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Seasonal relevance of agricultural diffuse pollutant with microplastic in the bay

Wei Ouyang (Conceptualization) (Methodology) (Writing - review and editing) (Supervision), Yu Zhang (Investigation) (Writing - original draft), Li Wang (Investigation), Damià Barceló (Resources) (Writing - review and editing), Yidi Wang (Software) (Visualization), Chunye Lin (Methodology) (Project administration)

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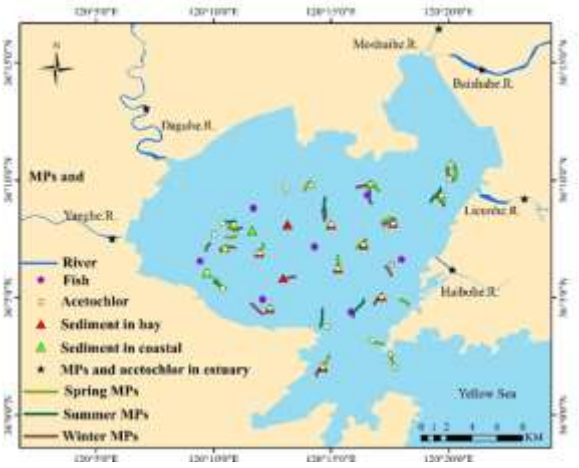
Seasonal relevance of agricultural diffuse pollutant with microplastic in the bay

Wei Ouyang[a,*], Yu Zhang[a], Li Wang[a], Damià Barceló[b], Yidi Wang[a], Chunye Lin[a]

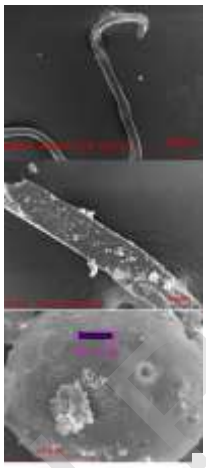
[a] State *Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, China*

[b] *Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research of the Spanish Council for Scientific Research (IDAEA-CSIC), Jordi Girona 18-26, 08034. Barcelona, Spain*

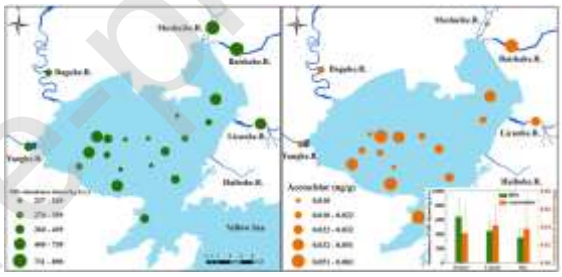
Graphical abstract



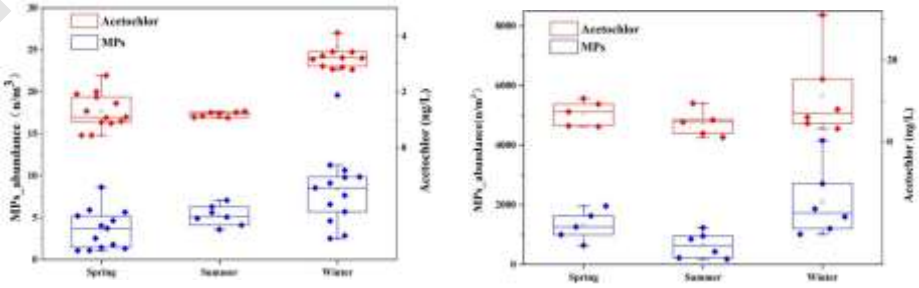
Seasonal water and sediment sampling in the bay



microplastic



Spatial correlations between acetochlor with microplastic



Seasonal correlations between acetochlor with microplastic

*Corresponding author. Tel.: +86 10 58804585; fax: +86 10 58804585. *E-mail address:* wei@itc.nl (W. Ouyang).

Highlights

- Microplastic particles (MPs) seasonal distributions in the bay are figured.
- MPs properties in water and sediment vary with deep water depth in the bay.
- MPs abundances in fish stomachs show biological accumulation.
- Seasonal relevance between MPs with acetochlor show similar transport process.

Abstract

Microplastic particles between 10 μm and 1 mm in the marine environment have attracted international attention due to their potential health risk. Based on the current field investigations and source identification studies, the transport pattern from territorial to marine environments is comparatively unknown. Acetochlor concentrations and the microplastic abundance in the water, sediment and fish of Jiaozhou Bay in spring, summer and winter were measured. The seasonal relevance of the typical diffuse agricultural pollutant acetochlor with microplastics in river water and seawater in three zones (estuary, coastal and bay) were analyzed, which demonstrated the similar transport path and source from land to the bay. The electron microscopy and energy spectra of microplastics in three seasons highlight varied characteristics of microplastics during the transport. The spatial distribution of microplastic abundance in the sediment in the bay presented a decreasing pattern from the estuary to the coastal and bay waters. Microplastics were detected in all of the stomach samples in the bay with an abundance of 7.45-10.11 n/g. dw, which show the biological transport from bay. The analysis of microplastic size, shape, color and composition properties in the water and sediment further demonstrated the transport of microplastics in the bay.

Key words: Microplastics; Diffuse pollution; herbicides; bay; transport

1. Introduction

Plastics are treated as hazardous pollutants with direct health concerns and significant ecological impacts (Geyer et al., 2017). Plasticulture refers to the use of plastic materials in agricultural tillage, which is mainly used for irrigation, packaging, plastic barriers and agricultural mulch (Steinmetz et al., 2016). The degradation of plastic materials causes the proliferation of microplastics (MPs), which have a small size between 10 μm and 1 mm and can

enter the food chain (Sanchez et al., 2014). Parts of MPs enter the ocean from territorial agricultural sources, which may share similar transport patterns with diffuse agricultural pollutants (Piehl et al., 2018; Zhang et al., 2019). It is hypothesized that MPs and acetochlor from agricultural system share similar patterns of transport to bay waters.

It is estimated that billions of tons of plastic are released into the environment (Vignieri, 2016), and the related research about the agricultural source is not plenty as industry source (Rochman, 2018). Increased dependence on plastic materials significantly improves agricultural productivity, but the used plastic becomes a pollution source and causes environmental damage. Plasticulture is widely used for higher crop yields with minimization of water resources and fertilizer cost and is composed of plastic mulch and drip irrigation systems. In the United States, plasticulture is a multibillion dollar business for food production (Hol et al., 2017). The plastics from agricultural systems are discharged as a kind of diffuse pollutant into the environment due to their low recycling rate and intensive applications. Worldwide plastic application in agriculture has reached a yearly load of 6.5 million tons in 2012 (Scarascia- Mugnozza et al. 2012), which is mainly composed of polyethylene (PE), Polyethylene terephthalate (PET), and polystyrene (PS) (Huang et al., 2020). The yearly consumption of plastic mulch in China was 2.60 million tons in 2016, and the recycling rate ranged from 50%-60%. The yearly load of agricultural plastic waste for covering films is 627 kg ha^{-1} in Italy (Blanco et al., 2018). Plastic waste is ultimately transported into the sea, and the world's oceans are polluted with thousands to 240,000 tonnes of plastic particles (Plastic pollution hurts perch. Nature, 2016). Field investigations have proven that the MPs in the sea ar mixed with other chemic pollutants (Schiermeier, 2017), which deliver physical and chemical risks to marine biota (Lönnstedt and Eklöv, 2016).

Bay waters, such as Chesapeake Bay, the largest estuary in the United States, and the delta area of the Yellow River basin, have received much diffuse pollution and sediments from the whole watershed (Fulweiler et al., 2007). Herbicide loading can present the dynamics of diffuse organic pollution loading in watersheds, which presents the general loading pattern for other diffuse pollutants with the combined impacts of hydrological parameters, tillage practice and climatic conditions (Huang et al., 2017; Ouyang et al., 2019). Acetochlor is a typical herbicide and widely applied in the farmlands around the bay. Similar to MPs, acetochlor also poses an unpredictable risk to human health and marine safety, which is still widely applied in the tillage practice and with relatively slow degradation process. Acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetomide) is the third most frequently detected herbicide in natural waters, and the knowledge of its sources, fate and transport are very clear (Foley et al., 2008). The transport of acetochlor is mainly through leaching, surface runoff and soil erosion, which is the same

route as that for MPs from farmland to the aquatic environment. Acetochlor is an effective indicator for the occurrence, transport, and distribution analysis of pollutantsfrom estuaries to bays (Mijangos et al., 2018; Woodward et al., 2019).

