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Tyre and road wear particles from source to sea

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Abstract

Tyre and road wear particles (TRWP) are an important microplastics contributor to the environment, although direct observations along suggested pathways are virtually absent. There are concerns for both human health and ecosystems from TRWP exposure and leached chemicals. Due to great analytical challenges in detection and characterization, almost nothing is known about the physicochemical characteristics, occurrence, fate and transport of TRWP in the environment. Diverse tyre types exist for different seasons and vehicle profiles, and their formulations are undisclosed proprietary information.

Here we show TRWP dispersion in marine sediments, and a direct link between tyre formulation, tread hardness and TRWP emissions. Softer tyres with higher natural rubber and carbon black content generate higher particle wear. Sediment TRWP dominates the microplastics assemblage close to the city, while showing a much more steeply reducing concentration gradient with distance from the source, suggesting different transport behaviour compared to lower density microplastics. This implies that urbanized coastal ecosystems are impacted by the accumulating TRWP, with consequences for sediment ecosystems.

One-sentence summary

Tyre and road wear particles—The link between tyre formulation, emissions and their spread in the marine environment.

Keywords Tyre and road wear particles, Microplastics, Sediment, Road simulator, Microscopy, Spectroscopy, Particle emission

Introduction

Microplastic particles are recognised as a global threat because of their ubiquitous distribution in water bodies all around the world [1-3], and their potential health impacts on animals, including humans, due to the many potential exposure pathways and risks [4-6]. Microplastics comprise a wide range of materials, without a

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standardised definition, but in the wider scope including particles of conventional thermoplastics (i.e., from common household plastics), polymer composites, rubbers, and elastomers, and synthetic fibres [7, 8]. Most critical reviews, often based on material flow modelling [9–11] conclude that the three main microplastic sources are tyre and road wear particles (TRWP), fibres and paint. Recent estimates suggest that emissions from tyres represent 5–10% of the worldwide dominating sources of microplastics [12]. Studies have shown that exposure to tyre particles, and to their chemical leachates, can have detrimental effects on aquatic organisms, [13–17]. Tyres are optimised for driving safety, rolling resistance, longevity, and noise, but chemical and particle emissions are



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poorly studied and not yet included in regulations or sustainability labelling. In order to design low particle emission tyres relation between composition, formulation and particle wear are needed.

Environmental TRWP analyses are scarce and compared to other microplastics there is disproportionately little known about their properties, fate or impacts in water bodies, mainly due to analytical challenges [18–21]. Therefor an aim was to develop a combination of analytical methods for identification, physiochemical characteristic in order to determine occurrence, fate and transport of TRWP in the environment. A secondary aim was to address the knowledge gap in relation between tyre tread composition, wear processes and TRWP characteristics. This was addressed through controlled tyre wear experiments in a road simulator infrastructure, supported by advanced multimethod analytical assessments of both tyres and generated particles.

Result and discussion

(A)

Distribution and identification of TRWP—from city to sea

TRWP are formed from friction between the tyre and the road, and are transported to aquatic environments via runoff [20] and air [22]. On release into coastal waters, TRWP residence time in the suspended state,

TRWP distribution

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versus sedimentation behaviour, is likely size and density dependent, but their distribution has previously not been shown. In this study, we have extracted and analysed TRWP and other microplastics, from surface sediments in a sill fjord, i.e., an enclosed bay of the sea, characterised by a stagnant basin. A city (pop. 50.000), associated with diverse potential sources of particulate pollution (traffic, residential and business areas, municipal wastewater plant effluent, commercial and yacht harbour, Fig. 1A), surrounds the fjord head. TRWP abundance and distribution was measured for the first time in the marine environment, and found ubiquitous in sampled sediments, dominating the overall microplastic, while, in contrast to other microplastic particles (Fig. 1B), not spreading very far from the city.

