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Metals associated with Beach plastic litter at Woodbridge Island and Derdesteen in Table Bay, South Africa

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Abstract

Plastics and associated metallic contaminants pose a significant ecological risk to marine ecosystems and human health. To evaluate the potential threat of plastic waste in the marine environment, the distribution of plastic litter and their associated metals at Woodbridge Island and Derdesteen Beaches, located in Table Bay, Cape Town, was investigated. Beach litter was collected over a 100-m stretch of the beaches during low tide. Plastic debris was the most dominant litter type, accounting for 88% of the 4583 litter items collected at Woodbridge Island and 78% of 713 items at Derdesteen Beaches by count. Overall, this represents a significant portion of the 5296 litter items collected. Plastic fragments were the predominant category of plastics identified. Using a Spectrum Two Universal Attenuated Total Reflectance Infrared (UATR-IR) spectrometer, 11 polymers were identified in plastic items ≤ 200 mm, with polypropylene (40%) and polyethylene (24%) being the dominant polymer categories. Of the plastic debris (≤ 200 mm) processed for metal content using an inductively coupled plasma mass spectrometer (ICP-MS), polystyrene plastics were found to contain a higher abundance of the analyzed metals. Overall, metals were detected in plastic items at frequencies ranging from 49% (Se and Cd) to 100% (Cr and Ni), with median concentrations between 0.04 mg/kg (Co) and 147.36 mg/kg (Al). Pb exhibited the highest overall median concentration (6.05 mg/kg) with a detection frequency of 53% of the non-essential metals. This study highlights plastics as a potential vector for toxic metals in the marine environment, posing a significant threat to the proper functioning of marine ecosystems and underscoring the urgent need for continuous monitoring, control, and abatement of plastic waste in marine environments.

Keywords Marine, ICP-MS, Polymer, Litter, Metals, Plastics

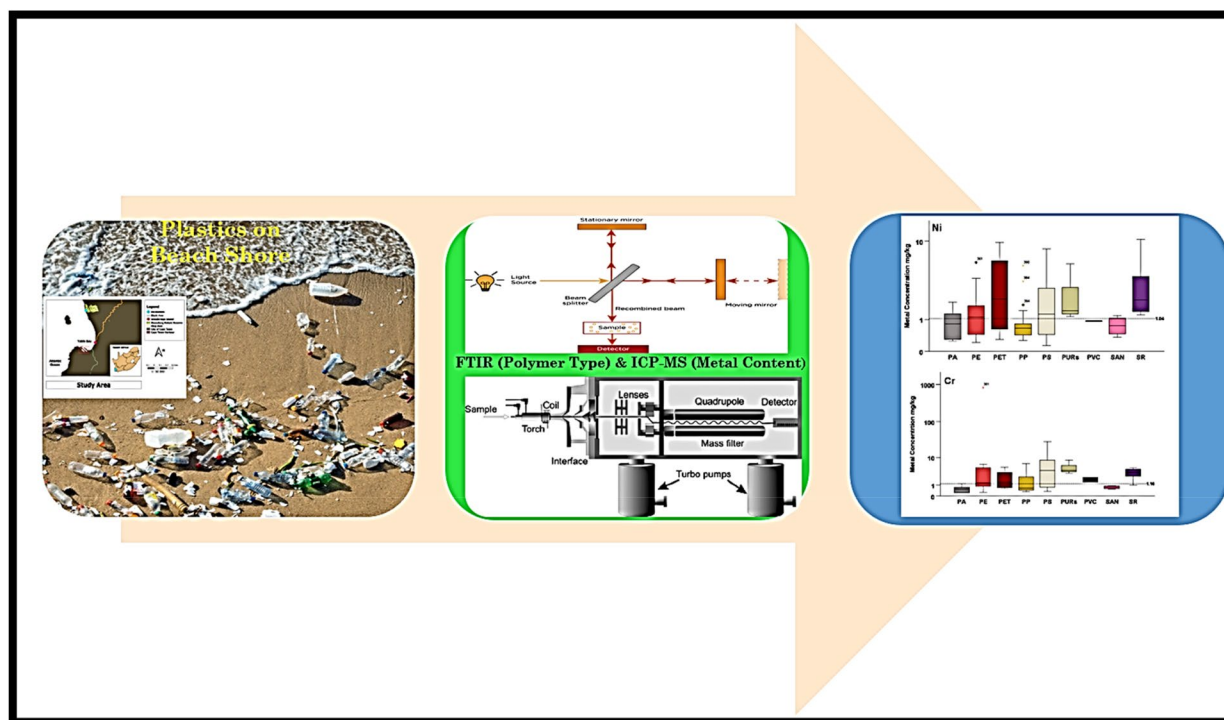
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Graphical Abstract



Introduction

Global plastic production and usage have seen year-on-year growth over the past decade, with annual global plastics consumption reaching up to 460 million metric tonnes in 2019 [1]. This figure is projected to triple by 2060, driven primarily by economic growth [1]. The increased use of plastics has consequently led to substantial and growing leakage into the environment, with an estimated 22 million metric tonnes of plastics leaked in 2019 alone, and this amount is projected to double by 2060 [1]. Plastic leakage places immense stress on the marine ecosystem, a major repository for plastic waste [2–4].

Marine species (e.g., mussels, limpets, starfish, turtles, sharks, rays, birds, corals, fish, and marine mammals amongst others) in the different marine compartments have encountered or accumulated plastics in various forms, leading to deleterious impacts on marine species, biodiversity, and the overall function of marine ecosystems [5, 6].

Plastics have been classified based on their size as very large (mega- > 1 m), large (macro- 25–1000 mm), small (micro- < 5 mm), and very small (nano- < 1 µm) [7]. Large (macro) to very large (mega) plastic litter impacts marine

organisms through entanglement, smothering, emission of embedded chemicals, harbouring and spreading of pathogens, and promoting the spread of alien species amongst others [8–11].

Also, large plastics break down into smaller forms, categorized as meso-, micro- and nano-plastics, because of photodegradation, oxidation, and mechanical abrasion [6]. The fragmentation and degradation of plastics promote their dispersal, hence increasing the number of organisms and marine compartments being affected by plastics. Overall, plastics, regardless of size, shape or colour, tend to significantly affect the behaviour and fate of pollutants in the environment, leading to increased pollutant adsorption and toxicity in exposed organisms [12].

Researchers have highlighted some of the environmental, social, and economic impacts of plastic waste in marine and coastal environments [13–15]. The study by Gómez et al. [15] showed plastic litter as a Trojan horse for perfluoroalkyl substances (PFASs), while acute toxic levels of metals were reported in plastic litter by Fernandes et al. [16] in the marine environment. In South Africa, high levels of metals were detected in microplastics associated with antifouling paint particles at a Marina in Simon's Town [17]. Notably, elevated concentrations

of toxic metals were reported, including chromium (Cr: 555 ± 99.43 $\mu\text{g/g}$), lead (Pb: 1202 ± 116.55 $\mu\text{g/g}$), and mercury (Hg: 0.55 ± 0.10 $\mu\text{g/g}$). Thus, plastic litter can hold toxic persistent metallic and organic pollutants, with enhanced persistency, bioavailability, and mobility. This makes marine plastic pollution one of the world's most daunting environmental challenges [6, 12, 18, 19].

Researchers have however focused more on plastic-associated organic contaminants (used in the production of various plastic items to impart specific properties or functions) that are endocrine disruptors such as phthalates, phenols, and perfluoroalkyl substances (PFASs) amongst others [15, 20–22]. Metallic catalysts are also commonly used in the production of plastics and the synthesis of organic plasticizers, stabilizers, and additives [22]. Additionally, metals such as lead (Pb) and cadmium (Cd), often in the form of metal soaps, were used as stabilizers in the production of polyvinyl chloride (PVC) before regulations and voluntary commitments restricted their use due to environmental and health concerns [22, 23]. Apart from these intrinsic plastic production metals, plastics in various polymer categories have the propensity to absorb metals from their surrounding environment [16]. Polyethylene, polypropylene, polystyrene, and PVC, amongst others, are some of the plastic items found in marine environments that have been shown to contain metals [24, 25].

