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

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Abstract

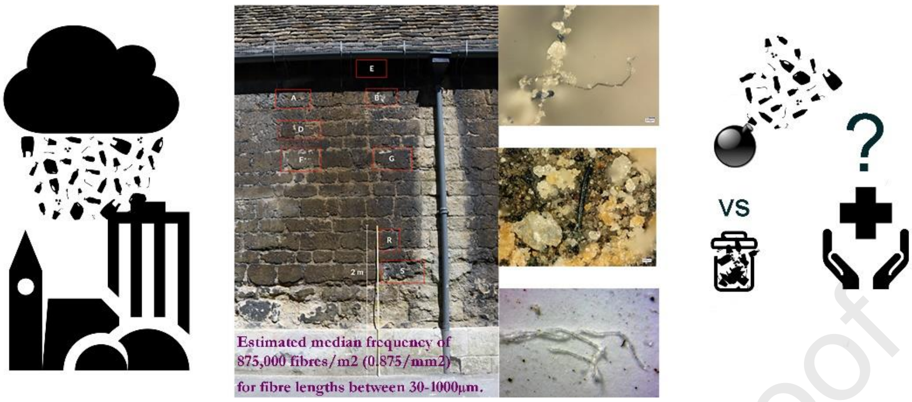
Despite the increasing concerns surrounding the health and environmental risks of microplastics (MPs), the research focus has primarily been on their prevalence in air and the oceans, consequently neglecting their presence on urban facades, which are integral to our everyday environments**.** Therefore, there is a crucial knowledge gap in comprehending urban MP pollution. Our pioneering interdisciplinary study not only quantifies but also identifies MPs on historic facades, revealing their pervasive presence in a medium-sized urban area in the UK. In this case study, we estimated a mean density of 975,000 fibres/m^2 (0.10 fibres/mm^2) for fibre lengths between 30-1000µm with a ratio of 1:5 for natural to artificial fibres.

Our research identifies three groups of fibre length frequencies across varied exposure scenarios on the investigated urban facade. Sheltered areas (4m height) show a high prevalence of 60-120 µm and 180-240 µm fibres. In contrast, less sheltered areas at 3m exhibit lower fibre frequencies but similar lengths. Notably, the lowest area (2-1.5m) features longer fibres (300-1000 µm), while adjacent area S, near a faulty gutter, shows no fibres, highlighting the impact of exposure, altitude, and environmental variables on fibre distribution on urban facades.

Our findings pave one of many necessary paths forward to determine the long-term fate of these fibres and provoke a pertinent question: do historic facades serve as an urban 'sink' that mitigates potentially adverse health impacts or amplifies the effects of mobile microplastics? Addressing MP pollution in urban areas is crucial for public health and sustainable cities. More research is required

to understand the multi-scale factors behind MP pollution in large cities and to find mitigation strategies, paving the way for effective interventions and policies against this growing threat.

Graphical abstract



1 Introduction

Microplastics (MPs), defined as particles ranging from 1 to 5000 µm, are becoming an environmental focal point due to their ubiquitous presence and potential threats to human health and ecosystems (Bergmann et al., 2015; Persson et al., 2022). This issue is exacerbated by a marked increase in global plastic production over the past 70 years, culminating in an estimated 10 billion metric tons (Brahney et al., 2021). In addition, inefficient waste management further contributes to environmental accumulation rates that sometimes exceed its production (Geyer et al., 2017). Importantly, MP concentrations and exposure are heightened in industrialised urban regions, accentuating risks within densely populated areas (Mokhtarzadeh et al., 2022; Qiu et al., 2020).

While existing MP research mainly covers air, oceans, and more recently freshwater and soils, vertical surfaces in urban settings remain largely overlooked (Akdogan and Guven, 2019; Allen et al., 2021; Athey and Erdle, 2022; Chen et al., 2020; Goodman et al., 2021; Li et al., 2018). These surfaces constituting both terrestrial and atmospheric interfaces, serve as critical, yet neglected accumulation points for MP pollution from diverse sources.

Furthermore, current MP research lacks standardised methodologies for the identification and quantification, particularly considering the unique degrading processes present in urban environments (Bergmann et al., 2022; Li et al., 2018; Xu et al., 2019). Once in the environment, plastics degrade, fragment, and become colonised by microorganisms. They may further chemically breakdown into novel compounds with yet-to-be-understood impacts, some decomposing more readily than others (Campanale et al., 2020). These modification complicate analytical processes due to a general lack of harmonised reference data for these altered states, although some attempts to provide such data exist (De Frond et al., 2021; Hirai et al., 2011; Suhrhoff and Scholz-Bottcher, 2016). In addition, MPs can also absorb harmful pollutants like heavy trace metals and pathogens, posing multiple threats to human health through exposure routes like inhalation, ingestion, or skin contact (Campanale et al., 2020; Jenner et al., 2022; Ragusa et al., 2021).

Moreover, MPs are not only a human health concern; they also affect wildlife, including both terrestrial and aquatic species (Akdogan and Guven, 2019; Zhu et al., 2019). Unexpected pathways, such as avian activity and mobile wildlife, further complicate the distribution and impact of MPs in various ecosystems (Masia et al., 2019; Ragusa et al., 2021; Wang et al., 2017; Zhao et al., 2016). Understanding these various sources and exposure routes is crucial for informing targeted interventions to mitigate MP pollution.

