Microplastic pollution on historic facades : hidden ‘sink' or urban threat?

Microplastic Pollution on Historic Built Surfaces: Hidden 'Sink' or Urban Threat?

Katrin Wilhelm[a*]; Sam Woor[a]; Michelle Jackson[b]; Dania Albini[b]; Neil Young[c]; Phani Karamched[c]; Miriam C. Policarpo Wright[d], Josep Grau-Bove[d], Scott Allan Orr [d], Jack Longman[e], Tim de Kock[f]

[a] Oxford Resilient Buildings and Landscapes Laboratory (OxRBL), School of Geography and the Environment, University of Oxford, South Parks Road, Oxford, OX1 3QY, UK; Katrin.wilhelm@ouce.ox.ac.uk; sam.woor@ouce.ox.ac.uk

[b] Department of Biology, University of Oxford, 11a Mansfield Road, OX1 3SZ, England, UK; michelle.jackson@biology.ox.ac.uk ; dania.albini@biology.ox.ac.uk

[c] David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH; neil.young@materials.ox.ac.uk; Phani.karamched@materials.ox.ac.uk

[d] UCL Institute for Sustainable Heritage, Central House, 14 Upper Woburn Pl, WC1H 0NN, London, United Kingdom; scott.orr@ucl.ac.uk ; miriam.wright@ucl.ac.uk ; josep.grau.bove@ucl.ac.uk

[e] Department of Geography and Environmental Sciences, Northumbria University, Newcastle-upon-Tyne, NE1 8ST, United Kingdom; jack2.longman@northumbria.ac.uk

[f] Antwerp Cultural Heritage Sciences (ARCHES), Faculty of Design, University of Antwerp, Mutsaardstraat 31, 2000 Antwerp, Belgium; Tim.DeKock@uantwerpen.be

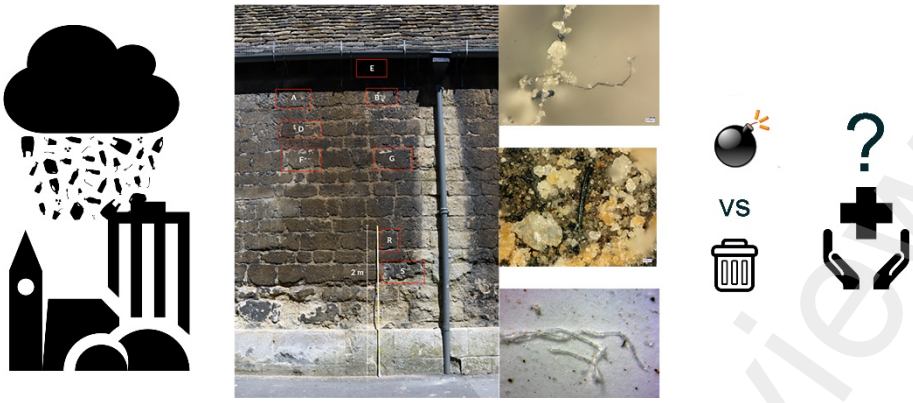
Abstract

Despite increasing concerns about the health and environmental risks of microplastics (MPs), research has largely overlooked their presence on urban surfaces— integral parts of our daily lives. The focus has often been on MPs in air and oceans, leaving a significant knowledge gap in understanding urban MP pollution. Our pioneering interdisciplinary study addresses this gap, quantifying and identifying MPs on vertical urban surfaces, subjected to MP pollution from both terrestrial and atmospheric domains. We have effectively integrated knowledge and methodologies from air pollution and terrestrial microplastics research.

We reveal the pervasive presence of MPs on historic masonry buildings in a medium-sized urban area in the UK, with an estimated median frequency of 875,000 fibres/m^2 (0.875/mm^2) for fibre lengths between 30-1000µm. These findings underscore the urgent need to determine the long-term fate of these fibres: do historic surfaces represent an urban 'sink' that can mitigate potentially negative health impacts or exacerbate effects of volatile microplastics?

Understanding the varied sources, pathways, and impacts of MPs on urban surfaces is paramount for gauging their ultimate fate. Addressing MP pollution in historic urban areas is essential for safeguarding human health and promoting sustainable cities. By developing a comprehensive understanding of these multi-scale factors, we can pave the way for effective interventions and policies to mitigate the threat of MPs.

Graphical abstract



1 Introduction

Microplastics (MPs) have become a global threat due to their ubiquity, unpredictable and potentially unmanageable risks to human health, ecosystems and the environment[1,2,3]. The gravity of this issue is intensified by the rapid increase in plastic production over the past 70 years, resulting in a staggering 10 billion metric tons of plastic having been produced globally[4]. Furthermore, mismanagement of plastic waste leads to it redistribution and accumulation in the environment at a rate that surpasses its production[5]. As plastic debris breaks down over time, it creates MPs, thereby turning the surge in plastic production into a direct feed for escalating MP pollution levels.

MP sources and exposure are highest in industrialised urban areas[6,7]. The extensive presence and diversity of MPs and their by-products in urban areas pose a significant concern due to the growing concentration of the global population in these environments. In 2019, pollution-related factors resulted in over 4.6 million premature deaths in urban areas. Alarmingly, nearly 99% of the global population resides in areas where the air quality guidelines established by the World Health Organization (WHO) are consistently unmet[8].

While research on MPs has increased recently, the majority of those studies focus on MPs in the air and oceans, and only recent attention has been given to freshwater and soils, while MPs on urban surfaces have been largely overlooked[9,10,11,12,13]. The built environment represents a crucial intersection for studies on microplastic (MP) pollution from both terrestrial and atmospheric perspectives, essentially acting as a 'missing link' in current MP research. More specifically, these urban surfaces, being both grounded and exposed to the air, are uniquely positioned to accumulate MP pollution from both land and air-based sources.

Investigating the presence of microplastics on vertical urban surfaces is crucial for several reasons. Firstly, vertical surfaces, such as building facades and walls, are often exposed to direct sunlight and weathering, which can contribute to the breakdown and release of microplastics. Understanding the extent of microplastic accumulation on these surfaces can provide insights into their persistence and potential for further environmental contamination. Additionally, vertical urban surfaces are in close proximity to everyday human activities and can serve as sources of microplastic exposure. Exploring the presence of microplastics on these surfaces can help assess the risks to human health and inform appropriate mitigation measures. Therefore, investigating microplastics on these surfaces is essential for a comprehensive understanding of microplastic pollution in urban environments. A significant gap remains in understanding the role of urban surfaces in the pathway of MPs, specifically whether they act as a long-term or temporary storage (‘sinks’) for MPs.