Metals in the environment are largely classified into two categories: essential metals and non-essential metals. Essential metals occur naturally and are vital for normal biological functioning in aquatic biota (e.g., Mn and Cu) and humans [26, 27]. Ten metals (sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), and molybdenum (Mo)) have been identified to be required for proper physiological functioning in humans [27]. Although these essential metals are vital for human health and the ecological functioning of aquatic biota, they are only needed in specific (trace) amounts and can become very toxic at elevated levels [28]. Non-essential metals (e.g., Hg, As, Cr, Cd, and Pb), on the other hand, are not required for biological functioning and are toxic to aquatic organisms and humans even at minute concentrations [17, 28].

The toxic effects of metals have been well-documented and established [29–33]. Vezzoni et al. [33] demonstrated the effects of metal-contaminated sediments on benthic amphipods and sea urchin embryos, reporting lack or abnormal embryonic development and increased mortality as significant ecological risks associated with metal exposure. Exposure to metals in marine organisms has also been linked to oxidative stress, leading to the overproduction of reactive oxygen species, which can cause cellular damage, including disruptions to membrane

integrity, protein oxidation, and nucleic acid damage [34]. Metals, such as cadmium (Cd) and lead (Pb), act as metabolic antagonists. Cd disrupts calcium (Ca) homeostasis by interfering with Ca-binding proteins, potentially contributing to hypocalcemia. Pb, when incorporated into metabolic processes, has been linked to neurotoxicity and gonadotoxicity, due to its ability to mimic essential metals [34]. Metals are persistent contaminants that tend to bioaccumulate in exposed marine organisms and, in turn, enter the food chain, potentially exposing humans who consume seafood to their toxic effects, which include neurological damage and developmental issues in children [35]. Arsenic (As), chromium (Cr), mercury (Hg), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), thallium (Tl), and lead (Pb) are considered among the most environmentally toxic metals [34, 36]. These metals are known for their high toxicity, persistence in the environment, and potential to cause severe health issues in humans and other living organisms [34, 36].

Metals in the environment have traditionally been assessed based on their ecotoxicological importance, with a significant focus on their occurrence in water, sediments, and aquatic organisms [26, 37–39]. Although the occurrence of macro litter in the marine environment in South Africa [40–42] and other parts of the world [43–47] has been reported, records on macro plastics and associated contaminants are still scarce. Therefore, this study aims to quantify and categorize marine litter from Table Bay, Cape Town, South Africa, with a focus on plastics, and subsequently determine the associated metal content in plastics.

Materials and methods

Study area

The Table Bay coastline of the Atlantic Ocean, in Cape Town was selected for the study, with beaches at Woodbridge Island and Derdesteen, as the sampling sites (Fig. 1). The two sites have similar exposure to weather conditions but differ in proximity to the harbour, river mouth, frequency of visitors and catchment area. Woodbridge Island ($33^{\circ}53'0.63''$ S, $18^{\circ}29'9.62''$ E) is located off the coast of Milnerton, approximately 12 km from Cape Town Harbour. It is close to the Diep River Mouth (about 1 km away) and the Black River Mouth (around 2 km away). The Woodbridge Island receives stormwater runoff from nearby residential and industrial areas, making it a suitable impact site for our study. Recreational activities at the Woodbridge Island site include sunbathing, kite surfing, walking, and angling, with the historic lighthouse (built in 1960), Milnerton golf club and several restaurants as tourist attractions at the site [48, 49]. Meanwhile, Derdesteen ($33^{\circ}46'1.03''$ S, $18^{\circ}26'39.22''$ E), located within

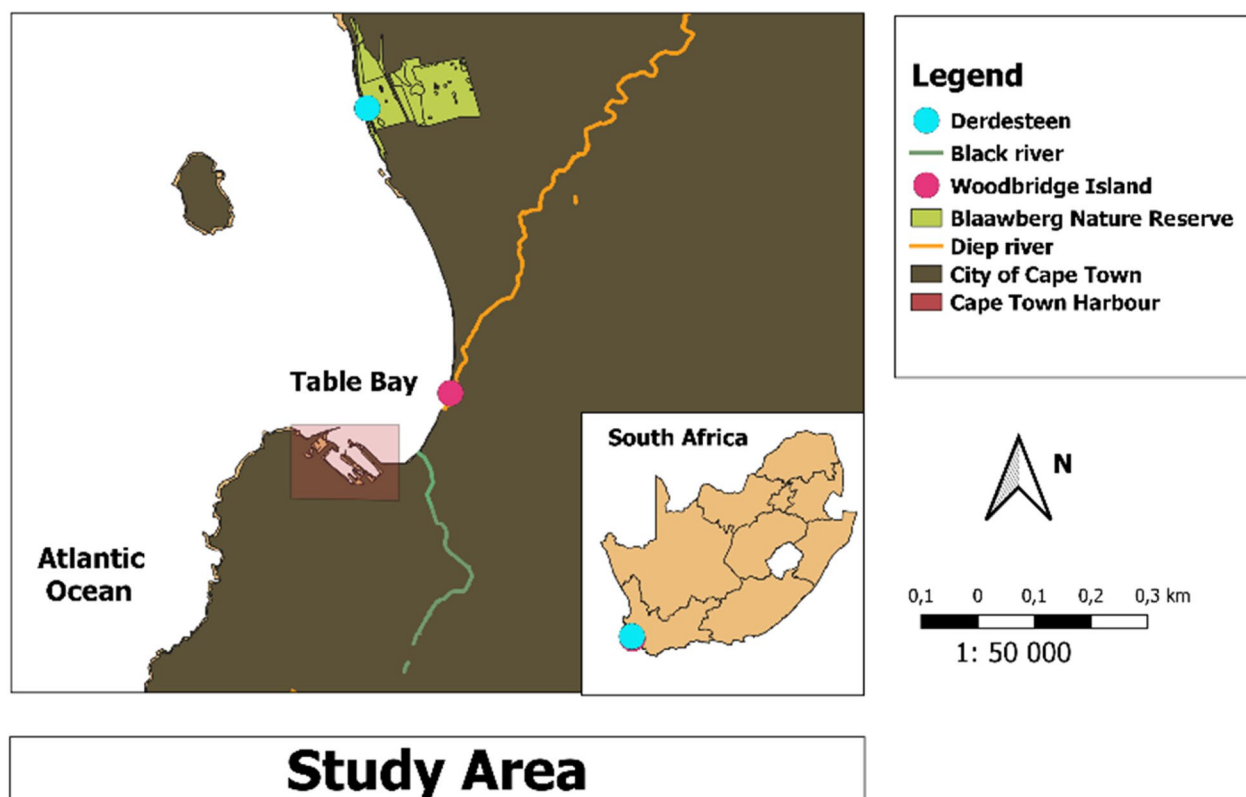


Fig. 1 Selected study sites at the Table Bay area

the Blaauwberg Nature Reserve along South Africa's west coast, was selected as the control site. Derdesteen Beach is located about 25 km from Cape Town Harbour, away from river mouth, residential area, industrial area, and restaurants, with board and kite surfing as the major activities observed.

