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INFLUENCIA DE LOS MICROPLÁSTICOS (MPs) Y PRODUCTOS FARMACÉUTICOS Y DE CUIDADO PERSONAL (PPCPs) DERIVADOS DE LA ACTIVIDAD HUMANA COSTERA Y SUS EFECTOS EN EL ECOSISTEMA ANTÁRTICO

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I. Resumen

El incremento de la actividad humana en la Antártica ha generado numerosos impactos en el ecosistema. Recientemente ha sido descrita la presencia de microplásticos (MPs) y Productos farmacéuticos y de cuidado personal (PPCPs) en ambientes costeros, principalmente en la Península Antártica. El objetivo de esta tesis fue evaluar la contribución de la actividad humana en las concentraciones de MPs y PPCPs en el ecosistema antártico. Para esto, se determinó la abundancia y composición de microplásticos en suelos y en sedimentos intermareales de la Bahía Fildes, Antártica. En los suelos se obtuvo un promedio de 13,6 partículas/50 ml de muestra, con una longitud máxima de partículas de <500 µm. Estas partículas fueron identificadas como fragmentos, caracterizados por su composición basada en resina fenoxi de color naranjo, idénticos a los revestimientos de las instalaciones de la base Frei. En contraste, en los sedimentos intermareales se registraron exclusivamente fibras en una menor abundancia (1,5 partículas/50 ml de muestra), pero mayor longitud (<2000 µm). Estas fibras se caracterizaron por una composición de tereftalato de polietileno (PET) de distintos colores, con mayores abundancias en los sitios cercanos a los efluentes de aguas residuales, donde además se encontraron fibras de algodón, lo que permite presumir que su principal fuente corresponde a aguas grises. Respecto a las variables ambientales evaluadas, si bien la materia orgánica se correlacionó positivamente con los fragmentos de plástico del suelo, esta variable parece explicarse más en la composición de los microplásticos. En tanto, las fibras de los sedimentos intermareales se correlacionaron positivamente al tamaño de partícula de los sedimentos. En general, las variables ambientales seleccionadas en este estudio parecen no explicar las concentraciones de microplásticos. Finalmente, se observó que, a pesar de las restricciones impuestas en zonas protegidas, la contaminación por microplásticos se ha expandido a éstas áreas.

Un objetivo adicional fue identificar las fuentes, concentraciones y distribución de PPCPs en el sistema costero antártico y sus efectos en la biota. De modo que se realizó una revisión de los artículos científicos disponibles en la Antártica, junto a la bibliografía del Consejo de Administradores de Programas Antárticos Nacionales (CONMAP) y la Secretaría del Tratado Antártico (ATS). Esto se complementó con los datos espaciales de Quantarctica. Los resultados muestran que existe una amplia variedad de PPCPs reportados en aguas costeras los que alcanzan concentraciones de hasta 60000 ng/l. Las mayores concentraciones se detectaron en base Esperanza debido a la ausencia de tratamiento, siendo significativamente elevados para los

analgésicos acetaminofén (48744 ng/l), diclofenaco (15087 ng/l) e ibuprofeno (10053 ng/l). No obstante, la implementación de un sistema de tratamiento terciario en base Scott igualmente arrojó altos valores para los filtros UV 4-metil-bencilidenoalcanfor (4-MBC) (<11700 ng/l) y 2,4- dihidroxibenzofenona (BP-1) (<6830 ng/l), así como el surfactante 4-t-octilfenol (OP) (<7050 ng/l). En general, se observó que el número de ocupantes de cada estación no fue tan determinante como la implementación de algún sistema de tratamiento de aguas residuales. Sin embargo, otras variables como la frecuencia de muestreo también deben ser consideradas. De este modo, se identificó a los efluentes como la principal fuente de PPCPs en la Antártica, siendo mayores las concentraciones en zonas aledañas a las bases en comparación de mar adentro. Además, la biota antártica ha sido poco estudiada, con solo una especie evaluada, por lo tanto, los eventuales efectos de los microplásticos son por ahora desconocidos.

Esta tesis demuestra que las actividades humanas en la Antártica han resultado en la contaminación por MPs y PPCPs de sus suelos, agua de mar y sedimentos costeros, y que existe un alto grado de desconocimiento de los eventuales efectos en la biota. Dado que la mayoría de las estaciones antárticas se localizan en las zonas costeras, sus efluentes tienen una gran influencia sobre el ambiente marino, siendo identificados como la principal fuente de contaminación por MPs y PPCPs. En contraste, los suelos son dominados por la contaminación de microplásticos que en bahía Fildes responde al uso de suelo mediante la infraestructura. En este sentido, debido a las restricciones que rigen del Protocolo Ambiental, las limitadas actividades efectuadas dentro del territorio antártico sólo permitirían el uso y posterior eliminación de PPCPs principalmente mediante los efluentes, de modo que su presencia en suelos se espera que sea escasa o nula. El principal inconveniente es que algunas de las estaciones de investigación carecen de tratamiento terciario, descrito como uno de los más efectivos en la remoción de PPCPs. Asimismo, se permite la liberación de efluentes sin tratamiento directamente al mar. En consecuencia, mayores esfuerzos por sobre lo dictado por el Protocolo Ambiental, como el mejoramiento voluntario de estos sistemas de tratamiento y el control, tanto en el ingreso como uso de estos contaminantes, son medidas que podrían compensar la deficiente remoción de algunos contaminantes, ante la espera de nuevas regulaciones de los contaminantes emergentes antes mencionados.

II. Abstract

The increase in human activity in Antarctica has generated numerous impacts on the ecosystem. The presence of microplastics (MPs) and pharmaceutical and personal care products (PPCPs) in coastal environments, mainly in the Antarctic Peninsula, has recently been described. The objective of this thesis was to evaluate the contribution of human activity in the concentrations of PMs and PPCPs in the Antarctic ecosystem. For this, the abundance and composition of microplastics in soils and intertidal sediments of Fildes Bay, Antarctica, were determined. In the soils, an average of 13.6 particles/50 ml of sample was obtained, with a maximum particle length of <500 µm. These particles were identified as fragments, characterized by their composition based on orange-colored phenoxy resin, identical to the coatings of the Frei base facilities. In contrast, in the intertidal sediments fibers were exclusively recorded in a lower abundance (1.5 particles/50 ml of sample), but greater length (<2000 µm). These fibers were characterized by a composition of polyethylene terephthalate (PET) of different colors, with greater abundances in the sites near the wastewater effluents, where cotton fibers were also found, which allows us to presume that their main source corresponds to grey waters. Regarding the environmental variables evaluated, although organic matter was positively correlated with plastic fragments in the soil, this variable seems to be explained more by the composition of microplastics. Meanwhile, intertidal sediment fibers were positively correlated to sediment particle size. In general, the environmental variables selected in this study do not seem to explain the concentrations of microplastics. Finally, it was observed that, despite the restrictions imposed in protected areas, microplastic contamination has spread to these sites.

An additional objective was to identify the sources, concentrations and distribution of PPCPs in the Antarctic coastal system and their effects on biota. A review of the scientific articles available in Antarctica was carried out, together with the bibliography of the Council of Administrators of National Antarctic Programs (CONMAP) and the Secretariat of the Antarctic Treaty (ATS). This was supplemented by spatial data from Quantarctica. The results show that there is a wide variety of PPCPs reported in coastal waters, reaching concentrations of up to 60,000 ng/l. The highest concentrations were detected in the Esperanza base due to the absence of treatment, being significantly high for the analgesics acetaminophen (48744 ng/l), diclofenac (15087 ng/l) and ibuprofen (10053 ng/l). However, the implementation of a Scott-based tertiary treatment system also yielded high values for the UV filters 4-methyl-benzylidenecamphor (4-MBC) (<11700 ng/l) and 2,4-dihydroxybenzophenone

(BP-1) (<6830 ng/l), as well as the surfactant 4-t-octylphenol (OP) (<7050 ng/l). In general, it was observed that the number of occupants of each station was not as decisive as the implementation of a wastewater treatment system. However, other variables such as sampling frequency must also be considered. In this way, effluents were identified as the main source of PPCPs in Antarctica, with higher concentrations in areas surrounding the bases compared to offshore. In addition, the Antarctic biota has been little studied, with only one species evaluated, therefore, the eventual effects of microplastics are unknown at this time.

This thesis demonstrates that human activities in Antarctica have resulted in contamination by PMs and PPCPs of its soils, seawater and coastal sediments, and little is known about the possible effects on the biota. Since most Antarctic stations are located in coastal areas, their effluents have a great influence on the marine environment, being identified as the main source of pollution by PMs and PPCPs. In contrast, the soils are dominated by microplastic contamination that in Fildes Bay responds to land use through infrastructure. In this sense, due to the restrictions that govern the Environmental Protocol, the limited activities carried out within the Antarctic territory would only allow the use and subsequent elimination of PPCPs, mainly through effluents, so that their presence in soils is expected to be scarce or null. The main drawback is that some of the research stations lack tertiary treatment, described as one of the most effective in removing PPCPs. Likewise, the release of effluents without treatment directly into the sea is allowed. Consequently, greater efforts beyond what is dictated by the Environmental Protocol, such as the voluntary improvement of these treatment systems and the control, both in the entry and use of these pollutants, are measures that could compensate for the poor removal of some pollutants, given waiting for new regulations of the aforementioned emerging pollutants.

III. Introducción

El continente Antártico tiene una superficie de 14 millones de km^2, en su mayoría cubierta por hielo y nieve, incluyendo las plataformas de hielo Ronne, Ross y Amery (Carrasco & González 2007). El continente está rodeado por los océanos Pacífico, Índico y Atlántico Sur, conocido como Océano Austral el cual geográficamente genera un aislamiento del resto de los continentes desde su separación de la Península Antártica de América del Sur hace 30 millones de años (Bargagli 2008, Lu et al. 2012). A pesar de esta separación, sucesivos descubrimientos en el continente se realizaron en el siglo XVIII, los que posteriormente dieron inicio a una actividad económica de explotación de los recursos biológicos como la caza de focas, la caza de ballenas y actualmente la pesquería (Basberg & Headland 2013). En el siglo XX, la presencia humana ya no se limitó a la actividad económica y paulatinamente dio origen a la investigación polar, especialmente luego del Año Geofísico Internacional en 1957 y, en consecuencia, al aumento de la presencia humana estableciéndose en bases a lo largo del continente (Bargagli 2008). Por esta razón, el año 1959 se firmó el Tratado Antártico entre los gobiernos de Argentina, Australia, Bélgica, Chile, República Francesa, Japón, Nueva Zelandia, Noruega, Unión del África del Sur, Unión de Repúblicas Socialistas Soviéticas, Reino Unido de Gran Bretaña e Irlanda del Norte y los Estados Unidos de América (ATS 2022). Este tratado incluía 14 artículos que declaraban a la Antártica exclusivamente para fines pacíficos y científicos (ATS 2022). A partir del tratado, se elaboraron instrumentos jurídicos y recomendaciones para el manejo de los recursos naturales y la protección del medio ambiente (Bargagli 2008, Bray 2016). El primero fue la Convención sobre la Conservación de los Recursos Vivos Marinos Antárticos (CCRVMA) en el año 1980 que establece un principio de conservación de los ecosistemas que incluye el uso racional de las poblaciones de kril y peces dentro de límites de sostenibilidad científicamente determinados y, posteriormente, el Protocolo sobre Protección del Medio Ambiente del Tratado Antártico en el año 1991 (Bargagli 2008, Bray 2016). Antes de la existencia de este Protocolo, los residuos antropogénicos eran a menudo depositados en vertederos o en el mar dando lugar a la contaminación de ambientes terrestres y marinos (Cunningham et al. 2005).

Actualmente, la creciente cantidad y diversidad de actividades humanas globales están afectando los entornos marinos, terrestres y criósfera del continente (Hughes et al. 2018). Estos cambios en el entorno de la Antártica y el Océano Austral influyen en los impulsores del impacto climático a nivel mundial con consecuencias tales como el cambio del nivel medio del mar, acidificación de los océanos, alteración de los ecosistemas, pérdida de biodiversidad, y eventos climáticos y meteorológicos extremos como sequías, incendios forestales e inundaciones (Chown et al. 2022). De igual forma, la evidencia demuestra que la Antártica está siendo fuertemente afectada no solo por estos factores estresantes del cambio climático, sino también por presiones no climáticas que intensifican la vulnerabilidad de los ecosistemas oceánicos y de la criósfera, como la sobrepesca, el desarrollo costero y la contaminación (Hughes et al. 2018, IPCC 2019). De modo que, a pesar de la lejanía de zonas densamente pobladas, este relativo aislamiento de fuentes de contaminación no ha impedido que el estado actual de su entorno sea similar al de otras regiones del planeta (Gröndahl et al. 2008, Esteban et al. 2016, Chown & Brooks 2019). Rockström et al. (2009) describieron los nueve límites planetarios, los cuales son interdependientes y traspasarlos durante periodos de tiempo prolongados, ponen en peligro el espacio operativo seguro para la humanidad. En estos límites planetarios se incluyó la contaminación química ya que influye en el funcionamiento del sistema terrestre tanto a través del impacto global y ubicuo en el desarrollo fisiológico y demográfico de los humanos y otros seres vivos, impactando el funcionamiento del ecosistema y estructura; y también como una variable que afecta otros límites planetarios (Rockström et al. 2009). Sin embargo, dada su complejidad Rockström et al. (2009) no determinaron un nivel límite para la contaminación química. Por lo tanto, es importante llenar los vacíos de conocimientos para identificar los umbrales del sistema terrestre y analizar los riesgos e incertidumbres (Rockström et al. 2009).

La introducción de comportamientos menos amigables del turista hacia la protección del medio ambiente han ocurrido desde que el turismo se ha convertido en la mayor actividad económica de la región (Kruczek et al. 2018). En general, las principales vías de ingreso provienen de Ciudad del Cabo (Sudáfrica), Christchurch (Nueva Zelanda), Hobart (Australia), Punta Arenas (Chile) y Ushuaia (Argentina) (Roldan, 2015). De acuerdo a los datos de la temporada 2019/20, se registró un ingreso de más de 74.000 turistas, cifra muy superior a las 5.000 personas que se hospedaron en las más de 80 bases distribuidas en su mayoría en zonas costeras y en la Península Antártica (Bruni et al. 1997, Gröndahl et al. 2008, Morales 2013, CONMAP 2019, IAATO 2020). En este contexto, las características de accesibilidad al continente junto a sus usos de suelo y la densidad humana han sido modelados, evidenciando una alta presión de la huella humana en la Península Antártica (Pertierra et al. 2017). Asimismo, Gao et al. (2021) evaluaron el impacto acumulativo en el ecosistema terrestre antártico, identificando un impacto muy alto en el área del medio oriente de la Península Antártica.

Al norte de la Península Antártica se localizan las Islas Shetland del Sur, siendo la Isla Rey Jorge la de mayor tamaño con 80 km de largo y 28 km de ancho (Carrasco & González 2007). En la esquina suroeste de Isla Rey Jorge se encuentra una zona libre de hielo denominada Península Fildes (Turner & Pendlebury 2004). Parte de su geografía está compuesta por la Península Ardley, una Zona Antártica Especialmente Protegida N°150 que alcanza una longitud de 2 km y ancho de 1,5 km (ATS 2009). Este es uno de los hábitats más importantes de pingüinos y ha sido seleccionado por el Comité Científico de Investigaciones Antárticas (SCAR) como un sitio especial para la investigación (Yin et al. 2008). Isla Rey Jorge debido a su ubicación tiene un clima marítimo en el verano y un clima de característica polar en invierno (Carrasco & González 2007). Para el periodo 1991-2020, la temperatura promedio máxima anual fue de - 0,5°C y el promedio de la temperatura mínima anual fue - 4,0°C en la Península Fildes (Dirección Meteorológica de Chile 2021). El año 2021 la estación Meteorológica de la base Frei, reportó una temperatura mínima de - 20,6°C y una temperatura máxima de 6,5°C (DGAC 2022). En general, las precipitaciones son frecuentes y en forma de nieve, lluvia o llovizna (Turner & Pendlebury 2004). Para el mismo año, se registró un total anual de 440 mm de precipitación de agua caída, un total anual 263 cm de nieve fresca, la presión atmosférica fue de 988 hPa y la humedad relativa del aire fue de 92% (DGAC 2022). El viento prevalece con una dirección del oeste y noroeste y su velocidad puede superar los 100 km/h (Carrasco & González 2007). En general, los suelos de la Antártica son considerados pobres en cuanto a nutrientes, lugares para las plantas y hábitats para los organismos (Bölter 2011). La Isla Rey Jorge tiene un 8% de su área libre de hielo, en su mayoría con suelos erosionados derivados de roca ígnea al igual que la Península Fildes, aunque la roca sedimentaria es importante en algunos sitios (Turner & Pendlebury 2004, Bölter 2011). Además, los componentes biológicos como la avifauna influyen fuertemente en la composición de sus suelos, acelerando la génesis de estos, la formación de arcilla y minerales poco cristalinos (Mendonça et al. 2013).

Isla Rey Jorge es una zona de gran impacto por las actividades humanas que se desarrollan en las estaciones de investigación, especialmente en la Península Fildes ya que cuenta con la única pista de aterrizaje de la isla y las seis estaciones científicas alrededor de su bahía concentran una ocupación mayor a 500 personas, las que desarrollan sus actividades alrededor de la Zona Antártica Especialmente Protegida de la Península Ardley (Turner & Pendlebury 2004, CONMAP 2017, ATS 2018a). Los residuos derivados de las actividades se encuentran regulados por el Protocolo al Tratado Antártico sobre Protección del Medio Ambiente. Por una parte, el Protocolo prohíbe la eliminación de basura al mar indicando que esta debe ser almacenada y devuelta al país de origen (ATS 1991a). Sin embargo, residuos sólidos como macroplásticos han sido reportados por Barnes et al. (2005) en el Océano Austral en cercanías a la Península Antártica. En sistemas terrestres, anteriormente fue descrita la presencia de macroplásticos en zonas protegidas de nidificación de aves en Cabo Shirreff, verificándose además un significativo aumento en la tasa de acumulación en islas antárticas (Torres & Gajardo 1985). Asimismo, para las aguas residuales y residuos líquidos domésticos, el Protocolo señala que los efluentes pueden ser descargados directamente al mar si la estación posee una ocupación semanal promedio menor a 30 personas y, en caso contrario, estos deben ser tratados previamente por maceración (ATS 1991b). No obstante, en la actualidad muchas de las bases que cuentan con sistemas de tratamiento presentan fallas de los procesos biológicos, falta de mantenimiento y requerimientos para la evacuación de sus lodos, generando la liberación de residuos al ambiente (Hughes & Blenkharn 2003, Gröndahl et al. 2008, Morales 2013). Estimándose que el 37% de las estaciones permanentes y el 69% de las estaciones no permanentes no poseen ningún tipo de tratamiento (Morales 2013). En síntesis, efluentes y desechos provenientes de sistemas terrestres constituyen una entrada importante de contaminantes emergentes al medio acuático costero. Este tipo de contaminantes corresponden a un grupo de productos químicos, no necesariamente nuevos, sin estado regulatorio que con frecuencia han estado presentes en el ambiente y cuyos impactos sobre este y en la salud humana son poco conocidos (EPA 2008, Emnet et al. 2015). Estos se clasifican en: Contaminantes orgánicos persistentes (COPs), Nanomateriales, Productos farmacéuticos y de cuidado personal (PPCPs), Microplásticos (MPs) y Disruptores endocrinos (EDCs) (EPA 2008, Wagner & Lambert 2017). Hace una década que se han realizado esfuerzos en evaluar la presencia e impactos de otro tipo de contaminantes como los COPs (Weber & Goerke 2003, Chiuchiolo et al. 2004, Goerke et al. 2004, Lana et al. 2014, Wild et al. 2015, Khairy et al. 2016, Mwangi et al. 2016), no obstante, la información acerca de los MPs y PPCPs es reciente, acotada y con escasa información en la biota antártica y sus eventuales efectos. Además, estos contaminantes no están regulados por el Protocolo Ambiental, por lo que incorporar monitoreos permanentes y estudios que permitan una comprensión de las tendencias temporales y de los efectos en el estado regional y global, contribuirán en la introducción de medidas de protección y gestión del ecosistema antártico (Arpin-Pont et al. 2016, Villarrubia-Gómez et al. 2018).

3.1 Productos farmacéuticos y de cuidado personal (PPCPs)

Globalmente, los PPCPs alcanzan una producción anual de 2×10^7 toneladas (Wang and Wang 2016). Esta elevada demanda ha generado su detección en aguas costeras de diversas regiones del mundo (Vidal-Dorsch et al. 2012, Ali et al. 2021, Chen et al. 2021). Además de los aportes derivados de la escorrentía, una fuente importante de PPCPs proviene de la remoción incompleta en los sistemas de tratamiento de aguas residuales, generando una liberación continua de compuestos originales, productos de transformación y metabolitos bioactivos, conduciendo a concentraciones altas a largo plazo que promueven efectos adversos continuos pero desapercibidos en los organismos acuáticos y terrestres (Barceló & Petrovic 2007, Yin et al. 2017). Ciertos tipos de hormonas sintéticas como el dietilestilbestrol y etinilestradiol se han detectado en efluentes de aguas residuales y en agua de mar en Isla Ross, Isla Seymour-Marambio, Isla Rey Jorge e Isla Decepción (Emnet et al. 2015, Esteban et al. 2016, González-Alonso et al. 2017). Esta última alcanzó concentraciones de 23,1 ng/L en almejas en bahía de Winter Quarters, organismos que utilizan los sedimentos como sustrato, de modo que otros organismos bentónicos como gusanos poliquetos y sus depredadores se encontrarán expuestos a estos compuestos (Emnet et al. 2015). Recientemente, ha sido reportado el hallazgo de otros grupos de PPCPs como surfactantes, analgésicos, anti-inflamatorios, beta-bloqueadores, reguladores lipídicos, diuréticos, ansiolíticos, antibióticos, antibacteriales, fungicidas, filtros UV y fragancias en aguas costeras, sedimentos y organismos marinos antárticos (Emnet et al. 2015, Esteban et al. 2016, González-Alonso et al. 2017, Vecchiato et al. 2017, Hernández et al. 2019, Domínguez-Morueco et al. 2021, Duarte et al. 2021 y Szopińska et al. 2022).

3.2 Microplásticos (MPs)

Estas partículas miden menos de 5 mm y derivan de la producción anual de la industria del plástico que alcanza los 368 millones de toneladas (GESAMP 2016, PlasticsEurope 2020). Industrialmente son fabricados con un tamaño microscópico para diversos fines como tecnologías de chorro de aire, productos de limpieza, cosméticos y como gránulos de producción de plástico, denominados microplásticos primarios. O bien, una vez liberados al ambiente y mediante la fragilización superficial y microfisuras, generan partículas apenas visibles denominadas microplásticos secundarios. Esta basura plástica ingresa al océano a través de la escorrentía, fluyendo hacia los cursos de agua o descargándose directamente en las aguas costeras, alcanzando su mayor acumulación en los giros subtropicales (Cózar et al. 2014, Van Sebille et al. 2015), siendo descrito también el transporte atmosférico de estas partículas (Cózar et al. 2014, Allen et al. 2019, Evangeliou et al. 2020). Actualmente, las estimaciones acerca de su abundancia global son aún débiles debido a la falta de comprensión de sus transformaciones hasta los sumideros finales y muestreos deficientes, especialmente en el hemisferio sur y en regiones remotas (Cózar et al. 2014, Eriksen et al. 2014). Por lo tanto, los MPs constituyen un creciente problema ambiental debido a su gran capacidad de dispersión, persistencia y acumulación en océanos de todo el mundo, incluyendo la Antártica, continente en el cual los conocimientos acerca de su concentración, extensión y distribución son muy escasos (Žitko & Hanlon 1991, Andrady 1993, Gregory 1996, Gregory & Ryan 1997, Gregory & Andrady 2003, Thompson et al. 2004, 2005; Betts 2008, Moore 2008, Barnes et al. 2009, Fendall & Sewell 2009, Patel et al. 2009, Ryan *et al*. 2009, Barnes et al. 2010, Costa *et al*. 2010, Zarfl & Matthies 2010, Andrady 2011, Cole et al. 2011, PlasticsEurope 2013, Waller et al. 2017). Adicionalmente, las vías de exposición que contribuyen a la bioacumulación de MPs no está clara y se requieren estudios más detallados ya que su ingestión en los organismos marinos puede facilitar la transferencia de aditivos químicos o contaminantes hidrofóbicos y cuyo potencial de efectos subletales es incierta (Cole et al. 2011, Gall & Thompson 2015, Miller et al. 2020). Cincinelli et al. (2017) reportaron los primeros datos de microplásticos en la Antártica, correspondiente a aguas subsuperficiales del mar de Ross, registrando concentraciones de 0,0032-1,18 partículas/m^3, predominantemente polietileno y polipropileno, alcanzando el mayor registro los fragmentos (71,9 ± 21,6%), seguido de las fibras (12,7 ± 14,3%) y otros tipos (15,4 ± 12,8%). Por otra parte, en Bahía Almirantazgo, Península Antártica, se detectó una abundancia promedio de 2,40 (± 4,57) microfibras 100 m^{-3} (Absher et al. 2019). Adicionalmente, Munari et al. (2017) registraron las primeras concentraciones de microplásticos en sedimentos antárticos con un tamaño de 0,3 a 22 mm de longitud, sin embargo, a diferencia de la columna de agua, la mayor abundancia de partículas correspondió a fibras. Posteriormente, Reed et al. (2018) reportaron concentraciones de hasta 5 partículas/10 ml de sedimentos cercanos a los efluentes de aguas residuales de base Rothera. En aves marinas, se ha descrito la ingestión de microplásticos (Amélineau et al. 2016, Holland et al. 2016), reportándose hasta en un 90% de los tractos digestivos analizados (Zhao et al. 2016). Hasta ahora, en sistemas terrestres antárticos no ha sido reportada la contaminación por microplásticos. A nivel global la información es escasa, lo cual podría deberse tanto a su poca compresión como a la falta de métodos estandarizados (Bläsing & Amelung 2018). No obstante, la presencia de microplásticos en los suelos es inminente, por esto, debería ser explorada ya que pueden persistir, acumularse y afectar el funcionamiento de la biota del suelo (Rilling 2012). Algunas fuentes importantes en los suelos corresponden a los vertederos, verificándose un movimiento vertical por bioturbación o lixiviación de pequeñas partículas plásticas (Bläsing & Amelung 2018). En este sentido, ha sido reportado que una exposición a suelos con microplásticos de polietileno disminuye la tasa de crecimiento y aumenta la mortalidad en *Lumbricus terrestris* (Linnaeus, 1758) (Huerta Lwanga et al. 2016).

La alta densidad humana en zonas costeras produce la liberación de MPs y PPCPs en las zonas costeras de la Antártica, sin embargo, se desconocen sus efectos en la biota. La presencia del hielo cubriendo las aguas costeras y los extensos períodos de oscuridad durante gran parte del año, generan una reducción de la actividad biológica en los procesos de degradación por actividad microbiana y fotodegradación, generando una mayor exposición de la cadena alimentaria debido a su mayor persistencia en el ambiente costero (Braga et al. 2005, Emnet et al. 2015, Esteban et al. 2016). Factores como la temperatura y estacionalidad determinan la fisiología, historia de vida y la biodiversidad de la biota antártica, caracterizándose por un metabolismo y crecimiento lentos (Peck et al. 2006, Emnet et al. 2015). En consecuencia, alcanzan bajas tasas de excreción de sustancias químicas potencialmente dañinas y períodos más largos de exposición in vivo, planteando problemas de toxicidad y transferencia de éstos contaminantes desde presas a organismos depredadores (Moore 2008, Andrady 2011, Browne et al. 2011, Cole et al. 2011, Emnet et al. 2015, Lusher 2015).

IV. Hipótesis

Considerando estos antecedentes, la población humana y las actividades que desarrollan involucran la utilización de contaminantes emergentes como Microplásticos (MPs) y Productos farmacéuticos y de cuidado personal (PPCPs), los cuales pueden ser liberados a través de fuentes puntuales y difusas al ambiente. Entonces, la presencia humana en la Antártica cuyas bases se distribuyen principalmente en las zonas costeras, generará un alto grado de contaminación por MPs y PPCPs en suelos, sedimentos y aguas de mar.

En base a estos antecedentes se espera que:

1. Suelos aledaños a las bases presentarán mayores abundancias de microplásticos en comparación a suelos distantes de las bases (*hipótesis 1*).
2. Sedimentos intermareales cercanos al efluente de base Frei presentarán mayores abundancias de microplásticos en comparación a sedimentos intermareales distantes del efluente (*hipótesis 2*).
3. Bases situadas en zonas costeras que no cuenten con sistemas de tratamiento de aguas residuales generarán altas concentraciones de PPCPs en el agua de mar donde liberan sus efluentes en comparación a bases con sistemas de tratamiento operativos (*hipótesis 3*).

V. Objetivos

Objetivo general

- Evaluar la contribución de la actividad humana en las concentraciones de microplásticos y PPCPs en el ecosistema antártico.

Objetivos específicos

• Identificar las fuentes, concentraciones y distribución de PPCPs en el sistema costero antártico y sus efectos en la biota.

• Determinar la abundancia y composición de microplásticos en suelos y en sedimentos intermareales de la Bahía Fildes, Antártica.

VI. Capítulo 1: Occurrence and Distribution of Microplastics in Soils and Intertidal Sediments at Fildes Bay, Maritime Antarctica

Este capítulo está basado en:

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6.1 Abstract

Increased human activity on the Antarctic Peninsula has generated microplastic contamination in marine systems; however, less attention has been paid to soils so far. We investigated the occurrence of microplastics in 11 surface soils and intertidal sediments collected from Fildes Bay, King George Island. A transect of soils at Antarctic stations until Fildes Bay was made (i.e., S1–S5). Intertidal sediments along the shore (i.e., IS1–IS5) and a reference sample from Ardley Island (i.e., IS6) were also collected. All samples were stored at 4°C and analyzed for the organic matter content, particle size, and pH. Plastic particles were counted and classified by shape using metal dissecting forceps and a stereomicroscope and further analyzed by Fourier transform infrared spectroscopy (FT-IR). They were classified by length as fibers (length: 500–2,000 µm) and fragments (length: 20–500 µm). In soil, fragments reached an average of 13.6 particles/50 ml sample, while in intertidal sediments, no fragments were found, but a fiber abundance of 1.5 particles/50 ml sample was observed. The principal component analysis shows a relationship between fibers and intertidal sediments, whereas fragments present a relationship with soils. There were differences between the numbers of fragments found in soils and intertidal sediments ($p = 0.003$), with a high abundance of fragments at site S5, but no significant differences were observed for fibers. The physicochemical soil analysis revealed that larger particle sizes were observed in intertidal sediments (average = 706.94 ± 230.51 µm) than in soils ($p = 0.0007$). The organic matter content was higher in soil than in intertidal sediments ($p = 0.006$) reaching an average of 6.0%. Plastic fragments and organic matter were significantly correlated ($r = 0.779$, $p = 0.005$), while fibers were positively correlated with particle size ($r = 0.713$, $p = 0.014$). The fragments were composed of phenoxy resin with the same appearance, shape, and bright orange color as the coatings of the facilities.

According to the FT-IR analysis, the fibers had different colors and were composed of polyethylene terephthalate (PET). Cotton was also present at the sites surrounding the sampling site close to the base effluent. The presence of fiber on Ardley Island (i.e., control) may indicate that microplastic contamination has reached protected areas. This is the first study to confirm the presence of plastic debris in Antarctic soils. Further studies should focus on the identification of plastic sources and on the management of human activities and their eventual effects on biota.

Keywords: fibers, fragments, PET, phenoxy resin, pollution, soil, intermareal sediment, Antarctica.

6.2 INTRODUCTION

Since the first expeditions, and especially since the 1950s, scientific interest in the Antarctic continent has increased; there are currently more than 80 facilities distributed mainly in coastal areas and on the Antarctic Peninsula (Bruni et al., 1997; Gröndahl et al., 2009; Lu et al., 2012; Morales Calvo, 2013). These facilities host more than 5,000 people a year; however, this number is much lower than the 74,000 tourists who arrived in the 2019/2020 season (Council of Managers of National Antarctic Program, 2020; International Association of Antarctica Tour Operators, 2020). Using the data of human density and accessibility features of the Antarctic continent along with land uses, Pertierra et al. (2017) concluded that the Antarctic Peninsula is one of the three regions with the greatest human footprint pressure. On coasts worldwide, a high human density has resulted in contamination by microplastics, spread over six continents from the poles to the equator, sustained by an annual worldwide production of 368 million tons of plastic (Browne et al., 2011; Plastics Europe, 2020). In Antarctica, Barnes et al. (2010) reported the presence of macroplastics, such as fishing buoys and packing material in the Durmont D'Urville, Davis, and Amundsen seas. Nevertheless, at present, the international scientific community does not regularly sample microplastics or record at-sea observations of macroplastics in the Southern Ocean region, and there are few peer-reviewed scientific publications that quantify plastics in Antarctic waters (Waller et al., 2017). In studies carried out in seawater, a high abundance of microplastics has been reported in the vicinity of the Antarctic continent, in contrast to the low abundances that they reach in the Southern Ocean, which probably derive from long-distance transport (Isobe et al., 2017). Also, microplastics reached higher concentrations along the Antarctic Peninsula than at open ocean sub-Antarctic stations (Jones-Williams et al., 2020). Cunningham et al. (2020) reported high levels of microplastic contamination in marine sediment cores from three regions in Antarctica and the Southern Ocean. This is consistent with the findings of Onink et al. (2021), who, using a Lagrange particle transport model, verified that coastlines and coastal waters are an important reservoir of plastic debris and that there is limited transport of the marine plastic debris with positive buoyancy between the coastal zone and the open ocean. In general, high microplastic abundance has been reported in seawater and marine sediments collected in the areas closest to scientific stations, with wastewater effluents identified as being among their main sources (Cincinelli et al., 2017; Waller et al., 2017; Reed et al., 2018).

