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From COVID-19 Personal Protective Equipment (PPE) to pollutants: A multi-analytical approach towards environmental weathering of gloves and face masks in beach sand and sea[☆]

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ABSTRACT

COVID-19 pandemic has led to an unprecedented global demand for personal protective equipment (PPE) such as gloves and face masks. While these items have been crucial in curbing the spread of viruses, their disposal poses significant environmental challenges. This study aims to provide insights on the effects resulting from exposure in seawater and beach sand on PPE, when accidentally disposed. For that purpose, three types of gloves (nitrile, latex and vinyl) and face masks (FFP2, surgical and generic) were 18 months exposed. The samples were then collected and analysed by Attenuated Total Reflectance infrared (ATR-FTIR) spectroscopy analyses to evaluate the aging/degradation state of the PPEs' surface, while Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC–MS) was conducted to elucidate potential degradation of the polymer structures. Finally, Direct Analysis in Real-Time coupled with Mass Spectrometry (DART-MS) was employed, to assess their chemical composition and potential leaching behavior.

ATR-FTIR and Py-GC–MS analyses revealed that polymer aging (oxidation) occurred in surgical masks exposed to seawater. In contrast, nitrile gloves aged in sand exhibited a loss of the characteristic nitrile absorption band. DART-MS further revealed that both masks and gloves exhibited limited degradation. Nevertheless, some noteworthy patterns emerged. Metal chlorides present in gloves were completely released, while phthalates were prone to oxidation when aged in beach sand. Regarding face masks, similar trends were discovered, again showing more pronounced chemical aging behavior in sand-aged samples. In conclusion, this study highlights that a multidisciplinary analytical approach is required to understand the impact of plastics towards the marine ecosystem.

1. Introduction

Since the start of the COVID-19 pandemic, 777 million infection cases have been reported to the World Health Organization (WHO) (World Health Organization, 2025), either or not resulting in a pathological condition. A possible mitigation strategy to reduce this viral transmission was personal protective equipment (PPE), such as face masks and gloves (Cook, 2020; Dogan et al., 2023; Roberts et al., 2022). This strategy resulted in a surge towards PPE usage, resulting in an estimated global use of 129 billion face masks and 65 billion gloves monthly (Ortega-Borchardt et al., 2024). Even though these measures were proven to safeguard the public health, the increased usage introduced new environmental challenges. The latter is primarily originating from its incorrect disposal (Ortega-Borchardt et al., 2024). Improper

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disposal of PPE places considerable stress on the environment, particularly in marine and coastal ecosystems, where these items frequently accumulate. Consequently, concerns raise about their long-term environmental impact and chemical stability, especially given that PPE contributes to the estimated 5 to 13 million tons of waste entering oceans annually (Aragaw, 2020; Mattan-Moorgawa et al., 2021). As a result, understanding the long-term environmental impact of discarded PPE is essential, especially regarding potential chemical degradation and pollutant release. This is especially critical because PPEs are mainly composed of synthetic polymers such as polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), among others, which are highly resistant to degradation (Akhtar et al., 2023).

Apart from the physical appearance and accumulation, concerns are also raising regarding the chemical stability of PPE under strong environmental conditions. This concern is highlighted by the fact that PPE often contains different chemical additives, such as plasticizers and antimicrobial agents, which may leach into the environment over time (Dogan et al., 2023; Oteef et al., 2023). These substances can exhibit toxic, bio-accumulative, or endocrine-disrupting properties (Chiu et al., 2020; Chung et al., 2019; Forner-Piquer et al., 2017; Qadeer et al., 2022), harming aquatic organisms (Zhang et al., 2021; Albarano et al., 2025) and potentially entering the human food chain. Environmental factors such as UV exposure, temperature fluctuations, and microbial activity can further accelerate PPE degradation, leading to the formation of degradation products or leaching with unknown ecological consequences. Despite these concerns, research on the long-term chemical fate of PPE in marine environments remains limited and is recommended to improve the understanding of the associated consequences (Ortega-Borchardt et al., 2024).

Therefore, to address the knowledge gap of the potential environmental impact introduced by improper PPE disposal, PPE items made from synthetic polymers, including nitrile, latex, vinyl gloves, and various face mask types (FFP2, surgical, and generic) were included into a long-term in-situ study, by exposing them to beach sand and seawater for 18 months. The study aimed to deploy a range of analytical techniques to investigate the chemical (i.e., additive disappearance and oxidation) and structural (i.e., polymer oxidation hypothetically induced by UV-irradiation) alterations of PPE materials following prolonged marine environmental exposure. Moreover, although the critical phase of the pandemic is essentially over, the potential impact on ecosystems, and in particularly marine ecosystems, remain significant (Ajaj et al., 2023; Du et al., 2022; Liu et al., 2024; Yang et al., 2022; Zhao et al., 2024). This persistence underscores the importance of considering both the long-term bioavailability of microplastics and the potential toxicity of associated additives to living organisms.

2. Material and methods

2.1. *Experimental design*

The in-situ experiment was conducted, as described by De Monte et al. (2022), in the Bay of Santa Teresa, a small inlet located within the touristic and commercial Gulf of La Spezia, Italy (Fig. 1), near the headquarters of the National Research Council (CNR) and the National Institute of Geophysics and Volcanology (INGV). The bay also serves as a test site for various scientific projects and is home to an underwater observatory called LabMARE (De Monte et al., 2022).

This underwater multi-parametric platform is managed by the Ligurian Cluster of Marine Technologies (DLTM), in collaboration with INGV, CNR, the Italian National Agency for New Technologies, energy and Sustainable Economic Development (ENEA), and the Hydrographic Institute of the Navy, as part of the LabMARE project funded by the Liguria Region. Its purpose is to assess new technologies and monitor the environmental status. The platform, placed on 10 m depth and 80 m far from the coast is equipped with CTD (conductivity, temperature and depth) sensors for monitoring environmental parameters such as temperature and salinity, and provides real time data via an underwater connected land-based station, as well as through internet data transmission. Additionally, for this specific experiment, a cage system, consisting out of two large cages (70 cm × 30 cm) and twice eight baskets with 1 mm mesh netting (19 cm × 14 cm and 14 cm × 14 cm), was built of stainless steel 316 by Vamp s.n.c. (a company specialized in the industrial and naval sectors in La Spezia) in November 2020. From this cage system two dedicated cages for studying plastic and bioplastic degradation in the marine environment were installed to the platform (Fig. 2). Moreover, metal was chosen over plastic as construction material for cages and baskets, to overcome potential contamination of the inserted samples, such as the possible release of additives from plastic materials (Accustandard, 2024). The only plastic elements used were large plastic ties, which were required to fix the cages to the underwater observatory. All components were equipped with sacrificial anodes to prevent galvanic corrosion. Besides the underwater station, a sandbox was also established on land near the LabMARE station, containing sand that was collected from the Gulf of La Spezia (Le Grazie Bay).

