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The Assessment of the Sewage and Sludge Contamination by Phthalate Acid Esters (PAEs) in Eastern Europe Countries

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Abstract: Phthalate acid esters (PAEs) are widely used as raw materials for industries that are well known for their environmental contamination and toxicological effects as “endocrine disruptors”. The determining of PAE contamination was based on analysis of dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), dibutyl phthalate (DBP), diisobutyl phthalate (DiBP), dicyclohexyl phthalate (DCHP) and di(2-ethylhexyl) phthalate (DEHP) in wastewater and sediment samples collected from city sewer systems of Lithuania and Poland, and Denmark for comparison. The potential PAE sources as well as their concentrations in the wastewater were analyzed and discussed. The intention of the study was to determine the level and key sources of pollution by phthalates in some Eastern European countries and to reveal the successful managerial actions to minimize PAEs taken by Denmark. Water and sludge samples were collected in 2019–2020 and analyzed by gas chromatography-mass spectrometry. The highest contamination with phthalates in Lithuania can be attributed to DEHP: up to 63% of total PAEs in water samples and up to 94% of total PAEs in sludge samples, which are primarily used as additive compounds to plastics but do not react with them and are gradually released into the environment. However, in water samples in Poland, the highest concentration belonged to DMP—up to 210 µg/L, while the share of DEHP reached 15 µg/L. The concentrations of priority phthalate esters in the water samples reached up to 159 µg/L (DEHP) in Lithuania and up to 1.2 µg/L (DEHP) in Denmark. The biggest DEHP concentrations obtained in the sediment samples were 95 mg/kg in Lithuania and up to 6.6 mg/kg in Denmark. The dominant compounds of PAEs in water samples of Lithuania were DEHP > DEP > DiBP > DBP > DMP. DPP and DCHP concentrations were less than 0.05 µg/L. However, the distribution of PAEs in the water samples from Poland was as follows: DMP > DEHP > DEP > DBP, and DiBP, as well as DPP and DCHP, concentrations were less than 0.05 µg/L. Further studies are recommended for adequate monitoring of phthalates in wastewater and sludge in order to reduce or/and predict phthalates’ potential risk to hydrobiots and human health.



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Keywords: PAEs; potential sources; phthalate concentrations; compound distribution; regulation

1. Introduction

Phthalate acid esters are micro-pollutants of great public concern due to their negative impact on the 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.

Phthalate acid esters (PAEs) are used to increase a material’s flexibility, transparency, pliability, plasticity, strength, endurance and longevity [1–3]. 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 [4]. PAEs can account for up to 40% of the final plastic product [5]. 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) and adhesives. Phthalates are also included in apparel, furniture (PVC flooring), car and public transport interiors, cosmetics, medical devices, toys and baby care products, food and packaging materials such as drinking straws, and food containers [6–11]. 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 usage in aquatic systems, paints, glue, lubricants and plastic bags [7,9,12–16].

PAEs are not chemically bound to the host polymer and exposed to a higher temperature can easily migrate in the contact matrix, which may lead to the release from the life cycle of commercial and domestic products into the environment—air, water, soil and biota [4,10,17–27].

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 [9,28–31].

Hereby, phthalate acid esters can enter the water ecosystem through wastewater treatment plants (WWTP). Because of the high lipophilicity of PAEs, they tend to be adsorbed and concentrated to suspended organic matter and sludge and are removed through biodegradation [3,29,31–33]. In addition, the use of fertilizers, pesticides and 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 the food chain [34–36].

Moreover, PAEs are not persistent and readily biodegrade in the aquatic environment under aerobic and anaerobic conditions [36,37]. Higher molecular weight PAEs biodegrade more slowly than the lower molecular weight chemicals and may accumulate in the sediments [3,32,38].

PAEs are classified as carcinogenic, toxic and endocrine-disrupting compounds (EDCs) that cause adverse effects on the developmental stage of organisms [9,39–48].

Previous investigations have shown that PAEs have potential risk to human health and can cause reproductive problems, birth defects, children growth-disrupting effects, decreased testosterone levels, thyroid-disrupting effects, hormonal and endocrine disruptions, respiratory allergic symptoms, asthma and can even cause breast cancer [2,49–55]. Moreover, exposure to phthalate acid esters can adversely affect various human organs, such as the respiratory system, kidneys, liver as well as the endocrine system [56].

