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**Microplásticos em Praias Arenosas da Ilha de Santa Catarina: ocorrência,
distribuição e caracterização**

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Daniela Gadens Zanetti

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distribuição e caracterização**

Dissertação submetida ao Programa de Oceanografia da Universidade Federal de Santa Catarina para a obtenção do Grau de Mestre em Oceanografia.
Orientador: Profa. Dra. Juliana Leonel

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Daniela Gadens Zanetti

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ocorrência, distribuição e caracterização**

O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Certificamos que esta é a **versão original e final** do trabalho de conclusão que foi julgado adequado para obtenção do título de mestre em Oceanografia.

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RESUMO

Microplásticos (MPs) receberam considerável atenção da comunidade científica por sua alta capacidade de dispersão e acúmulo em vários ambientes. Os microplásticos representam um risco para a biota devido ao seu tamanho e similaridade com itens alimentares, pela capacidade de acúmulo nos organismos, causando danos físicos, pelos aditivos adicionados nas etapas de manufatura que podem ser liberados da matriz polimérica e pela sua capacidade de concentrar poluentes orgânicos. Dez praias arenosas ao longo da Ilha de Santa Catarina foram amostradas para avaliar a variabilidade espacial na distribuição, composição, padrão de acúmulos e possíveis fontes de microplásticos. Todo material coletado foi analisado quanto à forma, cor, tamanho e estágio de degradação por processamento digital de imagens obtidas por lupa binocular e composição polimérica por espectrofotômetro de infravermelho por transformada de Fourier (FT-IR) com refletância total atenuada (ATR). Os pellets foram avaliados visualmente quanto ao grau de intemperismo (amarelamento e erosão) e quanto ao grau de oxidação pela formação de grupamentos que indicam a degradação polimérica. A concentração de MPs variou de 1,33 a 127,3 itens m⁻² na linha de deixa e de 0 a 37,33 itens m⁻² na porção pós praia. Destaca-se a importância dos ventos, energia das ondas e orientação da praia na distribuição dos microplásticos Sugere-se que os pellets chegam à Ilha de Santa Catarina depois de uma curta permanência no oceano e também não ficaram no litoral por um longo período de tempo.

Palavras-chave: FTIR. Pellets. Plástico. Poluição Marinha.

ABSTRACT

Microplastics (MPs) have received considerable attention from the scientific community for their high dispersion and accumulation capacity in various environments. MPs pose a risk to biota due to their size and similarity to food items, they may accumulate in organisms, resulting in physical harm; they can also leach contaminants such as plastic additives and concentrate hydrophobic persistent organic pollutants. Ten sandy beaches along Santa Catarina Island were sampled to study spatial variability in the distribution, composition, weathering pattern and possible sources of MPs. All material collected was analyzed for shape, color, size and degradation stage by digital processing of images obtained by stereomicroscope and polymer composition was estimated by Fourier Transform Infrared Spectrophotometer (FT-IR) with attenuated total reflectance (ATR). Pellets were visually evaluated for the degree of weathering (yellowing and erosion) and the degree of oxidation by the formation of peaks that indicate polymeric degradation. The concentration of MPs ranged from 1.33 to 127.3 particles m^{-2} in the strandline and from 0 to 37.33 particles m^{-2} in the backshore portion. The importance of winds, wave energy and beach orientation in the distribution of microplastics is highlighted. It is suggested that pellets arrive in Santa Catarina Island after a short period in the ocean and have not been on the coast for a long time.

Keywords: FTIR. Pellets. Plastic. Marine Pollution.

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1 INTRODUÇÃO

Os padrões vigentes de produção, gestão e descarte inadequado de resíduos sólidos ultrapassaram há tempos as fronteiras terrestres e hoje geram nos oceanos problemas que exigem atenção urgente. Além disso, os resíduos sólidos marinhos possuem grande capacidade de dispersão, exigindo soluções integradas que consideram múltiplos setores da sociedade e ação conjunta entre países (UNEP, 2005).

Ainda que a poluição marinha por resíduos sólidos englobe fontes difusas e variadas, incluindo qualquer resíduo gerado pelo homem, as atividades realizadas no continente são a principal fonte de aporte de material para o ambiente marinho (Andrady, 2011; UNEP, 2005). Outro fator importante é que a composição dos resíduos sólidos marinhos, ainda que diversa, é majoritariamente formada por material plástico, representando 90% dos resíduos sólidos encontrados nos ambientes marinhos (Galgani et al. 2015; Thiel et al. 2013, Stevenson, 2011; Derraik, 2002).

O termo plástico engloba uma variedade de polímeros artificiais que oferecem uma versatilidade incomparável em uma ampla gama de temperaturas de operação e diversas propriedades de acordo com as exigências do produto final e da área de aplicação, tais como elevada ductilidade, resistência à corrosão, bio-inércia, isolamento térmico/elétrico, e durabilidade excepcional em comparação com materiais concorrentes (Andrady e Neal, 2009). A quantidade de polímeros plásticos disponíveis hoje no mercado é imensa, dentre os tipos mais utilizados podem ser citados o polietileno (PE), o polipropileno (PP), o poliestireno (PS), o policloreto de polivinila (PVC), o polietileno tereftalato (PET), entre outros (GESAMP, 2010) (Quadro 1). O PE, PVC, PS, PP e PET são os mais empregados, representando 90% de toda a produção mundial de plástico (Andrady e Neal, 2009) que atualmente é de cerca de 322 milhões de toneladas por ano (PLASTICSEUROPE, 2016). No território brasileiro, somente em 2018, foram importados e exportados mais de 2 milhões de toneladas de resinas plásticas primária de PE, PS e PP (MDIC, 2019).

Quadro 1 Densidade específica de resinas de polímeros.

Polímero	Sigla	Densidade g mL ⁻¹
Polipropileno	PP	0,85 – 0,92
Polietileno de Baixa Densidade	LDPE	0,89 – 0,93
Polietileno de Alta Densidade	HDPE	0,94 – 0,97
Poliestireno	PS	1,04 – 1,08
Nylon 6	PA6	1,15
Policloreto de Vinila	PVC	1,16 – 1,41
Polietileno Tereftalato	PET	1,38 – 1,41

Fonte: Adaptado de Morét – Ferguson et al. 2010.

Embora o plástico ainda não seja usado estratigraficamente como marcador primário para definir o início do Antropoceno, a presença desse material é um sinal presente em estratos desse período (Zalasiewicz et al. 2016). Estimativas indicam que no mínimo 5,32 trilhões de partículas de plástico estão flutuando nos oceanos, correspondendo a 289 940 toneladas em massa (Eriksen et al. 2014).

A problemática dos plásticos nos ambientes marinhos e costeiro tem despertado a atenção da comunidade científica e da sociedade civil em todo o mundo, levantando questões relacionadas ao consumo e as divisões de responsabilidade acerca dos resíduos encontrados no ambiente (Hopewell et al. 2009).

Microplásticos

Os microplásticos são definidos como partículas de diâmetro menor que 5 mm, ou cuja maior dimensão não exceda 5 mm, e maior que 1 µm (Arthur et al. 2009; NOAA, 2015; Duis e Coors, 2016, GESAMP, 2015). Os microplásticos podem ser agrupados em duas categorias estabelecidas de acordo com a sua origem: primários e secundários (Figura 1).

Microplásticos primários compreendem partículas já produzidas em tamanhos reduzidos (Cole et al. 2011), como é o caso das microesferas usadas em esfoliantes, cremes e loções faciais (Sherrington et al. 2016). Eles se caracterizam por possuírem diâmetro menor que 1 mm e por serem constituídos, normalmente, de polietileno e poliestireno (Browne et al. 2007). Outra forma dos microplásticos primários são os pellets/resinas da pré-produção de produtos plásticos (Hidalgo-Ruz et al. 2012). Estes têm tamanho de 2 a 5mm (Costa et al. 2010) e apresentam

formatos e cores variados, os quais são produzidos e transportados a granel, antes de serem moldados, derretidos e transformados em outros itens plásticos.

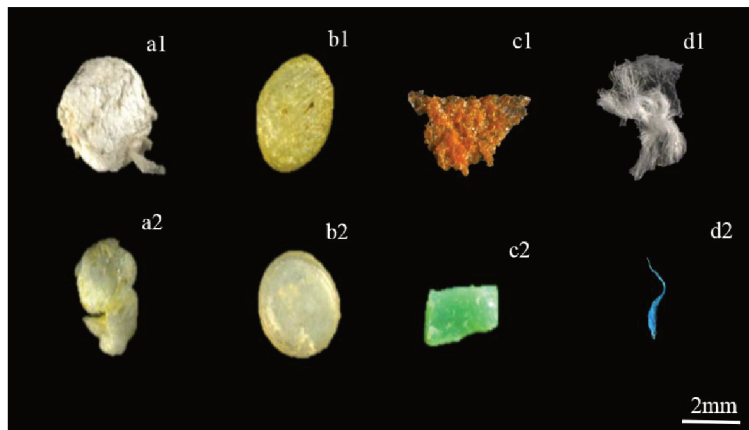


Figura 2 Diferentes formas, cores e tipos de microplásticos: agrupados em isopor (a1; a2), pellets (b1; b2), fragmentos (c1; c2) e fibras (d1; d2). Fonte: Elaborado pelo autor.

Já os microplásticos secundários são fragmentos derivados do fracionamento de partículas maiores, que tiveram sua integridade estrutural reduzida por processos físicos, químicos e biológicos (Ryan et al. 2009). Quando em contato com a luz ultravioleta, por exemplo, os plásticos sofrem fotodegradação e através da quebra da matriz polimérica ficam suscetíveis à fragmentação que pode ser causada por fatores externos como turbulência, ação de ondas, abrasão mecânica e degradação química (Costa et al. 2010; Van Sebille et al. 2015). Esses processos, ao se repetirem, contribuem para a quebra em frações cada vez menores, até atingirem o tamanho de microplástico (Browne et al. 2007).

Os microplásticos chegam aos oceanos por fontes e atividades que atuam diretamente no ambiente marinho, como lazer em praia e transporte marítimo de carga, por de fontes fluviais, drenagem urbana (Long et al. 2015; Ogata et al. 2009; Van Cauwenberghe, et al. 2015) e por transporte atmosférico (Dris et al. 2016).

Uma vez no ambiente marinho, os microplásticos podem ser ingeridos por peixes, aves, tartarugas, crustáceos, bivalves, e outros invertebrados (Lee et al. 2013; Li et al. 2015; Tourinho et al. 2010; Von Moss et al. 2012; Wright et al. 2013). A ingestão desses fragmentos pode causar danos físicos, sufocamento, problemas digestivos, redução do consumo de alimentos e inflamação (Browne et al. 2007; Cole et al. 2011; Watts et al. 2015). Além disso, a presença de microplásticos em

partículas orgânicas, tais como pellets fecais de zooplâncton, altera a densidade destas e interfere no transporte de carbono para regiões profundas dos oceanos (Cole et al. 2016).

Outro problema relacionado aos microplásticos marinhos envolve os aditivos adicionados aos polímeros durante as etapas de manufatura, os quais podem ser liberados da matriz polimérica (Vandenberget al. 2007), e causar danos relevantes para algumas espécies marinhas, como já evidenciados em poliquetas (Koelmans et al. 2014). Dependendo da aplicabilidade do material plástico final os componentes adicionados podem ser antioxidantes, antimicrobianos, antiestáticos, estabilizantes, lubrificantes, estabilizantes térmicos, anti-UV's e pigmentos, sendo que compostos com o Bisfenol A (BPA) e os ftalatos apresentam toxicidade potencial podendo bioacumular nos organismos e provocar distúrbios na reprodução e desenvolvimento de diversas espécies (Oehlmann et al. 2009).

