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Spider Webs as Passive Monitors of Microplastic and Its Copollutants in Indoor Environments

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Cite This: *ACS Omega* 2025, 10, 4418−4426
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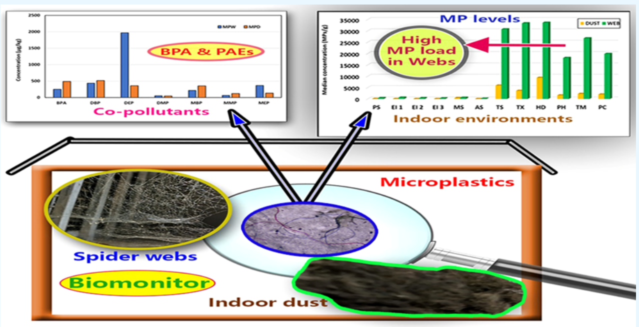
ABSTRACT: Indoor environments are particularly vulnerable to microplastics (MPs) and associated copollutants due to limited air circulation and particulate matter accumulation. Continuous monitoring is essential to evaluate exposure levels and health risks. We propose using indoor spider webs as passive monitors for MPs and their copollutants. MPs were found in both web and dust samples with nonuniform distribution ($p < 0.05$), indicating contamination hotspots. Web samples had significantly higher MP levels (138−33,570 MPs/g) compared to dust samples (59−9324 MPs/g). A strong positive correlation ($r = 0.93$, $p < 0.05$) between MPs in dust and webs suggests that spider webs are effective bioindicators of indoor MP contamination. The study also revealed the presence of Bisphenol A and various phthalic acid esters (PAEs). Co-pollutant concentrations ranged from 52.02−1971.78 μg/kg in webs and 43.18−518.42 μg/kg in dust. Diethyl phthalate (DEP) was more common in webs, while Dibutyl phthalate (DBP) predominated in dust. These findings highlight spider webs' potential as both effective biomonitoring tools and significant sinks for MPs and their cocontaminants in indoor environments.



INTRODUCTION

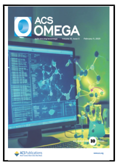
Airborne pollutants emitted from diverse industrial and human activities have become a growing concern due to their potential impact on human health. Among the various environments where these contaminants have been identified, indoor spaces stand out as areas with significantly higher contamination levels.[1] This is particularly relevant given the considerable amount of time that individuals spend in various indoor spaces.[2]

One emerging focus in the realm of indoor air quality is the presence and impact of microplastics (MPs).[3] MPs have gained prominence as a subject of interest in recent times, drawing attention from toxicological studies that delve into their adverse effects on human health. These minute plastic particles (<5 mm) are abundantly sourced within indoor environments, with textiles and single-use plastics identified as major contributors.[4] Interestingly, the toxicity associated with MPs extends beyond the particles themselves to include cocontaminants present within them. These cocontaminants, often introduced during the manufacturing of plastics as additives to prolong their lifespan, contribute to the overall health risks posed by MPs. Additionally, compounds may migrate from the indoor air environment to MPs, further complicating the relationship between pollutants and their sources in indoor spaces.[3]

Traditionally, indoor air quality studies focus on monitoring matrices such as vapor, particulate matter (PM), and dust particulates, with active samplers being the preferred method for collecting data.[5] However, a notable shift is occurring toward incorporating bioindicators for monitoring indoor air quality. This approach involves using living organisms, such as plants, lichens, and mosses, to provide a more holistic understanding of air quality.[5]

Bio monitors are utilized to track MPs in various environmental settings. Fish and other marine invertebrates are employed to monitor microplastic pollution in marine ecosystems. The MPs they ingest from their surroundings accumulate in their organs, and this accumulation is measured to evaluate environmental pollution levels.[6] Soft tissues of mussels and gastrointestinal tracts of fish are used to monitor MPs in wrecks.[7] Additionally, both artificial and natural leaves, especially those with trichomes and leaflets, are utilized for monitoring airborne MPs, with natural leaves proving more efficient than smooth leaves.[8] Yet, the complexity of pollutant

Received: August 11, 2024
Revised: November 16, 2024
Accepted: November 25, 2024
Published: November 30, 2024



https://doi.org/10.1021/acsomega.4c07373

identification is influenced by various factors, including metabolic processes, surface chemistry, and the inherent lack of uniformity among living systems, which poses significant challenges in maintaining live systems during air quality assessments.[5,9]

Spider webs, being ubiquitous and prevalent in various environments, exhibit a remarkable ability to trap a diverse range of contaminants.[10] They have been successful used as bio monitors for diverse air pollutants in various countries such as Nigeria, Poland, Germany, Sweden, Iraq and Brazil.[10−16] This characteristic makes them a compelling material for studying and monitoring indoor air quality.[16] In comparison to conventional monitoring techniques, webs offer distinct advantages, including cost-effectiveness, noninvasiveness, and ease of collection.[5,10] Webs are generally found in isolated locations, which provides an added layer of protection against environmental factors. Their temporal assessment capability allows investigators to remove existing webs and monitor the contaminants in newly woven webs when spiders reconstruct them.[5,17] Furthermore, spider webs can be transported from laboratory settings to designated monitoring sites, offering a controlled and reproducible environment for analysis.[5] Webs produced in the laboratory present an additional advantage, as they are not influenced by vegetation periods, a factor that can complicate studies involving living systems.[5]

While existing studies on spider webs as pollutant monitors have predominantly focused on outdoor environments, emerging research reveals their untapped potential as powerful tools for assessing indoor air quality.[12,13] A few pioneering studies have already explored the use of spider webs to capture MPs in the air.[13,14] However, the significant frontier lies in their potential to quantify both MP levels and their associated copollutants. In this context, the current investigation aims to evaluate the viability of spider webs as precise monitors for indoor MPs and their copollutants.