This finding indicated that the global coastal ecosystems, which are recipients of a large part of the world vehicle fleet (40% of world population within 100 km from the sea) [23], will be especially impacted by accumulated TRWP compared to other microplastics (Fig. S1). These sediment ecosystems are already negatively impaired by many other pollutants and anthropogenic stressors, with the consequence that TRWP exposure are adding to the other ecological risk factors. TRWP were identified by visual-tactile probing [24, 25] allowing

(B) Proportion between TRWP and plastic particles

Uddevalla TRWP **Plastic polymers** 20000 10000 25000 15000 10000 5000 5000 Number of particles per kg/DS Particles/kg/DS Blank 1: 0 TRWP 1000 Blank 2: 0 TRWP Depth (meters) Blank 3: 0 TRWP 5000 0 -50 Blank 4: 1 TRWP (30 particles/kg/DS) 10000 Blank 5: 0 TRWP 5000 5000

Number of particles per kg/DS

Fig. 1 (**A**) Geographical distribution of TRWP in marine sediments. Byfjord, the innermost basin in the fjord system between the island of Orust and the mainland, and the city of Uddevalla on the Swedish west coast (58,35359° N, 11,89502° E). Islands protect the system from the wind-driven influx of marine plastics from the wider North Sea, enabling local sources and transport in the area to be studied. Sampled concentrations of TRWP larger than 50 μ m are shown by circles with area proportional to abundance. Procedural blanks (*n* = 5) are shown for comparison where only one black elastomer were found in one sample (Blank 4) (Fig. S4). (**B**) The occurrence of TRWP in relation to other identified polymeric microplastic particles, are shown for the different groups of sample stations away from the city

elastomers to be distinguished from other black particles such as charcoal and condensed oil. The majority of TRWP, were between 50 and 100 μ m and only 0.5% of the identified particles were larger than > 300 μ m (Figs. S2 and S3). Until recently, spectroscopic analysis of TRWP composition was considered impossible, but by combining new pre-treatment techniques with FTIR, an identifiable signature was obtained from some of the probed environmental TRWP (Fig. 4E).

Physicochemical properties of tyres

(A)

Tyre treads are composed of natural (plant-based) and synthetic rubbers (mainly polybutadiene (PBD), and a styrene-butadiene copolymer (SBR)), carbon black, inorganic fillers, such as silica (SiO₂), zinc oxide (ZnO), elemental sulfur (S), as well as oils and various additives [26]. Tyre formulations vary with brands and specific use, including hundreds of different recipes and are not disclosed publicly. To understand the relation between formulation, composition and physicochemical properties of the tyre tread, a comprehensive chemical and physicochemical characterisation was conducted of the tested tyres (Fig. 2).

Thermal gravimetric analysis (TGA) measures pyrolytic mass-loss as a function of temperature. Coupling the instrument to a Fourier-transform infrared spectrometer (TGA-FTIR) enabled identification of products in the outgoing gas stream, and measurement of natural and synthetic rubber, carbon black, and inorganic filler proportions (Fig. 2A and E). Pyrolysis Gas Chromatography/ Mass Spectrometry (py-GCMS) provided complementary polyisoprene (PIP) and polybutadiene (PBD) decomposition data (Fig. 2A). PIP trend from the py-GCMS follows well the natural rubber (NR) results from TGA, while PBD, which is only one of the synthetic elastomers used in the tyres recipe, does not explain the TGA synthetic rubber results. This could be explained by the SBR content indicated in the summer tyres that are not guantified in the py-GCMS. On the other hand, TGA-FTIR provides qualitative identification of styrene in the synthetic rubber peaks of summer tyres indicating SBR content (Fig. S2).

For FTIR analysis, tyre tread samples were cut in thin slices using a cryo ultramicrotome and further spread in a diamond compression cell (Fig. 2B). Spectra from summer and winter tyres showed the same peaks, within each type, independently of brands (Fig. 2B). Thus, FTIR is able to separate summer from winter tyres, but not brands within each tyre type. Leads et al. [27], analysed black particles (\geq 500 µm) by ATR-FTIR in the

Winter tires



(E)

Fig. 2 Characteristics of tyre treads from summer, studless and studded winter tyres. (A) The proportion of natural and synthetic rubber from tyres measured with TGA-FTIR (diagram) and with Py-GCMS (pie charts). (B) FTIR spectra of tyre treads. (C) Two polymeric phases in tyre tread revealed with SEM using the EsB detector. (D) SEM–EDS with elemental constitution of tyre treads and (E) Polymeric content measured by TGA and Py-GCMS as a function of hardness (shore value). Tyre photos from http://www.pirelli.com

Charleston Harbor estuary (USA). One of these particles was positively identified as an acrylonitrile/butadiene/styrene compound. The other particles generated downward sloping spectra that were consistent with the spectra of butyl rubber containing carbon black. All these results are consistent with the polymer composition of tyres. Moreover, they described that carbon black is highly absorptive and scatters IR light which results in a distinctive ATR spectrum that slopes downward to the right (when displayed as percent (%) transmittance). From these results the particles were identified as TWP.