There is a lack of standard methods for the identification and quantification of MPs on urban surfaces, particularly in view of MP-degrading processes common in the environment [2,10,14,15]. Once in the environment, plastics not only degrade and fragment, altering their physical and chemical properties, but also become colonised by microorganisms[16,17]. These modifications complicate the analytical process, as most current reference spectra do not account for degraded, weathered, or otherwise altered microplastics (exception are e.g.[15]). Without standardised methods, the reliable quantification and identification of MPs become challenging. It also hampers the comparison of results across diverse contexts (such as regions, surfaces), thereby hindering the development of a comprehensive understanding of MP pollution and pathways in urban environments and beyond.

Furthermore, the lack of standardised methods to quantify and identify MPs makes monitoring mitigation efforts and implementing targeted interventions to reduce MP pollution difficult. MPs are small particles (1 – 5000 μm) that originate from a variety of primary and secondary sources, including the breakdown of commercially-produced plastics, the release of microbeads from a range of products, including those for personal care, abrasive cleaning , paint, blasting abrasives and the shedding of synthetic fibres from clothing and other textiles, surface coatings to protect against guano, and urban sewage sludge used as fertiliser for agricultural land[18,19,20,21]. Further, textiles, as sources for fibres, are used in a range of industries such as automotive production and construction, horticulture, mining, sports, transport[22,23.]

The complexity of microplastic (MP) pollution necessitates a holistic approach due to its diverse sources, varied physical and chemical transformations, and wide range of impacts across biological scales. MPs can be detrimental to human health and enter the human body through inhalation, ingestion, or skin contact[24,25,26.]

Microplastics (MPs) originate from a multitude of sources and, once in the environment, they undergo physical and chemical transformations, even potentially absorbing other harmful pollutants. Unanticipated pathways, such as avian activity, can further distribute these MPs[25,27]. Complicating the issue, MPs can also carry or adsorb detrimental pollutants, including heavy trace metals and pathogens, posing additional threats to human health. Furthermore, they may chemically breakdown into novel compounds with yet-to-be-understood impacts, some decomposing more readily than others as delineated by Campanale et al. 2020[24].

Furthermore, they exert significant effects not only on human health through various exposure routes, but also on wildlife, affecting both terrestrial and aquatic species[11,28.] Environments frequented by birds, for instance, could potentially serve as sources and conduits of MP pollution[29,30.] Given this multifaceted nature of MP pollution, it is essential to adopt a comprehensive approach that considers all these interconnected facets to effectively mitigate their impacts on the environment, ecosystems, and human health. This is especially critical in urban spaces, where the density of human activity intensifies the risk of exposure and where urban ecosystems might be uniquely vulnerable.

Our study investigated historic structures within the built environment. We focused on buildings of artistic and sociocultural value, often crafted with traditional materials such as limestone and preserved over extended periods. The weathering stress history of historic buildings makes them particularly sensitive to environmental changes, functioning much like a 'canary in the coal mine' — an early warning system for detrimental environmental changes. This provides opportunities for long-term pollution monitoring. We built upon existing research on long-term exposure to

environmental pollutants and stressors. Previous studies have demonstrated that vertical surfaces (and to a lesser extent, horizontal ones) can act as quasi-passive samplers for urban pollutants[31-33]. In this context, our research explores whether black weathering crusts—recently established as valuable long-term records of air pollution[34,35]—act as a potential source or sink of MP pollution.

Our study fills a significant gap in the existing literature by investigating MPs on historic urban surfaces, which, to our knowledge, has not been previously explored. We investigated selected areas of 8 m^2 of the south facing medieval outer limestone wall of New College Cloister on New College Lane, Oxford, UK, exposed to the atmosphere since c.1400c. We demonstrate the ubiquitous presence of MPs in a traffic-reduced urban setting, adding to our understanding of the overall urban MP budget. Our research lays the groundwork for considering (historic) built environment surfaces in future MP studies. The overall aim of our study is to advance the development of a reliable methodology for MP collection and analysis in these contexts to broaden the assessment of the real MP extent and, potentially, inform new policies towards healthier urban environments and more sustainable plastic usage[36,37]. Our findings are of great importance, given the unpredictable risks of MPs to human health, ecosystems, and the environment.

2 Material and Methods

2.1 Sampling strategy

Despite extensive research on microplastics (MPs) detection in various environmental settings, there is still a lack of standardisation in methodologies employed by different research groups and analytical methods vary widely[14,15]. Bergmann et al. (2022[2]) raise concerns as the lack of standardisation might lead to significant variations in results. Given the lack of standardization in MP research, we developed a comprehensive approach to investigate microplastics on vertical surfaces, which has not been previously explored. Our qualitative and quantitative methodology involved manual sample collection, density separation, visual 3D microscopy, scanning electron microscopy (SEM), FlowCAM® analysis, and Fourier-transform infrared spectroscopy (FTIR). This multi-dimensional approach enhanced the accuracy and reliability of our findings, considering the challenges posed by the absence of established research protocols in this particular field of urban MP research.

To ensure the integrity of our analysis, we took stringent measures to prevent cross-contamination at every step. These precautions included wearing appropriate protective clothing and gloves, as well as using containers that were specifically chosen to eliminate any electrostatic charge. These practices adhere to the guidelines proposed by [22,86,87].

2.2 Site

Oxford, UK has a population of approximately 162,000 residents (estimate based on ONS 2021 Census; Oxford City Council) with a relatively high population density of about 3,509 people per square kilometre. The urban environment of Oxford provides an interesting context for studying MPs on urban surfaces. On the one hand, the urban landscape of Oxford is characterised by a mix of historic buildings (serving as long-term passive samplers for air pollutants[35]; Figure 1), academic institutions, residential areas, and commercial establishments. On the other hand, the city's high population density and diverse activities (e.g., tourism, sports events, etc.) create potential sources and diverse pathways for MPs.

