# Monitoring of Organic Micropollutants in Effluents as Crucial Tool in Sustainable Development

## Monitoring mikrozanieczyszczeń organicznych jako ważne narzędzie realizacji zrównoważonego rozwoju

## \*Maria Włodarczyk-Makuła, \*\*Ewa Wiśniowska, \*\*\*Agnieszka Popenda

Katedra Chemii, Technologii Wody i Ścieków, Wydział Infrastruktury i Środowiska, Politechnika Częstochowska, ul. Dąbrowskiego 69, 42-200 Częstochowa, Poland E-mail: \*mwm@is.pcz.czest.pl; \*\*ewisniowska@is.pcz.czest.pl; \*\*\*apopenda@is.pcz.czest.pl

### **Abstract**

Water resources are crucial issues in sustainable development. From an economic perspective lack of clean water leads to long-lasting effects on human capital and growth. The key problem is to what extent can we give up on the economic growth to preserve the natural resources for future generations. Progress in monitoring will be critical in ensure to achieving sustainable development goals. However monitoring of the status quo is not the only strategy. The better one is monitoring of pollutants discharging in order to prevent or at least to limit their amounts. At present, the afore mentioned monitoring is not carried out with respect to municipal effluents despite the fact that these contaminants are found in the treated wastewater and should be monitored to avoid pollution of surface waters. The types of micropollutants that should be monitored have to be chosen individually for each wastewater treatment plant (WWTP) depending to local conditions that allows to fullfill the tasks in sustainable development. Recent changes in Polish legislations relying on which organic micropollutants are considered when classification of surface and underground water is made, are the proper directions.

**Key words:** organic micropollutants, environmental safety, sustainable development, surface water, effluents, monitoring

### Streszczenie

Zasoby wodne są kluczowym elementem zrównoważonego rozwoju. Z punktu widzenia ekonomii brak czystej wody prowadzi do długofalowych skutków dla rozwoju i wzrostu ludzkości. Kluczowym pytaniem jest co można zrobić, aby rozwój ekonomiczny odbywał się w sposób pozwalający na zachowanie zasobów naturalnych dla przyszłych pokoleń? Postęp w sposobie monitorowania będzie krytyczny dla sprawdzenia i oceny stopnia realizacji celów zrównoważonego rozwoju. Monitorowanie stanu istniejącego nie jest odpowiednio skuteczną metodą. Lepszą strategią jest monitorowanie zrzutów zanieczyszczeń, tak aby można było im zapobiegać lub je ograniczać. Obecnie tego rodzaju monitoring nie jest stosowany w odniesieniu do odpływów z oczyszczalni ścieków komunalnych pomimo tego, że wyniki badań wskazują, że organiczne mikrozanieczyszczenia występują powszechnie w oczyszczonych ściekach. Z tego względu należałoby wprowadzić obowiązek monitorowania stężeń wybranych mikrozanieczyszczeń w ściekach oczyszczonych. Zakres monitoringu powinien być dobrany indywidualnie dla każdej oczyszczalni ścieków w zależności od lokalnych czynników, co pozwoli na realizację zasady zrównoważonego rozwoju. Dobrym kierunkiem jest natomiast wprowadzony w Polsce obowiązek monitorowania wybranych organicznych mikrozanieczyszczeń w wodach powierzchniowych i podziemnych.

**Słowa kluczowe:** mikrozanieczyszczenia organiczne, bezpieczeństwo środowiskowe, zrównoważony rozwój, wody powierzchniowe, ścieki oczyszczone, monitoring

#### Introduction

Water resources play an import ant role in sustainable development. The Future we Want — outcome document of Rio +20 (United Nations Conference on Sustainable Development, 2012) recognizes water as a core of this kind of development (Water for a Sustainable World, 2015). From an economic perspective lack of clean water leads to long-negative lasting effects on human capital and growth because environmental, social and economic conditions are mutually dependent. About how important clean water is, shows e.g. the casus of ancient Romans. The researchers suggest that because of using lead pipes and lead plates by them damage in nervous systems occurred resulting in the fall of an empire.

The key problem is to what extent can we give up on the economic growth to preserve the natural resources for future generations. Economy of sustainable development offers three strategies in solving this problem:

- strategy of the effectiveness it aims to more efficient use of the existing resources, including decrease of harmful pollutants discharge,
- 2. strategy of coherence by development of new ecological products,
- 3. strategy of sufficiency by changing in attitude of people through limiting consumption of natural resources (Rogall, 2010).