The polymer content as a function of tyre hardness, turned out to be a key performance parameter, since harder tyres (summer tyres) were composed primarily of synthetic rubber and showed little variation in the rubber blend (natural and synthetic elastomers) between brands. Furthermore, the composition of winter tyres varied considerably between brands and showed that they can have a blend dominated by both natural and synthetic rubber. Furthermore, the difference between tyre brands of the same tyre type is larger than within a brand, comparing studless with studded winter tyres. In the case of winter tyres, the content of carbon black is high compared to the summer tyres, probably because the high proportion of natural rubber requires structural support, which could be improved by the insertion of reinforcing loads as the carbon black [28].

Further, scanning electron microscopy (SEM) with an energy selective backscattered detector (EsB), for the first time applied to tyre material, reveals at least two phases probably formed by different elastomers (Fig. 2C). Usually, the higher component fraction becomes the continuous matrix, and the lower component gives rise to dispersed phases [29]. As described, the amount of synthetic rubber in the tyres is higher than NR. Thus, NR are the spherical domains dispersed in the synthetic elastomer matrix.

A key process in the tyre production is the vulcanisation that cross-link the rubber chains, forming a threedimensional network, which improves the elasticity and tensile strength. The most commonly used chemical activator for vulcanisation is ZnO [30]. However, environmental concerns have led to attempts to reduce the use of zinc by replacing it with ZnO nanoparticles doped in different surfaces as SiO₂ and calcium carbonate (CaCO₃) [31, 32].

Different types of fillers are used to reduce the rolling resistance of the tyres. However, the fillers, both in their size and amount, differ between types and brands but $CaCO_3$ and SiO_2 are main components [32]. Figure 2D shows SEM-Energy Dispersive X-Ray (EDS) images of a tyre tread with the mapping of different elements found in the rubbery matrix of tyres.

TGA data also provide a pyrolytic residual, which is correlated to tyre tread inorganic sum from EDS. The residuals were highest in the summer tyres, showing a correlation with hardness and an inverse trend of the carbon black peak (Fig. 2E). The multimethod characterisation on one hand shows the complexity of tyre formulations, but also reveals that there is systematics in the composition between tyre types and its relation to rubber hardness.

Road simulated particles

The VTI road simulator was used to generate realistic TRWP from summer and winter tyres (Kumho, Pirelli and Nokian) for physical chemical characterisation and emission comparisons. Road simulator dust was collected using a specially built sampling hood (Fig. 3A). Emission rates were estimated from image segmentation measurements (Fig. 3B) and py-GCMS. Py-GCMS-based calculations indicated lower TRWP emissions than image analysis-based calculations (Fig. 3C). Both methods are associated with specific uncertainties and assumptions, one based on individual particles measurements and the other on bulk polymer mass analysis. However, both show a relatively higher emission rate for winter tyres. Harder rubber, characteristic of summer tyres, was associated with lower tyre wear, suggesting that, where winter tyres are commonly used, TRWP emissions are likely to be higher in winter. Summer TRWP are likely to be associated with higher concentrations of metals and oxides, indicated by the higher TGA-residues in Fig. 2E.

Physicochemical properties of TRWP

TRWP are generally described as elongated particles encrusted with minerals from the road surface [19]. TRWP generated in the road simulator (and with bitumen removed), as well as the particles found in marine sediments, included cigar-shaped and more irregular, knobbly, or twisted, elongate forms, (Fig. 4A). TRWP generated by studded tyres tended to be less elongated. From an imaged cross-section, it is possible to verify that mineral particles are not only present on the surface, but also within the entire TRWP volume (Fig. 4B and C). Kovochich et al. [33, 34] analysis the particles surface and identified, basically, the same elements (including S, Zn/ Na, Si, K, Mg, Ca, and Al) consistent with the chemical composition of tread material. TRWP from the tested tyres have similar size distributions (those generated by studded tyres were generally slightly smaller), and the majority were smaller than 200 μ m (Fig. 4D).

