Study on distribution of phthalate acid esters (PAEs) in water and sludge in Lithuania, Poland and Denmark

REPORT

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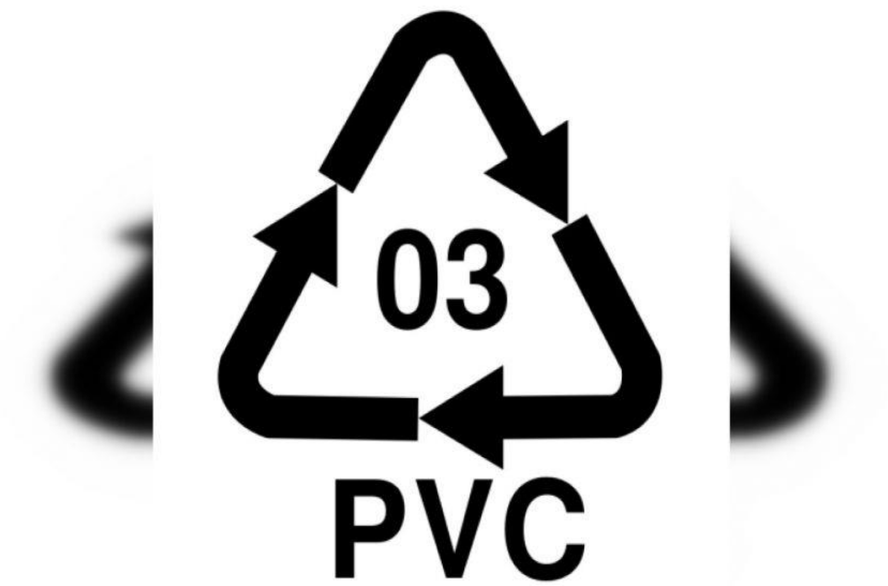

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ABSTRACT

Phthalate acid esters are widely used as raw materials for industry that are well known for their environmental contamination and toxicological effects as “endocrine disruptors.” In this study, seven phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), dibutylphthalate (DBP), diisobutyl phthalate (DiBP), dicyclohexyl phthalate (DCHP) and di(2-ethylhexyl) phthalate (DEHP) environmental levels were determined in different areas of Lithuania, Poland and Denmark. Water and sludge samples from the above water systems were collected in 2019–2020 and analysed by gas chromatography-mass spectrometry.

The highest contamination with phthalates in Lithuania was attributed to DEHP: 63 % of total PAEs in water samples and 94 % of total PAEs in sludge samples which is primarily used in plastic polymers. However, in Poland water samples the biggest concentration was determined of DMP – 67% of total PAEs in water samples, with only 17% of DEPH of total PAEs in water samples. The total concentrations of priority phthalate esters in the water samples ranged from 0.07 to 163.44 μl/l in Lithuania and from 1.48 to 22.7 μl/l in Poland and from 0.05 to 1.2 μl/l in Denmark respectively as well as from 4.8 to 95.6 mg/kg in the sediment’s samples in Lithuania.

The dominant PAEs in water samples of Lithuania sampling points were DEHP > DEP > DiBP > DBP > DMP as well as DPRP and DCHP concentrations were less than 0.05 μl/l. However, the distribution of PAEs in the water samples of Poland was as follow: DMP > DEPH > DEP >DBP and DiBP as well as DPRP and DCHP concentrations were less than 0.05 μl/l.

Further studies are recommended for adequate monitoring of phthalates in water and sludge in order to ensure human health.

Keywords: *Phthalates, dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutylphthalate, diisobutyl phthalate, dicyclohexyl phthalate, di(2-ethylhexyl) phthalate.*

1. INTRODUCTION

Phthalate acid esters (PAEs) are micro-pollutants of great public concern due to their negative impact on ecosystem and human health. Phthalates are dialkyl or alkyl aryl esters of phthalic acid, which are primarily synthesized from phthalic anhydride and the corresponding alcohol by the Fischer esterification in the presence of a catalyst.

PAEs are used to increase a material's flexibility, transparency, pliability, plasticity, strength, endurance and longevity (Kolarik et al. 2008; Serrano et al. 2014; Gao et al. 2014). They are important plasticizers and additives, which depending on the alcohol that makes up the alkyl chain are widely used in industrial production in numerous plastic applications due to their high performance and low cost (Li et al. 2020). PAEs can account for up to 40% of the final plastic product (Wittassek and Koch, 2011). Long-chain PAEs (di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DiNP), diisodecyl phthalate DiDP), are primarily used in plastic polymers and applications such as building and construction materials (wires and cables; electrical cords; flooring, roofing and cladding; wall coverings and floor tiles; films and sheets; paints and lacquers), adhesives, clothing, furniture (PVC flooring), car and public transport interior (automobile upholstery, leather for car interiors), cosmetic products, medical devices (plastic tubing and intravenous storage bags; gloves; teethers), toys and child care products, food and packaging material (drinking straws, food containers) (Ma et al. 2014; Net et al. 2015; Herrero et al, 2015; Palusellial et al. 2020; Kiralan et al. 2020; Weizhen et al. 2020). However, short-chain PAEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), butyl benzyl phthalate (BBzP), di-n-butyl phthalate (DnBP), diisobutyl phthalate (DiBP)) are often used in non-PVC applications such as personal care products, adjuvants in pesticide formulations for use in aquatic systems, paints, glue, lubricants and plastic bags (Rudel et al. 2011; Chen et al. 2013; Peng et al. 2013; Braun 2013; Net et al., 2015; Net et al. 2015; Abdolahnejad et al. 2019; Palusellial et al. 2020).

PAEs are not chemically bound to the host polymer and exposed on higher temperature can easily migrate in the contact matrix which may lead to the release from life cycle of commercial and domestic products into the environment – air, water, soil and biota (He et al. 2011; Zhang and Lee 2013; Zota et al. 2014; Luo et al. 2014; Moreira et al. 2014; Zhao et al. 2015; Wang et al. 2015; Olujimi et al. 2017; Lu et al. 2018; Yu et al. 2019; Chen et al. 2019; Li et al. 2020; Kiralan et al. 2020; Milosevic et al. 2020).

PAEs eventually can enter the environment through multiple pathways among which are industrial and municipal wastewaters, land application of sewage sludge, and leaching after the disposal of industrial and municipal solid waste (Paluselli et al., 2018; Abtahi et al., 2019; Palusellial et al. 2020; Gani et al. 2020).

