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Assessment of Quantity and Quality of Microplastics in the Sediments, Waters, Oysters, and Selected Fish Species in Key Sites Along the Bombong Estuary and the Coastal Waters of Ticalan in San Juan, Batangas

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Microplastics (or MPs; < 5 mm in size) pollution is largely unstudied in the Philippines. From an environmental sustainability standpoint, it is important to understand the characteristics, abundance, and environmental fate of plastic debris of various sizes, and these include MPs that are not more easily and readily detected. In this study, we assessed the extent of MPs contamination in the sediments, waters, oysters, and selected fishes found in the rivers and coastal areas of Ticalan, Batangas, which were identified from water quality parameters as Class C and CS, respectively. The MPs were extracted from these samples by chemical digestion of the matrix, series of filtration, and separation by flotation through a density gradient to finally isolate the MPs which were not dissolved by chemical digestion. The isolated samples were imaged by optical microscopy and characterized based on their descriptive attributes. The results showed the presence of microplastics in all the samples tested, which were found mostly in the form of filaments, fragments, films, and pellets – with most showing weathered, degraded, or angular and irregular surfaces. Identification was done through spectral matching of the Fourier transform infrared spectra of isolated fragments with that of known plastics, although identification in some cases is made uncertain by possibility of degradation of the plastics in the environment. The majority of the isolates showed signature absorption bands of the C-H stretching vibrations of polyethylene-based plastics.

Keywords: fishes, FTIR, microplastics, oysters, sediments, water

INTRODUCTION

Plastics can be intentionally produced in specifically small sizes (*e.g.*, microbeads in beauty products) or may undergo weathering resulting in the formation of MPs. MPs, which have size dimensions less than 5 mm, are ubiquitous and continually accumulate in the marine environment, with approximately 8.2 bn kg reported to be entering the ocean every year globally due to improper disposal, runoff, *etc.* (Wilcox *et al.* 2015). Due to their high stability and durability, MPs can be persistent pollutants of the marine environment (Cozar *et al*. 2014), that could reach far distances, thus widening their impact on ecosystems (Ryan *et al*. 2009). Increasing global plastic production since the 1950s has increased the concern for

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pollution from such materials (Comăniță *et al.* 2017). Commercial products and their packaging as single-use plastic items, coupled with the challenge of effective waste management in the Philippines, have exacerbated plastic waste pollution (Ang and Sy-Changco 2007, Magalang 2014, Greenpeace 2017).

From an environmental sustainability standpoint, it is important to understand the characteristics, abundance, and environmental fate of plastic debris of various sizes, and these include MPs that are not easily and readily detected. The risks that these materials pose to higher-order organisms, including humans, are seriously problematic given the potential for bioaccumulation and biomagnification of these pollutants through the food chain. There are very few papers published on MP pollution in the Philippines, such as that of Argamino and Janairo (2016) on mussels (*Perna viridis*), and Paler and co-authors (2019) on plastic occurrence in the beaches of Southwestern Luzon.

The Bombong estuary and the coastal waters of Ticalan, San Juan, Batangas provide various ecological services such as a source of irrigation water and site for various aquaculture industries for the culture of shellfish, tilapia, milkfish, giant tiger prawns, and others. The area is also a popular site for tourists for its beaches. Unfortunately, the growth in population and lack of compliance with the local government's solid waste management programs in the area as stated in the Solid Waste Management Plan 2015–2025 (Municipality of San Juan 2015), present significant risks of pollution to these aquatic habitats. Given its economic potential and in the absence of any studies about the environmental condition of the area, there is a need to obtain baseline information that may be used for the formulation of mitigation programs and policies to reduce pollution in the area. In this study, we assessed the extent of MPs contamination in this area. For holistic baseline information, we sampled the sediments, the water, and marine organisms (oysters and selected freshwater and reef fish species) found in the river and coastal areas of Ticalan, Batangas. Methods for isolation of the MPs from these various environmental samples were also developed from published protocols to incorporate less toxic and more readily available chemical reagents.

MATERIALS AND METHODS

Study Sites

The study was conducted during September and November 2018 in three sites in Ticalan, Batangas: (a) Site 1 – upstream of the Bombong estuary; (b) Site 2 – downstream of the Bombong estuary; and Site 3 – the adjoining coastal area (Figure 1). An ecological profile of the area was initially made that included land use, land cover, and floral and faunal diversity. Water quality parameters

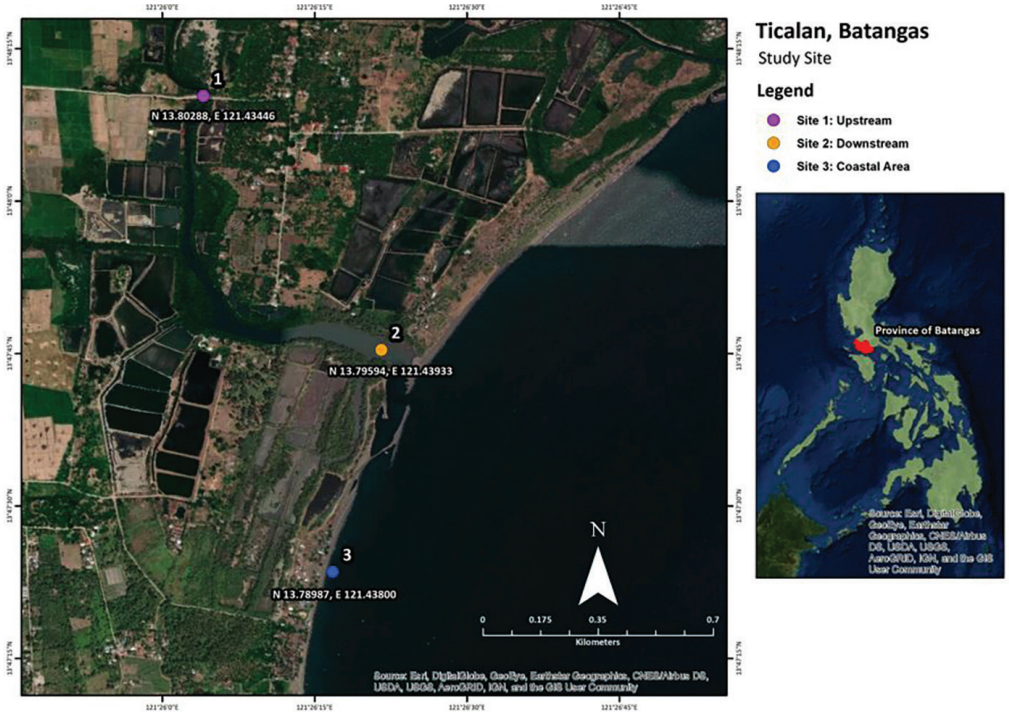

Figure 1. Satellite image of Ticalan, Batangas with area site markers (map adapted from PHILGIS.org).

such as pH, dissolved oxygen (DO), temperature, salinity, conductivity, and turbidity (TBD) were measured using standard field monitoring equipment.

General Experimental Design

The study was performed in accordance with the experimental design shown in Figure 2. The protocols for sampling and analysis of MPs in sediments and water samples were adapted from the methods described by Eriksen and co-authors (2013), Hidalgo-Ruz and co-authors (2012), Masura and co-authors (2015), and Quinn and co-authors (2017) with slight modifications to create the most feasible methodology for the isolation and testing of MPs in sediments and water samples. Sampling procedures described by Argamino and Janairo (2016) and Hammer and co-authors (2017), and processing procedures from Karlsson and co-authors (2017) and Lusher and co-authors (2017) were adapted for the biological samples.

Blank trials were done, which covered wet sieving, digestion, wet peroxide oxidation (WPO), and density separation. In addition, a blank sample with only potassium bromide (KBr) was used to generate the baseline spectra for the Fourier Transform Infrared Spectroscopy (FTIR) analysis for spectrum comparison (Shimadzu IRAffinity-1 FT-IR).