MP abundance has been detected in freshwater and marine conditions worldwide, and the concentrations range from 50 to 2500 particles per cubic meter (Sighicelli et al., 2018). Some reports have been published regarding the detection of MPs in marine fish bodies. However, little information is known about the discharge and transport pattern of MPs from agricultural sources and their correlation with agricultural pollutants. The discharge of both MPs and acetochlor from farmland is affected by degradation and transformation during transport to the bay (Scheurer and Bigalke, 2018), but the principle of acetochlor fate and transport is better understood. The aquatic variation from territorial to marine environments affects the behavior and transformation of MPs (Sagawa et al., 2018). However, detailed studies about MP transport patterns from agricultural sources to the bay and morphological responses are currently lacking.

In this study, we simultaneously investigated the seasonal patterns of a typical organic diffuse agricultural pollutant and MPs from an estuary to coastal and bay waters. Acetochlor is the main pesticide used for weed control in crop and vegetable cultivation in farmland around the bay (Ouyang et al., 2016). As a trace organic pollutant, it is possible that it has the same transport pattern as that of MPs under the driving forces of precipitation and farmland drainage (Accinelli et al., 2019; Brumovský et al., 2016). According to tillage practices, the application frequency of herbicides is one or two times during the growing period, and these herbicides may suffer similar degradation and sorption during transport as that of MPs (Andrade et al., 2019). As organic pollutants, they also share similar responses when changing from freshwater to seawater during transport to the bay. Thus, agricultural diffuse pollution is an important source for MPs. Our study is a first attempt to identify the synergistic interaction of acetochlor and MPs and estimate their dynamics during transport from the terrestrial environment to the marine environment.

2. Materials and Methods

2.1 Study area and sampling

Jiaozhou Bay is a shallow embayment in the west of the Pacific Ocean. It is a bay with an average depth of around 7 m and an area of 340 km^2. This area is in the warm temperate monsoon climate zone. The annual mean temperature is 12.7°C, and the annual average rainfall is 662.1 mm. The hydrodynamic environment is controlled by semidiurnal tides with a moderate tidal range of 2.7 m. The average plastic mulch residue was 23.91 kg/hm^2 in the farmlands around the bay (Xu et al., 2018). Acetochlor is a frequently applied herbicide in the surrounding farmlands, and the average yearly usage intensity is about 0.50 kg/ha.

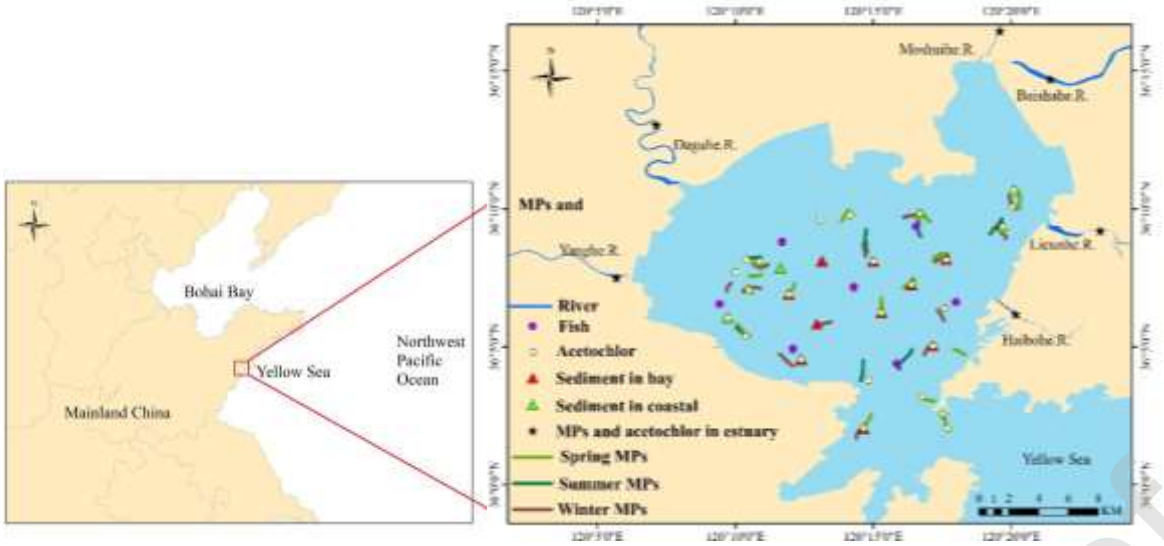


Fig. 1 Seasonal sampling locations of water, sediment, and fish in the bay

Surface river water sampling in the estuary at 1 meter depth was performed separately with metal buckets. In spring (2018) and winter (2019), surface freshwater samples were collected by dipping a steel bucket with a volume of about 0.15 m^3 into the water. In summer 2019, surface freshwater samples were collected with a 12 V DC pump for 15 min. The pump's flow rate was 4 m^3/h, and its efficacy was 0.8. The sampling information for freshwater samples is detailed in Fig. S1 and Table S2. To maintain consistency with the seawater samples, the collected freshwater was filtered by a net trawl with 48 μm mesh diameter. The pretreatments of the freshwater samples, including concentration and the storage conditions, are the same as those of the seawater samples.

Surface seawater sampling in the bay was conducted using plankton trawls with a 250 μm mesh net and a ϕ0.1 m circular-opening net (Frere et al., 2017). To avoid the wave caused by the vessel, the trawl was boarded on the no-drainage side of the vessel using 15 meters of rope. The trawl towed around 3 knots (5.55 km/h) for 5-10 min when the wind velocity was below 5 m/s. The volume of surface seawater filtered by the trawl was the multiple of the trawl opening area and towed distance. The towed distance was postprocessed by cumulative GPS (Law et al., 2014). The trawl was washed three times with ultrapure water to concentrate the samples, which were then stored in a 48 μm mesh (NITEX, Switzerland). The samples were kept in covered glass petri dishes at room temperature.

Surface sediment samples for MP extraction were collected by a Van Veen grab instrument and then rinsed and sieved by a 0.5 mm mesh screen. After identification, the fish samples collected with nets were stored at -20°C. The *Acanthogobius ommaturus*, *Hexagrammos otakii*, *Pleuronichthys cornutus*, and *Saurida elongata* were selected as the typical species in this study.

2.2 Sample digestion and separation

Surface water samples were rinsed from the mesh into a glass beaker (1 L) and then dried at 90℃. To avoid sample degradation by natural organic substances, such as zooplankton, the water samples were digested with 35% H_2O_2 for 1-3 d. As the density range of MPs is 0.8-1.4 g/cm^3 and the sediment density is 2.65 g/cm^3 (Frere et al., 2017; Hidalgo-Ruz et al., 2012), a $ZnCl_2$ solution (1.5g/cm^3) was used to separate MPs from the sediment. The suspended MPs in the $ZnCl_2$ solution were vacuum filtered onto a cellulose nitrate membrane (0.45 μm). A film containing MP samples from water was placed in a clean glass Petri dish and stored at room temperature. Before identification, filter membranes were dried in an oven at 55°C for 24 h to avoid water interference.

The pretreatment of sediments was performed according to Fries et al. (2013). a 100 g sediment (dry weight) sample was added to 200 mL $ZnCl_2$ solution (p=1.5 g/cm^3) in a 1 L glass beaker. To dissolve completely, the sediments in the beaker were oscillated for 1 h. The oscillation conditions were 120 rpm and 25℃. After deposition of the sediment, the supernatant was transferred to a 1 L glass funnel. To improve the recovery rate of MPs from the sediments, the process was repeated three times. The solution was precipitated in a glass funnel for 24 h. The sediment particles deposited at the bottom of the funnel were discharged from the funnel mouth. To overcome surface tension, the glass funnel was shaken (the tilt angle was not more than 90°) every 4 h. As there were few organic impurities in the sediment, the experiment did not include sample digestion. Finally, the supernatant in the funnel was vacuum filtered with a 0.45 μm nitrocellulose filter. The filter membrane was stored in a clean glass Petri dish and dried naturally.

The tropical fish samples of similar size were dissected to obtain stomach tissue. The length of the gastric tissue was measured with a Vernier caliper, and the wet weight (g/w.w.) was measured with a microbalance (accuracy to 0.0001 g). To avoid adherence of exogenous MPs to the surface during the anatomical process, the gastric tissue was washed with ultrapure water many times. Then, the biological tissue was wrapped with clean aluminum foil and dried in a cold environment. The gastric tissue was placed in a clean glass beaker (1 L) and then digested using 200 mL 10% KOH for digestion (Li et al., 2018). The beaker was placed in a water bath at 55℃ for 3 h to speed up the digestion and then incubated at room temperature for 24 h. The digestion solution was filtered by a 0.45 μm nitrocellulose filter. To reduce the sample loss caused by MPs adhering to the filter and funnel, the containers were rinsed with ultrapure water repeatedly. The filter was kept in a glass Petri dish for the following measurements.

To ensure the accuracy of the experimental data, a recovery experiment for MPs was carried out, and black polypropylene (PP) MPs were made using scissors and files. Their particle size ranged from 1 mm to 2 mm. The

homemade black MPs were mixed with the sediments evenly, and the density separation steps were carried out. The samples were examined under a stereoscope, and the recovery rates were more than 70%.

