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

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Concentrations and risk assessment of metals, antifouling paint particles and microplastics in 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 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 results, high levels of maritime traffic and associated activities (eg. boating maintenance) continues to be major sources of contaminants (metals, organics, microplastics, and pathogens amongst others) into marine ecosystem (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

al. 2017). 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; Vezzzone 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 Hanglip 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.

120 Sediment sampling and metal analyses

121 Six sites were sampled in June 2018 at spring low tide for sediment metal analyses. Site
122 1 was at the slipway of a shipyard (impact site), sites 2 to 4 within the marina, site 5 outside the
123 marina at the mouth of a storm water pipe and site 6 approximately one kilometre to the north
124 of site 1 (non-impact / control site) (Fig. 1). Notable activities at site 1 (adjacent to boatyard
125 slipway) included sandblasting and painting of yachts and small crafts. At the respective sites,
126 the upper 5 cm of sediment were sampled and stored in pre-cleaned jars. The samples were
127 stored on ice in the field and stored at -20° C until sample processing. Sediment samples for
128 sites 1, 3, 5 and 6 were sent to the University of Stellenbosch's Central Analytical Facility
129 (CAF) for metal analyses. Antifouling paint particles (APPs) from sites 1 and 3 were removed
130 from sediment and also sent for metal analyses. At the CAF, sediment and APPs were processed
131 using the US EPA method 6020A and metals analysed using an Agilent 7700x ICP-MS with
132 an Octopole Reaction System. Quality assurance of data was based on the NIST traceable
133 standard and the results presented percentage accuracy as relative standard deviations as
134 follows: B (116%), Al (104%), V (99%), Cr (100%), Mn (102%), Fe (106%), Co (102%), Ni
135 (103%), Cu (105%), Zn (103%), As (106%), Se (103%), Sr (102%), Mo (102%), Cd (103%),
136 Sn (108%), Sb (88%), Ba (103%), Hg (98%) and Pb (110%). All metal concentrations are
137 expressed as µg/g dry weight.

138 Various indices applied to sediment metals were included to assess the potential effects
139 of metals. Enrichment factor (EF) presents a ratio between concentrations of an element to that
140 of the Earth's upper continental crust (Eq. 1) (Turekian and Wedepohl 1961; Loring 1991). The
141 upper continental crust data normalises the data with pre-industrialised data for elements
142 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.

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

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)

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \dots \times CF_n} \quad (4)$$

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). Equation 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).

$$Er = Tr \times CF \quad (5)$$

$$Ri = \sum Er \quad (6)$$

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 $-20\text{ }^{\circ}\text{C}$ until extraction. Sediment samples were allowed to thaw to room temperature and placed in an oven at $50\text{ }^{\circ}\text{C}$ 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 $20\text{ }\mu\text{m}$ 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 Zeiss stereo microscope with magnifications set to $\times 20$, 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 $4000 - 450\text{ cm}^{-1}$, 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 ($C_{\text{microplastic}}$) compared to background concentrations

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

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

$$MPPLI_{\text{site}} = \sqrt[2]{MPCF_r \times MPCF_i} \quad (8)$$

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

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

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

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

where PRI_i indicates the ecological hazard of polymers when associated with the polymer risk index (H_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 $\pm$ 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 $\mu\text{g/g}$ dry weight, for Hg and Fe, respectively. The maximum concentrations for sediment metals ranged from 0.55 $\mu\text{g/g}$ (Cd) to 18062 $\mu\text{g/g}$ (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 $\mu\text{g/g}$) and Cu (up to 3673.88 $\mu\text{g/g}$) 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).

