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Sorption of organic substances to tire wear materials: similarities and differences with other types of microplastic

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Abstract

Tire materials are a significant proportion of the (micro)plastics in the environment that until today have been clearly overlooked. These materials are released into the environment, either unintentionally as an abrasion product from tire wear, that reaches the environment via road runoff, or intentionally as, for example, shredded "tire crumble rubber" used as filling material for playgrounds. Although there are a few estimates available the amount of tire-wear material to be found in aquatic environments, investigations on the fate tire materials and especially their interaction with organic substances are missing. Although the sorption processes associated with the complex constituents of tires are an important aspect of any environmental risk assessment for tire-wear materials, they have yet to be thoroughly investigated. In this review we elucidate the sorption properties of the polymeric rubbers and carbon black that form the main components of tires, within the context of current microplastic research.

Highlights

- Tire materials show different sorption properties from other microplastics
- Sorption to tire-wear rubber is expected to differ from sorption to tire crumb rubber
- Molecular interactions involving composite tire-wear materials remain poorly understood
- The aging of tire-wear materials and hydrochemistry have important influences on sorption

Keywords

adsorption, partitioning, black carbon, tire wear, tire crumb, rubber, environmental risk assessment

Abbreviations

BC	black carbon
CB	carbon black
DDT	dichlorodiphenyltrichloroethane
HOCs	hydrophobic organic compounds
NOM	natural organic matter
NR	natural rubber
LSER	linear solvation energy relationship
PP	polypropylene
ppLFER	poly-parameter linear free energy relationship
PAH	polycyclic aromatic hydrocarbon
PE	polyethylene
PBD	polybutadiene
PCBs	polychlorinated biphenyls
PS	polystyrene
PVC	polyvinyl chloide
$\log K_{ow}$	logarithmic octanol-water partitioning constant
SBR	styrene butadiene rubber
STXM	scanning transmission X-ray microscopy
T_g	glass transition temperature
TWP	tire wear particle
TCR	tire crumb rubber

1 Introduction

Plastics are ubiquitous in everyday life and their use in consumer products as well as in industry makes them one of the most common and widely used products. Although elastomers meet the International Organization for Standardization’s description of plastics (ISO; “plastic is a material which contains as an essential ingredient a high polymer and which, at some stage in its processing into finished products, can be shaped by flow”)[1], they are not considered as plastics in the ISO definition because of their reversible elastic deformation. As a result, they rarely feature in statistics concerning the quantity of plastic in the environment. However, tire materials are elastomers that are commonly found in the environment. If classified as microplastics, which is still under discussion, tire materials would account for up to 70% of the microplastic release into the natural environment.[2]

Tires generally consist largely (40-60%) of a complex mixture of polymers, mostly styrene butadiene rubber (SBR) but also polybutadiene (PBD) and natural rubber (NR). These elastomers are compounded with 20-35% carbon black (CB) as a reinforcing agent, 15-20% oils as softeners and extenders, and 1-2% vulcanization chemicals (e.g., zinc oxide and sulphur).[3] Tire materials are typically introduced into the environment through two different pathways (**Figure 1**): firstly as tire wear particle (TWP), an abrasion product that is washed off roads in runoff and makes up 5-30% of non-exhaust emissions from traffic,[4] and secondly, recycled and shredded tires known as “tire crumb rubber” (TCR), which is popular as a construction material and is also widely distributed through its use in artificial reefs,[5] as embankment fill material,[6] on turf fields, and as fill material for playgrounds.[7] Tire materials have complex compositions and are known to leach toxic substances such as zink[8,9] and PAHs[10]. Tire materials, and in particular TCR, have also been shown to have high sorption capacities for organic molecules and have therefore been proposed as a cost-effective alternative for removing organic pollutants from water.[11,12] However, to date our understanding of mechanisms controlling interactions between organic molecules and tire materials in the environment, and of how the complex composition of tires influences these interactions, remains quite limited.