At present, there are no studies on Antarctic soils. Li et al. (2016) concluded that land-based sources account for 80% of the plastic waste in the marine environment, with high human density and industrial activities playing a key role. While evidence of the ecological impacts of microplastics has increased worldwide, evidence of the potential consequences of microplastics in soil ecosystems is still relatively scarce (Huang et al., 2019). This lack of information is of an ecotoxicological concern, given that once in the soil, these particles decompose slowly and accumulate as relatively persistent pollutants (Rillig, 2018). Decades ago, harm to fur seals, gulls, and penguin species caused by the presence of macroplastics was reported; however, the situation has resulted in sustained increases in their accumulation rates on Antarctic islands (Torres and Gajardo, 1985; Torres and Jorquera, 1992, 1994). There is no information on the presence of microplastics in terrestrial Antarctic environments, although they were recently reported in a freshwater stream, with their presence attributed likely to air transport (González-Pleiter et al., 2020). Since 1968, various countries have established facilities on the Fildes Peninsula, generating great environmental pressure resulting from the scientific and logistical activities that take place in the area (Lu et al., 2012; Amaro et al., 2015). The high density of the facilities and the varied human activities in the region often clash with the environmental standards laid down in the Protocol on Environmental Protection to the Antarctic Treaty (Peter et al., 2013). Since human activities in the Antarctic are the main source of microplastic contamination, the objective of this study was to evaluate its occurrence and distribution on the adjacent soil and intertidal sediments of Fildes Bay, Antarctica.

6.3 MATERIALS AND METHODS

6.3.1 Study Area and Sampling Site

The study area is the Fildes Peninsula, King George Island (Antarctic Specially Protected Area No. 125), one of the areas in Antarctica with the greatest paleontological interest and an area with a great diversity of organisms, including vertebrates, invertebrates, and flora (Secretariat of the Antarctic Treaty [ATS], 2009). The area contains six permanent Antarctic stations belonging to different countries (i.e., Chile, Russia, Uruguay, and China), built between 1968 and 1994. In the 1980s, the construction of the airport turned the area into a major logistical hub for the Antarctic Peninsula (Braun et al., 2012). A part of the Fildes Peninsula is formed by Ardley Peninsula (62° 13'S, 58° 54'W), Antarctic Specially Protected Area No. 150, located on the southwest coast of King George Island (Fildes Bay). Ardley Island was designated as a protected area on account of the diverse assemblage of bird species that breed on it and to allow the study of their ecology and the factors that affect their populations. Ardley Island also has developed an outstanding flora, with species of lichens, mosses, and vascular plants (Secretariat of the Antarctic Treaty [ATS], 2009) (Figure 1).

The study area was divided into two sampling sites (Figure 1), namely, Antarctic stations and intertidal zones.

6.3.2 Sample Collection and Analysis

Sampling was performed in December 2018. In areas corresponding to Antarctic stations, five soil samples were collected along a transect stretching from the Frei Antarctic station to Fildes Bay (i.e., S1–S5) (Figure 1). In intertidal zones, five sediment intertidal samples were collected along the shore zone (i.e., IS1–IS5). In addition, an intertidal sediment sample (i.e., IS6) was collected from the shore of Ardley Island as a reference from an area free of human activities. An amount of 200 ml of soil and 500 ml of intertidal sediment was extracted at a depth of 0–1 cm using a metal spatula that had been previously washed with acetone. The soil samples were stored in aluminum foil, and the intertidal sediments were collected in glass bottles; they were then refrigerated at 4°C.

To extract the microplastics, the method described by Thompson et al. (2004) and modified by Browne et al. (2010) was used. In brief, 50 ml of the sample was suspended in 100 ml of supersaturated solution of NaCl (1.2 kg NaCl/L), previously filtered by filter paper with a pore size of 1 mm (Advantec Grade NO.5C size 11 cm). This solution was stirred for 30 s, and after 2 min, the particles in the supernatant were separated from the solution using a glass filter under a vacuum with a pore size of 1.6 mm (glass fiber prefilters; Merck Milipore Ltd.).

This step was repeated three times for each sample. To minimize contamination by airborne microplastics during drying at room temperature, the filters were placed in Petri dishes and kept inside a glass box.

The plastic particles were separated from non-plastic material and counted using metal dissecting forceps and a stereomicroscope (Olympus SZ61 40X, Japan). Particles with a length of less than 5 mm and greater than 1 mm were considered microplastics GESAMP, 2019 [Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) (United States)]. Fourier-transform infrared spectroscopy (FTIR) (Spotlight 400 Perkin Elmer) was used to identify the nature of the polymer in the microplastics from the sampling sites. The attenuated total reflectance (ATR) micro-imaging technique with a germanium crystal was used. A spectral range between 750 and 4,000 cm^{-1} and a pixel of size 6.25 mm was used. The spectra carry the data with an interval of 3 mm and a resolution of 6 cm^{-1}. Samples from soil and sediments are expressed in volumes to enable comparisons between sample types. All spectra were compared with fused deposition modeling (FDM) FT-IR and Raman spectral libraries and libraries created by the laboratory that analyzed the samples.

6.3.3 Analysis of Physicochemical Parameters in the Collected Samples

Organic matter: The organic matter content in the soil and intertidal sediment samples was determined based on the method described by Heiri et al. (2001). Soil and intertidal sediment were dried at 60°C for 72 h. One g of soil/sediment was homogenized in a mortar and combusted in a muffle furnace at 550°C for 4 h. Finally, the sample was weighed to determine the organic matter content (%) by loss ignition. The results are expressed in dry matter.

Particle size: Samples were dried at room temperature and sieved using a 2-mm sieve. Subsequently, organic matter was removed from each sample using 30% hydrogen peroxide. The sample was deposited in a funnel with a filter paper with a pore size of 1 mm (Advantec Grade NO.5C size 11 cm) and cleaned with milli-Q water. Then, the sample was introduced into a dispersion unit until 10–20% laser obscuration was reached (Malvern Mastersizer 3000S with Hydro EV dispersion unit, United Kingdom). Finally, the results were analyzed using Gradistat v.8 to obtain the average particle size (Blott, 2010).

pH: Soil and intertidal sediment samples were dried at room temperature and homogenized in a mortar. Subsequently, each sample was sieved using a 2-mm sieve. Subsequently, 1 g of sample was placed in 50 ml of Milli-Q water (20°C). To homogenize the sample, a magnetic stirrer was used for 5 min at

225 rpm. The sample was left to stand for 2 h, at which point, the pH in the supernatant was determined using a pH meter (Hanna Edge, United States).

6.3.4 Maps

The sampling area map was prepared using the QGIS 3.14 software (QGIS.org, 2020) and the layers were available in Quantarctica (2019).

6.3.5 Statistical Analyses

To explore the variance of the environmental variables (e.g., fibers, fragments, organic matter, particle size, and pH) in the data set, a Euclidean distance matrix was built, and then a principal component analysis (PCA) was performed. Then, a Shapiro-Wilk test was carried out to test the normal data distribution. A Kruskal-Wallis test and ANOVA were carried out to verify the existence of significant differences between soils and intertidal sediments. A Kendall correlation analysis between particles—whether fibers or fragments—and organic matter, particle size, and pH were performed. The level of significance was set at $p = 0.05$. All statistical analyses were performed with the R Studio software version 4.0.2.

6.4 RESULTS

This study revealed the presence of microplastics in soils and intertidal sediments at 81% of the sites analyzed at Fildes Bay, Antarctica. Five topsoil samples (i.e., S1–S5), five intertidal sediments (i.e., IS1–IS5), and a reference sample (i.e., IS6) were analyzed. Plastic debris after treatment was classified as fibers or fragments based on size, and the nature of the polymer was characterized using FT-IR. Microplastic occurrence (i.e., fibers and fragments), organic matter, particle size, and pH in soils and sediments, respectively, are shown in Figure 2. Plastic fragments (length < 500 mm) were detected in all soil samples, while the presence of fiber was only observed in sample S1 (1 particle/50 ml). The distribution of the fragments in the samples varied from 4 to 37 particles/50 ml sample. The highest occurrence was observed in S5, which is the sample from closest to the shore. Samples taken far from the shore (i.e., S1–S4) presented an occurrence of fragments between 4 and 11 particles/50 ml. The soil organic matter content varied from 4.4 to 8.2%. Similarly, the soil particle size in the samples ranged from 40.6 to 323.6 mm. The soil was considered neutral, with a pH ranging from 6.9 to 7.5. Regarding the evaluated physicochemical variables, no trends were identified in terms of proximity to the coast.

In the intertidal sediments, only fibers (length <2,000 mm) were observed, ranging from 1 to 4 particles/50 ml. Samples IS1 (4 particles/50 ml) and IS2 (3 particles/50 ml) presented the highest detected abundances; these samples were taken at sites close to the effluent. Abundances in the other intertidal samples (i.e., IS3–IS5) ranged from 0 to 1 particle/50 ml. The inspection of sample IS6 (i.e., protected area, control) revealed a transparent, brilliant, and hard fiber (Figure 3D).

We recognized its similarity to the ropes used on boats; however, during sample preparation for the FT-IR analysis, the sample was lost and could not be further identified. The physicochemical values are indicative of homogeneous organic matter in the intertidal sediments (2.2–2.6%). The particle size ranged from 318.9 to 1,042.8 µm. Similar to the soils, the intertidal sediments presented a neutral range (6.5–7.3).

Fragments and particle size presented the greatest variability along the PC1 axis, which captured 83.67% of the total variance (Figure 4). The abundance of the type of plastic debris (i.e., fibers and fragments) in soils and intertidal sediments was correlated with physicochemical variables. Specifically, intertidal sediments were characterized by the largest occurrence of fibers, whereas fragments were highly predominant in soil samples. In addition, intertidal sediment sites were influenced by particle size, although soils do not seem to show a significant relationship with other soil variables (i.e., pH and organic matter).

The number of fragments differed significantly between the investigated sample types, i.e., soils and sediments ($p = 0.003$). In terms of soil physicochemical parameters, organic matter differed significantly between the matrices ($p = 0.006$), with higher concentrations in soils (S5 = 7.3% and S1 = 8.2%) compared with sediments. Particle size differed significantly between sample types ($p = 0.0007$), with higher sizes in the intertidal matrix (S1 = 1,042 mm) than in soils. pH did not present significant differences between matrices. Positive correlations between fragments and organic matter ($r = 0.7786$, $p = 0.005$) were observed, as well as between fibers and particle size ($r = 0.7128$, $p = 0.014$).

All the fragments collected in the soils presented uniformity in color, which was classified as bright orange. The presence of mesoplastics with the same characteristics was also observed in the area, with evident secondary fragmentation in situ. The orange fragment had a high similarity to phenoxy resin (Figure 3A). In contrast, the intertidal plastic fibers presented different colors (i.e., black, blue, red, and transparent). The FT-IR analysis determined that 67% and 50% of all fibers recorded at sites IS1 and IS2, respectively, were cotton fibers (Figure 3C). In addition, for all sites, the analysis indicated that the remaining fibers had a high similarity to polyethylene terephthalate (PET) (Figure 3B).

6.5 DISCUSSION

6.5.1 Microplastics in Antarctic Soils

The largest amount of microplastics was detected in soils (1–37 particles/50 ml soil), with fragments predominating, which were associated with high concentrations of organic matter. A comparison with other reports is difficult due to the lack of similar studies on microplastics in Antarctic soils. According to Bläsing and Amelung (2018), our poor understanding of microplastics in soils may be due to the lack of standardized methods. In general, abundances of plastics are highly variable depending on land use and population density; so far plastic debris have been reported in agricultural soils in Shanghai, China (78 ± 12.91 particles/kg) (Liu et al., 2018); roadside soils (1,108 particles/kg) and agricultural soils (3,440 particles/kg) in Yeoju, Republic of Korea (Choi et al., 2021); soils of cultivated areas and the riparian forest zone of Dian Lake, China (7,100–42,960 particles/kg) (Zhang and Liu, 2018); agricultural soils in Nanjing and Wuxi, China (420–1,290particles/kg) (Li et al., 2019); and agricultural soils (2,200–6,875 particles/kg), parks (6,250 ± 3,776 particles/kg), industrial areas (5,780 ± 3,251 particles/kg), and dumps (2,429 ± 1,817 particles/kg) in Lahore, Pakistan (Rafique et al., 2020). The values found in the present study are far lower than those listed above, suggesting that the intensity of the land use and human activities clearly determine the occurrence of plastic debris in soils.

Fragments were observed in all investigated soils, while only one fiber, at site S1, was identified (Figure 2). The fragments had the same appearance, shape, and orange color as those observed in the coatings of the neighboring facilities, which present deterioration associated with local environmental and climatic conditions. This suggests that local land use is the main driver of soil fragments on Fildes Bay. Land use may in part explain the presence of a certain type of microplastic, such as in agricultural soils, which reach high fiber abundances due to the use of sewage sludge as fertilizer (Liu et al., 2018; Corradini et al., 2019; Jiang et al., 2020). Wind also plays an important role in the investigated area, as it reaches speeds of over 100 km/h (Cerda, 2006). In the province of Sakarya, Turkey, Kaya et al. (2018) reported that fibers were more abundant than fragments in the air, with microplastics having a presence of up to four orders of magnitude higher in the air than in soils. This is consistent with the findings of Wright et al. (2020) who recorded atmospheric deposition rates ranging from 575 to 1,008 microplastics/m^2/day in the city of London, with the representativeness of 92% of fibers. This finding could explain the low abundance of fibers in soils, which might have been constantly resuspended from the soils or transported to other areas. Furthermore, it has been shown that particle density is decisive in their deposition in coastal systems, since less dense particles tend to settle downwind, in contrast to denser particles, whose settling is not determined by wind, with deposition along the coast (Browne et al., 2010). Finally, once in the soil, the behavior of microplastics varies; according to Waldschläger and Schüttrumpf (2020), fibers that have a smaller diameter reach greater infiltration depths, in contrast to the fragments, which infiltrate less due to the entanglement of the angular particles in the pores.

The highest concentration of fragments was recorded at site S5, the closest to the sea and, therefore, the lowest, which could also suggest a certain degree of runoff as a result of melting snow. Site S5 is also an area with a high-degree of human activity, the use of which is mainly associated with the transit of towing machinery for small boats and motorized vehicles to assist in logistics and maintenance tasks for scientific and tourism purposes. Based on a visual inspection, the fragments even show a degree of secondary fragmentation in situ. The determination of their composition by FT-IR shows a high coincidence with phenoxy resin (Figure 3A), which has a high density and is used as a flexibilizer for cross-linked phenolic and epoxy formulations in adhesives, coatings, and compounds and to make compatible mixtures of various plastic materials (Song et al., 2015; Jones- Williams et al., 2020). Previous studies have not frequently reported the detection of synthetic resins in the environment; however, the detection of this material is very likely since these resins, especially phenoxy resins, are often blended with plastics (Paler et al., 2021). For example, microplastics derived from thermoplastic road-surface marking paints (Horton et al., 2017) and ship paints (Song et al., 2014) have been described. In terms of abundance, paint resins are comparable to microplastics, together reaching 75% of total particles in the surface waters of Jinhae Bay, South Korea (Song et al., 2015). In surface waters between Adelaide Island, Antarctica, and the mid Scotia Sea, it has been reported that, although phenoxy resin has local sources, it has a long range and, together with polyethylene, is one of the most common resins (41%) (Jones-Williams et al., 2020).

Therefore, although we did not verify its presence in the intertidal sediments, it is highly probable that it is present not only in the soils of Fildes Bay but also offshore. In addition, transport through biovectors from terrestrial to aquatic environments, such as that which took place via the adhesion of a piece of mesoplastic to the chest of an adult individual of the species *Pygoscelis papua* (Forster, 1781), should not be ruled out (Figure 3E).

Our study showed a relationship between the fragments and organic matter of the soils. This contrasts with the results reported by Watteau et al. (2018), who analyzed soils enriched with municipal compost in France and concluded that microplastics in soils do not present an association with organic matter. In experimental soils with different microplastic sizes, Dong et al. (2021) reported that the presence of polystyrene and polytetrafluoroethylene microplastics caused a reduction in the soil organic matter. In our research, organic matter (%) was determined using the method of Heiri et al. (2001), who indicate that weight loss is proportional to the amount of organic carbon contained in the sample. However, Rillig (2018) emphasized that the methods used for quantitation of organic carbon in soil can cover “invisible” microplastics because plastics are composed mainly of carbon. This could explain the relationship that we verified between the increase in organic matter in sites and a high abundance of fragments. As organic matter (%) does not seem to be a precise variable, it is suggested that future studies employ more specific analyses regarding the composition of the type of carbon present in soils.

The information available on exposure and effects of microplastics on Antarctic organisms is similarly scarce. Plastic particles can persist, accumulate, and eventually affect the functioning and biodiversity of terrestrial ecosystems (Rillig, 2012). Habib et al. (2020) isolated bacteria *Pseudomonas* sp. ADL15 and *Rhodococcus* sp. ADL35 from soil samples collected in Victoria Land, Ross Sea, Antarctica. They corroborated positive growth in a medium containing fragments of polypropylene (Habib et al., 2020). In addition, bacterial assemblages with distinct community structures colonized the PE microplastics (Huang et al., 2019). In general, soil fauna has an active intake of microplastics, with a consequent alteration of its intestinal microbiome and adverse effects on motility, growth, metabolism, reproduction, and mortality in various combinations (Büks et al., 2020), especially at high concentrations and with small particle sizes. The small size and large surface area of microplastics allow the adsorption of pollutants on their surfaces, increasing the local concentration in soils and generating potential ecological risks (Moore, 2008; Ashton et al., 2010; Rillig, 2012; Liu et al., 2018). Finally, although it was not found in the intertidal zone, phenoxy resin could be transported offshore; according to European Chemicals Agency (2021), this substance is toxic to aquatic life, with long-lasting effects.

6.5.2 Microplastics in Antarctic Intertidal Sediments

The intertidal sediments were dominated by fibers (up to 4 fibers/50 ml sediment) (Figure 2), which were associated with large particle sizes. Similar abundances have been reported by Reed et al. (2018), who recorded up to 3 fibers/10 ml sediment in North Cove, Adelaide Island, Antarctic Peninsula. A previous study carried out by Rebolledo and Franeker (2015) on Cape Shirreff did not record microplastics in intertidal sediments, despite the presence of macroplastics in the area. Although the information on microplastics in Antarctic intertidal sediments is limited (Table 1), these data could suggest a low abundance compared with those of deep sediments. Close to the study area, Waller et al. (2017) carried out research in semi-deep sediments (6–60 m) in Mackellar Inlet, Almirantazgo Bay. They reported between 16 and 766 particles/m^2; however, they did not find a clear pattern of abundance or distribution, and the proportion of fibers and fragments found was not reported. Consistent with our findings, the predominance of fibers (42.8%) was verified in semi-deep sediments (25–140 m) in Terra Nova Bay (Munari et al., 2017). Fibers also predominated for all recorded microplastics, with the exception of one particle, in shallow sediments (0–20 m) on Adelaide Island (Reed et al., 2018). This pattern of fiber prevalence has also been reported in Singapore mangroves (Nor and Obbard, 2014). In addition, Browne et al. (2010) analyzed the sediments in the high tide line of the Tamar Estuary, United Kingdom, finding values of up to 1 fiber/50 ml sediment, similar to those of Fildes Bay. A low abundance in the intertidal sediments of coastal systems in Plymouth, United Kingdom, was also described by Thompson et al. (2004), who indicated that fibers increased in subtidal sediments. In marine environments of the Alboran Sea (42 m deep), an abundance of 45 fibers/50 ml sediment has been described (Sanchez-Vidal et al., 2018). Although Sanchez-Vidal et al. (2018) did not include other forms of particles in deep sediments of southern European seas in their study, they estimated that around 20% of the fibers found had accumulated in the open sea beyond 2,000 m of water depth. This could be explained by the fibers having an abundance up to four orders of magnitude higher in deep sediments than in the surface waters of the Atlantic Ocean, Mediterranean Sea, and the Indian Ocean (Woodall et al., 2014). In contrast, very deep sediments (136–3,633 m) analyzed on the Antarctic Peninsula, South Sandwich Islands, and South Georgia were shown to be dominated by fragments, which accounted for 56% of the total (Cunningham et al., 2020). Density could partly explain the distribution of the fibers, once in the water, in the water column, and in the deep sediments (Thompson et al., 2004; Sanchez-Vidal et al., 2018). In general, depth seems to be a determining factor in the abundance of certain forms of microplastics, with fibers predominating in intertidal environments and shallow areas.

Regarding the values at each site, the highest abundances were recorded at the sites closest to the Frei base effluent (i.e., IS1 and IS2), and are consistent with those reported in marine sediments near wastewater from the Rothera station west of the Antarctica Peninsula (Reed et al., 2018). In addition, 67% and 50% of all fibers recorded at sites IS1 and IS2, respectively, were cotton fibers, confirming the contribution of wastewater effluents. Although sludge acts as a microplastic retention agent, with estimated retention rates of 75.7% to 90% (Corradini et al., 2019; Jiang et al., 2020), fibers have also been found in the effluents (37.7–60.8%) of secondary treatment systems (Jiang et al., 2020), and up to 14 fibers/L have been observed in primary treatment systems (Talvitie et al., 2015). Given this scenario, a negative situation is projected for some facilities, as their treatment systems are prone to failure due to both the low temperatures that impede biological processes and the lack of maintenance and sludge evacuation, resulting in continuous emission of waste into the environment (Hughes and Blenkharn, 2003; Gröndahl et al., 2009; Morales Calvo, 2013). In addition, 37% of permanent stations and 69% of non-permanent stations do not have any type of wastewater treatment (Morales Calvo, 2013). Due to the high population density in the north of the Antarctic Peninsula, microplastics derived from personal care products and laundry are likely to be concentrated there (Waller et al., 2017). Microfibres from laundry released in wastewater may be a more substantial source of microplastic pollution compared with other sources as personal care products (Waller et al., 2017). However, the contribution of fibers from sources related to other types of local human activities should not be ruled out.

Regarding sediment characteristics, we found that a greater fiber abundance is related to large particle sizes. In other regions, studies on intertidal sediments have not identified a pattern in terms of microplastic abundance and sediment particle size, with high abundances found in both sediments larger than 2 mm in Canada (Cluzard et al., 2015) and fine sediments in Singapore (Nor and Obbard, 2014). The physical interactions between microplastics and sediments are not yet fully understood due to the diversity of shapes, diameters, lengths, surface areas, and densities, among other characteristics, which makes it difficult to know where they will settle and at what sedimentation rate (Browne et al., 2010; Cluzard et al., 2015).

All the fibers found in the intertidal zone were made of PET, also called polyester (Figure 3B). This material is widely used in the manufacturing of cold-weather clothing (Gonzalez et al., 1998; Das and Gersak, 2014; Gnanauthayan et al., 2017). Polyethylene terephthalate has a density of 1.34–1.39 g/cm^3, and according to Browne et al. (2010), almost 80% of the microplastics recorded on the coastline are denser, which, as they state, maybe due to its slow degradation, longer contact time with abrasive particles in the sediment, or transport by the wind of less dense plastics toward the coasts and inland. This could explain the presence of this type of polymer composition at all sites and in other regions, as reported by Naji et al. (2017) in a study on intertidal sediments of Hormozgan, Persian Gulf, in which fibers predominated by 88%, PET was identified as the most abundant polymer (i.e., 41%), and high concentrations in wastewater release zones were found. In Portugal and Morocco, 29% of the fibers found in intertidal sediments were made of PET (Velez et al., 2019). Similarly, a large-scale study conducted at high tide in intertidal sediments (0–5 cm) in Auckland, New Zealand, reported that fibers predominated (i.e., 88%) and PET accounted for 22% of all microplastics analyzed (Bridson et al., 2020). This abundance of PET in relatively shallow sediments was also described by Woodall et al. (2014) in the Atlantic Ocean, the Mediterranean Sea, and the Indian Ocean. Similarly, it was reported that 12.9% of the fibers found in the deep sea were polyester (Sanchez-Vidal et al., 2018). It has been observed that many marine microplastics have this composition and that their distribution and sinking rate presumably differ from those of other high-density microplastics (Cunningham et al., 2020).

In marine environments of Victoria Land, Antarctica, Sfriso et al. (2020) collected benthic invertebrates, reporting that species contained between 0.01 and 3.29 items/mg^{-1}, and that bivalves and gastropods displayed the highest microplastic contamination. Despite these findings, no evident accumulation through the food web was detected. In other regions, the dominance of PET fibers in coastal ecosystems on the coast of Pará, Brazil, was described by Morais et al. (2020), who reported that plastic fibers accounted for 84% of plastics ingested by individuals of *Bunodosoma cangicum* (Belém and Preslercravo, 1973), with PET being the main polymer (44.7%), and that this organism presented a higher amount of plastic debris in the more populated sampling sites.

It is still not clear if the role of microplastics is that of pollutant or merely contaminant; however, it is necessary to deepen our knowledge on the distribution and effects of microplastics and additives at all levels of the food web to evaluate their effects on marine organisms and ecosystems from a broader perspective (Sfriso et al., 2020). Aragaw and Mekonnen (2021) have recommended that microplastic contamination investigation guidelines emphasize experimental ecotoxicological studies and risk assessments for aquatic organisms. Vighi et al. (2021) stressed that key aspects in the production of an adequate risk assessment are frequently overlooked and that the impacts of environmental variables on additive leaching must be included.

6.5.3 Pollution of Protected Areas

Ardley Island was selected to assess the base level of contamination in an area with less human activity and no residential, scientific, or military settlements, only two sporadically used shelters. However, it was possible to detect the presence of a fiber particle in the intertidal sediment, which indicates that Antarctic environments with restricted entry and protected for their biological value are not exempt from contamination by microplastics. Thus, the inspection of King George Island has shown clear deficiencies with respect to waste management at some stations in the form of waste storage and the existence of more than 40 waste dumps (Peter et al., 2013). Although in other locations of the continent, there has been an effort regarding the recovery of waste and mitigation of old landfills (Eriksen et al., 2020), the Protocol to the Antarctic Treaty on Environmental Protection has recognized the lack of data on plastics that would allow adequate decision-making and reduction of pollution and has recently made recommendations regarding the use of plastic on the continent (Secretariat of the Antarctic Treaty, 2019a). Among the recommendations are halting the use of personal care products that contain plastic microbeads and considering the use of filtration technologies to reduce the amount of microplastic particles that enter the Antarctic marine environment (Secretariat of the Antarctic Treaty, 2019a, b); however, there are no recommendations focused on soils. This is worrying as our study has shown that the soil-intertidal sediment interface is not necessarily a continuum and that there is a difference in the composition of plastic particles, suggesting specific sources of microplastics in each matrix at Fildes Bay. Therefore, an understanding of microplastic pollution in Antarctica requires an increased focus on identifying sources and sinks.

6.5.4 Methods Used in Microplastic Research in Antarctica

In general, few studies are available on marine sediments in Antarctica, with most focusing on subtidal sediments and none so far on soils (Table 1). Research efforts are made mainly on the Antarctic Peninsula, which makes it difficult to understand what occurs inside the Antarctic Continent. Antarctica is characterized by difficult-to-access sites, low temperatures, and strong winds; this last factor can generate a high degree of contamination during sample collection. Given this scenario, sample collection techniques, microplastic selection criteria, and sample treatment vary among studies. Although all authors have used FT-IR to determine the composition of the particles, the results are expressed in different units of abundance (e.g., particles/ml and particles/m^2). In these cases, we suggest the incorporation of a standardized expression of units whenever possible, such as particles per surface or per volume. In our study, for comparative purposes, we decided to use the same expression for both matrices, which allowed us to identify a greater abundance in soils (average = 13.8 particles/50 ml) than in intertidal sediments (average = 1.5 particles/50 ml). This expression of the results permitted us to corroborate that even though the studied environments are contiguous, their abundances were independent and that contrary to what we expected, surface intertidal sediments did not behave as a sink for land-based sources. For instance, at site IS5, the presence of microplastics was not recorded, even though the adjacent soils were visibly affected by high abundances of microplastics as a result of the infrastructure that had been affected by a fire. In addition, despite the continuous release of fibers from the effluents, a low abundance was found at all intertidal sediment sites, which could be due to environmental dynamics such as tidal waves that affect intertidal sediments. In this regard, Cluzard et al. (2015) observed that a greater influence of tides and waves caused a lower accumulation of microplastics. Thus, although the abundances alone did not allow us to explain the distribution of microplastics in the study area, improving their comparability facilitates understanding of the complex intrinsic processes associated with Antarctic matrices.

6.6 CONCLUSION

The results of this study revealed the occurrence of microplastics in soils and intertidal sediments at 81% of the analyzed sites at Fildes Bay, Antarctica. This is the first study to report the presence of microplastics in Antarctic soils, with a high abundance of phenoxy resin fragments in Antarctic soils near stations, probably associated with deterioration of infrastructure coatings. Compared with terrestrial abundances, the abundance of microplastics in intertidal sediments was lower and consistent with results previously reported in shallow Antarctic sediments. Polyethylene terephthalate fibers predominated in the intertidal sediments, especially at the sites near the effluent from the Frei base, where the presence of cotton fibers was confirmed. Although this base has a treatment system, the situation of the bases affected by logistical limitations or without treatment systems is worrying. In addition, microplastics were found on Ardley Island, corroborating that there is contamination in protected areas. Regarding the influence of environmental variables, we observed a relationship between fragments and organic matter; however, this relationship seems to be a result of the composition of the polymers. In addition, the observed relationship between fibers and particle size was not conclusive, and to date, there are no studies that confirm a clear relationship. This investigation shows the importance of the early identification and management of local sources of microplastics and the study of each matrix, as the behavior of microplastics seems to differ depending on the substrate into which they are released. Paint resins should be considered in future studies, as they have demonstrated their persistence in the environment despite local climatic conditions. It is suggested that the Fildes Bay area be monitored to evaluate the behavior of these microplastics in other matrices and their eventual interactions with local fauna. This will make it possible to strengthen efforts to reduce the presence of microplastics in areas of major human activity such as Fildes Bay.

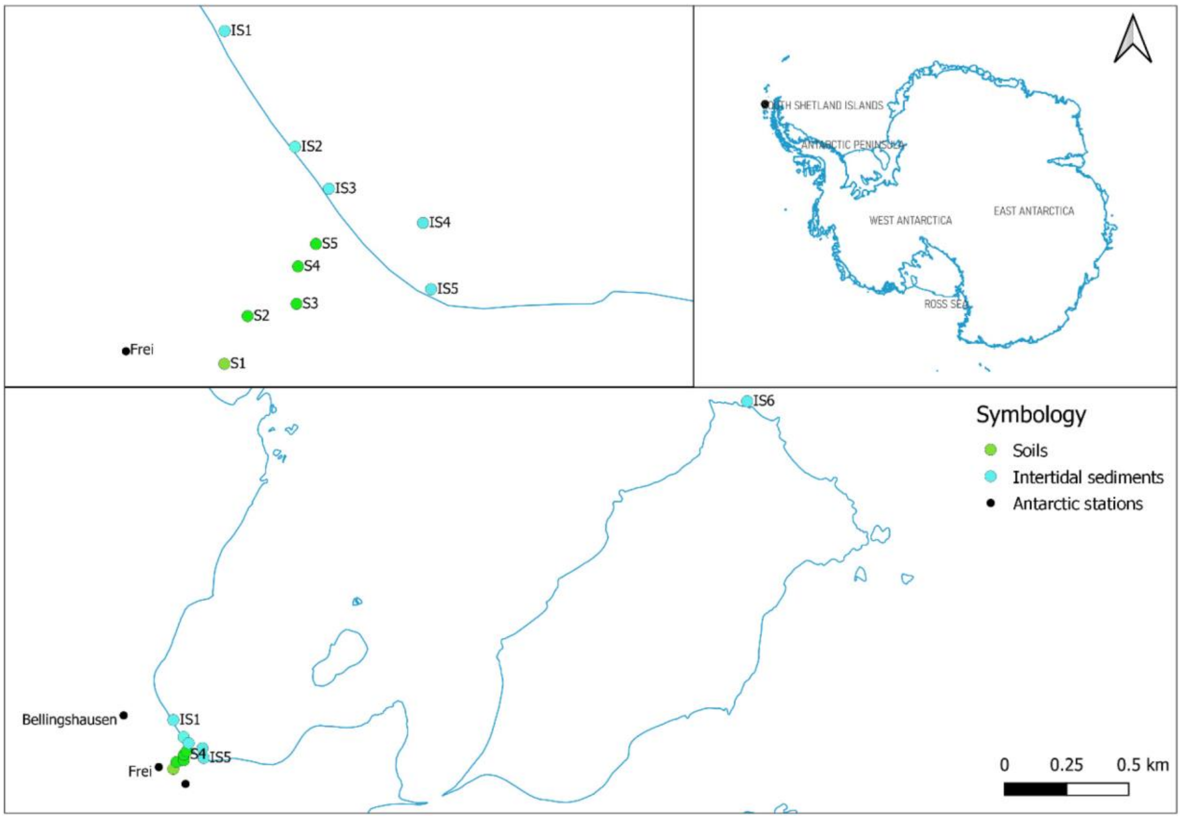

Figure 1. Sampling areas on Fildes Bay and Ardley Island, Antarctica. Green points indicate soil samples (i.e., S1–S5), and light blue points represent intertidal sediments (i.e., IS1–IS6).

