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RESEARCH ARTICLE

Concentrations and risk assessment of metals and microplastics from antifouling paint particles in the coastal sediment of a marina in Simon's Town, South Africa

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Abstract
Maintenance of maritime vessels includes the removal of paint from hulls that are sources of metals, antifouling paint particles (APPs) and microplastics (MPs) that end up in the coastal environment. Simon's Town is a small urban town in False Bay, Cape Town, South Africa, where maritime activities take place (there is a naval harbour, marina and shipyard). The aim of this study was to measure metals, APPs and MPs in Simon's Town, to assess the impact of maritime activities and a storm water pipe in a sheltered marina. Sediment samples were collected from six sites during winter 2018. Sediment and extracted APPs were analysed for metal concentrations (Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Sb, Sn, Sr, V and Zn) and MPs characterised based on type (shape and polymer), colour and size. Highest average metal concentrations in sediment for all sites were Fe (32228 ± SEM 4024), Al (12271 ± 1062) and Cu (1129 ± 407). Metals in paint particles were highest for Fe (80873 ± 19341), Cu (66762 ± 13082) and Zn (44910 ± 1400 µg/g). Metal and MP fragment concentrations were highest at the slipway of the shipyard, decreasing with increased distance from the slipway. MP filaments were highest close to the storm water outfall pipe. Our results suggest that shipyards are potential sources of metals and MP fragments (mainly APPs), with storm water pipes potential sources of MP filaments. Various indices applied to assess the potential impacts of metals and MPs suggest that these contaminants have the potential to adversely impact the intertidal ecosystem investigated.

Keywords Microplastics · Antifouling paint particles · Metals · Sediment · Risk index

Introduction

Coastal maritime activities are increasing globally, and this has resulted in more vessels requiring maintenance (Tillig et al. 2020). Harbours and marinas are hubs of maritime activities and are subsequently potential sites for contaminants to enter marine and coastal environments (Tanner et al. 2000; Stronkhorst and Hattum 2003; Luna et al. 2012; Poulsen et al. 2021). Anthropogenic activities at and around marinas/harbours include periodic harbour dredging, accidental discharge of oil and chemicals, ship painting and repair works, uncontrolled disposal and leakage of industrial and urban waste (Paradas and Amado Filho 2007). As a result, high levels of maritime traffic and associated activities (e.g. boating maintenance) continue to be major sources of contaminants (metals, organics, microplastics, and pathogens amongst others) into marine ecosystem (Soroldoni et al. 2018a).

The antifouling paints used as coatings on vessel hulls and other submerged structures for cost-effective maritime operations (in order to minimise biofouling by marine organisms) are also sources of contaminants into the marine environment (Muller-Karanassos et al. 2019). Tributyltin (TBT) and triphenyltin (TPT) compounds were the most used antifouling paints in the early 1970s as these were highly effective and affordable antifouling biocides used by shipping industries and small boat owners (Santillo et al. 2013). However, the undesirable consequences of TBT usage in antifouling paints led to a worldwide ban in 2008, based on the ban imposed by the International Maritime Organization (Champ 2000; Chambers et al. 2006). Consequently, new tin-free chemical compounds (intended to be less toxic) in

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commercial antifouling paints containing Cu(I) as the main biocide, with a combination of other booster biocides were developed, replacing the use of "toxic" TBT (Santillo et al. 2013; Soroldoni et al. 2017). However, toxic effects associated with these "newly" developed antifouling booster biocides have been reported (Soroldoni et al. 2017; Amara et al. 2018; Muller-Karanassos et al. 2019).

Particles stemming from antifouling paints, known as antifouling paint particles (APPs), are generated during repair, cleaning and painting of vessel hulls at boatyards, shipyards and marinas (Soroldoni et al. 2017, 2018a; Muller-Karanassos et al. 2019). These particles are poorly managed and end up in the local marine environment, with their toxic components leaching and potentially bioaccumulating in marine organisms (Molino et al. 2019). These APPs get deposited in sediments, along with various contaminants, depending on the type of paint, amount of paint layers, removal processes (scraping, blasting or hosing) and the influence of deposition time (Soroldoni et al. 2017). The secondary release of metals such as Sn, Cu, Zn and Pb into the marine environment has been linked to APPs (Soroldoni et al. 2017; Muller-Karanassos et al. 2019). Other metals that have been linked or used as markers for paint include Cd, Co and Sb (Pekey 2006; Williams and Antoine 2020). APPs also easily fragment and when released into the marine environment and are classified as microparticles known as secondary microplastics (MPs), because APPs contain polymers (epoxy and acrylates), resins, rubbers and synthetic copolymers (Muller-Karanassos et al. 2019; Torres and De-la-Torre 2021). The secondary release of metals and MPs by APPs, coupled with organic booster biocides, makes the occurrence of APPs in the coastal and marine environment a major health and environmental concern.

The toxic impact of metals in the marine environment has been highlighted over the years (Ahsanullah and Florence 1984; Diab et al. 2008; Vezzone et al. 2019). Thirteen (13) metals (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Tl, Zn and Se) are included amongst the priority pollutants by the United State Environmental Protection Agency (US EPA), due to their persistent nature, non-biodegradability and some are toxic even at low concentrations (US EPA 2014). To ensure that economical and nutritional values derived from the marine ecosystem are sustained, the assessment and control of these metals in the marine environment become imperative.

The occurrence of MPs in the marine environment has attracted research interests, as the effects of MPs are still poorly understood (Neves et al. 2015; Patti et al. 2020; Preston-Whyte et al. 2021). MPs are often mistaken as prey by marine organisms and, when ingested, have the potential to negatively affect nutrient assimilation, reproduction and behavioural changes (Qiao et al. 2019; Chen et al. 2020). Bioavailable MPs have the potential to transfer embedded/adsorbed contaminants to organism tissues and cells, resulting in acute and chronic toxicity to organisms (Amorim et al. 2020; Chen et al. 2020). Also, MPs have been shown to provide suitable surfaces for the formation of biofilms that could contain harmful pathogens that are transported within aquatic ecosystems (Gong et al. 2019; Feng et al. 2020). Thus, MPs can cause physical, chemical and biological damage in exposed organisms. Since APPs are comprised of polymers, these are also classified as MPs, but the contribution of APPs to marine MPs is often neglected or poorly understood (Torres and De-la-Torre 2021).

Records of the concentration of metals and MPs in coastal sediment in False Bay, Cape Town, are sparse (Pfaff et al. 2019), with available data suggesting that the bay is not highly contaminated with metals (Pfaff et al. 2019) or MPs (de Villiers 2018). Although not contaminated by metals as other parts of the country, metal concentrations in sediment within False Bay have increased over the past 30 years and there is evidence that metal contamination in Cape Town, South Africa, is influenced by localised sources of contamination (Sparks et al. 2014). Simon's Town is one of the oldest towns in South Africa, houses the country's major naval base and is a popular area for recreational activities (due to its protected beaches) and tourism (due the presence of penguin colonies) (Pfaff et al. 2019). Given the high economic value and sensitive ecological status of Simon's Town, the aim of this study was to assess the potential impacts of a boatyard and storm water pipe with regard to sedimentary levels of metals, APPs and MPs in a multi-impacted naval area, as the concentrations, characteristics and risks of these contaminants have not yet been investigated in the region.

Materials and methods

Study area

Simon's Town (34°11′31.3″S, 18°26′01."E) is a small town situated along the west coast of False Bay in Cape Town, South Africa. The bay is southward facing, approximately 1000 km^2 in size, with the Cape Peninsula to the west (where Simon's Town is situated) and Cape Hangklip to the east (Pfaff et al. 2019). Wind dynamics drive ocean circulation and wave dynamics in False Bay is dominated by south-easterly winds during summer and by north-westerly winds in winter (Jury et al. 1985). Sea surface temperature (SST) and upwelling events peak in summer (Jury et al. 1985; Dufois and Rouault 2012) due to intense wind. Circulation in the bay is generally clockwise as a result of cyclonically sheared southerly winds, moving surface currents westwards in the bay (Jury 2020). Simon's Town has an estimated population of 6700 (StatsSA 2021), is the major naval base for the

country and has boating activities such as a yacht club and boating maintenance site in a marina.

