

BOŻENA MROWIEC\*

## EFFECT OF BTX ON BIOLOGICAL TREATMENT OF SEWAGE

Aromatic hydrocarbons (BTX) are very often found in municipal sewage in the range from 0 to 933  $\mu\text{g}/\text{dm}^3$ . The concentration of toluene in the digested sludge liquor from primary settling tanks could increase to 42 000  $\mu\text{g}/\text{dm}^3$ . Other aromatic hydrocarbons are observed in lower concentrations of about 30  $\mu\text{g}/\text{dm}^3$ . Aromatic hydrocarbons have a more or less negative effect on the treatment. The effects were evaluated in laboratory experiments for synthetic and real sewage, both under anaerobic and aerobic conditions. BTXs were added in concentrations ranging from 250 to 1250  $\mu\text{g}/\text{dm}^3$ . The treatment permitted an almost complete BTX removal. However, the presence of aromatic hydrocarbons resulted in poor efficiency of COD, nitrification and total phosphorus removal.

### 1. INTRODUCTION

Such aromatic hydrocarbons as benzene, toluene and xylenes (BTX) are put on the list of basic water pollutants, made by the American Agency of Environmental Protection (US EPA) and the European Union. Taking account of environmental pollution, aromatic hydrocarbons, and especially benzene and its aliphatic derivatives, are considered to be very harmful. This is connected with their toxic properties, even if they occur in very low concentrations. In organic synthesis, benzene is the main substrate, which can be used for the production of its aromatic derivatives and cyclic compounds. The production of synthetic fibres and materials, synthetic rubber, dyes, resins, detergents and agricultural chemicals is based on toluene and xylenes. The compounds are used in the pharmaceutical industry and as organic solvents [1].

BTX are often present in municipal treatment plants. They can be discharged with industrial wastewater, from small factories and public utilities, and with domestic sewage [2]. Concentrations of these compounds are diverse, e.g. BELL et al. [3] and NAMKUNG and RITTMAN [4] have found BTX concentrations in municipal sewage on the level from 0.43  $\mu\text{g}/\text{dm}^3$  for benzene to 85.5  $\mu\text{g}/\text{dm}^3$  for toluene. The investigations of the content of BTX in the sewage collected from several municipal wastewater

---

\* Institute of Environmental Protection and Engineering, University of Bielsko-Biała, ul. Willowa 2, 43-309 Bielsko-Biała, Poland.

treatment plants in the Bielsko-Biała region performed in the last few years revealed that the concentration of the aforementioned compounds ranged from zero to tens  $\mu\text{g}/\text{dm}^3$ . The substance, which had always been present in sewage, usually in the highest concentration from 14 to 115  $\mu\text{g}/\text{dm}^3$ , was toluene [5].

The Enhanced Biological Nutrients Removal Processes (EBNRP) are working according to many different schemes, and the necessary volatile fatty acids (VFA) are produced from sludge for denitrification and dephosphatation processes. The retention time for effective hydrolyses of primary or secondary sludge, i.e. the production of optimal amounts of VFA, is assumed to be 2 to 8 days [6]. Concentration in the range from 3500 to 4000  $\text{mg}/\text{dm}^3$  of VFA expressed as acetic acid can be achieved.

Almost no attention is given to the other products of the hydrolyses of sludge organic substrate. It was found that, in parallel to VFA production, toluene formation occurred [7].

The investigations on real sewage sludge digestion process univocally showed that toluene was produced in the acid phase of fermentation. A considerably high increase of toluene concentration up to about 42 000  $\mu\text{g}/\text{dm}^3$  was measured, which was about 1000 times higher than its concentration measured in raw sewage.

