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

PHTHALATE ESTERS DELIVERY TO THE LARGEST EUROPEAN LAGOON: SOURCES, PARTITIONING AND SEASONAL VARIATIONS

Elise Lorre[1*], Federica Bianchi[2,3], Irma Vybernaite-Lubiene[1], Jovita Mėžinė[1], and Mindaugas Zilius[1,2]

[1] Marine Research Institute, Klaipeda University, 92295 Klaipeda, Lithuania

[2] University of Parma, Department of Chemistry, Life Science and Environmental Sustainability, Parco Area delle Scienze 17/A, 43124 Parma, Italy

[3] University of Parma, Interdepartmental Center for Energy and Environment (CIDEA), Parco Area delle Scienze, 43124 Parma, Italy

*Corresponding author:

Elise Lorre

Marine Research Institute of Klaipeda University,

Universiteto al. 17, 92295 Klaipeda, Lithuania.

E-mail.: elise.lorre@apc.ku.lt

Tel.: +370 46 398818

Abstract

Phthalate esters (PAEs) due to their ability to leach from plastics, widely used in our daily life, are 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 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 dissolved and particulate phases. The obtained results were later combined with hydrological inputs at the inlet and outlet of the lagoon to estimate system role in regulating the transport of pollutants to the sea. Plasticizers were detected during all sampling events with a total concentration ranging from 0.01 to 6.17 μg L^{-1}. Di(2-ethylhexyl) phthalate (DEHP) was the most abundant PAEs and was mainly found attached to particulate matter, highlighting the importance of this matrix in the transport of such contaminant. Dibutyl phthalate (DnBP) and diisobutyl phthalate (DiBP) were the other two dominant PAEs found in the area, mainly detected in dissolved phase. Meteorological conditions appeared to be an important factor regulating the distribution of PAEs in environment. During the river ice-covered season, PAEs concentration showed the highest value suggesting the importance of ice in the retention of PAEs. While heavy rainfall impacts the amount of water delivered to WWTP, there is an increase of PAEs concentration supporting the hypothesis of their transport via soil leaching and infiltration into wastewater networks. Rainfall could also be a direct source of PAEs to the lagoon resulting in net surplus export of PAEs to the Baltic Sea.

Keywords:

Phthalate esters (PAEs),

Suspended matter,

Curonian Lagoon,

Wastewater Treatment Plants,

Seasonal variation

Funding

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

1. Introduction

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

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

Considering a great hydrophobic nature of PAEs, they can be extensively adsorbed by organic and 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 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 et al., 2022; Liu et al., 2023). Therefore, estuarine systems can act as a trap or source for PAEs on their way to the open sea or ocean. The interplay between urbanization, commercial activities, and the effects on wildlife and human health in the estuarine systems is a societal concern and calls for an urgent management and sustainable use of these ecosystems (Adeogun et al., 2015). In Europe, most studies on PAEs have been focused on coastal systems subjected to tidal influence and high salinity variations (Prieto et al., 2007; Schmidt et al., 2021), but the distribution of PAEs in northern oligohaline systems with long water turnover remains understudied.

In present study, the external inputs of eight plasticizers were monitored via river, seawater inflow and wastewater effluents discharge to the largest European lagoon, the Curonian Lagoon. Consequently, the aims of this study were (1) to quantify the external sources of targeted plasticizers (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 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 different hydrometeorological conditions. By combining concentration measurements to hydrological inputs, the loads of PAEs were also estimated, highlighting the role of lagoon in regulating PAEs transport. To our knowledge, only few studies have performed PAEs analysis in oligohaline, microtidal estuarine ecosystems. The elucidation of PAEs origin, transport and fate in the largest European lagoon will help to better understand the role of estuarine systems in regulating their load to adjacent coastal sites, and will provide a scientific basis for formulating recommendations for environmental monitoring programs.

2. Material and methods

2.1. Study site and sampling collection

The Curonian Lagoon is a large (1,584 km^2), shallow (mean depth 3.8 m), microtidal estuarine system situated along the SE Baltic coast (Fig. 1). Freshwater input to the lagoon is dominated by the Nemunas River accounting for 96% of total inputs and representing the fourth largest tributary to the

