Environmental Pollution 326 (2023) 121511

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Identification and quantification of tire wear particles by employing different cross-validation techniques: FTIR-ATR Micro-FTIR, Pyr-GC/MS, and SEM☆

Beatrice Rosso [a], Elena Gregoris [a,b], Lucio Litti [c], Federico Zorzi [c,d], Maurizio Fiorini [e], Barbara Bravo [g], Carlo Barbante [a,b], Andrea Gambaro [a,b], Fabiana Corami [a,b,*]

[a] Department of Environmental Sciences, Informatics, and Statistics; Ca' Foscari University of Venice, Via Torino, 155, 30172, Venezia-Mestre, Italy
[b] Institute of Polar Sciences, CNR-ISP; Campus Scientifico - Ca' Foscari University of Venice, Via Torino, 155, 30172, Venezia-Mestre, Italy
[c] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy
[d] CEASC (Centro di Analisi e Servizi per la Certificazione), University of Padova, Via Jappelli 1a, 35121 Padova, Italy
[e] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Via Terracini 28, Bologna (BO), Italy
[g] Thermo Fisher Scientific, Str. Rivoltana, Km 4 - 20090 Rodano (MI), Italy

ARTICLE INFO

Keywords:
Tyre wear particles (TWPS)
Cross-validation techniques
Highway stormwater runoff
Quantification and identification

ABSTRACT

Tire wear particles (TWPs) are one of the environment's most important emission sources of microplastics. In this work, chemical identification of these particles was carried out in highway stormwater runoff through cross-validation techniques for the first time. Optimization of a pre-treatment method (i.e., extraction and purification) was provided to extract TWPs, avoiding their degradation and denaturation, to prevent getting low recognizable identification and consequently underestimates in the quantification. Specific markers were used for TWPs identification comparing real stormwater samples and reference materials via FTIR-ATR, Micro-FTIR, and Pyrolysis–gas-chromatography–mass spectrometry (Pyr-GC/MS). Quantification of TWPs was carried out via Micro-FTIR (microscopic counting); the abundance ranged from 220,371 ± 651 TWPs/L to 358,915 ± 831 TWPs/L, while the higher mass was 39,6 ± 9 mg TWPs/L and the lowest 31,0 ± 8 mg TWPs/L. Most of the TWPs analyzed were less than 100 μm in size. The sizes were also confirmed using a scanning electron microscope (SEM), including the presence of potential nano TWPs in the samples. Elemental analysis via SEM supported that a complex mixture of heterogeneous composition characterizes these particles by agglomerating organic and inorganic particles that could derive from brake and road wear, road pavement, road dust, asphalts, and construction road work. Due to the analytical lack of knowledge about TWPs chemical identification and quantification in scientific literature, this study significantly contributes to providing a novel pre-treatment and analytical methodology for these emerging contaminants in highway stormwater runoff. The results of this study highlight the uttermost necessity to employ cross-validation techniques, i.e., FTIR-ATR, Micro-FTIR, Pyr-GC/MS, and SEM for the TWPs identification and quantification in the real environmental samples.

1. Introduction

The global production of thermoplastics and synthetic rubber grew rapidly since the beginning of their large-scale production over the 1950s, reaching 370 million tonnes/year in 2019 and 11.3% of the entire European plastic demand distribution (Plastics Europe 2019). As a result of the growing automotive industry production, tire manufacturing is considered the world's most significant consumer of synthetic rubber, with a production of 1.5 billion tire units per year worldwide. Their extensive use and the mismanagement of waste have been dramatically increasing, resulting in millions of used tires being disposed of around the globe (Archibong et al., 2021; Mohajerani et al.,

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author. Institute of Polar Sciences, CNR-ISP, Campus Scientifico - Ca' Foscari University of Venice, Via Torino, 155, 30172, Venezia-Mestre, Italy.
E-mail addresses: beatrice.rosso@unive.it (B. Rosso), elena.gregoris@cnr.it (E. Gregoris), lucio.litti@unipd.it (L. Litti), federico.zorzi@unipd.it (F. Zorzi), maurizio.fiorini@unibo.it (M. Fiorini), barbara.bravo@thermofisher.com (B. Bravo), barbante@unive.it (C. Barbante), gambaro@unive.it (A. Gambaro), fabiana.corami@cnr.it (F. Corami).

https://doi.org/10.1016/j.envpol.2023.121511
Received 1 February 2023; Received in revised form 21 March 2023; Accepted 23 March 2023
Available online 24 March 2023

2020). Besides, the result of the friction heat and the wear of the tire is the production of black particles, called tire wear particles (TWPs), which are of different dimensions, from the nanosized particle fraction up to 220 μm, and of different shapes (Kole et al., 2017; Sommer et al., 2018; Wagner et al., 2018). Despite these particles having been described as environmental contaminants since the 1970s (Cadle and Williams, 1979), the distribution, sources, amount, and transport of TWPs into the environment with potential health issues have only recently been highlighted (Ding et al., 2023; Halle et al., 2021; Luo et al., 2021). TWPs have only recently been recognized as microplastics (MPs) since synthetic polymers are core constituents of tires (Vv. Aa, 2020; Hartmann et al., 2019). The composition of TWPs differs from brand and purpose, and it is made up of several layers (e.g., steel cords, synthetic textiles, rubbers, the sidewall, the belt, etc.), where the principal components consist of rubber (e.g., styrene butadiene rubber (SBR) or butadiene rubber (BR), natural rubber (NR) and isoprene rubber (IR)). Other components are fillers (carbon black and silica), reinforcement materials (steel, polyester, rayon, nylon), softeners (oils and resins), plasticizers, desiccants, chemicals for vulcanization, sulfur, zinc and cadmium oxide, etc.), preservatives, additives, and anti-aging agents (Andersson-Sköld et al., 2020; Baensch-Baltruschat et al., 2020; Wagner et al., 2018, 2022). Highway and road traffic vehicles are the primary source of TWPs in the environment (Goehler et al., 2022; Knight et al., 2020). Hence, these particles are generated by vehicle friction actions and are first deposited and accumulated in the road dust. During rainfall, TWPs are washed off through stormwater runoff (SW) to the roadside to receiving waters or resuspended during dry periods through the atmosphere and reach surrounding soils (Luo et al., 2021). Coarse TWPs are deposited on the road and transported to soils near the roadside. In contrast, the small-sized TWPs are likely to be washed away with runoff, suspended in the air, transported over longer distances, and easily ingested by the biota with potential toxic effects, providing an inhalation risk also to human health (Baensch-Baltruschat et al., 2020; Garrard et al., 2022; Knight et al., 2020; Rienda and Alves, 2021; Schell et al., 2022). A crucial concern arises from the chemicals that are incorporated into the tires, with the possibility of leaching into the surrounding environmental matrices (Rauert et al., 2021, 2022). Besides, TWPs may incorporate material from the road and the surrounding environment during their transport in the environment (e.g., asphalt, road dust, sediments, gravel, oils, and other pollutants), and may form conglomerates with various compositions (Baensch-Baltruschat et al., 2020; Sommer et al., 2018). Only recently, some studies have reported the presence of hundreds of chemicals (e.g., plastic additives), most of which are unknown and can be released during the wear of tires in their life cycle (Halle et al., 2021; Müller et al., 2022; Müller et al., 2022; Seiwert et al., 2020). Due to TWPs' complex chemical mixture composition, the incorporation of material from the surrounding environment, and the small-sized TWPs in the environment, the analytical methods for characterizing TWPs in real samples are challenging. To date, no standardized procedures have been developed; different sampling, pre-treatments, and measurement procedures were used, resulting in incomparable results, especially in real environmental samples (Baensch-Baltruschat et al., 2020; Mattonai et al., 2022; Rauert et al., 2022).

