What can we learn from studying plastic debris in the Sea Scheldt estuary?

Characterization of plastic debris from the Sea Scheldt estuary

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Abstract

The Sea Scheldt estuary has been suggested to be a significant pathway for transfer of plastic debris to the North Sea. We have studied 12,801 plastic items that were collected in the Sea Scheldt estuary (Belgium) during 3 sampling campaigns (in spring, summer, and autumn) using a technique called anchor netting. The investigation results indicated that the abundance of plastic debris in the Scheldt River was on average $1.6x10^{-3}$ items per m^3 with an average weight of $0.38x10^{-3}$ g per m^3. Foils were the most abundant form, accounting for more than 88% of the samples, followed by fragments for 11% of the samples and filaments, making up for less than 1% of the plastic debris. FTIR spectroscopy of 7% of the total number of plastic debris items collected in the Sea Scheldt estuary (n=883) revealed that polypropylene (PP), polyethylene (PE), and polystyrene (PS) originating from disposable packaging materials were the most abundant types of polymers. A limited number of plastic debris items (n=100) were selected for non-destructive screening of their mineral element composition using micro-X-ray fluorescence spectrometry (μXRF). The corresponding results revealed that S, Ca, Si, P, Al, and Fe were the predominant mineral elements. These elements originate from flame retardants, mineral fillers, and commonly used catalysts for plastic production. Finally, machine learning algorithms were deployed to test a new concept for forensic identification of the different plastic entities based on the most important elements present using a limited subset of PP (n=36) and PE (n=35) plastic entities.

Keywords: plastic pollution, mesoplastics, macroplastics, polymer type, Sea Scheldt estuary, multi-element fingerprint

1. Introduction

Plastic is considered one of the most important inventions of the 20th century, providing us with a range of very practical materials. The low production cost of plastics, as well as their very favorable characteristics, including light weight, durability, inertness, and resistance to corrosion and degradation, have led to significant technological and social progress. As an outcome, the global production of plastics has increased significantly over the past decades, rising from 1.5 million metric tons in 1950 to almost 367 million metric tons in 2020 (UNEP, 2021; Statista, 2021). Today, however, it also represents one of the greatest potential threats to the environment and human health. An astonishing 10% of the 8.3 billion tons of plastic produced globally to date accumulated in the world's oceans as plastic debris, making plastic a fast-growing environmental issue and an issue of major concern for policy makers, businesses, society representatives, and scientists (Geyer et al., 2017). These large amounts of plastic that are currently present in the ocean are exposed to a combination of several processes including photo-induced, mechanical, and biological degradation (Chamas et al., 2020). The slowly degrading/fragmenting plastic debris forms a highly heterogeneous group of particles with different sizes (i.e., from centimeter over millimeter and micrometer to nanometer scale), shapes, densities, and chemical compositions. The presence of small plastic fragments in open ocean water was first noticed in the 1970's and recently, plastic pollution of the marine environment has been recognized by the United Nations Environment Programme as an emerging global issue (UNEP, 2016). Researchers have meanwhile also pointed out that rivers may act as a sink for plastic from multiple sources and they are the dominant pathway for transporting plastic debris to the marine environment, thus presenting an environmental threat (Lebreton et al., 2017; Winton et al., 2020; Gonzalez-Fernandez et al., 2021). Moreover, it has also been found that plastic debris negatively impacts freshwater and terrestrial species (Blettler and Mitchell, 2021) and increases the flood risk by blocking hydraulic infrastructure

(van Emmerik and Schwarz, 2020). In addition, plastic fragmentation will lead to the release of micro- and nanoplastics that affect the river, as well as marine ecosystems, negatively, especially once they enter the food webs (Wong et al., 2020). However, in contrast to the emerging field of studies in the marine environment, little research has been conducted so far to obtain data and knowledge on plastic pollution in freshwater systems, thus leading to fundamental gaps in the understanding of the multiple sources, transformation pathways, fragmentation processes and fate of the plastic pollution in freshwater systems, while estimates of the riverine plastic flux in general are also still largely missing (Gonzalez-Fernandez et al., 2021).

To date, there has been little scientific attention for river basins, despite their role as main contributors of plastics to estuaries, where transportation and accumulation patterns are determined by flow regimes. To identify the most polluting rivers and to prioritize mitigation efforts, accurate estimates of riverine plastic inputs into the oceans are globally required. In 2017, two models were constructed to estimate the contribution of rivers. The first model was based on plastic waste management, population density, monthly catchment runoff and artificial barriers acting as particle sinks (Lebreton et al., 2017). Globally, this model estimated the influx of plastic via rivers into the sea to be between 1.15 and 2.41 million tons per year. The second study attempted to find a relationship between plastic waste management and field measurements, estimating a yearly influx between 51 thousand tons and 440 thousand tons for macroplastics (Schmidt et al., 2017). The total influx of plastics was estimated to be between 1.72 million tons and 4.38 million tons worldwide. However, field data are scarce, such that the results of the models presented cannot be validated and it is of the highest importance to enhance our knowledge on the sources, sinks, and transport mechanisms of plastic debris in rivers (Lebreton et al., 2022), thus enabling optimization of plastic pollution prevention and mitigation strategies.

For Belgium, there are currently limited field studies on plastic debris flowing from the Scheldt River towards the North Sea. A first study in 2013 roughly estimated the rate at which the Scheldt River discharges the coarse fraction of floating macro plastic litter (≥ 25 mm) into the North Sea at approximately 10 to 100 m^3/year in periods with average floods and tide (van der Wal et al., 2013). These authors also speculated that the discharge of the fine fraction of macroplastic litter (5-24 mm) might be much larger than that of the coarse fraction (van der Wal et al., 2013). The model of Lebreton et al. (2017) predicts a contribution of the Scheldt River to the plastic influx into the North Sea between 4.2 and 23.3 tons per year, with a peak between January and March. The model of Schmidt et al. (2017) estimates the contribution of the Scheldt River to the macroplastic influx into the North Sea at around 1.46 tons per year. Furthermore, a recent study by Liu et al. (2022) indicated that microplastics in the size range of ≤50–5000 μm were found in all surface waters and sediments collected from 25 sampling sites upstream of Antwerp city and down to the estuary of the Scheldt River. Considering the limited data available and that estuaries make the transfer dynamics of plastic debris complex and nonlinear (Tramoy et al., 2020), it is necessary to further explore the occurrence of plastic debris in the Sea Scheldt estuary.