Sediment sampling and metal analyses

Six sites were sampled in June 2018 at spring low tide for sediment metal analyses. Site 1 was at the slipway of a shipyard (site near to potential source of contamination), sites 2 to 4 within the marina, site 5 outside the marina at the mouth of a storm water pipe and site 6 approximately one kilometre to the north of site 1 (site away from contamination sources) (Fig. 1). Notable activities at site 1 (adjacent to boatyard slipway) included sandblasting and painting of yachts and small crafts. At the respective sites, the upper 5 cm of sediment was sampled and stored in pre-cleaned jars. The samples were stored on ice in the field and stored at -20° C until sample processing. Sediment samples for sites 1, 3, 5 and 6 were sent to the University of Stellenbosch's Central Analytical Facility (CAF) for metal analyses. APPs from sites 1 and 3 were removed from sediment and also sent for metal analyses. At the CAF, sediment and APPs were processed using the US EPA method 6020A and metals analysed using an Agilent 7700 × ICP-MS with an Octopole Reaction System. Quality assurance of data was based on the NIST traceable standard and the results presented percentage accuracy as relative standard deviations as follows: B (116%), Al (104%), V (99%), Cr (100%), Mn (102%), Fe (106%), Co (102%), Ni (103%), Cu (105%), Zn (103%), As (106%), Se (103%), Sr (102%), Mo (102%), Cd (103%), Sn (108%), Sb (88%), Ba (103%), Hg (98%) and Pb (110%). All metal concentrations are expressed as µg/g dry weight.

Various indices applied to sediment metals were included to assess the potential effects of metals. Enrichment factor (EF) presents a ratio between concentrations of an element to that of the Earth's upper continental crust (Eq. 1) (Turekian and Wedepohl 1961; Loring 1991). The upper continental crust data normalises the data with pre-industrialised data for elements reported.

$$EF = \left(\frac{\frac{x}{y}sediment}{\frac{x}{y}background} \right) \quad (1)$$

where x is the concentration of metals reported and y the reference element (Al) that is geochemically stable and characterised by the vertical mobility and/or degradation phenomena (Barbieri 2016). Scales for the risk categories of indices are provided in Table 1.

The geoaccumulation index (I_{geo}) is defined by the following equation

$$I_{geo} = log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (2)$$

where C_n is the concentration of metals in the sediment and B_n the geochemical background values of metals in the upper continental crust. The factor 1.5 is the background metric correction factor due the lithospheric effects (Müller 1979). See Table 1 for index category values.

The contamination factor (CF) is an index that assesses the status of contamination of a metal. It uses the same upper continental crust background values used to determine EF values.

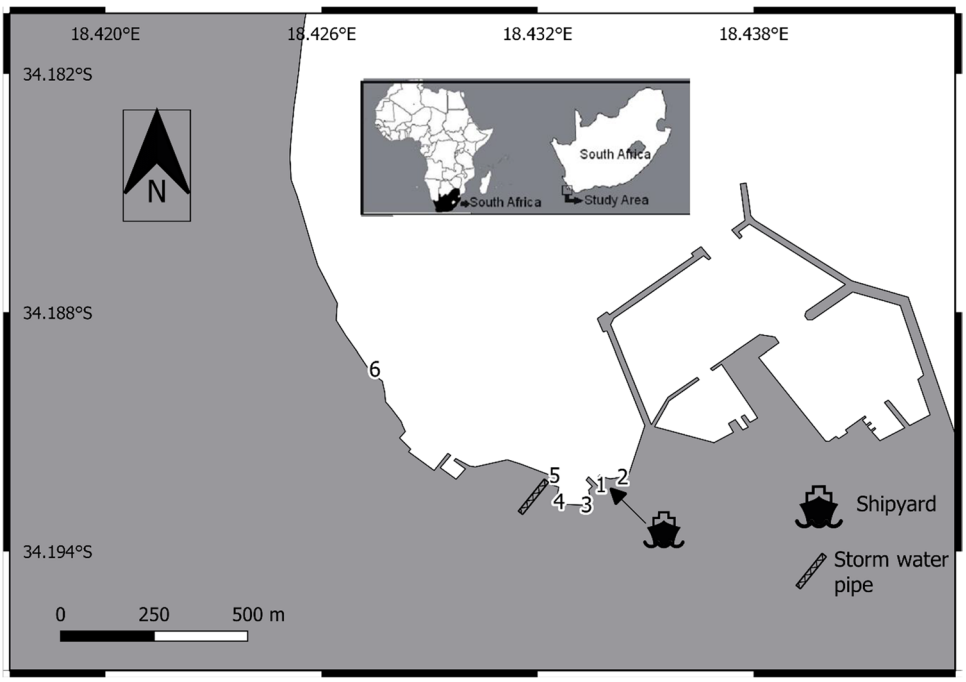

Fig. 1 Map of sites sampled in Simon's Town, Cape Town. Site 1 (impact site) was sampled adjacent to a shipyard maintenance facility, site 5 at the mouth of a storm water pipe (rectangle) and site 6 (non-impact site) approximately 1 km from site 1

Table 1 Risk categories of indices for metal and microplastic contamination in Simon's Town, Cape Town

Risk Category:	Low (I)	Moderate (II)	High (III)	Very High (IV)	Dangerous (V)
Metals:					
Enrichment Factor (EF)	< 5	5—10	10—25	25 – 50	> 50
Geoaccumulation Index (I_{geo})	< 1	1—2	2—4	4—5	> 5
Ecological Risk (Er)	< 40	40 – 80	80 – 160	160 – 320	> 320
Potential Ecological Risk Index (Ri)	< 150	150—300	300—600	> 600	
Microplastics:					
Polymer Risk Index (H)	< 10	10 – 100	101 – 1000	1000—10,000	> 10,000
Pollution Risk Index (PRI)	< 150	150 – 300	300 – 600	600 – 1200	> 1200
Metals and Microplastics					
Contamination Factor (CF)	< 1	1 – 3	3 – 6	> 6	
Pollution Load Index (PLI)	< 1	1—3	3—4	4—5	> 5

$$CF = \left(\frac{C_{metal}}{C_{background}} \right) \tag{3}$$

where C_{metal} and $C_{background}$ are the concentrations of metals analysed in sediment and the geochemical background values of metals, respectively. Contamination factor risk classification is provided in Table 1 (Hakanson 1980). Associated with CF values are the calculations of the pollution load index (PLI)

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \cdots \times CF_n} \tag{4}$$

where CF is the contamination factor measured and *n* the number of metals analysed.

An ecological risk (Er) assessment analyses the potential effect of metals in sediment on organisms in the marine environment (Hakanson 1980). Equations 5 uses a toxicity coefficient, the toxic-response factor for a given substance (Tr) and contamination factor (CF) to determine the potential ecological risk index (Ri) (Eq. 6).

$$Er = Tr \times CF \tag{5}$$

$$Ri = \sum Er \tag{6}$$

The toxicity coefficients for the respective metals are Cu = 5, Ni = 5, Pb = 5, Cd = 30, Zn = 1, Cr = 2 and Co = 2 (Hakanson 1980).