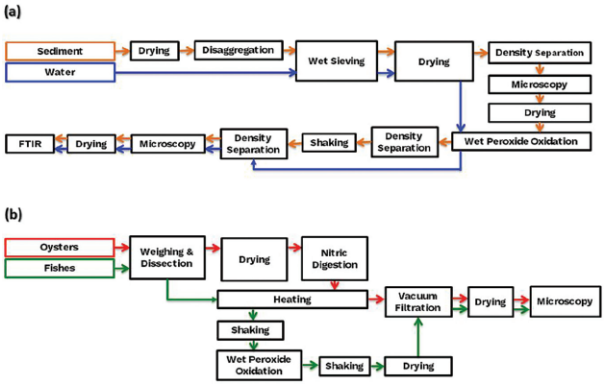

Figure 2. General experimental design for the analysis of MPs in (a) sediments and water samples; (b) oysters and selected fish species obtained from Ticalan, Batangas. Protocols were adapted from: Eriksen *et al.* (2013), Hidalgo-Ruz *et al.* (2012), Masura *et al.* (2015), and Quinn *et al.* (2017) for the sampling and analyses; Argamino and Janairo (2016) for the sediments and water samples; and Hammer *et al.* (2017), Karlsson *et al.* (2017), and Lusher *et al.* (2017) for the oysters and fish samples.

Sampling and Characterization of Sediments

Sediment samples were collected (4 L) from each site using a Ponar Grab sampler. These were placed in separately labeled 1 L glass jars, stored in a cooler with ice (*ca*. 0–4 °C), and transported to the laboratory for processing.

Sediment samples of 100 g each were placed in pre-weighed 600-mL beakers and were oven-dried at 90 °C until a constant dry weight was observed. The solidified mass of sediment was ground to a fine powder using a mortar and pestle with the addition of small amounts of distilled water until a ubiquitously fine-textured mixture was achieved.

The mixture underwent wet sieving with distilled water using stainless steel sieves with the following mesh sizes: 5 mm, 1 mm, 300 µm, and 45 µm. This resulted in a higher recovery of small-sized MPs and easier separation from other debris.

The materials collected in the final sieve were transferred to a beaker and returned to the oven to dry (at 90 °C) until they achieved a constant weight. The samples were allowed to cool at ambient temperature.

A sodium iodide brine solution (density range of 1.55–1.6 g/mL) was used for density separation of MPs from sediment instead of lithium metatungstate, as suggested by Masura and co-authors (2015). The brine solution was filtered (Whatman Grade 1, 10 µm) to remove any solids and other impurities. The filtered brine solution (100 mL) was added to the sediment sample and stirred. The mixture was left to stand for 10 min or until the MPs were visibly seen floating in the solution. All floating particles were collected with the use of metal tweezers and examined under a dissection microscope (40 x magnification). Potential MP particles were collected and oven-dried at 90 °C.

The potential MP particles were subjected to WPO to dissolve any remaining organic material and to further isolate the MPs. This was done by adding 20 mL of 0.05 M aqueous ferrous oxide, followed by 20 mL of 30% hydrogen peroxide (H_2O_2). The resulting mixture was left to stand at ambient temperature for 5 min to allow the mixture to settle and for the reaction to subside. Subsequently, the mixture was stirred and heated on a hot plate at 75 °C. When bubbles were observed, the sample was removed from the hot plate to cool and let the bubbling subside. The cycle of heating and cooling was repeated for an additional 30 min. Supplemental 5 mL of 30% H_2O_2 was added to the solution until no organic material remained.

Sodium chloride was added with a ratio of 6 g per 20 mL of solution to increase the density of the aqueous solution. The mixture was placed in a shaking incubator (60 °C at 100 rpm) for 10 min or until the salt was completely dissolved. The mixture was poured into a density separator (Masura *et al*. 2015) and left to settle overnight. Identifiable MPs were isolated from the sieve, examined under a dissection microscope (40x magnification), and characterized following Table 1 adopted from Hidalgo-

Table 1. Characterization of the MPs following Hidalgo-Ruz and co-authors (2012).

Characterization	Description
Sources	consumer product fragments (*e.g.*, fishing net) and raw industrial pellets
Type	plastic fragments, pellets, filaments, plastic films, foamed plastic, granules, and styrofoam
Shape	*for pellets*: cylindrical, disks, flat, ovoid, spheruloids
	for fragments: rounded, subrounded, subangular, angular
	general: irregular, elongated, degraded, rough, and broken edges
Erosion	fresh, unweathered, incipient alteration, and level of crazing (conchoidal fractures) weathered, grooves, irregular surface, jagged fragments, linear fractures, subparallel ridges, and very degraded
Color	transparent, crystalline, white, clear-white-cream, red, orange, blue, opaque, black, gray, brown, green, pink, tan, yellow, and pigmentation

Ruz and co-authors (2012). The particles were then placed in a glass vial and oven-dried at 40 °C in order to reduce sample noise for the succeeding FTIR analysis.

Assessment of MPs in River and Coastal Water Samples

Water samples were collected from each site using a WaterMark Plankton net (30 cm x 90 cm; with 363 µm mesh size) tethered to the side of the boat and dragged for 10 min. Samples were placed in labeled glass containers, stored in a cooler with ice (*ca*. 0–4 °C), and transported to the laboratory for further processing and analysis.

The samples were wet sieved with distilled water using stainless steel sieves (mesh sizes: 5 mm, 1 mm, 300 µm, and 45 µm). The collected solids were placed in pre-weighed beakers and oven-dried (90 °C) until they achieved a constant weight ($\pm$ 0.0001 g). The samples were then subjected to WPO as described previously with the exception of adding 20 mL of 30% H_2O_2, instead of 5 mL, to the beakers when natural organic material was still visible. The succeeding steps were followed as previously described.

Assessment of MPs in Oysters and Selected Species of Fish

Adult slipper-shaped oysters, *Crassostrea iredalei* (locally called *talaba*), were obtained from an oyster hatchery located downstream of the Bombong estuary. These were cleaned on-site to remove debris and mud, wrapped in a cotton cloth, and carefully placed in Ziploc bags to prevent stray MPs and other contaminants from coming into direct contact with the samples. These were stored in a cooler with ice (*ca*. 0–4 °C) and transported to the laboratory for further processing and analysis.

Dead oysters were discarded. The weight and length of the remaining oysters were measured before shucking. Replicates, each consisting of four shucked oysters, were placed in separate Erlenmeyer flasks and oven-dried at 60 °C. Subsequently, 20 mL of concentrated nitric acid was added to each sample, which was left to dry for at least four days to achieve optimum digestion. Each sample was heated on a hot plate at 80–90 °C for 20 min. Warm distilled water (80 °C; 20 mL) was added to each flask for dilution. The samples were then subjected to vacuum filtration (Whatman Grade GF/C). The filters were eventually placed on Petri dishes and dried in an oven at 50 °C for 1 h. After drying, the filter papers were examined under a dissection microscope (10x or 40x magnification) for the presence of MP particles. Identifiable MPs were documented and characterized using Table 1.

Various species of freshwater and reef fish species belonging to Mugilidae, Labridae, Serranidae, and Lutjanidae (Figure 3) were used. These were part of the catch obtained on the sampling day by the local fishermen of Sitio Dagat-Ilaya in Ticalan, Batangas. The fish samples were wrapped in aluminum foil and carefully placed in Ziploc bags and transported in a cooler with ice (*ca*. 0–4 °C) for further processing.