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**.**

Despite the growing concerns and increasing research on MPs in urban settings, a significant gap remains in understanding their interaction with built environments, particularly vertical surfaces, and facades. These surfaces could either contribute to further MP transport or function as potential 'sinks', yet they remain understudied. Capitalising on previous research that established vertical surfaces as quasi-passive samplers for urban pollutants (Farkas et al., 2018; García-Florentino et al., 2020b; Ozga et al., 2014), our hypothesis posits that historic surfaces, owing to their unique long-term weathering history and ability to superficially incorporate air pollutants such as trace metals, may also demonstrate effective MP accumulation capabilities.

For this study, we focussed on urban historic structures made of traditional materials like limestone. These buildings, often located in city centres, are invaluable not just culturally but also as environmental indicators. Urban vertical surfaces of historic buildings are ubiquitous in urban areas and the daily environments of many societies. Almost all of the listed buildings in England have a traditional masonry structure (97%; Historic England (2023)), with similar representation in Scotland, Wales, and Northern Ireland. This construction type also makes up about 25% of the UK's housing stock (CLG, 2012). The UK also has more than 8,000 conservation areas, which typically have specific management measures in place to protect the character and external appearance of the buildings within the area. More broadly, entire historic centres and cities feature prominently (at least 50 in Europe alone) on the UNESCO list of World Heritage Sites.

Their accumulated weathering stress history renders them especially sensitive to environmental changes. Prior research, exemplified by studies such as Bonazza et al. (2005) and Farkas et al. (2018), has significantly contributed to our understanding of the impact of various pollutants on historic buildings. These works primarily focus on traditional pollutants, including trace metals and polycyclic aromatic hydrocarbons (PAHs), establishing a foundational context for our current research into microplastics. Notably, there is an observable shift in the research landscape, moving from solely examining the effects of pollution on the structural integrity of buildings to a broader investigation into the environmental and public health implications of pollutants accumulated on these buildings. Recent studies exploring the consequences of lead and PAHs underscore this evolving trend (e.g., Navas-Acien et al. 2007; Jahandari et al. 2020; Wilhelm et al. 2023). In line with this shift, we propose that MPs, which may have been previously overlooked in the context of building pollutants, warrant similar investigative attention.

Our study is the first of its kind to investigate MPs on historic urban facades. We aim to establish a reliable methodology for MP collection and analysis for such surfaces, with the ultimate goal of informing future policies aimed at healthier urban environments and more sustainable plastic usage (Coffin, 2023; Cohen and Muñoz, 2016). By exploring the unique ab-/ad-sorption properties of historic buildings, we aim to expand the scope of MP research while addressing unknown risks to human and environmental health. Our findings are particularly relevant given the unpredictable risks of MPs to human health, ecosystems, and the overall environment.

2 Material and Methods

2.1 Identifying strategy

In light of the recognised gap in standardised methodologies for MP research on urban facades, we devised a sampling strategy mindful of the unique challenges presented by historical urban environments (Bergmann et al., 2022; Coffin, 2023; Xu et al., 2019). Our strategy considered factors such as long-term exposure to environmental and anthropogenic influences, and accessibility.

Specifically, we targeted a 8 m^2 area of the south-facing wall of New College Cloister in Oxford, UK (built between c. 1396 and 1400). Manual sample collection was performed in a grid-like pattern across this area to ensure a representative sampling (Figure 1; Table 1). Sample collection was conducted during a period in May with low precipitation to mitigate for run-off effects.

Density separation, visual 3D microscopy, SEM, FlowCAM® analysis, and FTIR were selected as our analytical methods to cater to the diverse and potentially degraded nature of MPs expected on aged, weathered surfaces. 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 (Renner et al., 2019; Robertson et al., 2018; Woodall et al., 2015).

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 facades. 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, academic institutions, residential areas, and commercial establishments (Wilhelm et al., 2023); Figure 1). 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) The inset on the right displays the sampling areas at a block scale. Within each block, several sub-areas were sampled, collectively covering a total area of 100 x 100 mm per block.

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 (Wilhelm et al., 2021). 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). Six areas at block scale were sampled at four different heights (1.60, 2, 3, and 4 m above street level). Within each block, several sub-areas were sampled, collectively covering a total area of 100 x 100 mm per block. 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) and the Malta Convention (1992). 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).

2.3 3D microscopy

Untreated crust samples from New College Lane were first visually inspected using a Keyence VHX 3D microscope at 100-500x magnification to identify the presence of microplastic fibres. The fibres were qualitatively identified by examining their morphology, colour and observing the ends of the fibres where fraying might indicate human-made products (Robertson et al., 2018). Both the qualitative SEM and FTIR analysis involved hand-picking the fibres with tweezers, a common procedure, which however imposes a size limitation (> 500 µm) that can be handled by a human (Aves et al., 2022; Li et al., 2018; Wang et al., 2017)

2.4 SEM

The samples were prepared on the 12.5mm Aluminium pin stub and mounted. A Zeiss EVO tungsten filament SEM equipped with an Oxford Instruments EDX detector was used to image and map the elemental compositions of the fibres. The samples were mounted on a carbon sticky pad and coated with a 4nm layer of Pt to improve conductivity in the SEM and a beam voltage of 10KV was used for the examination (Figure 4).

2.5 FTIR

Samples were not chemically pre-treated ('purified') to not affect low-density and sensitive materials such as Nylon (Razeghi et al., 2021) and maintain any environmental degradation process intact for analysis such as biological interaction with MPs, an area which remains understudied.

Individual microfibres were first picked using a Keyence VHX 3D microscope and transferred to a 12-spot reflection slide for analysis using the FTIR microscope. The slides were loosely covered with aluminium foil while being transferred between the 3D microscope and the FTIR microscope in order to avoid particle contamination (Nuelle et al., 2014; Renner et al., 2019; Woodall et al., 2015).