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

286 Contamination factors provide an index of the quality of sediments at sites (Tomlinson
287 et al. 1980). Contamination factor values > 3 (high risk, Category III) (Hakanson 1980) at all
288 sites were recorded for Co, Ni, Cu, As, Se, Mo and Pb (Table 3). The metals classified as high
289 risk contamination at sites 1, 3 and 5 were recorded for Ni, Zn, Sr, Cd and Hg. The pollution
290 load index (PLI) assesses the level of metal pollution and values > 3 indicates moderate
291 pollution risk polluted and values > 5 indicating dangerous pollution risks (Hakanson 1980).
292 The PLI risk category values decreased from sites 1 to 6 as follows: site 1 (9.2), site 3 (6.1), site
293 5 (3.8) and site 6 (1.5). The ecological risk factor (Er) (data only for selected metals) provides
294 a pollution index associated with the potential ecological risk for particular metals (Hakanson
295 1980) (see Table 1 for risk categories). The Er for the seven metals analysed was > 80 (high
296 risk, Category III) for Co (site 1), Ni (site 1 and 3), Cu (site 1, 3 and 5), Zn (sites 1 and 3), Cd
297 (sites 1, 3 and 5) and Pb (sites 1 and 5). Finally, the potential ecological risk index (Ri)
298 measures the summative ecological risks factors (Er) (Hakanson 1980). The general pattern
299 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

348 facility. Although Simon's Town is in a low populated area with minimal potential sources of
349 anthropogenic inputs (no major riverine input, no major industrial activities and low
350 commercial maritime activities), we are able to demonstrate that localised sources of MP have
351 the potential to have an effect on coastal ecosystems (see Table 1 and 3 for risk analyses). The
352 high filamentous MP concentrations and high PLI at site 5 (Fig. 6a) is cause for concern as
353 filamentous MP polymers are considered a greater risk for marine organisms than other types
354 MPs (Qiao et al. 2019). Polymer and pollution risk indices displayed similar trends (Fig. 6b and
355 c), with the sequence for the pollution risk index from highest to lowest at sites as follows: 4 >
356 1 > 2 > 5 > 6 > 3. The high PLI and PRI values at site 4 is of interest as site 4 was also the site
357 with the lowest PLI. This demonstrates the effect of polymer type on the risks posed by MPs as
358 site 4 recorded the lowest MP concentrations of all the sites sampled (Fig. 2), yet poses the
359 highest pollution risk. At site 4 we recorded 96% of MPs analysed as fragments and MP
360 polymer types for the fragments were epoxy resins (70%) and PVA (30%), which then suggests
361 that APPs from the nearby boating facility could be posing a considerable risk to the rocky
362 shore ecosystem in the marina.

363
364 The results reported here provides evidence that APPs from boatyards are sources of
365 MPs to ambient environments. Non-aqueous paints are classified as MPs as these are mainly
366 comprised of polymers and co-polymers such as alkyls, epoxies and polyesters (Zhou 2015).
367 These polymers end up as MPs stemming from maintenance of maritime vessels (eg
368 sandblasting) and are categorised as highly toxic to organisms (Lithner et al. 2011). APPs have
369 shown to comprise significant proportions of MPs in areas close to boatyards (Galafassi et al.
370 2019) that may be translocated to areas where they are taken up by aquatic biota. In areas with
371 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 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 dm³. 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 / m² 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 / m² 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 / m² in Simon's Town, which is lower than that reported elsewhere, such as 124000 MPs / m² in Guangdong Province, southern China (Dou et al. 2021), 17645 in Hawaiian beaches (McDermid and McMullen 2004) and 44000 MPs / m² 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.