Microplastics analyses

Sediment samples collected for metal analyses were used for MP extraction and digestion, and we used the methods adopted from GESAMP (2019). Briefly, samples were stored at -20 °C until extraction. Sediment samples were allowed to thaw to room temperature and placed in an oven at 50 °C for 24 h. Dried sediment was weighed, to which a hypersaline solution (359 g NaCl/L MilliQ water) was added and the sample stirred vigorously for two minutes and allowed to settle. The supernatant was extracted, and the process repeated again twice. The supernatants were filtered onto 20-µm nylon mesh and stored in pre-cleaned petri dishes until microscopic identification was done. MPs were identified and classified based on type, colour and size (GESAMP 2019) using a Zeis stereo microscope with magnifications set to × 20, depending on the field of view required to identify MPs. Polymer identification using spectroscopy (PerkinElmer Two ATR-FTIR spectrometer) was done following the methods of Sparks et al. (2021). Spectral wave numbers ranged from 4000 to 450 cm^{-1}, resolution set to 4 cm^{-1}, data interval set to 1 cm^{-1} and scans set to 10. A background scan was done before starting FTIR scans, and the ATR crystal was cleaned between scans. The minimum size limit of MPs analysed was set at 500 µm. Polymer identification was done by comparing spectral scans with the ST Japan Library and a Perkin spectral library provided by the supplier (Perkin Elmer). Identification of APPs were confirmed once MP fragments were identified by FTIR analyses.

Microplastics indices were applied in a similar manner as metals in order to provide comparative assessments of the potential effects of MPs, with risk categories presented in Table 1. The MPs contamination factor (MPCF) assesses the concentrations of MPs ($C_{microplastic}$) compared to background concentrations

$$MPCF_i = \left(\frac{C_{microplastic}}{C_{baseline}} \right) \tag{7}$$

where the $C_{baseline}$ value selected was the average microplastics sediment concentration for site 6 (control site) as there are no historic values for the region, and this method is considered acceptable (Kabir et al. 2021). Microplastic pollution index (MPPLI) calculations were similar to that of metals

$$MPPLI_{site} = \sqrt[2]{MPCFrXMPCFi} \quad (8)$$

where MPCFr and MPCFi were MPCFs for fragments and filaments, respectively. The chemical toxicity of polymers was analysed based on the method by Lithner et al. (2011), where hazard scores are assigned to polymer types to assess the risk of polymers

$$H_i = \sum P_n \times S_n \quad (9)$$

where H_i is the calculated polymer risk index, P_n the ratio of a polymer type recorded at a site and S_n the polymer hazard score assigned by Lithner et al. (2011). The pollution risk index (PRI) is calculated as follows

$$PRI_i = \sum H_i \times MPPLI_{site} \quad (10)$$

where PRI_i indicates the ecological hazard of polymers when associated with the polymer risk index (H_i).

Quality controls of MP analyses

MP quality control/assurance of sediment samples were absent in field sampling as QA protocols were not set when sampling took place. We acknowledge that the results reported may include MP contamination (mainly filaments) from sampling error. However, given the low filament MP concentrations in samples from site 1 to 4, we assume that field contamination was minimal. In the laboratory, we controlled for airborne contamination by placing empty wet petri dishes on workbenches for the duration of all laboratory work. These positive controls were checked at the start and end of each day and any contamination recorded. A total of six fibres were recorded and the data adjusted accordingly. Blanks (negative controls) were included in all sample filtrations and no MPs contamination reported. As far as possible, no plastic items were used in the laboratory, all glassware and items used were rinsed three times with MilliQ ultra-pure water. MilliQ water was used to make up all solutions used (e.g. hypersaline solutions). Petri dishes were kept closed at all times and only opened when being processed under the microscope to record MPs. Extraction efficiencies were done by filtering known quantities of filaments and fragments. Efficiencies were 90% for filaments and 96% for fragments.

Data analyses

Data were analysed to test significant differences in metal and MP concentrations between sites. Metal data in most cases met the assumptions for parametric analyses and analysed using ANOVAs, using Dunnett's t post hoc analysis to report significant difference in metal concentrations at sites to that of site 6 (control site). Metal data are expressed as mean ± standard error of the mean (SEM) concentrations and MP data reported as median concentrations. The data for MPs did not meet assumptions for parametric analyses and subsequently, Kruskal–Wallis (KW) tests used to determine differences in MP concentrations between sites. MP data are expressed as counts per Kg sediment. Significant values for all analyses were set at $p < 0.05$.

Results and discussion

Metals and antifouling paint particles

Mean concentrations of metals and metalloids in sediment for all sites ranged between 0.25 and 32228 µg/g dry weight, for Cd and Fe, respectively. The maximum concentrations for sediment metals ranged from 0.55 µg/g (Cd) to 18062 µg/g (Al) (see combined sediment metal data in Table 2). Ten (Cr, Ni, Cu, Zn, As, Se, Cd, Sb, Hg and Pb) of the metals presented are listed amongst the priority metal pollutants by the US EPA (US EPA 2014), of which some are extremely toxic and can effect toxicity even at low concentrations under certain conditions (Fatoki and Mathabatha 2001). The levels at which essential metals, especially Fe (up to 55102.85 µg/g) and Cu (up to 3673.88 µg/g) found in the sediment samples, are also cause for concern. Although essential metals (Mn, Zn, Fe and Cu) have valuable roles in biological processes of marine organisms, they are required at low concentrations and occur naturally in the marine environment (Rubal et al. 2014). The elevated concentrations of essential metals, coupled with the anthropogenic release of toxic non-essential metals (Hg, As, Cr, Cd and Pb amongst others) into the marine environment, pose a threat to the proper functioning of marine ecosystems (Zhang et al. 2020; Franco-Fuentes et al. 2021), and this may also be the case in Simon's Town. The general trend observed in this study was the decrease in metal concentrations with increased distance to site 1 (see Co, Cu, Zn, Sr, Mo, Cd, Sn and Ba). However, some metal concentrations were higher at sites 3 (Cr, Mn, Fe, Ni and As) and 5 (B, Al, Se, Hg and Pb) (Table 1) which corresponded to the presence of a storm water pipe (Fig. 1). Respective metal concentrations (for sediment only) that were significantly higher than site 6 are underlined in Table 2.

Increased anthropogenic activities have resulted in essential metals reaching levels that are toxic to marine organisms (Hudspith et al. 2017; Zhang et al. 2020). This is evident in metal concentrations analysed in MPs from sites 1 and 3, where all measurements were higher than metals in sediment by orders of magnitude for Cu (×59), Zn (×43), Ba (×33), Sn (×26), Pb (×11) and Cr (×10) (Table 2). Boatyards and marinas are potential sources of metals in sediment due to

Table 2 Metal concentrations (µg/g dry weight) in sediment and paint from sites 1, 3, 5 and 6 in Simon's Town, Cape Town. Data underlined indicates significance differences in sediment metals from site 6. Data in bold and italics indicate values that are higher than recommended guidelines values (see Table 4 for guideline values - threshold effects level)

