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Original Research

Variability of COD and TKN Fractions of Combined Wastewater

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Abstract

Our paper analyzes the quality of combined wastewater in the aspect of its biological treatment. Fractions of chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) in the inflow to the Group Wastewater Treatment Plant in Łódź were determined. The research revealed a distinct increase of inert fractions during wet weather caused by an increasing portion of contaminants bound with suspended solids.

Keywords: wet weather pollution, COD and TKN fraction, combined wastewater, biological treatment

Introduction

The efficiency of biological wastewater treatment plants depends both on pollutant concentration level and on their susceptibility to decay in the biological treatment processes.

The removal of carbon and nitrogen compounds depends on fractional composition of pollutants. Analyses of fractional composition made in the course of 24 hours after each treatment stage and during dry and wet weather conditions allows us to determine proportions between fractions of COD and TKN. On this basis, a proper assessment of biological treatment process effectiveness is possible.

In the paper, variability of the dry- and wet weather wastewater composition in the inflow to the Łódź Group Wastewater Treatment Plant (GWWTP) (of the dry weather capacity of 180,000 m^3/d) is analyzed.

In particular, fractionating of COD and TKN are demonstrated on the example of measurements carried out for the existing urban catchment of Łódź city equipped with the combined sewage system. The constituents mentioned above are determinants for the biological treatment process with nutrient removal (the biological stage works in the UCT system).

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Apart from the recognition of variations of the fractions' participation during the inflow of combined wastewater, one of the aims of our research was the collection of input data for simulation software. This software, called SymOS, uses the ASM1 model for a dynamic simulation of wastewater treatment plants [1].

Definitions of COD and TKN Fractions and Methodology of Their Determination

The fractional composition of COD and TKN was assumed on the basis of the ASM1 model [2]. Most often, the following COD fractions are specified [2-10]:

$$COD = S_S + S_i + X_S + X_i \quad (1)$$

The meaning of the particular fractions and the unified methodology of their determination used both for dry and weather inflow are presented in Table 1.

For the BOD_{tot} calculation the same factor 1.47 for dry- and wet weather was assumed, which is adequate for the dilution of domestic wastewater by stormwater and the absence of BOD-inhibiting contaminants during wet weather conditions. This was preliminarily confirmed by our own additional BOD tests, but has to be checked in detail in a new research campaign.

Table 1. Definitions of COD fractions and methodology of their determination.

Fractions of COD	Methodology of determination
S_s - soluble easily degradable	$S_s = COD_{mf} – S_i$
S_i - inert soluble	$0.9 \cdot COD_{eff}$
X_s - particulate slowly degradable	$COD_{BD} – S_s$
X_i - inert particulate	$X_{COD} – X_s$

COD – chemical oxygen demand of raw wastewater,
COD_{eff} – COD of effluent from secondary clarifiers, filtrated using 0.45 µm membrane filter,
COD_{mf} – soluble COD of raw sewage microfiltrated after coagulation with zinc chloride using 0.45 µm membrane filters,
$X_{COD} = X_s+X_i$ – total particulate COD; $X_{COD} = COD_{tot}-COD_{mf}$,
BOD_{tot} – total Biochemical Oxygen Demand of organic carbon compounds, assumed as $1.47 \cdot BOD_5$; BOD_5 determined with addition of a nitrification inhibitor,
$COD_{BD}=S_s+X_s$ – biodegradable fraction of COD; $COD_{BD}= BOD_{tot}/(1-f_{BOD})$ with the correction factor $f_{BOD}=0.15$ according to [9].

The relevant problem concerning the determination of COD fractions results in the absence the uniquivocal definition of soluble and suspended contaminants. For the purposes of our research presented in this paper, the colloidal fraction of contaminants has been assigned to suspended solids (in accordance with the used methodology) [3, 11].

The fraction S_s in most cases is totally assimilated and metabolized by activated sludge organisms (e.g. heterotrophic bacteria), whereas the fraction X_i associates itself to activated sludge flocs and therefore can be removed together with the surplus sludge or with the secondary clarifier outflow. Fraction X_s is entrapped by activated sludge flocs and next absorbed by heterotrophs and transformed into easily degradable compounds (S_s). The fraction S_i (inert soluble) leaves the treatment plant in the concentration equal to that of raw wastewater.

