



# UNIVERSITÀ DI PARMA

## ARCHIVIO DELLA RICERCA

University of Parma Research Repository

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

This is the peer reviewed version of the following article:

*Original*

Phthalate esters delivery to the largest european lagoon: sources, partitioning and seasonal variations / Lorre, Elise; Bianchi, Federica; Vybernaite-Lubiene, Irma; Mezine, Jovita; Zilius, Mindaugas. - In: ENVIRONMENTAL RESEARCH. - ISSN 1096-0953. - 235:(2023). [10.1016/j.envres.2023.116667]

*Availability:*

This version is available at: 11381/2954493 since: 2024-04-29T19:33:51Z

*Publisher:*

*Published*

DOI:10.1016/j.envres.2023.116667

*Terms of use:*

Anyone can freely access the full text of works made available as "Open Access". Works made available

*Publisher copyright*

note finali coverpage

(Article begins on next page)

02 May 2026



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  
33 exported to downstream situated estuarine systems. This study aimed to investigate the external  
34 sources of eight plasticizers to the largest European lagoon (the Curonian Lagoon, south-east Baltic  
35 Sea), focusing on their seasonal variation and transport behaviour through the partitioning between  
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  
39 0.01 to 6.17  $\mu\text{g L}^{-1}$ . Di(2-ethylhexyl) phthalate (DEHP) was the most abundant PAEs and was mainly  
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.

49

50

51

52 **Keywords:**

53 Phthalate esters (PAEs),

54 Suspended matter,

55 Curonian Lagoon,

56 Wastewater Treatment Plants,

57 Seasonal variation

58

59

60 **Funding**

61 This research was supported by the Doctorate Study Programme in Ecology and Environmental  
62 Sciences, Klaipėda University.

63

## 64 **1. Introduction**

65 Phthalate esters (PAEs), also known as phthalates, is a group of emerging pollutants frequently used  
66 as additives to modify physical properties (resistance and mouldability) of plastic materials. Their  
67 presence in synthetic polymers, especially in polyvinyl chloride (PVC), makes them the most widely  
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  
89  $1.3 \mu\text{g L}^{-1}$  for DEHP in fresh and marine waters (Net et al., 2015). Consequently, the monitoring of  
90 PAEs in various environmental matrices has become a necessity.

91 Aquatic environments, especially estuarine systems which act as the interface between land and  
92 sea, receive significant amounts of organic micropollutants through the large catchment runoff,  
93 wastewater discharge, and atmospheric precipitation, which seriously threaten these ecosystems (Li  
94 et al., 2017; Liu et al., 2023; Wu et al., 2023). The primary source of PAEs to estuarine systems is  
95 untreated or insufficiently treated municipal and/or industrial wastewater (European Environmental  
96 Agency, 2019; Schmidt et al., 2021; Kerienė and Maruška, 2022). However, input of PAEs through  
97 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  
100 accumulating in sediments (Chen et al., 2017, Staples et al., 1997b). Depending on the hydrodynamics  
101 of estuarine systems, some particulate-bound PAEs can settle to surface sediment, where they are  
102 mineralised, buried or later released back to water column (Paluselli and Kim, 2020; Hidalgo-Serrano  
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.

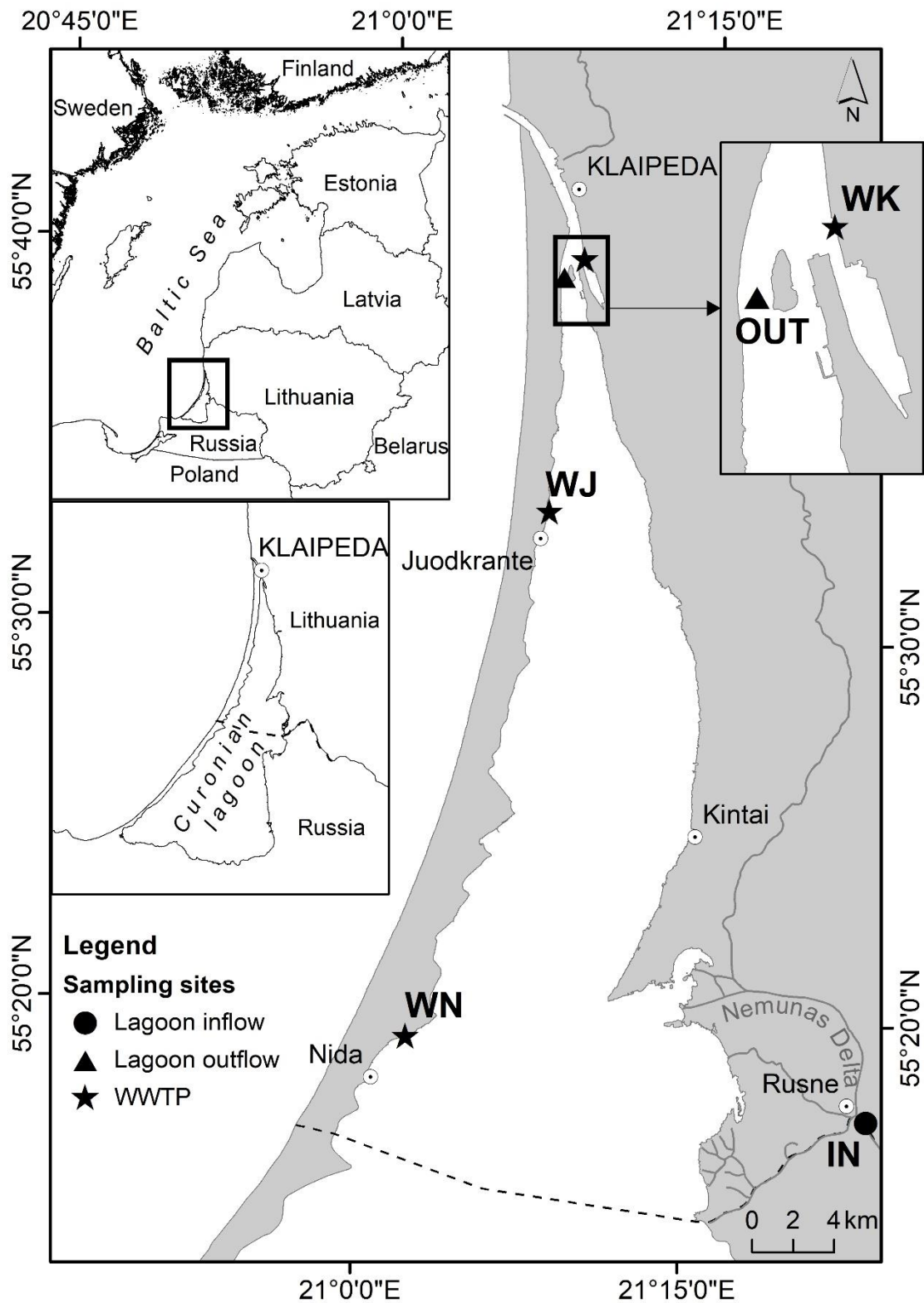
110 In present study, the external inputs of eight plasticizers were monitored via river, seawater  
111 inflow and wastewater effluents discharge to the largest European lagoon, the Curonian Lagoon.  
112 Consequently, the aims of this study were (1) to quantify the external sources of targeted plasticizers  
113 (DMP, DEP, DnBP, BBzP, DEHP, DOP, diisobutyl phthalate (DiBP), and bis-2-ethylhexyl adipate  
114 (DEHA)) discharged to the lagoon and exchange with a sea, by measuring their monthly  
115 concentration in water column, (2) to evaluate the partitioning of PAEs in the water column between  
116 dissolved and particulate phases, and (3) to assess the seasonal patterns of PAEs distribution under  
117 different hydrometeorological conditions. By combining concentration measurements to hydrological  
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.