### 2. Legislations of sustainable development in the aspect of micropollutants monitoring

According to H. Rogall, sustainable development requires consequent implementation of these three above mentioned strategies simultaneously (Rogall, 2010). The implementation of them should be supported by legislation both at international and national level. In that spirit in New York in September 2015 the world leaders adopted 2030 Agenda for Sustainable Development. It officially came into force on January 1st 2016. It comprises 17 Sustainable Development Goals, including the Goal 6 Clean water and sanitation (SDG 6). According to SDG 6: Clean, accessible water for all is an essential part of the world we want to live in. This goal should be achieved by 2030, among others, by improving water quality by reducing pollution, elimination dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater (Sustainable Development Goals, 2015). The goals included in Agenda results, among others, from the report of United Nations mentioned above (it was published in 2015) (Sustainable Development Goals, 2015). The report emphasizes the role of reliable data to monitor progress of the goal fulfilling. As it is advisable mentioned in report prepared by team managed by William Reidhead (Monitoring Water and Sanitation in the 2030) it is difficult to manage what is not measured, and what gets meas*ured is far more likely to get measured.* The authors envisage that progress in monitoring will be critical in ensuring the achieving Sustainable Development Goals of 2030 Agenda. In 2014 GEMI (Integrated Monitoring Initiative) was established. This is an inter-agency initiative focused on integrating and expanding existing monitoring efforts on, among others, water quality and integrated water management resources (www.sdg6monitoring.org/news/presenting-gemi) in United Nations member states. It should ensured harmonized monitoring of entire water cycle. Agencies involved in GEMI have also been reporting on innovative practices for water accounting and management. GEMI allows the Member States to achieve individual countries monitoring interests with flexibility (Monitoring Water and Sanitation in the 2030). Until 2018 GEMI implementation will focus on the development of monitoring methodologies. Protection of the environment against the pollutants should, however, concern not only monitoring, but protection as well. These two operations should be included in the practices of member countries as tools of the accomplishment of sustainable development idea. Protection of the environment is related with not only monitoring but also reducing discharges of pollutants into the environment.

### 3. Organic micropollutants in wastewater

In case of macropollutants such as: organic compounds (chemical oxygen demand -COD, Biochemical oxygen demand- BOD), nitrogen-N and phosphorus-P compounds even the legislation of not very well developed countries is involved in protection of water environment against them. For example, in Uganda standards for treated effluents were established by the Bureau of Standards and implemented by the National Environment Management Authority. The permissible values for BOD5 were set at level 50 mgO<sub>2</sub>/L, COD 100 mgO<sub>2</sub>/L, TSS 100 mgO<sub>2</sub>/L, TN 10 mg/L and TP 10 mg/L, respectively. In Kenya the permissible values for treated wastewater discharged into rivers are as follow BOD<sub>5</sub> 50 mg/L, COD 250 mg/L, TSS 50 mg/L, TN 50 mg/L and TP 6 mg/L (Muresan, 2013). The standards are less strict than in Europe and in the USA, however by their introducing also developing countries protect the environment and achieve goals in this area.

Micropollutants, especially the organic ones, are limited in wastewater very rarely. It is probably due to the fact that effects of micropollutants presence in the environment are not such spectacularly visible compare to those caused by nitrogen, phosphorus and high loads of organic compounds. The last ones cause euthrophisation and oxygen depletion, extinction of fish and other water organisms. In case of micropollutants the effects are most often to chronic exposure at low concentrations. The effects caused by micropollutants are less spectacular than damage in

the environment caused by biogen or organic compounds, but the threats are of high importance. For a long time it looked as if we decrease the loads of COD/BOD and biogenic compounds into surface waters we solve the problem of water resources intended for drinking purposes. We have thought that if we can treat wastewater and water for drinking and industrial purposes we are able to solve problem with expending natural water resources. That is not a true. At present, due to the lack of clean water half the population in the developing countries has been suffering from various diseases. According to the UNEP prognoses 3/4 of the humanity will live in areas of water shortage (Rogall, 2010). Even in well developed, European countries the situation is serious. Based on the results of monitoring we can say that organic micropollutants are common contaminants of our living environment (Popenda, 2016). They are found in personal care products and pharmaceutics, we use them in agriculture and various branches of industry. Human's activity is one of the main sources of pollution of the environment by organic micropollutants (Grotenhuis, 2003). Because of this also the humans are able to manage and decrease discharges of these compounds into the environment, including surface waters. Wastewater treatment plants, both industrial and municipal, should be considered as important sources of organic micropollutants of anthropogenic origin (Włodarczyk-Makuła, 2015). However, at present hardly any country has established standards for micropollutants in municipal effluents. Untill now only Switzerland has already decided to reduce micropollutants concentrations and toxicity connected with their presence in wastewater. The Swiss government decided to upgrade approximately 50% of wastewater treatment plants in the coming 20 years (microcropollutants.com).

