Concentrations and Risk Assessment of Metals, Antifouling Paint Particles and Microplastics in Coastal Sediment of a Marina in Simon’s Town, South Africa

Conrad Sparks (sparksc@cput.ac.za)  
Cape Peninsula University of Technology  https://orcid.org/0000-0001-9721-3544

Adetunji Awe  
Cape Peninsula University of Technology

Research Article

Keywords: Microplastics, antifouling paint particles, metals, sediment, risk index

Posted Date: November 2nd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-982346/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Concentrations and risk assessment of metals, antifouling paint particles and microplastics in coastal sediment of a marina in Simon’s Town, South Africa

Conrad Sparks* and Adetunji Awe

Department of Conservation and Marine Sciences, Cape Peninsula University of Technology, Cape Town, South Africa

*Corresponding author: sparks@cput.ac.za

Abstract

Maintenance of maritime vessels includes the removal of paint from hulls that ultimately ends up the aquatic environment. Coastal maritime vessel maintenance is a source of metals, antifouling paint particles (APPs) and microplastics (MPs) that ends 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 boat maintenance facility). 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 protected marina. Sediment samples were collected from 6 sites during winter 2018. Sediment and extracted APPs were analysed for metal content and MPs characterised based on type (visual and polymer), colour and size. Metal and MP fragment concentrations were highest at the slipway of a boatyard / maintenance facility, decreasing with increased distance from the slipway. MP filaments were highest close to the storm water outfall pipe. Our results suggest that boating maintenance facilities are potential sources metals and MP APP fragments, with storm water pipes potential sources of MP filaments. Various indices applied to assessed the potential impacts of metals and MPs, suggests that these contaminants have the potential to severely adversely impact the intertidal ecosystem investigated.
Keywords: Microplastics, antifouling paint particles, metals, sediment, risk index

Introduction

Coastal maritime activities are increasing globally and the increase in vessels at sea has resulted in an increase in demand for vessel 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 Van 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 ecosystems (Soroldoni et al. 2018).

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 utilised 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 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
However, toxic effects associated with these “newly” developed antifouling booster biocides that include zinc pyrithione (ZnPT), copper pyrithione (CuPT), Irgarol 1051, Diuron, Chlorotalonil, Dichlofuanid, (1,3-Benzothiazol-2-ylsulfanyl) methyl thiocyanate (TCMTB), Sea Nine 211 and 4,5-Dichloro-2-octyl-4-isothiazolin-3-one (DCOIT) amongst others, in marine organisms 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, 2018; 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 has 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 micro particles 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 the contained toxic 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 becomes imperative.

The occurrence of microplastics (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, has 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 then easily 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 are 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 is 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 as
contaminated by metals as other part of the country, metal concentrations in sediment within False Bay has increase 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 and 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 impact of a boatyard and storm water pipe by assessing the association between sediment metals, APPs and MPs in a marina, 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 km² 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 during summer is dominated by south-easterly winds and in winter by north-westerly winds (Jury et al. 1985). Sea surface temperature (SST) and upwelling events peaking 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.
Six sites were sampled in June 2018 at spring low tide for sediment metal analyses. Site 1 was at the slipway of a shipyard (impact site), 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 (non-impact / control site) (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 were 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. Antifouling paint particles (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 7700x 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.
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

\[
I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)
\]  

(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.

\[
CF = \left( \frac{C_{metal}}{C_{background}} \right)
\]  

(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 \( (PLI) \)

\[
PLI = \sqrt[\text{n}]{CF_1 \times CF_2 \times CF_3 \ldots \times CF_n}
\]  

(4)

where CF is the contamination factor measured and \( n \) the number of samples 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) (Equation 6).

\[ Er = Tr \times CF \]  
\[ Ri = \sum Er \]  

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 hours. 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 x20, depending on the field of view required to identify MPs. Polymer identification using spectroscopy (Perkin Elmer Two ATR-FTIR spectrometer) was done following the methods of Sparks et al. (2021). Spectral wave numbers ranged from 4000 – 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).