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441 **References**

- 442 Abu-Hilal A, Al-Najjar T (2009) Marine litter in coral reef areas along the Jordan Gulf of Aqaba, Red
443 Sea. *J Environ Manage* 90:1043–1049. doi: 10.1016/j.jenvman.2008.03.014
- 444 Ahsanullah M, Florence TM (1984) Toxicity of copper to the marine amphipod *Allorchestes*
445 *compressa* in the presence of water-and lipid-soluble ligands. *Mar Biol* 84:41–45. doi:
446 10.1007/BF00394525
- 447 Alyazichi YM, Jones BG, Mclean E Source identification and assessment of sediment contamination
448 of trace metals in Kogarah Bay, NSW, Australia. doi: 10.1007/s10661-014-4238-z
- 449 Amara I, Miled W, Slama R Ben, Ladhari N (2018) Antifouling processes and toxicity effects of
450 antifouling paints on marine environment. A review. *Environ Toxicol Pharmacol* 57:115–130.
451 doi: 10.1016/J.ETAP.2017.12.001
- 452 Amorim ALA de, Ramos JAA, Nogueira Júnior M (2020) Ingestion of microplastic by ontogenetic
453 phases of *Stellifer brasiliensis* (Perciformes, Sciaenidae) from the surf zone of tropical beaches.
454 *Mar Pollut Bull* 158:111214. doi: 10.1016/j.marpolbul.2020.111214
- 455 Arisekar U, Shakila RJ, Shalini R, et al (2021) Heavy metal concentration in reef-associated surface
456 sediments, Hare Island, Gulf of Mannar Marine Biosphere Reserve (southeast coast of India):
457 The first report on pollution load and biological hazard assessment using geochemical
458 normalization factors an. *Mar Pollut Bull* 162:111838. doi: 10.1016/j.marpolbul.2020.111838
- 459 Barbieri M (2016) The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to
460 Evaluate the Soil Contamination. doi: 10.4172/2381-8719.1000237
- 461 Bersuder P, Smith AJ, Hynes C, et al (2020) Baseline survey of marine sediments collected from the
462 Kingdom of Bahrain: PAHs, PCBs, organochlorine pesticides, perfluoroalkyl substances,
463 dioxins, brominated flame retardants and metal contamination. *Mar Pollut Bull* 161:111734. doi:
464 10.1016/j.marpolbul.2020.111734
- 465 Boitsov S, Newman BK, Muiambo HF, et al (2021) Distribution and possible sources of polycyclic
466 aromatic hydrocarbons (PAHs) and metals in marine surface sediments off northern
467 Mozambique. *Mar Pollut Bull* 163:. doi: 10.1016/j.marpolbul.2020.111952

468 Chambers LD, Stokes KR, Walsh FC, Wood RJK (2006) Modern approaches to marine antifouling
 469 coatings. *Surf Coatings Technol* 201:3642–3652. doi: 10.1016/J.SURFCOAT.2006.08.129
 470 Champ MA (2000) A review of organotin regulatory strategies, pending actions, related costs and
 471 benefits. *Sci Total Environ* 258:21–71. doi: 10.1016/S0048-9697(00)00506-4
 472 Chen JC, Chen MY, Fang C, et al (2020) Microplastics negatively impact embryogenesis and
 473 modulate the immune response of the marine medaka *Oryzias melastigma*. *Mar Pollut Bull*
 474 158:111349. doi: 10.1016/j.marpolbul.2020.111349
 475 de Souza AM, Rocha DS, Guerra JV, et al (2021) Metal concentrations in marine sediments of the Rio
 476 de Janeiro Coast (Brazil): A proposal to establish new acceptable levels of contamination. *Mar*
 477 *Pollut Bull* 165:. doi: 10.1016/j.marpolbul.2021.112113
 478 de Villiers S (2018) Quantification of microfibre levels in South Africa’s beach sediments, and
 479 evaluation of spatial and temporal variability from 2016 to 2017. *Mar Pollut Bull* 135:481–489.
 480 doi: 10.1016/j.marpolbul.2018.07.058
 481 Diab A, Minghetti M, Casadei E, et al (2008) Abstracts from Fourteenth International Symposium on
 482 Pollutant Responses in Marine Organisms (PRIMO 14) – Heavy metals: Mechanisms of
 483 detoxification and mechanisms of toxicity. *Mar Environ Res* 66:41–46. doi:
 484 10.1016/j.marenvres.2008.02.017
 485 Dou P-C, Mai L, Bao L-J, Zeng EY (2021) Microplastics on beaches and mangrove sediments along
 486 the coast of South China. doi: 10.1016/j.marpolbul.2021.112806
 487 Dufois F, Rouault M (2012) Sea surface temperature in False Bay (South Africa): Towards a better
 488 understanding of its seasonal and inter-annual variability. *Cont Shelf Res* 43:24–35. doi:
 489 10.1016/J.CSR.2012.04.009
 490 Fatoki OS, Mathabatha S (2001) An assessment of heavy metal pollution in the East London and Port
 491 Elizabeth harbours. 27:233–240
 492 Feng L, He L, Jiang S, et al (2020) Investigating the composition and distribution of microplastics
 493 surface biofilms in coral areas. *Chemosphere* 252:126565. doi:
 494 10.1016/J.CHEMOSPHERE.2020.126565
 495 Franco-Fuentes E, Moity N, Ramírez-González J, et al (2021) Metals in commercial fish in the