Consequently, six PAEs (DMP, DEP, DnBP, BBzP, DEHP, di-n-octyl phthalate (DnOP)) have been included in the priority list of pollutants by the European Union and the United States Environmental Protection Agency [41].

Effects of climate change as well as overuse and contamination put water resources under substantial pressure. The EU has some restrictions on the use of phthalates in materials and products. Therefore, industries should be prepared for and respond to the life cycle of their products. However, in Eastern European countries, many organizers of economic activity do not know what types of phthalates are released into the water and what their further qualitative and quantitative characteristics are. Taking into account the widespread use of PAEs and the evidence supported by scientific studies described in the literature, a research hypothesis was proposed. The hypothesis of this survey was that the primary level of pollution of wastewaters and their sludge by phthalates depends on domestic and industrial sources of pollution, and the higher the pollution, the more objects of economic activity are served. To clarify economic activity interactions with water pollution by PAEs in order to define their environmental impacts, the levels of DMP, DEP, DPP, DBP, DiBP, DCHP and DEHP in wastewater and sludge samples collected from domestic and industrial users were determined in 2019–2020.

Furthermore, in this paper, we present a comparative example of sewage pollution by microplastics in some Eastern European countries and Denmark that reflected the growing

awareness of the concern of wastewater monitoring and European legal requirement implementation regarding the manufacture, marketing and use of PAE compounds.

2. Materials and Methods

In 2019–2020 a total of 50 water and 8 sludge samples were collected from 50 locations in Lithuania, Poland and Denmark. Experimental data were expressed as the mean of 3 results. Details of each sampling site are included in Table S1, and sampling location maps are presented in Figures S1 and S2.

The Standard EN ISO 18856:2005 and ISO 18856:2004 (Water quality—Determination of selected phthalates using gas chromatography/mass spectrometry) specify a method for the determination of phthalates (Table 1) in water after solid-phase extraction and gas chromatography/mass spectrometry.

Table 1. List of phthalates that could be determined in the water by EN ISO 18856:2005 and ISO 18856:2004 standards.

Compound	Formula	Abbreviation	Molar Mass, g/mol	Method Detection Limit, µg/L	CAS-RN *
Dimethyl phthalate	C ₁₀ H ₁₀ O ₄	DMP	194.2	0.05	131-11-3
Diethyl phthalate	C ₁₂ H ₁₄ O ₄	DEP	222.2	0.05	84-66-2
Dipropyl phthalate	C ₁₄ H ₁₈ O ₄	DPP	250.3	0.05	131-16-8
Dibutyl phthalate	C ₁₆ H ₂₂ O ₄	DBP	278.4	0.05	84-74-2
Diisobutyl phthalate	C ₁₆ H ₂₂ O ₄	DiBP	278.4	0.05	84-69-5
Dicyclohexyl phthalate	C ₂₀ H ₂₆ O ₄	DCHP	330.4	0.05	84-61-7
Di(2-ethylhexyl) phthalate	C ₂₄ H ₃₈ O ₄	DEHP	390.6	0.05	117-81-7

* CAS-RN: Chemical Abstracts Service Registry Number.

This method could be used for the determination of phthalates in groundwater, surface water, wastewater and drinking water.

The principle of the water sample analysis method is solid-phase extraction of the compounds from the water. Then the separation is accomplished using capillary columns by the gas chromatography and followed by identification and quantification of the phthalates by mass spectrometry.

However, 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 phthalates in sludge, treated biowaste and soil, after extraction and gas chromatographic analysis with mass spectrometric detection (Table 1).

The principle of the sludge sample analysis method: the dried sample is extracted with ethyl acetate on the shaking device. An aliquot of the extract is cleaned with aluminum oxide (if necessary) followed by gas chromatographic separation using capillary columns and identification and quantification of the phthalates by mass spectrometry.