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

\[ MPCF_i = \left( \frac{C_{microplastic}}{C_{baseline}} \right) \]  

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

\[ MPPLI_{site} = \sqrt{MPCF_r \times MPCF_i} \]  

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

\[ H_i = \sum P_n \times S_n \]  

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

\[ PRI_i = \sum H_i \times MPPLI_{site} \]
where PRI\textsubscript{i} indicates the ecological hazard of polymers when associated with the polymer risk index (H\textsubscript{i}).

MP Quality Controls

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 lab, we controlled for airborne contamination by placing empty wet petri dishes on workbenches for the duration of all lab work. These positive controls were checked at the start and end of each day and any contamination recorded. A total of 6 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 lab, all glassware and items used were rinsed three times with MilliQ ultra-pure water. MilliQ water was used to make up all solutions used (eg 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 Dunett’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 determined 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 detected metals and metalloids in sediment for all sites ranged
between 0.36 to 32228 µg/g dry weight, for Hg and Fe, respectively. The maximum
concentrations for sediment metals ranged from 0.55 µg/g (Cd) to 18062 µg/g (Al). 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 indicated by being underlined values 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 (APPs) from sites 1 and 3, where all measurements were higher than metals in sediment by orders of magnitude for Cu (x59), Zn (x43), Ba (x33), Sn (x26), Pb (x11) and Cr (x10) (Table 2). The metals in APPs may have been a source of metal contamination that contributed to elevated sediment metals reported in sites sampled. Once released into the water column, APP transport is affected by hydrodynamic factors such as advection, resuspension, bioturbation and suspension (Turner 2010). 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). 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 activity 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).
The potential effect of metals in sediment were assessed using a variety of indices. 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 ($I_{\text{geo}}$) 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) $I_{\text{geo}} > 2$ 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 $I_{\text{geo}}$ 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 indicates moderate pollution risk polluted and values > 5 indicating dangerous pollution risks (Hakanson 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 ecologic 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), indicates the detrimental effect that metals associated with APPs poses. The lower Ri values at site 5 (mouth of a storm water pipe) further supports this postulation and may even suggest that areas adjacent to boatyards pose higher ecologic risks than storm water systems. Further research is needed to assess the ecological and biological effects that elevated metals in sediment potentially poses on coastal communities.

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 protected area of the marina, in close proximity to the boatyard, which could account for the higher prevalence of fragments (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 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 MPs 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 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 Table 1 and 3 for risk analyses). The high filamentous MP concentrations and high PLI at site 5 (Fig. 6a) is cause for concern as filamentous MP polymers are considered a greater risk for marine organisms than other types 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 PLI and PRI values at site 4 is 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 provides evidence that APPs from boatyards are sources of MPs to ambient environments. Non-aqueous paints 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 (e.g. 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 the marina where we sampled sediment), chemicals sorbed onto APP
MPs (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 (Gaylarde et al. 2021). For example, Molino et al. (2019) found that exposing 0.3 g/L of APPs to copepods resulted in 100% death within 88 hours, suggesting that APPs from boating maintenance facilities have toxic effects on copepod communities in surrounding waters of boatyards. In our study, we reported on the risk posed by metals and APPs (as MP polymers) but APPs also contain other chemicals such as antifouling booster biocides and organic pollutants, of which the effects of the latter on marine organisms is poorly known (Soroldoni et al. 2017).

The MP concentrations reported in our study is 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 APP 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 varies, and this makes comparisons between sites (and even at 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 is 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 when attempting to provide management authorities with data regarding the concentrations of contaminants in coastal areas.

**Conclusion**

The impact site we sampled was situated in a protected part of a marina in Simon’s Town, which has a high potential for metals and MPs to accumulate. Waste stemming from boatyards and runoff from storm water systems have the potential 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 poses pollution and ecological risks to the intertidal community in Simon’s Town. The high metal and MP concentrations reported here provides 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.

**Declarations**

**Ethical approval, consent to participate, Consent for publication**

Not Applicable
CRediT authorship contribution statement

Conrad Sparks: Conceptualization, Funding acquisition, Methodology, Investigation, Supervision, Writing – review & editing. Adetunji Awe: Methodology, Writing – review & editing.

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.

Availability of data and materials

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

Funding

This work was funded by the National Research Foundation, South Africa (Funding project reference: Thuthuka TTK190406427888, Grant No: 121970).

