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Environmental impacts of covid-19 pandemic: Release of microplastics, organic contaminants and trace metals from face masks under ambient environmental conditions

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ABSTRACT

The covid-19 pandemic era was characterized by heavy usage and disposal of medical face masks, now estimated at over 1.24 trillion. Few studies had attempted to demonstrate the release of microplastics from face masks using simulated conditions and application of mechanical forces, far different from the effects experienced by face masks dumped in the open environment, in landfills and dumpsites. In the current study, we monitored the release of microplastics, organic contaminants and toxic metals from medical face masks degraded under normal outdoor environmental conditions, over a period of 60 weeks. We showed that face mask’s decomposition proceeded via sunlight (UV) – initiated oxidative degradation, leading to the replacement of methylene (CH₂-) and alkyl (CH₃-) groups in face mask’s polypropylene backbone with hydroxyl and ketonic functional groups. Organic compounds released from decaying face masks into the surrounding soil included alkanes, alkenes, carboxylic acids/diesters and phthalate esters. Mean maximum concentration of phthalates in the soil ranged from 3.14 mg/kg (diethyl phthalate) to 11.68 mg/kg di(2-ethylhexyl) phthalate. Heavy metals, including Cu, Pb, Cd, As, Sn and Fe, were released into the soil, leading to contamination factors of 3.11, 2.84, 2.42, 2.26, 1.80 and 0.99, respectively. Together, the metals gave a pollution load index (PLI) of 2.102, indicating that they constitute moderate pollution of the soil surrounding the heap of face masks. This study provides a realistic insight into the fate and impacts of the enormous amounts of face masks, disposed or abandoned in soil environments during the covid-19 pandemic.

1. Introduction

The coronavirus (covid-19) outbreak was declared a pandemic and a global health emergency by the World Health Organisation (WHO) in January 2020, after spreading to several countries across the world (Saadat et al., 2020). There have been 583 million cases of the covid-19 infection, with over 6.4 million deaths recorded as at August 2022, based on the latest data from the Johns Hopkins University. The disease, caused by a novel severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), had spread rapidly and easily from person to person through contact with body fluids, such as saliva and nasal droplets. Typically, coronaviruses are single stranded RNA viruses that can cause infections in humans and animal species (Kooraki et al., 2020). The SARS-CoV-2 is widely believed to have originated from an animal market in Wuhan city, China in 2019 (Cao et al., 2020).

There have been diverse perspectives to the environmental consequences of the pandemic. Improvement in air quality was observed in many cities due to the lack of airplane travels and reduced level of industrial production, which typically releases pollutant gases into the atmosphere. Emission of pollutant gases reportedly dropped by over 50% in New York city, while atmospheric nitrogen dioxide concentration reduced significantly over Italy, Spain and the United Kingdom in 2020 (Ficetola and Rubolini, 2020). Similarly, quality of surface waters (e.g. streams and rivers) improved during the peak of the pandemic, as a result of closure of public places and the reduced vehicular and industrial activities. However, the most significant environmental impacts of the covid-19 pandemic would result from the use of personal protective items. It is notable that hand sanitizers, hand gloves, face shield and face
masks were recommended to curb the spread of the virus. This led to a widespread use of these items, resulting in the release of an unprecedentedly huge amount of plastic wastes into the environment (Oceans Asia, 2021; Farooq et al., 2022). The medical test kits, produced and packaged in plastic containers, have also added to the environmental burden of plastic wastes emanating from the pandemic.

By far, the singular most used item for covid-19 prevention was the medical face mask. Because of the lack of official guidelines for their disposal or recycling, indiscriminate disposal of the masks was very rampant. Based on estimate of usage and disposal by Benson et al. (2021), about 1.24 trillion of single-use face masks have ended up in the environment during the main 18 – month period of the pandemic, from December 2019 to May 2021. As expected, and given the humongous amounts of these face masks, a number of studies have attempted to demonstrate the release of contaminants from them. Of particular interest is the potential of the face masks to release microplastics, the tiny plastic materials with sizes below 5 mm (Thompson et al., 2004), known to be toxic to various life forms in the natural environment.

In addition to articles which had speculated the possibility of microplastics being released from face masks (for example Arigaw, 2020; Fadare and Okkoffo, 2020), studies by Salii et al. (2021), Shen et al. (2021) and Sullivan et al. (2021) reported that microplastics could be released by medical face masks, within the context of the covid-19 pandemic. However, these studies were conducted under laboratory conditions, with the application of external mechanical or chemical forces (such as shear stress, stirring, cutting into pieces, treatment with detergents/alcohol) on the face masks to elicit the release of microplastics. These laboratory scenarios are different from the conditions experienced by face masks dumped in the open environment, and thus could not provide an accurate estimate of microplastic particles released by medical face masks. Also, studies by Liang et al. (2022) and Morgana et al. (2021) employed mechanical simulations to elicit the release of microplastics from face masks into the water environment; thereby leaving knowledge gaps about the fate and release of microplastics by face masks dumped in soil environment, which is the first environmental phase that received used covid-19 face masks, and where many of them are permanently abandoned in dumpsites and landfills.

The current study therefore investigated the release of microplastics, organic contaminants and toxic trace metals from face masks dumped in soil environment over a period of 60 weeks. The face masks were allowed to degrade under natural environmental factors (sunlight, rainfall, humidity, atmospheric pressure, animal interactions, etc.) in the open environment, to provide a realistic understanding of the fate of face masks dumped in soil environment, and the extent of release of the various contaminants from the face masks under the natural environmental forces.