One-liter amber glass bottles with Teflon caps were used for sample collection to avoid exposure to light and contamination of plastic. Before taking the samples, bottles were washed with distilled water and acetone. Collected samples were extracted within 24–48 h with preservation at 4 °C [3]. Samples were taken from the sewer hatches where the mix of pipes from various activities was coming. Further, sludge samples were collected using a grab sampler and stored in special 0.5 L glass bottles at −20 °C. Sludge sample points:

- (1) Primary sludge—at the pumping station of the sludge gravity thickener;
- (2) Excess sludge—from the pipeline before secondary thickening;
- (3) Digestate—from the bottom of the sludge digester (biogas reactor);
- (4) Dried sludge—from the bottom of the dried sludge silage/bunker.

All experimental materials were made of borosilicate glass and were used after a series of cleaning processes. They were kept in a 10% hydrochloric acid bath for 24 h, rinsed with ultrapure water and finally rinsed with methanol and dichloromethane just before use.

The phthalate standards for DMP (99%), DEP (99%), DPP (99%), DBP (99%), DiBP (99%), DCHP (99%) and DEHP (98%) were purchased from Dr. Ehrenstorfer GmbH (Germany). Organic solvents such as acetonitrile and n-hexane were of HPLC-grade and obtained from Sigma-Aldrich (USA).

The analysis was performed using a Bruker SCION 436 gas chromatograph equipped with a SCION TQ/SQ mass spectrometer detector. Chromatographic separation was achieved using a SCION-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) with selected ion monitoring mode for quantitative determination. The flow rate of helium (a carrier gas, purity $\geq 99.999\%$) was 1.0 mL min^{-1} . The temperature of the GC-MS was as follows: initial $80 \text{ }^\circ\text{C}$, which was ramped to $180 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$, $230 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$ and $289 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C min}^{-1}$, with an isotherm hold of 5 min. Samples of $1 \mu\text{L}$ were injected in an automatic split-less injection mode at $289 \text{ }^\circ\text{C}$. Selected ion monitoring (SIM) data were acquired during the GC full scan electron MS analysis.

With every analysis regime, laboratory contaminations were adjusted by analysis of blank samples.

3. Results and Discussion

The concentrations of the DMP, DEP, DPP, DBP, DiBP, DCHP and DEHP in wastewater and sludge samples from Lithuania (Klaipeda), Poland (Goleniów) and Denmark (Rønne) sewer systems were analyzed in 2019–2020. WWTPs in Klaipeda, Goleniów and Rønne have similar mechanical and biological types of water cleaning. In order to find the common tendency of the level of the specific PAEs in sewage systems, the different pollution level sources and their cleaning at WWTPs with varied capacities were assessed. Klaipeda WWTP has the biggest capacity and serves domestic and industrial companies' sewage, while Goleniów and Rønne treat mostly domestic sewage and just a few industrial companies' effluents. In its turn, Rønne WWTP is similar to Goleniów but situated on the island and therefore has a direct impact on the surrounding hydro system. Such location demands specific attention to the quality of wastewater and sludge because, in the end, the ecology of the island depends on the state of the water ecosystem.

3.1. The Levels of PAEs in Wastewater and Sludge Samples Collected from Domestic and Industrial Users in Lithuania (Klaipeda).

All wastewater and sludge samples in Lithuania were taken from the places fitting to the unified Klaipeda sewage system. The Klaipeda WWTP is the main biological sewage treatment plant in Klaipeda, built in 1998, with a capacity of 305,333 population equivalent (PE). 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 (Klaipeda) was attributed to DEHP since it has the largest meaning in industrial production and consumption. Its concentration ranged from 0.05 to $159 \mu\text{g/L}$ at the water sampling points (Table 2). Due to the low water solubility and long side chain, DEHP is stable and difficult to be biodegraded [57,58].