2. METHODS AND MATERIALS

2.1. Chemicals and Reagents. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), Bisphenol A (BPA), Dibutyl phthalate (DBP), Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Monobutyl phthalate (MBP), Monomethyl phthalate (MMP), and Monoethyl phthalate (MEP), were sourced from Sigma-Aldrich. High-performance liquid chromatography (HPLC) grade solvents, such as acetonitrile, methanol, and formic acid, were procured from Fisher Scientific. Water from Cascada Lab Water systems, with a conductivity of 18.2 MΩ cm^{-1}, was used for both the preparation of chemical standards and the mobile phase.

2.2. Study Area and Sample Collection. The indoor spider web and dust samples were collected from various indoor spaces in Cochin City, India. Cochin City, situated on the southwestern coast of India, and serves as a prominent commercial hub and boasts a population density of 7100/km^2[18] The region experiences a warm and humid climate, characterized by two annual monsoon periods (Southwest and Northeast monsoons).[19] In total 120 samples were collected (n = 60 web and n = 60 dust samples) from various indoor micro environments such as paint shops (PS; n = 5), educational institutions (EI 1 (School), EI 2 (College), EI 3 (College); n = 15), medical shops (MS; n = 5), antique shops (AS; n = 5), tailoring shops (TS; n = 5), textile shops (TX; n = 5), home décor shops (HD; n = 5), photostat shops (PH; n = 5), table mat shops (TM; n = 5), and plastic collection units (PC; n = 5).

2.2.1. Dust Sample Collection. To gather dust samples, we utilized a brush to sweep dust from various surfaces, a method commonly employed in indoor dust research[20] and found to be both practical and effective for our study. We gently swept the indoor settled dust into a dustpan using a brush, then promptly transferred it into a securely sealed Ziplock cover. To prevent cross-contamination, the brush and dustpan were thoroughly cleaned with acetone before and after each sampling. In the laboratory, the samples were sieved using a stainless-steel mesh with a 100 μm cutoff. Postsieving, the samples were wrapped in aluminum foil and stored at 4 °C until they were analyzed.

2.2.2. Web Sample Collection. Spider web samples of spiders belonging to pholcidae family were obtained from the same indoor locations as the settled dust samples. To avoid contamination, glass rods were used to gather the webs. All visible indoor spider webs were collected from ceilings at heights of ~3−5 m above the floor. Once collected, the web samples were carefully transferred into 20 mL glass vials, which were sealed with a Teflon-coated septum and a synthetic rubber lid.

2.3. Sample Processing and Analysis. *2.3.1. Microplastic Analysis.* Initially, 1 g of dust/web samples was accurately measured and deposited into a clean glass beaker. The removal of organic matter from the samples was achieved with wet peroxide oxidation (WPO) with a 30% hydrogen peroxide (H_2O_2) solution. The samples were then kept for drying in a hot air oven for 24 h under a temperature not exceeding 50 °C. After drying the samples were introduced to 30 mL of zinc chloride ($ZnCl_2$) solution (density = 1.5 g cm^{-3}) to facilitate density separation. The mixture was then vigorously stirred with a glass rod for a period of 5 min, followed by being left undisturbed for 24 h. Subsequently, the resulting supernatant was filtered through a 25 mm Whatman glass fiber filter paper (pore size: 2.7 μm) and the filter papers were left to air-dry. The dried samples were initially analyzed using a stereomicroscope (OPTIKA microscopes, Italy) to determine the concentration of microplastic (MP) particles. Following the particle count analysis, the microplastic suspects were carefully transferred onto a glass slide using metal tweezers for Raman and ATR-FTIR analysis. The Raman analysis was conducted using a Micro-Raman spectrometer (WITec α 300RA, Germany) equipped with a 532 nm laser for excitation, a grating of 600 grooves/mm, and a 20× objective. The instrument was calibrated using spectra from a silicon wafer (standard provided by WITec, Germany).

Shimadzu Prestige-21 FTIR Spectrophotometer with a highly sensitive DLATGS detector along with a 45° ZnSe ATR crystal flat plate was used for the ATR-FTIR analysis. To validate the FTIR spectrum, polystyrene film (provided as a standard by Shimadzu) was measured, and peak wave numbers were noted to ensure accuracy. Each sample were subjected to 30 scans at a resolution of 4 cm^{-1}. A background spectrum was captured every 15 min. After each sampling, the ATR crystal was thoroughly cleaned with IPA (Iso-Propyl Alcohol) and ensured to be dry before subsequent sampling. Prior to acquiring the final sample spectrum, background subtraction and baseline correction of the IR spectrum were performed.

The quality assurance/quality control was as per the guidelines provided in earlier reports.[3] The glassware and other apparatus used for MP extraction were initially subjected to acid washing followed by cleaning with deionized water.

