

Article

# Anthropogenic Occurrence of Phthalate Esters in Beach Seawater in the Southeast Coast Region, South Korea

Huijin Heo <sup>1,†</sup>, Mi-Jin Choi <sup>1,†</sup>, Jongkwan Park <sup>2</sup>, Taewoo Nam <sup>1</sup> and Jaeweon Cho <sup>1,\*</sup>

<sup>1</sup> School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea; heohuijin@unist.ac.kr (H.H.); cmj111@unist.ac.kr (M.-J.C.); time\_free@nate.com (T.N.)

<sup>2</sup> School of Civil, Environmental and Chemical Engineering, Changwon National University, Changwon, Gyeongsangnamdo 51140, Korea; jkpark2019@changwon.ac.kr

\* Correspondence: jaeweoncho@unist.ac.kr; Tel.: +82-052-217-2833

† These authors contributed equally to this work.

Received: 4 December 2019; Accepted: 27 December 2019; Published: 30 December 2019



**Abstract:** In modern times, humans have contributed to the occurrence of phthalate esters (PEs) in various environmental matrices by consuming plastics that generally contain PEs, which are essential synthetic organic chemicals for fabrication of various consumer products. Five beaches in Ulsan and Busan, South Korea, were investigated for the anthropogenic occurrence of four PEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), and bis(2-ethylhexyl) phthalate (DEHP)) in beach seawater. Using stir-bar sorptive extraction-thermal desorption-gas chromatography/mass spectrometry, DnBP and DEHP were determined as generally dominant. At Ilsan Beach, both the northern and southern ends showed higher DnBP and DEHP concentrations than the middle of the beach, while DMP and DEP showed similar concentrations at all points. The differences in the DnBP and DEHP concentrations may be related to the fishery industry and domestic sewage inflow to the beach. In addition, a comparison among Ilsan, Imnang, and Songjeong beaches suggested the effects of neighboring industrial areas on the DnBP and DEHP ratio. This study provides information on the effects of seasons, weather events, the proximity of rivers, industrial behavior, and domestic sewage to PE concentrations in beach seawater.

**Keywords:** anthropogenic occurrence; beach; phthalate esters; SBSE-TD-GC/MS

## 1. Introduction

Phthalates, or more precisely phthalate esters (PEs), are an essential additive in the majority of plastic products and consumer products such as toys, packaging, building materials, cosmetics, and fragrance solvents, as they enhance plastic flexibility and fragrance persistence [1]. These PEs easily migrate from the products to other matrices due to the weak attraction between PE and plastic monomer molecules caused by a physically mixed rather than chemically bonded state [2]. For example, in everyday life, PEs generally migrate from consumer products to the hands and body by touch, even when present only at trace concentrations [3]. In addition, attention to PEs is increasing as concerns regarding their occurrence in the environment and human exposure have been raised. Some PEs affect organisms as endocrine-disrupting chemicals (EDCs) and are suspected carcinogens and developmental toxicants [4–6]. Therefore, the U.S. Environmental Protection Agency (EPA) designated six PEs as being of primary concern in 2007: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), butyl-benzyl-phthalate (BBP), bis(2-ethylhexyl)-phthalate (DEHP), and di-*n*-octyl phthalate (DnOP).

The occurrence and concentrations of PEs in the environment are affected by natural and anthropogenic factors. PEs are mainly emitted to environmental matrices as releases and leachates from the PE-containing products [3]. The concentrations of emitted PEs in environmental matrices are influenced by physicochemical interactions between PEs and the matrix. In addition, natural phenomena, such as rainfall and ocean currents, can affect the PEs concentration in a water body [7].

However, PEs in environmental matrices cannot be easily analyzed because of their trace-level concentrations, high background concentrations, contamination during analysis, and complex pretreatment methods [8]. To address these difficulties, many types of research efforts have been reported regarding improved methods to understand the fate and concentration of PEs in environmental matrices such as the hydrosphere, atmosphere, lithosphere, and anthroposphere [7,8]. For example, PE determination and monitoring in natural water systems, particulate matter, agricultural soil, house dust, and personal care products have been investigated [9–13]. In these studies, gas chromatograph/mass spectrometers (GC/MS) have generally been used as an analytical instrument followed by suitable pretreatment methods for each sample type. For efficient pretreatment of water samples, stir-bar sorptive extraction (SBSE) and thermal desorption (TD) have been suggested, which are extraction methods for organic chemicals in a liquid matrix and involve stirring with a polydimethylsiloxane (PDMS)-coated stir bar [14]. Pretreatment using TD facilitates simple sample preparation by inserting the stir bar directly into the extraction of the TD unit directly without any back extraction. The TD unit desorbs extracted compounds in the stir bar by heating, concentrates the desorbed compounds, and injects the concentrate into a GC/MS.

In addition, the SBSE-TD method is known as a green analytical chemistry technology because organic solvents are not required during the pretreatment process [8]. For example, the National Institute of Environmental Research (NIER) of Korea suggested that the standard method for PE determination should be via concentration by liquid–liquid extraction, purification with florisil columns, and analysis by GC/MS [15]. Throughout the pretreatment process, 200 mL of sample is required and more than 150 mL of organic solvent is used. The pretreatment process takes at least 80 min, and it is difficult to pretreat several samples simultaneously. However, the SBSE-TD method requires only 25 mL of sample and no organic solvent. It takes 60 min to stir but is efficient because several samples can be pretreated simultaneously. Desorption and concentration take place in the TD, which is directly connected to the GC, saving time and effort.

Although many types of environmental matrices have been selected for monitoring PEs, there are few studies of PE occurrences on beaches. Furthermore, PE concentrations in Korean seawater have hardly been reported. Here, we focused on beaches as they facilitate exposure to PEs as people frequent beaches and have direct contacts with the beach environment, such as seawater and sand. Furthermore, many types of plastic products and consumer products are indiscriminately used at beaches. There is inevitable PE exposure from seawater and sand, while beach users are without any perception regarding PEs.