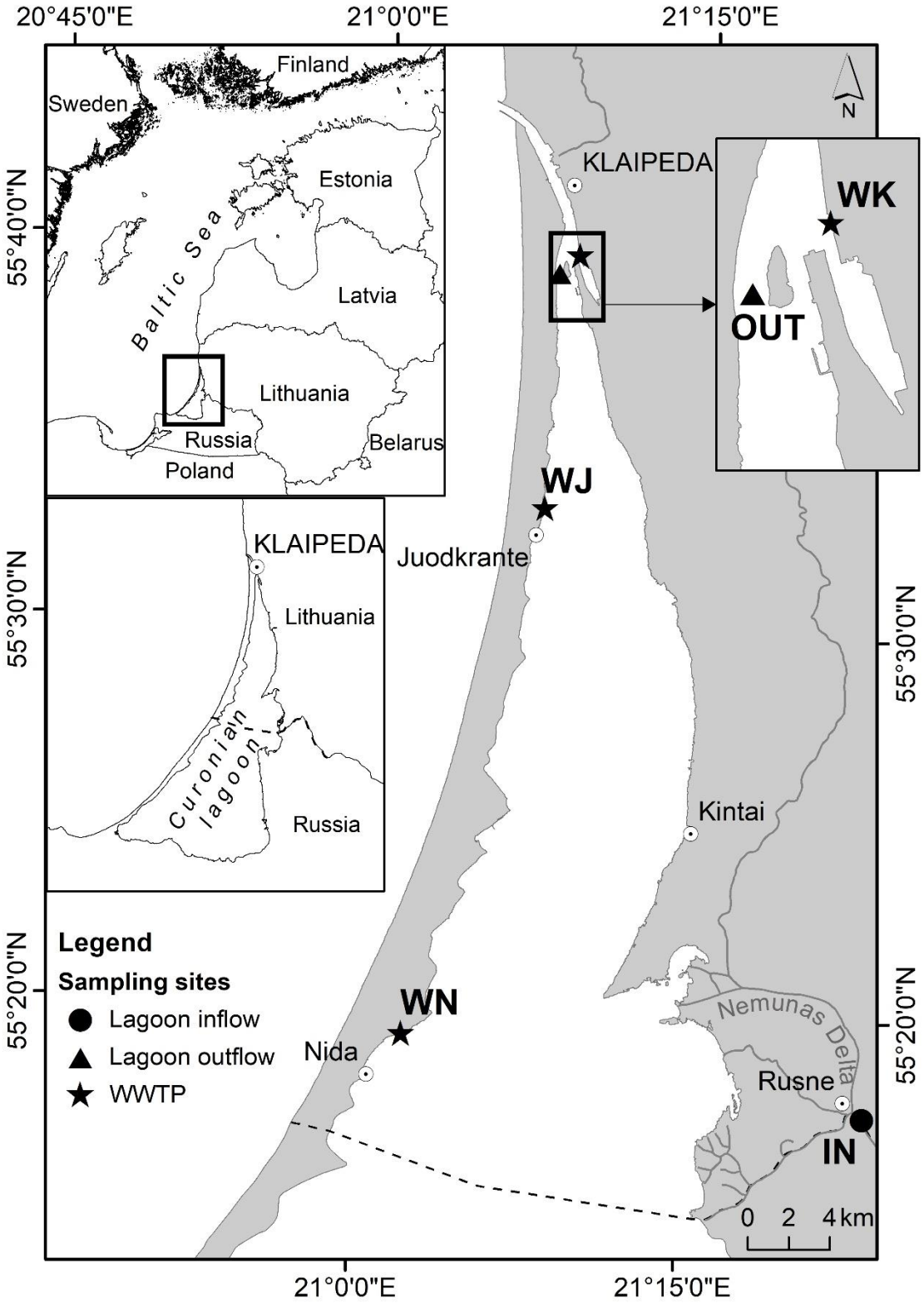

Fig. 1. Location of sampling stations in the study area.

Baltic Sea (Jakimavičius and Kriaučiūnienė, 2013; HELCOM, 2015). The river basin has a total area of 97,864 km^2 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.

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, Juodkrantė – WJ, and Klaipėda city - WK) situated around the lagoon perimeter (Lithuanian part; Fig. 1). The sampling strategy was based on previous studies carried out by Vybernaite-Lubiene et al. (2017, 2022) and Zilius et al. (2018), which were designed to estimate targeted compound inputs 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 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 studied period. In order to avoid contamination, plastic material was excluded during all the procedures. Water temperature and salinity was measured only at lagoon inflow and outflow using 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 for subsequent analyses.

2.2. Chemicals and materials

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 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 (Nagorka and Koschorreck, 2020). Due to a simplicity in the text we accounted DEHA as a sum of 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 purchased from HPC Standard GmbH (Germany). Capillary grade ethyl acetate (EA), supratrace grade dichloromethane (DCM), and supergradient grade methanol (MeOH) were purchased from VWR International GmbH (Austria). The solution of single plasticizer (1g L^{-1}) and the mixed stock solution (10 mg L^{-1}) were prepared in EA and stored in the dark at -20 °C until analysis.

Table 1

Physicochemical properties of target plasticisers.

	Name	Acronym	Molecular weight (g mol^{-1})	Boiling point(°C)	Vapour pressure[a] (mmHg)	Log K_{ow}[a]	Target ion (m/z)	Qualifier ions (m/z)	MDL[b] (µg L^{-1})
1	Dimethyl phthalate	DMP	194.2	282	$2x10^{-3}$	1.61	163	194-133	0.06
2	Diethyl phthalate	DEP	222.2	298	$1x10^{-3}$	2.38	149	177-222	0.06
3	Di-iso-butyl phthalate	DiBP	278.3	327	$2.9x10^{-4}$	4.11	149	223	0.05
4	Dibutyl phthalate	DnBP	278.3	340	$2.7x10^{-5}$	4.45	149	223-278	0.03
5	Butyl Benzyl phthalate	BBzP	312.4	370	$5x10^{-6}$	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	$1x10^{-7}$	7.5	149	167-279	0.04
8	Di(n-octyl) phthalate	DnOP	390.6	380	$1x10^{-7}$	8.06	149	279-261	0.04

K_{ow}: octanol–water partition coefficient

[a] Data from Staples et al., 1997b

[b] Method Detection limit (MDL) = 3*Ss (Ss – sample standard deviation of n replicates spiked sample analyses; n=10).