The highest DEHP concentration of $159 \mu\text{g/L}$ and $112 \mu\text{g/L}$ was observed at the truck wash and laundry sampling points, respectively. The concentrations of other PAEs at these sampling points were also high. At the truck wash water sampling point, the concentration of DiBP reached $2.2 \mu\text{g/L}$, DBP $1.8 \mu\text{g/L}$, DEP $0.26 \mu\text{g/L}$ and DMP $0.18 \mu\text{g/L}$. However, at the laundry sampling point, DBP concentration reached $6.9 \mu\text{g/L}$, DEP $4.8 \mu\text{g/L}$, DiBP $3.3 \mu\text{g/L}$ and DMP $0.14 \mu\text{g/L}$. PAE compounds are included in lubricants that influence the truck wash sewage's pollution. Phthalates were detected in the content of detergents that explain the laundry's wastewater pollution by PAEs. Moreover, according to the Environmental Working Group (EWG), fragrances are considered to be among the top five allergens and can trigger asthma attacks. Testing by the EWG also revealed that 75% of the fragrances contain phthalates [59].

Table 2. Results of the phthalate analysis of water samples (Lithuania), 2019.

No	Sampling Point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP
		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
2	PET factory	<0.05	2	<0.05	0.11	1.2	<0.05	0.05
3	Klaipeda region landfill	<0.05	0.47	<0.05	0.1	0.78	<0.05	7.2
4	Furniture production	0.06	4	<0.05	0.14	1	<0.05	19
5	Shopping center I	0.6	17	<0.05	6.1	26	<0.05	14
6	Wood processing	<0.05	0.23	<0.05	<0.05	0.5	<0.05	14
7	Laundry services	0.14	4.8	<0.05	6.9	3.3	<0.05	112
8	Cruise ship terminal	<0.05	<0.05	<0.05	0.07	0.43	<0.05	0.12
9	Tobacco factory	<0.05	3.2	<0.05	<0.05	0.74	<0.05	2.1
10	Fish processing	<0.05	1.2	<0.05	0.15	1.0	<0.05	0.67
11	Shopping center II	0.17	78.0	<0.05	2.6	4.9	<0.05	50
12	Food factory	0.06	1.9	<0.05	<0.05	0.33	<0.05	1.2
13	Bread factory	1.4	5.5	<0.05	0.32	0.56	<0.05	26
14	Biodiesel (methyl ester) production plant	3.1	1.8	<0.05	34	2.7	<0.05	6.8
15	Energy supply, maintenance and repair services	<0.05	0.3	<0.05	0.1	0.48	<0.05	0.41
16	Hotel	0.05	9.6	<0.05	1.3	2.5	<0.05	4.8
17	Concrete production	0.06	0.25	<0.05	<0.05	0.64	<0.05	0.13
18	Beer factory	0.05	<0.05	<0.05	0.06	0.17	<0.05	0.8
19	Domestic sewage	0.08	3.1	<0.05	0.6	1.8	<0.05	40
20	Sewage pumping station II	0.07	0.84	<0.05	0.4	1.5	<0.05	9.7
21	Sewage pumping station VI	0.41	6.6	<0.05	0.14	1	<0.05	2.7
22	Sewage pumping station XVII	0.07	0.14	<0.05	0.14	1.1	<0.05	9.5
23	Sewage pumping station XIX	0.27	2.6	<0.05	0.07	0.47	<0.05	0.7
24	Republican Hospital	0.68	2.5	<0.05	0.18	0.79	<0.05	0.39
25	Kindergarten	<0.05	0.64	<0.05	0.45	0.9	<0.05	1.8
26	Truck wash services	0.18	0.26	<0.05	1.8	2.2	<0.05	159
27	Publishing-printing house	<0.05	1.7	<0.05	<0.05	0.34	<0.05	0.22
28	Sewage pumping station in Gargzdai II	<0.05	0.84	<0.05	0.07	0.34	<0.05	1.6
29	Care home	<0.05	4.2	<0.05	0.05	0.3	<0.05	0.44
30	District WWTP outlet	<0.05	0.07	<0.05	<0.05	0.11	<0.05	0.14
31	Klaipeda WWTP outlet	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
32	Klaipeda WWTP inlet	0.08	3.35	<0.05	0.68	2.35	<0.05	2.51

Meanwhile, near the shopping center II entity (located near several car washing and repair shops and catering companies), the concentration of DEHP was also very high—50 µg/L. Moreover, the concentration of the DEP at this sampling point reached 78.0 µg/L, DiBP 4.9 µg/L, DBP 2.6 µg/L and DMP 0.17 µg/L. Since DEHP makes up most of the production of PAEs such as plasticizers for PVC and is present in food packaging materials, kitchen utensils, gloves and cleaning products, it is easily washed off to the sewage system [60]. Phthalates can be easily released into the environment through production, use and utilization because the chemical bond between them and main plastics is non-covalent [61].