Each fish was dissected to extract the entire gastrointestinal tract and gills, which were then placed in a 600-mL glass

Figure 3. Biological samples collected from Ticalan, Batangas. Clockwise: (a) oysters, (b–c) oyster preparation for processing; reef fishes under Families (d) Labridae, (e) Serranidae, (f) Lutjanidae, and (g–j) Mugilidae (*Banak*) showing initial weighing and dissection to obtain the gills and digestive systems.

beaker and heated on a hot plate (60 °C) for 15 min before being placed in a shaking incubator for 20 min (300 rpm) at approximately 25 °C (Karlsson *et al.* 2017).

The dried samples were subjected to WPO by adding 30% H_2O_2 in 5 mL increments followed by wet sieving using 1 mm and 300 µm mesh sizes steel sieves. The addition of 20 mL aqueous ferrous (II) sulfate was done before the beakers were placed in a shaking incubator (at 300 rpm, 60 °C) for 15 min. To further evaporate the liquid, the samples were oven-dried at 60 °C for 24–48 h. Distilled water was added before subjecting the samples to vacuum filtration (Whatman Grade GF/C).

Subsequently, each filter paper was placed on a Petri dish and dried in the oven for 1 h at 50 °C. These were then examined under a dissecting microscope (10–40x magnification). Identifiable MPs were photographed and characterized using the criteria shown in Table 1.

Water Analysis

The pH, DO, conductivity, TBD, total suspended solids (TSS), salinity, temperature, nitrates (NO_3–N), and phosphates (PO_4^{3-}) were analyzed using a HANNA Multiparameter Water Quality Meter. The probes were washed and calibrated and immersed in the electrolyte solution for direct reading of the water quality parameter.

FTIR Analysis

Individual MP particles were isolated using a metal tweezer. Each particle was mixed with KBr to form a pellet. The transmission spectrum was generated using a Shimadzu IRAffinity-1 FTIR using blank KBr as background and averaging 40 scans at 4 cm^{-1} resolution. The spectra were manually baseline-corrected where necessary.

Characterization of the MPs Obtained from Water, Sediment, and Biological Samples

The MPs were characterized by size (relative to a 5 mm scale bar), composition (based on the results of the FTIR spectroscopy), type of particle, shape, erosion history, and color using the criteria in Table 1. The identification of the possible sources, shape, and erosion history of MPs was also noted.

RESULTS AND DISCUSSION

Ecological Profiling and Water Quality Monitoring

Figure 4 shows a land cover map of the Bombong estuary and the surrounding coastal areas in Tayabas Bay. Croplands consisting of rice, sugarcane, and corn

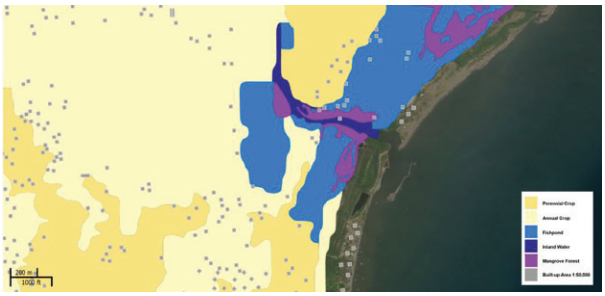

Figure 4. Land cover map of the Bombong estuary, Ticalan, San Juan, Batangas along with surrounding areas (map made with the Philippine Geoportal using ArcGIS Online – aerial base maps).

as well as perennial crops like pineapples, bananas, and coconuts dominate the western part of the northeastern portion of the river. Fishponds are also seen on the eastern and southwestern portions of the Bombong estuary where various species such as the Nile tilapia (*Oreochromis niloticus*), milkfish (*Chanos chanos*), giant tiger prawns (*Penaeus monodon*), and oysters (Order Ostreida) are cultured. Mangrove forests dominate the western and eastern sides of the Bombong estuary, providing protection from wind and tidal action and serving as nursery grounds for juvenile marine life. The western and eastern banks of the river consist of restaurants, gas stations, residential areas, schools, and plazas, which are likely contributors to the waste in the estuary. Due to the absence of a proper waste management program, the practice of burning and burying of trash along the coast is prevalent. Trash from nearby coastal provinces are also brought in through tidal action, particularly during the latter half of the year.

The results of the water quality monitoring are shown in Table 2. The Bombong estuary and the Ticalan coastal waters have yet to be officially classified by the Department of Environment and Natural Resources – Environmental Management Bureau for their intended beneficial use under the Department Administrative Order (DAO) 2016-08.

For the purposes of this study, the classifications Class C for the Bombong estuary and Class SC for the Ticalan coastal waters are adopted. Classes C and SC are given to freshwaters and marine waters, respectively, which are mainly used for harvesting and propagating aquatic products (DENR-EMB 2016). The study classified the Bombong estuary and the Ticalan coast accordingly due to their current uses for small-scale aquaculture.

Water quality measurements along the Bombong estuary were found to comply with the DAO 2016-08 standard limits for Class C waters for pH, temperature, NO_3–N, and PO_4^{3-}, while the levels of DO and TSS were noncompliant (Table 2). For the coastal waters, the results showed that DO and temperature were not compliant with the standard

Table 2. Water quality parameters of the Bombong Estuary and coastal waters of Ticalan, Batangas.

Parameter	DAO 2016-08 limit value for Class C	Bombong estuary		DAO 2016-08 limit value for Class SC	Coastal waters
pH	6.5–9.0	Upstream	7.65	6.5–8.5	8.2
		Downstream	8.32		
DO (mg/L, ppm)	Minimum of 5	Upstream	0.96*	Minimum of 5	2.45*
		Downstream	2.27*		
Conductivity (ps/cm)	Not specified	Upstream	36,720	Not specified	51,870
		Downstream	46,497		
TDS (mg/L)	Not specified	Upstream	18,060	Not specified	25,850
		Downstream	25,705		
TSS (mg/L)	80	Upstream	185	80	ND
		Downstream	168		
Salinity (psu)	Not specified	Upstream	23.07	Not specified	33.76
		Downstream	33.64		
Temperature (°C)	25–31	Upstream	30.71	25–31	32.35*
		Downstream	29.73		
NO_3–N [(a)]	7		5.2	10	ND
PO_4^{3-} [(a)]	0.5		0.175	0.5	ND

[(a)] Data from De Guzman and co-authors with permission
*Non-compliant with DAO 2016-08 limit
ND – no data

limits for Class SC waters. Additionally, while no official limits exist for TDS, conductivity, and salinity in coastal waters, the aforementioned parameters were measured to be within the normal range for marine environments.

Low DO concentrations from the estuary to the coast (*i.e.*, ranging from 0.96 mg/L upstream to 2.45 mg/L along the coast) may be attributed to wastewater effluent being discharged from agricultural activities, fishponds, and local informal settlers within the vicinity of the sampled sites. Discharge from these aforementioned sectors are likely ways of how MPs are introduced and transported into the immediate environment, especially since wastewater treatment facilities are reportedly absent in the area (Leslie *et al.* 2017). Temperature and salinity are inversely related to DO concentration. The Bombong estuary was noted to have brackish waters downstream (with a salinity ranging between 23.7–33.64 psu) and temperatures nearing the upper bound limit at 29.7–30.7 °C (the maximum ideal temperature being 31 °C). The observed DO concentrations may also be further attributed to the reduction processes undergone by bacteria in mangrove and estuarine ecosystems, like that of the Bombong estuary (Alongi 1994, Holomboe *et al.* 2001, Mattone 2018).

Fine silt and clay particles which characterize the sediments of the upstream benthic zone and riverbanks, coupled with runoff from anthropogenic activity, likely contribute to high concentrations of TSS in the Bombong estuary.

Assessment of MPs in Sediments and Water Samples

The results of the analyses of sediments and water samples for the presence of MPs are shown in Figure 5.