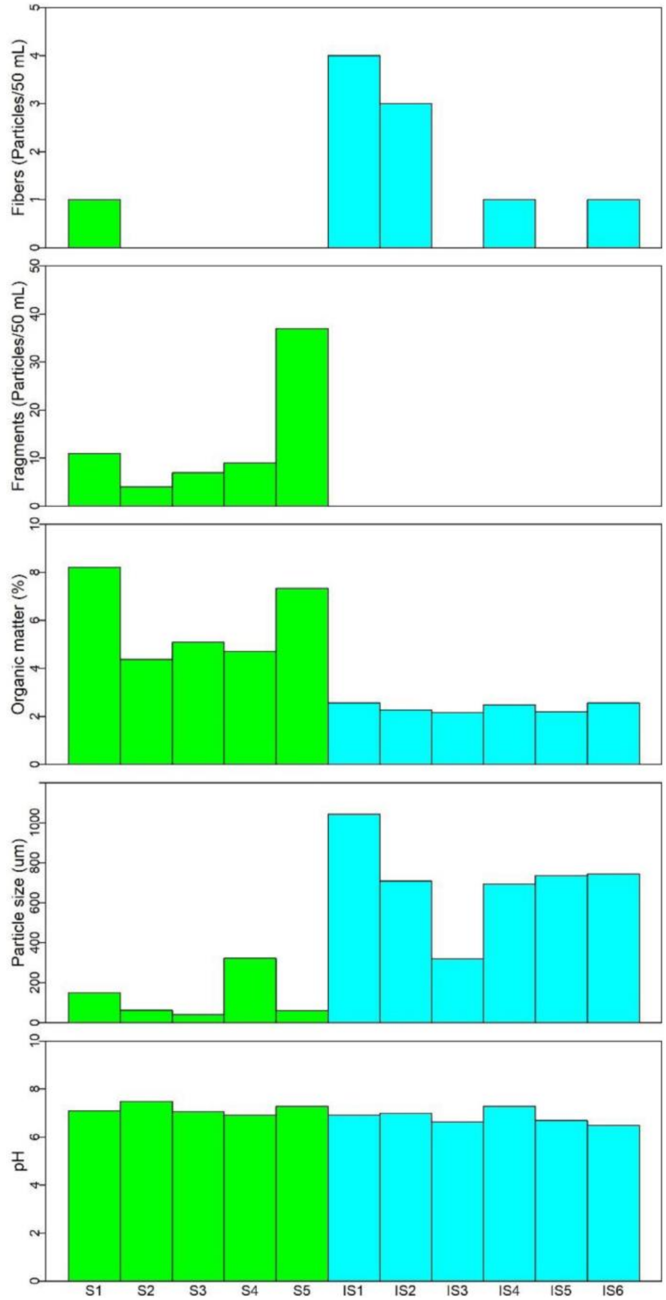

Figure 2. The abundance of microplastics (i.e., fibers and fragments) and determination of an organic matter, particle size, and pH in soils (i.e., S1–S5) and intertidal sediments (i.e., IS1–IS6) of Fildes Bay, Antarctica.

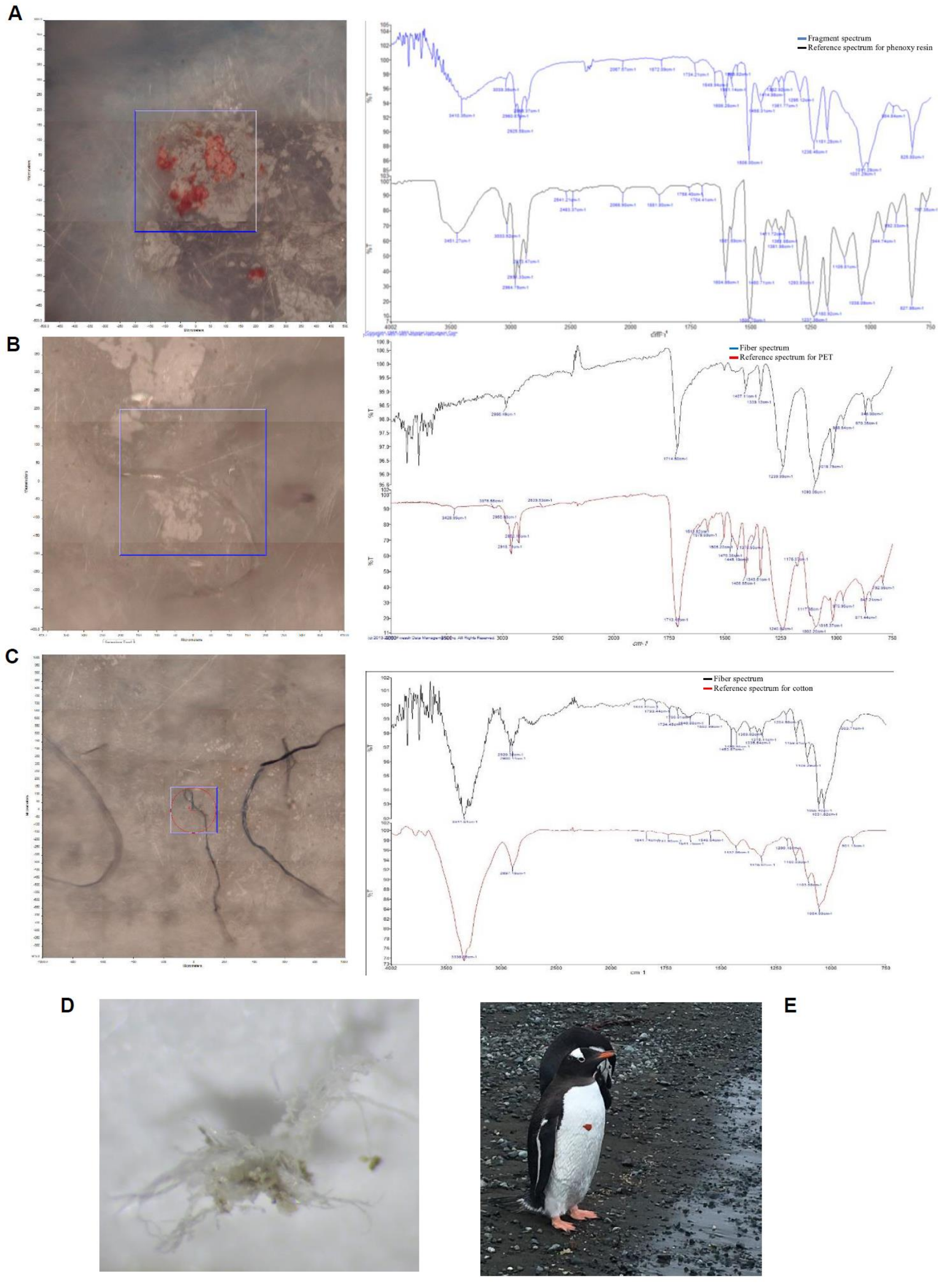

Figure 3. Photograph and spectrum of an orange tree fragment of phenoxy resin (A) collected in soils, PET fiber (B), cotton fiber (C) and a fiber found at the site IS6 (D) from intertidal sediments and a mesoplastic piece on *P. papua* (E) in Fildes Bay, Antarctica.

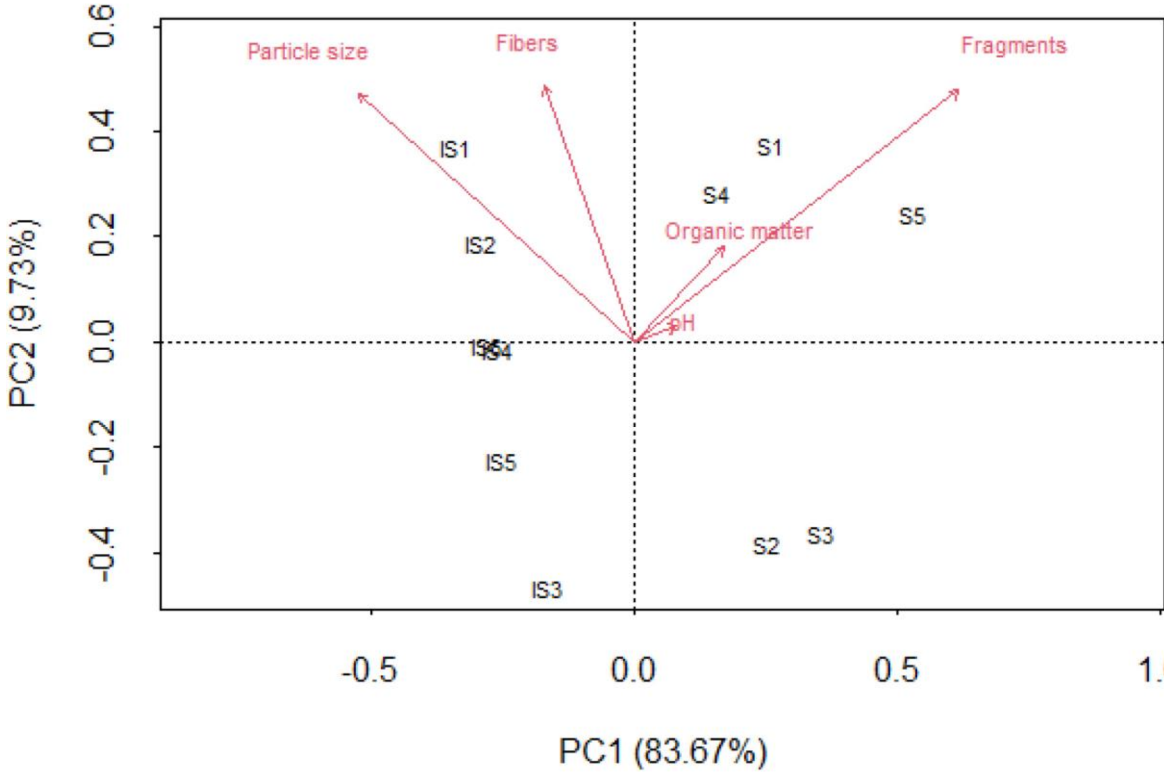

Figure 4. Principal component analysis (PCA) between fibers, fragments, organic matter, particle size, and pH in soils and intertidal sites.

Table 1. Microplastics in intertidal and subtidal sediments in Antarctica.

Matrix	Shape	Location	Sampling date	Collection method	Depth (m)	Size criteria	Sample digestion	Density Separation	FT-IR	Abundance	Reference
Subtidal sediment	Fibers (42.8%)	Terra Nova Bay, Ross Sea, Antarctica.	2015	Van Veen grab	25–140	< 5 mm			X	5–1,705 particles/m^2	Munari et al. (2017)
Intertidal and subtidal sediment	Fibers (except a spheric particle)	North Cove, Cheshire Island and South Cove, Adelaide Island, Antarctic Peninsula.	2016	Diving or box coring	0–20	< 5 mm		X	X	0–3 particles/10 ml	Reed et al. (2018)
Subtidal sediment	Fibers and fragments (no percentages)	Mackellar Inlet, South Shetland Islands, Antarctic Peninsula.	2013 and 2015	Van Veen grab and SCUBA	6–60	< 5 mm				16–766 particles/m^2	Waller et al. (2017)
Subtidal sediment	Fragments (56%). Fibers (39%)	Antarctic Peninsula.	2017–2019	OKTOPUS multicores	136–3,633	< 2 mm	X	X	X	1.30 ± 0.51 particles/g	Cunningham et al. (2020)

FT-IR, Fourier-transform infrared spectroscopy.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

AP-B and ROB conceptualized the study and provided funding for the study. AP-B performed the fieldwork and laboratory analysis. AP-B, AA, KM, and ROB wrote the manuscript. All authors contributed to the article and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

VII. Capítulo 2: Analysis of the contribution of locally derived wastewater to the occurrence of Pharmaceuticals and Personal Care Products in Antarctic coastal waters.

Este capítulo está basado en:

Perfetti-Bolaño, A., Muñoz, K., Kolok, A. S., Araneda, A., & Barra, R. O. (2022). Analysis of the contribution of locally derived wastewater to the occurrence of Pharmaceuticals and Personal Care Products in Antarctic coastal waters. Science of The Total Environment, 158116.

7.1 Abstract

Pharmaceuticals and Personal Care Products (PPCPs) are emerging pollutants detected in many locations of the world including Antarctica. The main objective of this review is to discuss the influence of the human population on the concentration, distribution and biological effects of PPCPs across the Antarctic coastal marine ecosystem. We carried out a review of the scientific articles published for PPCPs in Antarctic, supported by the information of the Antarctic stations reported by Council of Managers of National Antarctic Programs (CONMAP), Scientific Committee on Antarctic Research (SCAR) and Secretariat of the Antarctic Treaty (ATS). In addition, spatial data regarding the Antarctic continent was obtained from Quantarctica. Antarctic concentrations of PPCPs were more reflective of the treatment system used by research stations as opposed to the infrastructure built or the annual occupancy by station. The main problem is that most of the research stations lack tertiary treatment, resulting in elevated concentrations of PPCPs in effluents. Furthermore, the geographic distribution of Antarctic field stations in coastal areas allows for the release of PPCPs, directly into the sea, a practice that remains in compliance with the current Protocol. After their release, PPCPs can become incorporated into sea ice, which can then act as a chemical reservoir. In addition, there is no clarity on the effects on the local biota. Finally, we recommend regulating the entry and use of PPCPs in Antarctica given the difficulties of operating, and in some cases the complete absence of appropriate treatment systems. Further studies are needed on the fate, transport and biological effects of PPCPs on the Antarctic biota. It is recommended that research efforts be carried out in areas inhabited by humans to generate mitigation measures relative to potential adverse impacts. Tourism should be also considered in further studies due the temporal release of PPCPs.

Keywords: Pharmaceutical and Personal Care Product (PPCPs), Coastal seawater, Pollution, Wastewater Treatment Plant (WWTP), Antarctica.

7.2 Introduction

Emerging contaminants, or chemicals of emerging concern, are a subset of potentially toxic chemicals products, not necessarily new, but without regulatory status. When present in the environment their impact on ecosystem function and human health is very often not well understood. A key class of emerging pollutants are Pharmaceuticals and Personal Care Products (PPCPs) (EPA, 2008; Wagner & Lambert, 2017). Daughton & Ternes (1999) suggested a systematic strategy to determine if a research effort should be initiated to establish the incidence of PPCPs in the environment. Such a strategy would determine if there were adverse effects on aquatic organisms, and if cost-effective modifications of wastewater treatment could improve elimination efficiencies. While there is uncertainty regarding the environmental impact of PPCPs, enhanced analytic selectivity and sensitivity of technologies such as liquid chromatography and gas chromatography coupled with methods based on mass spectrometry have been used for the analysis of a greater diversity of these pollutants (Gago-Ferrero et al., 2012; CONMAP, 2014). Monitoring studies using these analytical approaches have allowed scientists to corroborate the presence of PPCPs in the surface water of rivers and coastal seawaters around the world, including U.K., U.S.A., Canada, China and Saudi Arabia (Boyd et al., 2003; Kasprzyk-Hordern et al., 2008; Vidal-Dorsch et al., 2012; Ali et al., 2017; Chen et al., 2021), with concentrations <14000 ng l-1 for a wide spectrum of reported compounds. The global detection of PPCPs can be explained by their high annual production (2×10^7 tons, Wang & Wang, 2016) as well as the recalcitrant nature of many of these compounds with respect to degradation and removal in treatment facilities. Consequently, after PPCPs have been used, they are often discharged, in parent form, from wastewater treatment plants (WWTPs) into rivers, lakes and coastal seas (Huber et al., 2016). In this aspect, the type of wastewater treatment is important given that conventional treatments, for example coagulation plus chlorination, achieve low efficiency in the removal of PPCPs compared to more advanced technologies such as activated carbon, ozone and reverse osmosis (Snyder et al., 2003; Westerhoff et al., 2005). Nevertheless, globally, over 80% of all wastewater is discharged without treatment (Connor et al., 2017). In developing countries, increasing urbanization and economic development, has increased the use of PPCPs, which increases the chemical load that treatment plants have to deal with. Furthermore, insufficient research, finances and human resources, coupled with innapropriate selection of treatment technologies that fit the local physical and climatic conditions, have only exacerbated the problem (Massoud et al., 2009; Gallego-Schmid & Tarpani, 2019).

Issues associated with the release of PPCPs also occur in the polar environments. In the Arctic, for example, the treatment of wastewater is often inadequate or completely lacking, due to absence of appropriated WWTPs and the widely used bucket toilets even in villages and towns, resulting in relatively high release rates for PPCPs into the aquatic environment (Gunnarsdóttir et al., 2013; Kallenborn et al., 2018). Research conducted on the Faroe Islands, Iceland and Greenland in treated and untreated wastewater streams, identified the occurrence of a large number of PPCPs such as diclofenac, ibuprofen, lidocaine, naproxen, metformin and citalopram (Huber et al., 2016). Since 2015, PPCPs such as estrogens, analgesics, anti-inflammatories, antibiotics, fungicides, preservatives, UV filters and surfactants have been demonstrated to occur in streams, glaciers drains, sea ice and polar organisms in Antarctica (Emnet et al., 2015; Esteban et al., 2016; González-Alonso et al., 2017; Vecchiato et al., 2017; Hernández et al., 2019; Domínguez-Morueco et al., 2021). This is due to the fact that, during the agreements of the Environmental Protocol, the prohibition on the disposal of untreated effluents was ruled out because of the high costs of its execution. As such, the Protocol allows for direct discharge of wastewater effluents into the sea when the station is occupied by fewer than 30 persons weekly, but for stations occupied by more than 30, at least one primary maceration treatment must be functioning (ATS, 1991; Smith & Riddle, 2009). Consequently, 37% of the permanent stations and 69% of summer stations, lack any kind of treatment whatsoever (Gröndahl et al. 2009). Antarctic polar stations also discharge different types of wastewater to the environment, including water derived from domestic, e.g., kitchens, toilets, laundry rooms, and bathrooms, and from technological sources as laboratories, repair workshops, etc. (Szopińska et al., 2021). This can result in a great variety of PPCPs being distributed into the environment, at wide ranging concentrations, and is in line with the global pattern showing high concentrations of PPCPs in areas of high human density (aus der Beek et al., 2016). The problem is exacerbated by the fact that many facilities account for operational problems and failures due to logistics, maintenance and unrealized energy requirements, all of which can result in increased specific labor for removal and subsequent treatment or evacuation of sludge (Hughes & Blenkharn, 2003; Gröndahl et al., 2009; Morales, 2013).

The main objective of this review is to compilate the literature regarding occurrence and diversity of PPCPs and to discuss the influence of the human population on the concentrations, distribution and effects of PPCPs in Antarctic coastal marine ecosystem.

7.3 Materials and Methods

Research articles available about the presence of PPCPs in the Antarctic were compiled from the Web Of Science (WOS) and Google Scholar (Emnet et al., 2015; Esteban et al., 2016; González-Alonso et al., 2017; Vecchiato et al., 2017; Hernández et al., 2019; Domínguez-Morueco et al., 2021; Duarte et al., 2021; Szopińska et al. 2022), for search key words including pharmaceuticals, drugs, Personal Care Products, PPCPs, pollution, contaminants of emerging concern and Antarctic. Studies that expressed PPCPs results as composite sums (e.g., Szopińska et al., 2021) were not included in this review.

Antarctic facilities and its infrastructure information published by the Council of Managers of National Antarctic Programs (CONMAP, 2017, 2020a) and Scientific Committee on Antarctic Research (SCAR, 2020) were classified for each country according to the operating time (Figure 1a), population and built infrastructure (Figure 1b). The information on occupants by Antarctic station provided by CONMAP (2020a) corresponds to the years 2017-2019. In addition, both the number of stations and the type of seasonality were ordered by country (Figure 2).

The implementation of the treatment for wastewater used by each Antarctic station was compiled from the Reports of the Antarctic Treaty Inspections from Secretariat of the Antarctic Treaty (ATS, 2003, 2005, 2009a, 2009b, 2010, 2011, 2012, 2013a, 2013b, 2013c, 2015, 2016a, 2016b, 2017a, 2017b, 2018, 2019a, 2019b, 2019c, 2020a, 2020b, 2020c). Additionally, publications from Council of Managers of National Antarctic Programs (CONMAP) (2014, 2016, 2019, 2020b) were also compiled. This information was complemented by that published by Delille & Delille (2000), Thomsen (2005), Tarasenko (2009), Martins et al. (2014), Australia State of the environment (2016), BAS (2019a, 2019b), Australian Government (2020), Swedish Polar Research Secretariat (2020), Szopińska et al. (2021) and updated information by direct request to Chilean institutions (Figure 3). The spatial data of Antarctic continent was obtained from Quantarctica 3 Data Package (Matsuoka et al., 2018) and the mapping was developed using QGIS 3.14.0 Software (QGIS.org, 2022).

7.4 PPCPs in the Antarctic: sources and occurrence

7.4.1 Operating scientific stations and population in numbers

According to the information published by CONMAP (2020a), currently scientific stations belonging to 29 nations are distributed on the Antarctic continent. The longest time of operation that any country has operated a station is 118 years by Argentina, meanwhile the youngest station correspond to Belgium. Figure 1a shows the operating time of the stations in the Antarctica. In addition, the human population is correlated with the built infrastructure (Figure 1b). In this context, the United States has both the largest population (1399 inhabitants) and the largest built infrastructure (51000 m2) (CONMAP, 2017, 2020a) (Figure 1b). In both aspects, values attributed to the United States more than double those of the next leading nation, Argentina. In the case of Australia, they have a similar infrastructure as Argentina, but with less than 300 inhabitants per year. The small station in terms of people per year and infrastructure corresponds to R. Belarus.

Although many of the PPCPs detected in Antarctica were not synthesized at the time that the earliest stations were developed, the greatest boom in the establishment of stations occurred during the 1950s, a period in which PPCPs, for example acetaminophen, were already marketed. Acetaminophen has proved to be useful, as it has become one of the most widely used drugs in the world, is a common ingredient in more complex drug formulations (McGill & Hinson, 2020; Shen et al., 2021), and is used to treat a wide spectrum of effects, i.e. to treat allergies, coughs, colds, flu and insomnia and moderate to severe pain (FDA, 2017). In this regard, depending upon the waste management of each station, countries with an extensive operating time (Figure 1a) may have generated a legacy of PPCPs in the Antarctic environment with a relatively long exposure time. Longer-dated stations could generate chronic effects through the probable chronic occurrence of some types of PPCPs. The human contribution to PPCPs in the Antarctic environment reaches even more importance for year-round stations. Based on information reported by CONMAP (2020a), we estimated that although year-round stations represent 52.6% of the stations, they house the most of the annual population, i.e. 82.4% (Figure 2). Of this total, 35.1% of the population is housed in the three year-round stations operated by the United States. Such year-round stations have particular importance relative to the occurrence of PPCPs both because they represent permanent point sources and because they support large numbers of habitants. Given the potential PPCPs load discharged from these year-round stations, the kind of wastewater treatment used acquires greater relevance in the management of emerging pollutants in the Antarctic environment.

Figure 3 shows the Antarctic stations according their facility information (CONMAP, 2020a), spatial distribution from Quantarctica (Matsuoka et al. 2018) and the status of their wastewater treatment capacity. Currently, 38 stations reported that they dispose of their effluents directly at sea, of these: 7 do not have treatment, 26 use treatment, 3 use septic tanks and 2 macerations (Figure 3). Maceration is allowed by the Protocol, nonetheless, Hale et al. (2008) have shown that this process may not deter the entry of chemicals into the Antarctic environment. Likewise, the presence of surfactants in wastewater from septic tanks in samples belonging to the Arctowski station has been confirmed (Szopińska et al. 2021). Due to the state of operation of wastewater treatment systems in the Antarctic, the presence of permanent and unregulated emissions in coastal waters of the continent is probable.

7.4.2 Occurrence and levels of PPCPs in the Antarctic environment

To the date, only eight studies have been conducted in relation to PPCPs in the Antarctic. Comparatively, it is the Antarctic Peninsula that presents the largest number of studies carried out (n = 6) relative to the rest of the continent (n = 2) (Figure 3). These studies have focused upon a variety of compounds, including: analgesics/antipyretics/antiinflammatories, antiasthmatics, antibiotics, antidepressants, antidiabetics, antidiarrheals, antifungals, antihistamines, antimicrobials/disinfectants, anxiolytics, cardiovascular agents, diuretics, fragrances, plasticizers and surfactants, preservatives, synthetic estrogens, UV filters, UV blockers and vasopressors (Figure 3). Usually, It is verified that the effluents showed the highest concentrations (Figure 4). Of the set of reported PPCPs there are six that stand out for their high concentrations (>6000 ng/l), and these were detected in Esperanza base (Argentina) and Scott base (New Zealand) (Figure 4), these PPCPs belong to the group of analgesics/antipyretics/antiinflammatories, UV filters and surfactants. All the studies were carried out during the austral summer, a common practice in Antarctica due mainly to the restrictions derived from the meteorological conditions and the accessibility for sampling in the peninsula. Thus, most of the studies were carried out during the 2012 - 2013 season, and permanent monitoring was not reported. This implies a lack of knowledge of the general dynamics of these pollutants due to the absence of reports during the seasons of low temperature. According to the methods used, the researchers basically used two types of analytical techniques based on target analysis via LC-MS/MS TSQ and GC-MS (Table 1). Despite the efforts, shortcomings are still observed, since a large part of the continent does not present basic information about these pollutants, such as coastal areas in the north of the continent.

Interestingly and despite of the high levels of solar radiation (Zeng et al., 2021), few studies have looked for UV filters. UV filters such as 4-methyl-benzylidenecamphor (4-MBC), are used in various types of personal care and hygiene products like sunscreens, cosmetic products, and hair-caring products; as well as other materials such as toys, outdoor furniture, textiles, rubber and plastic materials as protective agent (Tsui et al., 2019; Domínguez-Marueco et al., 2021; Gómez-Regalado et al., 2021). In general, prior to entering the Antarctic continent, it has become recommended that the use of UV filters be frequent during the stay, these products being available in all modules of the bases. UV filters can accumulate and expose the food chain (Gago-Ferrero et al. 2012), which, in turn, has potential adverse impacts for both organisms and the ecosystem due to its disruptive capacity observed, for example, in the decrease in fertility and reproduction (Díaz-Cruz et al., 2008; Fent et al., 2008; Kim & Choi, 2014; Astel et al., 2020). Increased worldwide demand for UV filters is associated with high temperatureand irradiance (Magi et al. 2013), and changes in the tourist market (Astel et al., 2020). In Antarctica, it has been observed that certain conditions favor frequent “very large” ozone holes in late spring which enable extreme surface UV events over the Antarctic Peninsula (Cordero et al., 2022). According to Gies et al. (2009), 80% of the human population in Antarctica is exposed to UV levels above those recommended, and over 30% reached more than 5 times the limits.

Another group for which data has been provided are surfactants. Surfactants, such as 4-t-octylphenol (OP), reduce surface tension and are widely used in industrial and domestic processes in a variety of areas such as cleaning, food, metallurgy, pharmacy, medicine, paints, varnishes and mining (Knepper & Berna, 2003; Ivanković & Hrenović, 2010). They have toxic effects on aquatic organisms and their release from wastewater can have serious effects on the ecosystem (Ivanković & Hrenović, 2010). As a consequence of the use of UV filters and surfactants, these were detected in the Scott, McMurdo and Esperanza base (Emnet et al. 2015, Domínguez-Morueco et al. 2021). Emnet et al. (2015) observed that WWTP discharge in the Scott Base strongly correlate with population over longer periods, such as the summer research season. This apply for 4-MBC whose concentrations increased steadily throughout the research season (from 321 ng l-1 in August to 2130 ng l-1 in January) (Emnet et al. 2015). Contrarily, the highest concentrations for OP were observed in August, before the start of the research season in the Scott base (Emnet et al. 2015). This station uses bio-degradation, aerated fixed thin-film bed, centrifuge and filtration to purify water and ozone disinfection since the 2009 - 2010 season (ATS, 2012; Emnet et al., 2015). Nevertheless, high concentrations were reached for the UV filters, 4-MBC (<11700 ng l-1) and 2.4-

dyhydroxybenzophenone (BP-1) (<6830 ng l-1), as well as the surfactant OP (<7050 ng l-1) during a seven-day study (Figure 5, Table 1).

4-MBC and BP-1 belong to the stable UV absorbents and are widely used in other personal care products, as well as in the textile industry (Gantz & Sumner, 1957). These UV filters are of concern in human and environmental context because of the potential endocrine-disrupting effects they exert (Nashev et al., 2010; Zhang et al., 2013; Juliano & Magrini, 2017). These high concentrations contrast with those recorded by the same authors during the monthly sampling: 4-MBC: 976 - 2020 ng l-1, BP-1: 24.3 - 124 ng l-1 and OP: 7.5 - 39.0 ng l-1. Later, Emnet et al. (2020) recorded even lower values in urban areas for 4-MBC (23.2 - 428.8 ng l-1), BP-1 (3.6 - 146.2 ng l-1) and OP (3 - 205.8 ng l-1), compared to those reported in Antarctica (Table 1). The high concentrations reported by Emnet et al. (2015) exceed even the records in effluents without treatments from Esperanza base, in which Domínguez-Morueco et al. (2021) could not detect 4-MBC, despite high concentrations of BP-1 (1400 ng l-1) (Table 1).

Globally, it has been recognized that the presence of pharmaceuticals in aquatic systems is a growing problem due to the potential consequences that these chemicals can have on aquatic biota at the molecular and population levels (Almeida et al., 2020). In Antarctica, weather conditions and human activities create an environment in which the use of analgesics and anti-inflammatories is commonplace. For example, injuries are frequently reported, however, other issues such as dental problems or disturbances of gastrointestinal tract are also described (Bhatia et al., 2013; Ohno et al., 2018; Olalla et al., 2020), together with a restricted provision of pofesional health care (Olson 2002). As a consequence, there is a concomitant increase in the release of analgesics and anti-inflammatories during periods of high human activity. High concentrations for acetaminophen (48,744 ng l-1), diclofenac (15,087 ng l-1) and ibuprofen (10,053 ng l-1) were reported in effluents from Esperanza base (González-Alonso et al. 2017). The hazard quotient values for these pharmaceuticals were over 10 at several sampling points (Figure 5). The samples were collected during the austral summer of 2012 - 2013, and at that point this station only had a biological sewage treatment plant, according to the ATS report corresponding to the inspection period 2013 (ATS, 2013c). However, Esteban et al. (2016) indicated that the station did not have a wastewater treatment system at the time of collecting the samples (22 December 2012 and 8 February 2013). Similar concentrations were verified for acetaminophen (>60,000 ng l-1) in effluents without chemical or microbiological treatment in Ny-Ålesund (Choi et al., 2020). The authors indicated that the concentration of the investigated pollutants ranged from 4–280,000 ng l-1 in the effluent and 2–98 ng l-1 in the seawater. At sub-Arctic locations, Huber et al. (2016) confirmed in effluents the presence of diclofenac (597 ng l-1) at Torshavn, Faroe Islands, despite the presence of 2 and 3-step microbial sludge digestion and filtration. In general, the release of PPCPs is observed despite the implementation of treatment systems, with some of the concentrations reported in Antarctica being higher than those in highly urbanized areas. In this context, the efficiency of removal of WWTPs in the Antarctic region should be demonstrated, and consistency between all of the research stations with respect to the type of treatment used, needs to be implemented in order to reduce the presence and concentration of PPCPs in effluents, in particular in periods of intensive human activity.

7.4.3 Status and efficiency of WWTPs in the Antarctic

Globally, high removal efficiencies, upwards toward 99%, have been described for pharmaceuticals after the implementation of 2 and 3-step microbial sludge digestion and filtration (Huber et al., 2016). Up to 95% of acetaminophen and ibuprofen, for example are removed using a primary physicochemical treatment followed by a secondary biological treatment (Biel-Maeso et al., 2018). Similarly, up to 100%, 94% and 48% removal was shown to occur for ibuprofen, acetaminophen and diclofenac, respectively, using a primary and secondary wastewater treatment with activated sludge, followed by tertiary treatment (Čelić et al., 2019). Pereira et al. (2016) analyzed the effluents from Santos Bay, Sao Paulo, Brazil, reaching lower concentrations of 2094 ng l-1 for ibuprofen, 17.4-34.6 ng l-1 for acetaminophen and 19.4 ng l-1 for diclofenac, using mechanical treatment and chlorination. More homogeneous concentrations were recorded in the effluents of Matosinhos, Portugal, but they did not exceed 300 ng l-1, principally because primary and secondary treatment treated the effluent prior to discharge (Paíga et al., 2015). In contrast, 4-MBC has a low removal which does not exceed 28% through ozone and 8.2% through continuous microfiltration (Li et al., 2007). OP achieved 60% removal rates using a stacked constructed wetland, that featured vertical and horizontal flow as well as an assembled biofilter (Dai et al., 2017). BP-1 had a removal of 74 ± 22% in 33 WWTPs across Australia (O'Malley et al., 2020).

Wastewater treatment systems in Antarctica do not easily remove micropollutants since their design, similar to most municiple systems to remove principally nutrients and organic matter (CONMAP, 2014). For PPCPs, advanced and effective tertiary treatment processes such as sequential UV and ozonation process eliminate most PPCPs, an elimination that does not occur in primary, secondary or biologic treatment (Westerhoff et al., 2005; Sui et al., 2014; Wang & Wang, 2016; Patel et al., 2019). For example, when studying various effluents with different types of treatments, it was confirmed that the lower concentrations of drugs such as diclofenac were the result of the implementation of UV as tertiary treatment, even when the population was substantially larger, 15 times or more (McEneff et al., 2014). However, variations in the concentrations and distribution of pharmaceuticals and UV filters, both in the same geographical areas and in different ones, depend not only on the implementation of treatments, but also on population density, the different uses of PPCPs and the concentrations used (Huber et al., 2016; Emnet et al., 2020). For example, Emnet et al. (2015) reported a reduction did not occur for 4-MBC during January, the research season with the highest floating population, probably due to a high chemical load at that time. This agrees with the study of Astel et al. (2020), in which they verified a high detection of BP-1 during the summer, which may be related to seasonal tourism. In this way, it is observed that the UV filters are not completely removed during the treatments (Li et al., 2007), but rather that their removal is dependent upon their concentration in the effluent. In the six-months monitoring study of Emnet et al. (2015), concentrations of the detected analytes did not correlate with the number of staff on base present at the time of sampling, or with the operating temperature of the WWTP.