Os microplásticos também podem contribuir com a introdução de compostos no ambiente e na malha trófica marinha, tais como metais pesados (Massos e Turner, 2017; Vedolin et al. 2017), hidrocarbonetos de petróleo (Fisner et al. 2013) e poluentes orgânicos persistentes (Taniguchi et al. 2016). Estudos indicam que os microplásticos também representam riscos à saúde humana pela sua presença em diversos produtos de origem marinha, incluindo em grânulos de sal (Yang et al. 2015) e frutos do mar (Li, 2015).

No ambiente, os microplásticos irão se distribuir de acordo com sua densidade e tamanho, se depositando no sedimento de fundo ou permanecendo na coluna d'água, onde serão transportados e distribuídos pelas correntes, podendo acumular nas regiões costeiras, principalmente em praias arenosas (Browne et al. 2011). Sendo assim, há diversos fatores que regem essa distribuição, como aporte de material, chuvas, ventos, tempestade, hidrodinâmica local e geomorfologia praial (Eriksson, et al. 2013), além da interferência antrópica na região (Turra et al. 2014).

Sendo assim, praias arenosas são frequentemente objeto de estudo para quantificação de resíduos sólidos (Moreira et al. 2016; De Carvalho e Neto 2016; Lozoya et al. 2016), nas quais, muitas vezes, o maior constituinte desse material é o microplástico primário na forma de pellets plásticos (Moore et al. 2001; Browne et al. 2010; Eriksen et al. 2014; Law e Thompson, 2014).

A Ilha de Santa Catarina, localizada na costa sul do Brasil, possui importantes atividades econômicas que estão relacionadas com as praias arenosas, como o turismo e a maricultura. Apesar de esses setores serem diretamente impactados pela presença de resíduos sólidos e poluentes no ambiente, os estudos que já avaliaram a presença de resíduos sólidos na região são escassos (Widmer e Hennemann, 2010; Vieira e Dias et al. 2011; Corraini et al. 2018; Oliveira, 2015). E apesar de não possuir atividades portuárias em sua extensão, a Ilha de Santa Catarina encontra-se entre o complexo portuário de Itajaí e o Porto de Imbituba que poderiam colaborar com o aporte de microplásticos secundários (pellets plásticos) para as praias. O porto de Itajaí localiza-se em uma região relevante econômica e ambientalmente, composta por uma diversidade de indústrias pesqueiras e pela maior bacia hidrográfica do estado de Santa Catarina, a bacia hidrográfica do Rio Itajaí-Açú, com 15.500 km² de drenagem (Pereira et al., 2010). A desembocadura do Rio Itajaí-Açú localiza-se aproximadamente a 100km ao norte da Ilha de Santa Catarina (Reis et al., 2010), e em períodos de verão é sugerido que o fluxo da pluma do Rio Itajaí-Açú esteja direcionado ao sul, até o Cabo de Santa Marta Grande, confirmadas pelas baixas salinidades ($S < 35,35$), observadas no verão, que se estendem para o sul da foz do Rio Itajaí-Açú ao longo da plataforma continental média (Campos et al., 2013).

O diagnóstico e o monitoramento de microplásticos nos ambientes e a sua identificação têm motivado a comunidade científica a padronizar termos, nomenclaturas e amostragem e definir critérios específicos para estimar a abundância e composição (Galgani et al, 2010). Analiticamente, a identificação dos microplásticos levanta diversos desafios, gerados por seus tamanhos reduzidos e seus variados estágios de degradação. Geralmente a identificação dos microplásticos é feita visualmente, o que tende a superestimar os valores encontrados e o que motiva a incorporação de técnicas confirmatórias de análises poliméricas, como é o caso do uso do FTIR.

As técnicas de caracterização polimérica, como o FTIR, também permitem a inferência do estágio de degradação do material. A degradação ocorre por conta dos processos de intemperismo físico, termo-oxidação, hidrólise, biodegradação e foto-oxidação que o material sofre no ambiente, impulsionados pela radiação UV,

presença de oxigênio, aumento da temperatura, ação dos ventos e ondas (Charles et al. 2013). A absorção do oxigênio presente na água levaria a formação de alguns grupos funcionais específicos, como grupamentos cetona, éster e vinil, e a nível molecular, a degradação impulsiona uma crescente quantidade desses compostos de baixo peso molecular (Corcoaran et al., 2009). Sendo assim a degradação poderia ser estimada pela leitura específica de índices, calculados pela razão entre seus picos de absorção e picos de referência – que não sofreriam alterações com os processos de degradação da matriz polimérica:

(1) Índice carbonil cetona = I_{1715}/I_{1465} (Artham et al. 2009, Albertsson et al. 1987, Roy et al. 2011)

(2) Índice carbonil cetona = I_{1715}/I_{1374} (Andrady et al. 1993)

(3) Índice carbonil cetona = I_{1715}/I_{720} (Endo et al. 2005)

(4) Índice Ester carbonil = I_{1740}/I_{1465} (Artham, 2009; Endo et al. 2005)

(5) Índice Vinil = I_{1640}/I_{1465} (Artham, 2009; Endo et al. 2005)

Visualmente, a degradação também pode ser identificada por alterações estruturais e pelo amarelamento da superfície do material, sendo os pellets plásticos um bom material para essas análises, uma vez que suas forma e coloração iniciais e características químicas são conhecidas.

Sendo assim, a degradação dos pellets forneceria uma variável informativa com relação à sua presença no ambiente, padrões e dinâmicas de introdução desse tipo de resíduo e de sua mobilidade de pellets nos compartimentos (McCormick e Hoellein, 2016).

Dessa forma, o presente trabalho tem como objetivo preencher essa lacuna de dados relativos à ocorrência, caracterização e distribuição dos microplásticos nas praias da Ilha de Santa Catarina, considerando que os estudos de abundância de microplásticos no ambiente devem levar em consideração não só a quantidade e a composição polimérica dos microplásticos amostrados, mas também suas

características de intemperismo. O entendimento do comportamento dos microplásticos em praias arenosas pode colaborar para uma melhor gestão dessa ameaça, uma vez que a poluição marinha e costeira é responsável por alterações na estrutura e função de comunidades de fitoplâncton, zooplâncton, bentos e essas alterações podem causar riscos à biodiversidade, prejuízos econômicos e à saúde pública (Islam e Tanaka, 2004).

2. HIPÓTESES

As características antrópicas das praias são os fatores determinantes na ocorrência e distribuição de microplásticos nas praias arenosas da Ilha de Santa Catarina, Brasil.

Os níveis de erosão e de amarelamento dos pellets correlacionam-se com os índices de oxidação.

As praias da região norte da Ilha de Santa Catarina apresentam maior número de pellets em decorrência das atividades portuárias localizadas no norte do estado.

3. OBJETIVOS

1.1 Objetivo Geral

Compreender a dinâmica, a ocorrência e a distribuição dos diferentes tipos de microplásticos nas praias arenosas da Ilha de Santa Catarina

1.2 Objetivos Específicos

Diagnosticar o estado de contaminação das praias em função da presença de microplásticos totais e dos pellets;

Avaliar a importância das características antrópicas e ambientais na ocorrência e distribuição de microplásticos;

Inferir sobre o tempo de residência dos pellets nas praias através da análise visual de erosão e amarelamento e do índice de oxidação.

4. RESULTADOS

Os resultados dessa dissertação serão apresentados na forma de um artigo científico, conforme permitido pelo regulamento da PPGOceano.

Distribution and characterization of microplastics in sandy beaches in the Island of Santa Catarina, Brazil.

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Conflict of Interest – No conflict of interest

1.3 ABSTRACT

Microplastics (MPs) have received considerable attention from the scientific community for their high dispersibility and accumulation capacity in various environments. MPs pose a risk to biota due to their size and similarity to food items, and for carrying chemical compounds that can bioaccumulate. Ten sandy beaches along Santa Catarina Island were sampled to study spatial variability in the distribution, composition, weathering pattern and possible sources of MPs. All material collected was analyzed for shape, color, size and degradation stage by digital processing of images obtained by microscopy and polymer composition by Fourier Transform Infrared Spectrophotometer (FT-IR) with attenuated total reflectance (ATR). The concentration of MPs ranged from 1.33 to 127.3 particles m^{-2} in the strandline and from 0 to 37.33 particles m^{-2} in the backshore portion. Natural characteristics, such as exposure to wind and wave energy, appears to be as important as anthropogenic characteristics for microplastics concentrations and distribution. The use of oxidation indices were also examined and highlighted the need for standardization of methods.

KEYWORDS: FTIR, pellets, weathering processes, plastic, coastal pollution

1.4 INTRODUCTION

Due to its properties, such as malleability, durability, low weight and low cost of production, plastic is used in a large range of products from consumer goods, food packaging, and textiles to construction, transportation, electronics, agriculture, among others (Plastics Europe, 2016). Its production and consumption increased quickly and has been encouraged for a society and industry ideologically focused on the disposable culture (Borodin et al. 2015). However, difficulties in managing their disposal make them an environmental problem (Mason et al. 2016; Guerrero et al. 2013).

Although plastics have been reported in the marine environment since the 1970s, it was only in the last decade that it was recognized as a major problem (Lo et al. 2018; Hopewell, et al. 2009; Nor and Obbard, 2014; Obbard et al.2014; Reisser et al. 2014; Turra et al. 2014). In the marine environment, plastics predominate among solid wastes (Galganiet al. 2015; Thielet al. 2013), reaching 60-80% of the debris found in the ocean (Stevenson, 2011; Derraik, 2002). Studies have estimated that there are at least 5.32 trillions of plastic particles floating in the oceans, corresponding to 289 940 tons of debris (Eriksen et al. 2014).

Plastic particles can be classified according to their size and environmental studies in this field of expertise have focused on microplastics (MPs, <5 mm) occurrence, distribution, fate and impacts. MPs can be grouped according to their origin into primary or secondary. Primary MPs are micro-beads used in body exfoliators, toothpaste, soaps (Sherrington et al. 2016), and pellets/resins from the pre-production of plastic products (Hidalgo-Ruzet al. 2012). Secondary MPs are plastic items resulted from fragmentation of larger particles due to physical, chemical and/or biological processes (Ryanet al. 2009; Browne et al. 2007).

MPs have already been found in the water column of coastal and oceanic regions, in beach sediments, ocean bottoms, biota, and air (Barnes et al. 2009; Engler, 2012; Eriksson et al. 2013; Lee et al. 2013; Smith, 2012; Dris et al. 2016; 2017). Their density determines if will deposit in the bottom sediment or remain in the water column, where they will be transported and distributed, and may accumulate in the coastal regions, especially in sandy beaches (Browne et al. 2011). The occurrence and distribution of MPs in coastal areas are often related to population density (Browne et al. 2011; Jayasiri et al. 2013), rainfall, winds, storm, local hydrodynamics and beach geomorphology (Eriksson, et al. 2013).

