364	-1.691	0.113	0.069	14.562
	P _{tot} .	-0.348	0.403	-0.052	-0.863	0.403	0.865	1.156

 Table 8. Model coefficients with collinearity statistics.

Note: Tolerance and VIF are collinearity statistics.

The R² factor, 0.95, is high and a little drop of the adjusted R², 0.93, shows robust model (probably not very high overfitting). The explained variance of the model is statistically highly significant (p < 0.001). Therefore, the variance inflation factor is more than 10 for COD (40.0), BOD (37.9), N-NO₂ (16.0) and N-NH₃ (14.6), so the multicollinearity in

an ordinary least square is high. Furthermore, a Bayesian Linear Regression was made (Table 9).

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Models	P(M)	P(M data)	BF _M	BF ₁₀	\mathbf{R}^2
$COD + BOD + N-NH_3$	0.004	0.337	141.804	1.000	0.947
$COD + BOD + N-NO_2$	0.004	0.123	39.034	0.364	0.940
$COD + BOD + N-NO_2 + N-NH_3$	0.004	0.078	23.586	0.231	0.952
$COD + BOD + N-NH_3 + P_{tot.}$	0.004	0.073	21.917	0.216	0.951
pH + COD + BOD + N-NH ₃	0.004	0.067	20.157	0.200	0.951
$OD + solids + BOD + N-NH_3$	0.004	0.041	11.833	0.121	0.948
$COD + BOD + N-NO_2 + N-NH_3 + P_{tot.}$	0.006	0.025	4.317	0.045	0.954
pH + COD + BOD + N-NH ₃ + P _{tot.}	0.006	0.023	3.847	0.040	0.954
$pH + COD + BOD + N-NO_2 + N-NH_3$	0.006	0.020	3.357	0.035	0.953
$COD + solids + BOD + N-NO_2$	0.004	0.018	5.173	0.054	0.942

Note: P(M): Prior model probabilities. P(M | data): Posterior probabilities of the models considered. BF_M : Posterior model odds. BF_{10} : Bayes factor. R^2 : Explained variance.

The prior probability of the respective models was between 0.004 and 0.006. The maximum posterior the model probabilities and the Bayes factor for model were 0.337 and 141.8 respectively—for COD + BOD + N-NH₃ variant. Maximum R² coefficient was calculated for the sum of all four factors ($R^2 = 0.954$) and the sum of them, without N-NO₂.

4.3. Air and Technological Wastewater Compounds

Figure 3 contains the heatmap of Spearman's rho correlation coefficient of air and TS compounds.



Figure 3. Heatmap of Spearman's rho correlation coefficient of air and technological wastewater compounds. Note: * p < 0.05, ** p < 0.01, *** p < 0.001.

For the pH of process wastewater, the correlation coefficients were negative. Statistically significant were six out of eleven—the correlation coefficient of pH and other parameters ranged from -0.4 to -0.5.

In the remaining cases, correlation analyses of technological wastewater compounds, odour and air pollution concentrations, Spearman's rho correlation coefficients ranged from 0.6 (VOCs-P_{tot.}) to 0.9 (c_{od} -COD). Very high (>0.8) correlation coefficients were also determined for BOD and all the air compounds, as well as COD and almost all air compounds, apart from VOCs, also for pairs: N-NO₂-NH₃ air, NO₂-VOCs, N-NH₃- c_{od} , and NH₃ air.