7.4.4 Additional factors influencing the concentration of PCPPs in effluents and coastal waters

PPCPs recorded by different authors in effluents and in coastal waters are highly variable in both chemical diversity and concentration. An argument explaining possible variations is the status and efficiency of the WWTPs in the Antarctic stations. However, additional factors such as geography and human activities may also contribute to the extent of the degree of contamination. Spatially, a pattern of higher concentrations of PPCPs is corroborated in samples such as ocean water, sea ice and sediments, from sites adjacent to WWTPs compared to samples obtained offshore in the Antarctica (Emnet et al., 2015; Vecchiato et al., 2017; Szopińska et al., 2022). The lower concentrations in ocean waters compared to that observed in effluents (Table 1) can be attributed to a dilution phenomenon, which increases towards the offshore, highlighting the important role of currents and water flows in the distribution of pollutants. This phenomenon has also been described in other regions such as Saronikos Gulf, Eastern Mediterranean Sea; Ebro Delta, Spain; Hong Kong and Japan (Alygizakis et al., 2016; Čelić et al., 2019; Tsui et al., 2019). In this sense, the distribution of PPCPs can be intensified in the coastal zone when the geography presents a closed or semi-enclosed coastal, with high concentrations PPCPs such as pharmaceuticals and UV filters compared to the open sea (Tsui et al., 2015; Biel-Maeso et al., 2018).

Temporarily, high discharge volumes, associated with a rise in the resident population at the field stations during the summer due to increased research activity and tourism generate an intensified discharge of PPCPs into the ecosystem (Emnet et al., 2015; Biel-Maeso et al., 2018; Astel et al., 2020; Emnet et al., 2020). According to data published by the CONMAP (2020) and the International Association of Antarctica Tour Operators (IAATO) (2020) the number of tourists is more than 14 times greater than that of the population occupying the stations. This rapid growth of tourism requires structural, institutional and legislative reforms, especially in the southwest coast of the Antarctic Peninsula, where disembarkation of passengers and marine traffic of tourists has been concentrated, compared to the low tourist activity carried out on the continent (Liggett et al., 2011; Bender et al., 2016; IAATO, 2018). It has been observed that for some PPCPs such as UV-filters, tourism is less important compared to personnel residing in the bases (Domínguez-Morueco et al., 2021), this because of the accumulation potential of the lipophilic substances in sediments and particulate material. In this sense, Emnet et al. (2015) reported increased concentrations of 4-MBC during research season with a significant increase in concentrations when they carried out daily sampling compared to monthly sampling. Emnet et al. (2015) highlighted that field studies conducted over long periods with low sampling frequencies may fail in assessing short-term fluctuations in concentrations of target analytes. This is due to the loads/flows of waste which are highly variable, and in temporal terms have been characterized by seasonal and even diurnal fluctuations (CONMAP, 2014). Additionally, during the colder months the efficiency of the treatment systems, which are temperature sensitive, requiring temperatures approaching 25°C, decreases leading to a possible increase of PPCPs in the effluent (Hedgespeth et al., 2012; CONMAP, 2014). Furthermore, it has been described that snow and ice act as a reservoir of PPCPs and that their subsequent melting generates pulses of pollutants in the Antarctic environment (CONMAP, 2014; Vecchiato et al., 2017). González-Alonso et al. (2017) observed the third highest total concentration of drugs, mainly ibuprofen in glacier drain water. The authors indicate that the occurrence of PPCPs in areas of low anthropogenic pressures may be related to sporadic research or touristic activities. In line with Emnet et a. (2015) who reported that the disposal of raw human waste and grey water from field research parties via tidal cracks in the sea ice may be a source of pollutants.

Along with the above mentioned factors, the extensive periods of darkness together with the low temperatures, reduce photodegradation such as biodegradation by bacteria and plankton, extending the persistence of these contaminants (Hedgespeth et al., 2012; Emnet et al., 2015). Also, certain PPCPs do not undergo transformation and can be transported over long distances, making difficult concentration predictions (Alygizakis et al., 2016). For example, BP-1 and OP has been recorded at Cape Evans, Antarctica, 25 km away from their source (Emnet et al., 2015). Biel-Maeso et al. (2018) demonstrated the presence of drugs up to 65 km offshore, indicating that some pharmaceuticals persist within the marine environment.

7.5 PPCPs in Antarctic biota and effects

7.5.1 Feeding strategies and bioaccumulation potential

In general, there is only a limited amount of information regarding the presence and effects of PPCPs on Antarctic organisms. Duarte et al. (2021) detected PPCPs in phytoplankton, the main component in the Antarctic food chain, at Deception Island, Antarctic Peninsula, which could have serious implications for the ecosystem. Emnet et al. (2015) studied the presence of PPCPs in organisms such as *Laternula elliptica* (King, 1832), *Sterichinus neumayeri* (Meissner, 1900) and *Trematomus bernachii* (Boulenger, 1902), mainly benthic marine organisms throughout Erebus Bay. Due to methodological limitations by matrix interferences, only some PPCPs could be quantified and detected within the organisms. Among these, OP was detected within the species *T. bernachii* with concentrations of up to 464 ng g-1 l.w. Furthermore, the authors reported the presence of OP in fish collected up to 25 km away, which may be possible due to the mobilization of contaminants through ocean currents or sources not considered.

At a global level, there are a number of published articles that use biota to study pharmaceuticals, UV filters and surfactants, with many of these studies focusing on marine bivalves, particularly the species *Mytilus galloprovincialis* (Lamarck, 1819). Mezzelani et al. (2016) conducted laboratory studies using an exposure dose of 25,000 ng l-1 for acetaminophen, diclofenac and ibuprofen, and a field research in Portonovo Bay, central Adriatic Sea. Diclofenac and ibuprofen were measured in mussels *M. Galloprovincialis*, both under laboratory conditions (diclofenac: 14.90 ± 7.89 ng g-1 and ibuprofen: 1.63 ± 1.00 ng g-1) and in Portonovo Bay (diclofenac: 16,11 ± 14,72 ng g-1 and ibuprofen: 9,39 ± 0,59 ng g-1) (Mezzelani et al., 2016). Acetaminophen, in the same study, was not identified in either the field or the laboratory. On the contrary, in *M. Galloprovincialis* from Granger Bay, Cape Town, Petrik et al. (2017) verified a degree of bioaccumulation of acetaminophen with concentrations approaching 9 ng l-1, in contrast to diclofenac which was identified in concentrations that were less than 2.5 ng l-1. However, after a 12-month monitoring of individuals of the species *M. galloprovincialis* and *M. edulis* (Linnaeus, 1758) on the coasts of Ireland, no bioaccumulation was recorded for diclofenac despite the presence of this drug in effluents (<3000 ng l-1) and sea water (<600 ng l-1) (McEneff et al., 2014). Levels in tissues were reported for OP in *M. galloprovincialis* with concentrations up to 10.5 ng g-1 d.w. en Thermaikos Gulf, Northern Aegean Sea, Greece (Arditsoglou & Voutsa, 2012). Xu et al. (2016) reported relatively low concentrations in Hong Kong seawaters (1.3-17.5 ng l-1), and an upward trend in sediments (15.8-37.9 ng g-1), addition to the bioaccumulation for species Chinese damsel (*Neopomacentrus bankieri* (Richardson, 1846)) (OP: 34.5-39.9 ng g-1), Chocolate hind (*Cephalopholis boenak* (Bloch, 1790)) (OP: 26.4-40.5 ng g-1), Brown goby (*Bathygobius fuscus* (Rüppell, 1830)) (OP: 84.2 ng g-1) and Green mussel (*Perna viridis* (Linnaeus, 1758)) (OP: 52.6-74.5 ng g-1). However, for its congener P. canaliculus (Gmelin, 1791) concentrations exceeded 2000 ng g-1 l.w. in Lyttelton Harbour, Christchurch, New Zealand (Emnet et al., 2020). BP-1 showed minimal concentrations in mussels *M. galloprovinciallis*, organisms with a slow rate of biotransformation because intake exceeds metabolism, or involve other metabolic pathways (Gómez-Regalado et al., 2021). 4-MBC bioaccumulated in the species *M. galloprovincialis* and the uptake of waterborne 4-MBC was very rapid, and after only 24 h of exposure to 1 µg L-1, the tissular concentrations were 418 ug kg-1 d.w. (Vidal-Liñán et al., 2018).

The Antarctic biota is subject to a heterogeneous habitat and to a stressful environment, including very cold temperatures, which structures the physiology, life history and biodiversity of the organisms living there (Peck et al., 2006; Block et al., 2009). Tests carried out by Freitas et al. (2019), using different temperatures (17°C and 21°C) and an exposure to 1 µg L-1 of triclosan and diclofenac in individuals of the species *M. galloprovincialis*, seems to indicate that the exposure time at a certain temperature would be relevant for the bioaccumulation of PPCPs. Dermal absorption should not be ruled out as it has been described as the main route of exposure to PPCPs in aquatic organisms (Ghosh et al. 2021). The dermal uptake of synthetic musks has been demonstrated, being the lipophilic substances the ones that have the highest absorption (Daughton 2007, Zhang et al. 2017). Additionally, the biology of the species is fundamental to the bioaccumulation of these pollutants. According to Block et al. (2009), antarctic organisms have developed a series of strategies to take advantage of resources during the austral summer through synchronization. For example, it has been described that the species *L. elliptica* hides its siphon under the sediment during the austral winter, with a reopening during the austral summer during the chlorophyll peak, a time when it also spawns (Brockington, 2001; Ahn et al., 2003). In this sense, species having seasonal feeding strategies would not be directly exposed during the winter months. Additionally, through the use of isotopes in sediments and biota in the vicinity of the McMurdo station, it was found that the species *L.elliptica*, did not have assimilate in proportion to its exposure to wastewater, probably due to their non-generalist diet (Conlan et al., 2006). In contrast to *L. elliptica*, the sea urchin *S. neumayeri*, a generalist feeder, showed an assimilation proportional to the input of wastewater in the benthos (Conlan et al., 2006). Low assimilation was observed for *T. bernachii* compared to other general consumers of benthos such as *S. neumayeri*, which may be due both to a low number of samples and to the analysis of a tissue different from that of the other species analyzed, since this species has a generalist diet (Conlan et al., 2006). Generally, feeding specialists exhibit lower concentrations of pollutants compared with generalist species (McLeod et al., 2014; Pinzone et al., 2019; de Mesquita et al., 2021).

7.6 Exposure and effects on biota

Regarding the risks of PPCPs, Olalla et al. (2020) determined that the analgesics/anti-inflammatories acetaminophen, ibuprofen and diclofenac present the highest environmental risks to the Antarctic Peninsula, as these substances exceeded the threshold considered to be “high risk” by up to 100-fold at wastewater discharge. Also, Tsui et al. (2015) suggested that UV filters pose higher potential risks to benthic communities during periods with stronger UV radiation when usage is higher (Tsui et al., 2015). The combined effect of mixtures of UV filters in sunscreens agents is so far largely unknown (Domínguez-Morueco et al., 2021). Domínguez-Morueco et al. (2021) and Olalla et al. (2020) did not observe environmental risk for UV filters, but given their possible oestrogenicity and their capacity for accumulation, they should be monitored continuously given their widespread use in Antarctica. Due to the paucity of information available, the eventual effects and risks of unmonitored PPCPs in the Antarctic ecosystem are unknown. This is alarming as the predominant source of PPCPs is direct discharge into the sea. Compared to terrestrial and intertidal antarctic systems, this habitat has been described as having great richness and diversity, reaching more than 8100 species, and some phyla represented at levels greater than global averages (Peck et al., 2006, De Broyer & Danis, 2011). Given this scenario, the number of new species recently described (López-González, 2020; Pinheiro, 2020; Buskowiak & Janussen, 2021; Maggioni et al., 2022) makes the impacts of PPCPs even more uncertain. This is particularly true for benthic fauna, described by De Broyer & Danis (2011), accounting for 88% of the total species. In addition, there is an information bias in this taxonomic group, because according to Griffiths et al. (2010) the monitoring is carried out on the platform, to the detriment of the knowledge of the deep-sea marine fauna. The combination of very poor functional scopes, with slow rates of adaptation and restricted available dispersal ranges make antarctic marine species among the most susceptible to environmental change (Peck et al., 2004).

Most Antarctic biotas are exposed to multiple stresses and considered vulnerable to environmental change due to narrow tolerance ranges, rapid change, projected circumpolar impacts, low potential for timely genetic adaptation, and migration barriers (Gutt et al. 2021). In gastropods of the species *Phorcus lineatus* (da Costa, 1778), chronically exposed to acetaminophen, significant increased the catalase and cholinesterase activities, thus, extrapolation of this results to phylogenetically close species may account for similar endpoints (Almeida & Nunes, 2019). Duarte et al. (2021) indicate that the diversity and concentrations of PPCPs in the Antarctica may lead to strong preasures on the marine food web with severe consequences for the whole ecosystem trophic structure. Impacts of climate change on antarctic biodiversity will likely vary for different communities and depend on species range (Rogers et al., 2020). Coastal communities and those of sub-Antarctic islands, especially range-restricted endemic communities, will likely suffer the greatest negative consequences of climate change (Rogers et al., 2020). The climate of the Western Antarctic Peninsula is the most rapidly changing in the Southern Hemisphere, with a rise in atmospheric temperature of nearly 3°C since 1951 (Meredith & King, 2005). Marine species in this region have extreme sensitivities to their environment, with population and species removal predicted in response to very small increases in ocean temperature (Meredith & King, 2005). In addition, this region has an important breeding and nursery ground for Antarctic krill is stablished, a key species in the Southern Ocean food web, highly susceptible to environmental changes modifying its abundance, distribution and life cycle (Meredith & King, 2005; Flores et al., 2012). Due to the influence of climate change and intense industrial fishing, this region is a priority area for Marine protected areas (MPAs), as paer the Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR) (Sylvester & Brooks, 2020). However, some CCAMLR members make it difficult to approve MPAs, so political and economic interests cast a shadow on international negotiations about adaptation strategies such as fisheries closure and the establishment of MPAs (Wendebourg, 2020; Teschke et al., 2021). Despite the above, Antarctica is not only facing these pressures, but also the Southern Ocean waters are among the most vulnerable to ocean acidification (Hancock et al., 2020). In ecological terms, Duffy et al. (2017) have been described that the Antarctic Peninsula and the islands of the Southern Ocean could have less effective barriers for the establishment of non-native species. If predicted warming occurs in the shallows around the Antarctic Peninsula region, native marine species may change in geographic and bathymetric range and/or become less competitive within parts of these ranges, facilitating the establishment and spread of any non-native species (Hughes et al. 2020).

7.7 Conclusions

The human population that has settled in Antarctica has contributed to the occurrence of widespread pollutants such as PPCPs, and the pattern of concentration of these compounds dependent upon whether each base is permanently or intermittently populated. In this way, wastewater management plays a key role in the eventual PPCPs loads in coastal marine waters and the exposure of organisms that live therein. In general, the concentrations of PPCPs in this environment, seem to be more influenced by the implementation or absence of wastewater treatment and the quality of the treatment, and less influenced by the annual number of people permanent living there. Although there are diffuse sources such as pulses of pollutants from melting ice, the highest concentrations of PPCPs were reported in point sources from the effluents, which shows a phenomenon similar to that described in other regions of the planet. The highest concentrations were reached for pharmaceuticals at the Esperanza base, which lacks treatment for its wastewater during field sampling. On the other hand, the implementation of treatment systems appears to be inefficient, since UV filters and surfactants were verified in Scott base probably due to the low removal efficiency and high persistence of these PPCPs. This is important considering that most of the stations are located in the coastal zone, being able to release their effluents without treatment directly at sea. Therefore, treatment systems, capable of withstanding fluctuations in the number of personnel, should be considered in the absence of appropriate legal regulations for wastewater discharge in the requirements of the Environmental Protocol to the Antarctic Treaty. The increasing of tourism in the region should be also evaluated in order to identify how anthropogenic pressure in the region contribute to temporal and spatial concentrations of PPCPs.

Information regarding wastewater treatment systems tend to be inaccessible, but where it exists, it is fragmented, scarce and in some cases outdated. This leads to a partial and unrealistic view of the risk to which the continent is subjected. Furthermore, information bias was verified due to the lack of studies in some groups of PPCPs. In this unfavorable scenario, the scarcity of studies of PPCPs in Antarctica can generate an underestimation of the concentrations, which could be even higher than those reported, to the detriment of an adequate understanding of the distribution and effects on the coastal aquatic ecosystems of Antarctica. Further, biota has been poorly studied, therefore, the possible bioaccumulation and effects are unknown, especially in benthic organisms surrounding effluents. It is suggested the implementation of a control of the PPCPs that enter the continent during the entry of people both by national and tourist operators, due the difficulties of the functioning of the treatment systems and the low removal of some types of treatment. This is particularly true for bases that do not have a treatment system. It is recommended to carry out research efforts in areas intervened by human activity with the presence of protected areas to generate mitigation measures to the possible impacts not currently studied.

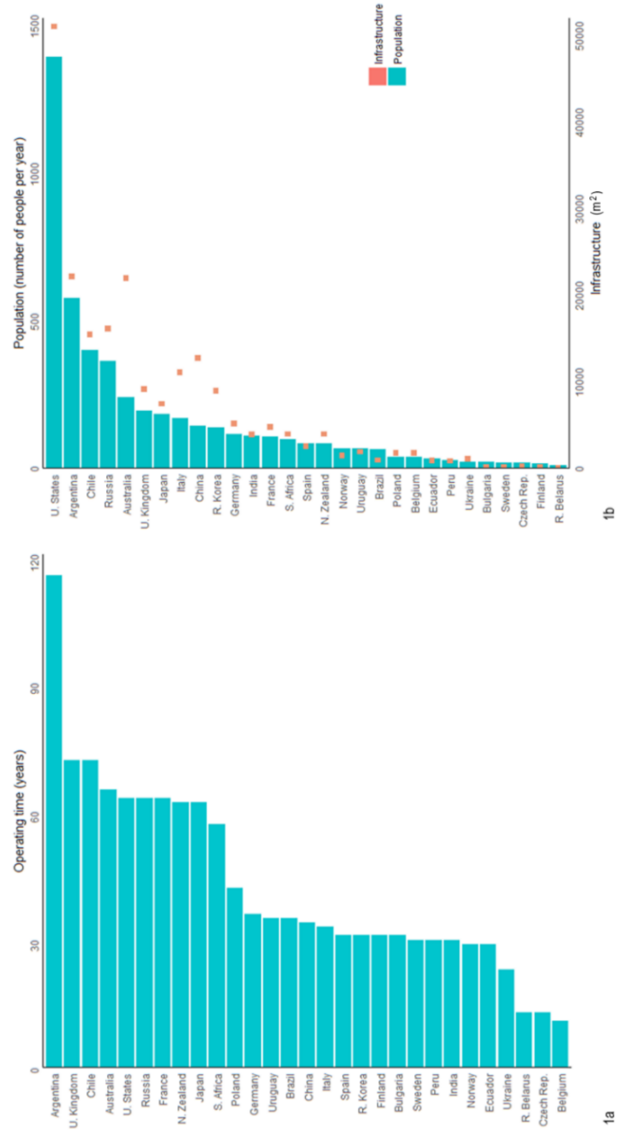

Figure 1. Operation time and population by country in the Antarctic continent.

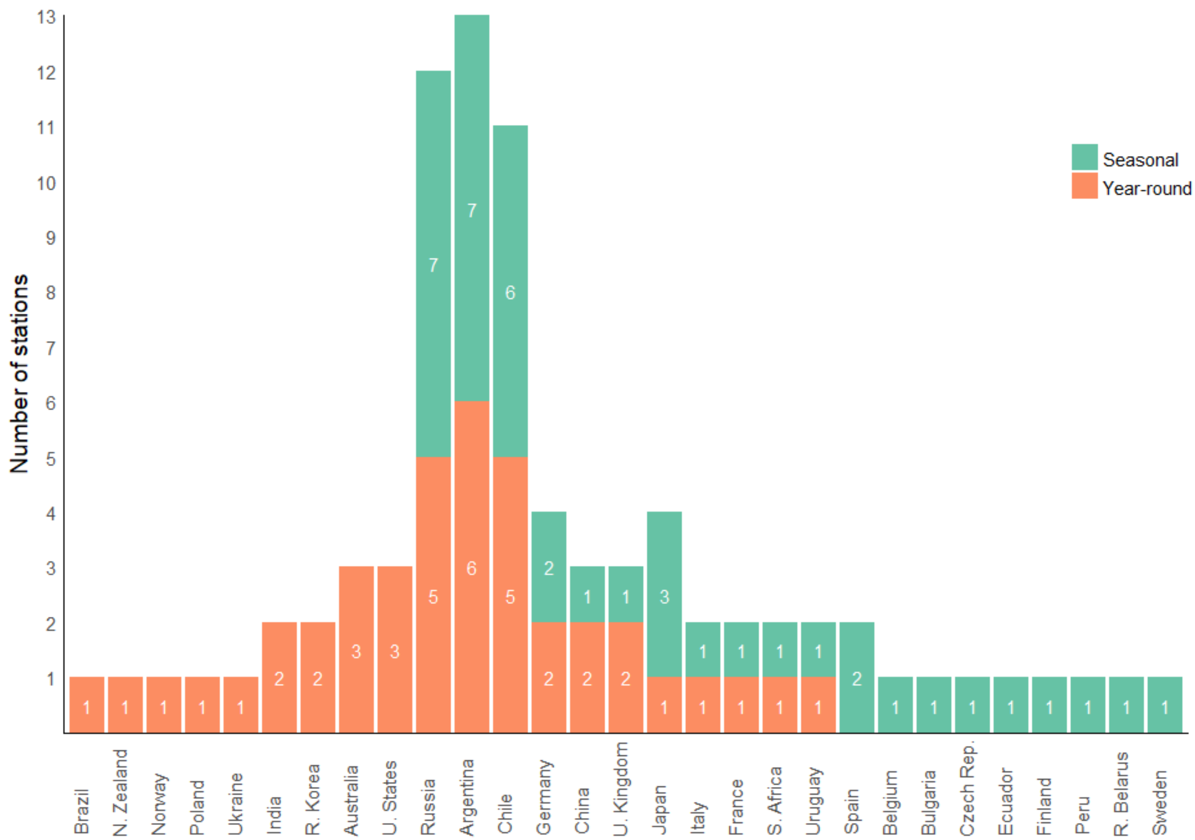

Figure 2. Number and seasonality of stations by country in the Antarctic continent.

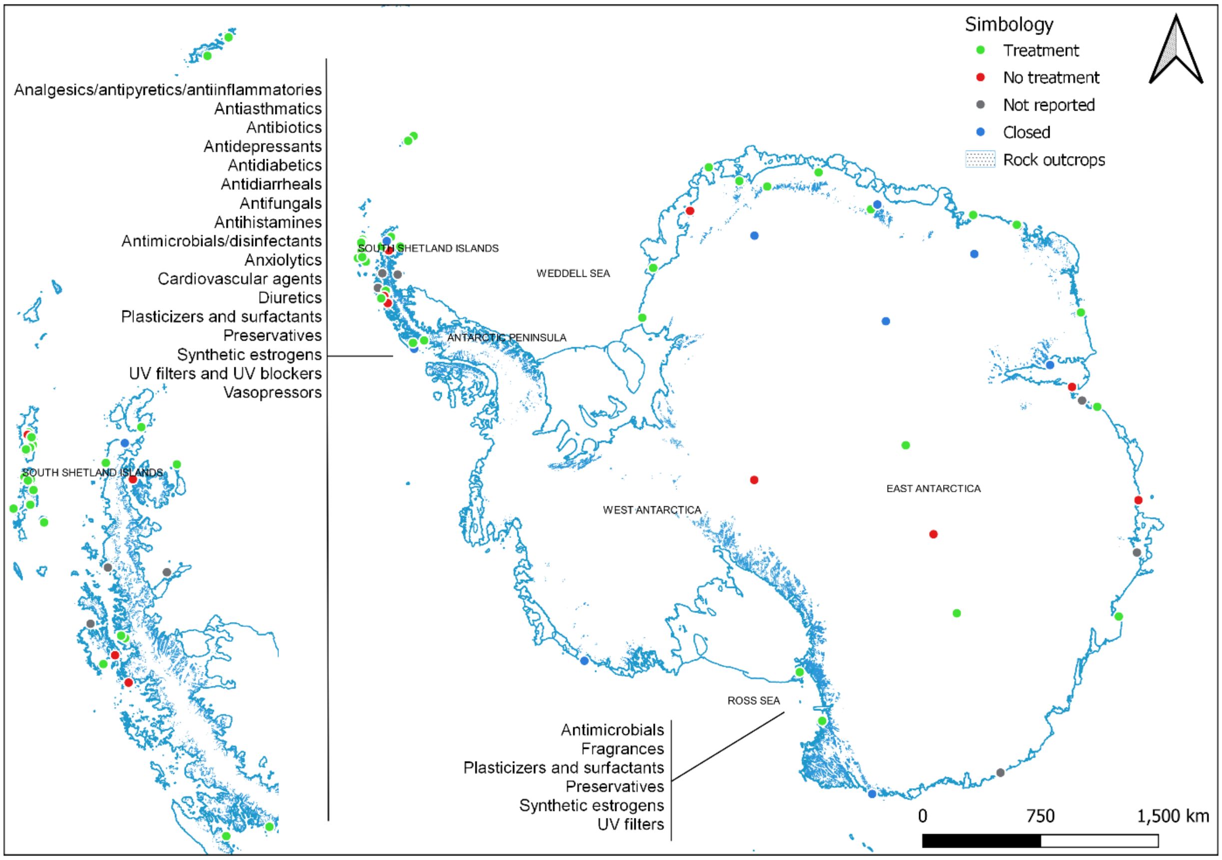

Figure 3. Status of the treatment system in the Antarctic bases and PPCPs reported in coastal aquatic systems.

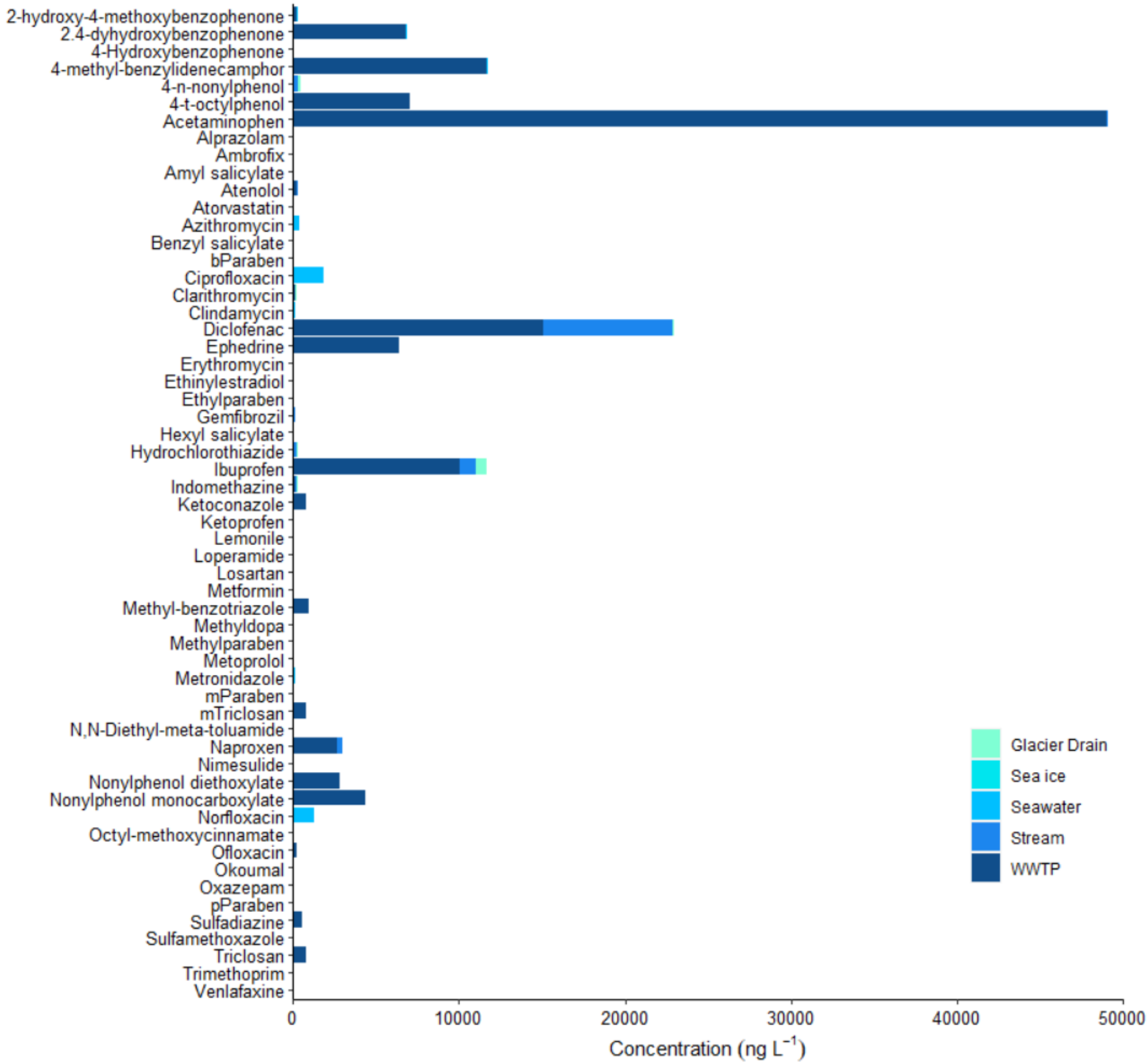

Figure 4. Pharmaceuticals and Personal Care Products (PPCPs) reported in Antarctic WWTP effluents and water matrices.

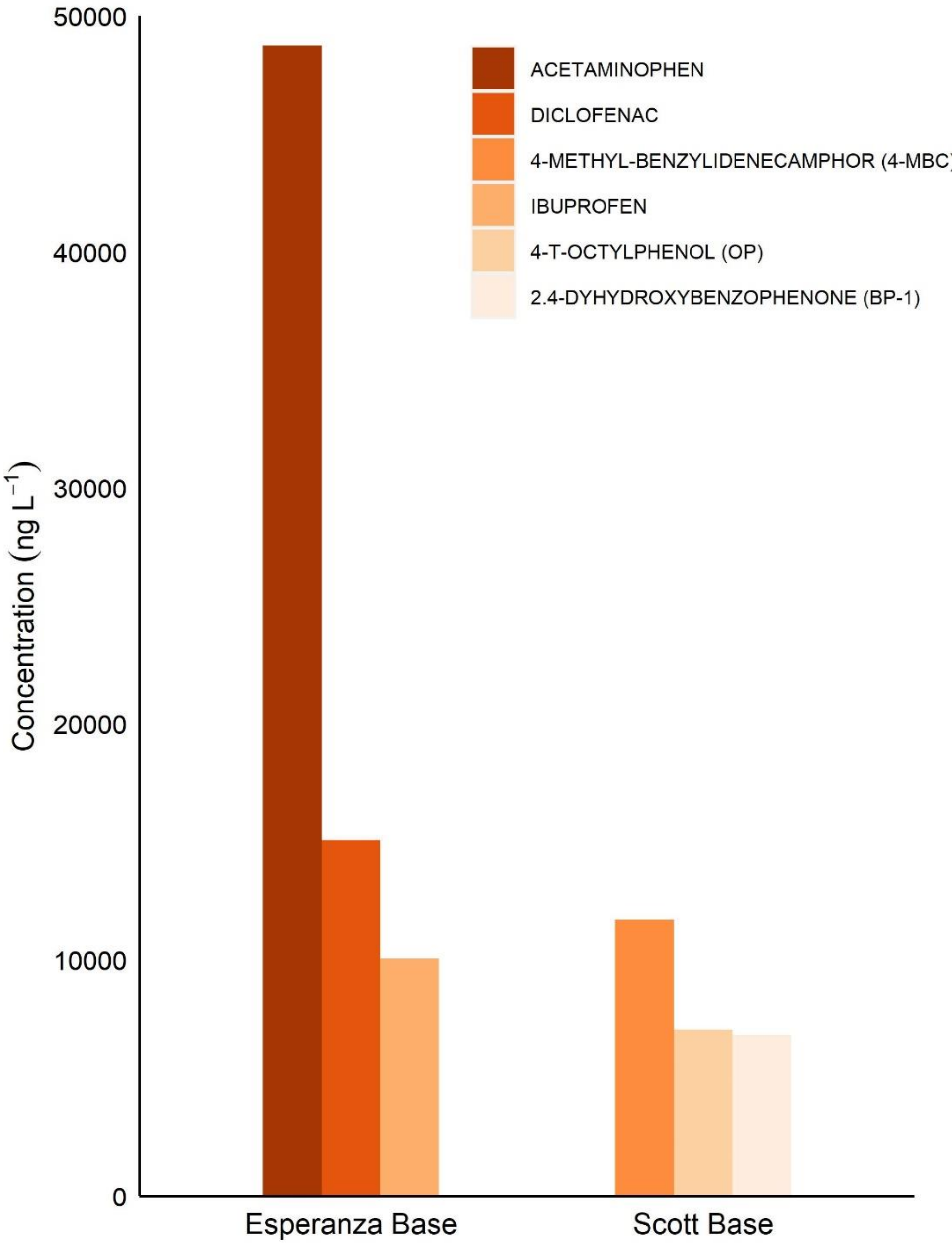

Figure 5. Maximum levels of pharmaceuticals and Personal Care Products (PPCPs) reported in effluents of Esperanza and Scott bases.

