

The invisible footprint of climbing shoes: high exposure to rubber additives in indoor facilities

Anya Sherman^{a,b,f,†}, Thibault Masset^{c,†}, Lukas Wimmer^{d,e}, Lea Ann Dailey^d, Thorsten H \ddot{u} ffer^{a,f}, Florian Breider^c, Thilo Hofmann^{a,f,*}

† These authors contributed equally.

a) University of Vienna, Centre for Microbiology and Environmental Systems Science, Environmental Geosciences EDGE, 1090 Vienna, Austria.

b) University of Vienna, Doctoral School in Microbiology and Environmental Science, 1090 Vienna, Austria.

c) EPFL – Ecole Polytechnique Fédérale de Lausanne, Central Environmental Laboratory, Institute of Environmental Engineering, ENAC, station 2, CH-1015 Lausanne, Switzerland

d) University of Vienna, Department of Pharmaceutical Sciences, 1090 Vienna, Austria.

e) University of Vienna, Doctoral School of Pharmaceutical, Nutritional and Sport Sciences, 1090 Vienna, Austria.

f) University of Vienna, Research Platform Plastics in the Environment and Society (PLENTY), 1090 Vienna, Austria.

*thilo.hofmann@univie.ac.at

1 **Abstract:**

2 There is increasing research focused on rubber additives, predominantly originating from tire and road
3 wear particles. Other consumer products including sports equipment also contain rubber additives and
4 the overall human exposure to these compounds is of concern due to demonstrated toxicity to animal
5 species. Rubber additives are intentionally incorporated into climbing shoes for specific performance.
6 We found high concentrations of rubber additives in shoe sole samples, aerosol particulate matter, and
7 settled dust in indoor climbing halls. The estimated daily intake via inhalation for climbers and
8 employees of these facilities exceeds the intake of rubber additives from all other known sources.
9 Abrasion powder resulting from friction of climbing shoes on the holds is responsible for the high
10 concentrations of rubber additives observed in aerosol particulate matter and settled dust, while other
11 emission sources could be excluded. We also show that atmospheric transformation of rubber
12 additives occurs in indoor environments. These findings identify a previously unknown human
13 exposure route to rubber additives and emphasize the global problem of the toxicity burden of plastic
14 additives.

16 **Introduction:**

17 Air quality has an important impact on human health. Concentrations of particulate matter (PM) are
18 linked to rates and outcomes of cancer^{1,2}, respiratory and cardiovascular disease^{2,3}, COVID19⁴, and
19 ultimately, life expectancy^{2,3,5,6}, especially in densely populated areas⁷. Currently, more than half of
20 the global population lives in cities, with a projected increase to 68% by 2050⁸. In parallel with
21 urbanization, the global population is spending less time outdoors⁹, with the US population estimated
22 to spend 90% of their time indoors¹⁰. Indoor air quality is a critical and increasing determinant of
23 human health and indoor air quality is relevant not only in the home and workplace, but also in places
24 of recreation. Due to safety, accessibility, and/or practical constraints, outdoor recreation is unrealistic
25 for many living in dense urban centers, so indoor recreational facilities serve as places to exercise, as
26 well as socialize. One increasingly popular form of indoor recreation is climbing. In 2018, an
27 estimated 1.5% of the UK population¹¹, and about 4.4% of the US population¹² visited indoor

28 climbing halls. Of these visitors, about 20% are regulars and spend several hours a day, multiple times
29 a week in climbing halls¹¹.

30 Very high PM concentrations in indoor climbing gyms have been previously reported¹³. Chalk used by
31 climbers was suggested as the primary source of PM, but other sources may also contribute. In
32 climbing halls, specialized climbing shoes are worn, with soles made of highly functionalized rubber.
33 The rubber is chemically engineered to be flexible and sticky. Soles are intentionally designed to
34 slowly abrade during climbing, due to desired friction with climbing holds. This leads to a constant
35 generation of rubber particles, which accumulate on the climbing footholds. Most climbers own
36 brushes to clean these climbing holds, which results in a constant aerosolization of rubber particles,
37 which may remain airborne long enough to be inhaled. Plastic additives in general have been
38 identified to increase the global toxicity burden on humans and the environment with over 13,000
39 substances across a wide range of sectors and product value chains^{14,15}. In tires, which are also highly
40 engineered and abrade during their intended use, rubber additive concentrations are very high¹⁶. Tire
41 additives and their transformation products, such as 6PPD-quinone, have been found to be responsible
42 for Coho salmon mass mortality¹⁷, as well as toxicity in rainbow trout, brook trout¹⁸, and white-
43 spotted char populations¹⁹. 6PPD-quinone is also toxic to human lung cells²⁰⁻²². Recent studies have
44 detected rubber additives in human urine^{23,24} and blood²⁵, with inhalation hypothesized to be a major
45 source of exposure. Due to the highly specialized properties of climbing shoes, we hypothesized that
46 these rubber particles contain high additive concentrations, and that climbing halls are a hot spot of
47 human exposure.

48 In this study, we explored climbing halls as an indoor source of exposure to rubber additives. We
49 collected air particulate matter samples in climbing halls and measured the concentrations of rubber-
50 derived compounds therein. Based on these concentrations, we calculated the exposure for employees
51 and recreational visitors to these rubber-derived compounds. We were able to implicate climbing
52 shoes as the source of these rubber-derived compounds.

53

54

55 Results & Discussion:

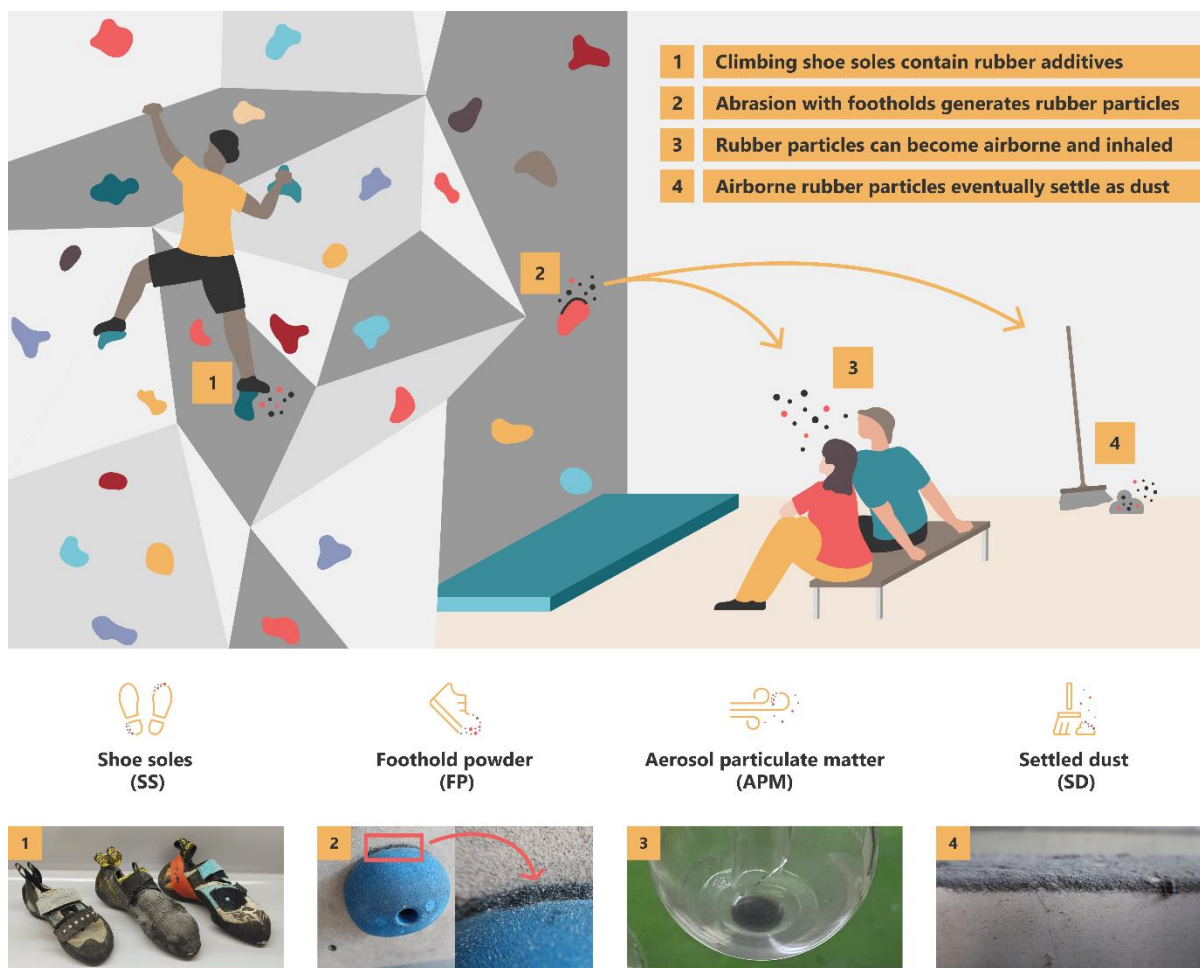


Figure 1: Schematic of a climbing hall, with photos of the four types of samples analyzed in our study. Specialized climbing shoes are worn with highly functionalized rubber soles (1 – shoe soles). Friction between these shoe soles and the footholds generates rubber particles (2 – foothold powder). Those can be aerosolized and be inhaled directly upon generation, due to the brushing of holds, or by climbers falling onto mats and resuspending rubber particles which had settled (3 – aerosol particulate matter). Eventually, airborne particles also settle elsewhere as dust (4 – settled dust).

