Inhalation of climbing shoe particles is highly relevant for the human exposure to rubber-derived chemicals in indoor facilities.

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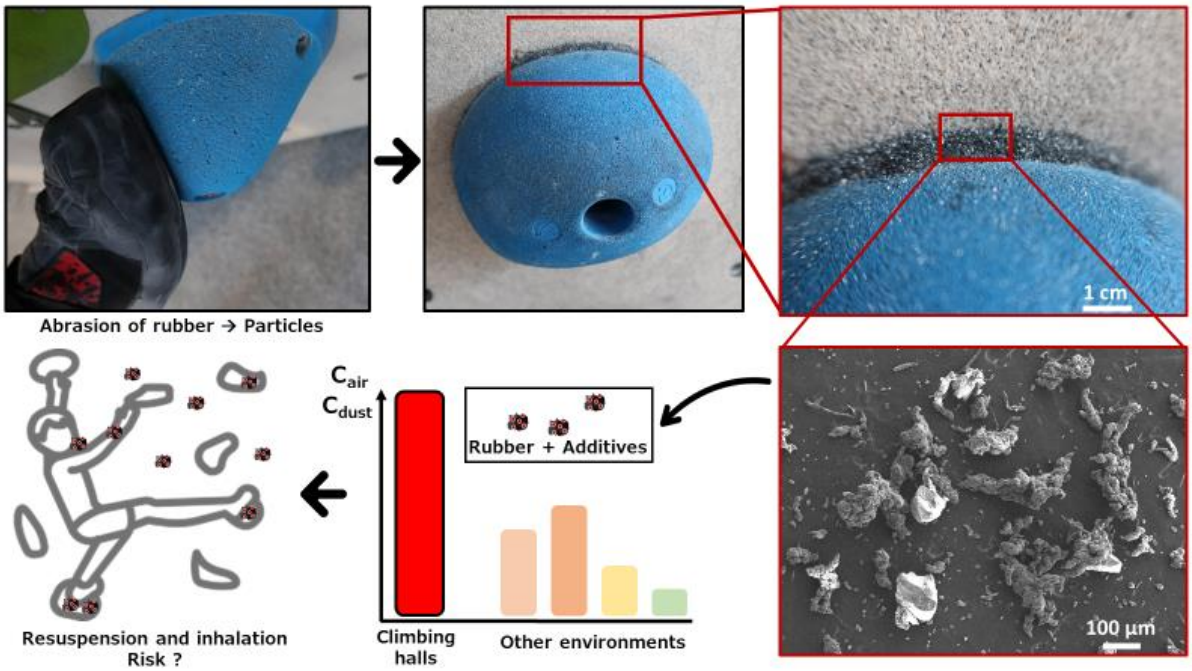
Synopsis: This work investigates the occurrence of rubber-derived chemicals in climbing shoes, as well as its presence in particulate matter in indoor climbing halls resulting in exposure for the facilities' visitors.



Abstract

There is increasing research focused on rubber-derived chemicals (RDCs), predominantly originating from tire and road wear particles. Other consumer products also contain RDCs, but the overall human exposure to these compounds is unknown. This study investigated climbing shoes as a potential contributor to human indoor exposure to RDCs, including potentially harmful substances such as benzothiazoles, p-phenylenediamines (PPDs), and PPD-quinones. The soles of climbing shoes contain high but variable concentrations of RDCs (mean 711 µg/g). In indoor climbing halls, abrasion particles from these shoes can be suspended in the air. Dust and air samples were collected in two climbing halls and particulate matter in the inhalable and respirable fractions were analyzed for 15 RDCs. Concentrations in dust (16 to 43 µg/g) and particulate matter (23 to 35 ng/m^3) exceed those reported from other environments. For most RDCs, estimated daily intake via inhalation (EDI_{inh}) for adults visiting or working in these facilities exceeds the EDI from other sources. This highlights the potential concerns with using large amounts of rubber additives in consumer products. RDCs profiles in shoe samples differed from those in dust and particulate matter, indicating that RDCs are chemically transformed in airborne rubber particles. This finding has broader implications as similar transformations are likely to occur in airborne tire wear particles.