2.3. Sample treatment

2.3.1. Dissolved phase analysis

Water samples (500 mL) were filtered through a pre-combusted (6 h at 500 °C) GF/F filters (0.7 µm 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 hydrochloric acid (VWR International GmbH, Austria). The extractions were performed following the standard method EN ISO 18856:2005 (European Committee for Standardization, 2005). Briefly, solid-phase extraction (SPE) was performed with C18ec cartridges (Chromabond®, 6 mL/500 mg) to extract the plasticizers from the water samples. Cartridges were preliminary rinsed with one bed volume of EA, dried with a gentle stream of N_2 gas, and then conditioned with two bed volumes of MeOH. The glass bottles containing 500 mL of samples spiked with internal standard, were connected 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 completed, the cartridge was dried with N_2 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) 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 (Cauwet, 1999).

2.3.2. Particulate phase analysis

The GF/F filters with precipitated suspended particulate matter (SPM) were dried at 60 °C for 3h prior to analysis. Then filters were spiked with the internal standard and ultrasonically extracted two 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).

2.4. GC-MS analysis

Samples were analysed using a Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu GCMS-TQ8040 mass spectrometer. The gas chromatograph was equipped with a Restek® Rxi-5Sil MS (5% polydiphenylsiloxane, 95% polydimethylsiloxane) capillary column (30 m × 0.25 mm internal diameter and 0.25 µm film thickness). Helium was used as carrier gas at a constant flow rate of 1 mL/min; the GC injector was operated in splitless mode at 250 °C. Oven temperature program 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 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 were carried out under selected ion monitoring (SIM). The current of the ions used for identification and quantification purposes is reported in Table 1.

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.

For each batch of samples, procedural blanks and instrumental blanks were performed. To monitor instrumental variations, control samples (mixed PAEs working solution at 30 µg L^{-1} and 100 µg L^{-1}; 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 between the precision calculated by the laboratory with that reported in the normalized method was assessed by performing 15 replicated measurements. The method detection limit (MDL) and method quantification limit (MQL) were calculated according to the following equations: MDL = 3*Ss and MQL = 10*Ss for each PAEs (Ss – sample standard deviation of n replicates spiked sample analyses; 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 µg L^{-1} range. Mandel's fitting test was used to assess linearity. Trueness was assessed by the participation to a proficiency test program (AGLAE 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.

2.6. Data analysis

The concentrations of each compound were measured separately in the dissolved (μg L^{-1}) and particulate phases (μg g^{-1} dry weight). Volumetric concentration of particulate phase (μg L^{-1}) was calculated by multiplying from the SPM concentration. A total concentration of PAEs was obtained 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 described methods for the lagoon (Zilius et al., 2018). Discharge data were provided by the Lithuanian Hydro-meteorological Service. Inputs from WWTPs were calculated from monthly measurements of PAEs concentration and daily discharge. Effluents discharge data were provided by AB "Klaipėdos Vanduo" and UAB "Neringos Vanduo". Net PAEs fluxes between the lagoon and the Baltic Sea were derived using estimates of hydrologic exchange obtained from a hydrodynamic model (SHYFEM; http://www.ismar.cnr.it/shyfem) previously calibrated for this site (Umgiesser et al., 2016). This 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 between the lagoon and Baltic Sea and measurements of PAEs concentration in the outflow. Inputs 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.

3. Results and discussion

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 μg L^{-1} to 0.06 μg L^{-1} and 0.08 μg L^{-1} to 0.19 μg L^{-1} 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 μg L^{-1} 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.

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

The concentration of PAEs found at the lagoon inflow and outflow was compared to the other studies carried out in Europe (Table 2). However, the number of PAEs congeners analyzed varies from study to study, therefore the direct comparison of total PAEs concentration between systems is challenging. Since DEHP is the most common studied plasticizer in aquatic environments, it can be used as an indicative measure to estimate the level of PAEs pollution. The results show that concentration of DEHP in the water column of the Curonian Lagoon was comparable to other studies, 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 μg L^{-1}, representing a relatively high concentration (Table 2).