496 Galapagos Marine Reserve: Contribution to food security and toxic risk assessment. *J Environ*
 497 *Manage* 286:112188. doi: 10.1016/j.jenvman.2021.112188
 498 Galafassi S, Nizzetto L, Volta P (2019) Plastic sources: A survey across scientific and grey literature
 499 for their inventory and relative contribution to microplastics pollution in natural environments,
 500 with an emphasis on surface water. *Sci Total Environ* 693:133499. doi:
 501 10.1016/j.scitotenv.2019.07.305
 502 Gaylarde CC, Neto JAB, da Fonseca EM (2021) Paint fragments as polluting microplastics: A brief
 503 review. *Mar Pollut Bull* 162:. doi: 10.1016/j.marpolbul.2020.111847
 504 GESAMP (2019) Guidelines for the monitoring and assessment of plastic litter in the ocean (Kershaw
 505 P.J., Turra A. and Galgani F. editors), (IMO/FAO/UNESCO-
 506 IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP/ISA Joint Group of Experts on the Scientific
 507 Aspects of Marine Environmental Prote. Rep Stud GESAMP no 99:130p
 508 Gong M, Yang G, Zhuang L, Zeng EY (2019) Microbial biofilm formation and community structure
 509 on low-density polyethylene microparticles in lake water microcosms. *Environ Pollut* 252:94–
 510 102. doi: 10.1016/J.ENVPOL.2019.05.090
 511 Gredilla A, Stoichev T, Fdez-Ortiz De Vallejuelo S, et al (2015) Spatial distribution of some trace and
 512 major elements in sediments of the Cávado estuary (Esposende, Portugal). doi:
 513 10.1016/j.marpolbul.2015.07.040
 514 Hakanson L (1980) An ecological risk index for aquatic pollution control.a sedimentological
 515 approach. *Water Res* 14:975–1001. doi: 10.1016/0043-1354(80)90143-8
 516 Hudspith M, Reichelt-Brushett A, Harrison PL (2017) Factors affecting the toxicity of trace metals to
 517 fertilization success in broadcast spawning marine invertebrates: A review. *Aquat. Toxicol.*
 518 184:1–13
 519 Jeong H, Choi JY, Lim J, et al (2020) Characterization of the contribution of road deposited sediments
 520 to the contamination of the close marine environment with trace metals: Case of the port city of
 521 Busan (South Korea). *Mar Pollut Bull* 161:. doi: 10.1016/j.marpolbul.2020.111717
 522 Jury MR (2020) Coastal gradients in False Bay, south of Cape Town: What insights can be gained
 523 from mesoscale reanalysis? *Ocean Sci* 16:1545–1557. doi: 10.5194/OS-16-1545-2020

524 Jury MR, Kamstra F, Taunton-Clark J (1985) Diurnal wind cycles and upwelling off the northern
 525 portion of the Cape Peninsula in summer. <http://dx.doi.org/102989/025776185784461216> 3:1–
 526 10. doi: 10.2989/025776185784461216

527 Kabir AHME, Sekine M, Imai T, et al (2021) Assessing small-scale freshwater microplastics
 528 pollution, land-use, source-to-sink conduits, and pollution risks: Perspectives from Japanese
 529 rivers polluted with microplastics. *Sci Total Environ* 768:144655. doi:
 530 10.1016/J.SCITOTENV.2020.144655

