Archives of Environmental Protection
Vol. 44 no. 4 pp. 50–57

PL ISSN 2083-4772
DOI 10.24425/aep.2018.122296

Correlations between organic pollution indicators in municipal wastewater

Tadeusz Siwiec[1], Lidia Reczek[1], Magdalena M. Michel[1], Beata Gut[1], Paulina Hawer-Strojek[1], Justyna Czajkowska*[1], Krzysztof Jóźwiakowski[2], Magdalena Gajewska[3], Piotr Bugajski[4]

[1]Warsaw University of Life Sciences, Poland
[2]University of Life Sciences in Lublin, Poland
[3]Gdańsk University of Technology, Poland
[4]University of Agriculture in Kraków, Poland

*Corresponding author's e-mail: justyna_czajkowska@sggw.pl

Keywords: BOD_5, COD_{Cr}, TOC, COD_{Mn}, wastewater, municipal wastewater treatment plant.

Abstract: The paper presents the results of a study of parameters used for determining the amount of organic pollutants in wastewater flowing into a collective wastewater treatment plant with a population equivalent of about 120 000 PE. The plant constituted part of a sewage system. Assays were performed for biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}), permanganete index (COD_{Mn}) and total organic carbon (TOC). In addition, the pH of wastewater and its alkalinity were determined. Sampling of incoming wastewater and measurement of physicochemical parameters were performed once a week, in the spring. A total of 44 samples of wastewater were collected. The correlations between the individual parameters and the correlations between the ratios of these parameters were determined. It was found that it was possible to estimate, with sufficient accuracy, the values of selected parameters for determining the concentrations of organic compounds in municipal wastewater, knowing the values of other parameters in this group. Moreover, it was shown that, knowing the relationship between the analyzed parameters, one can find multiple regression equations for a given type of wastewater, which allow one to calculate the remaining relationships with a good fit, i.e. a determination factor R^2 greater than 0.6.

Introduction

Wastewater is a multi-phase and multi-component system consisting of dissolved gases, liquids and solids. The organic and inorganic substances found in wastewater may be in the form of solutions, colloids or dispersed phases. The analytical ratios most commonly used to determine the overall concentration of organic substances in wastewater are chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and total organic carbon (TOC). COD and BOD_5 are conventional indicators of the amount of oxygen consumed in the oxidation of organic compounds. Because BOD_5 measurements are time-consuming (5 days), studies are being conducted to reduce the measurement time to up to 0.5 hour, which would enable extrapolation of results (Liu et al. 2015).

The total organic carbon content is not explicitly linked to the oxygen demand indicators such as BOD_5 or COD_{Cr} because TOC measurement consists in determining the concentration of organic carbon without taking into account its degree of oxidation. It is estimated that in domestic wastewater, about 42% of TOC is represented by dissolved solids, 31% is in colloidal form, and 27% is in suspended form (Liwarska-Bizukojć 2014).

There are three types of relationships between BOD_5 and COD_{Cr} (Miksch 2000):

$$BOD_5 = a \cdot COD_{Cr} \tag{1}$$

$$BOD_5 = a \cdot COD_{Cr} - b \tag{2}$$

$$BOD_5 = a \cdot COD_{Cr} + b \tag{3}$$

Relationship (1) is true when wastewater contains only biochemical oxidative substances and can be quantitatively oxidized chemically. Then, BOD_5/COD_{Cr} = a, and oscillates between 0.5 and 0.7. Relationship (2) is correct when wastewater contains undesirable substances or substances that decompose very slowly, and relationship (3) can be observed in industrial wastewater which contains biologically degradable compounds, but not matter that can be chemically oxidized by dichromate, and, when a correction for nitrification is used (Miksch 2000). The mutual linear relationships between BOD and COD have been confirmed by other researchers (Alsaqqar et al. 2017). The BOD_5/COD_{Cr} relationship is used to determine the stability index (Cossu et al. 2012) and to model wastewater treatment processes in a variety processes (Alsulaili et al. 2017).

The biodegradability of wastewater is commonly expressed as a COD_{Cr}/BOD_5 ratio or its inverse. Typical ratios in raw wastewater are BOD_5/TOC = 1.8–2.5, COD_{Cr}/TOC = 2.5–4.0 (Sadecka 2010), and BOD_5/COD_{Cr}= 0.3–0.96 (Abdalla and Hammam 2014). Liwarska-Bizukojć (2014) recognizes the BOD_5/COD_{Cr} ratio of 0.4–0.5 as typical of domestic and municipal wastewater, ratio greater than 0.5 – presence of biodegradable wastewater and less than 0.2 non-biodegradable. For example, in raw sewage from a cosmetic factory which was considered not susceptible to biodegradation, the BOD_5/COD_{Cr} ratio was 0.14 (Michel et al. 2015). In leachate from new landfills, the BOD_5/COD ratio was as high as 0.7 and decreased with time to 0.1, a value that is characteristic of stabilized landfills (Surmacz-Górska 2001). Samudro and Mangkoedihardjo (2010) assumed that with BOD_5/COD_{Cr} ratio <0.1 wastewater can be regarded as toxic, since living organisms have limited access to easily decomposed organic matter, and such drips usually contain a lot of mineral salts. Low BOD_5/COD_{Cr} ratios have been observed in rivers (Lee and Nikraz 2015).

The aim of the present study was to determine the statistical relationships among COD_{Cr}, BOD_5, COD_{Mn} and TOC in raw municipal wastewater entering a mechanical and biological wastewater treatment plant, as well as to find relationships between the ratios of pairs of these parameters which would allow for the estimation of selected parameters based on results of measurements of other parameters from this set.

Method

Tests were conducted from March to May at an urban wastewater treatment plant (WWTP) located in a small town (near Warsaw) in Poland. Three to five samples of wastewater were taken at 30 min intervals. The physicochemical composition of sewage entering the plant was analyzed. The technological diagram is shown in Fig. 1.