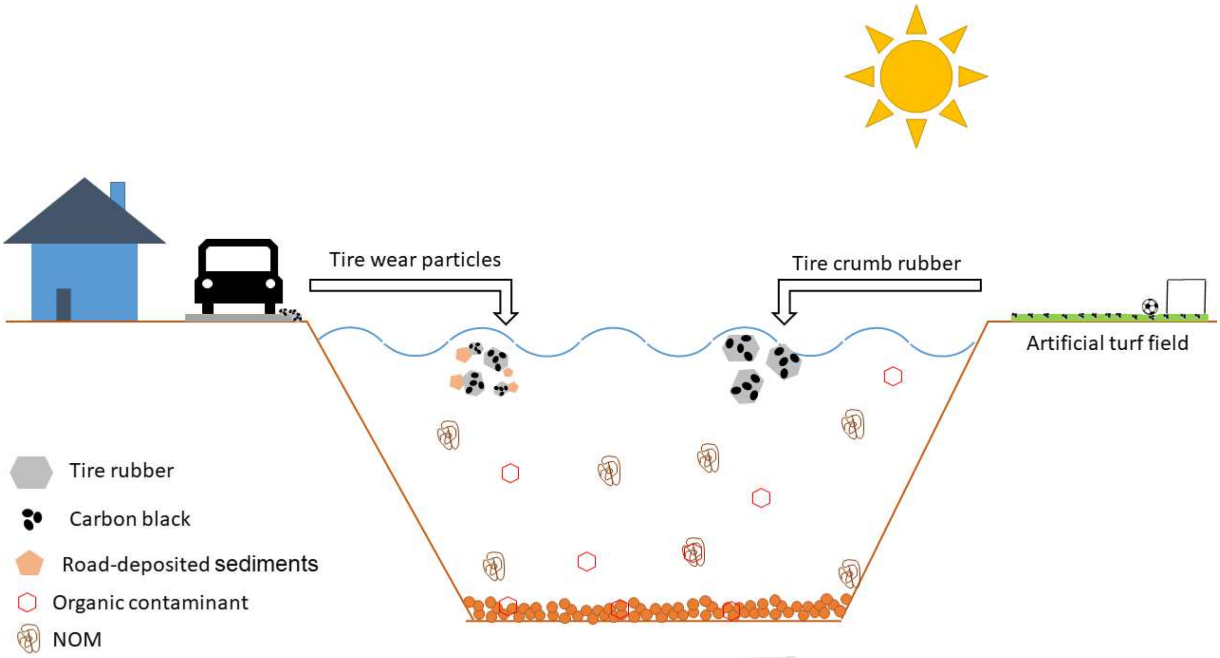

Figure 1: Introduction of tire materials into the environment.

As with microplastics, tire materials may play a role as a vector for organic contaminants. A large number of investigations into mechanisms controlling sorption of organic compounds by microplastics[13,14] have reported strong interactions,[15] supporting the hypothesis of a vector effect. Strong interactions between microplastics and organic contaminants can lead to an increase in the bioavailability of the contaminants due to the uptake of microplastics by aquatic organisms, thus allowing the contaminants to enter the food chain and to ultimately pose a threat to human health.[16] Arguing against the hypothesis of a vector effect for microplastics is the fact that microplastics compete as sorbent materials with other, naturally occurring, sorbents such as suspended particulate matter, which are present in far greater quantities and are therefore likely to outcompete microplastics, even if microplastics exhibit stronger sorption properties.[17] Similar considerations on the relevant molecular interactions and a critical assessment of the relevance of tire materials as a vector for the co-transport of organic contaminants would be required. Such an assessment for tire materials needs knowledge on their abundance in environmental compartments, also in relation to other suspended particulate matter, and understanding their sorption properties.

This review aims to assess the current state of knowledge on interactions between tire materials and organic molecules in the environment and to thereby (i) elucidate the processes controlling the interactions between tire materials and organic compounds, (ii) identify gaps in our knowledge that need to be filled, (iii) define future directions for research into the importance of relevance of tire materials as sorbents within the environment, and (iv) to facilitate assessment of the potential applications for using tire materials as sorbents.

2 Discussion

2.1 Tire materials are important sorbents in the environment

Tire materials are complex composites consisting mainly of various rubbers and carbon black, together with additional fillers, reinforcement agents, and other processing aids (**Table 1**). A passenger car tire typically contains almost 40 types of rubber (both synthetic and natural), 8 kinds of carbon black, steel for the belts, and 40 different chemicals.[18] The carbon black filling material in passenger car tires is today being increasingly replaced by silica. Despite consistency in the overall ingredients, the exact combination of these components in tire material is application dependent. For example, NR is used more in high-performance tires (e.g., for aircraft, buses, and trucks).[19] Truck tires typical contain 80% NR compared to only 15% in passenger car tires.[20]

TWP are defined as particles that are generated mechanically by the rolling shear of tire treads against road surfaces.[21] The abrasion of tires results in the generation of small particles, usually in the fine fraction (<2.5 µm). The composition and characteristics of these particles change as a result of the interactions between tires and road surfaces. The TWP are therefore likely to have different physio-chemical properties from the original tire tread, and consequently also from TCR. The properties of TWPs derived from tires consisting of a number of different materials (Table 1) have been investigated, as detailed in Wagner et al. (2018) and references therein.[4] The shape of TWP generated on roads was found to be very different from that of (cryogenically) ground tire material (such as, for example, TCR), which has sharper, relatively well-defined edges. Precise information on the physico-chemical properties of TWP (such as particle density, particle size distribution, and surface charge) has recently been shown to be of essential importance for understanding the transport and fate of TWP in surface waters.[4] These parameters are also expected to be important with respect to the sorption of organic compounds, affecting the available surface area, diffusion of the sorbate within the polymer, and electrostatic interactions with ionizable contaminants. The size distribution of TWP ranges from a few nanometers to several hundred micrometers, whereas TCR is mainly found in the coarse size fraction.[22–25] Sorption of organic compounds to TCR is therefore expected to be weaker than to TWP. A number of investigations have reported bimodal mass size distributions for TWP with one peak in the coarse fraction and another in the fine fraction.[26–28] These features of the observed particle size distributions can be a result of the conditions of particle formation, the sampling method used, or the analytical instrumentation used.[29] Such polydisperse particle size distributions are likely to have a significant effect on the interactions between TWP and organic compounds. Most of the finer particles were reported to consist mainly of carbon,[30] but the specific type of carbon (whether derived from rubber or from black carbon) was not determined. Following their release on road surfaces TWP are susceptible to aggregation, either with other TWP (homoaggregation) or with other particulate matter (heteroaggregation). Heteroaggregation is expected to be increasingly important relative to homoaggregation as the distance from the point of release increases and the relative concentrations of TWP compared to suspended matter is assumed to decrease. The precise form and composition of the aggregates is important, not only to the transport of TWP in aqueous environments but also to their interactions with organic molecules.