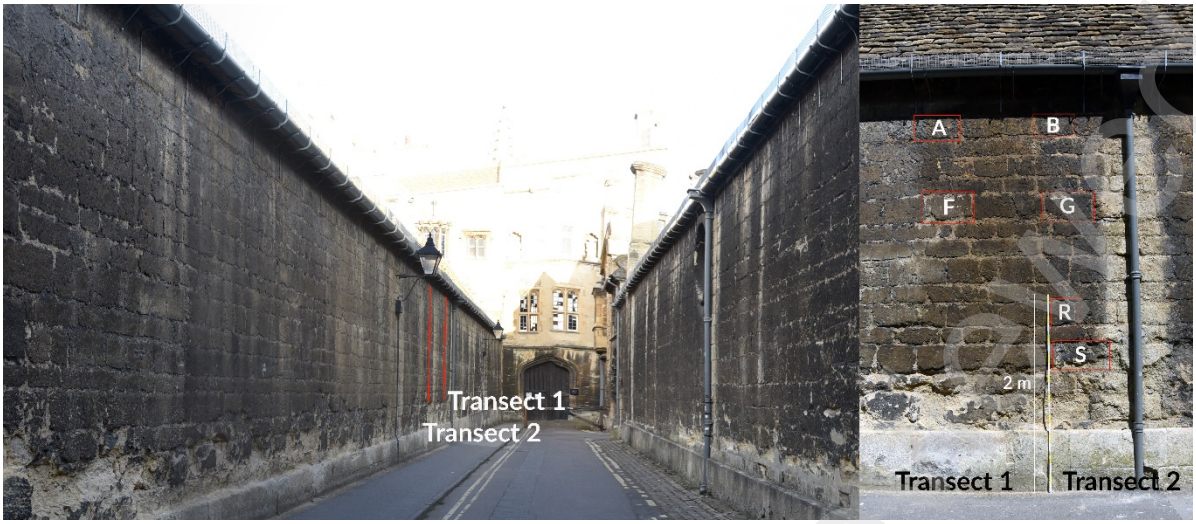


Figure 1 Sampling transects (red lines), New College Lane, Oxford (UK). GIS 51°45'15.2"N 1°15'09.9"W. The south-facing wall of New College Cloister on the left. Inlay (right) shows sampling locations.

The investigated samples of this study are a subset obtained as part of the 'Pollution Clock' project which has established black gypsum crusts on built historic environment as long-term geochemical archives for past air pollution providing a finer-scale resolution pollution record reconstruction[34]. Samples were taken in May 2021 in the traffic-reduced New College Lane, Oxford, UK (GIS 51°45'15.2"N 1°15'09.9"W) on the south-facing wall of New College Cloister (built between c. 1396 and 1400). Six areas were sampled at four different heights (1.60, 2, 3, and 4 m above street level). The size of the individual sampling areas was about 100 mm x 100 mm. We used a 420HC stainless-steel blade (Rockwell hardness 58) and only removed weathering crust to be as minimally invasive as possible (in line with the Venice Charter, 1964[88] and the Malta Convention, 1992[89]). During the sampling period in May 2021, a total of 18mm of rain was recorded at the Radcliffe Weather Station (Location: 450900E 207200N, Lat 51.761 Lon -1.262, 63 meters above mean sea level).

Table 1 Sample IDs, sampling area and height at the south-facing Cloister wall of New College (Oxford, UK) in New College Lane as well as the cumulative lengths of the fibres. Areas A and B (4 m height) are sheltered from rain and run-off through the open eave; areas F and G (3 m height) are neither sheltered nor in direct line of increased water run-off; area R (2 m) is potentially affected by wash off from upper parts of the wall. Area S at 1.6m height and close to the gutter has the most disturbed surface.

Sample	**A** (4m)	**B** (4m)	**F** (3m)	**G** (3m)	**R** (2m)	**S** (1.6)	**Total**
Sample area (mm²)	396	690	690	453	264	700	**3193**
Height (m)	4	4	3	3	2	1.6	-
Abundance	55	151	25	11	44	0	**286**
Median Abundance/mm²	0.14	0.22	0.04	0.02	0.17	0	**0.88**
Cumulative fibre length (µm)	6592.76	21993.31	4122.26	1207.43	18508.62	-	**52424.38**
min length (µm)	57.46	52.34	34.04	51.61	42.09	NA	**34.04**
max length (µm)	550.1	525.21	630.62	242.66	345.87	NA	**630.62**
mean length (µm)	119.87	145.65	164.89	109.77	420.65	NA	**192.166**
Standard Error	13.82	8.26	29.72	19.9	40.32	-	-
median length (µm)	78.69	118.95	97.72	84.56	320.62	NA	**97.72**
MAD fibre length	0	14.64	0	0	0	-	-
25th percentile (µm)	66.246	85.644	75.762	53.436	214.11	NA	-
75th percentile (µm)	147.864	163.602	159.21	146.034	566.934	NA	-

IQR	81.618	77.958	83.448	92.60	352.824		

177

178 ## 2.3 3D microscopy

179 Untreated crust samples from New College Lane were first visually inspected using a Keyence VHX 3D
180 microscope to identify the presence of microplastic fibres. The fibres were qualitatively identified by
181 examining their morphology, colour and observing the ends of the fibres where fraying might indicate
182 human-made products[22]. Both the qualitative SEM and FTIR analysis involved hand-picking the fibres
183 with tweezers, a common procedure, which however imposes a size limitation (> 500 µm) that can be
184 handled by a human[10,90,27].

185 ## 2.4 SEM

186 The samples were prepared on the 12.5mm Aluminium pin stub and mounted so that the cross-
187 section could be examined. A Zeiss EVO tungsten filament SEM equipped with an Oxford
188 Instruments EDX detector was used to image and map the elemental compositions. The samples
189 were mounted on a carbon sticky pad and coated with a 4nm layer of Pt to improve conductivity in
190 the SEM and a beam voltage of 10KV was used for the examination. Figure 2 shows an example
191 image (originally obtained at a magnification of 150X) and the elemental distribution maps.

192 ## 2.5 FTIR

193 Samples were not chemically pre-treated ('purified') with chemicals to not affect low-density and
194 sensitive materials such as Nylon[91] and maintain any environmental degradation process intact for
195 analysis and assuming that biological contamination is less compared to water samples or fish
196 intestines etc.[14,87]. Individual microfibres were first picked using a Keyence VHX 3D microscope and
197 transferred to a 12-spot reflection slide for analysis using the FTIR microscope. The slides were
198 loosely covered with aluminium foil while being transferred between the 3D microscope and the
199 FTIR microscope in order to avoid particle contamination[87,86,92.]

200 This study employed Fourier transform infrared (FTIR) spectroscopy as the most common approach
201 to analyse MPs[93,15, 94]). A Thermo Scientific Nicolet iN10 MX FTIR microscope was used to collect
202 infrared spectra for microfibres manually picked from the New College Lane crust samples. The
203 integrated microscope was used to locate the individual MPs, and to select targets for collecting IR
204 spectra. The IR reflection spectra were collected with the detector in liquid nitrogen-cooled mode,
205 and a spectral range of 4000 to 675 cm^{-1}. Three repeat measurements were taken at each target
206 location of eleven fibres in total. The three measurements were averaged using the median and a
207 simple linear baseline correction was applied.