2. Materials and methods

2.1. Materials

Single-use medical face masks used in this study were purchased from a pharmaceutical store in Akure city, Nigeria. The face masks (blue and white in colour) were of 3-ply type and had three layers of non-woven fabric material. Chemical reagents and solvents including anhydrous sodium sulphate, sodium chloride, n-hexane and dichloromethane were of analytical grade and obtained from Sigma Aldrich (UK). Concentrated HCl and HNO₃ were 99.9% pure based on trace metals content (Sigma Aldrich). Cellulose acetate membrane filters and hydrophilic lipophilic balance - solid phase extraction (HLB-SPE) cartridges were supplied by Hangzhou Scientific Co. (China). Phthalate esters mixture certified reference material (4828231) was obtained from Sigma Aldrich (UK). All glass wares were washed with detergent solution and rinsed sufficiently with deionized water, dried in an oven and covered with aluminium foil prior use.

2.2. The study area

This study was conducted in an experimental garden within the research farm at the Federal University of Technology Akure, Southwestern Nigeria. The university campus lies between longitude 5–20° E and latitude 7–9° N, and approximately 28–32 m above sea level. The Southwestern Nigeria experiences a tropical monsoon climate, characterized by high temperature and humidity. Annual average temperature is about 32 °C during the day and 23 °C at night. The region receives annual rainfall ranging from 1300 to 1650 mm, with peaks at June and September every year. The rainy season is usually followed by a long dry season, starting in October until March the following year.

Face masks in this study were exposed to the normal environmental conditions in the garden for 60 weeks, while data on temperature (°C), rainfall (mm), relative humidity (%), wind speed (m/s), solar power (irradiance, W/m²) and atmospheric pressure (mbar) were recorded at a meteorological station located within the research farm (Supplementary Material 2).

2.3. Monitoring of microplastics release from medical face masks

In order to investigate the extent of microplastics release from individual medical face mask, a 2 L glass beaker was half-filled with soil of the garden and a mask was placed on top of the soil inside the beaker, without touching the surface of the glass. The set up (180 pieces) were exposed in the garden and 3 sets were removed weekly (over 60 weeks) and processed for triplicate determination of microplastics. To provide control for air-borne microplastics that may be deposited in the beakers, 180 beakers half-filled with soil (but without face masks) were also placed beside those containing masks, and 3 of this control set up were removed weekly (over the 60-week period) and processed simultaneously for microplastics determination.

To determine microplastics in the soil of the beaker, 300 g of the soil was scraped gently from the top, using a stainless spatula. The soil was transferred into a clean 1 L conical flask and 600 mL saturated NaCl solution (prepared by dissolving 365 g in a litre of deionized water) was added (Klein et al., 2015). The mixture was stirred with a magnetic stirrer for 1 h and then allowed to stand for 1 h, to separate the supernatant layer from the bottom soil. The supernatant was filtered under vacuum through 0.45 μm cellulose nitrate membrane to collect floated microplastics, while avoiding the soil particles moving on to the filter. Fresh NaCl solution was added to the soil in the conical flask to top up the mixture to the initial soil-solution level. The mixture was again stirred, allowed to stand and filtered through the membrane to collect any remaining microplastics. For beakers that contained face masks, each mask (together with adhering soil material) was immersed in 500 mL NaCl solution to remove any loosely bound microplastics. This NaCl portion was also filtered through the cellulose acetate membrane. The membrane filters were transferred into clean petri dishes and dried in a desiccator for a week. Large particles (> 1 mm) were counted with naked eye and removed with a tweezer. Micro-range particles were enumerated under a digital binocular microscope (AmScope B120C-E1) at 40–2500× magnification. The number of fibres and fragments were also counted under the microscope.

Quality control and assurance measures were taken during microplastics determination to avoid contamination. Contact of samples and apparatus with plasticware was avoided throughout. Both deionized water and NaCl solution were filtered through 0.22 μm cellulose acetate membrane before use. All glassware and tweezers were rinsed copiously with the filtered deionized water prior use, and laboratory coats made of cotton were worn throughout. Microplastics floatation, filtration and enumeration under microscope were performed in a laminar flow cabinet to further prevent contamination from the laboratory environment (Coppock et al., 2017).
2.4. FTIR analyses of face masks and microplastics

Fourier transform infrared (FTIR) spectrometric analyses were performed to monitor changes in surface functional groups of the face mask polymer over the period of exposure. Initial analyses were performed on both the blue and white sides of the masks to determine their original polymer composition. Thereafter, face masks retrieved from beakers withdrawn on weekly basis (section 2.3) were rinsed thoroughly with deionized water and air-dried in a laminar flow cabinet for a week. Attenuated total reflectance (ATR) - FTIR analysis was then performed on the masks. All measurements were carried out on the Agilent Cary 630 instrument, between 4000 cm⁻¹ and 500 cm⁻¹, and at resolution of 8 cm⁻¹. FTIR spectra of the microplastics (> 1 mm) recovered from the face masks were also recorded.