Sample collection

Litter was collected in February 2021 during summer over a successive 10-day period, along a 100 m stretch (divided into four 25-m areas) of the selected sites from the edge of the water to the back of the beach and transported to the laboratory for further analysis. The litter were sorted and grouped as reported in our previous study [50]). Litter were collected, classified, counted, and weighed, using an adapted method from the African Marine Litter Monitoring manual by Barnardo and Ribbink [51]. For this study, shopping bags, straws, cigarette lighters, cigarette butts, bottles, lollipop sticks, hygiene, stationary, utensils, wrapping, fragment, and foam were the types of plastic litter surveyed and recorded as count or weight per 100 m.

Fourier transform infrared spectroscopy (FTIR) analysis

Plastic litter (not bigger than 200 mm) was processed for polymer type using a PerkinElmer Spectrum Two Universal Attenuated Total Reflectance (UATR-IR) spectrometer, equipped with ST Japan and PerkinElmer polymer libraries as previously described by Sparks and Awe [17]. The spectrum range covered was from 4000 to 450 cm^{-1} , with a resolution of 4 cm^{-1} and a data interval of 1 cm^{-1} . A background scan was performed after cleaning the ATR crystal surface with isopropanol and prior to sample scans. Each sample was scanned 10 times, and the ATR crystal was cleaned with isopropanol before scanning each new sample.

Metal analysis

Some of the plastic litter identified by the UATR-IR was further processed for metal analysis based on the differences in polymer type, colour, and category. The metal analysis was conducted using an Agilent 7800 ICP-MS equipped with an SPS 4 Autosampler (Agilent, Japan). Prior to the metal analysis on the ICP-MS, the plastic items were rinsed thoroughly with ultrapure MilliQ water and air dried. The dried plastics were then singly immersed in liquid nitrogen and crushed. After this,

an in-built method for plastic digestion on a MARS 6 One Touch microwave CEM system (CEM Matthews, NC, USA. Method: Polyethylene digestion) was then employed to digest crushed samples. In brief, 10 ml of concentrated ultrapure nitric acid (Millipore, 65% Suprapur Nitric acid) was added to 0.25 g of crushed samples in Teflon vessels. MAR 6 digestion program: 0 to 200 °C within 15 min and held at 200 °C for a further 15 min at 800 psi and power of 900–1050 W. Clear and particle-free digestates were quantitatively transferred and diluted to 50 ml with ultrapure MilliQ water. The samples were then centrifuged at 5000 rpm and a 10 mL aliquot of the supernatant was processed through the ICP-MS, which has been calibrated for the determination of As, Cd, Cr, Co, Cu, Ni, Pb, Zn and Se.

Quality assurance

To ensure quality assurance, the standard procedures for trace metal analysis were followed, such that the use of metallic and glassware was avoided, and reagent blanks were processed alongside the samples. All plastic wares utilised were soaked in 10% nitric acid overnight and washed copiously with distilled water before use. All standards, samples and blanks were processed in a specialised prep-station and fume hood dedicated to trace metal analysis. We only used supra pure reagents and analysed samples in duplicates.

Data analysis

Statistical analysis was conducted using the Statistical Package for the Social Sciences (SPSS, version 29.0.2.0 (20). Assumptions of normality and homogeneity of variances were not met. Therefore, non-parametric tests, specifically the Mann–Whitney U test (for two groups) and the Kruskal–Wallis H test (for more than two groups) were applied, with statistical significance set at $p < 0.050$.

Results and discussion

Litter

A total of 5296 litter items, at a median of 90.50 items/100 m that weighed 15,132.14 g (median=111.11 g/100 m) was collected. The litter count was significantly higher ($U=393.00$ and $p<0.001$) at Woodbridge Island (total=4583.00 items/100 m and median=238.50 items/100 m) relative to Derdesteen (total=713 items/100 m and median=22.00 items/100 m), as presented in Fig. 2a. However, the difference in litter weight was not statically different ($U=259.000$ and $p=0.114$) at both Woodbridge Island (total=8658.83 g/100 m and median=180.62 g/100 m) and Derdesteen (total=6473.32 g/100 m and median=91.41 g/100 m), as presented in Fig. 2b.

The surveyed litter items by count were mainly (86%) plastics, with a higher proportion of plastics at Woodbridge Island (88%) compared to Derdesteen (78%). Hygiene (e.g. condoms/condom wrappers, diapers, earbuds, medical containers/tubes, sanitary pads, syringes/needles and wet wipes/toilet paper) and marine (e.g. Buoys/floats, fishing line, fishing net/trap, glow/light stick, rope/string and sinker/hook) items accounted for 6% of the litter at each site and constitute the second most prevalent items after plastics. The study of Barnardo et al. [40] in Port Elizabeth, South Africa, also reported a high prevalence of plastics in marine litter items. They found that plastics had the highest accumulation rate by count at their studied sites, but a lower plastic proportion of 51.8% was recorded in their study compared to ours. In another study from South Africa, conducted in Kwa-Zulu-Natal by Meakins et al. [41], a higher plastic proportion of over 90% relative to our study was reported. Riverine inputs, illegal dumping of construction waste around the coastline, and inadequate wastewater treatment were identified as possible sources of plastics. The dominance of plastic in surveyed marine litter items in studies from other African countries has also been highlighted [52–54]. Although the study by Weideman et al. [54] assessed floating litter, riverine input was also identified as an important factor, especially regarding the density of surveyed litter.

In our study, the top three contributors to the overall weight of litter were plastic (46%), glass (27%) and clothing (15%). The accumulation of glass litter items at our sites was more pronounced at Woodbridge Island, where glass litter contributed the highest weight to the litter load at 39%. Whereas, at Derdesteen, plastic litter contributed the highest weight at 65%, followed by glass and clothing items at 10% each.

Since there were significant differences in litter count between our sites ($U=393.00$, $p<0.001$) but not in litter weight ($U=259.000$, $p=0.114$), this indicates that a few heavy glass items (mainly alcoholic beverage bottles) at Woodbridge Island and a few heavy plastic items at Derdesteen were the primary contributors to the litter weight at Table Bay. The differences in litter composition at our sites suggest that litter from Woodbridge Island originates primarily from the catchment area and beachgoers (i.e., the prevalence of light plastics, glass bottles, and hygiene items), whereas at Derdesteen, the litter items could potentially be linked to marine leakages (i.e., the prevalence of heavy plastics and marine items). The majority of items assessed at Derdesteen also appeared aged, likely due to weathering in contrast to those from Woodbridge Island. The study by Chitaka et al. [55] in South Africa ruled out direct littering by beachgoers based on the prevalence of items showing signs of

