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## Binational survey of personal protective equipment (PPE) pollution driven by the COVID-19 pandemic in coastal environments: Abundance, distribution, and analytical characterization

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### ABSTRACT

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In the present contribution, two nationwide surveys of personal protective equipment (PPE) pollution were conducted in Peru and Argentina aiming to provide valuable information regarding the abundance and distribution of PPE in coastal sites. Additionally, PPE items were recovered from the environment and analyzed by Fourier transformed infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) with Energy dispersive X-ray (EDX), and X-ray diffraction (XRD), and compared to brand-new PPE in order to investigate the chemical and structural degradation of PPE in the environment. PPE density ( $\text{PPE m}^{-2}$ ) found in both countries were comparable to previous studies. FTIR analysis revealed multiple polymer types comprising common PPE, mainly polypropylene, polyamide, polyethylene terephthalate, and polyester. SEM micrographs showed clear weathering signs, such as cracks, cavities, and rough surfaces in face masks and gloves. EDX elemental mapping revealed the presence of elemental additives, such as Ca in gloves and face masks and AgNPs as an antimicrobial agent. Other metals found on the surface of PPE were Mo, P, Ti, and Zn. XRD patterns displayed a notorious decrease in the crystallinity of polypropylene face masks, which could alter its interaction with external contaminants and stability. The next steps in this line of research were discussed.

## 1. Introduction

The COVID 19 pandemic has generated drastic changes in our daily lives, such as using face masks and other types of personal protective equipment (PPE) to slow down the transmission rate of the SARS-CoV-2 virus. Under this context, plastic production worldwide has increased considerably and, thus, long-term goals to secure the sustainability of fighting the pandemic are required (Ahmadifard, 2020). Mitigation strategies are being implemented. However, it was recently estimated that 11% of plastic waste generated globally (2016) entered the aquatic environment (Borrelle et al., 2020). Particularly, medical waste has grown up to 370% and packaging plastic demand up to 40% in some countries like Spain and China (Patrício Silva et al., 2021). The huge increase in plastic waste is overloading the capacity of the countries to manage it properly (Singh et al., 2022; Kalina and Tilley, 2020). Prata et al. (2020) estimated that 129 billion face masks and 65 billion gloves are used globally each month during the pandemic, leading to widespread plastic pollution. For this reason, large volumes of PPE waste have been generated and inadequately discharged during this pandemic (Mekonnen and Aragaw, 2021; De-la-Torre and Aragaw, 2021). This type of waste has become a severe environmental concern since it has been evidenced in rivers, beaches, coasts, lakes, and cities worldwide (Ardusso et al., 2021; Akhbarizadeh et al., 2021a; Ben Haddad et al., 2021; Okuku et al., 2020; Rakib et al., 2021; Thiel et al., 2021), potentially representing a new major type of plastic pollution.

PPE waste, particularly face masks, has impacted directly on wildlife since this waste can entanglement or be ingested by seabirds, mammals, and penguins, among others (Hiemstra et al., 2021). Also, they may leach pollutants with ecotoxicological effects, such as heavy metals (e.g., Cd, Pb), plastic additives (phthalate esters), organic contaminants, nanoparticles (NPs) (Ag and Cu) from the face masks, gloves, and wipes during their degradation in the environment (Kutralam-Muniasamy et al., 2022; Sullivan et al., 2021; Chen et al., 2021). On the other hand, this type of waste (in particular, face masks) could contaminate water bodies with the SARS-CoV-2 virus because these materials can be hosting sites for viruses and microorganisms (Tran et al., 2021) and be colonized by marine macroinvertebrates present in the water column (De-la-Torre et al., 2021a).

Most importantly, early observations of face masks pollution suggest that, due to the structural characteristics of the polypropylene (PP)-based material, the layers of most surgical face masks are prone to release microfibers (Aragaw, 2020; Fadare and Okoffo, 2020). Several studies have demonstrated the leaching of secondary micro/nanoplastics (MPs/PNPs) from face masks (Il Kwak and An, 2021). Depending on several factors, the release of MPs (< 5 mm) has been estimated to reach about 2230 MPs per mask, and more than  $2.43 \times 10^9$  PNPs (<1  $\mu\text{m}$ ) per mask (Ma et al., 2021). These plastic particles are widely known for their ubiquity in the environment, including water bodies, soil, sediment, atmosphere, and cryosphere (Dobaradaran et al., 2018; Akhbarizadeh et al., 2021b; Bergmann et al., 2019; Dioses-Salinas et al.,

2020; Torres and De-la-Torre, 2021), organisms from multiple taxa (Villagran et al., 2020; Hall et al., 2015; Meaza et al., 2021; Ory et al., 2018), mostly due to accidental ingestion, and foods and consumer goods (De-la-Torre, 2020; Barboza et al., 2018; Akhbarizadeh et al., 2020; Li et al., 2015). The ecotoxicological effects of MPs/PNPs have been demonstrated in multiple studies, and are generally associated with oxidative stress, cytotoxicity, neurotoxicity, behavioral changes, among other sublethal effects during the early stages of the development of model organisms (Webb et al., 2020; Kim et al., 2021; Prokić et al., 2019). Since PPE waste and its subproducts (MPs/PNPs) are threatening the well-being of aquatic and terrestrial organisms, it is imperative to investigate its reach (abundance and distribution), sources, and fragmentation in the environment under the current unprecedented scenario.

The presence and abundance of PPE waste have been reported in some coastal cities of South America during the first months of the COVID-19 pandemic. In particular, one study reported the abundance of face masks along the coast of Chile, while discussing the influence of COVID-19 infrastructure (signposts for PPE, PPE-specific bins, etc.) (Thiel et al., 2021). Other studies have quantified PPE pollution in very specific sites/cities rather than executing a broader survey (Gallo Neto et al., 2021; De-la-Torre et al., 2021b). However, no previous study has analytically characterized the collected PPE items to better understand their degradation in the environment. Aiming to provide a better understanding of the current situation regarding PPE pollution, including its abundance, distribution, and sources, as well as their chemical composition and effects of weathering conditions, in the present study we have conducted two nationwide surveys of PPE pollution in beaches of Peru and Argentina. The density and characteristics of littered PPE were described, and their possible sources were discussed. Also, a subsample of different types of PPE was recovered and analyzed by Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) with Energy dispersive X-ray (EDX), and X-ray diffraction (XRD), which provide further insights concerning their chemical composition, degradation in the environment, generation of MPs, and, ultimately, impact on the environment.

## 2. Materials and methods

### 2.1. Area of study

#### 2.1.1. Peru

Peru is located on the western coast of South America facing the Pacific Ocean and extending ~2250 km. The latest census (2017) reported a total population of 31.2 million, out of which 79.3% were living in urban cities or towns, while the remaining were in rural areas (INEI, 2018). Peru is administratively divided into 24 regions and subdivided into provinces. The capital of Peru (Lima) is an overpopulated metropolitan city located on the central coast of Peru with a population reaching almost 30% of the total population of Peru. The Peruvian

current system consists of one oceanic current (Peru current) that flows from south to north, one coastal branch (Peru Coastal Current), and the Peru-Chile Countercurrent flowing in the opposite direction between the two previous currents. Additionally, a subsurface current flows from north to south (Peru Undercurrent), fed by the Equatorial Undercurrent (Cabarcos et al., 2014).

Numerous beaches along the coast of Peru are popular tourist destinations and important grounds for artisanal and industrial fishing (Velez-Zuazo et al., 2021) and are home to coastal nature reserves. However, solid waste management across the country is very poor, mainly consisting of open dumpsites and a limited number of certified controlled landfills (Walmsley et al., 2018). Particularly, marine litter and microplastic pollution have been evidenced along the coast of Peru (De-la-Torre et al., 2020a, 2020b, 2021a; Santillán et al., 2020), which may be associated with poor coastal management and environmental awareness.

A total of 36 coastal sampling sites were selected in Peru (Table S1). The selected sites were well distributed along the coast and were representative of different coastal activities (tourism, recreational, fishing activities, or no specific activity) and proximity to highly urbanized/populated cities. Most of the fishing activities in coastal areas are small-scale or artisanal. Some beaches are well-known tourist destinations, while others are less popular. Regardless, recreational activities (bathing, aquatic or sand sports, gastronomic activities, among others) are mostly carried out. By the time the sampling campaign was carried out, most beaches were open to the public. However, the number of beachgoers (either local or tourists) was likely limited compared to previous years due to the COVID-19 pandemic restrictions (limited tourism and traveling with limited capacity). Some beaches had incorporated signposts indicating recommendations on the disposal of PPE-related waste, as well as the measures to prevent the transmission of the virus (e.g., wearing face masks, social distancing, etc.). The sites where no activity was carried out were observed to be less popular, of hard access or remote, or were highly contaminated, which made them less appealing to visitors. The categories assigned to each sampling site were based on observations, as specific activities are not enforced. Thus, the activities are not mutually exclusive and, in some sites, both touristic/recreational and fishing activities were carried out simultaneously. A site in Punta San Juan, which belongs to the Guano Islands, Islets, and Capes National Reserve System, was evaluated to determine whether coastal nature reserves were impacted by PPE. In addition to coastal sites, an urban canal in Lima was monitored for PPE. This canal directly feeds the lagoons and marshes of the Pantanos de Villa Wildlife Refuge (PVWR), a protected area within the overpopulated city of Lima.

### 2.1.2. Argentina

Argentina is located in the southern half of South America. It shares the bulk of the Southern Cone with Chile to the west and is also bordered by Bolivia and Paraguay to the north, Brazil to the northeast, Uruguay and the South Atlantic Ocean to the east, and the Drake Passage to the south. Argentina is a federal state, and it comprises 23 provinces and one autonomous city, Buenos Aires. The country's capital is the Autonomous City of Buenos Aires (CABA) located in the province of Buenos Aires. CABA together with 40 municipalities makes up the Buenos Aires Metropolitan Area (AMBA), which is the second-largest metropolitan area in South America after São Paulo (Mendiola and González, 2021). According to the National Institute of Statistics and Censuses (INDEC, 2021), as of 2021, the total estimated population of Argentina is about 45,808,747 inhabitants, where around 92% of their population live in cities or urban areas (INDEC, 2021; UNHABITAT, 2021). In particular, around 33% of the total population of Argentina live in AMBA (Mendiola and González, 2021).

Argentina has around 11,235 km of the Antarctic coastline and Austral islands, and 5117 km of the American coastline, out of which 537 km comprise a coastline of Rio of Plata (borders with Uruguay), and 4725 km corresponding to Atlantic littoral coastline (part of Buenos

Aires province and the provinces of Río Negro, Chubut, Santa Cruz, and Tierra del Fuego) (INDEC, 2017). Due to this long coastline, the tourism industry in summer is an essential item to some coastal areas of Argentina because it is the primary source of income, such as beaches of Buenos Aires Province (e.g., Monte Hermoso, Pehuén-Co). Around 70% of Argentine tourists go to the Atlantic coast of this province (Schlüter, 2001).