This step was performed before and after each extraction process. To prevent MP contamination from the air, we conducted the sample extractions within a laminar-flow fume hood. Furthermore, a glass Petri-dish was left open inside the fume hood to monitor MP contamination. Blank samples, consisting of extraction solvents, underwent the same extraction procedure as the dust/web samples. The Raman analysis on particles obtained from the Petri-dish and glass fiber filter did not reveal any airborne or solvent-induced MP contamination.

2.3.2. Co-Pollutant Analysis. The organic micropollutant analysis involved a slight adjustment to the MP extraction process from web and dust samples to preserve organic additives.[3] Both web and dust samples were homogenized before separating the MPs using a NaCl solution, omitting wet peroxide treatment. Approximately 0.1 g of MPs were weighed and transferred from glass fiber filters (GFF) into glass centrifuge tubes using metal tweezers for subsequent analysis. About 8 mL of a methanol/water solvent mixture (5:3 v/v) was added to the centrifuge tube containing MPs. Each MP-solvent mixture underwent 30 min of sonication followed by centrifugation at 4500 rpm for 5 min. The resulting supernatant was concentrated to 2 mL by purging with a stream of nitrogen gas. Approximately 1 mL of the resultant solution was then transferred into a glass vial through a 0.22 μm PTFE syringe filter. The solutions in the vials were subjected to target analysis of Bisphenol A (BPA), Dibutyl phthalate (DBP), Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Monobutyl phthalate (MBP), Monomethyl phthalate (MMP), and Monoethyl phthalate (MEP) using LC-MS/MS analysis equipped with a reverse phase C18 analytical column of 3 mm × 150 mm and 3 μm particle size. Delay column (AQUITY UPLC BEH C18 1.7 μm 2.1 mm × 100 mm) for was used for removing phthalate emerging from the mobile phase. The injected sample volume was 10 μL. The mobile phases were 0.1% formic acid in water and 0.1% formic acid in methanol for phthalates and PFAS, and 0.1% ammonia in water and 0.1% ammonia in ACN for BPA, respectively.

The flow rates were set at 0.3 mL/min for phthalates and 0.4 mL/min for BPA. For phthalates, the total run time was 22 min. The composition of solvent B was maintained at 20% from 0.00 to 1.00 min, increased to 95% by 9.00 min, and held at this level until 16.00 min. It was then reduced back to 20% at 16.50 min and kept constant until the end of the analysis.

For BPA, the total run time was 10 min. The composition of solvent B was held at 50% from 0.00 to 0.01 min, then increased to 75% by 7.00 min. It was reduced back to 50% at 9.00 min and maintained at this level until the end of the analysis.

To assess linearity, seven standard solutions with concentrations between 10 and 200 ppb (10, 20, 40, 60, 80, 100, and 200 ppb) were utilized. Standards of the target organic compounds were injected before and after the analysis of sample series to verify the instrument's parameters. The intercept, slope, correlation coefficient, maximum residual deviation, and relative standard deviation of the response factor were calculated. Calibration curves were constructed by plotting the peak area of the compounds against their concentrations (Supporting Information: Figure S1). The standards showed satisfactory linearity with R^2 values exceeding 0.99. The Limit of Detection (LOD) and Limit of Quantification (LOQ) were determined using the signal-to-noise ratio, with the eqs 3.3 N/S for LOD and 10 N/S for LOQ, where N represents the standard deviation of the y-intercepts of the regression line, and S is the slope of the calibration curve. The calculated LOD for the BPA, DBP, DEP, DMP, MBP, MMP and MEP ranged from 0.05 to 0.11 ng/L, while the LOQ ranged from 0.17 to 0.37 ng/L. The interday and intraday precision for the targeted compounds were consistently below 4%. The recovery values were within 80–120%.

2.4. Data Processing. Data processing was conducted using IBM SPSS 22, Originpro 2018, Jamovi 2.4.14 and Microsoft Excel software. The distribution of MPs across various indoor environments was monitored using normality tests such as the Shapiro–Wilk and Kolmogorov–Smirnov tests. The variation in MP levels among indoor dust and web samples was examined using the Kruskal–Wallis test. The tests were deemed statistically significant at a p-value less than 0.05.

3. RESULTS AND DISCUSSION

3.1. Distribution of MPs across Dust and Web. The concentration of MPs in the dust samples varied from 2–10,407 MPs/g, while the MP load in the web samples ranged from 120–34,570 MPs/g (Table 1). A recent study from parking lots reported MP counts ranging from 2500–505,000 MPs/g, with a median value of 20,830 MPs/g in spider webs.[13] In our study, the average and median MP concentrations were 13629 ± 14,106 MPs/g and 7225 MPs/g, respectively. The variability of MP levels within samples, estimated by the coefficient of variation (CV), can be an effective method to predict their dispersion in the study locations.[21] MPs in both dust and web samples displayed a CV > 100%, reflecting high variability and uneven dispersion within different indoor spaces. Furthermore, the distribution of MPs in web and dust samples indicate that the data is positively skewed (Table 1), with more skewness (1.43) observed in the dust samples compared to the web samples. In this context, the Shapiro–Wilk test was used to assess the normality of distribution of MPs in the samples. The resulting p-value of less than 0.05 (Table 1) indicates that the MP levels were non-normally distributed, suggesting that localized hotspots may influence elevated MP levels in certain sites.