Hereby, phthalate acid esters can enter the water system through wastewater treatment plants. Because of high lipophilicity of PAEs they tend to be adsorbed and concentrated to suspended organic matter and sludge and are removing through the anaerobic digestion (Liang et al., 2008; Stasinakis, 2012; Gao et al. 2014; Gani et al. 2017; Gani et al. 2020). In addition, the use of fertilizers, pesticides and the irrigation with polluted water in agriculture increase the diffusion of phthalate acid esters in the environment as well as its accumulation in plant biomass and introduction in food chain (Abdel daiem et al, 2012; He et al., 2015; Vannucchi et al. 2019).

Moreover, PAEs are not persistent and readily biodegrade in the aquatic environment under aerobic and anaerobic conditions (Bartsch et al. 2019; Vannucchi et al. 2019). Higher molecular weight PAEs biodegrading slowly than the lower molecular weight chemicals and may accumulate in the aquatic environment (Liang et al. 2008; Gao et al. 2014; Zhang et al. 2017).

In fact, PAEs are classified as carcinogenic, toxic and endocrine-disrupting compounds (EDCs) which cause adverse effects on the developmental stage of organisms (Bergé et al. 2013; Pant et al. 2014; Net et al., 2015; Axelsson et al. 2015; Liu et al. 2016; Sathyanarayana et al. 2016; Zarean et al. 2016; Wang et al. 2017; Song et al. 2019; Wei et al. 2020; Palusellial et al. 2020).

Previous investigations have shown that PAEs have harmful effects on human health such as reproductive problems, birth defects, children growth-disrupting effects, decreased testosterone levels, thyroid-disrupting effects, hormonal and endocrine disruptions, causes respiratory allergic symptoms, asthma and can even cause breast cancer (Casalscasas and Desvergne 2011; Serrano et al. 2014; Foster et al. 2015; Katsikantami et al. 2016; Faraji et al. 2017; Wenzel 2017; Hosney et al. 2018; Li et al. 2019;). Moreover, exposure to phthalate acid esters can adversely affect various human organs, such as respiratory system, kidneys, liver as well as endocrine system (Zaki and Shoeib 2018).

Consequently, six of PAEs (DMP, DEP, DnBP, BBzP, DEHP, di-n-octyl phthalate (DnOP)) have been included in apriority list of pollutants by the European Union and the United State Environment protection agency (Net et al. 2015).

The objective of this study was to determine the levels of dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutyl-phthalate, diisobutyl phthalate, dicikloheksil phthalate, di(2-ethylhexyl) phthalate in water and sediment samples collected from 35 locations in Lithuania, 9 locations in Poland as well as 4 locations in Denmark and to discuss their potential sources with the goal of helping decision-makers to develop strategies to minimize exposure.

2. MATERIALS AND METHODS

2.1. Study area and sampling strategy

In 2019–2020 a total of 44 water and 6 sludge samples were collected from 50 locations in Lithuania, Poland and Denmark. Details of each sampling site are included in Table 1.

Figure 1. Map of the location of the sampling sites in Poland.

