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Phthalate esters delivery to the largest european lagoon: sources, partitioning and seasonal variations

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1	PHTHALATE ESTERS DELIVERY TO THE LARGEST EUROPEAN
2	LAGOON: SOURCES, PARTITIONING AND SEASONAL VARIATIONS
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### 30 Abstract

31 Phthalate esters (PAEs) due to their ability to leach from plastics, widely used in our daily life, are 32 intensely accumulating in wastewater water treatment plants (WWTP) and rivers, before being exported to downstream situated estuarine systems. This study aimed to investigate the external 33 34 sources of eight plasticizers to the largest European lagoon (the Curonian Lagoon, south-east Baltic Sea), focusing on their seasonal variation and transport behaviour through the partitioning between 35 36 dissolved and particulate phases. The obtained results were later combined with hydrological inputs 37 at the inlet and outlet of the lagoon to estimate system role in regulating the transport of pollutants to 38 the sea. Plasticizers were detected during all sampling events with a total concentration ranging from 0.01 to 6.17  $\mu$ g L<sup>-1</sup>. Di(2-ethylhexyl) phthalate (DEHP) was the most abundant PAEs and was mainly 39 40 found attached to particulate matter, highlighting the importance of this matrix in the transport of 41 such contaminant. Dibutyl phthalate (DnBP) and diisobutyl phthalate (DiBP) were the other two 42 dominant PAEs found in the area, mainly detected in dissolved phase. Meteorological conditions 43 appeared to be an important factor regulating the distribution of PAEs in environment. During the 44 river ice-covered season, PAEs concentration showed the highest value suggesting the importance of 45 ice in the retention of PAEs. While heavy rainfall impacts the amount of water delivered to WWTP, 46 there is an increase of PAEs concentration supporting the hypothesis of their transport via soil 47 leaching and infiltration into wastewater networks. Rainfall could also be a direct source of PAEs to 48 the lagoon resulting in net surplus export of PAEs to the Baltic Sea.

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- 51
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- 53 Phthalate esters (PAEs),
- 54 Suspended matter,
- 55 Curonian Lagoon,
- 56 Wastewater Treatment Plants,
- 57 Seasonal variation
- 58
- 59

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# 64 1. Introduction

Phthalate esters (PAEs), also known as phthalates, is a group of emerging pollutants frequently used 65 as additives to modify physical properties (resistance and mouldability) of plastic materials. Their 66 presence in synthetic polymers, especially in polyvinyl chloride (PVC), makes them the most widely 67 68 used plasticizers worldwide (Rahman and Brazel, 2004). PAEs are also used as additives in many 69 daily used products, such as cosmetics, children's toys, kitchen floors, vinyl wall coverings, wires 70 and cables, food packaging, medical devices, and automobile parts (Gómez-Hens and Aguilar-71 Caballos, 2003; Rahman and Brazel, 2004) However, PAEs are not chemically bound to the plastic 72 matrix and exist in a free-mobile and leachable phase. Due to widespread use and ability to leach 73 from various products, PAEs are considered as ubiquitous environmental contaminants. They are 74 discharged mainly through domestic, agricultural, and industrial effluents to downstream situated 75 coastal areas, where they can be easily found in different ecosystem elements including water column, 76 sediments, aquatic organisms, and thus ultimately enter the food chain (Fatoki and Noma, 2002; 77 Labunska and Santillo, 2004; Latini, 2005; Liu et al., 2014; Wang et al., 2014).

78 However, PAEs in high concentrations can have adverse health consequences, such as 79 carcinogenic, teratogenic and mutagenic effects for human and wildlife. They can also act as 80 endocrine disruptors and induce damage to the reproductive system (Dearman et al., 1996; Srivastava 81 et al., 2010; Adeniyi et al., 2011; Net et al., 2014). Some PAEs were found to have acute or chronic 82 effects (i.e., mortality, growth inhibition, effect on reproduction or respiration inhibition) among 83 aquatic microorganisms, algae, invertebrates, and fishes (Staples et al., 1997), such consequences 84 could potentially affect the ecosystem functioning. Due to PAEs potential health and environmental 85 risks, six PAEs (dimethyl phthalate [DMP], diethyl phthalate [DEP], dibutyl phthalate [DnBP], butyl 86 benzyl phthalate [BBzP], di(2-ethylhexyl) phthalate [DEHP], di(n-octyl) phthalate [DOP]) have been 87 included as priority pollutants by the United States Environmental Protection Agency (USEPA), the 88 European Union (EU) and Chinese waters list. EU proposed a guideline for environmental quality of 1.3  $\mu$ g L<sup>-1</sup> for DEHP in fresh and marine waters (Net et al., 2015). Consequently, the monitoring of 89 90 PAEs in various environmental matrices has become a necessity.

Aquatic environments, especially estuarine systems which act as the interface between land and sea, receive significant amounts of organic micropollutants through the large catchment runoff, wastewater discharge, and atmospheric precipitation, which seriously threaten these ecosystems (Li et al., 2017; Liu et al., 2023; Wu et al., 2023). The primary source of PAEs to estuarine systems is untreated or insufficiently treated municipal and/or industrial wastewater (European Environmental Agency, 2019; Schmidt et al., 2021; Keriene and Maruška, 2022). However, input of PAEs through the rivers can often exceed that of waste water due to higher river discharge (Dargnat et al., 2009a).