Metal	Sediment (sites 1, 3, 5 and 6 combined)				APPs (sites 1 and 3 combined)				Sediment (sites 1, 3, 5 and 6)							
									1		**3**		**5**		**6**	
	Mean	SEM	Min	Max	Mean	SEM	Min	Max	Mean	SEM	Mean	SEM	Mean	SEM	Mean	SEM
B	20.85	3.52	5.34	40.75	43.77	7.79	26.57	69.65	21.56	3.61	18.45	1.51	37.41	2.64	5.98	0.48
Al	12271	1062	7383	18062	21385	2198	16227	27607	11802	553	12311	522	17362	543	7607	122
V	23.09	1.78	17.27	33.85	56.57	3.19	45.96	68.08	19.94	1.13	22.11	1.64	32.63	0.66	17.68	0.23
Cr	***55.5***	12.07	9.33	124.99	***555***	99.43	325.23	872.66	***70.06***	5.87	***112.62***	6.58	29.57	2.47	9.77	0.25
Mn	196.79	46.42	57.95	544.02	281.13	77.27	114.52	534.91	179.05	14.75	440.25	63.97	60.17	1.48	107.69	2.38
Fe	32228	4024	18,295	55,102	80873	19341	37648	133934	39064	2543	50340	2381	20691	368	18815	291
Co	11.01	3.77	2.09	39.2	22.13	2.6	15.14	30.88	31.92	3.72	7.18	0.75	2.72	0.19	2.23	0.08
Ni	***21.01***	4.31	6.67	49.63	***93.15***	18.59	47.22	150.14	***33.23***	8.20	***34.52***	2.79	9.25	1.11	7.04	0.19
Cu	***1129***	407.41	23.99	3673	***66763***	13082	35891	104672	***3369***	163.31	***988.42***	43.07	***130.36***	4.17	***28.85***	2.45
Zn	***1047***	294.87	67.45	2483	***44910***	1500	39704	50021	***2326***	119.53	***1658***	19.78	***135.93***	2.58	70.15	1.86
As	**12.02**	0.47	9.87	14.68	***24.15***	4.74	12.9	38.51	***11.78***	1.19	***12.96***	1.03	***12.90***	0.29	***10.45***	0.38
Se	0.38	0.05	0.21	0.67	0.85	0.06	0.69	1.09	0.28	0.03	0.37	0.01	0.64	0.02	0.22	0.01
Sr	426.25	76.55	42.18	790.07	565.87	109.4	316.23	886.9	742.85	42.48	421.47	32.56	496.90	17.23	43.80	1.32
Mo	10.26	3.07	0.65	28.34	41.06	1.97	34.82	45.63	25.04	1.65	13.45	3.12	1.89	0.15	0.66	0.01
Cd	0.25	0.05	0.04	0.55	***2.16***	0.72	0.52	4.13	0.48	0.03	0.22	0.01	0.24	0.04	0.05	0.00
Sn	***65.98***	15.43	10.45	149.78	***1707***	557.4	464.8	3225	***128.98***	11.02	***93.94***	24.88	***13.64***	1.81	***27.34***	2.16
Sb	4.01	0.9	1.5	10.53	44.72	7.47	21.81	65.77	8.75	0.93	2.00	0.29	3.57	0.94	1.71	0.14
Ba	367.85	142.24	33.86	1289.25	12194	703.71	10668	14721	1178	55.63	165.57	7.84	91.96	6.34	35.76	1.30
Hg	***0.36***	0.12	0.02	1.18	***0.55***	0.1	0.33	0.8	***0.25***	0.03	0.13	0.01	***1.05***	0.07	0.02	0.00
Pb	***111***	19.8	42.96	199.74	***1202***	116.55	908.24	1483	***151.12***	23.89	***56.80***	4.39	***193.98***	4.25	***43.17***	0.19

Underlined values are to indicate significant differences from site 6

Bold and italics values indicate above recommended concentrations

the presence of APPs (Soroldoni et al. 2018a, b). The metals in APPs are probably a source of contamination that contributed to elevated sediment metals reported at sites sampled (Table 3). Once released into the water column, APP transport is affected by hydrodynamic factors such as advection, resuspension, bioturbation and suspension (Turner 2010; Soroldoni et al. 2017, 2018a). Metals from APPs are more likely to leach into the environment and be sources of bioavailable metals (in higher than usual concentrations) to coastal invertebrates (Turner 2010; Soroldoni et al. 2017). APP prevalence was highest at site 1 (Fig. 2), a slipway adjacent to a boating maintenance facility at the marina in Simons Town (see Fig. 1). Boating maintenance activities observed included the sanding of hulls of vessels, and small paint particles were evident in streams running from the facility into the marina. Of the metal data available for sediment quality guidelines, metal concentrations in sediment sampled (mean for all sites) were above recommended guideline concentrations (see values in bold and italics in Table 2 and threshold effect levels in Table 4).

Enrichment factors were low for most elements at all sites (Table 3), but high enrichment (> 5) was recorded for Mn at site 5. The geoaccumulation index (I_{geo}) isolates anthropogenic pollution and used as an indicator to assess the presence and level of anthropogenic contamination in sediment (Barbieri 2016). Geoaccumulation index values generally decreased from sites 1 to 6. Based on the classification system by Müller (1979), $I_{geo} > 2$ are considered high risk and polluted, and these values (> 2) reported were recorded for Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Hg and Pb (Table 3). Average I_{geo} values at respective sites were as follows: site 1 = 2.6, site 3 = 2 (moderate pollution risk), sites 5 and 6 = 1.3, respectively (low pollution risk), and site 6 = -0.04 (not polluted). Site 6 risk category of not polluted further supports this site as a control site for data analysis comparisons with site 1 (impact site).

Contamination factors provide an index of the quality of sediments at sites (Tomlinson et al. 1980). Contamination factor values > 3 (high risk, Category III) (Hakanson 1980) at all sites were recorded for Co, Ni, Cu, As, Se, Mo and Pb (Table 3). The metals classified as high risk contamination at sites 1, 3 and 5 were recorded for Ni, Zn, Sr, Cd and Hg. The pollution load index (PLI) assesses the level of metal pollution, and values > 3 indicate moderate pollution risk and values > 5 indicate dangerous pollution risks (Hakanson

Table 3 Indices of sediment metal contamination in Simon's Town: enrichment factor (EF), geoaccumulation index (I_{geo}), contamination factor (CF), pollution load index (PLI), ecological risk factor (Er) and ecological risk index (Ri). Values in bold indicate risk index categories III and greater (ie. high risk and greater). See Table 1 for risk category values

Metal	Enrichment Factor (EF)				Geoaccumulation Index (I_{geo})				Contamination Factor (CF)				Ecological Risk Factor (Er)			
	Site 1	Site 3	Site 5	Site 6	Site 1 (mean)	Site 3 (mean)	Site 5 (mean)	Site 6 (mean)	Site 1	Site 3	Site 5	Site 6	Site 1	Site 3	Site 5	Site 6
B	1.29	1.07	1.55	0.56	-1.32	-1.52	-0.5	-3.14	0.62	0.53	1.10	0.20				
Al	**Reference element**				-1.67	-1.61	-1.11	-2.30	0.47	0.49	0.70	0.30				
V	0.47	0.45	0.43	0.34	-0.59	-0.45	0.12	-0.76	1.00	1.11	1.60	0.90				
Cr	0.24	0.15	0.83	1.09	0.41	1.10	-0.84	-2.43	2.00	3.22	0.80	0.30	4	6	2	1
Mn	2.27	0.99	**9.82**	2.41	-2.84	-1.57	-4.41	-3.57	0.21	0.52	0.10	0.10				
Fe	0.12	0.10	0.33	0.16	1.40	1.77	0.49	0.36	3.99	5.14	2.10	1.90				
Co	0.00	0.02	0.08	0.04	**6.13**	**3.98**	**2.59**	**2.31**	**106**	**23.9**	**9.10**	**7.40**	**213**	48	18	15
Ni	0.03	0.03	0.15	0.09	**3.39**	**3.52**	1.61	1.23	**16.62**	**17.2**	**4.60**	**3.50**	**83**	**86**	23	18
Cu	0.00	0.00	0.02	0.04	**9.13**	**7.36**	**4.44**	**2.25**	**842.3**	**247**	**32.6**	**7.20**	**4212**	**1236**	**163**	36
Zn	0.00	0.00	0.08	0.07	**6.60**	**6.11**	**2.50**	1.55	**145.4**	**103**	**8.50**	4.40	**145**	**104**	8	4
As	0.04	0.04	0.05	0.03	**2.96**	**3.10**	**3.10**	**2.80**	**11.78**	**12.9**	**12.9**	**10.4**				
Se	0.09	0.07	0.05	0.07	1.89	**2.28**	**3.09**	1.58	**5.63**	**7.30**	**12.8**	**4.50**				
Sr	0.01	0.02	0.03	0.14	**4.63**	**3.80**	**4.05**	0.54	**37.14**	**21.1**	**24.8**	2.20				
Mo	0.00	0.01	0.07	0.09	**6.38**	**5.41**	**2.65**	1.15	**125.2**	**67.2**	**9.50**	**3.30**				
Cd	0.03	0.07	0.09	0.18	**3.41**	**2.31**	**2.38**	0.20	**16.07**	**7.47**	**8.00**	1.70	**482**	**224**	**240**	52
Sn	0.02	0.04	0.32	0.07	**3.83**	**3.25**	0.57	1.59	**21.50**	**15.7**	2.30	**4.60**				
Sb	0.08	0.38	0.34	0.27	1.94	-0.20	0.57	-0.40	**5.84**	1.34	2.40	1.10				
Ba	0.23	1.73	4.42	4.95	0.43	-2.40	-3.25	-4.61	2.03	0.29	0.20	0.10				
Hg	0.06	0.12	0.02	0.50	**2.43**	1.46	**4.54**	-1.28	**8.23**	**4.18**	**34.9**	0.60				
Pb	0.02	0.06	0.03	0.05	**3.81**	**2.43**	**4.21**	**2.04**	**21.59**	**8.11**	**27.7**	**6.20**	**108**	41	**139**	31
PLI									**9.22**	**6.07**	**3.80**	**1.50**				
Ecological Risk Index (Ri)													**5247**	**1744**	**593**	**156**

