Toluene in sewage and sludge in wastewater treatment plants
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ABSTRACT

Toluene is a compound that often occurs in municipal wastewater ranging from detectable levels up to 237 μg/L. Before the year 2000, the presence of the aromatic hydrocarbons was assigned only to external sources. The Enhanced Biological Nutrients Removal Processes (EBNRP) work according to many different schemes and technologies. For high-efficiency biological denitrification and dephosphatation processes, the presence of volatile fatty acids (VFAs) in sewage is required. VFAs are the main product of organic matter hydrolysis from sewage sludge. However, no attention has been given to other products of the process. It has been found that in parallel to VFA production, toluene formation occurred. The formation of toluene in municipal anaerobic sludge digestion processes was investigated. Experiments were performed on a laboratory scale using sludge from primary and secondary settling tanks of municipal treatment plants. The concentration of toluene in the digested sludge from primary settling tanks was found to be about 42,000 μg/L. The digested sludge supernatant liquor returned to the biological dephosphatation and denitrification processes for sewage enrichment can contain up to 16,500 μg/L of toluene.

Key words | anaerobic sludge digestion, municipal wastewater, sewage sludge, toluene

INTRODUCTION

Commercial toluene is mainly (80%) used as an intermediate in the chemical industry, as a raw material in the organic synthesis of other chemicals (benzene, benzoic acid, phenol, xylene and other derivatives), as dye intermediates, in the synthesis of explosives (TNT) and as flavoring agents. Approximately 20% of commercial toluene is used as a solvent for paints, rubber products, thinners, adhesives, ink and finally as a processing aid (‘extraction solvent’) in the production of pharmaceutical and other chemical products. Most toluene is obtained through the distillation of refinery streams. This is a process that does not involve any contact with water. Toluene is released into the environment when substances containing toluene or some preparations (based on toluene-containing substances) are produced, distributed and handled. The emission into the environment is the result of its use as fuel (48–74%), its use as a solvent (25–52%) and its refining and production (2%). The emission into the environment also comes from other manufacturing processes (EU 2003).

The main reason for studying toluene is due to its frequent presence in wastewater. Studies into the presence of toluene in industrial wastewater have recorded its concentration to be 0.2–12,900 μg/L. Average levels were detected at a few hundred μg/L. (EU 2003). Toluene also occurs in municipal effluents ranging from detectable levels to 290 μg/L. Stripping and biodegradation in the sewage treatment processes can remove the compound. However, toluene is the compound most frequently measured in high concentrations in the stages following treatment (Namkung & Rittmann 1987; Bell et al. 1988; Suschka et al. 1996).

Toluene is relatively soluble in water compared to other aromatic hydrocarbons and can migrate to groundwater and pollute potable water sources. An amount may be adsorbed on biological flocs and solids. Even volatile chemicals, such as toluene, are commonly found in sewage sludges as a result of sorption with organic substances in the sludge matrix. As a result, the concentrations of the compound in sludge can be significantly higher than in the liquid state. In the environment it causes problems affecting water, soil, and indoor and outdoor air as well as creating health risks for humans and animals (Estebar et al. 2012).
Toluene seems to be aerobically and anaerobically biodegradable at high concentrations and when it is exposed to the right microorganisms. However, under aerobic and oligotrophic conditions the substance does not seem to be biodegradable if the concentration is low (0.05 mg/L level; EU 2003). Nahar et al. (2000) holds the opinion that toluene is not readily biodegradable and as such can be described as a toxic chemical.

**Toluene toxicity**

Although there is a general agreement that toluene does not have the hemotoxic properties of benzene, the narcotic and neurotoxic properties of toluene are its main health risks for humans. It should also be noted that there are conflicting reports in the literature on the clastogenic properties of toluene both in humans and animals experimentally (Mrowiec et al. 2005).

The physiological basis of toluene toxicity in relation to the activated sludge microorganisms, however, remains poorly characterized. Toxicity is apparently due to the interaction of toluene with the cytoplasmic membrane. This process results in the loss of the cations Mg$^{2+}$ and Ca$^{2+}$ as well as other small molecules. Consequently, toluene has a denaturing effect on the cytoplasmic membrane. Studies into *Pseudomonas putida* indicate that when toluene is present, the content of lipids in the cell membrane changes (Peña-Calva et al. 2004). The study suggests that problems with the biological treatment of the chemical at high concentrations can occur due to its water solubility (515 mg/L at 23°C). Therefore it can be present at high concentrations in wastewater. Concentrations of toluene from 15 to 70 mg/L inhibited the denitrifying pathway (NO$_3^-$ to N$_2$) at different enzymatic levels owing to differences in the accumulated intermediates. Similar findings have been presented in studies (Nunes-Halldorson et al. 2004) recording that biodegradation reduced toxicity of toluene from 88% to only 33%. Residual toxicity is probably due to the presence of toxic intermediates or end products. For example, catechol is an intermediate common to numerous aromatic biodegradation pathways and it has been found to be significantly more toxic than benzene in bacterial bioassay.