Introduction

Elastomers are used in many consumer and industrial products including tires with a tread usually composed of natural or synthetic rubber. In air samples taken near roads around the world, rubber from tire and road wear particles (TRWP) has been measured both in total particulate matter and in the PM_{10} fraction to represent between 0.15 and 3% of particulate matter[1–6]. The human health risk posed by airborne TRWP is not well understood. In a toxicity study of aerosolized TRWP in rats, no significant effects were observed[7], and a predicted no observed effect concentration of 55 µg/m^3 has been proposed[8]. However, inhaled tire wear particles induced pulmonary fibrotic injury in mice[9] and organic tire extracts induced toxicity in a human lung cell line[10]. In general, much of the toxicity of tire wear particles is attributed to leachable organic rubber-derived chemicals (RDCs)[11–18].

Organic RDCs have been detected in household dusts[19,20], which suggests that tires are not the sole source of exposure to these compounds. Zhao et al. screened a wide range of elastomeric consumer products for multiple organic RDCs[21] and several were found ubiquitously, although the concentrations

in most consumer products were 1-2 orders of magnitude lower than in tires. The additive profile of elastomeric products was proposed to depend on the properties required for their intended use[21]. Highly engineered soles of climbing shoes are likely to contain high quantities of additives and are so far overlooked. Over the past decades, specific rubber formulas have been developed to produce shoes that offer various combinations of softness, flexibility, stiffness, and stickiness[22]. The rubber on climbing shoes abrades due to the friction between shoes and footholds. This generates rubber particles which can easily become airborne upon generation or afterwards, since it is common practice for climbers to brush particles off holds. In the enclosed environments of indoor climbing halls, these rubber particles could be continuously generated and suspended, leading to high concentrations of inhalable rubber particles and RDCs.

The last decade has seen a massive rise in the popularity of indoor climbing. In 2018, an estimated 1.5% of UK population[23], and about 4.4% of the US population[24] visited indoor climbing halls. Of these visitors, about 20% are regulars and spend several hours a day, multiple times a week in climbing halls[23]. Therefore, indoor climbing halls might be a relevant but previously overlooked micro-environment where a noteworthy portion of the population is exposed to inhalable rubber particles and the organic RDCs they contain. This study aimed to (*i*) screen several commercial climbing shoe soles for commonly used RDCs, (*ii*) assess the contamination levels in several types of samples, including respirable particulate matter samples from indoor climbing halls and (*iii*) determine the potential exposure to RDCs for indoor climbing halls visitors and employees.

Materials and methods

Sample collection and analyses

Shoe powder (SP) samples resulting from the abrasion of climbing shoe soles on climbing holds were collected in Hall 1 (n=3) and Hall 2 (n=1) between March and April 2023, where there was visible accumulation of rubber particles (Table S1, Section S1). Dust samples were collected from uncleaned floor and wood surfaces away from the climbing walls from Hall 1 (n=3), Hall 2 (n=1) and Hall 3 (n=1) between March and April 2023 (Table S1, Section S1). All samples were collected using a clean metallic spatula and stored in cleaned amber glass vials at -20°C until further processing. A standardized glass liquid impinger (Copley Scientific Ltd), which divides aerosols into inhalable (> 6.4 µm aerodynamic diameter) and respirable (< 6.4 µm aerodynamic diameter) fractions, was used for active airborne particulate matter (PM) sampling in Hall 3 and Hall 4 (details in Section S2). Briefly, the air inlet was set at a height of 142 cm, facing the climbing wall at approximately 3 m distance. The air flow rate was 60 ± 2 L/min. Composite samples were collected on five consecutive days in April 2023 during peak activity (5-8 pm), for a total volume of 54 m^3 air per sample in each climbing hall. PM samples, suspended in ultrapure water or ethanol were stored in amber glass bottles at -20°C until further processing. Thirty shoe soles (SS) were collected from both used and new climbing shoes to represent the marketplace (Table S2). Shoe sole samples were collected from the tip of the sole, i.e., the most susceptible area to be abraded on the climbing holds during use. Samples were cut into 1 mm^2 pieces and ground into fine powder using cryo-ball milling (MM400, Retsch®) for 2 min at 25 Hz. After grinding, 50 mg powder was immediately suspended in 1 mL dichloromethane to prevent re-agglomeration. Liquid from the two glass impinger chambers containing captured PM was removed via rotary evaporation (ethanol) or lyophilization (ultrapure water). The residual particle mass was determined gravimetrically using a high precision balance and samples were then resuspended in ethanol. All samples were extracted with accelerated solvent extraction (Section S4). The following RDCs were analysed in all samples with UPLC-MS/MS: benzothiazole (BTZ), 2-hydroxybenzothiazole (20H-BTZ), 2-aminobenzothiazole (2amino-BTZ), 2-mercaptobenzothiazole (2SH-BTZ), aniline, 1,3-diphenylguanidine (DPG), hexa(methoxymethyl)melamine (HMMM), and the phenylenediamine compounds: 6PPD, IPPD, CPPD, DPPD and their associated quinones: 6PPDq, IPPDq, CPPDq,