During the study period, wastewater tests samples were collected from 6.03. until 15.05. once a week from 8:00 to 9:15 every 15 minutes using samples taken from the flow channel between the grit traps and the settling tank. A total of 44 sewage samples were collected and assayed for the following parameters using the methods given:

- biochemical oxygen demand (BOD_5), an OxiTop Control respirator. Pressure sensor that allows for the determination of a pressure drop in gaseous phase (ambient air) in a closed vessel at constant temperature (Malińska 2016)
- chemical oxygen demand (COD_{Cr}), the bichromate method using LCK 014 and LCK 514 cuvette tests HachLange firm,
- chemical oxygen demand, potassium permanganate (COD_{Mn}) (Clesceri 1999),
- total organic carbon (TOC) (Clesceri 1999),
- pH, the potentiometric method (Clesceri 1999),
- alkalinity, the alkalimetric titration method (Clesceri 1999).

BOD_5 tests were performed in two series: 1) using 2-chloro-6-trichloromethylpyrimidine (TCMP) as a nitrification inhibitor (BOD_{5inh}), and 2) without an inhibitor (BOD_5).

The results of the physicochemical assays which were methodologically illogical (e.g. cases in which BOD_5 was higher than COD) were excluded from further statistical assessment. The Grubbs test (Zięba 2013) was used to identify outliers. Results deviating from the trend were removed from the series. The normality of distribution of the results was verified using the Shapiro-Wilk test (Zięba 2013). It was found that the results had distributions close to the normal distribution with significant level a = 0.05. Descriptive statistics of the results were done according to Wasilewska's recommendations (2011). The following properties of distributions were analyzed:

- location of the distribution – arithmetic mean (x_{me}), minimum value (x_{min}), maximum value (x_{max}), median (x_{med}), first quartile (Q_1) and third quartile (Q_3),
- variability – standard deviation (s) and coefficient of variation (V_s) – formula (4),

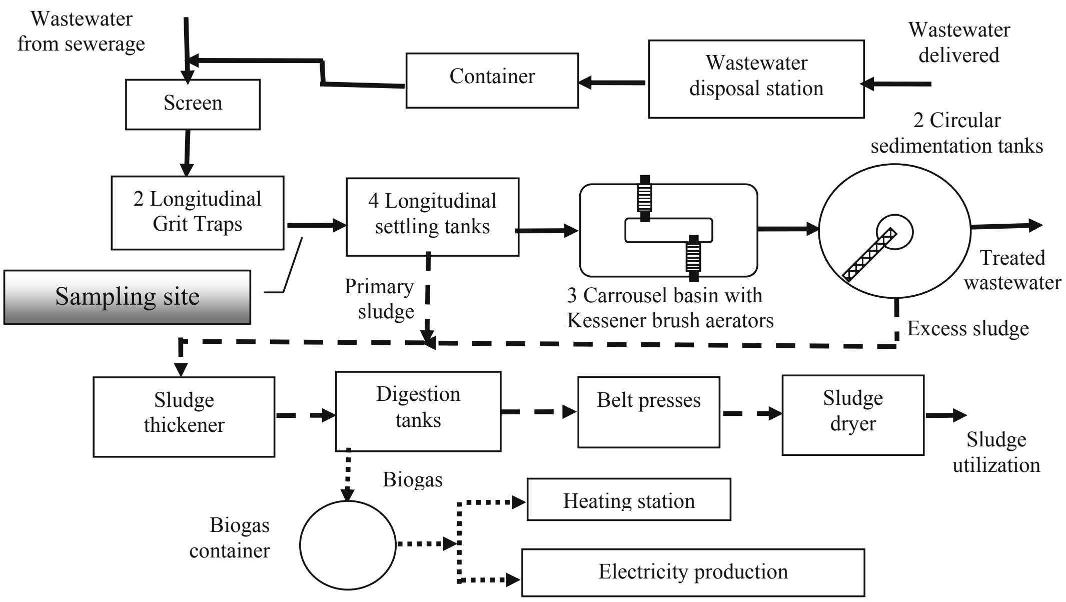

Fig. 1. Technological scheme of the wastewater treatment plant showing the location of the sampling site

- asymmetry – Pearson's coefficient of skewness (A_p) – formula (5) and classical asymmetry coefficient (A_s) – formula (6), where μ_3 – third central moment,
- concentration – kurtosis (K) – formula (7), where μ_4 – fourth central moment and Gini coefficient (G) according to Kot et al. (2011) – formula (8), where the values are in descending order, *n* is the number of results,
- standard deviation of the residual component Se (9) and coefficient of random variation Ve (10) where x_i – bservations, n – observations number, w – structural number in the regression equation (Kot et al. 2011):

$$V_s = \frac{\sigma \cdot 100\%}{x_{me}} \tag{4}$$

$$A_p = \frac{3 \cdot (x_{me} - x_{med})}{\sigma} \tag{5}$$

$$A_s = \frac{\mu_3}{\sigma^3} \tag{6}$$

$$K = \frac{\mu_4}{\sigma^4} \tag{7}$$

$$G = 1 + \frac{1}{n} - \frac{2}{n^2 \cdot x_{me}} \cdot \sum_{i=1}^{n} i \cdot n_i \tag{8}$$

$$S_e = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{me})}{n - w}} \tag{9}$$

$$V_e = \frac{S_e}{x_{me}} \cdot 100\% \tag{10}$$

Since in the calculations of Pearson's A_p, determination of mode was not possible, it was assumed, following the work of Kot et al. (2011), that the difference between mean and mode was roughly three times the difference between mean and median.