56

57 High exposure to rubber-derived compounds in climbing halls for visitors and employees

58 Our air sampling campaigns, carried out during peak activity hours, revealed very high particulate
59 matter (PM) concentrations (Figure 1). Inhalable PM concentrations ($PM > 6.4 \mu m$) in climbing halls
60 1 and 2 were $1,590 \mu g/m^3$ and $1,000 \mu g/m^3$, respectively, while respirable PM concentrations ($PM <$
61 $6.4 \mu m$) were $1,040 \mu g/m^3$ and $900 \mu g/m^3$ (Table 1). Despite differences in sampling techniques, the
62 measured respirable particle concentrations correspond well to PM_{10} concentrations previously

63 reported for indoor climbing halls (from 509 to 4,028 $\mu\text{g}/\text{m}^3$)¹³. These values exceed WHO guidelines
64 for indoor PM_{10} concentrations of 45 $\mu\text{g}/\text{m}^3$ for 24 hours²⁶, and exceed those of most indoor
65 environments²⁷ including indoor artificial turf halls²⁸. In aerosol PM (APM) samples from both
66 climbing halls, our chemical analyses performed for 15 rubber-derived compounds (RDCs) showed
67 that nine RDCs were detected above the limit of quantitation (LOQ) (Table 1). Among these, five
68 RDCs were identified as transformation products (TPs) of compounds commonly used in rubber
69 products. Of these TPs, aniline, 2-hydroxybenzothiazole (2OH-BTZ), benzothiazole (BTZ), as well as
70 two phenylenediamine-quinones (6PPDq and IPPDq) were among the compounds which dominated
71 the chemical profile in the aerosol fraction of the climbing hall samples (Figure 2a). Cumulative RDC
72 concentrations in inhalable APM were 17 and 27 ng/m^3 in halls 1 and 2, respectively, while RDC
73 concentrations in respirable APM were 6 and 8 ng/m^3 in halls 1 and 2, respectively.

74

75 It has been shown that concentrations of similar organic compounds in settled dust can be used as a
76 proxy for their concentrations in airborne PM^{29} , thus, we quantified RDCs in dust samples from three
77 climbing halls (#2-4). We detected 12 out of 15 RDCs in at least one dust sample (Tables 1, S1), and
78 the chemical profile was very similar to aerosol PM samples (Figure 2a). Overall, cumulative RDC
79 concentrations in settled dust samples were high (16 to 43 $\mu\text{g}/\text{g}$, Table S1). The origin of the RDCs
80 detected in aerosol PM and settled dust samples was at this point unknown, but the similarity in
81 chemical profile of settled dust and aerosol PM samples from different halls in three different
82 countries (France, Switzerland and Austria) suggests an important source of RDCs which is
83 ubiquitously present in climbing halls.

84

Table 1: Concentrations of particles and rubber-derived compounds (RDCs) in aerosol PM from Halls 1 and 2 and settled dust samples from Halls 2, 3 and 4.

| | Respirable PM ng/m ³ | | Inhalable PM ng/m ³ | | Total aerosol PM ng/m ³ | | Settled dust (n = 5) mean (SD) ng/g |
|---|------------------------------------|--------|-----------------------------------|--------|---------------------------------------|--------|---|
| | Hall 1 | Hall 2 | Hall 1 | Hall 2 | Hall 1 | Hall 2 | Halls 2-4 |
| Total particles (µg/m³) | 1040 | 900 | 1590 | 1000 | 2630 | 1900 | - |
| Aniline | 1.06 | 1.31 | 2.68 | 2.80 | 3.75 | 4.12 | 1266 (1644) |
| DPG | 0.84 | 1.96 | 4.97 | 4.56 | 5.81 | 6.52 | 4092 (3057) |
| 2OH-BTZ | 1.58 | 1.28 | 3.17 | 4.11 | 4.76 | 5.39 | 5123 (3393) |
| IPPD | 0.04 | 0.06 | 0.12 | 0.15 | 0.16 | 0.21 | 139 (126) |
| BTZ | 2.01 | 2.47 | 5.35 | 13.89 | 7.36 | 16.36 | 12950 (10020) |
| 2amino-BTZ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | 61.4 (55.3) |
| 2SH-BTZ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | 1222 (1201) |
| HMMM | 0.03 | 0.25 | 0.09 | 0.50 | 0.12 | 0.75 | 58.4 (17.0) |
| CPPD | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| 6PPD | <LOQ | 0.10 | 0.15 | 0.31 | 0.15 | 0.41 | 101 (61.0) |
| IPPDq | 0.01 | 0.02 | 0.01 | 0.04 | 0.01 | 0.06 | 25.0 (24.0) |
| DPPDq | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| 6PPDq | 0.15 | 0.37 | 0.50 | 0.71 | 0.66 | 1.08 | 119 (113) |
| CPPDq | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| DPPD | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | 0.30 (0.30) |

Compound Profile

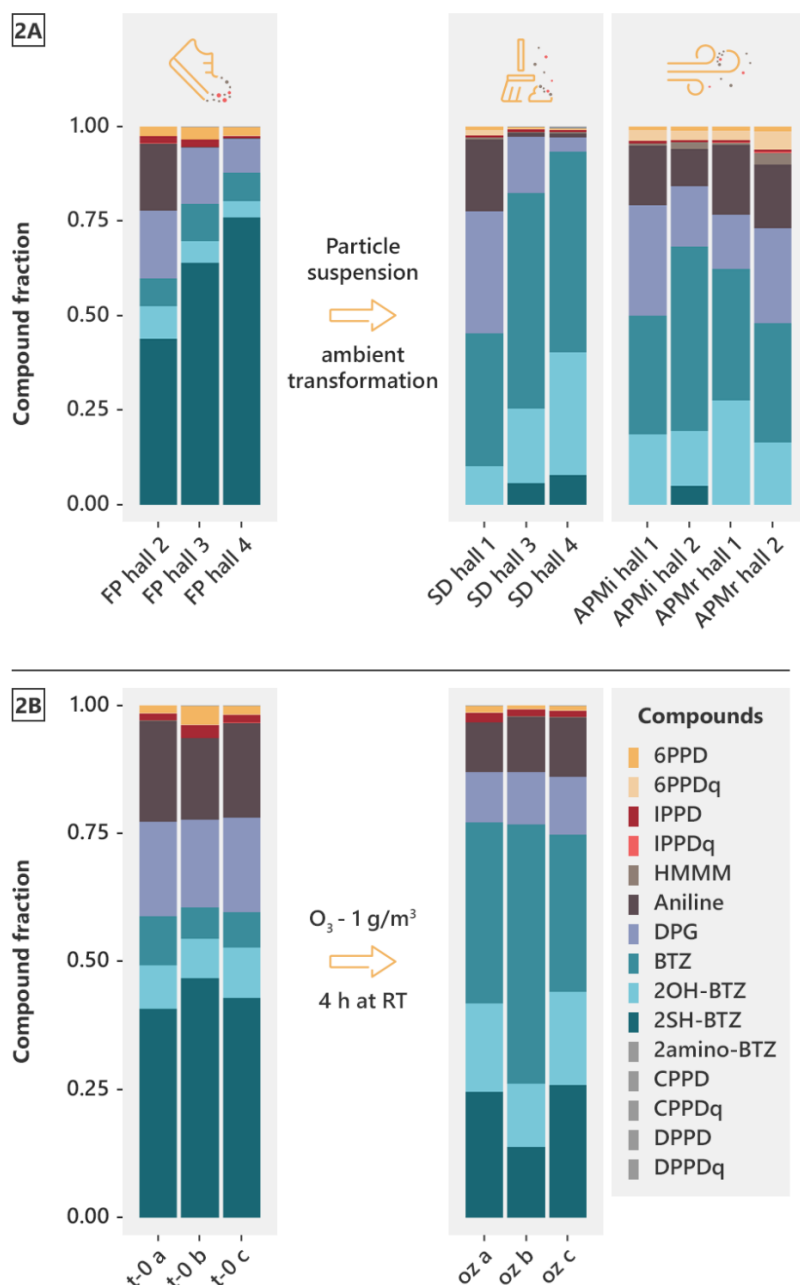


Figure 2: Rubber-derived compound profile in different samples. (a): Rubber-derived compound profile in foothold powder (FP), settled dust (SD), inhalable PM (APMi) and respirable PM (APMr) samples. (b) Rubber-derived compound profile of foothold powder samples before (t-0) and after ozonation experiments (oz). Ozone promotes profile shift which mirrors the shift seen in (a), indicating that the rubber-derived compounds in aerosol PM and settled dust samples can originate from climbing shoes.

85 Several recent studies report concentrations of RDCs in dust from outdoor and indoor environments,
 86 mostly driven by the increasing research about tire particles. Concentrations of most RDCs in our
 87 settled dust samples were higher than those reported for most dust samples from other indoor

88 environments (Figure 3, Table S2). Benzothiazole concentrations were one or two orders of
89 magnitudes higher in our samples than in house dust and even road dust³⁰⁻³². 6PPDq concentrations
90 were also higher than in most house dust samples collected around the world³³⁻³⁶ and were similar to
91 road dust samples^{37,38}. Concentrations of DPG were also high (mean= 4994 ng/g) and exceeded most
92 reported DPG concentrations in house dust^{39,40}.

93

94 Similar to dust, concentrations in the collected aerosol PM samples were very high compared to other
95 atmospheric environments for most RDCs (Figure 3 and Table S3 for concentrations of all RDCs).

96 PPDs and PPDqs concentrations in the respirable fraction were higher than those measured in Chinese
97 megacities^{41,42} and similar to roadside sites and city centres in China during air pollution events⁴³.

98 Concentrations of DPG, BTZ, and 2OH-BTZ in aerosol PM samples were one or two orders of
99 magnitude higher than in 18 megacities worldwide⁴⁴ and BTZ and 2OH-BTZ were up to 10-fold
100 above concentrations from industrial areas in Spain⁴⁵. So far, studies reporting RDC concentrations in

101 aerosol PM collected in indoor environments remain very scarce. Dye et al. (2006)²⁸ investigated
102 2OH-BTZ, 2-amino-BTZ, 2SH-BTZ and IPPD concentrations in PM collected in indoor artificial turf
103 halls. They reported higher concentrations of 2-amino-BTZ, 2SH-BTZ and IPPD compared to our
104 climbing hall samples, but lower concentrations of 2OH-BTZ. However, it should be noted that the
105 reported values in the study by Dye et al. were not direct measurements but based on RDC
106 concentrations in ground granulate and estimated concentrations of rubber in the airborne PM, so
107 these data should be treated with caution.