Quantity. A total of 38 MPs were isolated and characterized consisting of 22 particles in the sediments and 16 particles in water samples (see Figure 5a). From this total, the highest number of MPs were found in the downstream sample sites (*i.e.*, 6 MPs and 11 MPs in water and sediments, respectively) followed by the upstream sample sites (*i.e.*, 4 and 7 MPs in water and sediments, respectively), with the coastal areas having the least

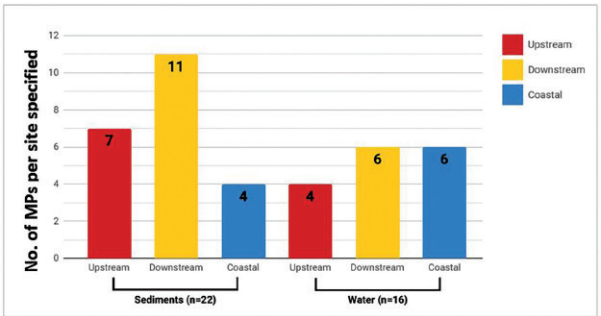

Figure 5. Total number of MP particles isolated from the water (n = 16) and sediment (n = 22) samples collected from the upstream (red), downstream (yellow), and coastal areas (blue) of Ticalan, Batangas. A total of 38 MP particles were found from all sites in all the samples (*i.e.*, 1.5 L of water and 1.2 kg of sediment) that were tested.

amount of isolated MPs (*i.e.*, 6 and 4 MPs in water and sediments, respectively).

The downstream site, where the oyster hatchery is located, is also a docking area for the boats used by the local fisherfolk and the coast guard. A higher quantity of MPs in this area could be attributed to human activities from the surrounding areas. These activities include the use of plastics such as in ropes, fishing nets, and plastic barrels. However, it should be noted that none of the isolated MPs from this study were clearly identified as nylon-based (which is a common plastic material used as rope, because of its fiber strength, *vide infra*). Plastic wastes from nearby towns can also accumulate in the river mouth and along the coast of Tayabas Bay in Ticalan due to tidal action, which carries plastics into this portion of the river during high tide.

Type. The type of MPs found in the sediment and water samples varied from filaments, fragments, films, pellets, and foam (see Figure 6a–b). The most abundant types were plastic films (*i.e.*, 11 MPs), followed by fragments (*i.e.*, 10 MPs), filaments (*i.e.*, 10 MPs), pellets (*i.e.*, 4 MPs), and foam (*i.e.*, 1 MP) per 1.2 kg of sediment and 1.5 L of water sample collected from all the sites. The sediment samples contained mostly filaments and fragments (10 and 7 MPs, respectively) while plastic films and pellets (7 and 3 MPs, respectively) were found to be more common in the water samples.

Fragments were found to be the most ubiquitous of the types because they can come from a larger variety of possible sources. Pellets and films, which are often composed of low-density polymers such as polystyrene or epoxy resin, tend to remain afloat in surface waters and are, thus, exposed to photochemical degradation and the effects of weathering. Filaments, on the other hand, likely reach the sediments as similarly reported in several studies. Sediment and bottom water samples taken from the Irish continental shelf revealed that up to 85% of the MPs that were observed were filaments (Martin *et al.* 2017). Similarly, Woodall and co-authors (2014) estimated that MPs in the form of filaments are more abundant in the deep-sea ocean sediments of the Atlantic Ocean, Mediterranean Sea, and Indian Ocean as compared to contaminated surface waters.

Shape. The MPs collected were observed to have irregular, ovoid, rounded, sub-rounded, angular, sub-angular, elongated, and degraded and crumpled shapes (see Figure 7a–b).

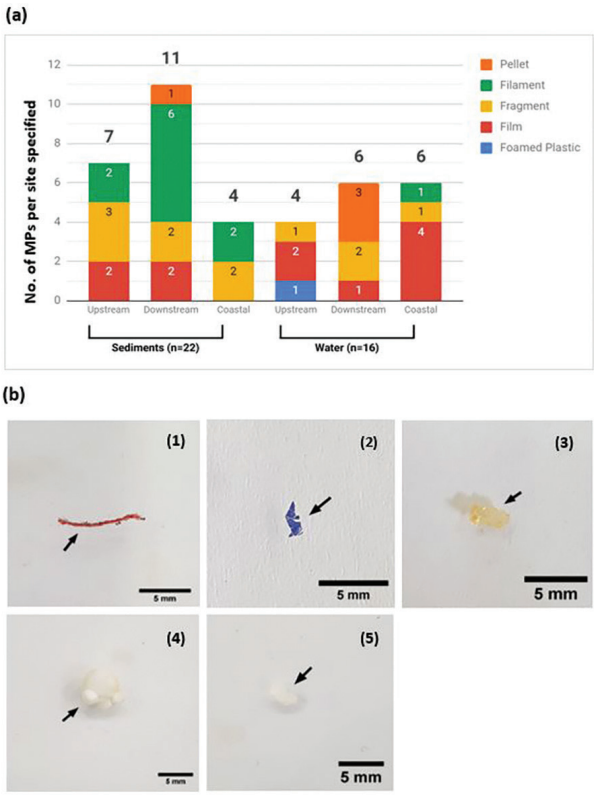

Figure 6. (a) Type and total number of MP particles obtained from the water (n = 16) and sediment (n = 22) samples obtained from the sampling sites in Ticalan, Batangas. The colors represent the different types of MPs that were isolated and the corresponding number for each type; (b) photos of the different types of MPs collected from sediments and water samples: (1) filament, (2) fragment, (3) film, (4) pellet, and (5) foamed plastic [scale: 5 mm].

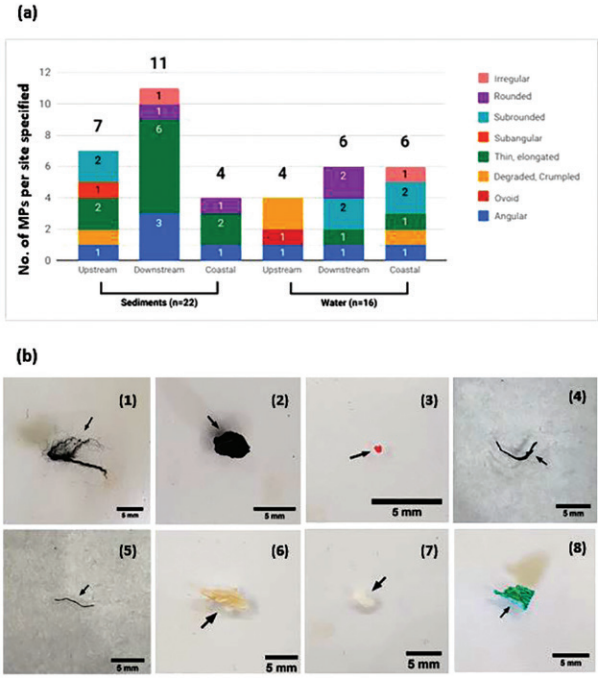

Figure 7. (a) The various shapes and corresponding number of MP particles isolated from the sediment (n = 22) and water (n = 16) samples obtained from the various sites in Ticalan, Batangas; (b) photos of the different types of MPs collected from sediments and water samples: (1) irregular, (2) rounded, (3) subrounded, (4) subangular, (5) thin and elongated, (6) degraded and crumpled, (7) ovoid, and (8) angular [scale: 5 mm].

Pellets are either round or ovoid and are often considered to be primary MPs used in the production of larger plastic products. These tend to enter the environment with very minimal alteration in shape. Larger and more spherical pellets may be indicative of shorter residence time, while smaller ones may be presumed to have undergone longer exposure to various weathering processes in that environment. Fragments were found to be angular, sub-angular, rounded, or sub-rounded with jagged edges or sharp corners, indicating that they are likely to be secondary MPs that had broken off from larger products. Filaments were classified as thin and elongated and found in high concentrations in the benthic zone. Their thin, fibrous shape offers very little surface area thus, their tendency to sink. Plastic films were observed to be degraded and crumpled or irregular in shape. Discoloration and tearing around the edges was indicative of a faster degradation rate. They were also found to be more abundant in the upstream site where the waters were calm.