There are still many obstacles to overcome for a quantitative chemical analysis in complex environmental samples. Variable levels of mineral encrustation can mask the polymeric matrix, making it difficult to distinguish



Fig. 3 Generation and sampling of particles from road simulator. Aliquots of road simulator dust were cleaned with xylene prior to light and electron microscopy (A) Road simulator with sampling hood mounted on one wheel. Road simulator was run at 50 km/h for four hours with each tyre set. (B) Analysis scheme for image segmentation (ImageJ) analysis to estimate particle volume and tyre mass. (C) Emissions calculated from Py-GCMS and microscopy measurements

TRWP from natural particles, based on elemental composition. Therefore, sample pre-treatment to dissolve or dissociate these, may be key to SEM–EDS characterisation. Promising initial results were achieved in our laboratory using a mixed acid pre-treatment; a decrease was observed in the Si, aluminium and oxygen concentrations, and a corresponding increase in the carbon concentration, related to the increased contribution of the elastomeric matrix to the X-ray signal (Fig. 4B). Thus, although TRWP carry certain differences in relation to their original matrix, it is necessary to monitor the rubber-polymer-blend composition in the particles, because it remains similar to the original elastomeric composition.

After cleaning the particles with an acid treatment the TRWP were cut in ultra-thin sections, with a diamond knife, and analysed by FTIR in a diamond compression cell. The spectra from road simulator generated particles and corresponding tyre treads are very similar except for peak 1727 and 1538 cm⁻¹ (stretching vibration of a methyl-assisted conjugated double bond ($-(CH=CH)_n$ -, where n > 6 from both NR and SBR) (Fig. 4E) [35]. Moreover, the spectra from environmental TRWP show the band at 1375 cm⁻¹, that are typical for PIP and natural rubbers, and the bands at 740 and 966 cm⁻¹ that are

characteristic for PBD rubber [36]. Thus, these bands prove the existence of the tyre rubber components in the probed environmental particles.

Implications

The consistent trend across tested tyre brands for relation between chemical formulation and rubber hardness, on one hand, and the observation that the softer winter tyres release more TRWP per driven distance (at the same tested temperatures), reveal that there are opportunities to optimize not only for driving safety, noise and rolling resistance but also for particle emission characteristics. The observed difference in emissions between tyre types suggest that industry efforts to create wear-reducing formulations, as well as consumer driven change, would have largest potential of emission reduction from winter tyres. Rolling resistance, wet friction and tread wear are the three performance components in the "magic triangle" [37, 38]. These three properties are often interrelated so that improving one or two will often deteriorate the other properties, making optimisations for all difficult. However, recent studies indicate possibilities to manufacture low-wearing tyres with good friction and rolling resistance properties by new additives and polymer developments [39–41].



Fig. 4 Physiochemical properties of TRWP (A) Light microscopy images of TRWP generated in the road simulator and extracted from marine surface sediments. (B) left top shows a light microscope image of a road simulator generated particle, left bottom shows the same particle after cleaning and the right shows a SEM image of the same particle after cleaning. (C) SEM–EDS of particle cross section (D) Shape and size distribution statistics of road simulator generated TRWP (green), tyre tread (black) and a particle extracted from marine surface sediment (blue)

The different rubber mixtures used in summer and winter tyres are related to optimisation of the tyre properties under prevailing road conditions, focusing on grip, driving experience and fuel consumption. These aspects are partly covered by today's European tyre labelling [42], which incorporate rolling resistance, wet friction and noise. On the other hand, tyre wear is not yet included in the labelling, which together with raised public awareness is a prerequisite for consumer driven change. Finally, even though TRWP emissions should be lowered by optimised tyre formulations, tyre air pressure, speed limits, driving behaviour, there will be an unavoidable TRWP emission. Thus, better stormwater management to avoid untreated flow of road runoff into the environment would both reduce TRWP dispersion and other traffic related contaminants.