98 Considering a great hydrophobic nature of PAEs, they can be extensively adsorbed by organic and 99 inorganic suspended particles in water column, which allows transport over longer distance before accumulating in sediments (Chen et al., 2017, Staples et al., 1997b). Depending on the hydrodynamics 100 101 of estuarine systems, some particulate-bound PAEs can settle to surface sediment, where they are mineralised, buried or later released back to water column (Paluselli and Kim, 2020; Hidalgo-Serrano 102 103 et al., 2022; Liu et al., 2023). Therefore, estuarine systems can act as a trap or source for PAEs on 104 their way to the open sea or ocean. The interplay between urbanization, commercial activities, and 105 the effects on wildlife and human health in the estuarine systems is a societal concern and calls for 106 an urgent management and sustainable use of these ecosystems (Adeogun et al., 2015). In Europe, 107 most studies on PAEs have been focused on coastal systems subjected to tidal influence and high 108 salinity variations (Prieto et al., 2007; Schmidt et al., 2021), but the distribution of PAEs in northern 109 oligohaline systems with long water turnover remains understudied.

110 In present study, the external inputs of eight plasticizers were monitored via river, seawater 111 inflow and wastewater effluents discharge to the largest European lagoon, the Curonian Lagoon. 112 Consequently, the aims of this study were (1) to quantify the external sources of targeted plasticizers 113 (DMP, DEP, DnBP, BBzP, DEHP, DOP, diisobutyl phthalate (DiBP), and bis-2-ethylhexyl adipate (DEHA)) discharged to the lagoon and exchange with a sea, by measuring their monthly 114 115 concentration in water column, (2) to evaluate the partitioning of PAEs in the water column between dissolved and particulate phases, and (3) to assess the seasonal patterns of PAEs distribution under 116 different hydrometeorological conditions. By combining concentration measurements to hydrological 117 118 inputs, the loads of PAEs were also estimated, highlighting the role of lagoon in regulating PAEs 119 transport. To our knowledge, only few studies have performed PAEs analysis in oligohaline, 120 microtidal estuarine ecosystems. The elucidation of PAEs origin, transport and fate in the largest 121 European lagoon will help to better understand the role of estuarine systems in regulating their load 122 to adjacent coastal sites, and will provide a scientific basis for formulating recommendations for 123 environmental monitoring programs.

124

### 125 **2. Material and methods**

126 2.1. Study site and sampling collection

127 The Curonian Lagoon is a large (1,584 km<sup>2</sup>), shallow (mean depth 3.8 m), microtidal estuarine system

128 situated along the SE Baltic coast (Fig. 1). Freshwater input to the lagoon is dominated by the

129 Nemunas River accounting for 96% of total inputs and representing the fourth largest tributary to the





Fig. 1. Location of sampling stations in the study area.

Baltic Sea (Jakimavičius and Kriaučiūnienė, 2013; HELCOM, 2015). The river basin has a total area
of 97,864 km<sup>2</sup> draining urban (over 5 million inhabitants), agricultural, and industrial areas over three
countries (Lithuania Republic, Belarus, Russian Federation). The Curonian Lagoon also receives
direct discharge from different wastewater treatment plants (WWTPs) along its perimeter. The largest
point source discharging to the lagoon is Klaipėda city WWTP (population 200,000). Additionally,

the temporal movement of the population to the coast during the touristic season (from June to September) impacts the discharge from the small WWTPs located on the Curonian Spit. The lagoon discharges to the Baltic Sea through a single narrow strait at Klaipėda.

140 Water samples were collected monthly from June 2021 to May 2022 at the lagoon inflow (Nemunas River - IN) and outflow (Klaipėda Strait - OUT), and from the 3 WWTPs (Nida - WN, 141 142 Juodkrantė – WJ, and Klaipėda city - WK) situated around the lagoon perimeter (Lithuanian part; 143 Fig. 1). The sampling strategy was based on previous studies carried out by Vybernaite-Lubiene et 144 al. (2017, 2022) and Zilius et al. (2018), which were designed to estimate targeted compound inputs 145 to the lagoon and its exchange with the sea. Integrated water samples, representing entire water column, were transferred to pre-treated borosilicate glass bottles (1 L). Effluent samples (1 L) at each 146 147 WWTP were collected in triplicates in outflow channel using a telescopic sampler. Thus, in total, 180 freshwater and waste water samples (12 months, 5 sampling sites, 3 replicates) were collected over 148 studied period. In order to avoid contamination, plastic material was excluded during all the 149 150 procedures. Water temperature and salinity was measured only at lagoon inflow and outflow using 151 YSI 460 multiple probe (YSI incorporated, USA) and CTD 90 (Sea & Sun Technology, Germany), respectively. All samples were cooled with ice packs and transported to the laboratory within the hour 152 153 for subsequent analyses.