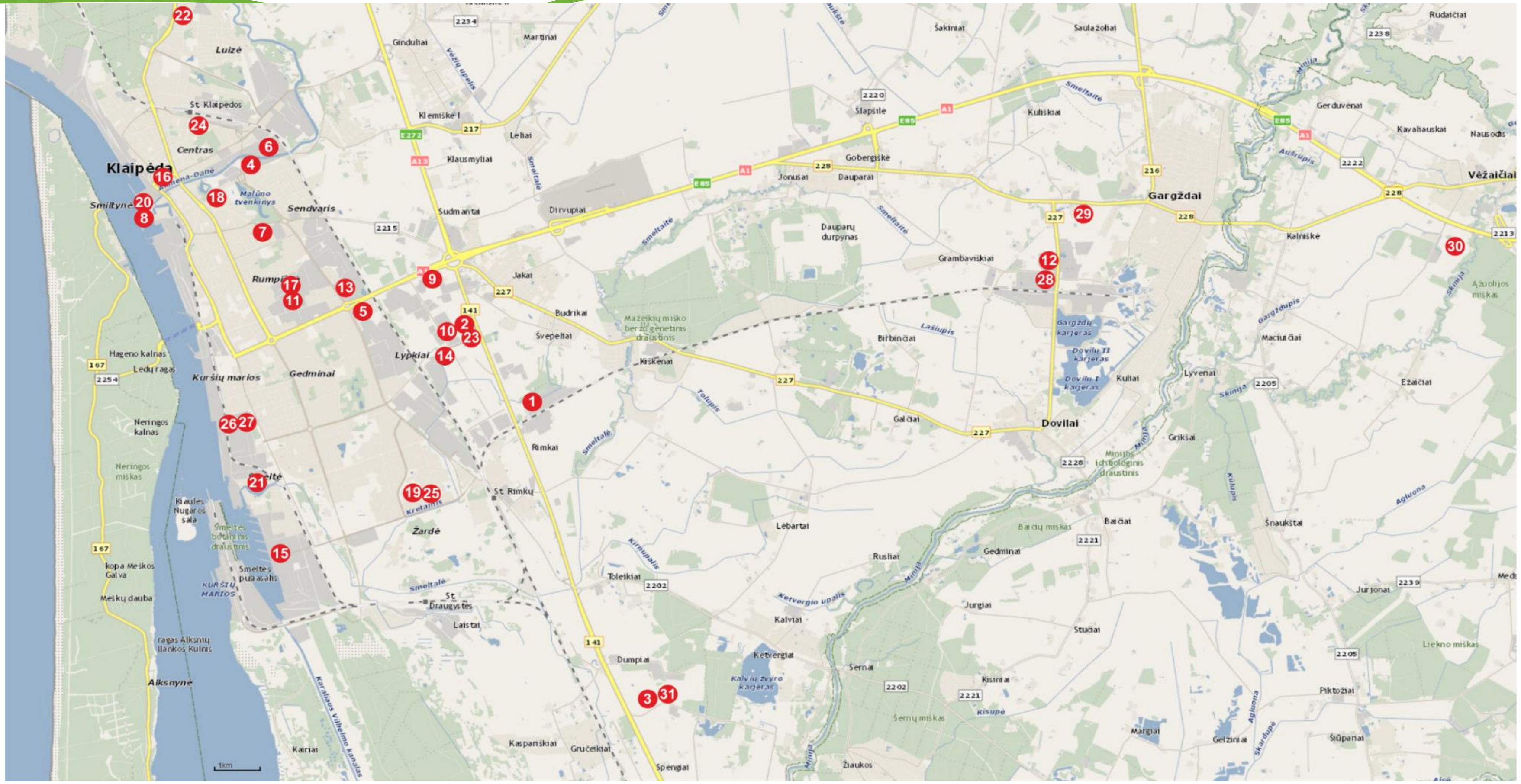

Figure 2. Map of the location of the sampling sites in Lithuania

Table 1. Sampling site description

Samples	Sampling points		
	Lithuania	Poland	Denmark
Water	No 1. PET factory No 2. PET factory No 3. Klaipeda region landfill No 4. Furniture production No 5. Shopping Center I No 6. Wood processing No 7. Laundry services No 8. Cruise ship terminal No 9. Tobacco Factory No 10. Fish processing No 11. Shopping center II No 12. Food factory No 13. Bread Factory No 14. Biodiesel production plant No 15. Energy supply, maintenance and repair services No 16. Hotel No 17. Concrete production No 18. Bear factory No 19. Domestic sewage No 20. Sewage pumping station II No 21. Sewage pumping station VI	No 0. Treated sewage from Goleniów sewage treatment plant (outlet) No 1. Sewage pumping station Source: cosmetics company, concrete plant, catering, laundry, processing of furskins. No 2. Sewage pumping station Source: restaurants, café. No 3. Manhole. Sewage from: fast-food restaurant, gas station, kindergarten. No 4. Manhole. Sewage from: restaurants, hairdresser, beautician. No 5. Manhole. Source: restaurants, café. No 6. Sewage pumping station Source: supermarket, market, restaurants, café. No 7. Manhole. Source: shopping center, production of cardboard packaging, train station. No 8. Manhole on the sewage treatment plant. Source: all Industrial Park. No 9. Raw sewage Goleniów sewage treatment plant (inlet). Source: Goleniów town and commune (inlet)	No 1. Inlet of the Rønne WWTP No 2. Outlet of the Rønne WWTP

Samples	Sampling points		
	Lithuania	Poland	Denmark
	No 22. Sewage pumping station XVII No 23. Sewage pumping station XIX No 24. Klaipeda Republican Hospital No 25. Kindergarten No 26. Truck wash services No 27. Publishing-printing house No 28. Sewage pumping station in Gargzdai II No 29. Care home No 30. District WWTP No 31. Klaipeda WWTP outlet No 32. Klaipeda WWTP inlet		
Sludge	Klaipeda WWTP: No 33. Primary sludge No 34. Excess sludge No 35. Digestate No 36. Dried sludge	-	Rønne WWTP: No 1. Sludge of the WWTP No 2. Sludge of the WWTP

2.2. METHODOLOGY

2.2.1. Water samples analysis

The Standard EN ISO 18856:2005 and ISO 18856:2004 (Water quality. Determination of selected phthalates using gas chromatography/mass spectrometry) specifies a method for the determination of phthalates (Table 2) in water after solid phase extraction and gas chromatography/mass spectrometry.

Table 2. List of the phthalates which could be determined in the water by EN ISO 18856:2005, ISO 18856:2004 standards

Compound	Formula	Abbreviation	Molar Mass, g/mol	CAS-RN*
Dimethyl phthalate	$C_{10}H_{10}O_4$	DMP	194,2	131-11-3
Diethyl phthalate	$C_{12}H_{14}O_4$	DEP	222,2	84-66-2
Dipropyl phthalate	$C_{14}H_{18}O_4$	DPP	250,3	131-16-8
Dibutylphthalate	$C_{16}H_{22}O_4$	DBP	278,4	84-74-2
Diisobutyl phthalate	$C_{16}H_{22}O_4$	DiBP	278,4	84-69-5
Dicyclohexyl phthalate	$C_{20}H_{26}O_4$	DCHP	330,4	84-61-7
di(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	DEHP	390,6	117-81-7

** - CAS-RN Chemical Abstracts Service Registry Number*

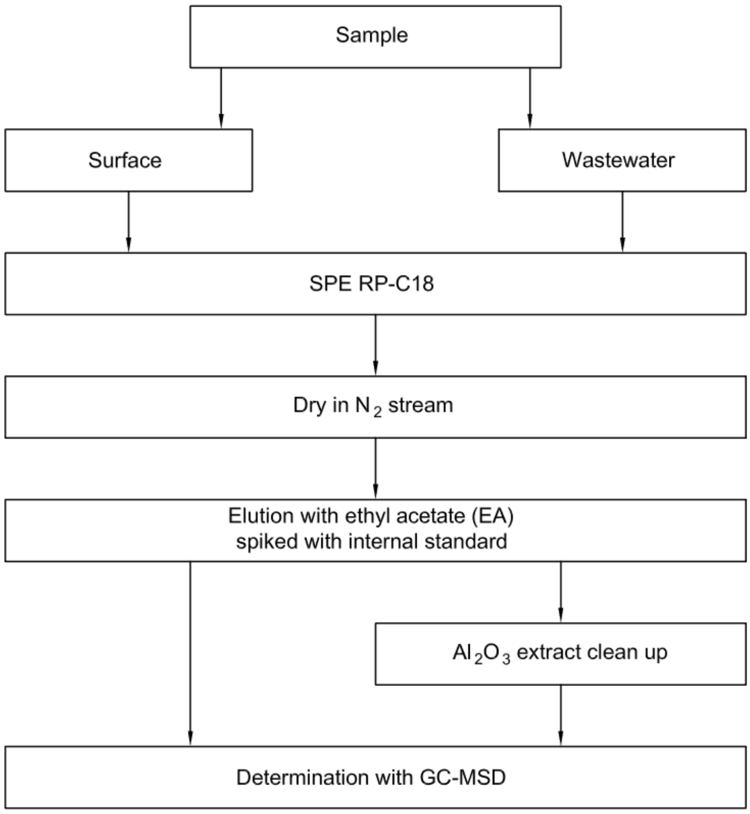

Figure 3. Flowchart of the analysis (Source: EN ISO 18856:2005)

The method is applicable to the determination of phthalates in ground water, surface water, wastewater and drinking water in mass concentrations ranging from above 0,02 μg/l up to 0,150 μg /l, depending on the individual substance and value of the blank.

Principle: extraction of the compounds from the water by solid-phase extraction. Then separation is accomplished using capillary columns by gas chromatography and followed by identification and quantification of the phthalates by mass spectrometry. The principle of this method is outlined in Figure 3.

2.2.2. Sludge samples analysis

CEN/TS 16183:2012 standard “Sludge, treated biowaste and soil – determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC-MS)”. Describes a method for the determination of selected phthalates in sludge, treated biowaste and soil, after extraction and gas chromatographic analysis with mass spectrometric detection.

The method is applicable for the determination of phthalates (Table 3) at the lowest mass content of 0,1 mg/kg to 0,5 mg/kg (expressed as dry matter), depending on the individual substance.

The applicability of the method to other phthalates not specified is not excluded except the isomeric mixtures e. g. DiNP (Di-isononylphthalate) but shall be verified in each case.