2.5. Monitoring of release of organic compounds from face masks

The experimental garden was divided into two large portions – one side for the placement of face masks directly on the ground and the other side to be without face masks (as control). Each side was further divided into several smaller (5 m × 5 m) portions. Face masks (30 pieces) were stacked on top of one another at the centre of the 5 m × 5 m portions, to form a small heap of masks. The heaps were immobilized by placing a large clean stone on them, to guide them from being blown away by wind. Similar large stones were placed at the centre of each 5 m × 5 m plot in the control portion. At four weeks interval over the period of 60 weeks, composite top soil samples (n = 10) were taken at 30 cm and 50 cm radii around the heap of face masks, and around the stone in the control plots which lacked the face masks. The samples were taken at depth not more than 10 cm, using a pre-cleaned stainless-steel hand trowel. Each sample collected at a given radius was air-dried in the lab for two weeks, sieved through a 2 mm size mesh, and divided into two equal portions (about 250 g each). One portion was processed for the extraction of organic compounds and the other portion was used for the determination of toxic trace metals (section 2.6).

For extraction of organic contaminants, 25 g of the soil was sub-sampled by quartering method and extracted twice with 75 mL portions of dichloromethane and n-hexane (2:1) mixture, using a glass separatory funnel. Organic solvent from the two extractions were combined, dried over anhydrous sodium sulphate, and evaporated to near dryness on a rotary evaporator at 30 °C. Clean-up of the extracts was performed with HLB-SPE cartridges (200 mg, 40 μm, 300 Å), with acetone as the eluting solvent. The cleaned extracts were analysed by gas chromatography – mass spectrometry (Agilent GC 7980 B coupled with 5977 B MSD) for detection of various organic contaminants released from the masks. DB5MS (30 m × 0.25 mm × 0.25 μm) was used as the separating column, while helium (1.2 mL/min) served as the carrier gas. Quantification of phthalate esters (diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate and di-sec-butyl phthalate) in the extracts was achieved with calibration curves prepared with the mixed certified reference material (Supelco 458231), containing 2000 μg/mL of each phthalate compound.

2.6. Determination of toxic trace metals in soil around face masks

From the 250 g portion of soil sample (obtained in section 2.5), 1 g was placed in a digestion flask and 25 mL of aqua regia was added. The aqua regia was prepared by mixing concentrated HCl and HNO₃ (3:1 by volume) under a fume hood. The soil – acid mixture was left to pre-digest overnight in the fume hood, and then heated at 150 °C to near dryness. Nitric acid (5 M, 25 mL) was then added to the sample, which was again heated at 150 °C until about 5 mL was left. The content was allowed to cool and filtered through a Whatman filter paper No.1 into a clean 50 mL standard volumetric flask, and made up to the mark with deionized water. Each soil sample was digested in triplicate. Similarly, fresh face mask samples were digested to determine toxic metals presence in them. Three face mask samples were snipped separately into tiny pieces and 1 g of each was digested in triplicate, as done for the soil samples. Addition of HNO₃ and heating continued until the materials were fully decomposed to release any trace metals present.

The heavy metals: arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), iron (Fe), antimony (Sb) and tin (Sn) were determined in the filtered digestate by inductively coupled plasma – optical emission spectrometry (Agilent 5000 Series, equipped with SPS 4 Autosampler). Details of the instrument’s operating conditions are presented in Table S1 (Supplementary Information). Limits of quantitation (LOQ) of the metals were between 0.051 μg/kg (Cd) and 0.27 μg/kg (Fe). The analytical procedure was validated by digesting and analyzing PACS-2 sediment certified reference material, produced by the National Research Council of Canada. The procedure used in this study showed good agreement with certified values, with accuracy of determination ranging from 94.7% (Cd) to 98.1% (Pb). Reagent blanks were also analysed after every ten sample determinations and no metals were detected in them.

2.7. Determination of trace metals pollution indices

Assessment of the extent of soil pollution resulting from the release of trace metals from the face masks was performed by determining contamination factors (CF), degree of contamination (Cdeg) and pollution load index (PLI).

\[ CF = \frac{C_m}{C_b} \] (1)

where \( C_m \) is the concentration of a metal in the soil around the dumped face masks and \( C_b \) is the background concentration of the metal in the soil (Ebong et al., 2018; Qingjie et al., 2008; Weissmannová and Pavlovs'ký, 2017). Metals concentrations determined in the control soil, where face masks were not placed, served as the background concentrations in this study.

\[ C_{\text{deg}} = \text{sum of contamination factors of all trace metals at a given location. According to } \text{Ebong et al. (2018)} \text{ and } \text{Hakanson (1980)}, C_{\text{deg}} < 8 \text{ is regarded as low degree of contamination; } 8 < C_{\text{deg}} < 16 \text{ is moderate; } 16 < C_{\text{deg}} < 32 \text{ is considerable; and } C_{\text{deg}} > 32 \text{ is very high degree of contamination.} \]

\[ \text{PLI was calculated from the relationship, } \text{PLI} = \left( CF_1 \times CF_2 \times CF_3 \ldots \times CF_n \right)^{1/n} \] (2)

where \( n \) is the number of individual trace metals under consideration. PLI below 1 is regarded as no pollution, 1 < PLI < 2 is moderate pollution, 2 < PLI < 3 is heavy pollution, and PLI > 3 is extremely heavy pollution (Tomilson et al., 1980; Ebong et al., 2018). The mean concentration of each metal released into the soil over the period of study was used in determining these indices.

2.8. Statistical analyses

Non-parametric Mann-Whitney U statistical test was performed to examine differences in metals concentration between soil samples around face masks and those around marked centres in the control soil (lacking face masks). Analysis of variance (ANOVA) was used to examine if there were significant changes in the concentration of organic compounds (phthalates) in soil samples over successive sampling instances. SPSS software (version 25) was used in all analyses and P values < 0.05 was considered as statistically significant.