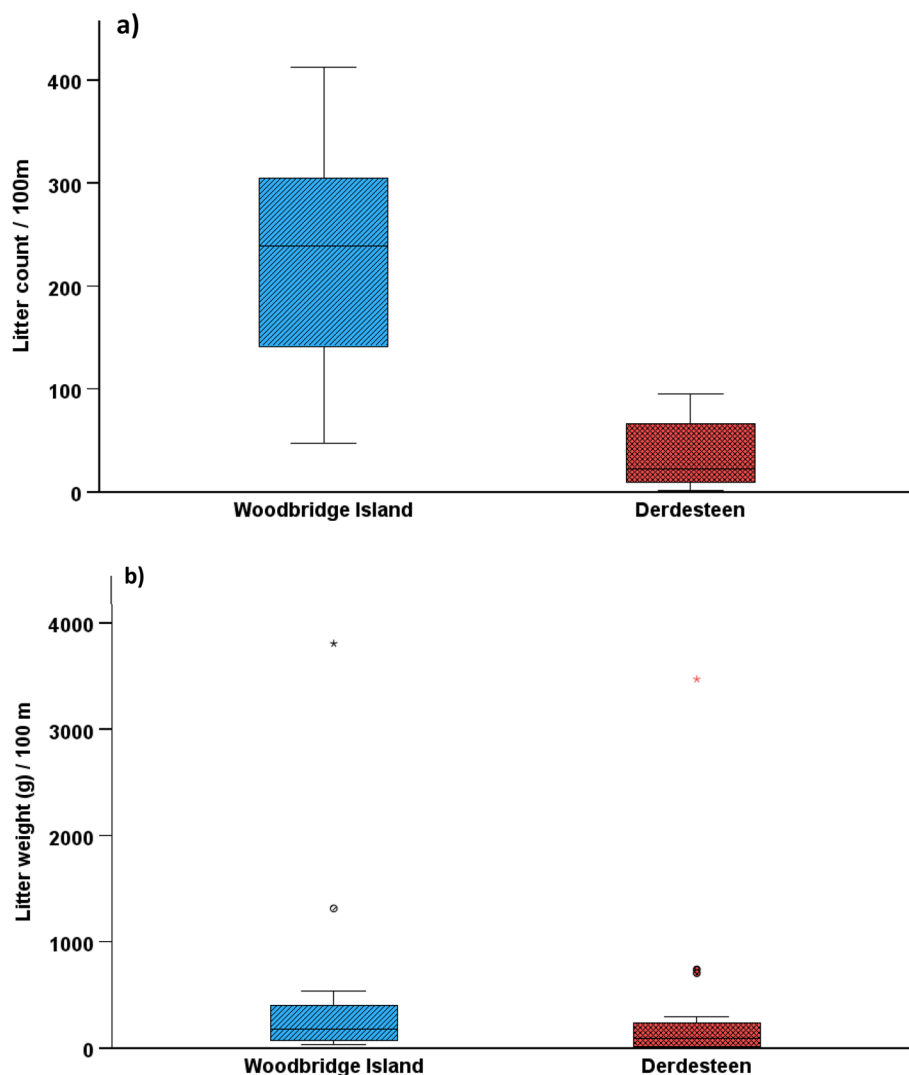


Fig. 2 a Distribution of litter count and b weight across study sites

weathering and water transport in the monitored beach litter, supporting our postulation. However, the marine environment is highly dynamic, with the occurrence and clearance of marine plastics influenced by various factors (such as catchment area, anthropogenic actions, ocean dynamics, clean-up efforts and environmental conditions, amongst others), making it challenging to identify the sources of observed items [55, 56].

Woodbridge Island is situated close to two rivers: the Diep and the Black Rivers. Studies have emphasized river mouths as significant pathways for litter into coastal and marine environments, as rivers transport residential and industrial debris from catchment areas to coastal and marine areas, from where it gets deposited into the ocean [57–60]. Hence, the accumulation of light plastics, and hygiene items at Woodbridge Island could be attributed to riverine litter from the residential catchment areas.

The report by Barnes et al. [57] highlighted that although plastics constitute roughly 10% of discarded waste, on coastal shorelines, plastics constitute a much larger proportion of marine litter, with river mouths being a significant conduit of fragmented plastics into the marine environment.

Evaluating plastic litter

Plastics items, including cigarette butts and lighters from the collected litter that were further analysed, showed that fragments dominated at 36%, followed by foam at 29%, wrapping at 12%, bottles at 7%, cigarette butts and lollipop sticks at 6% each and straws accounting for 4%, while the remaining analysed categories (shopping bag, cigarette lighter, hygiene, stationary, and utensil) only constituted approximately 1% of the total count. The dominance of fragmented plastics at the Woodbridge

Island site, near two river mouths, further highlights the importance of riverine inputs. However, the clean-up approach at the site could have also meant that more visible items like wrapping bags were picked up, leaving behind smaller fragmented ones, contributing 38% of the plastic litter counts at the site. Conversely, at the Derdesteen site with no direct riverine litter input and no observed clean-ups, wrapping was the most dominant item at 44%, followed by fragment at 17% and 12% recorded for foam. The dominance of wrapping items at our control site is suggestive of aeolian plastic deposition, as wind has been shown to be an important factor in beach plastic loading [61]. Polymer identification of surveyed plastics was carried out for more insight into the surveyed plastics.

Identifying the polymers in plastics

Plastic items (≤ 20 cm) were selected from the plastic litter items for polymer type identification. Approximately 6% of the total surveyed plastics had their polymers identified on the UATR-IR spectrometer with the aid of ST Japan and PerkinElmer polymer libraries. A total of 11 polymers were identified, with an average spectra quality match of 95%. Overall, most of the analysed plastics were polypropylene (PP) at 40%, followed by polyethylene (PE) at 24%, with polystyrene (PS) recorded at 12% and cellulose acetate (CA) at 10%. Other polymers recorded were 4% synthetic rubbers (SR), 3% polyamides (PA), 2% polyethylene terephthalate (PET), 2% styrene acrylonitrile copolymer (SAN), 2% Polyurethanes (PURs), 1% polyvinyl chloride (PVC) and natural fibre (NF) at just 0.4%. The proportion of each identified polymer type at each site is presented in Table 1.

Also, looking at the polymer types associated with the categorized plastics, PP dominated in most of the categories, except in caps/lids and hygiene (dominated by PE), cigarette butts (dominated by CA), foam (dominated by PS) and rubber (dominated by synthetic rubber) as shown in Fig. 3a. Six polymer types were recorded for food, fragment and wrapping items, three in caps/lids, foam, rope/line, rubber, and stationary, while only two polymer types were recorded in the rest of the categories as represented in Fig. 3b.

Most of the plastics identified as cellulose acetate (CA) and polystyrene were white in colour, polyamides (PA) and polypropylene were mainly transparent, polyethylene

was mostly blue/green, while polyurethanes (PURs) and synthetic rubbers (SR) were mainly brown/yellow as shown in Fig. 4a. PE has the highest variety of colours, appearing in all seven (7) colour categories, followed by PP and SR with six (6) colours each, PET and SAN with four (4) colours, PS and PVC had three (3), CA and PA had two (2), while NF and PURs were entirely brown/yellow as shown in Fig. 4b.

Metal content of selected plastic items

Based on the plastics analyzed with the FTIR, 47 samples were successfully quantitatively digested and analysed for metal content on an ICP-MS instrument. The 47 samples comprised of PA (3), PE (13), PET (2), PP (11), PS (7), PURs (2), PVC (1), SAN (2) and SR (6). The detected metal concentrations have high variance, and the overall median concentrations of analysed metals were mostly ≥ 1 mg/kg. Carnati et al. [62] and Klöckner et al. [24] also reported high variance in the metal contents of plastic items in their studies. The high variance in metal concentration could have stemmed from various factors, such as plastic polymer type, usage, production process, environmental exposure, and ageing level amongst others. In contrast however, Klöckner et al. [24] reported a median concentration below 1 mg/kg for most of the metals analysed except for Cu (1.8 mg/kg), Fe (51 mg/kg) and Zn (45 mg/kg). In our study, the overall median concentrations of Zn and Fe were also high at 33.15 and 54.46 mg/kg respectively, with Al level that was particularly high at 147.36 mg/kg and toxic Pb occurring at 6.05 mg/kg median concentration. The lowest overall median concentrations were recorded in Co (0.04 mg/kg), Cd and V (each at 0.11 mg/kg). Like our study, Klöckner et al. [24] also observed the lowest medians for Co (0.06 mg/kg) and Cd (0.041 mg/kg). Although low median levels were recorded for some of the toxic metals in our study, mixtures of toxic and essential metals at low doses have been shown to have a significant potential to produce deleterious outcomes on biological organisms [63].