Histograms with normal distribution overlay were constructed to visualize the results and a regression analysis was performed to find relationships between the individual parameters (BOD_5, BOD_{5inh}, COD_{Cr}, COD_{Mn}, TOC). The values of measured parameters were very diverse and random. Thus, in order to determine the relationships among them the corresponding ratios of the individual parameters were calculated and analyzed: BOD_5/COD_{Cr}, BOD_{5inh}/COD_{Cr}, COD_{Cr}/COD_{Mn}, TOC/COD_{Cr}, BOD_5/BOD_{5inh}, BOD_5/COD_{Mn}, BOD_{5inh}/COD_{Mn}, BOD_5/TOC, BOD_{5inh}/TOC, COD_{Mn}/TOC.

Results and discussion

The general characteristics of the investigated wastewater samples are presented in Table 1. The values of the analyzed physicochemical parameters of the wastewater vary over a wide range, which is a consequence of irregular inflow of waste from industrial plants, public utilities, service points etc. An analysis of the last four columns of Table 1 (minimum/maximum and quartiles values) shows that the wastewater entering the WWTP showed quite a high variability of pollutant concentrations. The large scattering resulted primarily from the impact of wastewater transported by wastewater trucks. Generally, wastewater coming from the trucks accounted for 3–4% of the amount of incoming wastewater, but, as reported by employees of the plant, sometimes several vacuum trucks came to the WWTP in a short space of time. The COD_{Cr} values in the delivered wastewater in the WWTP Piaseczno oscillated between 1,000 and 10,000 $mgO_2 \times L^{-1}$ and sometimes exceeded 10,000 $mgO_2 \times L^{-1}$. Comparable concentrations of organic substances (BOD_5, COD_{Cr}) occur in domestic wastewater (Pawęska and Kuczewski 2013, Mucha and Kułakowski 2016). The investigated parameters, with the exception of pH, were skewed to the right, with the median located clearly below the mean. The pH distribution was symmetrical.

Figure 2 shows the dependence of the tested indicators on the overall content of organic compounds, i.e. TOC, BOD_5, BOD_{5inh} and COD_{Mn} or COD_{Cr}, in the wastewater. The data show that the determination coefficients R^2 are at an acceptable level and, as reported by Bobrowski and Maćkowiak-Łybacka (2006), at R^2 in the range of 0.5–0.81, the dependence is strict. A significant effect of nitrification on the total BOD_5 value can be seen, as the values obtained from measurements performed without the use of the inhibitor are clearly higher. The average BOD_5/BOD_{5inh} ratio was 1.21±0.15. This means that some of the oxygen used in biochemical decomposition was utilized for the oxidation of ammonium nitrogen. Previous studies confirm

Table 1. Characteristic parameters of the tested wastewater

No.	Parameter	Unit	Mean	St. dev.	Median	Minimum	Maximum	First quartiles	Third quartiles
1.	BOD_5	$mgO_2 \times L^{-1}$	232.0	57.9	218.0	149.0	380.0	189	279
2.	BOD_{5inh}	$mgO_2 \times L^{-1}$	194.0	51.1	178.0	132.0	279.0	149	235
3.	COD_{Cr}	$mgO_2 \times L^{-1}$	283.6	66.6	257.8	178.3	415.2	243	337
4.	COD_{Mn}	$mgO_2 \times L^{-1}$	111.0	34.8	100.8	57.0	175.8	83	139
5.	TOC	$mgC \times L^{-1}$	118.7	33.9	103.7	57.6	171.2	92	154
6.	pH	–	7.9	0.2	7.9	7.5	8.3	7.78	7.93
7.	Alkalinity	$mval \times L^{-1}$	10.5	1.9	9.6	8.6	14.3	9.42	10.6

this observation (Scholes et al. 2016, Siwiec et al. 2012), demonstrating that nitrification of ammonium compounds influences the measurement of BOD_5 earlier than from day five on, as usually reported in the literature (Miksch 2000).

By analyzing the functions BOD_5=f(COD_{Cr}) and BOD_{5inh} = f(COD_{Cr}) (Fig. 2) and using the relationships given by Miksch (2000) (formulas (1)–(3)), we found that in the expressions BOD_5=0.6369COD_{Cr} + 61.1653 and BOD_{5inh}=0.6694COD_{Cr} + 6.5931, the absolute terms expressed the effect of nitrification and the impact of substances that cannot be chemically oxidated under bichromate. A similar relationship BOD_5 = 0.431×COD_{Cr} +21.08 was found for domestic wastewater (Jóźwiakowski et al. 2017). This gave us the opportunity to assess the relative percentage share of these two components in the BOD_5 values: the average nitrification share was about 89%, while the share of substances, for example ammonia, which were non-oxidable under the bichromatic method was about 11%.

Table 2 presents the descriptive statistics of the ratios of the tested parameters from which it can be concluded that the wastewater exhibited an excellent biodegradability, as evidenced by the very high ratios of organic decomposition (BOD_5) and organic decomposition in the presence of the nitrification inhibitor (BOD_{5inh}) to total organic impurities (COD_{Cr}) (0.822 and 0.685, respectively). The high BOD_5/COD ratio may have been due to the breakdown of difficult-to-decompose compounds in the sewage network (Jin et al. 2015). The speculation that the wastewater contained a high level of readily decomposable substances was confirmed by the fact that the WWTP easily generated treated wastewater with a BOD_5 below 10 mg×L^{-1} and a COD_{Cr} of 30 to 40 mg×L^{-1}. It is worth pointing to a significant share of nitrification in the BOD_5 values. The mean BOD_5 score was 27.6% higher than mean BOD_{5inh}. The medians did not differ significantly from the means and they were lower than the means, which meant that the distribution had positive skew, i.e. a slight dominance of higher measurement values.