208 Following the recommendation of Aves et al. (2022), this study visually investigated all sample and
209 relevant reference spectra. To identify the chemical components of each sample, we analysed the
210 spectra using the software Spectragryph, which compares the results to reference spectra based on
211 a full-spectrum Pearson correlation coefficient and provides an estimation of similarity, denoted as
212 the hit quality index (HQI)[14]. For our study we used the Primpke (2018[42]) FTIR spectra library
213 enhanced with 57 FTIR spectra of plastics from Birch et al. (2021[95]) as recommended by Menges
214 (2019) the Spectragryph software provider as well as two novel databases, FLOPP and FLOPP-e,
215 introduced by De Frond et al. (2021[15]) which contain spectra from common plastic items including
216 environmentally weathered. Following Aves et al. (2022[90]) and Renner et al. (2019[87]) matches of
217 >70% HQI against the library reference spectra were included in the results as MPs. From each
218 database HQI the highest scoring was accepted. Three spectra collected on any individual fibre were
219 averaged using the median. To compare our spectra to the database spectra, a simple automatic
220 baseline as vertical set off was applied.

Although our study does not specifically focus on MP degradation, it is crucial to consider the impact of degradation processes on MP analysis. While chemical degradation is a universal process, it can be accelerated on land due to the absence of water's (sea and fresh) buffering effect against temperature and UV impact[80,96]. Consequently, MP weathering and degrading patterns may differ significantly on vertical urban walls compared to sea and freshwater bodies as well as soil and sediments. However, these degradation processes are also influenced by the specific conditions and factors within each environment, combined with the respective MP chemistry and morphology, thereby affecting the rate and extent of degradation. Furthermore, different degradation mechanisms can interact simultaneously, adding to the complexity of the overall degradation process[9,15,22]

This complexity is reflected in the FTIR spectral reference database when analysing environmentally degraded MPs, where multiple matches are frequently encountered for a variety of reasons. Firstly, the reflection mode of the FTIR analysis can contribute to variability in matches. When collecting data in reflection mode (which was preferred in our instance to not damage the degraded MP sample further and to collect three readings per sample without losing the fibre), the spectra may be influenced by light scattering effects, which can vary depending on the morphology of the MP particles. This can lead to multiple matches in the database, as the collected spectra may not perfectly match the reference spectra due to the influence of scattering[14]. Secondly, the presence of degraded plastic can also contribute to multiple matches in the database. Degraded plastics can undergo chemical changes and structural modifications, which can result in variations in the FTIR spectra[97,98]. These variations may cause the spectra of degraded plastics to match multiple entries in the database, as the reference spectra may not fully capture the range of potential spectral changes that can occur during degradation. Thirdly, it is possible for a single MP fibre to contain more than one polymer type. This can occur due to various reasons such as the presence of multiple layers or coatings on the fibre, the use of polymer blends or composites, or the degradation and fragmentation of different polymers mixing together[23,99]. The EDX elemental map (Figure 2) of sample NCL-B2 demonstrates such an example which shows instead of carbon (the most common base element for MPs as they derive from oil), calcium and chlorine, indicating a treated textile used in sports cloths as described by Varan et al. (2021[23]).

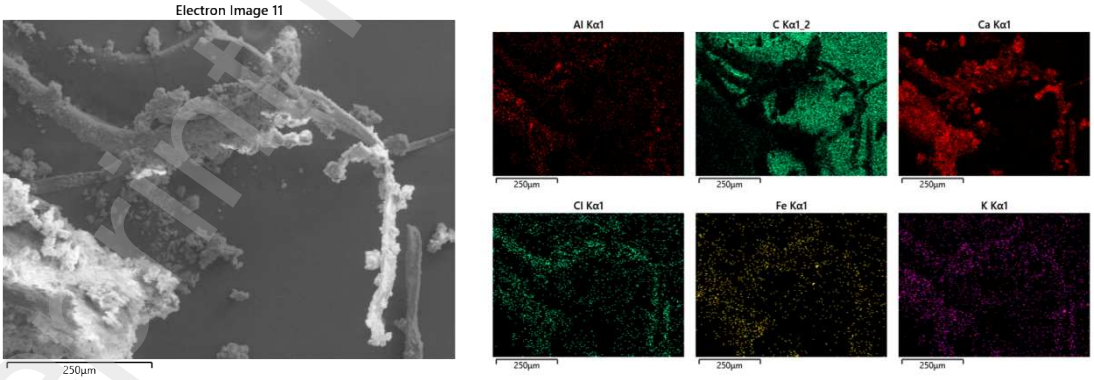


Figure 2 The SEM-EDX analysis of sample NCL-B2 reveals the presence of Calcium and Chloride, but interestingly, no Carbon. Typically, Carbon is the most prevalent base element in synthetic fibers, making this finding unusual.

2.6 Density separation

In order to separate microplastic fibres in preparation for the FlowCAM® analysis, 6 crust samples were processed (Table 1). Density separation involves the submergence and agitation of a sample made up of materials of mixed densities in a solution of known density which causes the submerged materials to either sink or float based on their density relative to that of the solution and is a common procedure in MP analysis[100]. Density separation is widely applied in studies of environmental microplastic, usually for their separation from sediments such as silt and sand[101]. There is a lack of consensus on what solution is best used for the density separation of microplastics, with NaCl being the most common as it is readily available and easily disposed of[102,100]. However, Quinn et al. (2017[100]) note that many common plastics have a density greater than that of NaCl (1.2 g cm^{-3}), thus may not be represented in resulting density separates. Added to the fact that there is no existing precedent for separating microplastics from heritage stone crusts, we believe that a higher density solution is more appropriate for capturing a potentially wider range of microplastic materials. Therefore, we used a 1.4 g cm^{-3} solution of sodium polytungstate (SPT) as it has been applied previously in microplastic density separations[103,104,105].

Crust samples were placed in the bottoms of beakers in a single layer and roughly 50 ml of SPT was added. Samples were then covered and agitated in an Ultrawave ultrasonic bath for 10 minutes, resulting in the disaggregation of the crusts. They were then left to settle, covered, for 24 hours. A 5 ml sub-sample was pipetted off for subsequent FlowCAM® analysis. The remaining solutions were vacuum filtered through 47 mm diameter cellulose nitrate filter papers with a 0.2 µm pore size. The papers were then rinsed with distilled water to prevent crystallisation of the SPT and dried in covered petri dishes at room temperature. The dilute SPT was recycled. All equipment was thoroughly rinsed, dried and inspected using a microscope prior to the procedures outlined above to ensure no contamination from microplastic in the laboratory. Visual inspection of the filter paper did not show MP contamination.