Analytical developments and harmonization of methods for physicochemical characterization and environmental detection is a prerequisite for both improved tyre formulations and better environmental regulation and management. Here we have shown that FTIR and SEM–EDX after customized sample preparation show potential of polymeric and elemental fingerprinting on single particle level, but need further developments. The complementary combination of py-GCMS and microscopy show promising results and implies that combining techniques can be successful tools in the future such as correlative microscopy in combination with py-GCMS.

Conclusions

By employing a multimethod comprehensive physicochemical characterization on TRWP both generated from a realistic road simulator as well as from the environment, we describe consistent chemical characteristics of the particles and the tyre rubber compositions, within the complex formulations, and additionally that the TRWP have incorporated significant amounts of road mineral microparticles. TRWP identified in the marine environment can be chemically validated by resemblance with both tyre tread material and with TRWP generated in the road simulator. The marine sediment distribution study shows that TRWP disperse into the marine environment, a dominating microplastic abundance in urban ecosystem, but are not transported very far from the sources compared to other lighter microplastics (Fig. S1), which in combination to recently revealed environmental hazard and impact from tyre associated chemicals,

emphasize ecological risk to sediment dwelling organism close to high traffic density areas. However, the full environmental impacts of these findings need to be further studied.

Materials and methods

Environmental particles

Sediment samples were collected with a Gemini corer on the 12–14 of September 2017. The top two centimetres from three to four cores were pooled with a metal spoon and transferred to a glass bottle until a volume of 200 mL were obtained. The samples were stored in 8 °C until further processed.

The samples were weighed and a separate subsample of 5 mL were taken to determine the ratio of wet weight to dry weight by drying the sediment in 105 °C for 24 h. The sediments were pre-treated with inorganic oxidative and dispersive chemicals, (0.67 mol/L sodium hypochlorite (NaClO), 0.45 mol/L potassium hydroxide (KOH) and 0.022 mol/L sodium pyrophosphate (Na₄P₂O₇)) [43].

Approximately 400 mL of the degradation agent were added to each glass bottles with sediments and incubated in room temperature for one hour on an oscillating stirring table (New Brunswick Scientific, Innova 40) at 160 rpm. After the treatment, the sediments were washed with Milli-Q water followed by shaking and centrifugation (Eppendorf Centrifuge 5804R) for 30 min at 1000 rpm. The washing procedure was repeated three times and the supernatant was removed and filtrated through a 50 µm mesh between repetitions and new Milli-Q were added. After centrifugation the sediment were moved back to the glass jars with the addition of $ZnCl_2$ (density of 1.8 g/cm³) which was gently mixed before it was introduced to the Kristineberg microplastic sediment separator (KMSS) sediment tower [43]. The standpipe part of the tower was mounted, and the rotor, positioned in the bottom of the tower, was turned on. The ZnCl2 was introduced through the bottom valve and filled to 85% of the volume of the tower. Three hours later. the rotor was turned off, and the sediment was allowed to settle. After 12 h of settling, the dividing chamber was mounted on top of the standpipe, and the tower was filled with ZnCl2. When filled, the ball valve was closed, the liquid level lowered, and the dividing chamber was removed. Next, the dividing chamber was turned upside down, and the solution was filtrated through three PA filters with mesh sizes 300 μ m, 100 μ m, and 50 μ m. After filtration, the filters were rinsed with Milli-Q water to remove salt crystals.

Particles on 300 and 100 μ m membranes were first visual classified according to the protocol Karlsson et al., [24], photographed under a stereomicroscope (Leica M205C software Leica Application Suite V4.8) and

chemical identified with FTIR (Thermo Scientific Nicolet iN10, software OMNIC Picta). For the FTIR measurements, reflection as collection mode, cooled detector, collection time at 1:30 min, giving 256 scans corrected against 256 background scans and high spectral resolution. All particles collected on the 50 μ m membranes, were moved to Pt coated membranes and analysed with FTIR.

Five blank samples without any sediment were processed. All blanks were treated as the sediment samples, from cleaning the bottles before sampling, in the field, during storage, treatment, separation, and analysis.