An example, in Polish legislation some micropolluare limited in industrial wastewater (Rozporządzenie, Dz.U. 1800, 2014). Mainly those considered as harmful the environment (hexachlorocyclohxane: HCH, tetrachloromethane: CCl4, pentachlorophenol: PCP, aldrine, dieldrine, endrine, izodrine, DDT, polychlorinated biphenyls: PCB, polychlorinated triphenyls: PCT, hexachlorobenzene: HCB, hexachlorobutadiene: HCBD, trichloromethane: CHCl<sub>3</sub>, 1,2-dichloroethane: EDC, trichloroethylene: TRI, tetrachloroethylene: PER and trichlorobenzene: TCB. Also insecticides (both chlorinated hydrocarbons, phosphoroorganic and carbaminates), petroleum hydrocarbons, benzene, toluene and xylene BTX andAdsorbable Organic Halides AOX are limited in the industrial wastewater. Germany has also established limits of organic micropollutants in industrial effluents. In Germany AOX and VHHC (volatile halogenated hydrocarbons) are limited in wastewater from manufacturing of coating materials and varnish resins (www. bmub.bund.de). This politics is connected with the fact that at present in ecological risk assessment attention is focused mainly on evaluation, identification and characterization of micropollutants and not on management. This is despite the rule of Environmental Law which says that the primary way that we should act is to avoid contamination, not clean surface water. The law systems seems to be still under furtherance of the idea of evaluation not protection. As a result micropollutant concentrations are measured in surface waters in most European countries, but their concentration is not monitored in municipal effluents.

However, there is data available on concentrations of the organic micropollutants in municipal effluents indicating that the afore mentioned contaminants make significant but still not noticeable problem (Table 1). In the table comparison of the concentrations of selected micropollutants in surface water and effluents is also included. The data indicate that many compounds such as: nonvlphenols, DEHP. polycyclic aromatic hydrocarbons-PAHs, polychlorinated biphenyls-PCBs, pharmaceuticals (diclophenac, carbamazpine, ibuprofene, naproxen, E2, EE2) occur in effluents originating from WWTPs at concentrations significantly higher than those in surface water. This is however, not a rule in case of the pollutants that are not used in households, such as MCPA or 2,4-D. What is important micropollutants are commonly found in effluents and the loads discharged into surface waters can pose a serious risk to the environment. This is the first argument supporting the idea of the necessity of organic micropollutants monitoring in municipal effluents, but the type of micropollutants should be matched individually as many conditions affects the pollution of wastewater. All the conditions should be taken into consideration in matching process. The second argument is that organic micropollutants are not efficiently removed from wastewater during treatment. The existing wastewater treatment plants are not designed for removing micropollutants.

This also means that the key question is not if, but which organic microcompounds should be analysed in the effluents. Concentrations of organic pollutants in rivers can be a clue when we choose the pollutants which are the most significant problem. For example, in Poland concentration of the following organic micropollutants in rivers and lakes was measured within national monitoring system in 2010-2015: alachlor, anthracene, atrazine, benzene, brominated diphenyloether, C<sub>10</sub>-13 chloroalkanes, chlorfenwinfos, chloropyriphos, EDC, dichloromethane, DEHP, diurone, endosulphane, fluoranthene, hexachlorobenzene, hexachlorobutadiene (HCBD), heksachlorocyclohexane (HCH), izoproturone, naphthalene, pnonylophenol, 4-(1,1',3,3'-tetramethylobutylo)-phenol, pentachlorobenzene, pentachlorophenol (PCP), benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, simazine, tributilocine compounds, tetrachlorobenzenes, trichloromethane, trifluraniline,

Table 1. Selected micropollutant concentrations in wastewater and surface water compared to the levels regared as having long-term and acute effects on living microorganisms, source: publications.jrc.ec.europa.eu; Bukhardt-Holm, 2011; Włodarczyk-Makuła, 2015; Min, 2014; Urbaniak, 2017; Nathália, 2011; Iglesias, 2014; Inventory on the presence of pharmaceuticals in Dutch water; Kummerer, 2013; Valdes, 2015; De Oude, 1992; Abd El-Gawas, 2014; Voulvoulis, 2004; Leonard, 2001; www.helcom.fi/Documents/HELCOM%20at%20work/ Projects/BASE/Indicators\_TBT.pdf; Nagy, 2013; Wang, 2017

