

RESEARCH ARTICLE

**Evaluation of the spatial distribution and potential ecological risk of some common alkylphenols in sediments from the northern coastline of Marmara Sea, Türkiye**

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**Abstract**

In this study, the spatial distribution of alkylphenols in the sediments of the Marmara Sea was investigated for the first time. The targeted alkylphenol analysis was made by gas chromatography with triple quadrupole (GC-MS/MS) system. The 4-tert-octylphenol and 4-nonylphenol were detected in the studied sediments, while 4-n-octylphenol was not quantified. The measured concentrations of 4-tert-octylphenol and 4-nonylphenol were in the range of <DL (below detection limit) – 35.24 and <DL – 8.45 ng/g DW (Dry Weight), respectively. Elevated alkylphenol concentrations were found in the sediments of Kumport and open sea area of the Marmara Sea. The detected 4-tert-octylphenol found in this region, therefore, indicates that alkylphenol contamination may reach far from the coast or maritime activities may be a cause. Based on the classification of the Norwegian Pollution Control Authority (NCPA), some sampling points are in class IV, which means that the sediment thus is posing a high risk for benthic organisms. The risk quotients (RQs) for the sediments investigated also showed that the concentration of 4-tert-octylphenol poses a serious risk.

**Keywords:** GC-MS/MS, sediment, potential ecological risk

**Received:** 20.07.2024, **Accepted:** 29.07.2024

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**Introduction**

Alkylphenols (nonylphenols, octylphenols) which are part of non-ionic surfactants used as household detergents, are emulsifiers, wetting agents, dispersants, and pesticide formulations of industrial products (Fiedler *et al.* 2007). Nonylphenol polyethoxylates and octylphenol polyethoxylates are 80% and 20% respectively, of total alkylphenol ethoxylates (APEO). These compounds could be biodegraded in wastewater treatment plants or released in to the environment

without an efficient degradation process. Subsequently, they lose their ethoxy groups in marine ecosystem, yielding octyl phenol, nonylphenol and their mono, di, tri ethoxylated compounds (Çetintürk 2003; Chen *et al.* 2006; David *et al.* 2009). Furthermore, nonyl and octyl phenols are the primary degradation by-products of alkylphenoxylates (Gu *et al.* 2016). The main route of entry of these compounds into the marine environment is through industrial and municipal wastes, while some studies claimed that the atmospheric route can also be considered (Koniecko *et al.* 2014; Graca *et al.* 2016).

Surface sediments are considered to be the main reservoir hydrophobic organic pollutants in marine ecosystems. However, when the alkylphenols are introduced into the seawater, they can be degraded with not only by microbial degradation but also volatility property, UV and photolysis. The degradation rate in seawater is of the order of 4-NP (2d.) > 4-*t*-OP (13d.). This rapid degradation profile was not directly related to biotic factors such as microbial activity; the easy volatilisation is the main factor. Regarding the degradation in marine sediments, under aerobic conditions, 4-NP showed the faster degradation ( $t_{1/2} = 5.8$  d.) than 4-*t*-OP ( $t_{1/2} > 20$ d.). On the other hand, according to Ying and Kookana (2003), 4-NP and 4-*t*-OP degrade rapidly under aerobic conditions in both seawater and marine sediments, but are likely to persist longer under anaerobic conditions (remained unchanged concentrations in  $\sim 70$ d.).

Alkylphenols in marine environment are classified as endocrine disrupting compounds (EDCs), leading to abnormalities in the alteration of the immune system, feminisation and other abnormalities in marine organisms (Arditsoglou and Voutsas 2012). For this reason, octylphenol and nonylphenol are included in the list of priority action chemicals of the Oslo Paris Commission on Hazardous Substances (OSPAR 2009). Nonylphenol in particular is recognised as the most potentially endocrine disruptor, due to its relatively similar chemical structure to 17 $\beta$ -estradiol. In addition, there are reports in the literature that either short or long-term exposure to nonyl and octylphenol at a wide range of concentrations has toxic effects on marine organisms. Nonylphenol carboxylate (NPEC) is an important stressor for the diatom community in sediments (Brix *et al.* 2012). Nonylphenol (18.74  $\mu\text{g/L}$ ) and octylphenol (160  $\mu\text{g/L}$ ) affect the sea urchin *Paracentrotus lividus* at the reproduction and embryonic developmental stages (Arslan *et al.* 2007); toxicity by growth inhibition, photosynthetic pigment, chlorophyll fluorescence, *etc.*, on the marine microalgae *Chlorella pyrenoidosa* and *Scenedesmus obliquus* (Yang *et al.* 2021); and the nonylphenol-contaminated sediments induce to estrogenic activity through vitellogenin on male mummichogs *Fundulus heteroclitus* (Kurihara *et al.* 2007). Conversely, nonylphenol exposure (1 -10  $\mu\text{g/L}$ ) does not affect sexual differentiation or testis ova in rainbow trout *Oncorhynchus mykiss*, but induces vitellogenin and zona radiata protein expression in the liver (Ackermann *et al.* 2002).

To investigate the impact of these toxic compounds on human health, the levels of alkylphenols in marine organisms have also been studied. In a study on the Italian coast of the Adriatic Sea, where nonylphenol concentrations in edible molluscs were found to be 30 times higher than octylphenol, the collected squid which are pelagic organisms, showed the highest concentration levels of alkylphenol contamination among the molluscs studied (Ferrara *et al.* 2001). According to Gu *et al.* (2016), higher concentrations of alkylphenols (4-*t*-OP, 4-OP, and 4-NP) were found in fish species (64 fish species were studied among 183 samples) which consume either benthic organisms or demersal fish species. For this reason, alkylphenol contamination needs to be investigated in sediment samples where human populations are densely concentrated as this would reflect the impacts on human health.

Therefore, it is necessary to investigate the distribution of alkylphenols and possible source contamination in the Marmara Sea coast, especially in the Istanbul coast, which is the most densely populated city in the Marmara region. Alkylphenols are widely used in industrial and household applications, relatively stable in sediments, and have estrogenic potential. However, to date, there is no data available on the distribution of alkylphenol concentrations. Therefore, we aimed to elucidate alkylphenol concentrations on the northern coast of the Marmara Sea region. This study will be the baseline data of these endocrine disrupting chemicals in the region. Furthermore, in order to protect the marine environment, the environmental risk assessment in high-risk areas will be carried out.