On the other hand, the Patagonia coasts and beaches are other popular destinations in Argentina due to fauna reserves, gastronomic activities, national parks, and exotic landscapes (glaciers). For the present study, we sampled beaches and coastal environments in the Northern, middle, and Southernmost parts of Argentina (Table S2). The North East and South West of the Buenos Aires province present a higher population density. Also, beaches located in the middle of the province have an intermediate population, and beaches or coastal environments at the southernmost part of the country present lesser inhabitants. Different services such as tourism, sport, and recreational activities, and artisanal fishing are prevalent in these coastal areas. Coastal cities such as Monte Hermoso and Pehuén-Co, and Rio de la Plata area in AMBA of the Buenos Aires province are beaches famous in the summer season while Puerto Madryn, Ushuaia, and Rio Grande cities are popular tourist destinations all year due to their beautiful landscape and national parks. In particular, many cruise ship tourists arrive in Ushuaia in summer to visit Beagle Channel, and Tierra del Fuego National Park, among other attractions. However, the COVID-19 pandemic affected the touristic and recreational activities in these coastal areas generating economic losses in the coastal cities. To mitigate the negative economic impacts in coastal cities due to the closure of most beaches in Argentina by the pandemic, some regional governments took measures to reopen the beaches such as limiting the number of tourists, practicing social distancing, the use of PPE, tourist accommodation protocols, among other measures for human life protection (Fig. S3).

### 2.2. Sampling strategy

A single sampling campaign involving both countries was carried out from the start of the Fall (March) to Winter (July) seasons of 2021. The sampling methodology followed previous studies conducted on the beaches of Bangladesh and Morocco (Ben Haddad et al., 2021; Rakib et al., 2021). In brief, a sampling area that covered the whole extent of the beach (from the low-tide line to the upper beach limit) was determined in each site and several transects (parallel to each other) separated by 8–10 m were established in order to visually cover all of the beach areas. PPE items were identified by the naked eye while walking along each transect and recording the find. The findings were categorized as either face mask, glove, face shield, hazmat suit, or bouffant cap. Several PPE items were carefully handled and stored in zip lock bags to be transported to the laboratory. The PPE density ( $C$ ,  $\text{PPE m}^{-2}$ ) in each sampling site was calculated as described by (Okuku et al., 2020):

$$C = n/a$$

Where  $n$  is the number of PPE items and  $a$  is the sampled area ( $\text{m}^2$ ). The sampling area was estimated using Google Earth (<https://www.google.com/earth/>). One of the urban canals that feed the PVWR was sampled by walking along the bank for 680 m. PPE items were counted if they were in contact with the water stream or up to  $\sim 2$  m from the berm into the vegetation. In this case, PPE density was expressed in  $\text{PPE m}^{-1}$ .

### 2.3. FTIR analysis

A subsample of PPE waste ( $n = 7$ ) found in the coastal areas of both countries was selected to be analyzed by Fourier-transform infrared (FTIR) spectroscopy (PerkinElmer Spectrum Two™) in transmittance mode and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy using a Nicolet iS5 spectrometer (Thermo Fisher)

equipped with an iD7 ATR module. To evaluate PPE waste with FTIR spectroscopy (transmittance mode), face masks were cut open and each layer was evaluated separately. A face shield was separated into a headband frame and visor (or shield). A square was cut from the fabric (face masks) and visor (face shield) and dried at 50–60 °C for 30 min to reduce moisture. In the case of the headband frame, a section was cut into small pieces and pressed into a pellet with KBr. The readings were carried out in transmittance mode at wavelengths between 500 and 3500  $\text{cm}^{-1}$  at a resolution of 8  $\text{cm}^{-1}$  (De-la-Torre et al., 2021a). The adsorption bands were analyzed manually to determine the presence of several functional groups and suspected polymer identities. For ATR-FTIR spectroscopy, the spectra were recorded between 500  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution. The obtained spectra from each PPE waste analyzed were automatically compared with the reference spectra of pure polymers in order to identify the type of material from which they are made.

#### 2.4. SEM/EDX

A Scanning Electron Microscope (SEM) coupled with an energy dispersive X-ray analyzer (EDX) (dual-stage ISI DS 130 with EDAX 9600) was used to examine the elemental composition and surface of some of the PPE ( $n = 5$ ) found in coastal areas with their respective patterns (brand new PPE). Fragments of three face masks and one glove were placed over an aluminum tape on an SEM holder and covered with gold before analysis, following the conditions described by Forero López et al. (2021).

#### 2.5. XRD

X-ray diffraction analysis was used to detect the changes of crystallinity of polymers due to aging in the environment or for the identification of NPs on the surface of face masks. X-ray Diffraction data were collected using a PANalytical Empyrean 3 diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation and a PIXcel<sup>3D</sup> detector. It was operated at a voltage of 45 kV and a current of 40 mA. The data were collected using a continuous scan mode with a divergence slit of  $1/2^\circ$  and a scan angular speed of  $0.042^\circ/\text{s}$  for the  $2\theta$  range  $20^\circ \leq 2\theta \leq 70^\circ$ .

#### 2.6. Data and statistical analyses

The results were expressed in terms of PPE density ( $\text{PPE m}^{-2} \pm \text{SD}$ ). Each sampling site was georeferenced, and the resulting PPE density was classified in 5 density ranges determined by the natural breaks method (ArcMap) for Peru and Argentina separately. Then, two maps displaying the results were constructed using ArcGIS 10.7. The assumption of normality of the datasets was invalidated (Shapiro-Wilk test,  $p < 0.05$ ) before statistical analysis. Thus, nonparametric tests were carried out. To determine the correlation between the independent variables 1) city/province total population (population) or 2) population density (population  $\text{km}^{-2}$ ) and the dependent variables 1) total PPE or 2) PPE density, four Spearman correlation tests were performed for the datasets of Peru and Argentina independently. To compare the PPE density between activities (recreational/tourism, fishing, none, and nature reserve), a Kruskal-Wallis test was conducted for the dataset of Peru. The latter test was not conducted with the dataset of Argentina because specific activities were very similar across sampling sites. Additionally, multi-dimensional scaling (MDS) graphs based on Euclidean distances were created to visually analyze the PPE density and total PPE (including different PPE types) based on activities and population density. The level of significance was set to 0.05. The Shapiro-Wilk, Spearman, and Kruskal-Wallis tests and graphs (box and scatter plots) were conducted in GraphPad Prism (version 8.4.3 for Windows). MDS graphs were performed in PRIMER 6 + PERMANOVA.

### 3. Results

#### 3.1. PPE occurrence, abundance, and distribution

A total of 462 PPE items were identified in 36 sampling sites along the coast of Peru. PPE items occurred in 91.7% of all sampling sites. The mean PPE density was  $6.60 \times 10^{-4} \text{ PPE m}^{-2}$  (range of  $0.00\text{--}5.01 \times 10^{-3} \text{ PPE m}^{-2}$ ) (Fig. 1a). Face masks represented 94.5% of all PPE items, followed by face shields (2.9%), and gloves (2.0%) (Fig. 1b). Only two bouffant caps and one hazmat suit were found. In the urban canal that feeds the lagoons and marshes of the PVWR, a total of 135 PPE items were found, which translates into about  $0.20 \text{ PPE m}^{-1}$ . Face masks were the main type of PPE (89.6%), followed by face shields (6.7%), bouffant caps (2.2%), and gloves (1.5%).

In Argentina, a total of 43 PPE items were identified in 15 sampling sites. Unlike Peru, PPE items occurred in 66.6% of all sites, but presented a slightly higher mean density ( $7.21 \times 10^{-4} \text{ PPE m}^{-2}$ ) ranging from 0.00 to  $5.60 \times 10^{-3} \text{ PPE m}^{-2}$  (Fig. 1a). Face masks and gloves were identified equally (48.8% each), and a single face shield was found (Fig. 1b). The distribution of PPE densities among sampling sites was displayed in nationwide maps (Fig. 2).

Spearman tests showed no significant correlation ( $p > 0.05$ ) between any of the predictor variables (total population and population density) and the response variables (total PPE and PPE density) evaluated with the dataset of Peru (Fig. 3). In the case of Argentina, the total PPE was positively correlated with the total population ( $p = 0.0434$ ) and inversely correlated with the population density ( $p = 0.0054$ ). However, data are very dispersed, and the Spearman coefficient value is very low, which indicates a low correlation (Fig. 4).

PPE densities were grouped based on the main activities carried out in each sampling site. The boxplot diagram displays individual values in each activity (Fig. 5). No significant differences were found among sampling sites (Kruskal-Wallis test,  $p > 0.05$ ). Differences in PPE density among activities were not tested for the datasets of Argentina because all the sampling locations presented similar activities. In the MDS graphs (Fig. S1), no clear pattern was observed. Individual values were dispersed and very close to each other regardless of the activity or population density level (predictor variables).

#### 3.2. FTIR results

The different components/layers of three face masks (1 white surgical and 2 cloth face masks) and one face shield were analyzed by FTIR spectroscopy. The surgical face mask was composed of two layers. In

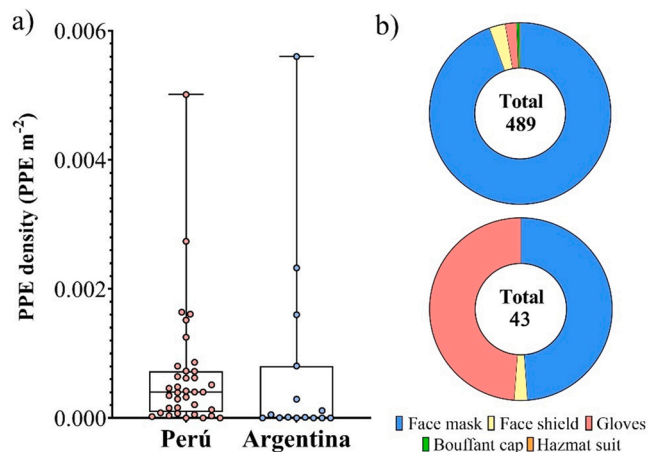


Fig. 1. (a) Boxplot displaying individual PPE densities across sampling sites in Peru and Argentina. (b) Pie charts displaying the contribution of different types of PPE items in Peru (top) and Argentina (bottom).