Table 1. Descriptives of MPs across the Sample Sites

	dust	web
N (samples)	60	60
mean (MPs/g)	2184	13,629
median (MPs/g)	798	8345
standard deviation	2929	14,106
minimum (MPs/g)	2	120
maximum (MPs/g)	10,407	34,570
skewness	1.43	0.283
std. error skewness	0.309	0.309
Shapiro–Wilk W	0.755	0.774
Shapiro–Wilk p	<.001	<.001

Figure 1 presents the variation in MP levels (median: MPs/g) in dust and web samples from diverse indoor environments. On comparing the concentrations across various indoor environments, a significant spike in MP levels can be noted in the samples from tailoring shops (TS), textile shops (TX), home décor shops (HD), photostat shops (PH), table mat shops (TM), and plastic collection units (PC). The highest MP load in both dust (9324 MPs/g) and web (33,570 MPs/g)

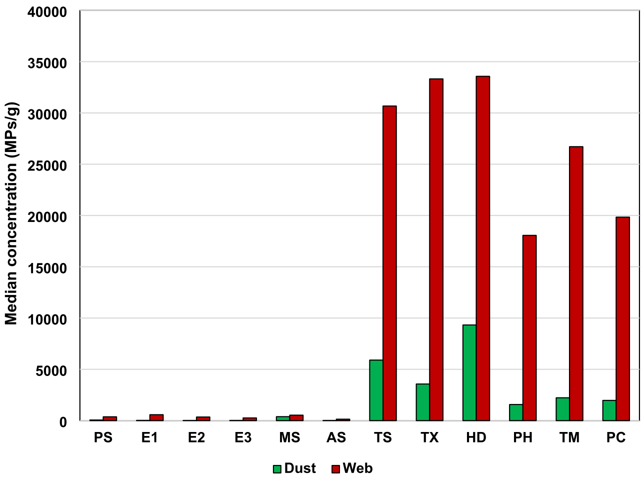


Figure 1. Comparative chart indicating the median concentration (MPs/g) in dust and web samples in different indoor spaces.*PS: Paint shops, EI: Educational institutions, MS: Medical shop, AS: Antique shops, TS: Tailoring shops, TX: Textile shops, HD: Home décor shops, PH: Photostat shops, TM: Table mat shops, PC: Plastic collection units.

samples were found in home décor shops. The high MP contamination in web and dust samples from TS, TX, HD, and TM can be attributed to textile fibers in these environments. The deposition rate of textile fibers in indoor dust is estimated to reach up to 1600 to 11,000 fibers/day/m^2.[22] In the case of PH and PC units, the source of MPs is likely related to MP contamination from electronic equipment, printing, and shredding activities.[23]

The box violin plots signifying the distribution of MPs between two groups (dust and web) along with Man-Whitney *U* test is presented in Figure 2. Man–Whitney *U* test was applied to assess differences in the abundance of MPs among between dust and web. The resulting *p*-value of less than 0.05 indicates that significant differences exist, indicating higher MP levels in web when compared to dust.

These observations clearly indicate that spider webs accumulate a higher density of MPs compared to indoor dust. Our finding aligns with the study by Iordachescu et al.,[13] which compared MP levels in road dust and spider webs. Thus, indicating that spider webs can play a substantial role for capturing MPs in indoor environments. Furthermore, a strong positive association ($r = 0.93$, $p < 0.05$) was noted between the MPs in dust and web samples. This clearly highlight the role of web being a good bioindicator of indoor MP contamination.

Webs situated indoors probably could have longer lifespans than dust samples.[13] The Pholcidae spiders whose webs were utilized in this study is reported to live for 3 years.[24] The dust is exposed to various factors in indoor spaces such as resuspension from indoor activities like cleaning, walking, and other mechanical stressors, providing a plausible explanation for the observed higher variation in MP concentrations.[23] Additionally, indoor ventilation and disintegration of larger particles from indoor materials can also be a significant factor affecting the concentration of MPs in dust samples.[23] Compared to dust sampling, which requires specialized vacuuming equipment, brushes, and other collection materials like paper bags, aluminum foils and ziplock covers all of which can introduce MPs and their copollutants, spider webs can be collected with a glass rod and stored in a glass vial avoiding cross contamination. This further reduces the wastage as part of sample collection which a huge environmental benefit. Furthermore, spider web samples offer a unique advantage as they are typically built in secluded environments, shielded from various environmental factors.[14] It is also found the webs could be stable up to 2 years ever if the spider is not using the web. Importantly, they spiders do not dismantle their old webs, which increases