This study employed Fourier transform infrared (FTIR) spectroscopy as the most common approach to analyse MPs (De Frond et al., 2021; Renner et al., 2018; Zarfl, 2019). A Thermo Scientific Nicolet iN10 MX FTIR microscope was used to collect infrared spectra for microfibres manually picked from the New College Lane crust samples. The integrated microscope was used to locate the individual MPs, and to select targets for collecting IR spectra. The IR reflection spectra were collected with the detector in liquid nitrogen-cooled mode, and a spectral range of 4000 to 675 cm^{-1}. Three repeat measurements were taken at each target location of eleven fibres in total. The three measurements were averaged using the median and a simple linear baseline correction was applied.

Following the recommendation of Aves et al. (2022), this study visually investigated all sample and relevant reference spectra. To identify the chemical components of each sample, we analysed the spectra using the software Spectragryph, which compares the results to reference spectra based on a full-spectrum Pearson correlation coefficient and provides an estimation of similarity, denoted as the hit quality index (HQI)(Xu et al., 2019). For our study, we utilised the Primpke (Primpke et al., 2018) FTIR spectra library, which was enhanced with 57 FTIR spectra of plastics from Birch et al. (Birch et al., 2021), as recommended by Menges (2019), the provider of the Spectragryph software. Additionally, we incorporated two novel databases—FLOPP and FLOPP-e—introduced by De Frond et al. (De Frond et al., 2021), which contain spectra from common plastic items, including those that are environmentally weathered. Following Aves et al. (2022) and Renner et al. (2019) matches of >70% HQI against the library reference spectra were included in the results as MPs. From each database HQI the highest scoring was accepted. To compare our spectra to the database spectra, a simple automatic baseline as vertical set off was applied.

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 (Quinn et al., 2017). Density separation is widely applied in studies of environmental MPs, usually for their separation from sediments such as silt and sand (Hidalgo-Ruz et al., 2012). There is a lack of consensus on what solution is best used for the density separation of microplastics, with saturated NaCl solution (~6M at 20 °C) being the most common as it is readily available and easily disposed of (Quinn et al., 2017; Thompson et al., 2004). However, Quinn et al. (2017) note that many common plastics have a density greater than that of saturated NaCl solution (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 (Corcoran et al., 2009; Stock et al., 2019).

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 prior 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 fibres and fragments using machine learning assisted data collection following established approaches of previous studies (e.g., Hyeon et al., 2023; Kaile et al., 2020; Woods et al., 2018). 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 (Sieracki et al., 1998). 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 (detection limit 30 µm). 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 (Figure 2a). Image libraries of plastic fibres 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. Any potential organic contaminants were excluded from the count through the visual inspection of the FlowCam images based on morphological characteristics such as not being uniform in thickness along their length, and particles lacking homogeneous clear or artificial coloration typical of microplastic fibres to exclude potential contamination through biology (cf. Hildago-Ruz et al. 2012; Bergmann et al. 2017; This meant that some green artificial fibres have been excluded; however, during our visual inspection of separated fibres under the microscope green was not a commonly observed colour; cf. section 3; for an example of excluded organic matter; Figure 2b)

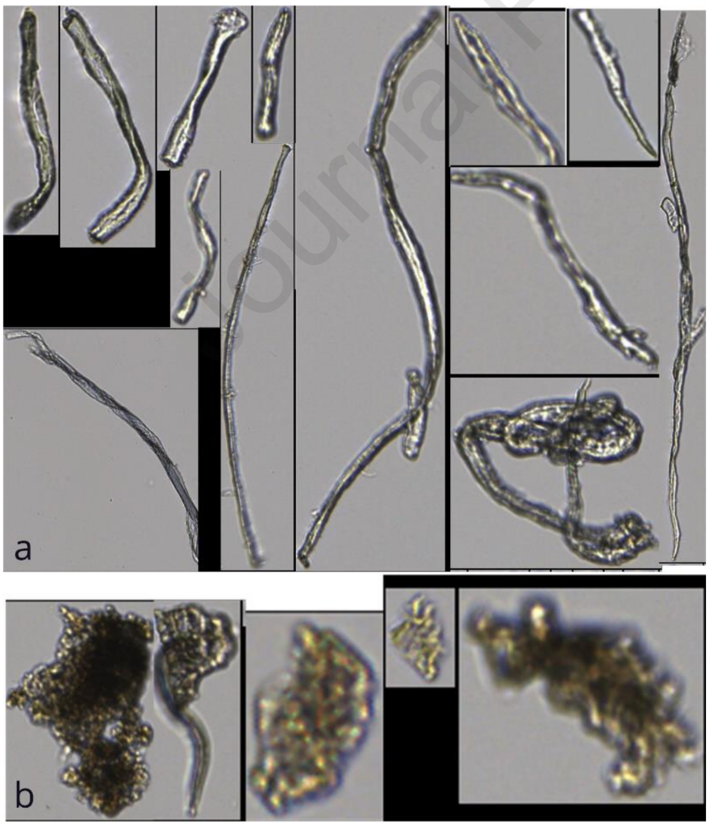


Figure 2: FlowCam image examples of microplastic (a) and for organic matter (b), the later has been excluded from the microfibre count in our study.

3 Results

Consistent with the findings of Allen et al. (2021), we observed a high count of fibres, common for urban areas. In the sheltered sampling areas of A and B at 4 m height, we found the highest fibre density 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 Sampling areas F and G at 3 m height, neither sheltered nor in direct line of increased water run-off, presented a lower fibre density 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 run-off and washed down fibres, shows a similar density 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.