In order to confirm the correctness of obtained results for the S_i fraction, two methods were compared: COD_{eff} as filtrated effluent, i.e. biologically treated wastewater, and COD_{eff} determined as COD of raw wastewater after a prolonged aeration (of 30 days). The maximum difference in results did not exceed 5%. Thereby the methodology with the filtered COD was finally accepted as quick and precise enough.

According to the ASM1 model (and to the distinction accepted in the papers [2, 3, 9, 12, 13]), the fractional composition of TKN can be described as follows:

$$TKN = S_{nh} + S_{nd} + S_{ni} + X_{nd} + X_{ni} \quad (2)$$

Nitrate- and nitrite nitrogen as a pollutant of raw wastewater have been ignored as their total content usually does not exceed 1%.

According to literature data, total biologically inert nitrogen ($X_{ni} + S_{ni}$) exhibits values of up to 5-13% (Table 5). Because only the Snh fraction can be determined directly, for two organic fractions (S_{nd} and X_{nd}) their fixed fractions for the adequate COD components were assumed. The two remained fractions (S_{ni} and X_{ni}) could then be calculated from the nitrogen balance.

Methodology of the determination of TKN fractions is shown in Table 2.

Results

Our analyses were devoted both to conditions of dry and wet weather. For dry weather grab samples every 2 hours during the day, for wet weather – every 1-2 hours during the time of the risen WWTP inflow. Composite samples weighted by flow were collected for each research series, too.

Table 3 summarizes the literature and our own data for dry weather periods.

The COD fractions determined for Łódź wastewater during dry weather conditions are close to the literature data. This dry weather composition may be assumed as quite stable and can be treated next as a background for analyses of variations of the combined wastewater composition.

In Table 4 a statement of our own results for COD fractions determined for dry and wet weather conditions is presented.

A most important item that can be noticed from Table 4 is an increase of inert (S_i and X_i) and a decrease of biodegradable (S_s and X_s) fractions in combined wastewater inflow.

Table 2. Definition of TKN fractions and methodology of their determination.

TKN fractions	Methodology of determination
S_{nh} - soluble ammonia nitrogen	$S_{nh\,mf}$*
S_{nd} - soluble organic nitrogen, biologically degradable	$S_{nd} \cong 0.02 \cdot S_s$ according to [9]
S_{ni} - soluble organic nitrogen, biologically undegradable	$S_{ni} = TKN_{mf} – S_{nh} – S_{nd}$
X_{nd} - particulate organic nitrogen, biologically degradable	$X_{nd} \cong 0.04 \cdot X_s$ according to [9]
X_{ni}- particulate organic nitrogen, biologically undegradable	$X_{ni} \cong TKN_{tot} – S_{nh} – S_{nd} – X_{nd}$

* $S_{nh\,mf}$ – soluble ammonia nitrogen determined in filtrated raw wastewater samples using 0.45µm membrane filters; identical values were obtained, for non-filtrated samples, either as inorganic ammonia nitrogen present in wastewater or as the soluble fraction only.
TKN_{mf} – total Kjeldahl nitrogen determined for filtrated samples using 0.45µm membrane filters;
TKN_{tot} – total Kjeldahl nitrogen in raw wastewater samples.

Table 3. Percentage contribution of particular fractions in total COD of raw dry weather wastewater.

COD fraction	Ekama 1989 2002	Kappeler and Gujer [16]	Carucci et al. [17]	Rössle and Pretorius [15]	Kalinowska and Oleszkiewicz [18]	Wisconsin Dep. of Nat. Res. [14]	Beck et al. [17]	Myszograj and Sadecka [13]	Own research* Łódź
S_s	20 -25	9	9	8-25	12.5-25	19 -30	5	22.6-29.2	13.6-29.8
S_i	8-10	11	4	7-20	8-10	4-7	27	2.4-2.7	4.8-7.0
X_s	60-65	58	77	50-77	50	48-67	65	51.3-56	39.1-68.2
X_i	5-7	22	10	4-10	15	7-15	3	17.1-18.7	6.8-42.1

* values for daily composite samples weighted by flow

Table 4. Percentage contribution of particular fractions in total COD of raw dry and wet weather wastewater.