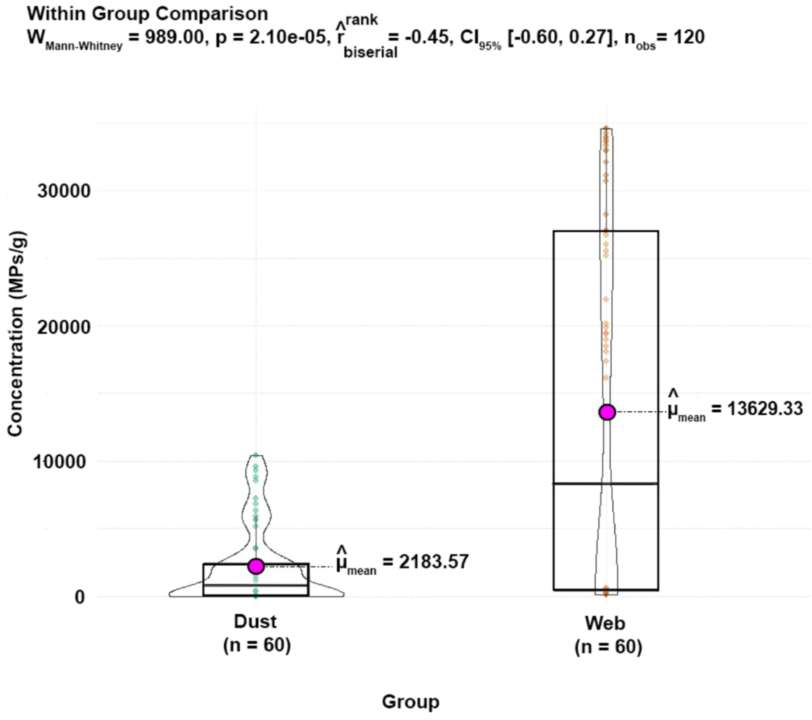


Figure 2. Box-Violin plot indicating the comparison between dust and web samples in the study sites.

the webs' longevity and enhances their potential to serve as passive samplers for airborne MPs over a fixed period.[24] This protective setting reduces the likelihood of significant fluctuations in MP concentrations over time. Moreover, spider webs remain suspended in indoor spaces, serving as effective collectors of airborne particles, including MPs.

3.2. Chemical Composition of MPs. Four reference polymers PE, PP, PS and PVC were utilized to identify the composition of MPs due to their widespread use of these plastics in the study area.[3] The known routes for the production of MPs from the above polymers in indoor spaces include abrasion, wear and chemical degradation.[25]

Both Raman and ATR-IR-spectroscopy was used in tandem for the polymer identification. IR analysis has advantages over Raman spectroscopy for analyzing certain colored particles because it does not produce fluorescence, which can interfere with Raman spectra.[26] This makes IR analysis particularly useful for examining colored MPs[27] and enhances the accuracy of polymer identification. The characteristic Raman and IR vibrations used for the identification is presented in Table 2.

Table 2. Characteristic Raman and IR Vibrations Used for the Polymer Identification

polymer type	Raman vibrations (cm^{-1})	IR vibrations (cm^{-1})	refs
PVC	638, 694, and 1430	1427 (CH_2 bend), and 1099 (C−C stretch)	27,28
PE	2850, 2883, and 2995	2915 (C−H stretch), and 2845 (C−H stretch)	27,28
PP	398, 809, 841, 1040, 1152, 1330, 1458, and 2853	2950 (C−H stretch), 2915 (C−H stretch), and 2838 (C−H stretch)	27,28
PS	1001, 1602, and 3054	3024 (aromatic C−H stretch), and 2847 (C−H stretch), 1601 (aromatic ring stretch)	27,28

Figure 3(a,b) presents the Raman spectra for the polymer types identified in both dust and web samples. The spectra displayed a stable baseline with distinct vibrational modes. In the dust samples, the occurrence of PE, PP, PS, and PVC was noted. However, we could only detect the presence of PE, PP, and PS. The differences observed in the spectra of PP in dust with that of web may be attributed to background fluorescence, which is frequently observed in complex environmental samples during Raman analysis.[29] This issue is likely related to our use of a laser with an excitation wavelength falling in visible range (532 nm). This could be reduced by using a laser with excitation in the near-infrared (NIR) range or completely avoid it by employing deep-ultraviolet (UV) wavelengths.[29] we could only detect the presence of PE, PP, and PS. It is essential to note that the density of MPs may influence their behavior in the air, with less dense MPs predicted to remain airborne for longer periods.[30] Considering that spider webs are often constructed in elevated spaces within indoor environments, it is plausible that they capture more of less dense MPs from the air due to their longer residence time. This fact is supportive of the observation that PVC is not found in web samples.

Figure 4(a−c) displays representative microscopic images of microplastics (MPs) and IR spectra of some colored MPs from both dust and web samples. A higher prevalence of MPs is observed in web samples compared to dust. Various shapes of MPs, such as fibers, films, and fragments, were identified. These shapes are indicative of secondary MPs, which form from the breakdown of larger plastic items, unlike primary MPs, which are typically spherical or bead-shaped.[31]

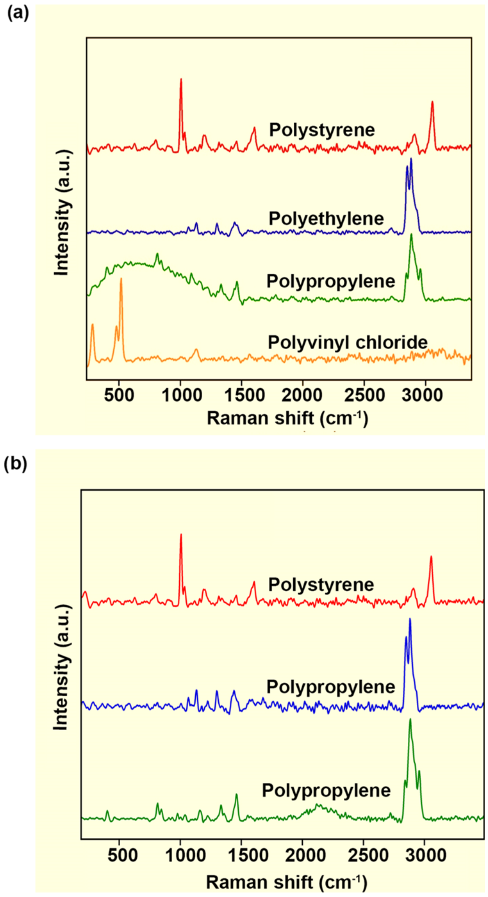


Figure 3. Raman spectra of different polymer types of MPs observed in (a) dust and (b) web samples.