Regarding pre-treatment procedures, the commonly employed solutions are aggressive digestion steps (e.g., alkali or acid solutions) with density extraction methods for separating them from interferences, such as biogenic organic matter and inorganic components. The degradation of TWPs and purification procedures might be crucial factors affecting the reproducibility and accuracy of TWPs' characterization (Liu et al., 2021; Mattonai et al., 2022). Visual identification and thermo-analytical methods have been commonly employed to identify TWPs. Although spectroscopic methods, e.g., FTIR spectroscopy, have been applied for TWPs measurements, several challenges arise from some fillers containing black carbon components, which adsorb light throughout the infrared region (Baensch-Baltruschat et al., 2020; Wagner et al., 2018). Thermo-analytical methods, such as pyrolysis gas chromatography-mass spectrometry (Pyr-GC/MS) and thermal extraction and desorption (TED-GC/MS), are used for qualitative fingerprinting of TWPs analysis, and the products of their thermal decomposition are employed as markers for their quantification and identification (Arias et al., 2022; Klöckner et al., 2020; Parker-Jurd et al., 2021). Using validated chemical markers to quantify TWPs in various environmental samples indirectly can be advantageous, including high time efficiency and low material costs. However, the selection of analytical markers is critical and should be considered case-by-case, including the different aging stages and brands of tires that could influence the accuracy and comparability of TWPs' measurements. Therefore, using these markers to calculate TWPs concentration might lead to an underestimation due to their chemical process in the environment (e.g., vaporization, photo-degradation) or overestimation due to the ubiquity of other related sources, which can generate the same substances also used for tire production (Baensch-Baltruschat et al., 2020; Luo et al., 2021; Rødland et al., 2021). Hence, researchers have underlined the need to employ cross-validation techniques to confirm the chemical composition of TWPs in real environmental samples (Liu et al., 2021).

In one of our previous studies on small microplastics (SMPs), and microlitter components (MCLs; e.g., plasticizers, antistatic agents, lubricants, vulcanizers, curing agents, etc., natural and non-plastic synthetic fibers, etc.) on highway stormwater runoff (HSW; Rosso et al., 2022), a highly significant number of black particles was observed in the samples analyzed, pointing to the presence of TWPs. For this reason, the same samples were analyzed to identify TWPs.

TWPs have been investigated in several studies since they have been assumed to be the most predominant source of MPs in the environment (Chang et al., 2020; Eisentraut et al., 2018; Halle et al., 2021; Leads and Weinstein, 2019; Luo et al., 2021; Goβmann et al., 2021). However, to our knowledge, this is the first study whose goal is the cross-validation of the chemical identification of TWPs in stormwater by employing several techniques together: FTIR-ATR, Micro-FTIR, Pyr-GC/MS, and SEM. The quantification of TWPs was carried out via Micro-FTIR. Besides, size and shape investigation were performed using the imaging of Micro-FTIR and SEM.

The pre-treatment method employed (i.e., extraction and purification) has been optimized without further degradation/denaturation of the particles under investigation (Corami et al., 2021; Rosso et al., 2022).

2. Materials and methods

2.1. Sampling

TWPs were present in samples of HWS collected along the trafficked highway (Passante of Mestre on the mainland of Venice in Italy; 32.3 km long, with average traffic of about 71,000 vehicles per day, including more than 20,000 heavy vehicles). The sampling procedure was described according to Rosso et al. (2022). Before sampling, explorations were performed to choose the right equipment and position of sampling devices along the highway. The number and the choice of the sampling devices and modality were tested (e.g., considering the slope, the access, etc.) to collect rainfall events greater than 5 mm. HSW samples were collected at the same site in three different drains along the highway (10 m from each other), where three decontaminated glass flasks (each flask's volume 1 L) were located in each drain. These flasks were inserted in the drains before a rainfall event to collect the HSW. The flasks were hung inside the drains with clean iron wire. After the rainfall, the three flasks were recovered, carefully transported to the laboratory, and stored at 4 °C. Technical operations, authorization accesses, and remote control were supported by StormWater Italia (SWI – Marghera-Venice) company and CAV (Concessioni Autostradali Venete) of Venice, Italy. Details on the sampling date are reported in Supplementary Information (Table S1).

2.2. Reagents

Ultrapure water (UW) is produced by a UW system (Elga Lab Water, Veolia, High Wycombe, UK). The employed reagents were: hydrogen peroxide (H_2O_2, 30%, ACS reagent, Sigma Aldrich), organic solvent-free and cold-pressed sunflower seeds oil (SSO, Crudolio, Camisano Vicentino (VI), Italy), hexane (puriss. P. a., ACS reagent, reag. Ph. Eur., ≥99% (GC) Sigma Aldrich, Merck, Darmstadt, Germany), ethanol (absolute, for HPLC, ≥99.8%, Sigma Aldrich, Merck, Darmstadt Germany), and methanol (for HPLC ≥99.9% Sigma Aldrich, Merck, Darmstadt, Germany). Aluminum oxide filters (0.2 μm, 47 mm diameter, ANODISC (Anopore Inorganic Membrane Whatman) were purchased from Merck (Merck, Darmstadt, Germany).

2.3. QA/QC

Plastic contamination was minimized at any step, from sampling to the analysis. The operators wore cotton lab coats and nitrile gloves during sampling, and in the plastic-free Clean Room ISO 7, a controlled laboratory, where all the furniture is stainless steel and the ceiling, as well as the floor and the walls, are covered with stainless steel. The pre-treatment procedures (i.e., extraction, purification, and filtration) were performed under a decontaminated steel fume hood in the clean room. All steelware and all glassware, including the glass flasks and jars, were decontaminated before use by rinsing with UW, followed by methanol, a 50% solution (v/v) methanol and ethanol, and ethanol at last. Inox steel containers and balls of the ball mill (Retsch MM400 Mixer Mill) were decontaminated accordingly. After filtration, filters were stored in decontaminated glass Petri dishes covered with aluminum foil under the fume hood in the cleanroom. Before the analysis, filters were transferred to the Micro-FTIR laboratory and carefully covered with aluminum foil to avoid external contamination. Reagent blanks (i.e., ultrapure water, methanol, ethanol, H_2O_2) and procedural blanks (i.e., UW and H_2O_2 were oleo-extracted, recovered, and filtered using the same reagents as for the samples) were tested for TWPs or other microplastic contamination and processed as samples for each batch. All the blanks were run in triplicate. No plastic particles were observed on the blanks.