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

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

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

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

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

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

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

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

551 Molino C, Angeletti D, Oldham VE, et al (2019) Effect of marine antifouling paint particles waste on

552 survival of natural Bermuda copepod communities. doi: 10.1016/j.marpolbul.2019.110492

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

556 Müller G (1979) Schwermetalle in den Sedimenten des Rheins. Veränderungen seit Umschau 79:778–
 557 783

558 Nel HA, Froneman PW (2015) A quantitative analysis of microplastic pollution along the south-
 559 eastern coastline of South Africa. Mar Pollut Bull 101:274–279. doi:
 560 10.1016/j.marpolbul.2015.09.043

561 Nel HA, Hean JW, Noundou XS, Froneman PW (2017) Do microplastic loads reflect the population
 562 demographics along the southern African coastline? Mar Pollut Bull 115:115–119. doi:
 563 10.1016/j.marpolbul.2016.11.056

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

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

568 Patti TB, Fobert EK, Reeves SE, da Silva KB (2020) Spatial distribution of microplastics around an
 569 inhabited coral island in the Maldives, Indian Ocean. Sci Total Environ 141263. doi:
 570 10.1016/j.scitotenv.2020.141263

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

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

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

578 Poulsen R, Gravert TKO, Tartara A, et al (2021) A case study of PAH contamination using blue
 579 mussels as a bioindicator in a small Greenlandic fishing harbor. Mar Pollut Bull 171:112688. doi:

580 10.1016/J.MARPOLBUL.2021.112688

581 Preston-Whyte F, Silburn B, Meakins B, et al (2021) Meso- and microplastics monitoring in harbour
582 environments: A case study for the Port of Durban, South Africa. *Mar Pollut Bull* 163:111948.
583 doi: 10.1016/J.MARPOLBUL.2020.111948

584 Qiao R, Deng Y, Zhang S, et al (2019) Accumulation of different shapes of microplastics initiates
585 intestinal injury and gut microbiota dysbiosis in the gut of zebrafish. *Chemosphere* 236:. doi:
586 10.1016/j.chemosphere.2019.07.065

587 Rubal M, Veiga P, Reis PA, et al (2014) Effects of subtle pollution at different levels of biological
588 organisation on species-rich assemblages. *Environ Pollut* 191:101–110. doi:
589 10.1016/j.envpol.2014.04.019

590 Santillo D, Johnston P, Langston WJ (2013) TBT antifoulants: a tale of ships, snails and imposex. In:
591 Harremoes P, Gee D, MacGarvin M, et al. (eds) *The Precautionary Principle in the 20th Century*,
592 1st edn. Routledge, pp 168–180

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

596 Soroldoni S, Abreu F, Castro ÍB, et al (2017) Are antifouling paint particles a continuous source of
597 toxic chemicals to the marine environment? *J Hazard Mater* 330:76–82. doi:
598 10.1016/j.jhazmat.2017.02.001

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

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

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

605 Sparks C, Odendaal J, Snyman R (2014) An analysis of historical Mussel Watch Programme data
606 from the west coast of the Cape Peninsula, Cape Town. *Mar Pollut Bull*. doi:
607 10.1016/j.marpolbul.2014.07.047

608 StatsSA (2021) Statistics South Africa. http://www.statssa.gov.za/?page_id=4286&id=343. Accessed
609 13 Jun 2021

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

612 Tanner PA, Leong LS, Pan SM (2000) Contamination of Heavy Metals in Marine Sediment Cores
613 from Victoria Harbour, Hong Kong. *Mar Pollut Bull* 40:769–779. doi: 10.1016/S0025-
614 326X(00)00025-4

615 Tillig F, Ringsberg JW, Psaraftis HN, Zis T (2020) Reduced environmental impact of marine transport
616 through speed reduction and wind assisted propulsion. *Transp Res Part D Transp Environ*
617 83:102380. doi: 10.1016/J.TRD.2020.102380

618 Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy-metal
619 levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen*
620 33:566–575. doi: 10.1007/BF02414780

621 Torres FG, De-la-Torre GE (2021) Environmental pollution with antifouling paint particles:
622 Distribution, ecotoxicology, and sustainable alternatives. *Mar Pollut Bull* 169:112529. doi:
623 10.1016/J.MARPOLBUL.2021.112529

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

626 Turner A (2010) Marine pollution from antifouling paint particles. *Mar Pollut Bull* 60:159–171. doi:
627 10.1016/j.marpolbul.2009.12.004

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

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

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

635 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) d 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.