MPs of different colors, including black/dark, white/transparent, blue, red, and green, were detected. We were able to observe a lot of dark/blue MPs in the web samples similar to the samples collected from the urbanized area in Brazil.[16] Dark MPs likely come from the degradation of furniture and building materials and may also result from the aging of colored MPs.[32] Transparent/white MPs may originate from single-use plastics and the photobleaching of colored plastics.[3,21] Colored MPs in the samples likely result from the wear and tear of various plastic products, such as furniture, textiles, footwear, and food and beverage containers.[21] While color alone is not the most reliable method for identifying MP sources, it still provides valuable insights into their origins and pathways.[3]

3.3. Human Exposure Risk. MPs act as carriers for toxic substances such as phthalates and heavy metals, significantly increasing health risks. These particles can enter the human body through inhalation, ingestion, or skin contact.[3] MPs themselves can cause respiratory and gastrointestinal irritation, and smaller particles, like nanoplastics, may penetrate cellular membranes, triggering oxidative stress and immune responses.[3] In addition, toxic substances carried by MPs, such as heavy metals pose even greater risks like kidney damage, skeletal issues, cognitive impairments and developmental problems.[33] Vulnerable populations, such as children, pregnant women, and the elderly, face higher risks from MP exposure due to their developing or compromised physiology. Children's

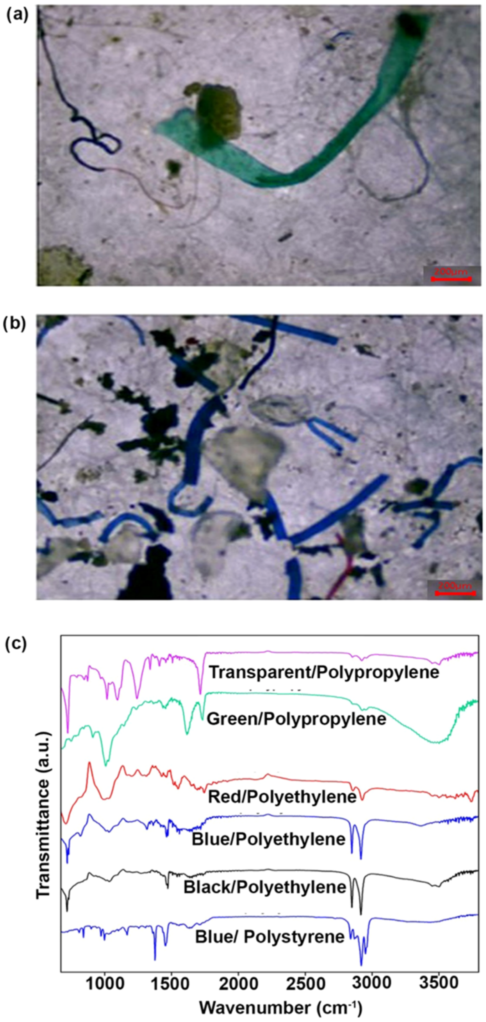


Figure 4. Optical microscope images of microplastics in (a) dust and web (b) sample and (c) IR spectra of some colored MPs.

frequent hand-to-mouth behavior increases their ingestion of contaminated dust, exacerbating exposure risks.[3,20] Understanding the pathways of human exposure to MPs and the toxic substances they carry is essential for developing public health policies.

In this study, since there was no established method for estimating human risk from MPs in spider webs, we focused solely on monitoring the exposure risk from MPs through the ingestion of dust. The present study monitored MPs larger than 50 μm; thus, the estimation of exposure to MPs in indoor dust was centered on the ingestion pathway, as it is the primary exposure route for MPs of this size.[21] Further details on the assessment of ingestion risk can be found in the Supporting Information. Table 3 provides a comparison of the estimated daily intakes (EDI) of MPs (MPs kg^{1-} day^{-1}) by ingestion across different indoor spaces.

Among various indoor spaces, the HD recorded the highest estimated daily intake, while the AS and EIs exhibited the lowest intake. This disparity can be attributed to the nature of activities and materials present in these environments. The elevated intake in the HD, as well as TS and TX, can be linked to the high density of textiles and their processing activities, which generate more MPs. Textiles, especially those undergoing frequent cutting, handling, and movement, release significant amounts of MPs into the environment, thereby increasing potential ingestion exposure.[34]

Table 3. Estimated Daily Intakes (EDI) of MPs (MPs kg^{-1} day^{-1}) by Ingestion across Different Indoor Spaces

indoor environments	children	teenagers	adults
PS	[a]n.a.	0.0020	0.0016
EI 1	0.0018	0.0007	0.0006
EI 2	n.a.	0.0005	0.0004
EI 3	n.a.	0.0006	0.0005
MS	n.a.	0.0128	0.0107
AS	n.a.	0.0005	0.0004
TS	n.a.	0.1959	0.1648
TX	n.a.	0.1185	0.0997
HD	n.a.	0.3096	0.2605
PH	n.a.	0.0521	0.0438
TM	n.a.	0.0739	0.0622
PC	n.a.	0.0653	0.0550

[a] n.a.—Not applicable.