The small differences between quartiles Q_3 and Q_1 show that, despite the fact that wastewater was sampled at various different times, the vast majority of the results are within a relatively narrow range. This conclusion is confirmed by the graphs in Fig. 3. The variability of the results shown by the V_s coefficient is not large, as, according to Wasilewska (2011)

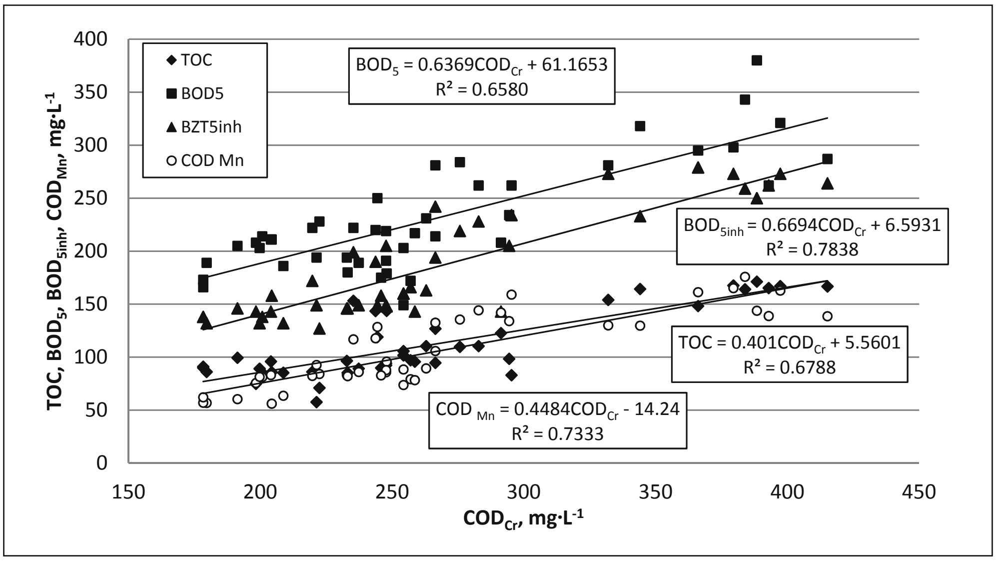

Fig. 2. Relationships between parameters of the effluent and COD_{Cr}

Table 2. Descriptive statistics for the ratios of the parameters tested

No.	Ratio	x_{min}	x_{me}	x_{max}	x_{med}	Q_1	Q_3	s	V_s	A_p	A_s	K	G
1.	BOD_5/COD_{Cr}	0.586	0.822	0.978	0.821	0.772	0.892	0.097	11.8%	0.041	−0.421	2.415	0.065
2.	BOD_{5inh}/COD_{Cr}	0.491	0.685	0.846	0.670	0.629	0.763	0.085	12.5%	0.513	0.158	2.322	0.068
3.	COD_{Mn}/COD_{Cr}	0.290	0.388	0.538	0.366	0.346	0.435	0.067	17.2%	0.973	0.589	2.234	0.094
4.	TOC/COD_{Cr}	0.260	0.420	0.651	0.412	0.375	0.441	0.081	19.3%	0.311	0.844	4.057	0.099
5.	BOD_5/ BOD_{5inh}	0.931	1.210	1.520	1.190	1.103	1.303	0.151	12.6%	0.412	0.371	2.226	0.070
6.	BOD_5/COD_{Mn}	1.464	2.163	2.925	2.105	1.887	2.329	0.374	17.3%	0.474	0.484	2.345	0.095
7.	BOD_{5inh}/COD_{Mn}	1.006	1.799	2.421	1.766	1.653	1.905	0.285	15.8%	0.350	0.026	3.706	0.084
8.	BOD_5/TOC	1.247	2.018	3.368	1.993	1.778	1.182	0.434	21.5%	0.173	1.124	5.076	0.110
9.	BOD_{5inh}/TOC	1.031	1.681	2.819	1.583	1.512	1.760	0.370	22.0%	0.798	1.217	4.674	0.111
10.	COD_{Mn}/TOC	0.634	0.957	1.916	0.866	0.815	0.985	0.274	28.6%	0.997	1.741	6.137	0.139

and Nankya and KyungSook (2016), a variance of up to 20% is considered to be a weak variance and a variance of up to 40% – moderate. In the present study, the highest coefficient was obtained for a COD_{Mn}/TOC ratio of about 28%. Both the Pearson's coefficient of skewness A_p and the classical asymmetry coefficient A_s show that the distribution of the results is not symmetrical. In general, except for one result, the coefficients are positive, which indicates that the distribution is skewed to the right, while the numerical values show that it is difficult to find some mathematical dependence. Wasilewska (2011) states that asymmetry is very small if A_p=0¸0.2 and A_s=0¸0.4. As the two values increase, the asymmetry becomes larger, and is considered to be a very large skew if A_p>0.8 and A_s>1.6. Practically all of these cases can occur. A similar pattern was observed in the case of concentration assessment. In five cases K<3, which meant that the distribution was less concentrated than the normal distribution (it was flatter), while in the other five it was more slender than the normal distribution. The Gini coefficient obtained using the Lorenz concentration curve showed that the concentration was weak, since G was less than 0.3.

Tables 3 and 4 give selected linear correlations between the investigated parameters along with coefficients of determination which allow for the estimation of one parameter on the basis of other, measured parameters. Only statistically significant relationships were selected.

As shown in Table 3, the oxygen parameters (BOD_5, BOD_{5inh}, COD_{Cr} and COD_{Mn}) correlate quite well with one another, with R^2>0.6; lower correlations are observed between TOC and BOD_5, $BOD_{5inh,}$ and COD_{Mn}. An acceptable correlation was obtained for TOC=f(COD_{Cr}). In spite of this, almost all the dependencies fell within the range of 0.5–0.81, which according to Bobrowski and Maćkowiak-Łybacka (2006) characterizes closely related parameters. The relationship between pH and alkalinity is not shown in the Table 3. The pH of the effluent did not show any statistically significant relationships, and R^2 values were low (from −0.12 to −0.26). Density, although statistically significant (R^2 from 0.63 to 0.80), is not a parameter that is technologically related to BOD_5, COD_{Cr}, or TOC. The mutual relationships among BOD_5, COD and TOC were strong dependencies, while no statistically significant relationships were found among pH and alkalinity (Lee and Nikraz 2014).