5. Conclusions

The carried out research allowed to draw the following conclusions:

- 1. None of the air pollution concentration values—ammonia, hydrogen sulphide and methyl mercaptan—meet the permissible reference values for assessing the degree of air pollution—respectively, 0.533 ppm, 0.013 ppm and 0.009 ppm (Regulation of the Minister of the Environment of 26 January 2010 on reference values for some substances in the air) [41].
- 2. At AMWTP, where sewage is stored in a tank and only periodically pumped out, much higher values of both sewage and air parameters were observed than in the case of biogas plant A equipped with a sewage system, thanks to which sewage is directed to a sewage treatment plant.
- 3. The analysis of the results of air compounds shown a significant positive correlation between the odour concentration and both the main odorogenic and volatile organic compounds. Analysing the individual compounds, a high positive correlation was also found—the strongest between H₂S, NH₃ and VOCs.
- 4. After analysis of the results of sewage compounds, the insignificant correlation between P total and other parameters was found. For the rest of the compounds, the highest positive correlation was found between COD and BOD and N-NO₂ and N-NH₃ as well as COD and N-NO₂.
- 5. According to the results, the impact of physico-chemical parameters of technological sewage on odour emission was significant—the strong correlation was observed between odour concentration and chosen air and wastewater parameters. To make these relationships more accurate, linear regression models were performed, which were characterized by high determination coefficients.
- 6. Municipal waste treatment plants, especially those equipped with a biogas installation, are an indispensable element of urban infrastructure as well as an important part of a circular economy. Therefore, it is important to support the technological processes carried out at plants by analysing them in scientific studies. TS from biological waste treatment processes is very persistent, due to its diverse and variable composition, as well as uncontrolled emission of odours from tanks intended for their storage. The presented research results show the essence and complexity of the raised issues.
- 7. It seems advisable to extend the research conducted in this study with an analysis related to the biomethane potential of technological wastewater after the fermentation process. Such a study for household food waste was conducted by Lytras et al. [12]. The mentioned researchers analysed the co-digestion of waste activated sludge and condensate, produced through drying and shredding of source-separated collected food waste, which proved to be an effective method for its valorisation.