Compound	Concentrations in	Concentrations in	Compound	Concentrations in	Concentrations in
_	effluents	surface water	_	effluents	surface water
	(ng/L)	(ng/L)		(ng/L)	(ng/L)
Dioxins PCDDs	$0.003 \div 0.177$	0.728 ÷ 6	Diclophenac	50 ÷ 2,500	2.8 ÷ 470
Furans	0.006 ÷	0.599	Carbamazepine	482 ÷ 950	n.d ÷ 230
PCDFs	0.05				
Polychlorinated	10 ÷ 908	$0.3 \div 150$	Ibuprofen	81 ÷ 2,100	10 ÷ 40
biphenyls (PCBs)	(7 congeners)				
Nonylphenol	880 ÷	$0.8^8 \div 18{,}000$	Naproxen	21 ÷ 12,500	< LOD ÷ 300
(NP)	22,690				
Diethyl phthalate	$6.01 \cdot 10^6 \div$	$110 \div 36,000$	17β-Estradiol	< 5 ÷ 631	369
(DEHP)	17.04 10 <sup>6</sup>		(E2)		
Polycyclic aro-	1,025 ÷	41 ÷ 437	17α-	< 5 ÷ 187	43
matic hydrocar-	3,056,000	(Nagy, 2013)	Ethynylestradiol		
bons (PAHs)		4 ÷ 29	(EE2)		
		(Wang, 2017)			
MCPA	25 ÷ 150	n.d. ÷ 370	2,4-D	13 ÷ 27	< 1000
Diuron	62 ÷ 1,379	$2.4 \div 2.849 \cdot 10^6$	Dieldrin	< 10	2.5
Aldrin	Production is	15.3	Atrazine	no data	$100 \div 4.9 \cdot 10^5$
	banned				
DDT	Production is	$0.12 \div 218$	Linear alkylben-	$6.10^3 \div 16.10^3$	$70.10^3 \div 2.45.10^6$
	banned		zene sulfonate		
			(LAS)		
Tributylocine	$2.5 \cdot 10^6$	$1.39 \cdot 10^{3}$	Endosulphane	≤ 220	$\leq 4 \cdot 10^3$
(TBT)		$1.44 \cdot 10^3$			

n.d.-not detected; LOD - limit of detection

trechloromethane, sum of atrazine, dieldrine, endrine and izodrine, DDT, trichloroethylene and tetrachloroethylene (gios.gov.pl/). Taking into consideration the analyzed micropollutants concentration most examined samples of river water were classified as of very good quality. The exceptions are listed in Table 2.

Table 2. High concentration of micropollutants in Polish river waters (2010-2015), source: www.gios.gov.pl/

Micropollutant	Place of sampling	
_	(river name)	
Benzo(g,hi)perylene,	Ina, Chełszcząca, Gowie-	
indene(1,2,3-cd)pyrene	nica, Wołczenica, Rega,	
	Dębosznica, Błotnica,	
	Dzierżęcinka, Głównica,	
	Parsęta, Wieprza, Pisa, El-	
	bląg, Wąska, Sajna, Bóbr,	
	Czernica, Czerna Mała,	
	Obra, Kwisa, Nysa Łu-	
	życka, Obrzyca, Odra, Ru-	
	rzyca, Tywa	
Benzo(a)pyrene	Głównica	
Benzo(b)fluoranthene	Głównica	
Benzo(k)fluoranthene	Głównica	
DEHP	Biała, Horodnianka	
Endosulphane	Warta	
Tributylocine	Odra, Martwa Wisła, No-	
compounds	gat Kanał Żerański	

The detailed analysis of the data typical for Poland indicates that the compounds that should be monitored, are polycyclic aromatic hydrocarbons, phthalates (DEHP) and selected biocides: tributilocine and endosulphane.

### 4. Toxicity of organic micropollutants

The considered organic compounds are also very dangerous to water organisms. The danger that comes from the presence of micropollutants discharges with effluents is spectacular if we compare the concentrations of the pollutants with LOEC (low observed effect concentrations) or NOEC (no observed effect concentration) values. Toxicity and effects on living organisms of the compounds mentioned above are listed in Table 3.

These compounds should be recommended to be monitored in effluents. The second group of micropollutants which should be controlled in effluents in Poland are the ones which LOEC values are significantly lower than LC50, but their concentrations are also at high level in the treated wastewater. It is because OECD classification (Table 4) of toxicity is not always representative for evaluation of environmental effects of micropollutants.

They are mainly pharmaceuticals, e.g.  $17\alpha$ -ethynylestradiol (EE2) concentration in effluent can be even 187 ng/L and NOEC for fish is only 5 ng/L, and LOEC for *Danio rerio* (survival) is only 100 ng/L.

Table 3. Acute and chronic toxicity of selected micropollutants, source: Holdway, 2008; www.sciencedirect.com/topics/agricultural-and-biological-sciences/endosulfan;