The changes of BTX concentration in the consecutive steps of treatment at two large municipal wastewater treatment plants in the south region of Poland were measured as the background to the laboratory investigations. The concentration of BTX in the sewage transported to biological reactors was high in relation to their concentration in raw sewage. The concentration of the aromatic hydrocarbons tested varied in the range from 0 to 933  $\mu\text{g}/\text{dm}^3$ . Toluene concentration measured ranged from 1 to 238  $\mu\text{g}/\text{dm}^3$  in raw sewage, and on an average it reached 20 000  $\mu\text{g}/\text{dm}^3$  in digested sludge supernatant returned to the dephosphatation stage of biological sewage treatment. Other aromatic hydrocarbons were observed in lower concentration, approaching 30  $\mu\text{g}/\text{dm}^3$  in sewage and supernatant. Exceptionally, in one case, the *o*-xylene concentration in raw sewage was 933  $\mu\text{g}/\text{dm}^3$ .

The laboratory investigations were carried out in order to estimate the impact of BTX on biological treatment process.

## 2. MATERIALS AND METHODS

The laboratory investigations of the biological treatment process were performed with the use of real activated sludge and municipal sewage taken from selected municipal treatment plants or synthetic wastewater. The treatment plants were designed and operated for enhanced biological nitrogen and phosphorous removal. Twenty seven batch series were carried out in a two-stage laboratory reactor (figure 1). Synthetic wastewater was used in 15 series, mechanically treated municipal sewage – in 5 series and municipal sewage with sludge supernatant (in the volume ratio of 10:1) – in

7 series. The primary sludge and excess sludge were stored for ten days under anaerobic conditions aiming at VFA and toluene generation. Synthetic wastewater of composition given by WU et al. [8] was prepared. The characteristics of different wastewaters used are presented in the table.



Fig. 1. Laboratory reactors for biological sewage treatment

Table

Characteristics of substrates used

Parameter	Synthetic wastewater	Municipal sewage	Mixture of municipal sewage and sludge supernatant
	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>
COD	115–730	134–502	895–1534
N-NH <sub>4</sub> <sup>+</sup>	16–64	10–48	48–94
N-NO <sub>3</sub> <sup>-</sup>	4–24	0–20	4–12
N <sub>K</sub>		12–85	50–188
P-PO <sub>4</sub> <sup>3-</sup>	8–27	2–11	9–46
P <sub>tot</sub>		5–13	12–47

The BTX concentrations measured in raw sewage varied in a wide range. The highest concentrations were observed for toluene (290 µg/dm<sup>3</sup>), for benzene (30 µg/dm<sup>3</sup>), for *o*-xylene (10 µg/dm<sup>3</sup>) and for *p*-xylene (8 µg/dm<sup>3</sup>).

Two parallel reactors, anaerobic and aerobic, each of the active volume of 5 dm<sup>3</sup>, were operated at a HRT of 20 hours. The activated sludge MLSS concentration was maintained on a level close to 5 g/dm<sup>3</sup>. Benzene, toluene, *p*-xylene and *o*-xylene (BTX) dissolved in methanol were added to the first reactor. Theoretical doses of each hydrocarbon added ranged from 250 to 1250 µg/dm<sup>3</sup>. The real concentration of BTX and COD was measured at the beginning of consecutive experimental steps. The sewage in the second reactor contained BTX only in the case of their presence in the real municipal sewage. Slow mixers continuously mixed the content of the reactors (anaerobic step). The aerobic reactor were supplied with compressed air. After 30 minutes of sedimentation, the samples were analysed for temperature, pH, COD, ORP dissolved oxygen, phosphorus (P<sub>tot</sub>, P-PO<sub>4</sub><sup>3-</sup>) and nitrogen (TKN, N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>3</sub><sup>-</sup>). All analyses were carried out according to Standard Methods [9]. The BTX were determined in cleared sewage and in the samples with activated sludge using a gas chromatograph (GC) equipped with a "purge-and-trap system" and thermal desorption. The GC had a capillary column HP-5 Crosslinked 5% ME Siloxane (30 m length, 0.32 mm internal diameter, 0.25 µm film thickness) and a FID detector.