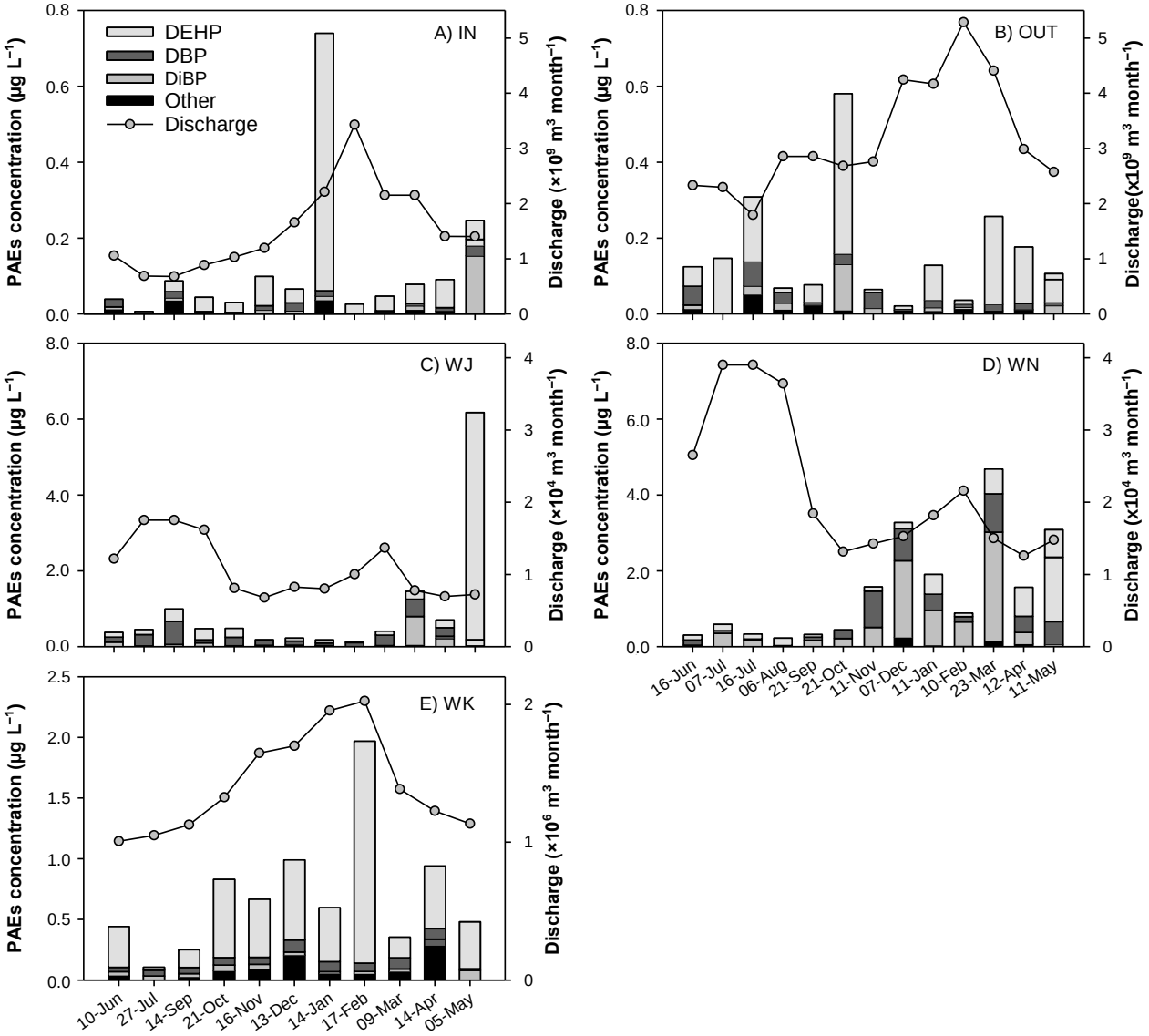

Fig. 2. Mean monthly discharge, concentration, and composition of dominant PAEs at the lagoon inflow (A), outflow (B), and WWTPs (C, WJ – Juodkrantė; D, WN – Nida; E, WK – Klaipėda).

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 µg L^{-1} with an average value of 1.06 µg L^{-1} (Fig. 2E), which globally is under the median concentration found in Europe (5.35 µg L^{-1}, Bergé et al., 2013). For example, the concentration of DEHP in effluents discharging to the lagoon varied from ND to 7.81 µg L^{-1}, which is comparable with those found in Spain (0.985–1.172 µg L^{-1}) and Netherland (ND–2.4 µg L^{-1}) but lower than in France (5–188 µg L^{-1}) (Table 2). Klaipėda city WWTP is the largest WWTP (annual discharge 0.017 km^3) discharging into the lagoon. The concentration of PAEs in effluents from this WWTP followed a seasonal dynamic with a minimum during warm and low discharge periods (0.11 µg L^{-1} in July 2021) and a maximum during colder and high discharge period (1.97 µg 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

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

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 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^3 $month^{-1}$) and tripled at Nida WWTP (from 12,595 to 39,008 m^3 $month^{-1}$). Despite the increased discharge of effluents, which are a proxy of wastewater production, PAEs concentration did not vary significantly (Fig. 2C, D). Indeed, increasing effluent discharge from Nida WWTP lowered the concentration of PAEs, which was in the range of 0.23–0.59 µg L^{-1} (June–October 2021), and increased from 0.89 up to 4.68 µg L^{-1} during low discharge period (November 2021–May 2022). This opposite pattern compared to larger Klaipėda city WWTP could be explained by dilution effect.

321

322

Table 2

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

Location	Type	PAEs congeners	PAEs range (μg L^{-1})	DEHP median (range) (μg L^{-1})	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.

323

324

325

3.2 Compositional profiles of PAEs

The analysis of the compositional profiles of PAEs in samples allows the investigation of the 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) of 49% (Table 3). This highlights that DEHP is an ubiquitous contaminant in river and effluents entering to the Curonian Lagoon. Although DnBP and DiBP had also high DF (≥94%), their average 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 China (Meng et al., 2014; Xu et al., 2022), represents a majority of PAEs in aquatic environments and WWTPs, followed by DnBP and DiBP (Table 2). However, some studies show the presence of other PAEs in higher concentration than DEHP, for example Dimethylpropyl phthalate (DMPP) and DEP were the most dominant PAEs in the Netherlands (Vethaak et al., 2005) and Spain (Prieto et al., 2007), respectively. This difference might be a result of specific applications of plasticisers in industry or households. Overall, in the present study, a general trend can be observed regarding the PAEs composition in WWTPs effluents. At large Klaipėda WWTP, DiBP and DnBP together accounted only for 22% of total PAEs, whereas at small Juodkrantė and Nida WWTPs they represented more than half of total PAEs (Table 3). By contrast, opposite patterns were observed for DEHP. Such different composition of PAEs in effluents could be likely ascribed to both the presence of different wastewater treatments and a different chemical composition of inputs (Bergé et al., 2014), due to the residential WWTPs located on the Curonian Spit (Juodkrantė and Nida WWTPs) and the industrial / residential WWTP (Klaipėda city WWTP). Although DiBP is not considered a priority pollutant, its high DF, suggests that this compound should be included as a relevant contaminant in the next future. DEHA was investigated in parallel to PAEs as it is a plasticiser which can be potentially used as an alternative to DEHP (Nagorka and Koschorreck, 2020). Compared to other 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, but since the replacement of some chemicals is still under evaluation, the monitoring of these 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		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