2.3 MPs measurement

Stereoscopy is an effective method for the preliminary identification of MPs. The suspected MPs on the filter were observed with an SMZ25 Nikon stereoscope (×10) and recorded with the camera attached to the stereoscope. The basic principles of identification are as follows: (1) gloss and uniform coloration; (2) no obvious cell or other biological structure; and (3) uniform thickness and three-dimensional curved shape (Hidalgo-Ruz et al., 2012).

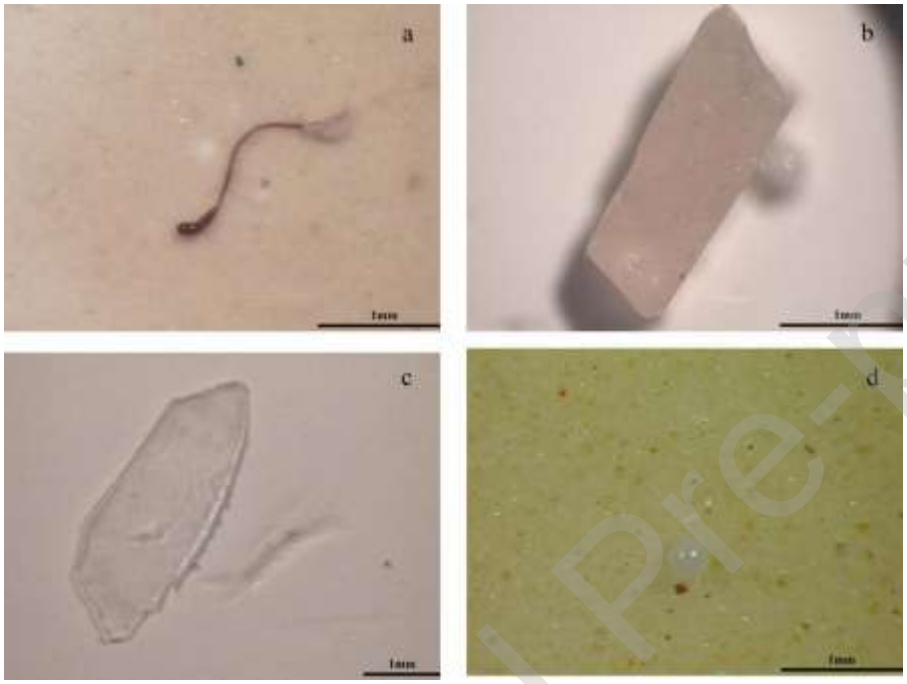


Fig. 2 The scanned microplastics in the water samples

$ZnCl_2$ solutions were filtered before use. All reagent bottles were washed with ultrapure water three times and covered with aluminum foil. Plastic products were avoided during the experiment to reduce exogenous pollution. Plastic products were washed with ethyl alcohol and ultrapure water three times. The instrument utilized for MP determination was washed to reduce fiber pollution. Procedure blanks were utilized to determine the procedure pollution.

Typical suspected MPs were selected for Raman spectroscopic analysis, and the detected nonplastic materials were removed from the list. The 100 suspected MPs were selected randomly for Raman measurements. The Raman instrument selected in this study was a laser confocal microscopic Raman scattering spectrometer (Horiba, LabRAM Aramis model), which has a fast measurement speed and high sensitivity. The test conditions were a green 532 nm excitation source (solid-state laser) and red 633 nm excitation source (He-Ne device). The spectrum range was 0-

4000 cm^{-1}, and the lamp current intensity was 25 mW. The cumulative time was 10-30 s, and the number of scans was 2. Although the sample had been digested by hydrogen peroxide, there were some natural organic residues still present in the sample, such as lipids. These caused fluorescence interference and increased the difficulty of spectral identification. Therefore, this study used a MATLAB algorithm to deduct the fluorescence background and optimize the atlas (https://github.com/ michaelstchen/ modPolyFit) (Ghosal et al., 2018). Then, the processed Raman spectra were compared with the KnowItAll® library. Only matching degrees greater than 60% were identified as MPs. To further characterize the MPs, the surface morphology and qualitative elemental analysis of MPs were studied by scanning electron microscopy (SEM/EDS) (Sobhani et al., 2020). A field emission scanning electron microscope with an EMAX-350 energy dispersive spectrometer (S-4800/EX-350) was selected as the instrument in this experiment.

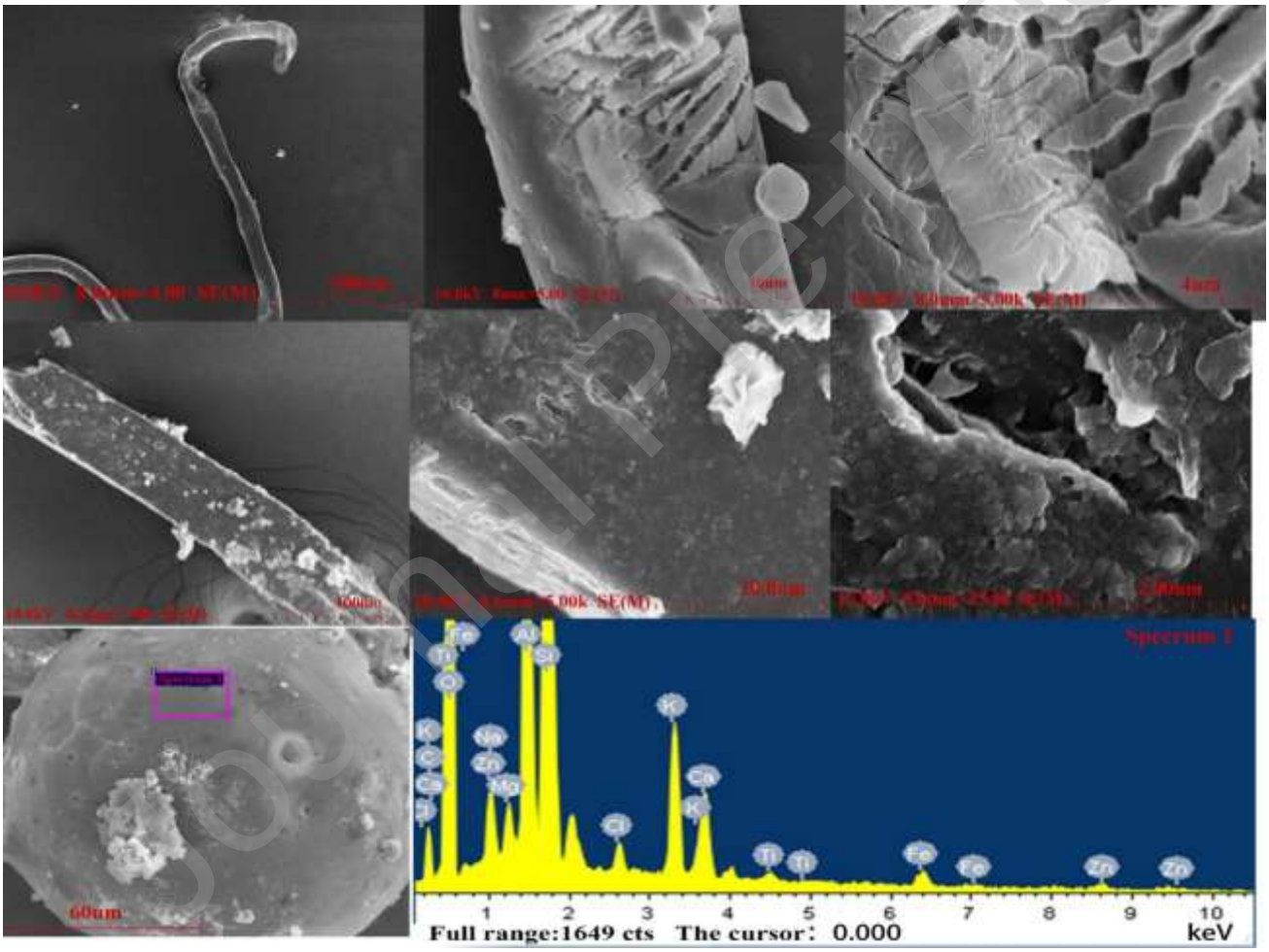


Fig. 3 Electron microscopy images and energy spectrum analysis of MPs

2.4 Acetochlor measurement

The extraction of acetochlor from the water samples was performed via solid-phase extraction (SPE). ENVI-Carb graphitized carbon black (GCB, SUPELCLEAN, 57094, 0.5 g, 6 mL) cartridges were used for extraction according

to Corcia et al., (1997) and Ouyang et al. (2019). The collected water samples were equilibrated to room temperature and filtered through glass fiber filters (0.77 μm, Whatman). Ace-D_{11} (30 ng) was added to samples as a surrogate before extraction. SPE cartridges were activated and eluted. The concentration of the target herbicide in the blank was below the limit of detection. All samples were analyzed in duplicate. The average relative percentage difference (RPD) for acetochlor was 15%. The average recovery rate of the surrogate was 84% ± 14. The method detection limits (MDLs) and method quantification limits (MQLs) were applied (Fig. S3-S4).