### 3. RESULTS AND DISCUSSION

In the laboratory investigations, theoretical concentration of each compound contained in BTX in sewage before treatment process ranged from 250 to 1250 µg/dm<sup>3</sup> (the total from 1.0 to 5.0 mg/dm<sup>3</sup>). Total real concentration of aromatic hydrocarbons oscillated between ca. 0.78 and 5.32 mg/dm<sup>3</sup>. Higher concentrations resulted from BTX presence in sewage and sludge supernatant. Practically in each of the series investigated, different sewage (with regard to contaminant concentrations) and different BTX concentrations were used. After the first step of treatment (anaerobic), the BTX concentrations on an average decreased by 45% (benzene), 59% (toluene), 65% (*o*-xylene) and 76% (*p*-xylene). The decrease of BTX concentration after the first stage of biological treatment is shown in figure 2. A part of BTX was adsorbed on activated sludge. Therefore, the concentration of BTX was determined in the samples without activated sludge and in the parallel samples in the sewage mixed with activated sludge. *p*-xylene was found to be most effectively adsorbed by activated sludge, on an average in 59%, and benzene – least effectively, about 15% (figure 3). This may result from different solubility of the compounds in the sewage. The next stage of treatment (aerobic process) permitted an almost complete BTX removal. Only toluene and xylenes remained in the treated sewage in concentration of up to 13 µg/dm<sup>3</sup>. Benzene was not observed in the sewage after both biological treatment stages.