Looking at the two sites monitored individually, the median concentrations for Pb, Zn, Fe, and Al were > 1 mg/kg, with a median Cu value of 9.15 mg/kg at Derdesteen (Table 2). The maximum detected values of toxic metals are of great concern relative to the United States Environmental Protection Agency (EPA)

Table 1 Polymer proportion at each site

Location	CA	PA	PE	PET	PP	PS	PVC	SAN	SR	NF	PURs
WI	14%	1%	26%	3%	37%	13%	1%	1%	2%	1%	3%
DS	3%	9%	19%	1%	47%	9%	1%	4%	8%	0%	0%

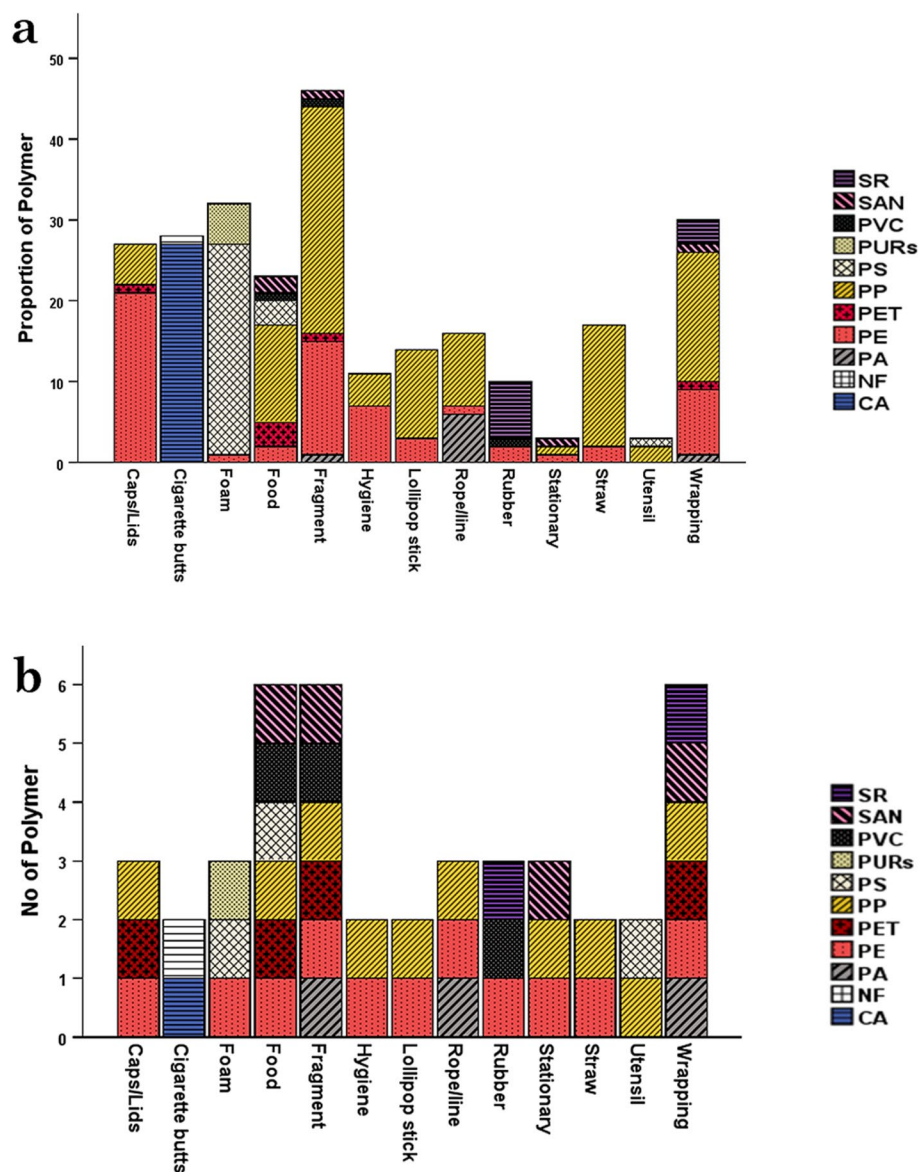


Fig. 3 **a** Proportion of Polymer and **b** number of polymers in categorized plastic items (SR: Synthetic Rubber; SAN: Styrene Acrylonitrile Copolymer; PVC: Polyvinylchloride; PURs: Polyurethanes; PS: Polystyrene; PP: Polypropylene; PET: Polyethylene Terephthalate; PE: Polyethylene; PA: Polyamide; NF: Natural fibre; CA: Cellulose Acetate)

Marine Sediment Screening Benchmarks, with toxic Pb and Cd having maximum values of 3988.98 mg/kg (recorded in a plastic item from Woodbridge) and 9666.94 mg/kg (recorded in a plastic item from Derdesteen), respectively as presented in Table 2. Plastics have the potential to serve as a pathway for toxic metals to enter marine organisms through leaching into the marine environment or direct ingestion. This process makes these metals bioavailable in exposed organisms, which can then transfer into the food web, with a propensity for bioaccumulation and biomagnification

across trophic levels [64]. As a result, both marine organisms and humans are exposed to the known deleterious effects of Pb and Cd, including neurotoxicity, cardiovascular toxicity, nephrotoxicity, reproductive toxicity, embryotoxicity, immunotoxicity, bone toxicity, osteotoxicity, carcinogenicity, pulmonary toxicity, hepatotoxicity, digestive system toxicity, genotoxicity, growth inhibitory toxicity, chronic protein dysregulation, mutagenesis, and oxidative stress, among others [34, 64]. These toxic effects pose a severe threat to marine ecosystems and human health, highlighting the

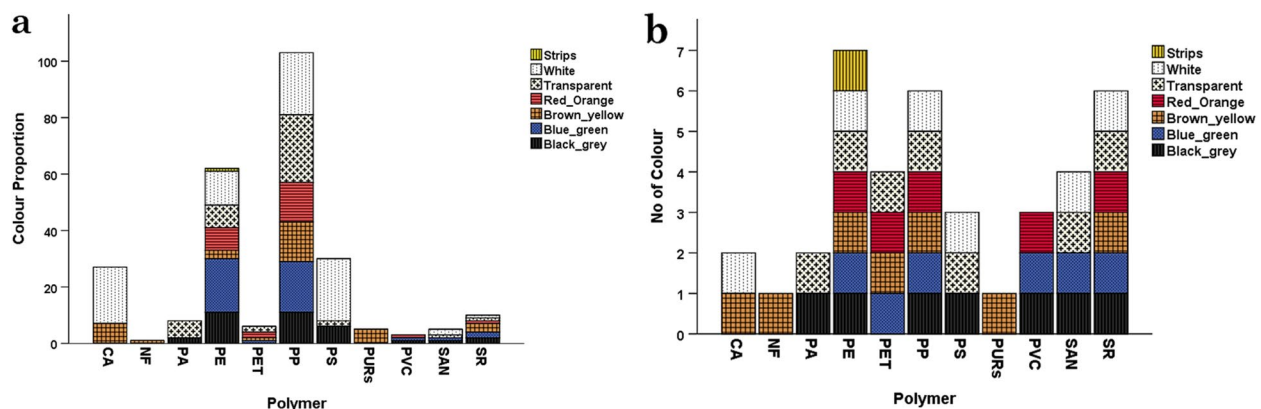


Fig. 4 Proportion of colour and **b)** number of colours in categorized plastic items

Table 2 Descriptive Statistics of detected metal concentrations (mg/kg)