Earlier studies concentrated on the presence of toluene in municipal wastewater treatment plants in Poland. The objective of this study was to determine the toluene concentration in influent and in sewage treated with biological treatment methods. The second issue discussed in the paper is the presence of toluene in sewage sludge and sludge liquor after anaerobic digestion.

**METHODS**

**Materials**

The toluene concentration was determined in sewage, sludge supernatant and sewage sludge samples.

For sewage, the influents and effluents of four municipal wastewater treatment plants (WWTPs) in southern Poland were monitored. In addition, at two municipal wastewater plants, samples were collected before the biological treatment process. The sludge supernatant was drawn from the centrifuge or filtration press effluent after dewatering the digested sludge. Sampling was carried out seasonally, 20 samples were taken from two treatment plants: A and B (5× influent, 5× effluent, 5× wastewater before the biological treatment process and 5× sludge supernatant) and 15 samples were taken from another two treatment plants: C and D (5× influent, 5× effluent and 5× sludge supernatant). Samples of wastewater before the biological treatment process were not taken from wastewater treatment plants C and D, due to the low concentration of toluene in the influent. The sewage samples were collected in 0.5 mL glass bottles in such a way that no air was left in the bottles. The analyses were performed immediately after transporting the samples to the laboratory.

**Anaerobic digestion**

Analyses of toluene presence and generation in the sewage sludge investigations of acid sludge digestion were performed. The sludge from a primary settling tank from WWTPs B and D was taken and sludge from a secondary settling tank at WWTP C was used. The sludge was digested in a small pilot scale bioreactor with a volume of 10 L under laboratory conditions. The contents were mixed manually twice a day. Five series of experiments on anaerobic sludge digestion were performed with a retention time of 12 days—two series of anaerobic digestion for secondary sludge and three for primary sludge. The process was controlled by the measurements of temperature, pH, oxidation–reduction potential (ORP), and volatile fatty acids (VFAs), e.g. acetic, proportionate and butyric acids.
Analytical procedures

Toluene was measured in the samples with a volume of 10 mL using gas chromatography (GC) equipped with a ‘purge and trap system’ and thermal desorption. The GC had a capillary column: HP-5 Crosslinked 5% ME Siloxane (length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm), oven temperature 35 °C (held 2.8 min) to 200 and 30 °C/min (held 3.5 min), injector/detector temperature 200 °C/300 °C, carrier gas nitrogen (N₂), liner velocity 38 mL/s, flow rate 2.4 mL/min, split vent 30:1 and a flame ionization detector (FID). The detection limit of the assay was 1 μg/L.

VFAs were also determined using GC with a FID on a capillary column: FFAP (length 30 m, internal diameter 0.53 mm, film thickness 1.0 μm), oven temperature 75 °C (held 2.0 min) to 150 and 25 °C/min (held 5.0 min), injector/detector temperature 250 °C/250 °C, carrier gas nitrogen (N₂), liner velocity 25 mL/sec, flow rate 3.1 mL/min. The detection limit of the assay was 1 mg/L.

The results of chromatographic analyses were calculated by HP ChemStation.

The pH and ORP measurements were carried out with a WTW inoLab Level2 meter equipped with a SenTix 41 and SenTix ORP electrodes respectively.

RESULTS AND DISCUSSION

The investigations of the content of toluene in sewage and sewage sludge were performed at four municipal wastewater treatment plants in the Bielsko-Biala region. These investigations were performed according to the Enhanced Biological Nutrient Removal Processes (EBNRP). The WWTPs treat typical municipal sewage involving about 10% of industrial wastewater. Industrial wastewater does not contain a specific substance like BTEX at high concentrations. Daily flows of sewage were about 90,000 m³/d for WWTP A and 20,000–30,000 m³/d for WWTPs B, C and D. In each WWTP the applied technology was the activated sludge process. In WWTPs B and D primary and secondary sludge were produced. In WWTPs A and C only secondary sludge was processed. Sludge disposal methanogenic digestion was used in WWTPs A and D, anaerobic digestion in open digesters was used in WWTP B and aerobic digestion in WWTP C.