Road simulator

The VTI road simulator [44] was used to generate TRWP. The simulator rotates four wheels on a circular road pavement track at speeds up to 70 km/h. Each wheel has an electric motor, i.e. the machine rotation is propelled by the wheels, not by a central vertical axle rotation. The simulator was used to wear sets of summer and winter (studded and studless) tyres to study differences in wear emissions and properties of generated particles. The pavement used was a stone mastic asphalt with a maximum stone size of 16 mm (SMA16) with two main aggregate materials (granite and porphyry). One of the wheels was equipped with a sampling hood, designed to sample TRWP behind the tyre (Fig. 3). In total, 12 sets of new tyres were used, four brands each of summer, studless winter and studded winter tyres. For analyses in this study, a subset of these were used. Each tyre type was run-in according to a type-specific procedure. Sampling was performed at a constant speed of 50 km/h during four hours, amounting to 200 km of driving. The start temperature (room and tyre) at each test was approximately 10 °C. Due to friction heat, temperatures in tyres, pavement and room slowly increased during the test and typically, room and pavement temperatures had increased by 5° C and the tyres by 10 °C at the end of the test. The hardness of the rubber was measured at room temperature (20 °C) using a hardness tester (HPE II, Bareiss Prüfgerätebau GmbH). Road simulator dust samples were cleaned (to remove bitumen) by 30 s of gentle agitation (slow rotation in a vertical plane) in xylenes, as a first step prior to all types of analysis.

Tyres and particles

Thermogravimetric (TGA) analyses were performed on a Mettler Toledo TGA1 connected to an FTIR (Thermo Scientific Nicolet iS50) via a Thermo Scientific TGA-IR Module. About 10–15 mg of sample from each tyre was heated from room temperature to 560 °C under nitrogen atmosphere at a heating rate of 10 °C/min to monitor the weight loss of oil and elastomers. At 560 °C, the gas flow was changed to an oxygen atmosphere and the samples were heated from 560 to 800 °C to observe the carbon black degradation.

The cryo fractured surfaces of the tyres were observed, without dyeing or phase extraction, using the scanning electron microscopy (SEM), Zeiss field emission SEM Gemini 300, with an energy selective backscattered detector (EsB) at an acceleration rate of 1 kV. The Energy selective Backscattered (EsB) Detector is suitable for composition contrast. In this case, the most influent parameters are brightness/contrast adjustment, Ep value, EsB grid voltage, and working distance (WD).

The tyres and the TRWP were cut in ultrathin sections and surfaces, using a diamond knife, at -140 °C in a Leica EM FC6 cryo-ultramicrotome. The samples were analysed by SEM–EDS (Zeiss field emission SEM Gemini 300 with the energy-dispersive X-ray spectrometer from Bruker) in VP mode (30 Pa) using the BSD detector and EHT 12 kV. Subsequently, these samples were used for FTIR analysis and analysed using a diamond compression cell and transmission mode (cooled detector, high resolution 45 s, background spectra obtained before sample).

Pyrolysis GCMS (py-GCMS)