Metal	Overall			Woodbridge			Derdesteen			US EPA MSSB ^a
	Detection frequency	Maximum (mg/kg)	Median (mg/kg)	Detection frequency	Maximum (mg/kg)	Median (mg/kg)	Detection frequency	Maximum (mg/kg)	Median (mg/kg)	
Al	91%	4385.21	147.36	90%	4385.21	147.49	94%	1038.74	124.45	
V	89%	6.63	0.11	88%	6.63	0.15	90%	1.43	0.10	
Cr	100%	829.34	1.16	100%	829.34	2.23	100%	6.48	0.92	52.30
Mn	89%	270.98	0.60	88%	270.98	0.77	90%	16.22	0.30	
Fe	95%	7215.75	54.46	96%	7040.64	62.24	94%	7215.75	48.22	
Co	75%	55.67	0.04	77%	1.92	0.07	71%	55.67	0.02	
Ni	100%	10.47	1.05	100%	9.73	1.23	100%	10.47	0.65	15.90
Cu	54%	247.94	2.49	58%	33.04	1.60	48%	247.94	9.15	18.70
Zn	91%	23,056.14	33.15	92%	4178.19	34.17	90%	23,056.14	32.74	124.00
As	61%	9.92	0.75	65%	9.92	0.99	55%	5.35	0.36	7.24
Se	49%	2061.11	0.82	58%	6.80	0.80	35%	2061.11	1.09	
Cd	49%	9666.94	0.11	52%	92.52	0.08	45%	9666.94	0.27	0.68
Pb	53%	3988.98	6.05	63%	3988.98	4.42	39%	67.77	6.10	30.20

US EPA MSSB United States Environmental Protection Agency Marine Sediment Screening Benchmarks

^a US EPA (2006) [65]

urgent need for continuous monitoring of these toxic metals, as well as stricter regulations and mitigation efforts to reduce metal contamination in plastics and the coastal environment.

The median concentration of most of the analysed metals did not however exceed the available safety standards/limits for metals in plastic articles (Table 3), except for Pb, Cr and Cu. The Pb content exceeded the concentration limit of 2 mg/kg, specified for contact with foodstuffs (CFS) safety standard, with an overall median Pb content of 6.05 mg/kg and median values of 4.42 mg/kg and 6.10 mg/kg at Woodbridge and Derdesteen, respectively. The CFS limit was also exceeded for Cr (limit = 1 mg/kg) at Woodbridge (Cr

median = 2.23 mg/kg), and for Cu (limit = 5 mg/kg) at Derdesteen (Cu median = 9.15 mg/kg).

The distribution of recorded median metal contents of plastic items (Fig. 5a) varied significantly, Kruskal–Wallis H Test $H(12)$ of 485.562 and $p < 0.001$ were obtained. High contents of Al, Fe and Zn were recorded in analysed plastic items, with Fe having the widest distribution range. Although Fe and Zn are essential metals and Al is also abundant in our environment, these elements could be harmful to sufficiently exposed organisms at elevated concentrations [17].

Comparing metal content in plastic articles between the two sites (Fig. 5b), the Mann–Whitney U test shows that there were no significant differences ($p > 0.050$) in

Table 3 Limit values (mg/kg) of some selected Metals regulated in Europe (adapted from Turner and Filella [22])

Metals	TS	RoHS	ELV	PPW	CFS	Hazardous
Al	70,000					
As	47				1	yes
Cd	17	100	100	100 ^a		yes
Cr (IV)	0.20	1000	1000	100 ^a	1 ^b	yes
Co	130					yes
Cu	7700				5	
Hg	160	1000	1000	100 ^a		yes
Mn	15,400					
Ni	930					
Pb	23	1000	1000	100 ^a	2	yes
Sb	560					
Se	460					
Zn	46,000				100	

TS Toy Safety (migratory limit in 0.07 M HCl), RoHS Restriction of Hazardous Substances, ELV End-of-Life Vehicles, PPW Packaging and Packaging Waste, CFS Contact with foodstuffs

^a The combined limit for Cd, Cr (IV), Hg and Pb is 100 mg/kg

^b When the oxidation number of Cr is not specified and assumed to be VI

the recorded levels of each metal content of analysed plastics between the two sites except for Cr ($U=947.000$, $p=0.042$), Cu ($U=131.000$, $p=0.044$), As ($U=381.000$, $p=0.011$). Cr and As were significantly higher at Woodbridge compared to Derdesteen, while Cu was significantly higher in Derdesteen compared to Woodbridge. This is suggestive of a higher prevalence of non-essential metals that may be toxic to marine life even at low concentrations at the Woodbridge site, likely due to the site's exposure to various anthropogenic inputs. In contrast, the Derdesteen site, located within a nature reserve and farther from residential, industrial, and riverine inputs, shows lower levels of these toxic metals and the prevalence of essential Cu. Non-essential Cr and Ni were detected at 100% frequency, across our sites and the majority of all the other analysed metals (Al, V, Mn, Fe, Co, and Zn) were detected at a frequency of over 70% across the sites, as presented in Table 2.

The distribution of metals across polymer types

The concentrations of analysed metals in the different polymers are presented in Fig. 6. Notably, in polystyrene (PS) and Polyurethanes (PURs), the median concentrations of analysed metals were above the overall recorded medians, except for Se and Cd, and Zn in PURs only. The highest median concentration of non-essential Cr (3.91 mg/kg) was recorded in PS and closely followed by that (3.90 mg/kg) recorded in PURs. This observation may be attributed to the porous nature of polystyrene (PS), especially expanded PS, and polyurethane foams (PURs), which provide a high number of adsorption

sites for metals. Additionally, ageing readily increases surface area and alters functional groups on foam-like plastics, leading to the formation of negatively charged sites (C–O and O–H) with an enhanced affinity for positively charged metal ions [66]. The median concentration of toxic Pb in PS and PURs were 10.60 and 6.41 mg/kg respectively. But the highest median concentrations of toxic Pb (20.70 mg/kg), Cd (9651.31 mg/kg) and Se (2057.76 mg/kg) were all recorded in the PVC polymer category, while the highest Zn was recorded in the synthetic rubber (SR) with a median value of 2696.04 mg/kg. The level of Pb and Cd in PVC may be due to the use of Pb- and Cd-based stabilisers in PVC production for many years, to proffer improved heat resistance in PVC articles, essential for the long service life of PVC [23, 67]. Whereas the high level of Zn in SR could be linked to the role played by zinc oxide in the production of rubber items, as ZnO is employed as an activator, vulcanisation agent, and reinforcing agent during rubber production [68, 69].

The Kruskal–Wallis H Test showed significant differences in the distribution of analysed metals across the polymer categories (H (8), $p<0.050$), except for Al, Ni and Pb that do not vary significantly across the polymer categories (H (8), $p>0.050$).

The distribution of metals across categorised plastic items

The distribution of the detected metals is presented in Fig. 7 and the distribution showed variability across the analysed plastic categories. The highest content of most of the analysed metals (Al, V, Cr, Mn, Fe, Co, Ni, and