This paper presents some first insight into the occurrence and variability of plastic debris in the Scheldt estuary within Belgium as a potential source of plastic pollution in the North Sea. To understand the extent of plastic debris contamination in 2018, 3 sampling campaigns (spring, summer, and autumn) were conducted to collect plastic debris at 4 different locations. This sampling was carried out during already planned monitoring campaigns conducted with the aim of studying fish populations in the Scheldt estuary and relied on the use of a commercial fishing boat and its nets. Specific objectives were to: (1) characterize plastic debris based on their appearance (morphology) and size, (2) determine the composition for a fraction of the plastic debris collected, using Fourier transform infrared (FTIR) spectroscopy, and (3) perform

statistical analysis and use machine learning algorithms to test a new concept for the forensic identification of different types of polymers present in plastic debris using their multi-element fingerprint as revealed by X-ray fluorescence spectrometry (XRF) as a proxy.

2. Materials and methods

2.1. Studying sites

The samples used in this study were collected in the context of a larger research project conducted by the Ecosystem Management Research Group at the University of Antwerp (Belgium) to study plastic pollution in the Scheldt River and characterize the flux of plastic towards the North Sea (Teunkens et al., 2021) and were shared with the Flemish Institute for Technological Research (VITO) to perform polymer analysis. The latter samples were collected in 2018 during 3 sampling campaigns (spring, summer, and autumn), using a technique called anchor netting. The sampling campaign itself was organized by the Institute for Nature and Forest (INBO) to survey the fish assemblage in the Maritime Scheldt (Breine et al., 2019). The Maritime Scheldt is the Belgian part of the Scheldt River which is located in one of the most densely populated areas of Europe (over 500 inhabitants per km^2). The Maritime Scheldt is still subjected to the tides and reaches from the sluice in Merelbeke (near Ghent) to the Belgian-Dutch border. This part of the Scheldt (**Figure 1**) is approximately 100 km in length and is fed by three major tributaries, the Upper Scheldt (near Ghent), the Dender (in Dendermonde) and the Rupel (in Rupelmonde). Between Steendorp and Antwerp (**Figure 1**), near Schelle, the river has a net discharge of 107 m^3/s. This can be as high as 253 m^3/s in winter and as low as 34 m^3/s in summer (Plancke et al., 2017).

Figure 1. Map of the different sampling sites (A) in the Maritime Scheldt in Belgium (adapted from Breine et al., 2019), (B) photo of TH16-Harder (Credit: INBO), and (C) collection of samples by deploying an anchored fishing vessel with stow nets on an anchor fastened to a frame.

2.2. Sample collection

Most studies on riverine plastic fluxes are focused on floating plastic debris, while concentrations of suspended plastic debris have been reported in a limited number of studies only. In order to take the plastic debris samples over the entire depth (from surface to bottom), a fishing vessel (TH16-Harder) was anchored and two large, 8 m wide, nets were submersed into the river. During sampling, the fishing vessel remained stationary, thus using the natural flow of the water for sample collection (Teunkens et al., 2021). In general, one of both nets is left for one hour, the other net is left for two hours. The total length of a single net is approximately 70 m. The mesh size of the net becomes progressively smaller towards the tip of the net. The mesh size is measured as half mesh knot to knot (hmkk), which is the length of one bar of mesh. At the opening of the net, the mesh size is 80 mm (for ± 16 m in length) followed by 60 mm (± 12 m in length), 40 mm (± 8 m in length), 20 mm (± 8 m in length), and 10 mm (± 4 m in length). The last 20 m of net has the smallest mesh size, being 5 mm hmkk. Sampling campaigns were organized at 4 different locations, in Branst, Steendorp, Antwerp (Kennedy) and Doel (**Figure 1**). These sampling campaigns were organized 3 times in 2018 (Breine et al., 2019), *i.e.,* in spring (23-26/04/2018), summer (16-19/07/2018), and autumn (24-27/09/2018). As the Maritime Scheldt is a tidal river, samples were taken both during ebb (towards low-tide) and flow (towards high-tide). A mechanical flowmeter was lowered into the river behind the boat and was positioned halfway between the surface and the riverbed. As the fishing vessel has a flat bottom with limited draught, the ship's hull is assumed to have no

effect on the measured flowrates. After collection, the plastic items were air dried overtime and stored in paper bags.

2.3. Plastic debris identification

2.3.1. Morphology and size

Firstly, the samples were separated into two categories based on their appearance (morphology), *i.e.,* items with a large surface to volume ratio (foils) and a rest fraction. Secondly, the foils were divided into 6 size categories: 0.5-2.5 cm representing mesoplastics; 2.5-5 cm; 5-10 cm; 10-20 cm; 20-30 cm; and larger than 30 cm, all representing macroplastics (GESAMP, 2019; Vriend et al., 2020). The rest fraction was additionally separated and can either consist of container, lid, filament, foam, etc. (**SI1-3**). Finally, all items were counted and weighed per category.