As a starting point of PE monitoring in South Korea, we selected the five beaches of Ulsan and Busan, which have their own characteristics, i.e., they are either in the vicinity of industrial and residential complexes or the estuary of Nakdong River, which is the longest river in South Korea. The five beaches were Ilsan (IS) and Jinha (JH) beaches in Ulsan, and Imnang (IN), Songjeong (SJ), and Dadaepo (DD) beaches in Busan. The aforementioned six PEs in beach seawater were determined using SBSE-TD-GC/MS. Among the six PEs, BBP and DnOP were usually below detection limits. Therefore, we were interested in determining the concentrations of the other four PEs (DMP, DEP, DnBP, and DEHP) in beach seawater. The results show that DnBP and DEHP were usually dominant and that DnBP concentrations were generally higher than DEHP concentrations at four beaches (IS, JH, IN, and DD), which are located in the vicinities of industrial complexes. In the case of DMP and DEP, DEP was present at a higher proportion than DMP in Spring while the proportions were similar in Summer. This study observed the effects of seasons, weather events, proximity of river, industrial activities, and domestic sewage to PE concentrations in the beach seawater.

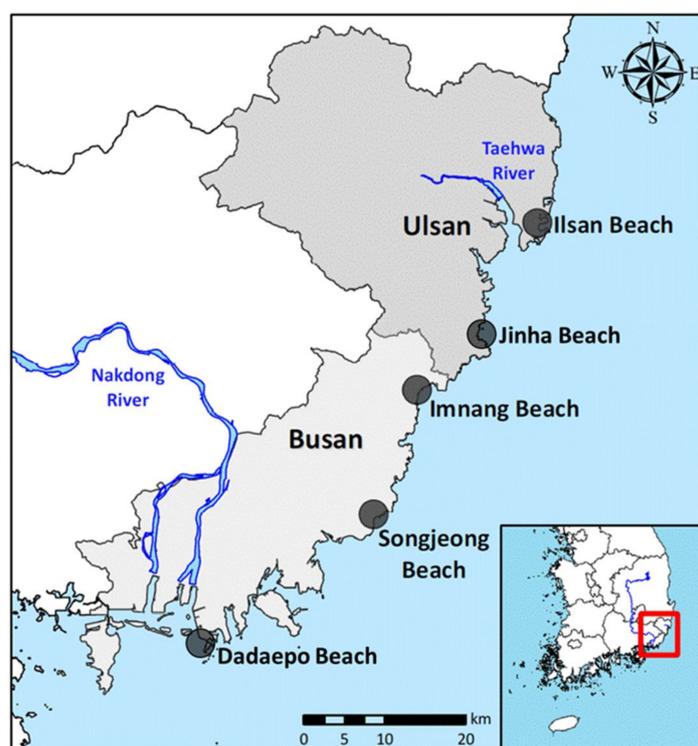
## 2. Materials and Methods

### 2.1. Materials and Reagents

A certified reference material (CRM) for the six PEs, an EPA Phthalate Esters Mix of 2000 µg/mL each in methanol, was purchased from Supelco (Bellefonte, PA, USA). Benzyl benzoate, for an internal standard (ISTD), and sodium chloride for adjusting the ionic strength of spiked samples, were supplied by Sigma–Aldrich (St. Louis, MO, USA). Deionized (DI) water (18.2 MΩ/cm) was prepared using a Barnstead Nanopure water purification system (Thermo Scientific, Marietta, OH, USA). All standard solutions were prepared in high-pressure liquid chromatography (HPLC)-grade methanol (Honeywell Burdick & Jackson, Muskegon, MI, USA) and all spiked solutions were prepared using DI water and the standard solutions. All glassware (except for the volumetric flask) were used after being thoroughly rinsed with DI water and baked at 550 °C for 3 h. Sodium chloride was also baked at 550 °C to remove organic compounds.

### 2.2. Sampling

Sampling sites for PE determination were Ilsan and Jinha beaches in Ulsan and Imnang, Songjeong and Dadaepo beaches in Busan, South Korea (Figure 1). These sites were selected considering popular density, the existence of adjacent industrial complex and river, and other factors that may affect the PE concentrations (Table 1). All five beaches are affected by the East Korean Warm Current [16]. Ilsan and Jinha beaches are cove terrain and stretch from north to south. Imnang and Songjeong beaches stretch from northeast to southwest. Dadaepo Beach stretches from northwest to southeast. Ilsan, Songjeong, and Dadaepo beaches are in the vicinity of large urbanized residential and commercial areas, while Jinha and Imnang beach are in rural areas with the lowest population density (221 and 179 people/km<sup>2</sup>, respectively). Particularly, four beaches (except Songjeong Beach) are in the vicinities of industrial complexes.



**Figure 1.** Target beaches in Ulsan and Busan and sampling locations at each beach, South Korea.

Table 1. Basic information on the sampling sites.