The measurements of toluene concentration have shown the presence of the compound in raw municipal sewage at levels of 0–115 μg/L (Figure 1). Toluene is a substance always recorded in sewage and usually at the highest concentrations in relation to other aromatic hydrocarbons (benzene, ethylbenzene, xylenes). In Figure 2 the chromatographic analysis of raw wastewater from treatment plant A is presented.

Polish legislation allows the maximum content sum of BTEX in influent to wastewater treatment plant at a level of 1 mg/L. During the investigations this value was not exceeded.

The highest concentrations of toluene were measured in wastewater treatment plant B but no clear dependence on specific characteristics of the wastewater can be stated. At the other wastewater treatment plants (A, C and D) toluene had been determined at low and very low concentration levels.

The presence of toluene and other volatile compounds (BTEX) at municipal wastewater treatment plants have been confirmed by several studies and described in research papers and reports. As mentioned before, toluene can be discharged into industrial wastewater from small factories, mills, public utilities and sewage. The concentrations of the compound are diverse, for example, Bell et al. (1993) and Namkung & Rittmann (1987) gave the content of toluene in municipal sewage as 87 μg/L. In Polish analysed wastewater treatment plants the toluene concentration was higher only in one case. It can therefore be asserted that the toluene concentration found in raw municipal wastewater was in the same range as in other studies in Poland.

In treated wastewater discharged from the treatment plants the toluene concentrations were 0–32 μg/L. The highest concentrations were recorded again for treatment plant B. Toluene removal during the wastewater treatment process was 34–85%. The fact that the toluene was not fully
removed during the biological treatment process under the aeration conditions was striking.

In the literature a higher concentration of the compound was determined in the wastewater transported to biological reactors compared to concentrations in raw sewage. The inflowing toluene concentrations into the biological reactor have varied from 4.5 to 237 μg/L. In the Skyway treatment plant (USA) the concentration of toluene in the aeration grit chamber was 3.6 μg/L (Bell et al. 1993). Considering only the release of the compound into the atmosphere, the toluene concentration was expected to decrease in the following stages of sewage treatment. Analysis of the inflow to the activated sludge process has recorded the concentration of toluene as almost triple at 10.5 μg/L. However, the studies did not explain the reason for the higher concentration of the compound.

The investigations and measurements of BTEX and particularly toluene undertaken at two of the studied municipal wastewater treatment plants have shown relatively high concentrations of toluene in the anaerobic digested sludge supernatant as well. The concentrations of toluene varied in widely: in the supernatant from the dewatering process (WWTPs A and D) after the methanogenic sludge digestion the compound was observed at 5–126 μg/L (minimum and maximum values of the measured concentration). However, after the anaerobic digestion in open digesters (WWTP B) it ranged from 31 to 1,767 μg/L. In the case of the supernatant after dewatering sludge which was stabilized in aerobic conditions (WWTP C), the toluene concentrations were measured between 1 and 24 μg/L. The values of the maximum and average toluene concentrations are presented in Figure 3. Supernatants were discharged into raw wastewater and could increase the toluene concentration but the toluene mass balance could not explain the high concentrations measured in anaerobically digested sludge liquor compared to measured concentrations in the raw wastewater.

The EBNRP works according to many different schemes and technologies. For the high efficiency of biological denitrification and dephosphatation processes the presence of easily biodegradable organic matter, such as VFAs, in sewage is required. In municipal wastewater treatment plants VFAs are produced in different places and from different procedures, from accidental production in primary settlers or thickeners to specifically designed hydrolysis tanks. VFAs are often generated in the acidic stage of the primary or secondary sludge anaerobic
digestion and the production is a crucial step for effective biological nutrient removal. The sludge retention time for effective hydrolysis (i.e. the production of optimal amounts of VFAs) is assumed to be 2 to 8 days. The average VFA concentration range is 3,500–4,000 mg/L in acetic acid. VFAs are the main product of organic matter sewage sludge hydrolysis. However, in studies no attention has been given to the other products of the process. It was found that in parallel with VFA production toluene formation occurred. The toluene concentrations in sewage sludge depended on the type of sludge and the stage of digestion. The changes of toluene concentration in supernatant sludge during anaerobic sludge digestion are presented in Figure 4. During the period of anaerobic digestion (12 days) the toluene concentration in the supernatant sludge from the primary settling tank at WWTP B increased from 13 to 1,683 μg/L on the 11th day. The toluene concentration in the supernatant sludge from the secondary settling tank at WWTP C increased from 10 to 526 μg/L on the 7th day.