Certified reference materials for MPs and TWPs in SW or other environmental samples are lacking. Therefore, several pieces (about 100 g) resulting from the tear and wear of commonly used commercial tires (taken from the dust formed inside the shredded end-of-life tires) provided by a mechanic were selected as homemade reference material (their dimensions range from 1 to 5 mm). An aliquot of these particles (several different pieces for a total weight of 20 g) was analyzed with FTIR-ATR. The other particles were frozen (−20 °C); then, these tire fragments were ball-milled to obtain a fine and homogenous mixture of particles. Five aliquots of this homogenous mixture (10 g each) were resuspended in UW (300 mL) and filtered on aluminum oxide filters. These filters were therefore employed as reference material for identifying TWPS for Micro-FTIR and Pyr-GC/MS validation methods and the morphological analysis with SEM.

As reported in Rosso et al. (2022), the average yield of the recovery test was 94%; therefore, the oleoextraction for SMPs, TWPs, and other microlitter components was efficient, replicable, and accurate.

2.4. TWPs in environmental samples: oleo-extraction, filtration, and purification

HWS samples were processed to extract (oleo-extraction) simultaneously SMPs, TWPs, and MCLs, which were later analyzed via Micro-FTIR for quantification and polymer identification (Rosso et al., 2022). The pre-treatment procedure was previously developed by Corami et al. (2021) and optimized for the HSW samples (Rosso et al., 2022). Briefly, 100 mL of HSW samples (the aliquot came from a composite mean sample derived from the HSW collected in the three sampling flasks for each event) were diluted 1:1 with UW in a decontaminated Erlenmeyer flask and thoroughly homogenized. The flasks were stirred for 3 h on a multipurpose orbital shaker at room temperature after having added 30 mL of H_2O_2 to pseudo-digest the organic matter possibly present in the samples and minimize/avoid spectral interferents. Then, the stirred aliquots were poured into decontaminated 500 mL separating funnels, adding 7 mL of SSO (more details on the use of SSO are described in Supplementary information). Separatory funnels were then stirred for 15 min at 100 rpm on an orbital shaker, forming an emulsion. After a resting time of 3 h for the two phases to separate completely, the aqueous phase was collected in a second decontaminated separating funnel, while the first oleo-extract was recovered in a decontaminated Erlenmeyer flask with 20 mL of *n*-hexane and 20 mL of ethanol. The oleo-extraction was repeated for a second time, adding 5 mL of SSO and 5 mL of H_2O_2 in the second separating funnel. After discarding the aqueous phase, the oleo-extract was recovered with 20 mL of hexane and 20 mL of ethanol and poured into the same Erlenmeyer flask. The oleo-extracts were filtered onto aluminum oxide filters using a decontaminated glass vacuum filtration system (VWR International, Milan, Italy), under the fume hood. After that, the purification procedure was carried out according to Corami et al. (2020, 2021). Briefly, every filter was cleansed before the filtration by pouring 50 mL of a 70% (v/v) solution of ethanol-methanol and 20 mL of ethanol. The oil phases from the HSW samples were poured several times, alternating with hexane and ethanol to allow the oil to be filtered more efficiently and quickly without leaving traces of oil on the filter and the particles. Finally, a 70% (v/v) solution of ethanol-methanol and ethanol were employed to rinse the filter. Reagent blanks (including UW) and procedural blanks were filtered accordingly. All the samples were run in triplicate.

Before the analysis via Micro-FTIR, filters were left to dry in decontaminated Petri dishes covered with aluminum foil in the cleanroom for at least 72 h.

2.5. Quantification (via microscopic counting) and identification of TWPs via FTIR-ATR and Micro-FTIR

Large pieces of homemade reference material for TWPs (≫100 μm) were firstly analyzed with FTIR-ATR Nicolet iS20 (Thermo Fisher Scientific, Madison, WI, USA) with a Smart iTX™ diamond accessory to characterize functional groups over a range of 500–4000 cm^{-1}.

TWPs were analyzed, simultaneously with SMPs and MCLs (Rosso et al., 2022) in HSW samples using a Micro-FTIR spectrometer (Nicolet™ iN™ 10 infrared microscope; Thermo Fisher Scientific, Madison, WI, USA), equipped with an ultra-fast motorized stage and liquid-nitrogen-cooled MCT detector (mercury cadmium telluride detector). The analysis was performed in transmittance mode, with a spectral range of 4000–1200 cm^{-1}, 100-μm step size scanning (spatial resolution), 100 × 100 μm aperture, and 64 co-added scans at a spectral resolution of 4 cm^{-1}.

According to Corami et al. (2020, 2021), microscopic counting was performed. Briefly, at least 20 known-sized areas (i.e., count fields) were randomly chosen with no overlapping on the surface of the filter, and a significant number of particles (an average of 300 particles per count field) were analyzed using the PARTICLE WIZARDS of the Omnic™ Picta™ software. The spectral background was acquired on a clean point in each count field. The FTIR spectrum of each particle was compared with spectra in previously selected reference libraries (the complete list is in the supplementary information). According to the similarity algorithm, the identification of each spectrum is expressed as a match percentage (match %). Particles were regarded as identified and counted for quantification only when the match percentage was ≥65% (optimal identification). Only optimally identified particles were quantified. A selection of previously analyzed particles was also regularly analyzed with the point-and-shoot technique to double-validate the identification. The length and the width of each particle (sizes of the particle) were retrieved thanks to the imaging of PARTICLE WIZARDS, and the

aspect ratio (AR) was calculated according to Corami et al. (2021, the equation is in the supplementary information). The abundance of particles was calculated using a slightly modified equation from Corami et al. (2020, 2021); specifically, the equation for the abundance of TWPs/L was

$$\frac{TWPs_{tot}}{L} = \frac{n * F}{V_{tot}} \quad (1)$$

Where n = number of TWPs counted on every field, V_{tot} = volume of HSW collected (L), and F = count factor, calculated as follows:

$$\frac{Filter\ area}{Count\ field\ area * n\ count\ fields} \quad (2)$$

The mass of each TWP is calculated according to its volume (V); the latter is calculated according to AR, and density (ρ). From other scientific papers, an average ρ was obtained (1.8 g cm^{-3}; Kayhanian et al., 2012; Klöckner et al., 2020; Parker-Jurd et al., 2021; Rhodes et al., 2012; Unice et al., 2019). This value considers different potential compositions of tire brands and degradation processes characterized by particle transport in the environment. Statistical analyses were performed using STATISTICA software (TIBCO, Palo Alto, CA, USA). TWPs follow the Poisson distribution since they are counted as SMPs (Courtene-Jones et al., 2017; Corami et al., 2021; Filella, 2015). The confidence interval (fiducial interval, FI) was calculated accordingly. The Fisher exact test (F test; $\alpha = 0.05$) was performed to test whether variances were homogenous. Non-parametric statistical tests, i.e., the Kruskal-Wallis test ($p < 0.05$) for multiple comparisons and the Mann-Whitney *U* test ($p < 0.05$) for pairwise comparisons, were performed to assess the meaningfulness of the differences observed, having verified the non-homogeneity of variances.