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. [a]Values in the 'Total' column are an average of the values in the row.

Sample	**A** (4m)	**B** (4m)	**F** (3m)	**G** (3m)	**R** (2m)	**S** (1.6)	**Total**
Sample area (mm^2)	396	690	690	453	264	700	**3193**
Height (m)	4	4	3	3	2	1.6	-
Abundance	55	151	25	11	44	0	**286**
Mean density/mm^2	0.14	0.22	0.04	0.02	0.17	0	**0.10[a]**
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 length	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**
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		

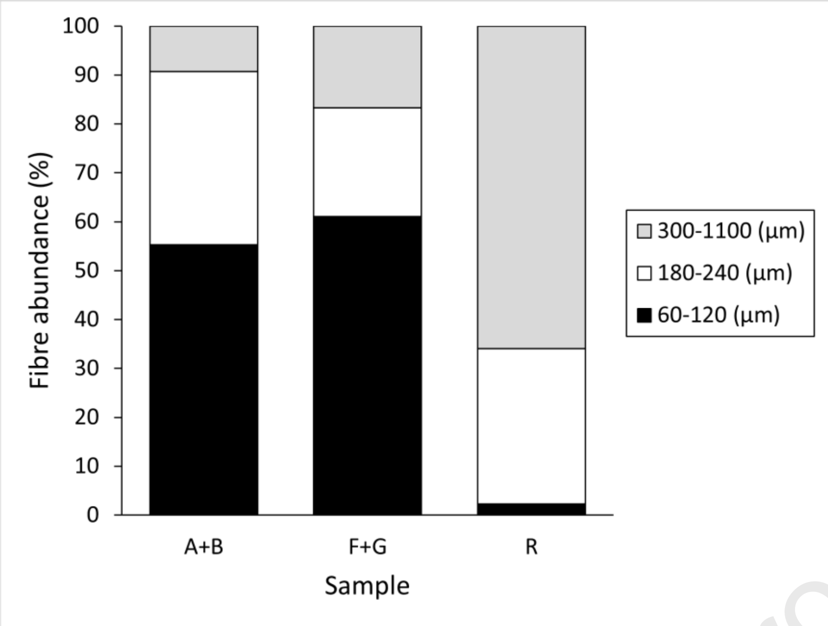


Figure 3 Distribution of fiber lengths categorised into three main bins, illustrating the relative abundance (%) of different fiber length ranges at varying heights, with sampling areas A and B at 4 m, areas F and G at 3 m, and area R at 2 m.

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 mean density of 975,000 fibres per square meter (or 0.10 fibres /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 length 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 with more severe detrimental effects (Campanale et al., 2020; Ma et al., 2021).

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, Figure 4). 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).