3. Results and discussion

3.1. Degradation of face masks and release of microplastics

The medical face masks placed on soil in the beakers decomposed gradually due to environmental factors. Physical signs of degradation
were clearly visible starting from week 14, with the degradation increasing as the number of weeks of exposure increased (Fig. S1). The gradual degradation of the masks was simultaneously accompanied by the release of microplastics into the soil in the beaker. Prior to week 14, the average number of microplastics recovered and determined in the soil ranged from 9.67 ± 1.53 to 17.53 ± 1.68 for beakers containing face masks, and from 6.79 ± 1.49 to 18.33 ± 3.46 for control beakers which lacked face masks. The similarity in the number of microplastics obtained from the two experimental set-ups at this initial stage, suggests that the values represent the background levels of microplastics in the soil used for the experiment.

However, at the 14th week of determination, average number of microplastics began to increase sharply and consistently in beakers that contained face masks compared to the control experiments (Fig. 1a). Thereafter, amount of microplastics in experiments with face masks increased exponentially, reaching an average of 3280.45 ± 173.88 MPs/face mask at 40th week and 3686.24 ± 80.39 MPs/face mask at the 60th week. It is noteworthy that the amounts of microplastics in the control experiments also increased steadily, but at a much lower rate compared to the experiments that contained masks. The value averaged 58.71 ± 7.51 at week 40, and rose only to 85.32 ± 14.51 MPs/face mask at week 60 in the control experiments. Since all beakers were left open in the garden, to subject the face masks to natural environmental effects (similar to those experienced by face masks dumped indiscriminately on soils and dumpsites), the little increase observed in the control experiments would have resulted from microplastics available in the atmospheric environment and deposited in the beakers over time. While the same effect may have contributed to the levels observed in the beakers containing face masks, the much higher concentration of microplastics detected in these beakers (in contrast to the controls) implies that such amount of microplastics could not have come from the open environment. Furthermore, observation of microplastics from the beakers containing masks confirmed that they were all dominated by blue and white particles (Fig. S2), typical of the materials used in making the face masks. These results provide empirical evidence for the release of microplastics from medical face masks. Some previous studies (e.g. Morgana et al., 2021; Liang et al., 2022; Wu et al., 2022) had used simulated conditions and application of mechanical effects such as stress forces, shaking, blending, pressure and/or heat to induce the release of microplastics from face masks. However, this current study demonstrates the release of the microplastics under normal ambient environmental conditions, similar to that experienced by the huge number of masks disposed on soil environments, and without application of any external pressure or heat. It therefore provides a better insight into the amount of microplastics that could be released from covid-19 face masks in soil environment.

Microplastics released from the face masks were mainly of fibre and fragment shapes. The fibres dominated with percentage range of 85.5–91.6%, while fragments ranged from 8.4 to 14.5% in all the samples. The largest sizes of the fibres and fragments were 1.6 and 0.5 mm, respectively. While the face masks appear as fabric materials and were normally expected to produce fibre-type microplastics, release of fragment-type microplastics resulted from the fabric material breaking down initially into smaller sizes, which were then degraded further to give the predominating fibre-type microplastics. The release of microplastics from face masks has serious potential implications for the environment, particularly in the light of the covid-19 pandemic, in which an estimated 1.24 trillion single-use face masks have been discarded (Benson et al., 2021). Many species inhabiting the soil environment may ingest the microplastics as food. Indeed, two soil insect types – the black carpenter ant (Camponotus haereticus) and the jumping spider (Salticidae sp.) were found living and mulching on plastic particles from

![Fig. 1. Microplastics recovered from experimental soils containing medical face masks and the controls (lacking face masks) at (a) weeks 0–20 (b) weeks 21–40 (c) weeks 41–60, of exposure to ambient environmental conditions.](image-url)
degrading face masks on the soil environment (Fig. 2). Ingestion of microplastics by species is known to cause effects such as blockage of the digestive system, internal lacerations, enzyme biotransformation and damage, oxidative stress, and reduced reproduction capabilities (Provencher et al., 2017; Wu et al., 2019). More so, the face masks contain and release other chemical contaminants (sections 3.2 and 3.4), which may be injurious to the species that ingest them. As it is the case with many contaminants in the soil environment, microplastics released by face masks may be transferred via run-off to surface waters, where the aquatic species may also be exposed to the numerous potential effects. Such transfers may be significant in some west-African countries and others, where dumpsites are commonly located near rivers and water ways (Dladla et al., 2016; Orhorhor and Ogbohgorie, 2019; Idowu et al., 2022). Being channels and corridors to the ocean, the rivers would ultimately carry the face masks’ particles to the marine environment, where they add to the already high burden of microplastics and plastic debris, against which the marine organisms are grappling.