Regarding daily intakes across various age groups, Table 1 indicates that in EI 1 (school), the observed order of estimated daily intake was children > teenagers > adults. This pattern reflects the greater vulnerability of children to MP exposure in indoor environments, likely due to their behaviors and physiological characteristics. Children have a higher respiration rate, increased surface area contact with their environment, and lower body weight compared to teenagers and adults, which collectively contribute to a higher intake of MPs.[3] In other environments, where exposure risk for children were not accounted for due to their absence, the teenagers exhibited a higher daily intake of MPs than adults. This variation can be explained by the different activity patterns (cleaning and arrangement) and environmental interactions of teenagers, who often spend more time in settings with higher MP concentrations. The combination of their active lifestyles, increased contact with various surfaces, and the same physiological factors affecting children (albeit to a lesser extent) contribute to this higher intake in teenagers.[3]

3.4. Co-Pollutants Levels. We specifically targeted BPA, DBP, DEP, DMP, MBP, MMP, and MEP for the copollutant analysis of MPs isolated from dust and web samples. These compounds were chosen for several reasons. BPA is a commonly used as a flame retardant, while phthalate esters such as DBP, DEP, DMP are widely applied as plasticizers. Even-though these compounds are integral to the manufacturing of plastics, they are well-known endocrine disruptors (EDCs). Furthermore, numerous studies have highlighted their ubiquitous presence in indoor environments.[15,35] MPs may significantly contribute to the existing levels of these EDCs since they often contain these chemicals in elevated amounts. However, there is very limited knowledge on their contribution to total EDC levels in indoor spaces.[36] The selection of monoesters of phthalates (MBP, MMP, and MEP) was based on the potential transformation of parent compounds within indoor spaces, suggesting that MPs could also harbors these transformed products.[2,3]

Figure 5 presents the results of the copollutant analysis, highlighting that the target analytes were ubiquitously present in both web and dust matrices. This study marks the first detection of BPA, phthalate esters, and their monoesters in MPs collected from spider web samples. Notably, DEP exhibited the highest concentration in web samples (1971.78

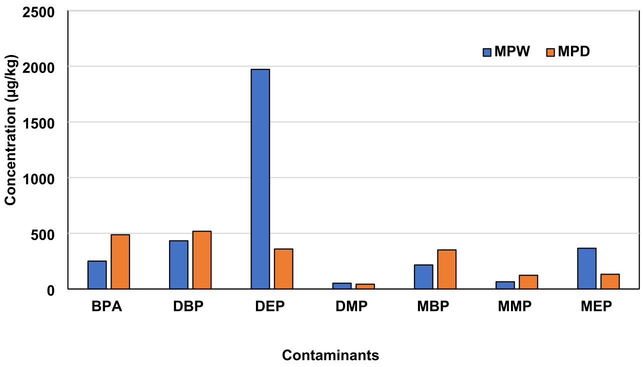


Figure 5. Concentration levels (mean) of pollutants in web and dust samples. *MPW: Microplastics in web, MPD: Microplastics in dust, BPA: Bisphenol A, DBP: Dibutyl phthalate, DEP: Diethyl phthalate, DMP: Dimethyl phthalate, MBP: Monobutyl phthalate; MMP: Monomethyl phthalate; MEP: Monoethyl phthalate.

μg/kg), while DBP (518.42 μg/kg) was the dominant phthalate ester (PAE) in dust samples. The total copollutant concentration was higher in MPs from webs (3354.58 μg/kg) compared to dust (2014.77 μg/kg), primarily due to the significantly elevated DEP levels in the web samples.

The concentration trends of contaminants varied between web and dust samples. Specifically, BPA, DBP, MBP, and MMP concentrations were higher in dust samples, whereas DEP, DMP, and MEP was more concentrated in web samples. The composition profile in Figure 6 shows DEP as the primary contributor to the total pollutant load in web samples (∼58.77%), while DBP had the highest contribution in dust samples (∼25.73%), closely followed by BPA (∼24.18%). These variations in concentration trends may be attributed to physical, chemical, and biological factors inherent to the respective matrices,[37] as well as their octanol-air, particle/gas and dust/gas partition coefficients.[38]

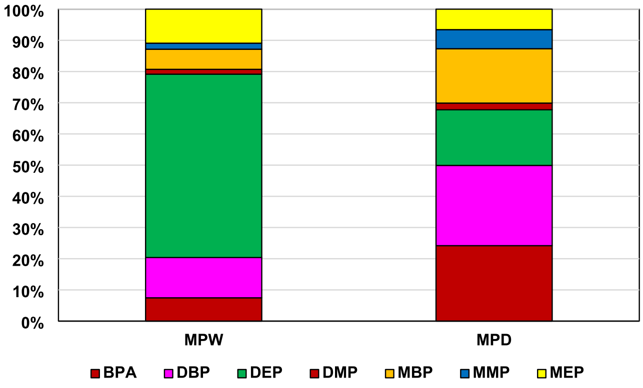


Figure 6. Percentage (%) composition of each contaminant to the total contaminant level in web and dust samples.*MPW: Microplastics in web, MPD: Microplastics in dust, BPA: Bisphenol A, DBP: Dibutyl phthalate, DEP: Diethyl phthalate, DMP: Dimethyl phthalate, MBP: Monobutyl phthalate; MMP: Monomethyl phthalate; MEP: Monoethyl phthalate.