690 Table 1. Risk categories of indices for metal and microplastic contamination in Simon's Town, Cape
691 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

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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)							
									1 (impact)		3	5		6 (control)		
	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	<u>21.56</u>	3.61	<u>18.45</u>	1.51	<u>37.41</u>	2.64	5.98	0.48
Al	12271	1062	7383	18062	21385	2198	16227	27607	<u>11802</u>	553	<u>12311</u>	522	<u>17362</u>	543	7607	122
V	23.09	1.78	17.27	33.85	56.57	3.19	45.96	68.08	19.94	1.13	<u>22.11</u>	1.64	<u>32.63</u>	0.66	17.68	0.23
Cr	<i>55.5</i>	12.07	9.33	124.99	<i>555</i>	99.43	325.23	872.66	<i>70.06</i>	5.87	<i>112.62</i>	6.58	<u>29.57</u>	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	<u>440.25</u>	63.97	60.17	1.48	107.69	2.38
Fe	32228	4024	18295	55102.	80873	19341	37648	133934	<u>39064</u>	2543	<u>50340</u>	2381	20691	368	18815	291
Co	11.01	3.77	2.09	39.2	22.13	2.6	15.14	30.88	<u>31.92</u>	3.72	7.18	0.75	2.72	0.19	2.23	0.08
Ni	<i>21.01</i>	4.31	6.67	49.63	<i>93.15</i>	18.59	47.22	150.14	<u>33.23</u>	8.20	<i>34.52</i>	2.79	9.25	1.11	7.04	0.19
Cu	<i>1129</i>	407.41	23.99	3673	<i>66763</i>	13082	35891	104672	<u>3369</u>	163.31	<i>988.42</i>	43.07	<i>130.36</i>	4.17	<i>28.85</i>	2.45

Zn	1047	294.87	67.45	2483	44910	1500	39704	50021	<u>2326</u>	119.53	<u>1658</u>	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	<u>0.37</u>	0.01	<u>0.64</u>	0.02	0.22	0.01
Sr	426.25	76.55	42.18	790.07	565.87	109.4	316.23	886.9	<u>742.85</u>	42.48	<u>421.47</u>	32.56	<u>496.90</u>	17.23	43.80	1.32
Mo	10.26	3.07	0.65	28.34	41.06	1.97	34.82	45.63	<u>25.04</u>	1.65	<u>13.45</u>	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	<u>0.48</u>	0.03	<u>0.22</u>	0.01	<u>0.24</u>	0.04	0.05	0.00
Sn	65.98	15.43	10.45	149.78	1707	557.4	464.8	3225	<u>128.98</u>	11.02	<u>93.94</u>	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	<u>8.75</u>	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	<u>1178</u>	55.63	<u>165.57</u>	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	<u>0.25</u>	0.03	0.13	0.01	<u>1.05</u>	0.07	0.02	0.00
Pb	111	19.8	42.96	199.74	1202	116.55	908.24	1483	<u>151.12</u>	23.89	56.80	4.39	<u>193.98</u>	4.25	43.17	0.19

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	Site	Site	Site	Site 1	Site 3	Site 5	Site 6	Site	Site	Site	Site	Site	Site	Site	Site
	1	3	5	6	(mean)	(mean)	(mean)	(mean)	1	3	5	6	1	3	5	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

Table 4. Range and mean ($\pm$ SEM) concentrations ($\mu\text{g/g}$) 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	0-0.66	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. 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)

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. 1993)
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.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Supplementary Files

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- [STData1.csv](#)