ANALYTE	CAS NUMBER	MOLECULAR FORMULA	AVERAGE MASS (Da)	LogKow	LogKoc	Level III Fugacity Model. Half-Life (hr)	MATRIX	SAMPLING DATE	ANALYTICAL TECHNIQUE	LOCATION	CONCENTRATION (ng/l)
ACETAMINOPHEN	103-90-2	$C_8H_9NO_2$	151.16	0.27	1.790	360	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	48744[c]
DICLOFENAC	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	4.02	2.921	900	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	15087[c]
IBUPROFEN	15687-27-1	$C_{13}H_{18}O_2$	206.28	3.79	2.596	360	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	10053[c]
4-MBC	36861-47-9	$C_{18}H_{22}O$	254.37	5.92	4.087	1.44e+003	effluent	2009	GC–MS	Scott Base.	173 – 217[a]
								2009	GC–MS	McMurdo.	ND[a]
								2012	GC–MS	Scott Base (seven-day monitoring).	3250 – 11700[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	321 – 785[a]
										Scott Base (monthly with ozone).	976 – 2020[a]
								2012-2013		Esperanza Base, Hope Bay.	<LOQ[d]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	42.7 – 47.5[a]
										Winter Quarters Bay, Erebus Bay.	ND[a]
										Scott Base.	ND[a]
										Cape Evans, Erebus Bay.	ND[a]
							Sea ice	2012	GC–MS	Erebus Bay.	<34.3[a]
BP-1	131-56-6	$C_{13}H_{10}O_3$	214.22	2.96	3.460	360	Effluent	2009	GC–MS	Scott Base.	143 – 171[a]
									GC–MS	McMurdo.	7.2 - 7.3[a]
								2012	GC–MS	Scott Base (seven-day monitoring).	265 - 6830[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	47.1 - 461[a]
										Scott Base (monthly with ozone).	24.3 - 124[a]
								2012-2013		Esperanza Base, Hope Bay.	1400[d]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	6.3 – 10.3[a]
										Winter Quarters Bay, Erebus Bay.	Nd[a]
										Scott Base.	1.3 – 2.6[a]
										Cape Evans, Erebus Bay.	ND[a]
							Sea ice	2012	GC–MS	Erebus Bay.	ND[a]
OP	140-66-9	$C_{14}H_{22}O$	206.32	5.28	4.189	900	Effluent	2009	GC–MS	Scott Base.	101 – 118[a]
								2009	GC–MS	McMurdo.	ND[a]

								2012	GC–MS	Scott Base (seven-day monitoring).	929 - 7050[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	27.1 - 4070[a]
										Scott Base (monthly with ozone).	7.5 – 39.0[a]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	1.6 – 1.7[a]
										Winter Quarters Bay, Erebus Bay.	0.3 – 1.5[a]
										Scott Base.	<1.8[a]
										Cape Evans, Erebus Bay.	0.3 – 0.5[a]
							Sea ice	2012	GC–MS	Erebus Bay.	0.5 - 0.9[a]
							WWD	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	1.13[b]

Table 1. Analgesics and anti-inflammatories, UV-filters reported and Plasticizers and surfactants reported in the Antarctic continent (a = Emnet et al. 2015; b = Esteban et al.2016; c = González-Alonso et al. 2017; d= Domínguez-Morueco et al. 2021).

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VIII. Discusión

Este trabajo de tesis reveló el estado actual de los contaminantes emergentes en sistemas costeros de la Antártica mediante la cuantificación y caracterización de la contaminación por MPs en suelos y sedimentos intermareales de bahía Fildes. Adicionalmente, se realizó una revisión de los PPCPs actualmente descritos en la Antártica, de modo que para ambos grupos de contaminantes fueron identificadas sus principales fuentes, concentraciones, distribución y eventuales efectos en la biota antártica.

A nivel global, altas concentraciones de MPs y PPCPs han sido vinculadas a zonas con alta densidad humana (Li et al. 2018, Mbedzi et al. 2020, Adeleye et al. 2022). En términos comparativos, la Antártica posee una densidad de población muy inferior al resto del mundo (United Nations 2019), con estaciones que poseen un bajo número de residentes, salvo excepciones como la estación McMurdo. Además, el Protocolo Ambiental ha designado a la Antártica como reserva natural, dedicada a la paz y la ciencia (ATS 1991c), por lo que está exento del nivel de actividades que se desarrollan en otros continentes como la industrialización, ganadería, agricultura, etc. A pesar de lo anterior, en la Antártica se observa el mismo patrón descrito globalmente, identificándose una mayor abundancia de MPs y PPCPs en zonas costeras en comparación a muestras extraídas mar adentro (Reed et al. 2018). Esto ha sido verificado exclusivamente en agua de mar y sedimentos marinos, ya que a la fecha la información acerca de estos contaminantes en sistemas terrestres era inexistente para MPs, y lo continúa siendo para PPCPs. En consecuencia, estas limitaciones complejizan la comprensión acerca de sus fuentes terrestres y sumideros en el ecosistema, en desmedro de una adecuada gestión. Ante la acotada información de MPs, es especialmente preocupante la falta de esfuerzos de investigación en las zonas terrestres, ya que ha sido descrito que cerca de un 80% de los hallazgos en ambientes acuáticos provienen de estas zonas (Li et al. 2016). Esto alcanza mayor relevancia debido a las altas abundancias de MPs reportadas por este trabajo en los suelos (1–37 partículas/50 ml suelo) en comparación a los sedimentos intermareales de bahía Fildes (1–4 partículas/50 ml suelo). Esto demostró que las abundancias de microplásticos en el ecosistema antártico podrían estar siendo subestimadas al no considerar otras matrices. En este sentido, se rechazó la hipótesis 1, ya que los suelos aledaños a las bases no presentaron mayores abundancias de microplásticos en comparación a suelos distantes de las bases. Esto debido a que la mayor abundancia fue reportada en el sitio IS5, el más alejado de las bases y el más cercano a la bahía. Además, se observó que las fuentes de contaminación por microplásticos en suelos están influenciadas por las actividades locales, ya que estuvieron dominadas por fragmentos de resina fenoxi de un color naranja brillante, idénticos a los observados en las instalaciones adyacentes pertenecientes a la base chilena Frei. En la otra matriz analizada, se confirmó la hipótesis 2, ya que los sedimentos intermareales cercanos al efluente de la base Frei (sitios IS1 e IS2) presentaron una mayor abundancia en comparación a los sedimentos más distantes del efluente. Estas abundancias fueron similares a las reportadas en sedimentos intermareales en North Cove, Isla Adelaide en la Península Antártica (Reed et al. 2018). Además, se confirmó la presencia de fibras de algodón en estos dos sitios, lo que permite corroborar su procedencia desde las aguas grises de la base, junto a la identificación de fibras de PET, material ampliamente utilizado en la fabricación de vestimenta para climas fríos (Gonzalez et al. 1998, Das & Gersak 2014, Gnanauthayan et al. 2017). En general, estos hallazgos van en consonancia con lo reportado globalmente, siendo las fibras predominantes en sedimentos intermareales y poco profundos, cuyo polímero más abundante ha sido PET (Woodall et al. 2014, Naji et al. 2017, Morais et al. 2020). Es relevante el hallazgo de microplásticos en la zona protegida de Isla Ardley, lo que implica que la distribución de estos contaminantes se ha ampliado a zonas que tienen grandes restricciones en los protocolos de ingreso debido a su valor biológico. A pesar de lo anterior, son numerosos los vertederos en la Isla y el Protocolo ha reconocido la falta de datos en plásticos para tomar decisiones y reducirlo (Peter et al. 2013, ATS 2019).

En contraste, el uso y consiguiente eliminación de los PPCPs en la Antártica está restringido a la red de alcantarillado debido a las restricciones de actividades impuestas por el Tratado Antártico, diferenciándose de otras regiones en las que su presencia se atribuye a diversas fuentes como por ejemplo la actividad agrícola debido a la reutilización de aguas residuales para riego (Xu et al. 2009, Karnjanapiboonwong et al. 2011). Por ende, la principal fuente de PPCPs en este continente son los efluentes y, en consecuencia, las fuentes terrestres podrían ser menos relevantes para estos contaminantes en comparación a los microplásticos. Tanto en bases permanentes como estacionales, una variable importante que modifica la composición de los efluentes de aguas residuales es el número de ocupantes (Stark et al. 2015). Sin embargo, altas concentraciones fueron informadas en base Esperanza, cuyo tratamiento de sus aguas residuales se encontraba fuera de operación, alcanzando altas concentraciones para el acetaminofén, diclofenaco e ibuprofeno. Esto contrasta con la base de mayor ocupación en territorio antártico, McMurdo, cuyas concentraciones en efluentes fueron bajas para PPCPs como BP-1 e incluso no detectadas para 4-MBC y OP, en comparación a los valores reportados en base Scott cuya ocupación es muy inferior. Esto indicaría que las concentraciones de contaminantes parecen estar más influenciadas por el tipo de sistema de tratamiento implementado que por el número de ocupantes. Esto permite confirmar la hipótesis 3, dado que bases situadas en zonas costeras que no cuentan con un sistema de tratamiento de aguas residuales, como la base Esperanza, generó altas concentraciones de PPCPs en el agua de mar donde liberan sus efluentes en comparación a bases con sistemas de tratamiento operativos como McMurdo o base Scott. Si bien, Emnet et al. (2015) describieron un aumento en las concentraciones del filtro solar 4-MBC en un periodo de mayor ocupación en la base Scott durante el verano, esto también podría responder a la baja remoción de los filtros solares informada como inferior al 30% (Li et al. 2007). En este contexto existen limitaciones en las eficiencias de los tratamientos, por ejemplo, estudios efectuados en Finlandia indicaron que el proceso de sedimentación del tratamiento primario libera en promedio 14 fibras y 290 partículas por litro de agua residual (Talvitie et al. 2015). Una situación similar ha sido descrita para PPCPs como el etinilestradiol en sistemas de tratamiento de aguas residuales de Kuwait, los cuales sólo eliminan el 79% de esta hormona (Saeed et al. 2017). En fármacos se ha verificado su persistencia, generando balances de masa negativos de algunos productos y metabolitos dentro del sistema, sugiriendo una posible retransformación (Archer et al. 2017). La remoción incompleta de microplásticos y PPCPs es preocupante dado el complejo escenario para un adecuado funcionamiento de los tratamientos, sumándose a la ya existente carga proveniente de las bases que no tratan sus efluentes. En términos temporales, considerando la larga data de algunas estaciones, estas podrían representar una ocurrencia crónica no sólo de PPCPs en el ambiente, sino también de MPs, acentuándose en bases cuya operación es permanente, ya que en total albergan a más del 80% de la población anual. Esto implicará que la cantidad de actividades realizadas tanto al interior de las bases como alrededor de ellas será relevante en la individualización de las fuentes de estos contaminantes.

En sistemas terrestres, ha sido descrito que los plásticos son persistentes, pueden acumularse y afectar a la biodiversidad (Rillig 2012). Es así como algunas especies de bacterias han proliferado en microplásticos, además la fauna puede consumir estas partículas, incluso con efectos letales (Büks et al. 2020, Habib et al. 2020). Lamentablemente, se desconoce el comportamiento de los microplásticos en los sistemas terrestres antárticos. En cambio, en sistemas acuáticos costeros se ha observado que ciertas especies efectúan una fragmentación digestiva de estas partículas a tamaños menores, es decir, nanoplásticos, como ya ha sido reportado en el krill antártico por Dawson et al. (2018). En ambientes marinos de la Tierra Victoria, Antártica, Sfriso et al. (2020) recolectaron invertebrados bentónicos, informando que las especies contenían entre 0,01 y 3,29 ítems/mg, y que los bivalvos y gasterópodos mostraron la mayor contaminación por microplásticos. A pesar de estos hallazgos, no se detectó una acumulación evidente a través de la red alimentaria. No obstante, esto no debe ser descartado en otras especies, ya que en organismos bentónicos filtradores de la especie *Mytilus edulis* (Linnaeus, 1798) se ha reportado que la exposición a pellets de polietileno (HDPE) produce su acumulación en branquias, estómago y glándula digestiva (von Moos et al. 2012) y que existe una transferencia de estas microesferas de poliestireno de 0,5 µm a su depredador, el cangrejo *Carcinus maenas* (Linnaeus, 1758) en el cual se observó su presencia en hemolinfa, estómago, hepatopáncreas, ovarios y branquias (Farrell & Nelson 2013). En zooplancton recolectado en el Mar Báltico, se observó la ingestión de perlas de poliestireno de 1,7-30,6 µm (Cole et al. 2013), evidenciándose un potencial de transferencia de estas microesferas fluorescente de 10 µm, desde organismos planctónicos desde un nivel trófico inferior (mesozooplancton) a un nivel superior (macrozooplancton) (Setälä et al. 2014). Respecto a las características de estos contaminantes, estos tienen un potencial para adsorber contaminantes hidrofóbicos en su superficie como metales, bifenilos policlorados (PCB) e hidrocarburos aromáticos policíclicos (HAP) (Moore 2008, Ashton et al. 2010, Rochman et al. 2013b). Paralelamente, la mezcla de monómeros y aditivos que componen a los plásticos pueden lixiviar al océano constituyendo una fuente de sustancias tóxicas persistentes y bioacumulativas, entre las que se encuentran los ftalatos de PVC, nonilfenol, retardantes de llama bromados y bisfenol A (Engler 2012, GESAMP 2016). Entre las consecuencias de la ingestión y transferencia de microplásticos se describen la disminución de reservas de energía hasta en un 50%, lo cual podría explicarse tanto en una disminución de la alimentación como en mayores tiempos de residencia intestinal e inflamación en gusanos marinos expuestos a sedimentos enriquecidos con cloruro de polivinilo no plastificado (Wright et al. 2013). Para los PPCPs, sólo ha podido ser analizado el surfactante OP en una especie de ictiofauna marina, siendo detectado incluso a 25 km de distancia de los efluentes (Emnet et al. 2015). No obstante, en otras regiones se ha reportado que PPCPs de baja lipofilicidad como el tetrazepam y diazepam son capaces de bioconcentrarse en bivalvos de la especie *M. galloprovincialis* (Lamark, 1819), junto a otras sustancias como el nonilfenol y octilfenol (Arditsoglou & Voutsa 2012, Gomez et al. 2012).

Los organismos antárticos hasta hace poco tiempo estaban sujetos a escasas influencias antropogénicas y probablemente se encuentran entre los organismos más vulnerables al estrés acumulativo causado por contaminantes y cambios en las condiciones climáticas y ambientales (Rota et al. 2022). Simultáneamente estas perturbaciones presionan el ecosistema antártico en un escenario de carencia de información acerca de los procesos que ocurrirán respecto a la circulación del Océano Austral y el hielo marino, y su influencia en el clima global (IPCC 2019). La falta de conocimiento también abarca las estimaciones y tendencias demográficas de su biodiversidad, incluidas especies clave como el krill antártico, aves marinas y focas, lo que desencadena una comprensión insuficiente de la dinámica del ecosistema antártico ante estos eventos (Chown & Brooks 2019, IPCC 2019). Aún frente a esta información limitada, las observaciones, modelamiento y las evaluaciones globales ya han descrito cambios significativos en los sistemas vivos y físicos de la Antártica, tanto marinos como terrestres (Chown et al. 2022). De este modo, el hallazgo de este tipo de contaminantes en la base de la red alimentaria con características únicas en la tierra donde los organismos suelen tener un desarrollo y un recambio generativo más lentos, y una tolerancia a la temperatura muy estrecha, puede tener graves implicaciones para toda la estructura trófica del ecosistema (Duarte et al. 2021). Chown et al. (2022) indicaron que a raíz del cambio climático es aconsejable seleccionar qué especies son las más vulnerables del ecosistema antártico debido a las altas probabilidades de extinción. Adicionalmente a esta consideración, se sugiere identificar cuáles de estas especies con alto riesgo de extinción son más propensas a la exposición a MPs y PPCPs tanto debido al consumo en la dieta como al uso de hábitat. Esto debería analizarse considerando las historias de vidas de las especies afectadas. Además, se sugiere realizar monitoreos de los niveles base de contaminación en el ecosistema considerando zonas de alta presencia humana para identificar sus fuentes y concentraciones, especialmente en fuentes ya confirmadas como los efluentes, pero con una investigación más detallada como el análisis de los efluentes antes de su eliminación por el emisario.

Son diversos los factores implicados en el actual estado de contaminación por MPs y PPCPs en la Antártica. La implementación de tecnologías avanzadas como los tratamientos de ozono, han arrojado altas concentraciones para filtros solares y surfactantes como el OP, alcanzando altas concentraciones de 4-MBC en contraste a los resultados no detectados por Domínguez-Morueco et al. (2021). Sin embargo, estos valores fueron obtenidos con un mayor esfuerzo de muestreo diario, lo que demuestra que el diseño de muestreo genera resultados altamente variables. En relación a los métodos de colección de muestras tampoco se ha llegado a un consenso, lo mismo sucede con la extracción de contaminantes en los ensayos de laboratorio, lo que implica que las comparaciones sean aún más difíciles ante la escasa información. Ante los hechos, el Protocolo Ambiental ha sugerido ciertas medidas preventivas, entre las que se ha incluido la limitación del uso de ciertos productos que contienen microplásticos tales como exfoliantes, etc. (ATS 2019), no obstante, a la fecha no se han incorporado sugerencias para PPCPs. Tampoco se han dilucidado las variables físico-químicas más importantes respecto a la contaminación, por lo que aún resta mayor claridad para una adecuado monitoreo y gestión.

Si bien el Protocolo Ambiental recientemente ha promovido el uso de productos sin MPs, estas medidas deberían ser fiscalizadas por los operadores nacionales para lograr resultados realmente efectivos. Se sugiere el control de ingreso y uso de estos contaminantes emergentes en la Antártica, medida a corto plazo que podría compensar las deficiencias ya existentes. Localmente, la instauración de áreas protegidas es una medida que limita el ingreso de estos contaminantes de forma indirecta debido al control de ingreso exclusivo para fines de investigación. Estas medidas pueden disminuir la carga contaminante del área protegida, sin embargo, debe ser una medida inicial a la espera de medidas más rigurosas de las fuentes y usos de estos contaminantes en territorio antártico. Además, cuando hay un mal manejo de la basura dentro del área protegida o en áreas vecinas no protegidas, estas medidas no logran su objetivo, tal como sucede en diversas áreas protegidas del mundo que hoy se han impactado por la contaminación (Kutralam-Muniasamy et al. 2021, Baroth et al. 2022). Esta medida debería ser empleada encarecidamente en aquellas estaciones donde los sistemas de tratamiento han demostrado una baja eficiencia debido a problemas de operación. Si bien, algunos de estos PPCPs son imprescindibles en la Antártica como lo son los filtros solares, medidas inmediatas como el mejoramiento de los sistemas de tratamiento ya existentes podrán contribuir en la contención del problema. Se ha observado que sistemas híbridos de MBR junto con la oxidación UV, el carbón activado y el ultrasonido, y la ozonización seguida de ultrasonidos, degradan por completo algunos contaminantes emergentes y muchos productos farmacéuticos (Dhangar & Kumar 2020). De forma complementaria a las tecnologías tradicionales, se ha empleado el uso de organismos o parte de sus estructuras, demostrando ser eficiente en la remoción de PPCPs. Un monitoreo de dos años en aguas residuales empleando un filtro de vegetación de álamo incluyó el análisis de analgésicos, bloqueador β-adrenérgicos, estimulantes, anticonvulsivos, antidepresivos, antiinflamatorios, antibióticos y metabolitos analgésicos y estimulantes, demostrando una eficiencia de eliminación superior al 90% (Martínez-Hernández et al. 2018). Así mismo, el uso de la microalga *Chlorella sorokiniana* condujo a una eliminación del 60% al 100% de diclofenaco, ibuprofeno, paracetamol y metoprolol (de Wilt et al. 2016). Ante estas ventajas, se recomienda el análisis de organismos endémicos del continente Antártico para evaluar su eficiencia en los sistemas de tratamiento locales. En comparación a los PPCPs, los estudios de remoción de MPs es limitada (Cristaldi et al. 2020, Hube & Wu 2021). En una investigación en la cual se compararon las tasas de eliminación de MPs en aguas residuales obtenidas en Rusia, Suecia, Francia, Finlandia, EE. UU., Reino Unido, Países Bajos, Alemania, Canadá, Australia, Italia, Turquía, Dinamarca, Polonia, China y Corea del Sur, se demostró que plantas de tratamiento con sistemas secundarios y terciarios eliminaron una media del 88% y el 94% de los MPs, respectivamente (Iyare et al. 2020). Paralelamente, la inspección de las bases en búsqueda de fuentes de microplásticos terrestres sería recomendable para detener su dispersión y eventual impacto en el ambiente. Estas medidas deberían ser adaptadas en todas las bases costeras, ya que actualmente se están edificando nuevas instalaciones y se prevé un aumento tanto de los residentes permanentes como de los turistas, hechos que ocurrirán en paralelo al ya creciente mercado de los MPs y PPCPs.

IX. Conclusiones

Esta tesis ha contribuido al estado del conocimiento de la contaminación por Microplásticos y Productos farmacéuticos y de cuidado personal en los ecosistemas costeros del Continente Antártico, brindando información que permite una mejor comprensión de las tasas y efectos de estos contaminantes y las eventuales implicancias en la biota antártica. Los capítulos que abordaron los objetivos han permitido obtener las siguientes conclusiones:

Capítulo 1

Hipótesis 1: Suelos aledaños a las bases presentarán mayores abundancias de microplásticos en comparación a suelos distantes de las bases.

Hipótesis 2: Sedimentos intermareales cercanos al efluente de base Frei presentarán mayores abundancias de microplásticos en comparación a sedimentos intermareales distantes del efluente.

1. Una alta ocurrencia de microplásticos se presentó en suelos en comparación a sedimentos marinos de Bahía Fildes, Antártica.
2. Altas abundancias de fragmentos de resina fenoxi en suelos en cercanías a las estaciones, fueron asociados al deterioro de los revestimientos de las infraestructuras.
3. Bajas abundancias en los sedimentos intermareales, similares a sedimentos antárticos poco profundos informados previamente. Predominaron las fibras de tereftalato de polietileno, principalmente cerca del efluente de la base de Frei, donde igualmente se confirmó la presencia de fibras de algodón.
4. La presencia de microplásticos en zonas protegidas como Isla Ardley es preocupante, al igual que las bases que carecen de sistema de tratamiento o presentan complejas limitaciones para su operación.
5. Respecto a las variables ambientales, se observó una relación entre los fragmentos y la materia orgánica, la cual parece basarse en la composición de los polímeros.
6. Además, la relación observada entre fibras y tamaño de partícula no fue concluyente, y hasta la fecha no existen estudios que confirmen una relación clara.
7. Se destaca la importancia de una temprana identificación de las fuentes locales de microplásticos y la particularidad de cada matriz en el comportamiento de estos contaminantes.

Capítulo 2

Hipótesis 3: Bases situadas en zonas costeras que no cuenten con sistemas de tratamiento de aguas residuales generarán altas concentraciones de PPCPs en el agua de mar donde liberan sus efluentes en comparación a bases con sistemas de tratamiento operativos.

1. La población humana establecida en la Antártica ha generado la síntesis de PPCPs de forma permanente o intermitente, con una estacionalidad dependiente de cada base.
2. Los sistemas de tratamientos de aguas residuales son determinantes en las concentraciones de PPCPs en el ambiente costero, alcanzando las mayores concentraciones ambientales en sus efluentes.
3. En consecuencia, la no operación del sistema de tratamiento en base Esperanza, arrojó las más altas concentraciones de PPCPs en el Continente Antártico. Sin embargo, la implementación de sistemas de tratamientos parece no ser completamente eficiente en la remoción de PPCPs como filtros UV y surfactantes en base Scott.
4. Esto es complejo debido a que algunas estaciones carecen de tratamiento terciario, cuyas tecnologías son más eficientes en la remoción de PPCPs. Además, la mayoría de las estaciones se localizan en zonas costeras del continente, las que de acuerdo al Protocolo Ambiental vigente, pueden liberar sus efluentes sin tratamiento dependiendo de la ocupación semanal en la estación. En último lugar, bases que efectivamente carecen de sistema de tratamiento, tampoco cuentan con estudios acerca de la presencia de PPCPs en estas localidades.
5. La visión global del problema por contaminación de PPCPs en la Antártica, se dificulta ante la fragmentada, escasa o desactualizada información acerca de los sistemas de tratamientos de aguas residuales. Además, se observa un sesgo de información al verificar una mayor cantidad de información para algunos grupos PPCPs. La escasez de estudios de PPCPs en la Antártica puede generar una subestimación de las concentraciones, que podrían ser incluso superiores a las reportadas, en detrimento de un conocimiento adecuado de la distribución y efectos sobre los ecosistemas acuáticos costeros de la Antártica. En adición, la biota ha sido poco estudiada, desconociéndose el grado de bioacumulación y efectos, especialmente en organismos bentónicos que rodean los efluentes.
6. En consecuencia, la problemática es afrontada de manera muy parcial y poco realista del riesgo. Un control en el ingreso de PPCPs al continente por parte de los operadores nacionales y turísticos, puede contribuir en la reducción

del impacto de los PPCPs en el ambiente, en un escenario que involucra sistemas de tratamientos inexistentes, con problemas logísticos o de baja eficiencia de remoción.

X. Capítulo 3: Referencias generales

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XI. ANEXO

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Occurrence and Distribution of Microplastics in Soils and Intertidal Sediments at Fildes Bay, Maritime Antarctica

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Increased human activity on the Antarctic Peninsula has generated microplastic contamination in marine systems; however, less attention has been paid to soils so far. We investigated the occurrence of microplastics in 11 surface soils and intertidal sediments collected from Fildes Bay, King George Island. A transect of soils at Antarctic stations until Fildes Bay was made (i.e., S1–S5). Intertidal sediments along the shore (i.e., IS1–IS5) and a reference sample from Ardley Island (i.e., IS6) were also collected. All samples were stored at 4°C and analyzed for the organic matter content, particle size, and pH. Plastic particles were counted and classified by shape using metal dissecting forceps and a stereomicroscope and further analyzed by Fourier-transform infrared spectroscopy (FT-IR). They were classified by length as fibers (length: 500–2,000 μm) and fragments (length: 20–500 μm). In soil, fragments reached an average of 13.6 particles/50 ml sample, while in intertidal sediments, no fragments were found, but a fiber abundance of 1.5 particles/50 ml sample was observed. The principal component analysis shows a relationship between fibers and intertidal sediments, whereas fragments present a relationship with soils. There were differences between the numbers of fragments found in soils and intertidal sediments ($p = 0.003$), with a high abundance of fragments at site S5, but no significant differences were observed for fibers. The physicochemical soil analysis revealed that larger particle sizes were observed in intertidal sediments (average = 706.94 ± 230.51 μm) than in soils ($p = 0.0007$). The organic matter content was higher in soil than in intertidal sediments ($p = 0.006$) reaching an average of 6.0%. Plastic fragments and organic matter were significantly correlated ($r = 0.779$, $p = 0.005$), while fibers were positively correlated with particle size ($r = 0.713$, $p = 0.014$). The fragments were composed of phenoxy resin with the same appearance, shape, and bright orange color as the coatings of the facilities. According to the FT-IR analysis, the fibers had different colors and were composed of polyethylene terephthalate (PET). Cotton was also present at the sites surrounding the sampling site close to the base effluent. The presence of fiber on Ardley Island (i.e., control) may indicate that microplastic contamination has reached protected areas. This is the first study to confirm the presence of plastic debris in Antarctic soils. Further studies should focus on the identification of plastic sources and on the management of human activities and their eventual effects on biota.

Keywords: fibers, fragments, PET, phenoxy resin, pollution, soil, intermareal sediment, Antarctica

INTRODUCTION

Since the first expeditions, and especially since the 1950s, scientific interest in the Antarctic continent has increased; there are currently more than 80 facilities distributed mainly in coastal areas and on the Antarctic Peninsula (Bruni et al., 1997; Gröndahl et al., 2009; Lu et al., 2012; Morales Calvo, 2013). These facilities host more than 5,000 people a year; however, this number is much lower than the 74,000 tourists who arrived in the 2019/2020 season (Council of Managers of National Antarctic Program, 2020; International Association of Antarctica Tour Operators, 2020). Using the data of human density and accessibility features of the Antarctic continent along with land uses, Pertierra et al. (2017) concluded that the Antarctic Peninsula is one of the three regions with the greatest human footprint pressure. On coasts worldwide, a high human density has resulted in contamination by microplastics, spread over six continents from the poles to the equator, sustained by an annual worldwide production of 368 million tons of plastic (Browne et al., 2011; Plastics Europe, 2020). In Antarctica, Barnes et al. (2010) reported the presence of macroplastics, such as fishing buoys and packing material in the Durmont D'Urville, Davis, and Amundsen seas. Nevertheless, at present, the international scientific community does not regularly sample microplastics or record at-sea observations of macroplastics in the Southern Ocean region, and there are few peer-reviewed scientific publications that quantify plastics in Antarctic waters (Waller et al., 2017). In studies carried out in seawater, a high abundance of microplastics has been reported in the vicinity of the Antarctic continent, in contrast to the low abundances that they reach in the Southern Ocean, which probably derive from long-distance transport (Isobe et al., 2017). Also, microplastics reached higher concentrations along the Antarctic Peninsula than at open ocean sub-Antarctic stations (Jones-Williams et al., 2020). Cunningham et al. (2020) reported high levels of microplastic contamination in marine sediment cores from three regions in Antarctica and the Southern Ocean. This is consistent with the findings of Onink et al. (2021), who, using a Lagrange particle transport model, verified that coastlines and coastal waters are an important reservoir of plastic debris and that there is limited transport of the marine plastic debris with positive buoyancy between the coastal zone and the open ocean. In general, high microplastic abundance has been reported in seawater and marine sediments collected in the areas closest to scientific stations, with wastewater effluents identified as being among their main sources (Cincinelli et al., 2017; Waller et al., 2017; Reed et al., 2018).

At present, there are no studies on Antarctic soils. Li et al. (2016) concluded that land-based sources account for 80% of the plastic waste in the marine environment, with high human density and industrial activities playing a key role. While evidence of the ecological impacts of microplastics has increased worldwide, evidence of the potential consequences of microplastics in soil ecosystems is still relatively scarce (Huang et al., 2019). This lack of information is of an ecotoxicological concern, given that once in the soil, these particles decompose slowly and accumulate as relatively persistent pollutants (Rillig, 2018). Decades ago, harm to fur seals, gulls, and penguin species caused by the presence of macroplastics was reported; however, the situation has resulted in sustained increases in their accumulation rates on Antarctic islands (Torres and Gajardo, 1985; Torres and Jorquera, 1992, 1994). There is no information on the presence of microplastics in terrestrial Antarctic environments, although they were recently reported in a freshwater stream, with their presence attributed likely to air transport (González-Pleiter et al., 2020).

Since 1968, various countries have established facilities on the Fildes Peninsula, generating great environmental pressure resulting from the scientific and logistical activities that take place in the area (Lu et al., 2012; Amaro et al., 2015). The high density of the facilities and the varied human activities in the region often clash with the environmental standards laid down in the Protocol on Environmental Protection to the Antarctic Treaty (Peter et al., 2013). Since human activities in the Antarctic are the main source of microplastic contamination, the objective of this study was to evaluate its occurrence and distribution on the adjacent soil and intertidal sediments of Fildes Bay, Antarctica.

MATERIALS AND METHODS

Study Area and Sampling Site

The study area is the Fildes Peninsula, King George Island (Antarctic Specially Protected Area No. 125), one of the areas in Antarctica with the greatest paleontological interest and an area with a great diversity of organisms, including vertebrates, invertebrates, and flora (Secretariat of the Antarctic Treaty [ATS], 2009). The area contains six permanent Antarctic stations belonging to different countries (i.e., Chile, Russia, Uruguay, and China), built between 1968 and 1994. In the 1980s, the construction of the airport turned the area into a major logistical hub for the Antarctic Peninsula (Braun et al., 2012). A part of the Fildes Peninsula is formed by Ardley Peninsula (62°13′S, 58°54′W), Antarctic Specially Protected Area No. 150, located on the southwest coast of King George Island (Fildes Bay). Ardley Island was designated as a protected area on account of the diverse assemblage of bird species that breed on it and to allow the study of their ecology and the factors that affect their populations. Ardley Island also has developed an outstanding flora, with

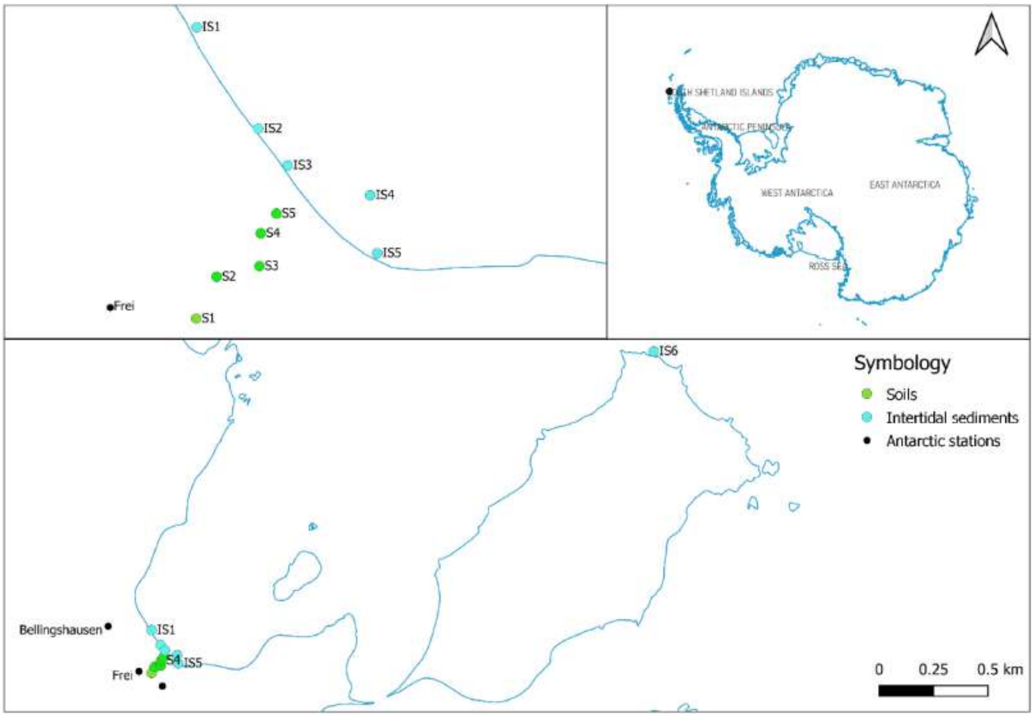

FIGURE 1 | Sampling areas on Fildes Bay and Ardley Island, Antarctica. Green points indicate soil samples (i.e., S1–S5), and light blue points represent intertidal sediments (i.e., IS1–IS6).

species of lichens, mosses, and vascular plants (Secretariat of the Antarctic Treaty [ATS], 2009) (**Figure 1**).