### 154 2.2. Chemicals and materials

155 The eight plasticisers analysed in this work were DMP, DEP, DnBP, BBzP, DEHP, DOP, DiBP, and DEHA (Table 1). We acknowledge that DEHA is not a part of PAEs, however since PAEs are under 156 157 strict regulations in Europe, many manufacturers have decided to replace them by phthalate free alternative such as adipate, increasing ultimately their use in plasticizer market and environment 158 (Nagorka and Koschorreck, 2020). Due to a simplicity in the text we accounted DEHA as a sum of 159 160 PAEs. The single standards for each compound (purity grade >98%) and internal standards D4-ring deuterated dibutyl phthalate (D4-DBP) and D4-ring deuterated di-n-octyl phthalate (D4-DnOP) were 161 purchased from HPC Standard GmbH (Germany). Capillary grade ethyl acetate (EA), supratrace 162 grade dichloromethane (DCM), and supergradient grade methanol (MeOH) were purchased from 163 VWR International GmbH (Austria). The solution of single plasticizer (1g  $L^{-1}$ ) and the mixed stock 164 solution (10 mg  $L^{-1}$ ) were prepared in EA and stored in the dark at -20 °C until analysis. 165

#### 167 **Table 1**

#### 168 Physicochemical properties of target plasticisers.

	Name	Acronym	Molecular weight (g mol <sup>-1</sup> )	Boiling point(°C)	Vapour pressure <sup>a</sup> (mmHg)	$egin{array}{c} { m Log} \ { m K_{ow}}^a \end{array}$	Target ion (m/z)	Qualifier ions (m/z)	$MDL^b$ (µg $L^{-1}$ )
1	Dimethyl phthalate	DMP	194.2	282	2x10 <sup>-3</sup>	1.61	163	194-133	0.06
2	Diethyl phthalate	DEP	222.2	298	$1 \times 10^{-3}$	2.38	149	177-222	0.06
3	Di-iso-butyl phthalate	DiBP	278.3	327	2.9x10 <sup>-4</sup>	4.11	149	223	0.05
4	Dibutyl phthalate	DnBP	278.3	340	$2.7 \times 10^{-5}$	4.45	149	223-278	0.03
5	Butyl Benzyl phthalate	BBzP	312.4	370	5x10 <sup>-6</sup>	4.59	149	206-312	0.03
6	Di(2-ethylhexyl) adipate	DEHA	370.6	417	-	-	129	57-147	0.02
7	Di(2-ethylhexyl) phthalate	DEHP	390.6	386	$1 x 10^{-7}$	7.5	149	167-279	0.04
8	Di(n-octyl) phthalate	DnOP	390.6	380	$1 x 10^{-7}$	8.06	149	279-261	0.04

169 K<sub>ow</sub>: octanol–water partition coefficient

170 <sup>a</sup> Data from Staples et al., 1997b

171 <sup>b</sup> Method Detection limit (MDL) = 3\*Ss (Ss – sample standard deviation of n replicates spiked sample analyses; n=10).

#### 172 2.3. Sample treatment

#### 173 2.3.1. Dissolved phase analysis

174 Water samples (500 mL) were filtered through a pre-combusted (6 h at 500 °C) GF/F filters (0.7 µm 175 nominal pore size; Frisenette, Denmark) to separate dissolved and particulate-bound phases. The filtered water was slightly acidified (pH between 2 and 5) using concentrated analytical grade 176 177 hydrochloric acid (VWR International GmbH, Austria). The extractions were performed following 178 the standard method EN ISO 18856:2005 (European Committee for Standardization, 2005). Briefly, 179 solid-phase extraction (SPE) was performed with C18ec cartridges (Chromabond®, 6 mL/500 mg) 180 to extract the plasticizers from the water samples. Cartridges were preliminary rinsed with one bed 181 volume of EA, dried with a gentle stream of N<sub>2</sub> gas, and then conditioned with two bed volumes of 182 MeOH. The glass bottles containing 500 mL of samples spiked with internal standard, were connected 183 with the conditioned cartridges via Chromabond® tubing adaptors. The water sample was passed through the cartridge at a flow rate of 2 mL/min using a vacuum pump. When the extraction was 184 185 completed, the cartridge was dried with N<sub>2</sub> and eluted with 2 mL of EA. In addition, 20 mL of nonacidified filtrate (only river and lagoon samples) was used for dissolved organic carbon (DOC) 186 187 analysis. DOC was analysed by the high temperature (680 °C) combustion catalytic oxidation/NDIR method using a Shimadzu TOC 5000 analyser. An anilide dilution series was used as a standard 188 189 (Cauwet, 1999).

190 2.3.2. Particulate phase analysis

191 The GF/F filters with precipitated suspended particulate matter (SPM) were dried at 60 °C for 3h 192 prior to analysis. Then filters were spiked with the internal standard and ultrasonically extracted two 193 times for 10 min with 10 ml of DCM using an ultrasonic homogeniser Bandelin Sonoplus HD 4200 equipped with TS103 probe (BANDELIN electronic GmbH & Co. KG, Germany). DCM was then
evaporated and PAEs were dissolved in 1.5 mL of EA. Prior to GC-MS analysis, the extracts were
filtered through 0.22 µm PTFE filters (Frisenette, Denmark).