## **Materials and Methods**

### *Study area*

The Marmara Sea is semi-closed and laid in between the Asian and European continents. It is connected via the Istanbul Strait (Bosphorus) to the Black Sea and through the Çanakkale Strait (Dardanelles) to the Mediterranean Sea. The Sea has unique halocline stratification and hydrodynamic conditions (Besiktepe *et al.* 1994). Thus, the Marmara Sea is an important storage sink of the vast range of organic pollutants due to its proximity to many densely industrial cities; one of them is Istanbul with the highest population in Türkiye. Generally, considering the status of Marmara Sea pollution, its ecosystem is prone to follow worst-case scenarios. While our coasts are under pollution pressure directly related to activities such as increasing population, industrialisation and tourism, they are also indirectly polluted due to increasing shipping activities. In addition to loading and unloading ports, fishing harbours and similar areas with different purposes of use are selected as pilot areas to determine the pollution extent, status and characteristics of coastal waters and bottom sediment.

In this study, two major port areas (Ambarlı and Kumport), a fisherman's shelter in the ferry port (Bostancı), an important creek outlet from Kalamış (Kadıköy) Bay to

the Marmara Sea, and the northwest coastline of the Marmara Sea were investigated (Figure 1).

Port area of Ambarlı (A1-19): Ambarlı Port complex, which is easily accessible from the E5 and TEM highways on the European side of Istanbul, is a private port consisting of seven separate port management terminals within the borders of Yakuplu Municipality of Büyükçekmece District, 30 km from the centre of Istanbul. Ambarlı port facilities are a port complex with 6025m berth length, 5400/year ship capacity and 1 152 793 m<sup>2</sup> area and plays an important role in the mobility of Türkiye's foreign trade goods.

Kumport (K1-14): Operating within the Ambarlı Port (AP) facilities, Kumport is one of the 3rd largest ports in Türkiye with its proximity to the Marmara Region, which plays an important role in the Turkish economy in container transportation.

Kurbağalıdere (K1-7): Kurbağalıdere (Kuşdili stream) originates from Kayışdağı and reaches the Marmara Sea north of Kalamış Bay. It is the longest and oldest stream of Kadıköy. It is approximately 9 km long. The stream has been the subject of complaints since the early 2000's due to intense odour and pollution. Starting in 2010, rehabilitation works were carried out.

Bostancı fisherman's shelter (B1-5) – In addition to loading and unloading ports, fishing harbours and similar areas with different purposes of use are selected as pilot areas to determine the pollution extent, status and characteristics of coastal waters and bottom sediment. Bostancı fishing harbour is one of the areas selected for the same purpose as the other sampling areas within the scope of the project.

#### *Sampling collection*

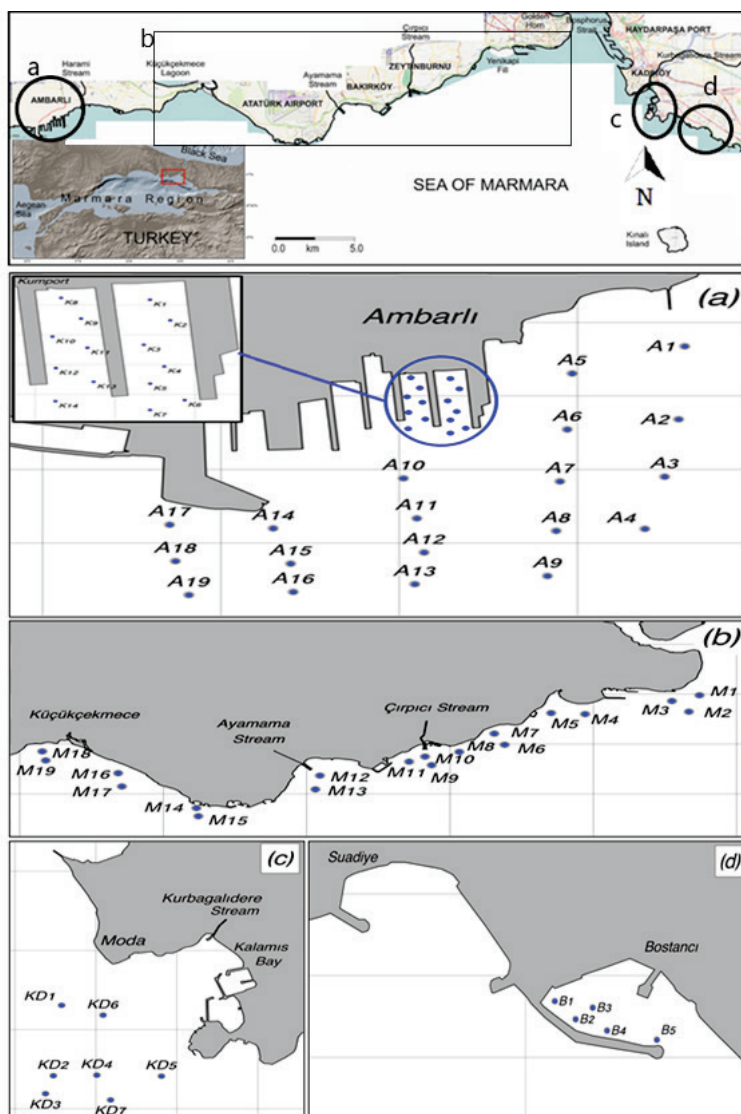
The sampling sites are shown in Figure 1. Sixty four surface sediments were collected from sites having water depths of 11 and 150 m with a Van Veen bottom grab a local boat named "Oğuz-N" in 2012 and 2014. The sampling stations were determined by Magellan ProFlex™ 500 global position system. The topmost 0-3 cm was carefully removed using clean stainless steel spatula. The samples were placed in solvent-cleaned glass-jars with foil-lined seals and they were frozen to -20°C immediately after collection till analysis. Twenty grams of each sample was extracted in 100 mL of dichloromethane solvent for 8 hours in an automated Soxhlet extraction apparatus according to US EPA method 3541. The extracts were then concentrated to 1 mL under a nitrogen stream and analyzed by GC-MS/MS. The analysis was performed in GC-MS/MS system on 2015.

#### *Analytical procedures*

##### *Chemical and reagents*

The individual standards of 4-tert-octylphenol (4-t-OP), 4-n-octylphenol (4-n-OP), 4-nonylphenol (4-NP) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The solvents used (such as acetic acid, methanol, n-hexane and dichloromethane) are analytical grade (Merck, Darmstadt, Germany). The

stock solution was prepared in acetone/hexane (50:50 v/v) at the concentration of 1000 mg/L in amber vials and then stored at -4°C in darkness. In order to perform instrumental analysis, a calibration set was prepared from the working standard solution (10 mg/L) in the concentration range between 10 and 500 ng/ml.