Characteristics	Ilsan Beach (IS)	Jinha Beach (JH)	Imnang Beach (IN)	Songjeong Beach (SJ)	Dadaepo Beach (DD)
<b>Regional</b>					
City	Ulsan	Ulsan	Busan	Busan	Busan
Coast classification	Ulsan Coast	Onsan Coast	Gijang Coast	Busan Coast	Nakdong River Estuary
Population density (people/km <sup>2</sup> ) <sup>a</sup>	3551	221	179	2244	5875
Number of visitors, 2017 <sup>b</sup>	518,300	480,035	265,700	4,305,000	7,320,000
Number of swimmers, 2017 <sup>b</sup>	22,566	247,115	265,700	286,950	4,993,700
Neighboring industrial areas	O	O	O	X	O
<b>Seawater</b>					
pH	8.3	8.0	7.9	8.0	8.1
Conductivity (mS/cm)	51	49	40	50	50
TOC (mg C/L)	0.8–1.3	1.2–1.5	1.4–2.2	1.2–1.4	1.7
TN (mg N/L)	0.2–0.3	0.3–0.4	0.5–1.3	0.2–0.3	0.2–0.5
UVA <sub>254nm</sub>	0.008–0.011	0.011–0.014	0.010–0.026	0.010–0.014	0.016–0.026
SUVA	0.7–1.4	0.7–1.2	0.7–1.2	0.7–1.2	0.9–1.6

TOC—total organic carbon, TN—total nitrogen, UVA<sub>254nm</sub>—UV absorbance measurements at 254 nm, SUVA—specific ultraviolet absorbance. <sup>a</sup> Statistics Korea, <sup>b</sup> Coastal Portal, Ministry of Oceans and Fisheries.

Surface seawater samples were collected at the middle point of each beach in baked amber glass bottles and stored in a refrigerator at 4 °C until pretreatment. Samples were analyzed as soon as possible to prevent the loss of any analytes.

### 2.3. Phthalate Ester (PE) Analysis Through Stir-Bar Sorptive Extraction-Thermal Desorption-Gas Chromatograph/Mass Spectrometer (SBSE-TD-GC/MS)

Seawater samples were pretreated using SBSE-TD. The PDMS-coated stir bars and TD unit (JTD-505 III) were supplied by Japan Analytical Industry Co., Ltd. (Tokyo, Japan). Stir bars were conditioned using nitrogen gas at 280 °C for 3 h prior to commencing the extraction. Spiked samples for SBSE optimization and calibration were prepared using DI water and sodium chloride, and standard solutions were diluted from the PE CRM and HPLC-grade methanol. Sodium chloride was added to reflect the seawater salinity based on the mean conductivity of the sampling sites (~50 mS/cm, Table 1). The sample volume for each extraction was 25 mL and the extractions were conducted at room temperature with the glass bottle closed using a polytetrafluoroethylene (PTFE)-coated cap. Following the extraction, the stir bar was dried with lint-free tissue and delivered into a TD vial. The desorption parameters and GC/MS conditions are listed in Table 2. After optimization of the SBSE condition, the samples were extracted using a PDMS stir bar at 1000 rpm for 60 min. The theoretical recovery of SBSE is known to be proportional to the  $K_{ow}$  of the analyte, and the calculated recovery of each PE is 20.8%, 62.4%, 99.5%, and 100% for DMP, DEP, DnBP, and DEHP, respectively [14]. However, these theoretical values differ from practical recovery because the theoretical recovery considers only the SBSE step, not the entire determination process. The experimental recovery of the optimized SBSE-TD-GC/MS conditions were 13.5%, 46.7%, 136.0%, and 102.0% for DMP, DEP, DnBP, and DEHP, respectively.

**Table 2.** Parameters of thermal desorption (TD) unit and gas chromatograph/mass spectrometer (GC/MS).

Parameters	Description
TD unit	
Transfer line temperature (°C)	280
Desorption temperature (°C)	280
Cryofocusing temperature (°C)	−40
Needle temperature (°C)	280
Injection time (min)	3
GC/MS	
Carrier gas	Helium (99.999%)
Temperature program	100 °C–(5 °C/min)–290 °C (4 min)
Column	DB-5MS (30 m × 0.25 mm, 0.50 µm, Agilent)
Ion source temperature (°C)	250
Interface temperature (°C)	280
Column flow (mL/min)	1.2
Split ratio	10:1

Each concentrated extract from seawater in the TD unit was injected automatically to a GC/MS (GCMS-QP2010 Ultra, Shimadzu Cor., Kyoto, Japan). Detailed conditions for the analysis are presented in Table 2. Detection was conducted in scan mode for the identification of PEs and selected ion monitoring (SIM) mode for quantification (Table 3).

**Table 3.** Retention time and selected ions for the determination of phthalate esters (PEs).

Compounds	Retention Time (min)	Selected Ions (Quantifier, Qualifier)	LOD (ng/L)
1 DMP	13.4	163, 77	5
2 DEP	16.7	149, 177	5
ISTD Benzyl-benzoate	21.1	105, 91	-
3 DnBP	24.8	149, 150	13
4 DEHP	35.2	149, 167	21

LOD—limit of detection; DMP—dimethyl phthalate; DEP—diethyl phthalate; ISTD—internal standard; DnBP—di-*n*-butyl phthalate; DEHP—bis(2-ethylhexyl)-phthalate.