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References

- 1. Fan, Y.V.; Klemeš, J.J.; Walmsley, T.G.; Bertók, B. Implementing Circular Economy in municipal solid waste treatment system using P-graph. *Sci. Total Environ.* 2020, 701, 134652. [CrossRef]
- Karak, T.; Bhagat, R.M.; Bhattacharyya, P. Municipal Solid Waste Generation, Composition, and Management: The World Scenario. *Crit. Rev. Environ. Sci. Technol.* 2012, 42, 1509–1630. [CrossRef]
- 3. Migliori, M.; Catizzone, E.; Giordano, G.; Le Pera, A.; Sellaro, M.; Lista, A.; Zanardi, G.; Zoia, L. Pilot Plant Data Assessment in Anaerobic Digestion of Organic Fraction of Municipal Waste Solids. *Sensors* **2019**, *7*, 54. [CrossRef]
- 4. Pires, A.; Martinho, G.; Chang, N.B. Solid waste management in European countries: A review of systems analysis techniques. J. Environ. Manag. 2011, 92, 1033–1050. [CrossRef] [PubMed]
- Wiśniewska, M.; Kulig, A.; Lelicińska-Serafin, K. Comparative analysis of preliminary identification and characteristic of odour sources in biogas plants processing municipal waste in Poland. SN Appl. Sci. 2019, 1, 550. [CrossRef]
- Oh, J.-I.; Lee, J.; Lin, K.-Y.A.; Kwon, E.E.; Tsang, Y.F. Biogas production from food waste via anaerobic digestion with wood chips. Energy Environ. 2018, 29, 1365–1372. [CrossRef]
- Xu, F.; Li, Y.; Ge, X.; Yang, L.; Li, Y. Anaerobic digestion of food waste—Challenges and opportunities. *Bioresour. Technol.* 2018, 247, 1047–1058. [CrossRef] [PubMed]
- 8. Pramanik, S.K.; Suja, F.B.; Zain, S.M.; Pramanik, B.K. The anaerobic digestion process of biogas production from food waste: Prospects and constraints. *Bioresour. Technol. Rep.* **2019**, *8*, 100310. [CrossRef]
- 9. Kader, F.; Baky, A.H.; Khan, M.N.H.; Chowdhury, H.A. Production of Biogas by Anaerobic Digestion of Food Waste and Process Simulation. *Am. J. Mech. Eng.* **2015**, *3*, 79–83. [CrossRef]
- Fisgativa, H.; Tremier, A. Influence of food waste characteristics variations on treatability through anaerobic digestion. In Proceedings of the 16th International Conference Rural-Urban Symbiosis (RAMIRAN), Hamburg, Germany, 8–10 September 2015.
- 11. Xu, Y.; Lu, Y.; Zheng, L.; Wang, Z.; Dai, X. Perspective on enhancing the anaerobic digestion of waste activated sludge. *J. Hazard. Mater.* **2020**, *389*, 121847. [CrossRef]
- 12. Lytras, G.; Koutroumanou, E.; Lyberatos, G. Anaerobic co-digestion of condensate produced from drying of Household Food Waste and Waste Activated Sludge. *J. Environ. Chem. Eng.* **2020**, *8*, 103947. [CrossRef]
- 13. Nkoa, R. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: A review. *Agron. Sustain. Dev.* **2014**, *34*, 473–492. [CrossRef]
- 14. Font, X.; Artola, A.; Sánchez, A. Detection, Composition and Treatment of Volatile Organic Compounds from Waste Treatment Plants. *Sensors* **2011**, *11*, 4043–4059. [CrossRef]
- 15. Nguyen, M.T.; Maeda, T.; Yusoff, M.Z.M.; Ogawa, H.I. Effect of azithromycin on enhancement of methane production from waste activated wastewater. *J. Ind. Microbiol. Biotechnol.* **2014**, *41*, 1051–1059. [CrossRef] [PubMed]
- 16. Capelli, L.; Sironi, S.; Del Rosso, R.; Guillot, J.M. Measuring odours in the environment vs. dispersion modelling: A review. *Atmos. Environ.* **2013**, *79*, 731–743. [CrossRef]
- Maurer, D.L.; Koziel, J.A.; Kalus, K.; Andersen, D.S.; Opalinski, S. Pilot-Scale Testing of Non-Activated Biochar for Swine Manure Treatment and Mitigation of Ammonia, Hydrogen Sulfide, Odorous Volatile Organic Compounds (VOCs), and Greenhouse Gas Emissions. *Sustainability* 2017, *9*, 929. [CrossRef]
- 18. Molleda, A.; Lopez, A.; Cuartas, M.; Lobo, A. Release of pollutants in MBT landfills: Laboratory versus field. *Chemosphere* **2020**, 249, 126–145. [CrossRef]
- 19. Monlau, F.; Sambusiti, C.; Ficara, E.; Aboulkas, A.; Barakat, A.; Carrere, H. New opportunities for agricultural digestate valorization: Current situation and perspectives. *Energy Environ. Sci.* **2015**, *8*, 2600–2621. [CrossRef]
- 20. Minière, M.; Boutin, O.; Soric, A. Combination of chemical and biological processes to enhance the treatment of hardly biodegradable matter in industrial wastewater: Selection parameters and performances. *Can. J. Environ. Eng.* **2019**, *97*. [CrossRef]
- 21. Filbakk, T.; Jirjis, R.; Nurmi, J.; Høibø, O. The effect of bark content on quality parameters of Scots pine (*Pinus sylvestris* L.) pellets. *Biomass Bioenergy* **2011**, 35, 3342–3349. [CrossRef]
- 22. Garbowski, T. Changes in the Physico-Chemical Parameters of Water as a Result of Long-Term Contact with Biomass, on the Example of Pine Bark (*Pinus sylvestris*). *Water Air Soil Pollut*. **2019**, *230*, 104. [CrossRef]
- 23. Mace, K.A.; Artaxo, P.; Duce, R.A. Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons. *J. Geophys. Res.* 2003, *108*, 1–10. [CrossRef]
- Vamvuka, D.; Sfakiotakis, S. Effects of heating rate and water leaching of perennial energy crops on pyrolysis characteristics and kinetics. *Renew. Energy* 2011, 36, 2433–2439. [CrossRef]
- 25. Vassilev, S.V.; Vassileva, C.G.; Vassilev, V.S. Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview. *Fuel* **2015**, *158*, 330–350. [CrossRef]