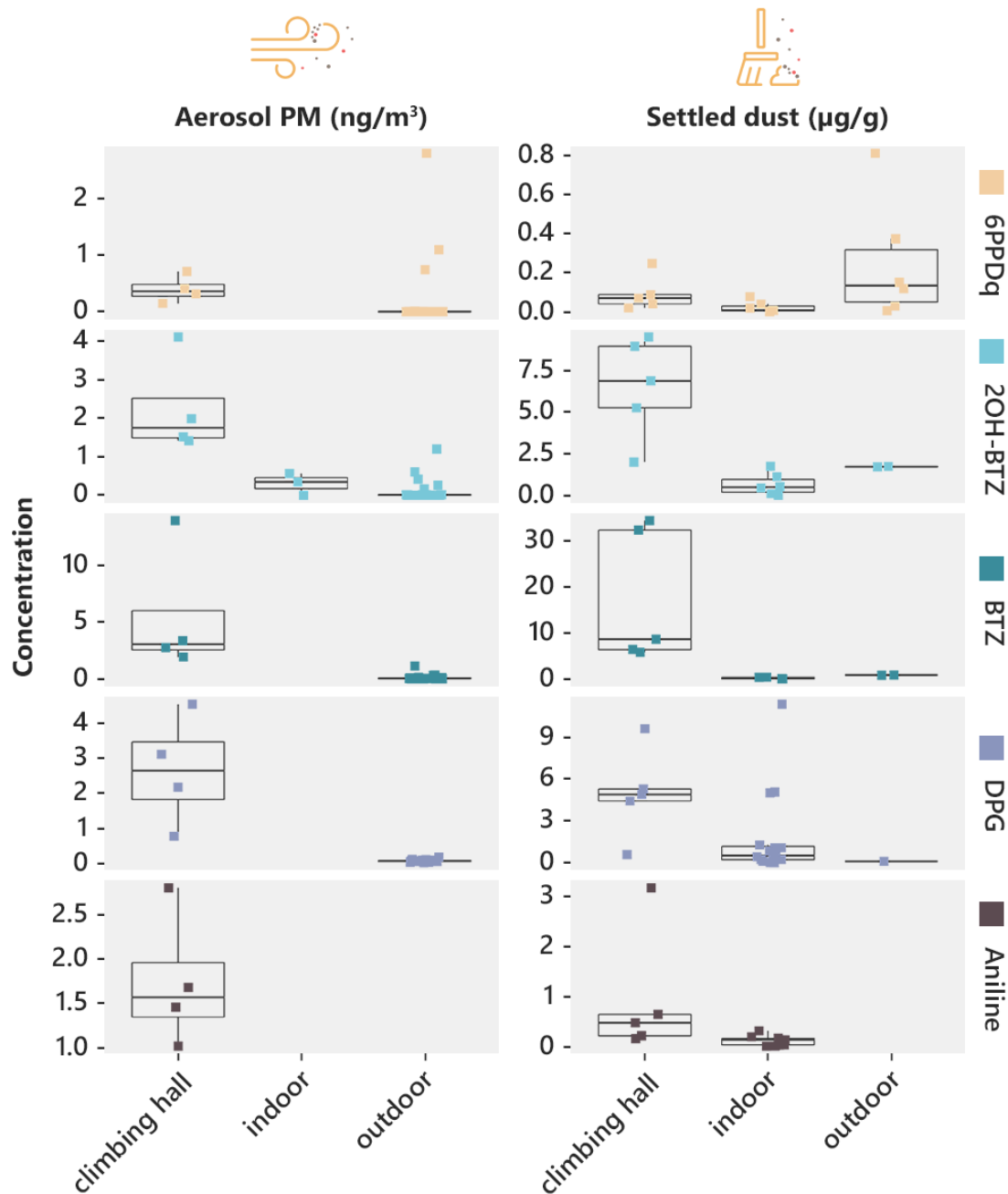


Figure 3: Rubber-derived compound concentrations measured in climbing hall airborne particulate matter (left) and settled dust (right) compared to concentrations reported in the literature for various indoor (houses, vehicles, shopping malls, dormitories, parking lot, sport halls) and outdoor (roadsides, city centers, playgrounds, recycling plants, industrial sites) environments. Details about literature values provided in Table S2.

108 Our data show that concentrations of RDCs found in the indoor air of climbing halls exceed those of
 109 most other environments that have been studied so far. Most climbers spend several hours in indoor
 110 climbing hall facilities and usually have a high respiration rate that could increase intake of RDCs.
 111 We explored the human exposure to RDCs in climbing halls by calculating the estimated daily intake

112 via inhalation (EDI_{inh}) for two groups: regular adult climbers and employees working at the halls
 113 (Table 2). Mean EDI_{inh} values estimated for the two sub-groups (adult climbers and employees)
 114 showed that employees would be subjected to a higher exposure than climbers due to their longer
 115 average exposure time, despite their lower inhalation rate (Tables 2, S4). EDI_{inh} for benzothiazoles
 116 ranged from 6.7 to 30 ng/kg/day and exceeded EDI_{inh} for Σ PPDs (0.2 to 0.8 ng/kg/day) which were
 117 similar to EDI_{inh} for Σ PPDqs (0.4 to 1.6 ng/kg/day). The EDI_{inh} derived for BTZs in this study was
 118 two orders of magnitude above those estimated for employees near industrial sites in Spain⁴⁵. EDI_{inh}
 119 for PPDs and PPDqs were up to 3.1 and 7.8-fold higher than EDI_{inh} for near-roadside workers in
 120 Chinese megacities and two orders of magnitudes higher than the EDI_{inh} for the adult population in
 121 Hong-Kong⁴². EDI_{inh} for DPG ranged from 4.9 – 8.7 ng/kg/day exceeding EDI via household dust
 122 ingestion in 11 countries (0.0 – 0.9 ng/kg/day)³⁹ (Table S5).

Table 2: Mean estimated dose intake (ng/kg/day) by inhalation from two sub-groups (adult climbers and employees) derived from Hall 1 and 2 aerosol PM data for a selection of rubber derived compounds.

| EDI (ng/kg/day) | Aniline | BTZ | 2OH-BTZ | DPG | HMMM | 6PPD | 6PPDq | IPPD | IPPDq |
|-------------------------------|---------|------|---------|------|------|------|-------|------|-------|
| EDI_{inh} Hall 2_(employee) | 5.85 | 22.8 | 7.59 | 9.22 | 1.06 | 0.58 | 1.54 | 0.26 | 0.09 |
| EDI_{inh} Hall 1_(employee) | 3.71 | 7.25 | 4.81 | 5.36 | 0.12 | 0.20 | 0.64 | 0.13 | 0.01 |
| EDI_{inh} Hall 2_(climber) | 3.24 | 12.7 | 4.21 | 5.12 | 0.59 | 0.32 | 0.85 | 0.14 | 0.05 |
| EDI_{inh} Hall 1_(climber) | 2.06 | 4.02 | 2.67 | 2.97 | 0.07 | 0.11 | 0.35 | 0.07 | 0.01 |

123 The contribution of climbing halls to the total daily intake of RDCs is significant for individuals
 124 exercising or working in these facilities. By comparing the EDI obtained in this study with the
 125 available EDI from literature derived for other environments, we highlight that exposure from indoor
 126 climbing halls exceeds every other exposure source known to date, including from such contaminated
 127 environments as roadsides in megacities (Table S5).

128 **Background levels of rubber derived compounds and evaluation of potential sources**

129 We performed several tests to eliminate sample contamination as the source of high RDC levels in
 130 aerosol PM and settled dust samples. Collection blanks were prepared to assess contamination that
 131 could have originated during aerosol PM sampling, subsequent storage, and laboratory processing;

132 storage blanks were prepared to assess contamination originating from sample storage and laboratory
133 processing; and laboratory blanks were prepared to isolate contamination originating during
134 laboratory processing. Laboratory blanks, which assessed background levels in solvents, glassware
135 and inadvertent contamination via laboratory aerosols, were mostly clean, except for low amounts of
136 2SH-BTZ and 2OH-BTZ, which were detected in one out of four blanks (Section S1). Collection and
137 storage blanks contained low levels of 2SH-BTZ, 2OH-BTZ, BTZ, DPG, and IPPD (Section S1). This
138 is unsurprising, since collection and storage blanks were prepared in the climbing halls, where RDCs
139 were present at high concentrations. RDC levels in these blanks were at least one order of magnitude
140 lower what was measured in aerosol PM samples (Section S1, Table 1), which confirms that the
141 majority of RDCs in our samples were not introduced via contamination. The total mass of RDCs
142 measured in collection blanks (representing contamination accumulated during sample collection,
143 storage, and laboratory processing) was subtracted from the mass of RDCs measured in aerosol PM
144 samples.

145
146 Levels of several RDCs in climbing hall aerosol PM and settled dust greatly exceed those reported in
147 other environments (Figure 3). Thus, we expected that the high concentrations of these RDCs were
148 specifically due to climbing activity. We collected reference samples in offices of climbing hall 1
149 (same building), where climbing is not practiced for confirmation. In these reference samples, we
150 detected 6PPD and IPPD (0.10 and 0.86 ng/m³, respectively) (Section S1), which is to be expected,
151 since the concentrations of 6PPD and IPPD in our aerosol PM samples are in the range of those
152 reported in other indoor²⁸ and outdoor^{33,45-50} environments (Figure S1), implying that these RDCs are
153 present at background levels, and not specifically derived from climbing activity. On the other hand,
154 BTZ, 2OH-BTZ, 6PPDq, IPPDq, DPG, aniline and HMMM were not detected in the reference
155 samples (Section S1), and their concentrations in our APM samples exceed previously reported values
156 (Figure 3), indicating that these compounds have a climbing-specific source.