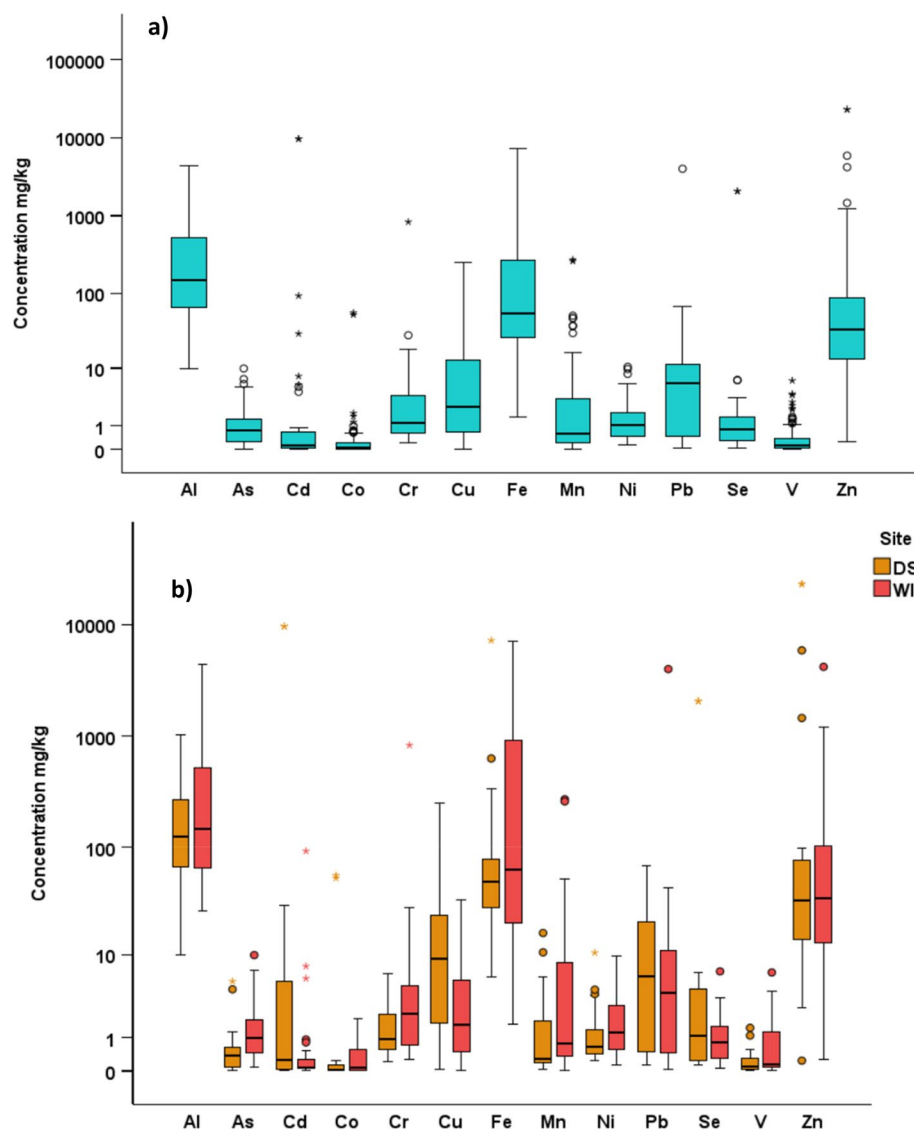


Fig. 5 Metal content of Plastics from **a)** both sites; **b** Woodbridge Vs Derdesteen. Charts were plotted on a logarithmic scale to better represent the wide range of values of metal concentrations

As) was found in Foam (Fig. 7), which consisted mostly of polystyrene. Presenting foam items as an important reservoir for metals.

The median levels of non-essential metals detected in our study are presented in Fig. 8. The highest content of most of the non-essential metals was recorded in foam, except for Cd (4.48 mg/kg) and Pb (14.07 mg/kg) which were both recorded in fragmented plastic items. The prevalence of Cr, Co, Ni, and As in foam items, exposes the marine environment to the well-established toxic effects of these metals [31, 70]. Also, according to the International Agency for Research on Cancer (IARC),

Cr and As are classified as Group 1 carcinogens to humans and are among the priority contaminants [71].

The highest median content of 33.04 mg/kg recorded for the essential and naturally occurring Cu, in the different plastic items was in Rope/line (made primarily of polyamide and polypropylene). Cu were predominant at the Derdesteen site relative to Woodbridge in our study and fishing activities could be opined as the potential Cu source. Whereby, the highest median content of Zn (1212.67 mg/kg) was in rubber, and that of Se (1.25 mg/kg) in plastic articles associated with food.

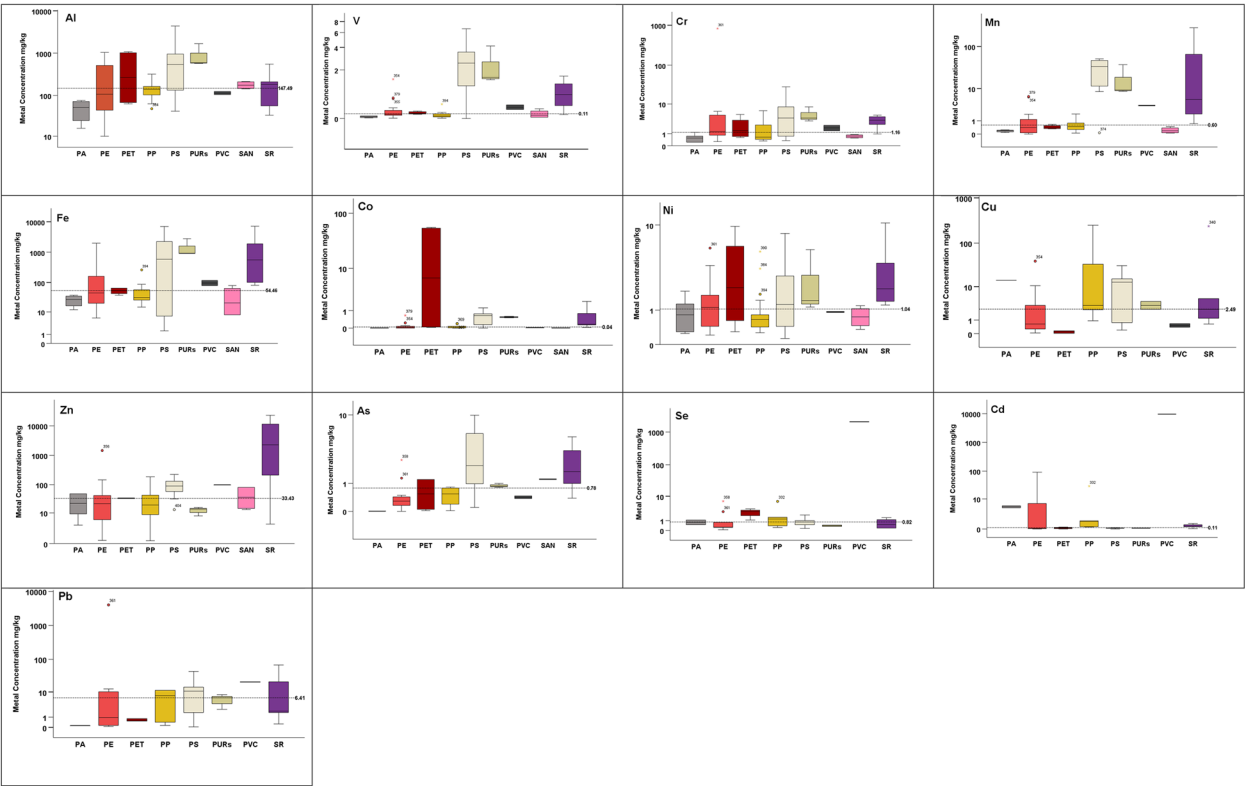


Fig. 6 Metal content in Different polymer types across the sites. The reference dotted line represents the median concentration and charts were plotted on a logarithmic scale, to better represent the wide range of values of metal concentrations