2.7 Flow Cam analysis

We used the Bench Top FlowCAM® 8000 (Fluid Imaging Technologies, Inc. Maine, USA) to fast identify, quantify and measure microplastic fibers and fragments. FlowCAM® uses a combination of flow cytometry, microscopy, and machine learning to fast detect and capture particles in a liquid sample, for semi-automatic image analysis[106]. Particles contained in a fluid sample are suctioned from a top inlet port through a glass flow chamber (i.e., flow cell) by a peristaltic pump. As particles pass through the flow chamber, they are illuminated by a laser, magnified by an objective and a camera creates a digital image for each single particle. The images are then stored in a computer for analysis. We used the FlowCAM® particle analysis software (VisualSpreadsheet©, version 4) in the AutoImage mode, to capture particle images with a 10x objective, 1mL pump, a flow rate of 0.15 ml/min, capturing 21 frames/second. Image libraries of plastic fibers were created prior to the experiment using a sub-sample (~10 samples) and were used as a reference for the auto-categorization of processed particles. Once the sample was photographed, images were auto identified by the VisualSpreadsheet© software and classified. Length measurements were automatically recorded by the software. Green fibres have been excluded from the count to exclude potential contamination through biology (accepting that this also excluded green artificial fibres; however during our visual inspection under the microscope green was not a commonly observed colour; cf. section 2)

3 Results

Consistent with the findings of Allen et al. (2021[12]), we observed a high count of fibres, common for urban areas. The FlowCAM® analysis (high-throughput image capture of particles suspended in liquid) identified a total of 286 individual fibres from the small sub-samples of weathering crusts

(total area = 32 cm^2; Table 1). The overall wall sampling area investigated in this study comprises approximately 32cm^2 of black weathering crust, which is considered to hold MPs either temporarily or permanently thus, function either as temporary storage (secondary source for near-future MPs) or longer-term incorporation as part of the surface crust ('sink'; Figure 1). When extrapolating our results, we estimate that there could be approximately 7,000,000 individual fibres across just this 8 m^2 surface. This corresponds to a median density of 875,000 fibres per square meter (or 0.88/mm^2).

The median length of the fibres ranged from 79 -320 µm with an Interquartile Range of 78 - 352 (Table 1). Based on median and mean values, we estimated a total cumulative fibre lengths of approximately 52 and 130 m, respectively. It is important to acknowledge that the estimation provided here is an extrapolation derived from the number of fibres detected in a 5 ml sample of the liquid separate from the crust sample. Specifically, the analysis focuses on fibres larger than 30 µm, which excludes the nano-sized fraction below <30 µm. Thus, our estimate is considered conservative as it does not account for the presence of smaller fibres within the nano-range, which have been reported elsewhere in significant quantities and more severe detrimental effects[24,38].

The microfibres in samples taken from the wall areas A and B when observed under SEM showed a diverse range of morphologies, including both smooth and pitted surfaces, as well as fibres that were straight, twisted, or bent, sometimes with frayed ends (Figure 2). In some instances, these fibres formed clusters or conglomerates on the surfaces. Notably, most of the fibres observed were single threads rather than bundled structures. These fibres exhibited a variety of hues with clear and white being the most common, but also including blue, red, and black. These findings are consistent with the observations of de Frond et al. (2021[15]).

Fibre chemistry. Both Energy Dispersive X-ray spectroscopy (EDX) and Fourier Transform Infrared spectroscopy (FTIR) results show the presence of MPs in and on the samples' crust. While we found common polymer types reported elsewhere such as polyethylene terephthalate (PET), polyethylene (PE), polyurethane (PU), polypropylene (PP), polyvinyl acetate (PVC), acrylic, black rubber and Nylon[39,40,21], different spectral reference libraries (cf. section 2.5) returned matches with different hit quality index (HQI%) values for a range of polymer types.

For example, the sample spectrum of NCL-A1 (Figure 3) shows the following peaks 3305.7 cm^{-1}, 2936.8 cm^{-1}, 2514 cm^{-1}, 1624.2 cm^{-1} ,1372.2 cm^{-1}, 1037.7 cm^{-1}, and 873.52 cm^{-1}. Both the Primpke[41] and FLOPP[15] spectra reference database return Nylon as the highest match. Yet, FLOPP-e, which contains spectra references of environmentally degraded plastic, returns Polypropylene (PP). De Frond et al. (2021[15]) identify three shifts in peaks for degraded PP to 3300−3400 cm^{-1} (hydroxyl), 1550−1810 cm^{-1} (carbonyl groups), and 1000−1200 cm^{-1} (carbon−oxygen). Thus, NCL-A1 could either indeed be Nylon or a degraded PP fibre.

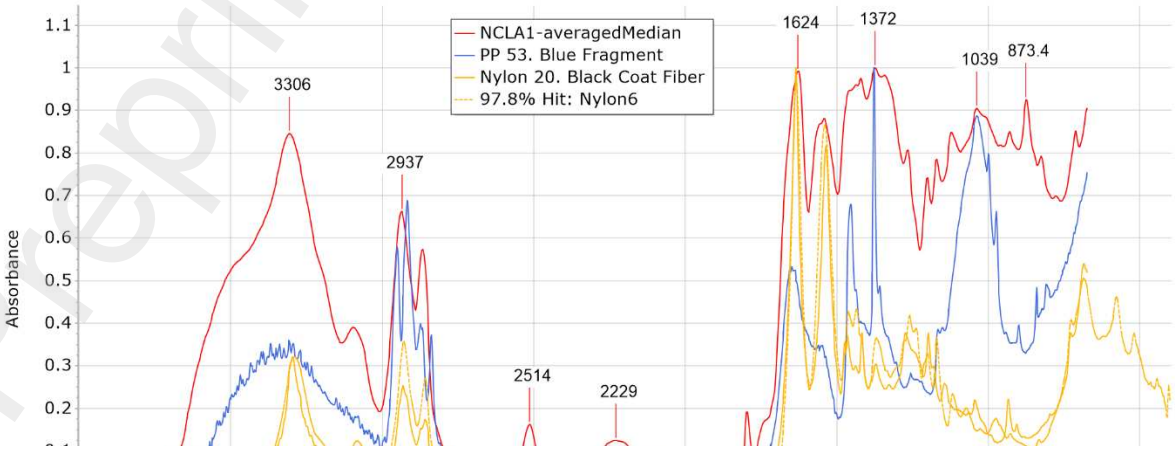


Figure 3 FTIR spectra with red showing NCLA1, blue the match from FLOPP-e indicating weathered Polypropylene (PP), and yellow-orange solid and dashed graphs from Primpke and FLOPP respectively matching Nylon and Nylon 6 respectively.