- Wiśniewska, M.; Kulig, A.; Lelicińska-Serafin, K. The Impact of Technological Processes on Odorant Emissions at Municipal Waste Biogas Plants. *Sustainability* 2020, 12, 5457. [CrossRef]
- 27. Wiśniewska, M.; Kulig, A.; Lelicińska-Serafin, K. Olfactometric testing as a method for assessing odour nuisance of biogas plants pro-cessing municipal waste. *Arch. Environ. Prot.* **2020**, *46*, 60–68. [CrossRef]
- 28. Szyłak-Szydłowski, M. Comparison of two types of field olfactometers for assessing odours in laboratory and field tests. *Chem. Eng. Trans.* **2014**, *40*, 67–72. [CrossRef]
- 29. Wang, X.; Parcsi, G.; Sivret, E.; Le, M.; Stuetz, R. Odorants and their contributions to overall odour emission from a landfill leachate. *Atmosphere* **2019**, *10*. [CrossRef]
- Fang, J.-J.; Jang, N.; Cen, D.-Y.; Shao, L.-M. Odor compounds from different sources of landfill: Characterization and source identification. *Waste Manag.* 2012, 32, 1401–1410. [CrossRef]
- 31. Kulig, A.; Szyłak-Szydłowski, M. Assessment of the effects of wastewater treatment plant modernization by means of the field olfactometry method. *Water* **2019**, *11*, 2367. [CrossRef]
- 32. Szyłak-Szydłowski, M. Odour Samples Degradation During Detention in Tedlar Bags. *Water Air Soil Pollut.* 2015, 226, 227. [CrossRef] [PubMed]
- Szyłak-Szydłowski, M. Validation of odour concentration from MBT piles using static chamber and wind tunnel with the different wind speed values. J. Air Waste Manag. Assoc. 2017, 67. [CrossRef] [PubMed]
- 34. The Polish Committee for Standardization. *PN-EN ISO 10523:2012. Water Quality. Determination of pH*; The Polish Committee for Standardization: Warsaw, Poland, 2012.
- 35. The Polish Committee for Standardization. *PN-EN 5664:2002. Water Quality. Determination of Ammonium Nitrogen. Distillation Method with Titration;* The Polish Committee for Standardization: Warsaw, Poland, 2002.
- 36. The Polish Committee for Standardization. *PN-EN ISO 6878:2006. Water Quality. Determination of Phosphorus. Ammonium Molybdate Spectrometric Method*; The Polish Committee for Standardization: Warsaw, Poland, 2006.
- 37. The Polish Committee for Standardization. PN-EN 6060:2006. Water Quality. Determination of Chemical Oxygen Demand. Titration Method. Chemical Index; The Polish Committee for Standardization: Warsaw, Poland, 2006.
- 38. The Polish Committee for Standardization. *PN-EN* 872:2007+*Ap* 1:2007. *Water and Wastewater. Determination of Solids. Method Using Filtration through Glass Fibre Filters;* The Polish Committee for Standardization: Warsaw, Poland, 2007.
- 39. The Polish Committee for Standardization. PN-EN 26777:1999. Water Quality. Determination of Nitrite. Molecular Absorption Spectrometric Method; The Polish Committee for Standardization: Warsaw, Poland, 1999.
- 40. The Polish Committee for Standardization. *PN-EN 1899-1:2002. Water Quality. Determination of Biochemical Oxygen Demand after n Days (BOD)—Part 1: Dilution Method and Vaccination with Allylthiourea;* The Polish Committee for Standardization: Warsaw, Poland, 2002.
- 41. FAO. Regulation establishing reference values for certain substances in the air. J. Laws 2010, 16, 87.