COD fractions		**S_s**		**S_i**		**X_s**		**X_i**	
Type of weather		Range* [%]	Mean ** [%]	Range* [%]	Mean** [%]	Range * [%]	Mean** [%]	Range * [%]	Mean** [%]
Dry weather		6-45	**22.0**	4-9	**5.5**	20-70	**56.0**	4-69	**16.5**
Wet weather	Rainfalls	1-35	**21.3**	3-11	**5.8**	13-79	**49.5**	7-79	**23.3**
	Storms	8-31	**14.0**	5-9	**7.0**	16-70	**47.6**	11-69	**31.2**
	Snowmelt	9-32	**21.1**	7-13	**8.0**	8-93	**26.6**	6-52	**44.3**

* the range for instantaneous samples
** mean values for composite samples weighted by flow

This may be attributed to the washout of biologically non-degradable pollutants by runoff from the urban catchment. Also, substantial differences in the composition of wet weather inflow dependently on investigated precipitation events can be observed. The fraction of soluble organic easily degradable compounds (S_s) is comparable in the case of rainfalls and snowmelt. Instead, combined storm inflows are characterized with the lower content of the S_s fraction and a simultaneous increase of both inert fractions. This seems to be taking big storm runoff intensity into consideration. From analyzing X_i values for various wet weather events, a considerable (more than doubled) increase for snowmelt events in comparison to dry weather conditions can be noted. Simultaneously, the particulate organic slowly degradable COD (X_s) decreases during wet weather and especially during snowmelt conditions.

Most likely, this can be explained by adsorption of inert contaminants bound with dust, exhaust fumes etc. on the long lying snow cover.

Hourly variations of COD and TKN fractions were investigated, too. Two examples of the results are shown in Fig. 1 for COD fractions in dry and wet weather conditions.

From the plots, a distinct influence of flow variations can be noticed: in dry weather conditions COD fractions vary according to flow variations. During increased flow caused by intense rainfall, the participation of the easily degradable fraction (S_s) decreases and of the particulate fraction (X_i) increases, respectively, in relation to dry weather conditions.

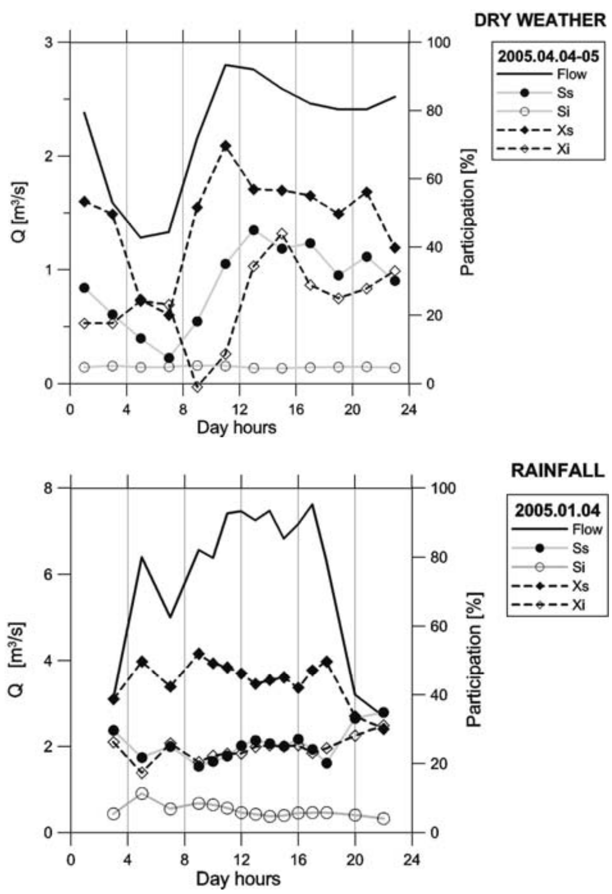

Fig. 1. Hourly variations of COD fractions for dry and wet weather conditions.

Table 5. Percentage contribution of particular fractions in TKN of raw dry weather wastewater.

TKN fraction	Szetela [3]	Rössle and Pretorius [15]	Beck et al. [19]	Own research Łódź
S_{nh}	60	75	73	66.5
S_{nd}	10	6	9	5.8
S_{ni}	*	*		8.4
X_{ni}	*	*		6.8
X_{nd}	25	6	12	12.5

* X_{ni}+S_{ni} – up to 5 % according to Szetela [3],
up to 13% according to Rössle and Pretorius [15].