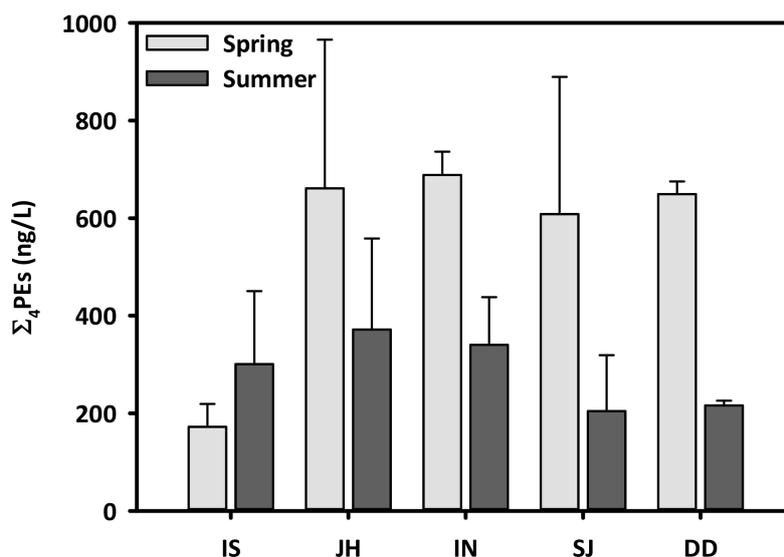
### 3. Results and Discussion

#### 3.1. Occurrence Tendency of PEs in the Southeast Coast Region, South Korea

During the Spring and Summer of 2017, four PEs occurred in seawater in five beaches located in the southeast coast region of South Korea. The sum of four PE concentrations ( $\sum_4$ PEs) showed different tendencies depending on the season and the site (Figure 2). The  $\sum_4$ PEs in Spring and Summer ranged from 172 ng/L to 689 ng/L and from 205 ng/L to 372 ng/L, respectively, with mean values of 556 ng/L and 287 ng/L. In Spring,  $\sum_4$ PEs were higher than in Summer except for at IS. Besides, four beaches (except IS) showed similar  $\sum_4$ PEs with a deviation less than 0.20% in Spring, and the  $\sum_4$ PEs at IS were four times lower than that at IN. In Summer, the highest  $\sum_4$ PEs (372 ng/L) were at JH, whereas SJ showed the lowest  $\sum_4$ PEs (205 ng/L), which were similar to that at DD.

The high PE concentrations in the areas near the river–sea border (JH and DD) with a range of salinities may have resulted from the close integration of soluble soil and humus derived from rivers containing macromolecular material, which resulted in increased apparent solubility and reduced apparent adsorption of macromolecular material [17]. The concentration of emitted PEs is affected by several natural phenomena such as seawater properties, weather, and other environmental factors [7]. In addition, PE concentrations in water are affected by partitioning among adjacent environmental matrices such as sediment and suspended particles [18,19]. In a different view, PEs are

emitted into seawater from adjacent residential and/or industrial complexes as well as anthropogenic factors including visitors and their personal belongings. It was reported that there were higher PE concentrations in sediment from an urbanized area than from a rural area, due to greater anthropogenic activity in the urban area [13]. Therefore, it was assumed that population density and the size of neighboring industrial complexes are related to the PE concentrations at each beach. Additionally, there are numerous potential industrial sources (such as machinery, textile, fabricated metal and electronic productions, and shipping activity) along the river, especially in the downstream and estuary regions of the sampling sites.

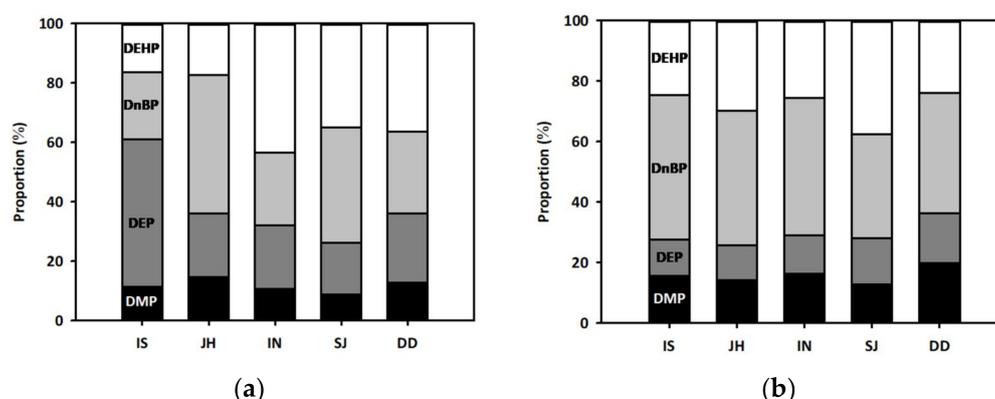


**Figure 2.** Sum of four phthalate ester (PE) concentrations ( $\Sigma_4$ PEs) in the seawater of five beaches in the Spring and Summer of 2017. IS—Ilsan Beach; JH—Jinha Beach; IN—Imnang Beach; SJ—Songjeong Beach; DD—Dadaepo Beach. The error bars indicate the standard deviation.

The proportional PE distributions were compared in Figure 3. The largest seasonal changes in the proportion of PEs were observed at IS, where DEP (50%) constituted half of the  $\Sigma_4$ PEs in Spring, while DnBP (48%) was dominant in Summer. At JH, DnBP contributed almost half of the  $\Sigma_4$ PEs in both seasons. The PEs were dominated by DnBP and DEHP in both seasons at SJ. Interestingly, DnBP was present at noticeably higher proportions at all sampling points in Summer (34~48%). Low proportions of DMP and DEP (13~20% and 11~17%, respectively) in Summer were recorded. However, in Spring, DEHP was dominant in seawater from Busan (IN, SJ, and DD). Additionally, there were higher proportions of DEP than DMP in Spring at all sites, and the ratio varied from 1.4 to 4.4 times while the ratio of DEP to DMP ranged from 0.8 to 1.2 times in Summer. These results are consistent with the water quality of the Nakdong River [17]. As mentioned previously, DD is located at an estuary of the Nakdong River, so the seawater quality at DD can be affected by the water quality of the Nakdong River. DEP and DEHP were the most frequently detected PEs in the effluent of a wastewater treatment plant (WWTP) in the Nakdong River Basin [17]. It was also reported that the DEHP concentration range was wide and that the highest concentration was 12.293  $\mu\text{g/L}$  due to the characteristic of the industrial complex occupying the Nakdong River, whereas the DMP detection rate was the lowest (47.4%) and the concentration was 0.954  $\mu\text{g/L}$  [17].

Additionally, the results in this study were compared to the concentrations of aquatic PEs in other countries. The minimum values were similar, whereas the maximum values were significantly lower (Table 4). In addition, DnBP and/or DEHP are generally the dominant PEs in other countries and in other water matrices. Therefore, additional PE monitoring will be helpful for understanding the anthropogenic occurrence and distribution of PEs in other matrices in the hydrosphere (such as rivers and estuaries), the lithosphere (such as beach sand), and in other environmental spheres. This will, in

turn, allow for a more comprehensive understanding of PE occurrence and its relationship to natural and anthropogenic factors.