The results show that the concentration of DEHP at the domestic sewage sampling point reached 40 µg/L and was several times higher than at some industrial sampling points such as the 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. In accordance with the obtained results, the DEHP concentrations in other industrial and mixed sewage pumping stations ranged from 0.7 µg/L (No. 23) to 9.7 µg/L (No. 20). Although the number of employees at each of the above-mentioned enterprises is not small (average 500 employees), the biggest effect on 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. This predominant effect of phthalates in domestic effluents in comparison to industrial ones can be elucidated by some industrial sector similarity to household activities, especially such as various services, catering, food, furniture and textile treatment [62].

Finally, the concentrations of DEHP in water samples of Klaipeda and nearby city district WWTP outlets ranged from 0.07 to 0.14 µg/L. The wastewater treatment plant

ensures effective phthalate precipitation at least two times per wastewater cleaning process and phthalate concentrate in the sedimentation.

It was determined that DEHP concentration in the water near the shopping center I sampling point (samples were taken from the sewer hatches where the mix of pipes from various center activities was coming) 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 the shopping center. Active catering services and products' plastic packaging also contribute to the total PAE compounds' concentration in the sewage.

DEHP concentration was also measured in the regional dump of the Klaipeda region landfill. It was found that DEHP concentration in the 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 0.78 µg/L (DBP). Based on the statistics [63], the amount of plastic waste has a tendency to increase in the world (380 million tons in 2015), and taking into account the low DEHP biodegradability in the water, the DEHP concentration is higher than other measured phthalates [64].

Furthermore, the diversity of the DEP concentrations at industrial sampling points varied from 0.23 µg/L at the wood processing factory to 5.5 µg/L at the bread factory. Diethyl phthalate, as a low molecular weight PAE, can be found in industrial solvents, solvents in perfumes, pharmaceutical products, insecticide materials, adhesives, waxes, inks and cosmetics [65]. DEP is quite volatile but very slowly evaporates from its aqueous solution [66] and is expected to be degraded by microorganisms of biological WWTP.

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

In this study, the distribution of total PAEs in the sludge samples was as follows: digestate sludge > primary sludge > dried sludge > excess sludge (Table 3). The highest concentrations of these samples were related to DEHP, where concentrations ranged from digestate sludge (95.0 mg/kg) to excess sludge (3.8 mg/kg). After sludge biodegradation in the biogas reactor, the sludge volume is decreased at least by one-third of the initial one, and the phthalates' concentration becomes higher in digestate sludge. The analysis of the sludge contamination by PAEs after the drying process showed a significant reduction in the DEHP. The most likely mechanism to explain the loss of DEHP in the sludge during the drying process is volatilization [67,68]. It is reported that the rates of the DEP and DEHP degradation in the sediments are very low and depend on pH, temperature, surfactants, pollutants and microbial inhibitors [41].

Table 3. Results of the phthalate analysis of sludge samples (Lithuania), 2019.

No	Sampling Point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP
		mg/kg						
33	Primary sludge	<0.05	0.52	<0.05	2.4	4.1	<0.05	23
34	Excess sludge	<0.05	<0.05	<0.05	0.25	0.7	<0.05	3.8
35	Digestate	<0.05	<0.05	<0.05	<0.05	0.6	<0.05	95
36	Dried sludge	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	16

It was found that DPP and DCHP phthalate concentrations in all water and sludge (except for the Klaipeda WWTP primary sludge sample with a slightly higher concentration of 0.052 mg/kg) samples were less than 0.05 mg/kg.

3.2. The Levels of PAEs in Wastewater Samples Collected from Domestic and Industrial Users in Poland (Goleniów).

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, where sewage from a supermarket and industrial area is collected before transferring it to the sewage treatment plant (Table 4). 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 reached 15 µg/L and 1.8 µg/L, respectively. The well-known method for phthalate removal from water is a biological treatment based on PAE aerobic and/or anaerobic degradation by microorganisms [69]. The obtained PAE concentrations showed that long-chain alkyl is quite resistible and requires effective biological treatment.