In the next part, the concentration of toluene in the sludge was measured in the acidity digestion of primary sewage sludge for VFA generation to biological nutrient removal processes. As discovered earlier, it was found that toluene was present at relatively high concentrations in almost every case of the tested sludge. The concentration of toluene was variable and during the 12-day period of digestion it increased from about 200 to almost 37,599, 32,931 and 37,524 μg/L in series 2, 4 and 5 respectively (Figure 5). As an example, the chromatographic analysis of the sludge sample from the anaerobic digestion is presented in Figure 6. In the tests the sludge from the primary settling tank WWPT B was used. Over a longer period of anaerobic sludge digestion (20 days) the concentration of toluene increased to a maximum level of about 42,000 μg/L. It was the highest toluene concentration measured in digested sludge. In series 1 and 3 the toluene concentrations were lower, closed to 8,671 and 15,175 μg/L respectively.

During the experiments the primary sludge from WWTP D was used. The changes of toluene concentrations in the sludge digestion process were very similar to changes of VFA concentrations. This was especially true for propionic acid in each series. In addition, propionic acid was recorded with the highest concentration in sludge digestion. Figure 5 shows the concentration of propionic acid as 10 times higher.

As mentioned, toluene and other compounds such as BTEX are adsorbed onto solid particles. Sorption of the compound depends on the kind of solid particles and on sewage sludge and it can be 5–58% (Mrowiec et al. 2014). The investigations showed that approximately 36% of toluene was adsorbed onto the sludge particles. Therefore in digested sludge the toluene concentrations are over two times higher than in sludge supernatant. The digested sludge supernatant (liquor) showed that the biological dephosphatation and denitrification for sewage enrichment can contain up to almost 16,500 μg/L of toluene. Therefore, it could explain the higher concentrations of toluene in wastewater introduced into biological reactors.

Wilson et al. (1994) have investigated the content of some VOCs in sewage sludge in 12 treatment plants located in Great Britain. They recorded the presence of toluene as 14.4–14,900 μg/L but no explanation was proposed. The biosynthesis of toluene in the anoxic hypolimnion in bottom sediments of lakes has been recorded by Juttner & Henatsch (1986). The authors discovered a 15-fold increase of toluene in the lake during the
anaerobic conditions from the spring turnover to October. Fischer-Romero et al. (1996) separated microorganisms from the anoxic sediment responsible for toluene production, calling it *Tolumonas auensis*. The authors observed the increase of toluene concentration from 0 to over 400 mmol/L during the anaerobic growth of the strain TA 4T in TP medium containing phenylacetic acid as a toluene precursor over the period of 28 days. In addition, the authors of the above studies stated that toluene is formed in a biological way (e.g. from phenylalanine and phenylacetate) only in presence of organic carbon sources, products of fermentation, e.g. ethanol, acetic acid and formic acid. Therefore, digested sewage sludge is a good material for toluene biosynthesis during organic matter decomposition. The phenomenon of toluene formation in the sewage sludge was presented earlier by Mrowiec (2000), Mrowiec et al. (2005) and Marczak et al. (2006) as the effect of microbial activity in anaerobic conditions.

Usually the presence of toluene in wastewater and sewage sludge is assigned only to external sources. Here it is shown that in the VFA production step, being a part of the EBNRNP system, relatively high concentrations of toluene may also be produced and then discharged into the bioreactors with the sludge supernatant. The presence of toluene in treated wastewater arising from the hydrolysis step for VFA production can have an influence on the removal of the compound from wastewater as well as on the efficiency of the treatment process. Toluene can be observed in the effluent of wastewater treatment plants, but the content of the compound depends on its concentration in wastewater, applied wastewater treatment technology and sludge disposal.

**CONCLUSIONS**

1. The toluene concentration in raw sewage meets the standards described by Polish regulations in relation to the content of specific substances (BTEX) in the wastewater discharged into municipal sewage treatment plants.
2. Biological wastewater treatment processes do not remove toluene completely. In wastewater effluent toluene concentrations over 10 μg/L can be present.
3. The highest toluene concentrations observed in sludge and sludge supernatant after anaerobic digestion were between 1.0 and 40.0 mg/L.
4. The sludge supernatant after anaerobic sludge disposal may be an additional source of toluene discharged into bioreactors in municipal wastewater treatment plants.

**REFERENCES**


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