Values in bold indicate in this table indicate values in Risk categories III and higher

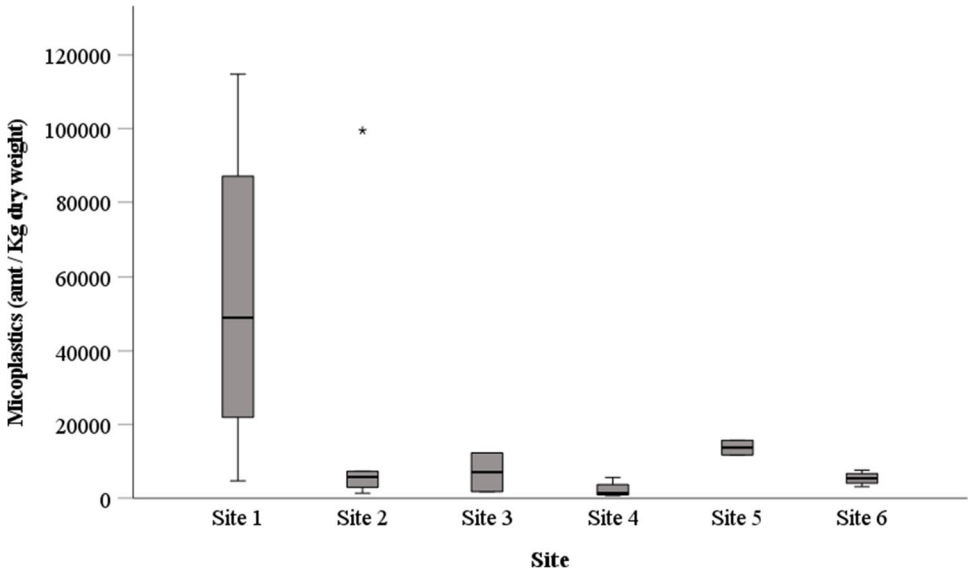

Fig. 2 Boxplot of median of microplastics abundance (counts per kg dry weight) in sediment from 6 sites in Simons Towns, Cape Town, South Africa

1980). The PLI risk category values decreased from sites 1 to 6 as follows: site 1 (9.2), site 3 (6.1), site 5 (3.8) and site 6 (1.5). The ecological risk factor (Er) (data only for selected metals) provides a pollution index associated with the potential ecological risk for particular metals (Hakanson 1980) (see Table 1 for risk categories). The Er for the seven metals analysed was > 80 (high risk, Category III) for Co (site 1), Ni (site 1 and 3), Cu (site 1, 3 and 5), Zn (sites 1 and 3), Cd (sites 1, 3 and 5) and Pb (sites 1 and 5). Finally, the potential ecological risk index (Ri) measures the summative ecological risks factors (Er) (Hakanson 1980). The general pattern observed for both Er and Ri was a decrease from site 1 to 6. The results obtained from all sediment indices measured indicated that site 1 was most contaminated with metals and posed the highest ecological risk and site 6 posing the lowest ecological risk. The high Ri values at sites 1 and 3, together with the metals analysed in paints from sites 1 and 3 (Table 2), indicate the detrimental effect that metals associated with APPs poses. The lower Ri values at site 5 (mouth of a storm water pipe) further support this postulation and may even suggest that areas adjacent to boatyards pose higher ecologic risks than storm water systems.

Microplastics

Microplastic (MP) analyses of sediments at the six sites sampled indicated MP concentrations were highest at site 1 (Fig. 2). For all sites combined, the median MP abundance was 5769 MPs / Kg dry weight. Median MP concentrations for the respective sites, from highest to lowest, were 49047 (site 1), 13710 (site 5), 7033 (site 3), 5769 (site 2), 5383 (site 6) and 1374 MPs / Kg dry weight (site 4). Site 1 was situated at a slipway of a boatyard and boating maintenance facility, which probably accounts for the high MPs recorded there. There were, however, no significant differences in MP concentrations between sites (KW = 11.1, p = 0.05). The low p value could suggest a type II error as evident from the high MP concentrations at site 1, and we consider MP concentrations at site 1 to be significantly higher than other sites sampled (Fig. 2). Only filaments and fragments were recorded at all sites sampled, and fragments were predominantly APPs (fragment prevalence for all sites = 89%), with the highest prevalence recorded at site 1 (Fig. 3a). Sites 1 to 4 were situated in the sheltered area of the marina, in close proximity to the boatyard, which could account for the higher prevalence APPs at these sites. Site 5 was directly in front of a storm water pipe (see Fig. 1) and site 6 at an open beach that is an area used for bathers that could have accounted for the higher prevalence of filamentous MPs at these sites.

Blue was the dominant colour recorded for filaments at sites 3 and 5 (Fig. 3b) and for fragments, red was most prevalent at site 2, black at site 3 and blue at sites 5 and 6 (Fig. 3c). Filament MP sizes varied across sites (Fig. 3d) with smaller MP filaments (< 1 mm) recorded at sites 1 to 3 and sites 4 to 6 were mainly larger than 2 mm. Fragments were generally smaller than 0.5 mm for all sites, with higher concentrations of MPs 2 to 5 mm in size at site 2 (Fig. 4e), further confirming the presence of APPs at the sites sampled.