2.6. Identification of TWPs using Pyr-GC/MS

After the Micro-FTIR analysis, selected filters of HSW samples were analyzed by Pyr-GC/MS. The apparatus comprises a Pyroprobe 5150 filament pyrolyzer (CDS Analytical) coupled with a high-resolution gas chromatograph HP 6890 - quadrupole mass spectrometer 5973 N (Agilent Technologies). Some fragments of HSW1 and HSW2 (about 1 mg) were inserted in a sample holder consisting of a pre-muffled (400 °C, 4 h) quartz tube (1,9 mm in diameter, 1 and 2.5 cm in length from CDS Analytical), between two pre-muffled quartz disks. Fragments of homemade reference material were inserted in the same way. The sample holder was introduced in the pyroprobe, and pyrolysis was conducted at 900 °C for 15 s. The interface (or accessory) was programmed to ventilate the samples for 3 min at 200 °C, to remove volatile and semi-volatile compounds before the pyrolysis started. The interface is then quickly heated to 280 °C and maintained at that temperature during and after the pyrolysis (3 min). The valve oven and transfer line were at 250 °C during the whole analysis. The probe was cleaned at 1200 °C for 10 s after each analysis. GC was equipped with an HP-5ms column (30 m × 0.25 mm x 0.25 μm, Agilent Technologies, He flow: 1 mL min^{-1}). The oven program was: 40 °C, 2 min, 13 °C/min to 261 °C, 6 °C/min to 300 °C, 2 min. GC inlet temperature was 300 °C; the split ratio was 1:5. The MS detector was used in scan mode from 31 to 400 m/z, with an ion source temperature of 230 °C (electron ionization source, 70 eV) and a quadrupole temperature of 150 °C. A scheme of the apparatus is in the Supplementary information. Polymer identification was based on the presence of indicator compounds in the resulting pyrogram. The identification of peaks was conducted by comparison of their mass spectra to those included in the NIST05 library by the National Institute of Standards and Technology (NIST).

According to the scientific literature, different pyrolysis products have been employed for the quantification and identification of TWP, e.g., additives and vulcanization accelerators, activators, antifreeze products, antioxidants, and antiozonants. However, some of these markers can be subjected to degradation. We decided to identify TWPs using markers of the most commonly used rubbers in tire production: natural (NR) or isoprene rubber (IR), butadiene rubber (BR), and styrene-butadiene rubber (SBR), bearing in mind that some of their monomers might come from different sources. For instance, rubber monomers can be emitted from other traffic-related sources, such as deicing salts, road barriers, leakage of antifreeze, galvanized metal in automobiles, brake wear, and road markings, but also from industry and building or natural material (Baensch-Baltruschat et al., 2020; Wagner et al., 2018; Wik and Dave, 2009). Besides, sources of styrene (monomer of SBR) include humic components, vegetables, fruit tannins, plastic residues, and diesel exhaust (Unice et al., 2012). The other monomer of SBR, 1,3-butadiene), is a component of vehicle exhaust formed from combustion products of olefins, alkanes, and aromatic compounds, while isoprene (monomer of NR and IR) can be present in environmental samples as organic matter (Unice et al., 2012). Hence, two dimers were selected as univocal markers of tire wear rubbers: 4-vinyl cyclohexene (VCH), which is not known to have other significant sources, except the presence of TWPs in the environment, and limonene (1-methyl-4-(1--methylethenyl)-cyclohexene, also known as dipentene), as it is the dominant dimer species and univocal marker for NR and IR rubbers used in literature (Panko et al., 2019; Rauert et al., 2021; Unice et al., 2012, 2013). Although rubber monomers could be originated from different sources in the environment, monitoring them can be useful for supporting the identification of NR/IR, SBR, and BR in the samples.

2.7. Morphological analysis of TWPs using SEM/EDX

After Micro-FTIR analysis, other HSW sample filters were analyzed at different magnifications with a Scanning Electron Microscope (FEI Quanta 200 ESEM with thermoionic gun) equipped with an EDAX Element C2B detector for qualitative EDX analysis at the Padua University (UniPd). The images and elemental analysis were employed to confirm the TWPs' sizes, morphology, and the particles on the TWPs' surface. Samples were gold sputtered with a Q150 R ES rotatory-pumped sputter coater (Quorum Technologies Ltd., East Sussex, UK) to make them conductive.

3. Results and discussion

3.1. Quantification and identification of TWPs via FTIR-ATR and Micro-FTIR

Regarding Micro-FTIR, removing other organic and inorganic interferences on the TWPs surface during pre-treatment was crucial for their quantification and identification with spectroscopic techniques (Worek et al., 2022). The purification procedure (Corami et al., 2020), employed in this study, provided a clear background and filters with no interferents (Fig. 1); however, several potential TWPs (black particles) had low transmittance across the spectrum caused by the absorption of the carbon black added to the tire material as a filler with the resulting that the base spectrum signal was altered. Hence, these spectra were processed post-map (after the acquisition), and a baseline correction was applied to the spectra from homemade reference materials and HSW samples using OMNIC PICTA software. While spectra of TWPs <100 μm in HSW samples and from the homemade reference material were collected via Micro-FTIR, the spectra of TWPs > 2 mm were collected via ATR-FTIR. All these spectra were identified similarly as cadmium, zinc, barium sulfide blend (Fig. 2). Different reference libraries were employed; in particular, these spectra were identified by two libraries: Polymer "Additives and Plasticizers" and "HR Polymer Additives and Plasticizers". The match of the spectra retrieved from HSW samples and homemade reference material had a percentage higher than 89–90% maximum (Fig. 2). Other additional spectra are in Supplementary Information (Fig. S1).