Quite often, in both theoretical and practical comparisons, authors use the ratios of the parameters investigated in this study. COD fractions are sometimes analyzed (Hocaoglu and Orhon 2013), which show the share of organic compounds in molecular and diffused fractions (Szaja et al. 2015). A particularly widely used relation is the BOD_5/COD_{Cr} ratio, which describes the fraction of easily decomposable organic compounds in the mass of organic compounds oxidized with $K_2Cr_2O_7$. A high value of this ratio confirms the possibility of conducting an effective biological wastewater treatment process. Other important relations are COD_{Cr}/COD_{Mn} and COD_{Cr}/TOC (Kowalski 2007), and especially the latter or its inverse, which specify the amount of oxygen needed to oxidize 1 g of carbon in the mass of organic pollutants (Kowalski 2007). A COD_{Cr}/TOC ratio above 4 refers to saturated hydrocarbons, a ratio of 4 to unsaturated fatty acids, and 3.75 to fatty acids. The lowest values, in the range of 2.6–2.8, refer to humic acids, carbohydrates and cellulose (Kowalski 2007). In this study, the mean was 2.46 with a range of 1.54–3.84 and quartiles Q_1=2.27 and Q_3=2.66. It can be concluded from these data that most of the pollutants in the wastewater were carbohydrates and cellulose derivatives with an oxygen/carbon atom (O/C) ratio of 0.77 (Kowalski 2007).

The spread of the determinants shown in Table 4 is very large since R^2 ranges from 0.149 to 0.721. The best correlation was obtained for the relationship $\frac{BOD_{5inh}}{TOC} = f\left(\frac{BOD_5}{TOC}\right)$. Values that were not much lower were obtained for $\frac{COD_{Mn}}{TOC} = f\left(\frac{BOD_{5inh}}{TOC}\right)$ and $\frac{COD_{Mn}}{TOC} = f\left(\frac{BOD_5}{TOC}\right)$. All the relationships in Table 4 are statistically significant because the probability test p was lower than the assumed significance level of 0.05, but it is difficult to treat them as satisfactory, as some of them have R^2 values below 0.2, which correspond to a correlation coefficient of less than 0.5. V_e informs that 10.1–24.3% is wrong to calculate the value of the variable using the regression equations in Table 4.

Multiple regression analysis yielded much better results, as shown in Table 5. The best- and the worst-fitting lines are shown in Figure 3.

Table 5 shows only those functions whose determination coefficient was greater than 0.6 and the coefficient of random variation is in the range of 9.1–12.6%. As already mentioned, such functions are quite useful for describing individual parameters (Fig. 3 a and b). A detailed analysis of the functions given in Table 5 shows that one parameter from each ratio on the left of the equality sign is repeated on the right. This implies that COD_{Cr} can be calculated from equations 1 and 2, COD_{Mn} – from equation 7, BOD_5 – from 3 and 5, and BOD_{5inh} – from 4 and 6. The correlations in which both parameters to the left of the equality sign were unknown could not be accepted because R^2 was very low. Also TOC did not correlate very well with the

Table 3. Selected functional relationships between the test parameters (mg×L^{-1})

Relation	R^2	Relation	R^2
$BOD_{5inh} = 15.6 + 0.769 \cdot BOD_5$	0.760	$COD_{Mn} = -3.115 + 0.58837 \cdot BOD_{5inh}$	0.748
$COD_{Cr} = 50.214 + 1.0058 \cdot BOD_5$	0.766	$TOC = 20.721 + 0.50509 \cdot BOD_{5inh}$	0.581
$COD_{Mn} = -6.755 + 0.5077 \cdot BOD_5$	0.716	$COD_{Mn} = -15.22 + 0.44527 \cdot COD_{Cr}$	0.728
$TOC = 15.319 + 0.44566 \cdot BOD_5$	0.581	$TOC = 2.4672 + 0.40996 \cdot COD_{Cr}$	0.650
$COD_{Cr} = 58.181 + 1.1617 \cdot BOD_{5inh}$	0.794	$TOC = 42.533 + 0.68612 \cdot COD_{Mn}$	0.496
$BOD = 1.813 \cdot TOC^{0,4244}$; $BOD = 3.376 \cdot 10^{-7} \cdot COD^3 + 6.82 \cdot 10^{-4} \cdot COD^2 + 3,69 \cdot 10^{-4} \cdot COD + 4.822$ (Bhat et al. 2003)			

other parameters. The values of the coefficient of determination R^2 for the ratios for calculating TOC $\frac{TOC}{COD_{Cr}}$ were 0.09; $\frac{BOD_5}{TOC}$ 0.20; $\frac{BOD_{5inh}}{TOC}$ 0.23; and $\frac{COD_{Mn}}{TOC}$ 0.47. This is logical since TOC is the only non-oxic indicator and, as such, is not expressed in the same units as the other indicators.

From the above analysis it can be seen that it is difficult to find a ready solution that would work in all conditions. However, it is worth running routine tests of wastewater because, given the repetitive habits of the users of a WWTP, such tests allow one to predict approximate ranges of the wastewater parameters, eliminating the need to measure them on every occasion.

The residual analysis was performed to assess the fit of the models. Points in the distribution of residuals are arranged randomly. The value of the W statistic from test Shapiro-Wilk for all models was greater than the critical value, hence it can be concluded that for $p<0.05$ the residual distribution is normal.