Eiler, 2000; Beyer, 1996; White Paper, 2008

Eller, 2000, Beye	r, 1996; White Pape	21, 2006
Compound	Levels of long-	Levels of acute
	term toxic	toxicity for water
	effects for wa-	organisms
	ter organisms	
Diethyl	LOEC	Daphnia magna LC50
phthalate	Daphmia	$(48h) 133 \div 2,000$
(DEHP)	magna 1,3000	μg/L
	μg/L	Rainbow trout LC50
	NOEC	(96h) 100,000 μg/L
	Daphmia	Gammarus
	magna 640	pseudolimnaeus
	μg/L	LC50 (96h) > 10,000
	1.0	μg/L
Polycyclic ar-	acenaphtene:	Freshwater fish:
omatic hydro-	fathed minnow	Acenaphtene:
carbons	embryos:	LC50 (96h) = 580-
(PAHs) (total	LOEC for	1730 μg/L
of 16 or 17	growth 495	Daphnia magna LC50
compounds)	μg/L and 682	$(48h) = 41000 \mu g/L$
compounds)	μg/L and 002 μg/L for	LC50 (96 h) for snail
	μg/L 101 survival	Aplexa hypnorum >
	NOEC 4 ÷	
	420 μg/L	2040 μg/L Anthracene: Sunfish
	Daphnia magna NOEC 600	(Lepomis macro-
		chirus)
	μg/L	$LC50 (96h) = 46 \mu g/L$
	Benzo(a)py-	EC50 (3h) Chlorella
	rene: LOEC (27	$vulgaris = 535 \mu g/L$
	d): rainbow	Benzo(a)anthracene:
	troat	LC50 (Daphnia pulex)
	0.21 μg/L	$(48h) = 10 \mu g/L$
	Phenenthrene	Benzo(a)pyrene: Da-
	LOEC:	<i>phnia magna</i> (4h
	8 μg/L	LC50)
	NOEC 5 µg/L	1.5 μg/L (toxicity in-
	(rainbow trout)	creases when UV irra-
		diation is involved)
		Fluoranthene: Ana-
		bena flosaque 38%
		growth inhibition after
		14d exposure for 147
		μg/L
		Fluorene: 96H LC50
		raibow troat 820 μg/L
		Naphthalene: P. pro-
		melas 96h
		$LC50 = 1990 \div 7900$
		μg/L
		Daphnia magna: 1000
		μg/L (LC50 96h)
Endosulphane	LOEC	LC50 (96h)
F	freshwater fish	Leiostomus xanthurus
	1 μg/L	$= 0.14 \mu\text{g/L}$
	NOEC	,ro
	freshwater fish	
	< 1 μg/L	
Tributylocine	No data	7.9 μg/L Danio rerio
Thoughoune	110 uata	7.9 μg/L Danio rerio (96 h)
		7.9 µg/L <i>Daphnia</i>
		magna (48 h)

LC50 – lethal concentration for 50% of tested organisms

Table 4. Classification criteria of chemicals toxicity according to their harmfulness to aquatic organisms according to EU, source: Commission of the European Communities, 1996

EC(LC)50 value, mg/L	Classification	
< 0.1	extremely toxic	
0.1 - 1	very toxic	
1-10	toxic	
10 - 100	harmful	
> 100	not toxic	

EC50 – effective concentration (50% of tested organisms exhibit the response)

LC50 and EC50 concentrations of the micropollutants are usually at a higher level. For E2 EC50 is in the range 120 ÷ 252 ng/L (fathead minnow) and for EE2 EC50 (Daphnia magna) is over 5,000,000 ng/L. For the group of pesticides the dieldrine for which NOEC (Brachionus calyciforus) population growth rate is 0.005 µg/L and LOEC (Brachionus calyciforus) population growth rate is 0.05 µg/L, while Daphnia magna LC50 (96h) 330 µg/L; Rainbow trout LC50 (96h)  $1.1 \div 9.9 \,\mu\text{g/L}$  (Karl, 2006). Despite these considerations it also should be emphasized that in most cases concentrations of organic micropollutants in effluents are lower than LOEC values. It indicates that the problem for the environment can be also caused by the ones which can accumulate and biomagnificate in water, sediments and water organisms. Humans are exposed to the micropollutans not only by water, but also by food, air etc. It makes difficult to distinguish between the dangerous for human from these sources, and distracts attention from the effect of quality of water intake from the environment and health effects (Bukhardt-Holm, 2011). In European Union regulations some of organic micropollutants are taken into consideration, but in surface and underground water, not in wastewater. In Water Framework Directive (WFD) (2000/60/EC) in article 16 Strategy against pollution of water has been established. Based on this article the list of priority substances which have been selected from the ones representing a significant risk for the environment has been prepared. They were listed in *Annex X* of the directive and established by decision No. 2477/2001/EC. Generally 33 priority substances are listed, among them 11 have been identified as priority hazardous substances, 15 as priority hazardous substances under review. Priority substances included both inorganic and organic compounds. Among 33 substances 29 were the organic ones. Water Framework Directive has set the quality standards and emission control measures for hazardous substances. It was also established that 11 priority hazardous substances emissions and discharges should be ceased not later than in 20 years. Priority substances under review should be examined until 2002 to decide if they should be classified as priority hazardous. For the remaining 8 substances in the Annex X, that are not classified as priority hazardous or under review (including) progressive reduction of the discharges was planned. The list of the priority pollutants was replaced in 2008 by Annex II of the Directive on Environmental Quality Standards (EQSD). This directive has set environmental quality standards for the substances representing a significant risk in surface waters (including rivers, lakes, transitional and coastal). It established the environmental quality standards for 33 priority substances and 8 priority hazardous substances. Both in WFD and EQSD two standards have been established: long-term standard (annual average concentration AA-EQS) and short-term standard (maximum acceptable concentration (MAC-EQS). The list of priority substances should be revised until 2011. According to this fact in 2012 the proposal of *Directive* Amending the Water Frame Directive and EOSD was published. It has included 15 additional priority substances, among them 6 were pointed out as priority hazardous ones. Two existing priority pollutants have been classified as priority hazardous ones. It also has established stricter quality standards for 4 of the priority substances from the previous lists, and revised slightly standard for next three. The fourth criterion which should be taken into consideration is the real possibility of removal of the compounds. To sum up, it can be stated that in the area of the protection of the water environment against to micropollutants no precise requirements are involved with respect to reduction of micropollutants discharges. However, in Poland micropollutants have been included in the system of both surface and underground water classification since 2016. It confirms the danger coming from the presence of the organic pollutants in water environment and it is an appropriate direction in legislation. It also should be emphasized that Polish legislation is similar to other European Union countries because they all follow the Directives mentioned above, however is removal of micropollutants economically reasonable?