These spectra were found to be closely consistent with those in the

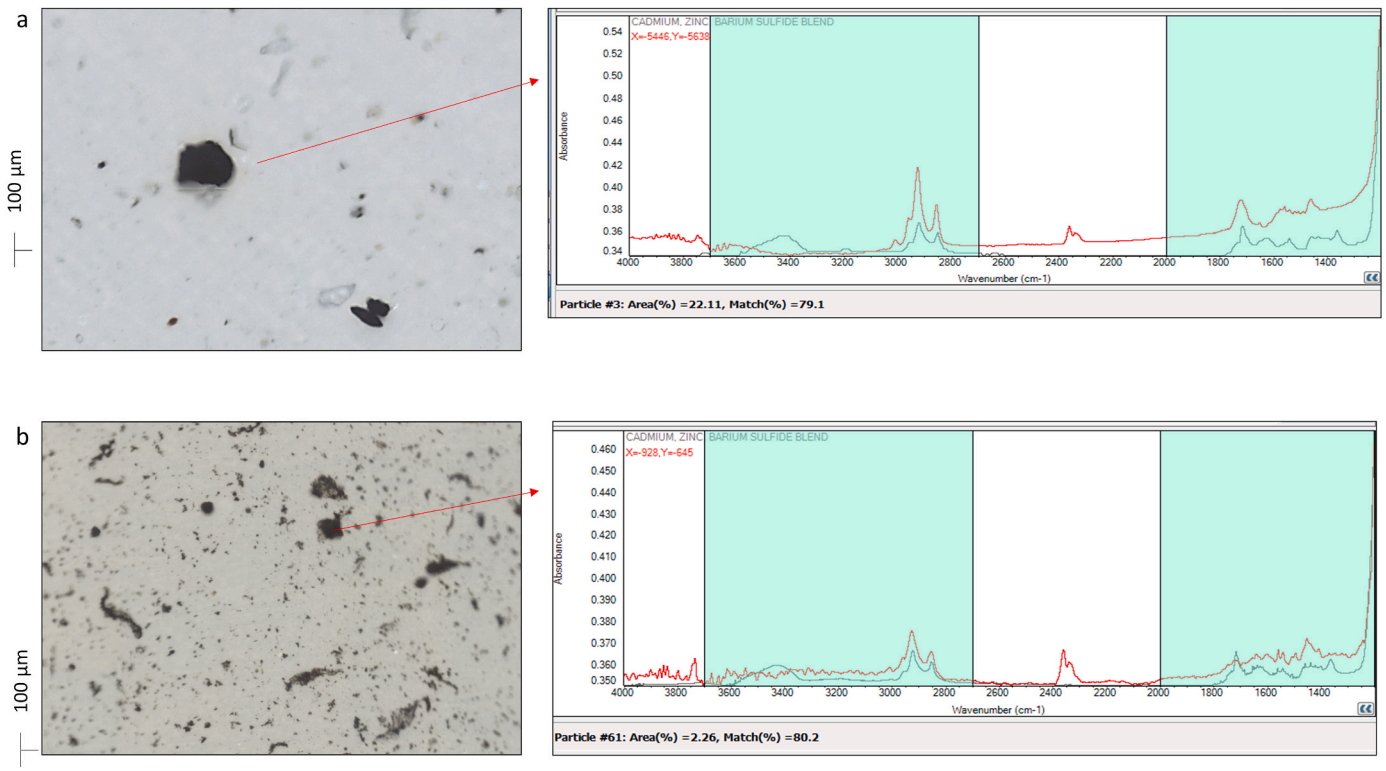

Fig. 1. Two count fields (a and b) analyzed with the Micro-FTIR. For each particle, a spectrum was obtained (in the right), and compared with specific and selected libraries. The pre-treatment methods employed provided clear background from organic and inorganic interferences that allowed the quantification and chemical identification of TWPs.

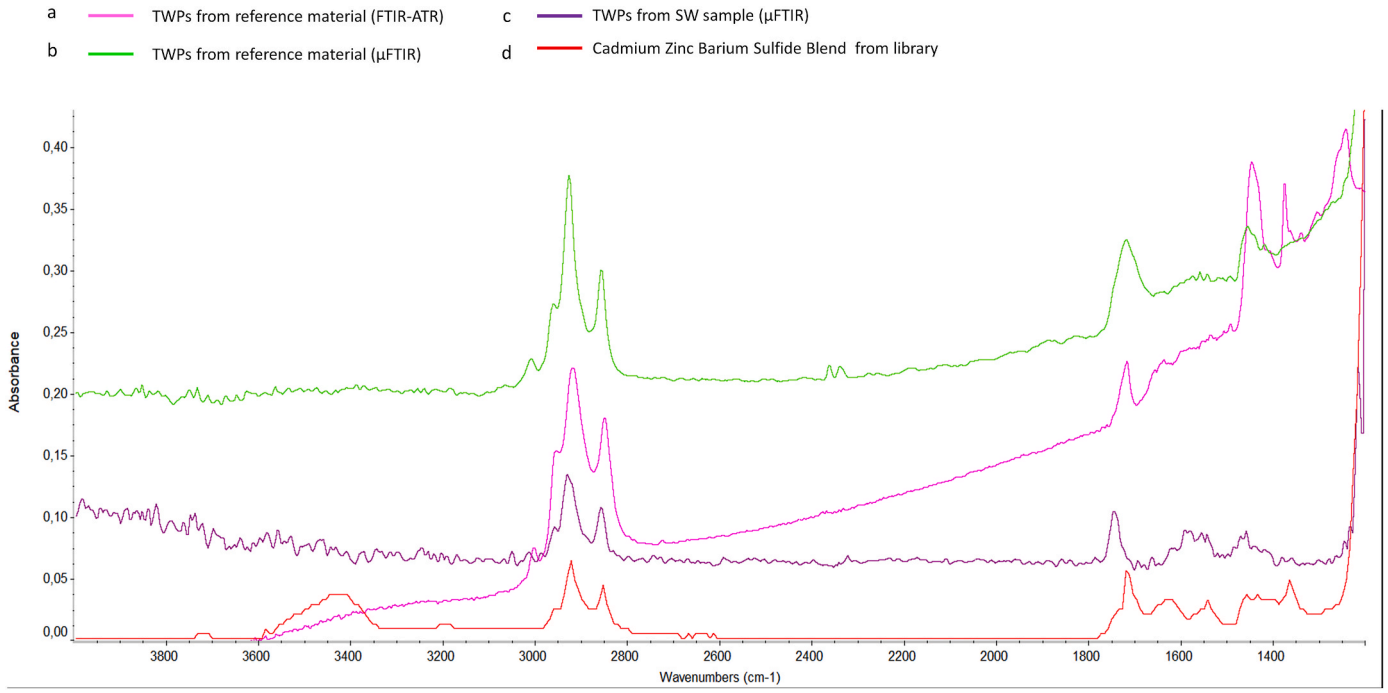

Fig. 2. All TWPs spectra obtained and compared to each other. Specifically, spectra *a)* derived from reference material employed FTIR-ATR, *b*) employed Micro-FTIR; spectra *c)* derived from TWPs from HSW samples using Micro-FTIR, and it is "Cadium zinc, barium sulfide blend" identified with specific libraries.

scientific literature (Figs. 1 and 2; Kovochich et al., 2021; Roychand and Pramanik, 2020; Thomas et al., 2022; Worek et al., 2022). Some characteristic bands were present in all the spectra. For instance, the intensities at 2913 and 2847 cm^{-1} are the repeating and characteristic bands that verify the presence of symmetrical and asymmetric stretching vibrations of methylene groups, while the peaks around 1450 cm^{-1} are from C–H bending. Some of the additional peaks present in the spectra could be originated from the different compositions of the tire or other

materials derived from the road (supplementary information, Fig. S1). In-depth investigations on the presence of other tire components in this complex mixture composition are needed in future studies to understand other potential TWPs markers. Besides, no standard procedures are described in scientific literature to purchase certified reference material or originate homemade TWPs materials as a reference; our preliminary results allowed us to confirm TWPs characterization in real environmental samples. Further studies need to evaluate potential variations in using TWPs reference materials for their chemical identification.