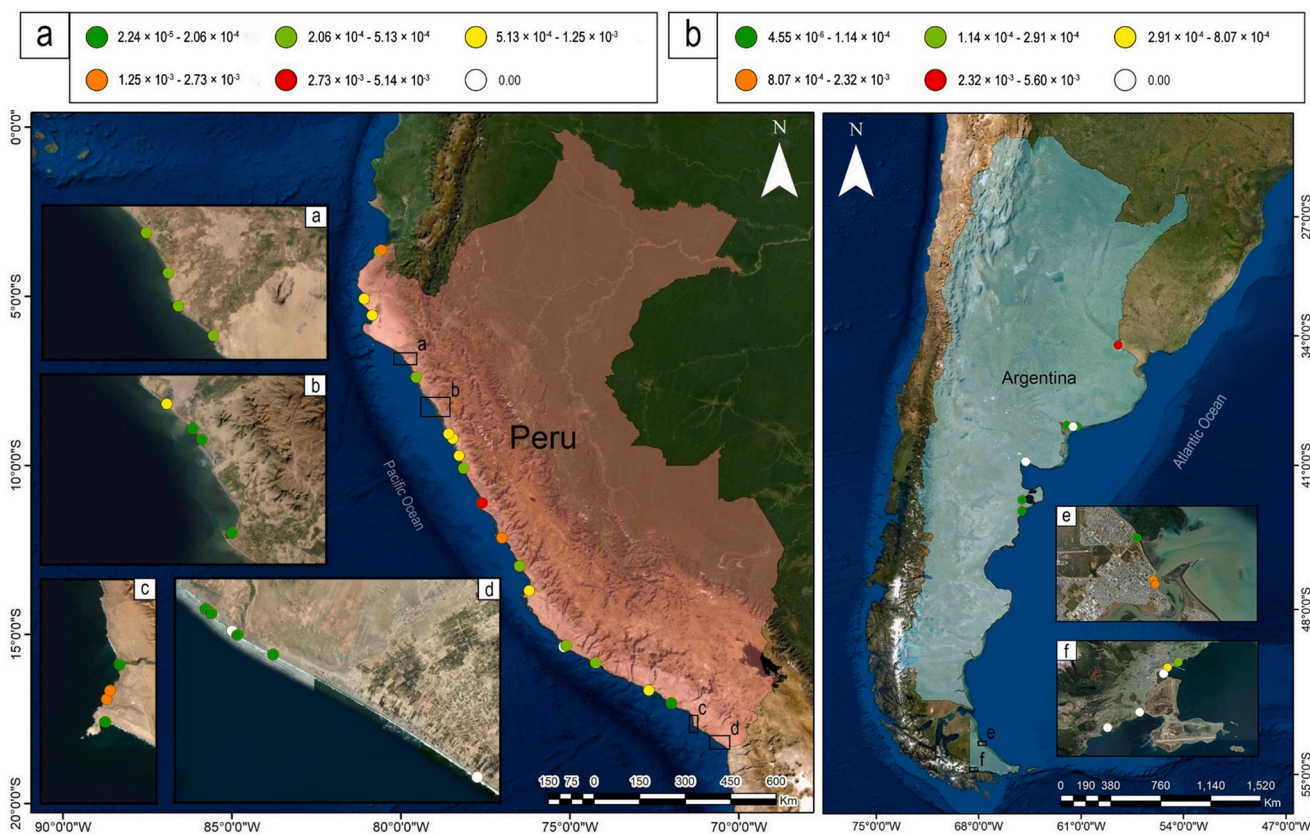


Fig. 2. Map of Peru (a) and Argentina (b) displaying the spatial distribution and level of PPE pollution (PPE m<sup>-2</sup>) across sampling sites.

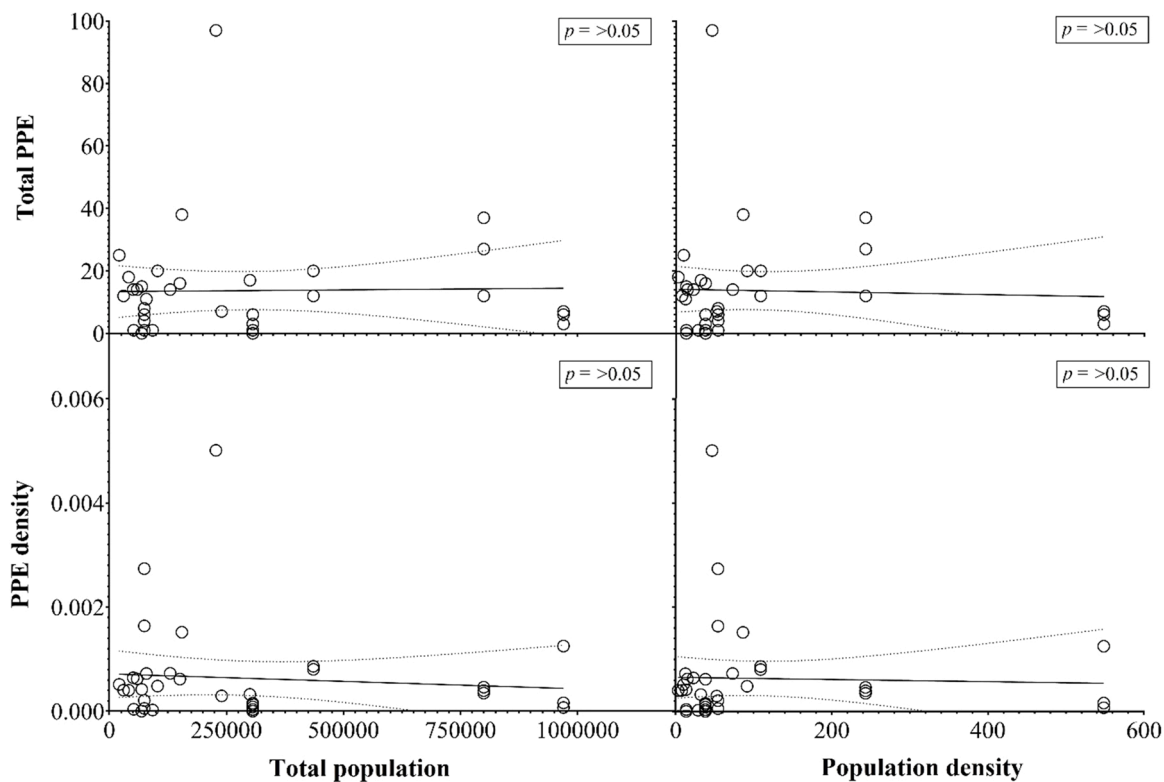


Fig. 3. Scatter plot diagrams and linear regression of the predictor and response variables in the datasets of Peru. P-values were determined by the Spearman correlation test.

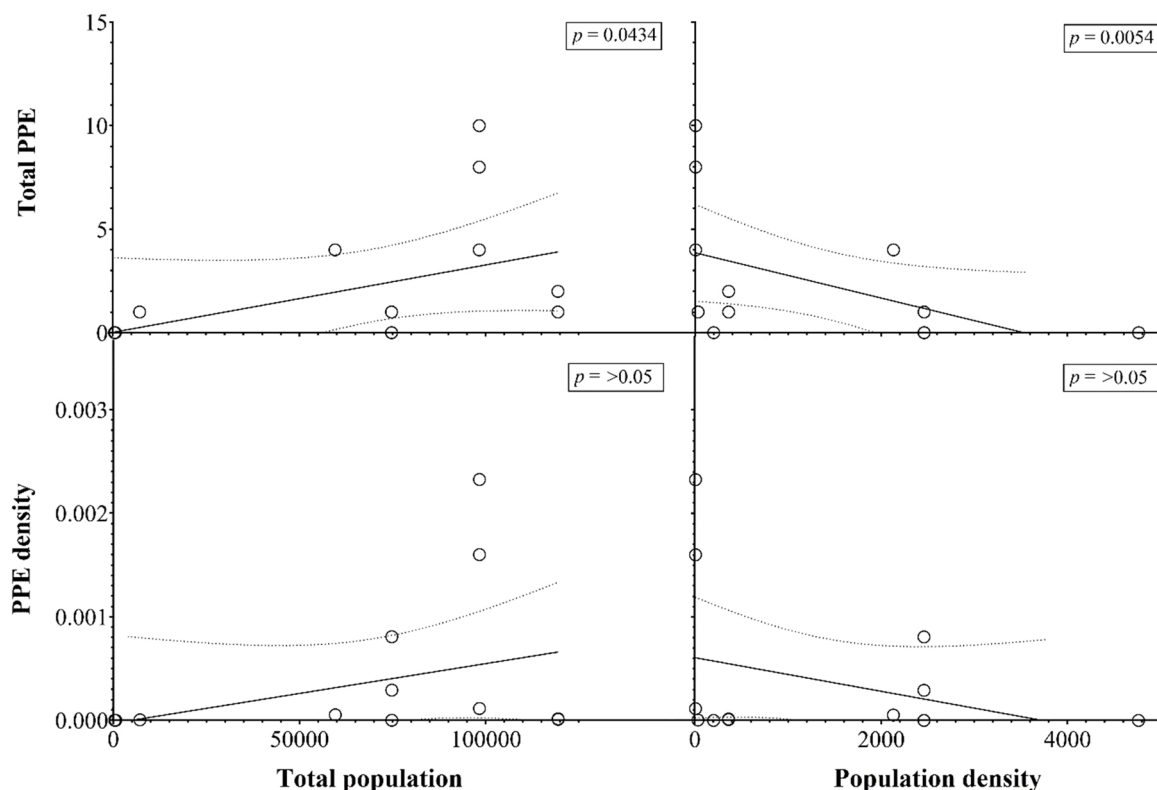


Fig. 4. Scatter plot diagrams and linear regression of the predictor and response variables in the datasets of Argentina. P-values were determined by the Spearman correlation test.

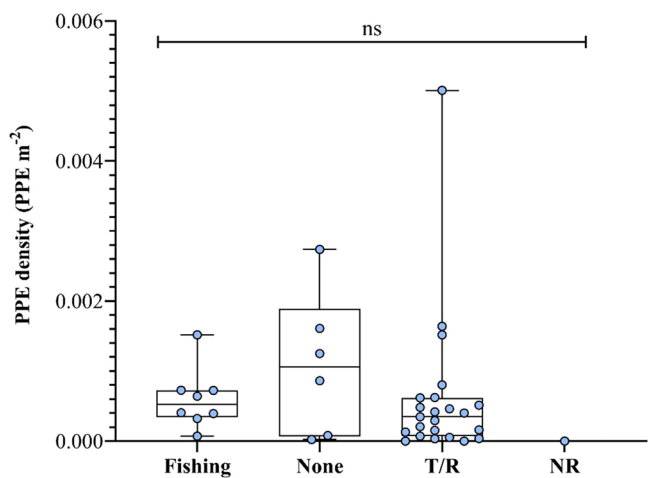


Fig. 5. Box plot and individual values of PPE density grouped per coastal activity in Peru. ns: No significant differences (Kruskal-Wallis test). T/R: Tourism or recreational. NR: Natural reserve.