Another example is the spectrum of NCL-A4 and the PP match of FLOPP-e for which we visually observe an additional peak at 1646.6 m^{-1} which De Frond et al. 2021 attribute to aged PP, but the peak is not detected automatically by the Spectragryph peak position finder even at a low threshold of 1% of the visible spectrum ordinate and a narrow search interval of 20.

Despite the uncertainty when analysing weathered MPs, our results (Table 2) show for the majority of the fibres an agreement between the three used reference spectra libraries in terms of the distinction between polymer and natural fibres. Among the seven fibres that scored an HQI >70%, five were identified as MPs, while one (NCL-A7) matched with a natural material, potentially cotton or hemp. Another fibre (NCL-A8) yielded contradictory results, resulting in an overall conservative MP to non-MP ratio of 5:1.

Table 2 List of seven fibres and the respective highest hit quality index (HQI%) matches derived from three different spectra libraries, Primpke[42], FLOPP and FLOPP-e[15].

#	Sample ID	Primpke Polymer HQI%		FLOPP Polymer HQI%		FLOPP-e Polymer HQI%		Polymer?
1	NCL-A1	Nylon6	74.47	Nylon	76.75	PP	88.55	Y
2	NCL-A2	PVC	80.12	PU	85.41	PU	85.16	Y
3	NCL-A3	PVC	84.8	PVC	83.76	PU	87.56	Y
4	NCL-A4	PVC	73.01	PVC	83.76	PP	87.52	Y
5	NCL-A5	PVC	75.11	Rubber	80	PP	76.32	Y
6	NCL-A7	Flax	79.14	cotton	77.1	cotton	77.32	N
7	NCL-A8	Fur	80.98	Nylon	77.61	PP	82.11	unclear

4 Discussion

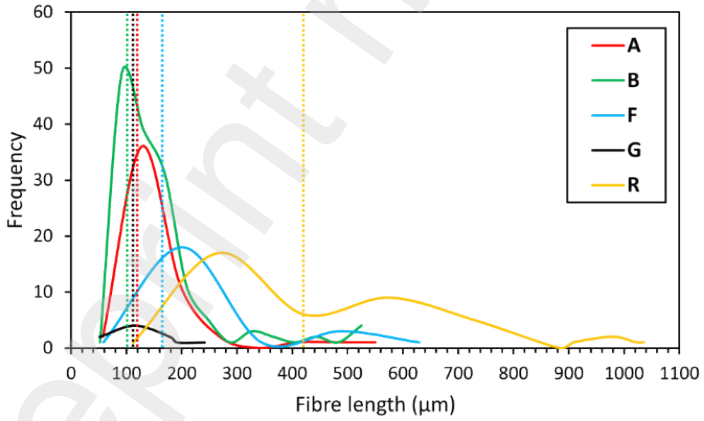
Contextualising our findings with other studies presents a challenge due to the lack of comparability in methods, such as the exclusion of certain size fractions from the MP count, variations in units (MPs kg^{-1} and m^{-3}; [2,27]), and limited comparability of MPs interaction (e.g., the residence time in oceans surfaces and the air are considerably different from sediments and likely different to those on urban surfaces). However, despite the small sample size, our findings suggest that, even though our study site is located on a low-traffic road in Oxford, we may be encountering a high frequency of fibres, estimated to be 875,000 fibres/m^2 (0.88 fibres/mm^2).

In our study, we propose that the majority of fibres identified likely originate from airborne deposition, which accumulates over time on the surfaces of the built environment. By linking these surface fibre counts to findings from atmospheric microplastic (MP) studies, we suggest that our method could serve as a passive sampler for future air pollution studies, underscoring the potential role of built environments in monitoring atmospheric microplastic pollution. However, it is important to note that the potential sources of MPs are not limited to industrial processes. Various non-industrial human activities can also contribute significantly to MP pollution. Everyday human behaviours, such as laundering synthetic clothing, use of personal care products containing microbeads, and general wear and tear of plastic materials, can release MPs into the environment[38,43]. These activities are likely more prevalent in areas with higher population densities,

providing a rationale for our use of population density as a proxy for human activity. For instance, a study conducted by Dris et al. (2016[44]) at a Paris test site (7,900 inhabitants k^m-2) found up to 355 particles/m^2/day (observation size lower limit 50µm), which, if undisturbed, would result in an annual accumulation of 129,575 particles. They extrapolated that between 3 – 10 tons of fibres derive from atmospheric fall-out. Allen et al. (2019[45]) observed a similar daily amount of MP particles in a remote mountain range in the French Pyrenees. Interestingly, both studies found that the majority of identified MP fragments are smaller than 50 µm.

While we cannot directly compare our findings to these daily estimates, the quantity of fibres we identified on built surfaces can offer valuable context for understanding airborne fibre levels. Given Oxford's population density of approximately 3,509 inhabitants^km-2 (ONS 2021 Census, Oxford City Council), one might expect fewer fibres per day in the city compared to Paris. If we hypothesize that all fibres on our test wall become airborne daily, we might anticipate roughly half the amount of fibres (64,787 fibres/m^2) found in Paris. However, our study reveals a stark difference; our findings exceed this estimation by a factor of 13.5, suggesting a greater than expected accumulation of fibres on our tested surfaces. This discrepancy underscores the importance of considering both airborne and surface-accumulated microplastics in future environmental pollution studies.

Wall vertical gradient of fibre frequency and length. We observed a notable gradient in the distribution and frequency of fibre lengths along the vertical wall at the scale of individual masonry blocks as seen in Figure 4. The true number of fibres across this surface could be greater than that obtained by our sampling approach, although spatial variability is highly likely based on our measurements from different areas of the wall (cf. Table 1 and Figure 4). This is in contrast to other pollutant studies (e.g., for trace metals on built structures) that have found height variations between 0 – 5 m to be insignificant in terms of accumulation distribution[46,47,48,49]. Building detailing, which mediates the interaction between the surface and environmental weathering agents (i.e., particulate matter deposition, wind-driven rain and runoff;[50,51,52,53]) also seemed to affect the observed distribution of MPs.