2.3.2. Polymer identification

Mesoplastic samples (0.5-2.5 cm) and hard plastics (rest fraction) from Steendorp, Kennedy and Doel (spring, summer, and autumn), as well as macroplastic samples (2.5-5 cm; 5-10 cm; 10-20 cm; 20-30 cm; and larger than 30 cm) collected during the summer season from Kennedy, were selected for polymer identification using FTIR spectroscopy (**SI2, SI3**). This selection accounted for 883 samples out of the 12,801 plastic items collected during the 2018 campaign (Breine et al., 2019), representing 7% of the total number of samples collected. The type of polymer was investigated using FTIR. Prior to analysis, all samples were carefully cleaned with Milli-Q water and dried. FTIR spectroscopy measurements were performed using a Nicolet™ iS™ 10 FTIR Spectrometer (Thermo Fisher Scientific, United States). The spectra were recorded in the region 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} averaging 32 scans for each measurement. The recorded FTIR spectra were processed using the OMNIC™ Specta software and compared to the reference spectra available in the FTIR Spectral Library (Thermo

Fisher Scientific, United States), which includes different libraries for, among other, (i) Polymers, (ii) the Hummel Polymer and Additives, (iii) Polymer Additives and Plasticizers, (iv) Polymers and Plasticizers. Before starting and after every 20 consecutive measurements the background was evaluated by recording a background spectrum to reduce the noise in the spectra and receive the most accurate match with the assigned reference spectra. Each measurement was performed once. The quality of the results was investigated by evaluating the differences between the sample and the reference spectra. For most of the samples, only minor differences were observed and the match between the sample and the reference spectra was better than 90%. However, if the match between the plastic debris sample and the reference spectra was below 75%, a duplicate measurement was performed (Primpke et al., 2018). If also for the duplicate measurement the match was below 75%, the result was considered as "undefined".

2.4. Elemental analysis

A subset of 100 plastic items obtained through simple random sampling from 883 plastic items characterized by FTIR, were selected for non-destructive screening of their mineral element composition using an Orbis PC Micro-XRF spectrometer (μXRF, EDAX, The Netherlands) with dedicated Orbis Vision software. This instrument is equipped with an Rh tube (max. 50 kV acceleration voltage and 1 mA tube current) and an LN-Free X-ray silicon drift detector (40 mm^2). Via a combination of a poly-capillary (30 μm) and a 1 mm and 2 mm collimator, the area to be measured on the sample can be selected. For plastic debris, the instrument was used at 40 kV and 0.8 mA. All samples were attached to a petri dish with a strip of double-sided tape to prevent them from moving during analysis. The analyses were performed under vacuum conditions. No X-ray filter was used for most of the samples. PVDC (polyvinylidene chloride) samples were additionally analyzed with an Al-filter. For the cross-validation and evaluation of the performance of μXRF, 16 plastic samples were acid digested

and analyzed by ICP-OES (Agilent 5100, CA, United States) for determination of the elemental composition in plastic, and the data obtained via μXRF and ICP-OES, respectively, showed a good correlation.

2.5. Statistical analysis and machine learning algorithms

Samples collected at four locations (Branst, Kennedy, Steendorp, Doel), in three seasons (spring, summer, autumn), at high and low tide, both at port and starboard of the vessel were used for the statistical analysis. The number of samples collected was counted and normalized for the volume of water sampled. The number of samples is expressed per million m^3 water. In addition, samples were weighted and reported as grams of items collected per million m^3 of water.

To assess the effect of location, season, tide, and boat side on the number of samples collected, a regression analysis was conducted (Hilbe, 2014). Since the dependent variable is a count variable, a Poisson regression was applied. In this case, a quasi-Poisson distribution was assumed, to properly handle overdispersion – occurring when the variance of the counts is larger than their mean. The estimated regression coefficients correspond to the multiplicative effect sizes of the independent variables. Confidence intervals were computed, from which significance could be evaluated.

In this study, a machine learning algorithm was used based on the multi-element fingerprint of 100 plastic items as determined using μXRF. More particularly, we employed a random forest binary classifier (RFC) to fit several decision tree classifiers and propose the fingerprint for several polymer types based on the feature importance. The latter exists as a built-in attribute of the RFC models computed using Gini importance and allows to quantify those features which are the most relevant (Gregorutti et al., 2017). The RFC model was trained on 100 estimators. A stratified K-fold was used for cross-validation with 5 folds. The folds are

made by preserving the percentage of samples for each class. The binary target for the classifier was obtained based on whether a specific plastic is present or not.

3. Results and discussion

3.1. What can we learn from the size and morphology of plastic debris?

Although the Scheldt River is seen as one of the best studied rivers, floating and/or suspended plastic debris pollution has never been part of such studies. During the sampling campaigns in 2018, a grand total of 12,801 plastic items were collected and individually counted. On average $1.6x10^{-3}$ ($\pm 1.3x10^{-3}$) plastic items per m^3 with an average weight of $0.38x10^{-3}$ ($\pm 0.36x10^{-3}$) g of plastics per m^3 were found in the Scheldt estuary (**Figure 2**). This concentration is in the same order of magnitude as for the suspended plastic debris reported for the river Rhine (Netherlands) and one order of magnitude lower than for the river Po in Italy (van Emmerik and Schwarz, 2020). Foils were most abundant, constituting more than 88% of the samples, followed by fragments for 11% of the samples and filaments making up less than 1% of the plastic debris occurrence in the Sea Scheldt estuary. No pellets or foams were observed. Foils, being elongated items, have the tendency to move in suspension because of their high surface to volume ratio, whilst fragments will either float or sink depending on the density of the polymer (Kuizenga et al., 2022). The most foils observed in this study were representing single-use packaging materials and it corresponds to the previous studies showing similar trends in the plastic abundance in the water column (Kiessling et al., 2021).

Figure 2. Distributions of the number of items collected per million m^3 of water, by size, at the four locations. The colors represent the three seasons, without correction for unbalanced sampling efforts.

The amount of plastic per m^3 water collected at Doel is lower compared to that found at the other locations (Kennedy, Steendorp and Branst), as shown in **Figure 2**. Results of the statistical analysis described in section 2.5 are shown in **Table 1**. The table shows exponentiated regression coefficients resulting from fitting a quasi-Poisson distribution, with an indication of the significance level. Hence, the numbers in the table are multiplicative differences between the respective category and the reference category. For example, the factor for Doel for the smallest size category is 0.122, which means that the number of items of that size collected at Doel is 12.2% of the number collected at Branst. This is a highly significant difference. In fact, the number of items collected at Doel is significantly lower than the corresponding number at Branst for all size categories. The counts at Branst and Kennedy are similar, while those at Steendorp are somewhat lower than those at Branst. Fewer items were collected in summer and autumn compared to spring. More items are collected during flow, again a fairly significant difference with factors higher by 50% - 80%, depending on the size class. Although less significant, a variation between port and starboard was also detected. This might indicate horizontal variation in a river, between riverbanks.