Changes in surface functional groups of the face mask were monitored through weekly FTIR analyses. Prior to the original FTIR analysis, the two sides (blue and white) were performed and the results gave exactly the same spectra pattern (Fig. S3), indicating that both outer sides were made of the same polymer material. The spectra gave all the characteristic FTIR peaks normally expected for polypropylene polymer (Jung et al., 2018), including the C–H stretch signals at 2952.1, 2918.5 and 2840.2 cm⁻¹; the CH₃ and CH₂ bend signals at 1453.7 and 1375.4 cm⁻¹, respectively; the CH– bend signal at 1166.7 cm⁻¹; the CH₃– rock signals at 998.9 and 972.3 cm⁻¹, as well as the CH₂– rock signals at 842.4 and 808 cm⁻¹. An additional signal, also attributable to the stretching of the C–H bonds of the alkyl (–CH₃) group of the polyethylene backbone, was observed at 2870.1 cm⁻¹. These results confirm that the outer parts of the face masks were made entirely of polypropylene polymer, and are consistent with previous reports that polypropylene is a major component of surgical face masks (Leonas and Jones, 2003; Aragaw, 2020). Following exposure of the masks to the environment, the FTIR analyses revealed changes in surface functional groups that occurred as the face mask gradually degraded. Table 1 provides details of key changes in surface functional groups on the face mask over the 50 weeks FTIR analyses period, and the approximate time when the changes occurred. FTIR spectra of the face masks exposed to the environment for up to week 11 showed no difference in signals to the original unexposed mask, suggesting that no changes in surface functionality occurred during this period. However, at week 12, three new peaks appeared on the spectra, in addition to the peaks observed on the original mask. These were the broad O–H stretch signal at 3362.1 cm⁻¹, the C=O stretch signal at 1640 cm⁻¹, and the C–O stretch signal at 1032.5 cm⁻¹. Notably, between weeks 13 and 36, these three signals gradually increased in intensity, while the four peaks for the alkyl group C–H stretch vibrations, and the signals at 1453.7 and 1375.4 cm⁻¹ for CH₃– and CH₂– bend vibrations, respectively, all reduced gradually. At week 36, the broad O–H peak and those attributed to the ketonic functional group had become very intense, while the alkyl C–H stretch signals and the CH₃– and CH₂– bend vibrations were almost completely gone, and remained so until week 50 (Fig. S4). The CH₂– rock signals at 998.9 and 972.3 cm⁻¹ were also completely disappeared. These results strongly suggest that the degradation of the face mask’s polypropylene material led to conversion of the alkyl (CH₃) group and the methylene (–CH₂)– group on the polymer backbone to alcohol and ketone. Observation of changes to the surface functional groups at week 12 (signaling the beginning of polymer degradation) is very consistent with the onset of microplastics release from the face mask at week 14.

The microplastics released by the face masks were in the form of fibres and fragments. Other shape types, such as film and nylon, were only found in negligible numbers in few experimental instances, and are believed to have resulted from deposition of contaminant particles normally suspended in air. Pellets and foams were not seen in both the main experiments and the controls. It is noteworthy that the average number of microplastics determined weekly in the control experiments was subtracted from the average number determined for the actual experiments (as background environmental contribution), to provide a realistic estimate of the amount of microplastics actually released by the face masks.

Based on the foregoing discussion and the observed FTIR signal changes, the steps leading to the face mask’s degradation may be proposed. Polymers such as polypropylene are susceptible to degradation by light, particularly the UV component of sunlight. In this case, the abandoning of face masks on the ground during the monitoring period, allowed for the incorporation of impurities from the environment, which made them more vulnerable to attack by light (Scott, 2002; Vasile and Pascu, 2005). We propose that the initial step in the face mask’s degradation is the attack by UV radiation in sunlight. The high intensity of sunlight in the outdoor tropical environment (where the experiment took place) further facilitates the initial attack by UV light. Also, the fact that the initial signs of degradation (in form of surface cracks) were first observed on the sides facing the sun in all cases, as against the side facing the ground, gives credence to our assertion that the degradation was initiated by the abiotic (sunlight) factor. The tertiary nature of the polypropylene polymer i.e. possession of alternating methyl groups in its chain, confers stability against microbial (biotic) degradation (Singh and Dwivedi, 2004), making microbial attack very unlikely at the initial stage. Thus, attack by sunlight leads to the formation of polypropylene radical, which reacts with molecular oxygen in the open environment to form a polypropylene peroxy radical intermediate (Fig. 3). This intermediate may abstract an atom of hydrogen.
from the nearest monomer unit (U) in the chain, to lead to the formation of a polypropylene hydroperoxide, bearing a hydroxyl functional group. In a completely radical-propagated pathway, oxidation of the polymer chain causes several random and end-chain scissions, leading to the formation of oxygen-containing final fragments, in which the alkyl (CH$_3$-) and the methylene (CH$_2$-) groups of the polypropylene polymer are retained (Gewert et al., 2015). However, results obtained in the current study imply that the products of the face mask’s degradation contain oxygen atoms, but lack the alkyl and methylene groups, as indicated by the loss of FTIR signals corresponding to these functional groups. Consistent with our observation of dominant hydroxyl and ketonic functional groups, we propose fragment compounds in which both the methylene and the alkyl groups of polypropylene backbone have been replaced by hydroxyl and ketonic functions (Fig. 3).

3.2. Release of organic contaminants from medical face masks

Release of chemical compounds from the face masks was investigated by performing GC-MS analyses on organic extracts of soil taken from around the masks, and those taken from the control plots which lacked face masks. Over the first four months of monitoring, similar compounds were detected in both types of soil extracts. The compounds detected during this period were highly diverse. Notable among them are pesticidal compounds such as carbamate derivates and their degradative metabolites, as well as organochloride and organobromide residues, all of which reflect a history of the use of chemical pesticides on the garden soil (Table S2). While these types of compounds were still being detected in the control soil, new set of compounds were found in soil around the face masks as from the fourth month of monitoring. The compounds were absent in the control soil extracts, indicating that they emanate from the decomposition of the medical face masks. These compounds may be categorized into four groups – alkanes, alkenes, phthalic acid esters (i.e. phthalates), and carboxylic acids and diesters of carboxylic acids (Table 2). The release of hydrocarbons (alkanes and alkenes) from decomposing face masks is consistent with studies which have demonstrated the possibility of obtaining such compounds from plastic materials (including the polypropylene-type plastics, of which the face mask is composed) under high temperature pyrolytic processes (Jia et al., 2016; Kumar et al., 2017; Ratnasari et al., 2017; Miandad et al., 2019). The current study implies that similar hydrocarbon compounds can be released from