Summary

As can be seen from literature reports and our own research, the relationships among the basic parameters of wastewater

Table 4. Selected functional relationships between the ratios of the test parameters obtained by the linear regression method

Relationship	R^2/V_e	Relationship	R^2/V_e
$\frac{BOD_5}{COD_{Cr}}=0.4222+0.5839\cdot\frac{BOD_{5inh}}{COD_{Cr}}$	0.267 10.1%	$\frac{BOD_5}{TOC}=3.7233-4.0591\cdot\frac{TOC}{COD_{Cr}}$	**0.573** 14.1%
$\frac{BOD_5}{BOD_{5inh}}=0.6319+0.7036\cdot\frac{BOD_5}{COD_{Cr}}$	0.200 11.2%	$\frac{BOD_{5inh}}{TOC}=3.0981-3.3738\cdot\frac{TOC}{COD_{Cr}}$	**0.545** 14.9%
$\frac{BOD_5}{COD_{Mn}}=0.8183+1.6364\cdot\frac{BOD_5}{COD_{Cr}}$	0.179 15.7%	$\frac{COD_{Mn}}{TOC}=1.891-2.2234\cdot\frac{TOC}{COD_{Cr}}$	0.432 21.7%
$\frac{BOD_5}{TOC}=0.5928+1.7344\cdot\frac{BOD_5}{COD_{Cr}}$	0.149 19.8%	$\frac{BOD_5}{COD_{Mn}}=0.8453+1.0891\cdot\frac{BOD_5}{BOD_{5inh}}$	0.196 15.5%
$\frac{COD_{Mn}}{COD_{Cr}}=0.1675+0.3219\cdot\frac{BOD_{5inh}}{COD_{Cr}}$	0.171 15.8%	$\frac{BOD_{5inh}}{COD_{Mn}}=0.6463+0.5327\cdot\frac{BOD_5}{COD_{Mn}}$	0.490 11.3%
$\frac{BOD_5}{BOD_{5inh}}=1.854-0.9402\cdot\frac{BOD_{5inh}}{COD_{Cr}}$	0.280 10.7%	$\frac{COD_{Mn}}{TOC}=1.7950-0.3873\cdot\frac{BOD_5}{COD_{Mn}}$	0.280 24.3%
$\frac{BOD_{5inh}}{TOC}=0.44721+1.8022\cdot\frac{BOD_{5inh}}{COD_{Cr}}$	0.173 20.0%	$\frac{COD_{Mn}}{TOC}=1.8874-0.5172\cdot\frac{BOD_{5inh}}{COD_{Mn}}$	0.289 24.1%
$\frac{BOD_5}{COD_{Mn}}=3.7216-4.0168\cdot\frac{COD_{Mn}}{COD_{Cr}}$	0.512 14.5%	$\frac{BOD_{5inh}}{TOC}=0.2205+0.7237\cdot\frac{BOD_5}{TOC}$	**0.721** 11.6%
$\frac{BOD_{5inh}}{COD_{Mn}}=2.9785-3.0414\cdot\frac{COD_{Mn}}{COD_{Cr}}$	**0.507** 11.1%	$\frac{COD_{Mn}}{TOC}=-0.0471+0.4976\cdot\frac{BOD_5}{TOC}$	**0.623** 17.6%
$\frac{COD_{Mn}}{TOC}=-0.0834+2.6824\cdot\frac{COD_{Mn}}{COD_{Cr}}$	0.426 21.7%	$\frac{COD_{Mn}}{TOC}=-0.0592+0.6046\cdot\frac{BOD_{5inh}}{TOC}$	**0.668** 16.5%

Table 5. Selected functional relationships between the ratios of the tested parameters obtained by the multiple regression method

No.	Function	R^2/V_e
1.	$\frac{COD_{Mn}}{COD_{Cr}}=0.782-0.306\frac{BOD_5}{BOD_{5inh}}+0.290\frac{BOD_5}{COD_{Mn}}-0.375\frac{BOD_{5inh}}{COD_{Mn}}-0.230\frac{BOD_5}{TOC}+0{,}112\frac{BOD_{5inh}}{TOC}+0{,}315\frac{COD_{Mn}}{TOC}$	0.719 9.1%
2.	$\frac{TOC}{COD_{Cr}}=1.656-0.962\frac{BOD_5}{BOD_{5inh}}+0.471\frac{BOD_5}{COD_{Mn}}-0.413\frac{BOD_{5inh}}{COD_{Mn}}-0.037\frac{BOD_5}{TOC}-0{,}334\frac{BOD_{5inh}}{TOC}+0{,}301\frac{COD_{Mn}}{TOC}$	0.671 11.0%
3.	$\frac{BOD_5}{COD_{Mn}}=3.914+7.687\frac{BOD_{5inh}}{COD_{Cr}}-15.753\frac{COD_{Mn}}{COD_{Cr}}-0.006\frac{TOC}{COD_{Mn}}-0.279\frac{BOD_{5inh}}{COD_{Mn}}-2{,}542\frac{BOD_{5inh}}{TOC}+4.048\frac{COD_{Mn}}{TOC}$	0.638 10.4%
4.	$\frac{BOD_{5inh}}{COD_{Mn}}=3.354+4.740\frac{BOD_5}{COD_{Cr}}-12.275\frac{COD_{Mn}}{COD_{Cr}}+0.938\frac{TOC}{COD_{Cr}}-0.541\frac{BOD_5}{COD_{Mn}}-1{,}082\frac{BOD_5}{TOC}+2.373\frac{COD_{Mn}}{TOC}$	0.654 9.4%
5.	$\frac{BOD_5}{TOC}=3.021+5.281\frac{BOD_{5inh}}{COD_{Cr}}-12.001\frac{COD_{Mn}}{COD_{Cr}}+0.412\frac{TOC}{COD_{Cr}}-1.092\frac{BOD_{5inh}}{COD_{Mn}}-0{,}701\frac{BOD_{5inh}}{TOC}+3.139\frac{COD_{Mn}}{TOC}$	0.814 9.3%
6.	$\frac{BOD_{5inh}}{TOC}=2.744+4.628\frac{BOD_5}{COD_{Cr}}-11.064\frac{COD_{Mn}}{COD_{Cr}}+0.428\frac{TOC}{COD_{Cr}}-1.083\frac{BOD_5}{COD_{Mn}}-0{,}401\frac{BOD_5}{TOC}+2.505\frac{COD_{Mn}}{TOC}$	0.829 9.1%
7.	$\frac{COD_{Mn}}{TOC}=-4.362-2.245\frac{BOD_5}{COD_{Cr}}+0.012\frac{BOD_{5inh}}{COD_{Cr}}+3.251\frac{TOC}{COD_{Cr}}+2.850\frac{BOD_5}{BOD_{5inh}}-0{,}796\frac{BOD_5}{TOC}+2.349\frac{BOD_{5inh}}{TOC}$	0.806 12.6%