Table 1. Results from quasi-Poisson analysis of the number of items per size category, using the regressors boat side, location, season, and tide. The numbers shown are exponentiated estimated regression coefficients, with significance as follows, *** if $p < 0.001$; ** if $p < 0.01$; * if $p < 0.05$;. if $p < 0.1$.

In contrast to what might be expected, our results show that both the smallest and largest size categories are less abundant. Some studies report an increasing abundance the smaller the size fraction becomes (Eriksen et al., 2014). Other studies report that the complex and nonlinear

transfer and deposition dynamics of plastic debris in estuaries is expected (Tramoy et al., 2020; Kuizenga et al., 2022). In this study an additional uncertainty in plastic debris abundance can be attributed to the nets used. As these nets are designed for commercial fishing, the mesh size becomes progressively smaller towards the end and only reaching 5 mm at the tip. This will result in an underestimation of the actual plastic concentrations. Although the main benefit of this technique is that it allows to collect plastic over the entire depth of the river and sample large volumes of water, this technique might not be entirely suitable to accurately estimate plastic concentrations. Yet, it clearly showed that most of the plastic present in the water column is below the surface and not visible from the surface. Furthermore, our analysis shows clear spatial and temporal variation. Spatially, the most striking conclusion from this sampling campaign is the low concentrations near Doel. Due to tidal pumping, plastics in an estuary are seemingly being retained in more upstream locations. On a temporal scale, most plastics were collected during spring sampling. This is similar to the predictions of Lebreton et al. (2017), predicting a peak between January and March.

As the river becomes deeper and especially wider as we move downstream, a dilution effect can occur, affecting the number concentration of items found per m^3 of water. Therefore, a compartment of 10 km length is created with the sampling site in the center. For each compartment, an average volume of water is calculated and multiplied with the concentration of items per m^3 water at each location (**Table 2**).

Table 2. The estimated number of plastic items in the 10 km compartment.

As can be seen in **Table 2** it is evident that, even with the dilution effect not taken into account, the estimated number of items in the 10 km long compartment is always lower in the most downstream location (Doel), compared to Kennedy. The highest number of items

observed for Kennedy suggest that the highest plastic input comes from the surrounding urban area (Antwerp city). In addition, due to friction and narrowing of the river, flood waves are deformed as they travel upstream the estuary (Wang et al., 2019). This causes tidal asymmetry in the estuary, where upstream, the flood phase becomes shorter with higher flow velocities. The ebb phase becomes longer, but with slower flow velocities (Bolle et al., 2010). Due to the higher peak velocities during the flood phase, this can give rise to a phenomenon called tidal pumping. Consequently, in the lower reaches of the estuary, a net upstream transport of, e.g., sediments is present (Eriksen et al., 2014; van Emmerik and Schwarz, 2019). In turn, this means that there is a zone where these two converging transport directions cause a very high suspended solids concentration. This zone is referred to as the estuarine turbidity maximum (ETM). In the Scheldt estuary this is located around 100 km from the mouth of the Western Scheldt (Bakker et al., 2016). Coincidently, this estuarine turbidity maximum is located between Steendorp and Branst. As plastics are also transported as a suspended load, this potentially explains the lower concentration near Doel.

The Sea Scheldt estuary presents an unique ecosystem, but also hosts different activities such as shipping, dredging, sand extraction, recreation, protection against floods, fishing, etc. (Maris et al., 2019; Van den Bergh et al., 2013). However, there is a knowledge gap on plastic debris mass concentration in the entire water column. As such, the mass of plastic items collected in the water column is also important (**Figure 3**).

Figure 3. Distributions of the weight in grams of items collected per million m^3 of water, by size, at the four locations. The colors represent the three seasons, without correction for unbalanced sampling efforts.

The lowest mass concentration of plastic debris has been observed for Doel, while the highest mass concentration of plastic debris has been observed in the most downstream location (Branst). It is evident that the season will play a significant role for the mass concentration of plastic debris present at all locations. This is particularly evident for samples collected during the autumn campaign at Branst. A high mass of the rest fraction is expected, as these samples present large objects that do not belong to any of 6 categories of mesoplastics and macroplastics.

The total amount of plastic debris and their mass concentration is important to understand plastic fluxes within the estuary zone and their potential contribution to the marine environment. However, detailed characterization of plastic debris including polymer type identification presents an important step in overcoming the big knowledge gap in the understanding of the multiple sources, transformation pathways, fragmentation processes and fate of the plastic pollution in estuarine zones. As such, polymer identification of plastic debris is of high importance to assess the current and future risks of plastic debris in aquatic environments.

3.2. What can we learn from plastic debris polymer composition?

Most studies up to now only report plastic fluxes in rivers and therefore, the origin and fate of plastic debris is not fully known. In this study, we have selected mesoplastic samples (0.5-2.5 cm) and hard plastics (rest fraction) from Steendorp, Kennedy and Doel (spring, summer, and autumn), as well as macroplastic samples (2.5-5 cm; 5-10 cm; 10-20 cm; 20-30 cm; and larger than 30 cm) collected during the summer season from Kennedy (**SI2**, **SI3**) to study the polymer composition of plastic debris. This selection contains a total of 883 samples from locations before and after the influence of Antwerp city (Kennedy) and presents one of the

most comprehensive datasets on the polymer composition of plastic debris in the Sea Scheldt estuary to date (**Figure 4**).