Tyre-tread samples were prepared for py-GCMS from nine tyre models. Each was cut from within the tread with a steel blade. Previously exposed surfaces of the tread were not included. In order to access the measurements availability one sample were analysed in triplicates. Kumho winter studless tyre. Two studded and two summer tyre solvent-cleaned road simulator dust samples were prepared by size fractionation on 26, 63 and 125 µm steel meshes. Each fraction was rinsed into precleaned bottles with milli-q water. One road simulator dust sample (Pirelli studless winter tyre) was prepared, and submitted for py-GCMS analysis, in triplicate. The remaining three samples (Pirelli summer, Nokian summer and Nokian studless road simulator dusts) were prepared in triplicate, but the triplicates within each sample were pooled before analysis. Samples were sent for py-GCMS analysis at Eurofins, Bergen. Cut tyre-tread samples (ranging from 113-680 µg) were placed directly in the sample cups. Sampled TRWP both as bulk powder and as size fractionated (26–63, 63–125 and >125 μ m) material were transferred from water suspensions to silver membrane filters (1.2 µm). Sample containers were triple rinsed with (0.2 µm) filtered milli-q water. Filtration funnels were thoroughly rinsed after filtration to ensure the collection of all material on the filter. The filters were placed in a glass petri dish (previously sterilised at 550 °C for 2 h) and stored in a desiccator until sample cup preparation. For the particulate samples, sample cups were prepared by inserting the filters into the sample cup. Sterile quartz wool was placed on top of both types of samples to keep material in place during analysis, and 10µL tetramethylammonium hydroxide (25%, in aqueous solution) was added to each cup. The sample run was programmed, and the sample cups were added to the autosampler. Thermal decomposition was controlled in a Frontier Laboratories EGA/PY-3030D pyrolysis system. Molecular fragments, carried in helium (1.0 mL/minute) along a Frontier Ultra Alloy 5 UA5-30 M-0.25F+Vent free column, were separated using an Agilent Technologies 6890N chromatograph. Ion mass-to-charge ratio was measured with an Agilent Technologies MSD 5975 detector. Dipentene (m/z 93) were used for polyisoprene and 4-vinylcyclohexene (m/z 79) were used for polybutadiene. SBR was only qualitatively detected in samples for the pyrolyzates 4-phenylcyclohexene (m/z 78, 104, 158). SBR also contributes to the amount of polybutadiene quantified as they both give response to 4-vinylcyclohexene. Polyisoprene and polybutadiene were guantified in relation to pure polyisoprene and polybutadiene standards (1–150 µg). The limits of rubber polymer quantification (LOQ) were 5 μ g for the particulate samples and 1 μ g for the cut tyre-tread samples. General QA/QC routines are empty cups between samples in order to find any potential carry-over between samples, and each sequence starts and ends with an empty cup. Quality controls are run for each sequence with known amounts of polymers to see if results are acceptable. No empty cups between the samples had any positive signals for polymers.

Microscopy image segmentation analysis using ImageJ script

In order to quantitatively determine the abundance and physical characteristics of collected particles wholefilter analysis in light microscopy was carried out. For this whole-filter image analysis, aliquots of 4 to 13 mg of each road simulator dust sample were solvent-cleaned and wet-sieved on stacked (26 µm and 100 µm) steel meshes. Both size fractions were filtered onto 47 mm alumina filters, Whatman Anodisks (if needed, to avoid overcrowding, fractions were spread over several Anodisks). Separation into 26 and 100 μm mesh fractions permitted use of fraction-appropriate objective magnifications (5×for the 100 μ m mesh-fraction, 10×for the 26 µm mesh-fraction). For mosaics covering 47 mm Anodisks, conversion of the original CZI format to an 8-bit grayscale, 27104×27040-pixel.TIF file, provided adequate resolution for smaller (20–100 μ m) particles. Prior to image analysis, ImageJ was used to paint over dark-coloured particles that did not appear to be TRWP (primarily fibres and mica-like crystals). A simple macro (SI) enabled batch analysis of same-scaled mosaics with

the open-source software Fiji (an ImageJ package), and increased measurement repeatability.

TRWP aspect-ratio was calculated from Feret's diameter / minimum calliper diameter (minFeret's). Based on observations of TRWP, a 3D ellipse was considered an appropriate geometric model for estimating particle volume from individual particle dimensions (Fig. 3B). The model used for this study incorporates measured particle Feret's diameter, minimum calliper diameter (minFeret's), and particle silhouette-area. The major horizontal axis of the projected 3D ellipse (x) is the measured Feret's diameter. The minor horizontal axis (y) is that of a projected 2D ellipse with a major axis equal to the particle Feret's diameter, and an area equal to the particle silhouettearea. A particle height factor was derived from a mean (n=40) relationship (particle height/minFeret's) between TRWP height and particle minFeret's. This factor, applied to all particles, was 0.72 minFeret's, $V = 4/3\pi (rx \cdot ry \cdot rz)$ where rx is the particle Feret's diameter/2, ry, is particle silhouette area/ $(\pi \cdot (particle \ Feret's \ diameter/2))$ and rzis (0.72 particle minFeret's)/2.