The study area was divided into two sampling sites (**Figure 1**), namely, Antarctic stations and intertidal zones.

Sample Collection and Analysis

Sampling was performed in December 2018. In areas corresponding to Antarctic stations, five soil samples were collected along a transect stretching from the Frei Antarctic station to Fildes Bay (i.e., S1–S5) (**Figure 1**). In intertidal zones, five sediment intertidal samples were collected along the shore zone (i.e., IS1–IS5). In addition, an intertidal sediment sample (i.e., IS6) was collected from the shore of Ardley Island as a reference from an area free of human activities. An amount of 200 ml of soil and 500 ml of intertidal sediment was extracted at a depth of 0–1 cm using a metal spatula that had been previously washed with acetone. The soil samples were stored in aluminum foil, and the intertidal sediments were collected in glass bottles; they were then refrigerated at 4°C.

To extract the microplastics, the method described by Thompson et al. (2004) and modified by Browne et al. (2010) was used. In brief, 50 ml of the sample was suspended in 100 ml of supersaturated solution of NaCl (1.2 kg NaCl/L), previously filtered by filter paper with a pore size of 1 μm (Advantec Grade NO.5C size 11 cm). This solution was stirred for 30 s, and after 2 min, the particles in the supernatant were separated from the solution using a glass filter under a vacuum with a pore size of 1.6 μm (glass fiber prefilters; Merck Milipore Ltd.). This step was repeated three times for each sample. To minimize contamination by airborne microplastics during drying at room temperature, the filters were placed in Petri dishes and kept inside a glass box.

The plastic particles were separated from non-plastic material and counted using metal dissecting forceps and a stereomicroscope (Olympus SZ61 40X, Japan). Particles with a length of less than 5 mm and greater than 1 μm were considered microplastics GESAMP, 2019 [Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) (United States)]. Fourier-transform infrared spectroscopy (FT-IR) (Spotlight 400 Perkin Elmer) was used to identify the nature of the polymer in the microplastics from the sampling sites. The attenuated total reflectance (ATR) micro-imaging technique with a germanium crystal was used. A spectral range between 750 and 4,000 cm^{-1} and a pixel of size 6.25 μm was used. The spectra carry the data with an interval of 3 μm and a resolution of 6 cm^{-1}. Samples from soil and sediments are expressed in volumes to enable comparisons between sample types. All spectra were compared with fused deposition modeling (FDM) FT-IR and Raman spectral libraries and libraries created by the laboratory that analyzed the samples.

Analysis of Physicochemical Parameters in the Collected Samples

Organic matter: The organic matter content in the soil and intertidal sediment samples was determined based on the method described by Heiri et al. (2001). Soil and intertidal sediment were dried at 60°C for 72 h. One g of soil/sediment was homogenized in a mortar and combusted in a muffle furnace at 550°C for 4 h. Finally, the sample was weighed to determine the organic matter content (%) by loss ignition. The results are expressed in dry matter.

Particle size: Samples were dried at room temperature and sieved using a 2-mm sieve. Subsequently, organic matter was removed from each sample using 30% hydrogen peroxide. The sample was deposited in a funnel with a filter paper with a pore size of 1 μm (Advantec Grade NO.5C size 11 cm) and cleaned with milli-Q water. Then, the sample was introduced into a dispersion unit until 10–20% laser obscuration was reached (Malvern Mastersizer 3000S with Hydro EV dispersion unit, United Kingdom). Finally, the results were analyzed using Gradistat v.8 to obtain the average particle size (Blott, 2010).

pH: Soil and intertidal sediment samples were dried at room temperature and homogenized in a mortar. Subsequently, each sample was sieved using a 2-mm sieve. Subsequently, 1 g of sample was placed in 50 ml of Milli-Q water (20°C). To homogenize the sample, a magnetic stirrer was used for 5 min at 225 rpm. The sample was left to stand for 2 h, at which point, the pH in the supernatant was determined using a pH meter (Hanna Edge, United States).

Maps

The sampling area map was prepared using the QGIS 3.14 software (QGIS.org, 2020) and the layers were available in Quantarctica (2019).

Statistical Analyses

To explore the variance of the environmental variables (e.g., fibers, fragments, organic matter, particle size, and pH) in the data set, a Euclidean distance matrix was built, and then a principal component analysis (PCA) was performed. Then, a Shapiro-Wilk test was carried out to test the normal data distribution. A Kruskal-Wallis test and ANOVA were carried out to verify the existence of significant differences between soils and intertidal sediments. A Kendall correlation analysis between particles—whether fibers or fragments—and organic matter, particle size, and pH were performed. The level of significance was set at $p = 0.05$. All statistical analyses were performed with the R Studio software version 4.0.2.

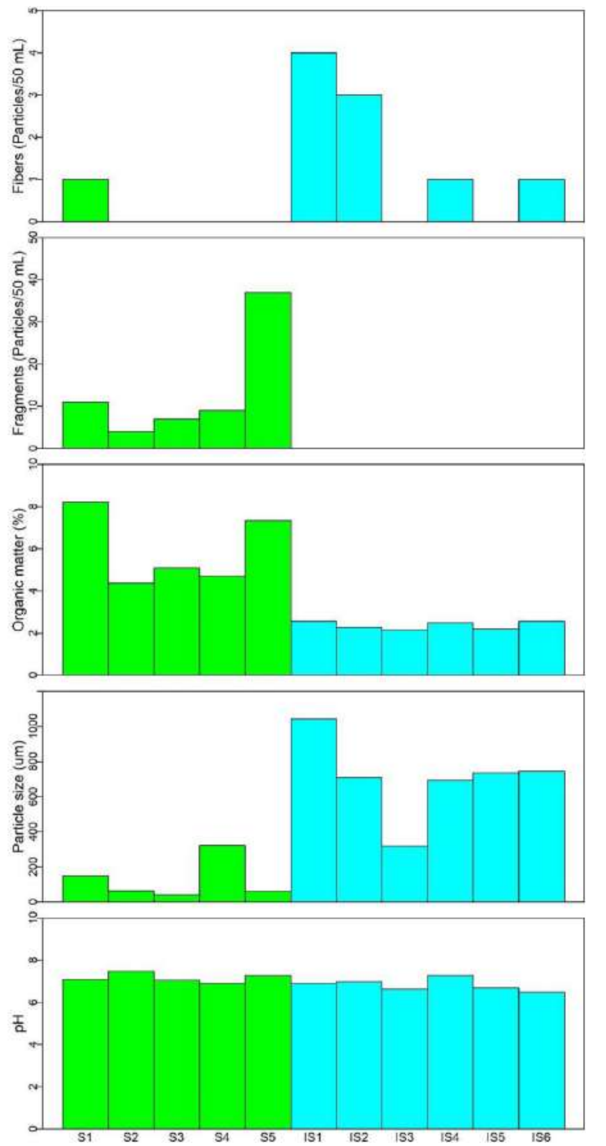

FIGURE 2 | The abundance of microplastics (i.e., fibers and fragments) and determination of an organic matter, particle size, and pH in soils (i.e., S1–S5) and intertidal sediments (i.e., IS1–IS6) of Fildes Bay, Antarctica.

RESULTS

This study revealed the presence of microplastics in soils and intertidal sediments at 81% of the sites analyzed at Fildes Bay, Antarctica. Five topsoil samples (i.e., S1–S5), five intertidal sediments (i.e., IS1–IS5), and a reference sample (i.e., IS6) were analyzed. Plastic debris after treatment was classified as fibers or fragments based on size, and the nature of the polymer was characterized using FT-IR. Microplastic occurrence (i.e., fibers and fragments), organic matter, particle size, and pH in soils and sediments, respectively, are shown in **Figure 2**. Plastic fragments (length < 500 μm) were detected in all soil samples, while the presence of fiber was only observed in sample S1 (1 particle/50 ml). The distribution of the fragments in the samples varied from 4 to 37 particles/50 ml sample. The highest occurrence was observed in S5, which is the sample from closest to the shore. Samples taken far from the shore (i.e., S1–S4) presented an occurrence of fragments between 4 and 11 particles/50 ml. The soil organic matter content varied from 4.4 to 8.2%. Similarly, the soil particle size in the samples ranged from 40.6 to 323.6 μm. The soil was considered neutral, with a pH ranging from 6.9 to 7.5. Regarding the evaluated physicochemical variables, no trends were identified in terms of proximity to the coast.

In the intertidal sediments, only fibers (length < 2,000 μm) were observed, ranging from 1 to 4 particles/50 ml. Samples

IS1 (4 particles/50 ml) and IS2 (3 particles/50 ml) presented the highest detected abundances; these samples were taken at sites close to the effluent. Abundances in the other intertidal samples (i.e., IS3–IS5) ranged from 0 to 1 particle/50 ml. The inspection of sample IS6 (i.e., protected area, control) revealed a transparent, brilliant, and hard fiber (**Figure 3D**). We recognized its similarity to the ropes used on boats; however, during sample preparation for the FT-IR analysis, the sample was lost and could not be further identified. The physicochemical values are indicative of homogeneous organic matter in the intertidal sediments (2.2–2.6%). The particle size ranged from 318.9 to 1,042.8 μm. Similar

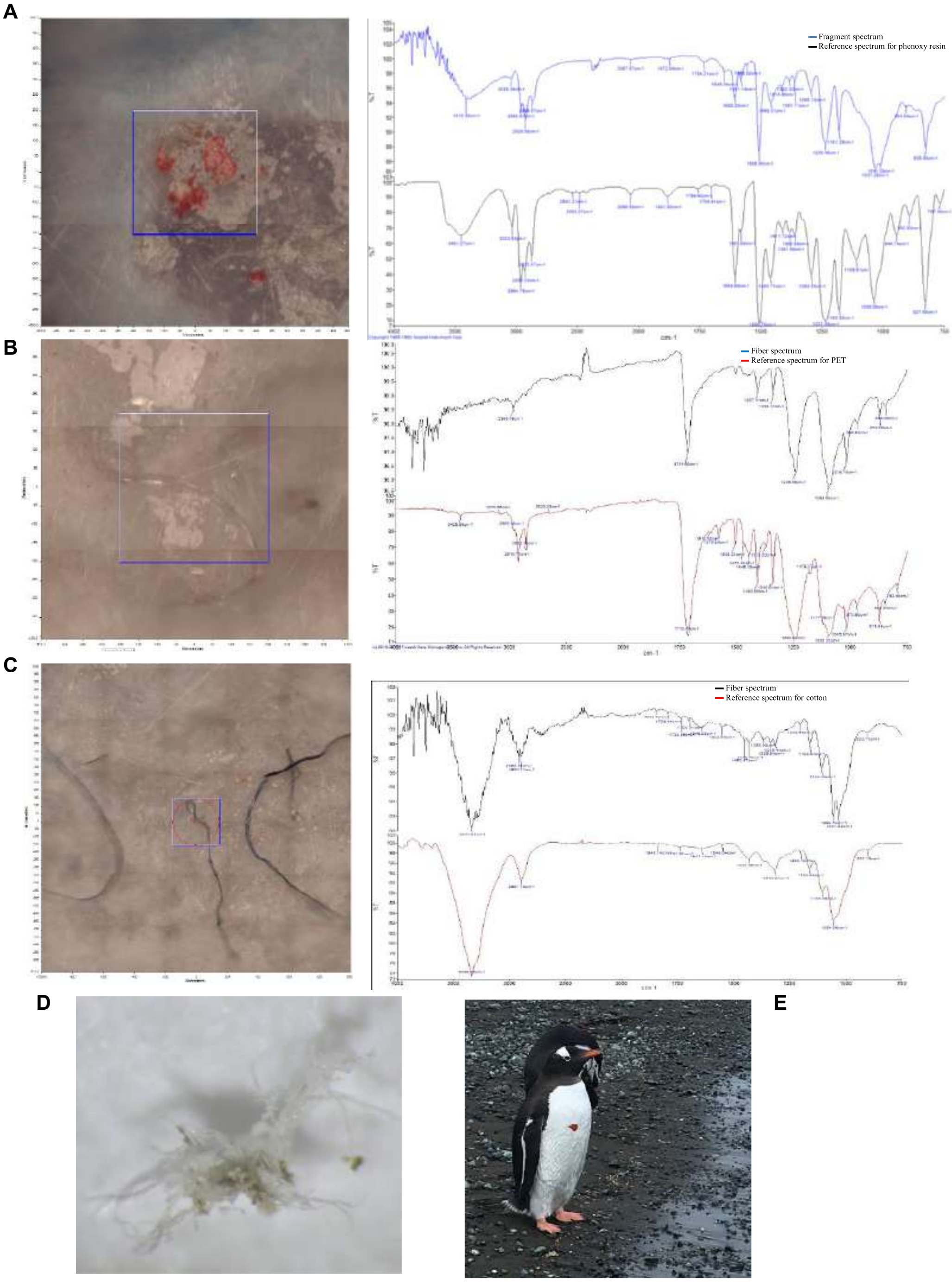

FIGURE 3 | Photograph and spectrum of an orange tree fragment of phenoxy resin **(A)** collected in soils, PET fiber **(B)**, cotton fiber **(C)** and a fiber found at the site IS6 **(D)** from intertidal sediments and a mesoplastic piece on *P. papua* **(E)** in Fildes Bay, Antarctica.

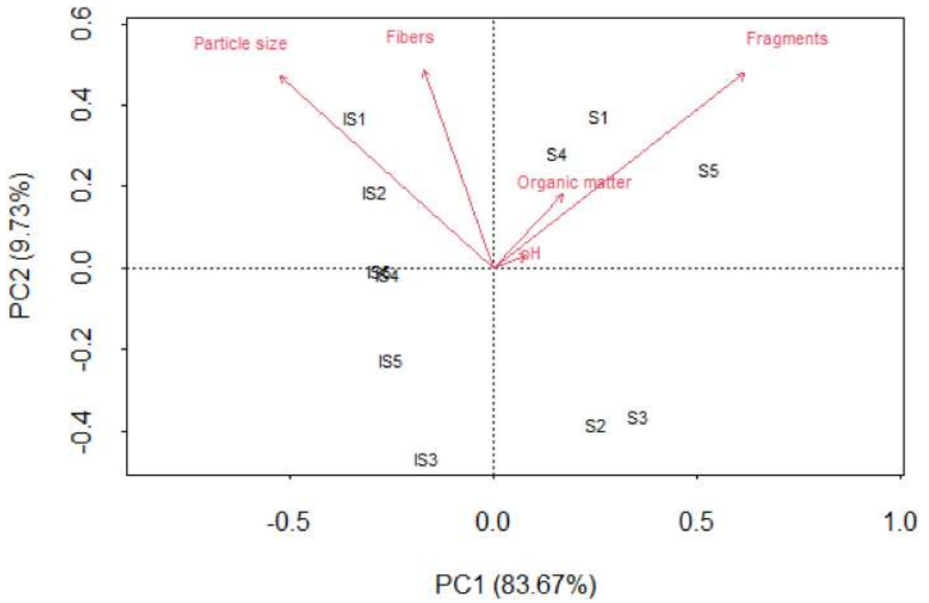

FIGURE 4 | Principal component analysis (PCA) between fibers, fragments, organic matter, particle size, and pH in soils and intertidal sites.

to the soils, the intertidal sediments presented a neutral range (6.5–7.3).

Fragments and particle size presented the greatest variability along the PC1 axis, which captured 83.67% of the total variance (**Figure 4**). The abundance of the type of plastic debris (i.e., fibers and fragments) in soils and intertidal sediments was correlated with physicochemical variables. Specifically, intertidal sediments were characterized by the largest occurrence of fibers, whereas fragments were highly predominant in soil samples. In addition, intertidal sediment sites were influenced by particle size, although soils do not seem to show a significant relationship with other soil variables (i.e., pH and organic matter).

The number of fragments differed significantly between the investigated sample types, i.e., soils and sediments ($p = 0.003$). In terms of soil physicochemical parameters, organic matter differed significantly between the matrices ($p = 0.006$), with higher concentrations in soils (S5 = 7.3% and S1 = 8.2%) compared with sediments. Particle size differed significantly between sample types ($p = 0.0007$), with higher sizes in the intertidal matrix (S1 = 1,042 μm) than in soils. pH did not present significant differences between matrices. Positive correlations between fragments and organic matter ($r = 0.7786$, $p = 0.005$) were observed, as well as between fibers and particle size ($r = 0.7128$, $p = 0.014$).

All the fragments collected in the soils presented uniformity in color, which was classified as bright orange. The presence of mesoplastics with the same characteristics was also observed in the area, with evident secondary fragmentation *in situ*. The orange fragment had a high similarity to phenoxy resin (**Figure 3A**). In contrast, the intertidal plastic fibers presented different colors (i.e., black, blue, red, and transparent). The FT-IR analysis determined that 67% and 50% of all fibers recorded at sites IS1 and IS2, respectively, were cotton fibers (**Figure 3C**). In addition, for all sites, the analysis indicated that the remaining fibers had a high similarity to polyethylene terephthalate (PET) (**Figure 3B**).

DISCUSSION

Microplastics in Antarctic Soils

The largest amount of microplastics was detected in soils (1–37 particles/50 ml soil), with fragments predominating, which were associated with high concentrations of organic matter. A comparison with other reports is difficult due to the lack of similar studies on microplastics in Antarctic soils. According to Bläsing and Amelung (2018), our poor understanding of microplastics in soils may be due to the lack of standardized methods. In general, abundances of plastics are highly variable depending on land use and population density; so far plastic debris have been reported in agricultural soils in Shanghai, China (78 ± 12.91 particles/kg) (Liu et al., 2018); roadside soils (1,108 particles/kg) and agricultural soils (3,440 particles/kg) in Yeoju, Republic of Korea (Choi et al., 2021); soils of cultivated areas and the riparian forest zone of Dian Lake, China (7,100–42,960 particles/kg) (Zhang and Liu, 2018); agricultural soils in Nanjing and Wuxi, China (420–1,290particles/kg) (Li et al., 2019); and agricultural soils (2,200–6,875 particles/kg), parks (6,250 ± 3,776 particles/kg), industrial areas (5,780 ± 3,251 particles/kg), and dumps (2,429 ± 1,817 particles/kg) in Lahore, Pakistan (Rafique et al., 2020). The values found in the present study are far lower than those listed above, suggesting that the intensity of the land use and human activities clearly determine the occurrence of plastic debris in soils.

Fragments were observed in all investigated soils, while only one fiber, at site S1, was identified (**Figure 2**). The fragments had the same appearance, shape, and orange color as those observed in the coatings of the neighboring facilities, which present deterioration associated with local environmental and climatic conditions. This suggests that local land use is the main driver of soil fragments on Fildes Bay. Land use may in part explain the presence of a certain type of microplastic, such as in agricultural soils, which reach high fiber abundances due to the use of sewage sludge as fertilizer (Liu et al., 2018; Corradini et al., 2019; Jiang et al., 2020). Wind also plays an important role in the investigated area, as it reaches speeds of over 100 km/h (Cerda, 2006). In the province of Sakarya, Turkey, Kaya et al. (2018) reported that fibers were more abundant than fragments in the air, with microplastics having a presence of up to four orders of magnitude higher in the air than in soils. This is consistent with the findings of Wright et al. (2020) who recorded atmospheric deposition rates ranging from 575 to 1,008 microplastics/m^2/day in the city of London, with the representativeness of 92% of fibers. This finding could explain the low abundance of fibers in soils, which might have been constantly resuspended from the soils or transported to other areas. Furthermore, it has been shown that particle density is decisive in their deposition in coastal systems, since less dense particles tend to settle downwind, in contrast to denser particles, whose settling is not determined by wind, with deposition along the coast (Browne et al., 2010). Finally, once in the soil, the behavior of microplastics varies; according to Waldschläger and Schüttrumpf (2020), fibers that have a smaller diameter reach greater infiltration depths, in contrast to the fragments, which infiltrate less due to the entanglement of the angular particles in the pores.

The highest concentration of fragments was recorded at site S5, the closest to the sea and, therefore, the lowest, which could also suggest a certain degree of runoff as a result of melting snow. Site S5 is also an area with a high-degree of human activity, the use of which is mainly associated with the transit of towing machinery for small boats and motorized vehicles to assist in logistics and maintenance tasks for scientific and tourism purposes. Based on a visual inspection, the fragments even show a degree of secondary fragmentation *in situ*. The determination of their composition by FT-IR shows a high coincidence with phenoxy resin (**Figure 3A**), which has a high density and is used as a flexibilizer for cross-linked phenolic and epoxy formulations in adhesives, coatings, and compounds and to make compatible mixtures of various plastic materials (Song et al., 2015; Jones-Williams et al., 2020). Previous studies have not frequently reported the detection of synthetic resins in the environment; however, the detection of this material is very likely since these resins, especially phenoxy resins, are often blended with plastics (Paler et al., 2021). For example, microplastics derived from thermoplastic road-surface marking paints (Horton et al., 2017) and ship paints (Song et al., 2014) have been described. In terms of abundance, paint resins are comparable to microplastics, together reaching 75% of total particles in the surface waters of Jinhae Bay, South Korea (Song et al., 2015). In surface waters between Adelaide Island, Antarctica, and the mid Scotia Sea, it has been reported that, although phenoxy resin has local sources, it has a long range and, together with polyethylene, is one of the most common resins (41%) (Jones-Williams et al., 2020). Therefore, although we did not verify its presence in the intertidal sediments, it is highly probable that it is present not only in the soils of Fildes Bay but also offshore. In addition, transport through biovectors from terrestrial to aquatic environments, such as that which took place via the adhesion of a piece of mesoplastic to the chest of an adult individual of the species *Pygoscelis papua* (Forster, 1781), should not be ruled out (**Figure 3E**).

Our study showed a relationship between the fragments and organic matter of the soils. This contrasts with the results reported by Watteau et al. (2018), who analyzed soils enriched with municipal compost in France and concluded that microplastics in soils do not present an association with organic matter. In experimental soils with different microplastic sizes, Dong et al. (2021) reported that the presence of polystyrene and polytetrafluoroethylene microplastics caused a reduction in the soil organic matter. In our research, organic matter (%) was determined using the method of Heiri et al. (2001), who indicate that weight loss is proportional to the amount of organic carbon contained in the sample. However, Rillig (2018) emphasized that the methods used for quantitation of organic carbon in soil can cover "invisible" microplastics because plastics are composed mainly of carbon. This could explain the relationship that we verified between the increase in organic matter in sites and a high abundance of fragments. As organic matter (%) does not seem to be a precise variable, it is suggested that future studies employ more specific analyses regarding the composition of the type of carbon present in soils.

The information available on exposure and effects of microplastics on Antarctic organisms is similarly scarce. Plastic particles can persist, accumulate, and eventually affect the functioning and biodiversity of terrestrial ecosystems (Rillig, 2012). Habib et al. (2020) isolated bacteria *Pseudomonas* sp. ADL15 and *Rhodococcus* sp. ADL35 from soil samples collected in Victoria Land, Ross Sea, Antarctica. They corroborated positive growth in a medium containing fragments of polypropylene (Habib et al., 2020). In addition, bacterial assemblages with distinct community structures colonized the PE microplastics (Huang et al., 2019). In general, soil fauna has an active intake of microplastics, with a consequent alteration of its intestinal microbiome and adverse effects on motility, growth, metabolism, reproduction, and mortality in various combinations (Büks et al., 2020), especially at high concentrations and with small particle sizes. The small size and large surface area of microplastics allow the adsorption of pollutants on their surfaces, increasing the local concentration in soils and generating potential ecological risks (Moore, 2008; Ashton et al., 2010; Rillig, 2012; Liu et al., 2018). Finally, although it was not found in the intertidal zone, phenoxy resin could be transported offshore; according to European Chemicals Agency (2021), this substance is toxic to aquatic life, with long-lasting effects.

Microplastics in Antarctic Intertidal Sediments

The intertidal sediments were dominated by fibers (up to 4 fibers/50 ml sediment) (**Figure 2**), which were associated with

TABLE 1 | Microplastics in intertidal and subtidal sediments in Antarctica.

Matrix	Shape	Location	Sampling date	Collection method	Depth (m)	Size criteria	Sample digestion	Density Separation	FT-IR	Abundance	Reference
Subtidal sediment	Fibers (42.8%)	Terra Nova Bay, Ross Sea, Antarctica.	2015	Van Veen grab	25–140	< 5 mm			X	5–1,705 particles/m^2	Munari et al. (2017)
Intertidal and subtidal sediment	Fibers (except a spheric particle)	North Cove, Cheshire Island and South Cove, Adelaide Island, Antarctic Peninsula.	2016	Diving or box coring	0–20	< 5 mm		X	X	0–3 particles/10 ml	Reed et al. (2018)
Subtidal sediment	Fibers and fragments (no percentages)	Mackellar Inlet, South Shetland Islands, Antarctic Peninsula.	2013 and 2015	Van Veen grab and SCUBA	6–60	< 5 mm				16–766 particles/m^2	Waller et al. (2017)
Subtidal sediment	Fragments (56%). Fibers (39%)	Antarctic Peninsula.	2017–2019	OKTOPUS multicores	136–3,633	< 2 mm	X	X	X	1.30 ± 0.51 particles/g	Cunningham et al. (2020)

FT-IR, Fourier-transform infrared spectroscopy.

large particle sizes. Similar abundances have been reported by Reed et al. (2018), who recorded up to 3 fibers/10 ml sediment in North Cove, Adelaide Island, Antarctic Peninsula. A previous study carried out by Rebolledo and Franeker (2015) on Cape Shirreff did not record microplastics in intertidal sediments, despite the presence of macroplastics in the area. Although the information on microplastics in Antarctic intertidal sediments is limited (**Table 1**), these data could suggest a low abundance compared with those of deep sediments. Close to the study area, Waller et al. (2017) carried out research in semi-deep sediments (6–60 m) in Mackellar Inlet, Almirantazgo Bay. They reported between 16 and 766 particles/m^2; however, they did not find a clear pattern of abundance or distribution, and the proportion of fibers and fragments found was not reported. Consistent with our findings, the predominance of fibers (42.8%) was verified in semi-deep sediments (25–140 m) in Terra Nova Bay (Munari et al., 2017). Fibers also predominated for all recorded microplastics, with the exception of one particle, in shallow sediments (0–20 m) on Adelaide Island (Reed et al., 2018). This pattern of fiber prevalence has also been reported in Singapore mangroves (Nor and Obbard, 2014). In addition, Browne et al. (2010) analyzed the sediments in the high tide line of the Tamar Estuary, United Kingdom, finding values of up to 1 fiber/50 ml sediment, similar to those of Fildes Bay. A low abundance in the intertidal sediments of coastal systems in Plymouth, United Kingdom, was also described by Thompson et al. (2004), who indicated that fibers increased in subtidal sediments. In marine environments of the Alboran Sea (42 m deep), an abundance of 45 fibers/50 ml sediment has been described (Sanchez-Vidal et al., 2018). Although Sanchez-Vidal et al. (2018) did not include other forms of particles in deep sediments of southern European seas in their study, they estimated that around 20% of the fibers found had accumulated in the open sea beyond 2,000 m of water depth. This could be explained by the fibers having an abundance up to four orders of magnitude higher in deep sediments than in the surface waters of the Atlantic Ocean, Mediterranean Sea, and the Indian Ocean (Woodall et al., 2014). In contrast, very deep sediments (136–3,633 m) analyzed on the Antarctic Peninsula, South Sandwich Islands, and South Georgia were shown to be dominated by fragments, which accounted for 56% of the total (Cunningham et al., 2020). Density could partly explain the distribution of the fibers, once in the water, in the water column, and in the deep sediments (Thompson et al., 2004; Sanchez-Vidal et al., 2018). In general, depth seems to be a determining factor in the abundance of certain forms of microplastics, with fibers predominating in intertidal environments and shallow areas.

Regarding the values at each site, the highest abundances were recorded at the sites closest to the Frei base effluent (i.e., IS1 and IS2), and are consistent with those reported in marine sediments near wastewater from the Rothera station west of the Antarctica Peninsula (Reed et al., 2018). In addition, 67% and 50% of all fibers recorded at sites IS1 and IS2, respectively, were cotton fibers, confirming the contribution of wastewater effluents. Although sludge acts as a microplastic retention agent, with estimated retention rates of 75.7% to 90% (Corradini et al., 2019; Jiang et al., 2020), fibers have also been found in the effluents (37.7–60.8%) of secondary treatment systems (Jiang et al., 2020), and up to 14 fibers/L have been observed in primary treatment systems (Talvitie et al., 2015). Given this scenario, a negative situation is projected for some facilities, as their treatment systems are prone to failure due to both the low temperatures that impede biological processes and the lack of maintenance and sludge evacuation, resulting in continuous emission of waste into the environment (Hughes and Blenkharn, 2003; Gröndahl et al., 2009; Morales Calvo, 2013). In addition, 37% of permanent stations and 69% of non-permanent stations do not have any type of wastewater treatment (Morales Calvo, 2013). Due to the high population density in the north of the Antarctic Peninsula, microplastics derived from personal care products and laundry are likely to be concentrated there (Waller et al., 2017). Microfibres from laundry released in wastewater may be a more substantial source of microplastic pollution compared with other sources as personal care products (Waller et al., 2017). However, the contribution of fibers from sources related to other types of local human activities should not be ruled out.

Regarding sediment characteristics, we found that a greater fiber abundance is related to large particle sizes. In other regions, studies on intertidal sediments have not identified a pattern in terms of microplastic abundance and sediment particle size, with high abundances found in both sediments larger than 2 mm in Canada (Cluzard et al., 2015) and fine sediments in Singapore (Nor and Obbard, 2014). The physical interactions between microplastics and sediments are not yet fully understood due to the diversity of shapes, diameters, lengths, surface areas, and densities, among other characteristics, which makes it difficult to know where they will settle and at what sedimentation rate (Browne et al., 2010; Cluzard et al., 2015).

All the fibers found in the intertidal zone were made of PET, also called polyester (**Figure 3B**). This material is widely used in the manufacturing of cold-weather clothing (Gonzalez et al., 1998; Das and Gersak, 2014; Gnanauthayan et al., 2017). Polyethylene terephthalate has a density of 1.34–1.39 g/cm^3, and according to Browne et al. (2010), almost 80% of the microplastics recorded on the coastline are denser, which, as they state, maybe due to its slow degradation, longer contact time with abrasive particles in the sediment, or transport by the wind of less dense plastics toward the coasts and inland. This could explain the presence of this type of polymer composition at all sites and in other regions, as reported by Naji et al. (2017) in a study on intertidal sediments of Hormozgan, Persian Gulf, in which fibers predominated by 88%, PET was identified as the most abundant polymer (i.e., 41%), and high concentrations in wastewater release zones were found. In Portugal and Morocco, 29% of the fibers found in intertidal sediments were made of PET (Velez et al., 2019). Similarly, a large-scale study conducted at high tide in intertidal sediments (0–5 cm) in Auckland, New Zealand, reported that fibers predominated (i.e., 88%) and PET accounted for 22% of all microplastics analyzed (Bridson et al., 2020). This abundance of PET in relatively shallow sediments was also described by Woodall et al. (2014) in the Atlantic Ocean, the Mediterranean Sea, and the Indian Ocean. Similarly, it was reported that 12.9% of the fibers found in the deep sea were polyester (Sanchez-Vidal et al., 2018). It has been observed that many marine microplastics have this composition and that their distribution and sinking rate presumably differ from those of other high-density microplastics (Cunningham et al., 2020).

In marine environments of Victoria Land, Antarctica, Sfriso et al. (2020) collected benthic invertebrates, reporting that species contained between 0.01 and 3.29 items/mg^{-1}, and that bivalves and gastropods displayed the highest microplastic contamination. Despite these findings, no evident accumulation through the food web was detected. In other regions, the dominance of PET fibers in coastal ecosystems on the coast of Pará, Brazil, was described by Morais et al. (2020), who reported that plastic fibers accounted for 84% of plastics ingested by individuals of *Bunodosoma cangicum* (Belém and Preslercravo, 1973), with PET being the main polymer (44.7%), and that this organism presented a higher amount of plastic debris in the more populated sampling sites.

It is still not clear if the role of microplastics is that of pollutant or merely contaminant; however, it is necessary to deepen our knowledge on the distribution and effects of microplastics and additives at all levels of the food web to evaluate their effects on marine organisms and ecosystems from a broader perspective (Sfriso et al., 2020). Aragaw and Mekonnen (2021) have recommended that microplastic contamination investigation guidelines emphasize experimental ecotoxicological studies and risk assessments for aquatic organisms. Vighi et al. (2021) stressed that key aspects in the production of an adequate risk assessment are frequently overlooked and that the impacts of environmental variables on additive leaching must be included.