Once in the marine environment MPs can be ingested by biota and may lead to both physical and chemical damages. These damages could include suffocation, clogging of the digestive tract, decrease of appetite, inflammation and decrease of lysosomal membrane stability (Setälä et al. 2016; Von Moss et al. 2012; Browne et al. 2007; Cole et al. 2011; Watts et al. 2015). In addition, MPs can carry contaminants, either added during their production or adsorbed from the environment, which present a large range of harmful effects to the biota (Teuten et al. 2009). Plastic fragments may act as substrate, sustaining an epiplastic community

that could lead to ecological changes (Reisser et al. 2014), as well as they interfere in the sinking rate of fecal pellets which may disturb the biological pump (Cole et al. 2016).

Qualitative and quantitative analysis to identify the most likely sources and accumulation patterns of plastics are underlying to support management of marine plastic litter and to create public policies (Xanthos and Walker et al. 2017). In this context, monitoring represents an important step towards the analysis of spatial and temporal trends, aiming to promote the increase of environmental quality (Galgani et al. 2010). Sandy beaches are frequently studied for identification and quantification of solid wastes, especially plastics (Moreira et al. 2016; De Carvalho and Neto, 2016; Lozoya et al. 2016). It is necessary to consider that transport of plastic particles depends on the size, shape and density of the material (Browne et al. 2010). The tidal floods contribute to a tendency of MPs deposition along the high tide lines (Costa et al. 2010; Corcoran et al. 2009). However, the constant remobilization of this material characterizes the accumulation of MPs material in the strandline as temporary, and the post-beach compartments offer better conditions for deposition and accumulation of the particles (Hidalgo-Ruz et al. 2012).

In Brazil, studies regarding occurrence and distribution of MPs on sandy beaches are still sparse and very recent, mostly focus on Northeast and Southeast coasts. Microplastics have been reported in Brazilian coast biota contamination and plankton association (Lima et al. 2015b; Lima et al 2014; Ivar do Sul et al. 2014; Castro et al. 2016) as well as within in sediments and interacting with other pollutants (Vedolin et al. 2018). Sediments samples reveal that fragments are, usually, the most common type of MPs founded (Ivar do Sul et al. 2009, Costa et al. 2010; Carvalho and Baptista Neto, 2016). Sources identification as well as the influence of anthropogenic and environmental conditions in MPs distribution remains limited, but primary source contamination, fishing, and port activity have already been identified as some of the main sources of microplastics (Castro et al. 2016; Carvalho and Baptista Neto, 2016; Costa et al. 2010, Turra et al. 2014). In Brazil, only one study identified MPs regarding polymer composition (Castro et al. 2016), revealing urgency in the classification of the polymer type found in order to provide more accurate data and confirm visually the identification of microplastics.

In the present study, MPs occurrence and distribution in ten different sandy beaches from Santa Catarina Island, Southern Brazil, were evaluated considering the distinct characteristics in each of them. Additionally, the influence of environmental factors, such as coastal geomorphology and hydrodynamic (waves, currents, tide pattern), in MPs incidence were also discussed. Besides levels and pattern of distribution, composition of pellets collected were also investigate and degradation indexes were used to assess information about the quality of pellets that reach Santa Catarina Island. Understanding the behavior of MPs on sandy beaches may contribute to a better management of this threat, since marine and coastal pollution are responsible for changes in the structure and function of communities and such changes may cause biodiversity impact, economic and public health damage (Islam and Tanaka, 2004).

1.5 MATERIALS AND METHODS

1.5.1 Study area

Santa Catarina Island (Figure 1), located in Southern Brazil, has an area of 424.4 km², warm and humid subtropical climate, and a microtidal regime, with neap and spring tides ranging between 0.4 and 1.2 m, respectively. The Island is separated from the continent by a 500 m strait divided in two bays: North and South.

Santa Catarina Island has beautiful beaches that attract a growing number of tourists every year. Although tourism is the main activity in the region (Andrés et al. 2018), it is also sought by the technology and the entrepreneurship sectors (BRASIL, 2017); the regions has 20% of all Brazilian startups. Moreover, the region is known nationally for shellfish production, since more than 90% of all bivalves cultivated in Brazil come from Santa Catarina State (Sabry et al. 2011). Fishing is a traditional activity and the main source of income for many families in the Island, such as in Sambaqui, Barra da Lagoa and Pântano do Sul. Santa Catarina Island lies between Itajaí Harbor and Imbituba Harbor. Itajaí Harbor is located in a region of economic and environmental importance, composed of a diversity of fishing industries and the largest hydrographic basin in the state of Santa Catarina, the Itajaí-Açú river basin, with 15,500 km² of drainage (Pereira et al 2010). The mouth of the Itajaí-Açú River is located approximately 100 km north of Santa Catarina Island (Reis et al., 2010) and,

in the summer periods, it is suggested that the flow of the Itajaí-Açú River plume should be directed to the south, confirmed by the low salinity-tongue ($S < 35.35$) observed in summer, extending southward from the mouth of Itajaí-Açú River along the middle-shelf region (Campos et al., 2013).

Figure 1 Location map and main features of the study

1.5.2 Sampling

The study was conducted during January 2018, in ten sandy beaches from Santa Catarina Island: a) Brava, b) Joaquina, c) Lagoinhado Norte, d) Moçambique



(northern and southern part), e) Pântano do Sul, f) Ribeirão da Ilha, g) Sambaqui, and h) Solidão (Figure 1, Table S1). Sampling location targeted beaches with different environmental (wave energy, declivity, sediment size etc) and anthropogenic (urbanization, beach uses, etc) characteristics.

Sampling method follows the procedures described by Dekiff et al. (2014) and Zhao et al. (2015) with modifications. At each beach a total of 12 samples were collected, 6 from each of the sections: a) strandline, defined here as the highest high tideline; and b) backshore, defined here as the place where the first obstacle was encountered (e.g dune, construction, vegetation). During sampling, 0.5 x 0.5 m quadrats were placed every 20 m in a 100 m line and surface sediment (2 cm) were collected with metal spoons, stored and taken to the laboratory. Sampling took place

during low tide and early in the morning to avoid beach cleaning and the presence of beachgoers.

1.5.3Plastics separation and characterization

Laboratorial procedures were defined following those described by Hidalgo-Ruz et al (2012), Fanini and Bozzeda (2018) and Veerasingam et al (2016) with few alterations. Briefly, sediments were oven dried at 60 °C, weighted and poured through 5 mm and 500 µm mesh sieves. Materials retained in the 500 µm sieve were examined and quantified using a stereomicroscopy (Leica S8APO Wetzlar, Germany), measured, and classified by in the follow categories: fibers, pellets, styrofoam or fragments. To allow comparison with other studies, MPs concentrations were expressed both as number of particles on a weight basis (particles kg⁻¹ of dry sediment) and on an area basis (particles m⁻²). Also, to standardize pellets occurrence measurements and compare the data of all nine beaches, the Pellet Pollution Index (PPI) was calculated, using the ratio between the number of pellets and the volume of sediment sampled (Fermandino et al. 2015).

For polymer identification, part of the sampled particles (50%) was analyzed using a FTIR spectroscopy (Agilent Carry, 660 Model) equipped with an attenuated total reflectance (ATR) diamond crystal attachment. Samples were placed directly on the crystal and the mean of 20 scans, in the range 4000 - 650 cm⁻¹ and resolution of 4 cm⁻¹, was measure for each sample (Figure 2). Prior polymer identification, all baseline spectra were normalized, spectra with low signal, high noise and those who did not have references peaks well defined were removed. Spectra of polyethylene (PE) were identified by presenting absorption peaks around 2920, 2851, 1475, 1374 and 720 cm⁻¹, due to asymmetric and symmetric stretching vibration of C-H bond in ethylene (2920 and 2851 cm⁻¹) and bending vibration of the C-H bond (at 1475 and 720 cm⁻¹). Polypropylene (PP) was identified according to absorption peaks between 2720 and 2950 cm⁻¹ and between 1453 and 809 cm⁻¹ (Guilmine et al. 2002, Kassouf et al. 2014). Polystyrene (PS) was identified by absorption peaks at 3026 and 2849, 1601 and 1493, 758 and 700 cm⁻¹, corresponding respectively to aromatic and aliphatic C-H stretching, aromatic C=C stretching, C-H benzene ring hydrogen's deformation, and ring deformation (Kaniappan and Latha, 2011).

1.5.4 Pellets analysis

A total of 101 pellets, mostly from Brava beach, were evaluated regarding their relative aging. It was assessed by two methods: a) visual evaluation of weathering state and degree of yellowing (Fanini and Bozzeda, 2018), and b) measurement of carbonyl content indexes, ester carbonyl bond index and vinyl double bond index, based on the light-induced photo-oxidative degradation of plastic in the environment which usually increase with the exposure time (Endo et al. 2005). A Spearman correlation test was used to measure the strength of a linear relationship between a) visual evaluation of weathering state and degree of yellowing and b) carbonyl content indexes, ester carbonyl bond index and vinyl double bond index.

Keto carbonyl, ester carbonyl and vinyl bond indexes were calculated based in the ratio between their, respectively, absorption peak and distinct reference peaks, using the following formulas:

$$(5) \text{ Ketone carbonyl bond index} = I_{1715}/I_{1465} \text{ (Artham et al. 2009, Albertsson et al. 1987, Roy et al. 2011)}$$

$$(6) \text{ Keto carbonyl bond index} = I_{1715}/I_{1374} \text{ (Andrady et al. 1993)}$$

$$(7) \text{ Keto Carbonyl bond index} = I_{1715}/I_{720} \text{ (Endo et al. 2005)}$$

$$(8) \text{ Ester carbonyl bond index} = I_{1740}/I_{1465} \text{ (Artham, 2009; Endo et al. 2005)}$$

$$(5) \text{ Vinyl bond index} = I_{1640}/I_{1465} \text{ (Artham, 2009; Endo et al. 2005)}$$

where absorption peaks at 1715 cm^{-1} , 1740 cm^{-1} , 1640 cm^{-1} , 1465 cm^{-1} , 1374 cm^{-1} , and 720 cm^{-1} correspond to keto carbonyl, ester carbonyl, double bond, methylene bands, symmetric bending vibrations of CH_3 and minimum of four methyl groups $(\text{CH}_2)_4$. Principal components analysis of Carbonyl indices was used to observe trends for the relationships between indexes.