**Figure 1.** Location of the study area and sampling sites (a) Port area of Ambarlı (A1-19) and Kumport (K1-K4), (B1-5), (b) the northwest coastline of the Marmara Sea (M1-19), (c) Kurbagalıdere (KD1-7), (d) Bostancı fishermen's shelter (B1-5).

### *Instrumental Analysis*

Gas chromatography with triple quadrupole mass spectrometry (GC-MS/MS) system was used to quantify the targeted alkylphenols to allow for lower detection limits and matrix effect. Instrument optimisation was performed with the 1 µg/ml concentration mixture. The multiple reaction monitoring (MRM) transition, the collision cell energy voltage (CE) for each ion transition and the ion source temperature were optimised within the instrumental range. The six-point calibration points were injected into the system and calibration curves were obtained. The acquired regression coefficients ( $r^2$ ) of the 4-tert-octylphenol and 4-nonylphenol were 0.9891 and 0.9883, respectively. The procedural blank was always injected at the interval of ten injections to check the possible contamination or carry-over between the injection of samples. The retention time and MRM transitions of each targeted chemical were presented in Table 1. The instrumental analysis was performed with a gas chromatograph 7890B (Agilent Technologies, Palo Alto, USA) combined with triple quadrupole mass spectrometry 7000D (Agilent Technologies, Palo Alto, USA). The GC system was fitted with a multimode inlet (MMI) and HP-5MS UI capillary column (30m x 0.25 mm id x 0.25 µm, Agilent Technologies, USA). The chromatographic separation was achieved by injecting 1 µl in split mode (20:1) and the column flow was set to 1.2 ml/min. The MS transfer line temperature was set to 300°C, the ion source temperature was 230°C, and both quadrupoles were held at 150°C. The oven was programmed as initiated 70°C (held for 3 min.) ramped 40°C/min to 170°C (held for 2min.) then 10°C/min to 300°C (held for 10min.).

**Table 1.** The mass spectrometry analysis parameters of the target analytes, retention time ( $t_R$ ; min.), MRM transitions, and collision energies (CEs, eV)

Analytes	$t_R$	1 <sup>st</sup> Transition		CE	2 <sup>nd</sup> Transition		CE	3 <sup>rd</sup> Transition		CE
		(a)	(b)		(a)	(b)		(a)	(b)	
4- <i>t</i> -OP	10.597	135.0	107.0	13	135.0	77.0	32	107.0	77.0	17
4-NP	11.673	220.0	107.0	14	107.0	77.0	19	107.0	51.0	41

(a) Precursor Ion, (b) Product Ion

### *Quality assurance and quality control (QA/QC)*

The limit of detection (LOD) and limit of quantification (LOQ) levels were calculated based on signal to noise ratio of 3:1 and 10:1, respectively (ICH, Q2 R1, 2006). The measured LOD levels of 4-tert-octylphenol, 4-nonylphenol were 1.39 and 2.11 ng/g, and the LOQ levels were 4.63 and 7.04 ng/g. For the recovery assessment, the reference sediment that were taken in the same sampling region in the open sea Marmara Sea was spiked with 100 ng/g concentration of alkylphenols. Followingly, the same extraction procedure was applied on the recovery sample. The measured recoveries for 4-*t*-OP, 4-NP were found 85% and 92%, respectively. The calculated reproducibility for these analytes was 5.6% and 7.2% (n=3), respectively.

### *The calculation of predicted no-effect concentration and risk values*

The sediment alkylphenol risk assessment values for marine organisms were obtained from the European Chemical Bureau (Assessment E.R. 2002) as for NP and OP 39.0 and 0.75 ng/g, respectively. The risk quotient (RQ) value is calculated as the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration in sediment (PNEC) value ( $RQ = MEC / PNEC$ ). Risk ranking criteria were applied based on Hernando *et al.* (2006); e.g.  $RQ < 0.1$  minimal risk,  $RQ = 0.1 - 1$  moderate risk, and  $RQ > 1$  high risk.

## **Results and Discussion**

### *Distribution of alkylphenol levels in the sediment samples*

It was observed that the spatial distribution of the investigated alkylphenols in the Marmara Sea region variable. The concentrations of the targeted alkylphenols in the investigated sediments in the Marmara Sea are shown in Table 2, although the 4-*n*-octylphenol was measured below the instrumental detection limit in the investigated sediments. A similar 4-*n*-OP result was observed in Thermaikos Bay, Greece (Arditsoglou and Voutsas 2012) and Qingduizi Bay, China (Wang *et al.* 2019). The concentrations of 4-*t*-OP and 4-NP ranged from <DL – 35.24 and <DL – 8.45 ng/g DW, respectively. In general, NP concentrations in water and sediments were found to be higher than OP in the literature due to the percentage of NP used in the ethoxylate formula. In addition, alkylphenol concentrations in coastal and estuarine sediments (lagoons, bights, and harbours) are higher than in open sea sediments. As a consequence, nonylphenol concentrations are expected to exceed octylphenol concentrations (David *et al.* 2009; Wu *et al.* 2013; Duan *et al.* 2014; McLaren and Rawlins 2022).

Conversely, in this study, the 4-*t*-OP showed a significantly higher concentration profile than NP in the sediments investigated. The higher concentration of OP than NP at most sites could be due to the deep water temperature, the amount of oxygen at the stations and the fact that OP has a longer residence time in the environment. Under aerobic conditions, NP degrades faster than OP, due to microbial activity (Ying and Kookana 2003). Deeper water has a lower temperature than surface water, so degradation of ethoxylate forms may be slower or reduced. It could also be an explanation that OP which has a more branched form than NP is not as strongly bound to sediment as NP. Previous studies confirmed that there was a weak correlation between carbon forms (total carbon, organic carbon, and black carbon) and OP, while a strong correlation was observed for NP (Koniecko *et al.* 2014). This phenomenon was previously reported in sediments from the Gulf of Gdansk, Baltic Sea (Koniecko *et al.* 2014) and Qingduizi Bay, China (Wang *et al.* 2019). Another important point is that the occurrence of colloids affects the sorption process of 4-*tert*-octylphenol in marine sediments and as for the desorption process it is mainly determined by the status of fresh (rapidly desorbing) or old sediments (Zhou 2006).