Acknowledgements

We thank the Cape Peninsula University of Technology for their support in granting space and facilities for sampling and lab analyses. Mr Siviwe Yuyu is acknowledged for his contribution in sample collection and laboratory work.
References

Abu-Hilal A, Al-Najjar T (2009) Marine litter in coral reef areas along the Jordan Gulf of Aqaba, Red Sea. J Environ Manage 90:1043–1049. doi: 10.1016/j.jenvman.2008.03.014

Ahsanullah M, Florence TM (1984) Toxicity of copper to the marine amphipod Allorchestes compressa in the presence of water-and lipid-soluble ligands. Mar Biol 84:41–45. doi: 10.1007/BF00394525

Alyazichi YM, Jones BG, Mclean E Source identification and assessment of sediment contamination of trace metals in Kogarah Bay, NSW, Australia. doi: 10.1007/s10661-014-4238-z

Amara I, Miled W, Slama R Ben, Ladhari N (2018) Antifouling processes and toxicity effects of antifouling paints on marine environment. A review. Environ Toxicol Pharmacol 57:115–130. doi: 10.1016/J.ETAP.2017.12.001

Amorim ALA de, Ramos JAA, Nogueira Júnior M (2020) Ingestion of microplastic by ontogenetic phases of Stellifer brasilensis (Perciformes, Sciaenidae) from the surf zone of tropical beaches. Mar Pollut Bull 158:111214. doi: 10.1016/j.marpolbul.2020.111214

Arisekar U, Shakila RJ, Shalini R, et al (2021) Heavy metal concentration in reef-associated surface sediments, Hare Island, Gulf of Mannar Marine Biosphere Reserve (southeast coast of India): The first report on pollution load and biological hazard assessment using geochemical normalization factors an. Mar Pollut Bull 162:111838. doi: 10.1016/j.marpolbul.2020.111838

Barbieri M (2016) The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. doi: 10.4172/2381-8719.1000237

Bersuder P, Smith AJ, Hynes C, et al (2020) Baseline survey of marine sediments collected from the Kingdom of Bahrain: PAHs, PCBs, organochlorine pesticides, perfluoroalkyl substances, dioxins, brominated flame retardants and metal contamination. Mar Pollut Bull 161:111734. doi: 10.1016/j.marpolbul.2020.111734

Boitsov S, Newman BK, Muiambo HF, et al (2021) Distribution and possible sources of polycyclic aromatic hydrocarbons (PAHs) and metals in marine surface sediments off northern Mozambique. Mar Pollut Bull 163:. doi: 10.1016/j.marpolbul.2020.111952
Chambers LD, Stokes KR, Walsh FC, Wood RJK (2006) Modern approaches to marine antifouling coatings. Surf Coatings Technol 201:3642–3652. doi: 10.1016/J.SURFCOAT.2006.08.129

Champ MA (2000) A review of organotin regulatory strategies, pending actions, related costs and benefits. Sci Total Environ 258:21–71. doi: 10.1016/S0048-9697(00)00506-4

Chen JC, Chen MY, Fang C, et al (2020) Microplastics negatively impact embryogenesis and modulate the immune response of the marine medaka Oryzias melastigma. Mar Pollut Bull 158:111349. doi: 10.1016/j.marpolbul.2020.111349

de Souza AM, Rocha DS, Guerra JV, et al (2021) Metal concentrations in marine sediments of the Rio de Janeiro Coast (Brazil): A proposal to establish new acceptable levels of contamination. Mar Pollut Bull 165:. doi: 10.1016/j.marpolbul.2021.112113

de Villiers S (2018) Quantification of microfibre levels in South Africa’s beach sediments, and evaluation of spatial and temporal variability from 2016 to 2017. Mar Pollut Bull 135:481–489. doi: 10.1016/j.marpolbul.2018.07.058

Diab A, Minghetti M, Casadei E, et al (2008) Abstracts from Fourteenth International Symposium on Pollutant Responses in Marine Organisms (PRIMO 14) – Heavy metals: Mechanisms of detoxification and mechanisms of toxicity. Mar Environ Res 66:41–46. doi: 10.1016/j.marenvres.2008.02.017

Dou P-C, Mai L, Bao L-J, Zeng EY (2021) Microplastics on beaches and mangrove sediments along the coast of South China. doi: 10.1016/j.marpolbul.2021.112806