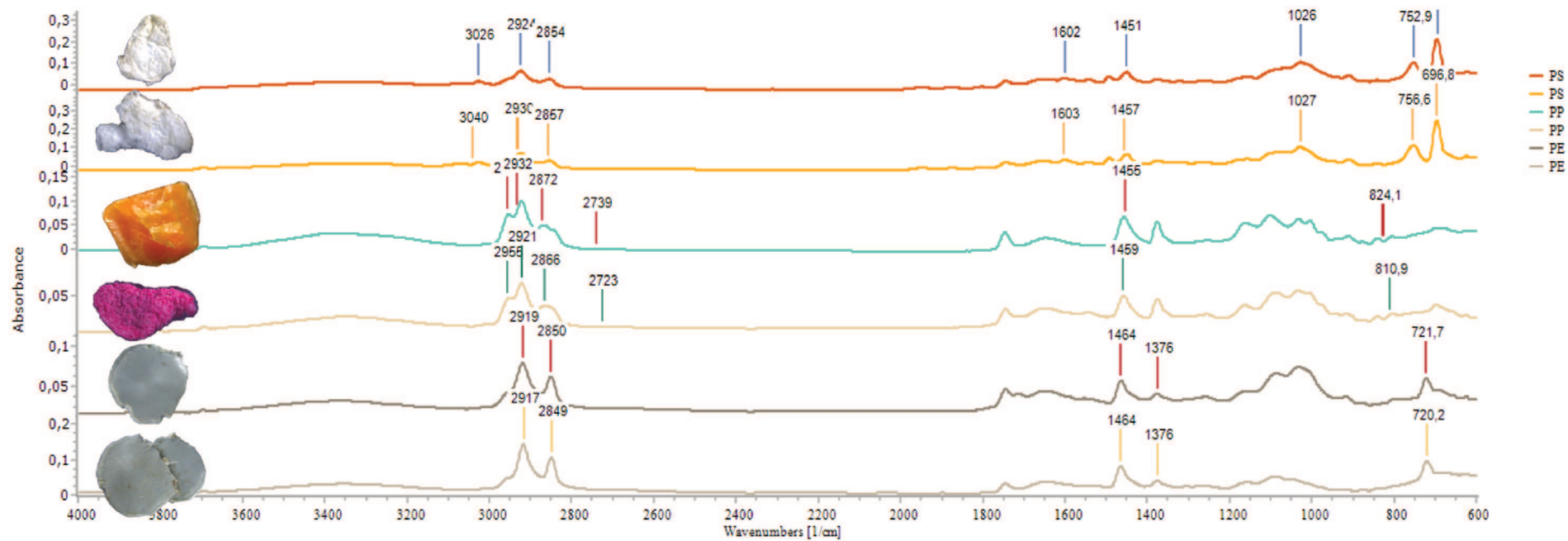


Figure 2 FTIR spectra of a, b) PS (Polystyrene); c, d) PP (Polypropylene); and e, f) PE (Polyethylene) samples.

1.6 RESULTS AND DISCUSSION

1.6.1 Microplastic abundance and spatial distribution

It is worth to note that the period of study (Jan/2018) was characterized by a precipitation ratio higher (315.2 mm) than the average values expected for the period

Table 1 Density, size and methods of sampling of plastic debris from beaches throughout the world.

*only pellets.

(149.2) (INMET). Therefore, it is possible that data reported here did not represent a typical summer in the region. Indeed, it was noted that the high precipitation increased the abundance of organic matter particles (for example, algae and leaves) found in the strandline portions of some beaches, such as Lagoinha do Norte and Brava, which may have contributed to the large amount of items detected in the area. Both Van Cauwenberghe et al. (2015) and Strand et al. (2013) reported that aggregation with organic matter plays an important role in the movement and abundance of MPs.

MPs were found in all ten beaches sampled in a total of 588 particles (Table 1, Table S2). MPs concentration range from 1.33 to 127.3 particles m^{-2} at strandline, and from 0 to 37.33 particles m^{-2} at back shore portion. Although some studies indicate that backshore portion could accumulate more MPs than strandline portion, it was not observed in most beaches sampled here; only Joaquina, Pântano do Sul and Solidão showed higher MPs concentration at the strandline (Figure 3). This pattern is consistent with data reported by McDermid and McMullen (2004) throughout the Hawaiian Islands, on which 18 559 MPs were founded at the strandline portion and only 541 MPs at the backshore portion. Lee et al. (2015) and Heo et al. (2013) also reported a higher abundance of marine plastic debris in the backshore zone compared to the strandline area.

MPs accumulation at the backshore portion is, in general, due to trapping by vegetation and transport during storm events (McDermid and McMullen, 2004; Turner et al. 2011). Also, some studies suggest that type and density of MPs may be related with the portion of preferential accumulation and that the backshore portion tends to accumulate a higher abundance of small plastics than the strandline, suggesting that the small plastic debris can be moved more easily to the upper littoral zone due to wind and tidal (Heo et al. 2013; Turner et al. 2011). The fact that it was not observed at Santa Catarina Island could be related to the period at which sampling happened.

During summer beach occupation could play an important role in MPs distribution, since municipal workers and sellers sweep the areas cleaning from large litters, but also remobilizing and mixing material from different areas.

Beach	Density (itens m ⁻²)	PPI index	Size	Meth od	Reference
10 beaches in Santa Catarina Island (Santa Catarina, Brazil)	127.3 (strandline) 0 (backshore)	Low	-5 mm	Backshore and Strandline 50 x 50 x 2 cm	Present study.
Boa Viagem Beach (Pernambuco - Brazil)	2900	-	1 mm	Strandline 10 x 10 x 2 cm	Costa et al. 2010
Portuguese coastline	1 - 393	Very High		Last high tide mark 50 x 50 cm 2 x 2 m	Martins and Sobral, 2011
12 beaches in Korea	51019 (backshore) 3313 (high strandline)	Very High Very High	-5 mm	High strandline 50 x 50 x 2 cm	Lee et al. 2015
13 beaches in São Paulo (Brazil)	0 to 5.3 (backshore) 0 to 131.3 (coastal dunes)*	-	1mm	Coastal dunes and backshore	Moreira et al. 2016
8 beaches in Island of Malta	<1 to 1000*	-		11 morphological zones except dune systems 100 x 100 cm	Turner and Holmes, 2011
9 beaches in the Hawaiian archipelago	4 to 17645	Very High	-15mm	High tideline and berm 61 x 61 x 5.5 cm	McDemid and McMullen, 2004
Pituba (Bahia, Brazil)	-	High		1 x 1 x 0,05 m	Fernandino et al 2015
Boa Viagem Beach (Pernambuco - Brazil)	642.6 (protected areas) 130 (exposed areas)	-	1mm-20mm	Strandline 10 x 10 x 2 cm	Pinheiro et al.2019

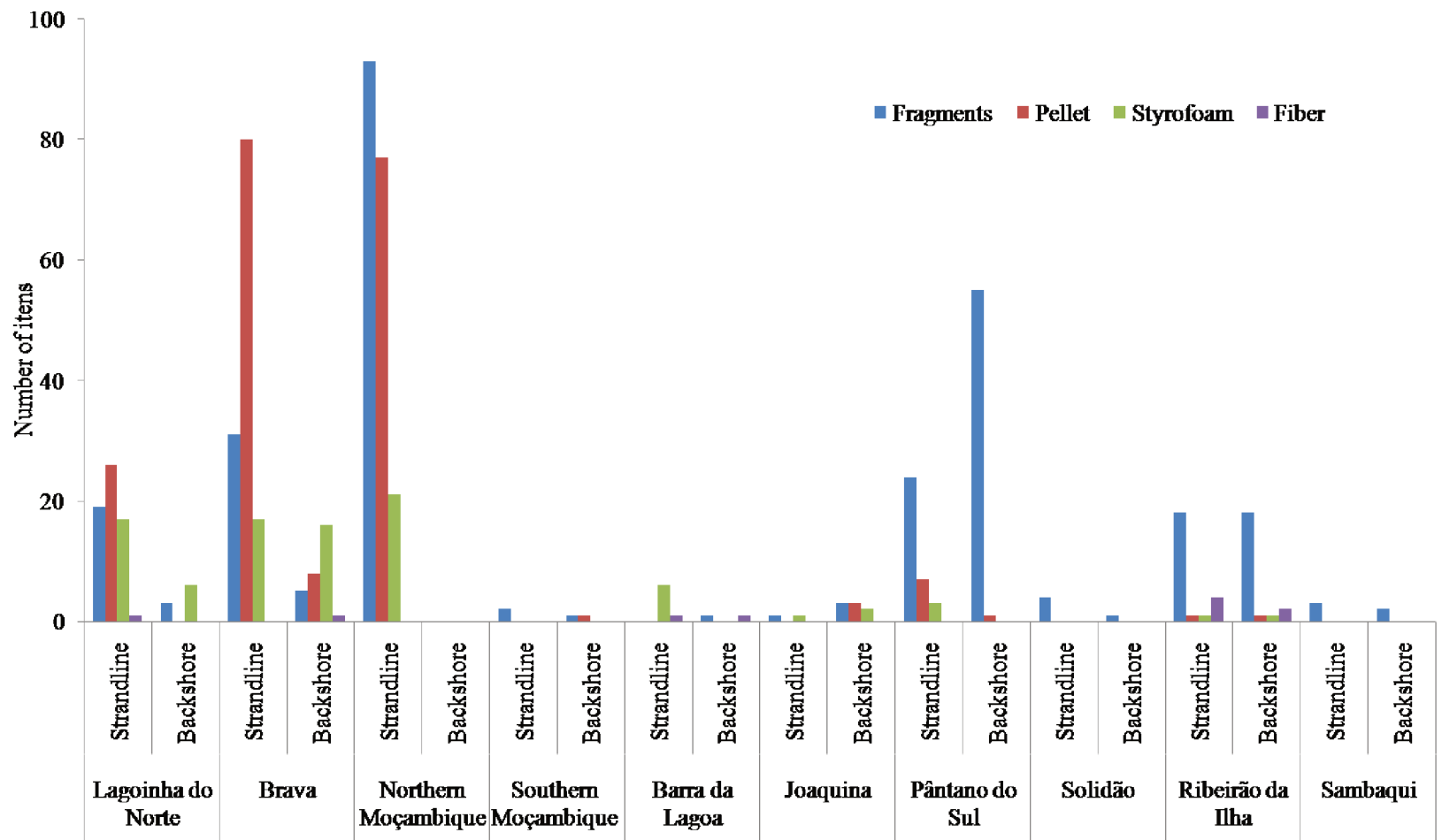


Figure 3 Number of items collected in ten beaches from Santa Catarina Island divided by category and beach portion.

Northern Moçambique was the beach with the highest concentrations of MPs (items m^{-2}), followed by Brava >Pântano do Sul ~ Lagoinha do Norte >Ribeirão da Ilha> Barra da Lagoa> Joaquina >Sambaqui ~ Solidão ~ Southern Moçambique (Figure 3). Although several studies detected a positive relationship between densely populated areas and/or recreational beaches use and the abundance of MPs in coastal sediments (De Carvalho and Neto, 2016; Browne et al.2011, Yu et al, 2016, Van Cauwenberghe et al. 2015), this relationship was not observed for most beaches studied here; not even for fibers, an indicative of sewage origin (Browne et al. 2011). It suggests currents, winds, waves, beach orientation, also as a dominant mechanism for MPs distribution in Santa Catarina Island. Similar results were found by Nel and Froneman (2015) and Nel et al. (2017) along the South Africa coast.

The importance of natural characteristics of each area on MPs abundance could be exemplified by Barra da Lagoa - Moçambique system that shows a morphodynamic gradient resulted from the combination of grain size, sediment transport and beach exposure to the wave energy (Miot da Silva et al.2012). Moçambique, the longest beach in the island (11.2 km), is inserted and protected by the Rio Vermelho State Park and, therefore, is neither a highly urbanized area nor a popular place for tourism, contrasting with Barra da Lagoa Beach, characterized by a densely urbanized area and fishing activity. Even though Moçambique and Barra da Lagoa received distinct names, they are not physically separated. Both are composed of fine sand and are dissipative beaches, but Barra da Lagoa is a low energy zone with a moderate width while Northern Moçambique is wider and more exposure to high energy waves (Miot da Silva et al. 2012). MPs distribution in the area shows higher values in Northern Moçambique (63.7 itens m^{-2}) and low values in Southern Moçambique (1.3 itens m^{-2}) and Barra da Lagoa (3.0 itens m^{-2}); actually Northern Moçambique presented the highest values from all beaches sampled in Santa Catarina Island. The mechanism responsible for maximum accumulation of MPs in Northern Moçambique appears to be wind and wave energy exposure, predominantly S-SE, that results in a northward littoral drift system already reported to be responsible for similar sediment transport in the area (Miot da Silva et al. 2012).