**Table 2.** The concentrations (ng/g DW) of 4-*tert*-octylphenol (4-*t*-OP), 4-nonylphenol (4-NP) at the surface sediments.

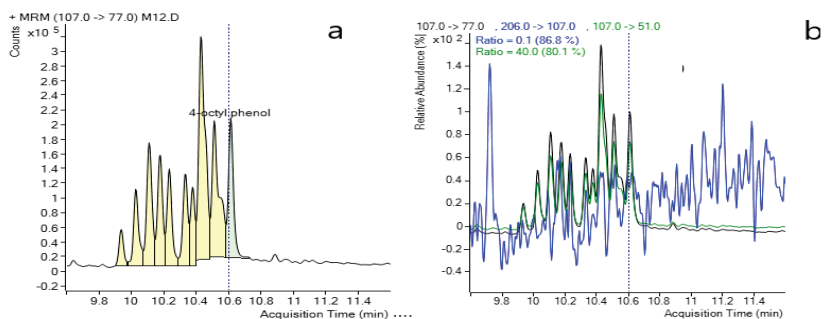
	4- <i>t</i> -OP	4-NP	Sta.	4- <i>t</i> -OP	4-NP	Sta.	4- <i>t</i> -OP	4-NP	Sta.	4- <i>t</i> -OP	4-NP
<b>K1</b>	<DL	<DL	<b>A1</b>	<DL	1.51	<b>M1</b>	<DL	<DL	<b>KD1</b>	<DL	<DL
<b>K2</b>	<DL	2.11	<b>A2</b>	<DL	<DL	<b>M2</b>	<DL	<DL	<b>KD2</b>	1.18	<DL
<b>K3</b>	<DL	<DL	<b>A3</b>	<DL	<DL	<b>M3</b>	<DL	<DL	<b>KD3</b>	<DL	<DL
<b>K4</b>	<DL	<DL	<b>A4</b>	<DL	1.29	<b>M4</b>	<DL	<DL	<b>KD4</b>	<DL	<DL
<b>K5</b>	<DL	<DL	<b>A5</b>	3.16	<DL	<b>M5</b>	<DL	<DL	<b>KD5</b>	<DL	<DL
<b>K6</b>	<DL	0.68	<b>A6</b>	1.73	<DL	<b>M6</b>	<DL	<DL	<b>KD6</b>	<DL	<DL
<b>K7</b>	<DL	1.07	<b>A7</b>	0.65	<DL	<b>M7</b>	<DL	<DL	<b>KD7</b>	<DL	<DL
<b>K8</b>	<DL	2.66	<b>A8</b>	3.22	<DL	<b>M8</b>	<DL	<DL			
<b>K9</b>	8.76*	<DL	<b>A9</b>	<DL	<DL	<b>M9</b>	<DL	<DL	<b>B1</b>	<DL	<DL
<b>K10</b>	<DL	<DL	<b>A10</b>	<DL	<DL	<b>M10</b>	<DL	<DL	<b>B2</b>	<DL	<DL
<b>K11</b>	<DL	<DL	<b>A11</b>	<DL	<DL	<b>M11</b>	<DL	<DL	<b>B3</b>	<DL	<DL
<b>K12</b>	<DL	<DL	<b>A12</b>	2.58	<DL	<b>M12</b>	35.24*	<DL	<b>B4</b>	<DL	<DL
<b>K13</b>	9.02*	<DL	<b>A13</b>	<DL	<DL	<b>M13</b>	<DL	<DL	<b>B5</b>	<DL	8.45*
<b>K14</b>	1.18	<DL	<b>A14</b>	<DL	<DL	<b>M14</b>	<DL	<DL			
			<b>A15</b>	<DL	<DL	<b>M15</b>	3.32	<DL			
			<b>A16</b>	<DL	<DL	<b>M16</b>	<DL	<DL			
			<b>A17</b>	<DL	<DL	<b>M17</b>	<DL	<DL			
			<b>A18</b>	<DL	<DL	<b>M18</b>	<DL	4.21			
			<b>A19</b>	<DL	<DL	<b>M19</b>	2.46	<DL			

<DL; lower than detection limit., \*: higher concentrations than guideline, K: Kumport, A: Ambarlı port, M: Sea of Marmara, KD: Kurbağalidere, B: Bostancı fisherman's shelter

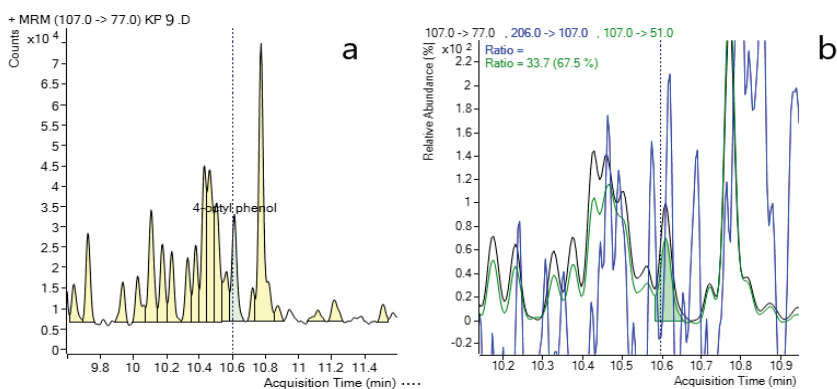
The calculated concentrations of alkylphenols were relatively lower than the instrumental detection limit at some stations, indicating that the contamination could be degraded by microbial activity, oxygen levels or sediment age. In addition, local hydrodynamic conditions (circulation, currents, enhanced weathering and sediment resuspension, etc.) and the rapid evaporation rate of alkylphenols on the surface water should also be considered.

The results of the gas chromatography with triple quadrupole mass spectrometry (GC-MS/MS) analyses of the sediment samples are given in Table 2. The higher concentrations of 4-*t*-OP were detected in the Sea of Marmara (M12; 35.24 ng/g DW, Figure 2) and in the stations of the Kumport (K9; 8.76 ng/g DW and K13; 9.02 ng/g DW, Figure 3), after the sediments of the Ambarlı port area (A5; 3.15 ng/g DW and A8; 3.22 ng/g DW). Meanwhile, the highest concentration of NPs was measured at the Kumport (K8: 2.66 ng/g DW), Bostancı fisherman's shelter (B5; 8.45 ng/g DW, Figure 4) and Marmara Sea (M18: 4.21 ng/g DW).