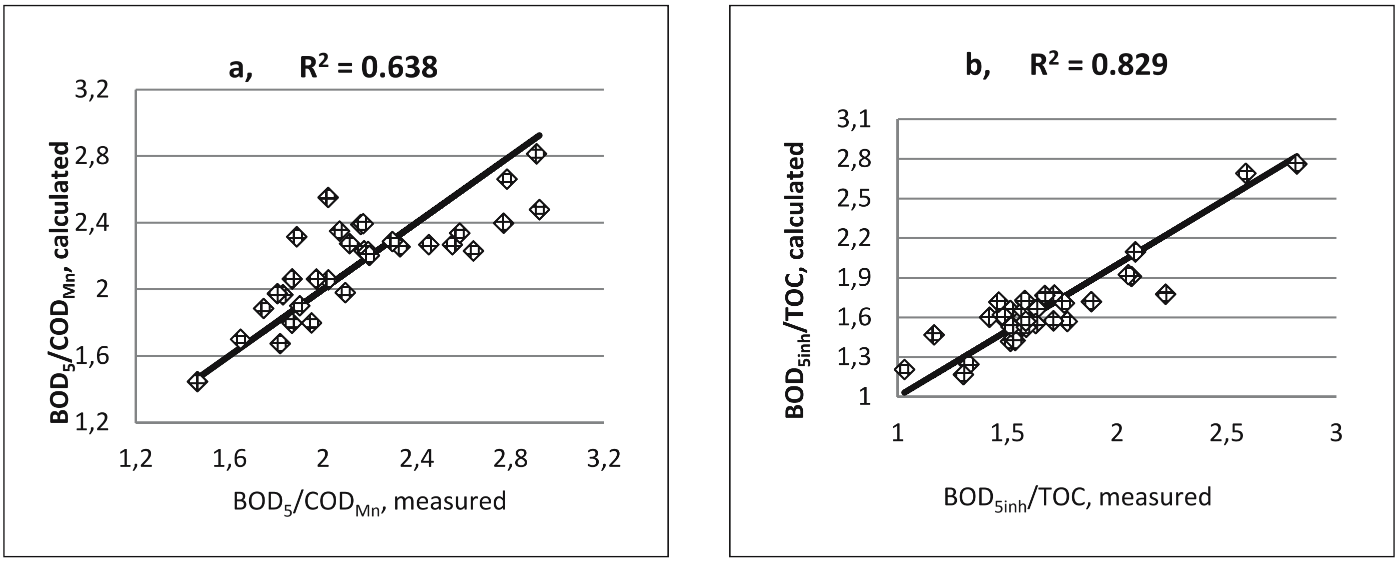

Fig. 3. Scatterplots with the worst – (a) and best-fitting (b) multiple regression lines

can be described by various different types of equations. It is difficult to find a universal equation for all the different cases. The diversity is due to the nature of sewerage system, and, above all, the presence and types of industrial plants, the types and sizes of public utilities and the amount of rainwater entering the sewer network. Nevertheless, computational effort can be reduced by running statistical tests for a particular wastewater parameter and using the results to calculate the other parameters. This suggestion is confirmed by the data given in Table 2, which shows an abundance of samples between the extreme quartiles. Coefficients of determination have very different values – from very low, or even statistically insignificant, to quite high-close to unity.

Linear regression does not produce satisfactory results, as its ability to estimate the parameters sought is limited. The best results are obtained by using multiple regression. This method requires more measurements, but when the appropriate functions are found for a given facility (as shown in Table 5), multiple regression can be used to evaluate further wastewater parameters in a simple and convenient manner.

Models can be used in other wastewater treatment plants, but the numerical coefficients should be verified by own studies of incoming sewage.

References

Abdalla, K.Z. & Hammam, G. (2014). Correlation between biochemical oxygen demand and chemical oxygen demand for various wastewater treatment plants in Egypt to obtain the biodegradability indices, *International Journal of Sciences: Basic and Applied Research* (IJSBAR), 13, 1, pp.42–48.

Alsaqqar, A.S., Khudair, B.H. & Al-Sulaimen, A.M. (2017). Performance evaluation of the organic matter removal efficiency in wastewater treatment plants; case study Al-Diwaniyah WWTP in Iraq, *International Journal of Science and Research* (IJSR), 6, 2, pp. 334–338.

Alsulaili, A.D., Hamoda, M.F., Al-Jarallah, R. & Alrukaibi, D. (2017). Treatment and potential reuse of graywater from schools: a pilot study, *Water Science and Technology,* 75, pp. 2119–2129. DOI: 10.2166/wst.2017.088

Bhat, M.R., Hiremath, R.S. & Kulkarni, V.R. (2003). Correlation between BOD, COD and TOC, *Journal of Industrial Pollution Control*, 19,2, pp. 187–191.

Bobrowski, D. & Mackowiak-Łybacka, K. (2006). *Selected methods of statistical inference*, Edit. Politechniki Poznańskiej, Poznań 2006. (in Polish)

Clesceri L.S., Greenberg A.E. & Eaton A.D. (1999). *Standard methods for the examination of water and wastewater* (20st edition), American Public Health Association, AWWA and Wat, Environ. Fed. 1999.

Cossu, R., Lai, T. & Sandon, A. (2012). Standardization of BOD_5/COD ratio as a biological stability index for MSW, *Waste Management*, (32), pp. 1503–1508.