2.5 Data analysis process

Vertical distribution was important for understanding the MP dispersion in the seawater. The empirical equation was suitable for the estimation of MPs in the surface water of a 0-5 m depth (Song et al., 2018), and the equation was as follows (Law et al., 2014; Isobe et al., 2015; Kukulka et al., 2012):

$$N = N_0 e^{\frac{w}{A_0} z}$$

where N_o is the concentration of MPs collected using the net, w is the plastic rise velocity (5.3 mm/s) obtained experimentally by Reisser et al. (2015), and z is the vertical axis perpendicularly extending from the marine surface. The parameter A_0 was computed as:

$$A_0 = 1.5 u_* k H_S$$

where u_* is the water frictional velocity (=0.0012 W_{10}), k is the von Karman coefficient (0.4), H_s is the significant wave height, the average annual value was used in this study, and W_{10} is the 10-m wind speed the average annual value of which was used.

Statistics were performed in SPSS 20.0. The significance of MP intensity differences between groups was evaluated using t-tests, and $p<0.05$ was considered significant. ArcGIS 10.2, Origin 9.1, and R 3.1.0 were used to generate graphs.

3. Results

3.1 Spatial pattern of MPs and acetochlor in the sediment

The spatial distribution of the MPs and acetochlor in sediments in the bay were analyzed (Fig. 6), which were classified into three groups with varying water depths. The average abundance of MPs in the estuary and coastal and bay waters decreased from 643±270 n/kg d.w to 358±129 n/kg d.w with increasing distance from the shore. The decreasing pattern proved that the MPs settle during transport.

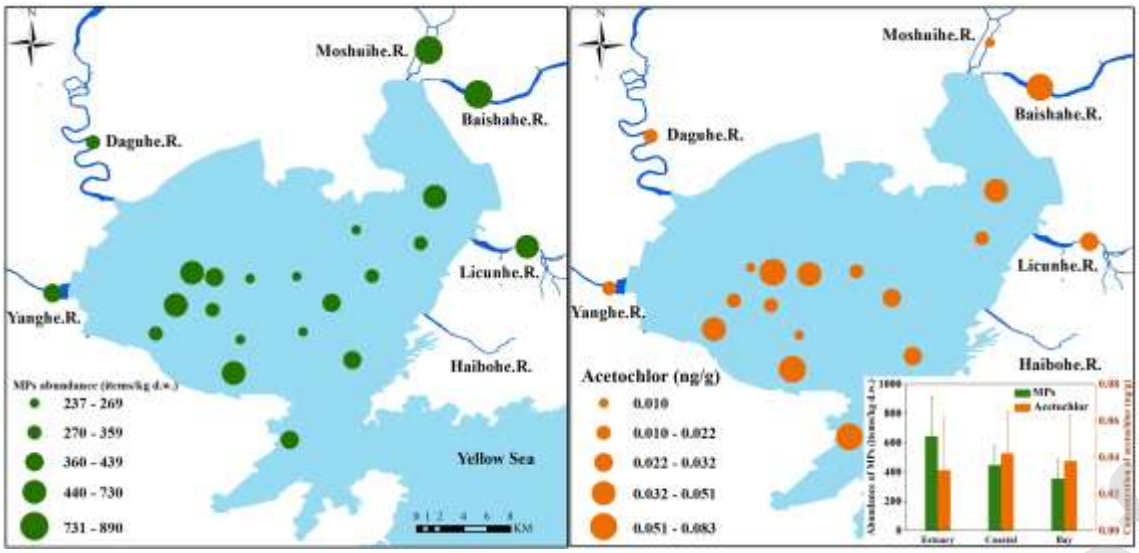


Fig. 4 Spatial distribution of MPs from 10 μm to 5 mm and acetochlor concentrations in sediment

The MP properties in sediments varied with the water depth. The average size was 1.45 mm in the estuary and larger than in the bay. The MPs of 1.0 mm-2.0 mm in size were largely observed in the sediment and had low distribution in the water, which indicated that MPs of this size tended to settle into the sediment. The transparent, blue and black MPs (68.69%) were found in sediments. The transparent MPs (36.25%) were the only ones with a distinct abundance difference between the estuary and the bay. The shape composition in the sediments was similar to that in the water, and the fibrous MPs were prevalent (53.5%). Regarding the MP material, PP was still the largest percentage of MP polymer (23.51%).

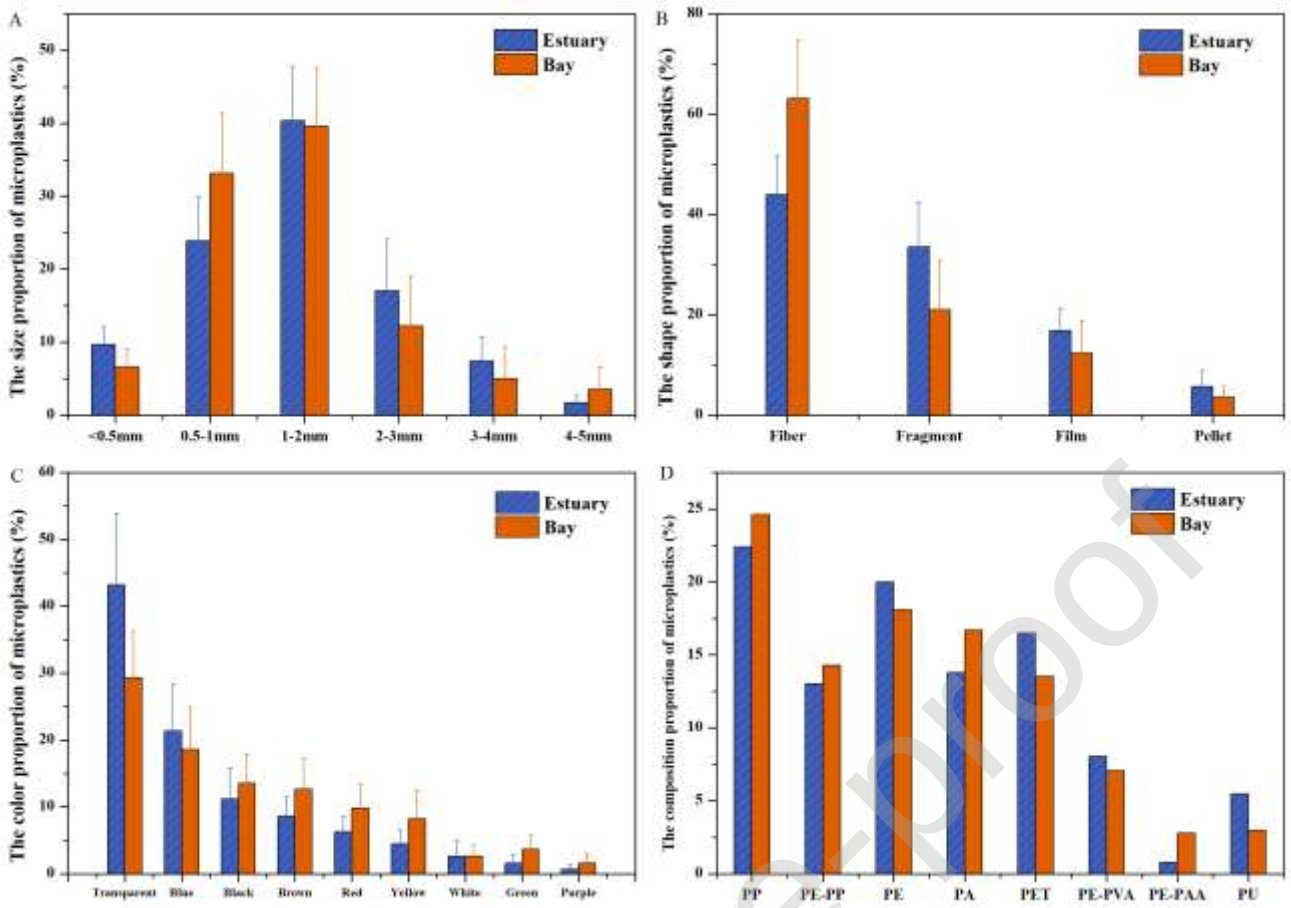


Fig. 5 Component characteristics of MPs observed in the sediment

3.2 Temporal pattern of MP properties in the estuary and bay

The size of the MPs in the estuary and bay ranged from 0.1 mm to 0.5 mm. The average size was 2.33 mm, and the range was 0.5-4 mm in the estuary, which was larger than the average value of 1.45 mm observed in the bay. Transparent, blue and black were the dominant colors among the MPs in the water, accounting for 66.34% of the colors. The proportion of transparent MPs in the estuary (23.18%) was lower than in the bay (43.49%). Fibers were the main shape of the MPs, and the fibrous proportion in the bay increased by 13.33% from that in the estuary. The ratios of the shapes across the seasons were similar. The Raman spectral analysis of the MP polymer makeup with BioRad KnowItAll® software showed that PP was a prevalent material with a higher composition in the estuary than in the bay. The summed proportions of PU, PET and PA in the estuary were 60.56%, which was lower than that in the bay.