Emission estimates

Py-GCMS analysis on xylene treated road dust material were compared with tyre tread samples with respect to both PIP and PBD content for Pirelli and Nokian summer and studless tyres.

Microscopy base image segmentation analysis (Pirelli, Nokian and Kumho summer and studless tyres) were used to measure particle size and geometry with a shape model derived for TRWP. The effect of inclusion of minerals were corrected for based on observed literature density values [12, 45–47]. There may be more uncertainties in the volume overestimation by the ellipse-based model, while the small sample sizes dictated by py-GCMS may have been influenced by the presence or absence of a few very large particles due to incorporation of road-derived material.

SEM-EDS analysis

TRWP were cut in ultrathin sections, using a diamond knife, at -140 °C in a Leica EM FC6 cryo-ultramicrotome to subsequent SEM–EDS and FTIR analysis (as described before).

To remove the excess of minerals in the tyre wear particles an acid treatment protocol containing 20% of hydrofluoric acid (48–50%) and 10% hydrochloric acid (37%) was applied. The platinum-coated polycarbonate filter membrane has been carefully inserted into a filled polypropylene In-Line Filter Holder from Merck and exposed to the acid solution inside the system. The particles were kept 4 h in the acid solution, at room temperature (20 $^{\circ}$ C), and then filtered with Milli-Q water.

The workflow includes the light microscope (Zeiss AxioImager) and the SEM–EDS (Zeiss field emission SEM Gemini 300 with the energy-dispersive X-ray spectrometer from Bruker) in VP mode (30 Pa) using the BSD detector and EHT 12 kV.

Abbreviations

CaCO ₃	Calcium carbonate
EDS	Energy Dispersive X-Ray
EsB	Energy selective backscattered detector
FTIR	Fourier-transform infrared spectroscopy
KMSS	Kristineberg microplastic sediment separator
KOH	Potassium hydroxide
NaClO	Sodium hypochlorite
Na ₄ P ₂ O ₇	Sodium pyrophosphate
PBD	Polybutadiene
PIP	Polyisoprene
Py-GCMS	Pyrolosis Gas Chromatography/Mass Spectrometer
S	Sulfur
SBR	Styrene-butadiene copolymer
SEM	Scanning electron microscopy
SiO ₂	Silica
TGA	Thermal gravimetric analysis
TRWP	Tyre and road wear particles
ZnCl ₂	Zinc chloride
ZnO	Zink oxide

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s43591-023-00060-8.

Additional file 1: Fig. S1. Geographical distribution of lower density microplastics in marine sediments. Byfjord, the innermost basin in the fjord system between the island of Orust and the mainland, and the town of Uddevalla on the Swedish west coast (58,35359° N, 11,89502° E). Islands protect the system from the wind-driven influx of marine plastics from the wider North Sea, enabling local sources and transport in the area to be studied. Surface sediments were pre-treated with digestive agents (1) to degrade organic matter, and a high-density liquid (zinc chloride solution $(ZnCl_2)$ at 1.8 g/cm³) was used to separate the mineral grains from the anthropogenic particles. Sampled concentrations of lower density microplastics larger than 50 µm are shown by circles with area proportional to abundance. Procedural blanks (n=5) are shown for comparison. Fig. S2. Number of identified particles (plastics (yellow) and TRWP (red) at the different sites according to their names in figure S3. (A) DTGA curves of the tires; (B) FTIR spectra made from tire pyrolysis products. Fig. S3. Samples station names. Fig. S4. Blank samples. Number of particles (plastics (yellow) and TRWP (red) per kg/DS found in the blank samples, no TRWP were found in Blank 1, 2, 3 and 5.

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Authors' contributions

Conceptualization: All. Investigation: KM, JAL, TW, IJ, EE, MH. Visualization: KM, JAL, MH. Funding acquisition: KM, YAS, MG, MH. Supervision: KM, JAL, YAS, MG, MH. Writing – original draft: KM, JAL, MH. Writing – review & editing: All authors. The author(s) read and approved the final manuscript.

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Availability of data and materials

All data are available in the main text or the supplementary materials.

Declarations

Ethics approval and consent to participate 'Not applicable'.

Consent for publication

The authors consent publication of the manuscript.

Competing interests

The authors declare no competing interests.

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