#### 197 2.4. GC-MS analysis

198 Samples were analysed using a Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu 199 GCMS-TQ8040 mass spectrometer. The gas chromatograph was equipped with a Restek® Rxi-5Sil 200 MS (5% polydiphenylsiloxane, 95% polydimethylsiloxane) capillary column (30 m  $\times$  0.25 mm 201 internal diameter and 0.25 µm film thickness). Helium was used as carrier gas at a constant flow rate 202 of 1 mL/min; the GC injector was operated in splitless mode at 250 °C. Oven temperature program 203 was as follows: 60 °C, held for 2 min, 240 °C at 25 °C/min., held for 2 min., and 300 °C at 10 °C/min 204 held for 3 min. The mass spectrometer was equipped with an electron ionization ion source (70 eV). Transfer line and ion source were maintained at 280 °C and 230 °C, respectively. GC-MS analyses 205 206 were carried out under selected ion monitoring (SIM). The current of the ions used for identification 207 and quantification purposes is reported in Table 1.

### 208 2.5. Quality control and quality assurance

To avoid background pollution, the laboratory equipment used for sampling and analysis, was exclusively made of glass, stainless steel and polytetrafluoroethylene (PTFE). Each sample was analysed in triplicates in the case of dissolved phases, whereas 5 replicates were performed when particulate phases had to be analysed to improve repeatability. Prior to use, all glass apparatus was soaked in HCl (10%) for 12 h, rinsed with distilled water, dried, burned at 500 °C for 6 h, and finally pre-rinsed with MeOH.

215 For each batch of samples, procedural blanks and instrumental blanks were performed. To 216 monitor instrumental variations, control samples (mixed PAEs working solution at 30  $\mu$ g L<sup>-1</sup> and 100 217  $\mu$ g L<sup>-1</sup>; EPA 506 phthalate Mix, Sigma Aldrich) were injected at regular intervals and monitored in a "X-diagram". In order to verify the applicability of the EN ISO 18856: 2005 method, the agreement 218 219 between the precision calculated by the laboratory with that reported in the normalized method was 220 assessed by performing 15 replicated measurements. The method detection limit (MDL) and method 221 quantification limit (MQL) were calculated according to the following equations: MDL = 3\*Ss and 222 MQL = 10\*Ss for each PAEs (Ss – sample standard deviation of n replicates spiked sample analyses; 223 n=10) by using spiked sample solutions. For each analyte, linearity was assessed on 6 concentration levels (3 replicate measurements per level) in the 10–200  $\mu$ g L<sup>-1</sup> range. Mandel's fitting test was used 224 to assess linearity. Trueness was assessed by the participation to a proficiency test program (AGLAE 225 226 Association, France) for natural water and wastewater obtaining satisfactory results for all tested analytes (DMP, DEP, DiBP, DnBP, DEHP, DOP) with recovery rates from 70% for DMP to 105%for DnBP.

#### 229 2.6. Data analysis

The concentrations of each compound were measured separately in the dissolved ( $\mu g L^{-1}$ ) and 230 particulate phases ( $\mu g g^{-1}$  dry weight). Volumetric concentration of particulate phase ( $\mu g L^{-1}$ ) was 231 calculated by multiplying from the SPM concentration. A total concentration of PAEs was obtained 232 233 by sum of dissolved and particulate phases. Riverine inputs were calculated from monthly measurements of PAEs concentration and daily discharge of the Nemunas River using previously 234 235 described methods for the lagoon (Zilius et al., 2018). Discharge data were provided by the Lithuanian 236 Hydro-meteorological Service. Inputs from WWTPs were calculated from monthly measurements of 237 PAEs concentration and daily discharge. Effluents discharge data were provided by AB "Klaipedos Vanduo" and UAB "Neringos Vanduo". Net PAEs fluxes between the lagoon and the Baltic Sea were 238 239 derived using estimates of hydrologic exchange obtained from a hydrodynamic model (SHYFEM; 240 http://www.ismar.cnr.it/shyfem) previously calibrated for this site (Umgiesser et al., 2016). This 241 approach was previously used to estimate nutrient exchange between lagoon and sea (Zilius et al., 2018; Vybernaite-Lubiene et al., 2022). Fluxes were derived based on the volume of exchange 242 243 between the lagoon and Baltic Sea and measurements of PAEs concentration in the outflow. Inputs 244 were expressed as an absolute unit (tons month $^{-1}$ ).

The linear regression was used to predict PAEs concentration based on selected environmental variables (salinity, debit, SPM and DOC). The assumption of data normality was checked using Shapiro-Wilk test. In the case of heteroscedasticity, data were log(x) transformed. The significance level was set at  $\alpha = 0.01$ . Analyses were performed using R Statistical Software. All graphical work was done using the SigmaPlot 14.0 software.

250

251

# 3. Results and discussion

252 3.1. Determination of PAEs in lagoon inputs and outflow

Prior to the use of a normalized method containing reproducibility data, an analytical laboratory has to verify the compliance between the repeatability calculated by the laboratory with that reported in the method. Since a good agreement was observed, the EN ISO 18856:2005 method was applied to determine PAEs in inputs to the Curonian Lagoon. MDL and MQL values for targeted plasticizers ranged from 0.02  $\mu$ g L<sup>-1</sup> to 0.06  $\mu$ g L<sup>-1</sup> and 0.08  $\mu$ g L<sup>-1</sup> to 0.19  $\mu$ g L<sup>-1</sup> respectively, thus proving the reliability of the method for the determination of PAEs at trace levels. PAEs were detected during all sampling events with concentration levels in the 0.02–6.17  $\mu$ g L<sup>-1</sup> range, regrouping dissolved and particulate-bound DMP, DEP, DiBP, DnBP, BBzP, DEHA, DEHP, and DOP (Fig. 2). These findings
are in line with the contamination levels usually found in Europe (Bergé et al., 2013 and Table 2).
Obviously, the concentrations of PAEs varied among sampling sites and were dependent on specific
environmental conditions, such as heavy rainfall or ice cover.