The global increase in road traffic has led to an increase in the quantity of end-of-life tires. In the United States around 2.5 million tons of tires are disposed every year,[31] while Europe is estimated to produce three million tons of end-of-life tires per annum.[32] Although the total end-of-life tire stockpile in the U.S. has been reduced by more than 87% since 1990, up to 85% of the remaining end-of-life tires may remain in the stockpile.[31] To avoid the problems associated with end-of life tire disposal, such tires are increasingly sent for recovery or material recycling.[32] TCR is produced by grinding tires and removing the fiber and steel belts; it is used in a variety of applications, for example as infill for turf fields, in mulches, and in crumb rubber modified asphalt and other civil engineering applications.[33] TCR has a granular texture and ranges from very fine powder up to 1 cm fragments, which are far larger than TWP.[32]

While the number of applications utilizing TCR is steadily increasing; there are concerns regarding environmental and human health.[34,35] Far less information is available on the characterization of TCR and its effects and fate within the environment than of TWP. In view of the broad range of compositions and uses of tire materials, the physico-chemical properties of TWP and TCR can be expected to be very heterogeneous. This makes the extensive characterization of the aqueous particle dispersions of tire materials used in environmental fate and effects studies a very important issue (for example in terms of their particle size distribution, composition, and age).[36,37] This is of particular importance with respect to the sorption properties of TWP and TCR, not only to critically assess the importance of tire materials as potential environmental sorbents but also bearing in mind that the possibility has been raised of using tires as an alternative sorbent materials for the removal of contaminants.

Table 1: Characteristics of tire materials compared with those of microplastics.[4,36]

	Tire materials	**Microplastics**
Composition	poly-butadiene, styrene-butadiene, neoprene isoprene, polysulphide, carbon black, silica	polyethylene, polypropylene, polycarbonate, polyvinyl chloride, polyamide
Additives	Mineral oils, thiazoles, organic peroxides, nitrocompounds, halogenated cyanoalkanes, amines, phenols, calcium oxides, aromatic and aliphatic esters, peptisers, ZnO, S, Se, Te	Plasticizers: phthalates, phosphates, bisphenols
Size	TWP: 100 µm - 1 nm; TCR: depending on the application mm - µm range	5 mm - 1 µm, nanoplastics < 100 nm
Density	Carbon black: 1.8 g/cm^3; SBR: 0.94-1.04 g/cm^3; TCR: 1.13 – 1.16 g/cm^3	0.9 - 1.1 g/cm^3
Morphology	Irregular, elongated, near spherical, jagged, granules	Mainly irregular, fragments and fibers, sometimes spherical

2.2 Sorption by tire materials and its major components carbon black and styrene-butadiene/natural rubber is complex; predictions are needed

The complexity of tire materials and their different input pathways into the environment, be it through unintentional input of TWP or intentional input of TCR, makes it particularly important to achieve a comprehensive understanding of the interactions between these materials and organic compounds and to be able to make accurate predictions. An in-depth understanding of the sorption mechanisms affecting organic compounds in environmental systems is critical in a number of different fields, not least in ecotoxicology. Contaminant transport in the environment, bioavailability and bioaccumulation, toxic effects on organisms, and transformation reactions, are all strongly dependent on sorption.

Research into possible applications for tire materials has been growing as a result of increases in the production, usage, disposal, and recycling of tires.[38,39] TCR has been proposed as a sorbent material that could provide a sustainable means of removing contaminants from aqueous solutions and as an inexpensive alternative to activated carbon.[12,40,41] It is therefore important to first address the sorption properties of the individual composite materials, and then relate this to sorption by the composites as a whole.

The exact composition of the rubber fraction in a tire varies according to its intended application, but SBR and NR are the main types of rubber used. NR is a linear polymer of isoprene (2-methyl butadiene) and due to its high structural regularity, it tends to crystallize spontaneously at low temperatures or when it is stretched. The NR polymer network allows its elasticity and flexibility to be combined with crystallization-induced strength and toughness through the vulcanization of raw NR. Synthetic petroleum-based rubbers (mostly polyisoprene, chloroprene or SBR, among others) are frequently used as substitutes for NR.[18] SBR has a glass transition temperature (T_g, which is a measure of intermolecular bonding energy for polymers) as low as -55 °C,[42] indicating that SBR has a flexible rubbery structure at room temperature.

The transport of organic solvents or gases through polymer rubbers has been extensively investigated as the use of polymer-based membranes has become increasingly important in a variety of barrier applications. Transport through polymers is controlled by the physico-chemical properties of the polymer, its crosslink density, the size of the organic molecules, and the temperature.[43–45] The degree of vulcanization (i.e. cross-linking) is an important factor in the diffusion of low molecular weight substances into the rubber phase: the higher the crosslink density, the slower the diffusion. These transport experiments typically involve placing pieces of rubber membrane into bulk organic sorbates (as solvents) and measuring the uptake of organic molecules into polymer by weighing the membranes at regular time intervals.[46–49] These experimental approaches are, however, unable to accurately mimic sorption and diffusion in the environment. It is therefore important to investigate the mass transfer characteristics of the organic molecules in the rubber components of tire materials under conditions found in the environment by, for example, varying the hydrochemical conditions and sorbate concentrations. An understanding of the mass transfer mechanisms involved in sorption and diffusion into the polymer matrix will be required to establish any links between the structure and properties of the organic sorbates and those of the polymer sorbents, and to predict their interactions in the environment.