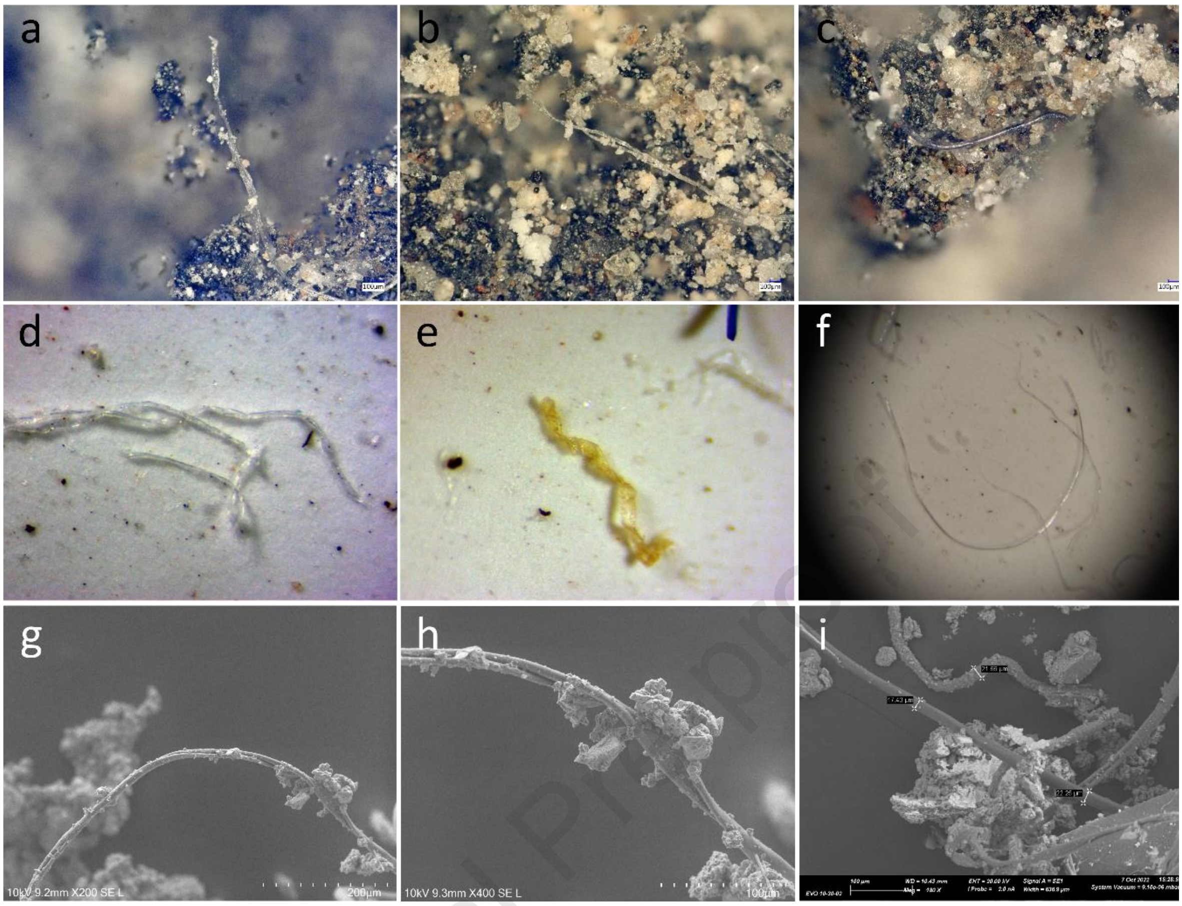


Figure 4 Examples of microplastic fibres imaged with a variety of microscope techniques. (a-c) In-situ fibres observed on samples of weathering crusts taken from New College Lane. (d-f) Fibres observed using a Leica stereomicroscope with 80x zoom following liberation from sample NCL A through density separation with SPT and filtration through cellulose nitrate filter papers. (g-i) Fibres extracted from NCL A observed using an SEM displaying coiled morphology and very regular thickness along their lengths.

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 (Biltcliff-Ward et al., 2022; Renner et al., 2017; Wright et al., 2020), 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 5) 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 (Primpke et al., 2020) and FLOPP (De Frond et al., 2021) spectra reference database return Nylon as the highest match. Yet, FLOPP-e, which contains spectra references of environmentally degraded plastic, returns Polypropylene (PP). Cowger et al. (2020) 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.

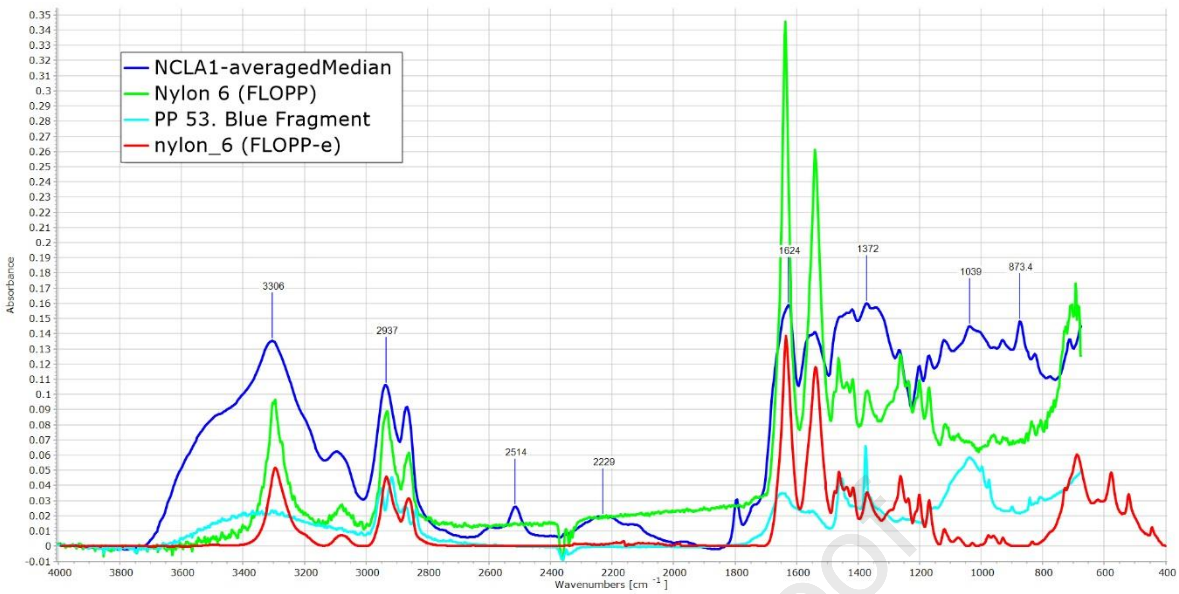


Figure 5 FTIR spectra with red showing NCLA1, blue the match from FLOPP-e indicating weathered Polypropylene, and yellow-orange solid and dashed graphs from Primpke and FLOPP respectively matching Nylon and Nylon 6 respectively.

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 (A7) matched with a natural material, potentially cotton or hemp. Another fibre (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(Primpke et al., 2018), FLOPP and FLOPP-e(De Frond et al., 2021). PP=Polypropylene, PU=Polyurethan, PVC=Polyvinylchloride.

#	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

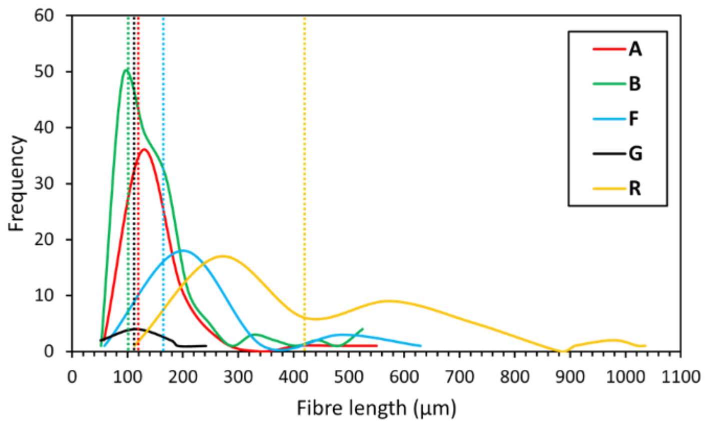
Contextualising our findings with other studies presents a challenge due to the lack of comparability in methods, such as the exclusion of certain size fractions from the MP count, variations in units

(MPs kg^{-1} and m^{-3}; (Bergmann et al., 2022; Wang et al., 2017)), 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 facades). 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 density of fibres, estimated to be 975,000 fibres/m^2 (0.10 fibres/mm^2).