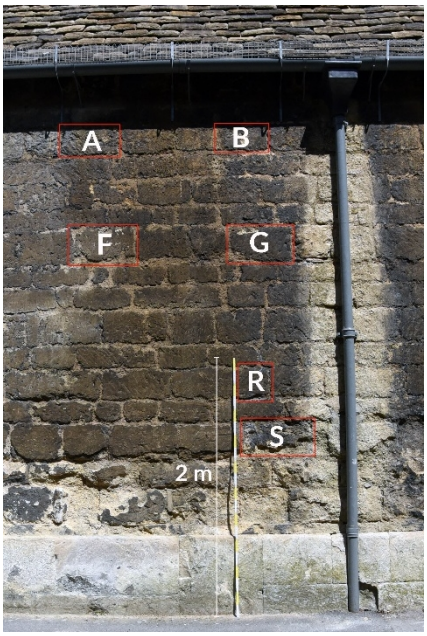


Figure 4 FlowCAM® analysis graph shows the frequency of various fibre lengths in relation to their sampling area on the wall (right). Dashed vertical lines show mean fibre length (µm). Areas A and B (4 m height) are sheltered from rain and run-off through the open eave; areas F and G (3 m height) are neither sheltered nor in direct line of increased water run-off; area R is potentially affected by wash down due to its lower position (2 m) and S

(1.60 m) is in direct water run-off vicinity to the gutter area (compare to Table 1 and Figure 1).

Shorter fibres were more prevalent in higher areas of the wall (4 m) compared to lower areas (1.6 – 3 m). Figure 4 shows that sampling areas A and B are sheltered from rain and water run-off through the open eave and, thus, exhibit the highest frequency of fibres, whereas no fibres were detected at sampling location S, which is directly affected by increased water run-off as indicated by the whitewashed areas around the dysfunctional gutter. On the other hand, sampling location R displays a wider range of fibre lengths but with a frequency less than half that of areas A and B. Sample areas F and G are neither sheltered nor in direct line of increased water run-off.

Based on these three exposure scenarios, the fibre length frequencies can be classified into three main categories. In the sheltered sampling areas of A and B at 4 m height, we found the highest fibre frequency of up to 0.14-0.22 fibres/mm^2 with an abundance of 55.34% for the 60-120 µm fibre length fraction and 35.44% for the 180-240 µm fibre length fraction (Figure 5). Sampling areas F and G at 3 m height, neither sheltered nor in direct line of increased water run-off, presented a lower fibre frequency with 0.02 – 0.04 fibres/mm^2 but a similar fibre lengths distribution compared to A and B with 61.11% for the 60-120 µm fibre length fraction and 22.22% for the 180-240 µm fibre length fraction. In contrast, sampling area R at 2 m height, and with the highest exposure to washed down fibres, shows a similar frequency of fibres compared to A and B with 0.17 fibres/mm^2 but with a shift towards a higher abundance of longer fibres with 31.82% for the 60-120 µm fibre length fraction and 65.91% for 180-240 µm fibre length fraction. Area S at 1.60 m and in direct vicinity of the dysfunctional gutter did not exhibit any fibres.

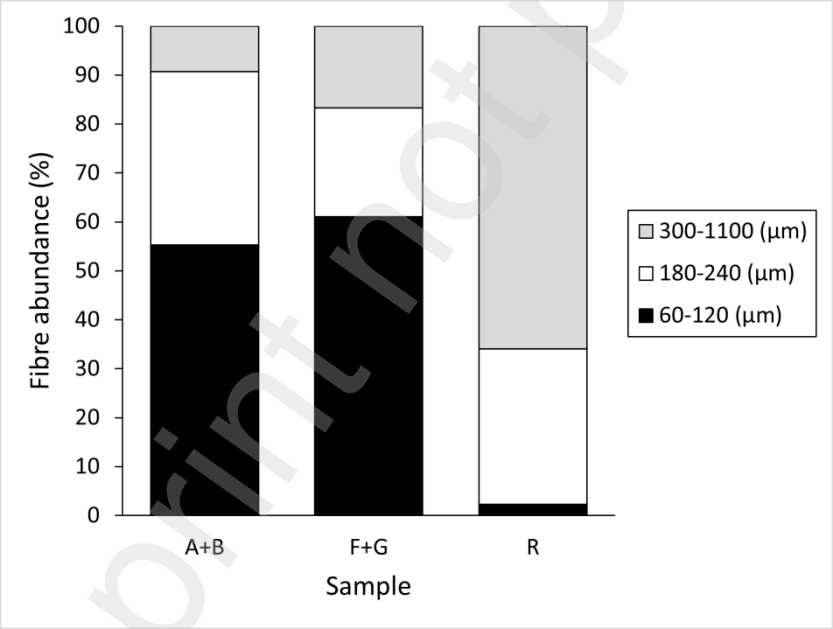


Figure 5 Fibre lengths in this study organised in three main bins to compare the percentage abundance of fibre lengths related to height with sampling areas A and B being at 4 m height, F and G at 3 m, and R at 2 m.

Urban wall surface interaction with MPs – Sink or thread? The significant quantity of fibres detected in this study, coupled with evidence of chemical degradation, strongly suggests that these

fibres persist on the urban wall for an extended period of time. The study also highlights the crucial role of building detailing in mediating the interaction between surfaces and environmental weathering agents, which appears to influence the distribution of MPs. While previous research on stone-built heritage has provided insights into the role of microclimate and surface morphology in the formation of black crusts that accumulate pollutants in sheltered areas[35], the investigation of MPs in relation to these factors remains limited and requires further exploration. Thus, while little is known about the mechanisms that cause MPs to adhere to surfaces and their mobility (e.g., residence time on the surface), our observations and previous work has demonstrated that urban surfaces subject to wind, water and other mobilising weathering agents (such as our sample area NCL-S, Figure 4), may act only as temporary stores between the precipitation and remobilisation of MPs to their eventual sequestration in down-system stores like river sediments and the ocean, although questions remain about the duration of this storage[54,55]. However, for less disturbed areas (such as our sample areas NCL-A and -B, and to a lower extend F, G and R, Figure 4), the gradual formation of weathering crusts (i.e., gypsum) has the potential to incorporate and trap MPs. The process of incorporating airborne particulate matter is a well-studied phenomenon[56,31,34].

The incorporation of MPs over time might result in their long-term sequestration. Consequently, historic urban surfaces with crust-forming properties not only become partial long-term sinks for MPs but also serve as environmental monitors. These surfaces allow us to understand the past and present pathways of MPs and predict their future routes and fate, thereby acting as valuable archives for urban MP flows.