CB, which is used as a filler material and to improve UV-resistance, is a quasi-graphitic form of almost pure elemental carbon, produced commercially under controlled conditions. It is designed to yield a range of elemental carbon particles with different properties, distinguished by their very low quantities (<1%) of extractable organic and inorganic compounds.[50,51] CB has a characteristic particle morphology, containing grape-like aggregates of highly fused spherical primary particles, with the aggregates clustered into larger agglomerates. It is physically and chemically distinct from “black carbon” (BC), which is a collective term used to describe a variety of carbonaceous materials that are mainly generated as (undesired) byproducts of incomplete combustion or pyrolysis of carbon-containing materials.[52] In contrast to CB, there is no universally accepted chemical definition of the term “black carbon” and it is often referred to as soot, graphitic carbon, or elemental carbon.[53] Different kinds of CB (e.g. thermal black and furnace black) are distinguished on the basis of their particle sizes and structure. About 90% of CB use in the U.S., Europe and Japan is as a reinforcing agent in rubber products and vehicle tires.[50] Many carbonaceous sorbent materials (such as black carbons,[54] zeolites,[55] clay minerals[56] and polymeric materials[57]) have been investigated for the removal of hazardous organic and inorganic compounds from polluted waters. The most commonly used sorbent is activated carbon.[56,58]

Experiments involving two tire materials with different proportions of the rubber components showed that the tire rubber composition had no significant effect on the sorption of hydrophobic organic compounds (HOCs) and that sorption by rubber correlated well with the hydrophobicity of the investigated sorbates (toluene and naphthalene).[41] A more diverse probe compound set would be required to investigate the importance of hydrophobic interaction to sorption by tire materials with more statistically significance. Alamo-Nole et al. (2011) investigated the sorption of toluene and xylene by TCR, and also by its main components (CB and SBR).[40] Linear sorption by SBR was interpreted to be mainly driven by polymer-water partitioning rather than by adsorption to the sorbent’s surface. The sorption by TCR (as a composite sorbent) was interpreted to be a combination of adsorption by CB and absorption by the SBR matrix. Alamo-Nole et al. (2012)[12] proposed the mechanism illustrated in **Figure 2** for sorption by TCR on the basis of results obtained from PAH sorption experiments using TCR, CB and SBR as sorbents. This mechanism involves the organic sorbate molecules initially (Figure 2a) adsorbing (at low sorbate concentrations) onto the CB surfaces that are exposed on the surfaces of the TCR (Figure 2b). Those molecules absorbing into rubber matrix around a CB particle also adsorbed onto the CB surface, which prevented the molecules from diffusing into the polymeric matrix (Figure 2c). With higher sorbate concentrations the CB surfaces reached saturation, after which any additional sorbate molecules are free to diffuse into the polymer matrix (Figure 2d). The conclusion that sorption by TCR is a combination of adsorption and absorption is not surprising, bearing in mind characteristics of the two major components of TCR.

While there may be considerable value in investigating sorption under controlled, reproducible, laboratory conditions in order to discriminate between effects due to different phenomena (which also occur within the environment), fitting experimental isotherm data to typical sorption models may not, on its own, be sufficient to allow valid conclusions to be drawn with regard to the dominant sorption mode. In fact conclusions regarding the dominant sorption mode of environmentally significant polymer particles on the basis of sorption linearity and sorption model fit (as indicators) need to be treated with caution.[13,14] Other approaches such as comparing experimental sorption data for different alkanes, as proposed by Endo et al. (2008),[59] or direct methods such as two-step laser desorption/laser ionization mass spectrometry[60–63] or scanning transmission X-ray microscopy (STXM),[64] have been successfully used to determine the dominant sorption mode of black carbon, and may also be complementary tools to investigate the sorption mode of tire materials with varying compositions of rubber and carbon black.

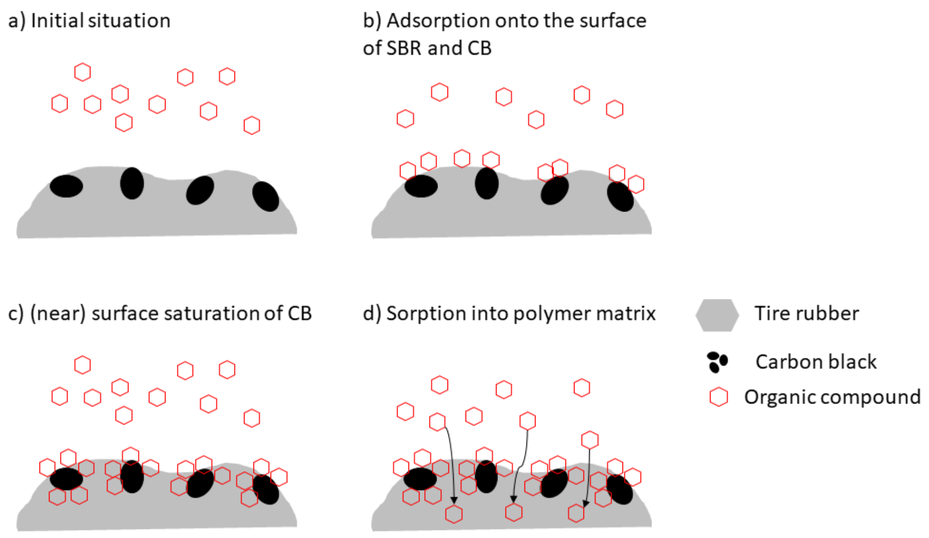

Figure 2: Mechanism for sorption by tire crumb rubber, modified from Alamo-Nole et al (2012).[12] *SBR: styrene-butadiene rubber, CB: carbon black.*