The detection of monophthalate esters (MBP, MEP, and MMP) on MPs in both web and dust samples is significant because these compounds are transformation products of their parent phthalates. Previous studies have documented the presence of these transformation products in indoor dust.[2,39] Phthalates are known to undergo both chemical and biological degradation in the environment, and their monoester metabolites serve as efficient biomarkers for assessing human exposure to parent phthalates in indoor settings.[40] While most research has focused on detecting these metabolites in human biological samples such as urine, milk, serum, and saliva, there is limited information on their occurrence in indoor environmental matrices.[2]

A study in China revealed the presence of phthalate metabolites in dust samples collected from residential areas, showing median concentrations of 21.54 μg/g for MBP, 1.11 μg/g for MEP, and 9.44 μg/g for MMP.[39] In our investigation, we could only compare these concentrations with MPs found in web and dust samples, as we did not directly analyze web and dust samples. The concentrations of MBP, MEP, and MMP in MPs from dust were 0.351, 0.123, and 0.132 μg/g, respectively. Similarly, in web samples, the concentrations were 0.216, 0.065, and 0.365 μg/g, respectively. These results suggest that MPs present in both dust and web samples contribute to the overall pollutant load of monoesters in indoor spaces and can serve as reservoirs for these compounds.

Despite previous reports noting the occurrence of transformation products of organic micropollutants in indoor dust, the mechanisms behind the transformation of these parent compounds remain poorly understood. Additionally, the residence time of organic micropollutants in indoor spaces is underexplored. Recent research highlighted the residence time of parabens (MeP and BuP) in indoor dust, showing the production of transformation products during their residence.[20] This suggests that compound transformation occurs in indoor spaces, though the specific mechanisms were not detailed in that study. Research in other matrices indicates that biotransformation is a key pathway for the transformation of phthalates, producing compounds such as monophthalate esters, phthalic acid, and phthalic anhydrides, which were detected in our previous report on indoor dust.[2]

Further research is necessary to understand the fate and transformation mechanisms of compounds in indoor environments, as transformation products may pose greater risks to residents due to increased bioavailability, reactivity, and persistence compared to parent compounds. Spider webs offer significant potential for these studies as they often undergo less disturbance compared to dust samples. Previous literature has shown that spider webs are effective in monitoring pollutants like heavy metals and organic micropollutants such as polycyclic aromatic hydrocarbons (PAHs) and dioxins.[41] Therefore, spider webs could be a valuable tool for investigating the dynamics of pollutant transformation and accumulation in indoor environments.

■ CONCLUSIONS

In conclusion, this study provides valuable insights into the distribution of microplastics (MPs) within indoor dust and spider webs. Spider webs were identified as significant collectors of MPs in indoor settings, highlighting their potential as effective biomonitoring tools. The presence of various polymer types and colored MPs underscores the complex nature of plastic sources indoors. Additionally, the detection of copollutants such as Bisphenol A (BPA), Dibutyl phthalate (DBP), Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Monobutyl phthalate (MBP), Monomethyl phthalate (MMP), and Monoethyl phthalate (MEP) in MPs isolated from both web and dust samples raises significant health concerns. This research contributes to our understanding of MP contamination in indoor environments, highlighting the associated health risks and underscoring the pivotal role of spider webs as essential sinks for MPs. Furthermore, spider webs tend to preferentially accumulate less dense MPs and their copollutants. This reflects the selective ability of spider webs to capture lighter particles suspended in the air. This selective accumulation demonstrates the webs' capacity to mimic the air phase of indoor contamination.

Given these findings, future research should explore the mechanisms governing microplastic dynamics in indoor environments, considering both dust and spider webs as integral components. Robust risk assessments and mitigation strategies need to be formulated, taking into account the varied sources and potential health impacts associated with microplastic ingestion. Ultimately, this study advocates for a comprehensive approach to addressing the complex challenges posed by microplastic contamination and their copollutants in indoor settings, emphasizing the need for ongoing investigation and proactive management to protect human health.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request. The data underlying this study are not publicly available since the observations in the present research is going to become part of explaining certain phenomena another work, which is not yet published. However, the data are available from the corresponding author upon reasonable request with a statement that such data will be used only for personal/study purpose.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c07373.

> Calibration plots of target analytes (DEP, DBP, DMP, BPA, MEP, MBP, and MMP); detailed description of parameters used for estimation of human exposure risk (PDF)

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Conceptualization, Methodology, Formal analysis, Writing−original draft: K.S.A.; Conceptualization, Methodology, Formal analysis, Writing−original draft: V.S.M.; Editing, Supervision: T.J.; Review & editing, Supervision: C.T.A.; Conceptualization, Writing−review and editing, Supervision: U.K.A.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the partial financial support from SPARC project (ID: P3847) (MHRD), New Delhi, and RUSA 2.0 CUSAT. Inter University Instrumentation Centre (IUIC), and Sophisticated Analytical Instrumentation Facility (SAIF), Mahatma Gandhi University, Kottayam for instrumental support. We also acknowledge the technical help provided by Shiny Thomas and Annu Mathew during the sample analysis. K.S.A. is thankful to CUSAT for research fellowship. V.S.M. is thankful to UGC for SRF fellowship.

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