Thus, it is clear that stormwater introduces a considerable inert COD load to the combined wastewater and for the S_s fraction a strong dilution effect appears.

It is also well-known that organic compounds determined as COD are the basic source of carbon in the biological treatment process. Moreover, a sufficient amount of carbon is necessary for an efficient run of the removal process of nitrogen compounds. Therefore, a decrease of the contribution of easily degradable COD fractions (S_s) (which can happen during wet weather conditions) can be a reason for nitrogen removal efficiency abatement. Especially, such a situation impedes the management of the efficient denitrification process.

During the inflow of combined wastewater to the WWTP, the proportions of nitrogen compounds undergo changes, too. The results of analyses of the TKN fractions obtained for dry weather raw wastewater are presented in Table 5.

To a great extent, the fractional composition of TKN for the Łódź dry weather wastewater corresponds to that found by Beck et al. [19]. Discrepancies in S_{nd} and X_{nd} fraction values obtained in our investigations and those found in the literature result most likely from the simplified method of fraction calculations.

Table 6 shows results of TKN composition obtained for wet weather conditions in comparison to dry weather results.

An analysis of Table 6 shows that ammonia nitrogen prevails in TKN and amounts up to 66% for dry weather and from 43% to 52% for wet weather.

With the inflow of wet weather wastewater the fraction S_{nd} increases not much, whereas S_{ni} doubles. Also, the content of organic particulate biologically inert nitrogen (X_{ni}) increases considerably. In particular, its contribution increases during storm and snowmelt events. The X_{nd} fraction increases, apart from snowmelt events when a distinct decrease was observed.

Similar conclusions, confirming an increase of particulate organic nitrogen in wet weather inflows, were drawn by Taylor et al. [20].

To summarize, in combined wastewater inflows a considerable change is observed for four TKN fractions: the percentage contribution of ammonia nitrogen (S_{nh}) decreases and the contribution of the S_{ni}, X_{ni} and X_{nd} fractions usually increase in relation to dry weather conditions.

Because of the intensity and type of precipitation events, an increase of the TKN fractions bound with suspended solids is comprehensible, since a greater part of pollutants passing into the combined sewage during wet weather events is just bound with suspended solids.

Conclusions

Knowledge of the participation of particular COD fractions enables more exact estimation of the biological degradablity of wastewater contaminations than the generally applied COD/BOD_5 ratio. Moreover, knowledge of the participation value of easily degradable fraction S_s is very useful for estimating nitrification and denitrification efficiency.

The presented analysis of fractional composition of COD and TKN for dry and wet weather wastewater proves distinct differences between these conditions. A significant

Table 6. Percentage contribution of particular TKN fractions of raw dry and wet weather wastewater.

TKN fractions / Type of the weather		S_{nh}		S_{nd}		S_{ni}		X_{ni}		X_{nd}	
		Range * [%]	Mean ** [%]	Range * [%]	Mean ** [%]	Range * [%]	Mean ** [%]	Range * [%]	Mean ** [%]	Range * [%]	Mean ** [%]
Dry weather		53-86	**66.5**	5-7	**5.8**	2-18	**8.4**	1-18	**6.8**	2-24	**12.5**
Wet weather	Rainfalls	28-72	**49.5**	0-23	**7.9**	1-56	**13.9**	4-27	**9.9**	1-42	**18.7**
	Storms	31-60	**42.8**	4-7	**5.5**	0-29	**15.8**	7-64	**18.4**	11-30	**17.5**
	Snowmelts	33-74	**50.5**	3-10	**7.3**	9-46	**13.4**	10-31	**26.4**	1-25	**2.3**

* the range for instantaneous samples
** mean values for composite samples weighted by flow
For dry weather the composite sample were taken during the whole day, for wet weather – during the risen WWTP inflow time.

increase of the inert and particulate fractions of COD and the particulate fraction of TKN in wet weather conditions was observed.

Simultaneous increase of the participation of the particulate organic biologically degradable fraction of nitrogen, with a deficit of the easily degradable carbon source, can cause deterioration of nitrogen compound removal.

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