Experimental sorption data are usually fitted to the Freundlich model (Equation 1, below) or the Langmuir model (Equation2) because of the usefulness of their model parameters, their simplicity, and their easy interpretability.[65] These models have also been used to evaluate sorption data derived for microplastics[13,66] and carbonaceous sorbents.[67]

$$C_s = K_F C_w^n \qquad \text{(Equation 1)}$$

where C_s is the concentration of sorbate on the sorbent [mg/kg], K_F is the Freundlich sorption coefficient [(mg/kg)/(mg/L)^n], C_w is the sorbate concentration in the aqueous phase at equilibrium [mg/L], and n is the Freundlich exponent [-].

$$C_s = \frac{C_{s,max} K_L C_w}{1 + K_L C_w} \qquad \text{(Equation 2)}$$

where $C_{s,max}$ is the maximum monolayer sorbate concentration on the sorbent surface [mg/kg] and K_L is the Langmuir sorption constant [L/kg].

The significance of such a statistical fit of experimental data and the conclusion that one sorption model fits the data better than the other clearly depend on a number of factors, for example the quality of the experimental data and the concentration range over which the sorption isotherms were determined. A comprehensive understanding of the models applied to sorption isotherms is necessary to avoid not only misapplication but also inaccurate discussions and conclusions. For example, depending on the aqueous concentration that the isotherm was determined for, it may not be clear which of the two sorption models yields the better fit for a rubber-like polymer. The Langmuir model for the adsorption of gases onto a solid surface was developed assuming that: (1) there are a limited number of accessible sites on the sorbent surface, each with identical sorption site energies, (2) sorption is reversible, (3) a monolayer forms on the sorbent surface, and (4) there is no interaction between sorbate molecules.[68] The Freundlich equation is one of the earliest empirical equations used to describe equilibrium data and adsorption characteristics for a heterogeneous surface.[69] Unlike the Langmuir isotherm, the Freundlich isotherm can describe neither the linearity range at very low concentrations nor the saturation effect at very high concentrations. Conceptually, both models describe adsorption processes onto a sorbent surface. While this may be valid for a hard, glass-like polymer such as polystyrene[13,14,70] or carbonaceous sorbents,[67] sorption by soft rubber-like polymers more closely resembles a partitioning process into the polymer matrix.[13,70] For sorption to complex composite tire materials the relative contributions of adsorption onto the carbonized phase (for example carbon black), and partitioning into the non-carbonized phase (SBR/NR), can be quantified by more complex sorption models, such as the dual-mode Langmuir model (Equation 3).[71]

$$C_s = \frac{C_{s,max} K_L C_w}{1 + K_L C_w} + K_p C_w \qquad \text{(Equation 3)}$$

where K_p is the partitioning constant [L/kg].

This model has been successfully used to describe the sorption of organic compounds by geosorbents and biochars.[72–74] Using this dual mode sorption model revealed a reduction in the relative contribution of absorption for SBR and its pyrolysis-derived chars, as a result of reductions in the polymeric rubber phase. With increasing proportions of CB in tire materials the contribution of adsorption can be expected to become increasingly important.

Another approach fundamentally distinct from the Langmuir model involves the Flory–Huggins theory, which has been shown to be valid for numerous polymer-solvent systems, especially for elastomeric materials and pure non-polar solvents. Details of the Flory-Huggins theory can be found in Favre et al. (1993).[75] Despite the fact that this model has been successfully used (even in ternary systems containing polymers, water, and an organic bulk solvent phase) its ability to explain the sorption of organic molecules at environmentally realistic (i.e. very dilute) concentrations has yet to be demonstrated.

An understanding of the relevant molecular interactions is of paramount importance for understanding (and predicting) sorption to tire materials in the environment. The main molecular interactions relevant to sorption by carbonaceous sorbents involve non-specific van der Waals forces, hydrophobicity, H-bond-interactions, and π electron donor-acceptor interactions (for neutral sorbates), as well as electrostatic interactions (for ionic or ionizable sorbates).[76]

Among π electron donor-acceptor interactions, π−π bond interactions between the conjugated C=C bonds of organic sorbates and benzene-like structures of carbonaceous sorbents via π−π coupling are expected to be of major importance in sorption.[67] Other π bond interactions include n−π interactions between electron-depleted regions of the sorbent and n-electron donors of organic compounds (with lone electron pair functional groups containing, for example, oxygen or nitrogen) and π bond interactions with cations or anions.[77] Halogen bond interactions have also been reported to play a role in the sorption of organic sorbates to PVC microplastics.[78] These interaction occur between –Cl groups in PVC acting as electron acceptors and conjugated C=C bonds or –OH groups of organic sorbates acting as electron donors. The contribution of the individual molecular interactions to overall sorption depends not only on the sorbate and sorbent properties but also on environmental factors such as pH and ionic strength. Differences in sorption to microplastics could not be explained by surface area or dispersivity, but were more likely related to the nature of the monomeric subunits.[13] For example, weak sorption by aliphatic polyethylene (PE) was found to result from non-specific van-der Waals interactions and hydrophobicity, whereas strong sorption by aromatic polystyrene (PS) was explained by the additional contribution from π-π electron donor-acceptor interactions.[13,15,79]