both cases, the FTIR spectra displayed bands typically representative of PP (Fig. 6). In brief, intense C-H stretching ( $2950$ ,  $2916$ , and  $2839$   $\text{cm}^{-1}$ ), as well as  $\text{CH}_2$  and  $\text{CH}_3$  ( $1454$  and  $1377$   $\text{cm}^{-1}$ , respectively) bending bands were observed (Hummel, 2012). CH bending and  $\text{CH}_3$  rocking were observed at  $1166$  and  $972$   $\text{cm}^{-1}$ , C-C stretching at  $997$   $\text{cm}^{-1}$ , and additional  $\text{CH}_3$ ,  $\text{CH}_2$ , C-C, and C- $\text{CH}_3$  vibrations bands at  $840$  and  $809$   $\text{cm}^{-1}$  (Noda et al., 2007). Cloth mask 1 was composed of two layers or sides. The first layer (used in contact with the mouth/skin) presented typical PP absorption bands aforementioned. However, the second layer showed different patterns. Moderately intense bands at  $1709$  and  $1959$   $\text{cm}^{-1}$  are assigned to the C=O symmetric stretching of

carbonyl groups and anhydride groups, respectively (Parvinzadeh and Ebrahimi, 2011a). Weaker bands at  $727$ ,  $1022$ , and  $1413$   $\text{cm}^{-1}$  are assigned to aromatic CH out of plane bending, aromatic CH in-plane bending, and aromatic ring in-plane bending, respectively (Neves et al., 2015). Additional bands at  $2969$  and  $3430$   $\text{cm}^{-1}$  were associated with C-H stretching and intermolecular O-H bonded to C=O groups, respectively (Parvinzadeh and Ebrahimi, 2011a). Based on the bands displayed in the spectrum, it is likely the second layer was mainly composed of polyester, probably polyethylene terephthalate (PET). Cloth mask 2 was composed of two outer layers and one inner filter. In any case, the spectra displayed bands in the carbonyl regions of PET ( $1700$ – $1720$   $\text{cm}^{-1}$ ) (Pietrelli et al., 2017) and aromatic ring vibrations (Neves et al., 2015; Jung et al., 2018) with minor shifts. Similarly, the face shield visor displayed the typical commercial transparent PET film spectrum (Singh et al., 2005). However, the headband showed bands at  $1738$   $\text{cm}^{-1}$ , and between  $1600$  and  $1400$   $\text{cm}^{-1}$ , possibly attributed to carboxylic and aromatic stretching vibrations, respectively. Regardless, the quality of the spectrum was insufficient to suggest a dominant polymer composition with certainty.

Photographs of face masks and gloves with their respective ATR-FTIR spectra are presented in Fig. 7. A zoomed picture of the single face mask is also presented (small insert, in Fig. 7a), where loose microfibrers derived from the inner zone can be observed. After observing the single face mask spectrum compared to the PP reference spectrum (Fig. 7a1), it can be appreciated that there is a high coincidence among the spectra. The spectrum of the elastic cord of the face mask (Fig. 7a2) is also compared with a reference spectrum, where the elastic is made from PET. On the other hand, Fig. 7b showed the ATR-FTIR spectrum of latex glove pattern (red spectrum) and sample (blue spectrum), where the presence of the characteristic peaks of natural rubber (polyisoprene) or latex are observed. It is well known that gloves are made of nitrile butadiene rubber, polyethylene (PE), polyvinyl chloride (PVC), and natural rubber. Moreover, according to the

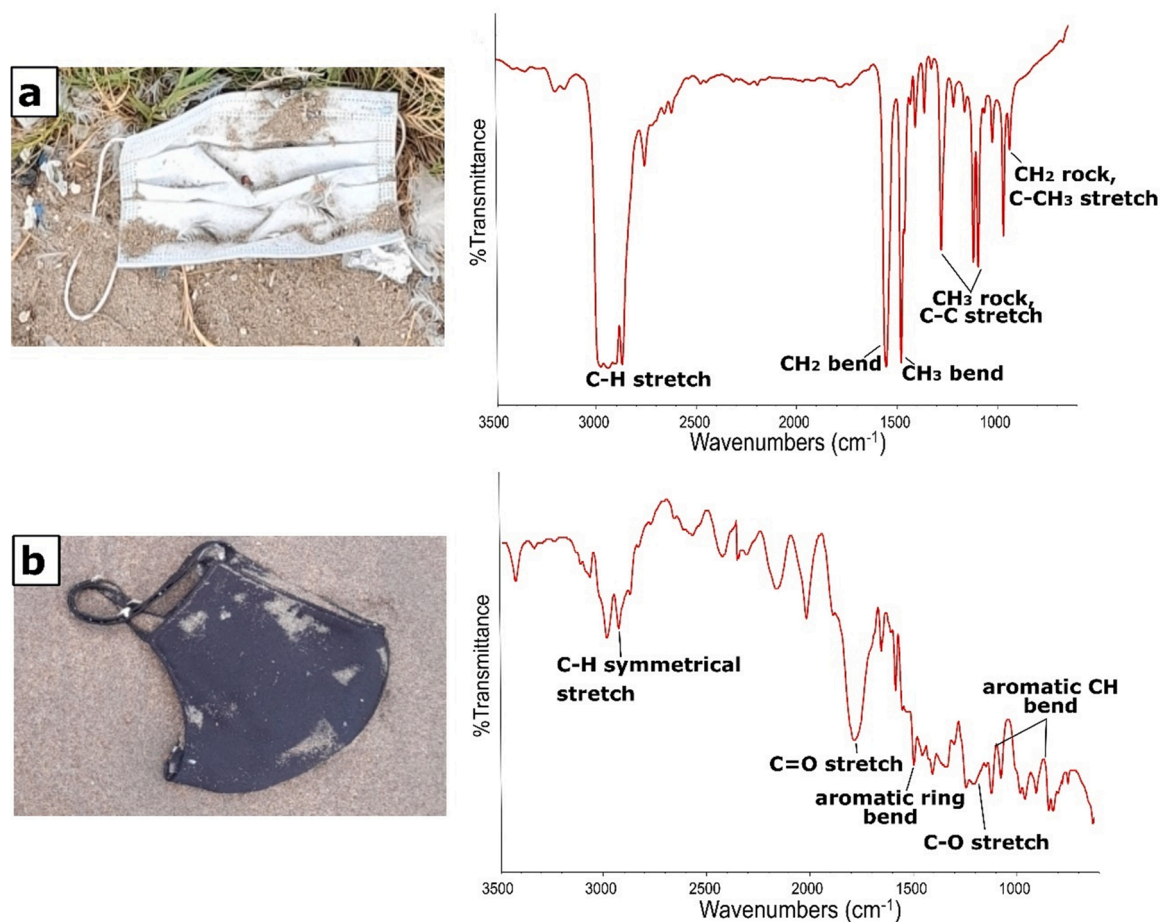


Fig. 6. Photographs of a white surgical face mask (top) and cloth mask (bottom) and their corresponding FTIR spectrum (outer face mask layer).

bibliography, the signal characteristics of CaCO<sub>3</sub> were also identified in both spectra (black spectrum). CaCO<sub>3</sub> is widely used in the gloves industry as a filler because it can improve latex stiffness and simultaneously reduce the cost of production since they replace a part of rubber with this chemical compound (Wijesinghe et al., 2016). The ATR-FTIR spectrum of the glove sample (blue spectrum) shows an additional peak at 3450 cm<sup>-1</sup>, generally attributed to the intermolecular O-H bonded to C=O groups. Moreover, a small peak at 1735 cm<sup>-1</sup> is attributed to the stretching C=O of the carbonyl group. In particular, this PPE waste had a rubbery and yellowish aspect due to its exposure to the environment.

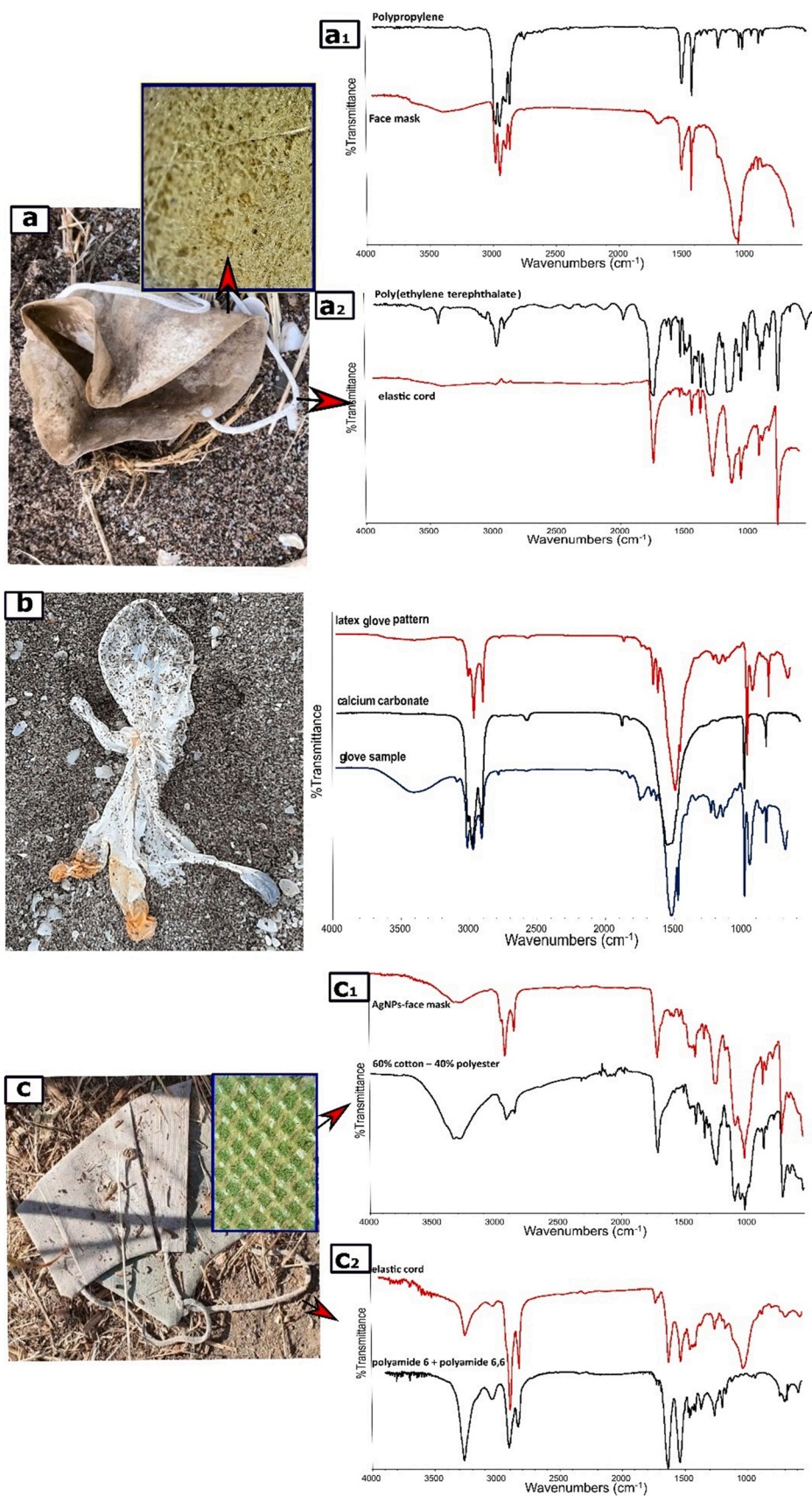
Face masks impregnated with nanoparticles (NPs-face masks) are very popular in Argentina (Ardusso et al., 2021) because the Ag and Cu nanoparticles are effective agents against the SARS-Cov-2 virus (Gulati et al., 2021; SS et al., 2020). There are two types of these reusable face masks: A washable (up to 15 washes) two-layer mask and a disposable three-layer mask. In this study, only one NPs-impregnated antiviral face mask was found during sampling in the coastal areas. However, previous unpublished observations on some city streets, such as Bahía Blanca and AMBA, have shown a significant number of this type of mask. Nanomaterials such as Ag and Cu-NPs are emerging contaminants and may negatively affect the environment and organisms (Turan et al., 2019). In this way, images of the NPs-face mask with their respective FTIR spectrum (inner face mask layer) are presented in Fig. 7c. A picture of the inner layer from the NPs-face mask is also presented (small insert, in Fig. 7c). Like the single face mask (Fig. 7, small insert), loose microfibrers are also observed on the surface of the inner layer of the NPs-face mask. On the other hand, the spectrum originated by cotton-polyester reference, and the spectrum from the inner layer from the NPs-face mask is presented in Fig. 7c1. The peak observed at 3570–3200 cm<sup>-1</sup> is assigned