Cadmium (Cd), zinc (Zn), and barium (Ba) are currently employed in tire manufacturing. Zn, and can be present in high concentration in tires, playing an irreplaceable role as an activator in the vulcanization process because it activates and promotes the highest number of crosslinks in the rubber chain, imparting strength, stability and other valuable properties in a finished tire. Zn turns sticky rubber compounds into stable and durable components that allow a tire to carry a vehicle's mass and stop safely (US Tire Manufacturers Association, 2019; Wik and Dave, 2009). Cd in tires is used as an attendant substance of Zn (Shakya et al., 2006); barium is usually used as barium sulfate to enhance the aging resistance and weatherability of rubber products in tire rubber (9X Minerals 2017). Zn is widely used as a TWPs marker in the scientific literature using different techniques (Klöckner et al., 2020; Müller et al., 2022), as it is considered the primary source of trace elements in the vicinity of waterbodies of highways and urban roads deriving from vehicles traffic (Councell et al., 2004; Degaffe and Turner, 2011). Zn (or other trace elements connected) markers can also be released from other traffic-related sources such as deicing salts, road barriers, galvanized metal in automobiles, brake wear, and road markings; thus, they cannot be used alone to identify TWPs (Kovochich et al., 2021; Unice et al., 2013; Wagner et al., 2018; Wik and Dave, 2009). For these reasons, cross-validation using other techniques, e.g., Pyr-GC/MS, was performed to confirm the identification of these particles.

In all HSW samples, fragments identified as cadmium zinc, barium sulfide blend were identified and quantified via Micro-FTIR. The abundance and mass of TWPs are reported (Fig. 3) with the respective confidence limit (error). The highest abundance was detected in SW4 (358,915 ± 831 TWPs/L), while the lowest abundance was observed in SW3 (220,371 ± 651 TWPs/L). The same trend was observed for mass: the higher amount was calculated for SW 4 (40 ± 9 mg TWPs/L) and the lowest for SW 3 (31 ± 8 mg TWPs/L). AR showed that ellipsoid (e) was the most common shape among TWPs in these HSW samples (Fig. S2 in supplementary information). Particles of different shapes can potentially cause different effects on the organisms in case of ingestion (Andersson-Sköld et al., 2020); hence, assessing the TWPs' shape is extremely important to evaluate potential toxicological effects in the environment. Since variances were not homogenous (F test, $\alpha = 0.05$), non-parametrical statistical tests were applied. The TWPs' abundance in HSW samples under exam was significantly different according to the Mann-Whitney *U* test ($\alpha = 0.05$). The differences observed were highly statistically significant according to the Kruskal-Wallis test ($p < 0.01$). Different rain events may significantly affect the abundance and distribution of SMPs, TWPs, and other microlitter components in HSW, which could potentially reach the environment and pose a threat to biota and human beings, as well.

Most of the TWPs observed in the HSW samples were smaller than 100 μm in length. Herein, the average length was 82 μm, while the average width was 34 μm. The length ranged from the minimum LOD (limit of detection) size of the Imaging of the Micro-FTIR (5 μm; Corami et al., 2021, 2022) to the maximum of 3000 μm, while the width varied from 5 μm to 157 μm (the size distribution in length of one of the HSW samples was shown in Fig. S3, in supplementary information). The efficiency of different treatment technologies for TWPs, rubber particles, and MPs in the storm and urban runoff (e.g., gross pollutant trap, vegetated and sand-only filter, bio-retention systems, etc.) from the highway and urban sources were evaluated in some studies, where only particles >100 μm in size were considered (Gilbreath et al., 2019; Lange et al., 2021). Although the data are still scarce (Baensch-Baltruschat et al., 2020), it should be underlined that the smaller TWPs from the highway may not be effectively trapped by stormwater treatment plants and spill into the environment. Once released into the environment, particles <100 μm can pose an additional threat to terrestrial and aquatic biota since they can enter the trophic web and be ingested, providing toxic effects due to the leachate compounds (Halle et al., 2021; Koski et al., 2021; Luo et al., 2021; Parker et al., 2020; Sheng et al., 2021). Hence, more studies on technologies and monitoring should be encouraged and integrated in the future to realize long-term solutions to mitigate and control TWPs' pollution (Luo et al., 2021).

Comparing our results with scientific literature is quite challenging due to the different markers, units of measure, matrices, and techniques employed for analyzing TWPs in stormwater runoff. Only limited studies provided a quantification of TWPs in stormwater or receiving water from road and highway systems. For example, a lower concentration in

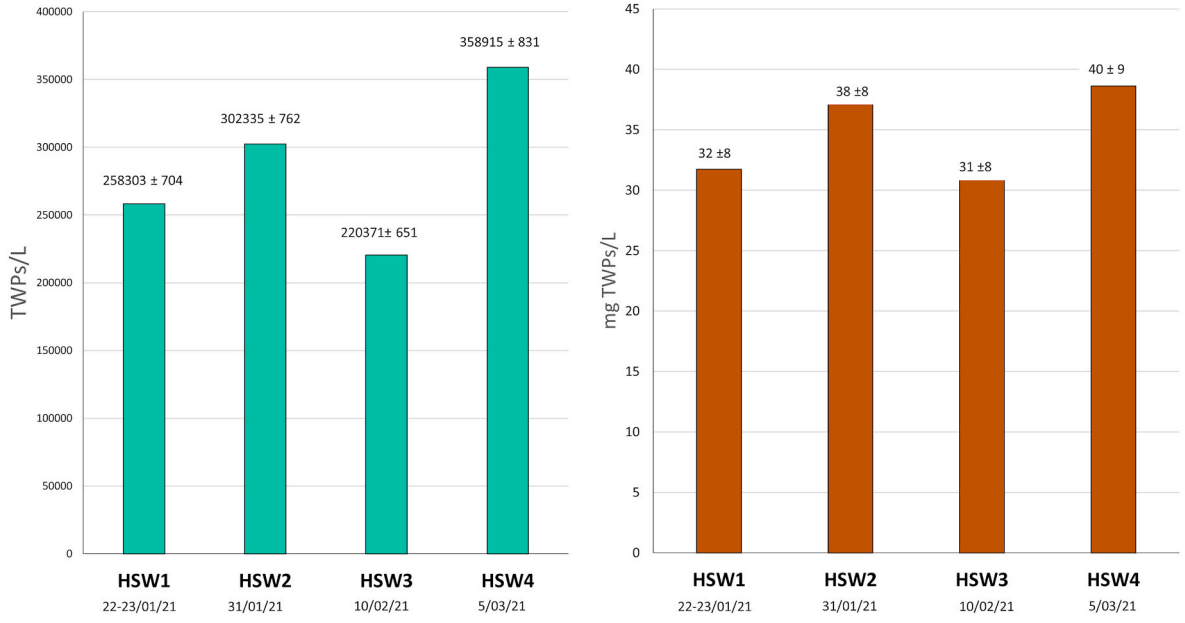

Fig. 3. The abundance (TWPs/L) and mass (mg TWPs/L) of TWPs with the respective confidence limit (error).

stormwater (4.0 ± 2.4 microplastic particles/L) was detected from a stormwater floating treatment wetland in Australia; while in sediment, the concentration was higher (595 ± 120 microplastic particles/kg dry sediment). However, only about 15–38% of these particles were identified by FTIR as synthetic rubber-carbon-filled particles (Ziajahromi et al., 2020). Regarding the mass, lower concentrations from 0.8 mg L^{-1} of TWPs to 2.5 mg L^{-1} were found in river water in China (Ni et al., 2008) and in stormwater rain (Parker-Jurd et al., 2021), respectively. On the other hand, higher concentrations were observed in USA and Japan (from 1.6 to 179 mg L^{-1}; Kumata et al., 2000; Wik and Dave, 2009), and Klöckner et al. (2020) found higher concentrations of up to 480 mg g^{-1} in highway runoff sediments from Germany using TED-GC/MS and benzothiazole as markers (details on these studies comparison were shown in Table S3).