157
158 To investigate potential climbing-related sources of RDCs, we first extracted samples of climbing
159 holds and mats used in the climbing areas. IPPD was detected in one climbing hold (66.0 ng/g), and in

160 one of the mats measured (83.1 ng/g). IPPDq was detected in the same mat (5.8 ng/g). In contrast,
161 dust samples contain 139 ng/g IPPD and 25 ng/g IPPDq which is higher than concentration in mats
162 and holds. Climbing holds and mats are made from durable materials with very low abrasion, so they
163 probably did not contribute substantially to the aerosol PM or settled dust present in climbing halls
164 and no other RDCs were found in these items (Section S1). Therefore, we concluded that another
165 climbing related source must be the main contributor to the high concentrations of RDCs measured in
166 settled dust and aerosol PM samples.

167

168 **Engineered climbing shoes contain high quantities of rubber-derived compounds**

169 Sports products are highly engineered materials, and so are climbing shoes. Their soles are composed
170 of rubber for an optimal friction on the climbing holds. Specific rubber formulas have been developed
171 to produce shoes that offer various combinations of softness, flexibility, stiffness, and stickiness.
172 These properties, as well as rubber durability, are typically optimized using additives. Thus, soles of
173 climbing shoes could be responsible for the high RDC levels found in the air and dust samples from
174 climbing halls.

175 We screened 30 shoe sole (SS) samples from various brands for RDCs (Table S6). All 15 RDCs were
176 found in at least one shoe sole sample. Concentrations were highly variable between shoe models with
177 cumulative RDC concentrations ranging from 25 to 3,405 $\mu\text{g/g}$ (mean: 711 $\mu\text{g/g}$) (Fig 4, Table S1).
178 Benzothiazoles exhibited high concentrations with 2SH-BTZ being the main constituent (mean: 538
179 $\mu\text{g/g}$) representing on average 67% of the total mass of RDCs detected (Fig S2). BTZ, 2OH-BTZ and
180 2-amino-BTZ were detected in lower concentrations (mean: 58, 53 and 3 $\mu\text{g/g}$, respectively). These
181 results suggest that, as in other rubber products, 2SH-BTZ is used as a vulcanization accelerator
182 during the curing process. Other benzothiazoles are also present and are typically considered to be
183 impurities or degradation products^{51,52}. Unlike benzothiazoles, DPG and aniline were not detected in
184 every shoe sole sample, with concentrations ranging from <LOQ to 814 $\mu\text{g/g}$ and <LOQ to 225 $\mu\text{g/g}$,
185 respectively. DPG is another vulcanization accelerator and may be used together with or instead of

186 2SH-BTZ (S18 and S19; Fig 4). *p*-Phenylenediamine compounds were detected in most shoe sole
187 samples in variable concentrations, with 6PPD and IPPD as the compounds with the highest
188 concentrations (mean: 1303 ng/g and 661 ng/g, respectively). This is not surprising, since of the
189 numerous PPDs available, 6PPD and IPPD are the most commonly used rubber antiozonants⁵³. CPPD
190 and DPPD were only detected sporadically and at trace levels (Table S1). The respective quinone
191 transformation products, 6PPDq and IPPDq, were consistently detected (mean: 23 ng/g and 15 ng/g,
192 respectively) and as expected, their concentration in the samples were correlated to the concentration
193 of the parent compounds. CPPDq and DPPDq were also occasionally detected along with their parent
194 compounds, but at very low concentrations (Table S1). Overall, RDC concentrations in shoe sole
195 samples were highly variable and likely due to different compounding strategies used by
196 manufacturers as well as the target product characteristics (i.e., stiffness, durability, performance,
197 adhesiveness). RDC concentrations in shoe sole samples were generally lower (DPG and PPDs) or
198 similar (benzothiazoles) to those in tire tread^{51,52} but higher than in other elastomeric consumer
199 products⁵².

200

201

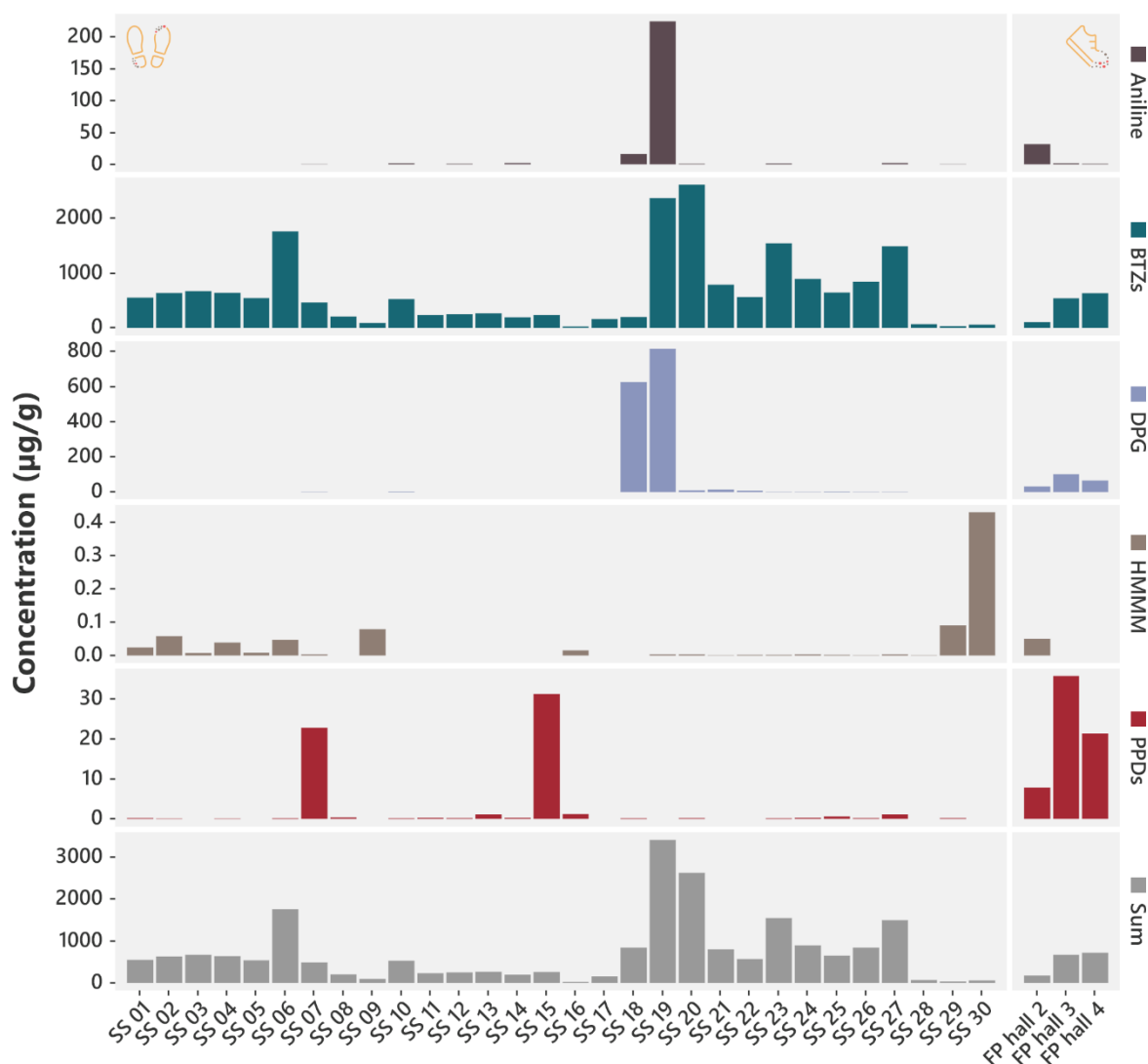


Figure 4: RDC concentrations in 30 climbing shoe soles (left), and foothold powder from three climbing halls (right). Concentrations of RDCs vary substantially between different shoe models. Foothold powder samples are representative of the variety of different shoe models. Information about shoe model can be found in Table S6.

202 We also collected powder samples from the top of several climbing footholds (Figures 1 and 5)
 203 which, based on visual inspection, were comprised primarily of abraded climbing shoe soles (in
 204 contrast to settled dust samples, which was more heterogenous in composition). As these foothold
 205 powder (FP) samples were collected in public climbing halls, where visitors wear a variety of
 206 different climbing shoe models, these samples should represent the diversity of shoe soles prevalent in
 207 climbing hall environments. Indeed, the foothold powder samples were highly representative of the
 208 variability found among individual shoe samples, both in terms of RDC concentrations and profile
 209 (Figures 4, S2). The abrasion of shoe soles generates fine elongated rubber particles (Figure 5) which

210 can become airborne over time, since it is common practice for climbers to brush particles off holds. It
211 has been previously shown that abrasion of particles and fibers containing additives drives the
212 chemical composition of indoor dust⁵⁴, and it is highly likely that the fine rubber particles emitted via
213 abrasion were captured by our air sampler. With SEM imaging, we confirmed that elongated particles,
214 visually very similar to those in shoe powder, were present in settled dust samples, including in the
215 respirable size fraction (Figure 5). Although some RDCs were indeed found in all four sample types,
216 i.e., shoe soles, foothold powder samples, settled dust and aerosol PM, the chemical profile did not
217 fully match across the four sample types (Figure 2). We thus decided to explore the possibility that
218 chemical transformations of some RDCs in airborne particles could link the chemical profiles of
219 RDCs in climbing shoes to those in aerosol PM and settled dust samples.