Dufois F, Rouaulet M (2012) Sea surface temperature in False Bay (South Africa): Towards a better understanding of its seasonal and inter-annual variability. Cont Shelf Res 43:24–35. doi: 10.1016/J.CSR.2012.04.009

Fatoki OS, Mathabatha S (2001) An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. 27:233–240

Feng L, He L, Jiang S, et al (2020) Investigating the composition and distribution of microplastics surface biofilms in coral areas. Chemosphere 252:126565. doi: 10.1016/J.CHEMOSPHERE.2020.126565

Franco-Fuentes E, Moity N, Ramírez-González J, et al (2021) Metals in commercial fish in the
Galapagos Marine Reserve: Contribution to food security and toxic risk assessment. J Environ Manage 286:112188. doi: 10.1016/j.jenvman.2021.112188

Galafassi S, Nizzetto L, Volta P (2019) Plastic sources: A survey across scientific and grey literature for their inventory and relative contribution to microplastics pollution in natural environments, with an emphasis on surface water. Sci Total Environ 693:133499. doi: 10.1016/j.scitotenv.2019.07.305

Gaylarde CC, Neto JAB, da Fonseca EM (2021) Paint fragments as polluting microplastics: A brief review. Mar Pollut Bull 162:. doi: 10.1016/j.marpolbul.2020.111847

GESAMP (2019) Guidelines for the monitoring and assessment of plastic litter in the ocean (Kershaw P.J., Turra A. and Galgani F. editors), (IMO/FAO/UNESCO-IoC/UNIDO/WMO/IAEA/UN/UNEP/UNDP/ISA Joint Group of Experts on the Scientific Aspects of Marine Environmental Prote. Rep Stud GESAMP no 99:130p

Gong M, Yang G, Zhuang L, Zeng EY (2019) Microbial biofilm formation and community structure on low-density polyethylene microparticles in lake water microcosms. Environ Pollut 252:94–102. doi: 10.1016/J.ENVPOL.2019.05.090

Gredilla A, Stoichev T, Fdez-Ortiz De Vallejuelo S, et al (2015) Spatial distribution of some trace and major elements in sediments of the Cávado estuary (Esposende, Portugal). doi: 10.1016/j.marpolbul.2015.07.040

Hakanson L (1980) An ecological risk index for aquatic pollution control. a sedimentological approach. Water Res 14:975–1001. doi: 10.1016/0043-1354(80)90143-8

Hudspith M, Reichelt-Brushett A, Harrison PL (2017) Factors affecting the toxicity of trace metals to fertilization success in broadcast spawning marine invertebrates: A review. Aquat. Toxicol. 184:1–13

Jeong H, Choi JY, Lim J, et al (2020) Characterization of the contribution of road deposited sediments to the contamination of the close marine environment with trace metals: Case of the port city of Busan (South Korea). Mar Pollut Bull 161:. doi: 10.1016/j.marpolbul.2020.111717

Jury MR (2020) Coastal gradients in False Bay, south of Cape Town: What insights can be gained from mesoscale reanalysis? Ocean Sci 16:1545–1557. doi: 10.5194/OS-16-1545-2020
Jury MR, Kamstra F, Taunton-Clark J (1985) Diurnal wind cycles and upwelling off the northern portion of the Cape Peninsula in summer. http://dx.doi.org/10.2989/025776185784461216 3:1–10. doi: 10.2989/025776185784461216

Kabir AHME, Sekine M, Imai T, et al (2021) Assessing small-scale freshwater microplastics pollution, land-use, source-to-sink conduits, and pollution risks: Perspectives from Japanese rivers polluted with microplastics. Sci Total Environ 768:144655. doi: 10.1016/J.SCITOTENV.2020.144655

Lithner D, Larsson Å, Dave G (2011) Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. doi: 10.1016/j.scitotenv.2011.04.038

Long ER, Macdonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage 19:81–97. doi: 10.1007/BF02472006

Loring DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. ICES J Mar Sci 48:101–115. doi: 10.1093/icesjms/48.1.101

Luna GM, Dell’Anno A, Pietrangeli B, Danovaro R (2012) A new molecular approach based on qPCR for the quantification of fecal bacteria in contaminated marine sediments. J Biotechnol 157:446–453. doi: 10.1016/J.JBIOTEC.2011.07.033