3.2. TWPs' identification via PyrGCMS

The presence of SBR and NR in the homemade reference material was confirmed by identifying VCH and limonene with matches above 95% and by identifying the supporting monomers (Table S2). Other aromatic and aliphatic compounds were identified in the reference material (Fig. S4), which can be helpful in further studies. The same markers were also identified in the selected HSW samples analyzed (example of pyrogram in Fig. 4 and Fig. S5, complete identification in Table S2), corroborating the presence of TWPs in HSW samples (Unice et al., 2012; Youn et al., 2021). Using Pyr-GC/MS allows for identifying the presence of the most common rubbers in tire production, whereas the additives could change based on the product brand and type (Gueissaz and Massonnet, 2017; Sarkissian, 2007). There are a few limitations to using Pyr-GC/MS markers, and more future developments are needed. For instance, other polymers with similar building blocks, such as acrylonitrile-butadiene-styrene (ABS) or styrene-butadiene-styrene block copolymer (SBS), often used as a bitumen modifier in asphalt, could originate from the same pyrolysis products of SBR (Airey, 2004). However, alternative use of this method has not been identified to date, and the relative magnitude of any potential positive bias is expected to be low (Unice et al., 2013).

3.3. Morphological and size analysis of TWPs via SEM

Selected filters of HSW samples and homemade reference material were analyzed via SEM/EDX to compare the aspect, morphological evaluation, preliminary elemental analysis, and size measurement (Fig. 5).

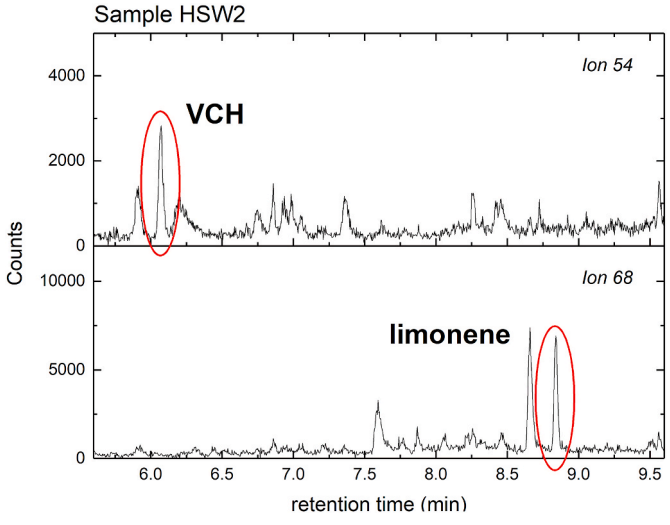

Fig. 4. Example of pyrogram with the presence of SBR and NR in the selected HSW samples analyzed confirmed by the identification of VCH and limonene.

The round and elongated shapes evaluated from the analysis via Micro-FTIR were confirmed with the morphological examination of TWPs (Fig. 5a and b, and Figs. S6a and S6b in the supplementary information, respectively). The "rolled up" shape may result from the shear and friction forces, which impact on tire tread through contact with the road surface during driving processes (Adachi and Tainosho, 2004; Baensch-Baltruschat et al., 2020; Knight et al., 2020; Kreider et al., 2010). Most of the TWPs in the samples under study were scratched, crumbled, micro-cut and fragmented, potentially due to braking or abrasion of the tire tread, whose fragments, upon contact with the road surface, were repeatedly cut, run over, and rolled by other vehicles (Fig. 5c and d for reference material and HSW sample, respectively). Besides, the repeated contact of TWPs with asphalt allowed other materials to be included in TWPs during their rolling up (Fig. 5e and f, respectively). Other parameters, e.g., tire characteristics, tread depth, construction, pressure and temperature, contact patch area, vehicle characteristics, speed, braking systems, and the road surface, can significantly affect tire wear and drive to a huge variability of the resulting TWPs'shapes (Boulter et al., 2006). Only a few smallest particles were observed as spheroidal shapes (Fig. S5c), as verified by other authors (Kim and Lee, 2018; Park et al., 2018). Hence, when elongated particles are formed, they could be broken down into smaller pieces due to shear forces driven by friction, and secondary wear processes can then smooth their surface.

The TWPs' lengths ranged from 10 μm to 100 μm in size, corroborating the average length retrieved with the imaging of the Micro-FTIR. It should be highlighted that about 40% of the total particles analyzed were less than 30-25 μm in length (see also Figs. S6c and S6d in supplementary information), as observed in the analysis via Micro-FTIR. As aforementioned, these particles can be spilled into the environment, posing a threat to different aquatic and terrestrial organisms that can eventually ingest them. Besides, the smallest black smallest particles (<1 μm) were observed with SEM analysis in HSW samples (Figs. S6a and S6b), which can probably be assimilated to nano TWPs. By comparing the result of this research with the very few studies in literature, the presence of nano TPWs (from just below 1 nm up to 300 nm, Polukarova et al., 2020) was observed in sweeping street road dust and stormwater. Besides, a case study in Austria confirmed that 6% of the TWPs released to air, soil or surface water were between 0.1 and 10 μm, while 0.3% were nanoscale below 0.1 μm (Prenner et al., 2021). However, given the sparse studies regarding nano TWPs, future investigations are needed, especially regarding their quantification. Bearing in mind that TWPs are a complex heterogenous mixture, analysis via SEM/EDX highlighted the encrustation of other fragments in most of the particles (Fig. 5e and f, and Figs. S6e and S6f). During the abrasion processes of a tire with a thermal, mechanic, and physical degradation, other organic and inorganic particles from the surrounding environment can easily roll over the road surface and be incorporated in TWPs, making their final composition even more complex and heterogenous (Sommer et al., 2018). According to the element analysis of SEM/EDX (Fig. and S8), a high abundance of carbon was observed, which is related to the rubbers present in tires; it can also be related to other materials, such as biogenic (spores, pollen) or organic matter (plant fragments, bitumen-rich particles, etc.) or to the presence of carbon black filler in some formulations, such as calcite/chalk ($CaCO_3$ filler). Other elements such as Si, Ca, and Mg (Figs. S7a, S7b, S7c) were present in crystals, phase (e.g., silica filler), or aggregates derived probably from silicates, calcite, clay, albite, or mixtures. These compounds could derive from brake wear, road wear, pavement, dust, asphalts, and construction road work. Besides, other particles mainly contain metals (e.g., Fe and Ni, Figs. S8a and S8b) probably derived from brake wear and disc deposited on the road surface and/or bitumen wear (Changarnier et al., 2018; Kovochich et al., 2021; Rausch et al., 2022; Sommer et al., 2018).