Foils (N=787) were the predominant morphology at all 3 sampling locations (Steendorp (N=228), Kennedy (N=516) and Doel (N=43)). The polymer composition of hard plastic samples from Kennedy (N=96) was also analyzed. Polypropylene (PP) and polyethylene (PE) are the most common polymers found with more than 70% for foils, followed by polystyrene (PS, 2-5%). This can be expected, as PP and PE make up for more than 50% of the plastic production.[1,2] In addition, PP and PE have a low production cost and display good mechanical properties, which make them ideal for use in disposable packaging materials (food packaging, pharmaceuticals, cosmetics, detergents, etc.) (Marsh and Bugusu, 2017). On the other hand, plastic items with a high density will sink to the bottom and are most probably not collected by the sampling technique used during the sampling campaigns. PP is the plastic with the lowest density, between 0.895 and 0.92 g/cm^3. The density of PE can vary from as low as 0.857 g/cm^3 to a maximum of 0.975 g/cm^3. In the case of the hard plastic samples obtained from Kennedy (N=96), PS (normally used in food packaging) was found to be the most common polymer with a share of 32%, followed by PP (25%) and PE (13%). These data are in accordance with other studies in which PE and PP, together with polyethylene terephthalate (PET), represent the most abundant plastic types found in aquatic environments (Bai et al., 2022; Schwarz et al., 2019).

Figure 4. Polymer composition of foils samples collected at Steendorp, Kennedy and Doel and hard plastic samples collected at Kennedy.

3.3. What can we learn from plastic debris multi-element fingerprint?

In most plastics currently used, the basic polymer is mixed with additives to improve the functionality and properties of the polymer. The most common additives are: (1) **plasticizers** (e.g. phthalates) (Hahladakis et al., 2018), (2) **flame retardants** (e.g., boron- and phosphorus-based compounds) (Klöckner et al., 2021; Resano et al., 2020) , (3) **heat stabilizers** (metal mixtures of lead, calcium, barium and cadmium) (Bakker et al., 2016; Al-Malack, 2001) , (4) **dyes or inorganic pigments** (e.g., oxides, sulfides, chromates and complexes based on metals such as cadmium, zinc, antimony, manganese, cobalt, aluminum, iron, copper and molybdenum) (Takada and Karapanagioti, 2019; Campanale et al., 2020), (5) **catalysts** (e.g., Ti and Al nanoparticles) (Kunwar et al., 2016; Wang and Mao, 2013; Zhong et al., 2018), and (6) **fillers** (e.g., kaolin, talc, chalk, zinc oxide) (Bakker et al., 2016; Hahladakis et al., 2018; Li et al., 2016). A considerable proportion of the common additives (metal impurities) present in the plastics are accessible using ICP-mass spectrometry (ICP-MS) after total digestion of samples (Maris et al., 2019; Roosen et al., 2020; Pereira et al., 2011; Vanhaecke et al., 2020). The quantification of metal impurities in plastics has been performed successfully by ICP-MS using bulk analysis recently (Maris et al., 2019). This study, however, only included a limited number of types of plastic entities only, such that a rather basic statistical interpretation sufficed to reliably identify certain polymer types on the basis of their metal content, e.g., Zn for tire tread rubber (Maris et al., 2019). Here, we applied μXRF for 100 selected plastic debris samples (**Table 3**) to examine their elemental composition and provide essential information on the additives present, thus providing a "mineral element fingerprint" which could possibly be relied on for distinguishing between the types of plastic.

Table 3. Elemental composition of plastic debris (100 samples in total) from two selected (the most abundant) types of plastic debris: PE (35 items) and PP (36 items).

Examination of the elemental composition of 100 selected plastic debris (**Table 3**) revealed that S occurred in all samples, while Ca occurred in 99 out of the 100 samples. Si, P, Al, and Fe were also found to be widely present. The widespread detection of these elements can be clarified considering that P and S are elements present in flame retardants (Jian et al., 2017), while $CaCO_3$ and SiO_2 are widely used mineral fillers. In addition, the presence of Ti can be explained using TiO_2 rutile as the most widespread white pigment in the plastics industry. In addition to TiO_2, the presence of Cu, Cr, Mg, and Mn in the selected plastic debris can be related to the pigments used. Finally, Fe, Al, and Zn are commonly used as catalysts for plastic production (Hahladakis et al., 2018).

Finally, in order to test if a multi-element fingerprint can act as a proxy for a plastic entity and if this approach can be exploited for the identification of the type of plastic a debris item in the water is manufactured from, machine learning algorithms were used. Due to the limited numbers of samples for other types of plastic debris, we only considered binarization of the original dataset with respect to the two most abundant groups of plastic debris, i.e., PE and PP.

To prove that such multi-element fingerprint can act as a proxy for the type of plastic entity, several steps have been taken to prepare and clean up the data. For that purpose, only the signal intensity for the element was considered as relevant, while all other features, including season, place, tidal direction, starboard/port, size, and morphology, were considered irrelevant. Based on the element intensity, four different groups for every element were considered: not present (0), low amount (1), medium amount (2), and high amount (3) **(SI4)**. Furthermore, all elements that show no difference according to the plastic type were removed from our dataset; this was the case for Co, Ni, Br, Ag, Cd, Sn, Sb, Ba, and Pb.

As the results from former studies indicate that one single element is not sufficient to define a fingerprint,[22] a combination of elements must be considered. Multi-element fingerprints for

PP and PE were obtained using the feature importance of the trained binary random forest classifier (**Figure 5**).

Figure 5. Elemental feature importance obtained from random forest classifier for PE and PP.

Finally, the relation between different plastic entities and the multi-element fingerprint was elucidated and the fingerprint elements that are essential for distinguishing between different plastic materials/types were identified. In the case of PE, the most important elements for polymer identification were Ti, Ca, K, Cu, Fe, and Mn, while for PP identification Ti, Ca, Fe, K, Cu, and Zn were the most important elements. As a result, we have shown that a well-trained machine learning model can be a suitable approach to identify the most important mineral elements for polymer identification. However, additional research is needed to prove that multi-element fingerprinting can be approached for distinguishing different types of plastic materials.

In a future study, more samples are required to improve the outcome achieved using machine learning algorithms. Verification of learning curves against a test set as varying the number of training instances in addition to the already applied cross-validation techniques offers opportunities to reach the best possible outcome.

4. Conclusion

Although the Scheldt River is one of the best studied rivers, macroplastic pollution has never been part of such studies. The aim of this study was to provide a first insight into the occurrence and variability of the plastic debris in the Sea Scheldt estuary within Belgium using

a one-year sample set collected through an anchor netting technique as an important step in the development of plastic mitigation and management strategies.