Table 3. List of the phthalates which could be determined in the water by CEN/TS 16183:2012 standard

Compound	Formula	Abbreviation	Molar Mass, g/mol	CAS-RN
Dimethyl phthalate	$C_{10}H_{10}O_4$	DMP	194,2	131-11-3
Diethyl phthalate	$C_{12}H_{14}O_4$	DEP	222,2	84-66-2
Dipropyl phthalate	$C_{14}H_{18}O_4$	DPP	250,3	131-16-8
Dibutylphthalate	$C_{16}H_{22}O_4$	DBP	278,4	84-74-2
Dicyclohexyl phthalate	$C_{20}H_{26}O_4$	DCHP	330,4	84-61-7
di(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	DEHP	390,6	117-81-7

Principle: the dried sample, dried by freeze-drying or with sodium sulphate is extracted with ethyl acetate on the shaking device. An aliquot of the extract is cleaned with aluminium oxide (if necessary) followed by gas chromatographic separation using capillary columns and identification and quantification of the phthalates by mass spectrometry.

3. RESULTS AND DISCUSSION

This study aimed to determine the presence of phthalates and their concentrations in different areas of Lithuania (Klaipeda), Poland (Goleniów) and Denmark, Bornholm (Rønne).

3.1. Lithuania

The Klaipeda WWTP is the main biological sewage treatment plant in Klaipeda, build in 1998 with a capacity of 305.333 PE based on the challenge of total nitrogen amount. Wastewater and sludge quality reflect that it is household and industrial wastewater from cigarette production, paper mill, wood timber, wood processing, furniture as well as food production and service companies.

The highest contamination with phthalates in Lithuania was attributed to DEHP which ranged from 0,05 to 159 µg/l in water sampling points (Table 4). Moreover, the mean concentration of DEHP reached 15,7 µg/l. This kind of phthalate is primarily used in plastic polymers and wares such as building and construction materials, furniture, cosmetic products, medical devices, toys and child care products, food and packaging material etc.

The highest DEPH concentrations of 159 µg/l and 112 µg/l was observed in the Truck wash and Laundry sampling points respectively. The concentrations of others PAEs at those sampling points were also very high. In the Truck wash water sampling point the concentration of DiBP reached 2,2 µg/l, DBP – 1,8 µg/l, DEP – 0,26 µg/l and DMP – 0,18 µg/l. However, in the Laundry sampling point DBP concentration reached 6,9 µg/l, DEP – 4,8 µg/l, DiBP – 3,3 µg/l and DMP – 0,14 µg/l. PAEs compounds include in lubricants that influence the truck wash sewage's pollution. Phthalates have been detected in content of detergents that explain laundry's wastewater pollution by PAEs.

Meanwhile, near Real estate rental services providing company sampling point the concentration of DEHP was also very high – 50 µg/l. Moreover, the concentration of the DEP in this sampling point reached – 78,0 µg/l, DiBP – 4,9 µg/l, DBP – 2,6 µg/l and DMP – 0,17 µg/l. It can be explained by the fact that the site is located near several car washing and repair shops, and catering companies as well.

The results showed that the concentration of DEHP in domestic sewage sampling point reached 40 µg/l and was several times higher than in some industrial sampling points such as Bread Factory (26 µg/l), Furniture Production (19 µg/l), Wood Processing Factory (14 µg/l), Biodiesel Production Plant (6,8 µg/l), Tobacco Factory (2,1 µg/l), Food Factory (1,2 µg/l) etc. Moreover, the DEHP concentrations in different Sewage pumping stations ranged from 0,7 µg/l (No. 19) to 9,7 µg/l (No. 2). Although the number of employees at each of above-mentioned enterprises is not small (average 500 employees), the biggest affect to the water pollution by phthalates was detected by household activities provided by citizens and based on phthalates active usage as part or substitute of PVC and other resins products. However, the concentrations of DEHP in water samples of Klaipeda and Vėžaičiai WWTPs ranged respectively only 0,07 and 0,14 µg/l. The wastewater treatment plant ensures effective phthalates precipitation at least two times per wastewater cleaning process and phthalates concentrate in the sedimentation.

Furthermore, the concentrations of some analysed PAEs in industry sampling points were high enough and in DEP case reached 5,5 µg/l in Bread Factory, 4 µg/l – in Furniture Factory, 3,7 µg/l – In PET factories, 3,2 µg/l – Tobacco Factory, 1,9 µg/l – Food Factory, 1,8 µg/l – in Biodiesel Production Plant, 1,7 µg/l – in Publishing – printing house, 1,2 µg/l – Fish Processing Factory, and 0,23 µg/l – Wood Processing Factory.

It was determined that DEHP concentration in water near Shopping center "Banginis" sampling point reached 14 µg/l as well as DiBP – 26 µg/l, DEP – 17,0 µg/l and DBP – 6,1 µg/l. It can be explained by the fact that cars' washing as well as filling stations are situated close to shopping center. Active catering services and products' plastic packaging also contribute to the total PAEs compounds' concentration in the sewage.

DEHP concentration was also measured in regional dump of Klaipeda region waste management center. It was found that DEHP concentration in water sample was up to 7,2 µg/l as well as concentrations of other PAEs ranged from less than 0,05 µg/l to 0,1 µg/l (DBP). Based on the statistics (Ritchie et al. 2018) shown that the amount of the plastic waste has tendency to increase over the world (380 million tons in 2015) and taking into account the low DEHP biodegradability in the water, the DEHP concentration is higher than others measured phthalates (Marttinen, et al., 2003).

The distribution of PAEs in the water samples of Klaipeda WWTP (outlet) was as follow: concentration of DMP, DEP, DPP, DBP, DiBP and DCHP were less than 0.05 µg/L, but DEHP concentration was 0.07 µg/L.

In this Study, distribution of total PAEs ($\sum_7$PAEs) in the sludge samples was as follow: Decomposed sludge (95,6 mg/kg) > Primary sludge (30,02 mg/kg) > Dried sludge (16,2 mg/kg) > Excess sludge (4,8 mg/kg) (Table 5). The highest concentrations of phthalates in all samples were associated with DEHP, which concentrations ranged from 95.0 mg kg^{-1} in digestate to 3.8 mg kg^{-1} in excess sludge. After the biodegradation of sludge in the biogas reactor, its volume decreases by 1/3 of the original, and the concentration of phthalates in both sludge becomes higher.

It was determined that DPP and DCHP phthalates concentrations in all water and sludge (exception Klaipeda WWTP primary sludge sample with slightly higher concentration of 0,052 mg/kg) samples were less than 0,05 mg/kg.