Erosion patterns. The erosion pattern observed on the collected MPs ranged from weathered, degraded, incipient alteration, parallel fracturing, irregular surface, and fresh. The particle was labeled *not applicable* if the particle did not fit any of the characteristics mentioned (see Figure 8). The pellets and fragments with scratches, grooves, irregular edges, or were more rounded in shape from weathering and exposure were often classified as *weathered.* Fragments that had no obvious signs of erosion were considered *fresh*. Those that showed new, shallow marks on their surface were categorized under *incipient alteration,* which may indicate that the particle had only just been introduced into the environment or had recently broken away from a larger plastic product. Plastic films that were considerably deteriorating were categorized as *degraded*. Finer particles such as filaments and fibers were categorized under *not applicable* due to the difficulty in examining their surfaces. Examining the surface texture of MPs and characterizing MP erosion is important in inferring the role of MPs in the transport of pollutants in the environment through adsorption. MPs with weathered surfaces have an increased surface area, thus enhancing effective diffusivity, allowing them to become vessels for contaminants (Lohmann 2009, Hidalgo-Ruz *et al*. 2012).

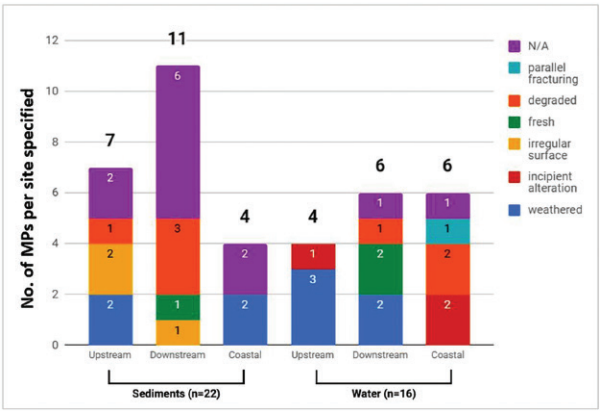

Figure 8. Type of erosions that were observed and the corresponding number of MP particles isolated from the sediment (n = 22) and water (n = 16) samples obtained in Ticalan, Batangas.

Composition. Several reviews (Song *et al*. 2015, Hidalgo-Ruz *et al.* 2012, Shim *et al*. 2017) have been published comparing different methods for identification of MPs though at present there is still no current standard method. Mere physical identification alone by microscopy could lead to misidentification and this, therefore, necessitates chemical identification through a number of techniques such as FTIR (Song *et al*. 2015, Hidalgo-Ruz 2012, Shim *et al.* 2017, Simon *et al.* 2018, Jung *et al.* 2018) or Raman spectroscopy (Lenz *et al.* 2015), pyrolysis-gas chromatography-mass spectroscopy in tandem with scanning electron microscopy with energy dispersive X-ray analysis (Fries *et al*. 2013), among others. The most widely used is FTIR-based, and a more recent mode of detection using this is the focal plane array, which also allowed for estimation of mass of the material (Simon *et al.* 2018). In this study, however, FTIR was done on samples that could be physically separated and then incorporated into a KBr pellet for spectral measurement in transmission mode. This made possible to still measure the spectrum of the MPs samples or samples collected from the extraction, as shown in Appendix Table I. One limitation, however, is the separation of individual components – especially when they are already too small to be segregated or picked up by a tweezer; in such case, the FTIR spectrum is a composite of the entire mixture that is KBr pelleted. Only the samples from the sediments and water were analyzed by FTIR because the MPs from the fish tissues were embedded in the filter membrane – this could be analyzed by Raman or FTIR microscopy in future studies.

It has long been a problem for researchers to isolate pure plastics for identification purposes, given that most will also contain organic plastic additives such as dyes and pigments used as a colorant, as well as inorganic plastic additives such as titania, zinc, *etc.*, which are used as fillers or stabilizers. Furthermore (Fries *et al.* 2013), interpretation is complicated by the fact that these MPs may have already undergone chemical transformation due to UV, heat, or bio-degradation (Lenz *et al.* 2015). It may still be possible to infer the identity of the plastic from the composite FTIR spectrum even of mixtures or partially degraded plastic material by careful analysis of the characteristic infrared bands of the polymers, including those of the additives (Lenz *et al.* 2015, Jung *et al.* 2018). Here, the general flow for interpreting the FTIR spectra

was based on identification of the main absorption bands in the spectra and comparing them against those of the most common MPs that have so far been identified in the environment. The recent work by Jung and co-authors (2018) used attenuated total internal reflection (ATR) – FTIR mode of analysis, which identified MPs including those that have been ingested by marine organisms, and the collection of spectra in their published work served as reference for the analysis of the FTIR spectra collected in the present work. ATR is a sampling technique that results in slight band broadening and shifting, and modification of relative intensities compared with transmission FTIR, although the positions of the main absorption bands remain the same within the resolution of spectral data collection (4 cm^{-1}). The ATR-FTIR spectra's main absorption bands of 16 polymers found as MP were reported by Jung and co-authors (2018) and their most prominent absorption bands. In the absence of a more thorough database for FTIR spectral matching, it is assumed, therefore, that the MPs isolated will be any one of these 16 most common commercial polymers – given also that previous works have shown that the most commonly found MPs in marine environment are polypropylene, high-density polyethylene, low-density polyethylene, polystyrene, polyvinyl chloride, and polyethylene terephthalate (Hidalgo-Ruz *et al.* 2012).

HDPE, LDPE, EVA, nitrile, and PP all have strong bands in the C-H stretching region and are nearly all identical-looking in terms of band profile except for PP, which shows multiple bands compared with the doublet formed by the 2915 and 2845 cm^{-1} bands. Their profile in the fingerprint region (< 1800 cm^{-1}) is also quite simple which allows for easy identification – although, however, resolving HDPE from LDPE poses a challenge given the subtle differences in this region that may not be resolved for the samples tested. On the other hand, the esters would have a strong carbonyl stretch appearing around 1713 cm^{-1} such as that of PET. Thus to identify the composition of the samples, the spectral bands of the spectra shown in Appendix Table I were tabulated and separated into three regions – the N-H, O-H, and C-H stretching frequency regions around 2800–3500 cm^{-1}, the fingerprint region around 1800–900 cm^{-1}, and the low-frequency region. These regions served as basis for inferring the identity of the samples, as shown in Appendix Table I.

It was observed that the samples showed to have residual water, as evidenced by the signature bands of water appearing in 3424 cm^{-1} (O-H str.) and 1630 cm^{-1} (H-O-H bending). Thus, these peaks were not tabulated anymore, considering that they also swamped any O-H or N-H stretching absorption bands that could be from the MP themselves. Identification of the characteristic peaks was, therefore, limited to those not interfered by the presence of water bands. In summary, nearly all samples showed the characteristic C-H vibrational modes indicative of polyethylene-based plastics – and where there is an additional peak around 1720–1740 cm^{-1}, which is assigned to the carbonyl bond stretching vibration – the spectra appear similar to that of ethylene-vinyl acetate (EVA). Partially decomposed PE would have oxidized functional groups in the form of carbonyl and, thus – in these samples – they were identified as EVA or degraded PE, where the latter is the most likely case. Oxidative degradation of PE results in formation of carbonyl groups, which appear in the FTIR spectra (Khabbaz *et al.* 1998). This is also not to discount the abovementioned other components (fillers) that could contribute to extra bands in the fingerprint region even of a PE-based material. Two samples showed what could be silica and not really MPs (C1WAT S6 and C1WAT S7) – this could be from extracted diatoms or diatomaceous materials that are ubiquitous in water environment. Two samples from sediments appear to be cellulose acetate materials given that the C-H peaks are not aligned with those of PE.