On the other hand, the importance of anthropic characteristics could be observed in the values reported for Sambaqui and Ribeirão da Ilha, both beaches with similar natural characteristics located facing the continent, respectively in Northern and Southern Bay, present distinguished values for MPs occurrence (Figure 3). The hydrodynamics of North and South Bay is mainly controlled by river discharge and tidal fluctuation (Schetini et al, 2000). North and South Bays receive a number of small estuaries and the largest of these being Cubatão River, on the continental margin of the South Bay, impacted with anthropogenic inputs from agricultural activities and domestic sewage (Parizzotto, 2012). Ribeirão da Ilha and Sambaqui are located in very low hydrodynamic environments and have a very narrow sand extension with no dunes. Both are a well known place for its oysters production with restaurants bordering the sand, and Ribeirão da Ilha as well as several houses whereas in Sambaqui the beach is bordered by a street.

Overall, MPs concentrations on beaches from Santa Catarina Island were lower than most in beaches from around the world (Table 1). The higher density values in Santa Catarina Island are for Brava and Northern Moçambique correspond to 48.62 items m^{-2} (11.69 item kg^{-1}) and 63.7 items m^{-2} (9.52 item kg^{-1}), respectively, both exposed areas. Considering only the strandline portion, this abundance values increase to 64 items m^{-2} (Brava Beach) and 127.3 items m^{-2} (Northern Moçambique). This results are lower than those founded in Jordan coast, (44 000 pellets m^{-2} , Abu-Hilal and Al-Najjar, 2009), and places that acts like a filter for MPs transported by oceanic surface currents, like Easter Island (805 items m^{-2} , Hidalgo-Ruz and Thiel, 2013) and Hawaii (17 645 items m^{-2} , McDermid and McMullen, 2004). Abundance of MPs in strandline portion of Northern Moçambique could be compared to those reported in exposed areas from Boa Viagem beach (130 items m^{-2} , Pinheiro et al. 2019), and in areas nearby sources of plastic pellets (120 items m^{-2} , Hidalgo-Ruz and Thiel, 2013 and 130 items m^{-2} , Moreira et al. 2016).

1.6.2 Microplastic composition

MPs sampled at Florianópolis beaches were classified as fragments (48%), pellets (35%), Styrofoam (15%), or fibers (2%) (Figure 3, Table S3). Fragments were the MPs predominant on 5 out of 10 beaches sampled (Solidão, Sambaqui, Ribeirão da

Ilha, Pântano do Sul, and Northern Moçambique), whereas pellets were predominant in 2 beaches (Brava and Lagoinha do Norte). In Southern Moçambique and Joaquina, pellets and fragments were detected in similar proportions. On the other hand, in Barra da Lagoa Styrofoam was the predominant MPs. Overall, it seems that composition depends on the local use of each beach and the environmental conditions responsible for the supply dynamic of MPs.

For example, located in the northern region of the Santa Catarina Island, Brava and Lagoinha do Norte beaches are important for tourism (Oliveira, 2015) and receive a large amount of people every year, especially during the summer. Even though, Brava and Lagoinha do Norte presented the second and the fourth largest amount of MPs in this study, the predominant class of MPs in the both areas is pellets, a kind of particle no related to recreational use of beaches. Pellets are primary plastics used by industry to produce all other plastic products and they enter the environmental by accidental spills (either on land or sea) or due to poor handle in harbors. Since there are neither plastic industries nor harbor in Santa Catarina Island, pellets seem to originate from Itajaí Harbor, located 80 km north of Santa Catarina Island at Itajaí-Açu Estuary. Itajaí Harbor is the major route of international trading in Santa Catarina State and responsible for almost 100% of all plastic resin imported to State (received more than 600 tons in 2018, Figure S1). During summer, the predominant northeastern winds favor the transport of the Itajaí-Açu plume to south (Figure S2) and could be responsible for transport of pellets to the north portion of Santa Catarina Island.

1.6.3 Polymer Identification

For polymer identification, 47% of all fragments and 49% of all pellets were analyzed by FTIR, mostly from Brava beach (70 %) and Northern Moçambique (20 %). Regarding fragments, 46 % were identified as PP, 40 % as PE and 13 % as PS (Figure 4). For pellets, 82 % were identified as PE and 18 % as PP, as expected, since PE represents most of the global plastic production worldwide, followed by PP production (PlasticEurope, 2016; Andrady and Neal, 2009). PE is the primary material for bottles, bags, storage containers, straws and films, while PP is the primary material for plastic tools, packing, rugs, carpets, caps, cups, ropes and fishing nets. Higher values of PP than PE could be expected in coastal areas (Rios et al. 2007) since sampling occurred

during summer when consume of cups, caps, fishing gear (for sport and recreational fishing), and packing increase.

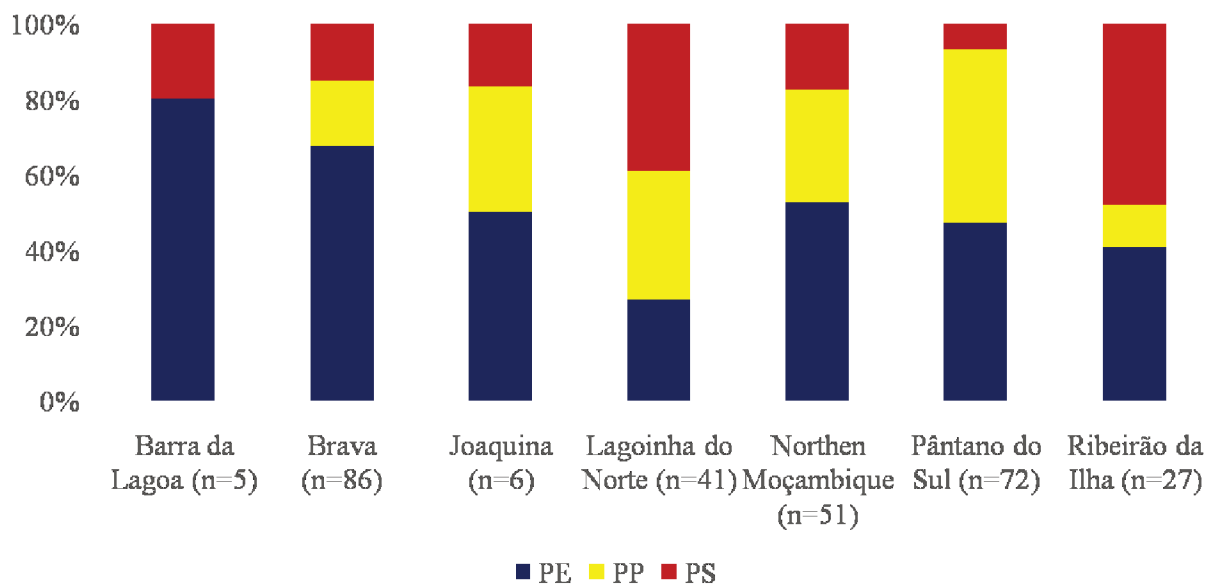


Figure 4 Polymeric distribution of MPs sampled in Santa Catarina Island beaches.

1.6.4 Pellets

In the total 205 pellets are sampled in sandy beaches from Santa Catarina Island which were divided by color: 73 % transparent, 20 % white and 7 % other colors (red, blue, black). All white/transparent pellets were also visually classified according to degree of erosion (Figure S3) and the degree of yellowing (Figure S4). According to the PPI index (Table 2), Brava and Lagoinha do North beaches are classified as very high contaminated by pellets while most beaches (7 out of 10) were classified as very low contaminated.

Table 2 PPI index and beach classification according to pellets concentration (based on Fernandino et al. 2015) for Santa Catarina Island beaches.

Beach	PPI	Classification
Barra Da Lagoa	0	Very Low
Brava	3.52	Very High

Joaquina	0.12	Very Low
Lagoinha Do Norte	1.04	Moderate
Northern Moçambique	3.08	Very High
Southern Moçambique	0.04	Very Low
Pântano Do Sul	0.32	Very Low
Ribeirão Da Ilha	0.08	Very Low
Solidão	0	Very Low
Sambaqui	0	Very Low

Most pellets (75 %) showed some level of erosion. Among them, highly eroded pellets represented only 17 % of the total and are distributed mostly on the strandline portion (Figure 5). Transparent/white pellets were divided into pellets with no apparent yellowing (35%), with yellowish spots (31%), moderately yellowish (12%), highly yellowish (11%) and very high yellowing (4%). Pellets yellowing arises from many causes, specially from photo-oxidation that extinguish free radicals, originated from phenolic antioxidants (a type of additive) being exposure to UV radiation, and form quinonoidal structures (Albertsson et al. 1987). Pellets that spent more time in the marine environment have more time to oxidize. Therefore, degree of yellowing is suggested as an index of resident time of pellets in the marine environment and/or exposure to UV light (Carson et al., 2011). The fact that most pellets from Santa Catarina Island beaches presented low levels of erosion and yellowing and that they were sampled mostly at the strandline portion (Figure 5 and Figure 6) suggests that pellets arriving on the island are young and probably do not spend a lot of time on the beaches.

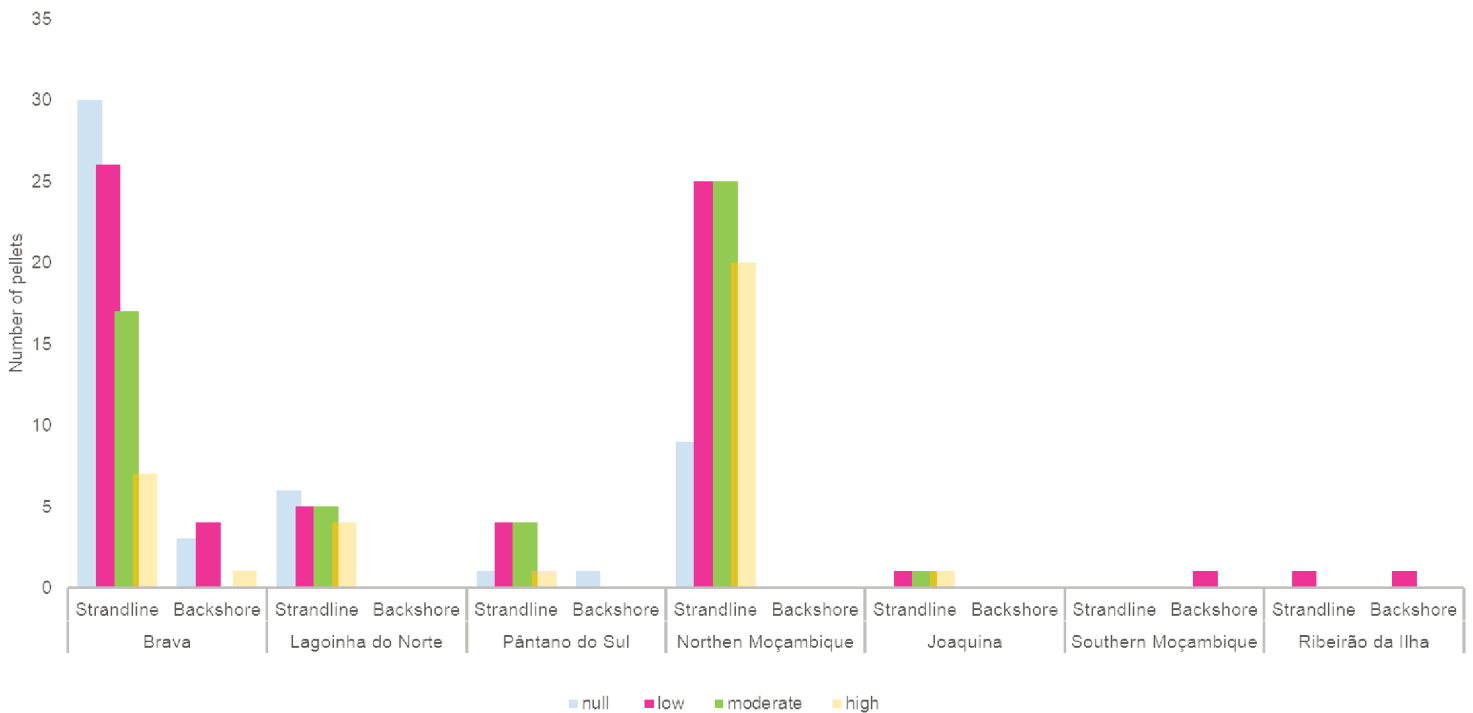


Figure 5 Distribution of pellets from Santa Catarina Island beaches considering degree of erosion on each beach compartment.