Implications for Urban Environments. Studies in the past have shown variable relationships between urban factors, such as population density, and microplastic pollution[57,58,59.] Nonetheless, it is widely accepted that densely populated urban areas with high levels of human activity tend to significantly contribute to the production of microplastics[60,61,62.] Our study, though conducted in Oxford, a small UK city, reveals concerning microplastic pollution levels that are likely magnified in larger, densely populated urban areas, particularly in rapidly industrialising countries. As urban populations continue to rise and city boundaries expand, we anticipate the issues highlighted in our research to become increasingly significant. Urbanisation is likely to lead to an increase in urban microplastic pathways and accumulation, resulting in elevated human exposure[63]. This is particularly concerning for countries with high levels of plastic pollution such as the USA, India, and China, whose plastic pollution levels exceed those of the UK[64].

To gain a comprehensive understanding of urban microplastics, we must establish a firm link between research on urban microplastics and the ecology of urban walls. For example, surfaces within the historic built environment are often home to microorganisms that interact with, oxidise, and metabolise air pollution. These interactions, when explored further, could shed light on the full impact of microplastics on our urban environments[65,66,67].

Our research provides an essential complement to high-resolution atmospheric chemistry transport dispersion models, frequently used for predicting urban air quality[68]. These models reflect changes in urban emissions, and have been crucial in understanding the conditions in various cities. However, the models have largely been driven by health authorities' need for insights into air-borne pollutants, while potentially overlooking crucial aspects of environmental pollution such as microplastics.

The strength of our study lies in its ability to provide high-resolution, real-world data on microplastic pollution within the urban environment, specifically on vertical surfaces. This data can be used to complement existing models, offering a more comprehensive perspective. By integrating our

findings with these models, we can broaden our understanding of urban pollution, accounting not only for traditional air pollutants, but also for microplastics. This integrated approach can lead to more holistic strategies for mitigating urban pollution and improving public health.

Health and climate change implications. Our study reveals a significant presence of microplastics (MPs), especially fibers, on urban surfaces, which raises substantial concerns for human and environmental health[69]. Detrimental health effects are associated with MPs within the range of our findings (30-1000 µm), including potential ingestion or inhalation leading to biopsies in lung tissue[70] and traversal of the digestive tract wall[71]. Both examples coincide with the modal peaks of fibre length found in our study(Figure 4). Notably, we did not capture the smallest particle size fraction (<10 µm), which is thought to have potentially the most harmful impacts on health when inhaled or ingested and has, for example, been found in human placenta[25,72].

This issue is further magnified in the context of climate change and its association with plastic pollution, where the expected doubling of plastic deposition over the next three decades warrants urgent attention. These climate pressures could exacerbate existing pollution, possibly intensifying urban heat islands and trapping pollutants[2,73,74]. Microbial activities, potentially linked to Nitrous oxide (N_2O) emissions, are also anticipated to rise, though their exact interaction with MPs remains unclear [75,76,77,78]. Thus, our findings underscore the need to explore the role of microorganisms in promoting MP incorporation, accelerating their chemical breakdown, or aiding in their sequestration.

Urgent need for standard protocols and future research. The findings of this study are concerning and emphasise the urgent need for improved and standardised analytical methods to ensure greater accuracy in the results for urban MP research echoing the concerns raised by numerous studies in established fields of MP research[2,14,20,21,79.] Developing methodologies for assessing rapidly large vertical urban surfaces is critical, enabling accurate quantification, extrapolation, and modelling of MP contamination. Future studies should consider the degradation processes of microfibers in the context of the historic built environment, potential health risks of secondary compounds, challenges posed by plastic degradation, and the role of MPs as vectors for microorganisms and other pollutants including further exploration into factors such as surface charge and zeta potential [12,80,79,81,82,83.]

In-depth field studies across diverse urban settings are essential to understand variations in microplastics (MP) types, distribution, and accumulation. Our findings prompt further research to elucidate the full extent of MPs in different historic urban environments. Crucially, we must identify and monitor the unexplored pathways and sinks of MPs. A holistic understanding will be achieved by integrating the complex dynamics at various scales—from MPs and microorganisms to built environment features, regional urban conditions, and macro-climatic factors. Furthermore, incorporating findings from local and regional climate studies, as well as soil, sediment, and freshwater contamination research, will augment our evidence base.

Reliable microplastic (MP) quantification on urban surfaces is crucial for developing mitigation strategies and accurate risk assessments. This research is essential for creating effective policies to mitigate environmental and health impacts. Delays in standardising methods and interventions may cause long-term harm. Prioritizing an understanding of MP sources could shift attitudes towards plastic consumption, providing a more holistic understanding of MP's budget, pathways, and fate in urban settings.

5 Conclusion

Our study provides ground-breaking evidence of the significant potential for large-scale accumulation of microplastics (MPs) on urban surfaces, specifically the weathering crusts of historic buildings. We emphasise the urgent need for standardised methodologies to comprehensively understand and investigate the sources, mobility, pathways, and impacts of MPs on human health and the environment. The anticipated doubling of plastic deposition in landfills and the environment over the next two decades further emphasises the long-lasting legacy of the MP issue[84].

This is further compounded by the prolonged response through an inherent accumulation capacity of the built environment system. Similar to the persistent legacy of leaded petrol pollution, still evident in urban historic surfaces' weathering crusts long after the Pb phase-out in the 1980s and final ban in 2000, serves as a reminder of the long-term impacts of past practices[34,85,33].

The significant presence of microplastics (MPs) in large quantities, with a frequency of 0.88/mm^2 for fibre lengths between 30-1000µm, as observed in this study, raises the question of the extent of MPs in larger cities with developed industrial areas. As Persson et al. (2021[3]) highlight, the production, diversity, and global release of novel entities (NEs), including plastics, are increasing at a rate that exceeds society's capacity to assess and effectively manage them. This raises concerns about transgressing the safe operating space of the planetary boundary for NEs. Consequently, addressing the issue of MPs on urban surfaces should be given high priority to inform policies aimed at promoting healthy urban environments and fostering a shift in people's attitudes towards plastic consumption. Our study provides a tangible local example that reflects a large-scale global problem, offering a concise perspective on a complex issue and suggesting practical pathways for addressing the problem with potential regional, national, and global implications.

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8 Author contributions

K.W. and S.W. initiated, designed, and lead the research. M.J. and D.A. performed FlowCam analysis and evaluation. N.Y. and P.K. conducted the SEM analysis and evaluation. M.W., J.G. and S.A.O. preformed the FTIR analysis. T.d.K. Validation, Methodology. All authors wrote, reviewed and edited the manuscript. J.L. Methodology, Funding Aquisition, Writing - Reviewing & Editing. All authors have read and agreed to the published version of the manuscript.

9 Competing interests statement

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