In summary, the FTIR results indicate that the predominant composition of the MPs isolated from the water or sediments in either coastal, downstream, or upstream samples in the study were most likely PE-based. This is not surprising because of the widespread use of PE-based plastic bags that usually find their way into the marine environment (Yurtsever and Yurtsever 2018). In the Philippines, there is much concern on the current widespread use of oxo-biodegradable type PE plastic bags; these are initially disintegrated by UV light or heat into smaller fragments and, in the ideal case, eventually be absorbed and degraded by microbes into oligomeric products (Eyheraguibel *et al.* 2018). However, these may be reduced into non-fully degraded debris as MPs could lead to their persistence because they also do not fully degrade even after three years of exposure to the environment (Napper and Thompson 2019).

Assessment of MPs in Biological Samples

MPs in oysters. A total of 40 MP particles were found and characterized, including those obtained from the oyster secretions (see Figure 9a–c). Out of the total, 39 were filaments varying only in color, length, and thickness, and one fragment was identified. The filaments also showed signs of physical degradation caused by actions such as gill movement of fish, siphoning, and digestion processes of both fish and oysters.

Oysters are filter-feeders and the predominance of filaments in the sample is indicative of the origin of these MPs such as fishing nets, ropes, commercial textiles, and cloths, as also observed in the study by Hidalgo-Ruz and co-authors (2012). The presence of MPs in adult oysters

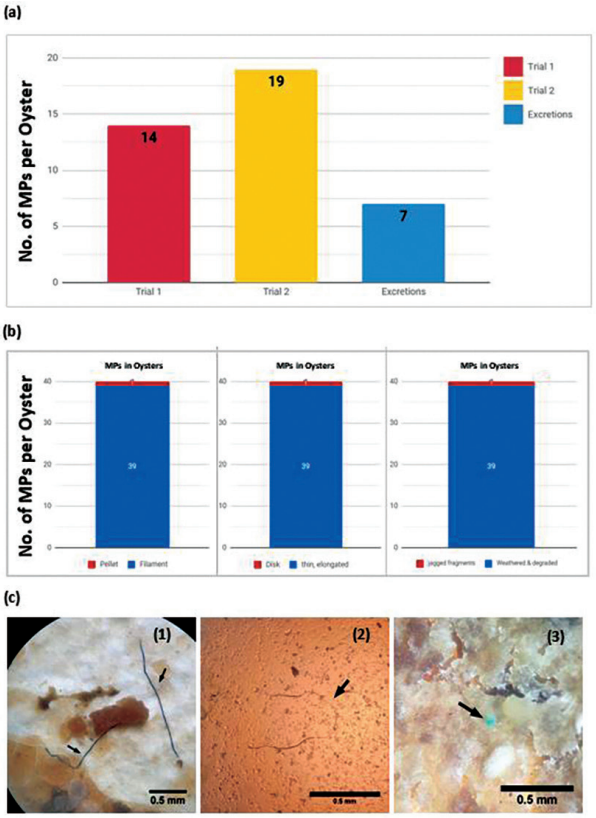

Figure 9. Results of the MPs assessment in oysters obtained from Ticalan, Batangas: (a) total number of particles isolated per trial; (b) type, shape, and extent of erosion: and (c) images showing the common types of MPs as indicated by the arrow: (1) thin and elongated blue filaments, (2) clear filament with jagged fragments, and (3) disk-shaped pellet [scale: 0.5 mm].

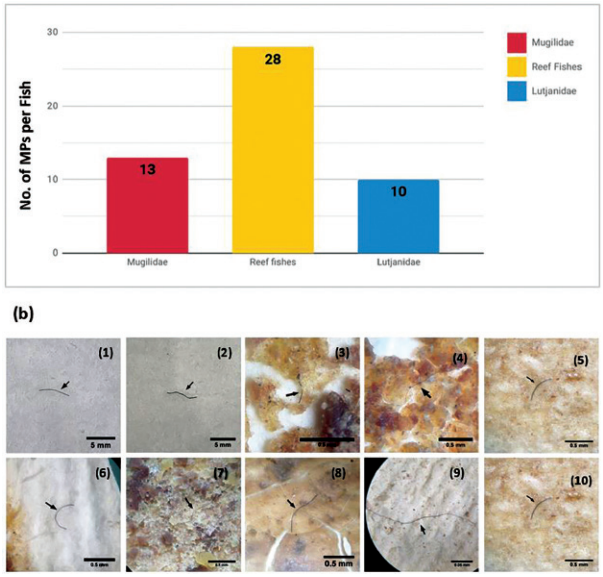

Figure 10. Results of the MP assessment in the various fish species obtained from Ticalan, Batangas. (a) total number of MPs; (b) images of the MPs that were collected in the various sites (as indicated by the arrow): (1) in downstream sediments; (2) in coastal sediments; (3–6) compared with adult oysters; (7) compared with oyster secretions; (8) in reef fishes; and (9–10) in Lutjanidae [scale: 0.5 mm].

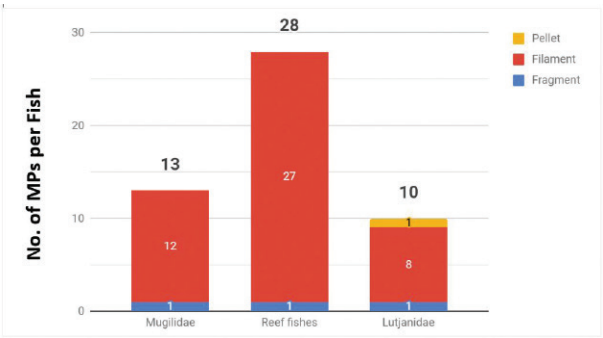

Figure 11. Types of MP particles (total = 51) obtained from the fish (n = 38) samples obtained from the coast of Ticalan. The colors represent different types of MPs that were isolated and the corresponding number for each characterization.

may cause feeding modifications, reproductive disruption, as well as a reduction in oocyte number, diameter, and sperm velocity (Sussarellu *et al.* 2016).

Difficulties were encountered in separating the MPs from the organic material due to the small sizes of the filaments, which did not allow for FTIR analyses. On the other hand, this was indicative of how MPs are embedded into internal organs of such aquatic organisms.

MPs in various fish species. A total of 51 MPs were isolated from the various fish species – 51 from *Mugilidae*, 28 from the reef fishes (*i.e.*, *Labridae*, *Serranida*e, *Lutjanidae*), and 14 from juvenile *Lutjanidae* (Figure 10a–b). FTIR analysis was not possible due to difficulties encountered in isolating the MPs from the organic material because of their minute sizes and the fact that they were deeply embedded in the organic material. Microscopic examination of the particles, however, showed a predominance of filaments (47 MPs), fragments (3 MPs), and pellet (1 MP) (see Figure 11) – which could have come from products like fishing nets, commercial textiles and cloth, as well as household and industrial products, as similarly reported by Hidalgo-Ruz and co-authors (2012).