FTIR spectroscopy revealed that PP and PE were the most common types of plastic debris occurring in the Sea Scheldt estuary for foils, while polystyrene was the most abundant for hard plastics. Multi-element fingerprinting of plastic debris using μ-XRF and handling of the multivariate data thus obtained using machine learning was successful to distinguish between PE and PP. However, further investigation is mandatory for exploiting this new strategy for the forensic identification of the type of plastic. In addition, further development of new and advanced analytical tools will be needed for comprehensive monitoring and understanding of the behavior of small plastic debris in distinct types of environmental samples (e.g., surface water, sea water, sediment, air, biota).

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supported by COST (European Cooperation in Science and Technology). We also thank two anonymous reviewers who provided valuable suggestions on the manuscript.

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Figure 1

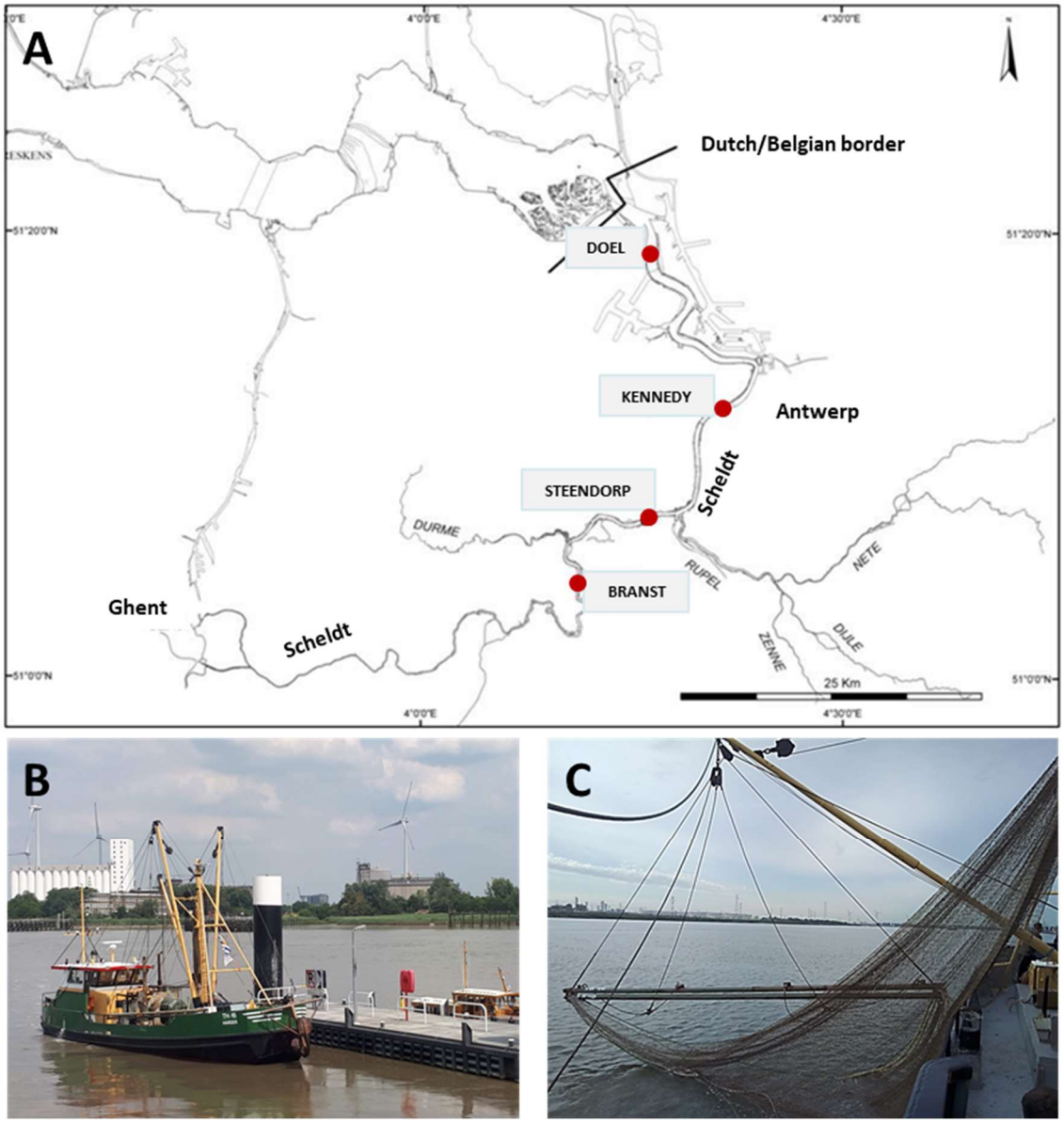
A
Dutch/Belgian border
DOEL
KENNEDY
Antwerp
Scheldt
STEENDORP
DURME
RUPEL
NETE
BRANST
Ghent
Scheldt
ZENNE
DIJLE
25 Km
51°20'0"N
51°0'0"N
4°0'0"E
4°30'0"E
B
C