According to Andrady et al. (1993) yellowing is faster in shorelines than in the ocean. Therefore, considering that pellets accumulated at the backshore portion would spend more time in the beach than those in the strandline, it was expected that pellets from the backshore portion would also present higher erosion and yellowing levels due to alteration of their surface area caused by natural agents. However, erosion and yellowing levels did not present preferences regarding portions (Figure 5 and Figure 6).

Photooxidation reactions, responsible for pellets yellowing, also increased surface area through embrittlement, thus degree of yellowing could correlate to erosion degree and production of smaller particles (micro- and nanoplastics) from pellets (Albertsson et al. 1987). A Spearman correlation test indicates that there is a compatibility between visual scales of yellowing and surface erosion ($r^2 = 0.64$ at $p < 0.05$).

Finally, besides yellowing, oxidation also leads to formation of functional groups, such as ketone and ester, that reduce polymer hydrophobicity and favors sorption of organic compounds, as PCBs. Hence, pellets from Santa Catarina Island should have a lower affinity for these compounds, but chemical analyses are necessary to test this hypothesis.

1.6.5 Oxidation Index

Ketone carbonyl, ester carbonyl and vinyl bond indices were used to address formation of new functional groups or change in the amount of functional groups and are related to level of weathering in polyolefins (Albertsson et al. 1987). Once in the environment, polymers structure can change due to biotic and abiotic reaction that show different intensities if on the ocean or in the shoreline (Biber et al. 2019). While aquatic environment support biofilm formation, over the shore particles were exposure to higher temperatures and UV radiation as well as to higher levels of oxygen. Initially, auto-oxidation due to abiotic factors (more intense at shoreline) increases carbonyl indices as a result of new functional groups formation, like esters and ketones (Biber et al. 2019). If at the sea, due to hydrophobicity reduction, this step will enhance the fouling process. Moreover, if the particle stays in the water for a long period of time, carbonyl indices will decrease due to biodegradation through Norrish type I and/or II reactions, leading to formation of double bonds in the polymer chain. Therefrom, decrease in carbonyl indices and presence of double bonds suggests degradation due to action of microorganisms.

Since beached pellets faces higher exposure to UV radiation and mechanical erosion when at shoreline than in the oceans (Corcoaran et al., 2009; Gregory and Andrady, 2003; Andrady, 2011) carbonyl oxidation indexes could lead to an indication of the time that the pellets are in the beaches. The use of indices instead of the absorption peak corresponded to the functional groups of interest is to compensate for differences in polymer thickness (Albertsson et al. 1987).

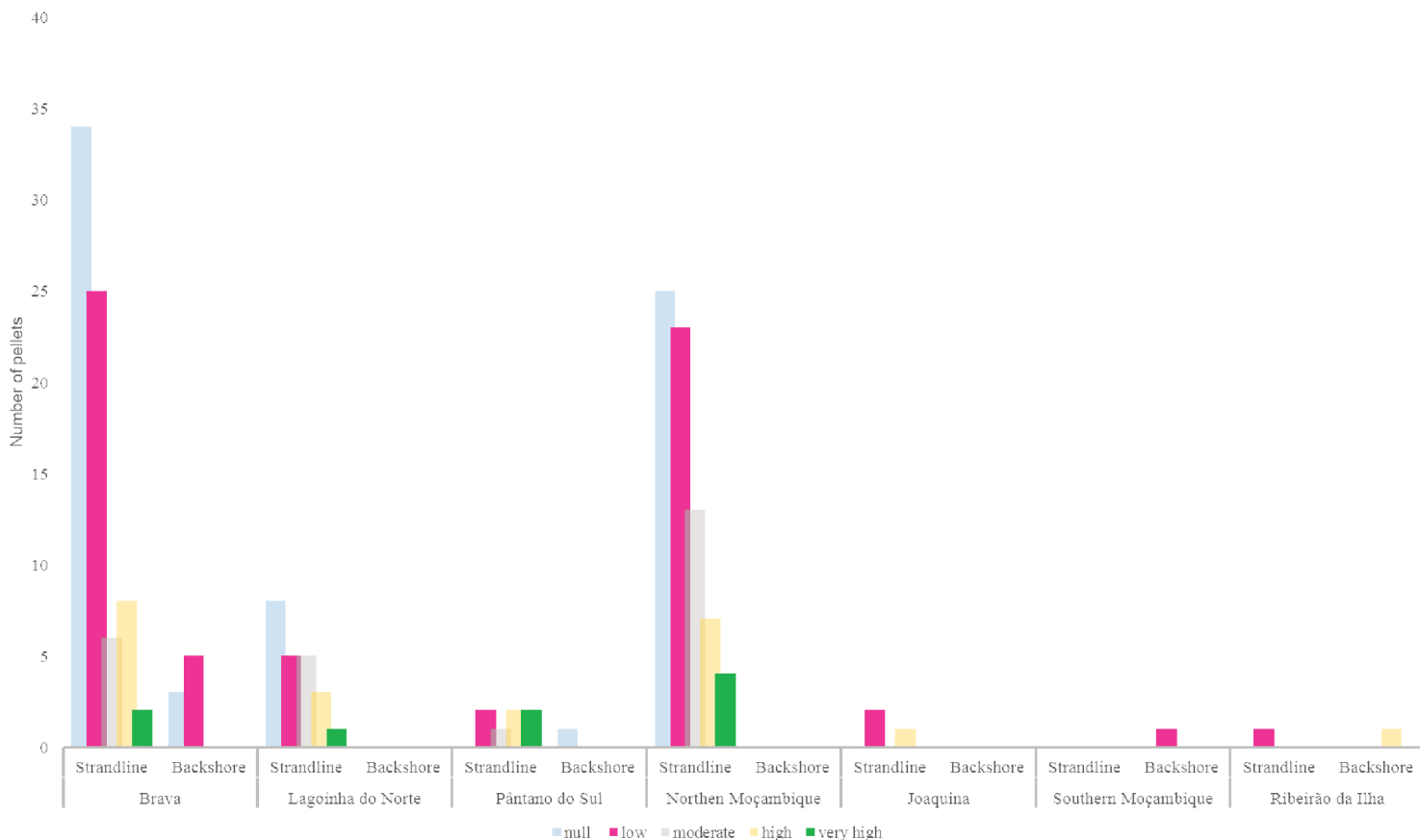


Figure 6 Distribution of pellet from Santa Catarina Island beaches considering degree of yellowing on each beach compartment.

However, there is no consensus on how to calculate the carbonyl index. For example, ketone carbonyl index is calculated dividing the absorption peaks, at 1715 cm^{-1} , by a reference peak which varies among authors: 1465 cm^{-1} or 1374 cm^{-1} or 720 cm^{-1} (Artham et al. 2009, Albertsson et al. 1987, Roy et al. 2011, Andrady et al. 1993, Endo et al. 2005) representing methylene bands, symmetric bending vibrations of CH_3 and minimum of four methyl groups $(\text{CH}_2)_4$, respectively. Applying those indices for pellets sampling at Santa Catarina Island beaches, very different results were found (Figure S5 and S6) making difficult to choose which show the most realistic results. Such results advocate the urgency for standardization of carbonyl index calculations.

Additionally to ketone carbonyl index, the ester carbonyl index and the vinyl bond index were also used to study polymer degradation. Here, the same reference

peak (1465 cm^{-1}) was used to calculate them in an effort to improve results comparisons with yellowing degree and erosion degree (Figures S7 and S8). Overall no relationship was observed among level of yellowing and indices, but for erosion a slightly increase was observed for ketone carbonyl index and a decrease for vinyl bond index. Considering that low erosion is related to low degradation, these results were opposite of what was expected, since the number of ketone carbonyl groups were expected to increase in the early stages of degradation and vinyl bonds were expected to increase with the advancement of degradation. Therefore, since bond indices not always indicate a direct relationship with the weathering of plastic as well as the chemical bonds did not change linearly with time, bond indices alone could not lead to age determination (Brandon et al., 2016).

Finally, there are other factors to be considering: a) in this study the number of pellets in each class of yellowing and erosion were not equally since only 40 % of all transparent/white pellets were analyzed; b) yellowing is no uniform as showed by studies where sliced pellets revealed a darker coloration on the outside that became progressively lighter towards the centre, so erosion may lead to the exposure of no-yellowed pellets parts that will influence FTIR results and work as a confounder during oxidation indices interpretation (Turner et al. 2011); c) the fact that pellets stayed in the ocean before arriving on the shoreline is also a confounder for oxidation indices interpretation, since there are degradation difference due to the nature of each compartment.

Weathering processes and degradation of pellets exposed to UV radiation and mechanical erosion are enhanced mainly by photo-oxidation (Corcoaran et al., 2009). Oxidation can be visually identified by the yellowing processes and the increasing amount of low molecular weight compounds. The adsorption of the oxygen present in the water leading to formation of some specific groups, like the carbonyl group, ester carbonyl and vinyl double bound group. Thus, the oxidative degradation of polyolefins can be indicated by the level of these groups.

1.7 CONCLUSION

Sampling of 10 sandy beaches from Santa Catarina Island revealed a relatively low microplastic concentration with higher values over the strandline (1.33 to 127.3 particles m^{-2} in the strandline and 0 to 37.33 particles m^{-2} in the backshore). Even though, Northern Moçambique is considered one of the pristine beached in the Island, it presented the higher values among all beaches, and a very high PPI value, highlighting the importance of winds, wave energy and beach orientation on MPs distribution. For pellets, proximity to potential source (Itajaí Harbor) appears to be the reason for the higher values detected in the beaches from the Northern part of the Island, especially Brava beach. Even though a few hotspot for pellets were detected, overall Santa Catarina Island sandy beaches show lower values of plastic material when compared to other region. Yellowing and erosion degree suggests that pellets arrive at the beach after a short stay in the ocean and also did not stay in the shoreline for a long period of time. Regarding oxidation indices is clearly the need for method standardization since different reference peaks will yield distinct results.

This study points out that a monitoring program are needed to evaluate and better understand the spatial or temporal trends of MPs on Santa Catarina Island, Identification of microplastic sources is also essential to prevent littering. Also, methodology and sampling techniques should be addressed and standardized in order to harmonize the data collected and allow comparisons on geographic and temporal scales.