Macdonald DD, Carr RS, Calder FD, et al (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5:253–278. doi: 10.1007/BF00118995

Macdonald DD, Ingersoll CG, Berger T. (2000) Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch Environ Contam Toxicol 39:20–31. doi: 10.1007/sOM440010075

Mansour AM, Askalany MS, Madkour HA, Assran BB (2013) Assessment and comparison of heavy-metal concentrations in marine sediments in view of tourism activities in Hurghada area, northern Red Sea, Egypt. Egypt J Aquat Res 39:91–103. doi: 10.1016/j.ejar.2013.07.004

McDermid KJ, McMullen TL (2004) Quantitative analysis of small-plastic debris on beaches in the Hawaiian archipelago. Mar Pollut Bull 48:790–794. doi: 10.1016/j.marpolbul.2003.10.017

Molino C, Angeletti D, Oldham VE, et al (2019) Effect of marine antifouling paint particles waste on
survival of natural Bermuda copepod communities. doi: 10.1016/j.marpolbul.2019.110492

Muller-Karanassos C, Turner A, Arundel W, et al (2019) Antifouling paint particles in intertidal estuarine sediments from southwest England and their ingestion by the harbour ragworm, Hediste diversicolor * Environ Pollut 249:163–170. doi: 10.1016/j.envpol.2019.03.009

Müller G (1979) Schwermetalle in den Sedimenten des Rheins. Veränderungen seit Umschau 79:778–783

Nel HA, Froneman PW (2015) A quantitative analysis of microplastic pollution along the south-eastern coastline of South Africa. Mar Pollut Bull 101:274–279. doi: 10.1016/j.marpolbul.2015.09.043

Nel HA, Hean JW, Noundou XS, Froneman PW (2017) Do microplastic loads reflect the population demographics along the southern African coastline? Mar Pollut Bull 115:115–119. doi: 10.1016/j.marpolbul.2016.11.056

Neves D, Sobral P, Ferreira JL, Pereira T (2015) Ingestion of microplastics by commercial fish off the Portuguese coast. Mar Pollut Bull 101:119–126. doi: 10.1016/j.marpolbul.2015.11.008

Paradas WC, Amado Filho GM (2007) Are metals of antifouling paints transferred to marine biota? Brazilian J Oceanogr 55:51–56. doi: 10.1590/s1679-87592007000100006

Patti TB, Fobert EK, Reeves SE, da Silva KB (2020) Spatial distribution of microplastics around an inhabited coral island in the Maldives, Indian Ocean. Sci Total Environ 141263. doi: 10.1016/j.scitotenv.2020.141263

Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar Pollut Bull 52:1197–1208. doi: 10.1016/j.marpolbul.2006.02.012

Persaud D, Jaagumagi R, Hayton A (1993) GUIDELINES FOR THE PROTECTION AND MANAGEMENT OF AQUATIC SEDIMENT QUALITY IN ONTARIO. ONTARIO

Pfaff MC, Logston RC, P N Raemaekers SJ, et al (2019) A synthesis of three decades of socio-ecological change in False Bay, South Africa: setting the scene for multidisciplinary research and management. Elem Sci Anthr 7:49. doi: 10.1525/elementa.367

Poulsen R, Gravert TKO, Tartara A, et al (2021) A case study of PAH contamination using blue mussels as a bioindicator in a small Greenlandic fishing harbor. Mar Pollut Bull 171:112688. doi:
Preston-Whyte F, Silburn B, Meakins B, et al (2021) Meso- and microplastics monitoring in harbour environments: A case study for the Port of Durban, South Africa. Mar Pollut Bull 163:111948. doi: 10.1016/J.MARPOLBUL.2020.111948

Qiao R, Deng Y, Zhang S, et al (2019) Accumulation of different shapes of microplastics initiates intestinal injury and gut microbiota dysbiosis in the gut of zebrafish. Chemosphere 236:. doi: 10.1016/j.chemosphere.2019.07.065

Rubal M, Veiga P, Reis PA, et al (2014) Effects of subtle pollution at different levels of biological organisation on species-rich assemblages. Environ Pollut 191:101–110. doi: 10.1016/j.envpol.2014.04.019