3.3 PAEs partitioning between particulate and dissolved phases

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 hydrophobic properties of the individual compound. The log K_{ow} (Table 1) value can be used to explain the tendency of PAEs to be partitioned between phases (Staples et al., 1997b). In particulate phase, DEHP, a highly hydrophobic compound (log K_{ow} 7.5), was representing over 78% (at Nida WWTP arriving up to 95% at Klaipėda city and Juodkrantė WWTPs) of PAEs congeners, whereas it 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 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 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 individually, however, no evident features have been elucidated.

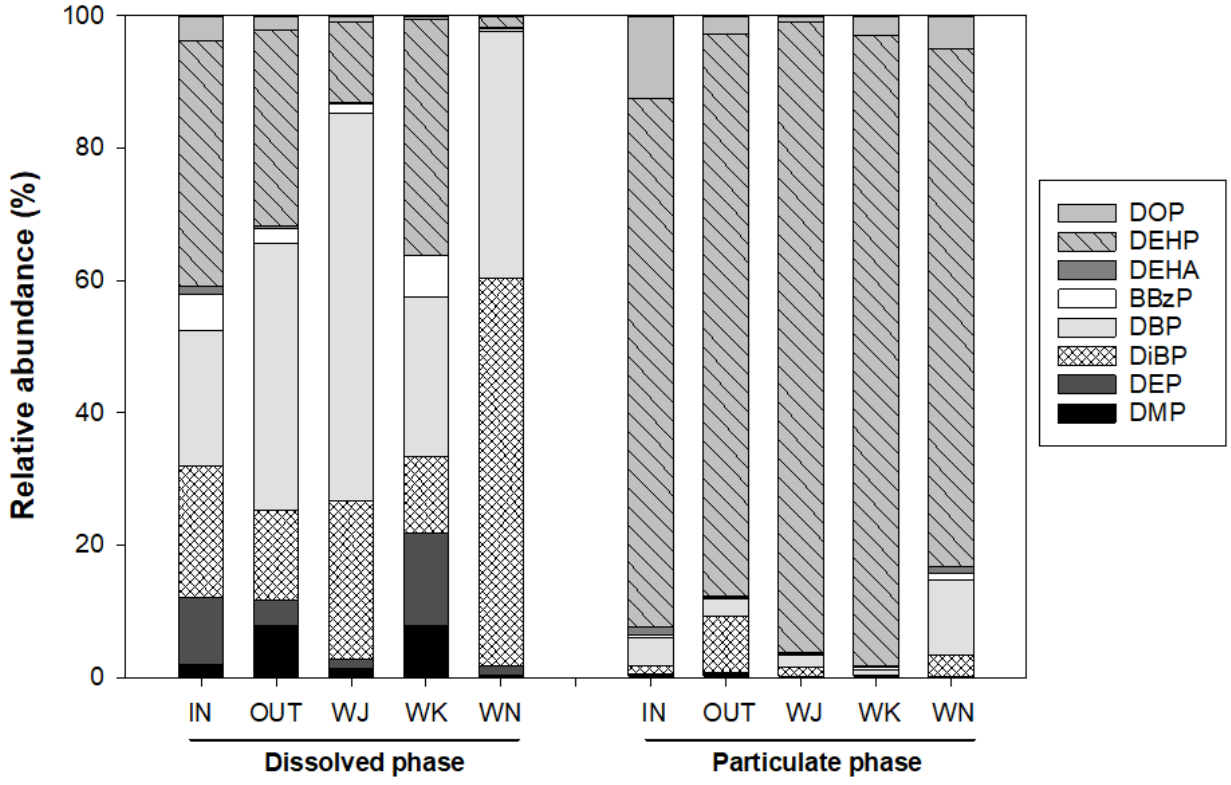

Fig. 3. Relative distribution of 8 plasticizers in dissolved and particulate-bound phases in samples collected at the study sites (IN: Lagoon inflow; OUT: Lagoon outflow; WJ: Juodkrantė WWTP; WK: Klaipėda city WWTP; WN: Nida WWTP).