Pollution of Protected Areas

Ardley Island was selected to assess the base level of contamination in an area with less human activity and no residential, scientific, or military settlements, only two sporadically used shelters. However, it was possible to detect the presence of a fiber particle in the intertidal sediment, which indicates that Antarctic environments with restricted entry and protected for their biological value are not exempt from contamination by microplastics. Thus, the inspection of King George Island has shown clear deficiencies with respect to waste management at some stations in the form of waste storage and the existence of more than 40 waste dumps (Peter et al., 2013). Although in other locations of the continent, there has been an effort regarding the recovery of waste and mitigation of old landfills (Eriksen et al., 2020), the Protocol to the Antarctic Treaty on Environmental Protection has recognized the lack of data on plastics that would allow adequate decision-making and reduction of pollution and has recently made recommendations regarding the use of plastic on the continent (Secretariat of the Antarctic Treaty, 2019a). Among the recommendations are halting the use of personal care products that contain plastic microbeads and considering the use of filtration technologies to reduce the amount of microplastic particles that enter the Antarctic marine environment (Secretariat of the Antarctic Treaty, 2019a,b); however, there are no recommendations focused on soils. This is worrying as our study has shown that the soil-intertidal sediment interface is not necessarily a continuum and that there is a difference in the composition of plastic particles, suggesting specific sources of microplastics in each matrix at Fildes Bay. Therefore, an understanding of microplastic pollution in Antarctica requires an increased focus on identifying sources and sinks.

Methods Used in Microplastic Research in Antarctica

In general, few studies are available on marine sediments in Antarctica, with most focusing on subtidal sediments and none so far on soils (**Table 1**). Research efforts are made mainly on the Antarctic Peninsula, which makes it difficult to understand what occurs inside the Antarctic Continent. Antarctica is characterized by difficult-to-access sites, low temperatures, and strong winds; this last factor can generate a high degree of contamination during sample collection. Given this scenario, sample collection techniques, microplastic selection criteria, and sample treatment vary among studies. Although all authors have used FT-IR to determine the composition of the particles, the results are expressed in different units of abundance (e.g., particles/ml and particles/m^2). In these cases, we suggest the incorporation of a standardized expression of units whenever possible, such as particles per surface or per volume. In our study, for comparative purposes, we decided to use the same expression for both matrices, which allowed us to identify a greater abundance in soils (average = 13.8 particles/50 ml) than in intertidal sediments (average = 1.5 particles/50 ml). This expression of the results permitted us to corroborate that even though the studied environments are contiguous, their abundances were independent and that contrary to what we expected, surface intertidal sediments did not behave as a sink for land-based sources. For instance, at site IS5, the presence of microplastics was not recorded, even though the adjacent soils were visibly affected by high abundances of microplastics as a result of the infrastructure that had been affected by a fire. In addition, despite the continuous release of fibers from the effluents, a low abundance was found at all intertidal sediment sites, which could be due to environmental dynamics such as tidal waves that affect intertidal sediments. In this regard, Cluzard et al. (2015) observed that a greater influence of tides and waves caused a lower accumulation of microplastics. Thus, although the abundances alone did not allow us to explain the distribution of microplastics in the study area, improving their comparability facilitates understanding of the complex intrinsic processes associated with Antarctic matrices.

CONCLUSION

The results of this study revealed the occurrence of microplastics in soils and intertidal sediments at 81% of the analyzed sites at Fildes Bay, Antarctica. This is the first study to report the presence of microplastics in Antarctic soils, with a high abundance of phenoxy resin fragments in Antarctic soils near stations, probably associated with deterioration of infrastructure coatings. Compared with terrestrial abundances, the abundance of microplastics in intertidal sediments was lower and consistent with results previously reported in shallow Antarctic sediments. Polyethylene terephthalate fibers predominated in the intertidal sediments, especially at the sites near the effluent from the Frei base, where the presence of cotton fibers was confirmed. Although this base has a treatment system, the situation of the bases affected by logistical limitations or without treatment systems is worrying. In addition, microplastics were found on Ardley Island, corroborating that there is contamination in protected areas. Regarding the influence of environmental variables, we observed a relationship between fragments and organic matter; however, this relationship seems to be a result of the composition of the polymers. In addition, the observed relationship between fibers and particle size was not conclusive, and to date, there are no studies that confirm a clear relationship. This investigation shows the importance of the early identification and management of local sources of microplastics and the study of each matrix, as the behavior of microplastics seems to differ depending on the substrate into which they are released. Paint resins should be considered in future studies, as they have demonstrated their persistence in the environment despite local climatic conditions. It is suggested that the Fildes Bay area be monitored to evaluate the behavior of these microplastics in other matrices and their eventual interactions with local fauna. This will make it possible to strengthen efforts to reduce the presence of microplastics in areas of major human activity such as Fildes Bay.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

AP-B and ROB conceptualized the study and provided funding for the study. AP-B performed the fieldwork and laboratory analysis. AP-B, AA, KM, and ROB wrote the manuscript. All authors contributed to the article and approved the submitted version.

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Review

Analysis of the contribution of locally derived wastewater to the occurrence of Pharmaceuticals and Personal Care Products in Antarctic coastal waters

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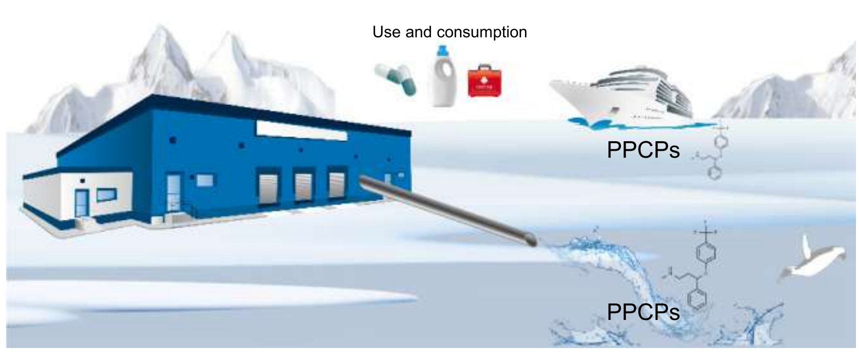
HIGHLIGHTS

- The concentration of PPCPs in Antarctica is driven by human activities.
- WWTPs are not completely effective reducing PCPPs in Antarctic coastal environment.
- Drugs, UV filters and plasticizers attained highest concentrations.
- The tourism should be included in monitoring due to its large floating population.

GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceuticals and Personal Care Products (PPCPs) are emerging pollutants detected in many locations of the world including Antarctica. The main objective of this review is to discuss the influence of the human population on the concentration, distribution and biological effects of PPCPs across the Antarctic coastal marine ecosystem. We carried out a review of the scientific articles published for PPCPs in Antarctic, supported by the information of the Antarctic stations reported by Council of Managers of National Antarctic Programs (CONMAP), Scientific Committee on Antarctic Research (SCAR) and Secretariat of the Antarctic Treaty (ATS). In addition, spatial data regarding the Antarctic continent was obtained from Quantarctica. Antarctic concentrations of PPCPs were more reflective of the treatment system used by research stations as opposed to the infrastructure built or the annual occupancy by station. The main problem is that most of the research stations lack tertiary treatment, resulting in elevated concentrations of PPCPs in effluents. Furthermore, the geographic distribution of Antarctic field stations in coastal areas allows for the release of PPCPs, directly into the sea, a practice that remains in compliance with the current Protocol. After their release, PPCPs can become incorporated into sea ice, which can then act as a chemical reservoir. In addition, there is no clarity on the effects on the local biota. Finally, we recommend regulating the entry and use of PPCPs in Antarctica given the difficulties of operating, and in some cases the complete absence of appropriate treatment systems. Further studies are needed on the fate, transport and biological effects of PPCPs on the Antarctic biota. It is recommended that research efforts be carried out in areas inhabited by humans to generate mitigation measures relative to potential adverse impacts. Tourism should be also considered in further studies due the temporal release of PPCPs.

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Contents

1. Introduction

Emerging contaminants, or chemicals of emerging concern, are a subset of potentially toxic chemicals products, not necessarily new, but without regulatory status. When present in the environment their impact on ecosystem function and human health is very often not well understood. A key class of emerging pollutants is Pharmaceuticals and Personal Care Products (PPCPs) (Environmental Protection Agency (EPA), 2008; Wagner and Lambert, 2017). Daughton and Ternes (1999) suggested a systematic strategy to determine if a research effort should be initiated to establish the incidence of PPCPs in the environment. Such a strategy would determine if there were adverse effects on aquatic organisms, and if cost-effective modifications of wastewater treatment could improve elimination efficiencies. While there is uncertainty regarding the environmental impact of PPCPs, enhanced analytic selectivity and sensitivity of technologies such as liquid chromatography and gas chromatography coupled with methods based on mass spectrometry have been used for the analysis of a greater diversity of these pollutants (Gago-Ferrero et al., 2012; Council of Managers of National Antarctic Program (CONMAP), 2014). Monitoring studies using these analytical approaches have allowed scientists to corroborate the presence of PPCPs in the surface water of rivers and coastal seawaters around the world, including U.K., U.S.A., Canada, China and Saudi Arabia (Boyd et al., 2003; Kasprzyk-Hordern et al., 2008; Vidal-Dorsch et al., 2012; Ali et al., 2017; Chen et al., 2021), with concentrations <14,000 ng l^{-1} for a wide spectrum of reported compounds. The global detection of PPCPs can be explained by their high annual production (2×10^7 tons, Wang and Wang, 2016) as well as the recalcitrant nature of many of these compounds with respect to degradation and removal in treatment facilities. Consequently, after PPCPs have been used, they are often discharged, in parent form, from wastewater treatment plants (WWTPs) into rivers, lakes and coastal seas (Huber et al., 2016). In this aspect, the type of wastewater treatment is important given that conventional treatments, for example coagulation plus chlorination, achieve low efficiency in the removal of PPCPs compared to more advanced technologies such as activated carbon, ozone and reverse osmosis (Snyder et al., 2003; Westerhoff et al., 2005). Nevertheless, globally, over 80 % of all wastewater is discharged without treatment (Connor et al., 2017). In developing countries, increasing urbanization and economic development, has increased the use of PPCPs, which increases the chemical load that treatment plants have to deal with. Furthermore, insufficient research, finances and human resources, coupled with inappropriate selection of treatment technologies that fit the local physical and climatic conditions, have only exacerbated the problem (Massoud et al., 2009; Gallego-Schmid and Tarpani, 2019).

Issues associated with the release of PPCPs also occur in the polar environments. In the Arctic, for example, the treatment of wastewater is often inadequate or completely lacking, due to absence of appropriated WWTPs and the widely used bucket toilets even in villages and towns, resulting in relatively high release rates for PPCPs into the aquatic environment (Gunnarsdóttir et al., 2013; Kallenborn et al., 2018). Research conducted on the Faroe Islands, Iceland and Greenland in treated and untreated wastewater streams, identified the occurrence of a large number of PPCPs such as diclofenac, ibuprofen, lidocaine, naproxen, metformin and citalopram (Huber et al., 2016). Since 2015, PPCPs such as estrogens, analgesics, anti-inflammatories, antibiotics, fungicides, preservatives, UV filters and surfactants have been demonstrated to occur in streams, glaciers drains, sea ice and polar organisms in Antarctica (Emnet et al., 2015; Esteban et al., 2016; González-Alonso et al., 2017; Vecchiato et al., 2017; Hernández et al., 2019; Domínguez-Morueco et al., 2021). This is due to the fact that, during the agreements of the Environmental Protocol, the prohibition on the disposal of untreated effluents was ruled out because of the high costs of its execution. As such, the Protocol allows for direct discharge of wastewater effluents into the sea when the station is occupied by fewer than 30 persons weekly, but for stations occupied by >30, at least one primary maceration treatment must be functioning (ATS, 1991; Smith and Riddle, 2009). Consequently, 37 % of the permanent stations and 69 % of summer stations, lack any kind of treatment whatsoever (Gröndahl et al., 2009). Antarctic polar stations also discharge different types of wastewater to the environment, including water derived from domestic, e.g., kitchens, toilets, laundry rooms, and bathrooms, and from technological sources as laboratories, repair workshops, etc. (Szopińska et al., 2021). This can result in a great variety of PPCPs being distributed into the environment, at wide ranging concentrations, and is in line with the global pattern showing high concentrations of PPCPs in areas of high human density (Aus Der Beek et al., 2016). The problem is exacerbated by the fact that many facilities account for operational problems and failures due to logistics, maintenance and unrealized energy requirements, all of which can result in increased specific labor for removal and subsequent treatment or evacuation of sludge (Hughes and Y Blenkharn, 2003; Gröndahl et al., 2009; Morales, 2013). The main objective of this review is to compilate the literature regarding occurrence and diversity of PPCPs and to discuss the influence of the human population on the concentrations, distribution and effects of PPCPs in Antarctic coastal marine ecosystem.

2. Materials and methods

Research articles available about the presence of PPCPs in the Antarctic were compiled from the Web Of Science (WOS) and Google Scholar (Emnet et al., 2015; Esteban et al., 2016; González-Alonso et al., 2017; Vecchiato et al., 2017; Hernández et al., 2019; Domínguez-Morueco et al., 2021; Duarte et al., 2021; Szopińska et al., 2022), for search key words including pharmaceuticals, drugs, Personal Care Products, PPCPs, pollution, contaminants of emerging concern and Antarctic. Studies that expressed PPCPs results as composite sums (e.g., Szopińska et al., 2021) were not included in this review.

Antarctic facilities and its infrastructure information published by the Council of Managers of National Antarctic Programs (Council of Managers of National Antarctic Program (CONMAP), 2017, 2020) and Scientific Committee on Antarctic Research (Scientific Committee on Antarctic Research (SCAR), 2020) were classified for each country according to the operating time (Fig. 1a), population and built infrastructure (Fig. 1b). The information on occupants by Antarctic station provided by Council of Managers of National Antarctic Program (CONMAP) (2020) corresponds to the years 2017–2019. In addition, both the number of stations and the type of seasonality were ordered by country (Fig. 2).

The implementation of the treatment for wastewater used by each Antarctic station was compiled from the Reports of the Antarctic Treaty Inspections from Secretariat of the Antarctic Treaty (ATS, 2003, 2005, 2009a, 2009b, 2010, 2011, 2012, 2013a, 2013b, 2013c, 2015, 2016a, 2016b, 2017a, 2017b, 2018, 2019a, 2019b, 2019c, 2020a, 2020b, 2020c). Additionally, publications from Council of Managers of National Antarctic Program (CONMAP) (2014, 2016, 2019); Council of Managers of National Antarctic Program (CONMAP) (2014, 2016, 2019; 2020) were also compiled. This information was complemented by that published by Delille and Delille (2000), Thomsen (2005), Tarasenko (2009), Martins et al. (2014), Australia State of the Environment (2016), British Antarctic Survey (BAS) (2019a, 2019b), Australian Government (2020), Swedish Polar Research Secretariat (2020), Szopińska et al. (2021) and updated information by direct request to Chilean institutions (Fig. 3). The spatial data of Antarctic continent was obtained from Quantarctica 3 Data Package (Matsuoka et al., 2018) and the mapping was developed using QGIS 3.14.0 Software (QGIS.org, 2022).

3. PPCPs in the Antarctic: sources and occurrence

3.1. Operating scientific stations and population in numbers

According to the information published by Council of Managers of National Antarctic Program (CONMAP) (2020), currently scientific stations belonging to 29 nations are distributed on the Antarctic continent. The longest time of operation that any country has operated a station is 118 years by Argentina, meanwhile the youngest station correspond to Belgium. Fig. 1a shows the operating time of the stations in the Antarctica. In addition, the human population is correlated with the built infrastructure (Fig. 1b). In this context, the United States has both the largest population (1399 inhabitants) and the largest built infrastructure (51,000 m^2) (Council of Managers of National Antarctic Program (CONMAP), 2017, 2020) (Fig. 1b). In both aspects, values attributed to the United States more than double those of the next leading nation, Argentina. In the case of Australia, they have a similar infrastructure as Argentina, but with <300 inhabitants per year. The small station in terms of people per year and infrastructure corresponds to R. Belarus.

Although many of the PPCPs detected in Antarctica were not synthesized at the time that the earliest stations were developed, the greatest boom in the establishment of stations occured during the 1950s, a period in which PPCPs, for example acetaminophen, were already marketed. Acetaminophen has proved to be useful, as it has become one of the most widely used drugs in the world, is a common ingredient in more complex drug formulations (McGill and Hinson, 2020; Shen et al., 2021), and is used to treat a wide spectrum of effects, i.e. to treat allergies, coughs, colds, flu and insomnia and moderate to severe pain (FDA, 2017). In this regard, depending upon the waste management of each station, countries with an extensive operating time (Fig. 1a) may have generated a legacy of PPCPs in the Antarctic environment with a relatively long exposure time. Longer-dated stations could generate chronic effects through the probable chronic occurrence of some types of PPCPs. The human contribution to PPCPs in the Antarctic environment reaches even more importance for year-round stations. Based on information reported by Council of Managers of National Antarctic Program (CONMAP) (2020), we estimated that although year-round stations represent 52.6 % of the stations, they house the most of the annual population, i.e. 82.4 % (Fig. 2). Of this total, 35.1 % of the population is housed in the three year-round stations operated by the United States. Such year-round stations have particular importance relative to the occurrence of PPCPs both because they represent permanent point sources and because they support large numbers of habitants. Given the potential PPCPs load discharged from these year-round stations, the kind of wastewater treatment used acquires greater relevance in the management of emerging pollutants in the Antarctic environment.

Fig. 3 shows the Antarctic stations according their facility information (Council of Managers of National Antarctic Program (CONMAP), 2020), spatial distribution from Quantarctica (Matsuoka et al., 2018) and the

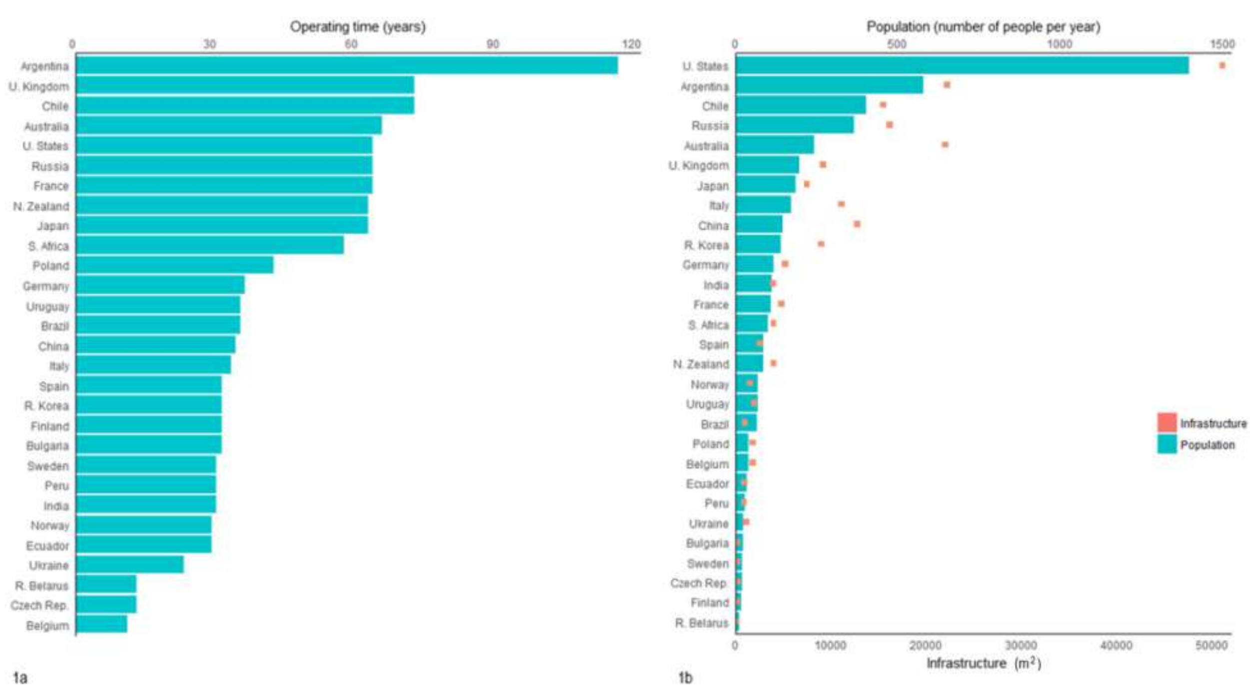

Fig. 1. Operation time and population by country in the Antarctic continent.

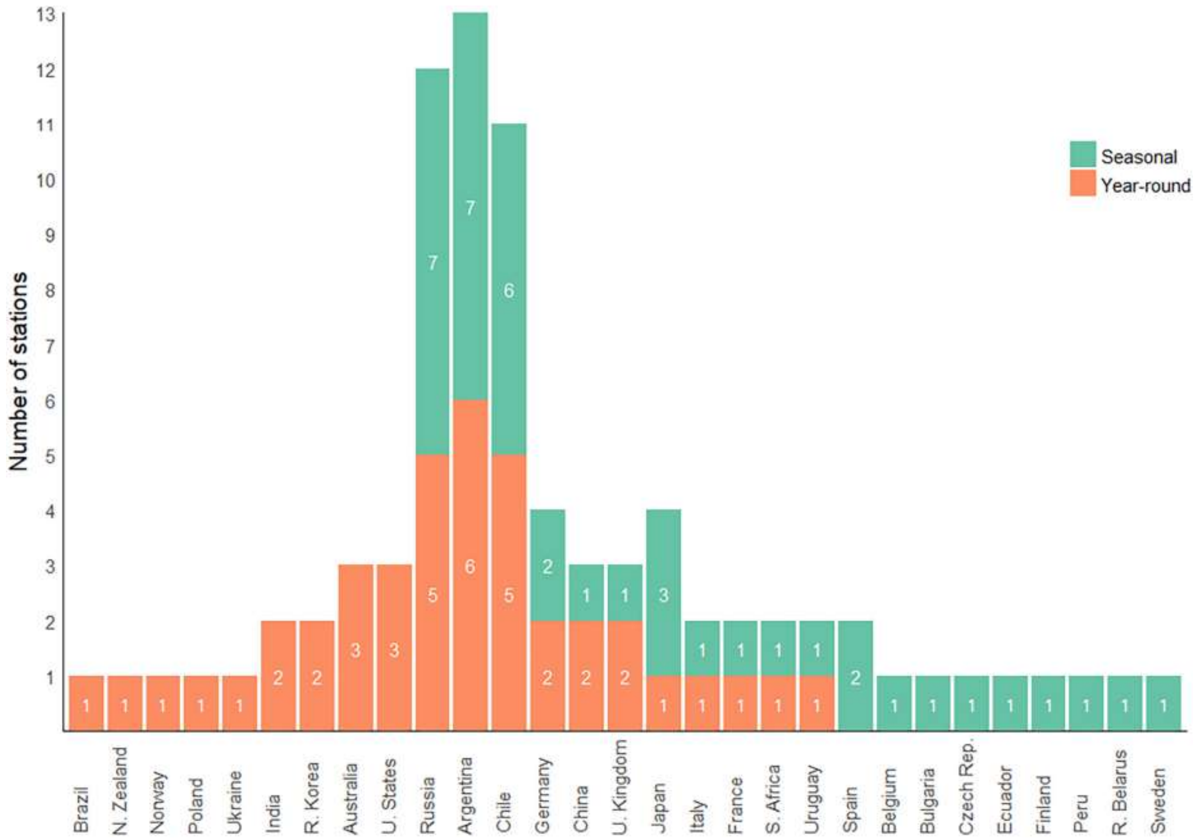

Fig. 2. Number and seasonality of stations by country in the Antarctic continent.

status of their wastewater treatment capacity. Currently, 38 stations reported that they dispose of their effluents directly at sea, of these: 7 do not have treatment, 26 use treatment, 3 use septic tanks and 2 macerations (Fig. 3). Maceration is allowed by the Protocol, nonetheless, Hale et al. (2008) have shown that this process may not deter the entry of chemicals into the Antarctic environment. Likewise, the presence of surfactants in wastewater from septic tanks in samples belonging to the Arctowski station has been confirmed (Szopińska et al., 2021). Due to the state of operation of wastewater treatment systems in the Antarctic, the presence of permanent and unregulated emissions in coastal waters of the continent is probable.

3.2. Occurrence and levels of PPCPs in the Antarctic environment

To the date, only eight studies have been conducted in relation to PPCPs in the Antarctic. Comparatively, it is the Antarctic Peninsula that presents the largest number of studies carried out ($n = 6$) relative to the rest of the continent ($n = 2$) (Fig. 3). These studies have focused upon a variety of compounds, including: analgesics/antipyretics/antiinflammatories, antiasthmatics, antibiotics, antidepressants, antidiabetics, antidiarrheals, antifungals, antihistamines, antimicrobials/disinfectants, anxiolytics, cardiovascular agents, diuretics, fragrances, plasticizers and surfactants, preservatives, synthetic estrogens, UV filters, UV blockers and vasopressors (Fig. 3). Usually, It is verified that the effluents showed the highest concentrations (Fig. 4). Of the set of reported PPCPs there are six that stand out for their high concentrations (>6000 ng l^{-1}), and these were detected in Esperanza base (Argentina) and Scott base (New Zealand) (Fig. 4), these PPCPs belong to the group of analgesics/antipyretics/antiinflammatories, UV filters and surfactants. All the studies were carried out during the austral summer, a common practice in Antarctica due mainly to the restrictions derived from the meteorological conditions and the accessibility for sampling in the peninsula. Thus, most of the studies were carried out during the 2012–2013 season, and permanent monitoring was not reported. This implies a lack of knowledge of the general dynamics of these pollutants due to the absence of reports during the seasons of low temperature. According to the methods used, the researchers basically used two types of analytical techniques based on target analysis via LC-MS/MS TSQ and GC–MS (Table 1). Despite the efforts, shortcomings are still observed, since a large part of the continent does not present basic information about these pollutants, such as coastal areas in the north of the continent.

Interestingly and despite of the high levels of solar radiation (Zeng et al., 2021), few studies have looked for UV filters. UV filters such as 4-methylbenzylidenecamphor (4-MBC), are used in various types of personal care and hygiene products like sunscreens, cosmetic products, and hair-caring products; as well as other materials such as toys, outdoor furniture, textiles, rubber and plastic materials as protective agent (Tsui et al., 2019; Domínguez-Morueco et al., 2021; Gómez-Regalado et al., 2021). In general, prior to entering the Antarctic continent, it has become recommended that the use of UV filters be frequent during the stay, these products being available in all modules of the bases. UV filters can accumulate and expose the food chain (Gago-Ferrero et al., 2012), which, in turn, has potential adverse impacts for both organisms and the ecosystem due to its disruptive capacity observed, for example, in the decrease in fertility and reproduction (Díaz-Cruz et al., 2008; Fent et al., 2008; Kim and Choi, 2014; Astel et al., 2020). Increased worldwide demand for UV filters is associated with high temperatureand irradiance (Magi et al., 2013), and changes in the tourist market (Astel et al., 2020). In Antarctica, it has been observed that certain conditions favor frequent "very large" ozone holes in late spring which enable extreme surface UV events over the Antarctic Peninsula (Cordero et al., 2022). According to Gies et al. (2009), 80 % of the human population in Antarctica is exposed to UV levels above those recommended, and over 30 % reached >5 times the limits.

Another group for which data has been provided are surfactants. Surfactants, such as 4-t-octylphenol (OP), reduce surface tension and are widely used in industrial and domestic processes in a variety of areas such as cleaning, food, metallurgy, pharmacy, medicine, paints, varnishes and mining (Knepper and Berna, 2003; Ivanković and Hrenović, 2010). They have

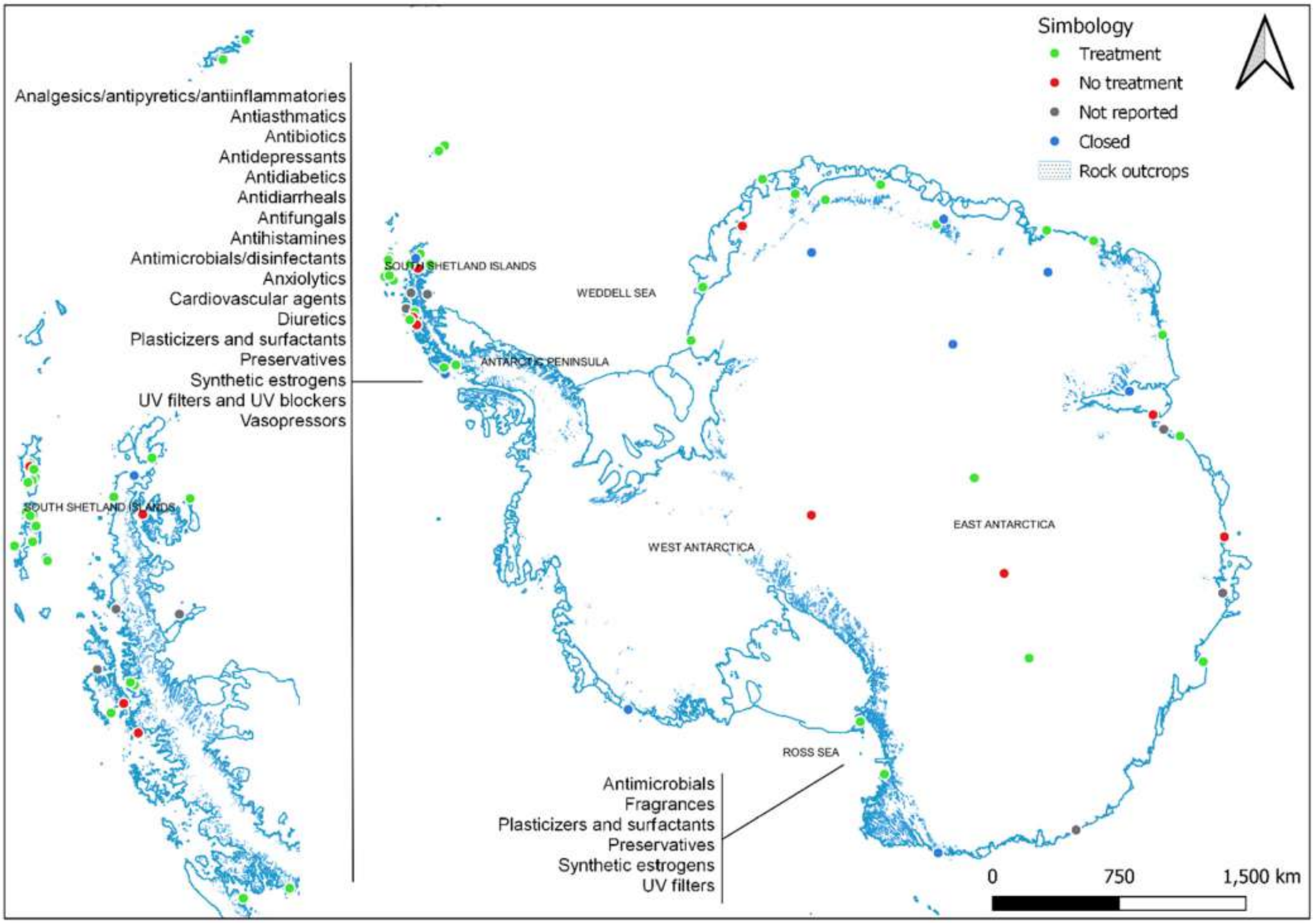

Fig. 3. Status of the treatment system in the Antarctic bases and PPCPs reported in coastal aquatic systems.

toxic effects on aquatic organisms and their release from wastewater can have serious effects on the ecosystem (Ivanković and Hrenović, 2010). As a consequence of the use of UV filters and surfactants, these were detected in the Scott, McMurdo and Esperanza base (Emnet et al., 2015; Domínguez-Morueco et al., 2021). Emnet et al. (2015) observed that WWTP discharge in the Scott Base strongly correlate with population over longer periods, such as the summer research season. This apply for 4-MBC whose concentrations increased steadily throughout the research season (from 321 ng l^{-1} in August to 2130 ng l^{-1} in January) (Emnet et al., 2015). Contrarily, the highest concentrations for OP were observed in August, before the start of the research season in the Scott base (Emnet et al., 2015). This station uses bio-degradation, aerated fixed thin-film bed, centrifuge and filtration to purify water and ozone disinfection since the 2009–2010 season (ATS, 2012; Emnet et al., 2015). Nevertheless, high concentrations were reached for the UV filters, 4-MBC (<11,700 ng l^{-1}) and 2.4-dyhydroxybenzophenone (BP-1) (<6830 ng l^{-1}), as well as the surfactant OP (<7050 ng l^{-1}) during a seven-day study (Fig. 5, Table 1).

4-MBC and BP-1 belong to the stable UV absorbents and are widely used in other personal care products, as well as in the textile industry (Gantz and Sumner, 1957). These UV filters are of concern in human and environmental context because of the potential endocrine-disrupting effects they exert (Nashev et al., 2010; Zhang et al., 2013; Juliano and Magrini, 2017). These high concentrations contrast with those recorded by the same authors during the monthly sampling: 4-MBC: 976–2020 ng l^{-1}, BP-1: 24.3–124 ng l^{-1} and OP: 7.5–39.0 ng l^{-1}. Later, Emnet et al. (2020) recorded even lower values in urban areas for 4-MBC (23.2–428.8 ng l^{-1}), BP-1 (3.6–146.2 ng l^{-1}) and OP (3–205.8 ng l^{-1}), compared to those reported in Antarctica (Table 1). The high concentrations reported by Emnet et al. (2015) exceed even the records in effluents without treatments from Esperanza base, in which Domínguez-Morueco et al. (2021) could not detect 4-MBC, despite high concentrations of BP-1 (1400 ng l^{-1}) (Table 1).