### 5. Costs of treatment of organic micropollutants

According to the data given by Wahlberg et al. (2018) conventional treatment of wastewater costs less than 0,2 EUR/m $^3$ . The balance has been done for pharmaceuticals. This treatment remains about 47% of these micropollutants in wastewater. They are discharged into the surface water. Removal of remaining amount of organic micropollutants increases treatment costs only by 0.06 EUR/m $^3$  – Table 5.

The development of physico-chemical methods takes place mainly due to the fact that chlorinated organic compounds are persistent to biodegradation and they are not sufficiently removed in the biological treatment plants (Bagal, 2013; Naresh, 2010; Niu, 2004; Pouran 2014, Bernal-Martinez, 2009; Barbusiński, 2013; Czaplicka, 2015; Wiśniowska 2008). Not only advanced oxidation can be used in

Table 5. Costs of various treatment technologies for removal of pharmaceutical micropollutants from wastewater, source: micropollutants.com/Portals/0/Downloads/Cost-of-treatment-water-micropollutants.pdf)

Treatment method	Costs,	Residues left
	EUR/m <sup>3</sup>	after treatment,
		%
Conventional treatment		
(without micropollutants		
removal)	0,17	47
Ozone oxidation	0,23	2
UV radiation	0,3	13
Activated carbon	0,48	3%
Reverse osmosis	0,65	4

micropollutants removal, but desorption, extractionand adsorption as well. Moreover, ion exchange, distillation as well as electrochemical methods can also be applied. There are also known thermal methods of destruction chlorinated organic derivatives. The combination of various degradation methods are usually used in micropollutants removal. However, it should be of aware that the costs of the processes and reagents consumption are relatively quite high. Due to these new, economically effective, methods of micropollutants removal in water environment are still of great interest.

### 6. Conclusions and future recommendations

It is confirmed in the literature data both the presence of dioxins, furans, pesticides, hexachlorobenzene, polychlorinated biphenyls, organic chlorine derivatives, polycyclic aromatic hydrocarbons in effluents from municipal wastewater treatment plants as well as their toxic effect on organisms. At the present state of knowledge, it is not possible to eliminate micropollutants from the wastewater environment completely using both biological and other methods. However, recent changes in legislation based on which organic micropollutants are considered when classification of surface and underground water is made, are the proper directions. The conducted studies are mainly concentrate on the limitation of emission into the individual environmental elements and as a consequence to the food. In order to limit emission of furans, dioxins, and other chlorine derivatives compounds the most important is replace them with others, non-chlorine cellulose and paper bleaching and developing technologies limiting formation of toxic compound long lasting effects s of incineration. Legislation is not precise when we consider the limitation of micropollutants discharges into the water environment. Future studies and acts on the organic micropollutants should focus on:

 legislation of micropollutants discharges control to water environment with respect to organic micropollutants, it must be emphasized that micropollutants which should be analyzed should be individually matched according to the needs for individual WWTPs,

- the limitations with the use of preparation in the agriculture,
- development of technological parameters of unit and integrated processes for removal and degradation of micropollutants in wastewater.

At present and in the future we have to put in place a law regulations which will support innovation and sustainability at the same time.

The research was carried out as a part of BS-PB-402-301/11.