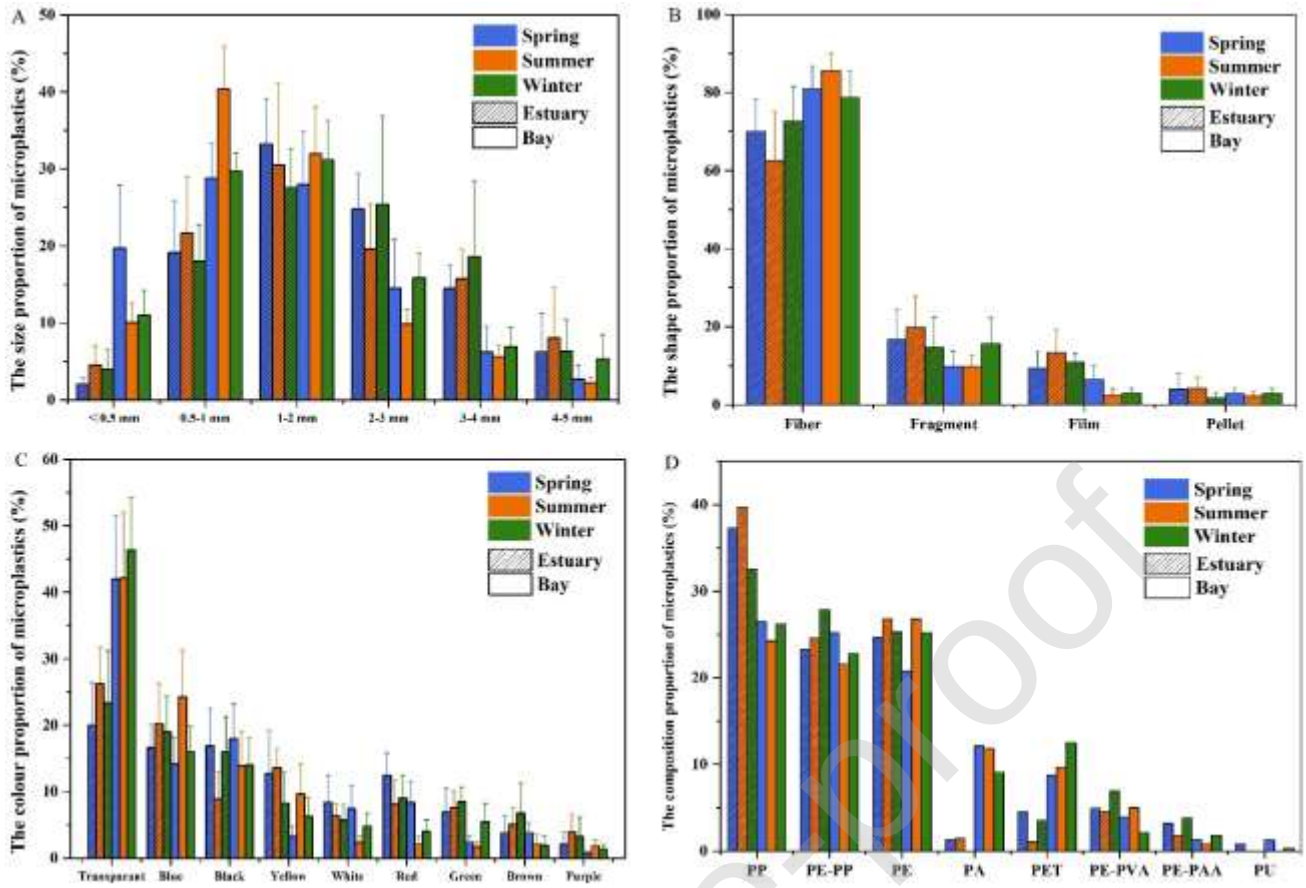


Fig. 6 Component characteristics of the MPs observed in the bay seawater

3.3 MP component characteristics in fish stomachs

The MPs were detected in the stomachs of four kinds of fishes, and the average abundance was 7.59±4.66 items/ind. (2.67 items/g w.w., or 9.17 items/g d.w., Table S7). The largest abundance was 13.5 items/ind. in *Pleuronichthys cornutus*. This result indicated that the accumulation of MPs in the fish stomach was due to food intake. The abundance in *Saurida elongata* was also relatively high. Compared with the abundance in the seawater, the abundances in the fish stomachs were relatively small, but the potential health risk was significant.

The MPs in the fish stomachs were mainly 0.5 mm-3.0 mm in size (77.34%), and the average size was 1.92±1.15 mm. The proportion of large sized MPs (4-5 mm) in the fish stomach (16.41%) was higher than that in both the water (9.67%) and sediments (8.55%). The transparent and blue MPs were dominant in the fish stomachs, accounting for 82.31% of the total observed MPs. This percentage was higher than that in the surface water (61.62%) and sediments (76.25%). The fibrous MPs in the fish stomachs accounted for 86.73% of the total MPs, constituting the largest shape classification. Similar to that in the water and sediments, PP accounted for the largest proportion (35.38%) of the polymer composition of MPs in the fish stomachs.

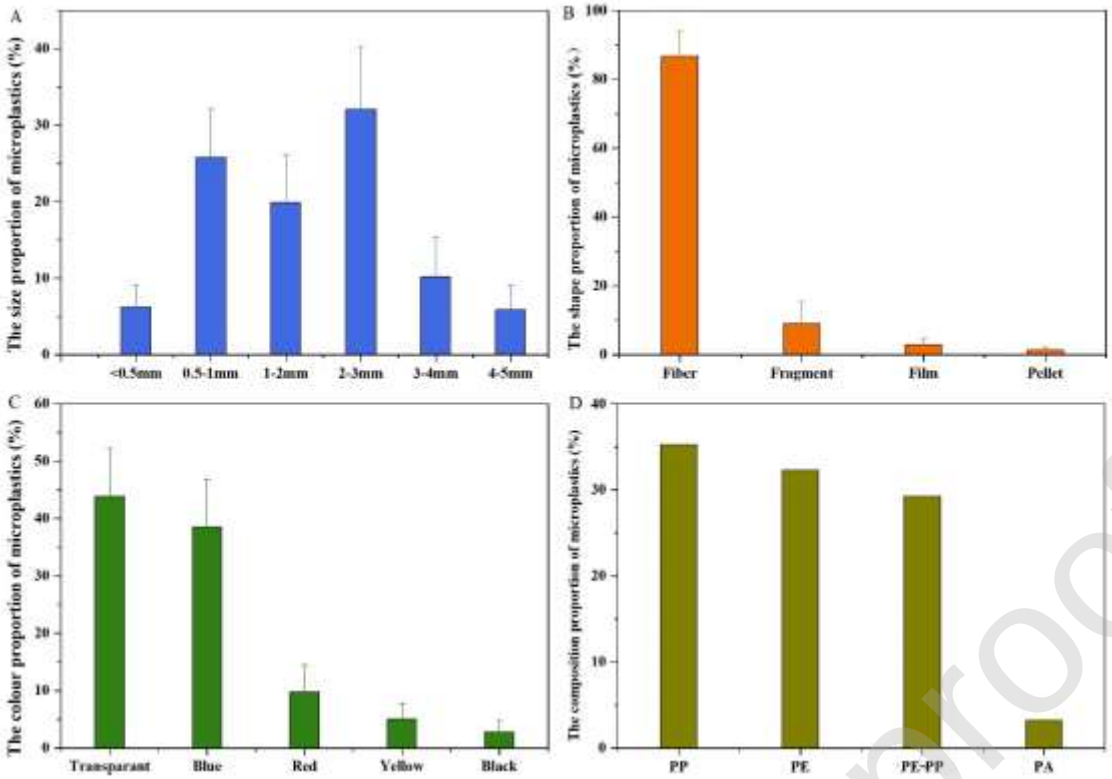


Fig. 7 Component characteristics of MPs observed in fish stomachs

3.4 Temporal correlation of MPs and acetochlor in the estuary and bay

The sampling of the river mouth in the estuary presented the discharge from territorial sources to the bay. The seasonal distributions of MP abundance and acetochlor concentration in the river waters showed close temporal correlations (Fig. 8). The MP abundance in the estuary was the highest in winter and the lowest in summer. Acetochlor showed a similar seasonal trend, and the highest concentrations were observed in the winter (12.7±13.6 ng/L). The correlation coefficient (R^2) between the averaged values of the two pollutants over the seasons was 0.926. The ranges of the two indicators at all the sampling locations in the spring and summer were much smaller than in winter. The concentration values in the winter were relatively high due to the low stream flow discharge and the discharged load after tillage in autumn.