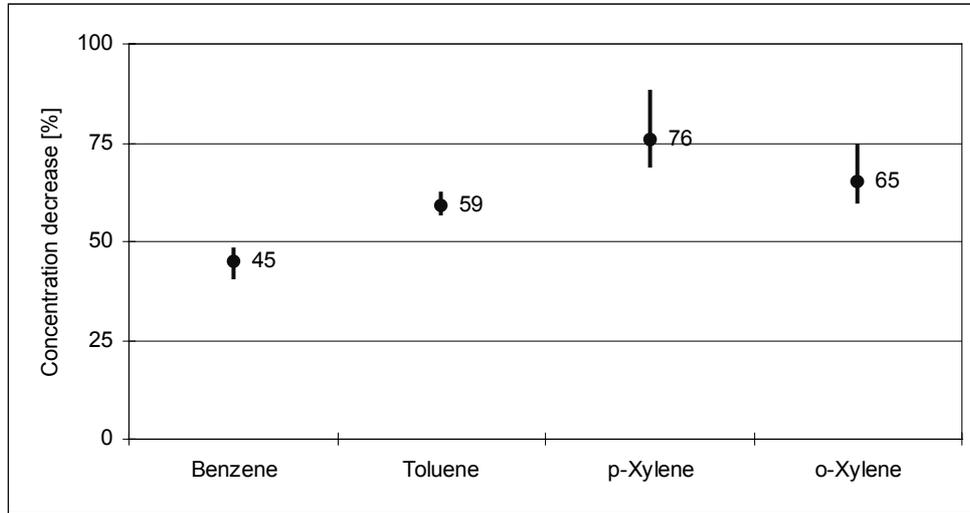


Fig. 2. Decrease of BTX concentration after anaerobic stage of treatment

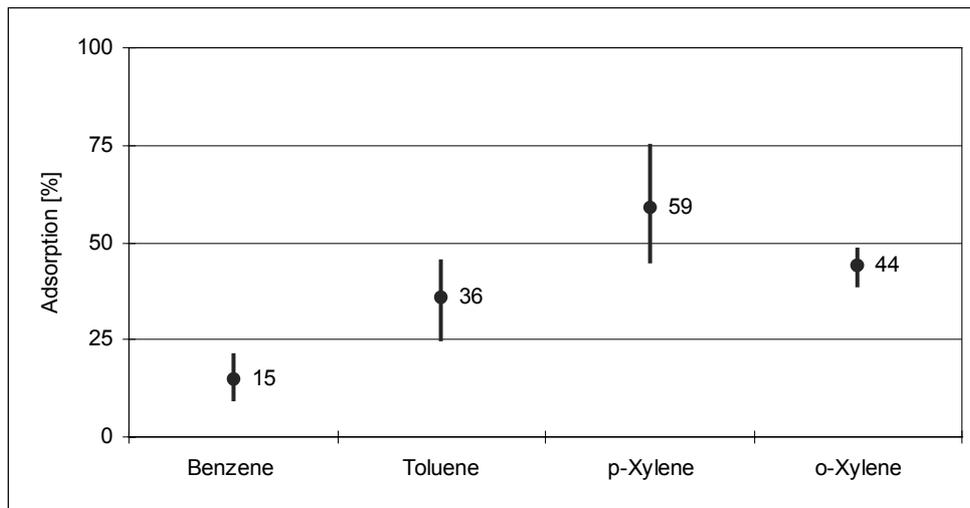


Fig. 3. Adsorption of BTX on activated sludge after anaerobic stage of treatment

The main aim of the laboratory investigations was to evaluate the impact of BTX on COD and phosphorus removal as well as on the nitrification efficiency.

Different values of COD in raw sewage were investigated. In the samples of synthetic sewage, COD values ranged from 115 to 730 mg O<sub>2</sub>/dm<sup>3</sup>, while in real municipal sewage, COD oscillated between 135 and 503 mg O<sub>2</sub>/dm<sup>3</sup>. Seven series were per-

formed with the addition of digested sludge supernatant. In these samples, COD values in the mixture varied from 895 to 1534 mg O<sub>2</sub>/dm<sup>3</sup>.

Comparing the effectiveness of COD removal for sewage (synthetic or natural) with and without the addition of BTX in various concentrations, a negative effect of their presence was found. The effectiveness of COD removal from municipal sewage or synthetic sewage, without the addition of BTX, was in the range between 71 and 97%. When those sludges were mixed with BTX the effectiveness of COD removal decreased distinctly, ranging from 30 to 82%. This efficiency depended on an initial COD value of sewage and BTX dose. At less COD, BTX dose increases its value in the range from tens to over hundred per cent. In the mixtures of sewage and digested sludge supernatant, COD values were close to thousand mg/dm<sup>3</sup> and higher. Therefore, BTX addition raised these values to twenty per cent at the maximum.

The negative effect of the aromatic hydrocarbons presence in the supplied sewage on COD removal can be attributed to the increase of COD in the sewage after the BTX addition. The differences in COD values in the treated samples with and without BTX are clearly shown in figure 4.

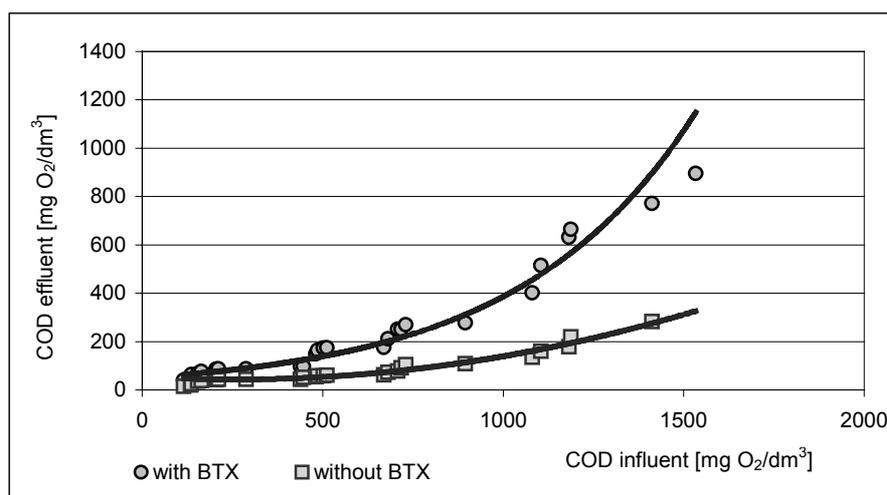


Fig. 4. COD values in treated sewage in samples with and without BTX

In contrary, and to some extent surprisingly, BTX in the influent contributed to higher efficiency of phosphate removal. The concentration of remaining phosphates after the aerobic stage of treatment was definitively lower in the case of sewage mixed with BTX. It is possible that higher values of COD caused by BTX presence in the first anaerobic step of biological treatment can be explained by the presence of easily biodegradable substrates being favourable for phosphorous bacteria. However, such a correlation was observed only in the case of synthetic wastewater where phosphates

occur as the only form of phosphorus. The phosphate concentration in the effluent is shown in figure 5.