to hydroxyl (OH) groups present in both the polymer structures. A strong peak appearing at 1014 cm<sup>-1</sup> is assigned to hydroxyl (OH) groups out-of-plane bending in the terminal carboxylic groups of the polyester structure (Parvinzadeh and Ebrahimi, 2011b). Another strong peak at 1710 cm<sup>-1</sup> is associated with C=O symmetric stretching of the carbonyl groups of polyester. In particular, the peak at 2970 is assigned to C-H and the peaks appearing at 821 and 721 cm<sup>-1</sup> are associated with aromatic bonds C=C and C-H of polyester. On the other hand, the ATR-FTIR spectrum of the elastic cord is also presented in Fig. 7c2, where signals at 3300 and 3070 cm<sup>-1</sup> are associated with N-H stretching. The signals at 1640 and 1540 cm<sup>-1</sup> are assigned to C=O stretching (amide I) and N-H deformation and C-N stretching (amide II), respectively (Liu et al., 2018). Thus, this material was identified as polyamide 6 and polyamide 6,6 mixes.

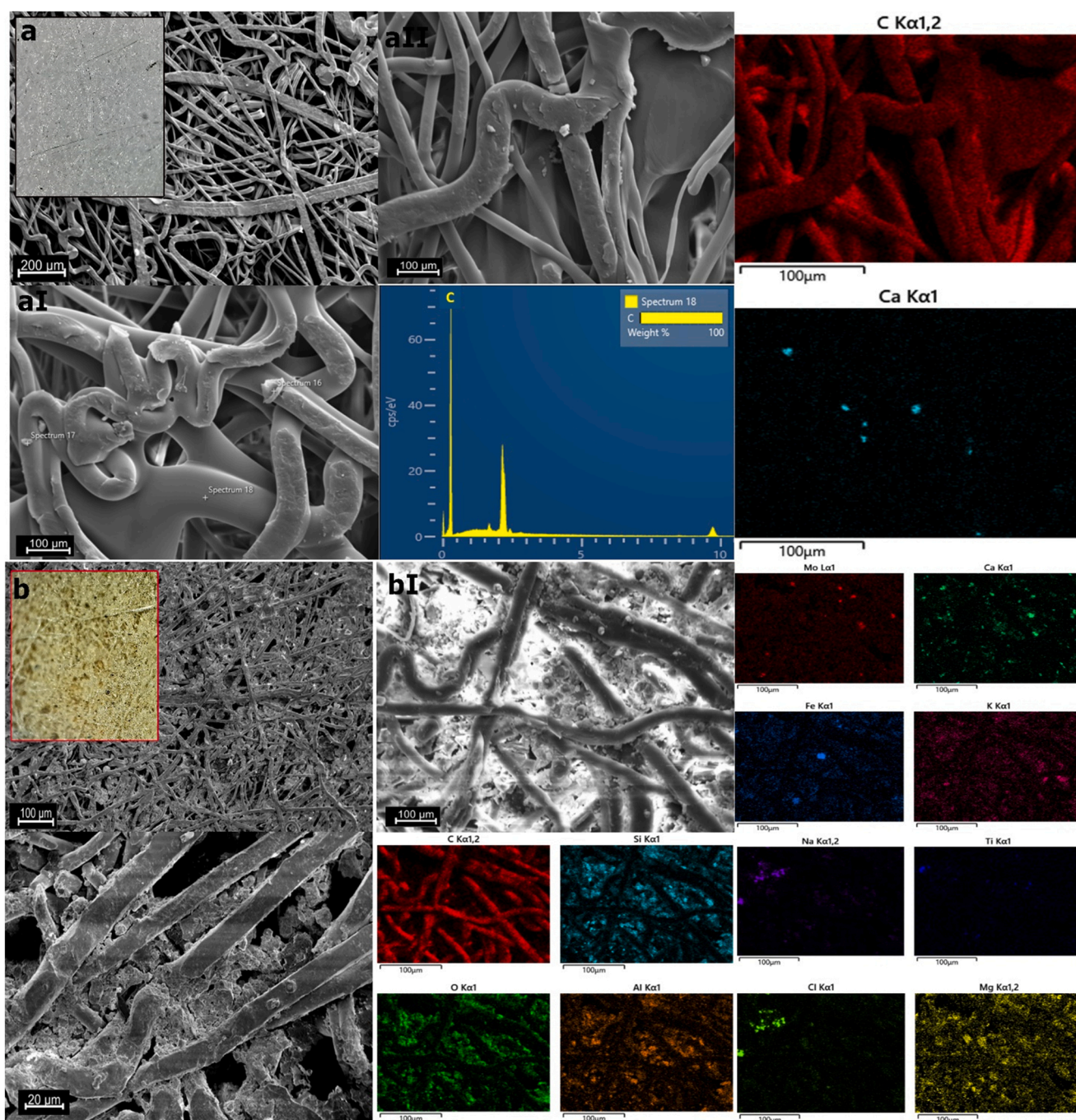
### 3.3. SEM/EDX results

SEM micrographs and EDX analysis of the PPE patterns and samples are shown in Figs. 8 and 9. Fig. 8a shows that some fibers from face mask patterns have a smooth surface while others have rough surfaces. Moreover, small particles adhered to the fiber surface also are observed. An EDX punctual spectra (Fig. 8aI) and SEM-EDX elemental mapping of PP-face mask patterns showed strong C signals in both analyses, while the Ca signal was only observed in the mapping (Fig. 8aII), indicating that Ca signal from the particles is adhered to the surface of PP-face masks pattern. Likewise, Na, K, Al, S, and Si peaks are only exhibited in punctual spectra 2 and 3 (spectral from particles adhered to PP-face mask) (Fig. S5). On the other hand, Fig. 8b shows that the face mask fibers are covered with mineral particles and between the weave of the layer of the PP-face mask. An SEM-EDX elemental mapping of the PP-





**Fig. 7.** (a) Photograph of white surgical face mask. a1. zoomed face mask image and its spectrum. a2. elastic cord spectrum. (b) Photograph glove and their corresponding ATR-FTIR spectrum and (c) photograph of the NPs-face mask. c1 ATR-FTIR spectrum from the inner layer of the NPs-face mask, and c2 ATR-FTIR spectrum from the elastic cord. Zoomed image of the inner layer of NPs-face mask image (small insert).



**Fig. 8.** (a-aII) SEM micrographs, EDX punctual spectra of PP-face mask pattern, and SEM-EDX elemental mapping of the weave of the layer of the PP-face mask pattern. (b-bI) SEM micrographs and SEM-EDX elemental mapping of the weave of the PP-face mask sample.

face mask (sample) weave showed signals of C, Si, O, Al, Cl, Mg, Mo, Ca, Fe, K, Na, and Ti (Fig. 8bI), indicating that synthetic fibers of the weave transport these elements of the particulate matter (PM).

On the other hand, Fig. 9a shows some protruding fibers from the surface of the inner layer of the NPs-face mask pattern. Moreover, except for some protuberances and small particles adhered to the surface microfibers, their surfaces are smooth. Fig. 9aI shows an SEM/EDX analysis on three different surface sites of the NPs-face mask pattern. All the EDX spectra exhibit a strong C peak and O. In particular, small peaks of Ag and Ca are also detected on the surface of fibers from NPs-face masks (spectra 1). EDX analysis on two different particles adhered to the surface of microfibers is also detailed. Both particles exhibit elemental signals of Fe, K, Si, Mg, and Al, but additional peaks of Mo, P,

and Ca in particle 1 (spectra 2). Likewise, the fibers of the inner layer of the NPs-face mask sample exhibited a great number of particles adhered to their surface (Fig. 9b). Finally, SEM-EDX elemental mapping confirms the signal of the same elements in some particles adhered to the surface of microfibers with the exception of Ti (Fig. 9 bI).

Finally, the micrographs of rubber gloves samples are shown in Fig. 10. The SEM image shows that the surface of the glove has microvoids, cavities, cracks, and crystals adhered to their surface (Fig. 10a). The weathering process of rubber gloves due to environmental exposition may generate an increase of defects on their surfaces as crazes and cracks (Canning et al., 1998). Fig. 10b shows SEM/EDX analysis on three different particles adhered to the surface of the worn glove. In particular, spectrum 2 shows a peak of Zn, suggesting that Zn is part of PM. An

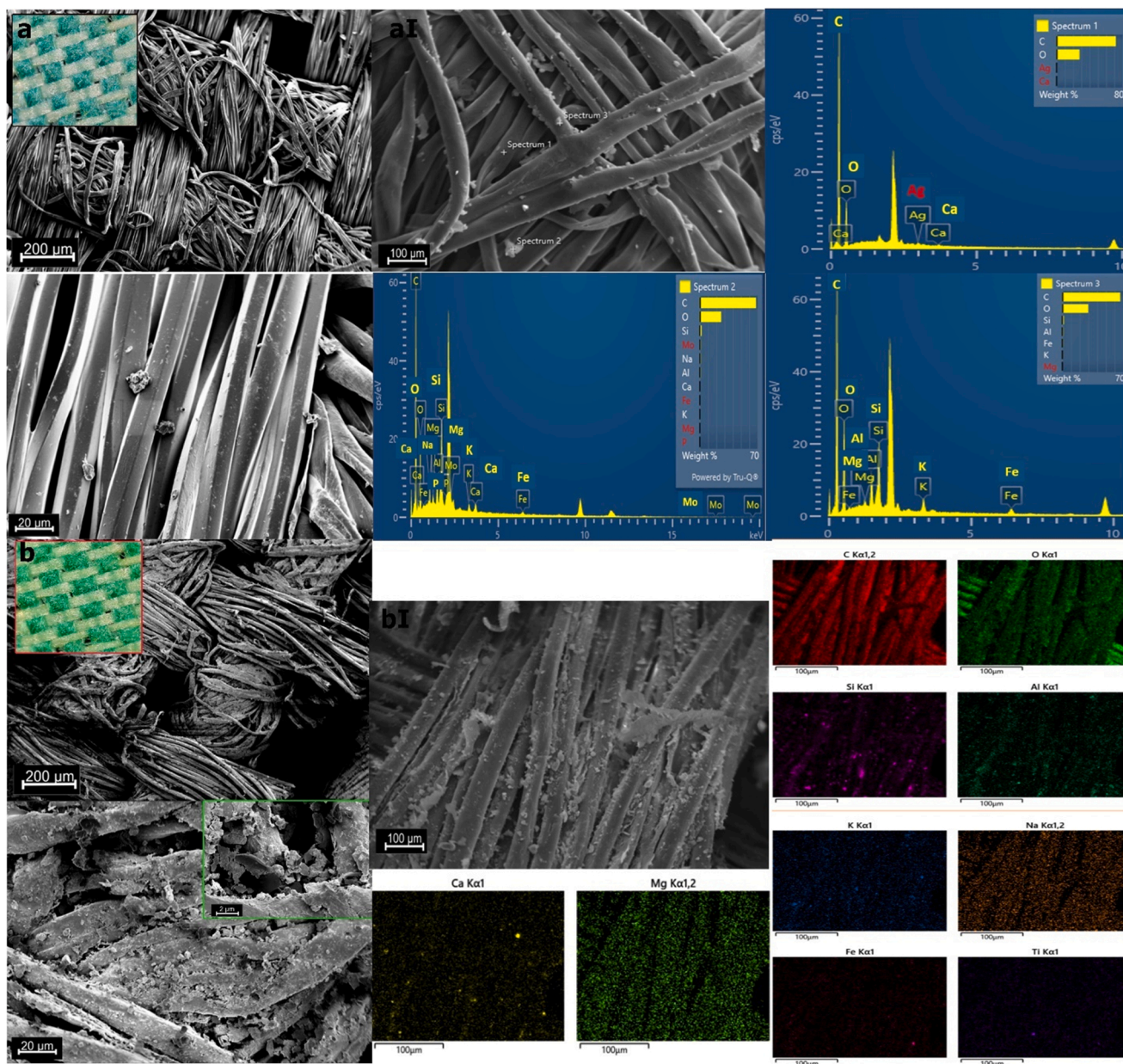


Fig. 9. (a-aI) SEM micrographs and EDX punctual spectra of NPs-face mask pattern, and (b-bI) SEM micrographs and SEM-EDX elemental mapping of NPs-face mask sample.

SEM-EDX elemental mapping shows the presence of Ca on the entire glove surface and confirms that  $\text{CaCO}_3$  has been used as an additive (Fig. S6).

### 3.4. XRD results

Fig. 11 shows the X-ray diffraction (XRD) patterns of the brand-new face masks, and the face masks found during sampling. In Fig. 11a, the PP-face mask pattern exhibited several sharp diffraction peaks at around  $2\theta = 14.0, 16.7, 18.45, 21.03,$  and  $21.6^\circ$ . These signals correspond to the isotactic  $\alpha$ -form of PP (curve a) (Chrissopoulou and Anastasiadis, 2011). The PP face mask sampled in the field shows the same characteristic peaks of PP but with less intensity (curve b). Some authors have reported that virgin polymers such as PP and Nylon had a higher degree of crystalline (semi-crystalline) than aged polymers (Saquing et al., 2010; Tang et al., 2020). On the other hand, Fig. 11b shows XRD patterns of the inner and outer layer of NPs-face mask blanks (pattern) and NPs-face

mask samples. Characteristic peaks of cotton (cellulose I) are observed at  $2\theta = 14.91, 16.3, 22.67,$  and  $34.12^\circ$  while the peaks  $22.67$  and  $25.38^\circ$  correspond to polyester (Doh et al., 2014; Hong, 2014; Shao and Wei, 2018; da et al., 2020).

### 4. Discussions

As previously mentioned, the use of face masks was recommended to reduce SARS-CoV-2 contagion (Adyel, 2020) and in both studied countries are being mandatory. For this reason, PPE has become more common in some coastal environments around the world (Akhbarzadeh et al., 2021a; Ben Haddad et al., 2021; Rakib et al., 2021; Fadare and Okoffo, 2020; Gallo Neto et al., 2021; De-la-Torre et al., 2021b; Ryan et al., 2020; Akarsu et al., 2021; Ammendolia et al., 2021). In Peru, PPE abundance and density showed great variability across sampling sites. Several factors could drive PPE pollution in coastal areas. In the analyzes conducted, no statistical significance was found between sampling sites

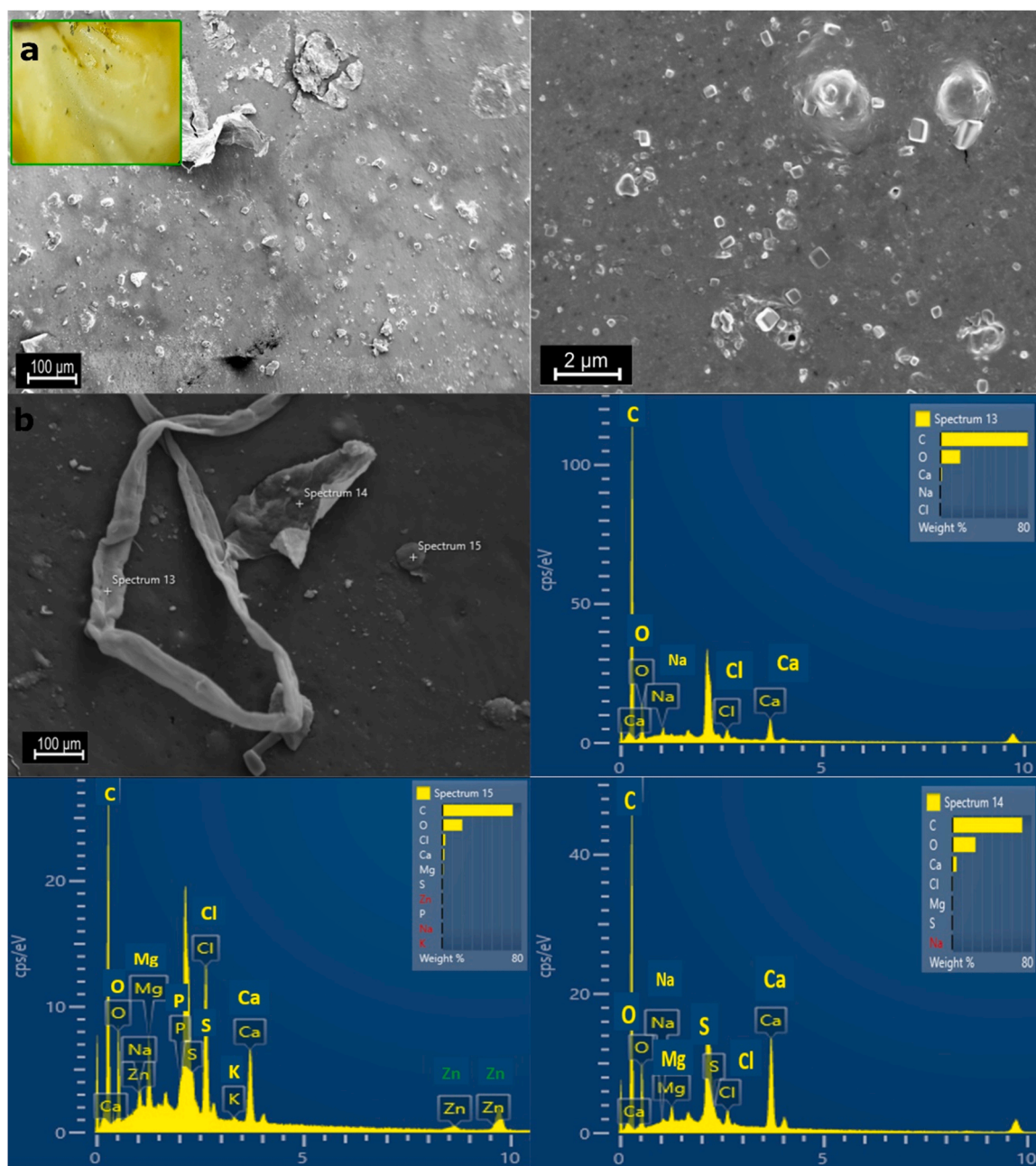
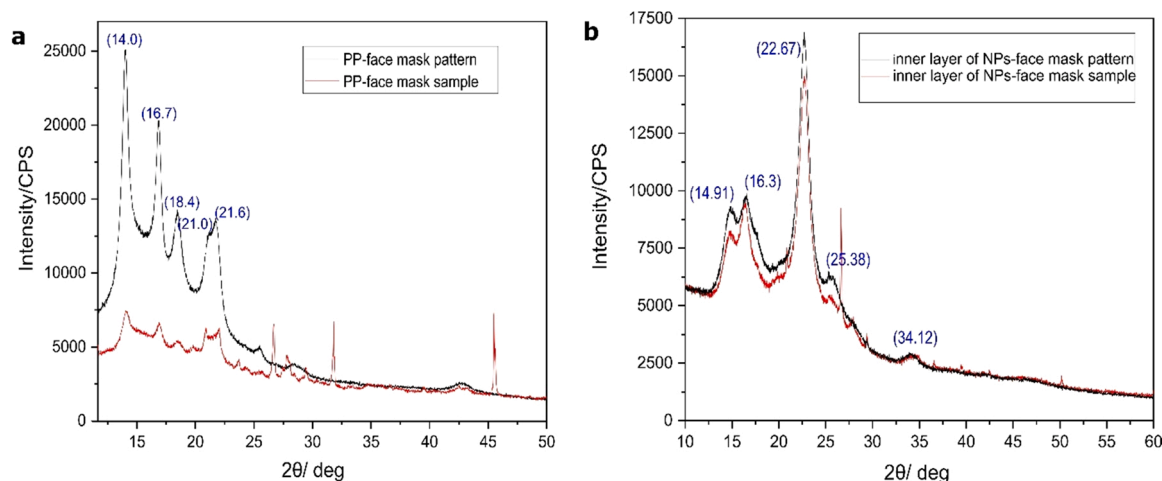


Fig. 10. (a) SEM micrographs and (b) EDX punctual spectra of gloves found in coastal areas.

grouped per activity (tourism/recreational, none, fishing, or nature reserve). Conversely, in our previous research carried out on 11 beaches of Lima (summer season), recreational beaches were significantly more polluted than other types (De-la-Torre et al., 2021b). It should be noted that the latter focused on the city of Lima, while this study was nationwide. We believe that by grouping sites from multiple regions in Peru, behavioral and cultural aspects may interfere with the observable PPE densities. For instance, the “Caleta” beach (9°04′32.4″S; 78°36′14.2″W) in Ancash Region, where no apparent activity was observed, demonstrated a relatively high PPE density ( $8.63 \times 10^{-4}$  PPE  $m^{-2}$ ). Apart from PPE, large amounts of fishing gear and municipal solid waste were found (Fig. S2a). This is likely due to its proximity to a large artisanal fishing pier and lack of beach cleaning. Moreover, the fact that a higher number of beachgoers was observed during the summer season, particularly on recreational beaches, may have gathered notoriously more people depending on the activity. Concerning the influence of

population densities, no significant correlation was observed in the analyzes conducted. It is likely that popularity and accessibility, which are beach-specific, could play a role in waste PPE generation. This is observed by comparing “Playa Hermosa” (15°21′20.65″S; 75°10′09.46″W) and the beach site within the Punta San Juan Nature Reserve (15°22′01.45″S; 75°11′14.54″W), both located in the Province of Nazca and very close to each other. Although no PPE was found in Punta San Juan, “Playa Hermosa” was contaminated with 15 face masks ( $4.19 \times 10^{-4}$  PPE  $m^{-2}$ ). We believe that Punta San Juan was PPE-free because it is not open to the public, unlike “Playa Hermosa”. COVID-19 related infrastructure, such as signposts providing recommendations for beachgoers were found indicating to maintain social distance and wear face masks (Fig. S3a). However, none of these infrastructures specified the correct way to dispose of PPE items or other types of litter. Moreover, some bins located within the beach area or at the entrance of public beaches were full and lacked maintenance



**Fig. 11.** The X-ray diffraction (XRD) spectra of (a) PP-face mask pattern and the PP-face mask sample, and (b) NPs-face masks pattern and NPs-face masks found during sampling in coastal areas.

(Fig. S3b). Solid waste management plans and infrastructure in Peru are very poor and mainly dependent on informal dumpsites (Walmsley et al., 2018). Regardless, our study shows that most PPE reaching coastal areas are driven by individual actions, such as littering on site. Moreover, it is possible that land-based generated PPE is being transported through urban waterways, including rivers and canals. For instance, almost 30% of the solid was generated in the lower basin of one of the most relevant rivers in Lima is improperly discarded, including in the vicinity of the river itself (Bertha, 2007). On the other hand, urban and irrigation canals are another possible transportation pathway of land-based PPE. Since PPE items have become ubiquitous in most urban areas (e.g., streets, residential and commercial sites) (Ammendolia et al., 2021), it is plausible that this material reaches waterways by the action of the wind. However, the exact contribution of fluvial transport of PPE on the abundance of marine litter found stranded along the coast is unknown and requires further research.

Regarding the sampling procedures, it is worth mentioning that the size of the sampled area could also influence the calculated PPE density. We have constructed a scatter plot considering the sampled area ( $m^2$ ) and resulting PPE density ( $PPE\ m^{-2}$ ), which shows an inverse correlation between the two variables (Fig. S4). It is likely that the number of beachgoers attending recreational sites may have been limited, despite the extent of the beach. On the other hand, extensive beaches are generally visited in particular subareas that are popular for beachgoers. This is the case of “Pimentel” beach, where vegetation and natural dunes occur within the beach area ( $106,542\ m^2$  of sampling area) (Fig. S1b) and most of the PPE items were found in a specific subarea located near the dock ( $3.47 \times 10^{-4}\ PPE\ m^{-2}$ ). Conversely, “Puerto Inglés” is a very small ( $\sim 610\ m^2$ ) touristic destination located in Ilo Province (Fig. S1c), where a single face mask was found but resulted in one of the highest PPE densities ( $1.64 \times 10^{-3}\ PPE\ m^{-2}$ ). To this end, it is necessary to standardize the sampling procedures in order to avoid bias, including the minimum and maximum sampling area.

The PVWR is located within the urban area of the city of Lima. This area ( $\sim 263.3\ ha$ ) is home to a wide diversity of animals and has been recognized as an important place for the reproduction of multiple bird species as well as a rookery and place of passage on their migration route along the Pacific coast of South America (Pulido, 2018; Pulido et al., 2020). Because of this, the PVWR has been designated as a wetland ecosystem of international importance (RAMSAR site). However, the economic growth and rapid urbanization of the city pose several threats to this area. While the PVWR is very well managed and preserved within its designated area by the competent authorities, the urban canals that feed the lagoons and marshes are heavily impacted by anthropogenic activities. The high density of PPE items ( $0.20\ PPE\ m^{-1}$ ) along the canal

shows the major weakness in the conservation efforts carried out by the authorities. Although PPE items were not identified inside PVWR or along any of the touristic routes at all, many of the PPE items, especially face masks, in contact with the water stream could release high concentrations of microplastics and chemical contaminants (Wang et al., 2021). These are suspected to be transported into the wetland, but the extent of the impact generated by this behavior is unknown.

The low densities of PPE in some coastal areas and beaches in Buenos Aires province (Monte Hermoso y Pehuén-Co) could be attributed to the fact that these coastal cities have nearly zero flow of tourists in the autumn/winter season and a low residential population density. On the other hand, citizens of Puerto Madryn (Chubut province) and Ushuaia (Tierra del Fuego Province) in the South of Argentina, have been carrying out voluntary work for cleaning beaches all year, which could have affected the counting of PPE waste in these beaches. In the center of the country, Coronel Rosales, a semi-urban beach near the Naval Base in Punta Alta city, presents a high density of PPE. This beach does not receive any kind of cleaning procedures. Besides, it receives high marine traffic and presents local marine currents that deposit litter on this beach. On the other hand, the high abundance of PPE found in CABA is related to the high population density, and the lack of cleanliness on the coast. CABA is the capital of Argentina and for this reason, is the most populated city in the country. People in this city voluntarily or involuntarily discard the PPE increasing their presence on the coasts where there are no bins and signposts. Thus, weather conditions, population density, the season of the year, and voluntary work could have affected the density of PPE found on sampling coastal areas in Argentina.

On the other hand, PPE in Argentinian coasts at the present study are the first records in the country. Previous studies were qualitative (Arduoso et al., 2021). Considering other South American countries, the average density of PPE in Argentina was considerably lower than the neighboring country Chile. At the end of 2020, Thiel et al. (2021) recorded a mean of  $0.006\ face\ masks\ m^{-2}$  and a maximum density of  $0.028\ face\ masks\ m^{-2}$ . Besides, the higher abundances were recorded in summer, and they found the average density of face masks during this time period was more than ten times higher than during the fall/winter period. Studies in Bangladesh (Rakib et al., 2021) also recorded higher PPE mean abundance ( $6.29 \times 10^{-3}\ m^2$ ) despite the sampled area ( $516,683\ m^2$ ) being slightly higher than the one of the present study ( $474,719\ m^2$ ).

Mean abundance in Argentina was slightly higher than PPE recorded in Morocco ( $2.79 \times 10^{-4}\ m^2$ ) under non-lockdown conditions (Ben Haddad et al., 2021). This difference between the density and the number of PPE is explained by the difference in the sampled area between the two studies (Morocco:  $282,374\ m^2$ ; Argentina:  $474,719\ m^2$ ).

Finally, the weather and strong winds may influence the abundance of PPE waste in coastal areas during the winter. The temperature in some regions in Argentina may reach 0 °C, with strong winds causing a low flow of people in these coastal areas.

Like Peru, Argentina also has poor infrastructure and waste management; these shortcomings were exacerbated during the COVID-19 pandemic (Arduso et al., 2021). Moreover, there are many open dumpsites active in some cities and towns, which aggravates the pollution in this region. Although urban areas have coverage in the solid waste collection and its final disposition, there are inequalities in these services in some country regions, such as the North and Cuyo-Mesopotamia (<https://www.argentina.gob.ar/ambiente/control/rsu>). Moreover, the lack of monitoring over the generation of waste and its final disposal has generated outdated statistical information or unknown over its magnitude.

Unlike most studies, Argentina presented an equal representation of face masks and gloves as PPE (48.8% each). In Morocco, for instance, face masks accounted for 100% in Tetouan and 96.8% in Agadir (Ben Haddad et al., 2021; Mghili et al., 2021). Similarly, the proportion of littered masks in Cox's Bazar beach (Bangladesh) and Peru were 97.8% (Rakib et al., 2021) and 94.5%, respectively. However, Peru presented a wider diversity of PPE. In particular, bouffant caps and hazmat suits were found. These types of materials have been found in the river outlets of Jakarta Bay, Indonesia (Cordova et al., 2021). Less reported PPE items, such as hazmat suits, caps, and food protectors, are uncommon because their use is not enforced for the general public. Regardless, the vast majority of face masks found were surgical (single-use masks) and cloth (reusable masks) in a significantly lower proportion. The type of PPE litter found in beach monitoring studies provides an overview of the consumer behavior and perception of protection against the pandemic, as well as the laws regarding PPE use in each country. While in the present study we considered PPE as any wearable equipment used by the consumer to prevent the infection of the virus, there are several plastic and non-plastic items driven by PPE consumption and protection that should be included in future monitoring programs. For instance, face mask wrappings (plastic), packaging (paperboard or plastic), alcohol containers (plastic), and wet wipes (synthetic fibers) have been overlooked by previous studies, as well as other pandemic-associated materials, including disposable syringes, COVID-19 diagnostic test materials, paper, and plastic wrappings from food delivery (de Sousa, 2021; Celis et al., 2021).

The results of the FTIR analysis are in accordance with previous reports. In this sense, the dominance of PP in the outer layers of surgical face masks from the environment has been reported in previous studies (Aragaw, 2020; Fadare and Okoffo, 2020). Besides, reusable cloth masks were found to be composed of polyester or cotton-polyester layers. Microfibers shed easily from this type of mask, similar to the release of polyester fibers from textiles during laundry (Rathinamoorthy and Balasaraswathi, 2021). Importantly, it has been estimated that microfibers released from face masks range between 284.9 and 823 particles per wash (De Felice et al., 2022). While most studies overlook the smaller components of PPE, here we identified PET and PA as the main composition of the elastic cords in two face masks, similar to the report by Shen et al. (2021). These two synthetic polymers have been previously identified in MPs from the aquatic environment (Huang et al., 2020; Zaki et al., 2021). Other than face masks, latex and PET were the main components of the analyzed glove and face shield visor, respectively. Analyzing the latter is of particular interest in PPE pollution since most studies have focused on face masks (Sullivan et al., 2021; Ma et al., 2021). However, the use of face shields is significant in countries like Peru (De-la-Torre et al., 2021b), but may be fairly uncommon in other countries. Based on its polymeric composition, it is evident that different types of PPE will become important sources of MPs. For instance, Morgana et al. (2021) reported that the single face mask with a low level of degradation could release up to  $10^8$  plastic particles of different sizes to the aquatic environment. Finally, Ma et al. (2021) informed the presence

of MPs in the nasal mucus of mask wearers, indicating that the plastic particles could be inhaled while using a face mask.