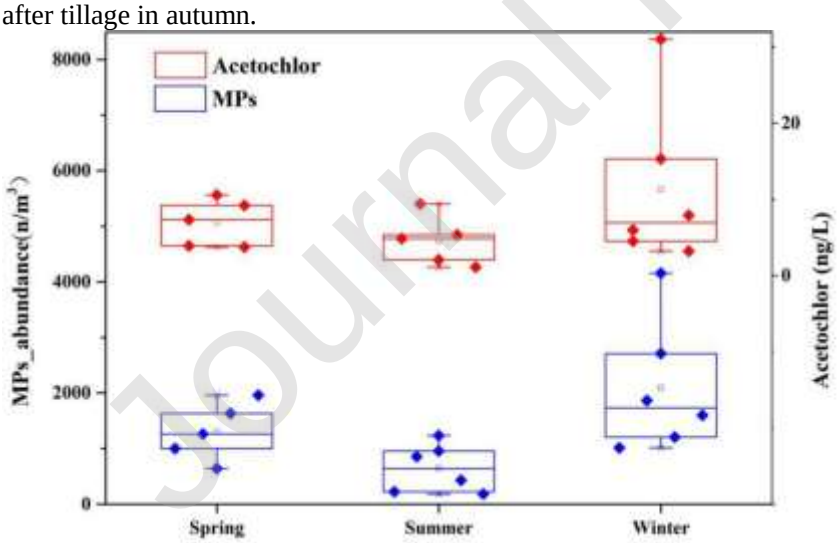


Fig. 8 Seasonal pattern of MP abundance and acetochlor concentration in the water of estuary (points in the box were was the value of each sampling site in the corresponding season)

The seasonal distributions of MPs and acetochlor in the surface seawater were then compared (Fig. 9). Their temporal patterns were similar within the estuary, and the summer concentrations were the lowest. The R^2 value

between the average values of the two pollutants over the seasons was 0.860. The average values in the spring was slightly larger than in the summer. The largest value still appeared in the winter, which coincided with the highest value in the estuary. The variation of pollutants in the summer was much smaller (1.2±0.1 ng/L) than in the other seasons. The seasonal correlations of the two pollutants between the two locations demonstrated that they shared the similar temporal-spatial patterns, and the MPs observed similar transport principles with acetochlor originating from agricultural systems.

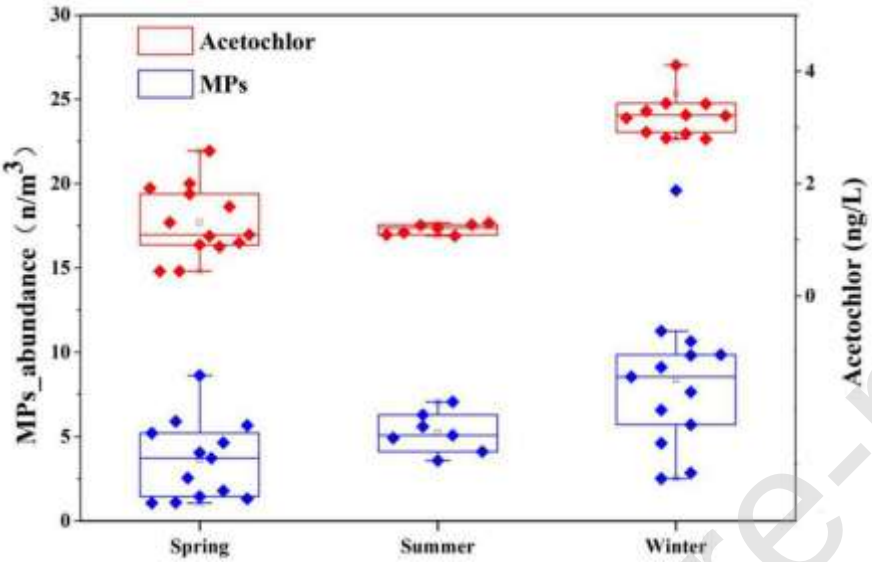


Fig. 9 Seasonal patterns of MPs and acetochlor in the seawater in the bay (points in the box were was the value of each sampling site in the corresponding season)

4. Discussion

4.1 Microplastic pollution dynamics in a bay with intensive cultivation

The agricultural tillage around the studied bay is very intensive, and the application of plastics as soil fumigation films, mulch films, and irrigation drip tape is very high (Yang et al., 2017). The observations in this bay demonstrate a higher MP load than in other similar estuaries (Fig. 10a). The seasonal patterns in the water of the estuary and bay also prove that the patterns coincide with the tillage practices. The higher loads in the winter are the direct consequence of the annual pattern of farmland maintenance. The main plastic particulates found in the estuary were transported after the weathering and fragmentation of plastic litter in the farmland (Auta et al., 2017). The decreased abundance from the estuary to the bay and in the sediment indicates that there was MP settling and degradation occurring during transport. Compared with those of other similar bays, the MP abundances in the water and sediment of this bay were slightly higher.

The MP abundance per unit weight of fish stomach detected in the bay ranged widely from 2.5-13.5 items/ind.

among the different species. The MP size and shape proprieties in the fish stomachs were clearly different from those of the MPs in the bay, which indicated that the biological accumulation in the fishes was of fibrous MPs with sizes of 2-3 mm. These types of MPs were also the dominant size of MPs in the bay. These MPs are associated with other toxic trace pollutants and are readily accumulated in fishes via ingestion. The composition of the MP size and properties in the water shared much similarity with those of the MPs found in the sediments, which also demonstrates the settling process from water to sediment that explains the abundance gap. Synthetic fibers are globally produced from polyesters, polyamides, acrylics and polyolefins (Schmiedgruber et al., 2019). The polyethylene is the dominant material for mulching film, which coincided with the main observed composition of MPs in the bay. The fiber was the dominant type of MPs in this bay, which indicated that fibrous MPs were the primary MP pollutant in the bay.

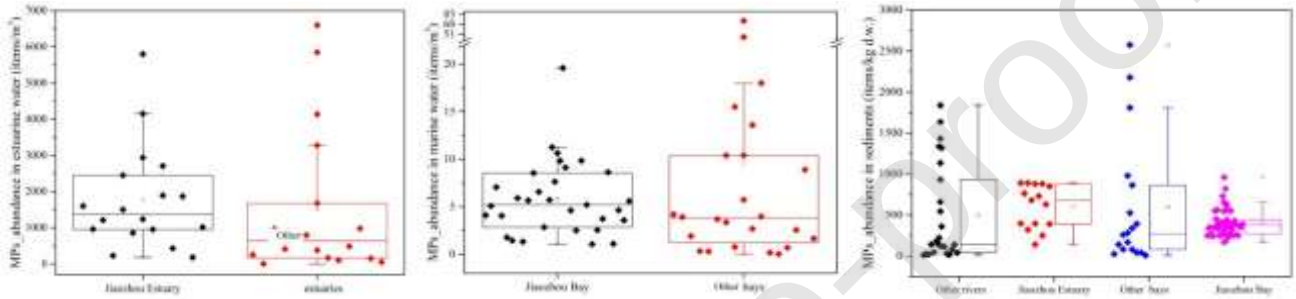


Fig. 10 Comparison of microplastics in water and sediment between these studies and those of similar areas

4.2 Transport pattern from the estuary to bay as diffuse pollution

The sampling location and period affected the MP abundance, and the mean values of acetochlor and MPs from the estuary to the bay decreased. The color properties of MPs had a clear spatial difference, and the transparent MPs decreased in abundance during transport to the bay. The MPs were mainly composed of PP, PE-PP and PE, which were commonly similar in the estuary and bay across the seasons. Differences in sizes of MPs in the surface water and sediment were relatively small, which was not similar to that of other similar bays (Barletta et al., 2019; Frère et al., 2017). This is mainly because the water depth in the studied bay is shallow, which caused the mixture of the surface and subsurface waters and the sediment by wind (Ouyang et al., 2019). The close correlation of MP abundance and acetochlor concentration in the estuary and bay demonstrated that agricultural diffuse pollution is the main source of both of these pollutants.