264 More precisely, the concentration of PAEs in the main lagoon tributary, the Nemunas River, ranged from 0.01  $\mu$ g L<sup>-1</sup> (July 2021) to 0.25  $\mu$ g L<sup>-1</sup> (May 2022) on average (Fig. 2A). However, in 265 January 2022, the average concentration of PAEs tripled up to 0.74  $\mu$ g L<sup>-1</sup> when water samples were 266 267 collected under congestions of frozen snow. This behavior could be explained taking into account 268 that snowfall could be a hotspot of PAEs as it can efficiently trap organic contaminants from the 269 atmosphere thus concentrating them in a frozen layer before their release to surrounding water during 270 melting process (Lei and Wania, 2004; Meyer and Wania, 2008). At the lagoon outlet, PAEs 271 concentration was generally higher than in the Nemunas River and depended on salinity (R<sup>2</sup>=0.54, p 272 < 0.01). When salinity was < 1.5, representing the outflow from the lagoon to the sea, the concentration of PAEs ranged from 0.02 to 0.26  $\mu$ g L<sup>-1</sup> on average (Fig. 2B). When sampling events 273 274 coincided with a seawater intrusion into lagoon (salinity > 3), PAEs concentration was in higher range of 0.18–0.58  $\mu$ g L<sup>-1</sup>. This likely reflects a contamination of seawater on its way through the Klaipėda 275 276 Strait to the lagoon (Fig. 1), where high concentration levels of organic micropollutants (e.g., PAHs) 277 exist due to harbor activities (Stakeniene et al., 2019). Although punctual measurements in the Baltic 278 Sea (Palanga Bridge station, 25-10-2021) were carried out, low concentration levels of PAEs (0.26 279  $\mu$ g L<sup>-1</sup>) were observed, thus supporting the idea of a potential contamination in the Klaipėda Strait.

280 The concentration of PAEs found at the lagoon inflow and outflow was compared to the other 281 studies carried out in Europe (Table 2). However, the number of PAEs congeners analyzed varies 282 from study to study, therefore the direct comparison of total PAEs concentration between systems is 283 challenging. Since DEHP is the most common studied plasticizer in aquatic environments, it can be 284 used as an indicative measure to estimate the level of PAEs pollution. The results show that 285 concentration of DEHP in the water column of the Curonian Lagoon was comparable to other studies, 286 including the Seine River, Marseille Bay, aquatic systems in the Netherlands and Spain, with the exception of the Somme River, where the average concentration of DEHP was 10.23  $\mu$ g L<sup>-1</sup>, 287 representing a relatively high concentration (Table 2). 288



290

Fig. 2. Mean monthly discharge, concentration, and composition of dominant PAEs at the lagoon inflow (A),
outflow (B), and WWTPs (C, WJ – Juodkrantė; D, WN – Nida; E, WK – Klaipėda).

293 The Curonian Lagoon also receives effluents from several WWTPs along its perimeter. The total PAEs concentration in the effluents ranged from 0.11to 6.17  $\mu$ g L<sup>-1</sup> with an average value of 294 1.06  $\mu$ g L<sup>-1</sup> (Fig. 2E), which globally is under the median concentration found in Europe (5.35  $\mu$ g L<sup>-</sup> 295 <sup>1</sup>, Bergé et al., 2013). For example, the concentration of DEHP in effluents discharging to the lagoon 296 varied from ND to 7.81  $\mu$ g L<sup>-1</sup>, which is comparable with those found in Spain (0.985–1.172  $\mu$ g L<sup>-1</sup>) 297 and Netherland (ND-2.4  $\mu$ g L<sup>-1</sup>) but lower than in France (5–188  $\mu$ g L<sup>-1</sup>) (Table 2). Klaipėda city 298 299 WWTP is the largest WWTP (annual discharge 0.017 km<sup>3</sup>) discharging into the lagoon. The 300 concentration of PAEs in effluents from this WWTP followed a seasonal dynamic with a minimum 301 during warm and low discharge periods (0.11  $\mu$ g L<sup>-1</sup> in July 2021) and a maximum during colder and high discharge period (1.97  $\mu$ g L<sup>-1</sup> in February 2022). A high discharge at this WWTP typically 302 303 occurs during intensive rainfall infiltration into wastewater networks, which in fall 2021-spring 2022

304 contributed nearly ~40% of total volume of collected wastewater (AB "Klaipėdos vanduo" annual 305 report). Therefore, rainfall infiltration is likely an uncounted source of PAEs, transporting them from 306 ground surface to WWTP networks or aquifers (Cao et al., 2022b). Similar situation was found in the 307 catchment of Yangtze River where during wet season increased rainfall runoff washed soil surface 308 and affected the efficiency of wastewater treatment resulting in to higher PAEs concentrations in river 309 (Qi et al., 2014; Xu et al., 2022).