| Table 1 | Important FTIR peaks that characterized the degradation of medical face masks exposed to ambient environmental conditions in soil environment. |
|---------|-------------------------------------------------------------------------------------------------------------------------------------|
| Stage of exposure | Comments | Observed FTIR Peaks (cm$^{-1}$) | Signal assignment |
| Initial (Unexposed) | Peaks confirm polypropylene presence | 2952.1, 2918.5, 2870.1, 2840.2 | C=H stretch of alkyl (-CH$_3$) group |
| | | 1453.7, 1375.4, 1166.7, 998.9, 972.3 | CH$_3$ bend |
| | | 842.4, 808.8 | CH$_2$ - rock, C-H$_2$ stretch |
| week 1 - week 11 | Same peaks as for the initial (unexposed) mask | As in initial | As in initial |
| week 12 | New peaks appeared in addition to the initial peaks | broad 3362.1 | O-H stretch |
| | | 1640 | C-O stretch |
| week 13 - week 35 | Decrease in signal strength for initial peaks; Increase in signal strength for new peaks | As in initial and week 12 | As in initial and week 12 |
| week 36 - week 50 | Disappearance of initial peaks; Retention of new peaks | intense broad 3362.1 | O-H stretch |
| | | intense 1640 | C-O stretch |
| | | intense 1022.5 | C-O stretch |

Fig. 3. Proposed pathway for degradation of polypropylene medical face masks under natural environmental conditions; n is a large number for polymer, U is a single unit of the polymer.

| Table 2 | Compounds detected in soil around decomposing medical face masks. |
|---------|---------------------------------------------------------------------|
| Carboxylic acids and Diesters | Phthalates | Alkanes | Alkenes |
| Dodecanoic acid | Diethyl phthalate | Nonacosane | 1-eicosene |
| n-Hexadecanoic acid | 5-methylhex-2-yl | Heptacosane | 1-docosene |
| Octadecanoic acid | Di(2-methylpropyl) | Eicosane | 1-octadecene |
| Dioctyl hexane-1,6-dioate | Di-sec-butyl phthalate | Tricosane | Z-8-hexadecene |
| Di(2-ethylhexyl)hexane-1,6-dioate | Dibutyl phthalate | | |
| Di(2-ethylhexyl)decane-1,10-dioate | Di(2-ethylhexyl)phthalate | | |
| | Dibutyl isophthalate | | |
polypropylene face masks, subjected to environmental effects (temperature, precipitation, humidity, etc.) over a long period of time. Of greater environmental and ecological concern is the release of phthalate esters from the face masks. Phthalates are prominent among the group of compounds known as endocrine disrupting chemicals (EDCs), which interfere or mimic hormones in living systems, thereby causing reproductive and developmental impairments (Bergman et al., 2013; Diamanti-Kandarakis et al., 2009). Many EDCs also exert impact on energy metabolic homeostasis, altering adipose tissue and promoting obesity, cancer, cognitive deficits and metabolic syndromes (Zarean et al., 2016; Amin et al., 2018; Lauretta et al., 2019; La Merrill et al., 2020). Phthalates are particularly toxic to crustaceans and amphibians in the environment. The large volume of face masks used and disposed due to the covid-19 pandemic may have caused an increase in global environmental burden of the phthalate diesters. While phthalates are not expected to be used directly in polypropylene (face mask) plastics production, they have also been detected as non-intentionally added substances (NIAS) in many types of plastics where their use is not permitted. Such presence is attributed to random and inadvertent formation during initial polymerization reactions, and from residues of catalysts used in the production process (Bach et al., 2012; Stenmarck et al., 2017). These side reactions may also be responsible for the presence of aliphatic acid diesters, which are subsequently leached from the polymer and are detected in the surrounding soil samples.

Fig. 4 shows frequency of detection of the compounds around face masks, presented as a percentage of the total number of times the soil was sampled and analysed for organic contaminants, and taking into consideration the fact that no release of compounds was observed for the first 12 weeks of the study, corresponding to 3 sampling times. Diethyl phthalate, di(2-methylpropyl) phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate and di(2-ethylhexyl) decane-1,10-dioate were detected most frequently at 83% each. The alkane compounds were detected less frequently compared to the other compound types. There is a possibility that some of the released compounds undergo reactions in the environment to convert to related analogues or derivatives. For instance, dibutyl isophthalate was not found in the soil samples until the 36th week of monitoring, whereas the related compound, dibutyl phthalate, was detected from the 16th week, when the organic compounds were first observed. The lack of detection of dibutyl isophthalate before the 36th week of face mask’s decomposition suggests that this contaminant is not released directly from the masks. Thus, part of the released dibutyl phthalate may be undergoing isomerization to the dibutyl isophthalate under the prevailing environmental conditions, leading to the detection of the isophthalate much later in the study period. Such transformation may be an attempt towards conversion of the dibutyl phthalate to its less harmful analogues, as isophthalates are known to be generally more ecofriendly, compared to their phthalate counterparts (Kim et al., 2019). Similarly, it is very unlikely that highly functionalized and reactive molecules such as the long chain carboxylic acids are released directly from inert face mask materials. Rather, the alkane compounds released by the decomposing face masks may undergo series of oxidation steps, facilitated by the abundance of oxygen and water molecules in the open-air environment, to eventually produce the carboxylic acids which are detected. Because the compounds are obtained from the soil environment, the seemingly difficult initial step (i.e. the oxidation of alkanes to alkanols) may be equally facilitated by the presence of transition metal oxides (Martin et al., 2021), such as Fe and Mn oxides, which are usually present in the soil. Indeed, high levels of Fe were found in all the soil samples in this study (section 3.4).