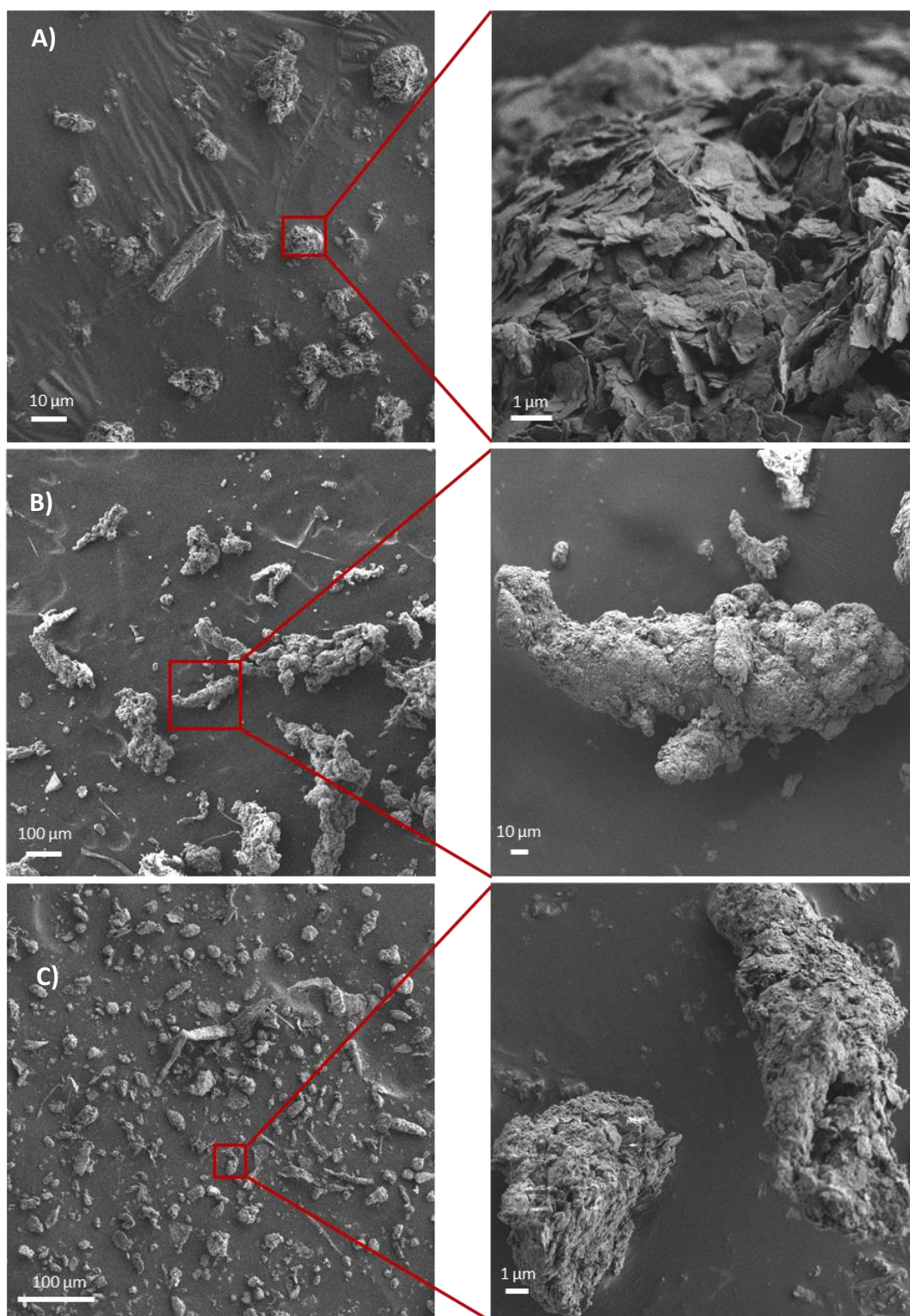


Figure 5: Representative scanning electron microscopy images of (A) chalk (calcium carbonate powder), (B) a foothold powder sample and (C) a settled dust sample collected in climbing halls. Rubber particles resulting from the abrasion of shoe soles are visible in the foothold powder and settled dust samples (B,C). Rubber particles are distinguishable from chalk particles (A) due to their elongated shape and surface physical characteristics with a smooth carbon-based surface compared to chalk. Surface roughness appears to increase between recently generated rubber particles identified in the foothold powder samples (B) and particles found in settled dust (C).

220 **Transformations in indoor air implicate climbing shoes as the source of rubber-derived**
221 **compounds**

222 While shoe sole and foothold powder samples were likely comprised mostly of rubber, the aerosol
223 PM and settled dust samples were more heterogeneous, so concentrations of RDCs cannot be directly
224 compared across the sample types. Therefore, we normalized all individual RDC concentrations to
225 \sum RDCs. All settled dust and aerosol PM samples had remarkably similar RDC profiles, which
226 differed distinctly from shoe sole and foothold powder samples (Figure 2a). Strikingly, the mean
227 fraction of 2SH-BTZ dropped from 69.9% in the foothold powder samples to 2.6% in the settled dust
228 and aerosol PM samples. At the same time, the fractions of BTZ and 2OH-BTZ increased from 8.7%
229 to 41.8% and 5.1% to 19.9%, respectively. A similar pattern emerged for the PPDs. The fraction of
230 6PPD dropped from 2.8% in the foothold powder samples to 0.8% in the settled dust and aerosol PM
231 samples, while the fraction of 6PPDq increased from 0.0% in the foothold powder samples to 2.1% in
232 the settled dust and aerosol PM samples. Likewise, the fraction of IPPD dropped from 1.3% to 0.5%,
233 while IPPDq increased from 0.0% to 0.1% (Figures 2a, S3).

234 All observed shifts (2SH-BTZ \rightarrow 2OH-BTZ + BTZ; 6PPD \rightarrow 6PPDq; IPPD \rightarrow IPPD-q) are likely the
235 result of transformation reactions on particle surfaces. The rubber particles collected in our aerosol
236 PM samples must by virtue of the collection technique, exhibit small aerodynamic diameters with a
237 correspondingly larger surface area, since larger rubber particles likely do not remain airborne long
238 enough to be inhaled (or captured by our sampling device). Rubber particles present in the collected
239 settled dust samples were also postulated to be enriched in smaller sized particulates after aerosol
240 transport. Such small particles have a high specific surface area, which allows for rapid reactions with
241 reactive species in the surrounding gas phase. Ozone, as well as secondary species, such as the
242 hydroxyl radical and NO_x drive chemical reactions on particle surfaces in indoor air⁵⁵. In contrast, it
243 was hypothesized that the foothold powder samples exhibited a lower specific surface area due to the
244 larger particle sizes and was too freshly generated to have undergone extensive transformation
245 reactions prior to collection.

246 To test whether ozone and associated secondary species could catalyze the observed transformations,
247 we conducted ozonation experiments on foothold powder samples, using an ozone exposure
248 chamber⁵⁶. This method exposes particles to elevated ozone concentrations (and associated secondary
249 species), without altering other parameters like temperature or light. Thus, transformations should
250 proceed via the mechanisms which we expect are most relevant in climbing halls. After four hours of
251 exposure to elevated ozone (1 g/m³), the chemical profile of the foothold powder samples shifted
252 substantially and corresponded to the chemical profile of the aerosol PM and settled dust samples
253 (Figure 2b, S4, Table S7).

254 Transformation of 2SH-BTZ is well studied in the aquatic environment⁵⁷, where 2OH-BTZ and BTZ
255 are frequently reported as transformation products, including when transformation is catalyzed by
256 ozone^{58,59}. In our ozonation experiments, the mean concentration of 2SH-BTZ decreased from 78 µg/g
257 to 23 µg/g, while the mean concentrations of 2OH-BTZ and BTZ increased from 15 µg/g to 17 µg/g,
258 and 13 µg/g to 39 µg/g respectively. Likewise, it is well documented that PPDs react with ozone to
259 form PPD-quinones^{17,60,61}, and the 6PPDq/6PPD ratio in crumb rubber has been related to the extent
260 of environmental weathering⁵². In our ozonation experiments, the mean 6PPDq/PPD ratio increased
261 from 0.04 to 0.12, and the mean IPPDq/IPPD ratio from 0.02 to 0.04. Based on the transformations
262 reported in the literature, and the results of our ozonation experiments, we conclude that the observed
263 shift of RDC profile in our samples results from atmospheric transformations of the RDCs after
264 generation of the rubber particles on the climbing holds. This conclusion is further supported by the
265 fact that we did not find any significant alternative sources of the RDCs to aerosol PM or settled dust
266 in climbing halls.

267 **Implications**

268 In indoor climbing halls, concentrations of several RDCs significantly exceed previously reported
269 values. Total daily intake of RDCs for individuals visiting or working in these facilities exceeds
270 exposure via all other known routes. The inhalable fraction of PM usually deposits in the nose and
271 upper airways, and is subsequently swallowed⁶². Respirable particles have a higher probability of

272 deposition within deeper regions of the lung⁶³. Thus, exposure to RDCs in climbing halls will be via
273 both the gastrointestinal and respiratory systems. Future research needs to address the leaching
274 kinetics and bioavailability of RDCs within the human body, including in epithelial lung fluid, and
275 gastrointestinal fluids, as well as the toxicological risk that RDCs pose. So far, there is concerning
276 existing literature on toxicity of several RDCs; in particular PM-bound PPDs and PPDqs may
277 contribute to the oxidative potential of PM, as recently demonstrated for outdoor environments⁶⁴.
278 Oxidative potential of PM induces oxidative stress and inflammation in the respiratory and
279 cardiovascular systems^{65,66}. Indeed, organic tire extracts and tire wear particles have been shown to
280 induce DNA damage, inflammation, and cell death in human lung cells²⁰⁻²².