Santillo D, Johnston P, Langston WJ (2013) TBT antifoulants: a tale of ships, snails and imposex. In: Harremoes P, Gee D, MacGarvin M, et al. (eds) The Precautionary Principle in the 20th Century, 1st edn. Routledge, pp 168–180

Simonetti P, Botté SE, Marcovecchio JE (2017) Occurrence and spatial distribution of metals in intertidal sediments of a temperate estuarine system (Bahía Blanca, Argentina). Environ Earth Sci 76:1–12. doi: 10.1007/s12665-017-6975-0

Soroldoni S, Abreu F, Castro ÍB, et al (2017) Are antifouling paint particles a continuous source of toxic chemicals to the marine environment? J Hazard Mater 330:76–82. doi: 10.1016/j.jhazmat.2017.02.001

Soroldoni S, Castro ÍB, Abreu F, et al (2018) Antifouling paint particles: Sources, occurrence, composition and dynamics. Water Res 137:47–56. doi: 10.1016/j.watres.2018.02.064

Sparks C (2020) Microplastics in Mussels Along the Coast of Cape Town, South Africa. Bull Environ Contam Toxicol 104:423–431. doi: 10.1007/s00128-020-02809-w

Sparks C, Awe A, Maneveld J (2021) Abundance and characteristics of microplastics in retail mussels from Cape Town, South Africa. doi: 10.1016/j.marpolbul.2021.112186

Sparks C, Odendaal J, Snyman R (2014) An analysis of historical Mussel Watch Programme data from the west coast of the Cape Peninsula, Cape Town. Mar Pollut Bull. doi: 10.1016/j.marpolbul.2014.07.047
StatsSA (2021) Statistics South Africa. http://www.statssa.gov.za/?page_id=4286&id=343. Accessed 13 Jun 2021

Stronkhorst J, Van Hattum B (2003) Contaminants of Concern in Dutch Marine Harbor Sediments. doi: 10.1007/s00244-003-0191-5

Tanner PA, Leong LS, Pan SM (2000) Contamination of Heavy Metals in Marine Sediment Cores from Victoria Harbour, Hong Kong. Mar Pollut Bull 40:769–779. doi: 10.1016/S0025-326X(00)00025-4

Tillig F, Ringsberg JW, Psaraftis HN, Zis T (2020) Reduced environmental impact of marine transport through speed reduction and wind assisted propulsion. Transp Res Part D Transp Environ 83:102380. doi: 10.1016/J.TRD.2020.102380

Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer Meeresuntersuchungen 33:566–575. doi: 10.1007/BF02414780

Torres FG, De-la-Torre GE (2021) Environmental pollution with antifouling paint particles: Distribution, ecotoxicology, and sustainable alternatives. Mar Pollut Bull 169:112529. doi: 10.1016/J.MARPOLBUL.2021.112529

Turekian K, Wedepohl KH (1961) Distribution of the Elements in Some Major Units of the Earth’s Crust. Geol Soc Am Bull 72:175–192. doi: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2

Turner A (2010) Marine pollution from antifouling paint particles. Mar Pollut Bull 60:159–171. doi: 10.1016/j.marpolbul.2009.12.004

US EPA (United States Environmental Protection Agency) (2014) Priority Pollutant List

Vezzone M, Cesar R, Moledo de Souza Abessa D, et al (2019) Metal pollution in surface sediments from Rodrigo de Freitas Lagoon (Rio de Janeiro, Brazil): Toxic effects on marine organisms. Environ Pollut. doi: 10.1016/j.envpol.2019.05.094

Williams JA, Antoine J (2020) Evaluation of the elemental pollution status of Jamaican surface sediments using enrichment factor, geoaccumulation index, ecological risk and potential ecological risk index. doi: 10.1016/j.marpolbul.2020.111288

Zhang L, Yan W, Xie Z, et al (2020) Bioaccumulation and changes of trace metals over the last two
decades in marine organisms from Guangdong coastal regions, South China. J Environ Sci (China) 98:103–108. doi: 10.1016/j.jes.2020.05.007

Zhou F (2015) Antifouling Surfaces and Materials: from land to marine environment. Springer
Figure Captions

Figure 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 (red line) and site 6 (non-impact site) approximately 1 km from site 1.