Table 4. Results of the phthalate analysis of water samples (Poland), 2020.

No	Sampling Point	DMP	DEP	DPP	DBP	DiBP	DCHP	DEHP
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
0	Treated wastewater outlet to the river Sewage pumping station. Source: cosmetics	<0.05	N/A	N/A	N/A	N/A	<0.05	8.1
1	company, concrete plant, catering, laundry, processing of furskins	1.1	2.2	<0.05	0.92	0.21	<0.05	2.6
2	Sewage pumping station. Source: restaurants, café	N/A (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
4	Manhole. Sewage from: restaurants, hairdresser, beautician	<0.05	3.7	<0.05	0.68	0.92	<0.05	8.8
5	Manhole. Source: restaurants, café	0.18	0.22	<0.05	0.70	0.12	<0.05	0.44
6	Sewage pumping station. Source: supermarket, market, restaurants, café	210	15	<0.05	0.27	0.46	<0.05	1.8
7	Manhole. Source: shopping center, production of cardboard packaging, train station	<0.05	3.0	<0.05	0.54	0.84	<0.05	15
8	Manhole on the sewage treatment plant. Source: industrial park	0.94	7.7	<0.05	0.52	0.31	<0.05	2.7
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

However, it was determined that the total concentrations of seven PAEs in the sewage No. 1 of the industrial park was much lower. It could be explained by a variety of a 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 compounds at this sampling point.

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

Wastewater treatment plants have an important role in the reduction of the risk of micropollutants, such as phthalates [70]. The dominant PAEs in the inlet of the sewage treatment plant No. 9 were DEHP > DEP > DiBP > DBP. DMP, DPP and DCHP concentrations were less than 0.05 µg/L.

It is important to state that the concentration of DPP and DCHP at all sampling points was less than 0.05 µg/L, which is in accordance with the proposition of the other scientists [71] and based on a small industrial/domestic sewage proportion at the wastewater treatment plant.

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

3.3. The Levels of PAEs in Wastewater and Sludge Samples Collected from Domestic and Industrial Users in Denmark (Rønne)

Rønne WWTP is the largest of the seven biological WWTPs in Denmark, built in 1995, with a 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 the inlet and outlet of sampling stations during the summer of 2020 in order to analyze the efficiency of the WWTP regarding phthalate reduction based on biotechnological sewage treatment.

The results of Rønne's wastewater pollution by phthalates are presented in Table 5. The analysis of the data showed the main trends of the PAE compound amounts' distribution in the samples. The predominant quantity of the DEHP and following DEP concentrations are in the same proportion as in above-analyzed Lithuanian and Polish WWTPs and reflect the common tendency of sewage pollution for small and middle-sized water treatments. The positive alteration of the total amount of PAEs after sewage treatment at Rønne WWTP does not connect with special or additional sewage handling. The reduction of the total phthalate concentration at the wastewater outlet point supports the statement that the biological water treatment and its microorganisms have the main role in phthalate concentrations' decline [70]. These results confirm the hypothesis that sustainable maintenance of biological wastewater treatment is an essential factor of micro-organic pollutant diminishing under present conditions.

Table 5. The concentration of phthalates in samples of the wastewater (Rønne, Denmark), 2020.

	CAS-RN	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

The distribution of PAEs in the water samples of Rønne WWTP was as follows: DEHP > DEP > DBP > DiBP. DMP, DPP and DCHP concentrations were less than 0.05 µg/L. A similar trend has been reported in the review by Chinese scientists [58].

It is well-known that wastewater pollution can be judged by the quality of the sludge. Such an organic pollutant as DEHP is an oily organic carcinogen, can slightly (0.27 mg/L at 25 °C) dissolve in water [72] and has the inclination to bind to the sludge. The main samples for the determination of the Rønne wastewater quality came from the inlet and outlet of the Rønne sewage system. Besides that, the results of the samples of sludge, which were collected on-site for DEHP determination every month then mixed and analyzed every three months, were taken into account for correct evaluation of the sludge pollution by DEHP at Rønne WWTP in 2019 (Figure 1).