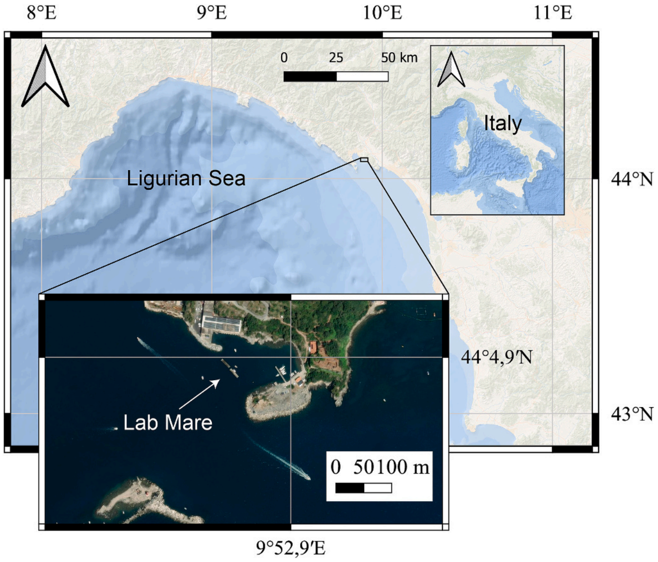

Fig. 1. Geographic location of LabMARE research station, inside La Spezia Gulf, Italy.

The experimental setup was fully established on March 3rd 2020, with the deployment of the LabMARE station and the cages. However, due the COVID-19 health emergency that enacted the national lockdown in Italy from start of March to June 2020, the sandbox was relocated near Sarzana (44°7′51.04″ N; 9°57′28.88″ E), to ensure the monitoring and protection of the samples. On September 18th 2020, six surgical masks (Type 1 “Protect96”), one generic mask (Bonzonella Care PF2ST-PO1, Type I, Class I Medical Device), two FFP2 masks (KN95 HRD) and three pairs of gloves (latex gloves “VWR international”, Class I, AQL 1.5 powder free; nitrile gloves “DOC zero veloforte” AQL < 1.5, powder free; Vinyl gloves “R36 Reflex” AQL 1.5 powder free, thickness 0.07 mm ± 0.02) were added into the sea cages and the sandbox, separately. The aforementioned masks were selected based on the common usage and availability on the market following the end of the first COVID-19 lockdown in Italy (Li et al., 2020; Rahman et al., 2022; Santarsiero et al., 2021; Xie et al., 2021). On the other hand, the used gloves were selected based on the types commonly used (Phalen and Meibach, 2022) and sourced from the CNR laboratories. Further, the PPE materials were removed only after 18 months. This timeframe was chosen to mimic long-term exposure and due to practical constraints of prolonging the experiments.

Fig. 2. Visual overview of PPE samples: (a) pristine condition; (b) placed in a cage for seawater submersion; (c) positioned in a sandbox for terrestrial exposure; (d, f) after 18 months of seawater exposure; and (e, g) after 18 months of sand exposure. Samples include various glove types (vinyl, latex and nitrile) and face masks (generic, FFP2 and surgical).

2.2. Polymer alteration analysis

2.2.1. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

To elucidate the potential alterations on the surface of the exposed materials, ATR-FTIR analyses were performed using a Nicolet™ iS20 FTIR Spectrometer equipped with ATR ID7/ITX AR at single-reflection coated diamond crystal. After background correction, a minimum of three spectra per sample were acquired over the spectral range of 4000 and 500 cm^{-1}, with 64 scans collected at different points across the sample's surface. The obtained spectra were then normalized using a characteristic absorption band specific to each material. To ensure consistent comparison, the spectra were averaged using Origin 2023 considering 1000 data points per spectrum in order to standardize the scale for comparison. All spectra were recorded for the pristine materials, as well as those aged for 18 months in the sea and sand conditions.

2.2.2. Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC–MS)

Potential changes in the polymer composition induced by the weathering conditions were further qualitatively investigated by Py-GC–MS. A part of the samples (i.e. nitrile, latex and vinyl gloves, and FFP2, surgical and generic face masks) were transferred into a pyrolysis cup (PY1-EC80F, 80 μL, Frontier Lab Ltd.), in duplicate. Following the sample transfer, the cups were introduced into the EGA/Py-3030D multi-shot microfurnace pyrolyzer using an AS2020-E autosampler, both from Frontier Lab Ltd. All samples were pyrolyzed under a helium atmosphere using the single shot approach at 590 °C for 0.3 min. Subsequent to the pyrolysis, the produced pyrolyzates were injected into the gas chromatograph (7890B, Agilent Technologies) with a split ratio of 100:1 and a constant helium flow of 1 mL/min. The separation was executed using an Agilent Technologies DB-5 MS column (30 m × 0.25 mm × 0.25 μm) of which the oven program started at 40 °C for 2 min and further ramped to 320 °C at a ramping rate of 5 °C/min, and finally held for 14 min. Lastly, the separated pyrolyzates were detected using a 5977B MSD single quadrupole mass spectrometer from Agilent Technologies. The MS was operated in scan mode between 40 and 550 m/z with a scan rate of 2.9 scans per second, while electron ionization was used in positive ionization mode (70 eV).

The data obtained were treated using the Agilent MassHunter Qualitative Analysis 10.0 software, and the F-Search software version 3.6.4 from Frontier Lab Ltd.

2.3. Determination of additive composition, leaching and degradation

2.3.1. Direct Analysis in Real Time Mass Spectrometry (DART-MS)

To gain deeper insight into the additive chemical composition of the various samples and to elucidate the effect of different weathering conditions, an exploratory screening was conducted using a high-resolution, accurate mass Q Exactive Orbirtrap mass spectrometer (MS) from ThermoFisher, equipped with a Direct Analysis in Real Time (DART) ion source from IonSense. The DART-SVP software interface was used as controller of the DART-source.