The importance of different molecular interactions to sorption can be assessed using a diverse set of molecular probe compounds.[67,80] Similar approaches using nonpolar molecular probe sorbates have been previously tested for tire materials, revealing that sorption by these sorbents was mainly driven by hydrophobicity, expressed by the logarithmic octanol-water partitioning constant (log K_{ow}).[71],[81] The stronger sorption of non-polar compounds than of polar compounds has been explained as being due to the non-polar character of the SBR copolymer in tire rubber. Other molecular interactions have been considered to explain sorption, including (i) π electron donor-acceptor interactions, (ii) H bond interactions between -OH groups of an organic sorbate and the O-containing groups on the carbonized fraction of tire materials, and/or between the -NO_2 sorbate functional groups and H-donors (e.g., -COOH) of tire materials, and (iii) π-H bonding between -OH sorbate functional groups and the aromatic surfaces of tire materials.[67,71,82] The relative importance of the individual interactions may vary for the different rubber component of tires, as shown by the pH-dependence of dichlorophenol sorption by tire rubber at high pH values, which could be largely attributed to the loss of H-bonding donor ability and an increase in its solubility as a result of dissociation of the sorbate.[71]

Surface properties (and consequently sorption) are significantly different for silica, which is increasingly being used as a replacement for CB (for details on the sorption of organic compounds to silica surfaces, see Parida et al., 2006)[83]. Silicon dioxide (silica) has a well-characterized surface and contains active hydroxyl groups. The oxygen-containing functional groups result in the surfaces of silica having a predominately negative charge at environmentally realistic pH values. Cation exchange therefore makes silica in important sorbent for organic cations (for example for pharmaceuticals).[84,85]

Determining sorption data may not always be feasible because of the time and cost involved, as well as the susceptibility of such determinations to experimental errors. In certain cases direct measurement of sorption can be practically impossible, for example if sorption is extremely high or extremely low, if the sorbates to be investigated are very expensive or not commercially available, or if sorption data is required for an extensive set of molecules. This clearly indicates the importance of methods that will allow reliable predictions to be made for sorption. The concepts of linear solvation energy relationships (LSER) or poly-parameter linear free energy relationships (ppLFER) yield more robust and accurate methods for the prediction of sorption than quantitative structure–activity relationships or simple correlations with log K_{ow}.[86,87] One of the major advantages of using ppLFER approaches is that they split the sorption between different molecular descriptors, which can in turn be attributed to different molecular interactions such as, for example, H-bond donor-acceptor interactions. These ppLFER approaches have previously been used to describe and predict sorption by a variety of sorbents, including environmental phases, polymers such as microplastics (aged and pristine),[14,88] and carbonaceous materials.[87] ppLFER may therefore for future research be a promising approach for obtaining precisely descriptions and predictions of sorption to composite tire materials.

2.3 The predictions of sorption to tire wear materials needs to include environmental factors

When assessing the environmental significance of tire materials and other particulate contaminants such as microplastics or nanomaterials, one question that arises is whether or not particles used in laboratory experiments are consistent with those found in the field. For example, pristine microplastics can be purchased as powder or as beads of different sizes for a variety of different polymers. These particles are often used for sorption investigations through laboratory experiments,[13,70,89] and are certainly necessary for robust and comparable experiments investigating sorption and to determine the mechanisms involved. However, the well-defined, pristine particles that are typically used in laboratory experiments are unlikely to be representative of the particles found in nature. Following their release into the environment, particles are subjected to various aging and fragmentation processes (**Figure 3**) that can alter their surface properties.[90] It has therefore often been suggested that more realistic particles, similar to those typically encountered in the environment, should be used for investigations into their toxicity and fate.[36,90–93] This suggestion is also extremely relevant to investigations into sorption by tire materials.