### References

- ABD EL-GAWAS H., 2014, Aquatic environmental monitoring and removal efficiency of detergents, in: *Water Science*, vol. 28, Issue 1, p. 51-64.
- BAGAL M. V., GOGATE P. R., 2013, Degradation of 2,4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes, in: *Ultrasonics Sonochemistry*, vol. 20, p.1226-1235.
- BARBUSIŃSKI K., 2013, Zaawansowane utlenianie w procesach oczyszczania wybranych ścieków przemysłowych, Wydawnictwo Politechniki Śląskiej, Monografie, Gliwice.
- BERNAL-MARTINEZ A., PATUREAU D., DELE-GENES J-P., CARRERE H., 2009, Removal of polycyclic aromatic hydrocarbons (PAH) during anaerobic digestion with recirculation of ozonated sewage sludge, in: *Journal of Hazardous Material*, vol.162, p.1145-1150.
- BEYER W.N., HEINZ G., REDMON-NORWOOD A.W., 1996, Environmental Contaminants in Wildlife. Interpreting Tissue Concentrations, Lewis Publishers.
- BUKHARDT-HOLM P., 2011, Linking Water Quality to Human Health and Environment: The Fate of Micropollutants, National University Singapure, Working Paper Series, August 2011.
- Commission of the European Communities, 1996, Technical guidance document in support of commission directive 93/67/EEC on risk assessment for existing substances, Part II-Environmental risk assessment, Brussels.
- 8. CZAPLICKA M., 2015, Zaawansowane procesy utleniania w oczyszczaniu wód i ścieków, Instytut metali Nieżelaznych, Gliwice.
- 9. DE OUDE N.T., 1992, Detergents, Anthropogenic compounds, in: *Handbook of Environmental Chemistry*, Springer-Verlag, Berlin, vol. 3, part F.
- EILER R., 2000, Handbook, Chemical Risk Assessment. Health Hazards to Humans, Plants and Animals, Volume 2, Organics, Lewis Publishers.
- Endosulfan, https://www.sciencedirect.com/topics/ agricultural-and-biological-sciences/endosulfan (1.02.2018).
- 12. EU, EU Wide Monitoring Survey on Waste Water Treatment Plant Effluents, http://publications.jrc.ec.europa.eu/repository/bitstream/JRC76400/lb-na-255 63-en.pdf.pdf (1.02.2018).
- 13. FENT K, WESTON A.A., CAMINADA D., 2006, Ecotoxicology of human pharmaceuticals. Review, in: *Aquatic Toxicology* vol. 76 p. 122-159.
- GEMI, http://www.sdg6monitoring.org/news/present ing-gemi (1.02.2018).

- GIOS, http://www.gios.gov.pl/pl/stan-srodowiska/ raporty-o-stanie-srodowiska (1.02.2018).
- GROTENHUIS T., MALINA G., SATIJN H.M.C, SMIT M.P.J., POPENDA A., 2003, Surface Water as Receptor for Persistent Organic Pollutants and Heavy Metals, Proceedings of the 8th International FZK/TNO Conference on Contaminated Soil, Con-Soil, Gent, Belgium.
- 17. HELCOM, http://www.helcom.fi/Documents/HEL-COM%20at%20work/Projects/BASE/Indicators\_TBT.pdf (1.02.2018).
- 18. HOLDWAY DA., HEFFERMAN J, SMITH A., 2008, Multigeneration assessment of nonylphenol and endosulfan using a model Australian freshwater fish, Melanotaenia fluviatilis, in: *Environmental Toxicology*, vol. 23, no 2 p. 253-262.
- IGLESIAS A., NEBOT C., VAZQUEZ B., CORO-NEL-OLIVARES C., ABUIN C., CEPEDA A., 2014, Monitoring the Presence of 13 Active Compounds in Surface Water Collected from rural areas in Northwestern Spain, in: *International Journal of Environ*mental Research and Public Health, vol. 11 no 5, p. 5251-5272.
- 20. Inventory on the presence of pharmaceuticals in Dutch water.
- 21. KUMMERER K., 2013, Pharmaceuticals in the environment: Sources, Fate, Effects and Risks, Springer.
- LEONARD A.W., HYNE R.V., LIM R.P., LEIGH K.A., LE J., BECKETT R., 2001, Fate and toxicity of endosulfan in Namoi River water and bottom sediment, in: *Journal of Environmental Quality*, vol. 30 no 3, p. 750-759.
- MICROPOLLUTANS, http://micropollutants.com/ About-micropollutants (1.02.2018).
- MICROPOLLUTANTS, http://micropollutants.com/ Portals/0/Downloads/Cost-of-treatment-water-micropollutant.pdf (1.02.2018).
- MIN Y., ZHONGIJAN L., XINGWANG Z., LECHENG L., 2014, Polychlorinated biphenyls in the centralized wastewater treatment plant in a chemical industry zone: source, distribution, and removal, in: *Journal of Chemistry*, article ID 352675, http://dx.doi.org/10.1155/2014/352675
- 26. Monitoring Water and Sanitation in the 2030 Agenda for Sustainable Development, An introduction.
- MURESAN V.A., ROMAN M.D., PICA E.M., 2013, Comparative analysis of the legislative requirements of wastewater disposal in water bodies for Africa and North America, in: *International Journal of the Lat*est Research in Science and Technology, vol. 2, issue 6, p. 32-37.
- NAGY A.S., SZABO J., VASS I., 2013, Occurrence and distribution of polycyclic aromatic hydrocarbons in surface water of the Raba River, Hungary, in: *Jour*nal of Environmental Science and Health A Toxic Hazard Substance Environmental Engineering, vol. 48 no 10, p.1190-1200.
- NARESH N. M., ADEWUYI Y.,G., 2010, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation, in: *Ultrasonics Sonochemistry*, vol. 17, p. 990-1003.
- 30. NIU J., CHEN J., MARTENS D., HENKELMANN B., QUAN X., YANG F., SEIDLITZ H.K., SCHRAMM K.W., 2004, The role of UV-B on the