Data accessibility statement— Data pertaining to this manuscript are deposited in figshare at <https://doi.org/10.6084/m9.figshare.9585914.v1>

Conflict of Interest – No conflict of interest

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1.9 SUPPORT INFORMATION

Distribution and characterization of microplastics in sandy beaches in the Island of Santa Catarina, Brazil.

Table S3 spatial and temporal localization of sampling area in Santa Catarina Island.

Beach	Latitude	Longitude	Date
Joaquina	-27°63'00.6"	-48°45'05.1"	Jan-08-19
Barra da Lagoa	-27°56'94.1"	-48°42'78.3"	Jan-08-19
Lagoinha do Norte	-27°23'32.9"	-48°25'66.2"	Jan-18-19
Brava	-27°24'17.4"	-48°24'76.7"	Jan-18-19
Northern Moçambique	-27°29'56.3"	-48°23'68.1"	Jan-19-19
Pântano do Sul	-27°46'86.5"	-48°30'71.8"	Jan-16-19
Sambaqui	-27°29'13.3"	-48°31'45.0"	Jan-23-19
Ribeirão	-27°29'73.4"	-48°31'44.9"	Jan-22-19
Solidão	-27°47'61.9"	-48°32'0.05"	Jan-16-19
Southern Moçambique	-27°31'44.1"	-48°25'0.26"	Jan-19-19

Table S4 MPs sampled from Santa Catarina Island beaches separated by media item m-2 and mediana item m-2, media item kg-1 and mediana item kg-1.

Beach	Média Item m-2 Total	Mediana Item m-2 Total	Média Item kg-1 Total	Mediana Item kg-1 Total	Portion	Média Item m-2	Mediana Item m-2	Média Item kg-1	Mediana Item kg-1	Total
Barra da Lagoa	3	0	0,7	0	Strandline	4,67	2	1,15	0,60	7
					Backshore	1,32	0	0,26	0	2
Brava	48,62	44	11,69	9,7	Strandline	64	64	13,74	13,74	128
					Backshore	20	6	4,26	1,4	30
Joaquina	2,67	2	0,42	0,22	Strandline	1,32	0	0,27	0	2
					Backshore	4	4	0,58	0,49	8
Lagoinha do Norte	24	28	1,31	1,22	Strandline	42	38	1,21	1,15	63
					Backshore	6	0	1,41	1,25	9
Northern Moçambique	63,7	2	9,52	0,28	Strandline	127,3	82	19,04	15,04	191
					Backshore	0	0	0	0	0
Southern Moçambique	1,33	0	0,23	0	Strandline	1,33	0	0,21	0	2
					Backshore	1,33	0	0,24	0	2
Pântano do Sul	30	26	7,65	5,78	Strandline	22,67	22	5,71	5,78	34
					Backshore	37,33	34	9,60	7,69	56
Ribeirão da Ilha	13,54	4	2,01	0,92	Strandline	16	4	2,45	0,89	24
					Backshore	11,43	8	1,64	1,43	20
Solidão	1,67	0	0,50	0	Strandline	2,67	4	0,84	0	4
					Backshore	0,67	0	0,17	0	1
Sambaqui	1,67	0	0,2	0	Strandline	2	0	0,24	0	3
					Backshore	1,33	0	0,15	0	2

Table S5 MPs sampled from Santa Catarina Island beaches separated by classes, color and polymers

Beach	Portion	Classes				Colour				Polymer			
		Fragments	Pellet	Styrofoam	Fiber	White	Transparent	Blue	Others	PS	PP	PE	Not Analyzed
Barra da Lagoa	Strandline	0	0	6	1	7	0	0	0	3	-	-	4
	Backshore	1	0	0	1	1	0	0	1	1	0	1	2
Brava	Strandline	31	80	17	0	36	69	8	15	13	15	58	42
	Backshore	5	8	16	1	13	7	3	7	-	-	-	30
Joaquina	Strandline	1	0	1	0	1	0	1	0	-	-	-	2
	Backshore	3	3	2	0	3	2	1	2	1	2	3	2
Lagoinha do Norte	Strandline	19	26	17	1	25	23	7	8	11	14	8	30
	Backshore	3	0	6	0	8	0	1	0	5	-	3	1
Northern Moçambique	Strandline	93	77	21	0	60	44	15	72	10	17	30	134
	Backshore	0	0	0	0	0	0	0	0	-	-	-	-
Southern Moçambique	Strandline	2	0	0	0	0	0	0	2	-	-	-	2
	Backshore	1	1	0	0	0	1	1	0	-	-	-	2
Pântano do Sul	Strandline	24	7	3	0	7	6	7	14	3	8	8	15
	Backshore	55	1	0	0	12	1	11	32	-	20	20	16
Ribeirão da Ilha	Strandline	18	1	1	4	1	1	8	14	11	1	4	8
	Backshore	16	1	1	2	4	1	3	12	2	2	7	9
Solidão	Strandline	4	0	0	0	3	0	0	1	-	-	-	4
	Backshore	1	0	0	0	0	0	0	1	-	-	-	1
Sambaqui	Strandline	3	0	0	0	0	0	2	1	-	-	-	3
	Backshore	2	0	0	0	0	0	1	1	-	-	-	2

(NA = not analyzed).

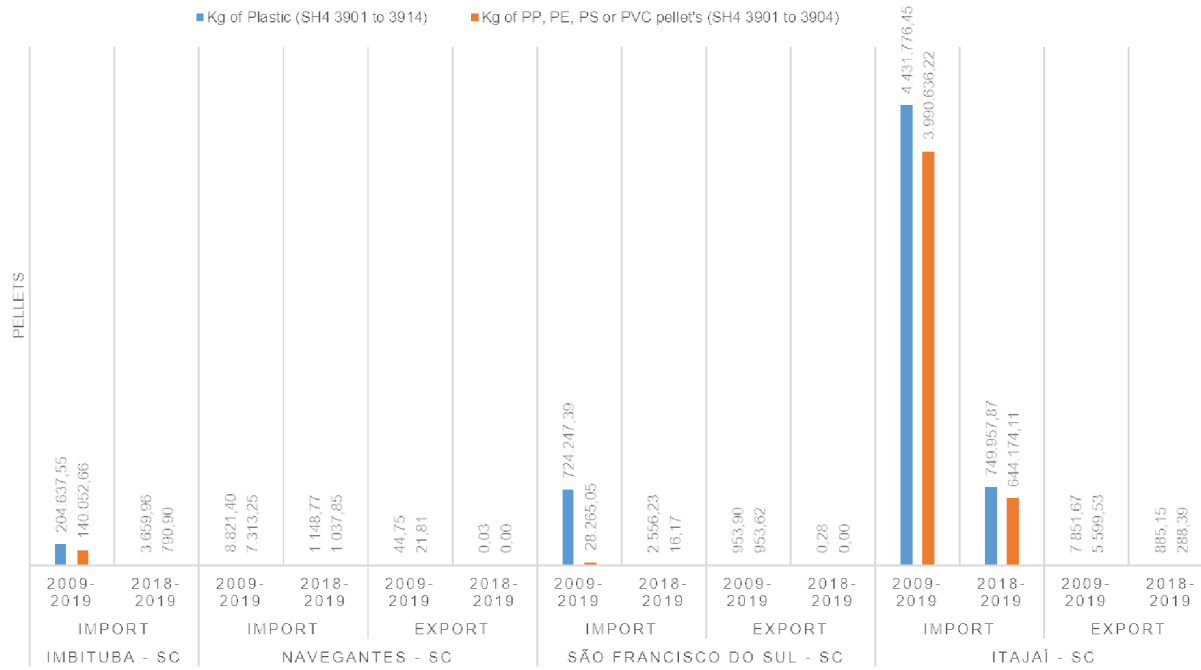


Figure S7 Total amount of plastic and pellets received by harbors from Santa Catarina State in 2018.

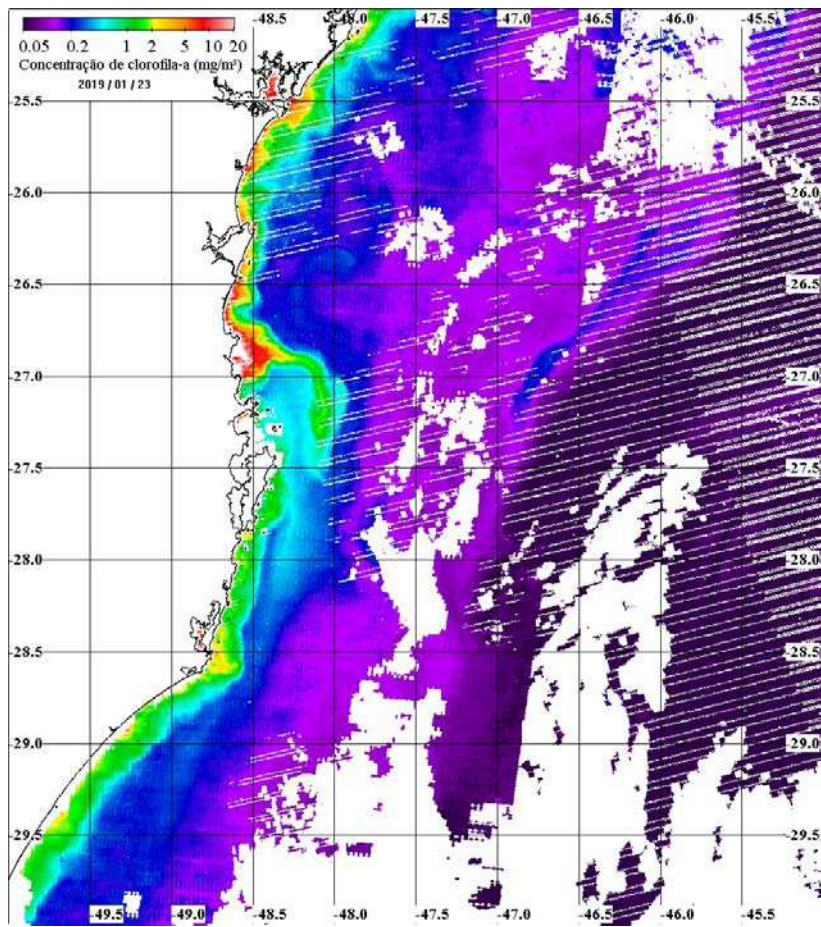


Figure S8 Surface Chlorophyll-0 distribution in Santa Catarina coastline showing the Itajaí-Açu plume (Jan/2019) toward Santa Catarina Island (Image from MODIS-Aqua, MODIS-Terra VIIRS-SNPP and VIIRS-JPSS, courtesy of Serrato, G.)

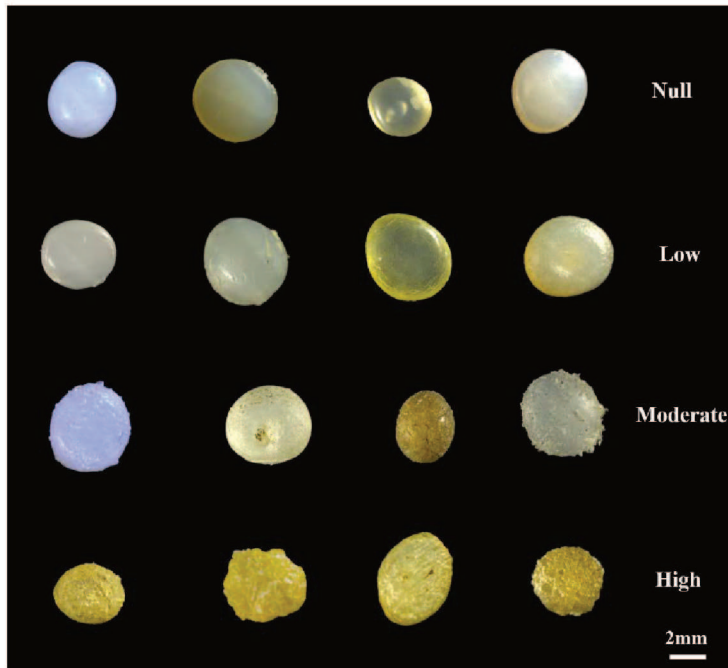


Figure S9 Degree of erosion scale for pellets (adapted from Acosta-Coley and Olivero-Verbel, 2015).