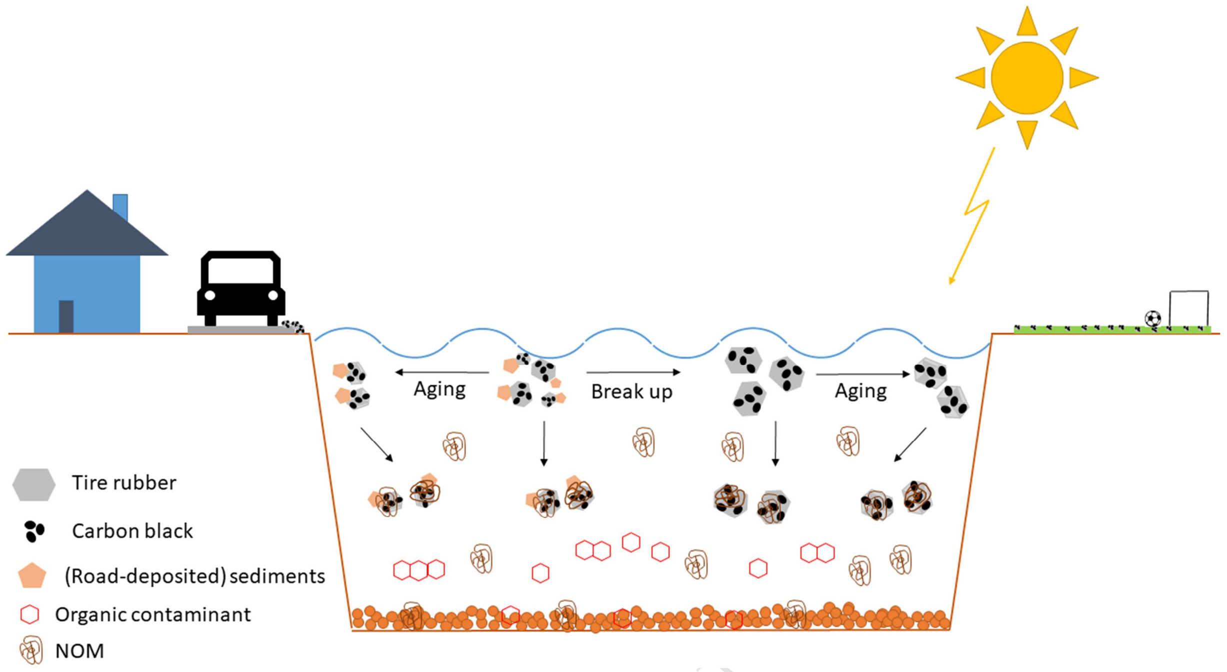

Figure 3: Overview of the most important transformation processes affecting the surface properties of tire materials.

Aging processes can change the properties of tire materials following their release into the environment. These processes involve mechanical stress and oxidation, as well as microbial colonization and degradation. The major components of tire materials are expected to be degraded slowly in the environment, which makes them persistent particulate contaminants, as is also the case for microplastics. In view of their different input pathways the aging processes may differ between TCR and TWP. Aging induced by irradiation is expected to be relevant aging processes for TCR that is used, for example, in artificial turf fields.

Photo-induced aging seems to be less relevant for TWPs which, following their generation in urban environments, are likely to be washed into sewage systems and to end up in sediment.[4] Aging processes and rates can be expected to differ between the various components of tire material, especially between CB and the polymer components. Solar UV radiation initiates autocatalytic oxidation of microplastics, especially on the exposed surfaces of particles.[94] Depending on the polymer type, this oxidation process can result in the formation of different functional groups such as ketones, esters, carboxylates, or hydroxyl groups. This will increase the material's hydrophilic properties and can consequently reduce the sorption of hydrophobic organic compounds.[95]

UV-induced aging was found to alter the physico-chemical properties of polystyrene microplastic sorbent materials and consequently to reduce sorption compared to pristine material.[14,96] In contrast, however, UV-aging had no effect on sorption by polypropylene (PP).[96] There have been inconsistent reports on the effect that aging has on the sorption properties of microplastics, for example sampled from a beach, compared to pristine microplastics. While Endo et al. (2005) found higher concentrations of polychlorinated biphenyls (PCBs) in discolored and/or fouled PE pellets obtained from Japanese beaches than in non-discolored PE pellets, there was no clear relationship between PCB concentrations and crystallinity or weathering.[97] Any possible reduction in sorption resulting from a decrease in hydrophobicity due to the introduction of oxygen, as discussed above, could be counteracted by an increase in surface areas due to the development of fine cracks that lead to an increase in sorption. When working with particles isolated from the environment it is important to keep in mind that the more aged PE particles have had longer ocean residence times, allowing more time for PCBs to be sorbed.[97] Photooxidative aging of carbonaceous materials such as fullerenes leads to a significant increase in surface oxidation and has also been shown to affect interactions with organic compounds.[98]

In contrast to photooxidation, thermal oxidative aging of tire materials has been thoroughly investigated because it limits the life of rubber products.[99,100] In this type of aging, the concentration of C=C-double bonds in the main chain of the polymer has been found to have a significant influence on its thermal oxidative stability, while the crosslink density of the rubber did not appear to have any effect on aging. As with plastics (for which aging processes have been widely investigated from the perspective of material science), one of the major challenges will be to assess the transferability of results obtained from aging in controlled (and accelerated) laboratory conditions to aging processes occurring under environmental conditions.

The interactions between tire materials and natural organic matter (NOM) are another important aspect of investigations into the sorption properties of these particulate contaminants under natural (realistic) conditions. The influence of NOM on sorption to carbonaceous sorbents has been extensively investigated, but with contradictory results. Some investigations found that sorption of NOM-coated particles was greater than that of uncoated particles as a result of new sorption sites becoming available due to an increase in the dispersity of the particles,[101] while other investigations found that sorption decreased as a result of sorption sites being occupied by the NOM coating.[102] Two scenarios have been proposed to explain the decrease in sorption of organic compounds to carbonaceous sorbents resulting from NOM coating. In the first scenario, NOM competes directly with organic compounds for sorption sites on the sorbent's surface, a process that represents a realistic scenario for the environment as it combines low sorbate concentrations with high NOM concentrations.[101] For the second scenario, in which the sorbent is assumed to be a porous material, a reduction in sorption is attributed to large NOM molecules blocking the entrances of the pores that would otherwise be accessible to smaller sorbate molecules.[103,104] While pristine microplastics are typically considered to be a non-porous sorbents, the embrittlement of particles can result in the formation of small cracks, which can serve as the equivalent of (relatively large) pores. This makes the mechanisms of how NOM influences the surface properties of carbonaceous sorbents transferable to microplastic [36] and tire materials. Preliminary results for microplastics suggest that the presence of NOM leads to reduced aggregation of micro-sized polystyrene particles,[105]. For microplastic there could be an offset between the increase in sorption resulting from an increase in surface area due to crack formation and a counteracting decrease in sorption as a result of NOM coating. NOM can be expected to have a similar effects on the surface properties of particles derived from tire materials, and on their interactions with organic compounds but this has not been addressed yet.