281 We have shown that from the time of particle generation to the time of entrance into a target organism
282 or environment, the RDC profile can shift substantially, including towards more toxic species, e.g.,
283 6PPD to 6PPDq. Previous work has relied on concentrations of RDCs in unweathered material to
284 estimate exposure²⁸ or even toxicity^{67,68}, but this approach should be treated with caution. In fact, a
285 recent review has called for a need to understand atmospheric transformations of organic RDCs in tire
286 wear particles⁶⁹. Due to elevated ozone and NO_x levels above the road surface, we expect that tire
287 wear particles will initially undergo similar atmospheric transformation reactions to those we
288 observed. Thus, our findings provide insights which can guide future research on the impact of
289 atmospherically aged tire wear particles.

290 With a global increasing urbanization, we expect to live, work, and recreate in safe indoor
291 environments. Particularly in indoor sports facilities, where respiration increases, air quality standards
292 need to be high and safe. Rubber formulations containing potentially toxic RDCs should not be used
293 in climbing shoes, or other consumer products where elevated human exposure is likely to occur.
294 Spurred mostly by the ongoing research about tire wear particles, the tire industry is under pressure to
295 find alternatives for some additives, such as 6PPD. Upcoming research and legislation must not
296 overlook consumer products, such as climbing shoes, which contain a high additive content, and
297 dominate the human exposure for a subset of the population. A recent study screening RDCs in a
298 multitude of rubber consumer products found that most products had RDC concentrations much lower

299 than those in climbing shoes⁵². This contrast shows that although rubber is widely used, only highly
300 engineered consumer products, such as climbing shoes and tires, contain a high additive content. This
301 knowledge can focus future work to identify “hotspots” of RDC exposure, but also sustains the global
302 problem of the toxicity burden of plastic additives. Until rubber becomes safer, potential strategies to
303 minimize exposure in climbing halls should also be considered, such as more frequent cleaning,
304 mobile and stationary HEPA air filters, or banning of certain shoe models.

305 **Materials and methods**

306 **Sample collection and characterization**

307 Four types of samples were collected: aerosol PM, settled dust, shoe soles, and foothold powder
308 samples (Figure 1).

309

310 Particulate matter in the aerosol fraction was sampled with a standardized glass liquid impinger
311 (Copley Scientific Ltd), which is an active sampling device which divides airborne PM into inhalable
312 ($> 6.4 \mu\text{m}$ aerodynamic diameter) and respirable ($< 6.4 \mu\text{m}$ aerodynamic diameter) fractions.

313 Composite aerosol PM samples were collected in Hall 1 and Hall 2 on five consecutive days in April
314 2023 during peak activity (17:00-20:00). The glass liquid impinger was operated as described in the
315 European Pharmacopoeia (Ph. Eur.). Before the device was assembled, 7 mL of MilliQ-water was
316 introduced into the upper chamber and 475 g (=130 mL) of ceramic beads (9730, ZY-P, 2.6-3.3 mm,
317 SiLibeads, Sigmund Lindner GmbH, Warmensteinach, Germany) and 25 mL of MilliQ-water were
318 introduced into the lower chamber. The air inlet was set at a height of 142 cm, facing the climbing
319 wall at approximately 3 m distance. The air flow rate was $60 \pm 2 \text{ L/min}$, for a total volume of 54 m^3
320 air per sample in each climbing hall. Temperature, humidity, and liquid levels of the upper and lower
321 chambers were monitored every 15 minutes, and liquids were replenished as needed. At the end of
322 each day of composite sampling, every part of the device was rinsed three times with 6 mL MilliQ-
323 water, and three times with 6 mL ethanol and collected. MilliQ water and ethanol rinses were stored
324 separately at -20°C in amber glass vials until analysis. Samples from the mouth / throat piece and the
325 upper chamber were combined to represent the inhalable fraction of PM; samples from the lower

326 chamber were collected separately to represent the respirable PM fraction. Further details about
327 aerosol sampling are provided in Section S2.

328

329 Settled dust samples were collected from uncleaned floor and wood surfaces 5 to 10 m from the
330 climbing walls (where rubber particles in dust would most likely have been aeri ally transported, rather
331 than falling directly from the climbing walls). Settled dust samples were collected from Hall 1 ($n=1$),
332 Hall 3 ($n=3$) and Hall 4 ($n=1$) between March and April 2023 (Table S8). All samples (1 – 5g) were
333 collected using a clean metallic spatula and stored in cleaned amber glass vials at -20°C until further
334 processing.

335

336 Thirty shoe sole samples were collected from both used and new climbing shoes to represent the
337 marketplace (Table S6). Shoe sole samples were cut out from the tip of the sole, i.e., the area most
338 susceptible area to abrasion on the climbing holds during use. Samples were cut into 1 mm^2 pieces
339 and ground into fine powder using cryo-ball milling (MM400, Retsch®) for 2 min at 25 Hz. After
340 grinding, 50 mg powder was immediately suspended in 1 mL dichloromethane to prevent re-
341 agglomeration.

342

343 Samples (1 – 5g) of material accumulated in the clefts of climbing footholds (foothold powder
344 samples) were collected in Hall 1 ($n=3$), Hall 2 ($n=1$), and Hall 3 ($n=3$) between March and October
345 2023 (Figure 1, Table S8).

346 Sub-samples of pure solid chalk, foothold powder samples and settled dust samples were coated with
347 a gold nanolayer (10 nm) and visually characterized with a scanning electron microscope (Gemini
348 SEM 300, Zeiss) at various magnification levels.

349

350 Sample extraction and measurement

351 Liquid was removed from the aerosol PM samples via rotary evaporation (ethanol) or lyophilization
352 (MilliQ-water). The residual particle mass was determined gravimetrically using a high precision

353 balance and samples were then resuspended in ethanol. All samples were then extracted with
354 accelerated solvent extraction (details Section S4). The following RDCs were analysed in all samples
355 with UPLC-MS/MS: benzothiazole (BTZ), 2-hydroxybenzothiazole (20H-BTZ), 2-
356 aminobenzothiazole (2-amino-BTZ), 2-mercaptobenzothiazole (2SH-BTZ), aniline, 1,3-
357 diphenylguanidine (DPG), hexa(methoxymethyl)melamine (HMMM), and the phenylenediamine
358 compounds: 6PPD, IPPD, CPPD, DPPD and their associated quinones: 6PPDq, IPPDq, CPPDq,
359 DPPDq. Details are provided in the SI regarding the chemicals and internal standards used (Section
360 S3), UPLC-MS/MS methods (Section S5) and extraction recovery (Table S9) for analyses of all
361 samples.

362 QA/QC

363 We investigated contamination that may have arisen during collection, storage, or laboratory
364 processing of samples. Collection blanks were collected before each composite sampling event. The
365 glass liquid impinger was assembled in the climbing hall (without air flow), then immediately rinsed
366 with exactly the same protocol as the samples. Storage blanks were also prepared in the climbing hall
367 by filling amber glass storage vials with MilliQ-water or ethanol, and then opening and closing the
368 vials five times, to simulate the collection of samples. Collection and storage blanks were stored and
369 extracted in the same manner as aerosol PM samples. Laboratory blanks were prepared in the same
370 manner as samples, beginning with accelerated solvent extraction.

371
372 To investigate background levels of RDCs (not arising from climbing activity), we collected reference
373 samples in an office of climbing hall 2, which was in the same building, but not connected to the
374 climbing area. Sampling procedure and duration were the same. Finally, to account for other potential
375 sources of RDCs in climbing areas, we obtained samples of climbing holds, as well as two types of
376 climbing mats from climbing hall 2. These control samples were extracted with the same procedure as
377 the shoe sole samples.

378

379 Exposure Calculations

380 To determine the human exposure to RDCs in climbing halls, estimated daily intake via inhalation
381 values were calculated based on total aerosol PM (inhalable plus respirable fraction) using equation
382 (2) for two types of individuals: regular adult climbers and employees working at the halls:

383

$$384 \quad EDI_{inh} = \frac{C_{air} IR ET EF}{BW Cf} \quad (2)$$

385

386 whereby EDI_{inh} is the estimated daily intake *via* inhalation (ng/kg/day), C_{air} the concentration of
387 RDCs in the aerosol (ng/m³), IR the inhalation rate (m³/hour), ET the exposure time (hours/day), EF
388 the exposure frequency (days/year), BW the body weight (kg) and Cf the number of days per year.
389 Details regarding exposure parameters obtained from the US EPA exposure factor handbook⁷⁰ are
390 available in Table S4.

391

392 Transformation Experiments

393 Ozonation experiments were performed to investigate whether the compound profile shift from
394 foothold powder to aerosol PM and settled dust could be explained by transformations of the
395 compounds in foothold powder. Foothold powder was collected from climbing hall 1 immediately
396 before experiment start and divided into six sub-samples. An ozone chamber⁵⁶ was employed to
397 expose three sub-samples to elevated ozone concentrations (1g/m³) at room temperature for 4 hours.
398 NO_x concentration was also measured to be 9 ppm during the experiment. After ozonation, all sub
399 samples were spiked with internal standards, and extracted and measured as described above.

400

401 Data Availability

402 All analytical data that support the findings of this study are available in the corresponding Supporting
403 Information.

404

405 **Acknowledgements**

406 The authors would like to acknowledge and thank Kristina Primerano and Professor Dr. Hinrich
407 Grothe from the CD Laboratory for chemo-mechanical analysis of bituminous materials (TU Wien)
408 for the support with ozonation experiments. The authors would like to warmly thank APDV resole for
409 providing various samples of climbing shoes soles as well as the climbing halls managers who have
410 continuously supported this project, and repeatedly allowed sampling in their facilities. Lukas
411 Wimmer's work was supported by IMPTOX European Union's Horizon 2020 research and innovation
412 program (grant number [965173](#)). Thilo Hofmann acknowledges funding from the Austrian Science
413 Fund, Cluster of Excellence COE7.