310 Regarding the small WWTPs located on the Curonian Spit (WJ and WN; Fig. 1), the temporal movement of the population to the coast during the touristic season (from June to September) affected 311 312 effluents discharge to the lagoon. For example, during the 2021 touristic season, the amount of effluents doubled at Juodkrantė (from 6,794 to 17,512 m<sup>3</sup> month<sup>-1</sup>) and tripled at Nida WWTP (from 313 12,595 to 39,008 m<sup>3</sup> month<sup>-1</sup>). Despite the increased discharge of effluents, which are a proxy of 314 wastewater production, PAEs concentration did not vary significantly (Fig. 2C, D). Indeed, increasing 315 316 effluent discharge from Nida WWTP lowered the concentration of PAEs, which was in the range of 0.23–0.59 µg L<sup>-1</sup> (June–October 2021), and increased from 0.89 µp to 4.68 µg L<sup>-1</sup> during low 317 318 discharge period (November 2021-May 2022). This opposite pattern compared to larger Klaipėda city WWTP could be explained by dilution effect. 319 320

# Table 2

Comparison of PAEs occurrence in Surface water and wastewater effluent with other European regions

Location	Туре	PAEs congeners	PAEs range (µg L <sup>-1</sup> )	DEHP median (range) (µg L <sup>-1</sup> )	Predominant PAEs	Reference
Surface water						
Nemunas River (Lithuania)	River	7 (+DEHA)	ND-1.8	0.03 (ND-1.2)	DEHP, DiBP, DnBP	This study
Curonian Lagoon (Lithuania)	Lagoon	7 (+DEHA)	ND-0.49	0.03 (ND-0.45)	DEHP, DiBP, DnBP	This study
Marseille Bay (France)	Sea	7	0.13-1.33	0.317*(0.016-0.924)	DEHP, DiBP, DnBP	Paluselli et al. 2018
Marseille Bay (France)	Sea	7	0.1–0.527	- (0.06-0.45)	DEHP, DiBP	Schmidt et al. 2021
Seine River Basin (France)	River	6	0.059-1.74	- (0.049-0.98)	DEHP, DEP	Teil et al. 2014
Somme River (France)	River	6	6.93–23.34	10.23*(5.16-20.76)	DEHP, DEP, DnBP	Net et al. 2014
Netherlands	Surface water	9	_	0.32 (0.9–5.0)	DMPP, DEHP, DEP	Vethaak et al. 2005
Nervión Estuary (Spain)	Estuarine water	6	0.999–2.638	- (0.323-0.463)	DEP, DEHP, DnBP	Prieto et al. 2007
Waste water effluent						
Lithuania, Curonian Lagoon	WWTP (n=108)	7 (+DEHA)	0.11-6.17	0.19 (ND-7.81)	DEHP, DiBP, DnBP	This study
Poland	WWTP (n=36)	8	ND-553.0	- (ND-27.1)	DnBP, DiNP, DiBP	Kotowska et al. 2020
Spain	WWTP (n=8)	5	_	- (0.985-1.172)	DEP, DMP, DEHP	Prieto et al. 2010
France, Marne Aval Station	WWTP (n=7)	6	_	5.02*-	DEHP, DEP	Dargnat et al. 2009b
France, Paris	WWTP (n=5)	5	-	22/27 (5-188)	DEHP, DEP	Gasperi et al. 2008
Netherlands	WWTP (n=9)	9	-	1.5 (ND-2.4)	DEHP, DEP, DMPP	Vethaak et al. 2005

\*- the value represents the mean rather than median; ND - not detected; "-" - no value founded in literature; DMPP - Dimethylpropyl phthalate.

#### 326 3.2 Compositional profiles of PAEs

327 The analysis of the compositional profiles of PAEs in samples allows the investigation of the 328 distribution and behaviour of PAEs in the environment. On average, among the 8 plasticizers studied, DEHP had the maximum detection frequency (DF) of 94% and the highest relative contribution (RC) 329 330 of 49% (Table 3). This highlights that DEHP is an ubiquitous contaminant in river and effluents 331 entering to the Curonian Lagoon. Although DnBP and DiBP had also high DF (≥94%), their average 332 RCs were relatively lower (26% and 16%, respectively). Indeed, these results agreed with those reported from other sites (Table 2). DEHP, being the most common used plasticizer in Europe and 333 334 China (Meng et al., 2014; Xu et al., 2022), represents a majority of PAEs in aquatic environments 335 and WWTPs, followed by DnBP and DiBP (Table 2). However, some studies show the presence of 336 other PAEs in higher concentration than DEHP, for example Dimethylpropyl phthalate (DMPP) and 337 DEP were the most dominant PAEs in the Netherlands (Vethaak et al., 2005) and Spain (Prieto et al., 338 2007), respectively. This difference might be a result of specific applications of plasticisers in 339 industry or households. Overall, in the present study, a general trend can be observed regarding the 340 PAEs composition in WWTPs effluents. At large Klaipėda WWTP, DiBP and DnBP together 341 accounted only for 22% of total PAEs, whereas at small Juodkrante and Nida WWTPs they represented more than half of total PAEs (Table 3). By contrast, opposite patterns were observed for 342 343 DEHP. Such different composition of PAEs in effluents could be likely ascribed to both the presence 344 of different wastewater treatments and a different chemical composition of inputs (Bergé et al., 2014), 345 due to the residential WWTPs located on the Curonian Spit (Juodkrante and Nida WWTPs) and the 346 industrial / residential WWTP (Klaipėda city WWTP). Although DiBP is not considered a priority 347 pollutant, its high DF, suggests that this compound should be included as a relevant contaminant in 348 the next future. DEHA was investigated in parallel to PAEs as it is a plasticiser which can be 349 potentially used as an alternative to DEHP (Nagorka and Koschorreck, 2020). Compared to other 350 PAEs, its concentration and relative contribution was at a very low level of pollution in the Curonian Lagoon. Many alternative plasticizers have been used to replace the PAEs, and DEHA is one of them, 351 352 but since the replacement of some chemicals is still under evaluation, the monitoring of these 353 substances could be relevant to forecast a potential increase in their daily use.