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

Figure 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).

Figure 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).

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

Figure 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.
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 – 10000   | > 10000       |
| 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           |
Table 2: Metal concentrations in sediment and paint from sites 1 (impact site), 3, 5 and 6 (control site) in Simon’s Town, Cape Town. Data underlined indicates significance differences in sediment metals from site 6. Data in bold and italics indicates values that are higher than recommended guidelines values (see Table 4 for guideline values).

| Metal | Sediment (sites 1, 3, 5 and 6 combined) | Paint (sites 1 and 3 combined) | Sediment (site 1, 3, 5 and 6) |
|-------|----------------------------------------|-------------------------------|-----------------------------|
|       | Mean        | SEM | Min | Max | Mean        | SEM | Min | Max | 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 |
| Al    | 12271       | 1062 | 7383 | 18062 | 21385       | 2198 | 16227 | 27607 | 11802   | 553  | 12311 | 522  | 17362 | 543  |
| 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 |
| Cr    | 555         | 12.07 | 9.33 | 24.99 | 555         | 99.43 | 325.23 | 872.66 | 70.66   | 5.87 | 112.62 | 6.58 | 29.57 | 2.47 |
| 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 |
| Fe    | 32228       | 4024 | 18295 | 55102. | 80873       | 19341 | 37648 | 133934 | 39064   | 2543 | 50340 | 2381 | 20691 | 368  |
| 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 |
| 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 |
| Cu    | 1129        | 407.41 | 23.99 | 3673 | 66763       | 13082 | 35891 | 104672 | 3369    | 163.31 | 988.42 | 43.07 | 130.36 | 4.17 |

30
| Element | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | Value 7 | Value 8 | Value 9 | Value 10 | Value 11 | Value 12 | Value 13 | Value 14 | Value 15 | Value 16 | Value 17 | Value 18 | Value 19 | Value 20 | Value 21 | Value 22 | Value 23 | Value 24 | Value 25 | Value 26 | Value 27 | Value 28 | Value 29 | Value 30 | Value 31 | Value 32 | Value 33 | Value 34 | Value 35 | Value 36 | Value 37 | Value 38 | Value 39 | Value 40 | Value 41 | Value 42 | Value 43 | Value 44 | Value 45 | Value 46 | Value 47 | Value 48 | Value 49 | Value 50 |
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 (mean) Site 3 (mean) Site 5 (mean) Site 6 (mean) | Site 1 Site 3 Site 5 Site 6 | Site Site Site Site | Site Site Site Site |
| 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 |
| 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 |
| 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 |
| Cu    | 0.00 0.00 0.02 0.04  | 9.13 7.36 4.44  | 2.25 842.3 247 32.6 | 7.20 |
| Element | Concentration | | | | | | | | | | | Ecological Risk Index (Ri) |
|--------|---------------|---|---|---|---|---|---|---|---|---|---|---|---|
| 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)
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.)              |
|             |                     | 33  | 12   | 36   | 158   | 12   | -    | -    | -   | -    | 87    |                                 |
| Egypt       | Hurghada Coast      | -   | 0.02-72 | 0.05-23 | 0.01-49 | -    | -    | -    | 0.03-0.68 | 0.0-0.66 | 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 |      |      |      |       |                                 |
| 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 | - | 0.14-1.4 | 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  | -    |      | (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. 1993) |

**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) |
|     | LEL | TEL | ERL | PEL | ERM | SEL | TET | Average Background |
|-----|-----|-----|-----|-----|-----|-----|-----|---------------------|
| PEL | 160 | 42.8| 108 | 271 | 41.6| -   | -   | 4.21 0.7 112        |
| ERM | 370 | 51.6| 270 | 410 | 70  | -   | -   | 9.6 0.71 218        |
| SEL | 110 | 75  | 110 | 820 | 33  | -   | -   | 10 2 250            |
| TET | 100 | 61  | 86  | 540 | 17  | -   | -   | 3 1 170             |
| Average Background | 35  | 2   | 4   | 16  | 1   | 0.05| 1.5 | 0.03 0.03 7         |

(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.)

(Turekian and Wedepohl 1961)
Figure 1.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- STData1.csv