In Peru, MP pollution has been the subject of concern in recent years. A baseline study conducted in the city of Lima revealed PP, HDPE, PS, and polyester as the main polymer types constituting MPs in sandy beaches (De-la-Torre et al., 2020a). Also, the colonization of LDPE, PP, PA, and latex macroplastics by marine macroinvertebrates has been reported and discussed as a potential source of spreaders of potentially invasive species (De-la-Torre et al., 2021a). Also, according to the structure and layers topography of the face mask, there may be preferential growth of microorganism communities (i.e., bacteria and/or fungi) on the face mask surface during the first stages of biofilm formation. Moreover, this microbial composition on the surface of plastic layers is also influenced by the bacteria living in a free-living state in the environment and the physical properties of the polymeric surface such as hydrophobicity, charge surface, and rugosity (Jacquin et al., 2019). However, most studies on plastic pollution in Peru lack chemical analytical analyses (such as FTIR or Raman spectroscopy) due to the lack of accessibility to advanced equipment. In the case of Argentina, the current literature provides a more comprehensive understanding of plastic pollution. For instance, MP pollution has been evidenced in surface water and organisms of the heavily impacted Bahía Blanca Estuary and Claromeco beach, where PP, PE, polyester, PA, cellulose-based, among others have been the dominant polymer types (Forero López et al., 2021; Díaz-Jaramillo et al., 2021; Truchet et al., 2021; Fernández Severini et al., 2020; Forero-López et al., 2021). In Ushuaia Bay, the southernmost city of Argentina, fibers, and fragments consisting of PA, cellulose-based, and PVC copolymers were found in the mussel *Mytilus chilensis* (Pérez et al., 2020). Likewise, PS and cellulose-based were found in intertidal limpets *Nacella magellanica* from the Beagle channel (Ojeda et al., 2021). Similar polymeric materials and the dominance of microfibers are reported in different locations across Argentina (Díaz-Jaramillo et al., 2021; Pazos et al., 2021; Montecinos et al., 2021). Based on previous studies and the occurrence of PPE in the marine environment, we believe that the COVID-19 pandemic is contributing significantly to the already widespread issue of plastic pollution in South America.

Marine environmental conditions and the high temperature to which the PPE are exposed on sands can lead to the fragmentation and release of MPs/PNPs from PPE, such as face masks. The micro-fibrous matrix of the external layer of face masks (either PP or Ag-NPs) reported in the present study is similar to those in the literature. Laboratory tests have demonstrated that UV irradiation resulted in the appearance of cracks and rough surfaces and a clear rupture of the fibers comprising the micro-fibrous matrix in PP face masks (Wang et al., 2021; Saliu et al., 2021). Akarsu et al. (2021) analyzed face masks found littering the streets of three cities in Turkey. Like our results, the SEM images displayed the initial stages of a fragmentation process of PP microfibers. Since the oxidation of PP induces the embrittlement of the polymer material (Fayolle et al., 2000), face masks could potentially become a source of MPs with high release rates due to fibrous structure and high surface area.

On the other hand, the presence of some metals in PPE waste is evident either as additives as Ca or Ag (as NPs). Other metals were detected in the particles adhered to the surface of PPE waste, such as Mo, P, Ti, and Zn. In this way, Sullivan et al. (2021) reported the presence of heavy metals such as Cd, Co, Cu, Pb, Sn, and Ti in disposable face masks manufactured in China. In the case of Ti, it is also likely to originate from common additives used in polyester fibers, such as TiO<sub>2</sub> (Rashid et al., 2021). On the other hand, some authors have reported the presence of hazardous metals such as Cr and Mo on the surface of MPs fibers found in Claromeco sandy beaches in Argentina (Truchet et al., 2021). Likewise, the same authors have also informed the presence of P as an additive in suspended MPs in a highly impacted estuarine wetland in Argentina (Forero-López et al., 2021).

The case of the face mask impregnated with Ag-NPs is more

interesting because these NPs are only detected through EDX due to their low concentrations. EDX spectrum of NPs-face mask pattern showed an atomic percentage around  $\approx 0.3\%$  Wt. of Ag-NPs, while the spectra and mapping of NPs-face mask waste did not detect the signal of NPs. This behavior could be due to possible masking of Ag signal due to the great quantity of PM adhered on the surface of fibers or leaching of NPs due to tendency to suffer transformations during the washing process or with contact with sweat (Mohan et al., 2019). According to the physico-chemical characteristics of NPs, and environmental conditions, they can interact with other pollutants generating synergic toxicological effects in microorganisms and animals (Zhu et al., 2020; Malakar et al., 2021; Singh et al., 2021). Moreover, NPs can be adsorbed on cell walls or skin, inhaled, or consumed involuntarily by organisms thus generating possible toxicological effects (Turan et al., 2019).

The results of XRD show that there were changes in the intensity of signals of peaks of the XRD spectra of face mask samples compared to the XRD patterns. The degree of crystallinity of the polymers is another property that plays a role in the sorption of some contaminants as organic pollutants onto MPs (Fu et al., 2021; Torres et al., 2021). The sorption mechanisms of the organic pollutants onto plastic particles are conditioned by the degree of crystallinity of the plastics, where the absorptive partitioning mechanism is predominant in amorphous polymers, and surface adsorption occurs on polymers with a high degree of crystallinity (Yao et al., 2021). However, both mechanisms could occur in semicrystalline polymers such as PE (Fu et al., 2021; Yao et al., 2021). For instance, carbonaceous by-products derived from masks (namely, microfibers) have shown a high affinity for crystal violet and methylene blue in controlled studies, thus acting as dye carriers (Anastopoulos and Pashalidis, 2021). Experiments with PP MPs in simulated marine media revealed an increase in the degree of crystallinity after several weeks of treatment (11 weeks) (Chen et al., 2021). However, the crystallinity decreased significantly after 23 weeks. The initial change in crystallinity is probably due to polymer chain scission caused by weathering conditions, which induces higher polymer chain alignability with shorter chains or secondary crystallization (Fabiya and McDonald, 2014; Law et al., 2008). Later on, the reduction of the degree of crystallinity could be attributed to the lower regulation of the material structure induced by the appearance of oxygen-containing groups as a result of photooxidation (Chen et al., 2021; Rajakumar et al., 2009). In this case, despite showing notorious aging signs, we are unsure of the time the face masks analyzed in the present study spent in the environment. Regardless, the appearance of a small peak at around  $1715\text{ cm}^{-1}$  in the FTIR spectrum of the PP face mask (Fig. 7a1) is attributed to oxygen-containing groups as a sign of prolonged environmental aging. Finally, Wang et al. (2021) reported the presence of phthalate esters (PAEs) as plasticizers additives in PP and PET face masks. This type of organic pollutant has been associated with the presence of plastics in water streams and may have teratogenic, mutagenic, and carcinogenic effects on organisms (Zhang et al., 2015; Hajjoui et al., 2022).

To mitigate the presence of PPE in Argentina and Peru coasts and those coastal areas with high abundances, it is recommended the presence of signposts and bins for the correct PPE final disposal. These signposts should warn about the hazards of PPE litter and provide instructions (along with sufficient and accessible infrastructure) for its correct disposal. Also, continuously raise awareness regarding the consequences of PPE pollution, such as the increase of MPs in the form of fibers (face masks), plastic remains, increase of metal NPs (face masks impregnated with antivirals of Ag). As well as encouraging the population to reuse PPE as much as possible and give recommendations about the correct final disposal of these elements. Besides, communication to local, national, and international media, citizens, and decision-makers about this serious problem is of uttermost importance (Aragaw, 2021). Media diffusion and citizen science are some of the most powerful tools to create awareness about plastic pollution under the current scenario (Ammendolia and Walker, 2022). We recommend further studies to investigate the degradation of different types of PPE (apart from

conventional single-use PP face masks) under controlled conditions and carry out in vitro and in situ colonization tests with different types of PPE items.

## 5. Conclusions

There are few studies of PPE pollution in South America and the results of this binational research represent an important contribution to this global problem. Face masks, gloves, and face shields were the most conspicuous PPE considering both countries and urgent measures should be carried out. Our results confirm that PPE pollution is ubiquitous, and policy and decision-makers must take action to prevent the exacerbation of plastic pollution under the COVID-19 pandemic scenario. Furthermore, analytical procedures (FTIR spectroscopy, XRD, and SEM-EDX) elucidated the chemical and structural changes that PPE undergo after entering the marine environment. In particular, PP was the most popular material the comprised the polymeric composition of multilayered face masks (i.e., surgical). Other types of masks, such as reusable masks, consisted of other synthetic fibers, such as polyester and cotton-polyester mats. Other less investigated materials identified were PET and nylon (earloops and face shield) and latex (gloves). The XRD patterns showed a notorious decrease in the crystallinity of PP-based face masks, which could alter their ability to adsorb hydrophobic chemicals, potentially acting as vectors of external pollutants. Furthermore, SEM images displayed a notorious deterioration of the fibrous microstructure in reusable and surgical face masks. These changes could promote the release of MPs/PNPs and other contaminants into the environment. Future research must focus on revealing the suitability of different PPE items as substrates for different types of marine organisms and pathogenic microbes through in situ and in vitro tests. Deteriorated face masks must be evaluated by multiple analytical techniques in order to provide a thorough understanding of their degradation in the environment, as well as mechanisms of MPs/PNPs release.

## CRedit authorship contribution statement

**Gabriel Enrique De-la-Torre:** Project administration, Conceptualization, Funding acquisition, Software, Writing – original draft, Writing – review & editing, Supervision. **Diana Carolina Dioses-Salinas:** Investigation, Formal Analysis, Writing – original draft, Data curation. **Carlos Ivan Pizarro-Ortega:** Investigation, Formal analysis, Writing – original draft, Data curation. **Melisa D. Fernández Severini:** Investigation, Data curation, Conceptualization, Funding acquisition, Software, Writing – original draft, Writing – review & editing. **A.D. Forero López:** Investigation, Data curation, Conceptualization, Funding acquisition, Software, Writing – original draft, Writing – review & editing. **Romina Mansilla:** Investigation, Formal analysis, Writing – review & editing. **Félix Ayala:** Investigation, Formal analysis, Writing – review & editing. **Luzby María Jimenez Castillo:** Investigation, Formal analysis. **Elizabeth Castillo-Paico:** Investigation, Formal analysis. **Daniel A. Torres:** Investigation, Formal analysis. **Liseth Meliza Mendoza-Castilla:** Investigation, Formal analysis. **Carolina Meza-Chuquizuta:** Investigation, Formal analysis. **Jhonson K. Vizcarra:** Investigation, Formal analysis. **Melissa Mejía:** Investigation, Formal analysis. **Javier Jeirzinho Valdivia De La Gala:** Investigation, Formal analysis. **Eduardo Alonso Sayra Ninaja:** Investigation, Formal analysis. **Danny Lewis Siles Calisaya:** Investigation, Formal analysis. **Walter Eduardo Flores-Miranda:** Investigation, Formal analysis. **Johan Leandro Eras Rosillo:** Investigation, Formal analysis. **Dante Espinoza-Morriberón:** Investigation, Data curation, Software. **Karen N. Gonzales:** Investigation, Data curation, Software, Formal analysis, Writing – review & editing. **Fernando G. Torres:** Investigation, Software, Funding acquisition. **Guido Noé Rimondino:** Investigation, Data curation, Software. **Mohamed Ben-Haddad:** Investigation, Formal analysis, Writing – review & editing. **Sina Dobaradaran:** Investigation, Formal analysis, Writing – review & editing. **Tadele Assefa Aragaw:** Investigation, Formal analysis,

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### 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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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.128070](https://doi.org/10.1016/j.jhazmat.2021.128070).

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