**Figure 3.** Proportions of phthalate esters (PEs) in the seawater of five beaches in South Korea in; (a) Spring, and (b) Summer in 2017. IS—Ilsan Beach; JH—Jinha Beach; IN—Imnang Beach; SJ—Songjeong Beach; DD—Dadaepo Beach; DMP—dimethyl phthalate; DEP—diethyl phthalate; DnBP—di-*n*-butyl-phthalate, DEHP—bis(2-ethylhexyl)-phthalate.

**Table 4.** The concentrations of the four phthalate esters (PEs) in various aquatic environments ( $\mu\text{g/L}$ ).

Matrix	Location	DMP	DEP	DnBP	DEHP	References
Rainwater	France	0.07–0.11	0.14–0.25	0.10–0.16	0.36–0.85	[20]
River	China	<loq–1.45	0.01–0.71	0.02–7.19	0.02–28.4	[21–24]
	France	-	0.07–0.18	0.07–0.32	0.16–0.31	[25]
	Iran	0.87	0.67	-	-	[26]
	Spain	-	0.05–0.28	-	0.12–4.98	[27]
Estuary	Spain	0.21–0.28	0.07	1.25–1.26	0.22	[28]
Seawater	Iran	0.49	0.52	-	-	[26]
	Canada	-	-	0.18–3.00	0.01–0.95	[29]
	Spain	<loq–0.25	0.02–0.48	0.25–0.40	0.03–0.62	[27,28]
	South Korea	0.02–0.10	0.02–0.15	0.04–0.36	0.03–0.30	This study

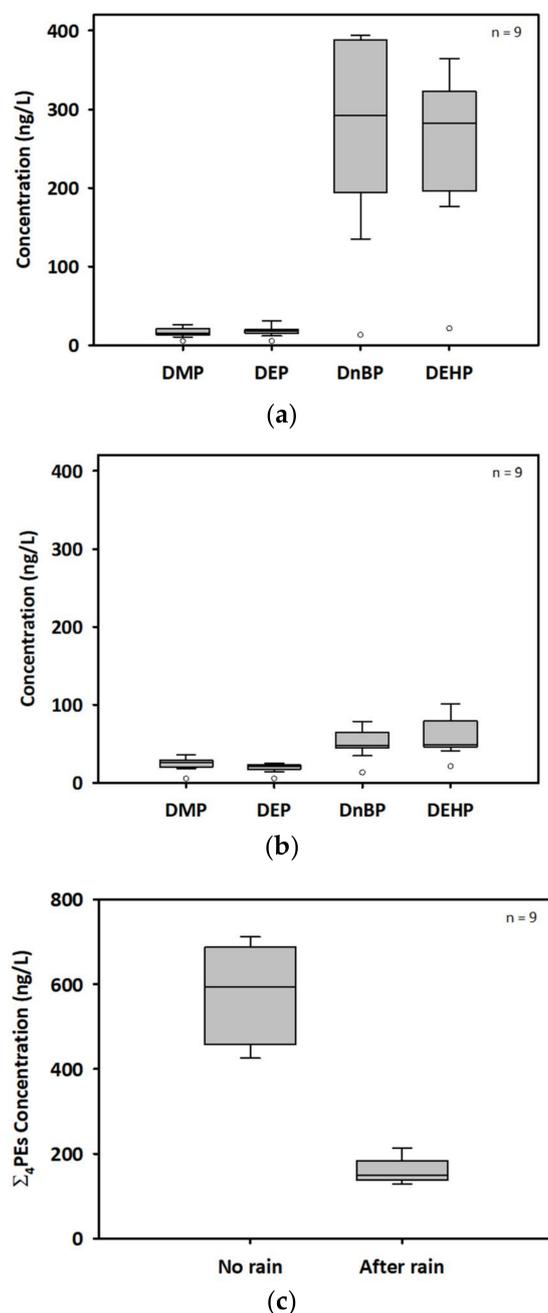
DMP—dimethyl phthalate; DEP—diethyl phthalate; DnBP—di-*n*-butyl-phthalate; DEHP—bis(2-ethylhexyl)-phthalate.

### 3.2. Influence of Rainfall Events on PE Concentrations in Beach Seawater

In South Korea, there is considerable variation in the amount of precipitation between seasons. Dry weather occurs in Spring while local torrential rainfalls and humid weather often occur in Summer. For example, in Ulsan, 26% and 52% of the annual precipitation (671.4 mm) fell in Spring and Summer 2017, respectively. In Busan, 19% and 58% of the annual precipitation (1014.4 mm) fell in Spring and Summer 2017, respectively [15]. Therefore, to observe the seasonality of PEs occurrence, seasonal characteristics must be considered. Prior to Summer sampling, rainfall had occurred for three consecutive days; the rainfall amount in Ulsan and Busan was 29 mm and 45 mm, respectively. It was indicated that heavy rainfall events dilute the PE concentrations in the seawater of the beaches, except IS (data not shown). Similarly, both increases and decreases in pharmaceutical concentrations in seawater due to heavy rainfall events have previously been reported [30,31].