3.3. Concentration of phthalate esters in soil around face masks

In order to provide an understanding of the level of release of the organic compounds from decomposing medical face masks, concentrations of phthalate compounds were determined in the soil samples around the decomposing face masks, and the results are summarized in Table 3. Although seven individual phthalate esters were detected in the soil, analytical standards were available only for the four phthalates shown in the table. The results indicate that quantifiable amounts of the phthalate esters are released from the medical face masks. Mean concentrations over the period of study revealed the order: di(2-ethylhexyl) phthalate (DEHP) > dibutyl phthalate (DBP) > di-sec/iso-butyl phthalate (DIBP) > diethyl phthalate (DEP). An analysis of variance (ANOVA) performed to examine relationship in the levels of each phthalate released over the monitoring period showed that the concentrations in the soil differ significantly (p < 0.05) between successive sampling instances (Tables S3–S6). Concentration of the four phthalates determined at radius 50 cm away from the masks (and at the same times as for the 30 cm radius), gave much lower concentrations than those determined at the 30 cm distance. This indicates that the phthalate concentrations decreased with distance away from the face masks, and provides a strong confirmation that the phthalates indeed emanated from the face masks.

There is no available standard regulatory limit for phthalate esters in soil environments. However, a widely cited work by van Wezel et al. (2000), which utilized data on environmental chemistry and toxicology.

Table 3

| Phthalate ester | Range (mg/kg) | Mean (mg/kg) | Environmental limit (mg/kg) | Reference |
|-----------------|--------------|--------------|----------------------------|-----------|
| Dibutyl phthalate | 1.98–11.48 | 8.24 ± 3.23 | 0.70 | van Wezel et al. (2000) |
| Di(2-ethylhexyl) phthalate | 7.11–18.27 | 11.68 ± 3.76 | 1.00 | van Wezel et al. (2000) |
| Diethyl phthalate | 0.76–5.81 | 3.14 ± 1.82 | NA | – |
| Di-sec-butyl phthalate | 1.74–9.02 | 4.89 ± 2.67 | NA | – |

* Data are mean ± standard deviation (n = 3 replicates); NA – not available.
of phthalates (with effects on endocrine disruption, growth, reproduction and survival as endpoints), obtained environmental risk limits of 0.700 and 1.00 mg/kg for DBP and DEHP, respectively. The average concentration of DBP measured in this study is 11.8 times higher than the stated risk limit for DBP, while that of DEHP is 11.7 times higher than the corresponding limit. These results suggest serious potential risks to species of organisms, particularly those inhabiting soil environments near the dumped face masks. Presence of phthalates has been shown to decrease catalase, urease and phosphatase enzyme activities in soil, leading to reduction in microbial metabolic activities and in the diversity of culturable bacterial species (Chen et al., 2004; Xie et al., 2009; Guo et al., 2010). Amphibians, molluscs and crustaceans are also very sensitive to phthalates. Biological effects such as genetic aberration and poor organ development have been reported at environmentally relevant concentrations in parts per billion range (Oehlmann et al., 2009), much lower than the levels found in the soil samples in the current study. Within the context of the covid-19 pandemic, the dumping of huge amounts of face masks (as observed in some hospital waste dumpsites) may have far-reaching effects on survival and reproduction of soil invertebrate and microbial species, and consequently on their population and diversity.

It is noteworthy that the detection of the phthalates began at the 16th week of monitoring, after there had been observation of physical signs of degradation on the masks, as well as an observation of microplastics release. Higher concentrations of all the phthalates were observed during the rainy months, between the 20th and 32 nd weeks of monitoring (corresponding to the period from June to September), and suggesting that rainfall was a crucial environmental factor in the leaching of compounds out of the face masks. Surprisingly, the phthalates could not be detected at the latter.

Periods of the monitoring, after the 40th week, which coincided with the driest period of the year. This lack of detection at the latter period suggests that the phthalates released earlier into the soil had been rapidly degraded. Indeed, some previous reports (Liang et al., 2008; Boll et al., 2020) had confirmed that phthalates could be biodegraded by fungi and bacteria under aerobic conditions, such as presented by the open environment in which the experiments were conducted.

3.4. Release of toxic trace metals by medical face masks in soil environment

The face mask materials, being industrially generated polymers, may contain traces of metals from catalysts used in the production process, and from contacts with internal machine surfaces. In particular, the nose strip that provides rigidity and support to the mask also contains a thin metal piece, which is a potential source of trace metals to the environment. In order to investigate the remote possibility of the medical face masks to release toxic metals into the environment when discarded, pieces of chopped face mask material were subjected to digestion by concentrated acid and the resulting solution was analysed by ICP-OES for As, Cd, Cu, Pb, Fe, Sb and Sn. Whereas Sb was not detected in this sample, mean concentrations of As, Cd, Pb, Sn, Cu and Fe were 0.22 ± 0.042, 0.35 ± 0.21, 1.72 ± 0.23, 3.21 ± 0.07, 6.31 ± 0.47 and 139.86 ± 33.52 mg/kg of face masks, respectively. This result shows that the face masks indeed have heavy metals inherent in them, with concentrations of Cu and Fe being particularly high.