The DEHP concentration increased twice during the year. The analysis of the data presented in Figure 1 showed that the amount of phthalates in the sludge has a tendency to change during the year, but there is no seasonal relationship [73]. The main reasons for an increase in the concentration of DEHP in sludge depend on the quality of wastewater, especially its industrial component, the type of treatment facilities and their efficiency.

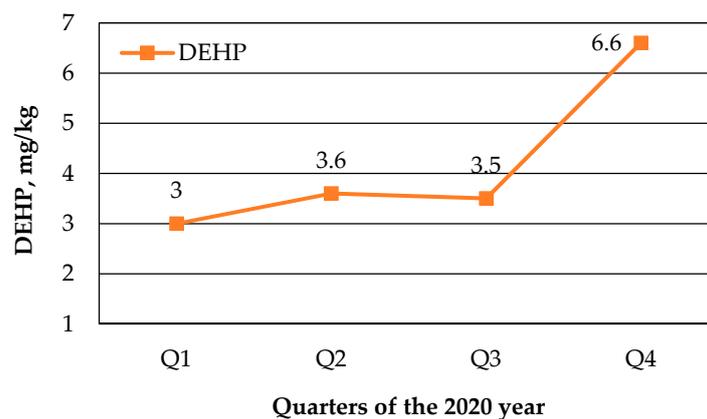


Figure 1. DEHP concentrations in the Rønne WWTP dewatered sludge in 2020.

3.4. Obtained Data and Conditions Comparison

The study results show that three various capacity wastewater systems, situated in three different places have common trends in the wastewater and sludge pollution by PAEs.

The most evident finding is related to the hypothesis that the level of sewage contamination depends on domestic and industrial pollution sources and is higher as more economic activity objects are served by WWTP. For instance, the bigger-capacity Klaipeda WWTP should clean the sewage of the objects whose DEHP and DEP concentrations in the sewage reached, respectively, 112 and 78 $\mu\text{g/L}$ and depend on a big shopping center and combined household services. The contribution of the specific industry of biodiesel production is reflected in DBP concentration (34 $\mu\text{g/L}$). A similar pollution tendency was observed in the Goleniów sewage system. A bigger amount of DEHP and DEP are also coming with shopping centers and household services objects' sewage (15 $\mu\text{g/L}$). The samples' analysis done at Rønne WWTP showed that among PAE compounds, DEHP concentration in the inlet is the highest (1.2 $\mu\text{g/L}$).

Therefore, the next important output is connected to the determination of the DEHP as the predominant phthalate compound in the sewage. In Klaipeda as well as Rønne sewage, the DEHP concentrations are the highest. However, in Goleniów, the biggest amount of PAEs belongs to DMP (210 $\mu\text{g/L}$). It falls short against Klaipeda and Rønne data as well as Western Europe and China scientists' reports [58]. Due to the fact that, in water, the DMP loss mechanism is related to biodegradation [3,29,31–33] and anaerobic condition, it could be suggested that the sampling condition or sewage biological treatment were temporarily damaged. The low DMP concentration at the Goleniów outlet point supports our assumption and confirms that the DEHP amount in the sewage is a broad issue.

It was found that although the DEHP concentration in the wastewater from different sources is high, it is still possible to significantly reduce pollution by PAEs using biological water treatment [62,64]. The concentration of DEHP at the outlet of Klaipeda and Rønne wastewater treatment plants is 0.07 $\mu\text{g/L}$, which is less than the Lithuanian limit for treated wastewater entering surface waters (<2 $\mu\text{g/L}$). The DEHP concentration in the outlet point of Goleniów WWTP was 8.1 $\mu\text{g/L}$, but officially there is no limit for DEHP concentration for the treated water in Poland. The evaluation of the wastewater sludge's contamination by PAEs was available at Klaipeda and Rønne WWTPs. In both cases, sludge pollution by DMP, DEP, DPP, DBP, DiBP, DCHP and DEHP were investigated and showed the biggest pollution by DEHP. The biggest concentration of the DEHP in Rønne's dewatered sludge was 6.6 mg/kg. Taking into consideration that Klaipeda WWTP technology includes excess sludge use for biogas production and digestate drying for further utilization, PAE pollution analysis was performed for four types of sludge. A significant amount of DEHP was found in digestate (95 mg/kg), but due to the drying process, DEHP concentration decreased six times to 16 mg/kg [67,68]. The comparison of the sludge pollution level in Klaipeda and Rønne was demonstrated to be effective Danish sludge quality management for its lasting utilization. Furthermore, the smallest,