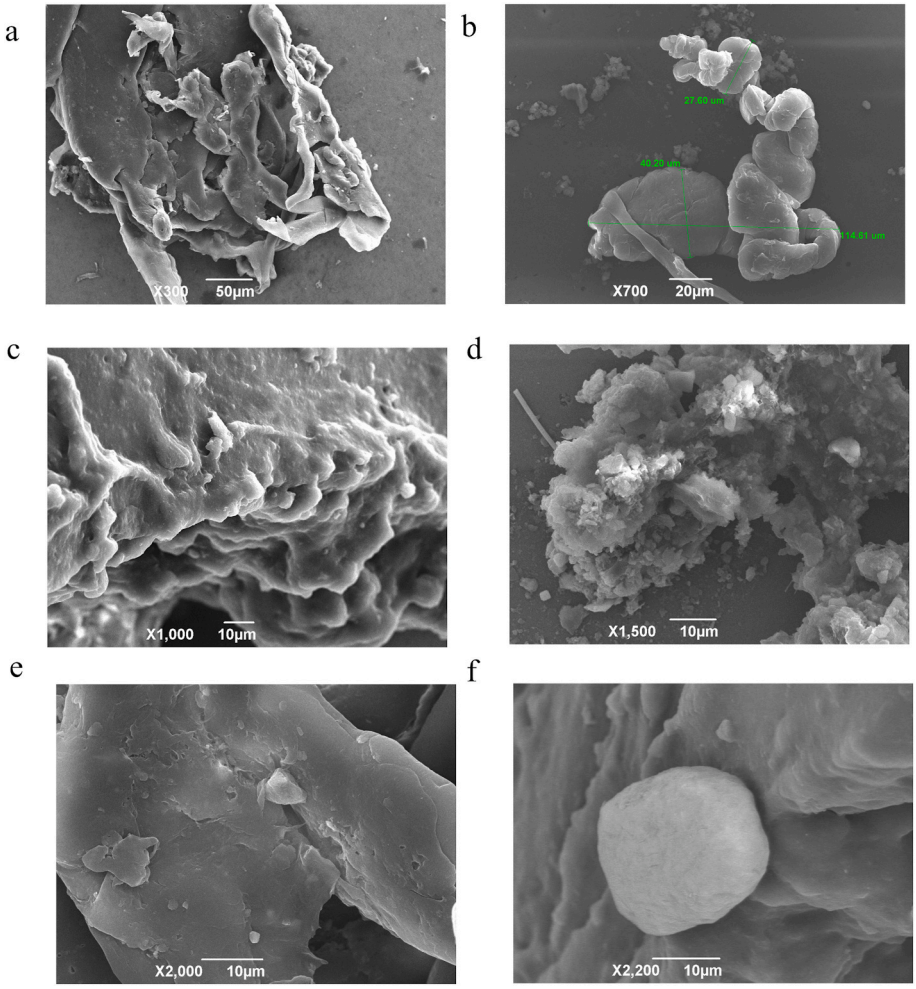

Fig. 5. Selected filters of HSW samples and homemade reference material were analyzed via SEM/EDX to compare the aspect, morphological evaluation, and size measurement. Fig. 5 a b show the "rolled up" TWPs shape result from the shear and friction forces; Fig. 5 c d show TWPs scratched, crumbled, micro-cut and fragmented, potentially due to braking or abrasion of the tire tread; Fig. 5 e f show the complex TWPs heterogeneous mixture and encrustation of other compounds in TWPs surface.

4. Conclusions

To the best of our knowledge, for the first time, different analytical techniques, i.e., FTIR-ATR, Micro-FTIR, Pyr-GC/MS, and SEM, were employed to cross-validate the chemical characterization of TWPs, together with their size and shape, in real environmental samples. Besides, employing these techniques gave complementary information about the TWPs' heterogeneous composition. TWPs were quantified via microscopic counts using the Micro-FTIR. Micro-FTIR spectra of the homemade reference material and TWPs in HSW samples were compared with each other, identified by comparison with reference libraries, and found to be cadmium, zinc, barium sulfide blend, suggesting that this spectrum may allow identification via Micro-FTIR of TWPs in other environmental matrices. The Pyr-GC/MS analysis ascertained the presence of TWPs in all the HSW samples, employing limonene and VCH as markers for identifying natural/isoprene rubbers and butadiene/styrene-butadiene rubbers, respectively, the most common rubbers used in the tire production. Besides, the chemical characterization of other additional pyrolysis products supported the identification of TWPs in environmental samples. Spheroidal and elongated shapes of TWPs, probably derived from shear and friction forces, were evaluated using Micro-FTIR and corroborated by the morphological analysis via SEM/EDX. By employing these two techniques, it has been highlighted that many of these particles are <100 µm and, once spilled in the environment, can be ingested by organisms, representing a hazard to the entire trophic net. Besides, the size range of TWPs observed via Micro-FTIR was also validated by SEM/EDX. In HSW samples, nano TWPs (<1 µm) were observed; however, future in-depth investigations are needed. The cross-validation with three different analytical techniques ascertained that TWPs are a complex mixture of various organic and inorganic components. Identifying specific markers in such a complex material is quite challenging. For this reason, various cross-validation techniques are needed to obtain robust results in identifying and quantifying TWPs and detailed information about their chemical composition in environmental samples.

Credit author statement

Beatrice Rosso: Methodology, Validation, Investigation, Data curation, Visualization, Writing – original draft; Writing – review & editing. Elena Gregoris: Methodology; Validation, Investigation, Data curation, Visualization, Resources; Writing – review & editing. Lucio Litti: Resources, Writing – review & editing; Federico Zorzi: Resources; Maurizio Fiorini: Resources,Writing – review & editing; Barbara Bravo: Resources, Writing – review & editing Carlo Barbante: Supervision, Writing – review & editing; Andrea Gambaro: Supervision, Resources, Writing – review & editing. Fabiana Corami: Conceptualization; Methodology; Validation; Formal analysis, Visualization, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgments

The authors thank Elga Lab water, High Wycombe, UK, for the pure water system used in this study. The authors thank the staff of Storm-Water Italia (SWI - Marghera-Venice) company, DTU (Technical University of Denmark), and CAV (Concessioni Autostradali Venete) of Venice, Italy for their support for technical operations, , authorizations, and accesses The authors also thank two anonymous English-speaking reviewers for carefully editing the proper English language, grammar, punctuation, spelling, and style. The authors would like to thank the mechanic that kindly provided the tire dust to produce the homemade reference materials. The authors thank the editor Prof. Eddy Zeng and three anonymous reviewers for their comments and suggestion that helped improve the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121511.

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