130

131

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

137 the temporal movement of the population to the coast during the touristic season (from June to  
138 September) impacts the discharge from the small WWTPs located on the Curonian Spit. The lagoon  
139 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  
141 (Nemunas River - IN) and outflow (Klaipėda Strait - OUT), and from the 3 WWTPs (Nida - WN,  
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  
146 column, were transferred to pre-treated borosilicate glass bottles (1 L). Effluent samples (1 L) at each  
147 WWTP were collected in triplicates in outflow channel using a telescopic sampler. Thus, in total, 180  
148 freshwater and waste water samples (12 months, 5 sampling sites, 3 replicates) were collected over  
149 studied period. In order to avoid contamination, plastic material was excluded during all the  
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),  
152 respectively. All samples were cooled with ice packs and transported to the laboratory within the hour  
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  
156 DEHA (Table 1). We acknowledge that DEHA is not a part of PAEs, however since PAEs are under  
157 strict regulations in Europe, many manufacturers have decided to replace them by phthalate free  
158 alternative such as adipate, increasing ultimately their use in plasticizer market and environment  
159 (Nagorka and Koschorreck, 2020). Due to a simplicity in the text we accounted DEHA as a sum of  
160 PAEs. The single standards for each compound (purity grade >98%) and internal standards D4-ring  
161 deuterated dibutyl phthalate (D4-DBP) and D4-ring deuterated di-n-octyl phthalate (D4-DnOP) were  
162 purchased from HPC Standard GmbH (Germany). Capillary grade ethyl acetate (EA), supratrace  
163 grade dichloromethane (DCM), and supergradient grade methanol (MeOH) were purchased from  
164 VWR International GmbH (Austria). The solution of single plasticizer ( $1\text{ g L}^{-1}$ ) and the mixed stock  
165 solution ( $10\text{ mg L}^{-1}$ ) were prepared in EA and stored in the dark at  $-20\text{ }^{\circ}\text{C}$  until analysis.

166

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)	Log K <sub>ow</sub> <sup>a</sup>	Target ion (m/z)	Qualifier ions (m/z)	MDL <sup>b</sup> (µg L <sup>-1</sup> )
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	1x10 <sup>-3</sup>	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	2.7x10 <sup>-5</sup>	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	1x10 <sup>-7</sup>	7.5	149	167-279	0.04
8 Di(n-octyl) phthalate	DnOP	390.6	380	1x10 <sup>-7</sup>	8.06	149	279-261	0.04

169 K<sub>ow</sub>: octanol–water partition coefficient170 <sup>a</sup>Data from Staples et al., 1997b171 <sup>b</sup>Method Detection limit (MDL) = 3\*S<sub>s</sub> (S<sub>s</sub> – 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; Frisette, Denmark) to separate dissolved and particulate-bound phases. The  
176 filtered water was slightly acidified (pH between 2 and 5) using concentrated analytical grade  
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  
184 through the cartridge at a flow rate of 2 mL/min using a vacuum pump. When the extraction was  
185 completed, the cartridge was dried with N<sub>2</sub> and eluted with 2 mL of EA. In addition, 20 mL of  
186 nonacidified filtrate (only river and lagoon samples) was used for dissolved organic carbon (DOC)  
187 analysis. DOC was analysed by the high temperature (680 °C) combustion catalytic oxidation/NDIR  
188 method using a Shimadzu TOC 5000 analyser. An anilide dilution series was used as a standard  
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

194 equipped with TS103 probe (BANDELIN electronic GmbH & Co. KG, Germany). DCM was then  
195 evaporated and PAEs were dissolved in 1.5 mL of EA. Prior to GC-MS analysis, the extracts were  
196 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 × 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).  
205 Transfer line and ion source were maintained at 280 °C and 230 °C, respectively. GC-MS analyses  
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

209 To avoid background pollution, the laboratory equipment used for sampling and analysis, was  
210 exclusively made of glass, stainless steel and polytetrafluoroethylene (PTFE). Each sample was  
211 analysed in triplicates in the case of dissolved phases, whereas 5 replicates were performed when  
212 particulate phases had to be analysed to improve repeatability. Prior to use, all glass apparatus was  
213 soaked in HCl (10%) for 12 h, rinsed with distilled water, dried, burned at 500 °C for 6 h, and finally  
214 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 µg L<sup>-1</sup> and 100  
217 µg L<sup>-1</sup>; EPA 506 phthalate Mix, Sigma Aldrich) were injected at regular intervals and monitored in  
218 a “X-diagram”. In order to verify the applicability of the EN ISO 18856: 2005 method, the agreement  
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\*S<sub>s</sub> and  
222 MQL = 10\*S<sub>s</sub> for each PAEs (S<sub>s</sub> – 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  
224 levels (3 replicate measurements per level) in the 10–200 µg L<sup>-1</sup> range. Mandel’s fitting test was used  
225 to assess linearity. Trueness was assessed by the participation to a proficiency test program (AGLAE  
226 Association, France) for natural water and wastewater obtaining satisfactory results for all tested

227 analytes (DMP, DEP, DiBP, DnBP, DEHP, DOP) with recovery rates from 70% for DMP to 105%  
228 for DnBP.

## 229 2.6. Data analysis

230 The concentrations of each compound were measured separately in the dissolved ( $\mu\text{g L}^{-1}$ ) and  
231 particulate phases ( $\mu\text{g g}^{-1}$  dry weight). Volumetric concentration of particulate phase ( $\mu\text{g L}^{-1}$ ) was  
232 calculated by multiplying from the SPM concentration. A total concentration of PAEs was obtained  
233 by sum of dissolved and particulate phases. Riverine inputs were calculated from monthly  
234 measurements of PAEs concentration and daily discharge of the Nemunas River using previously  
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 “Klaipėdos  
238 Vanduo” and UAB “Neringos Vanduo”. Net PAEs fluxes between the lagoon and the Baltic Sea were  
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.,  
242 2018; Vybernaite-Lubiene et al., 2022). Fluxes were derived based on the volume of exchange  
243 between the lagoon and Baltic Sea and measurements of PAEs concentration in the outflow. Inputs  
244 were expressed as an absolute unit ( $\text{tons month}^{-1}$ ).

245 The linear regression was used to predict PAEs concentration based on selected environmental  
246 variables (salinity, debit, SPM and DOC). The assumption of data normality was checked using  
247 Shapiro-Wilk test. In the case of heteroscedasticity, data were  $\log(x)$  transformed. The significance  
248 level was set at  $\alpha = 0.01$ . Analyses were performed using R Statistical Software. All graphical work  
249 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

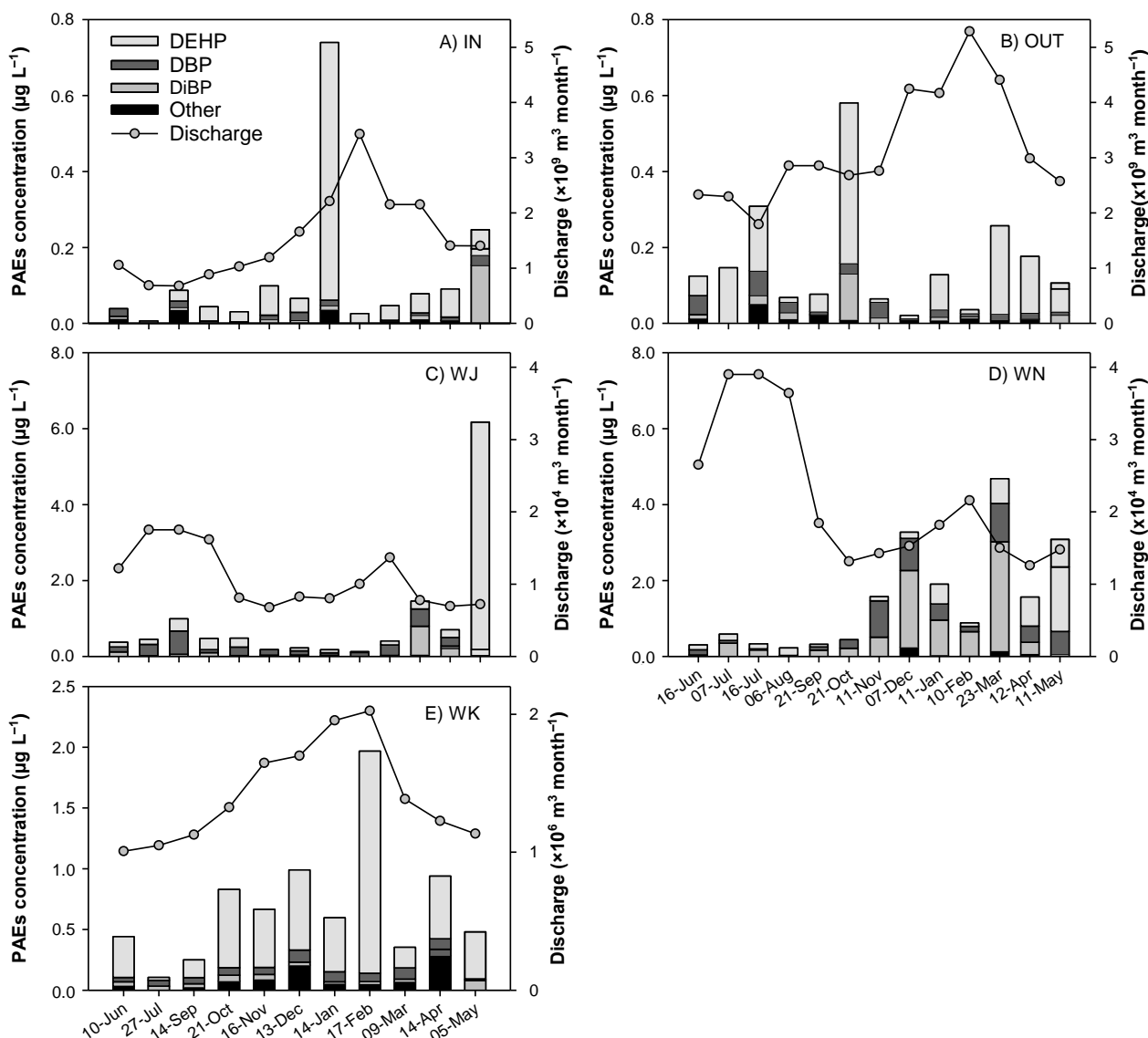
253 Prior to the use of a normalized method containing reproducibility data, an analytical laboratory has  
254 to verify the compliance between the repeatability calculated by the laboratory with that reported in  
255 the method. Since a good agreement was observed, the EN ISO 18856:2005 method was applied to  
256 determine PAEs in inputs to the Curonian Lagoon. MDL and MQL values for targeted plasticizers  
257 ranged from  $0.02 \mu\text{g L}^{-1}$  to  $0.06 \mu\text{g L}^{-1}$  and  $0.08 \mu\text{g L}^{-1}$  to  $0.19 \mu\text{g L}^{-1}$  respectively, thus proving the  
258 reliability of the method for the determination of PAEs at trace levels. PAEs were detected during all  
259 sampling events with concentration levels in the  $0.02\text{--}6.17 \mu\text{g L}^{-1}$  range, regrouping dissolved and

260 particulate-bound DMP, DEP, DiBP, DnBP, BBzP, DEHA, DEHP, and DOP (Fig. 2). These findings  
261 are in line with the contamination levels usually found in Europe (Bergé et al., 2013 and Table 2).  
262 Obviously, the concentrations of PAEs varied among sampling sites and were dependent on specific  
263 environmental conditions, such as heavy rainfall or ice cover.

264 More precisely, the concentration of PAEs in the main lagoon tributary, the Nemunas River,  
265 ranged from 0.01  $\mu\text{g L}^{-1}$  (July 2021) to 0.25  $\mu\text{g L}^{-1}$  (May 2022) on average (Fig. 2A). However, in  
266 January 2022, the average concentration of PAEs tripled up to 0.74  $\mu\text{g L}^{-1}$  when water samples were  
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 ( $R^2=0.54$ ,  $p$   
272  $< 0.01$ ). When salinity was  $\leq 1.5$ , representing the outflow from the lagoon to the sea, the  
273 concentration of PAEs ranged from 0.02 to 0.26  $\mu\text{g L}^{-1}$  on average (Fig. 2B). When sampling events  
274 coincided with a seawater intrusion into lagoon (salinity  $> 3$ ), PAEs concentration was in higher range  
275 of 0.18–0.58  $\mu\text{g L}^{-1}$ . This likely reflects a contamination of seawater on its way through the Klaipėda  
276 Strait to the lagoon (Fig. 1), where high concentration levels of organic micropollutants (e.g., PAHs)  
277 exist due to harbor activities (Stakenienė 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  $\mu\text{g L}^{-1}$ ) 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  
287 exception of the Somme River, where the average concentration of DEHP was 10.23  $\mu\text{g L}^{-1}$ ,  
288 representing a relatively high concentration (Table 2).

289



290

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

293

294 The Curonian Lagoon also receives effluents from several WWTPs along its perimeter. The  
 295 total PAEs concentration in the effluents ranged from 0.11 to 6.17  $\mu\text{g L}^{-1}$  with an average value of  
 296 1.06  $\mu\text{g L}^{-1}$  (Fig. 2E), which globally is under the median concentration found in Europe (5.35  $\mu\text{g L}^{-1}$ ,  
 297 Bergé et al., 2013). For example, the concentration of DEHP in effluents discharging to the lagoon  
 298 varied from ND to 7.81  $\mu\text{g L}^{-1}$ , which is comparable with those found in Spain (0.985–1.172  $\mu\text{g L}^{-1}$ )  
 299 and Netherland (ND–2.4  $\mu\text{g L}^{-1}$ ) but lower than in France (5–188  $\mu\text{g L}^{-1}$ ) (Table 2). Klaipėda city  
 300 WWTP is the largest WWTP (annual discharge 0.017  $\text{km}^3$ ) discharging into the lagoon. The  
 301 concentration of PAEs in effluents from this WWTP followed a seasonal dynamic with a minimum  
 302 during warm and low discharge periods (0.11  $\mu\text{g L}^{-1}$  in July 2021) and a maximum during colder and  
 303 high discharge period (1.97  $\mu\text{g L}^{-1}$  in February 2022). A high discharge at this WWTP typically  
 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  
311 movement of the population to the coast during the touristic season (from June to September) affected  
312 effluents discharge to the lagoon. For example, during the 2021 touristic season, the amount of  
313 effluents doubled at Juodkrantė (from 6,794 to 17,512 m<sup>3</sup> month<sup>-1</sup>) and tripled at Nida WWTP (from  
314 12,595 to 39,008 m<sup>3</sup> month<sup>-1</sup>). Despite the increased discharge of effluents, which are a proxy of  
315 wastewater production, PAEs concentration did not vary significantly (Fig. 2C, D). Indeed, increasing  
316 effluent discharge from Nida WWTP lowered the concentration of PAEs, which was in the range of  
317 0.23–0.59 µg L<sup>-1</sup> (June–October 2021), and increased from 0.89 up to 4.68 µg L<sup>-1</sup> during low  
318 discharge period (November 2021–May 2022). This opposite pattern compared to larger Klaipėda  
319 city WWTP could be explained by dilution effect.

320

321

322

**Table 2**

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

Location	Type	PAEs congeners	PAEs range ( $\mu\text{g L}^{-1}$ )	DEHP median (range) ( $\mu\text{g L}^{-1}$ )	Predominant PAEs	Reference
<b>Surface water</b>						
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
<b>Waste water effluent</b>						
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.

323

324

325

## 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,  
329 DEHP had the maximum detection frequency (DF) of 94% and the highest relative contribution (RC)  
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 ( $\geq 94\%$ ), their average  
332 RCs were relatively lower (26% and 16%, respectively). Indeed, these results agreed with those  
333 reported from other sites (Table 2). DEHP, being the most common used plasticizer in Europe and  
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 Juodkrantė and Nida WWTPs they  
342 represented more than half of total PAEs (Table 3). By contrast, opposite patterns were observed for  
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 (Juodkrantė 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  
351 Lagoon. Many alternative plasticizers have been used to replace the PAEs, and DEHA is one of them,  
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.

354

355

356 **Table 3**

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

359

Station	DMP		DEP		DiBP		DnBP		BBzP		DEHA		DEHP		DOP	
	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