Figure 2

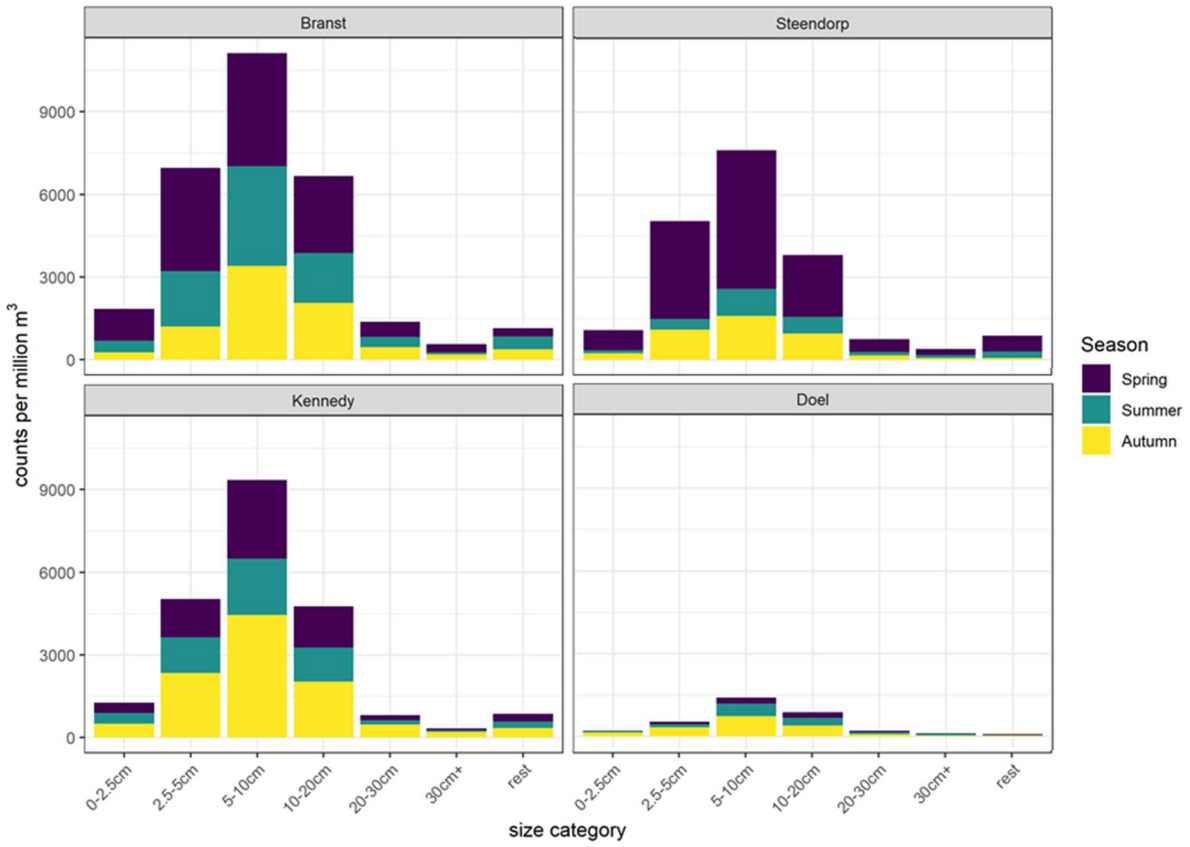
Branst
Steendorp
Kennedy
Doel
counts per million m3
9000
6000
3000
0
0-2.5cm
2.5-5cm
5-10cm
10-20cm
20-30cm
30cm+
rest
size category
Season
Spring
Summer
Autumn

Figure 3

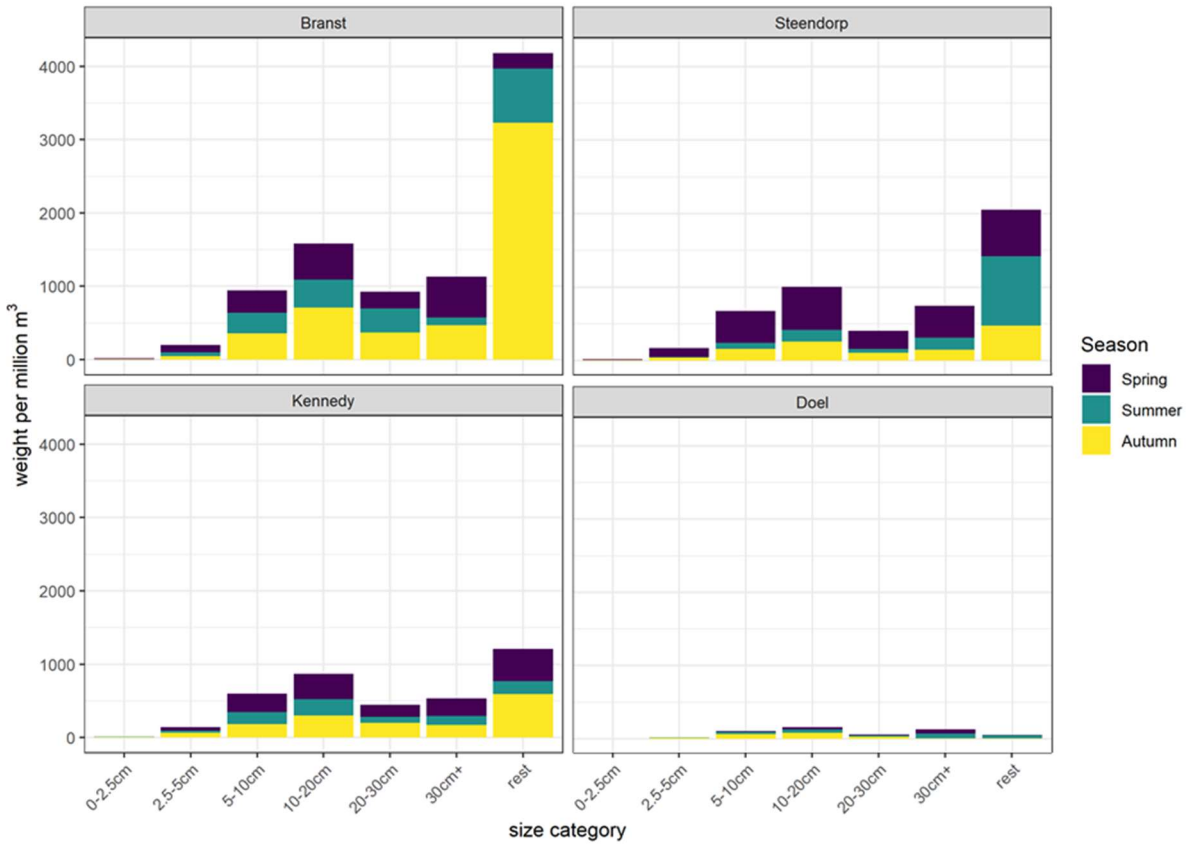
Branst
Steendorp
Kennedy
Doel
weight per million m3
4000
3000
2000
1000
0
0-2.5cm
2.5-5cm
5-10cm
10-20cm
20-30cm
30cm+
rest
size category
Season
Spring
Summer
Autumn