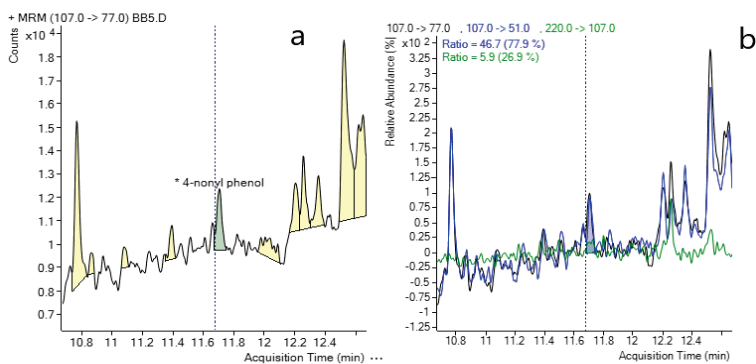




**Figure 2.** The MRM chromatograms of quantitative (a) and qualitative (b) ion transitions of M12 station.



**Figure 3.** The MRM chromatograms of quantitative (a) and qualitative (b) ion transitions of KP9 station



**Figure 4.** The MRM chromatograms of quantitative (a) and qualitative (b) ion transitions of B5 station

Based on the results obtained, the concentration of alkylphenols was detected only at one station in the sediments of Bostancı fisherman's shelter and Kurbağalidere Stream area sediments. For the investigated ports, it was found that the Kumport

(4-*t*-OP: <DL – 9.02 ng/g DW; NP: <DL – 2.66 ng/g DW) was more polluted than the Ambarlı Port (4-*t*-OP: <DL – 3.22 ng/g DW; NP: <DL – 1.51 ng/g DW). Although, alkylphenols were measured at a lower frequency (16%) at the sampled stations, the highest concentration level was observed in the Marmara Sea sediments (especially, in front of Ayamama Creek, at station M12).

Based on the premise of published studies, alkylphenol ethoxylates have also been used in oil and gas fields as emulsifiers in drilling mud formulations, thus their concentrations may be higher offshore than at coastal and estuarine source points (McLaren and Rawlins 2022). There is no oil or gas application infrastructure in the Marmara Sea. The plausible explanation for the finding of the highest octylphenol concentration in the M12, therefore, could be a reflection of the use of non-ionic surfactants for cargo cleaning, oil, dispersal and accidental spillage domestic waste by ship's crew. Therefore, the maritime activities in this area could be the cause of alkylphenol contamination.

#### *Comparison with alkylphenol distribution in sediments from different regions*

No data are available on the distribution of alkylphenols in the sediments of the Marmara Sea region. Therefore, it is not possible to compare the present measured concentrations with previous regional studies. A further comparison was made with the worldwide sediment data published in the literature (Table 3); it was found that in the NP concentrations in this study were higher than Qingduizi Bay, Yellow Sea, China (NP: 0.32 – 0.80 ng/g; Wang *et al.* 2019), while they were lower than Kalamazoo River, Michigan, United States (NP: <5.5 – 15.3 ng/g; Kannan *et al.* 2003), Tai-Shi and Chi-ku coasts, Taiwan (NP: 130 – 190 ng/g; Cheng *et al.* 2006), Pearl River Delta and northern South China Sea (NP: 59 – 7808 ng/g; Chen *et al.* 2006), Masan Bay, Korea (NP: 92 – 557 ng/g; Li *et al.* 2008), Thermaikos Bay, Greece (NP: 223 – 2695 ng/g; Arditoglou and Voutsas 2012), Llobregat, Spain (NP: 0 – 79 ng/g; Brix *et al.* 2012), Huangpu River, Shanghai, China (NP: 10.34 – 337.73 ng/g; Wu *et al.* 2013), Yellow Sea, China (NP: 349.5 – 1642.8 ng/g; Duan *et al.* 2014), East China Sea, China (NP: 31.3 – 1423.7 ng/g; Duan *et al.* 2014), Pearl River Delta, China (NP: 8.7 – 95.2 ng/g; Chen *et al.* 2014), Gulf of Gdansk, Poland (NP: 0.08 – 49 ng/g; Koniecko *et al.* 2014), Kaohsiung Harbor, Taiwan (NP: 18 – 27882 ng/g; Dong *et al.* 2015), Thane Creek, India (NP: 234.56 – 537.78 ng/g; Tiwari *et al.* 2016), Iberian coastal areas, Spain (NP: 201 – 601 ng/g; Salgueiro-Gonzalez *et al.* 2019).

The OP concentrations were higher than in Llobregat, Spain (OP: 2 – 3 ng/g; Brix *et al.* 2012), Yellow Sea, China (OP: 0.8 – 9.3 ng/g; Duan *et al.* 2014), East China Sea, China (OP: 0.7 – 11.1 ng/g; Duan *et al.* 2014), Pearl River Delta, China (OP: 0.3 – 3.0 ng/g; Chen *et al.* 2014); while, it is similar level to, Tai-Shi and Chi-ku coasts, Taiwan (OP: 27 – 49 ng/g; Cheng *et al.* 2006), Thermaikos Bay, Greece (OP: 6.0 – 25 ng/g; Arditoglou and Voutsas 2012), Huangpu River, Shanghai, China (OP: 0.54 – 27.41 ng/g; Wu *et al.* 2013), Iberian coastal areas, Spain (OP: 9.9 – 40.3 ng/g; Salgueiro-Gonzalez *et al.* 2019). While it is lower than Northern

South China Sea (OP: 1 – 93 ng/g; Chen *et al.* 2006), Gulf of Gdansk, Poland (OP: 0.08 – 250 ng/g; Koniecko *et al.* 2014), Kaohsiung Harbor, Taiwan (OP: 1.1 – 1150 ng/g; Dong *et al.* 2015), Thane Creek, India (OP: 107.35 – 268.89 ng/g; Tiwari *et al.* 2016), Qingduizi Bay, Yellow Sea, China (OP: 0.88 – 79.49 ng/g; Wang *et al.* 2019).