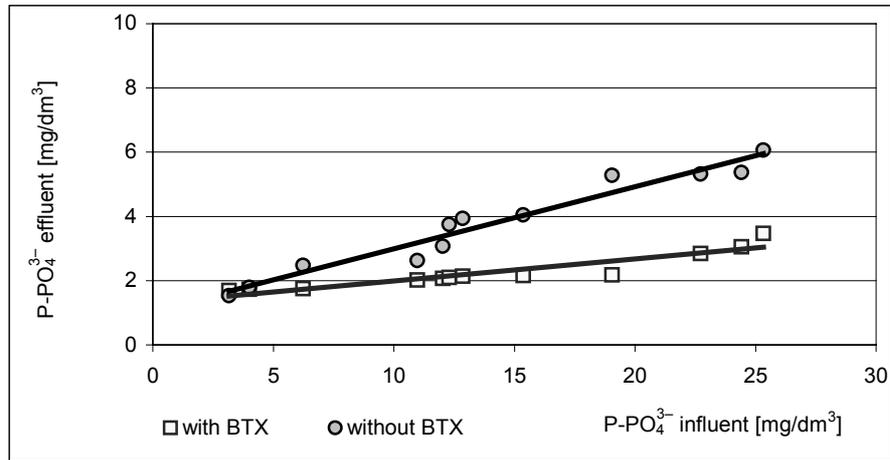


Fig. 5. Remaining phosphates after two steps: anaerobic-aerobic treatment

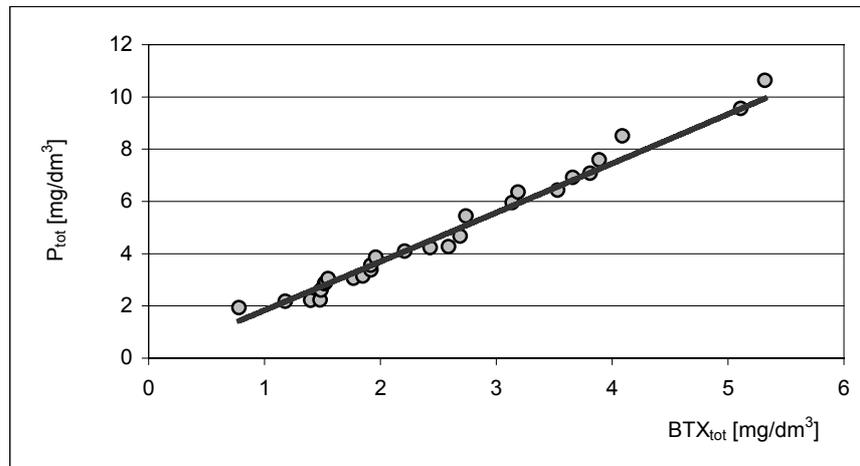


Fig. 6. Correlation between  $P_{\text{tot}}$  concentration in effluent and BTX concentration in influent

Different relationship was observed between BTX and total phosphorus in real sewage. BTX in sewage contributed to a limited total phosphorus removal. Total phosphorus concentration in the effluent was higher in the samples with BTX added, and higher concentration of BTX in sewage decreased the efficiency of phosphorus removal. Unequivocal differences were observed for the total BTX concentration

exceeding  $1.5 \text{ mg/dm}^3$ . The correlation between  $P_{\text{tot}}$  concentration in the effluent and BTX concentration clearly shows the negative effect of their presence (figure 6).

After the anaerobic treatment, the concentration of ammonia nitrogen was measured as the effect of ammonification process, and after the aerobic one, the concentrations of ammonia nitrogen and nitrate nitrogen were determined as the final products.

As in the case of the total phosphorus removal, the nitrification processes were disadvantageous for the samples to which BTX were added. Nitrate nitrogen concentration in the sewage after aeration stage in all the samples varied from 0 to  $8 \text{ mg/dm}^3$ . In the case of higher ammonia nitrogen concentration in raw sewage (samples with sludge supernatant), higher concentration of ammonia nitrogen in the effluent was observed. For lower ammonia concentration, the nitrification process was more pronounced, and the dominating form of nitrogen were nitrates.