The site at IS was selected for additional sampling because it showed the largest change rate (74.6%) of  $\sum_4\text{PEs}$  between Spring and Summer. To observe concentration changes following the rainfall event, seawater samples were collected before and after rainfall from IS in Spring, 2018 (Figure 4). Rainfall of 24 mm occurred in one day. In the seawater samples taken prior to the rainfall event, DnBP and DEHP were much higher than DMP and DEP, constituting more than 90% of  $\sum_4\text{PEs}$ . Following

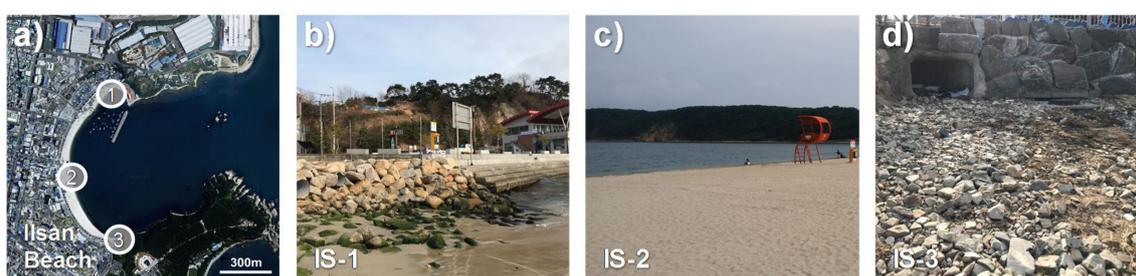
the rainfall event, DnBP and DEHP were reduced by 83% and 84%, respectively, while DMP and DEP were present at similar concentrations before and after the rainfall event. Accordingly, the portions of DMP and DEP increased to 12~19% of  $\sum_4$ PEs. These results imply that PE concentrations are sensitive to extreme external impacts like heavy rainfall events. Therefore, it can be helpful to combine grab sampling with passive sampling for observing temporal tendencies of PE concentrations in seawater.



**Figure 4.** Phthalate ester (PE) concentrations at Ilsan Beach in Spring of 2018: (a) before rain, (b) after rain, and (c)  $\sum_4$ PEs in seawater. n—number of analyzed samples. ○ means LOD of each PE. DMP—dimethyl-phthalate; DEP—diethyl-phthalate; DnBP—di-*n*-butyl-phthalate; DEHP—bis(2-ethylhexyl)-phthalate;  $\sum_4$ PEs—sum of the four PE concentrations. The error bars indicate the standard deviation.

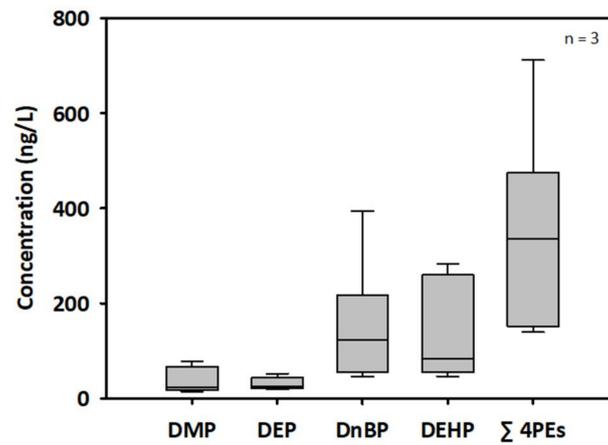
### 3.3. Influence of Sampling Sites at Ilsan Beach

Generally, PEs are not homogeneous in seawater near coastal areas and have both vertical and horizontal distributions. Furthermore, PEs generally showed high concentrations in surface water and may be affected by industrial and domestic sewage inflow [32,33]. Therefore, this study targeted surface seawater at three points that could indicate the influence of industries (especially fisheries), sewage inflow, and human activity (Figure 5a). Around the northern end of the beach, IS-1, there are several restaurants, two sewage outlets (that were not flowing at the sampling time), and several anchored fishing boats (Figure 5b). Near the southern end, IS-3, a flowing sewage outlet was observed, and the effluent appeared to be domestic sewage from neighboring residential areas and restaurants (Figure 5d). Unlike both ends, the middle of the beach, IS-2, was considered to have relatively minimal influence from the fishery industry and sewage. That is, the main source of PEs in IS-2 can be assumed to be beach visitors and swimmers.

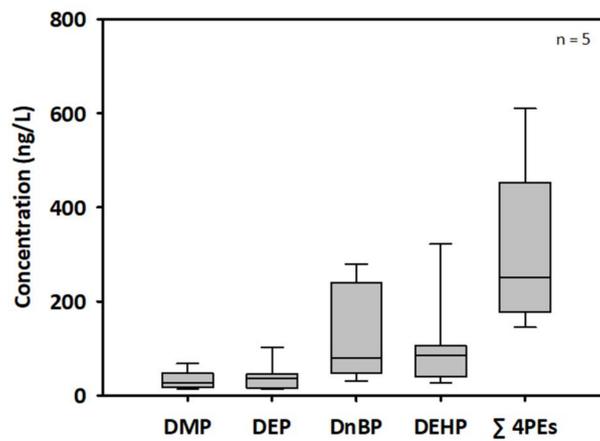


**Figure 5.** (a) Satellite photograph of Ilsan Beach, South Korea, and sampling locations at the beach: beach seawater samples were collected at: (b) the northern end (1, denoted as IS-1), (c) the middle of the beach (2, denoted as IS-2), and (d) at the southern end (3, denoted as IS-3).