We processed 10% of MPs counted for FTIR analyses and confirmed that 95% of MPs analysed were polymers (the remaining 5% were all cotton filaments). For all sites combined, the main polymers recorded were polyvinyl acetate (PVA) (36%), polyethylene terephthalate (PET 25%) and epoxy resin (18%) (Fig. 4a). The remainder polymers were unsaturated polyesters (UP) (9%), polymethyl methacrylate (PMMA) (5%) with ethylene vinyl acetate (EVA), polyamide-nylon (PA) and polyacrylonitrile (PAN) each comprising 2%. Filaments were mainly PET (44%) and UP (25%), with

Table 4 Range and mean (± SEM) concentrations (µg/g) of commonly monitored priority metals around the world in comparison with this study

Country	Location	Cr	Ni	Cu	Zn	As	Se	Sb	Cd	Hg	Pb	References
Australia	Kogarah Bay	6.6–91	1.3–28	4.8–100	10.6–433	1.5–27	-	-	-	-	5.4–235	(Alyazichi et al. 2015)
		33	12	36	158	12	-	-	-	-	87	
Egypt	Hurghada Coast	-	0.02–72	0.05–23	0.01–49	-	-	-	0.03–0.68	0–0.66	0.01–9.83	(Mansour et al. 2013)
		-	7.21	4.57	12.41		-		0.11	0.02	1.15	
Argentina	Rosales Port	9.1–19	8.2–12	19.3–43	46.5–111	-	-		0.04–0.11		6.8–11	(Simonetti et al. 2017)
		14.82	10.33	31.32	78.82	-	-		0.07		9.97	
Portugal	Cavado estuary	20.2	9.4	54.9	94	6.1	-		0.13	-	30.3	(Gredilla et al. 2015)
India	Bay of Bengal	1.6–6.3	0.3–5.2	0.1–6.4	0.01–6.2	0.14–2.0	0.55–6.4	-	0–1.14	0.01–0.9	0.01–1.05	(Arisekar et al. 2021)
Brazil	Costa Verde	49.2	19.8	56.8	223.6	-	-	-	2.0	-	19.8	(de Souza et al. 2021)
Mozambique	Northern Coast	1.7–26	< 5.0–17	0.12–23	< 1.0–34	< 0.5–7.6	-	-	< 0.1–0.22	-	< 1.0–57	(Boitsov et al. 2021)
South Korea	Busan	71.2	25.8	321	322	12.6	-	1.7	0.46	0.20	67.4	(Jeong et al. 2020)
South Korea	Busan	58.6	24.4	35.6	130	9.5	-	0.9	0.19	0.07	32.4	(Jeong et al. 2020)
Bahrain	Bahrain	25–71	16.6–42	10.7–213	25–239	2.77–10	-	-	< 0.08–0.75	< 0.03–0.54	3.69–277	(Bersuder et al. 2020)
South Africa	Simons Town	9.3–125	6.7–49.6	24–3674	67–2483	9.9–14.7	0.2–0.67	1.5–10.5	0.04–0.55	0.02–1.18	43–199.7	This study
		55.5 ± 12	21.0 ± 4.3	1129 ± 407	1047.8 ± 295	12 ± 0.47	0.38 ± 0.05	4.01 ± 0.9	0.25 ± 0.05	0.36 ± 0.12	111 ± 19.8	
Sediment Quality Guidelines values in µg/g												
LEL		26	16	16	120	6	-	-	0.6	0.2	31	(Persaud et al. 1996)
TEL		52.3	15.9	18.7	124	7.24	-	-	0.68	0.13	30.2	(Macdonald et al. 1996)
ERL		81	20.9	34	150	8.2	-	-	1.2	0.15	46.7	(Long et al. 1995)
PEL		160	42.8	108	271	41.6	-	-	4.21	0.7	112	(Macdonald et al. 1996)
ERM		370	51.6	270	410	70	-	-	9.6	0.71	218	(Long et al. 1995)
SEL		110	75	110	820	33	-	-	10	2	250	(Persaud et al. 1996)
TET		100	61	86	540	17			3	1	170	(Macdonald et al. 2000)
Average Background		35	2	4	16	1	0.05	1.5	0.03	0.03	7	(Turekian and Wedepohl 1961)

LEL = Lowest effect level; TEL = Threshold effects level; ERL = Effects range-low; PEL = Probable effect level; ERM = effect range-median; SEL = Severe effect level; TET = Toxic effect threshold

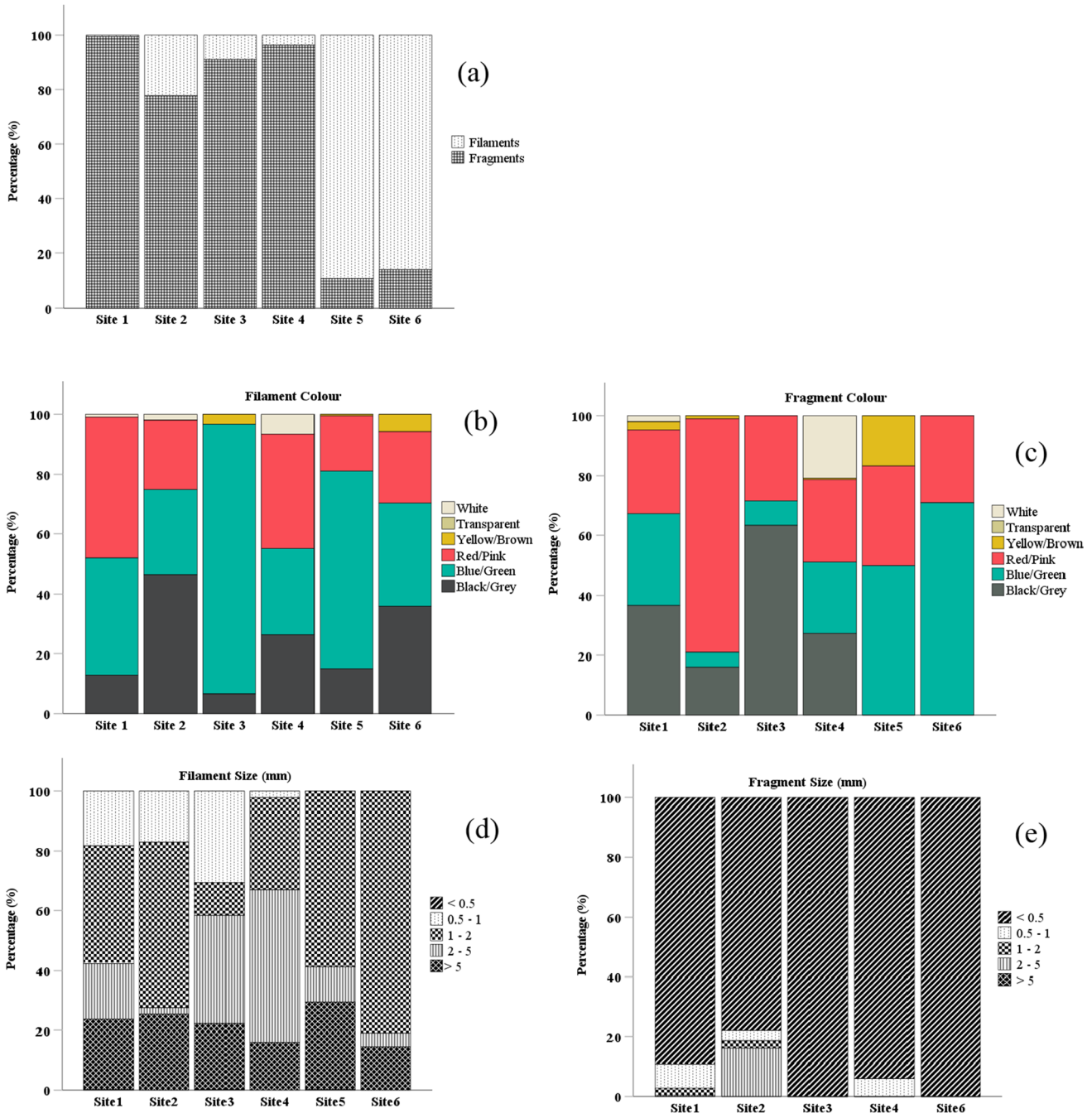

Fig. 3 Percentage characteristics of MPs at 6 sites in Simon's Town based on filaments and fragments (a), filament colour (b), fragment colour (c), filament size (d) and fragment size (e)

fragments mainly comprising PVA (50%) and epoxy resins (29%) (Fig. 4b). Fragment polymer identification for sites 1, 2 and 4 indicated that PVA (site 1), EVA (site 2) and epoxy resins (site 4) were the main polymers types present (Fig. 4c). Filaments were predominantly PET (Fig. 5) at sites 1 and 6, PVA at site 3 and PA at site 5 (Fig. 4c). Site 2 filaments were 50% PAN and UP, and site 4, 33.3% PET, PVA and UP, respectively.