among three target systems, amount of the DEHP in the sewage and its sludge in Rønne demanded sustainable environmental management decisions during a long period of time in accordance with the Danish review regarding sludge operation in 1993–2003, and the amount of sludge production had a tendency to reduce [74]. Regarding the DEHP amount in the sludge, the cut-off value for this compound (50 mg/kg d.w.) caused an important decrease of this contaminant. As a result, in 2003, more than 95% of sludge had a phthalate concentration below the cut-off criteria and was suitable for agricultural purposes [75]. Figure 1 data also confirm the positive trend of the DEHP concentration diminishing at the Rønne WWTP sludge from 2016 to 2020. Perhaps, such result was a 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 a voluntary agreement with manufacturers for the environmentally friendly alteration in products' production and use. Total/partial prohibition of PAEs, stricter standards, emission controls, environmental labeling, green guidelines and information campaigns, as well as the guideline for manufacturers and taxation, were the main actions, which helped to reduce the PAEs in the environment [76].

Although Denmark, Lithuania and Poland follow the same EU regulations on phthalates, the measurement results indicated differences in phthalate amounts in the sewage and sludge of Eastern countries and Denmark. Furthermore, in Denmark, there is a special regulation about toys, which, since 1999, has banned the manufacturing, import and selling of toys and certain articles for young children with phthalates, especially for children under three 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 have 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 16 January 2007, the sale of these products has also been banned.

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

The recent European document, which could affect the wastewater and sludge quality, is the 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) [77]. It is expected that this restriction will help to reduce such PAEs as DEHP, BBP, DBP and DIBP in consumer products in the EU market and respectively diminish the air, water, soil and sediment contamination by target organic pollutants.

4. Conclusions

The current study revealed the emergence of the phthalate acid esters in the aquatic environment originating due to extensive plastics' commercial and domestic usage.

The conducted research disclosed as well, the influence of economic activity on the pollution of the sewer system by PAEs.

It was found that the biggest PAE sources were concentrated in the vicinity of industrial parks, residential areas and roadside drains at some instances with emerging concentrations above the maximum permissible concentrations.

It was found that there is not a lot of research based on PAE analysis in Eastern countries' sewer systems while Western Europe, USA and China sewage systems are well investigated. This comparative analysis of the level of wastewater and sludge pollution by DMP, DEP, DPP, DBP, DiBP, DCHP and DEHP of sewage systems situated in Eastern countries (Lithuania, Poland) and Denmark is a major contribution to knowledge in this field.

It was determined that the DEHP is the predominant PAE in Eastern countries and Denmark's sewage systems as well as in Western Europe countries due to its widespread utilization and low solubility in water.

It was assessed that the Danish and the Lithuanian biological wastewater treatment facilities were more effective for lowering the concentration of DEHP and other analyzed PAEs in the outlet comparing to facilities in Poland.

It was found that during the phase of sludge drying, an effective reduction of DEHP concentration is achieved, based on the organic compound volatilization process.

It was disclosed that the investigated Danish wastewater and sludge were less polluted by DEHP and other analyzed PAEs in comparison to the Lithuanian or Polish wastewater and sludge.

It was displayed, that an active Danish Environmental Protection Agency policy and strategy grounded on numerous legal, educational and managerial actions boosts a new behavior in PAE use and disposal.

The research findings may provide reliable data for decision-makers regarding a phthalate reduction strategy's development in Lithuania, Poland and other countries based on a precedent of successful PAE pollution prevention policy in Denmark.

Considering the risk of phthalates' presence in the environment, more studies are needed to determine PAE; contamination dynamics in Eastern countries.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2071-1050/13/2/529/s1>, Figure S1: Map of the location of the sampling sites in Poland, Figure S2: Map of the location of the sampling sites in Lithuania, Table S1: Sampling site description.

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