**Table 3.** Comparison of octylphenol and nonylphenol concentrations (ng/g, DW) in sediments from different regions

Region	Number of sample	Range Min. – Max.		References
		4- <i>t</i> -OP	4- NP	
Masan Bay, Korea	18	-	92.0 – 557.0	Li <i>et al.</i> 2008
Llobregat, Spain	7	2.0 – 3.0	0 – 79.0	Brix <i>et al.</i> 2012
Thermaikos Bay, Greece	11	6.0 – 25.0	223.0 – 2695.0	Arditsoglou and Voutsas 2012
Huangpu River, Shanghai, China	21	0.54 – 27.4	10.3 – 337.7	Wu <i>et al.</i> 2013
Yellow Sea	41	0.8 – 9.3	349.5– 1642.8	Duan <i>et al.</i> 2014
East China Sea	25	0.7 – 11.1	31.3 – 1423.7	Duan <i>et al.</i> 2014
Gulf of Gdansk, Poland	12	0.08 – 250.0	0.08 – 49.0	Koniecko <i>et al.</i> 2014
Kaohsiung Harbor, Taiwan	20	1.1 – 1150.0	18.0 – 27882.0	Dong <i>et al.</i> 2015
Thane Creek, India	10	107.4 – 268.9	234.6 – 537.8	Tiwari <i>et al.</i> 2016
Qingduizi Bay, Yellow Sea, China	31	0.9 – 79.5	0.3 – 0.8	Wang <i>et al.</i> 2019
Iberian coastal Acaas, Spain	16	9.9 – 40.3	201.0 – 601.0	Salgueiro-Gonzalez <i>et al.</i> 2019
Kumport Marmara Sea, Türkiye	14	<DL – 9.0	<DL – 2.6	This study
Ambarlı port area, Türkiye	19	<DL – 3.2	<DL – 1.5	This study
Bostancı Fisherman's Shelter, Marmara Sea, Türkiye	5	<DL	<DL – 8.4	This study
Kurbağalıdere Marmara Sea, Türkiye	7	<DL – 1.2	<DL	This study
Northern coastline of Marmara Sea Türkiye	19	<DL – 35.2	<DL – 4.2	This study

–: no data available for 4-*t*-OP, <DL: lower than detection limit.

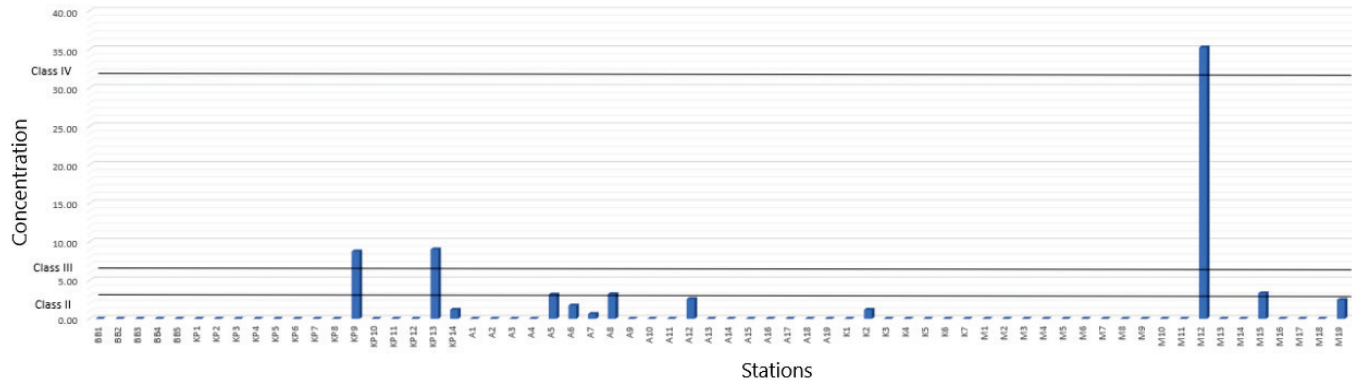
#### *Marine environmental risk assessment*

In order to interpret possible risk to the benthic organisms, the measured concentrations of OP and NP were compared with the Norwegian Pollution Control Authority's PNEC (predicted no effect concentration) values (NPCA

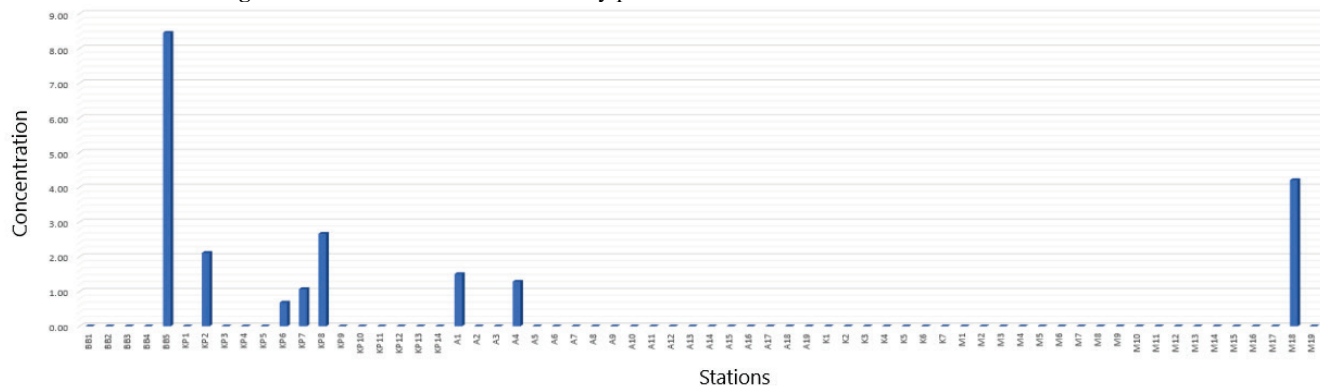
2007). It can be seen that the NP concentrations do not pose a risk to benthic organisms, whereas the OP concentrations of stations K9, K13 (the stations in the port of Kumport) and M12 (in front of the Ayamama stream) are within class IV. According to the Norwegian guidelines, class IV is regarded as poor conditions (Figures 5 and 6 ) for benthic organisms and acute toxic effects from short-term exposure concentration levels. Due to the high amount of OP in station M12 it may have been possible to cause estrogenic disruption to benthic organisms in this area. Therefore, these stations could be accepted as hot spots in the Marmara Sea for alkylphenols and should be monitored in the near future.

The calculated RQ values indicated that 17.46 % and 82.54% of the investigated sediments were at high risk, respectively, for octylphenols in the Marmara Sea region. On the other hand, most of the sediments were at minimal risk for nonylphenol. These results suggested that the alkylphenol risk are not significant for nonylphenol; however, the octylphenol might pose at high toxic effects on benthic organisms in some hot point stations. Similar assessment results were obtained between NPCA and risk quotient values.

It should be emphasised that the synergistic effect of endocrine disrupting chemicals should be considered rather than the effect of individual compounds, in order to protect the biodiversity of the benthic community in the study area.