Hocaoglu, S.M. & Orhon, D. (2013). Particle size distribution analysis of chemical oxygen demand fractions with different biodegradation characteristics in black water and gray water, *Clean – Soil, Air, Water,* 41, 11, pp. 1044–1051.

Jin, P., Wang, Bi., Jiao, D., Sun, G., Wang, Ba. & Wang, X.C. (2015). Characterization of microflora and transformation of organic matters in urban sewer system, *Water Research*, 84, pp. 112–119

Jóźwiakowski, K., Bugajski, P., Mucha, Z., Wójcik, W., Jucherski, A., Nastawny, M., Siwiec, T. & Gajewska, M. (2017). Reliability and efficiency of pollutions removal during long-term operation of one-stage constructed wetland system with horizontal flow, *Separation and Purification Technology*, 187, pp. 60–66.

Kot, S.M., Jakubowski, J. & Sokołowski, A. (2011). *Statistics*. Edit. Difin Warszawa 2011. (in Polish)

Kowalski, T. (2007). *Use and treatment of contaminated water*, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2007. (in Polish)

Lee, A.H. & Nikraz, H. (2014). BOD:COD ratio as an indicator for pollutants leaching from landfill, *Journal of Clean Energy Technology*, 2, 3, pp. 263–266.

Lee, A.H. & Nikraz, H. (2015). BOD:COD ratio as an indicator for river pollution, *International Proceedings of Chemical, Biological and Environmental Engineering*, 88, 15, pp. 89–94.

Liu, L, Bai, L., Yu, D., Zhai, J. & Dong, S. (2015). Biochemical oxygen demand measurement by mediator method in flow system, *Talanta*, 138, pp. 36–39.

Liwarska-Bizukojć, E. (2014). *Activated sludge modeling of wastewater treatment processes*, Edit. Seidel-Przywecki Sp zo.o. (in Polish)

Malińska, K. (2016). Application of a modified OxiTop® respirometer for laboratory composting studies, *Archives of Environmental Protection*, 42, 1, pp. 56–62

Miksch, K. (2000). *Wastewater biotechnology. A collection of paper*, Edit. Politechniki Śląskiej, Gliwice 2000. (in Polish)

Michel. M.M., Siwiec, T., Tytkowska, M. & Reczek, L. (2015). Analysis of flotation unit operation in coagulation of wastewater from a cosmetic factory, *Przemysł Chemiczny,* 94, 11, pp. 2000–2005. (in Polish)

Mucha, Z. & Kułakowski, P. (2016). Turbidity measurements as a tool of monitoring and control of the SBR effluent at the small wastewater treatment plant – preliminary study, *Archives of Environmental Protection*, 42,3, pp. 33–36

Nankya, M. & KyungSook, Ch. (2016). Temporal and spatial analysis of water quality in Saemangeum watershed using multivariate statistical techniques, *Paddy and Water Environment*, 14,1, pp. 3–17

Pawęska, K. & Kuczewski, K. (2013). The small wastewater treatment plants – hydrobotanical systems in environmental protection, *Archives of Environmental Protection*, 39, 1 pp. 3–16.

Sadecka, Z. (2010). *Foundations of biological wastewater treatment*, Edit. Seidel-Przywecki Sp. z o.o. (in Polish)

Scholes, E., Verheyen, V. & Brook-Carter, P. (2016). A review of practical tools for rapid monitoring of membrane bioreactors, *Water Research,* 102, pp. 252–262.

Siwiec, T., Kiedryńska, L., Abramowicz, K. & Rewicka, A. (2012). Analysis of chosen models describing the changes in BOD_5 in sewages, *Environment Protection Engineering,* (38), 2, pp. 61–76.

Surmacz-Górska, J. (2001). *Degradation of organic compounds in landfill leachate.* Komitet Inżynierii Środowiska PAN, Monograph, no. 5, Lublin. (in Polish)

Szaja, A., Aguilar, J.A. & Łagód, G. (2015). Estimation of chemical oxygen demand fractions of municipal wastewater by respirometric method – case study, *Annual Set Environmental Protection*, 17, pp. 289–299.

Wasilewska, E. (2011). *Descriptive statistics from scratch*, Edit. SGGW, Warszawa 2011. (in Polish)

Zięba, A. (2013). *Data analysis in science and technology*, Edit. PWN Warszawa 2013. (in Polish)

Korelacje pomiędzy wskaźnikami zanieczyszczeń organicznych w ściekach komunalnych

Streszczenie: W pracy przedstawiono wyniki badań parametrów wykorzystywanych do oznaczania ilości zanieczyszczeń organicznych w ściekach wpływających do zbiorczej oczyszczalni ścieków o równoważnej liczbie ludności około 120 000 mieszkańców. Zakład stanowi część systemu kanalizacyjnego. Testy przeprowadzono dla biochemicznego zapotrzebowania na tlen (BZT_5), chemicznego zapotrzebowania na tlen (COD_{Cr}), utlenialności (COD_{Mn}) i ogólnego węgla organicznego (TOC). Ponadto określono wartość pH ścieków i ich zasadowość. Pobieranie próbek dopływających ścieków i pomiar parametrów fizykochemicznych przeprowadzano raz w tygodniu, na wiosnę. Zebrano łącznie 44 próbki ścieków. Określono korelacje między poszczególnymi parametrami i korelacje między stosunkami tych parametrów. Stwierdzono, że możliwe było oszacowanie, z wystarczającą dokładnością, wartości wybranych parametrów do oznaczania stężeń związków organicznych w ściekach komunalnych, znając wartości innych parametrów w tej grupie. Ponadto wykazano, że znając zależność między analizowanymi parametrami, można znaleźć równania regresji wielokrotnej dla danego typu ścieków, które pozwalają obliczyć pozostałe zależności przy dobrym dopasowaniu, o współczynniku determinacji R^2 większym niż 0,6.