Our research provides a first account in South Africa of the prevalence of MP fragments that are predominantly APPs in an enclosed area adjacent to a boating maintenance facility. MPs were present in every sample and were higher at potential sources of MPs, as more filaments were recorded close to a storm water pipe and fragments recorded close to a boating maintenance facility. Although Simon's Town is in a low populated area with minimal

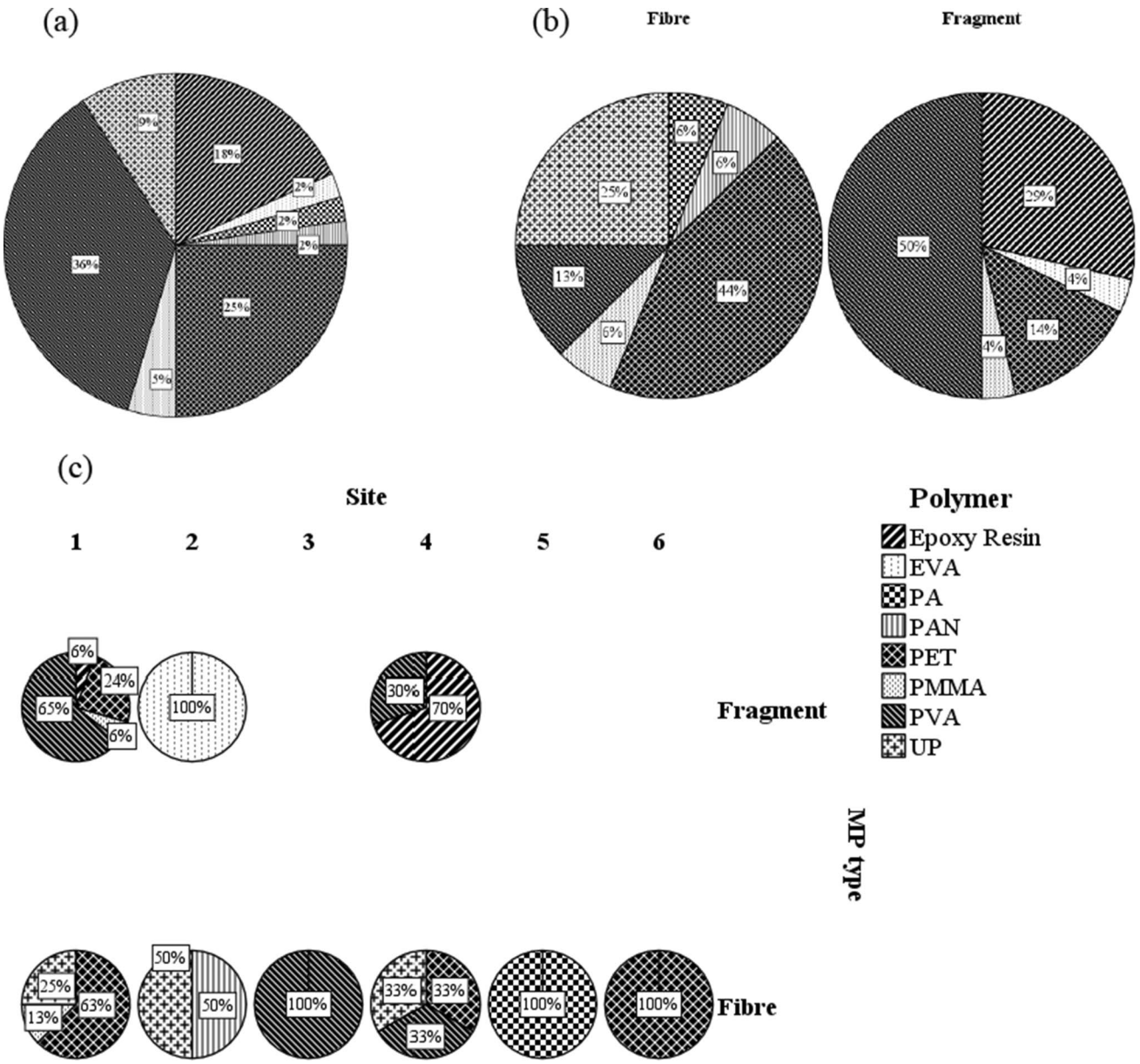

Fig. 4 Pie charts indicating percentage polymer types for all sites (a), filaments and fragments for all sites (b) and filaments and fragments per site (c)

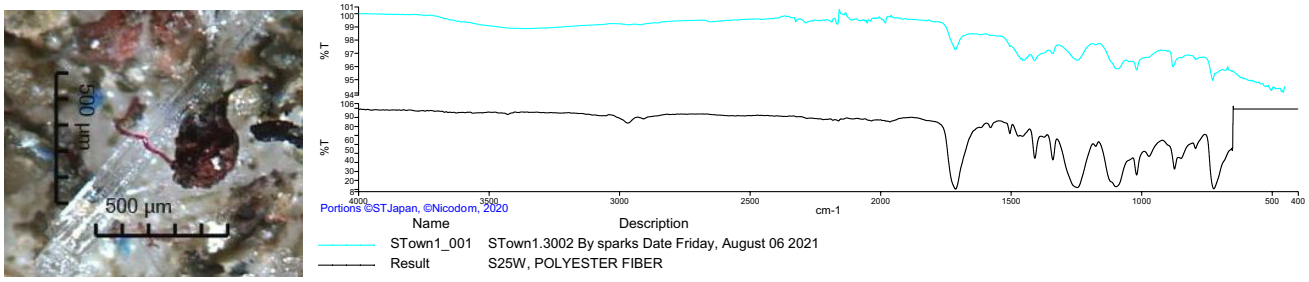

Fig. 5 Selected example of an FTIR scan and picture of a filamentous MP

potential sources of anthropogenic inputs (no major riverine input, no major industrial activities and low commercial maritime activities), we are able to demonstrate that localised sources of MP have the potential to have an effect on coastal ecosystems (see Tables 1 and 3 for risk analyses). The high filamentous MP concentrations and high PLI at site 5 (Fig. 6a) are causes for concern as filamentous MP polymers are considered a greater risk for marine organisms than other types of MPs (Qiao et al. 2019). Polymer and pollution risk indices displayed similar trends (Fig. 6b and c), with the sequence for the pollution risk index from highest to lowest at sites as follows: 4 > 1 > 2 > 5 > 6 > 3. The high H and PRI values at site 4 are of interest as site 4 was also the site with the lowest PLI. This demonstrates the effect of polymer type on the risks posed by MPs as site 4 recorded the lowest MP concentrations of all the sites sampled (Fig. 2), yet poses the highest pollution risk. At site 4, we recorded 96% of MPs analysed as fragments and MP polymer types for the fragments were epoxy resins (70%) and PVA (30%), which then suggests that APPs from the nearby boating facility could be posing a considerable risk to the rocky shore ecosystem in the marina.