3.2 Poland

Goleniów WWTP is the biological WWTP situated in Goleniów city, West Pomeranian District, North-western Poland, built – in 2004 and rebuilt in 2011 with the current capacity of 63 805 PE. Wastewater and sludge quality reflects that it is mostly household wastewater with some industrial sewage from the sectors of plastics production, meat processing, car washes and sewage delivered from septic tanks.

The highest contamination with phthalates was observed in sewage pumping station No 6 (Fig. 1), where sewage from supermarket and industrial area are collected before transferring them to the sewage treatment plant (Table 6). The concentration of DMP reached 210 µg/l. Moreover, the concentrations of DEP as well as DEHP in this sampling point were high as well and reach 15 µg/l and 1.8 µg/l respectively. The concentration of DiBP and DBP exceeded the maximum permitted concentration of 0.05 µg/l by 9 and 5 times respectively. The well-known method for phthalates removal from water is biological treatment based on PAEs aerobic and/or anaerobic degradation by microorganisms [Adhoum et al, 2004]. The obtained PAEs concentrations shown that long-chains alkyl are quite resistible and require effective biological treatment.

However, it was determined that the total concentrations of seven PAEs (**$\sum_7$PAEs**) in the sewage No 1 of Industrial Park was much lower – 7.03 µg/L. It could be explained by variety of smaller number of companies and their size. The DEHP (2.6 µg/l), DEP (2.2 µg/l) and DMP (1.1 µg/l) were the main phthalate's compounds in this sampling point.

The results of manhole observation No 3, No 4, No 5 and No 7 points showed that the highest concentration has DEHP – up to 15 µg/L and DMP – up to 7.7 µg/L. The main source of the high concentrations of PAEs at that observation points are fast-food restaurants, hairdresser, and beautician, shopping center, gas and train stations.

It was found that the total concentrations of seven PAEs in the inlet of the sewage treatment plant (No 9) reached 22.7 µg/l. The dominant PAEs were DEHP > DEP > DiBP > DBP. DMP, DPP and DCHP concentrations were less than 0.05 µg/l.

It is important to state that concentration of DPP and DCHP in all sampling points were less than 0.05 µg/l that in accordance with proposition of the other scientists [Menga et al., 2014] and based on small industrial/domestic sewage proportion at the wastewater treatment plant.

The distribution of PAEs in the water samples from Goleniów was as follow: DMP > DEHP > DEP > DBP and DiBP. DPP and DCHP concentrations were less than 0.05 µg/l.

Table 4. Results of phthalates analysis of water samples (Lithuania), 2019

No	Sampling point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP	$\sum_7$PAEs
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
1	PET factory	2.5	3.7	<0.05	0.22	1.1	<0.05	0.16	7.68
2	PET factory	<0.05	2	<0.05	0.11	1.2	<0.05	0.05	3.36
3	Klaipeda region landfill	<0.05	0.47	<0.05	0.1	0.78	<0.05	7.2	8.55
4	Furniture production	0.06	4	<0.05	0.14	1	<0.05	19	24.2
5	Shopping center I	0.6	17	<0.05	6.1	26	<0.05	14	63.67
6	Wood processing	<0.05	0.23	<0.05	<0.05	0.5	<0.05	14	14.73
7	Laundry services	0.14	4.8	<0.05	6.9	3.3	<0.05	112	127.14
8	Cruise ship terminal	<0.05	<0.05	<0.05	0.07	0.43	<0.05	0.12	0.62
9	Tobacco Factory	<0.05	3.2	<0.05	<0.05	0.74	<0.05	2.1	6.04
10	Fish processing	<0.05	1.2	<0.05	0.15	1.0	<0.05	0.67	3.02
11	Shopping center II	0.17	78.0	<0.05	2.6	4.9	<0.05	50	135.67
12	Food factory	0.06	1.9	<0.05	<0.05	0.33	<0.05	1.2	3.49
13	Bread Factory	1.4	5.5	<0.05	0.32	0.56	<0.05	26	33.78
14	Biodiesel (methyl ester) production plant	3.1	1.8	<0.05	34	2.7	<0.05	6.8	48.4
15	Energy supply, maintenance and repair services	<0.05	0.3	<0.05	0.1	0.48	<0.05	0.41	1.29

No	Sampling point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP	$\sum_7$PAEs
16	Hotel	0.05	9.6	<0.05	1.3	2.5	<0.05	4.8	18.25
17	Concrete production	0.06	0.25	<0.05	<0.05	0.64	<0.05	0.13	1.08
18	Bear factory	0.05	<0.05	<0.05	0.06	0.17	<0.05	0.8	1.08
19	Domestic sewage	0.08	3.1	<0.05	0.6	1.8	<0.05	40	45.58
20	Sewage pumping station II	0.07	0.84	<0.05	0.4	1.5	<0.05	9.7	12.51
21	Sewage pumping station VI	0.41	6.6	<0.05	0.14	1	<0.05	2.7	10.85
22	Sewage pumping station XVII	0.07	0.14	<0.05	0.14	1.1	<0.05	9.5	10.95
23	Sewage pumping station XIX	0.27	2.6	<0.05	0.07	0.47	<0.05	0.7	4.11
24	Republican Hospital	0.68	2.5	<0.05	0.18	0.79	<0.05	0.39	4.54
25	Kindergarten	<0.05	0.64	<0.05	0.45	0.9	<0.05	1.8	3.79
26	Truck wash services	0.18	0.26	<0.05	1.8	2.2	<0.05	159	163.44
27	Publishing-printing house	<0.05	1.7	<0.05	<0.05	0.34	<0.05	0.22	2.26
28	Sewage pumping station in Gargzdai II	<0.05	0.84	<0.05	0.07	0.34	<0.05	1.6	2.85
29	Care home	<0.05	4.2	<0.05	0.05	0.3	<0.05	0.44	4.99
30	District WWTP outlet	<0.05	0.07	<0.05	<0.05	0.11	<0.05	0.14	0.32
31	Klaipeda WWTP outlet	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	0.07
32	Klaipeda WWTP inlet	0.08	3.35	<0.05	0.68	2.35	<0.05	2.51	9.07

Table 5. Results of phthalates analysis of sludge samples (Lithuania), 2019

No	Sampling point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP	$\sum_7$PAEs
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
33	Primary sludge	<0.05	0.52	<0.05	2.4	4.1	<0.05	23	30.02
34	Excess sludge	<0.05	<0.05	<0.05	0.25	0.7	<0.05	3.8	4.8
35	Digestate	<0.05	<0.05	<0.05	<0.05	0.6	<0.05	95	95.6
36	Dried sludge	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	16	16.2