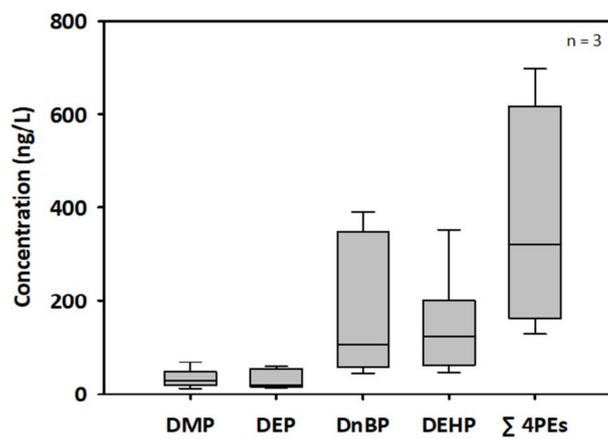
In terms of sampling points at Ilsan Beach,  $\sum_4$ PEs was higher at both ends than at IS-2 (Figure 6). The DMP and DEP concentrations were similar at all points (approximately 61 ng/L and 50 ng/L, respectively), however, there were differences in the DnBP and DEHP concentrations. At IS-2, the DnBP concentration was 80 ng/L, which was approximately half the concentrations at IS-1 (158 ng/L) and IS-3 (167 ng/L), and the proportion of DnBP (31%) was also lower than that at both IS-1 (45%) and IS-3 (40%). Ilsan Beach has coastal fishery-related activities, such as fishing boats and a seaweed farm near IS-1 and IS-3, respectively. Therefore, the coastal fishery industry could be a source of DnBP, considering the DnBP concentration at both ends. In addition, IS-3 showed the highest DEHP concentration (131 ng/L) that was 1.5 and 1.7 times higher than that at IS-1 (88 ng/L) and IS-2 (76 ng/L), respectively. It is thought that domestic sewage could be a source of DEHP; thus, sewage may have contributed to the high DEHP concentration [7].



(a)



(b)



(c)

**Figure 6.** The occurrence of four phthalate esters (PEs) at three sites: (a) the northern end, (b) the middle, and (c) the southern end of Ilsan Beach, South Korea, during Winter and Spring of 2018. n = number of sampling; DMP—dimethyl phthalate; DEP—diethyl-phthalate; DnBP—di-*n*-butyl-phthalate; DEHP—bis(2-ethylhexyl)-phthalate;  $\Sigma$ <sub>4</sub>PEs—sum of the four PE concentrations. The error bars indicate the standard deviation.

#### 4. Conclusions

Among the many factors affecting PE concentrations, this study focused on anthropogenic effects on PE concentrations in beach seawater. To investigate the characteristics of PE occurrences in South Korea, Ilsan, Jinha, Imnang, Songjeong, and Dadaepo beaches were monitored. It was revealed that PE proportions and distributions were affected by effluent from industrial wastewater, the wastewater treatment plant, and human activities. In the case of Ilsan Beach, the  $\sum_4$ PEs were higher during Summer than Spring, while the other 4 beaches showed opposite results in the  $\sum_4$ PEs. In addition, both ends of the beach showed higher concentrations than at the middle of the beach, which appeared to be related to the fishery industry and domestic sewage inflow. According to the surrounding environments of five target beaches, the ratio of DnBP and DEHP concentrations seemed to be influenced by the neighboring industrial areas. Because PEs have been used in various products, clear indicators connecting PE concentrations and specific human activities have not yet been revealed. Therefore, observations will continue in terms of temporal extension and various effects from other matrices on the beaches. Moreover, the relationships of demographic and geographic factors to PE concentrations to categorize PE occurrence patterns and associated human activities will be further explored in future studies.

**Author Contributions:** Conceptualization, J.C.; data curation, M.-J.C.; formal analysis, H.H. and T.N.; investigation, H.H., M.-J.C., and T.N.; methodology, H.H. and J.P.; supervision, J.C.; validation, J.P.; visualization, H.H. and M.-J.C.; writing—original draft, H.H.; writing—review and editing, M.-J.C. and J.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (MSIT) (No.: NRF-2015R1A5A7037825 & NRF-2017K1A3A9A01013898).

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Net, S.; Sempere, R.; Delmont, A.; Paluselli, A.; Ouddane, B. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environ. Sci. Technol.* **2015**, *49*, 4019–4035. [[CrossRef](#)] [[PubMed](#)]
2. Serôdio, P.; Nogueira, J.M.F. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Res.* **2006**, *40*, 2572–2582. [[CrossRef](#)] [[PubMed](#)]
3. Stanley, M.; Robillard, K.; Staples, C. Series Anthropogenic Compounds, Phthalate Esters, the Handbook of Environmental Chemistry. Springer: Berlin, Germany, 2003.
4. Grandjean, P.; Landrigan, P.J. Neurobehavioural effects of developmental toxicity. *Lancet Neurol.* **2014**, *13*, 330–338. [[CrossRef](#)]
5. Kluwe, W.M.; McConnell, E.E.; Huff, J.E.; Haseman, J.K.; Douglas, J.F.; Hartwell, W.V. Carcinogenicity testing of phthalate esters and related compounds by the National Toxicology Program and the National Cancer Institute. *Environ. Health Perspect.* **1982**, *45*, 129–133. [[CrossRef](#)]
6. Roy, J.R.; Chakraborty, S.; Chakraborty, T.R. Estrogen-like endocrine disrupting chemicals affecting puberty in humans—A review. *Med. Sci. Monit.* **2009**, *15*, RA137–RA145.
7. Gao, D.-W.; Wen, Z.-D. Phthalate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. *Sci. Total Environ.* **2016**, *541*, 986–1001. [[CrossRef](#)]
8. Net, S.; Delmont, A.; Sempéré, R.; Paluselli, A.; Ouddane, B. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. *Sci. Total Environ.* **2015**, *515*–516, 162–180. [[CrossRef](#)]
9. Kong, S.; Ji, Y.; Liu, L.; Chen, L.; Zhao, X.; Wang, J.; Bai, Z.; Sun, Z. Spatial and temporal variation of phthalic acid esters (PAEs) in atmospheric PM 10 and PM 2.5 and the influence of ambient temperature in Tianjin, China. *Atmos. Environ.* **2013**, *74*, 199–208. [[CrossRef](#)]
10. Koniecki, D.; Wang, R.; Moody, R.P.; Zhu, J. Phthalates in cosmetic and personal care products: Concentrations and possible dermal exposure. *Environ. Res.* **2011**, *111*, 329–336. [[CrossRef](#)]