414

415 **Author Contribution**

416 Anya Sherman and Thibault Masset contributed equally to this manuscript and conceived the
417 experiments together with Lukas Wimmer. All authors contributed to design of the study and
418 interpretation of data. Anya Sherman and Thibault Masset led the writing of the manuscript. Lea Ann
419 Dailey, Thorsten Hüffer, Florian Breider and Thilo Hofmann revised and edited the text. All authors
420 read and commented on the manuscript.

421

422 **Competing Interests**

423 The authors declare no competing interests.

424

425 **References**

- 426
- 427 1. Li, J., Li, W. X., Bai, C. & Song, Y. Particulate matter-induced epigenetic changes and lung
428 cancer. *The Clinical Respiratory Journal* **11**, 539–546 (2017).
- 429 2. Pope III, C. A. *et al.* Lung Cancer, Cardiopulmonary Mortality, and Long-term Exposure to Fine
430 Particulate Air Pollution. *JAMA* **287**, 1132–1141 (2002).
- 431 3. Brook, R. D. *et al.* Particulate Matter Air Pollution and Cardiovascular Disease. *Circulation* **121**,
432 2331–2378 (2010).
- 433 4. Hoang, T., Nguyen, T. Q. & Tran, T. T. A. Short-term exposure to ambient air pollution in
434 association with COVID-19 of two clusters in South Korea. *Tropical Medicine & International*
435 *Health* **26**, 478–491 (2021).
- 436 5. Lim, S. S. *et al.* A comparative risk assessment of burden of disease and injury attributable to 67
437 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global
438 Burden of Disease Study 2010. *The Lancet* **380**, 2224–2260 (2012).
- 439 6. Apte, J. S., Marshall, J. D., Cohen, A. J. & Brauer, M. Addressing Global Mortality from
440 Ambient PM_{2.5}. *Environ. Sci. Technol.* **49**, 8057–8066 (2015).
- 441 7. Gurjar, B. R. *et al.* Human health risks in megacities due to air pollution. *Atmospheric*
442 *Environment* **44**, 4606–4613 (2010).
- 443 8. World Urbanization Prospects 2018 | Population Division.
444 <https://www.un.org/development/desa/pd/news/world-urbanization-prospects-2018>.
- 445 9. Matz, C. J., Stieb, D. M. & Brion, O. Urban-rural differences in daily time-activity patterns,
446 occupational activity and housing characteristics. *Environmental Health* **14**, 88 (2015).
- 447 10. *Report to Congress on Indoor Air Quality Volume II: Assessment and Control of Indoor Air*
448 *Pollution*. (1989).
- 449 11. Berry, N. Social Climbers - The Evolving Indoor Climbing Industry. *UKC* (2018).
- 450 12. *The Market of Climbing Gyms Germany*. [https://www.businesscoot.com/en/study/the-market-of-](https://www.businesscoot.com/en/study/the-market-of-climbing-gyms-germany)
451 [climbing-gyms-germany](https://www.businesscoot.com/en/study/the-market-of-climbing-gyms-germany) (2023).
- 452 13. Weinbruch, S., Dirsch, T., Ebert, M., Hofmann, H. & Kandler, K. Dust exposure in indoor
453 climbing halls. *Journal of Environmental Monitoring* **10**, 648 (2008).
- 454 14. Hofmann, T. *et al.* Plastics can be used more sustainably in agriculture. *Commun Earth Environ*
455 **4**, 1–11 (2023).
- 456 15. Environment, U. N. Chemicals in Plastics - A Technical Report. *UNEP - UN Environment*
457 *Programme* <http://www.unep.org/resources/report/chemicals-plastics-technical-report> (2023).
- 458 16. Wagner, S. *et al.* Tire wear particles in the aquatic environment - A review on generation,
459 analysis, occurrence, fate and effects. *Water Research* **139**, 83–100 (2018).
- 460 17. Tian, Z. *et al.* A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon.
461 *Science* **371**, 185–189 (2021).
- 462 18. Brinkmann, M. *et al.* Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-quinone to Four
463 Fishes of Commercial, Cultural, and Ecological Importance. *Environ. Sci. Technol. Lett.* **9**, 333–
464 338 (2022).
- 465 19. Hiki, K. & Yamamoto, H. The Tire-Derived Chemical 6PPD-quinone Is Lethally Toxic to the
466 White-Spotted Char *Salvelinus leucomaenis pluvius* but Not to Two Other Salmonid Species.
467 *Environ. Sci. Technol. Lett.* **9**, 1050–1055 (2022).
- 468 20. Gualtieri, M., Rigamonti, L., Galeotti, V. & Camatini, M. Toxicity of tire debris extracts on
469 human lung cell line A549. *Toxicology in Vitro* **19**, 1001–1008 (2005).
- 470 21. Karlsson, H. L., Ljungman, A. G., Lindbom, J. & Möller, L. Comparison of genotoxic and
471 inflammatory effects of particles generated by wood combustion, a road simulator and collected
472 from street and subway. *Toxicology Letters* **165**, 203–211 (2006).
- 473 22. Wu, J., Cao, G., Zhang, F. & Cai, Z. A new toxicity mechanism of N-(1,3-Dimethylbutyl)-N'-
474 phenyl-p-phenylenediamine quinone: Formation of DNA adducts in mammalian cells and
475 aqueous organisms. *Science of The Total Environment* 161373 (2023)
476 doi:10.1016/j.scitotenv.2022.161373.
- 477 23. Li, Z. & Kannan, K. and 1, 2, 3-Triphenylguanidine in Human Urine Using Liquid
478 Chromatography-Tandem Mass Spectrometry. (2023) doi:10.1021/acs.est.3c00412.

- 479 24. Du, B. *et al.* First Report on the Occurrence of N-(1,3-Dimethylbutyl)-N'-phenyl-p-
480 phenylenediamine (6PPD) and 6PPD-Quinone as Pervasive Pollutants in Human Urine from
481 South China. *Environ. Sci. Technol. Lett.* **9**, 1056–1062 (2022).
- 482 25. Tang, S. *et al.* Prenatal Exposure to Emerging Plasticizers and Synthetic Antioxidants and Their
483 Potency to Cross Human Placenta. *Environ. Sci. Technol.* **56**, 8507–8517 (2022).
- 484 26. World Health Organization. *WHO Global Air Quality Guidelines: Particulate Matter (PM_{2.5}
485 and PM₁₀), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide.* (World Health
486 Organization, 2021).
- 487 27. Morawska, L. *et al.* Airborne particles in indoor environment of homes, schools, offices and aged
488 care facilities: The main routes of exposure. *Environment International* **108**, 75–83 (2017).
- 489 28. Dye, C., Bjerke, A., Schmidbauer, N. & Manø, S. Measurement of air pollution in indoor
490 artificial turf halls. *Report number NILU OR 3*, (2006).
- 491 29. Weschler, C. J., Salthammer, T. & Fromme, H. Partitioning of phthalates among the gas phase,
492 airborne particles and settled dust in indoor environments. *Atmospheric Environment* **42**, 1449–
493 1460 (2008).
- 494 30. Wang, L., Asimakopoulos, A. G., Moon, H. B., Nakata, H. & Kannan, K. Benzotriazole,
495 benzothiazole, and benzophenone compounds in indoor dust from the United States and East
496 Asian countries. *Environmental Science and Technology* **47**, 4752–4759 (2013).
- 497 31. Deng, C., Huang, J., Qi, Y., Chen, D. & Huang, W. Distribution patterns of rubber tire-related
498 chemicals with particle size in road and indoor parking lot dust. *Science of The Total
499 Environment* **844**, 157144 (2022).
- 500 32. Zhu, Q., Liao, C. & Jiang, G. Occurrence of Human Exposure to Benzothiazoles and
501 Benzotriazoles in Indoor Dust in Suizhou and Beijing, China. *Chem. Res. Chin. Univ.* **39**, 508–
502 515 (2023).
- 503 33. Wu, Y., Venier, M. & Hites, R. A. Broad Exposure of the North American Environment to
504 Phenolic and Amino Antioxidants and to Ultraviolet Filters. *Environ. Sci. Technol.* **54**, 9345–
505 9355 (2020).
- 506 34. Zhang, Y.-J. *et al.* Widespread N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine Quinone in
507 Size-Fractioned Atmospheric Particles and Dust of Different Indoor Environments. *Environ. Sci.
508 Technol. Lett.* **9**, 420–425 (2022).
- 509 35. Huang, W. *et al.* Occurrence of Substituted p-Phenylenediamine Antioxidants in Dusts. *Environ.
510 Sci. Technol. Lett.* **8**, 381–385 (2021).
- 511 36. Liu, R., Li, Y., Lin, Y., Ruan, T. & Jiang, G. Emerging aromatic secondary amine contaminants
512 and related derivatives in various dust matrices in China. *Ecotoxicology and Environmental
513 Safety* **170**, 657–663 (2019).
- 514 37. Deng, C., Huang, J., Qi, Y., Chen, D. & Huang, W. Distribution patterns of rubber tire-related
515 chemicals with particle size in road and indoor parking lot dust. *Science of The Total
516 Environment* **2022**,.
- 517 38. Hiki, K. & Yamamoto, H. Concentration and leachability of N-(1,3-dimethylbutyl)-N'-phenyl-p-
518 phenylenediamine (6PPD) and its quinone transformation product (6PPD-Q) in road dust
519 collected in Tokyo, Japan. *Environmental Pollution* **302**, (2022).
- 520 39. Li, Z.-M. & Kannan, K. Occurrence of 1,3-Diphenylguanidine, 1,3-Di- o -tolylguanidine, and
521 1,2,3-Triphenylguanidine in Indoor Dust from 11 Countries: Implications for Human Exposure.
522 *Environmental Science & Technology* **57**, 6129–6138 (2023).
- 523 40. Jin, R. *et al.* Ubiquity of Amino Accelerators and Antioxidants in Road Dust from Multiple Land
524 Types: Targeted and Nontargeted Analysis. *Environ. Sci. Technol.* acs.est.3c01448 (2023)
525 doi:10.1021/acs.est.3c01448.
- 526 41. Zhang, Y. *et al.* p-Phenylenediamine Antioxidants in PM_{2.5}: The Underestimated Urban Air
527 Pollutants. *Environmental Science & Technology* **56**, 6914–6921 (2022).
- 528 42. Cao, G. *et al.* New Evidence of Rubber-Derived Quinones in Water, Air, and Soil. *Environmental
529 Science & Technology* **56**, 4142–4150 (2022).
- 530 43. Wang, W. *et al.* Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of their
531 Quinone Derivatives in PM_{2.5}. (2022) doi:10.1021/acs.est.2c02463.