Table 6. Results of phthalates analysis of water samples (Poland), 2020

No	Sampling point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP	$\sum_7$PAEs
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
0	Treated wastewater outlet to the river	<0.05	NA	NA	NA	NA	<0.05	12,2 / 23,6	NA
1	Sewage pumping station Source: cosmetics company, concrete plant, catering, laundry, processing of furskins.	1.1	2.2	<0.05	0.92	0.21	<0.05	2.6	7.03
2	Sewage pumping station Source: restaurants, café.	NA (Lost during transportation)							
3	Manhole. Sewage from: fast-food restaurant, gas station, kindergarten.	<0.05	1.3	<0.05	1.2	1.8	<0.05	7.4	11.7
4	Manhole. Sewage from: restaurants, hairdresser,	<0.05	3.7	<0.05	0.68	0.92	<0.05	8.8	14.1

No	Sampling point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP	$\sum_7$PAEs
	beautician.								
5	Manhole. Source: restaurants, café.	0.18	0.22	<0.05	0.70	0.12	<0.05	0.44	1.66
6	Sewage pumping station Source: supermarket, market, restaurants, café.	210	15	<0.05	0.27	0.46	<0.05	1.8	227.53
7	Manhole. Source: shopping center, production of cardboard packaging, train station.	<0.05	3.0	<0.05	0.54	0.84	<0.05	15	19.38
8	Manhole on the sewage treatment plant. Source: all Industrial Park.	0.94	7.7	<0.05	0.52	0.31	<0.05	2.7	12.17
9	Raw sewage Goleniów sewage treatment plant (inlet). Source: Goleniów town and commune.	<0.05	4.2	<0.05	1.7	1.8	<0.05	15	22.7 / 43,7

3.3 Denmark

Background and objectives *(Source: Nature Agency, Ministry of the Environment)*

The Danish national surveillance programme for the aquatic environment (formerly NOVA in 2003, now NOVANA) has since 1998 included monitoring of trace elements and organic xenobiotics in discharges from sewage treatment plants (STPs) and other point sources. The aim of the point source programme is to ensure that Denmark meets its international reporting obligations within this area and to monitor the effect of various action plans, not least the different generations of the national Action Plan for the Aquatic Environment. The results of the surveillance programme from 1998-2003 has previously been summarized and reported, and a similar report is being prepared for the period 2004-2009. In addition to this, the Agency for Spatial and Environmental Planning (BLST) has wished to investigate whether it is possible to exploit the substantial number of data generated e.g. to establish general correlations between substance concentrations and other factors associated with the sewage or with treatment plant characteristics. Hence, the objective of this study has been to analyse and report the point source data on metals and xenobiotics for the period 1998-2009 in a way enabling use of the information in the planning of future surveillance programmes and for assessment of the total amount of substances discharged from Danish sewage treatment plants. The means to achieve this has been to establish “Nation Mean Concentrations” (NMCs) for substance concentrations in inlets and outlets from STPs and to identify possible correlations with relevant variables.

The main results of the Danish national surveillance programme for the aquatic environment presented in Table 7-9.

Table 7. Key figures for plasticizers (phthalates and adipates) at WWTPs

Compound	Inlet (µg/l)		Outlet (µg/l)	
	Key factor	65%-85% interval	Key factor	65%-85% interval
Benzylbutylphtalate	0.69	0.46-1.2	0	0-0
DEHP	29	22-37	2.8	1.4-6.0
Di(2-ethylhexyl)adipat	0.43	0.23-0.75	0	0-0
Dibutylphthalate	1.4	1.1-2.1	0.138	0-0.50
Diethylphthalate	6.2	5.1-7.7	0.328	0.20-0.63
Diisononylphthalate	30	23-36	0.37	0.19-0.56
Di-n-octylphthalate	0	0-0.21	0	0-0

Table 8. Average reduction factors for organic pollutants in wastewater as well as annual discharges to the aquatic environment (2008)

Compound	Key factor, inlet (µg/l)	Key factor, outlet (µg/l)	Reduction factor (%)	Annual discharges (kg/year)
Tributylphosphate	0.59	0.2175	63.14	160
Triphenylphosphate	0.25	0.044	82.40	32
DEHP	28.75	2.8	90.26	2000
Dibutylphthalate	1.4	0.1375	90.18	98
Diethylphthalate	6.2	0.3275	94.72	230
Diisononylphthalate	30.25	0.37	98.78	270
Alkylbenzensulfonate (LAS)	1575	23	98.54	16000
Cation detergents, sum	117.5	42	64.26	30000
AOX	80	37	53.75	26000

Table 9. Detailed data regarding key figures and fractiles

Compound	Antal data	Andel >DG	Min	5%	10%	25%	50%	65%	75%	85%	90%	95%	Max
SOFTENERS													
Inlet													
Benzylbutylphtalate	347	0,65	0	0	0	0	0,23	0,46	0,685	1,2	1,6	2,74	15
DEHP	62	0,98	0	0,671	1,3	5,625	14	21,65	28,75	36,55	38,9	43,95	63
Di(2-ethylhexyl)adipat	62	0,42	0	0	0	0	0	0,226	0,425	0,746	0,944	1,87	3,7
Dibutylphthalate	347	0,69	0	0	0	0	0,73	1,1	1,4	2,1	2,5	3,65	31
Diethylphthalate	339	0,91	0	0	0,198	1,4	3,8	5,07	6,2	7,73	9,02	12	34
Diisononylphthalate	62	0,85	0	0	0	7,2	15,5	22,65	30,25	35,85	40,8	50,7	84
Di-n-octylphthalate	62	0,19	0	0	0	0	0	0	0	0,211	0,301	0,659	8,8
Outlet													
Benzylbutylphtalate	350	0,13	0	0	0	0	0	0	0	0	0,1	0,23	2,2
DEHP	63	0,71	0	0	0	0	0,61	1,43	2,8	5,95	10,62	15,7	27
Di(2-ethylhexyl)adipat	63	0,05	0	0	0	0	0	0	0	0	0	0	0,75
Dibutylphthalate	350	0,27	0	0	0	0	0	0	0,138	0,5	0,703	1,055	2,9
Diethylphthalate	342	0,39	0	0	0	0	0	0,2	0,328	0,63	0,997	3,3	12
Diisononylphthalate	59	0,41	0	0	0	0	0	0,187	0,37	0,559	0,826	1,96	3,8
Di-n-octylphthalate	63	0,02	0	0	0	0	0	0	0	0	0	0	0,51

The main conclusions and recommendations of the project are the following:

- The sewage treatment plants (STPs) included in the point source programme represent a significant fraction of the total volume of treated sewage effluent from Danish STPs. The plants are less representative with regard to the composition at national scale (i.e. in numbers), with regard to size and technology (type of treatment).
- The statistical analysis of data showed that the coefficient of determination (R2) is not sufficient to enable establishment of reliable, quantitative models for the content of the hazardous substances (trace elements and xenobiotics) as a function of size, treatment type or relative load of the STP. NMC signifies in this report the best estimate of the national annual mean value of the concentration of a substance in urban sewage at the inlet to and outlet from a sewage treatment plant, respectively.
- Further, it has been demonstrated that there is a considerable co-variance between a general sewage parameter such as chemical oxygen demand (COD) and the hazardous substances but with the data available it was not possible to determine with sufficient certainty to what extent and how such a co-variance can be exploited and made operational.
- National Mean Concentrations have been established for a total of 76 substances at inlets to and outlets from Danish STPs, 18 metals/trace elements and 58 organic xenobiotics, based on the total number of monitoring data of each substance but without correlating these to possible explanatory variables. Inlet NMCs were established for all 76 substances while outlet NMCs were established for 37 of these.