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.,

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

3.4. PAEs load and lagoon effect

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

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

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

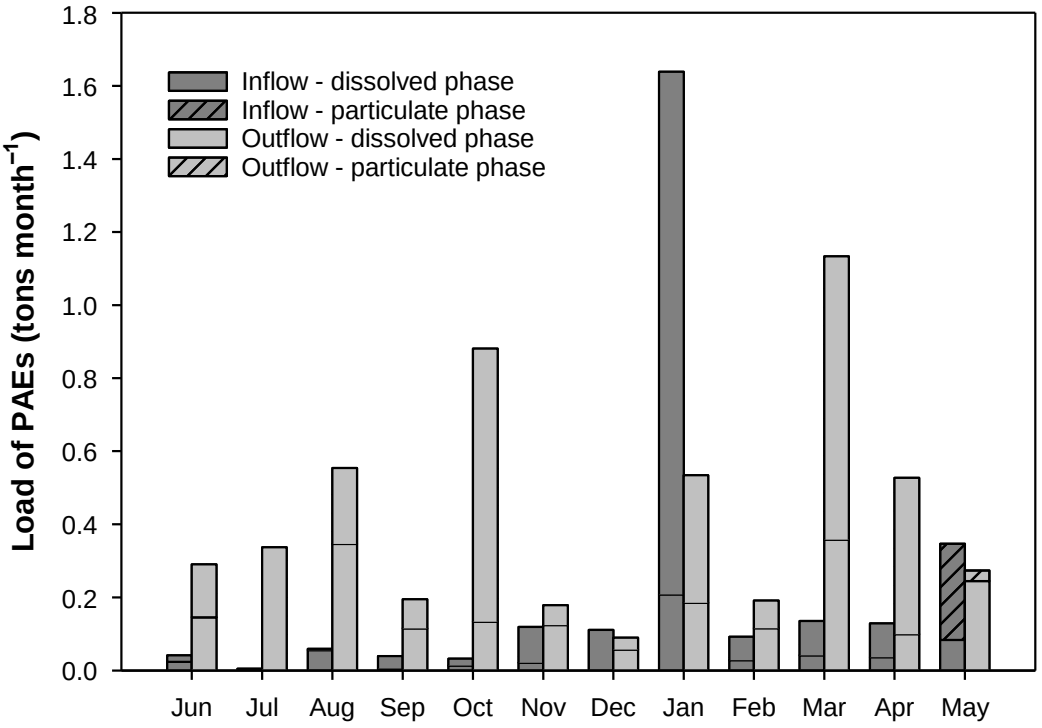

Fig. 4. Monthly loads of ΣPAEs at the inflow (Nemunas River) and outflow (Klaipėda Strait) of the Curonian Lagoon and proportion of dissolved or particulate-bound PAEs.

Conclusions

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 trend was found, high concentration levels can be observed, mainly depending on specific hydrological and meteorological events, thus underlining the importance of implementing monitoring activities for a better estimate of PAEs in estuarine environment. In the inputs of the Curonian 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 particulate matter, thus indicating the importance of SPM in the distribution of these pollutants in environment. On annual basis the Curonian Lagoon seems to act predominantly as a source of PAEs for the Baltic Sea suggesting the presence of another uncounted, important source, probably via atmospheric pollution.

Acknowledgements

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

References

Adeniyi, A.A., Okedeyi, O.O., and Yusuf, K.A., 2011. "Flame Ionization Gas Chromatographic Determination of Phthalate Esters in Water, Surface Sediments and Fish Species in the Ogun River Catchments, Ketu, Lagos, Nigeria." *Environmental Monitoring and Assessment* 172 (1): 561–69. https://doi.org/10.1007/s10661-010-1354-2.

Adeogun, A.O., Ibor, O.R., Omogbemi, E.D., Chukwuka, A.V., Adegbola, R.A., Adewuyi, G.A., and Arukwe, A., 2015. "Environmental Occurrence and Biota Concentration of Phthalate Esters in Epe and Lagos Lagoons, Nigeria." *Marine Environmental Research* 108: 24–32. https://doi.org/10.1016/j.marenvres.2015.04.002.

Anglada, J.M., Martins-Costa, M.T.C., Francisco, J.S., Ruiz-López, M.F., 2020. Photoinduced Oxidation Reactions at the Air–Water Interface. J. Am. Chem. Soc. 142, 16140–16155. https://doi.org/10.1021/jacs.0c06858

Bergé, A., Cladière, M., Gasperi, J., Coursimault, A., Tassin, B., and Moilleron, R., 2013. "Meta-Analysis of Environmental Contamination by Phthalates." *Environmental Science and Pollution Research* 20 (11): 8057–76. https://doi.org/10.1007/s11356-013-1982-5.

Bergé, A., Gasperi, J., Rocher, V., Gras, L., Coursimault, A., Moilleron, R., 2014. Phthalates and alkylphenols in industrial and domestic effluents: Case of Paris conurbation (France). Sci. Total Environ. 488–489, 26–35. https://doi.org/10.1016/j.scitotenv.2014.04.081

Cao, Y., Lin, H., Wang, Q., Li, J., Liu, M., Zhang, K., Xu, S., Huang, G., Ruan, Y., Wu, J., Leung, K.M.Y., Lam, P.K.S., 2022a. Significant riverine inputs of typical plastic additives-phthalate esters from the Pearl River Delta to the northern South China Sea. Sci. Total Environ. 849, 157744. https://doi.org/10.1016/j.scitotenv.2022.157744

Cao, Y., Xu, S., Zhang, K., Lin, H., Wu, R., Lao, J.Y., Tao, D., Liu, M., Leung, K.M.Y., andLam, P.K.S., 2022. "Spatiotemporal Occurrence of Phthalate Esters in Stormwater Drains of Hong Kong, China: Mass Loading and Source Identification." *Environmental Pollution* 308: 119683. https://doi.org/10.1016/j.envpol.2022.119683.

Cauwet, G, 1999. Determination of dissolved organic carbon and nitrogen by high temperature combustion, in: Methods of seawater analysis, edited by Grasshoff, K., Kremling, K, and Ehrhardt, M., Wiley- VCH Verlag GmbH, Weinheim, Germany, 407–420, 1999

Chen, C.F., Chen, C.W., Ju, Y.R., and Dong, C.D., 2017. "Determination and Assessment of Phthalate Esters Content in Sediments from Kaohsiung Harbor, Taiwan." *Marine Pollution Bulletin* 124 (2): 767–74. https://doi.org/10.1016/j.marpolbul.2016.11.064.