- 532 44. Johannessen, C., Helm, P., Lashuk, B., Yargeau, V. & Metcalfe, C. D. The Tire Wear
533 Compounds 6PPD - Quinone and 1,3 - Diphenylguanidine in an Urban Watershed. *Archives of*
534 *Environmental Contamination and Toxicology* **82**, 171–179 (2022).
- 535 45. Maceira, A., Marcé, R. M. & Borrull, F. Occurrence of benzothiazole, benzotriazole and
536 benzenesulfonamide derivatives in outdoor air particulate matter samples and human exposure
537 assessment. *Chemosphere* **193**, 557–566 (2018).
- 538 46. Liao, X. *et al.* Contamination profiles and health impact of benzothiazole and its derivatives in
539 PM_{2.5} in typical Chinese cities. *Science of The Total Environment* **755**, 142617 (2021).
- 540 47. Nuñez, A., Vallecillos, L., Marcé, R. M. & Borrull, F. Occurrence and risk assessment of
541 benzothiazole, benzotriazole and benzenesulfonamide derivatives in airborne particulate matter
542 from an industrial area in Spain. *Science of The Total Environment* **708**, 135065 (2020).
- 543 48. Cao, G. *et al.* New Evidence of Rubber-Derived Quinones in Water, Air, and Soil. *Environmental*
544 *Science & Technology* **56**, 4142–4150 (2022).
- 545 49. Zhang, Y. *et al.* p-Phenylenediamine Antioxidants in PM_{2.5}: The Underestimated Urban Air
546 Pollutants. *Environmental Science & Technology* **56**, 6914–6921 (2022).
- 547 50. Wang, W. *et al.* Beyond Substituted p-Phenylenediamine Antioxidants: Prevalence of Their
548 Quinone Derivatives in PM_{2.5}. *Environmental Science & Technology* **56**, 10629–10637 (2022).
- 549 51. Masset, T. *et al.* Bioaccessibility of Organic Compounds Associated with Tire Particles Using a
550 Fish In Vitro Digestive Model: Solubilization Kinetics and Effects of Food Coingestion.
551 *Environmental Science & Technology* (2022) doi:10.1021/acs.est.2c04291.
- 552 52. Zhao, H. N. *et al.* Screening p-Phenylenediamine Antioxidants, Their Transformation Products,
553 and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products.
554 *Environmental Science & Technology* (2023) doi:10.1021/acs.est.2c07014.
- 555 53. Datta, R. N., Huntink, N. M., Datta, S. & Talma, A. G. Rubber Vulcanizates Degradation and
556 Stabilization. *Rubber Chemistry and Technology* **80**, 436–480 (2007).
- 557 54. Rauert, C. *et al.* Test chamber and forensic microscopy investigation of the transfer of brominated
558 flame retardants into indoor dust via abrasion of source materials. *Science of The Total*
559 *Environment* **493**, 639–648 (2014).
- 560 55. Weschler, C. J. & Carslaw, N. Indoor Chemistry. *Environmental Science & Technology* **52**,
561 2419–2428 (2018).
- 562 56. Mirwald, J., Maschauer, D., Hofko, B. & Grothe, H. Impact of reactive oxygen species on
563 bitumen aging – The Viennese binder aging method. *Construction and Building Materials* **257**,
564 119495 (2020).
- 565 57. Liao, C., Kim, U. J. & Kannan, K. A Review of Environmental Occurrence, Fate, Exposure, and
566 Toxicity of Benzothiazoles. *Environmental Science and Technology* **52**, 5007–5026 (2018).
- 567 58. Fiehn, O., Wegener, G., Jochimsen, J. & Jekel, M. Analysis of the ozonation of 2-
568 mercaptobenzothiazole in water and tannery wastewater using sum parameters, liquid- and gas
569 chromatography and capillary electrophoresis. *Water Research* **32**, 1075–1084 (1998).
- 570 59. Derco, J., Kassai, A., Melicher, M. & Dudas, J. Removal of the 2-mercaptobenzothiazole from
571 model wastewater by ozonation. *The Scientific World Journal* **2014**, (2014).
- 572 60. Hu, X. *et al.* Transformation Product Formation upon Heterogeneous Ozonation of the Tire
573 Rubber Antioxidant 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine).
574 *Environmental Science & Technology Letters* **9**, 413–419 (2022).
- 575 61. Zhao, H. N. *et al.* Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous
576 Gas-Phase Ozonation: Identification and Environmental Occurrence. *Environmental Science &*
577 *Technology* **57**, 5621–5632 (2023).
- 578 62. Ferro, A. & Hidemann, L. Inhalation Exposure, Uptake, and Dose. in *Exposure Analysis* (eds.
579 Ott, W. R., Steinemann, A. C. & Wallace, L. A.) (CRC Press, New York, 2006).
- 580 63. Scheuch, G., Kohlhäufel, M. J., Brand, P. & Siekmeier, R. Clinical perspectives on pulmonary
581 systemic and macromolecular delivery. *Advanced Drug Delivery Reviews* **58**, 996–1008 (2006).
- 582 64. Wang, W. *et al.* p-Phenylenediamine-Derived Quinones as New Contributors to the Oxidative
583 Potential of Fine Particulate Matter. *Environmental Science & Technology Letters* **9**, 712–717
584 (2022).

- 585 65. Crobeddu, B., Aragao-Santiago, L., Bui, L.-C., Boland, S. & Baeza Squiban, A. Oxidative
586 potential of particulate matter 2.5 as predictive indicator of cellular stress. *Environmental*
587 *Pollution* **230**, 125–133 (2017).
- 588 66. Liu, Q. *et al.* Oxidative Potential and Inflammatory Impacts of Source Apportioned Ambient Air
589 Pollution in Beijing. *Environ. Sci. Technol.* **48**, 12920–12929 (2014).
- 590 67. Capolupo, M., Sørensen, L., Jayasena, K. D. R., Booth, A. M. & Fabbri, E. Chemical
591 composition and ecotoxicity of plastic and car tire rubber leachates to aquatic organisms. *Water*
592 *Research* **169**, 115270 (2020).
- 593 68. Redondo-Hasselerharm, P. E., De Ruijter, V. N., Mintenig, S. M., Verschoor, A. & Koelmans, A.
594 A. Ingestion and Chronic Effects of Car Tire Tread Particles on Freshwater Benthic
595 Macroinvertebrates. *Environmental Science and Technology* **52**, 13986–13994 (2018).
- 596 69. Johannessen, C., Liggio, J., Zhang, X., Saini, A. & Harner, T. Composition and transformation
597 chemistry of tire-wear derived organic chemicals and implications for air pollution. *Atmospheric*
598 *Pollution Research* **13**, 101533 (2022).
- 599 70. US Environmental Protection Agency. Exposure Factors Handbook: 2011 Edition. *U.S.*
600 *Environmental Protection Agency EPA/600/R-*, 1–1466 (2011).

601
602

603 **Figure legends**

604

605 Figure 1: Schematic of a climbing hall, with photos of the four types of samples analyzed in our
606 study. Specialized climbing shoes are worn with highly functionalized rubber soles (1 – shoe soles).
607 Friction between these shoe soles and the footholds generates rubber particles (2 – foothold powder).
608 Those can be aerosolized and be inhaled directly upon generation, due to the brushing of holds, or by
609 climbers falling onto mats and resuspending rubber particles which had settled (3 – aerosol particulate
610 matter). Eventually, airborne particles also settle elsewhere as dust (4 – settled dust).

611

612 Figure 2: Rubber-derived compound profile in different samples. (a): Rubber-derived compound
613 profile in foothold powder (FP), settled dust (SD), inhalable PM (APMi) and respirable PM (APMr)
614 samples. (b) Rubber-derived compound profile of foothold powder samples before (t-0) and after
615 ozonation experiments (oz). Ozone promotes profile shift which mirrors the shift seen in (a),
616 indicating that the rubber-derived compounds in aerosol PM and settled dust samples can originate
617 from climbing shoes.

618

619 Figure 3: Rubber-derived compound concentrations measured in climbing hall airborne particulate
620 matter (left) and settled dust (right) compared to concentrations reported in the literature for various
621 indoor (houses, vehicles, shopping malls, dormitories, parking lot, sport halls) and outdoor (roadsides,

622 city centers, playgrounds, recycling plants, industrial sites) environments. Details about literature
623 values provided in Table S2.

624

625 Figure 4: RDC concentrations in 30 climbing shoe soles (left), and foothold powder from three
626 climbing halls (right). Concentrations of RDCs vary substantially between different shoe models.
627 Foothold powder samples are representative of the variety of different shoe models. Information about
628 shoe model can be found in Table S6.

629

630 Figure 5: Representative scanning electron microscopy images of (A) chalk (calcium carbonate
631 powder), (B) a foothold powder sample and (C) a settled dust sample collected in climbing halls.
632 Rubber particles resulting from the abrasion of shoe soles are visible in the foothold powder and
633 settled dust samples (B,C). Rubber particles are distinguishable from chalk particles (A) due to their
634 elongated shape and surface physical characteristics with a smooth carbon-based surface compared to
635 chalk. Surface roughness appears to increase between recently generated rubber particles identified in
636 the foothold powder samples (B) and particles found in settled dust (C).

637