In order to determine whether the medical face masks could actually release trace metals when dumped in soil environments (as seen in dumpsites during the covid-19 pandemic), the metals were determined in soil samples obtained around heaps of face masks at four weeks intervals over a 60-week period. Table 4 presents the concentration of the metals in the soil samples from week 20–60. Because soil also normally contains trace metals, either as part of the natural (geogenic) formation or through deposition from diverse anthropogenic sources, control soil samples taken around demarcated centres on the adjacent experimental plots (which lacked face masks) were analysed simultaneously over the 60 - week period. Results of the metals determined in these control soil samples are shown in Table 5 for the period between weeks 20 and 60.

Concentrations of the metals obtained for the initial period of these experiments (weeks 0–16) were within the same range of values in both the soil around the face masks and in the control soil samples (Tables S7 and S8), indicating that there was no release of trace metals from the face masks during this period. In this case, the concentrations reveal the levels of the metals present in the garden soil, regardless of the presence of face masks. However, a clear difference in concentration of the metals around the heap of face masks became noticeable as from week 20, when compared with values in the control soils. Table 4 shows that the concentration of the metals in soil around the face masks were greater at all sampling times (from week 20 to week 60) than the corresponding concentrations in the control soils where face masks were absent (Table 5), with Fe as the only exception. Indeed, the Mann-Whitney U statistical tests performed to examine differences in the concentrations between experiments with face masks and those without face masks for each metal revealed that the levels in soils around face masks are significantly greater (p < 0.05 in all cases) than in the control soils (Tables S9–S14). It is particularly noteworthy that the concentrations of each metal increased continuously at three successive sampling times (weeks 20, 24 and 28) in the soil surrounding the face masks, while values at the other sampling times remained higher than those recorded at corresponding sampling times in the control soils. Given that the plots in both experiment types are located side-by-side within the same garden area, having identical physico-chemical properties (Table S15), and are exposed to the same environmental conditions, with the only difference in the treatments being the presence of face masks in one experiment type; the higher concentration of metals in soils around the face masks provide evidence of their release from the decomposing face masks. Concentration of the metals in soil at 50 cm radius from the masks are lower than those determined for 30 cm distance, which again
implies that the concentrations decrease with distance away from the face masks (the source of release of the metals). Similar to the observations at the 30 cm radius, concentrations of the metals (As, Cd, Cu, Pb and Sn) in soil around the face masks at 50 cm distance were all higher than the corresponding concentrations in the control soil samples. Antimony (Sb) was not detected in the soil samples at all distances higher than the corresponding concentrations in the control soil samples. Whereas other metals were detected at trace concentrations in all the soil samples. This is fully consistent with the fact that the metal was absent in the face mask material, as it could not be detected in the digested sample of the original face mask. The lack of Sb in the control soil samples also implies that the metal is not naturally present in geogenic formation of the garden soil, and has not been deposited by anthropogenic pollution.

Iron (Fe) concentrations were highest in the soil samples at all sampling instances. Whereas other metals were detected at μg/kg (or parts per billion) levels, Fe was present at mg/kg (parts per million) concentrations in all the soil samples. However, the levels of release of the metal from face masks to the soil could not be ascertained. Both the soil around the dumped face masks and the controls have Fe within similar concentration ranges, determined as 25.1 ± 0.051 to 36.6 ± 0.166 μg/kg. For the control samples, the highest Fe concentration was 36.6 × 10^6 μg/kg. The Fe concentration in the soil may also retard the growth of plants and cause the metal to accumulate in soil organisms such as earthworms (Wang et al., 2013). Overall, the Cdeg value obtained due to the concentrations of all the released metals was 13.4, while the PLI was 2.102, being only slightly above 2. Putting together, these results imply that the soil is only moderately polluted, due to the release of metals from the decomposing medical face masks.

4. Conclusions

This study has investigated the release of microplastics, organic compounds and inorganic (heavy metal) contaminants into the soil environment from medical face masks, the type used widely during the covid-19 pandemic. We have answered the hitherto elusive, but important question of “how much microplastics could be released from a single medical face mask under normal/natural environmental conditions without the application of mechanical forces?”. We showed that an average of 3686.24 microplastics were released from a single face mask, after a natural degradation period of 60 weeks. Structural replacement of methyl and methylene groups in the face mask’s polypropylene material with oxygenated functional groups paved the way for release of microplastics and other contaminants. Four classes of organic compounds were released into the soil from face masks, with endocrine-disrupting phthalate esters particularly released at quantifiable amounts. Concerns with heavy metals may relate with As, Cd, Pb and Cu, whose contamination factors exceeded 2 in the soil surrounding the masks.

It is worth emphasizing that single face masks and small heaps of face masks were used in this study, to elicit the levels of the various contaminants observed. In reality, much higher levels of these contaminants may have been released into the environment, due to the enormous amounts of face masks utilized and disposed of during the covid-19 era. The current study, conducted under tropical African climatic conditions, has offered deep insight into the fate and impacts of surgical face masks. Similar natural degradation and monitoring studies in other climatic environments would provide further and broader understanding of the scale of impact, resulting from the recent global covid-19 pandemic.

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