**Figure 5.** NPCA class limits for 4-t-octylphenol concentrations in Marmara Sea sediments



**Figure 6.** NPCA class limits for 4-nonylphenol concentrations in Marmara Sea sediments

## Conclusions

The distribution of two alkylphenols (OP and NP) in the sediment samples from the north coast of the Istanbul region and the Marmara Sea was investigated. The measured concentrations indicated that the 4-*t*-OP was the dominant contaminant in the studied sediments. The concentration of 4-*t*-OP and NP distribution is a significant spatial variable. The concentrations of the studied alkylphenols in the Marmara Sea region were found to be variable even in each of the sampled regions. The data that is significant contamination status in the M12 sediment sample (in front of the Ayamama stream) provided in this study is that the offshore Marmara Sea sediment samples are also under the burden of alkylphenol contamination than the estuarine and coastal regions. It could be said that the contamination of these compounds is attributable mainly due to anthropogenic activities. However, alkylphenol contamination source was not obvious in the distribution profile in sediment samples. The hydrodynamic conditions, the oxic/anoxic sediment profile and the activity of microorganisms were the main influences on the distribution of alkylphenol compounds. The calculated environmental risk assessment criteria suggest that the concentrations of 4-*t*-OP may expose estrogenic activities to the possible presence of specific benthic fauna. Especially, in the open sea sediment sampling sites were found in poor conditions and exceeding the limit values. The alkylphenol concentrations measured in this study emphasize once again the need for future monitoring programmes, also to investigate possible synergetic estrogenic potency on the benthic fauna.

## Acknowledgments

The sample collection in this study were supported by the Scientific and Technological Research Council of Turkey, Projects number, 111G153, TÜBİTAK KAMAG 1007, and CAYDAG-111Y216.

**Competing interest:** The authors declare that they have no known competing financial interest or personal relationship.

**Ethics committee approval:** There is no necessity fo ethical approval for this research

**Financial disclosure:** This research did not receive any specific grant from funding agencies.

**Author contributions:** K.Ç. conceptualization, methodology, formal analysis, validation, writing – original draft, writing – review & editing. S.Ü. conceptualization, methodology, formal analysis, writing – original draft, writing – review & editing, Supervision.

# Marmara Denizi'nin kuzey kıyı şeridindeki sedimanlarda bazı yaygın alkilfenollerin mekansal dağılımının ve potansiyel ekolojik riskinin değerlendirilmesi

## Öz

Bu çalışmada, alkilfenollerin mekansal dağılımı ilk kez Marmara Denizi sedimanlarında araştırılmıştır. Hedeflenen alkilfenollerin analizi için gaz kromatografisi üçlü kuadrupol (GC-MS/MS) sisteminde belirlenmiştir. Çalışılan sedimanlarda 4-tert-oktilfenol ve 4-nonilfenol tespit edilmiş, 4-*n*-oktilfenol ise ölçülememiştir. Ölçülen 4-tert-oktilfenol ve 4-nonilfenol konsantrasyonları sırasıyla <DL - 35.24 ve <DL - 8.45 ng/g DW (dry weight) aralığındadır. Kumport ve açık Marmara Denizi sediman örnekleme noktalarında yüksek alkilfenol konsantrasyonları bulunmuştur. Bu durum, bu bölgede tespit edilen 4-tert-oktilfenolün, alkilfenol kontaminasyonunun Marmara Denizi kıyı şeridinden çok uzaklara ulaşabileceğini veya denizcilik faaliyetlerinin bir neden olabileceğini gösterdiğini düşündürmüştür. Norveç Kirlilik Kontrol Kurumu (NCPA) sınıflandırmasına göre bazı örnekleme noktaları Sınıf IV'te yer almaktadır, bu da sedimanın bentik organizmalar için yüksek risk oluşturduğunu göstermektedir. Ayrıca, incelenen sedimanlar arasında risk katsayıları (RQ'lar) 4-tert-oktilfenol konsantrasyonunun ciddi bir risk oluşturduğunu kanıtlamıştır.

**Anahtar kelimeler:** GC-MS/MS, sediment, potansiyel ekolojik risk

## References

- Ackermann, G.E., Schwaiger, J., Negele, R.D., Fent, K. (2002) Effects of long-term nonylphenol exposure on gonadal development and biomarkers of estrogenicity in juvenile rainbow trout (*Oncorhynchus mykiss*). *Aquatic Toxicology* 60: 203-221.
- Arditsoglou, A., Voutsas, D. (2012) Occurrence and partitioning of endocrine disrupting compounds in the marine environment of Thermaikos Gulf, Northern Aegean Sea, Greece. *Marine Pollution Bulletin* 64: 2443-2452.
- Arslan, O.C., Parlak, H., Oral, R., Katalay, S. (2007) The effects of nonylphenol and octylphenol on embryonic development of sea urchin (*Paracentrotus lividus*). *Archives of Environmental Contamination and Toxicology* 53: 214-219.
- Assessment, E.R. (2002) 4-nonylphenol (branched) and nonylphenol, European Commission. Institute for Health and Consumer Protection, European Chemicals Bureau. Available at: <https://echa.europa.eu/documents/10162/43080e23-3646-4ddf-836b-a248bd4225c6>. (accessed 28 Feb 2023).

Besiktepe, S.T., Sur, H.I., Ozsoy, E., Latif, M.A., Oguz, T., Unluata, U. (1994) The circulation and hydrography of the Marmara Sea. *Progress in Oceanography* 34(4): 285-334.

Brix, R., Lopez-Doval, J., Ricart, M., Guasch, H., de Alda, M.L., Munoz, I., Orendt, C., Romani, A.M., Sabater, S., Barcelo, D. (2012) Establishing potential links between the presence of alkylphenolic compounds and the benthic community in a European river basin. *Environmental Science and Pollution Research* 19: 934-945.

Chen, B., Duan, J.C., Mai, B.X., Luo, X.J., Yang, Q.S., Sheng, G.Y., Fu, J.M. (2006) Distribution of alkylphenols in the Pearl River Delta and adjacent northern south China Sea, China. *Chemosphere* 63: 652-661.

Chen, R., Yin, P., Zhao, L., Yu, Q., Hong, A., Duan, S. (2014) Spatial-temporal distribution and potential ecological risk assesment of nonylphenol and octylphenol in riverine outlets of Pearl River Delta, China. *Journal of Environmental Sciences* 26: 2340-2347.

Cheng, C.Y., Liu, L.L., Ding, W.H. (2006) Occurence and seasonal variation of alkylphenols in marine organisms from the coast of Taiwan. *Chemosphere* 65: 2152-2159.