During the analysis, samples (i.e. nitrile, latex and vinyl gloves, and FFP2, surgical and generic face masks) were held in front of the DART-source without any sample preparation. Helium, used as carrier gas, was heated to 400 °C and exited the source in an excited state. These excited helium species were used to ionize the molecules present in the samples, which were subsequently introduced into the mass spectrometer. The HRMS was operated in both negative and positive ionization modes, with a scan range of 50–750 m/z, a resolution of 140,000, and a scan rate of 3.7 scans per second. Prior to data acquisition, the HRMS was calibrated in both ionization modes using the Pierce™ FlexMix™ calibration solution (ThermoFisher).

After performing the experimental analysis, the obtained data was processed with an in-house built workflow using the FreeStyle™ 1.8 SP2 QF1 from ThermoFisher, an in-house developed database containing the accurate masses of numerous chemical compounds, and a custom python script. After comparing the obtained accurate masses with the database, compounds were assigned, while the unassigned compounds were manually evaluated and based on their isotopic pattern and accurate mass, a chemical formula was proposed.

3. Results and discussions

3.1. Polymer alteration analysis

3.1.1. Surface polymer alteration investigation by ATR-FTIR analysis

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) is a widely used technique for characterizing chemical compositions of material surfaces. In this study, ATR-FTIR analysis was employed to investigate the surface chemical alterations in various types of PPE (face masks: generic, surgical and FFP2, and gloves: latex, vinyl and nitrile) in their pristine state and after 18 months of environmental aging under marine and sandy conditions. This non-destructive method enables the detection of molecular alterations such as oxidation, polymer degradation, and the formation of new functional groups (Beltran-Sanahuja et al., 2020; Campanale et al., 2023; De Monte et al., 2022).

The degradation of PPE in the marine environment can vary significantly depending on material composition and exposure conditions, with presumable factors such as salinity, UV radiation, and biofouling potentially leading to distinct chemical and physical alterations over time.

Generic masks are primarily composed of synthetic fibers, such as polyester and polyamide (nylon), often used in combination with natural fibers like cotton to enhance breathability, comfort, durability and flexibility. The ATR-FTIR spectra of the generic mask samples (Fig. 3A) display features consistent with polyamide-based fabrics, like N—H stretching around 3300 cm^{-1}, C—H stretching near 2900 cm^{-1}, C=O stretching (amide I band) between 1630 and 1650 cm^{-1}, N—H bending and C—N stretching (amide II band) around 1540 cm^{-1} and C—O and C—N stretching between 1000 and 1300 cm^{-1} (Bhullar et al., 2021; Fernandez-Gonzalez et al., 2021). However, specific alterations were observed that provide insights into degradation mechanisms occurring in marine and sandy environments. In the pristine generic mask, a distinct absorption band is observed at 1736 cm^{-1}, which is typically assigned to the C=O stretching vibration of ester or carbonyl-containing functional groups. This absorption band is not typical of the polyamide backbone and may be attributed to residual additives like for instance plasticizers containing ester or carbonyl functionalities (Lievens et al., 2022a, 2022b; Verleye et al., 2001). After 18 months exposed to the marine environment (Fig. 3A, blue line), this carbonyl band at 1736 cm^{-1} disappears, suggesting possible hydrolytic degradation or leaching of ester-based compounds upon prolonged exposure to water. This may indicate chemical alterations of surface layers or additive leaching in aqueous conditions. In contrast, the samples aged in the sandbox environment (Fig. 3A, orange line) show a noticeable increase in the intensity of the band at 1036 cm^{-1}, likely related to C—O or Si—O stretching. The latter possibly due to adherence of silicate particles (sand) or to surface oxidation products (De Monte et al., 2022). This may presumably reflect photooxidative and/or mechanical degradation processes, resulting from prolonged UV exposure and physical abrasion. The stability of the main polyamide bands suggests that the polymer backbone remains largely intact under the applied environmental conditions.

FFP2 and surgical face masks, although designed for different protective purposes, are commonly manufactured using similar materials. Both types of masks are typically composed of multiple layers of nonwoven polypropylene (PP), a thermoplastic polymer widely used in personal protective equipment due to its lightweight, breathable, and chemically resistant properties. The shared use of polypropylene allows for effective filtration and mechanical strength, making it a preferred choice for disposable respiratory protection (Hossain et al., 2023; Venkataraman et al., 2023). Despite differences in structural design and filtration efficiency, their material similarity makes them similarly susceptible to environmental degradation processes when exposed to environmental conditions. The ATR-FTIR spectra of surgical and FFP2 masks initially show the characteristic absorption bands of PP (Fig. 3B and C, black line). In both cases the spectra exhibited bands between 1778 cm^{-1}. These are typically associated with the C=O stretching of potential additives (Lievens et al., 2022a, 2022b; Verleye et al., 2001). However, when the mask is exposed to environmental conditions such as sand or seawater, significant spectral variations were observed. In both exposure scenarios, no intensity increase of the broad absorption band around 3330 cm^{-1} was observed. This band is generally attributed to O—H stretching vibrations, suggesting the adsorption or incorporation of water, possibly due to increased surface oxidation or biofilm formation on the mask's surface. On the white side of the surgical mask, after environmental exposure, a broad band between 1719 and 1512 cm^{-1} centered around 1649 cm^{-1} appears, this could indicate the presence of new carbonyl-containing functional groups (like esters, acids, or ketones), which are indicative of oxidative degradation or contamination from organic matter (Lievens et al., 2022a, 2022b; Szymanska-Chargot and Zdunek, 2013). Additionally, the region between 1160 and 960 cm^{-1}, centered at 1045 cm^{-1}, became more prominent. This spectral area is typically associated with C—O stretching vibrations, possibly from alcohols, esters, or residual sand on the sample. Interestingly, in the marine environment, the original bands between 1778 and 1503 cm^{-1} completely disappeared. This could be due to a few phenomena, like for instance physical erosion of the mask's surface, leaching of certain chemical additives or degradation by the marine environment. Moreover, the growth of biofilms and the accumulation of organic materials might suppress the original polymer signals, or even chemically alter the surface, leading to the disappearance of the characteristic bands.