- degradation of PCDD/Fs and PAHs sorbed on surfaces of spruce (Picea abies(L) Karst) needles, in: *Science of the Total Environment*, vol. 322, p. 231-241.
- 31. POPENDA A., WŁODARCZYK-MAKUŁA M., 2016, Sediments contamination with organic Micropollutants, Current State and Perspectives, in: *Civil and Environmental Engineering*, vol. 21, no 2, p. 89-107.
- POURAN S. R., RAMAN A.A.A, WAN DAUD W.M.A., 2014, Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions, in: *Journal of Cleaner Production*, vol. 64, p.24-35.
- ROGALL H., 2010, Economy of sustainable development Theory and practice, Wydawnictwo Zysk i Spółka, Poznań (in Polish).
- 34. Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014 r. w sprawie warunków, jakie należy spelnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz.U. 1800, 2014.
- 35. UNESCO, 2015, Water for a Sustainable World. The United Nations World Water Development report 2015, United Nations Educational, Scientific and Cultural Organization, France.
- 36. UNITED NATIONS, 2015, The Millennium Development Goals Report, New York 2015.
- 37. UNITED NATIONS, *Sustainable Development Goals*, https://www.un.org/sustainabledevelopment/sustainable-development-goals/ (1.02.2018).
- 38. Ustawa Prawo ochrony środowiska, 2001, Dz.U. 2017, poz. 519.
- 39. URBANIAK M., KIEDRZYŃSKA E., GROCHO-WALSKI A., 2017, The variability of PCDD/F concentrations in the effluent of wastewater treatment plants with regard to their hydrological environment, in: *Environmental Monitoring Assessment*, vol. 189 no 2 p. 90,
  - DOI: 10.1007/s10661-017-5794-9.
- VALDES M., MARINO D., WUNDERLIN D., SO-MOZA G., RONOCO A., CARRIQURI BORDE P., 2015, Screening concentration of E1, E2 and EE2 in

- sewage effluents and surface waters of the 'Pampas' region and the 'Rio de la Plata' estuary (Argentina), in: *Bulletin of Environmental Contamination Toxicology*, vol. 94 no 1, p. 29-33.
- VIECELLI N. C., LOVATEL E.R, CARDOSO E.M., NASCIMENTO FILHO I., 2011, Quantitative analysis of plasticizers in a wastewater treatment plant: influence of the suspended solids parameter, in: *Journal of Brazilian Chemistry Society*, Vol. 22, no 6, http://dx.doi.org/10.1590/S0103-50532011000600021.
- 42. VOULVOULIS N., SCRIMSHAW M.D., LESTER J.N., 2014, Removal of organotins during sewage treatment: a case study, in: *Environmental Technology*, vol. 25 no 6, p. 733-740.
- WANG C., ZHOU S., WU J., SONG J., SHI Y., LI B., CHEN H., 2017, Surface water polycyclic aromatic hydrocarbons in urban areas of Nanjing, China, in: Water Science & Technology, DOI:10.2166/wsr.2017.387
- WASTEWATER ORDINANCE, http://www.bmub. bund.de/fileadmin/bmu-import/files/pdfs/allgemein/ application/pdf/wastewater\_ordinance.pdf (1.02.2018).
- 45. WHITE PAPER, Aquatic life criteria for contaminants of emerging concern. Part I. General challenges and recommendations, OW/ORD Emerging Contaminants Workgroup, June 03, 2008.
- WIŚNIOWSKA E., 2008, Effect of chemical stabilisation of sewage sludge on the fate of PAHs, in: *Archives of Environmental Protection*, vol. 34, no. 3, p. 249-257.
- 47. WŁODARCZYK-MAKUŁA M., POPENDA A., 2015, Quantitative changes of PAHs in water and in wastewater during treatment processes, Wastewater Treatment, Occurrence and Fate of Polycyclic Aromatic Hydrocarbons (PAHs), in: Advances in Water and Wastewater Transport and Treatment, A series, Series Editor Amy J. Forsgren, Xylem, Sweden, Taylor and Francis Group, p. 47-70.
- 48. WŁODARCZYK-MAKUŁA M., 2015, *Physical and* chemical *fates of organic micropollutants*, Scholar's Press, Saarbrucken.