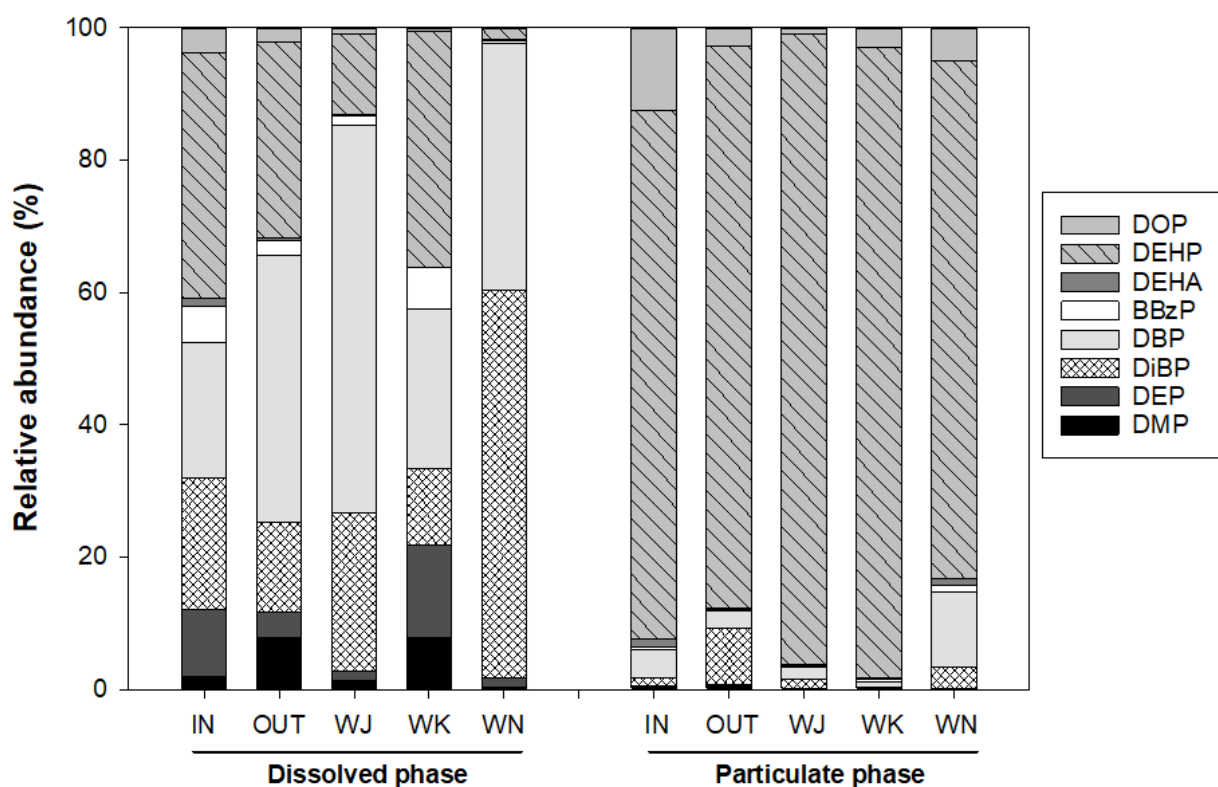
360

361

362

363 3.3 PAEs partitioning between particulate and dissolved phases

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



377  
378 **Fig. 3.** Relative distribution of 8 plasticizers in dissolved and particulate-bound phases in samples collected at  
379 the study sites (IN: Lagoon inflow; OUT: Lagoon outflow; WJ: Juodkrantė WWTP; WK: Klaipėda city  
380 WWTP; WN: Nida WWTP).

381  
382 In addition, the concentration of SPM, DOC, and debit can be used to predict seasonal patterns  
383 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 Klaipėda  
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 mg L<sup>-1</sup>) in  
388 river and lagoon outflow. Neither the concentration of total PAEs nor particulate-bound corresponded  
389 to the seasonal dynamic of DOC (4.07 – 11.60 mg L<sup>-1</sup>) and debit at the lagoon inlet and outlet. This  
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

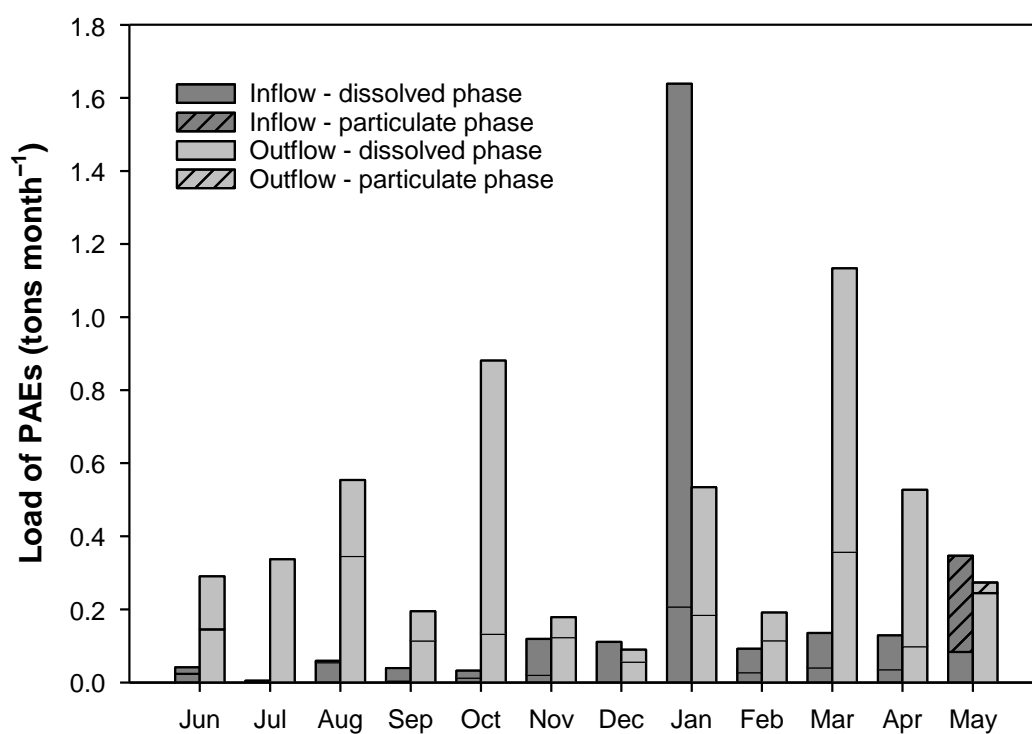
395

#### 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  
402 relatively higher than total inputs (0.23 tons of PAEs month<sup>-1</sup>), suggesting that lagoon is mainly a  
403 source of PAEs to adjacent coastal area of the Baltic Sea. Annually, 2.74 tons of PAEs was delivered  
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  
406 in south Europe (2.91–4.75 tons year<sup>-1</sup> by Seine River Estuary (France), Dargnat et al., 2009a), but  
407 relatively low to that in China (38–1060 tons year<sup>-1</sup>; Cao et al., 2022a). However, the role of lagoon  
408 in regulating PAEs fluxes can change between seasons. In summer, PAEs efflux with lagoon outflow  
409 exceeded by ~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.



438  
 439

440 **Fig. 4.** Monthly loads of ΣPAEs 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  
446 results show that water entering the lagoon is relatively polluted by PAEs. Although no clear seasonal  
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  
451 pollutants. The most common PAEs found in samples was DEHP, preferentially attached to  
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  
455 atmospheric pollution.

## 456 **Acknowledgements**

457 This research was supported by the Doctorate Study Programme in Ecology and Environmental  
458 Sciences, Klaipėda University. We gratefully thank AB “Klaipėdos Vanduo” and UAB “Neringos  
459 Vandensys” for access to collect effluents from WWTPs, and Environmental Protection Agency and  
460 Dr. Tobia Politi for logistic support in collecting samples.