Similarly, Figure 12 shows that the MPs were also predominantly filaments with thin and elongated shapes, possibly originating from fishing paraphernalia such as nylon nets and lines. Others were angular (1 MP from *Mugilidae*), irregular (1 MP from reef fishes), and disk-shaped pellets (1 MP from juvenile *Lutjanidae*). Figure 13 shows that the majority of the particles had weathered and degraded erosional patterns (50 MPs), with one having an irregular surface that could be attributed to exposure to factors inside and outside the living organism. Juvenile

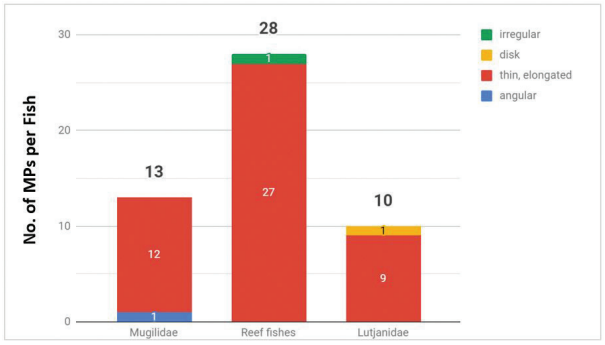

Figure 12. Shapes of MP particles (total = 51) obtained from the fish (n = 38) samples obtained from the coast of Ticalan. The colors represent different shapes of MPs that were isolated and the corresponding number for each characterization.

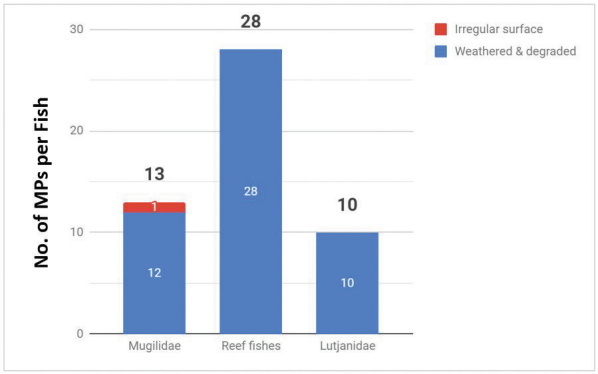

Figure 13. Erosion of MP particles (total = 51) obtained from the fish (n = 38) samples obtained from the coast of Ticalan. The colors represent different types of erosion of MPs that were isolated and the corresponding number for each characterization.

fish have several predators in the wild, such as bigger fish, seabirds, jellyfish. They are also caught for human consumption. There are several effects induced by MPs on aquatic organisms, including reduced feeding activity and enhanced absorption of contaminants on benthic aquatic systems (Besseling *et al.* 2013, Hammer *et al.* 2017).

Since the samples were caught by local fishermen, the presence of MPs in these organisms is a risk to the health of the various higher-order consumers, including humans.

CONCLUSIONS

The study found the presence of MPs in the sediments, waters, and biological organisms from the Bombong estuary and the coastal waters of Ticalan, Batangas. Of the sites that were sampled, the downstream site was found to have the highest number of MPs followed by the upstream site, with the least being found at the coastal sites – a trend that points to the effect of proximity of the population to these sites. The MPs isolated from the sediments and water samples were determined to be predominantly likely composed of polyethylene-based material, which could be partially degraded based on the presence of carbonyl bands in the FTIR spectra. These were further characterized according to particle type, shape, and erosion in order to better understand the history and environmental fate of each of the MPs found. The differences observed between the number and characteristics of the MPs in the different ecological components of Ticalan (*i.e.*, the upstream and downstream benthic zone and waters from the Bombong estuary, coastal sediments, surface seawater, oysters, and varying fish species) point to variations in the environmental fate, transport, and accumulation of these MPs. Such information can be used as environmental indicators of anthropogenic influences, which can help local communities, policymakers, and researchers address issues that impact human and environmental health like bioaccumulation risk on humans and other organisms.

The conclusive evidence of MPs that find their way into various ecological components further point to the added concern for the impact of plastic pollution on ecosystems.

Further studies are needed to ascertain the main sources of the MP pollution and their dynamics in these ecosystems, as well as to develop and promote mitigation protocols and policies that could reduce plastic pollution, in general.