- Mean national level reduction factors for passage of substances through an STP have been calculated for the 37 substances for which inlet as well as outlet NMCs was possible to establish. Based on these factors, estimates were made of the mean national annual discharges of the 37 substances to the Danish aquatic environment. These mean reduction factors should not be mistaken for treatment efficiencies in the traditional sense, i.e. they cannot be used for calculations at individual STPs.
- The quality and completeness of the data material has put some limitations on the possibilities of performing statistical analyses and obtaining operational results. In our opinion it is possible to improve on this in forthcoming generations of the point source surveillance programme without significant economic consequences and some outstanding issues can probably be addressed through more detailed analyses of the existing material. Further analysis will probably lead to assessment of NMCs for an additional number of substances.

Rønne WWTP is the largest of the seven biological WWTPs in Bornholm, build in 1995 with capacity of 60 000 PE. Wastewater and sludge quality reflects that it is mostly household wastewater without much industry, except the slaughterhouse, the hospital, and a few metal processing industries in Rønne.

Sewage samples were taken at inlet and outlet of sampling stations during the summer 2019 in order to analyse the efficiency of the WWTP regarding phthalates reduction based on technological sewage's sludge sedimentation.

The results of the Rønne's wastewater pollution by phthalates are presented in the Table 10. The analysis of the data showed the main trends of the PEAs compounds amounts' distribution in the samples. The predominant quantity of the DEHP and following DEP concentrations are in the same proportion as in above analysed Lithuanian and Polish WWTPs and reflect the common tendency of sewage pollution characterizing small and middle water treatments. The positive alteration of the total amount of PEAs after sewage treatment at Rønne WWTP does not connect with special or additional sewage handling regarding microorganic pollution.

Table 10. Concentration (µg/l) of PAEs in water samples (Denmark), 2019.

	Cas No	Method detection limit, µg/l	Inlet	Outlet
DMP	131-11-3	0.05	<0.05	<0.05
DEP	84-66-2	0.05	0.20	<0.05
DPP	131-16-8	0.05	<0.05	<0.05
DBP	84-74-2	0.05	0.14	<0.05
DiBP	84-69-5	0.05	0.05	<0.05
DCHP	84-61-7	0.05	<0.05	<0.05
DEHP	117-81-7	0.05	1.2	0.07
$\sum_6$PAEs	-	-	**<1.74**	**<0.37**

Due to the fact that DEHP concentrations in Rønne sewage in comparison with Eastern neighbours were quite modest the measurement of diethylhexylphthalate amount in the sewage during June-July of 2020 has been taking into account (Fig. 4). Although the concentrations of the DEHP in the inlet point were higher in the summer, the significant reduction of the pollution by PEAs is evident, especially in the second part of the June. It is in line with others scientist statement regarding DEHP degradation's rate and its dependence on temperature, nutrition, other pollutants and microbial community [Net et al, 2015]. These results confirm the hypothesis that sustainable maintenance of biological wastewater treatment is essential factor of micro organic pollutants diminish under present conditions.

The distribution of PAEs in the water samples of Rønne WWTP was as follow: DEHP > DEP > DBP > DiBP. DMP, DPP and DCHP concentrations were less than 0.05 µg/l.

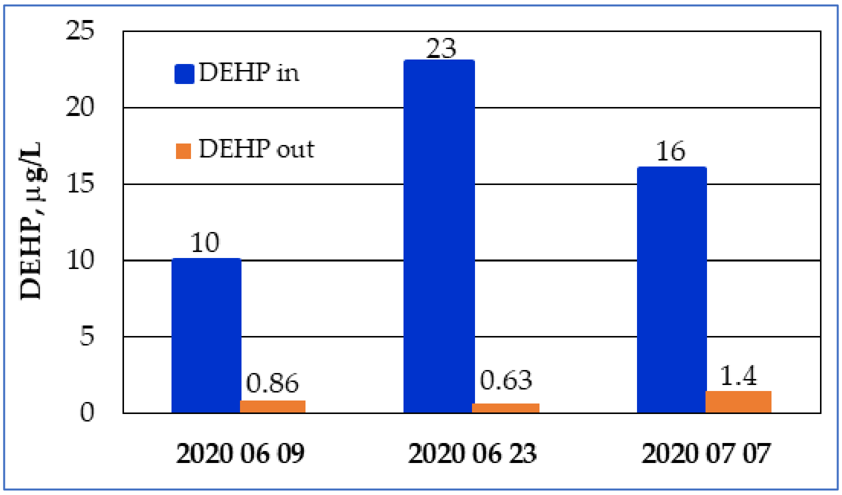

Figure 4. The DEHP concentrations in the sewage's inlet and outlet in Rønne WWTP summer, 2020.

By the quality of the sludge can be judged on wastewater pollution. Such organic pollutant, as DEHP is oily organic carcinogen and slightly ($2.70x10^{-1}$ mg/l at 25 °C) dissolve in the water [Defoe et al, 1990], and has the inclination to bind to the sludge. The main samples for determination of the Rønne wastewater quality came from inlet and outlet of the Rønne sewage system. Besides that, the results of the samples of sludge, which were collected on-side for DEHP determination every month, then mixed and analysed every 3 months, were taking into account for correct evaluation of the sludge pollution by DEHP at Ronne WWTP in 2019 (Fig. 5). The DEHP concentration increased twice during the year. The analysis of the data presented at Figure 4 and 5 shows that the amount of the phthalates in the sludge has tendency to change during the year, but there is no seasonal relationship [Nature Agency, 2011]. The main reasons for an increase in the concentration of DEHP in sludge depend on the quality of wastewater, especially on its industrial component, the type of treatment facilities and their efficiency.