### 

# **Table 3**

Average detection frequencies (DF, %) and Relative contributions (RC, %) of different PAEs at the study sites (IN: Lagoon inflow; OUT: Lagoon outflow; WJ:
 Juodkrantė WWTP; WK: Klaipėda city WWTP; WN: Nida WWTP).

Station	DMP		D	DEP		DiBP		DnBP		BBzP		DEHA		DEHP		DOP	
Station	DF	RC	DF	RC	DF	RC	DF	RC	DF	RC	DF	RC	DF	RC		DF	RC
IN	46	0.8	54	2.9	92	7.6	100	20.1	38	0.9	54	2.4	85	59.3		46	5.9
OUT	62	2.7	31	2.0	85	9.3	92	23.8	38	2.7	38	0.6	100	52.4		69	6.5
WJ	46	0.3	38	0.8	100	12.5	100	44.0	62	1.6	38	0.3	92	40.3		38	0.3
WN	46	0.4	62	1.2	100	41.3	100	28.7	62	0.6	38	0.1	92	27.0		46	0.6
WK	64	2.8	82	4.9	91	7.5	100	14.1	73	2.6	45	0.3	100	65.8		55	2.0
Total	53	1.4	53	2.4	94	15.7	98	26.1	55	1.7	43	0.7	94	49.0		51	3.1

363 3.3 PAEs partitioning between particulate and dissolved phases

364 The composition of targeted plasticizers congeners in dissolved and particulate phases is presented in Fig. 3. The relative abundance of the dissolved and particulate-bound PAEs mainly depend on the 365 hydrophobic properties of the individual compound. The  $\log K_{ow}$  (Table 1) value can be used to 366 explain the tendency of PAEs to be partitioned between phases (Staples et al., 1997b). In particulate 367 phase, DEHP, a highly hydrophobic compound (log  $K_{ow}$  7.5), was representing over 78% (at Nida 368 WWTP arriving up to 95% at Klaipeda city and Juodkrante WWTPs) of PAEs congeners, whereas it 369 370 accounted for less than 37% in dissolved phase. In comparison, compounds with lower hydrophobic properties like DiBP and DnBP ( $\log K_{ow}$  4.11 and 4.45, respectively) were dominant PAEs congeners 371 372 in dissolved phase, ranging from 12 to 59% and from 20 to 59%, respectively. Similar patterns were observed in WWTPs of France where DEHP was preferentially associated to the suspended solid 373 374 particles comparing to DEP and DnBP, which were mainly found in dissolved phase (Bergé et al., 2014). The seasonal patterns of each PAEs congener in effluents have been also investigated 375 376 individually, however, no evident features have been elucidated.



377

Fig. 3. Relative distribution of 8 plasticizers in dissolved and particulate-bound phases in samples collected at
the study sites (IN: Lagoon inflow; OUT: Lagoon outflow; WJ: Juodkrantė WWTP; WK: Klaipėda city
WWTP; WN: Nida WWTP).

381

In addition, the concentration of SPM, DOC, and debit can be used to predict seasonal patterns and partitioning of PAEs in natural waters and discharged waste water effluents (e.g., Dong et al.,

384 2022). The results of present study show that the concentration of particulate-bound PAEs (primarily 385 dominated by DEHP) was explained by SPM concentration solely in effluents from the Klaipeda 386 WWTP ( $R^2 = 0.33$ , p < 0.01), whereas SPM was a negligible predictor of particulate-bound PAEs in 387 other monitoring sites even if amount particulate matter varied over seasons  $(3.3-63.8 \text{ mg L}^{-1})$  in 388 river and lagoon outflow. Neither the concentration of total PAEs nor particulate-bound corresponded to the seasonal dynamic of DOC  $(4.07 - 11.60 \text{ mg L}^{-1})$  and debit at the lagoon inlet and outlet. This 389 390 suggests that temporal patterns of PAEs are affected in different manner than we may expect. It could 391 be a complex regulation of PAEs in downstream situated systems including biotransformation and 392 photolytic transformation, which are rarely studied in parallel to the monitoring studies (Paluselli et 393 al. 2018; Schmidt et al., 2020, 2021; Anglata et al., 2020; Puri et al., 2023 and references therein).