Sorption tests are typically performed using single-solute batch experiments. While these experiments may be very useful for investigating the relevant molecular interactions and sorption mechanisms for a specific sorbent, under realistic conditions there can be a number of different sorbates competing for sorption sites. Sorption competition can be illustrated through bi-solute or multi-solute experiments.[106] No competitive sorption of organic solutes by soft rubber-like polymers, such as polyethylene and cellulose, has been observed.[107,108] Single solute experiments have shown that sorption by SBR remains virtually unchanged in the presence of another sorbate, which clearly supports the notion that the sorption of organic compounds to SBR tire rubber is dominated by partitioning into the rubber matrix. Bi-solute sorption experiments indicated significantly weaker sorption of organic sorbates with increasing proportions of the carbonized phase in SBR, which suggests that competition for sorption sites and adsorption become increasingly relevant.[71] In contrast, Bakir et al. (2012) observed that DDT outcompeted PAHs for sorption by micro-sized plastics made of PE (a typical soft, rubber-like polymer) and PVC (commonly considered to be hard and glass-like). However, stronger interactions between DDT and PVC than between DDT and PE, together with the absence of competitive sorption in binary experiments, suggested that the interactions between microplastics and organic molecules are more influenced by the properties of the sorbate than by those of the sorbent.[109]

In addition to competitive sorption of multiple sorbates onto a particular sorbent, there is also the question of whether a particular sorbate will sorb preferentially to one sorbent or another. The majority of investigations into sorption to microplastics and tire materials have only considered the affinity of organic molecules in single sorbent experiments, in contrast to the conditions in the environment where contaminants are present as complex mixtures and a number of different sorbents are available. Sorption to plastics was found to be stronger than to natural sediments,[110] but the experiments were conducted using single sorbents and it is not clear whether the solid to liquid ratios at which the experiments were conducted represent realistic concentrations in the environment. In addition to investigating the thermodynamics of sorption to tire materials it is critically important to understand the sorption kinetics of the individual sorbents, as well as of mixtures of sorbents at typical naturally occurring concentrations.

As with microplastics, it is important to include in any investigations certain aspects of environmental realism in order to be able to extrapolate from the sorption of organic compounds by tire materials in controlled laboratory experiments to more realistic scenarios.[91] This could include aging of the tire materials prior to the sorption experiments, varying the duration of sorption batch experiments, varying the hydrochemical conditions, and investigating sorption by tire materials under (simulated) physiological conditions that mimic those in biota. For this one would need to distinguish between TWP and TCR. TCR can, for example, be fairly easily sampled and its physico-chemical properties characterized. For TWP, the sampling, separation, and analysis of particles is more complex because of their mode of formation.[4]

3 Future perspectives

Tire materials inevitably enter the environment as either tire wear particles or tire crumb rubber. Recent estimates indicate that tire materials account for a significant proportion (up to 60%) of plastics released into the environment.[111] Their role as sorbents for organic compounds has, to date, not been adequately investigated. The particle properties for both types of tire material, and consequently their sorption properties, vary as result of their different input pathways. The complex main components of these composites, polymeric rubber and carbon black, make the sorption properties of tire materials difficult to assess. Adsorption to carbon black and absorption into the rubber material are likely to be the dominant sorption mechanisms. However, diffusion rates within the rubber components under conditions found in the environment remain largely unknown. Once released into the environment their particle properties, and hence their sorption, are expected to change because of aging processes and interactions with natural organic matter. The following knowledge gaps therefore need to be addressed:

- The physico-chemical properties of tire wear materials (e.g. particle density, particle size distribution, surface properties) need to be thoroughly investigated in order to be better able to assess sorption phenomena.
- The influence of the different components of tire materials on their molecular interactions with organic compounds and sorption mechanisms also need to be comprehensively understood.
- For the assessment of the relevance of sorption to tire materials for the transport of organic compounds in the environment the establishment of a mass balance including the formation of tire wear particles is necessary.
- The influence of sorbed organic compounds on the fate of tire materials requires further investigation.
- The significance of tire wear material for contaminant transport, sequestration, and leaching in the environment needs to be evaluated under realistic environmental conditions using field site materials.

Another aspect of the sorption properties of tire materials is the assessment of their environmental application as sorbents for remediation purposes. The use of ground tires in a soil-bentonite slurry wall has been shown to retard the movement of organic contaminants, with tire material being mainly responsible. The addition of 7.5% tire material led to an increase of up to 80-fold in sorption affinity.[41] Although there have been investigations into the sorption of organic chemicals to tire materials and their pyrolysis products for the use in environmental remediation,[79] the interactions of tire-derived chars with organic chemicals remain poorly understood and require further research in order to fully assess their potential. A comprehensive assessment of the potential for using tire materials as environmental sorbents would need to address the problem of recovering microparticles and nanoparticles from the environment, as well and how this remediation method compares with other sorbents or approaches such as the direct elimination of organic molecules through biodegradation. One concern about the use of tire material as a sorbent in environmental applications is the leaching of hazardous tire-derived components that could counteract any potential benefits. Although the release of metals from TCR into aqueous systems has been shown to be below U.S. EPA regulatory limits,[40] these aspects of their use will need to be thoroughly investigated prior to any further exploration of their potential for remediation purposes.

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