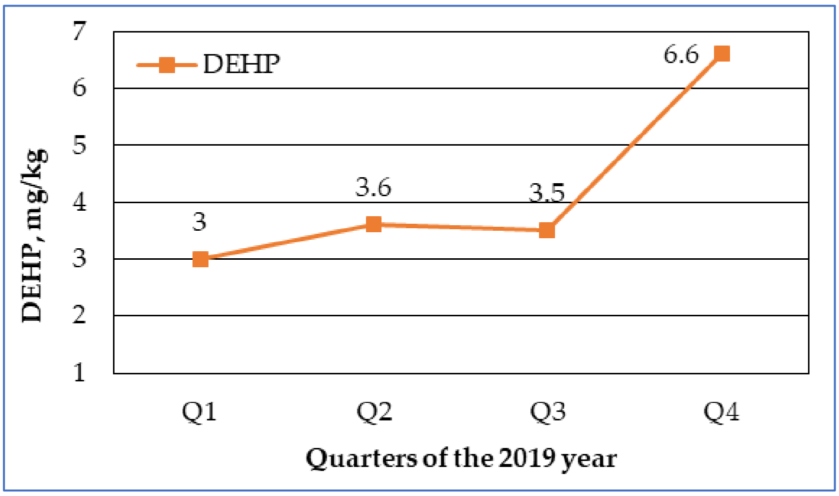

Figure 5. The Diethylhexylphthalate (DEHP) in the Rønne dewatered sludge in 2019.

As was point before, most of the DEHP in wastewater is decomposed in the WWTPs due to anaerobic digestion and a large amount of phthalates could be found in the sludge (Fig. 6).

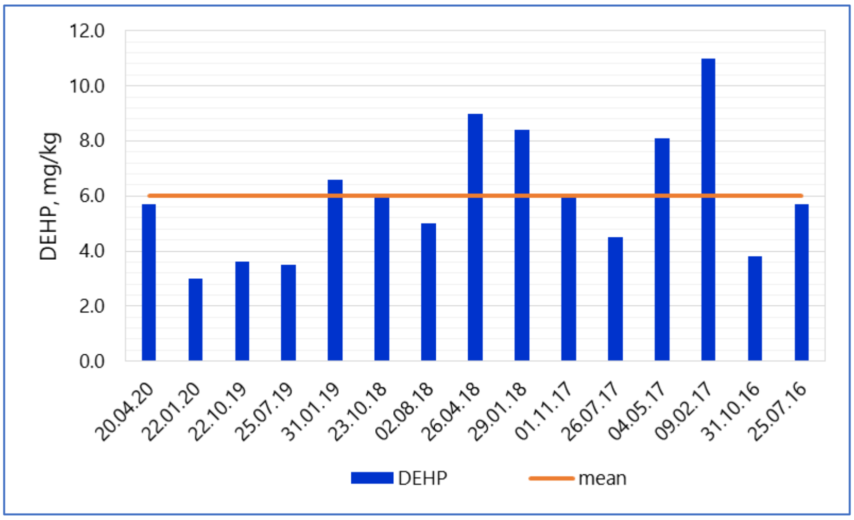

Figure 6. DEPH in sludge Rønne WWTP (Denmark), mg/kg

In accordance with Danish review regarding sludge operation in 1993-2003, the amount of sludge production has tendency to reduce [Çifci et al, 2013]. The cut-off value for DEHP (50 mg/kg d.w.) in 2003 has caused in an important decrease of this organic contaminant. As the results, in 2003 more than 95% of sludge has phthalate concentration below the cut-off criteria [Jensen et al, 2005]. The Fig. 6 data also confirm the positive trend of the DEHP concentration diminishing at the Ronne WWTP sludge from 2016 to 2020. Perhaps, such result was as consequence of the active Danish Environmental Protection Agency (EPA) policy and attention to pollution sources identification as well as publishing a list of undesirable substances and other numerous actions, such as voluntary agreement with manufacturers for the environmentally friendly alteration in products' production and use. Total/partial prohibition of PEAs, stricter standards, emission controls, environmental labelling, green guidelines, and information campaigns as well as the guideline for manufacturer and taxation are the main actions, which helped to reduce of the PEAs in environment [EPA, 2001].

The resent document, which could affect the wastewater and sludge quality, is REACH-ECHA document: “Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles” (XVII annex of REACH/ ECHA) [ECHA, 2020].

Although Denmark, Lithuania and Poland are followed by the same EU-regulations on phthalates, the measurement results have been indicated difference in phthalates’ amount in sewage and sludge of Eastern countries and Bornholm.

Furthermore, in Denmark there are a special regulation about toys, which since 1999 has banned the manufacturing, import and selling toys and certain articles for young children with phthalates, especially for children under 3 years of age.

From 16 January 2007, the manufacture and import of toys and articles for children up to the age of 14 with the phthalates DEHP, DBP and BBP has been forbidden as well. In the case of a toy or a toddler article that can be put in the mouth, the ban also applies to the phthalates DINP, DIDP and DNOP. As of April 16, 2007, it has also banned the sale of these products.

Denmark successfully adopted directive, regarding harmful substances monitoring implementation on the state level (priority substances in the field of water policy). Lithuania is still under preparation for directive’s implementation. Each middle and big size economic unit should organise air and water pollution control, inform regional environmental protection agency on PEAs compounds and their concentrations. Monitoring of the entity is carried out in Poland as well.

Also, the EC has adopted a decision to amend the REACH Regulation and restrict the use of the phthalates – DEHP, BBP, DBP and DIBP in consumer products on the EU market. The restriction started from 8 July 2020 and is expected to reduce organic contaminants amount in the air, water, soil and sediments.

CONCLUSIONS

The purpose of this study was to evaluate the degree of PAEs contamination in Lithuania, Poland and Denmark. This study was aimed at improving knowledge of wastewater and sludge pollution by phthalate through measuring and collecting data of industrial and domestic flows and their contribution to pollution carried within sewerage systems on the scale of small and medium agglomerations. The research was focused precisely on evaluation the degree of dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), dibutylphthalate (DBP), diisobutyl phthalate (DiBP), dicyclohexyl phthalate (DCHP) and di(2-ethylhexyl) phthalate (DEHP) contamination in wastewater and sludge of the Lithuania, Poland and Denmark.

This study found that the concentration of PAEs is very high in the vicinity of industrial parks, residential areas, and roadside drains, which shows that the concentration and distribution of PAEs in water are more affected by human activities.

Considering the risk of phthalates presence in the environment more studies are needed to identify and quantify the main sources of PAEs contamination and their dynamics, especially in Lithuania (Klaipeda) and Poland (Goleniow).

At the same time, the next step should be addressed to pollution by phthalate's prevention's challenge created on producers' and consumers' education, economic incentives application, and environmental management. Moreover, the findings may provide reliable data for decision-makers regarding phthalates reduction strategy's development in Lithuania, Poland, and similarly Eastern countries.

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