In our study, we propose that fibres found on urban facades primarily originate from airborne deposition, settling over time. Drawing parallels with atmospheric microplastic (MP) studies allows us to conceptualise these accumulated fibres as indicators of historical atmospheric MP deposition, positioning our method as a viable passive sampler for scrutinising airborne MP over extended periods in urban environments. While industrial processes are known contributors, MP pollution can also originate from everyday human activities, such as wearing and laundering synthetic clothing, using personal care products with microbeads, and the attrition of materials like car tires (Ma et al., 2021; Wardrop et al., 2016). In areas with denser populations, where these activities are presumably more frequent, we employ population density as a proxy for human activity, aligning with the methodological approaches of Dris et al. (2016) and Allen et al. (2019). Notably, these studies found that up to 355 particles/m^2/day (lower limit 50µm) and a comparable daily number of MPs respectively accumulate in urban (Paris) and remote environments, highlighting the ubiquity of MPs and validating our approach to exploring urban facades as repositories and potential monitors of atmospheric MP.

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 hypothesise that all fibres on our test wall become airborne daily, we might anticipate roughly half the number 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 15, 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 (Figure 6). Although the actual number of fibres across this surface may differ from what our sampling approach obtained, our measurements from different areas of the wall suggest that spatial variability is highly likely (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 (Biltcliff-Ward et al., 2022; Cowger et al., 2020; McCabe et al., 2015; Monna et al., 2008; Turkington et al., 2003a). Building detailing, which mediates the interaction between the surface and environmental weathering agents (i.e., particulate matter deposition, wind-driven rain and runoff;(Blocken et al., 2013; Mulvin and Lewis, 1994; Wilhelm et al., 2020; Wood, 1993) also seemed to affect the observed distribution of MPs.



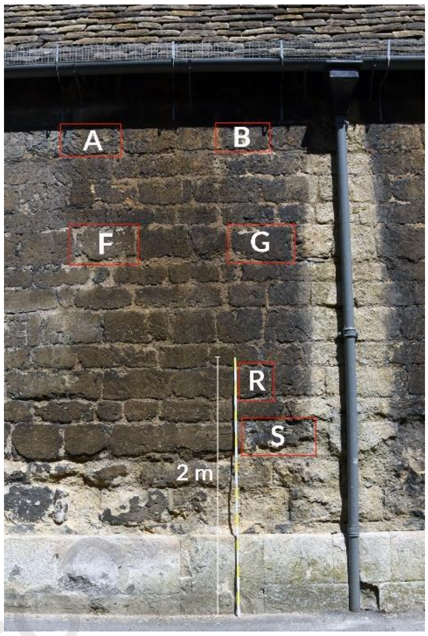


Figure 6 FlowCAM® analysis graph shows the frequency of various fibre lengths in relation to their sampling area on the wall (right). Dashed vertical lines show mean fibre length (µm). Areas A and B (4 m height) are sheltered from rain and run-off through the open eave; areas F and G (3 m height) are 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 (cf. 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). The sampling was performed under three exposure scenarios (Figure 6). Sampling areas A and B are sheltered from rain and water run-off through the open eave and exhibit the highest frequency of fibres. Sampling areas F, G and are neither sheltered nor in direct line of increased water run-off. Area F and R show a frequency of fibres less than half of the sheltered areas A and B, with lower area R showing also a wider range of fibre lengths. Sampling area S is directly affected by increased water run-off as indicated by the whitewashed areas around the dysfunctional gutter. No fibres were found at this sampling area.

While our findings group the fibre length frequencies into three categories across various exposure scenarios, it is crucial to examine the implications of these categorisations and their impact on our understanding of fibre distribution and deposition in urban settings. The marked prevalence of 60-120 µm and 180-240 µm fibre lengths in sheltered, elevated areas A and B (at 4m) suggests altitude and shielding potentially influence fibre deposition. In contrast, areas F and G (at 3m) show lower fibre frequencies but similar fibre length distribution, pointing to other influential factors governing these patterns. Additionally, the pronounced shift towards longer fibres in the exposed area R, and the complete absence in the adjacent lower area S (beside a malfunctioning gutter), highlight the combined roles of exposure, altitude, and other environmental variables resulting in differential fibre distribution patterns on urban facades. This brings forth critical questions regarding the kinetics of microplastic deposition: Does the topology of the built environment influence the capture and retention of fibres? And, how do exposure levels alter both the abundance and type of fibres on various urban surfaces?

Urban wall surface interaction with MPs – Sink or threat? In our exploration of historic built surfaces, we have unveiled their dynamic and complex nature, revealing a nuanced interplay with MPs. These urban facades, constantly undergoing moisture-induced changes and chemical transformations, serve as critical interfaces for environmental interactions. Our study finds that the permanence of MPs on these surfaces is highly context-dependent, shaped by both the architectural details and the urban ecosystem.