461

462

## 463 **References**

- 464 Adeniyi, A.A., Okedeyi, O.O., and Yusuf, K.A., 2011. “Flame Ionization Gas Chromatographic  
465 Determination of Phthalate Esters in Water, Surface Sediments and Fish Species in the Ogun  
466 River Catchments, Ketu, Lagos, Nigeria.” *Environmental Monitoring and Assessment* 172  
467 (1): 561–69. <https://doi.org/10.1007/s10661-010-1354-2>.
- 468 Adeogun, A.O., Ibor, O.R., Omogbemi, E.D., Chukwuka, A.V., Adegbola, R.A., Adewuyi, G.A., and  
469 Arukwe, A., 2015. “Environmental Occurrence and Biota Concentration of Phthalate Esters  
470 in Epe and Lagos Lagoons, Nigeria.” *Marine Environmental Research* 108: 24–32.  
471 <https://doi.org/10.1016/j.marenvres.2015.04.002>.
- 472 Anglada, J.M., Martins-Costa, M.T.C., Francisco, J.S., Ruiz-López, M.F., 2020. Photoinduced  
473 Oxidation Reactions at the Air–Water Interface. *J. Am. Chem. Soc.* 142, 16140–16155.  
474 <https://doi.org/10.1021/jacs.0c06858>
- 475 Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., and Moilleron, R., 2013. “Meta-  
476 Analysis of Environmental Contamination by Phthalates.” *Environmental Science and  
477 Pollution Research* 20 (11): 8057–76. <https://doi.org/10.1007/s11356-013-1982-5>.
- 478 Bergé, A., Gasperi, J., Rocher, V., Gras, L., Coursimault, A., Moilleron, R., 2014. Phthalates and  
479 alkylphenols in industrial and domestic effluents: Case of Paris conurbation (France). *Sci.  
480 Total Environ.* 488–489, 26–35. <https://doi.org/10.1016/j.scitotenv.2014.04.081>
- 481 Cao, Y., Lin, H., Wang, Q., Li, J., Liu, M., Zhang, K., Xu, S., Huang, G., Ruan, Y., Wu, J., Leung,  
482 K.M.Y., Lam, P.K.S., 2022a. Significant riverine inputs of typical plastic additives-phthalate  
483 esters from the Pearl River Delta to the northern South China Sea. *Sci. Total Environ.* 849,  
484 157744. <https://doi.org/10.1016/j.scitotenv.2022.157744>
- 485 Cao, Y., Xu, S., Zhang, K., Lin, H., Wu, R., Lao, J.Y., Tao, D., Liu, M., Leung, K.M.Y., and Lam,  
486 P.K.S., 2022. “Spatiotemporal Occurrence of Phthalate Esters in Stormwater Drains of Hong  
487 Kong, China: Mass Loading and Source Identification.” *Environmental Pollution* 308:  
488 119683. <https://doi.org/10.1016/j.envpol.2022.119683>.
- 489 Cauwet, G, 1999. Determination of dissolved organic carbon and nitrogen by high temperature  
490 combustion, in: *Methods of seawater analysis*, edited by Grasshoff, K., Kremling, K, and  
491 Ehrhardt, M., Wiley- VCH Verlag GmbH, Weinheim, Germany, 407–420, 1999
- 492 Chen, C.F., Chen, C.W., Ju, Y.R., and Dong, C.D., 2017. “Determination and Assessment of  
493 Phthalate Esters Content in Sediments from Kaohsiung Harbor, Taiwan.” *Marine Pollution  
494 Bulletin* 124 (2): 767–74. <https://doi.org/10.1016/j.marpolbul.2016.11.064>.
- 495 Dargnat, C., Blanchard, M., Chevreuil, M., Teil, M.J., 2009a. Occurrence of phthalate esters in the  
496 Seine River estuary (France). *Hydrol. Process.* 23, 1192–1201.  
497 <https://doi.org/10.1002/hyp.7245>
- 498 Dargnat, C., Teil, M.-J., Chevreuil, M., Blanchard, M., 2009b. Phthalate removal throughout  
499 wastewater treatment plant: Case study of Marne Aval station (France). *Sci. Total Environ.*  
500 407, 1235–1244. <https://doi.org/10.1016/j.scitotenv.2008.10.027>

- 501 Dearman, R.J., Cumberbatch, M., Hilton, J., Clowes, H.M., Fielding, I., Heylings, J.R, and I Kimber.  
 502 1996. "Influence of Dibutyl Phthalate on Dermal Sensitization to Fluorescein Isothiocyanate."  
 503 *Toxicological Sciences* 33 (1): 24–30.
- 504 Dong, L., Lin, L., Pan, X., Zhang, S., Lv, Z., Mi, C., 2022. Distribution Dynamics of Phthalate Esters  
 505 in Surface Water and Sediment of the Middle-Lower Hanjiang River, China. *Int. J. Environ.*  
 506 *Res. Public. Health* 19. <https://doi.org/10.3390/ijerph19052702>
- 507 European Environmental Agency. 2019. "Urban Waste Water Treatment: Existing Approaches,  
 508 Challenges and Opportunities". [https://forum.eionet.europa.eu/nrc-eionet-](https://forum.eionet.europa.eu/nrc-eionet-freshwater/library/urban-waste-water-treatment/urban-waste-water-treatment-challenges-and-opportunities)  
 509 [freshwater/library/urban-waste-water-treatment/urban-waste-water-treatment-challenges-](https://forum.eionet.europa.eu/nrc-eionet-freshwater/library/urban-waste-water-treatment/urban-waste-water-treatment-challenges-and-opportunities)  
 510 [and-opportunities](https://forum.eionet.europa.eu/nrc-eionet-freshwater/library/urban-waste-water-treatment/urban-waste-water-treatment-challenges-and-opportunities) [Google Scholar]
- 511 European Committee for Standardization, 2005. EN ISO 18856. Water quality - Determination of  
 512 selected phthalates using gas chromatography/mass spectrometry (ISO 18856:2004). ISO  
 513 copyright office, Geneva, pp. 1–32
- 514 Fatoki, O.S., and Noma, A., 2002. "Solid Phase Extraction Method for Selective Determination of  
 515 Phthalate Esters in the Aquatic Environment." *Water, Air, and Soil Pollution* 140 (1): 85–98.  
 516 <https://doi.org/10.1023/A:1020134707450>.
- 517 Gasperi, J., Garnaud, S., Rocher, V., Moilleron, R., 2008. Priority pollutants in wastewater and  
 518 combined sewer overflow. *Sci. Total Environ.* 407, 263–272.  
 519 <https://doi.org/10.1016/j.scitotenv.2008.08.015>
- 520 Gómez-Hens, A., and Aguilar-Caballos M.P., 2003. "Social and Economic Interest in the Control of  
 521 Phthalic Acid Esters." *TrAC Trends in Analytical Chemistry* 22 (11): 847–57.  
 522 [https://doi.org/10.1016/S0165-9936\(03\)01201-9](https://doi.org/10.1016/S0165-9936(03)01201-9).
- 523 HELCOM. 2015. Updated Fifth Baltic Sea pollution load compilation (PLC-5.5). Baltic Sea  
 524 Environment Proceedings No. 145.
- 525 Hidalgo-Serrano, M., Borrull, F., Marcé, R.M., Pocurull, E., 2022. Phthalate esters in marine  
 526 ecosystems: Analytical methods, occurrence and distribution. *TrAC Trends Anal. Chem.* 151,  
 527 116598. <https://doi.org/10.1016/j.trac.2022.116598>
- 528 Jakimavičius, D., and Kriauciūnienė, J., 2013. "The Climate Change Impact on the Water Balance of  
 529 the Curonian Lagoon." *Water Resources* 40 (2): 120–32.  
 530 <https://doi.org/10.1134/S0097807813020097>.
- 531 Kerienė, I., Maruška, A., 2022. A review on the presence and removal of phthalates from wastewater.  
 532 *Urban Water J.* 19, 769–781. <https://doi.org/10.1080/1573062X.2022.2087095>
- 533 Kotowska, U., Kapelewska, J., Sawczuk, R., 2020. Occurrence, removal, and environmental risk of  
 534 phthalates in wastewaters, landfill leachates, and groundwater in Poland. *Environ. Pollut.* 267,  
 535 115643. <https://doi.org/10.1016/j.envpol.2020.115643>
- 536 Labunska, I., and Santillo, D., 2004. "Environmental and Human Health Concerns Relating to Diethyl  
 537 Phthalate (DEP), a Common Ingredient in Cosmetics and Other Personal Care Products."  
 538 Greenpeace Research Laboratories Technical Note 06.
- 539 Latini, G., 2005. "Monitoring Phthalate Exposure in Humans." *Clinica Chimica Acta* 361 (1): 20–29.  
 540 <https://doi.org/10.1016/j.cccn.2005.05.003>.
- 541 Lei, Y.D., and Wania, F., 2004. "Is Rain or Snow a More Efficient Scavenger of Organic Chemicals?"  
 542 *Atmospheric Environment* 38 (22): 3557–71.  
 543 <https://doi.org/10.1016/j.atmosenv.2004.03.039>.
- 544 Li, R., Liang, J., Duan, H., and Gong, Z., 2017. "Spatial Distribution and Seasonal Variation of  
 545 Phthalate Esters in the Jiulong River Estuary, Southeast China." *Marine Pollution Bulletin*  
 546 122 (1): 38–46. <https://doi.org/10.1016/j.marpolbul.2017.05.062>.
- 547 Liu, H., Cui, K., Zeng, F., Chen, L., Cheng, Y., Li, H., Li, S., Zhou, X., Zhu, F., Ouyang, G., Luan,  
 548 T., and Zeng, Z., 2014. "Occurrence and Distribution of Phthalate Esters in Riverine  
 549 Sediments from the Pearl River Delta Region, South China." *Marine Pollution Bulletin* 83  
 550 (1): 358–65. <https://doi.org/10.1016/j.marpolbul.2014.03.038>.
- 551 Liu, Y., He, Y., Zhang, J., Cai, C., Breider, F., Tao, S., Liu, W., 2020. Distribution, partitioning  
 552 behavior, and ecological risk assessment of phthalate esters in sediment particle-pore water