Based on the concentration difference of acetochlor and MPs between freshwater in the estuary and seawater in the bay (Fig. 8 and Fig. 9), it is clear that the majority of the diffuse pollutants were retained in the sediment. The decreasing pattern of MPs in the sediment from the estuary to the bay was relatively small (Fig. 8). Due to the even smaller abundance of MPs in the seawater in the bay than in the estuary, a measurable fraction was still released from

the sediment to the water with the disturbance of the current tide (Fischer et al., 2016). It has been widely proven that acetochlor is mainly transported via sorption to organic particles in the river course or the bay (Calderon et al., 2016). Based on similar seasonal patterns (Eo et al., 2019), it can be concluded that the MPs may also be attached to organic particles for transportation. Therefore, soil erosion control and particle interception from rivers to marine areas may be an effective method to prevent MP pollution in the sea.

4.3 Implication for agricultural diffuse pollution control

The MPs in the bay had multiple sources, including atmospheric deposition and discharge from the sewage into the bay (Barrows et al., 2018). An observation in Germany showed that the dominant atmospheric MPs are fragments (Klein and Fischer, 2019), which is different from the dominant shape of MPs in this bay and indicates that territorial discharge may the main source. A previous study showed that the MP concentrations in the Japanese river are closely correlated with biochemical oxygen demand (BOD) (Kataoka et al., 2019) and demonstrate the dependence on human activities in the basin. The close correlation between MPs with acetochlor across the seasons identified that agricultural diffuse pollution was the main source of pollution in the bay. The shape and color properties of the MPs in the water and sediment in the bay further confirm the agricultural source. Plasticulture is necessary for tillage practices, but its adverse effects on the environment need to be carefully assessed. The observation of MP formation, transport and degradation from the agricultural system is still inconclusive and they can accumulate in the soil similarly to other diffuse pollutants. From the aspect of MP prevention, the PE and PP fibers from plasticulture waste are the major concerns.

More research is needed to prove that the MPs in marine water have significant negative impacts on marine ecosystems and human health. Similar to other studies, the detection of MPs still has many uncertainties due to the limits of observation. The visual identification of MP color and material is difficult to accurately repeat (Kapp and Yeatman, 2018). Additionally, as this study demonstrated, the SMZ25 Nikon stereoscope cannot detect the low nanometer size ranges of MPs from water samples.

5. Conclusion

This study generated unique data for the bay environment in the western Pacific and provided new insights into MP source identification and transport principles. The main aim of this work was to mechanistically understand the discharge pattern of agricultural diffuse pollution with the temporal and spatial correlation of MPs with the concentration of acetochlor. The similar temporal patterns showed the possibility of using typical organic diffuse pollution to quickly express the discharge and transport pattern of MPs. The transport of MPs in the freshwater and

sediments from the estuary to the bay presented seasonal patterns, which are the direct consequence of discharge under seasonal tillage and climatic conditions. With the MP observations in the fish stomachs, the sediment in the bay acted as a sink for MPs and as the MP source for the fishes.

The relatively high measured MP abundance in the water and sediment of the estuary compared to that of other bays further supports that they were discharged from land into the marine environment. The higher abundance in this bay compared to that of other bays suggests that the agricultural system is the main source for the MPs in this bay, which is surrounded by intensively cultivated farmlands. With the observed concentration trend from the estuary to the bay, it was clear that a clear majority of the MPs in the bay originated from the agricultural system, indicating that this transport pathway is a major source for pollution prevention. Beyond the case studies highlighted, trace herbicides are reliable for studying the source, transport and fate of MPs and their correlations, which is useful for quickly understanding the fundamental processes and implications of these pollutants.

Author credit

Wei Ouyang, Conceptualization, Methodology, Writing - Review & Editing, Supervision

Yu Zhang, Investigation, Writing - Original Draft

Li Wang, Investigation

Damià Barceló, Resources Writing - Review & Editing

Yidi Wang, Software, Visualization

Chunye Lin, Methodology, Project administration

Conflict of interest statement

We declare that the undersigned manuscript entitled “Seasonal relevance of agricultural diffuse pollutant with microplastic in the bay” is original, has not been full or partly published before, and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by the undersigned.

We understand that the Corresponding Author is the sole contact for the editorial process. The corresponding author "**Wei Ouyang**" is responsible for communicating with the other authors about process, submissions of revisions, and final approval of proofs.

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References

Accinelli, C., Abbas, H.K., Shier, W.T., Vicari, A., Giacomini, S., 2019. Degradation of microplastic seed film-coating fragments in soil. Chemosphere. 226, 645-650.

Andrade, J., Fernández-González, V., López-Mahía, P., Muniategui, S., 2019. A low-cost system to simulate environmental microplastic weathering. Marine Pollut. Bull. 149, 110663.

Auta, H.S., Emenike, C.U., Fauziah, S.H., 2017. Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions. Environ. Int. 102, 165-176.

Barrows, A., Christiansen, K., Bode, E.T., Hoellein, T.J., 2018. A watershed-scale, citizen science approach to quantifying microplastic concentration in a mixed land-use river. Water Res. 147, 382-392.

Blanco, I., Viviana Loisi, R., Sica, C., Schettini, E., Vox, G., 2018. Agricultural plastic waste mapping using GIS. A case study in Italy. Resour. Conserv. Recy. 137, 229-242.

Brumovsky, M.,Becanova, J., Kohoutek, J., Thomas, H., Petersen, W., Sorensen, K., Sanka, O., Nizzetto, L., 2016. Exploring the occurrence and distribution of contaminants of emerging concern through unmanned sampling from ships of opportunity in the north sea. J Marine Syst. 162, 47-56.

Calderon, M.J., Luna, E.D., Gomez, J.A., Hermosin, M.C., 2016. Herbicide monitoring in soil, runoff waters and sediments in an olive orchard. Sci. Total Environ. 569–570, 416-422.

Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K., R. Janssen, C., 2011. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. Mar. Pollut. Bull. 62(10), 2199-2204.

Corcia, A.D., Crescenzi, C., Guerriero, E., Samperi, R., 1997. Ultratrace determination of atrazine and its six major degradation producets in water by solid-phase extraction and liquid chromatography-electrospray/mass spectrometry. Environ. Sci. Technol. 31 (6), 1658-1663.

Cózar, A., Martí, E., Duarte, C.M., Juan, Lomas, J., van Sebille, E., Ballatore, T.J., et al., 2017. The arctic ocean as a dead end for floating plastics in the north atlantic branch of the thermohaline circulation. Sci. Adv. 3(4), e1600582.

Elert, A.M., Becker, R., Duemichen, E., Eisentraut, P., Falkenhagen, J., Sturm, H., et al. Comparison of different methods for MP detection: what can we learn from them, and why asking the right question before measurements matters? Environ. Pollut. 231, 1256-1264.

Enfrin, M., Dumée, L.F., Lee, J., 2019. Nano/microplastics in water and wastewater treatment processes – Origin, impact and potential solutions. Water Res. 161, 621-638.

Eo, S., Hong, S.H., Song, Y.K., Han, G.M., Shim, W.J., 2019. Spatiotemporal distribution and annual load of microplastics in the Nakdong River, South Korea. Water Res. 160, 228-237.

Fischer, E.K., Paglialonga, L., Czech, E., Tamminga, M., 2016. Microplastic pollution in lakes and lake shoreline sediments – -A case study on Lake Bolsena and Lake Chiusi (central Italy). Environ. Pollut. 213, 648-657.

Foley, M.E., Sigler, V., Gruden, C.L., 2008. A multiphasic characterization of the impact of the herbicide acetochlor on freshwater bacterial communities. The ISME J. 2(1), 56-66.

Frère, L., Paul-Pont, I., Rinnert, E., Petton, S., Jaffré, J., Bihannic, I., et al., 2017. Influence of environmental and anthropogenic factors on the composition, concentration and spatial distribution of microplastics: a case study of the Bay of Brest (Brittany, France). Environ. Pollut. 225, 211-222.

Fries, E., Dekiff,J.H., Willmeyer, J., Nuelle, M.T., Ebert, M., Remy, D., 2013. Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. Environ. Sci. Proc. Impacts. 15(10), 1949-1956.

Fulweiler, R.W., Nixon, S.W., Buckley, B.A., Granger, S.L., 2007. Reversal of the net dinitrogen gas flux in coastal marine sediments. Nature. 448, 180–182.

Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. Sci. Adv. 3(7), e1700782.