The presence of BTX in the sewage treated biologically can have a negative effect and limit the nitrification process. For comparison, the quantity of ammonia nitrogen oxygenated under aerobic conditions in the sewage with and without BTX is given in figure 7. The differences in the nitrification efficiency were distinctly shown by the Kjeldahl nitrogen concentrations. The nitrification process was adversely affected in all the samples tested. For high Kjeldahl nitrogen concentration in raw sewage, the differences were greater and the highest concentration of ammonia nitrogen in the treated sewage was measured.

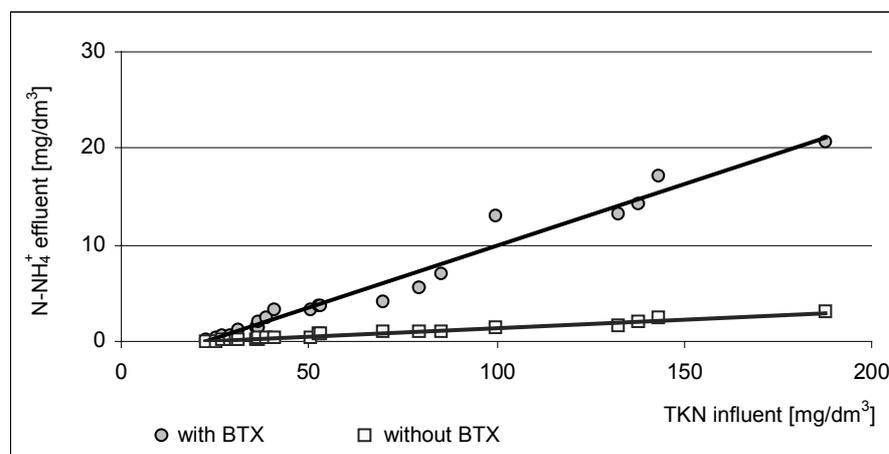


Fig. 7. TKN changes in aerobic stage of treatment for samples with and without BTX

The presence of BTX in sewage definitely affected the oxidation of ammonia nitrogen and the removal of Kjeldahl nitrogen. Correlations between concentrations of nitrogen ammonia and TKN in the effluent and BTX concentration in raw sewage

clearly show the negative effect of their presence. Also the negative effect of BTX was clearly observed for the total hydrocarbon concentration exceeding  $1.5 \text{ mg/dm}^3$ . The correlations are shown in figure 8.

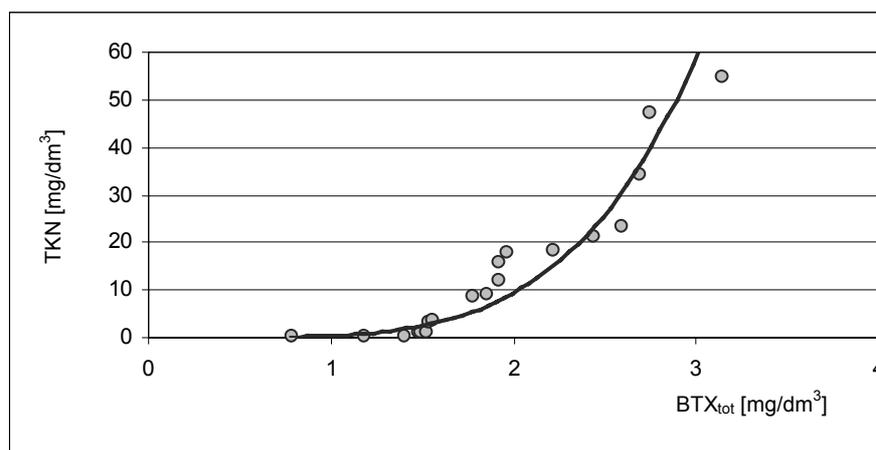


Fig. 8. Correlation between Kjeldahl nitrogen concentration in effluent and BTX concentration in influent

#### 4. CONCLUSIONS

Aromatic hydrocarbons (BTX) often present in municipal sewage have not attracted sufficient attention so far and this problem should be properly explained.