- 553 systems from the main stream of the Haihe River, Northern China. *Sci. Total Environ.* 745,  
554 141131. <https://doi.org/10.1016/j.scitotenv.2020.141131>
- 555 Liu, Y., Tang, Y., He, Y., Liu, H., Tao, S., Liu, W., 2023. Riverine inputs, spatiotemporal variations,  
556 and potential sources of phthalate esters transported into the Bohai Sea from an urban river in  
557 northern China. *Sci. Total Environ.* 878, 163253.  
558 <https://doi.org/10.1016/j.scitotenv.2023.163253>
- 559 Meng, X.-Z., Wang, Y., Xiang, N., Chen, L., Liu, Z., Wu, B., Dai, X., Zhang, Y.-H., Xie, Z.,  
560 Ebinghaus, R., 2014. Flow of sewage sludge-borne phthalate esters (PAEs) from human  
561 release to human intake: Implication for risk assessment of sludge applied to soil. *Sci. Total*  
562 *Environ.* 476–477, 242–249. <https://doi.org/10.1016/j.scitotenv.2014.01.007>
- 563 Meyer, T., and Wania, F., 2008. “Organic Contaminant Amplification during Snowmelt.” *Water*  
564 *Research* 42 (8): 1847–65. <https://doi.org/10.1016/j.watres.2007.12.016>.
- 565 Nagorka, R., and J. Koschorreck. 2020. “Trends for Plasticizers in German Freshwater Environments  
566 – Evidence for the Substitution of DEHP with Emerging Phthalate and Non-Phthalate  
567 Alternatives.” *Environmental Pollution* 262: 114237.  
568 <https://doi.org/10.1016/j.envpol.2020.114237>.
- 569 Net, S., Delmont, A., Sempéré, R., Paluselli, A., and Ouddane, B., 2015. “Reliable Quantification of  
570 Phthalates in Environmental Matrices (Air, Water, Sludge, Sediment and Soil): A Review.”  
571 *Science of The Total Environment* 515–516: 162–80.  
572 <https://doi.org/10.1016/j.scitotenv.2015.02.013>.
- 573 Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., and Ouddane, B., 2014. “Case Study of  
574 PAHs, Me-PAHs, PCBs, Phthalates and Pesticides Contamination in the Somme River Water,  
575 France.” *International Journal of Environmental Research* 8 (4): 1159–70.
- 576 Paluselli, A., Fauvelle, V., Schmidt, N., Galgani, F., Net, S., Sempéré, R., 2018. Distribution of  
577 phthalates in Marseille Bay (NW Mediterranean Sea). *Sci. Total Environ.* 621, 578–587.  
578 <https://doi.org/10.1016/j.scitotenv.2017.11.306>
- 579 Paluselli, A., Kim, S.-K., 2020. Horizontal and vertical distribution of phthalates acid ester (PAEs)  
580 in seawater and sediment of East China Sea and Korean South Sea: Traces of plastic debris?  
581 *Mar. Pollut. Bull.* 151, 110831. <https://doi.org/10.1016/j.marpolbul.2019.110831>
- 582 Prieto, A., Schrader, S., Moeder, M., 2010. Determination of organic priority pollutants and emerging  
583 compounds in wastewater and snow samples using multiresidue protocols on the basis of  
584 microextraction by packed sorbents coupled to large volume injection gas chromatography–  
585 mass spectrometry analysis. *J. Chromatogr. A* 1217, 6002–6011.  
586 <https://doi.org/10.1016/j.chroma.2010.07.070>
- 587 Prieto, A., Zuloaga, O., Usobiaga, A., Etxebarria, N., Fernández, L.A., 2007. Development of a stir  
588 bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry  
589 method for the simultaneous determination of several persistent organic pollutants in water  
590 samples. *J. Chromatogr. A* 1174, 40–49. <https://doi.org/10.1016/j.chroma.2007.07.054>
- 591 Puri, M., Gandhi, K., Kumar, M.S., 2023. The occurrence, fate, toxicity, and biodegradation of  
592 phthalate esters: An overview. *Water Environ. Res.* 95, e10832.  
593 <https://doi.org/10.1002/wer.10832>
- 594 Qi, W., Müller, B., Pernet-Coudrier, B., Singer, H., Liu, H., Qu, J., Berg, M., 2014. Organic  
595 micropollutants in the Yangtze River: Seasonal occurrence and annual loads. *Sci. Total*  
596 *Environ.* 472, 789–799. <https://doi.org/10.1016/j.scitotenv.2013.11.019>
- 597 Rahman, M., and Brazel, C.S., 2004. “The Plasticizer Market: An Assessment of Traditional  
598 Plasticizers and Research Trends to Meet New Challenges.” *Progress in Polymer Science* 29  
599 (12): 1223–48. <https://doi.org/10.1016/j.progpolymsci.2004.10.001>.
- 600 Schmidt, N., Castro-Jiménez, J., Fauvelle, V., Ourgaud, M., Sempéré, R., 2020. Occurrence of  
601 organic plastic additives in surface waters of the Rhône River (France). *Environ. Pollut.* 257,  
602 113637. <https://doi.org/10.1016/j.envpol.2019.113637>
- 603 Schmidt, N., Castro-Jiménez, J., Oursel, B., Sempéré, R., 2021. Phthalates and organophosphate  
604 esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring

605 links with microplastic abundance and accumulation in the marine food web. *Environ. Pollut.*  
606 272, 115970. <https://doi.org/10.1016/j.envpol.2020.115970>

607 Srivastava, A., Sharma, V.P., Tripathi, R., Kumar, R., Patel, D.K., and Mathur, P.K., 2010.  
608 “Occurrence of Phthalic Acid Esters in Gomti River Sediment, India.” *Environmental*  
609 *Monitoring and Assessment* 169 (1): 397–406. <https://doi.org/10.1007/s10661-009-1182-4>.

610 Stakėnienė, R., Jokšas, K., Galkus, A., and Raudonytė-Svirbutavičienė, E., 2019. “Polycyclic  
611 Aromatic Hydrocarbons in Surface Sediments from the Curonian Lagoon and the Nemunas  
612 River Delta (Lithuania, Baltic Sea): Distribution, Origin, and Suggestions for the Monitoring  
613 Program.” *Environmental Monitoring and Assessment* 191 (4): 212.  
614 <https://doi.org/10.1007/s10661-019-7367-6>.

615 Staples, C.A., Adams, W.J., Parkerton, T.F., Gorsuch, J.W., Biddinger, G.R., and Kevin H. Reinert,  
616 K.H., 1997. “Aquatic Toxicity of Eighteen Phthalate Esters.” *Environmental Toxicology and*  
617 *Chemistry* 16 (5): 875–91. <https://doi.org/10.1002/etc.5620160507>.

618 Staples, C.A., Peterson, D.R., Parkerton, T.F., and William J. Adams, W.J., 1997b. “The  
619 Environmental Fate of Phthalate Esters: A Literature Review.” *Chemosphere* 35 (4): 667–  
620 749. [https://doi.org/10.1016/S0045-6535\(97\)00195-1](https://doi.org/10.1016/S0045-6535(97)00195-1).

621 Stocker, J., Scheringer, M., Wegmann, F., Hungerbühler, K., 2007. Modeling the Effect of Snow and  
622 Ice on the Global Environmental Fate and Long-Range Transport Potential of Semivolatile  
623 Organic Compounds. *Environ. Sci. Technol.* 41, 6192–6198.  
624 <https://doi.org/10.1021/es062873k>

625 Teil, M.-J., Tlili, K., Blanchard, M., Labadie, P., Alliot, F., Chevreuil, M., 2014. Polychlorinated  
626 Biphenyls, Polybrominated Diphenyl Ethers, and Phthalates in Roach from the Seine River  
627 Basin (France): Impact of Densely Urbanized Areas. *Arch. Environ. Contam. Toxicol.* 66,  
628 41–57. <https://doi.org/10.1007/s00244-013-9955-8>

629 Umgiesser, G., Zemlys, P., Erturk, A., Razinkova-Baziukas, A., Mėžinė, J., and Ferrarin, C., 2016.  
630 “Seasonal renewal time variability in the Curonian Lagoon caused by atmospheric and  
631 hydrographical forcing”, *Ocean Sci.*, 12, 391–402, [https://doi.org/10.5194/os-12-391-](https://doi.org/10.5194/os-12-391-2016)  
632 2016.Vybernaite-Lubiene, I., Zilius, M., Giordani, G., Petkuvienė, J., Vaiciute, D.,  
633 Bukaveckas, P.A., and Bartoli, M., 2017. “Effect of Algal Blooms on Retention of N, Si and  
634 P in Europe’s Largest Coastal Lagoon.” *Estuarine, Coastal and Shelf Science* 194: 217–28.  
635 <https://doi.org/10.1016/j.ecss.2017.06.020>.

636 Vybernaite-Lubiene, I., Zilius, M., Bartoli, M., Petkuvienė, J., Zemlys, P., Magri, M., and Gianmarco  
637 Giordani, G., 2022. “Biogeochemical Budgets of Nutrients and Metabolism in the Curonian  
638 Lagoon (South East Baltic Sea): Spatial and Temporal Variations.” *Water* 14 (2).  
639 <https://doi.org/10.3390/w14020164>.

640 Wang, J., Bo, L., Li, L., Wang, D., Chen, G., Christie, P., and Teng, Y., 2014. “Occurrence of  
641 Phthalate Esters in River Sediments in Areas with Different Land Use Patterns.” *Science of*  
642 *The Total Environment* 500–501: 113–19. <https://doi.org/10.1016/j.scitotenv.2014.08.092>.

643 Wu, Y., Jin, R., Chen, Q., Du, X., Yang, J., Liu, M., 2023. Organic contaminants of emerging concern  
644 in global estuaries: Environmental occurrence, fate, and bioavailability. *Crit. Rev. Environ.*  
645 *Sci. Technol.* 53, 550–575. <https://doi.org/10.1080/10643389.2022.2077062>

646 Xu, H., Liu, Y., Xu, X., Lan, H., Qi, W., Wang, D., Liu, H., Qu, J., 2022. Spatiotemporal variation  
647 and risk assessment of phthalate acid esters (PAEs) in surface water of the Yangtze River  
648 Basin, China. *Sci. Total Environ.* 836, 155677.  
649 <https://doi.org/10.1016/j.scitotenv.2022.155677>

650 Zilius, M., Vybernaite-Lubiene, I., Vaiciute, D., Petkuvienė, J., Zemlys, P., Liskow, I., Voss, M.,  
651 Bartoli, M., and Bukaveckas, P.A., 2018. “The Influence of Cyanobacteria Blooms on the  
652 Attenuation of Nitrogen Throughputs in a Baltic Coastal Lagoon.” *Biogeochemistry* 141 (2):  
653 143–65. <https://doi.org/10.1007/s10533-018-0508-0>.

654

655