In areas where increased water run-off and erosion are prominent (area S in our study), the absence of MPs suggests that such factors may preclude their long-term deposition. Here, historic facades 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 (Gulotta et al., 2012; Sanjurjo Sanchez, 2009). Conversely, in less disturbed areas such as A, B, and to a lower extend F, G, and R in our study (Figure 6), the gradual formation of weathering crusts appears to facilitate the trapping and incorporation of MPs. This phenomenon aligns with broader atmospheric studies on MP deposition and suggests that urban facades could play a significant role in the environmental accumulation of MPs. The process of incorporating airborne particulate matter is a well-studied phenomenon and previous research on stone-built heritage has provided insights into the accumulation of pollutants in black crusts that form in sheltered areas (García-Florentino et al., 2020a; Nord et al., 1994; Wilhelm et al., 2021; Wilhelm et al., 2023).

Moreover, the presence of minerals with positive surface charges, like iron and aluminium oxy-hydroxides, within these crusts may enhance the sorption of MPs (Nie et al., 2023; Rauchschwalbe et al., 2022; Zhang et al., 2020). These minerals have been previously identified in weathering crusts, similar to those in this study. This finding opens up new avenues for understanding how urban surfaces interact with microplastics at a chemical level.

Adding to this complexity, the colonisation of these surfaces by microorganisms further influences the fate of MPs. It is hypothesised that in certain conditions, microorganisms rapidly assimilate MPs into biofilms, potentially prolonging their retention on these surfaces (Ahmed et al., 2022; Gadd, 2017; Gulotta et al., 2012; Nord et al., 1994; Sanjurjo Sanchez, 2009). Historic built environment surfaces are frequently inhabited by microorganisms that engage with, oxidise, and metabolise airborne pollutants (Fronteau et al., 2010; Machill et al., 1997; Moroni and Pitzurra, 2008). Bridging urban MP research with the ecology of urban walls, therefore, becomes imperative to comprehend the full spectrum of MP dynamics in urban settings.

The significant quantity of fibres we detected, coupled with signs of chemical degradation, suggests a prolonged persistence of MPs on these urban facades. This indicates that historic urban facades, especially those forming weathering crusts, might act as both temporary repositories and long-term sinks for MPs, effectively serving as environmental monitors. These facades, by chronicling the past and present trajectories of MPs, could be invaluable in predicting their future pathways and impact, thus acting as archives for urban MP flows.

Implications for Urban Environments. While past studies have demonstrated variable relationships between factors like population density and microplastic pollution (Dikareva and Simon, 2019; Fan et al., 2019; Xu et al., 2021), it is broadly agreed that areas with dense populations and heightened human activity are significant contributors to microplastic production (Chen et al., 2020; Koop and van Leeuwen, 2016; Koutnik et al., 2021). Although our research focused on Oxford, a smaller UK city, it uncovers levels of microplastic pollution that, when extrapolated, may be exacerbated in larger, densely populated urban zones, especially in rapidly industrialising nations. With global urbanisation trends showing a rise in urban populations and the expansion of city boundaries, the challenges highlighted in our study are projected to become increasingly significant. This trend in urban growth is expected to intensify urban microplastic pathways, leading to increased human exposure (Seto et al., 2012). Such projections are especially concerning for nations with pronounced plastic pollution like the USA, India, and China, which already exceed the UK in terms of pollution levels (Ritchie and Roser, 2018).

Our study provides an essential complement to the understanding provided by high-resolution atmospheric chemistry transport dispersion models, which are pivotal in predicting urban air quality but have historically emphasised airborne pollutants while potentially overlooking crucial aspects of environmental pollution such as microplastics (Hamilton et al., 2009). Our data captures high-resolution, real-world data on microplastic pollution on vertical urban surfaces, complementing these models for a broader understanding of urban pollution. Integrating our insights with existing models could lead to holistic urban pollution mitigation strategies, considering both traditional air pollutants and microplastics.

Health and Climate Change Implications. Our study reveals a significant presence of MPs, especially fibres, on urban facades, which raises substantial concerns for human and environmental health. Detrimental health effects are associated with MPs within the range of our findings (30-1000 µm). Inhalation or ingestion of these MPs may result in health conditions that could require medical investigations, such as lung tissue biopsies (Pauly et al., 1998) or result in traversal of the digestive tract wall (Volkheimer, 1974). These concerns are particularly notable given that they coincide with the modal peaks of fibre length observed in our study. Notably, the smallest particle size fraction (<10 µm), which poses potentially severe health threats, was not captured in our study (Prata et al., 2020; Ragusa et al., 2021).

Local climate and environmental changes, including weather extremes, could influence MP interactions with historical structures (Bergmann et al., 2022; Fallmann et al., 2016; Sesana et al., 2021). Factors such as increased weathering might alter MP deposition on buildings, and changing microbial activities could affect MP breakdown (Baggs and Philippot, 2010; McCabe et al., 2011; Smith, 2010; Viles and Cutler, 2012). While acknowledging the broader climate change context, our study emphasises the localised implications of MPs in historical urban settings.

Urgent need for standard protocols and future research. Our findings underscore the pressing need for standardised analytical methods in urban MP research, resonating with concerns voiced in established MP studies (Bergmann et al., 2022; Biltcliff-Ward et al., 2022; Nirmala et al., 2023; Revell et al., 2021; Xu et al., 2019). Developing methodologies for assessing rapidly large urban facades is critical, enabling accurate quantification, extrapolation, and modelling of MP contamination.

Future studies should consider the degradation processes of microfibres within historic built environments, potential health risks from secondary compounds, and the role of MPs as vectors for pollutants and microorganisms (Allen et al., 2021; Andrady, 2015; Godoy et al., 2019; Kirstein et al., 2021; Roveri et al., 2018).

Our study highlights the importance of FTIR in analysing MPs, particularly in urban settings. While FTIR has been crucial for identifying the chemical makeup of microfibres, its limitations in analysing complex or degraded MPs need addressing in future research. This aligns with the urgent need for standardised MP research protocols.