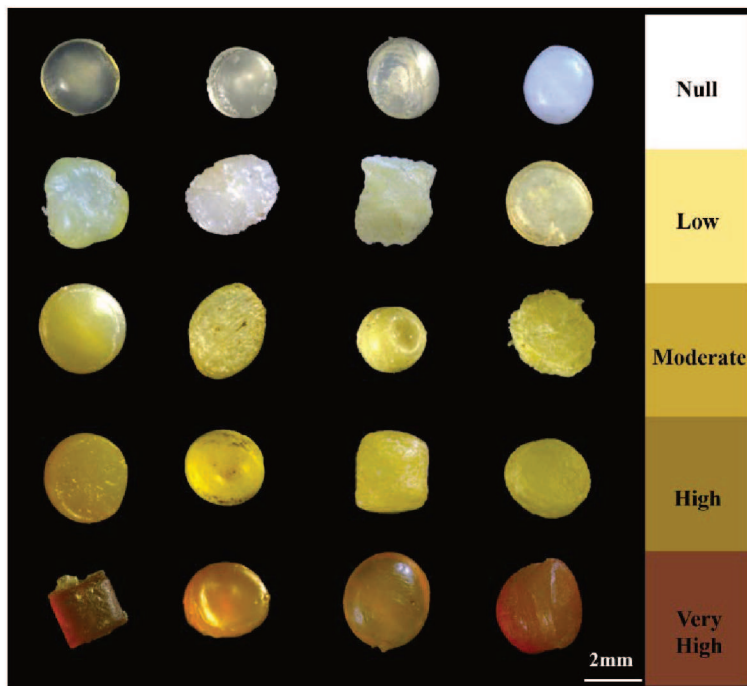


Figure S10 Degree of yellowing scale for pellets (based on Fanini and Bozzeda (2018)).

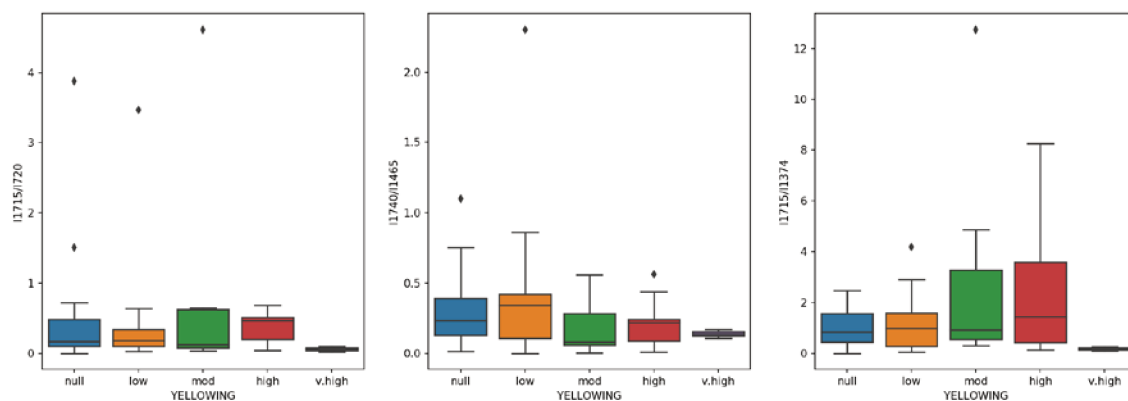


Figure S11 Ketone carbonyl indices calculated using distinct reference peaks for each degree of yellowing for pellets from Santa Catarina Island beaches.

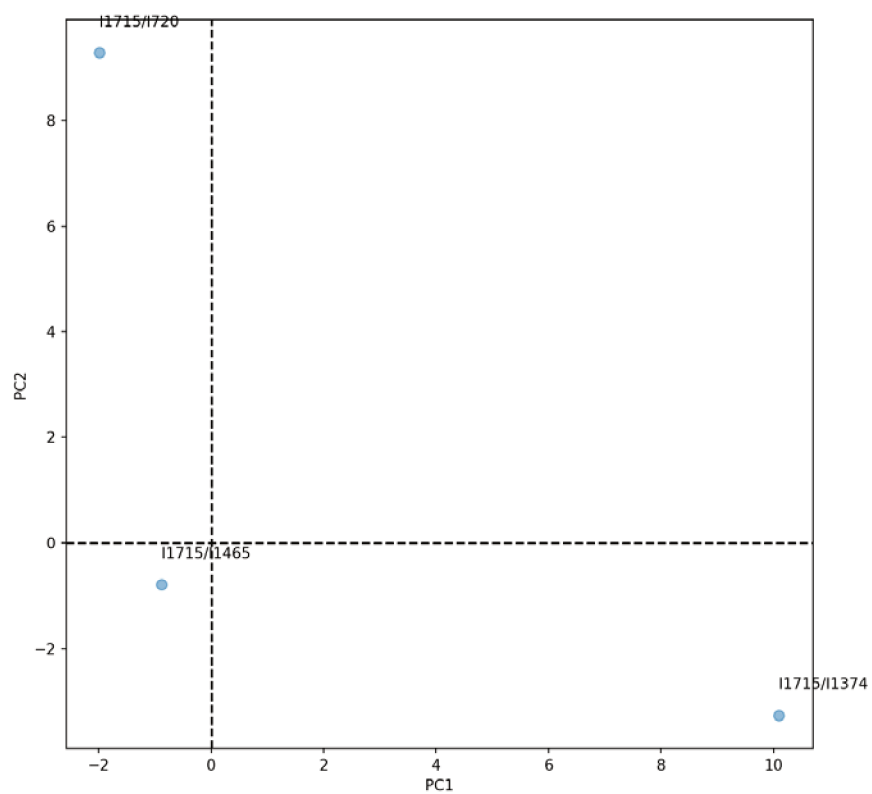


Figure S12 Principal components analysis of Carbonyl indices for pellets from Santa Catarina Island beaches.

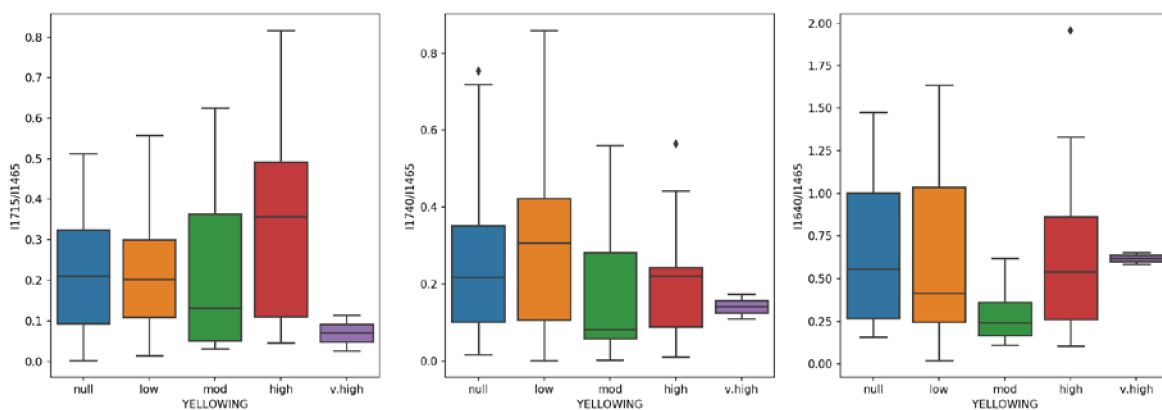


Figure S13 Ketone carbonyl index, ester carbonyl index and vinyl bond index for each degree of yellowing for pellets from Santa Catarina Island beaches.

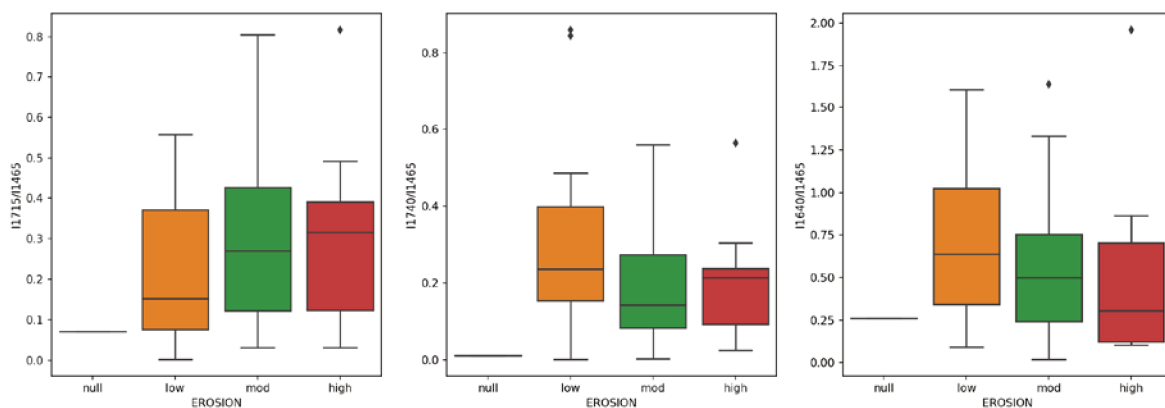


Figure S14 Ketone carbonyl index, ester carbonyl index and vinyl bond index for each degree of erosion for pellets from Santa Catarina Island beaches.

5. CONCLUSÕES E CONSIDERAÇÕES FUTURAS

- A porção Norte da praia de Moçambique apresentou os valores mais elevados de MPs entre todas as praias amostradas e um valor PPI muito elevado, destacando a importância dos ventos, energia das ondas e orientação da praia na distribuição dos MPs.
- Para os pellets, destaca-se a proximidade com a fonte potencial (Porto de Itajaí) como possível contribuinte dos valores detectados nas praias ao norte da Ilha, especialmente na praia Brava.

- Embora alguns hotspots de pellets tenham sido detectados, as praias arenosas da Ilha de Santa Catarina apresentam valores mais baixos de material plástico quando comparadas a outras regiões.
- O grau de amarelamento e erosão sugere que pellets chegam à praia depois de uma curta permanência no oceano e também não ficaram no litoral por um longo período de tempo.
- No geral, não foi observado relações entre o nível de amarelamento e índices de oxidação, no caso da erosão foi observado um leve aumento no índice de carbonila cetona e uma diminuição no índice vinil, diferente do esperado, uma vez que se esperava que o número de grupos carbonila cetona aumentasse nos estágios iniciais de degradação e que as ligações vinílicas aumentassem com o avanço da degradação.
- Programas de monitoramento são necessário para avaliar as tendências espaciais ou temporais da Ilha de Santa Catarina e identificar fontes de microplásticos. A metodologia e as técnicas de amostragem devem ser abordadas e padronizadas, a fim de harmonizar os dados coletados e permitir comparações em escalas geográficas e temporais.

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