Dargnat, C., Blanchard, M., Chevreuil, M., Teil, M.J., 2009a. Occurrence of phthalate esters in the Seine River estuary (France). Hydrol. Process. 23, 1192–1201. https://doi.org/10.1002/hyp.7245

Dargnat, C., Teil, M.-J., Chevreuil, M., Blanchard, M., 2009b. Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). Sci. Total Environ. 407, 1235–1244. https://doi.org/10.1016/j.scitotenv.2008.10.027

Dearman, R.J., Cumberbatch, M., Hilton, J., Clowes, H.M., Fielding, I., Heylings, J.R, and I Kimber. 1996. "Influence of Dibutyl Phthalate on Dermal Sensitization to Fluorescein Isothiocyanate." *Toxicological Sciences* 33 (1): 24–30.

Dong, L., Lin, L., Pan, X., Zhang, S., Lv, Z., Mi, C., 2022. Distribution Dynamics of Phthalate Esters in Surface Water and Sediment of the Middle-Lower Hanjiang River, China. Int. J. Environ. Res. Public. Health 19. https://doi.org/10.3390/ijerph19052702

European Environmental Agency. 2019. "Urban Waste Water Treatment: Existing Approaches, Challenges and Opportunities". https://forum.eionet.europa.eu/nrc-eionet-freshwater/library/urban-waste-water-treatment/urban-waste-water-treatment-challenges-and-opportunities [Google Scholar]

European Committee for Standardization, 2005. EN ISO 18856. Water quality - Determination of selected phthalates using gas chromatography/mass spectrometry (ISO 18856:2004). ISO copyright office, Geneva, pp. 1–32

Fatoki, O.S., and Noma, A., 2002. "Solid Phase Extraction Method for Selective Determination of Phthalate Esters in the Aquatic Environment." *Water, Air, and Soil Pollution* 140 (1): 85–98. https://doi.org/10.1023/A:1020134707450.

Gasperi, J., Garnaud, S., Rocher, V., Moilleron, R., 2008. Priority pollutants in wastewater and combined sewer overflow. Sci. Total Environ. 407, 263–272. https://doi.org/10.1016/j.scitotenv.2008.08.015

Gómez-Hens, A., and Aguilar-Caballos M.P., 2003. "Social and Economic Interest in the Control of Phthalic Acid Esters." *TrAC Trends in Analytical Chemistry* 22 (11): 847–57. https://doi.org/10.1016/S0165-9936(03)01201-9.

HELCOM. 2015. Updated Fifth Baltic Sea pollution load compilation (PLC-5.5). Baltic Sea Environment Proceedings No. 145.

Hidalgo-Serrano, M., Borrull, F., Marcé, R.M., Pocurull, E., 2022. Phthalate esters in marine ecosystems: Analytical methods, occurrence and distribution. TrAC Trends Anal. Chem. 151, 116598. https://doi.org/10.1016/j.trac.2022.116598

Jakimavičius, D., and Kriaučiūnienė, J., 2013. "The Climate Change Impact on the Water Balance of the Curonian Lagoon." *Water Resources* 40 (2): 120–32. https://doi.org/10.1134/S0097807813020097.

Kerienė, I., Maruška, A., 2022. A review on the presence and removal of phthalates from wastewater. Urban Water J. 19, 769–781. https://doi.org/10.1080/1573062X.2022.2087095

Kotowska, U., Kapelewska, J., Sawczuk, R., 2020. Occurrence, removal, and environmental risk of phthalates in wastewaters, landfill leachates, and groundwater in Poland. Environ. Pollut. 267, 115643. https://doi.org/10.1016/j.envpol.2020.115643

Labunska, I., and Santillo, D., 2004. "Environmental and Human Health Concerns Relating to Diethyl Phthalate (DEP), a Common Ingredient in Cosmetics and Other Personal Care Products." Greenpeace Research Laboratories Technical Note 06.

Latini, G., 2005. "Monitoring Phthalate Exposure in Humans." *Clinica Chimica Acta* 361 (1): 20–29. https://doi.org/10.1016/j.cccn.2005.05.003.

Lei, Y.D., and Wania, F., 2004. "Is Rain or Snow a More Efficient Scavenger of Organic Chemicals?" *Atmospheric Environment* 38 (22): 3557–71. https://doi.org/10.1016/j.atmosenv.2004.03.039.

Li, R., Liang, J., Duan, H., and Gong, Z., 2017. "Spatial Distribution and Seasonal Variation of Phthalate Esters in the Jiulong River Estuary, Southeast China." *Marine Pollution Bulletin* 122 (1): 38–46. https://doi.org/10.1016/j.marpolbul.2017.05.062.

Liu, H., Cui, K., Zeng, F., Chen, L., Cheng, Y., Li, H., Li, S., Zhou, X., Zhu, F., Ouyang, G., Luan, T., and Zeng, Z., 2014. "Occurrence and Distribution of Phthalate Esters in Riverine Sediments from the Pearl River Delta Region, South China." *Marine Pollution Bulletin* 83 (1): 358–65. https://doi.org/10.1016/j.marpolbul.2014.03.038.