BTX in treated sewage are formed due to a hydrolysis in VFA production and negatively affect COD and phosphorus removal as well as the efficiency of the nitrification process, which can increase ammonia nitrogen concentration in the treated sewage. However, under anaerobic conditions the hydrolysis of organics, yielding simpler products that are apparently favourable substrates for phosphorus-accumulating bacteria, improves the uptake of phosphates. At high BTX concentration (above  $1.5 \text{ mg/dm}^3$ ) in sewage, the hydrocarbons added to the samples before the treatment affected this process. Although so high BTX concentrations were not observed in real municipal sewage, the problem of BTX presence, their impact on the efficiency of the biological treatment processes and effluent quality are important and require adequate explanation.

#### REFERENCES

- [1] CHODKOWSKI J., *Słownik Chemiczny*, Wiedza Powszechna, Warszawa, 1995
- [2] ESCALAS A., GUADAYOL J., CORTINA M., RIVERA J., *Time and space patterns of volatile organic compounds in a sewage treatment plant*, Water Research, 2003, 37, 3913–3920.

- [3] BELL J., MELCER H., MONTEITH H., OSINGA I., STEEL P., *Stripping of volatile organic compounds at full-scale municipal wastewater treatment plants*, Water Environment Research, 1993, 65, 6, 708–716.
- [4] NAMKUNG E., RITTMAN B.E., *Estimating volatile organic compound emission from publicly owned treatment works*, J. Wat. Pollut. Control Fed., 1987, 59, 7, 670–678.
- [5] SUSCHKA J., MROWIEC B., KUSZMIDER G., *Volatile organic compounds (VOCs) at some sewage treatment plants in Poland*, Water Sci. Tech., 1996, 33, 12, 273–276.
- [6] OLESZKIEWICZ J.A., BARNARD J.L., *Fermentacja kwaśna osadu wstępnego dla intensyfikacji biologicznego usuwania fosforu i azotu*, Nutrient Removal from Wastewater – International Conference, Cracov, 1997, Poland.
- [7] MROWIEC B., SUSCHKA J., KEENER T.C., *Formation and biodegradation of toluene in the anaerobic sludge digestion process*, Water Environment Research, 2005, 77, 3, 274–278.
- [8] WU Y.C., ASCE M., HSIEH H.N., CAREY D.F., OU K.C., *Control of activated sludge bulking*, Journal of Environmental Engineering, 1984, 2, 110, 472–491.
- [9] *Standard Methods for the Examination of Water and Wastewater*, 1995, 19th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

#### WPLYW BTX NA BIOLOGICZNE OCZYSZCZANIE ŚCIEKÓW KOMUNALNYCH

Węglowodory aromatyczne typu BTX dosyć często występują w ściekach komunalnych. Ich stężenia wahają się od 0 do 933  $\mu\text{g}/\text{dm}^3$ . W cieczach fermentowanych osadów z osadników wstępnych stężenie toluenu może dochodzić nawet do 42 000  $\mu\text{g}/\text{dm}^3$ . Pozostałe węglowodory tej grupy mają niższe stężenia (do 30  $\mu\text{g}/\text{dm}^3$ ). Obecne w ściekach węglowodory mogą niekorzystnie wpływać na efektywność ich oczyszczania. W badaniach laboratoryjnych analizowano wpływ BTX na biologiczne oczyszczanie ścieków rzeczywistych i syntetycznych. Proces prowadzono w warunkach beztlenowo-tlenowych, stosując dawki BTX w zakresie od 250 do 1250  $\mu\text{g}/\text{dm}^3$  i uzyskując prawie całkowite usunięcie BTX. Jednak ich obecność w ściekach poddawanych oczyszczaniu obniżała usuwanie substancji organicznych (ChZT) i fosforu ogólnego oraz ograniczała proces nityfikacji.