Ghosal, S., Chen, M., Wagner, J., 2018. Molecular identification of polymers and anthropogenic particles extracted from oceanic water

and fish stomach–A Raman micro-spectroscopy study. Environ. Pollut. 233, 1113-1124.
Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. Environ. Sci. Technol. 46(6), 3060-3075.
Holt, H., Shukla, S., Hochmuth, G., Muñoz-Carpena, R., Ozores-Hampton, M., 2017. Transforming the food-water-energy-land-economic nexus of plasticulture production through compact bed geometries. Adv. Water Resour. 110, 515-527.
Huang, Y., Liu, Qin., Jia, W.Q., Yan, C.R., Wang, J., 2020. Agricultural plastic mulching as a source of microplastics in the terrestrial environment. Environ. Pollut. 260, 114096.
Isobe, A., Uchida, K., Tokai, T., Iwasaki, S., 2015. East Asian seas: a hot spot of pelagic microplastics. Mar. Pollut. Bull. 101(2), 618-623.
Kapp, K.J., Yeatman, E., 2018. Microplastic hotspots in the Snake and Lower Columbia rivers: A journey from the Greater Yellowstone Ecosystem to the Pacific Ocean. Environ. Pollut. 241, 1082-1090.
Kataoka, T., Nihei, Y., Kudou, K., Hinata, H., 2019. Assessment of the sources and inflow processes of microplastics in the river environments of Japan. Environ. Pollut. 244, 958-965.
Klein, M., Fischer, E.K., 2019. Microplastic abundance in atmospheric deposition within the Metropolitan area of Hamburg, Germany. Sci. Total Environ. 685, 96-103.
Kukulka, T., Proskurowski, G., Morét- Ferguson, S., Meyer, D.W., Law, K.L., 2012. The effect of wind mixing on the vertical distribution of buoyant plastic debris. Geophys. Res. Lett. 39(7).
Lares, M., Ncibi, M.C., Sillanpää, M., Sillanpää, M., 2018. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. Water Res. 133, 236-246.
Law, K.L., Morét-Ferguson, S.E., Goodwin, D.S., Zettler, E.R., Deforce, E., Kukulka, T., et al., 2014. Distribution of surface plastic debris in the eastern Pacific Ocean from an 11-year data set. Environ. Sci. Technol. 48(9), 4732-4738.
Li, H.X., Ma, L.S., Lin, L., Ni, Z.X., Xu, X.R., Shi, H.H., et al., 2018. Microplastics in oysters Saccostrea cucullata along the Pearl River Estuary, China. Environ. Pollut. 236, 619.
Li, H.X., Ma, L.S., Lin, L., Ni, Z.X., Xu, X.R., Shi, H.H., et al., 2018. Microplastics in oysters Saccostrea cucullata along the Pearl River Estuary, China. Environ. Pollut. 236, 619.
Li, X.W., Chen, L.B., Mei, Q.Q., Dong, B., Zeng, E.Y., 2018. Microplastics in sewage sludge from the wastewater treatment plants in China. Water Res. 142, 75-85.
Löder, M.G.J., Imhof, H.K., Ladehoff, M., Löschel, L.A., Lorenz, C., Mintenig, S., et al., 2017. Enzymatic purification of microplastics in environmental samples. Environ. Sci. Technol. 51(24), 14283-14292.
Lönnstedt, O., Eklöv, P., 2016. Environmentally relevant concentrations of microplastic particles influence larval fish ecology. Science 352(6290), 1213-1216.
Maes, T., Jessop, R., Wellner, N., Haupt, K., Mayes, A.G., 2017. A rapid-screening approach to detect and quantify microplastics based on fluorescent tagging with Nile Red. Sci. Rep. 7, 44501.
Mário B., Lima, A.R.A., Costa, M.F., 2019. Distribution, sources and consequences of nutrients, persistent organic pollutants, metals and microplastics in South American estuaries. Sci. Total Environ. 651, 1199-1218.
Ouyang, W., Wu, Y.Y., Hao, Z.C, Zhang, Q., Bu, Q.W., Gao, X., 2018. Combined impacts of land use and soil property changes on soil erosion in a mollisol area under long-term agricultural development. Sci. Total Environ. 613-614, 798-809.
Ouyang, W., Zhang, Y., Gu, X., Tysklind, M., Lin, C.Y., Wang, B.D., Xin, M., 2019. Occurrence, transportation, and distribution difference of typical herbicides from estuary to bay. Environ. Int. 130, 104858.
Ouyang, W., Zhang, Y., Gu, X., Tysklind, M., Lin, C.Y., Wang, B.D., Xin, M., 2019. Occurrence, transportation, and distribution difference of typical herbicides from estuary to bay. Environ. Int. 130, 104858.
Ouyang, W., Zhao, X.C., Tysklind, M., Hao, F.H., 2016. Typical agricultural diffuse herbicide sorption with agricultural waste-derived biochars amended soil of high organic matter content. Water Res. 92, 156-163.
Piehl, S., Leibner, A., Löder, M.G.J., Dris, R., Bogner, C., Laforsch, C., 2018. Identification and quantification of macro- and microplastics on an agricultural farmland. Sci. Rep. 8(1), 17950.
Plastic pollution hurts perch. 2016. Nature. 534, 155.
Reisser, J.W., Slat, B., Noble, K.D., du Plessis, K., Epp, M., Proietti, M., de Sonneville, J., Becker, T., Pattiaratchi, CPlessis, K.D., Epp, M., Proietti, M.C., et al., 2015. The vertical distribution of buoyant plastics at sea: an observational study in the North Atlantic Gyre. Biogeosciences. 12(4), 1249-1256.
Rochman, C.M., 2018. Microplastics research—from sink to source. Science. 360(6384), 28-29.
Sagawa, N., Kawaai, K., Hinata, H., 2018. Abundance and size of microplastics in a coastal sea: Comparison among bottom sediment, beach sediment, and surface water. Mar. Pollut. Bull. 133, 532-542.
Sanchez, W., Bender, C., Porcher, J.M., 2014. Wild gudgeons (Gobio gobio) from French rivers are contaminated by microplastics: preliminary study and first evidence. Enviro. Res. 128, 98-100.
Scarascia-Mugnozza, G., Sica, C., Russo, G., 2012. Plastic materials in European agriculture: actual use and perspectives. J. Arg. Eng. Res. 42, 15-28.
Scheurer, M., Bigalke, M., 2018. Microplastics in swiss floodplain soils. Environ. Sci. Technol. acs.est.7b06003.
Schiermeier, Q., 2017. Investigation finds swedish scientists committed scientific misconduct. Nature.
Schmiedgruber, M., Hufenus, R., Mitrano, D.M., 2019. Mechanistic understanding of microplastic fiber fate and sampling strategies: Synthesis and utility of metal doped polyester fibers. Water Res. 155, 423-430.
Sighicelli, M., Pietrelli, L., Lecce, F., Iannilli, V., Falconieri, M., Coscia, L., et al., 2018. Microplastic pollution in the surface waters of Italian Subalpine Lakes. Environ. Pollut. 236, 645-651.
Silva-Cavalcanti, J.S., Silva, J.D.B., de França, E.J., de Araújo, M.C.B., Gusmão, F., 2017. Microplastics ingestion by a common tropical freshwater fishing resource. Environ. Pollut. 221, 218-226.
Sobhani, Z., Zhang, X., Gibson, C., Naidu, R., Fang, C., 2020. Identification and visualisation of microplastics/nanoplastics by Raman imaging (i): Down to 100 nm. Water Res. 1741, 115658.

Song, Y.K., Hong, S.H., Eo, S., Jang, M., Han, G.M., Isobe, A., Shim, W.J., 2018. Horizontal and vertical distribution of microplastics in Korean coastal waters. Environ. Sci. Technol. 52(21), 12188-12197.

Steinmetz, Z., Wollmann, C., Schaefer, M., Buchmann, C., Schaumann, G.E., 2016. Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation? Sci. Total Environ. 550, 690-705.

Vignieri, S., 2016. Microplastic's triple threat. Science. 352(6290), 1185.

Vignieri, S., 2016. Microplastic's triple threat. Science. 352(6290), 1185.

Weithmann, N., Möller, J.N., Löder, M.G.J., Piehl, S., Laforsch, C., Freitag, R., 2018. Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci. Adv. 4(4), 8060.

Weithmann, N., Möller, J.N., Löder, M.G.J., Piehl, S., Laforsch, C., Freitag, R., 2018. Organic fertilizer as a vehicle for the entry of microplastic into the environment. Sci. Adv. 4(4), 8060.

Woodward, E.E., Kolpin, D.W., Zheng, W., Holm, N.L., Meppelink, S.M., Terrio, P.J., et al., 2019. Fate and transport of nitrapyrin in agroecosystems: Occurrence in agricultural soils, subsurface drains, and receiving streams in the Midwestern US. Sci. Total Environ. 650, 2830-2841.

Yang, D.D., Chen, J., Zhou, Y., Chen, X., Cao, X., 2017. Mapping plastic greenhouse with medium spatial resolution satellite data: Development of a new spectral index. ISPRS J. Photogramm. 128, 47-60.

Zhang, M.J., Zhao, Y., Qin, X., Jia, W.Q., Huang, Y., 2019. Microplastics from mulching film is a distinct habitat for bacteria in farmland soil. Sci. Total Environ. 688, 470-478.

Zhu, X., 2015. Optimization of elutriation device for filtration of microplastic particles from sediment. Mar. Pollut. Bull. 92(1-2), 69-72.