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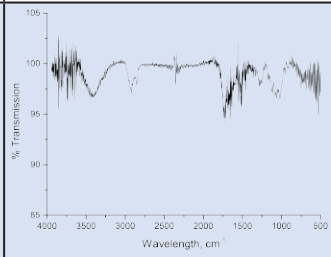
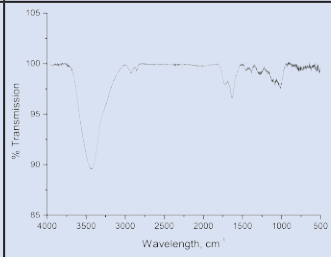
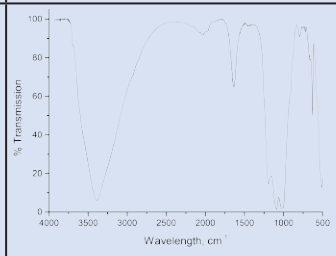
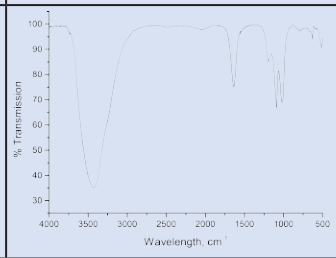
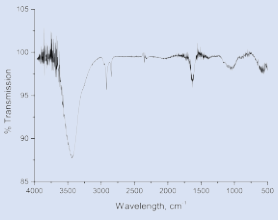
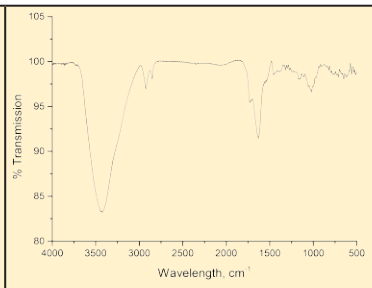
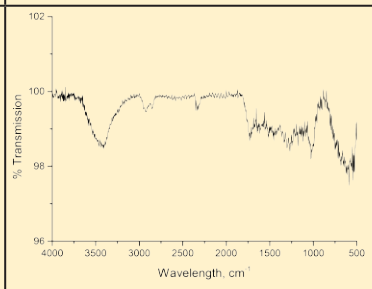
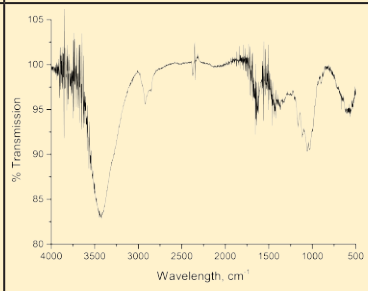
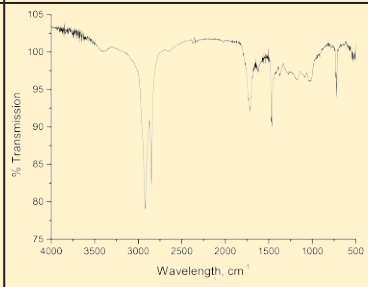
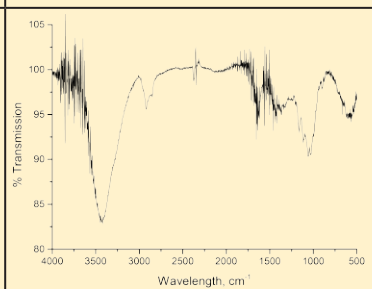
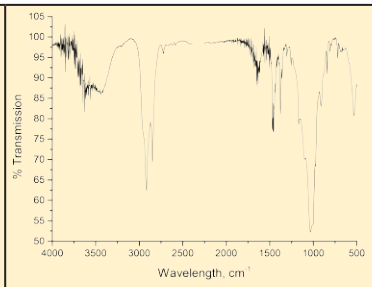
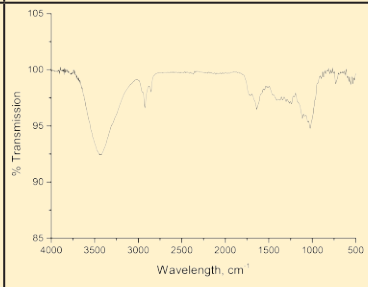
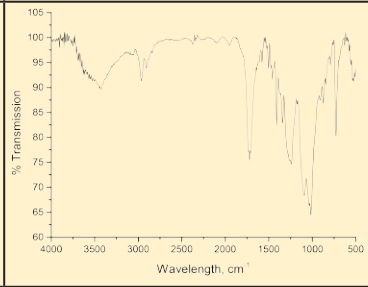
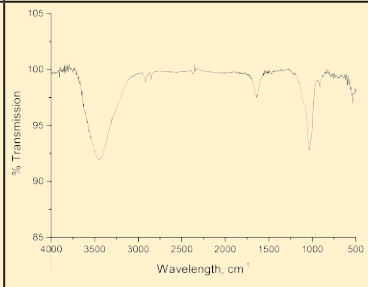
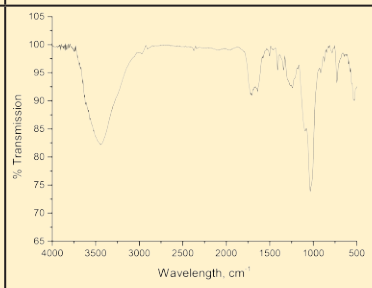
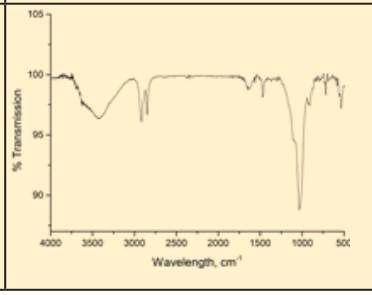
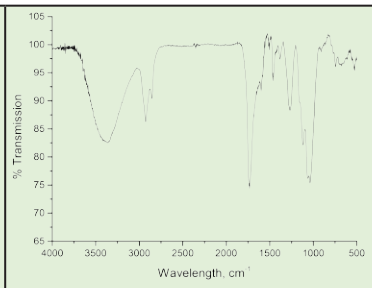
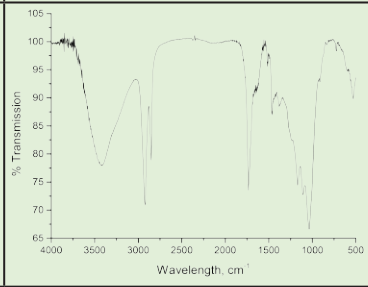
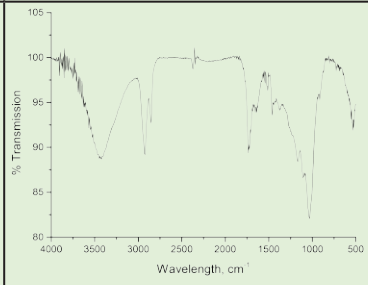
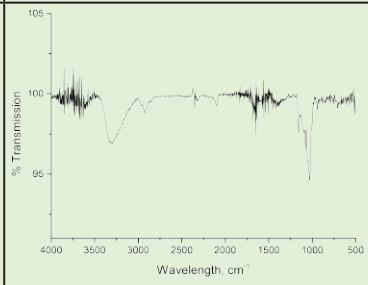
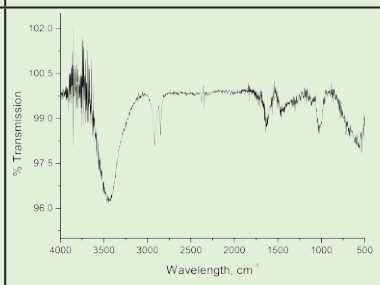
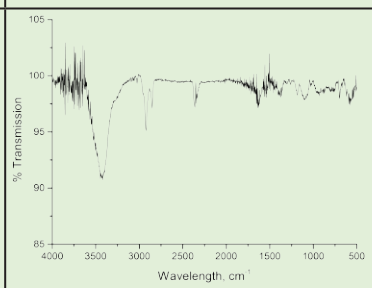
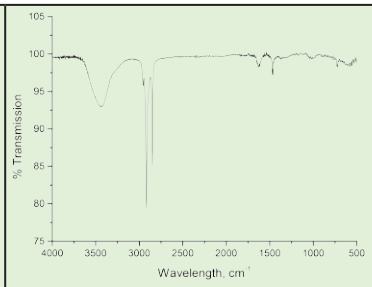
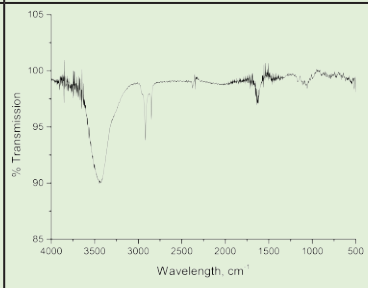
Appendix Table I. Identification of MPs sediment and water samples of Ticalan, Batangas based on the main FTIR absorption bands and comparison with published reference spectra in Jung and co-authors (2018).

Sample details			FTIR spectra obtained	Absorption peaks* (cm^{-1})			
Location	Compartment	Sample number		N-H, O-H*, C-H bond stretching region	Fingerprint region*	Low-frequency region	Possible composition
Coastal area	Water	2		2920, 2855	1726, 1275, 1116, 1077, 1021	738	EVA or degraded PE
		6		2920, 2847	1719, 1003	759	EVA or degraded PE
		7		2016	1192,1103, 1008	626,503, 470	Not plastic, possibly silica
		8		---	1190, 1097, 1014	627, 515, 473	Not plastic, possibly silica
	Sediment	4		2956, 2911, 2846	1057		PE (HDPE or LDPE) with silica

Downstream	Water	3		2930, 2851	1727, 1454, 1154, 1028		EVA or degraded PE
		4		2926, 2861	1730, broad band, 1021	606	EVA or PP
		5		2919, 2856	1056	592	EVA or degraded PE
		6		2919, 2848	1719, 1461, 1376, 1271, 1178, 1093, 1021	715	EVA or degraded PE
		7		2922, 2851	1434, 1351, 1169, 1115, 1057, 1027	580	EVA or degraded PE

	Sediment	1		2920, 2855	1459, 1376, 1158, 1103, 1021, 912	535, 471	PE (HDPE or LDPE) with silica
		3		2924, 2851	1709, broad bands, 1017	728	EVA or degraded PE
		5		3424, 2965, 2910	1730, 1461, 1410, 1339, 1241, 1095, 1034, 1016	876, 843, , 727, 462	Possibly CA
		6		2917, 2852	1034, 906	535	PE (HDPE or LDPE) with silica
		8		2962, 2906	1716, 1505, 1410,1337, 1232, 1090, 1029,	725, 525, 456	Possibly CA
		9		2916, 2851	1462, 1028, 905	719, 535	PE (HDPE or LDPE) with silica

Upstream	Water	1		2921, 2855	1734, 1598, 1464, 1382, 1264, 1117, 1037	744, 667, 531	EVA or degraded PE
		2		2920,2859	1737, 1457, 1383, 1171, 1105, 1029	525, 460	EVA or degraded PE
		4		2927, 2853	1728, 1465, 1379, 1171, 1107, 1035	537	EVA or degraded PE
	Sediment	1		2964, 2927	1156, 1081, 1030		PE (HDPE or LDPE) with silica
		2		2915, 2847	1443, 1025	571	PE (HDPE or LDPE)
		3		2917, 2851	1396, 1182, 1090		PE (HDPE or LDPE) with silica

		4		2959, 2918, 2846	1466	720	PE (HDPE or LDPE)
		5		2914, 2850	1052		PE (HDPE or LDPE)

*Bands that appear together in these regions (cm^{-1}) are assigned as follows and not reported in this table anymore: 3434, 1630 = H_2O vibrational bands; 2359, 2339 = CO_2 rotational-vibrational bands, which are either in the sample or that did not subtract completely from the background. Almost all spectra indicate the presence of residual water, perhaps adsorbed, in the samples; and so, the large O-H stretch and bending vibrational bands are present