Çetintürk, K. (2003) Determination of LAS (linear alkyl benzene sulfonate) in seawater by different methods and the effect of seawater salinity on these determinations. Master Thesis, İstanbul University, Institute of Marine Sciences and Management (in Turkish).

David, A., Fenet, H., Gomez, E. (2009) Alkylphenols in marine environments: Distribution monitoring strategies and detection considerations. *Marine Pollution Bulletin* 58: 953-960.

Dong, C.D., Chen, C.W., Chen, C.F. (2015) Seasonal and spatial distribution of 4-nonylphenol and 4-tert-octylphenol in the sediment of Kaohsiung harbor, Taiwan. *Chemosphere* 134: 588-597.

Duan, X.Y., Li, Y.X., Li, X.G., Zhang, D.H., Gao, Y. (2014) Alkylphenols in surface sediments of the Yellow Sea and East China Sea inner shelf: Occurrence, distribution and fate. *Chemosphere* 107: 265-273.

Ferrara, F., Fabietti, F., Delise, M., Bocca, A.P., Funari, E. (2001) Alkylphenolic compounds in edible molluscs of the Adriatic Sea (Italy). *Environmental Science and Technology* 35: 3109-3112.



Fiedler, S., Foerster, M., Glaser, B., Zech, W. (2007) Alkylphenols in sediments of the Atlantic rainforest south-west of Sao Paulo, Brazil. *Chemosphere* 66: 212-218.

Graca, B., Staniszewska, M., Zakrzewska, D., Zalewska, T. (2016) Reconstruction of the pollution history of alkylphenols (4-tert-octylphenol, 4-nonylphenol) in the Baltic Sea. *Environmental Science and Pollution Research* 23: 11598-11610.

Gu, Y., Yu, J., Hu, X., Yin, D. (2016) Characteristics of the alkylphenol and bisphenol A distributions in marine organisms and implications for human health: A case study of the East China Sea. *Science of the Total Environment* 539: 460-469.

Hernando, M.D., Mezcua, M., Fernandez-Alba, A.R., Barcelo, D. (2006) Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta* 69: 334-342.

ICH (2006), International Conference on Harmonization. Harmonized tripartite guideline, validation and analytical procedures, text and methodology. ICH Q2R1, 2006, p 12-4, Available at: <https://database.ich.org/sites/default/files/Q2%28R1%29%20Guideline.pdf> (accessed 22 Jul 2024).

Kannan, K., Keith, T.L., Naylor, C.G., Staples, C.A., Snyder, S.A., Giesy, J.P. (2003). Nonylphenol and nonylphenol ethoxylates in fish, sediment and water from Kalamazoo River, Michigan. *Archives of Environmental Contamination and Toxicology* 44: 77-82.

Koniecko, I., Staniszewska, M., Falkowska, L., Burska, D., Kielczewska, J., Jasinska, A. (2014) Alkylphenols in surface sediments of the Gulf of Gdansk (Baltic Sea). *Water, Air & Soil Pollution* 225: 2040-2052.

Kurihara, R., Watanabe, E., Ueda, Y., Kakuno, A., Fujii, K., Shiraishi, F., Hashimoto, S. (2007) Estrogenic activity in sediments contaminated by nonylphenol in Tokyo Bay (Japan) evaluated by vitellogenin induction in male mummichogs (*Fundulus heteroclitus*). *Marine Pollution Bulletin* 54: 1315-1320.

Li, D., Dong, M., Shim, W.J., Yim, U.H., Hong, S.H., Kannan, N. (2008) Distribution characteristics of nonylphenolic chemicals in Masan Bay environments, Korea. *Chemosphere* 71: 1162-1172.

Mclaren, D.E.K., Rawlins, A.J. (2022) Occurrence of alkylphenols and alkylphenol ethoxylates in North Sea sediment samples collected across oil and gas fields. *Marine Pollution Bulletin* 178: 113655.

NPCA (2007) Norwegian Pollution Control Authority. Revidering Avlassifisering Av Metaller Og Organiske Miljøgifter I Vann Og Sedimenter. TA-2229. Available at: <https://www.miljodirektoratet.no/globalassets/publikasjoner/klif2/publikasjoner/2229/ta2229.pdf> (accessed 28 Feb 2023).

Oslo and Paris Commission (OSPAR) (2009) Status and trend of marine chemical pollution. Hazardous Substances Series. 396/2009. Available at: <https://www.ospar.org/documents?v=7199> (accessed 28 Feb 2023).

Salgueiro-Gonzalez, N., Campillo, J.A., Vinas, L., Beiras, R., Lopez-Mahia, P., Muniategui-Lorenzo, S. (2019) Occurrence of selected endocrine disrupting compounds in Iberian coastal areas and assessment of the environmental risk. *Environmental Pollution* 249: 767-775.

Tiwari, M., Sahu, S.K., Pandit, G.G. (2016) Distribution and estrogenic potential of endocrine disrupting chemicals (EDCs) in estuarine sediments from Mumbai, India. *Environmental Science and Pollution Research* 23: 18789-18799.

Wang, L., Yang, X., Zhang, A., Bidegain, G., Li, R., Na, G., Yuan, X. (2019) Distribution patterns and ecological risk of endocrine-disrupting chemicals at Qingduizi Bay (China): A preliminary survey in a developing maricultured bay. *Marine Pollution Bulletin* 146: 915-920.

Wu, M., Wang, L., Xu, G., Liu, N., Tang, L., Zheng, J., Bu, T., Lei, B. (2013) Seasonal and spatial distribution of 4-tert-octylphenol, 4-nonylphenol and bisphenol A in the Huangpu River and its tributaries, Shanghai, China. *Environmental Monitoring and Assessment* 185: 3149-3161.

Yang, W., Gao, X., Wu, Y., Wan, L., Lu, C., Huang, J., Chen, H., Yang, Ding, H., Zhang, W. (2021) Chemical and species specific toxicity of nonylphenol and octylphenol to microalgae *Chlorella pyrenoidosa* and *Scenedesmus obliquus*. *Environmental Toxicology and Pharmacology* 81: 103517.

Ying, G.G., Kookana, R.S. (2003) Degradation of five selected endocrine-disrupting chemicals in seawater and marine sediment. *Environmental Science and Technology* 37: 1256-1260.

Zhou, J.L. (2006) Sorption and remobilization behaviour of 4-tert-octylphenol in aquatic systems. *Environmental Science and Technology* 40: 2225-2234.