Figure 4

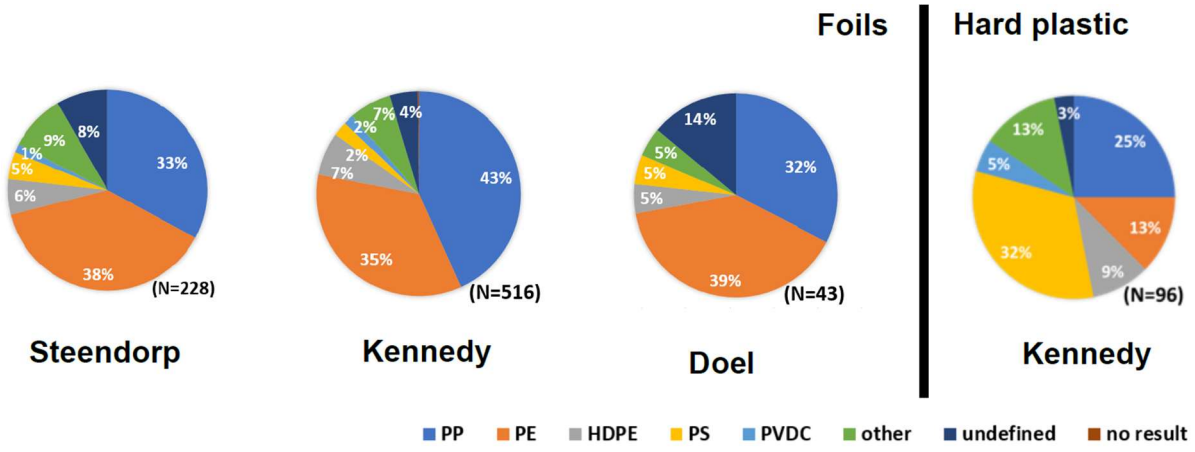
Foils
Hard plastic
33%
38%
6%
5%
1%
9%
8%
(N=228)
Steendorp
43%
35%
7%
2%
2%
7%
4%
(N=516)
Kennedy
32%
39%
5%
5%
5%
14%
(N=43)
Doel
25%
13%
9%
32%
5%
13%
3%
(N=96)
Kennedy
PP
PE
HDPE
PS
PVDC
other
undefined
no result

Figure 5

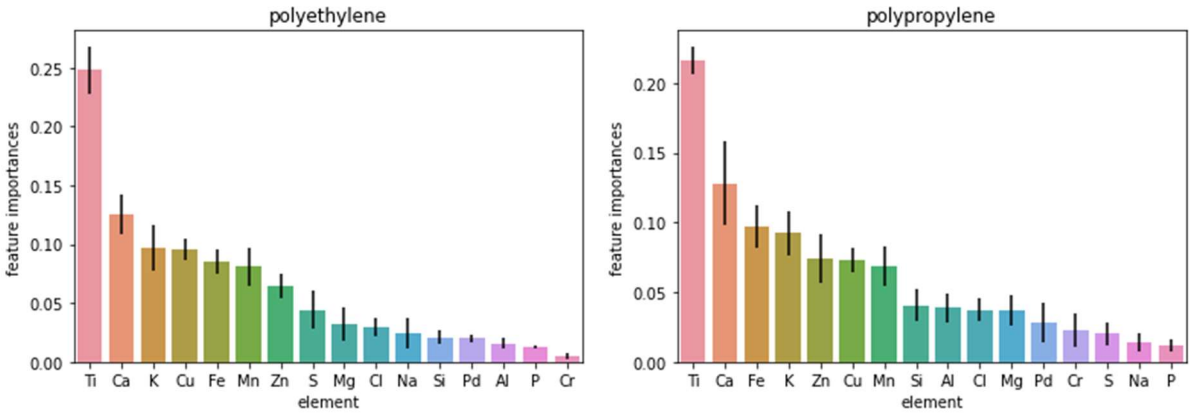
polyethylene
feature importances
0.25
0.20
0.15
0.10
0.05
0.00
Ti Ca K Cu Fe Mn Zn S Mg Cl Na Si Pd Al P Cr
element
polypropylene
feature importances
0.20
0.15
0.10
0.05
0.00
Ti Ca Fe K Zn Cu Mn Si Al Cl Mg Pd Cr S Na P
element

Table 1

	0.5-2.5cm	2.5-5cm	5-10cm	10-20cm	20-30cm	30cm+	rest
Side of boat (ref = port)							
starboard	1,070	1,164	1,376 *	1,315 *	1,503 *	1,245	1,712
Location (ref = Branst)							
Doel	0,122 ***	0,084 ***	0,134 ***	0,141 ***	0,150 ***	0,216 ***	0,068 **
Kennedy	0,842	0,867	1,002	0,844	0,702 .	0,674	0,924
Steendorp	0,500 **	0,634 *	0,612 **	0,512 ***	0,487 **	0,621 *	0,703
Season (ref = spring)							
Autumn	0,463 ***	0,539 **	0,764	0,745 *	0,876	0,797	0,640
Summer	0,392 ***	0,415 ***	0,533 ***	0,540 ***	0,534 **	0,486 **	0,726
Tide (ref = ebb)							
Flow	1,884 **	1,514 *	1,796 ***	1,629 ***	1,741 **	1,491 *	1,870 *

Table 2

	Number of items			
	Branst	**Steendorp**	**Kennedy**	**Doel**
Spring	28511	81336	83897	23922
Summer	18662	16137	47936	25101
Autumn	16218	24833	91454	58527

Table 3

Number of samples	Polymer	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
36	PP	0	1	33	35	35	36	2	28	35	18	1	3	32	11	27
35	PE	1	0	34	34	34	35	1	27	35	24	0	4	33	16	30
3	PS	0	0	3	3	3	3	0	3	3	2	0	0	3	3	3
11	HDPE	0	1	11	11	11	11	0	9	11	8	0	0	9	3	9
2	PVDC	0	0	1	1	1	2	2	2	2	1	0	0	2	0	2
7	undefined	0	1	6	6	6	7	2	5	7	6	0	1	7	2	5
6	other	0	1	4	4	4	6	2	2	6	4	0	0	4	0	3