Liu, Y., He, Y., Zhang, J., Cai, C., Breider, F., Tao, S., Liu, W., 2020. Distribution, partitioning behavior, and ecological risk assessment of phthalate esters in sediment particle-pore water

systems from the main stream of the Haihe River, Northern China. Sci. Total Environ. 745, 141131. https://doi.org/10.1016/j.scitotenv.2020.141131

Liu, Y., Tang, Y., He, Y., Liu, H., Tao, S., Liu, W., 2023. Riverine inputs, spatiotemporal variations, and potential sources of phthalate esters transported into the Bohai Sea from an urban river in northern China. Sci. Total Environ. 878, 163253. https://doi.org/10.1016/j.scitotenv.2023.163253

Meng, X.-Z., Wang, Y., Xiang, N., Chen, L., Liu, Z., Wu, B., Dai, X., Zhang, Y.-H., Xie, Z., Ebinghaus, R., 2014. Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: Implication for risk assessment of sludge applied to soil. Sci. Total Environ. 476–477, 242–249. https://doi.org/10.1016/j.scitotenv.2014.01.007

Meyer, T., and Wania, F., 2008. "Organic Contaminant Amplification during Snowmelt." *Water Research* 42 (8): 1847–65. https://doi.org/10.1016/j.watres.2007.12.016.

Nagorka, R., and J. Koschorreck. 2020. "Trends for Plasticizers in German Freshwater Environments – Evidence for the Substitution of DEHP with Emerging Phthalate and Non-Phthalate Alternatives." Environmental Pollution 262: 114237. https://doi.org/10.1016/j.envpol.2020.114237.

Net, S., Delmont, A., Sempéré, R., Paluselli, A., and Ouddane, B., 2015. "Reliable Quantification of Phthalates in Environmental Matrices (Air, Water, Sludge, Sediment and Soil): A Review." *Science of The Total Environment* 515–516: 162–80. https://doi.org/10.1016/j.scitotenv.2015.02.013.

Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., and Ouddane, B., 2014. "Case Study of PAHs, Me-PAHs, PCBs, Phthalates and Pesticides Contamination in the Somme River Water, France." *International Journal of Environmental Research* 8 (4): 1159–70.

Paluselli, A., Fauvelle, V., Schmidt, N., Galgani, F., Net, S., Sempéré, R., 2018. Distribution of phthalates in Marseille Bay (NW Mediterranean Sea). Sci. Total Environ. 621, 578–587. https://doi.org/10.1016/j.scitotenv.2017.11.306

Paluselli, A., Kim, S.-K., 2020. Horizontal and vertical distribution of phthalates acid ester (PAEs) in seawater and sediment of East China Sea and Korean South Sea: Traces of plastic debris? Mar. Pollut. Bull. 151, 110831. https://doi.org/10.1016/j.marpolbul.2019.110831

Prieto, A., Schrader, S., Moeder, M., 2010. Determination of organic priority pollutants and emerging compounds in wastewater and snow samples using multiresidue protocols on the basis of microextraction by packed sorbents coupled to large volume injection gas chromatography–mass spectrometry analysis. J. Chromatogr. A 1217, 6002–6011. https://doi.org/10.1016/j.chroma.2010.07.070

Prieto, A., Zuloaga, O., Usobiaga, A., Etxebarria, N., Fernández, L.A., 2007. Development of a stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry method for the simultaneous determination of several persistent organic pollutants in water samples. J. Chromatogr. A 1174, 40–49. https://doi.org/10.1016/j.chroma.2007.07.054

Puri, M., Gandhi, K., Kumar, M.S., 2023. The occurrence, fate, toxicity, and biodegradation of phthalate esters: An overview. Water Environ. Res. 95, e10832. https://doi.org/10.1002/wer.10832

Qi, W., Müller, B., Pernet-Coudrier, B., Singer, H., Liu, H., Qu, J., Berg, M., 2014. Organic micropollutants in the Yangtze River: Seasonal occurrence and annual loads. Sci. Total Environ. 472, 789–799. https://doi.org/10.1016/j.scitotenv.2013.11.019

Rahman, M., and Brazel, C.S., 2004. "The Plasticizer Market: An Assessment of Traditional Plasticizers and Research Trends to Meet New Challenges." *Progress in Polymer Science* 29 (12): 1223–48. https://doi.org/10.1016/j.progpolymsci.2004.10.001.

Schmidt, N., Castro-Jiménez, J., Fauvelle, V., Ourgaud, M., Sempéré, R., 2020. Occurrence of organic plastic additives in surface waters of the Rhône River (France). Environ. Pollut. 257, 113637. https://doi.org/10.1016/j.envpol.2019.113637

Schmidt, N., Castro-Jiménez, J., Oursel, B., Sempéré, R., 2021. Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: Exploring

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

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

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

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

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

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

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

Umgiesser, G., Zemlys, P., Erturk, A., Razinkova-Baziukas, A., Mėžinė, J., and Ferrarin, C., 2016. "Seasonal renewal time variability in the Curonian Lagoon caused by atmospheric and hydrographical forcing", *Ocean Sci*., 12, 391–402, https://doi.org/10.5194/os-12-391-2016.Vybernaite-Lubiene, I., Zilius, M., Giordani, G., Petkuviene, J., Vaiciute, D., Bukaveckas, P.A., and Bartoli, M.,. 2017. "Effect of Algal Blooms on Retention of N, Si and P in Europe's Largest Coastal Lagoon." *Estuarine, Coastal and Shelf Science* 194: 217–28. https://doi.org/10.1016/j.ecss.2017.06.020.

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

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

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

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

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