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 (Andrady, 2015; Andrady, 2017). Consequently, MP weathering and degrading patterns may differ significantly on urban facades 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 (Athey and Erdle, 2022; De Frond et al., 2021; Robertson et al., 2018)

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 (Xu et al., 2019). 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 (Brandon et al., 2016; Ioakeimidis et al., 2016). 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 (Shi et al., 2023; Varan and Caydamli, 2021). The EDX elemental map of sample B demonstrates such an example which shows instead of carbon (the most common base element for MPs as they derive from oil), calcium and chloride, indicating a treated textile used in sports cloths as described by Varan and Caydamli (2021; Figure SI 1).

Improving FTIR methods will not only enhance our understanding of MPs in environments like historic urban areas but also help assess their health and environmental impacts. Future studies should focus on refining these analytical techniques alongside exploring the broader implications of MPs.

In-depth field studies across diverse urban settings are essential to understand variations in MP types, distribution, and accumulation. Efforts should be directed towards discerning underexplored MP pathways and repositories, incorporating an understanding of factors ranging from microorganisms and MPs to larger urban and climatic influences. Incorporating insights from regional climate, soil, sediment, and water contamination studies can bolster our understanding.

Accurate MP quantification on urban facades is crucial for devising effective mitigation strategies and conducting risk assessments. Standardising these methods is a priority, as delays might induce long-term harm. By prioritising the understanding of MP sources, we can potentially influence perceptions on plastic consumption, providing a more holistic understanding of MP's budget, pathways, and fate in urban settings.

5 Conclusion

Our study highlights a potential global issue, revealing a pronounced presence of microplastics (MPs) on historic urban facades. Notably, we found a significant mean density of 975,000 fibres/m^2 (0.10 fibres/mm^2) for fibre lengths between 30-1000µm, underscoring the importance of further local and broader investigations.

Despite extensive research into MPs in various environments such as air, oceans, and, more recently, freshwater and soils, vertical surfaces (facades) in urban contexts— which constitute significant interfaces for both terrestrial and atmospheric elements— remain largely unexplored as potential accumulation points for MP pollution from multiple sources.

This pioneering evidence of substantial microplastic accumulation on these facades aligns with our initial hypothesis regarding the pollutant-accumulation capabilities of historic surfaces, establishing a crucial link between present plastic pollution and potential future impacts comparable to enduring legacies of past practices, such as leaded petrol pollution.

As highlighted by Persson et al. (2022), the rising production and global dissemination of novel entities, including plastics, often outpace societies' capacity for effective management. This imbalance risks crossing critical environmental (planetary) boundaries. Therefore, addressing MP accumulation on urban facades is paramount, not just for current mitigation but to inform forward-thinking policies promoting healthier urban spaces and shifts in plastic consumption behaviours.

Given the intensifying global crisis of plastic waste and the anticipated doubling of plastic deposition in coming decades (e.g., Persson et al., 2022), our findings underscore the urgency of addressing the silent accumulation of microplastics on urban facades to safeguard public health and ecological well-being. 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 (Farkas et al., 2018; Wilhelm et al., 2021).

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. Navigating the complex pathways and impacts of microplastics on urban facades necessitates a concerted, interdisciplinary effort that complements rigorous scientific exploration with robust policy-making, enabling not only the mitigation of current pollution but also the foresight to pre-emptively address emerging environmental threats of the future.

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

The authors declare no conflict of interests.

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10 Supplement Information

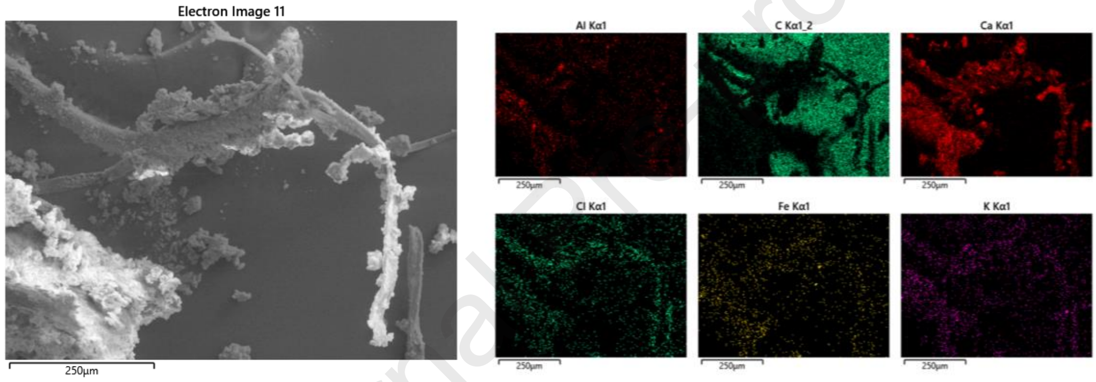

Figure SI 1: The SEM-EDX analysis of sample NCL-B2 reveals the presence of Calcium and Chloride, but interestingly, no Carbon. Typically, Carbon is the most prevalent base element in synthetic fibres, making this finding unusual.

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

Wilhelm et al.

Highlights

- We present the first study quantifying microplastics on vertical urban surfaces and show the pervasive presence of microplastics (MPs) on urban surfaces.
- Concentrations of microplastics on our study walls are up to 875,000 fibres/m^2.
- Fibres are more prevalent in more sheltered areas of the surfaces, and not present in areas of regular runoff.
- Our research suggests historic facades might act as urban sinks of MPs.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: