# Assessing the potential risk and relationship between microplastics and phthalates in surface seawater of a heavily human-impacted metropolitan bay in northern China

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**Abstract:** The impacts of microplastics (MPs) and phthalates (PAEs), a class of MP-associated contaminants, on the marine environment are not thoroughly understood despite concern over their adverse effects on humans and ecosystems. Field studies linking MPs and PAEs in seawater have not yet been reported. We investigate for the first time the correlation between MPs contamination and the presence of PAEs in the surface seawater of Jiaozhou Bay (JZB), a semi-enclosed metropolitan bay in northern China heavily impacted by human activity. The abundance of MPs, dominated by polyethylene and polyethylene terephthalate mostly smaller than 2 mm, ranged between 24.44 items/$m^3$ and 180.23 items/$m^3$, with the majority being black and transparent fibers and fragments. Concentrations of PAEs varied from 129.96 ng/L to 921.22 ng/L. Relatively higher abundances of MPs and higher concentrations of PAEs were generally found in areas near riverine inputs and sewage treatment plants. There was a strong correlation between PAEs concentration and MPs abundance, suggesting that they are closely linked. In a risk assessment combining PAEs and MPs, the risk quotients (RQs) indicated that the ecological risk of di-n-butyl phthalate in JZB was relatively high ($0.046<RQ<0.516$); the risk of the other PAEs were low. The overall ecological hazard index (HI) of PAEs was low to medium ($0.098<HI<0.897$). The risk of MPs pollution in JZB, as indicated by Pollution Load Index (PLI), was moderate ($PLI_{JZB}=11.76$), and mainly due to polyvinyl chloride.

**Key words:** Microplastics; phthalates; risk assessment; surface seawater; Jiaozhou Bay.

## 1. Introduction

Plastics and their products are widely used because of their convenience, light weight, and other advantageous properties (Andrés et al., 2014). However, the overuse and improper disposal of plastics have caused severe environmental problems (Rochman et al., 2013), because they can persist in the environment for tens to hundreds of years (Thompson et al., 2009). Large quantities of microplastics (MPs, size below 5mm) are released and transported into the ocean through rivers, sewage, and the atmosphere (Barnes et al., 2009). They originate either from intentional manufacturing (such as in facial cleansers, toothpastes, and plastic raw material; primary origin) or subsequent fragmentation of large plastics via mechanical, photochemical, and biological degradation (secondary origin) (Wright et al., 2013). MPs in marine systems are dispersed by waves, tides and ocean currents. They may sink through the water column (Cincinelli et al., 2019) and be incorporated into sediments (Klein et al., 2015; Tsang et al., 2017) or be assimilated by marine organisms (Kang et al., 2015) and hence transferred into the whole food web (Van et al., 2015), including marine mammals (Lusher et al., 2015a).

MPs easily adsorb heavy metals (Wang et al., 2017) and persistent organic pollutants (Guo et al., 2012a; Mai et al., 2018) due to their small particle size and high specific surface area, increasing their potential toxicity. Many harmful additives are also added during the production of plastics, such as plasticizers, flame retardants, and antioxidants (Hermabessiere et al., 2017). When MPs are immersed in seawater, they can release some of these poisonous substances (Hahladakis et al., 2018) and act as

vectors for pollutant transfer into the marine biota (Zhang et al., 2018a).

Plasticizers are polymer additives used to make plastics flexible, lightweight, and durable. Phthalic acid esters or phthalates (PAEs) have been the most commonly used plasticizers in the plastics industry for decades. PAEs as plasticizers are not chemically bonded with the plastic matrices, and are easily released into the surrounding environment (Dargnat et al., 2009). According to a report by the Information Handling Services (IHS) Chemistry, the amount of PAEs used to produce plasticizers worldwide was nearly 5.9 million tons in 2014 and is expected to rise to about 6.7 million tons by 2019 (Zhang et al., 2018c). Because of the large quantity and widespread application, PAEs are prevalent in the environment, and have been widely found in air, sea, and land environments (Wang et al., 2008; Zhang et al., 2018b). In addition, PAEs have been detected in some aquatic organisms, such as fish (Adeogun et al., 2015) and algae (Babu and Wu, 2010). PAEs are endocrine disruptive to animals and humans, and may be mutagenic, teratogenic, and carcinogenic (Guo et al., 2012b). Six PAEs, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-Ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DnOP), were listed as environmental priority pollutants by the United States Environmental Protection Agency in 2013 (USEPA, 2013).

Jiaozhou Bay (JZB) is a typical semi-enclosed shallow bay in Qingdao, China, which forms a complex and diverse ecosystem with the surrounding land environment (Fu et al., 2007). JZB is also an important fishery and aquatic base, a sea-salt

production base, and a shipping and tourism economic zone in north China (Gao et al., 2003). With the rapid urbanization and industrialization along the JZB coast, large amounts of industrial waste and anthropogenic pollutants are discharged into JZB directly or via several rivers (Shi et al., 2011). The bay has a low water exchange, with an average residence time of 80 days, ranging from less than 20 days in the deep channel up to 120 days in the shallower northwest area (Liu et al., 2004). This long residence time is favorable for the accumulation of pollutants with a high ecological risk. Owing to its special and distinct location and features, JZB has been and continues to be strongly impacted by anthropogenic activities, providing a good system for the study of MPs and related plasticizers.

Although Zheng et al. (2019) measured MPs in JZB seawater and sediment samples, the level of PAEs has not yet been determined, and no study has evaluated the combined risk of MPs and PAEs using observation data. The influence of environmental parameters, such as water level, water temperature, pH, dissolved oxygen, salinity and conductivity, on the distribution and abundance of MPs and PAEs in semi-enclosed metropolitan bays has also not been reported. Therefore, the objectives of this study are: 1) to determine the level of PAEs in JZB surface seawater and the correlation, if any, between MPs and the environmental parameters; 2) to evaluate the ecological risk of MPs and PAEs. This study also provides a preliminary of the chemical additives in plastics that could be used to trace the source of MPs in the environment, and acts as a reference for the study of the environmental effects of and means of reducing MPs.

## 2. Materials and methods

### *2.1. Study area and sample collection*

Located southeast of Shandong Peninsula and west of the Yellow Sea, JZB (35°55′ N–36°18′ N, 120°04′ E–120°23′ E) is surrounded by Qingdao, a metropolitan city in northern China (Fig. 1). The seawater area of JZB is about 370 $km^2$, with an average water depth of 7 m (Sun and Sun, 2015). The significant wave height of the bay is generally less than 5 m, with typical semidiurnal tides (Chen et al., 2012). Several seasonal rivers discharge water, waste, and sediments into the bay including the Dagu, Moshui, Licun, Haibo, and Yang Rivers (Dai et al., 2006; Liang et al., 2015). Several sewage treatment plants are also located on coastline of the bay, including the Tuandao, Haibo, and Licun sewage plants (Fig. 1).

MPs samples were collected from surface seawater at 22 sites (Fig. 1) using a seawater intake system on board the *R/V Yuan Jian 1* on 22 August, 2018 (Stations A1–A6), 10 September, 2018 (Stations C1–C9) and 2 January, 2019 (Stations D1–D7). All samples were collected at low tide. Table S1 in the Supplementary Information provides details of the sampling sites and environmental water parameters. An onboard flowmeter was used to measure the volume of pumped water. Typically, 300 L of seawater was filtered at each collection site using an online system with a 32μm steel sieve (Zhao et al., 2014). The retained particulate material was immediately back-flushed with Milli-Q water (Millipore Co., USA) into a 500 mL glass bottle and fixed in 2.5% formalin (Lattin et al., 2004).

For the PAEs analysis, seawater samples were collected at each station using a clean stainless-steel bucket and placed in clean 4L amber-glass bottles, with roughly 2 mL of 100 mg/L sodium azide added to each bottle to inhibit microbial activity (Gong et al., 2019). One field duplicated sample was randomly collected and examined at every three stations to check the representativeness of sampling. The water samples were stored in the dark at 4°C and processed as soon as possible. The water temperature (WT), pH, dissolved oxygen (DO), salinity (Sal.) and conductivity (Cond.) were measured in the field using an HQ40d multimeter (Hach, Loveland, CO, USA). The water level (WL) data were read from the sonar system on the ship.

*2.2. Sample pretreatment and analysis*

For the MPs measurement, samples were first oxidized to remove organic matter and then filtered. A stereoscopic microscope was used to examine the sample filters for MPs. When these were found, the polymer types were identified with a micro-Fourier transform infrared spectroscope (μ-FT-IR, PerkinElmer Spectrum Spotlight 400, PerkinElmer, USA). For detailed information about the procedure, readers should refer to the Supplementary Information Section S1.

Six USEPA priority PAEs (DMP, DEP, DBP, BBP, DEHP and DnOP) were identified and quantified in our study. Each seawater sample was filtered, the PAEs solid-phase extracted and then quantified with a GC-MS system (Agilent 7890A-5975C, Agilent Technologies Inc., California, USA). An internal calibration method was used for quantification. Detailed information can be found in Supplementary Information Section S2.

155 *2.3. Quality assurance (QA) and quality control (QC)*

156 Nitrile gloves and cotton lab coats were worn throughout the field work and
157 laboratory experiments. All containers were non-plastic, and were cleaned with
158 Milli-Q water. Blank membrane controls were run in the field and in the laboratory as
159 background checks. Between each sample test, anhydrous ethanol was used to wipe
160 the crystal on the μ-FT-IR to avoid cross-contamination (Zheng et al., 2019).

161 Non-plastic labware was also used for the PAEs analysis, and was cleaned three
162 times with n-hexane before use to prevent any contamination. Detailed procedures
163 and results of the QA/QC for the PAEs analysis, including blanks, spiked-matrix
164 recoveries, duplicated sample analysis, and method detection limit (MDL), are
165 described in Supplementary Information Section S3.

166 2.4. Risk assessment related to MPs and PAEs

167 Since MPs and PAEs are recent marine pollutants, there is still no systematic and
168 standardized model specifically developed for assessing their potential ecological risk.
169 Therefore, we adopted here the pollution load index (PLI) method (Tomlinson et al.,
170 1980) for the risk assessment of MPs; this is based on both the abundance and the
171 chemical components of the MPs (Xu et al., 2018). The risk evaluation of the PAEs
172 was based on the risk quotient (RQ) and potential hazard index (HI) methods,
173 following the guidance from the European Commission (EC, 2003). Detailed
174 descriptions of the assessment methods can be found in Supplementary Information
175 Section S4.

176 *2.5. Data analysis*

177 The abundance of MPs in seawater samples was expressed as items/$m^3$. All
178 PAEs concentrations were expressed as ng/L. The spatial distributions of the MPs and
179 PAEs were processed using Kriging by Surfer (version 15.0). All statistical analyses
180 were processed using SPSS (version 22.0). Statistical significance was considered at
181 the 0.05 alpha level. The figures were drawn using Origin (version 9.1). Pearson
182 correlation was performed to study the relationships between MPs, PAEs, and
183 environmental water parameters using Matlab.
184
185 **3. Results and discussion**
186 *3.1. MPs*
187 *3.1.1. MPs abundance in surface seawater*
188 MPs were detected at all sampling stations (Fig. 2a, Table S1), with abundance
189 ranging from 24.44 to 180.23 items/$m^3$. The mean abundance was 80.46 ± 44.82
190 items/$m^3$ with a median value of 65.34 items/$m^3$. These values were compared with
191 those found in surface waters in systems around the world, including JZB (Zheng et
192 al., 2019), in order to calibrate the contamination level of MPs in JZB (Fig. 3). This
193 comparison took into account the sampling method used in each study: bulk sampling
194 (used in the present study) or trawling-net sampling. The abundance of MPs observed
195 in this study was very similar to that reported by Zheng et al. (2019) in JZB (20–120
196 items/$m^3$). Of the other studies using the bulk sampling method, a relatively higher
197 abundance was recorded in the Yangtze Estuary, China (1675.8–6598.8 items/$m^3$,
198 Zhao et al., 2014), in the South China Sea (799–4339 items/$m^3$, Cai et al., 2018), and

199 in the Incheon/Kyeonggi coastal region of South Korea (328–2876 items/$m^3$, Chae et
200 al., 2015). In contrast, significantly lower abundances of MPs were reported in many
201 studies that used trawling-net sampling, for instance the Mediterranean Sea (0.15
202 items/$m^3$; de Lucia et al., 2014), the Seto Inland Sea (0.39 items/$m^3$; Isobe et al.,
203 2014), and the East China Sea (0.029–0.305 items/$m^3$; Zhao et al., 2014). In these
204 studies, the lowest abundance of MPs in surface waters was four orders of magnitude
205 lower than the highest for the bulk sampling method. Our results show that MPs were
206 present in the surface seawater of JZB but, compared with other documented systems,
207 the pollution level was still relatively low for a semi-enclosed bay heavily affected by
208 human activity.

209 Spatially, the highest abundance of MPs, 180.23 items/$m^3$, was found at Station
210 D1 near the Tuandao sewage treatment plant; the lowest abundance, 24.44 items/$m^3$,
211 was observed at Station D4 near the mouth of the bay. The abundance was therefore
212 up to seven times higher at sites near estuaries and sewage treatment plants than at the
213 other stations in the bay. For example, the MPs abundance at Stations C6 and C7,
214 close to the Lichun River and Haibo River estuaries, ranged from 98.82 to 159.42
215 items/$m^3$, and the abundance at D1 and C7, close to the Tuandao and Haibo sewage
216 treatment plants, ranged from 159.42 to 180.23 items/$m^3$. These results suggest that
217 MPs from rivers and sewage treatment plants were the major contributors to MPs in
218 JZB. This agrees with previous studies that found rivers to be one of the major
219 sources of marine MPs pollution (Schmidt et al., 2017), while estuaries are also
220 potential MPs hot spots (Wright et al., 2013). Municipal sewage treatment plants have

long been considered important sources of MPs (Xu et al., 2019). Significant amounts of MPs still enter the environment from these despite the high removal rates of MPs in current sewage treatment (Murphy et al., 2016).

The distribution of MPs is not only related to human activity, but also closely related to specific geographical locations (Lusher et al., 2014) and ocean currents. The overall level of MPs in the surface seawater of JZB decreased gradually from east to west. The presence of residual currents, such as the clockwise circulation in the eastern region (Li et al., 2014; Yuan et al., 2019), and the low water exchange rate of the bay (Liu et al., 2004) favor the trapping of MPs near the sources. On the other hand, mixing processes combined with strong, flood-dominant tidal currents (Gao et al., 2014) tend to disperse the MPs to different regions of the bay. Clearly, the hydrodynamics plays a significant role in the abundance, distribution, and trapping of MPs. A detailed study of the transport mechanisms that determine the trajectories and distribution patterns of the MPs (e.g. Jalón-Rojas et al, 2019a, b) is a subject of our on-going modelling of JZB.

The D-series of samples were collected in a different season to the A- and C-series. Even though seasonal variations have been frequently reported (e.g. Pelamatti et al., 2019), this seems not to be the case in the present study. The MPs abundances were in a similar range at Stations A1–A6 (26.67–133.33 items/$m^3$, average 66.85 items/$m^3$), C1–C9 (40.00–159.42 items/$m^3$, average 88.52 items/$m^3$), and D1–D7 (24.44 –180.23 items/$m^3$, average 81.77 items/$m^3$) (distribution in Fig. 2, data in Table S1). While significant differences were observed between the different

243 geographical locations (within the same A, C or D series of samples), the variations
244 between sampling times (between A, C and D series of samples) were relatively
245 small.

246 *3.1.2. MPs characteristics in surface seawater*

247 MPs are generally classified into six categories according to their size: < 0.5 mm,
248 0.5–1 mm, 1–2 mm, 2–3 mm, 3–4 mm, and 4–5 mm. Fig. 4a shows that, except at
249 Station D6, the surface seawater of JZB mainly contained MPs of size less than 2 mm,
250 accounting for up to 71.80% of the total MPs (see Fig. S1a in Supplementary
251 Information Section). In contrast, MPs with a size of 4–5 mm were the least abundant
252 (7.72%). This dominance of smaller MPs is similar to that in many previous
253 observational studies (e.g. Zhao et al., 2014; Zheng et al., 2019). In general, large
254 plastics are gradually broken up into smaller pieces or particles in the marine
255 environment. As a result, the number of small pieces of plastic increase as the size
256 decreases. The toxicity of MPs particles is related to particle size: the smaller the size,
257 the more toxic they are to marine zooplankton (Jeong et al., 2016).

258 Based on their morphological characteristics, MPs were classified into fibers,
259 fragments, films, and granules. Typical MP samples are shown in Fig.S2 of
260 Supplementary Information Section. Fibers and fragments were the main shapes here,
261 accounting for 75.62% and 20.82% of the total MPs, respectively (Fig.S1b in
262 Supplementary Information Section). MPs at Stations A4, A5, C3, and D4 were all
263 fibers (Fig. 4b). Films were detected in five samples, accounting for 1.32% of the total
264 MPs abundance. Granules were found only in three samples, accounting for 2.24% of

265 the abundance. Microbeads used in personal-care exfoliating products were not
266 detected in this study.

267 Fishery activities in JZB contributed most to the presence of fibrous MPs, since
268 plastic nets and ropes are the main fishing tools. Urban sewage has long been
269 considered a major source of fibrous plastics, mainly from laundry (Zhao et al., 2015).
270 The high presence of fibers supports the argument in Section 3.1.1 that the relatively
271 high abundance of fiber MPs at the study sites may come, to a large extent, from
272 domestic sewage. Although the use of plastic shopping bags has been restricted, they
273 remain a source of film MPs (Sruthy and Ramasamy, 2017). Plastic granules from
274 raw/unprocessed plastic materials, regarded as primary MPs (Law et al., 2010), were
275 only detected in a few samples in our study area, consistent with previous studies in
276 the East China Sea and Yangtze River Estuary (Zhao et al., 2014).

277 Colored MPs are more likely to be ingested by organisms, as they are more
278 similar to their prey (Abayomi et al., 2017; Wang et al., 2017). Different colors of
279 MPs were observed in the samples, including black, white, transparent, and colored
280 ones. Black was the dominant color found in our study area (Fig. 4c), accounting for
281 51.17% of the total MPs (Fig. S1c), followed by colored MPs, including red, blue and
282 green, accounting for 3.30~31.51% of the MPs. Transparent and white MPs,
283 accounting for 12.45% and 4.87%, respectively, were also observed. These
284 observations are consistent with a previous study by Zheng et al. (2019) that also
285 observed large number of black fibers.

286 The color of MPs is usually derived from their original plastic products, but it

can also be changed because of photodegradation and other processes. Consequently, residence times of MPs in the water may be a controlling factor in the degree of color alteration. For example, some blue and green lines might lose most of their original colors and appear white (Zhang et al., 2017). In our study area, white MPs had a relatively higher abundance at Stations C6 (19%) and C7 (17%), which are close to the estuaries of the Licun and Haibo Rivers and municipal sewage treatment plants (Fig. 1). The waste-water treatment processes and the potential weathering undergone during the transport by rivers probably had a bleaching effect on the MPs, resulting in an increased proportion of lightly colored MPs in the effluent. Xu et al. (2019) also found that the abundance of light-colored MPs (white, transparent, yellow, yellow-brown) accounted for the highest proportion in sewage waters (58.54% and 65.38% in the influent and effluent, respectively). White or lightly colored MPs (e.g. discolored yellow, transparent) usually form a higher proportion in surface water (Campanale et al., 2020) due to their higher mass production and their subsequent improper disposal (Wang et al., 2020).

Eight different polymer types were identified in the surface seawater samples (Fig. 4d and Fig. S1d), including polyethylene (PE, accounting for 46.71% of the total abundance), polyethylene terephthalate (PET, 26.86%), rayon (14.80%), polypropylene (PP, 3.66%), polyvinyl chloride (PVC, 3.35%), polyamide (PA, 2.60%), polystyrene (PS, 1.09%), and polyester (0.92%). PE, PET, rayon, PP, and PVC were the dominant types of MPs (Fig. 5), with PE and PP were the most widely used in our daily life and industry (Klein et al., 2015), such as food packaging and

309 water pipeline. PE (with a density of 0.86–0.96 g/cm$^3$) and PP (0.85–0.91 g/cm$^3$) are
310 readily transported by surface currents because of their lower specific densities
311 compared to seawater (Jalón-Rojas et al., 2019a; Zheng et al., 2019). The fate of these
312 MPs depends on biofouling or biological metabolism processes (Katija et al., 2017)
313 which increase their density, causing their ultimate deposition onto the seafloor
314 (Jalón-Rojas et al., 2019a).

315 *3.2.PAEs*

316 *3.2.1. Concentration of PAEs in surface seawater*

317 Fig. 2b and Table S1 summarize the PAEs concentrations in the JZB surface
318 seawater at each site. All the PAEs, except DnOP, were detected in all samples (Table
319 1), with detection frequencies ranging from 41.38 to 100.00 %. The concentrations of
320 $\Sigma_6$PAEs (sum of the concentrations of the six PAEs) ranged from 129.96 to 921.22
321 ng/L, with an average of 342.01 ng/L. The concentration of DEHP was lower than the
322 values reported for the Yellow River and Yangtze River in China (Sha et al., 2007;
323 Wang et al., 2008), but significantly higher than that detected in the Tama River in
324 Japan (Suzuki et al., 2001). In addition, DBP and DEHP were found to be much more
325 abundant than any other four congeners (DMP, DEP, BBP and DnOP), with
326 concentrations varying from < MDL to 248.03 ng/L (averaged at 158.09 ng/L,
327 accounting for 46.22% of $\Sigma_6$PAEs) and 60.42 to 617.18 ng/L (averaged at 140.31
328 ng/L, 41.02% of $\Sigma_6$PAEs), respectively. This is consistent with environmental water
329 samples from nine rivers and two seas in seven areas in China (Wu et al., 2013). DBP
330 is widely used in cosmetics (Giulivo et al., 2016), and the DEHP came mainly from

plastics and the chemical industry (Simoneit et al., 2005). DBP and DEHP are also major PAEs in household garbage (in toys, plastic packaging materials, etc) (Gao and Wen, 2016). In summary, PAEs in JZB surface water mainly come from plastics, the chemical industry and household waste.

It is well documented that the octanol-water partitioning coefficient ($\lg K_{ow}$) of a PAE is closely related to its alkyl chain length: the longer the alkyl chain, the greater the octanol-water partitioning coefficient (as summarized in Table S2), which was proven by many previous studies including a recent correlation analysis (Li et al., 2020). In turn, the greater the octanol-water partitioning coefficient, the higher the lipophilicity (or fat-solubility) of PAEs, and the more difficult the degradation of PAEs by photolysis, hydrolysis, and biological processes (Gao and Wen, 2016). Therefore, it is not a surprise that the concentrations of DBP and DEHP (with relatively longer alkyl chains) in seawater are higher than those of the other PAEs. In addition, the higher the lipophilicity, the greater the threat to aquatic organisms (Dordio et al., 2011).

Legislation in China is continuously refining the standards for various pollutants in a wide range of wastes. However, MPs and PAEs discharge limits are not included in the current national standard for sewage discharge implemented by the Ministry of Environmental Protection of China (MEP, 2002a, b). In addition, there are still great challenges for removing organic pollutants in domestic sewage water, with biodegradation a key step. Technologies are still under development, which may be greatly benefited from identification of highly efficient degradation bacteria and

353 microbial communities. At most 18% of PAEs are removed by the current treatment
354 equipment in sewage plants (Zhang et al., 2018b). Even if the sewage plants ensured
355 strict observance of standards, the discharge of treated water would be still a
356 significant source of PAEs.

357 Compared with other rivers, lakes, and oceans (Dargnat et al., 2009; Zhang et al.,
358 2018b, c), the current PAEs concentration in JZB surface water is moderate to slightly
359 low. However, with the rapid development of the marine economic zone along the
360 coast of the Shandong Peninsula, pollution in JZB, including MPs and PAEs (and
361 many other organic pollutants), is increasing markedly.

362 *3.2.2. Spatial distribution of PAEs*

363 The total PAEs concentrations in the east JZB, at Stations C6, C7, and D7 near
364 the mouth of the Licun and Haibo Rivers, and at Stations D1and C7 near the Tuandao
365 and Haibo sewage treatment plants, were all relatively high (Fig. 2b, S3). The total
366 PAEs concentration at Station D1 was as high as 921.22 ng/L. As for PAE congeners,
367 the spatial variation trend of DBP and DEHP were similar to that of $\sum_6$PAEs in
368 seawater. This is not a surprise, since DBP and DEHP were the major components
369 accounting for 87.24% of $\sum_6$PAEs, as presented in Section 3.2.1.

370 In general, the PAEs concentrations at nearshore stations were higher than those
371 in the middle of the bay, and the eastern-shore concentration higher than the
372 western-shore. The higher concentrations of PAEs in the east probably come from
373 surface runoff into JZB, with industries in Qingdao mainly located on the east coast.
374 The Licun, Haibo, and several other rivers east of Qingdao are heavily polluted, with

very low flows, carrying a large amount of organic pollutants from various sources in the city into JZB. Several sewage plants, such as the Tuandao and Haibo sewage treatment plants, also discharge effluent directly into JZB. Many mariculture farms located in the northeastern waters close to the city also contributed to the high levels of PAEs in the region (Ting et al., 2017).

The seasonal variation in PAEs concentrations, reported in previous studies (e.g. Zeng et al., 2009), were much less than the variations between different sampling stations, similar to the case for MPs abundance discussed in Section 3.1.1. The PAEs' concentration ranges and mean values were of the same order of magnitude for Stations A1–A6 (188.51–391.62 ng/L, average 284.61 ng/L), C1–C9 (235.73–507.14 ng/L, average 347.54 ng/L) and D1–D7 (129.96–921.22 ng/L, average 384.10 ng/L).

*3.3.Correlations between MPs, PAEs and environmental parameters.*

As PAEs are used for plastics production, we investigated the correlation between the MPs abundance (items/$m^3$) and PAEs concentrations ($\Sigma_6$PAEs, ng/L) in JZB surface seawater to explore the possible relationship between the two pollutants. A significantly positive correlation was found ($r^2$=0.745, $p$<0.01, $n$=22; Fig. 6).

As discussed in Section 3.2, MPs and PAEs are correlated each other, both of which are the result of human activity. After they enter the marine system via either atmospheric deposition, surface runoff or riverine input, MPs are prone both to the adsorbing of waterborne contaminants and to the leaching of their plasticizers (Koelmans et al., 2016), leading to the strong correlation between MPs and PAEs found in JZB seawater. The adsorption of waterborne contaminants by MPs and the

397 release of additives are concurrent processes, and their relative contributions to PAEs
398 levels are still a question to be resolved. It might be helpful to combine field studies
399 with numerical simulations to establish the relationship between contaminant
400 concentration and MPs abundance in specific samples, as well as to investigate the
401 spread through the food chain of these contaminants.

402 Previous studies also found relationships between PAEs and MPs in a variety of
403 cases. Baini et al. (2017) found correlations between four PAEs and MPs in neustonic
404 samples from the northwestern Mediterranean Sea. Fossi et al. (2016) reported that
405 PAEs were used as indirect (adsorbed contaminants) and plastic (component
406 contaminants) tracers for MPs in the baleen-whale food chain. The present study
407 reports their relationship in seawater samples, which further confirms that the
408 migration behavior of organic pollutants, such as PAEs, is a possible indirect method
409 to trace the source of MPs in the environment.

410 We also studied the correlations between MPs, PAEs, and various environmental
411 water parameters (Fig. S4). Water level (WL) was significantly negatively correlated
412 with MPs and PAEs ($r$= −0.532, $p$ < 0.05; $r$= −0.512, $p$ < 0.05, respectively). This
413 suggests that WL is an important environmental factor in the distribution of MPs and
414 PAEs. It could be that shallower waters are characterized by shorter residence times
415 and slower currents, but the transport mechanisms of MPs in JZB need to be
416 investigated in depth. It is interesting to note that pH, DO, Sal., and Cond. are strongly
417 associated with WT (5.4−28.2°C), which is related to sampling time or season.
418 However, there was no clear correlation between these parameters and MPs

419 abundance, neither with PAEs concentration.

420 *3.4. Assessment of ecological risk*

421 *3.4.1 MPs risk assessment*

422 The MPs polymer risk index H in JZB surface water varied from I to IV, with an
423 uneven distribution (Fig. 2C). These high values were mainly due to the presence of
424 high-risky polymers such as PVC, one of the most widely used plastics (Ye et al.,
425 2017). Once PVC enters the marine environment, it can release carcinogenic
426 monomers and other pollutants, impacting the wildlife (Green et al., 2016). Unreacted
427 monomers and polymeric impurities in plastic products can also be released into the
428 environment, threatening human health and ecosystem health (Araújo et al., 2002).

429 The MPs pollution load in JZB based on the Pollution Load Index (PLI) is given
430 in Fig. 2d. Fifteen sites were moderately polluted, the other seven mildly polluted.
431 According to this result, the MPs pollution risk in JZB surface seawater is not
432 dramatic. The whole area is characterized by a medium level of pollution risk (Fig. 2c,
433 d) with a $PLI_{JZB}$ value of 11.76, which falls into risk category Ⅱ.

434 *3.4.2 Potential ecological risk related to PAEs*

435 We assessed the ecological risk of the four main PAEs in JZB surface seawater.
436 The risk quotient (RQ) of DMP, DEP, and DEHP were lower than 0.1 at the 22
437 sampling stations, except at Stations C7, C8, D1 and D7, indicating an overall low
438 ecological risk. Relative higher RQs were found for DBP ($0.1 < RQ < 1$, except at
439 Stations D4 and D7; Fig. S5), which indicates that DBP is a medium ecological risk.
440 These results demonstrate that PAEs are becoming a potential threat to the ecology of

JZB, which deserves further study.

The hazard index (HI) values, ranging between 0.098 and 0.897, indicate medium-to-low ecological risk in JZB surface seawater. The HI value at Station D1 (0.897) was significantly higher than elsewhere, indicating that areas near sewage treatment plants are generally at a higher level of ecological risk. Higher HI levels were also observed at Station C6 (0.572) and C7 (0.588), which may be related to riverine input.

The risk assessment presented here has some limitations. For instance, it is difficult to determine the PNEC (Predicted No Effect Concentration) for each PAE congener because the environmental toxicology and ecotoxicological information on these pollutants are very limited. Further assessment of the ecological risks of these emerging pollutants is needed to provide more toxicity data (Gong et al., 2019).

## 4. Conclusions

The present study offers novel insights into the occurrence, distribution, correlation, and potential ecological risks of microplastics (MPs) and phthalates (PAEs) in surface seawater of a semi-enclosed bay heavily impacted by human activity, Jiaozhou Bay (JZB) in northern China.

The abundance of MPs in the bay was relatively low compared to other similar areas. The MP and PAE pollution was relatively severe near the estuaries and sewage plants, suggesting that rivers and sewage plants were the main sources of MPs and PAEs. A strong correlation between the abundance of MPs and concentration of PAEs

was observed in surface seawater.

The ecological risk assessment of PAEs, based on risk quotients, indicated that PAEs, presently at low-to-medium level, are becoming a potential threat to the JZB ecosystem. The risk-assessment model, based on MPs concentrations and polymer chemical hazards showed a high risk related to the presence of hazardous polymers such as PVC. The risk of MPs pollution in the bay was evaluated as medium.

Further studies on the impact of MPs on the transport of organic pollutants in marine environment are important in providing basic data for a source-to-sink study on pollutants in the ocean and a theoretical basis for the control of MPs pollution, as is more comprehensive modeling to help understand MP transport dynamics in a highly urbanized estuarine environment such as JZB.

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485 Australia.

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731

**Figure Captions**

**Fig. 1** The geographic location of JZB and sampling stations of surface seawater. The red dots represent water sampling sites, the red pentagram represents the location of Qingdao municipal government, the transparent pentagrams represent the locations of district governments, and the blue rhombuses represent the locations of sewage treatment plants.

**Fig. 2** The abundance of MPs (a), concentration of $\sum_6$PAEs (b), MPs' polymer risk index H (c) and pollution load index PLI (d) in JZB surface seawater.

**Fig. 3** Comparison of MPs abundance in JZB surface water with previously reported data.

**Fig. 4** Proportion of different sizes (a), shapes (b), colors (c), polymer types (d) of MPs from JZB surface seawater at each sampling site.

**Fig. 5** Identification of typical MPs in JZB surface seawater using μ-FT-IR. Values in brackets indicate the matches of the spectra with the standards. Scale bar of the right of photograph is 100μm.

**Fig. 6** Linear regression of MPs abundance and $\Sigma_6$PAEs observed in JZB surface seawater.

**Fig. 1**

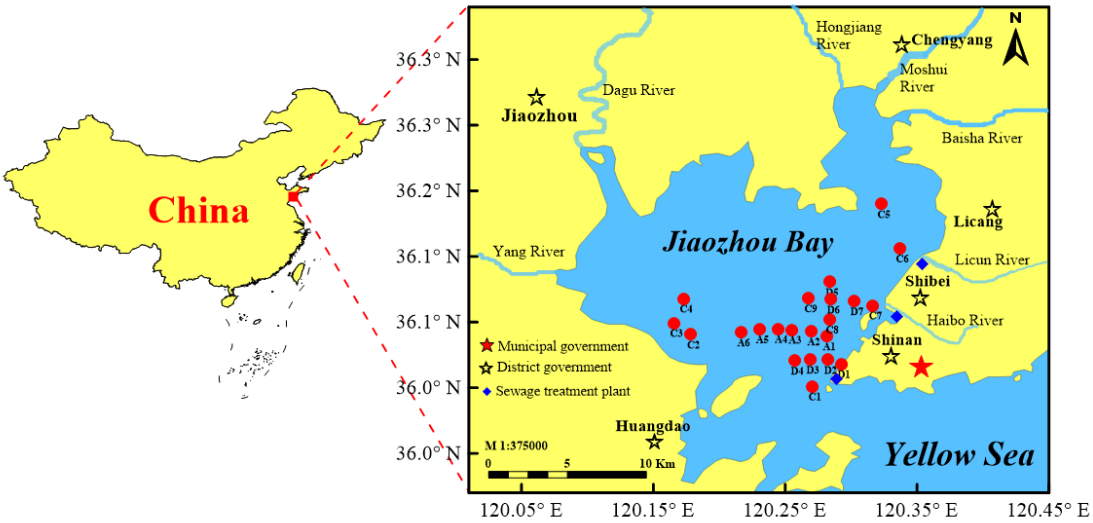

China
Jiaozhou
Dagu River
Hongjiang River
Chengyang
Moshui River
Baisha River
Licang
Jiaozhou Bay
Yang River
Licun River
Shibei
Haibo River
Shinan
Huangdao
Yellow Sea
Municipal government
District government
Sewage treatment plant
M 1:375000
0
5
10 Km
N
36.3° N
36.3° N
36.2° N
36.1° N
36.1° N
36.0° N
36.0° N
120.05° E
120.15° E
120.25° E
120.35° E
120.45° E

**Fig. 2**

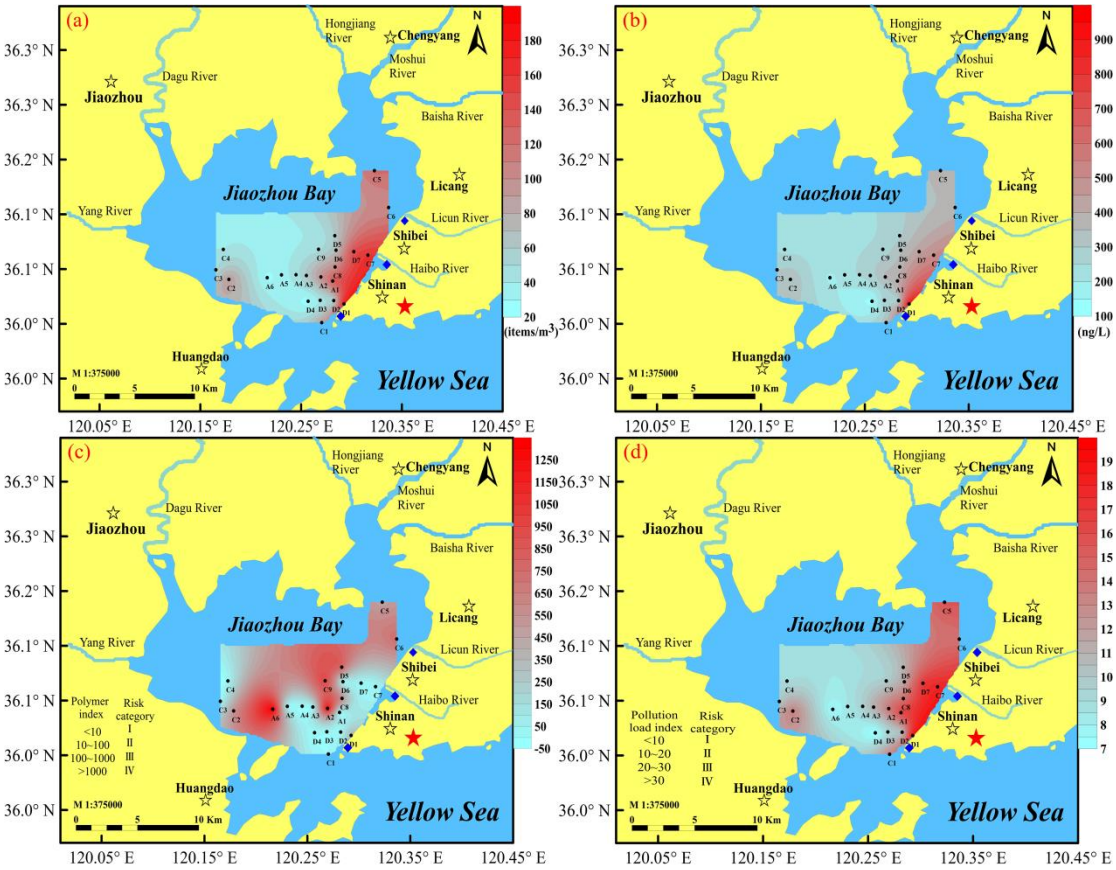

(a)
(b)
(c)
(d)
Hongjiang River
Chengyang
Moshui River
Dagu River
Jiaozhou
Baisha River
Licang
Jiaozhou Bay
Yang River
Licun River
Shibei
Haibo River
Shinan
Huangdao
Yellow Sea
M 1:375000
0 5 10 Km
N
36.3° N
36.2° N
36.1° N
36.0° N
120.05° E
120.15° E
120.25° E
120.35° E
120.45° E
(items/m3)
(ng/L)
Polymer index
Risk category
<10 I
10~100 II
100~1000 III
>1000 IV
Pollution load index
Risk category
<10 I
10~20 II
20~30 III
>30 IV

**Fig. 3**

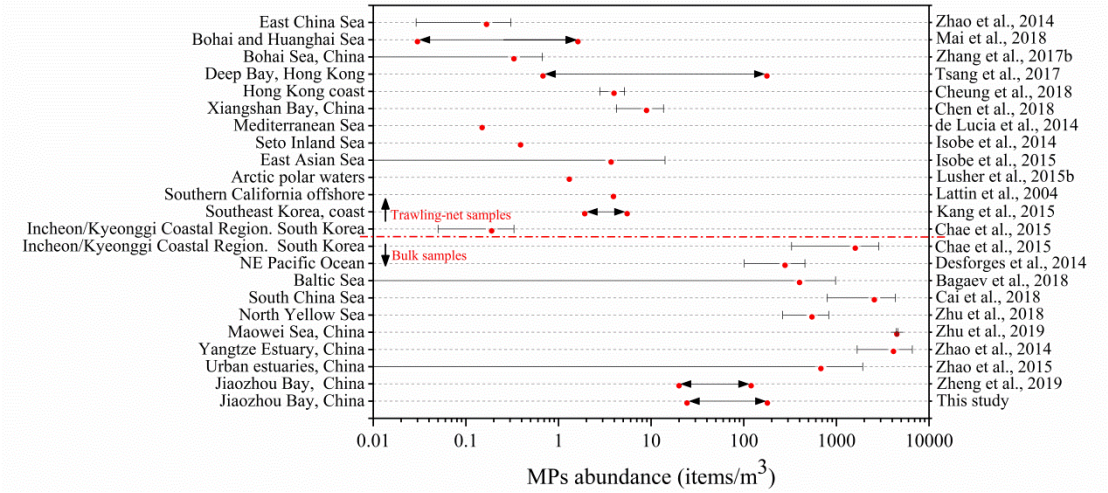
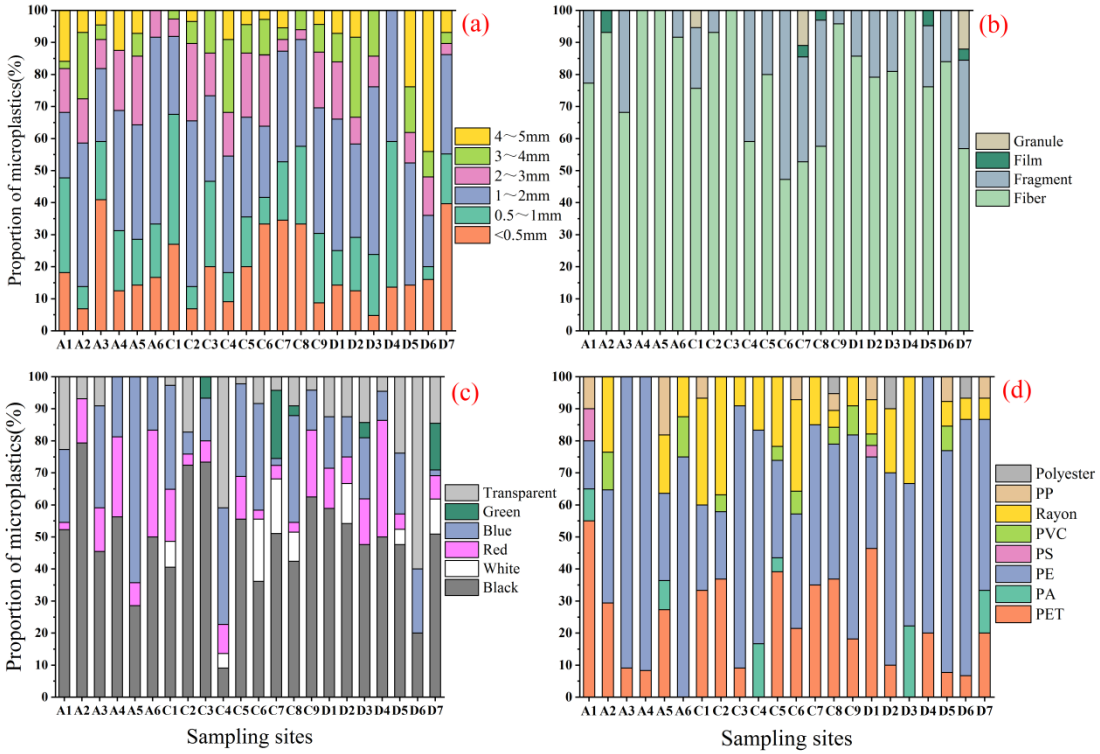
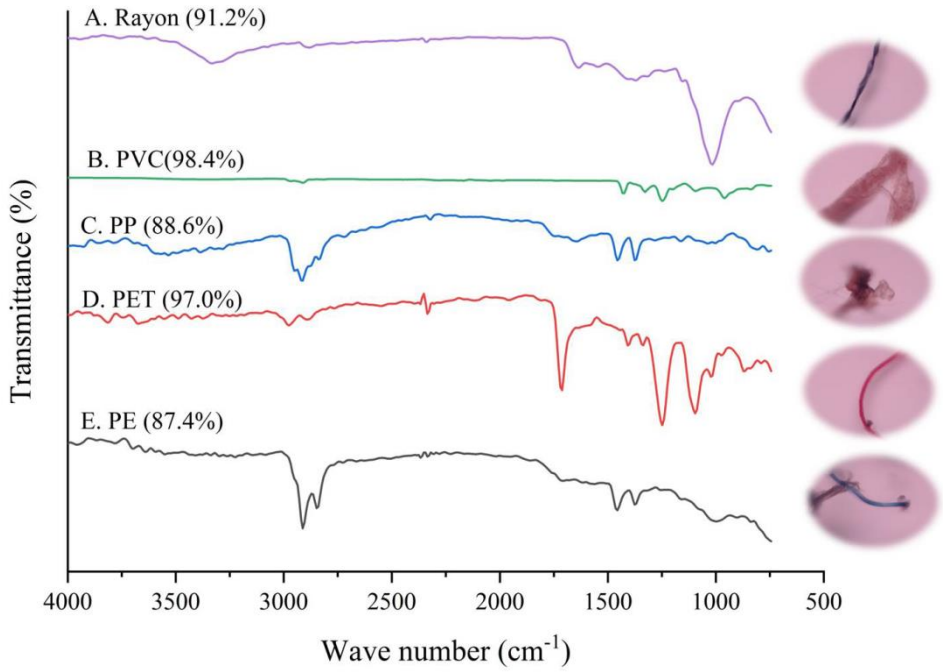

East China Sea
Bohai and Huanghai Sea
Bohai Sea, China
Deep Bay, Hong Kong
Hong Kong coast
Xiangshan Bay, China
Mediterranean Sea
Seto Inland Sea
East Asian Sea
Arctic polar waters
Southern California offshore
Southeast Korea, coast
Incheon/Kyeonggi Coastal Region. South Korea
Incheon/Kyeonggi Coastal Region. South Korea
NE Pacific Ocean
Baltic Sea
South China Sea
North Yellow Sea
Maowei Sea, China
Yangtze Estuary, China
Urban estuaries, China
Jiaozhou Bay, China
Jiaozhou Bay, China
Trawling-net samples
Bulk samples
Zhao et al., 2014
Mai et al., 2018
Zhang et al., 2017b
Tsang et al., 2017
Cheung et al., 2018
Chen et al., 2018
de Lucia et al., 2014
Isobe et al., 2014
Isobe et al., 2015
Lusher et al., 2015b
Lattin et al., 2004
Kang et al., 2015
Chae et al., 2015
Chae et al., 2015
Desforges et al., 2014
Bagaev et al., 2018
Cai et al., 2018
Zhu et al., 2018
Zhu et al., 2019
Zhao et al., 2014
Zhao et al., 2015
Zheng et al., 2019
This study
0.01
0.1
1
10
100
1000
10000
MPs abundance (items/m3)

**Fig. 4**


(a)
Proportion of microplastics(%)
4～5mm
3～4mm
2～3mm
1～2mm
0.5～1mm
<0.5mm
(b)
Granule
Film
Fragment
Fiber
(c)
Transparent
Green
Blue
Red
White
Black
(d)
Polyester
PP
Rayon
PVC
PS
PE
PA
PET
Sampling sites
Sampling sites

873 **Fig. 5**

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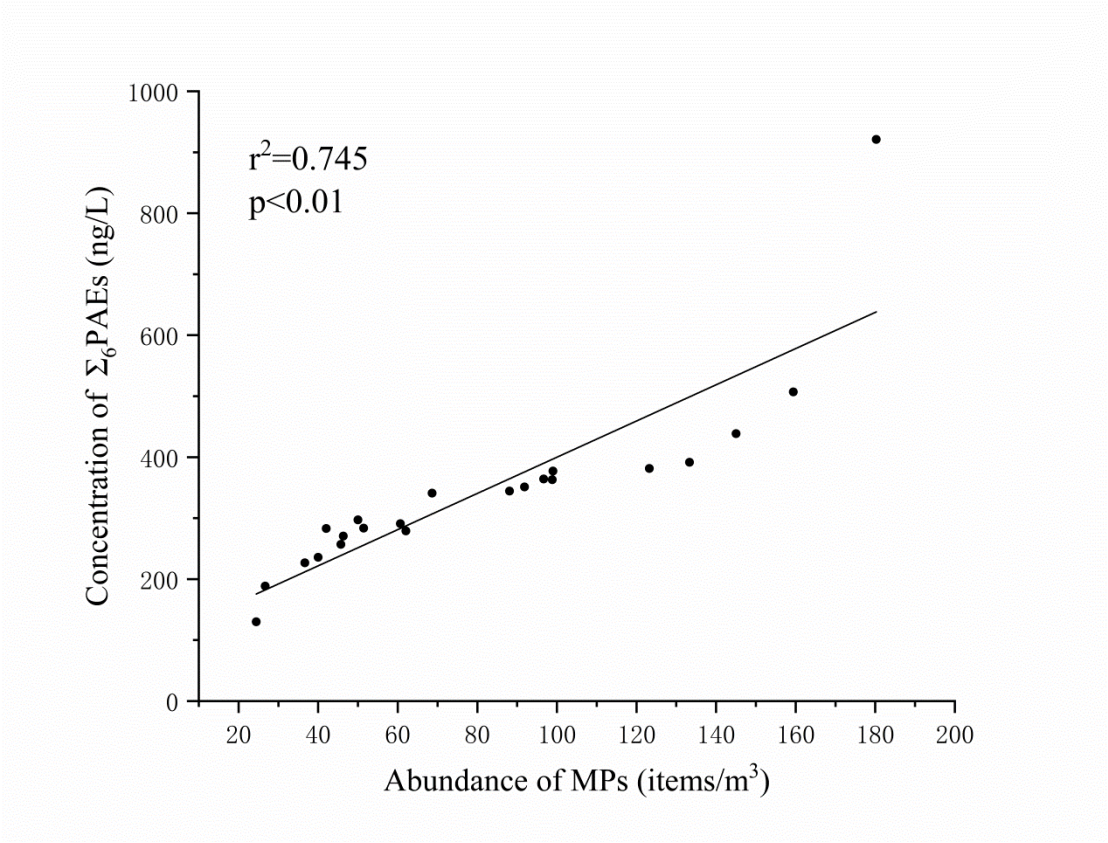
899 **Fig. 6**


$r^2$=0.745
p<0.01
Concentration of $\Sigma_6$PAEs (ng/L)
Abundance of MPs (items/m$^3$)
0
200
400
600
800
1000
20
40
60
80
100
120
140
160
180
200

900