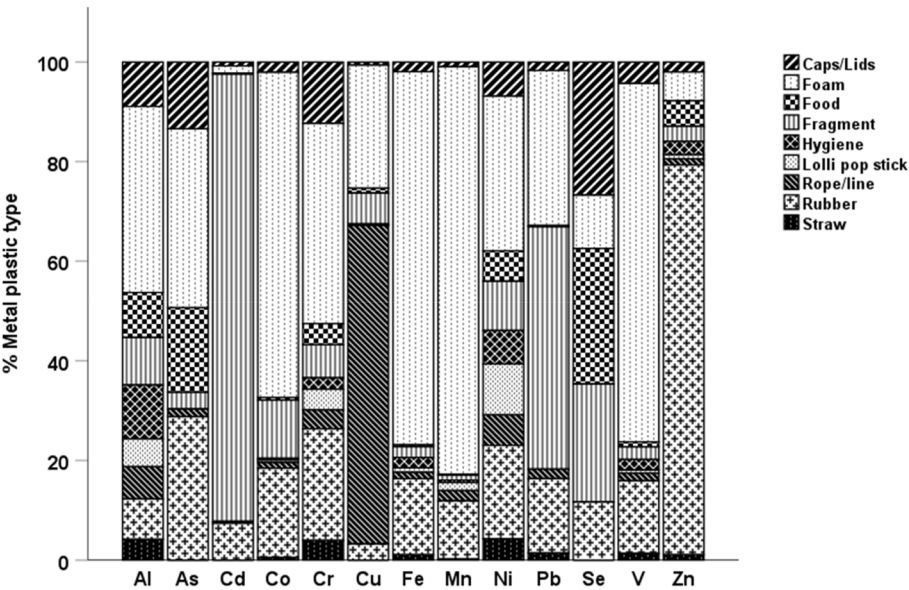


Fig. 7 Proportion of detected metals across the categorized plastic types

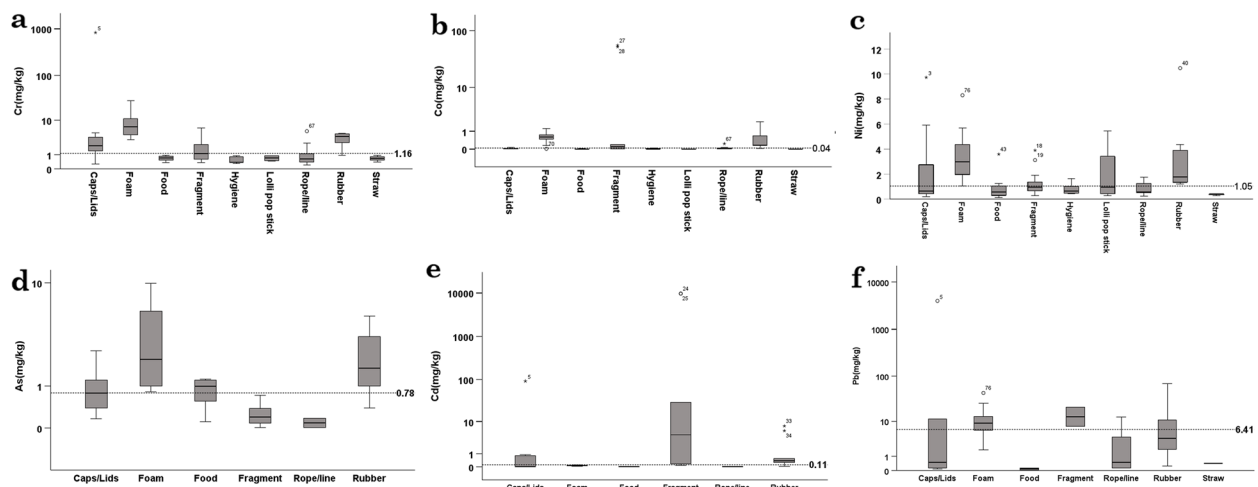


Fig. 8 Metal content of (a) Cr, b Co, c Ni, d As, e Cd and f Pb in the different plastic categories across the sites. The reference dotted line represents the median concentration and charts were plotted on a logarithmic scale except for c, to better represent the wide range of values of metal concentrations

The distribution of metals across the different plastic colour categories

Metal contents in plastics have been linked to pigments [24], hence the association between analysed metals and the colour of plastics was explored. The distribution of most of the analysed metals varied significantly across the different colours of plastic items (Kruskal–Wallis H Test $p < 0.050$), except for Co ($H(5) = 9.079$, $p = 0.106$), Se ($H(5) = 2.895$, $p = 0.716$), V ($H(5) = 10.040$, $p = 0.074$), and Zn ($H(5) = 5.795$, $p = 0.327$). The distribution of Al and Cu recorded were prominent in plastics categorized as blue-green, As in white, Cd and Pb were highest in black-grey, V, Cr, Mn, Fe, Co, and Ni were highest in the brown-yellow category, while Se

and Zn dominated in plastics coloured red-orange (Fig. 9). Our result indicates possible pigmentation, which is quite evident with Cu and Fe being dominant in blue-green and brown-yellow, respectively. For instance, copper phthalocyanine has been utilized in the production of blue and green pigments, which also acts as a stabilizer, enhancing the weathering resistance of plastics [72]. Whereby limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) pigment with a shade of yellow and brown has been widely employed as coloring agent [73, 74]. The study of Carnati et al. [62] also reported a linkage between plastic colours and metal contents, and similar to our study, reported a high abundance of Cu in blue and green plastics.

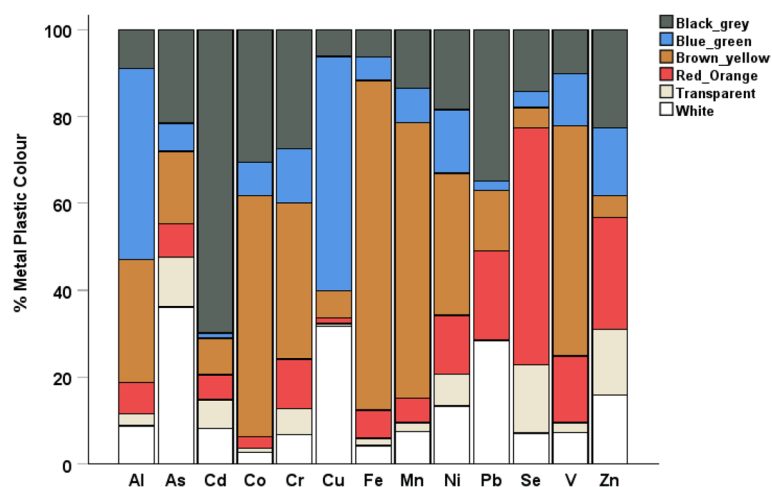


Fig. 9 Median proportion of detected metals across the categorized plastic colours

Conclusion

Our study showed the prevalence of plastic items among marine beach litter at both our impacted site (Woodbridge Island) and control site (Derdesteen) along the Table Bay coastline in Cape Town, South Africa. Plastics accounted for over 75% (by count and weight) of the litter items surveyed at each site. Fragmented plastic items dominated at the impacted site, indicating riverine plastic input, while wrapping items were predominant at the control site, suggesting wind deposition of floating plastic items from the open ocean, as the control site is distant from direct land-based plastic input.

Polypropylene, accounting for 40% of the plastics analysed for polymer type, was the most common, with most of these plastics being transparent. Additionally, the study confirmed the occurrence of metals in marine plastics, with polystyrene plastics showing a high capacity for metal accumulation. PVC, fragmented and black-grey plastics were found to have particularly high levels of lead (Pb) and cadmium (Cd).

Hence, further studies are needed to assess the mechanisms of metal accumulation and their fate in foam and fragmented plastics. Measures should also be implemented to control the release and accumulation of plastics in marine environments. Furthermore, the use of heavy metals, such as toxic Pb and Cd, as additives in PVC production should be investigated, and commercially available PVC items should be monitored for metal additives.

Although developing a suitable response to combat PVC pollution requires legislative policies, corporate action, and community efforts, short-term community initiatives such as public awareness campaigns can yield immediate benefits. These campaigns can educate people about the harm caused by indiscriminate use and disposal of PVC articles and promote beach clean-up initiatives. In the long term, we encourage the development of PVC alternatives and government-implemented take-back programs. A more rigid long-term approach involves policy restrictions on PVC use, including plastic deposit schemes and extended producer responsibility programs to encourage recycling.

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Authors' contributions

Adetunji Awe: Conceptualization, grant acquisition, Methodology, Investigation, Writing – review and edits. Oputu Oghenechuko: Methodology, review and edits. Uyiosa Aigbe: Writing – review and edits. Conrad Sparks: Conceptualization, grant acquisition, Investigation, review and edits.

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Data availability

The data supporting the findings of this study are included within the paper, and additional raw datasets used and/or analyzed during the study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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