Globally, it has been recognized that the presence of pharmaceuticals in aquatic systems is a growing problem due to the potential consequences that these chemicals can have on aquatic biota at the molecular and population levels (Almeida et al., 2020). In Antarctica, weather conditions and human activities create an environment in which the use of analgesics and anti-inflammatories is commonplace. For example, injuries are frequently reported, however, other issues such as dental problems or disturbances of gastrointestinal tract are also described (Bhatia et al., 2013; Ohno et al., 2018; Olalla et al., 2020), together with a restricted provision of professional health care (Olson, 2002). As a consequence, there is a concomitant increase in the release of analgesics and anti-inflammatories during periods of high human activity. High concentrations for acetaminophen (48,744 ng l^{-1}), diclofenac (15,087 ng l^{-1}) and ibuprofen (10,053 ng l^{-1}) were reported in effluents from Esperanza base (González-Alonso et al., 2017). The hazard quotient values for these pharmaceuticals were over 10 at several sampling points (Fig. 5). The samples were collected during the austral summer of 2012–2013, and at that point this station only had a biological sewage treatment plant, according to the ATS report corresponding to the inspection period 2013 (ATS, 2013c). However, Esteban et al. (2016) indicated that the station did not have a wastewater treatment system at the time of collecting the samples (22 December 2012 and 8 February 2013). Similar concentrations were verified for acetaminophen (>60,000 ng l^{-1}) in effluents without chemical or microbiological treatment in Ny-Ålesund (Choi et al., 2020). The authors indicated that the concentration of the investigated pollutants ranged from 4 to 280,000 ng l^{-1} in the effluent and 2–98 ng l^{-1} in the seawater. At sub-Arctic locations, Huber et al. (2016) confirmed in effluents the presence of diclofenac (597 ng l^{-1})

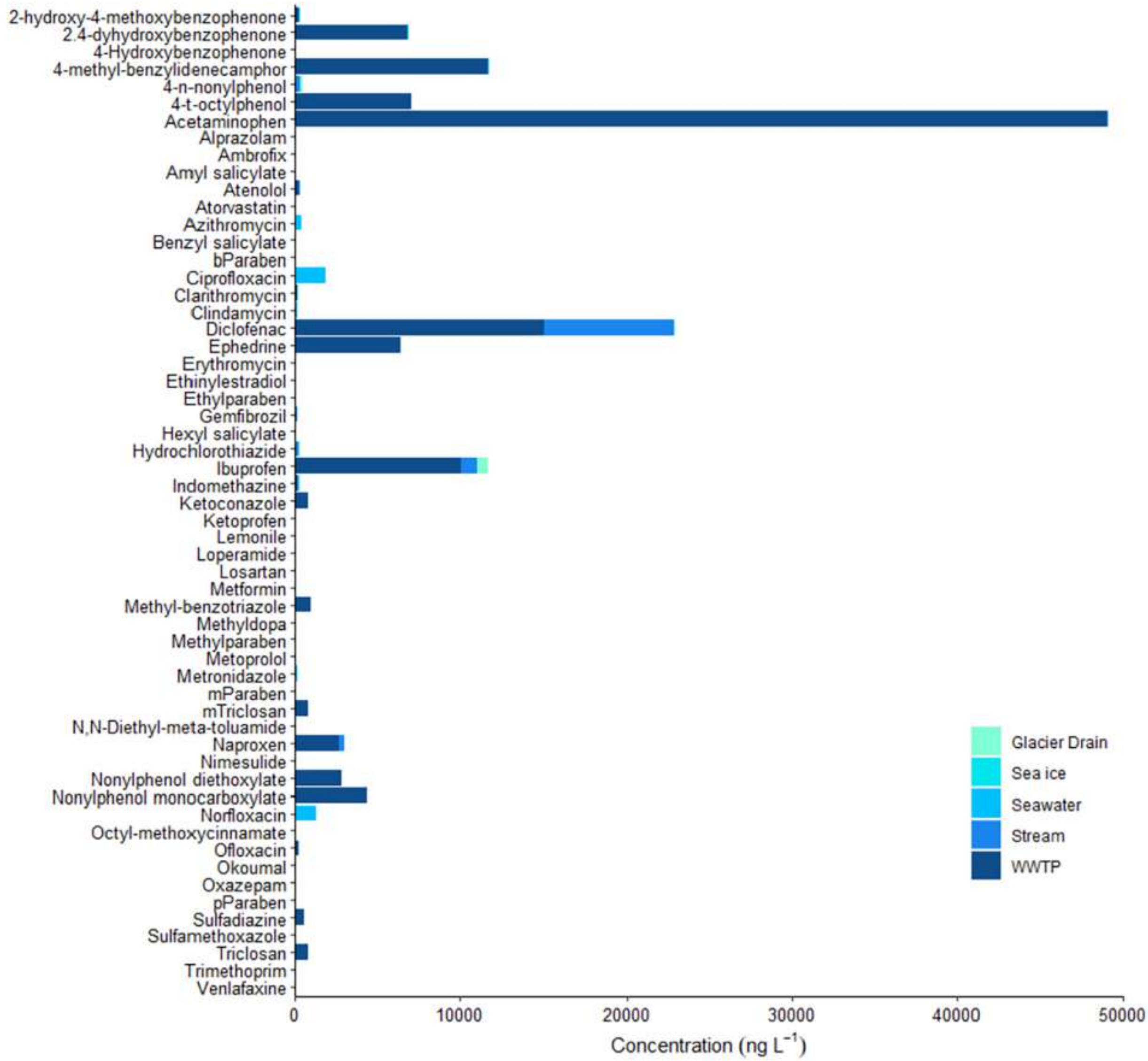

Fig. 4. Pharmaceuticals and Personal Care Products (PPCPs) reported in Antarctic WWTP effluents and water matrices.

at Torshavn, Faroe Islands, despite the presence of 2 and 3-step microbial sludge digestion and filtration. In general, the release of PPCPs is observed despite the implementation of treatment systems, with some of the concentrations reported in Antarctica being higher than those in highly urbanized areas. In this context, the efficiency of removal of WWTPs in the Antarctic region should be demonstrated, and consistency between all of the research stations with respect to the type of treatment used, needs to be implemented in order to reduce the presence and concentration of PPCPs in effluents, in particular in periods of intensive human activity.

3.3. Status and efficiency of WWTPs in the Antarctic

Globally, high removal efficiencies, upwards towards 99 %, have been described for pharmaceuticals after the implementation of 2 and 3-step microbial sludge digestion and filtration (Huber et al., 2016). Up to 95 % of acetaminophen and ibuprofen, for example are removed using a primary physicochemical treatment followed by a secondary biological treatment (Biel-Maeso et al., 2018). Similarly, up to 100 %, 94 % and 48 % removal was shown to occur for ibuprofen, acetaminophen and diclofenac, respectively, using a primary and secondary wastewater treatment with activated sludge, followed by tertiary treatment (Čelić et al., 2019). Pereira et al. (2016) analyzed the effluents from Santos Bay, Sao Paulo, Brazil, reaching lower concentrations of 2094 ng l^{-1} for ibuprofen, 17.4–34.6 ng l^{-1} for acetaminophen and 19.4 ng l^{-1} for diclofenac, using mechanical treatment and chlorination. More homogeneous concentrations were recorded in the effluents of Matosinhos, Portugal, but they did not exceed 300 ng l^{-1}, principally because primary and secondary treatment treated the effluent prior to discharge (Paíga et al., 2015). In contrast, 4-MBC has a low removal which does not exceed 28 % through ozone and 8.2 % through continuous microfiltration (Li et al., 2007). OP achieved 60 % removal rates using a stacked constructed wetlands, that featured vertical and horizontal flow as well as an assembled biofilter (Dai et al., 2017). BP-1 had a removal of 74 ± 22 % in 33 WWTPs across Australia (O'Malley et al., 2020).

Wastewater treatment systems in Antarctica do not easily remove micropollutants since their design, similar to most municipal systems to remove principally nutrients and organic matter (Council of Managers of National Antarctic Program (CONMAP), 2014). For PPCPs, advanced and effective tertiary treatment processes such as sequential UV and ozonation process eliminate most PPCPs, an elimination that does not occur in primary, secondary or biologic treatment (Westerhoff et al., 2005; Sui et al., 2014; Wang and Wang, 2016; Patel et al., 2019). For example, when studying various effluents with different types of treatments, it was confirmed that the lower concentrations of drugs such as diclofenac were the result of the implementation of UV as tertiary treatment, even when the

Table 1
Analgesics and anti-inflammatories, UV filters reported and Plasticizers and surfactants reported in the Antarctic continent (a = Emnet et al., 2015; b = Esteban et al., 2016; c = González-Alonso et al., 2017; d = Domínguez-Morueco et al., 2021).

Analyte	CAS number	Molecular formula	Average mass (Da)	LogKow	LogKoc	Level III fugacity model. half-life (hr)	Matrix	Sampling date	Analytical technique	Location	Concentration (ng l^{-1})
Acetaminophen	103-90-2	$C_8H_9NO_2$	151.16	0.27	1.790	360	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	48744[c]
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	4.02	2.921	900	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	15087[c]
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.28	3.79	2.596	360	Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	10053[c]
4-MBC	36861-47-9	$C_{18}H_{22}O$	254.37	5.92	4.087	1.44e + 003	Effluents	2009	GC–MS	Scott Base.	173–217[a]
								2009	GC–MS	McMurdo Base.	ND[a]
								2012	GC–MS	Scott Base (seven-day monitoring).	3250–11700[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	321–785[a]
										Scott Base (monthly with ozone).	976–2020[a]
								2012–2013		Esperanza Base, Hope Bay.	<LOQ[d]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	42.7–47.5[a]
										Winter Quarters Bay, Erebus Bay.	ND[a]
										Scott Base.	ND[a]
										Cape Evans, Erebus Bay.	ND[a]
							Sea ice	2012	GC–MS	Erebus Bay.	<34.3[a]
BP-1	131-56-6	$C_{13}H_{10}O_3$	214.22	2.96	3.460	360	Effluents	2009	GC–MS	Scott Base.	143–171[a]
								2009	GC–MS	McMurdo.	7.2–7.3[a]
								2012	GC–MS	Scott Base (seven-day monitoring).	265–6830[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	47.1–461[a]
										Scott Base (monthly with ozone).	24.3–124[a]
								2012–2013		Esperanza Base, Hope Bay.	1400[d]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	6.3–10.3[a]
										Winter Quarters Bay, Erebus Bay.	ND[a]
										Scott Base.	1.3–2.6[a]
										Cape Evans, Erebus Bay.	ND[a]
							Sea ice	2012	GC–MS	Erebus Bay.	ND[a]
OP	140-66-9	$C_{14}H_{22}O$	206.32	5.28	4.189	900	Effluents	2009	GC–MS	Scott Base.	101–118[a]
								2009	GC–MS	McMurdo.	ND[a]
								2012	GC–MS	Scott Base (seven-day monitoring).	929–7050[a]
								2012/2013	GC–MS	Scott Base (monthly without ozone).	27.1–4070[a]
										Scott Base (monthly with ozone).	7.5–39.0[a]
							Seawater	2009	GC–MS	Cape Armitage, Erebus Bay.	1.6–1.7[a]
										Winter Quarters Bay, Erebus Bay.	0.3–1.5[a]
										Scott Base.	<1.8[a]
										Cape Evans, Erebus Bay.	0.3–0.5[a]
							Sea ice	2012	GC–MS	Erebus Bay.	0.5–0.9[a]
							Effluents	2012/2013	LC-MS/MS TSQ	Esperanza Base, Hope Bay.	1.13[b]

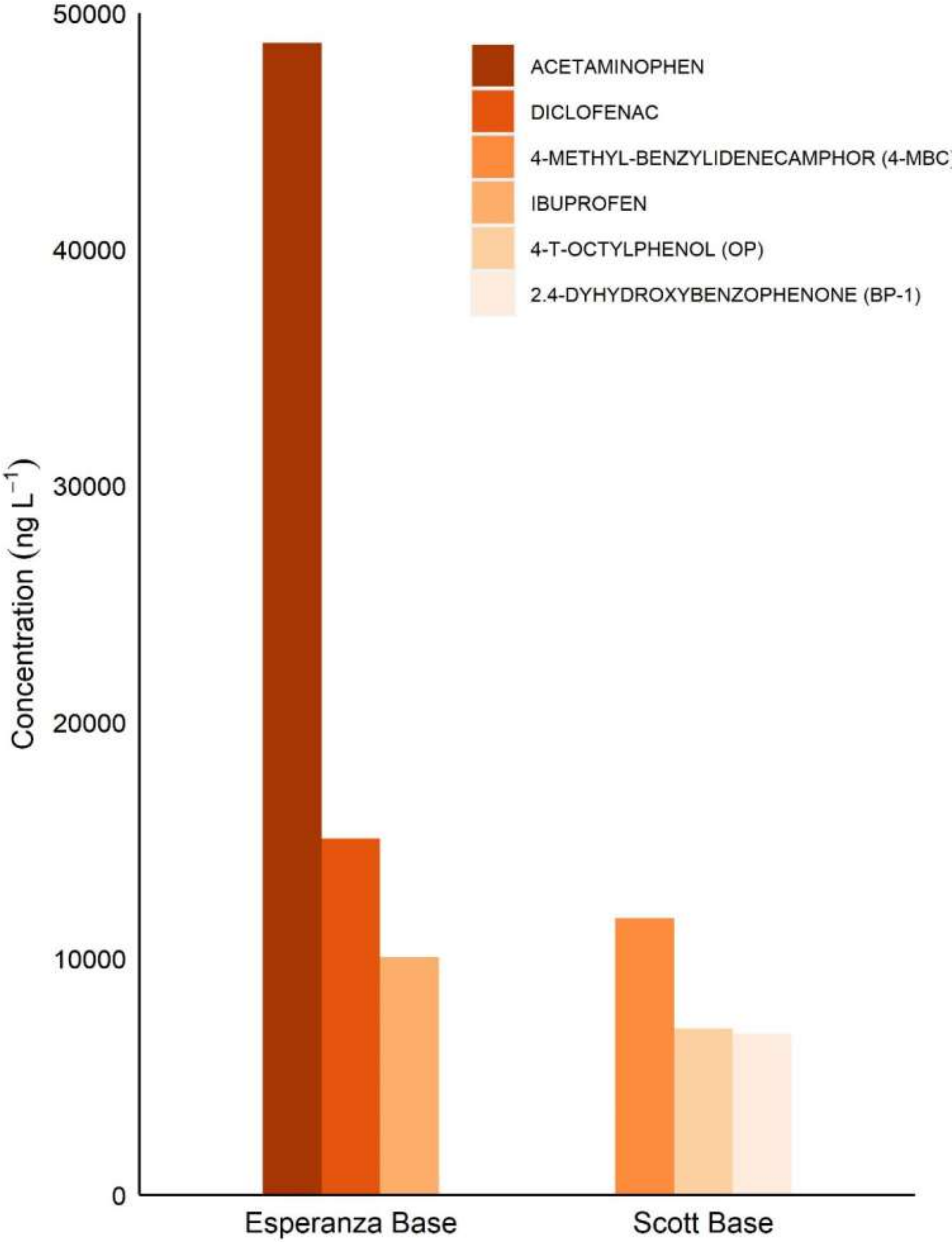

Fig. 5. Maximum levels of pharmaceuticals and Personal Care Products (PPCPs) reported in effluents of Esperanza and Scott bases.

population was substantially larger, 15 times or more (McEneff et al., 2014). However, variations in the concentrations and distribution of pharmaceuticals and UV filters, both in the same geographical areas and in different ones, depend not only on the implementation of treatments, but also on population density, the different uses of PPCPs and the concentrations used (Huber et al., 2016; Emnet et al., 2020). For example, Emnet et al. (2015) reported a reduction did not occur for 4-MBC during January, the research season with the highest floating population, probably due to a high chemical load at that time. This agrees with the study of Astel et al. (2020), in which they verified a high detection of BP-1 during the summer, which may be related to seasonal tourism. In this way, it is observed that the UV filters are not completely removed during the treatments (Li et al., 2007), but rather that their removal is dependent upon their concentration in the effluent. In the six-months monitoring study of Emnet et al. (2015), concentrations of the detected analytes did not correlate with the number of staff on base present at the time of sampling, or with the operating temperature of the WWTP.

3.4. Additional factors influencing the concentration of PCPPs in effluents and coastal waters

PPCPs recorded by different authors in effluents and in coastal waters are highly variable in both chemical diversity and concentration. An argument explaining possible variations is the status and efficiency of the WWTPs in the Antarctic stations. However, additional factors such as geography and human activities may also contribute to the extent of the degree of contamination. Spatially, a pattern of higher concentrations of PPCPs is corroborated in samples such as ocean water, sea ice and sediments, from sites adjacent to WWTPs compared to samples obtained offshore in the Antarctica (Emnet et al., 2015; Vecchiato et al., 2017; Szopińska et al., 2022). The lower concentrations in ocean waters compared to that observed in effluents (Table 1) can be attributed to a dilution phenomenon, which increases towards the offshore, highlighting the important role of currents and water flows in the distribution of pollutants. This phenomenon has also been described in other regions such as Saronikos Gulf, Eastern

Mediterranean Sea; Ebro Delta, Spain; Hong Kong and Japan (Alygizakis et al., 2016; Čelić et al., 2019; Tsui et al., 2019). In this sense, the distribution of PPCPs can be intensified in the coastal zone when the geography presents a closed or semi-enclosed coastal, with high concentrations PPCPs such as pharmaceuticals and UV filters compared to the open sea (Tsui et al., 2015; Biel-Maeso et al., 2018).

Temporarily, high discharge volumes, associated with a rise in the resident population at the field stations during the summer due to increased research activity and tourism generate an intensified discharge of PPCPs into the ecosystem (Emnet et al., 2015; Biel-Maeso et al., 2018; Astel et al., 2020; Emnet et al., 2020). According to data published by the Council of Managers of National Antarctic Program (CONMAP) (2020) and the International Association of Antarctica Tour Operators (IAATO) (2020) the number of tourists is >14 times greater than that of the population occupying the stations. This rapid growth of tourism requires structural, institutional and legislative reforms, especially in the southwest coast of the Antarctic Peninsula, where disembarkation of passengers and marine traffic of tourists has been concentrated, compared to the low tourist activity carried out on the continent (Liggett et al., 2011; Bender et al., 2016; International Association of Antarctica Tour Operators (IAATO), 2018). It has been observed that for some PPCPs such as UV-filters, tourism is less important compared to personnel residing in the bases (Domínguez-Morueco et al., 2021), this because of the accumulation potential of the lipophilic substances in sediments and particulate material. In this sense, Emnet et al. (2015) reported increased concentrations of 4-MBC during research season with a significant increase in concentrations when they carried out daily sampling compared to monthly sampling. Emnet et al. (2015) highlighted that field studies conducted over long periods with low sampling frequencies may fail in assessing short-term fluctuations in concentrations of target analytes. This is due to the loads/flows of waste which are highly variable, and in temporal terms have been characterized by seasonal and even diurnal fluctuations (Council of Managers of National Antarctic Program (CONMAP), 2014). Additionally, during the colder months the efficiency of the treatment systems, which are temperature sensitive, requiring temperatures approaching 25 °C, decreases leading to an possible increase of PPCPs in the effluent (Hedgespeth et al., 2012; Council of Managers of National Antarctic Program (CONMAP), 2014). Furthermore, it has been described that snow and ice act as a reservoir of PPCPs and that their subsequent melting generates pulses of pollutants in the Antarctic environment (Council of Managers of National Antarctic Program (CONMAP), 2014; Vecchiato et al., 2017). González-Alonso et al. (2017) observed the third highest total concentration of drugs, mainly ibuprofen in glacier drain water. The authors indicate that the occurrence of PPCPs in areas of low anthropogenic pressures may be related to sporadic research or touristic activities. In line with Emnet et al. (2015) who reported that the disposal of raw human waste and grey water from field research parties via tidal cracks in the sea ice may be a source of pollutants.

Along with the above mentioned factors, the extensive periods of darkness together with the low temperatures, reduce photodegradation such as biodegradation by bacteria and plankton, extending the persistence of these contaminants (Hedgespeth et al., 2012; Emnet et al., 2015). Also, certain PPCPs do not undergo transformation and can be transported over long distances, making difficult concentration predictions (Alygizakis et al., 2016). For example, BP-1 and OP has been recorded at Cape Evans, Antarctica, 25 km away from their source (Emnet et al., 2015). Biel-Maeso et al. (2018) demonstrated the presence of drugs up to 65 km offshore, indicating that some pharmaceuticals persist within the marine environment.

3.5. PPCPs in Antarctic biota and effects

3.5.1. Feeding strategies and bioaccumulation potential

In general, there is only a limited amount of information regarding the presence and effects of PPCPs on Antarctic organisms. Duarte et al. (2021) detected PPCPs in phytoplankton, the main component in the Antarctic food chain, at Deception Island, Antarctic Peninsula, which could have serious implications for the ecosystem. Emnet et al. (2015) studied the presence of PPCPs in organisms such as *Laternula elliptica* (King, 1832), *Sterichinus neumayeri* (Meissner, 1900) and *Trematomus bernachii* (Boulenger, 1902), mainly benthic marine organisms throughout Erebus Bay. Due to methodological limitations by matrix interferences, only some PPCPs could be quantified and detected within the organisms. Among these, OP was detected within the species *T. bernachii* with concentrations of up to 464 ng g^{-1} l.w. Furthermore, the authors reported the presence of OP in fish collected up to 25 km away, which may be possible due to the mobilization of contaminants through ocean currents or sources not considered.

At a global level, there are a number of published articles that use biota to study pharmaceuticals, UV filters and surfactants, with many of these studies focusing on marine bivalves, particularly the species *Mytilus galloprovincialis* (Lamarck, 1819). Mezzelani et al. (2016) conducted laboratory studies using an exposure dose of 25,000 ng l^{-1} for acetaminophen, diclofenac and ibuprofen, and a field research in Portonovo Bay, central Adriatic Sea. Diclofenac and ibuprofen were measured in mussels *M. galloprovincialis*, both under laboratory conditions (diclofenac: 14.90 ± 7.89 ng g^{-1} and ibuprofen: 1.63 ± 1.00 ng g^{-1}) and in Portonovo Bay (diclofenac: 16,11 ± 14,72 ng g^{-1} and ibuprofen: 9,39 ± 0,59 ng g^{-1}) (Mezzelani et al., 2016). Acetaminophen, in the same study, was not identified in either the field or the laboratory. On the contrary, in *M. galloprovincialis* from Granger Bay, Cape Town, Petrik et al. (2017) verified a degree of bioaccumulation of acetaminophen with concentrations approaching 9 ng l^{-1}, in contrast to diclofenac which was identified in concentrations that were <2.5 ng l^{-1}. However, after a 12-month monitoring of individuals of the species *M. galloprovincialis* and *M. edulis* (Linnaeus, 1758) on the coasts of Ireland, no bioaccumulation was recorded for diclofenac despite the presence of this drug in effluents (<3000 ng l^{-1}) and sea water (<600 ng l^{-1}) (McEneff et al., 2014). Levels in tissues were reported for OP in *M. galloprovincialis* with concentrations up to 10.5 ng g^{-1} d.w. en Thermaikos Gulf, Northern Aegean Sea, Greece (Arditsoglou and Voutsa, 2012). Xu et al. (2016) reported relatively low concentrations in Hong Kong seawaters (1.3–17.5 ng l^{-1}), and an upward trend in sediments (15.8–37.9 ng g^{-1}), addition to the bioaccumulation for species Chinese damsel (*Neopomacentrus bankieri* (Richardson, 1846)) (OP: 34.5–39.9 ng g^{-1}), Chocolate hind (*Cephalopholis boenak* (Bloch, 1790)) (OP: 26.4–40.5 ng g^{-1}), Brown goby (*Bathygobius fuscus* (Rüppell, 1830)) (OP: 84.2 ng g^{-1}) and Green mussel (*Perna viridis* (Linnaeus, 1758)) (OP: 52.6–74.5 ng g^{-1}). However, for its congener *P. canaliculus* (Gmelin, 1791) concentrations exceeded 2000 ng g^{-1} l.w. in Lyttelton Harbour, Christchurch, New Zealand (Emnet et al., 2020). BP-1 showed minimal concentrations in mussels *M. galloprovinciallis*, organisms with a slow rate of biotransformation because intake exceeds metabolism, or involve other metabolic pathways (Gómez-Regalado et al., 2021). 4-MBC bioaccumulated in the species *M. galloprovincialis* and the uptake of waterborne 4-MBC was very rapid, and after only 24 h of exposure to 1 μg L^{-1}, the tissular concentrations were 418 μg kg^{-1} d.w. (Vidal-Liñán et al., 2018).

The Antarctic biota is subject to a heterogeneous habitat and to a stressful environment, including very cold temperatures, which structures the physiology, life history and biodiversity of the organisms living there (Peck et al., 2006; Block et al., 2009). Tests carried out by Freitas et al. (2019), using different temperatures (17 °C and 21 °C) and an exposure to 1 μg L^{-1} of triclosan and diclofenac in individuals of the species *M. galloprovincialis*, seems to indicate that the exposure time at a certain temperature would be relevant for the bioaccumulation of PPCPs. Dermal absorption should not be ruled out as it has been described as the main route of exposure to PPCPs in aquatic organisms (Ghosh et al., 2021). The dermal uptake of synthetic musks has been demonstrated, being the lipophilic substances the ones that have the highest absorption (Daughton, 2007; Zhang et al., 2017). Additionally, the biology of the species is fundamental to the bioaccumulation of these pollutants. According to Block et al. (2009), antarctic organisms have developed a series of strategies to take advantage of resources during the austral summer through synchronization. For example, it has been described that the species

L. elliptica hides its siphon under the sediment during the austral winter, with a reopening during the austral summer during the chlorophyll peak, a time when it also spawns (Brockington, 2001; Ahn et al., 2003). In this sense, species having seasonal feeding strategies would not be directly exposed during the winter months. Additionally, through the use of isotopes in sediments and biota in the vicinity of the McMurdo station, it was found that the species *L. elliptica*, did not have assimilate in proportion to its exposure to wastewater, probably due to their non-generalist diet (Conlan et al., 2006). In contrast to L. *elliptica*, the sea urchin *S. neumayeri*, a generalist feeder, showed an assimilation proportional to the input of wastewater in the benthos (Conlan et al., 2006). Low assimilation was observed for *T. bernachii* compared to other general consumers of benthos such as *S. neumayeri*, which may be due both to a low number of samples and to the analysis of a tissue different from that of the other species analyzed, since this species has a generalist diet (Conlan et al., 2006). Generally, feeding specialists exhibit lower concentrations of pollutants compared with generalist species (McLeod et al., 2014; Pinzone et al., 2019; de Mesquita et al., 2021).

3.5.2. Exposure and effects on biota

Regarding the risks of PPCPs, Olalla et al. (2020) determined that the analgesics/anti-inflammatories acetaminophen, ibuprofen and diclofenac present the highest environmental risks to the Antarctic Peninsula, as these substances exceeded the threshold considered to be “high risk” by up to 100-fold at wastewater discharge. Also, Tsui et al. (2015) suggested that UV filters pose higher potential risks to benthic communities during periods with stronger UV radiation when usage is higher (Tsui et al., 2015). The combined effect of mixtures of UV filters in sunscreens agents is so far largely unknown (Domínguez-Morueco et al., 2021). Domínguez-Morueco et al. (2021) and Olalla et al. (2020) did not observe environmental risk for UV filters, but given their possible oestrogenicity and their capacity for accumulation, they should be monitored continuously given their widespread use in Antarctica. Due to the paucity of information available, the eventual effects and risks of unmonitored PPCPs in the Antarctic ecosystem are unknown. This is alarming as the predominant source of PPCPs is direct discharge into the sea. Compared to terrestrial and intertidal Antarctic systems, this habitat has been described as having great richness and diversity, reaching >8100 species, and some phyla represented at levels greater than global averages (Peck et al., 2006; De Broyer and Danis, 2011). Given this scenario, the number of new species recently described (López-González, 2020; Pinheiro et al., 2020; Buskowiak and Janussen, 2021; Maggioni et al., 2022) makes the impacts of PPCPs even more uncertain. This is particularly true for benthic fauna, described by De Broyer and Danis (2011), accounting for 88 % of the total species. In addition, there is an information bias in this taxonomic group, because according to Griffiths (2010) the monitoring is carried out on the platform, to the detriment of the knowledge of the deep-sea marine fauna. The combination of very poor functional scopes, with slow rates of adaptation and restricted available dispersal ranges make Antarctic marine species among the most susceptible to environmental change (Peck et al., 2004).

Most Antarctic biotas are exposed to multiple stresses and considered vulnerable to environmental change due to narrow tolerance ranges, rapid change, projected circumpolar impacts, low potential for timely genetic adaptation, and migration barriers (Gutt et al., 2021). In gastropods of the species *Phorcus lineatus* (da Costa, 1778), chronically exposed to acetaminophen, significant increased the catalase and cholinesterase activities, thus, extrapolation of this results to phylogenetically close species may account for similar endpoints (Almeida and Nunes, 2019). Duarte et al. (2021) indicate that the diversity and concentrations of PPCPs in the Antarctica may lead to strong pressures on the marine food web with severe consequences for the whole ecosystem trophic structure. Impacts of climate change on Antarctic biodiversity will likely vary for different communities and depend on species range (Rogers et al., 2020). Coastal communities and those of sub-Antarctic islands, especially range-restricted endemic communities, will likely suffer the greatest negative consequences of climate change (Rogers et al., 2020). The climate of the Western Antarctic Peninsula is the most rapidly changing in the Southern Hemisphere, with a rise in atmospheric temperature of nearly 3 °C since 1951 (Meredith and King, 2005). Marine species in this region have extreme sensitivities to their environment, with population and species removal predicted in response to very small increases in ocean temperature (Meredith and King, 2005). In addition, this region has an important breeding and nursery ground for Antarctic krill is stablished, a key species in the Southern Ocean food web, highly susceptible to environmental changes modifying its abundance, distribution and life cycle (Meredith and King, 2005; Flores et al., 2012). Due to the influence of climate change and intense industrial fishing, this region is a priority area for Marine protected areas (MPAs), as per the Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR) (Sylvester and Brooks, 2020). However, some CCAMLR members make it difficult to approve MPAs, so political and economic interests cast a shadow on international negotiations about adaptation strategies such as fisheries closure and the establishment of MPAs (Wendebourg, 2020; Teschke et al., 2021). Despite the above, Antarctica is not only facing these pressures, but also the Southern Ocean waters are among the most vulnerable to ocean acidification (Hancock et al., 2020). In ecological terms, Duffy et al. (2017) have been described that the Antarctic Peninsula and the islands of the Southern Ocean could have less effective barriers for the establishment of non-native species. If predicted warming occurs in the shallows around the Antarctic Peninsula region, native marine species may change in geographic and bathymetric range and/or become less competitive within parts of these ranges, facilitating the establishment and spread of any non-native species (Hughes et al., 2020).

4. Conclusions

The human population that has settled in Antarctica has contributed to the occurrence of widespread pollutants such as PPCPs, and the pattern of concentration of these compounds dependent upon whether each base is permanently or intermittently populated. In this way, wastewater management plays a key role in the eventual PPCPs loads in coastal marine waters and the exposure of organisms that live therein. In general, the concentrations of PPCPs in this environment, seem to be more influenced by the implementation or absence of wastewater treatment and the quality of the treatment, and less influenced by the annual number of people permanent living there. Although there are diffuse sources such as pulses of pollutants from melting ice, the highest concentrations of PPCPs were reported in point sources from the effluents, which shows a phenomenon similar to that described in other regions of the planet. The highest concentrations were reached for pharmaceuticals at the Esperanza base, which lacks treatment for its wastewater during field sampling. On the other hand, the implementation of treatment systems appears to be inefficient, since UV filters and surfactants were verified in Scott base probably due to the low removal efficiency and high persistence of these PPCPs. This is important considering that most of the stations are located in the coastal zone, being able to release their effluents without treatment directly at sea. Therefore, treatment systems, capable of withstanding fluctuations in the number of personnel, should be considered in the absence of appropriate legal regulations for wastewater discharge in the requirements of the Environmental Protocol to the Antarctic Treaty. The increasing of tourism in the region should be also evaluated in order to identify how anthropogenic pressure in the region contributes to temporal and spatial concentrations of PPCPs.

Information regarding wastewater treatment systems tends to be inaccessible, but where it exists, it is fragmented, scarce and in some cases outdated. This leads to a partial and unrealistic view of the risk to which the continent is subjected. Furthermore, information bias was verified due to the lack of studies in some groups of PPCPs. In this unfavorable scenario, the scarcity of studies of PPCPs in Antarctica can generate an underestimation of the concentrations, which could be even higher than those reported, to the detriment of an adequate understanding of the distribution and effects on the coastal aquatic ecosystems of Antarctica. Further, biota has been poorly studied, therefore, the possible bioaccumulation and effects are unknown, especially in benthic organisms surrounding effluents. It is suggested the implementation of a control of the PPCPs that enter the continent during the entry of people both by national and tourist operators, due the difficulties of the functioning of the treatment systems and the low removal of some types of treatment. This is particularly true for bases that do not have a treatment system. It is recommended to carry out research efforts in areas intervened by human activity with the presence of protected areas to generate mitigation measures to the possible impacts not currently studied.

CRediT authorship contribution statement

Alessandra Perfetti-Bolaño: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization, Funding acquisition. **Katherine Muñoz**: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration. **Alan S. Kolok**: Writing - Review & Editing. **Alberto Araneda**: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration. **Ricardo O. Barra**: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

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

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