Overall, due to the observed alterations, it can be presumed that polypropylene surgical masks undergo considerable chemical and physical transformations in natural environments. The marine setting seems to promote more advanced degradation or fouling processes, effectively altering or eliminating some of the original spectral features of the material (Dimassi et al., 2023; Ma et al., 2022).

Furthermore, analyzing the FFP2 masks exposed to a sand environment, also a completely different ATR-FTIR spectrum was observed on the inside layer of the mask (Fig. 3C, orange dotted line). This new spectrum was characterized by distinct and sharp absorption bands at 1703 cm^{-1}, 1255 cm^{-1}, 1100 cm^{-1}, and 725 cm^{-1}, suggesting that the inner layer is composed of a material different from the typical polypropylene used in the outer layers. In conclusion, the observed spectral features strongly indicate that the exposed inner layer of the FFP2 mask is composed of a polyester-type material, most likely polyethylene terephthalate (PET) or a related copolyester (Verleye et al., 2001). These materials are commonly employed in filtration layers owing to their structural stability, and chemical and bacterial resistance (Venkataraman et al., 2023), which is an essential property for maintaining the filtration efficiency of FFP2 masks. The detection of this inner layer suggests that environmental stressors in the sandbox, such as mechanical abrasion, UV irradiation or thermal cycling, may have contributed to the degradation or removal of the outer layers, thereby revealing the internal filtering component.

Nitrile gloves are predominantly composed of acrylonitrile butadiene rubber (NBR), a copolymer synthesized from acrylonitrile and butadiene monomers. This composition imparts excellent chemical resistance, mechanical strength, and flexibility, making them suitable for various applications, such as gloves (Herkins et al., 2024). The ATR-FTIR spectrum of NBR exhibits several characteristic absorption bands. First, the sharp peak around 2237 cm^{-1}, indicative of the nitrile functional group (C≡N stretching), C—H stretching bands between 2850 and 3000 cm^{-1}, corresponding to aliphatic C—H bonds, C=C stretching near 1640–1660 cm^{-1}, associated with the butadiene units, CH_2 bending at 1450 cm^{-1} and C—H out-of-plane bending observed between 700 and 900 cm^{-1} (Chakraborty et al., 2007; Ouyang et al., 2009; Smith, 2019). When nitrile gloves were subjected to sandy environments, the lack of the nitrile absorption band at 2237 cm^{-1} in the ATR-FTIR spectrum after environmental exposure suggests chemical transformations of the nitrile groups. It can be hypothesized that this transformation is cause by the cyclization phenomenon, where nitrile groups undergo intramolecular reactions to form cyclic structures. In polymers like polyacrylonitrile, thermal treatment leads to the formation of ladder-like structures through cyclization, resulting in the loss of the nitrile peak and the emergence of new bands corresponding to conjugated C=N and C=C bonds in the 1610–1660 cm^{-1} and 1450–1600 cm^{-1} (Fig. 3D, orange line) (Ouyang et al., 2009; Smith, 2019). However, when nitrile gloves were exposed to a marine environment, instead, ATR-FTIR spectrum reveals considerable changes, indicating chemical and physical alterations of the material surface. Two notable spectral features were observed, being a broad and intense band at 3435 cm^{-1}, which was also present when exposed to sand environments, and a narrow peak at 1265 cm^{-1}. The broad absorption band centered around 3435 cm^{-1} is characteristic of O—H stretching vibrations, typically associated with hydroxyl groups or water molecules that may arise due to formation of

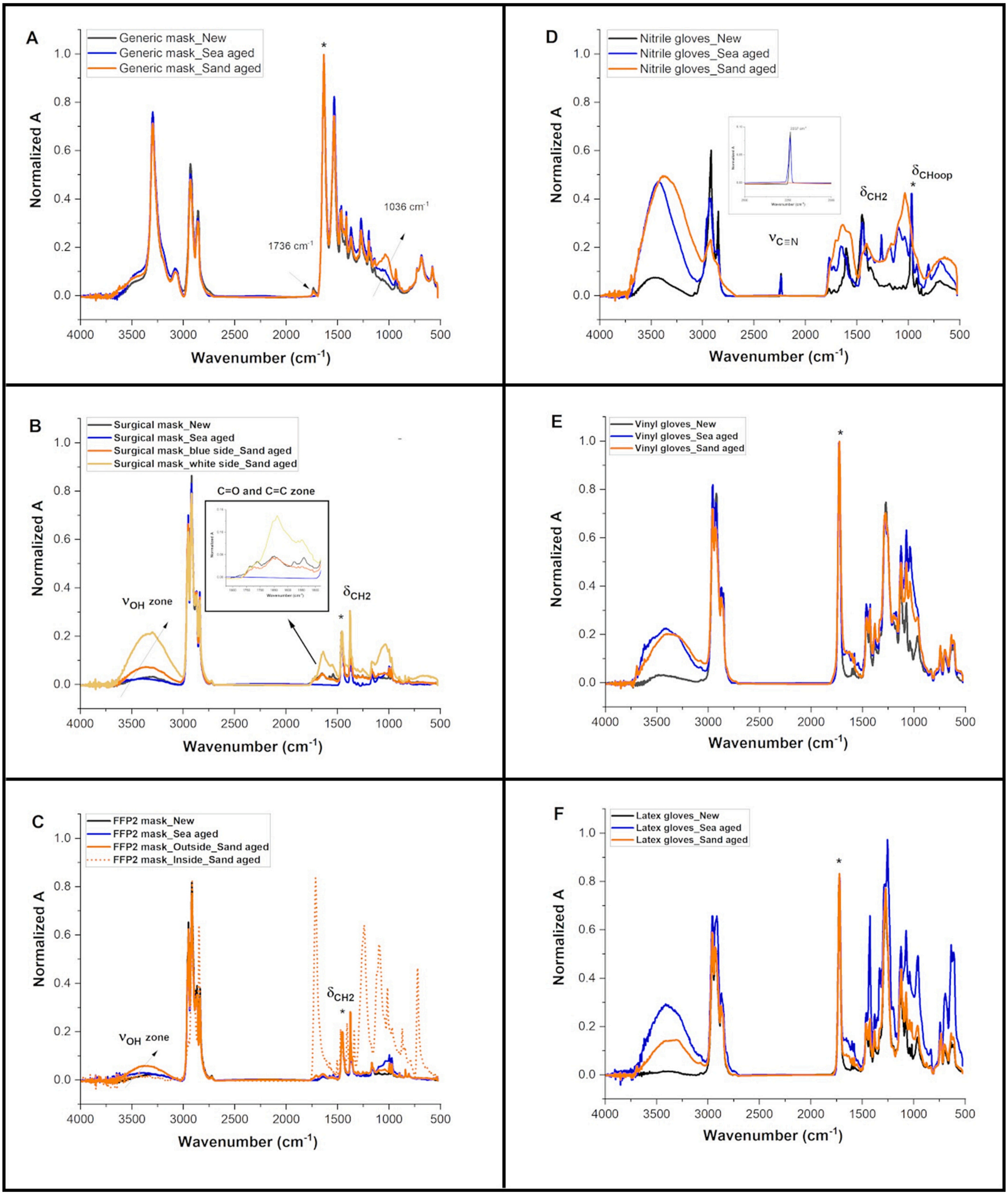

Fig. 3. ATR spectra overlays of A) generic, B) surgical and C) FFP2 masks, and D) nitrile, E) vinyl and F) latex gloves. The asterisk (*) highlights the band used for spectral normalization. The black, blue, and orange lines correspond to new, sea-aged, and sand-aged samples, respectively. The yellow line in panel B represents the white side of the surgical mask after sand exposure, while the dotted line in panel C refers to the inner side of the FFP2 mask after sand exposure. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

hydroxyl groups in marine conditions (UV light, salt ions, oxygen), potentially inducing oxidative degradation, resulting in the formation of alcohol or hydroxyl-containing functional groups on the surface of the polymer chains. The narrow peak at 1265 cm^{-1} indicates C—O stretching or O—H bending, which can also arise from alcohol groups formed during oxidation of the polymer (Campanale et al., 2023). Alternatively, this band may also correspond to C—N stretching vibrations arising from degradation byproducts, depending on the specific formulation of the glove material (Vouvoudi et al., 2022).

Unlike nitrile gloves, vinyl and latex gloves exhibited dominant absorption bands associated to plasticizers, which are commonly added to increase their flexibility and softness (Gee, 2023). These plasticizer bands can dominate the spectrum, potentially masking the characteristic signals of the base polymer. In contrast, nitrile gloves typically do not require such additives in the same quantities, allowing the IR spectrum to more clearly reflect the intrinsic features of the used polymer. This distinction enables more direct identification of the glove material in nitrile samples compared to vinyl or latex.

Vinyl gloves are primarily composed of polyvinyl chloride (PVC), a synthetic thermoplastic polymer. The ATR-FTIR spectrum of PVC exhibits several distinctive absorption bands and in particular the strong absorption of C—Cl Stretching near 600–700 cm^{-1}, due to the presence of carbon-chlorine bonds (Verleye et al., 2001). Latex gloves, on the other hand, are made of natural rubber, which is mainly composed of cis-1,4-polyisoprene (Gee, 2023; Martin-Martinez, 2002). As shown in Fig. 3E and F, the presence of the dominant band around 1722–1726 cm^{-1} in the ATR-FTIR spectra of both vinyl and latex gloves corresponds to C═O stretching vibrations of ester groups, suggesting the presence of plasticizers (e.g., phthalates) (Verleye et al., 2001), which may migrate to the surface over time. Given the surface-sensitive nature of ATR-FTIR, even trace amounts of migrated additives can generate strong spectral signals, potentially overshadowing the characteristic bands of the bulk polymer.

When vinyl gloves were exposed to marine and sand environments, an increase in the absorption band around 1040 cm^{-1} was observed. This band is associated with C—O stretching vibrations of additives, like plasticizers, present in the material and indicates accumulation or chemical modification of plasticizers or other additives in vinyl gloves during aging. Additionally, an increase of the O—H stretching band was observed, indicating the formation of hydroxyl groups, which indicates oxidation and hydrolysis reactions, probably promoted by exposure to humidity, UV irradiation and environmental factors present in both sand and seawater. These processes lead to the formation of hydroxylated compounds and alter the chemical structure of the surface layer. Plasticizers present in latex gloves can also undergo significant chemical changes when exposed to harsh environments such as seawater and sand combined with UV irradiation. These changes are reflected in the ATR-FTIR spectra by the appearance or increase of specific absorption bands. In marine environments, latex gloves began to show the characteristic infrared bands of natural rubber latex (Fig. 3F, blue line), indicating the exposure of the underlying polymer structure (Fig. 3F, marked with §). Meanwhile, the plasticizer tends to migrate out of the glove material and may accumulate or condense on the surface (Fig. 3F, framed bands). The broad band at 3434 cm^{-1} corresponds to O—H stretching vibrations, indicating the formation of hydroxyl groups or the adsorption of water molecules on the plasticizer molecules. Exposure to seawater promotes hydrolytic and oxidative degradation of plasticizers, leading to the formation of hydroxylated and oxidized compounds. These chemical changes result in an increase in absorption bands linked to —OH groups and an alteration of carbon-hydrogen vibrations. The presence of water and salt ions catalyzes these reactions, causing degradation of plasticizers and modification of the surface chemistry of latex gloves (Baskaran and Sathiavelu, 2020).

3.1.2. *Polymer weathering by Py-GC–MS*

Py-GC–MS was employed to further elucidate potential alterations in the polymer structure after 18 months of exposure. Initially, minimal differences were observed in the pyrograms when a ramping rate of 20 °C/min was applied, indicating that structural modifications were limited. To enhance the resolution of the potential alterations, particularly oxidative transformations, a slower ramp rate of 5 °C/min was applied, allowing for improved separation of potential degradation products (see Fig. 4 and Figs. S1–S5).

Py-GC–MS analysis identified diisononyl phthalate (DINP) as the primary additive in both vinyl and latex gloves, confirming the results obtained by ATR-FTIR and its widespread use as a plasticizer in these types of protective gloves (Gee, 2023; Oteef et al., 2023). Apart from detecting the main plasticizers and the marker compounds of the glove polymers (i.e., acrylonitrile, benzonitrile, naphthalene) (Hiltz, 2000; Kaal et al., 2023; Kusch, 2013), minimal signs of environmental weathering were observed, as evidenced by the similarity across all pyrograms, i.e. virgin and weathered gloves (Figs. S1–S3). The lack of visible degradation effects may be attributed to the inherent chemical stability and resistance of the polymers (Zhang et al., 2024) or alternatively, to the possibility that the employed technique lacked the capacity to detect subtle alterations across the samples injected. In contrast to the protective gloves, more pronounced aging and weathering effects were observed in the face masks. Py-GC–MS analysis confirmed that both surgical and FFP2 masks are composed of polypropylene (PP), exhibiting similar pyrogram profiles, confirming the FTIR analysis. Interestingly, signs of polymer aging, and more particularly oxidation, were more prominent in surgical masks. However, the underlying reason remained unclear, as both masks were composed of PP. A potential hypothesis may involve the differences in mechanical properties of the materials used. As shown in Fig. 4, the characteristic PP fingerprint pattern is visible, but additional peaks emerge approximately half a minute before the main PP peak. These newly observed peaks are likely associated with oxidation, although confirmation of its identity is limited by the low resolution of the mass spectrometer and strong compound fragmentation. Given that a non-polar column was used, the earlier retention time suggests that the compounds are more polar, possibly due to oxygen incorporation into the polymer structure.

Interestingly, contrary to expectations, the oxidation pattern was only observed in surgical face masks that had been exposed to seawater for 18 months, while it was absent in masks subjected to UV irradiation in beach sand. Furthermore, the oxidation pattern was not detected in FFP2 masks (Fig. S4), despite their similar PP composition. Instead, benzoic acid was more pronounced in these samples, presumably originating from the degradation of phthalate-based plasticizers. This degradation may be facilitated by *Achromobacter* species, which are known to have the ability to convert phthalates into phthalic acid and benzoic acid (Zhang et al., 2018; Wang et al., 2021), and have been identified in deep-sea environments (Zhang et al., 2014).

Lastly, for generic face masks (Fig. S5), minor differences were observed in seawater-exposed samples, but no clear explanation could be determined. Given the limited signs of degradation across the different samples, alternative analytical approaches should be considered in future investigations. In order to elucidate potential oxidation fragments, the use of soft ionization techniques (e.g., chemical ionization) could provide more detailed insights into oxidation products. Additionally, to enhance the detection of potential alterations, future studies could benefit from the application of pyrolysis coupled to comprehensive two-dimensional gas chromatography (GC × GC) and high-resolution Time of Flight mass spectrometry (HR-ToF-MS) for non-target screening. The extra chromatographic dimension enhances separation, which supports discovering co-eluting compounds, enabling a more detailed characterization of structural or compositional differences. Finally, employing alternative ionization sources is recommended to expand the chemical area covered. For the latter purpose, Atmospheric Pressure Photo-Ionization (APPI) facilitates the detection of less polar to non-polar, thermally stable compounds, providing valuable insight into polymer aging and chemical leaching behavior.

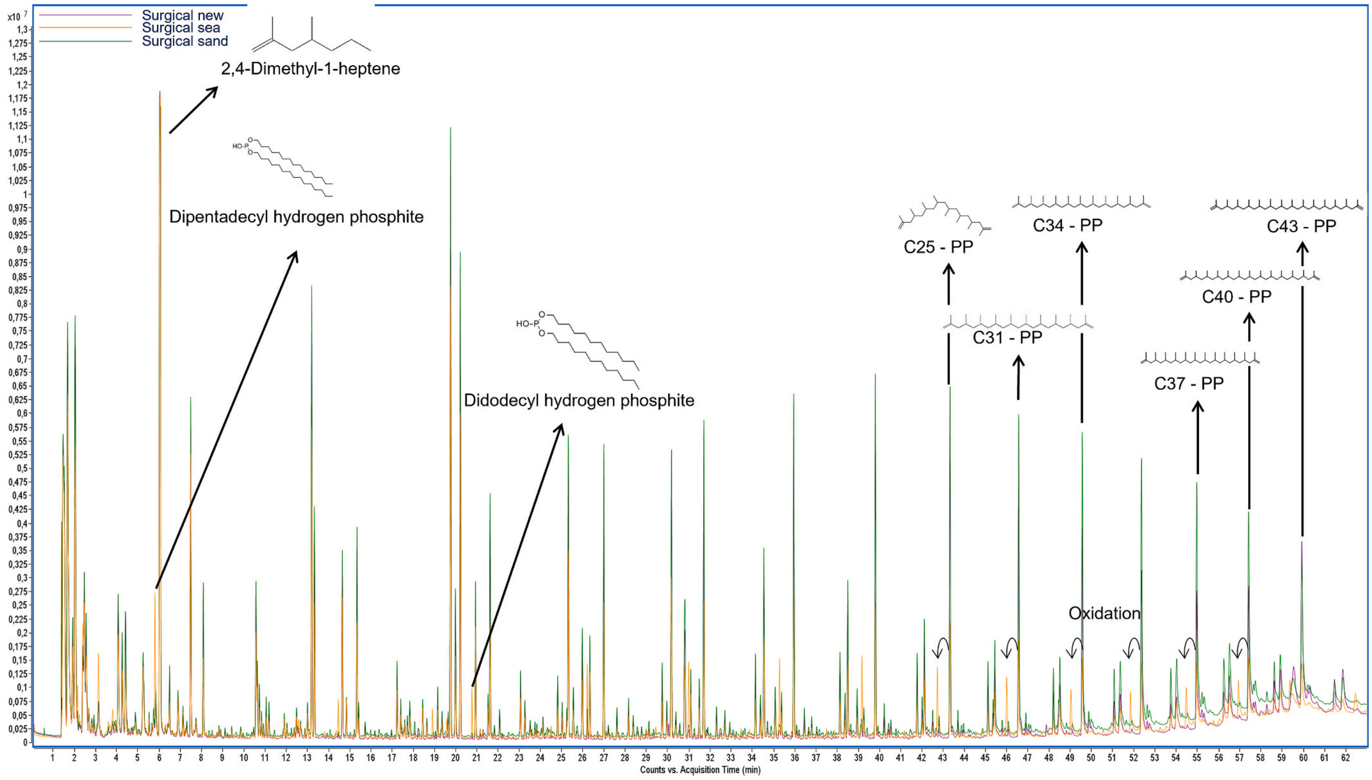

Fig. 4. Overlay of three pyrograms of surgical face masks. The purple line displays the pyrogram of a virgin face mask, while yellow and green lines correspond to surgical masks aged for 18 months in sea and sand conditions, respectively. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

3.2. Determination of the Additive disappearance and Alteration (DART-MS)

To elucidate potential leaching of additive chemicals a non-target screening approach using DART-MS was employed. To the best of our knowledge, this method has not been previously applied to detect environmental changes induced to PPEs. It enabled the identification of various chemical compounds present in different types of protective gloves (nitrile, vinyl and latex) under environmental exposure conditions (i.e., 18 months in sea or beach sand). The analysis revealed that

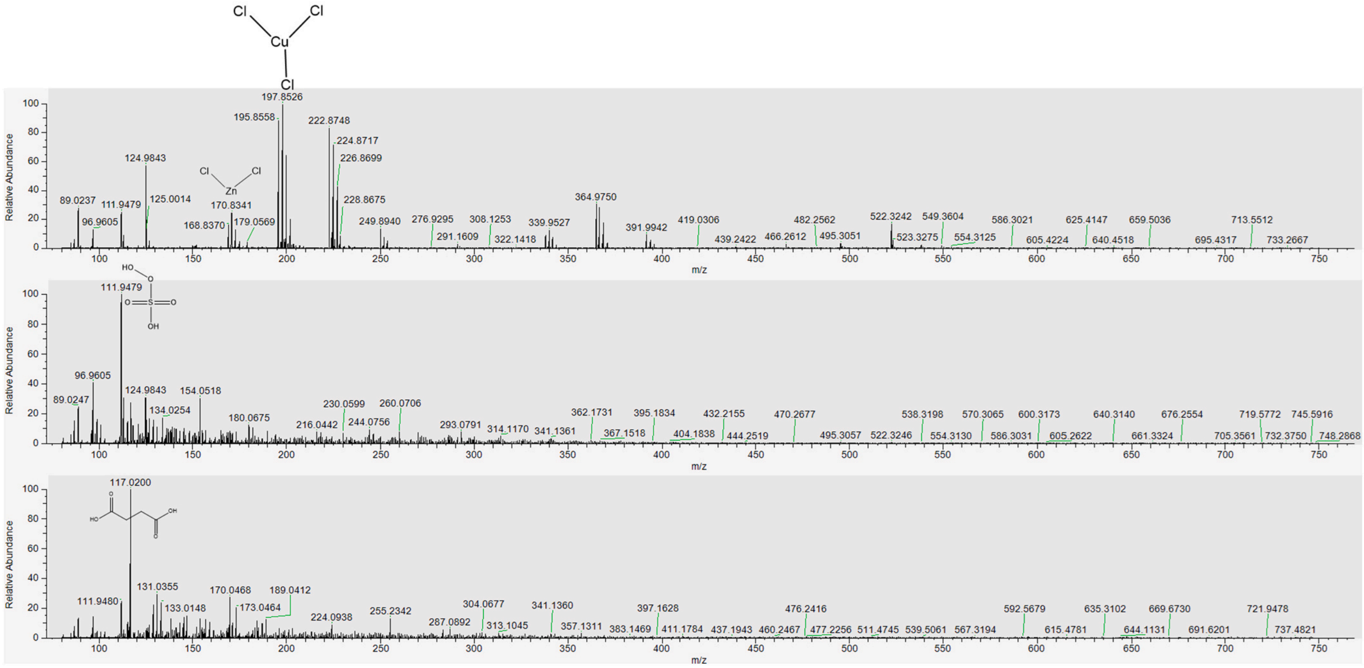

Fig. 5. The mass spectra (negative ionization mode) from the Direct Analysis in Real Time coupled to High-Resolution Mass Spectrometry analyses of nitrile gloves. The top figure represents new gloves, while the middle and bottom figures depict 18 months sea and sand aged nitrile gloves, respectively.

nitrile gloves contained metal chloride compounds, likely added as antibacterial agents (Gee, 2023; Dogan et al., 2023). However, following exposure to environmental conditions such as beach sand and seawater, these compounds were completely leached out as depicted in Fig. 5. This behavior indicates the potential of unintended release of metal chlorides (e.g. $ZnCl_2$ and $CuCl_3$), and thus heavy metals, into the surrounding environment, potentially contributing to aquatic pollution and negatively affecting marine organisms (e.g. inducing carcinogenic effects) or transferred to humans through the food chain (Ahamad et al., 2024; Santhosh et al., 2024). Despite the observed leaching of metals, no other major compounds appeared to leach from nitrile gloves under these conditions. Interestingly, DART-MS analyses of nitrile gloves that were exposed to beach sand for 18 months revealed the presence of surfactants, as shown in Fig. S6. Their detection suggests environmental contamination of the gloves rather than an inherent compound of the material. This hypothesis is supported by the fact that surfactants are highly released into the environment via, for instance, agrochemical products or wastewater treatment plant effluents (Badmus et al., 2021).

In addition to nitrile gloves, vinyl gloves were subjected to the DART-HRMS screening. Consistent with the Py-GC–MS and ATR-FTIR measurements, results demonstrated that they primarily contained plasticizers, such as terephthalates or phthalates (see Figs. S7 and S8). These plasticizers are commonly added in order to functionalize the polymer material by enhancing its flexibility and usability (Gee, 2023; Poitou et al., 2021). Unlike nitrile gloves, the leaching behavior of vinyl gloves varied depending on the environmental conditions. When exposed to a marine environment for 18 months, no considerable release of plasticizers was observed, probably due to their hydrophobic character. This is supported by the high octanol/water partition coefficient (Kow), which is defined as the ratio of a chemical concentration in n-octanol and water at equilibrium (Bialecka-Florjanczyk and Florjanczyk, 2007; Shaikh et al., 2018). As a result, plasticizers like diisononyl phthalate, having a Kow of 9.37 (National Center for Biotechnology Information, 2025), are not prone to leach out as they are considered as highly hydrophobic (Cumming and Rücker, 2017). However, exposure to beach sand resulted in the leaching of certain phthalate compounds (e.g. mono and diisononyl phthalate) into the environment. These compounds are well-documented toxicants, capable of inducing endocrine disruption and other adverse effects in biota (Chung et al., 2019; Forner-Piquer et al., 2017; Lievens et al., 2024; Qadeer et al., 2022). Additionally, some phthalate compounds (e.g., diisononyl phthalate) underwent oxidative transformation during sand exposure, presumably driven by UV irradiation. Since UV is strongly attenuated in coastal water penetration is limited in underwater environments (Tedetti and Sempere, 2006), photochemical oxidation cannot occur, underscoring the critical role of sunlight exposure in shaping the degradation pathways and environmental fate of these compounds.

The last type of gloves included in this study was latex gloves, which share a similar chemical composition to vinyl gloves, including the presence of plasticizers such as phthalates, exhibited comparable leaching behavior (Figs. S9 and S10). Under sand exposure, certain phthalates (e.g., mono and di isononyl phthalate) were released, while others underwent oxidative transformation (i.e., di isononyl phthalate), likely due to UV irradiation. In contrast, no significant leaching was observed under marine environment, further supporting the role of environmental conditions in dictating leaching and degradation behavior.

These findings highlight the environmental risks associated with the use and disposal of protective gloves. The leaching of toxic compounds, such as metal chlorides and phthalates, into marine and terrestrial ecosystems poses a threat to aquatic and terrestrial organisms. Moreover, the oxidative transformation of phthalates under UV exposure introduces additional complexity, as the transformation products may exhibit distinct toxicological profiles. Further research is warranted to comprehensively assess the long-term effects of these leached and transformed compounds on the ecosystem's health. Additionally, minimizing improper disposal of PPE is critical to mitigating their environmental footprint. Addressing the latter requires a multi-faceted strategy encompassing public awareness, regulatory framework, additional complementary measures.

In addition to the three different gloves, three different face masks (FFP2, surgical and generic) were subjected to DART-HRMS screening. The analyses of the face masks revealed a similar pattern to those observed in the various glove types (see Figs. S11–S16). All face mask types contained plasticizers (e.g., di isononyl phthalate), which in all cases leached to a limited extent when exposed for 18 months to sand weathering conditions, while it was not the case for sea weathered samples. Also here, it can be presumed that the plasticizers preferably remain in the polymer structure due to the high Kow as described earlier. As a result, those plasticizers might end up and accumulate in beach environments potentially causing adverse effects due to their carcinogenic properties (Chung et al., 2019; Forner-Piquer et al., 2017; Qadeer et al., 2022). In contrast to the gloves, the plasticizers did not exhibit any oxidation patterns. However, the reasoning remained unclear. It can be presumed that the measured part of the face masks was not directly in contact with sun rays, resulting in a lack of oxidation fragments.

In addition to the similar leaching behavior between face masks and gloves, interestingly an additional phenomenon, deposition, was observed for all face masks. For all samples iodine deposition was observed in samples exposed to the marine environment for 18 months. Even though it is obvious that it is not present on sand aged samples, it is apparent that it only occurs for face masks and not with other samples. It can be hypothesized that this phenomenon is more likely to occur in samples exhibiting specific surface roughness characteristics, as increased roughness corresponds to a larger surface area and more pronounced deposition.

Lastly, regarding generic face masks (Figs. S15 and S16), a surprising phenomenon took place. In both weathering cases, but more pronounced when sand-aged, the generic masks contained a recombination of fatty acids with sugars forming sugar fatty acid esters or so-called sugar esters (SEs) (Zheng et al., 2015). Unfortunately, it was not feasible within this study to elucidate the structural formula of these compounds, which complicates further elaboration. Therefore, future research should be performed, in order to elucidate the formed chemical structure and to better understand the degradation pathways of generic face masks in the marine environment.

In summary, several molecules disappeared from the studied samples or were further formed indicating their leaching into the environment. However, this study aimed to gain analytical insights into the behavior of PPE and its accompanying additive chemicals, but bioaccumulation and toxicity is not addressed due to the approach selected upfront. Therefore, it's highly recommended in future studies to explore the fate of the identified chemicals, using a targeted approach. It will provide numerical data to further address the loopholes towards potential bioaccumulation and toxicity.

4. Conclusions

This study shows the potential environmental effect of protective gloves and face masks through additive and polymer disappearance and degradation, respectively, under extensive exposure to seawater and beach sand. ATR-FTIR analyses revealed that after 18 months in marine and sandy conditions, considerable spectral changes occurred, indicating several degradation processes such as oxidation, hydrolysis, additive leaching and mechanical abrasion, mainly visible in nitrile gloves. Next, Py-GC–MS showed limited polymer degradation in gloves, likely due to the inherent stability of the polymer. In contrast, surgical face masks exhibited, to a limited extent, oxidation patterns after 18 months of seawater exposure, while FFP2 masks contained benzoic acid, possibly resulting from microbial degradation. Py-GC–MS also revealed the presence of phthalate plasticizers in the pristine samples. Further, DART-MS confirmed diisononyl phthalate as major additive in vinyl and latex gloves which disappeared mainly if exposed to a sand environment and underwent oxidative transformations, presumably driven by UV irradiation. Plasticizers were also present in face masks, however, limited oxidation occurred. Interestingly, DART-MS analyses also revealed the release of metal chlorides from nitrile gloves, potentially introducing heavy metal contamination in both marine environments studied. Furthermore, iodine deposition was discovered on masks exposed for 18 months to seawater due to the presence of iodine in the marine environment. Additionally, the unexpected formation of sugar esters in generic indicated alternative degradation pathways that require further investigation. In conclusion, these findings highlight the urge for improved waste management to reduce plastic pollution and consequently the leachable compounds in the marine environment.

Future research should focus on long-term degradation, toxicological effects of leached compounds, and mitigation strategies to reduce their ecological impact. The latter is of crucial importance since the contamination is still highly present even though COVID-19 is over. Therefore, a multidisciplinary approach is crucial to further elucidate the environmental impact of plastics. Advanced multi-analytical approach is required to provide deeper insight into degradation and leaching mechanisms. For this approach, soft ionization sources could ameliorate the detection of oxidation products, while comprehensive two-dimensional gas chromatography could be employed for a comprehensive non-target screening of polymer degradation.

CRediT authorship contribution statement

Siebe Lievens: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Lucia Ricci:** Writing – original draft, Methodology, Investigation, Conceptualization. **Géraldine Dumont:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Stefano Pezzini:** Writing – review & editing, Formal analysis. **Simona Bronco:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Cristina De Monte:** Writing – review & editing, Methodology, Conceptualization. **Jan Jordens:** Writing – review & editing, Supervision, Methodology. **Aline Reis De Carvalho:** Writing – review & editing, Supervision. **Marina Locritani:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Conceptualization. **Milica Velimirovic:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Silvia Merlino:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization.

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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2025.118530.

Data availability

Data will be made available on request.

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