394

# 395

### 396 3.4. PAEs load and lagoon effect

397 The Curonian Lagoon is well-suited for an analysis of input and output of specific compounds (e.g., 398 Vybernaite-Lubiene et al., 2017, 2022; Zilius et al., 2018) as it is connected to the Baltic Sea by a 399 single, narrow strait, and its principal tributary accounts for a most of inputs. Therefore, the 400 approximated inputs and outputs of total PAEs in the Curonian Lagoon were estimated on monthly 401 basis (Fig. 4). On average the flux of PAEs leaving the lagoon (0.43 tons of PAEs month<sup>-1</sup>) was relatively higher than total inputs (0.23 tons of PAEs month<sup>-1</sup>), suggesting that lagoon is mainly a 402 source of PAEs to adjacent coastal area of the Baltic Sea. Annually, 2.74 tons of PAEs was delivered 403 404 to the lagoon with Nemunas River discharge and 5.19 tons of PAEs was exported with lagoon outflow 405 to the adjacent coastal area of the Baltic Sea. The estimated riverine input is comparable to that found in south Europe (2.91–4.75 tons year<sup>-1</sup> by Seine River Estuary (France), Dargnat et al., 2009a), but 406 relatively low to that in China (38–1060 tons year<sup>-1</sup>; Cao et al., 2022a). However, the role of lagoon 407 408 in regulating PAEs fluxes can change between seasons. In summer, PAEs efflux with lagoon outflow 409 exceeded by  $\sim 90\%$  of inputs to the system. The opposite situation was observed in winter when inputs 410 exceeded efflux by 159% indicating that a large amount of PAEs was retained within the Curonian 411 Lagoon. Several explanations for these seasonal patterns can be proposed. First, it is important to 412 consider that the lagoon surface in wintertime is covered by ice with snowfall on the top, which can 413 trap organic micropollutants creating a large, temporal reservoir in the system (Stocker et al., 2007). 414 Whereas low water temperatures during winter period slows down microbial PAEs degradation (Xu 415 et al., 2022), which may keep elevated concentration of measured PAEs. Second, we acknowledge 416 that such PAEs mass balance estimation has limitation as considers a single measurement per month 417 which can lead to some over- or underestimation, especially during high hydrological period.

418 Therefore, further studies should take into consideration the variation over the weeks to focus more 419 attention towards specific meteorological and/or hydrological conditions (e.g., flood, debacle). 420 Finally, we have not taken into account the atmospheric deposition of PAEs, which could be one of 421 the important sources of PAEs to the lagoon, especially in Europe where the PAEs concentration in 422 atmosphere seems higher than the rest of the world (Bergé et al. 2013). Additionally, Berge et al. 423 (2013) concluded that PAEs flux with rainfalls to aquatic ecosystems is more important in Northern 424 European countries than in Southern ones, which would encourage the idea of high contamination by 425 rainfalls in Lithuania.

426 To better understand the transport mechanism of PAEs over the lagoon, we partitioned PAEs 427 in dissolved and particulate-bound phases (Fig. 4). The results showed that fraction of PAEs in SPM 428 at the lagoon outflow remained quite consistent (55–75% on average) over seasons. In comparison, 429 at the inflow this fraction varied from  $24 \pm 27$  % in summer to  $86 \pm 15$  % in winter. During low 430 discharge period (summer), sedimentation can occur along riverbed, removing the polluted SPM from 431 water column. Liu et al. (2020) suggest that during the dry season suspended sedimentary particles 432 in river water have a higher affinity for PAEs, which may result in a relative drop in the concentration 433 from the aqueous phase. Whereas in winter period, the high discharge of the river can greatly enhance 434 the sediment resuspension of riverbed, resulting in the increase of PAEs concentration in SPM. To 435 date many studies solely consider the contribution of dissolved PAEs on surface water pollution, 436 however, the results of present study underlines the importance of particulate-bound phase in which 437 PAEs is circulated downstream located estuarine systems.



440 Fig. 4. Monthly loads of  $\Sigma$ PAEs at the inflow (Nemunas River) and outflow (Klaipėda Strait) of the Curonian

- 441 Lagoon and proportion of dissolved or particulate-bound PAEs.
- 442
- 443

# 444 **Conclusions**

445 This study provides the first overview on potential sources of PAEs in the Curonian Lagoon. The results show that water entering the lagoon is relatively polluted by PAEs. Although no clear seasonal 446 447 trend was found, high concentration levels can be observed, mainly depending on specific 448 hydrological and meteorological events, thus underlining the importance of implementing monitoring 449 activities for a better estimate of PAEs in estuarine environment. In the inputs of the Curonian 450 Lagoon, three main PAEs were found including DiBP, which is still lacking in the priority list of pollutants. The most common PAEs found in samples was DEHP, preferentially attached to 451 452 particulate matter, thus indicating the importance of SPM in the distribution of these pollutants in 453 environment. On annual basis the Curonian Lagoon seems to act predominantly as a source of PAEs 454 for the Baltic Sea suggesting the presence of another uncounted, important source, probably via atmospheric pollution. 455

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- 461
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