The results reported here provide evidence that APPs from boatyards are sources of MPs to ambient environments. Antifouling paint particles are classified as MPs as these are mainly comprised of polymers and co-polymers such as alkyls, epoxies and polyesters (Zhou 2015). These polymers end up as MPs stemming from maintenance of maritime vessels (eg sandblasting) and are categorised as highly toxic to organisms (Lithner et al. 2011). APPs have shown to comprise significant proportions of MPs in areas close to boatyards (Galafassi et al. 2019) that may be translocated to areas where they are taken up by aquatic biota. In areas with poor circulation (such as marinas and harbours), chemicals sorbed onto APPs (eg metals, biocides and organic chemicals) can leach and reach toxic levels in the water column, while MPs can also become biofouled and consumed by aquatic biota such as invertebrates (Soroldoni et al. 2018a; Gaylarde et al. 2021). For example, Molino et al. (2019) found that exposing copepods to 0.3 g/L of APPs resulted in 100% death within 88 h, suggesting that APPs from boating maintenance facilities have toxic effects on copepod communities surrounding boatyards, with similar

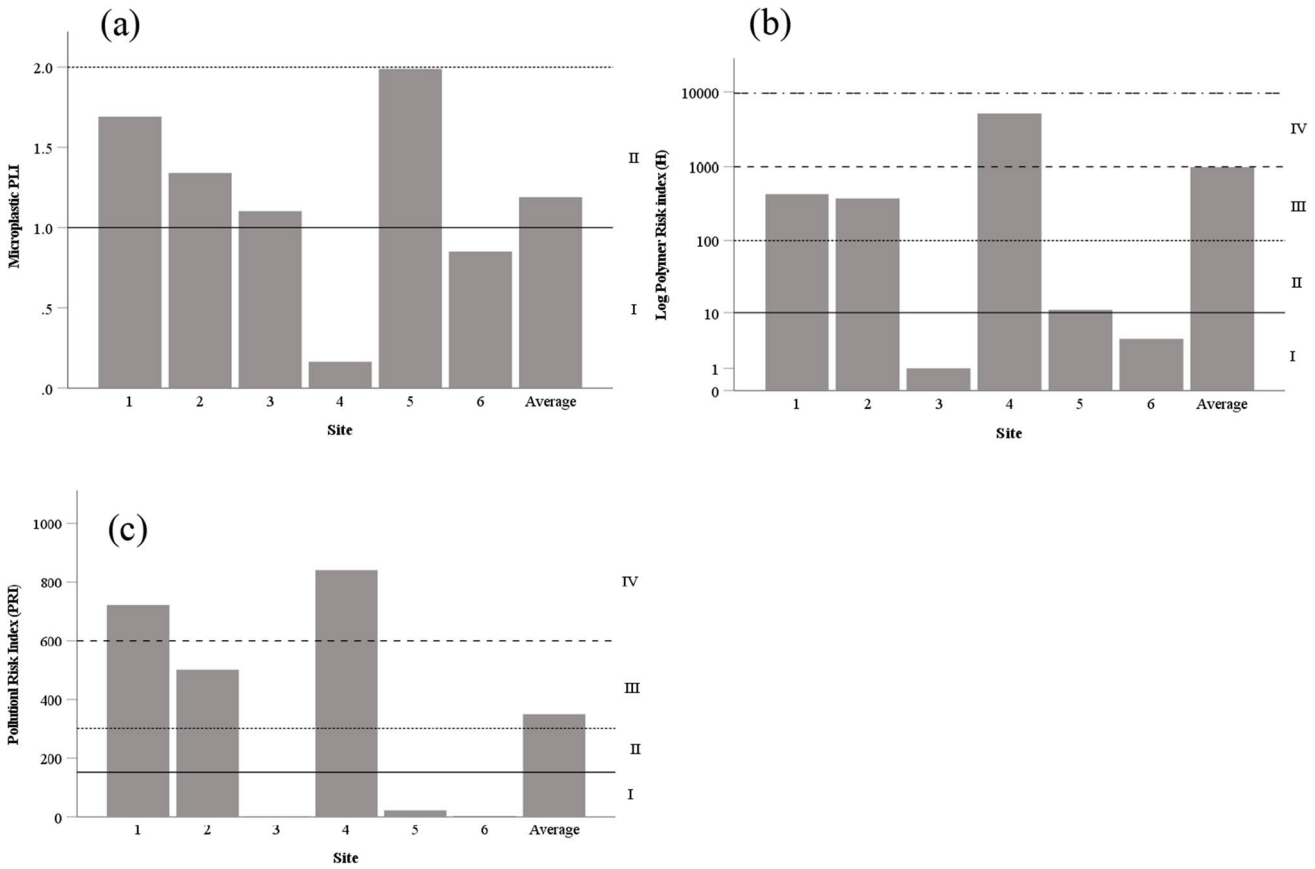

Fig. 6 Pollution load index (a), log polymer risk index (b) and pollution risk index (c) of microplastics sampled in sediment at 6 sites in Simon's Town. See Table 4 for categories of indices. Note the log scale for the polymer risk index

results being reported in Brazil (Soroldoni et al. 2017, 2018a; Abreu et al. 2020). In our study, we reported on the risk posed by metals and APPs, but APPs also contain other chemicals such as antifouling booster biocides and organic pollutants, of which the effects are poorly known (Soroldoni et al. 2017; Abreu et al. 2020).

The MP concentrations reported in our study are the highest yet recorded in southern Africa (median MP count was 5769 MPs / Kg dry weight for all sites and 49047 at site 1). Only a single previous report on MPs in Simon's Town sediment was done by de Villiers (2018) who analysed MP filaments in sediment, and recorded 40 filaments per dm^3. Sparks (2020) analysed mussels from Simon's Town for MPs and recorded 13 MPs / mussel. Interestingly, Sparks (2020) reported mainly MP fragments in the mussels processed (the only site out of 27 analysed in Cape Town to have > 80% fragments in mussels), with the predominant (> 80%) size of MPs being smaller than 0.5 mm and blue in colour. The MP loads reported here are still, however, somewhat higher than that reported previously in other parts of South Africa. Nel et al. (2017) recorded MP counts ranging from 86 to 755 MPs / m^2 from 16 beach sites sampled in 2016 along the entire coastline of South Africa, and these values were lower than that recorded by Nel and Froneman (2015), who recorded between 688 and 3308 MPs / m^2 from 21 beaches along the south coast of South Africa. One of the major challenges regarding analysis of MP data (globally) is that sampling, processing and reporting units of MPs vary, and this makes comparisons between sites (and even the same sites) very difficult. These factors are compounded when making comparisons between seasons (rainy and dry for example).

The high MP concentrations reported here are not as high as that reported in some other parts of the world. In an attempt to standardise units, we recorded 9201 MPs / m^2 in Simon's Town, which is lower than that reported elsewhere, such as 124000 MPs / m^2 in Guangdong Province, southern China (Dou et al. 2021), 17645 in Hawaiian beaches (McDermid and McMullen 2004) and 44000 MPs / m^2 in beaches in Jordan (Abu-Hilal and Al-Najjar 2009). Nevertheless, our results indicated that localised sources of contaminants from boatyards and storm water pipes are sources of metals and MPs, and careful consideration is needed when developing monitoring protocols of coastal systems and when attempting to provide management authorities with data regarding the concentrations of contaminants in coastal areas.

Conclusion

Our research provides data of high concentrations of metals and MPs in a sheltered part of a marina in Simon's Town, Cape Town. Waste stemming from boatyards and runoff from storm water systems have the potential to cause localised contamination that may go undetected if not monitored. We clearly demonstrate in this research that boatyards are sources of metal contamination and MP fragments (APPs), and storm water pipes sources of MP filaments, all which pose pollution and ecological risks to the intertidal community in Simon's Town. The high metal and MP concentrations reported here provide a baseline for future studies, and it is evident that there is a need for investigations to focus on the effects of metals and MPs on coastal biota in South Africa.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-022-18890-z.

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Authors' contributions Conrad Sparks did conceptualisation, funding acquisition, methodology, investigation, supervision, writing—review and editing. Adetunji Awe performed methodology and writing—review and editing.

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Data availability Base data used in the present research are provided as a CSV file. Further data are available on request.

Declarations

Ethical approval Not Applicable

Consent to participate Not Applicable

Consent for publication Not Applicable

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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