11. Otake, T.; Yoshinaga, J.; Yanagisawa, Y. Exposure to phthalate esters from indoor environment. *J. Expo. Sci. Environ. Epidemiol.* **2004**, *14*, 524–528. [[CrossRef](#)]
12. Wang, J.; Bo, L.; Li, L.; Wang, D.; Chen, G.; Christie, P.; Teng, Y. Occurrence of phthalate esters in river sediments in areas with different land use patterns. *Sci. Total Environ.* **2014**, *500*, 113–119. [[CrossRef](#)] [[PubMed](#)]
13. Zheng, X.; Zhang, B.-T.; Teng, Y. Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities. *Sci. Total Environ.* **2014**, *476*, 107–113. [[CrossRef](#)] [[PubMed](#)]
14. Baltussen, E.; Sandra, P.; David, F.; Cramers, C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcolumn Sep.* **1999**, *11*, 737–747. [[CrossRef](#)]
15. National Institute of Environmental Research. Available online: <https://www.nier.go.kr/NIER/kor/index.do> (accessed on 23 December 2019).
16. Choi, B.-J.; Byun, D.-S.; Lee, K.-H. Satellite-altimeter-derived East Sea Surface Currents: Estimation, Description and Variability Pattern. *Sea* **2012**, *17*, 225–242. [[CrossRef](#)]
17. Kim, G.-A.; Seo, C.-D.; Lee, S.-W.; Ryu, D.-C.; Kwon, K.-W. Monitoring of Hazardous Chemicals for Effluents of STPs and WWTP in the Nakdong River Basin. *J. Environ. Sci. Internat.* **2014**, *23*, 1253–1268. [[CrossRef](#)]
18. Peijnenburg, W.J.; Struijs, J. Occurrence of phthalate esters in the environment of the Netherlands. *Ecotox. Environ. Safe.* **2006**, *63*, 204–215. [[CrossRef](#)] [[PubMed](#)]
19. Preston, M.; Al-Omran, L. Phthalate ester speciation in estuarine water, suspended particulates and sediments. *Environ. Pollut.* **1989**, *62*, 183–193. [[CrossRef](#)]
20. Dargnat, C. Sources, Transfert et Devenir des Phtalates sur le Bassin Versant de la Seine: Caractérisation des Dangers pour l'Environnement et les Ecosystèmes. Ph.D. Thesis, Université Pierre et Marie Curie - Paris VI, Paris, France, 2008.
21. Shi, W.; Zhang, F.-X.; Hu, G.-J.; Hao, Y.-Q.; Zhang, X.-W.; Liu, H.-L.; Wei, S.; Wang, X.-R.; Giesy, J.P.; Yu, H.-X. Thyroid hormone disrupting activities associated with phthalate esters in water sources from Yangtze River Delta. *Environ. Int.* **2012**, *42*, 117–123. [[CrossRef](#)]
22. Zeng, F.; Cui, K.; Xie, Z.; Wu, L.; Liu, M.; Sun, G.; Lin, Y.; Luo, D.; Zeng, Z. Phthalate esters (PAEs): Emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou, China. *Environ. Pollut.* **2008**, *156*, 425–434. [[CrossRef](#)]
23. Zhang, L.; Dong, L.; Ren, L.; Shi, S.; Zhou, L.; Zhang, T.; Huang, Y. Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China. *J. Environ. Sci.* **2012**, *24*, 335–342. [[CrossRef](#)]
24. Zhu, X.J.; Qiu, Y.Y. Measuring the phthalates of xiangjiang river using liquid-liquid extraction gas chromatography. *Proc. Adv. Mater. Res.* **2011**, *301*, 752–755.
25. Dargnat, C.; Teil, M.-J.; Chevreuil, M.; Blanchard, M. Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). *Sci. Total Environ.* **2009**, *407*, 1235–1244. [[CrossRef](#)] [[PubMed](#)]
26. Hadjmohammadi, M.; Fatemi, M.; Taneh, T. Coacervative extraction of phthalates from water and their determination by high performance liquid chromatography. *J. Iran. Chem. Soc.* **2011**, *8*, 10–106. [[CrossRef](#)]
27. Sánchez-Avila, J.; Tauler, R.; Lacorte, S. Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. *Environ. Int.* **2012**, *46*, 50–62. [[CrossRef](#)] [[PubMed](#)]
28. Prieto, A.; Zuloaga, O.; Usobiaga, A.; Etxebarria, N.; Fernández, L.A. 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* **2007**, *1174*, 40–49. [[CrossRef](#)]
29. Keil, R.; Salemme, K.; Forrest, B.; Neibauer, J.; Logsdon, M. Differential presence of anthropogenic compounds dissolved in the marine waters of Puget Sound, WA and Barkley Sound, BC. *Mar. Pollut. Bull.* **2011**, *62*, 2404–2411. [[CrossRef](#)]
30. Gani, K.M.; Tyagi, V.K.; Kazmi, A.A. Occurrence of phthalates in aquatic environment and their removal during wastewater treatment processes: A review. *Environ. Sci. Pollut. R.* **2017**, *24*, 17267–17284. [[CrossRef](#)]
31. Gaw, S.; Thomas, K.V.; Hutchinson, T.H. Sources, impacts and trends of pharmaceuticals in the marine and coastal environment. *Philosophical Trans. R. Soc. B Biol. Sci.* **2014**, *369*, 20130572. [[CrossRef](#)]

32. Paluselli, A.; Aminot, Y.; Galgani, F.; Net, S.; Sempéré, R. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Prog. Oceanogr.* **2017**, *163*, 221–231. [[CrossRef](#)]
33. Zhang, Z.-M.; Zhang, H.-H.; Zhang, J.; Wang, Q.-W.; Yang, G.-P. Occurrence, distribution, and ecological risks of phthalate esters in the seawater and sediment of Changjiang River Estuary and its adjacent area. *Sci. Total Environ.* **2018**, *619*, 93–102. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).