DPPDq. Details are provided in the SI regarding the chemicals and internal standards used (Section S3), UPLC-MS/MS methods (Section S5) and QA/QC (Table S3, Section S6) for analyses of all samples.

Calculations

DPG was used as a chemical marker to estimate the quantity of collected PM derived from shoe sole abrasion ($Fraction\ PM_{shoe\ powder}$) (µg/m^3), since its relative concentration did not change from shoe powder to dust to PM samples (Figure 2, S2) using equation (1):

$$Fraction\ PM_{shoe\ powder} = \frac{[DPG_{PM}]}{[DPG_{SP}]} \cdot [PM] \quad (1)$$

With $[DPG_{PM}]$ being the measured concentration of DPG in a PM sample (ng/g), $[DPG_{SP}]$ the mean concentration of DPG in the shoe powder samples (ng/g), and $[PM]$ the concentration of total particulate matter in the sample (µg/m^3).

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

$$EDI_{inh} = \frac{C_{air}\ IR\ ET\ EF}{BW\ 365} \quad (2)$$

whereby EDI_{inh} is the estimated daily intake *via* inhalation (ng/kg/day), C_{air} the concentration of RDCs in the aerosol (ng/m^3), IR the inhalation rate (m^3/hour), ET the exposure time (hours/day), EF the exposure frequency (days/year), BW the body weight (kg) and 365 the number of days per year. Details regarding exposure parameters obtained from the US EPA exposure factor handbook[25] are available in Table S4.

Results and Discussion

RDCs concentrations in the 30 shoe samples were highly variable as the sum of fifteen RDCs ranged from 25 to 3,405 µg/g (mean: 711 µg/g) (Fig 1, Table S5). Benzothiazoles exhibited high concentrations with 2SH-BTZ being the main constituent (mean: 538 µg/g) representing on average 67% of the total mass of RDCs detected (Fig S1). BTZ, 2OH-BTZ and 2amino-BTZ were detected in lower concentrations (mean: 58, 53 and 3 µg/g, respectively). These results suggest that, as in other rubber products, 2SH-BTZ is used as a vulcanization accelerator during the curing process[26]. Other benzothiazoles are also present and are typically considered to be impurities or degradation products[21,27]. Unlike benzothiazoles, DPG and aniline were not detected in every shoe sample, with concentrations ranging from <LOQ to 814 µg/g and <LOQ to 225 µg/g, respectively. DPG is another vulcanization accelerator[26] and may be used together with or instead of 2SH-BTZ (S18 and S19; Fig 1). *p*-Phenylenediamine compounds were detected in most shoe samples in variable concentrations, with 6PPD and IPPD as the compounds with the highest concentrations (mean: 1303 ng/g and 661 ng/g, respectively). This is not surprising, since of the numerous PPDs available, IPPD and 6PPD are the most commonly used rubber antiozonants[28]. CPPD and DPPD were only detected sporadically and at trace levels (Table S5). 6PPDq and IPPDq were consistently detected (mean: 23 ng/g and 15.4 ng/g, respectively) and as expected, their concentration in the samples were correlated to the concentration of the parent compounds (Table S5). Overall, RDCs concentrations in shoe samples were highly variable and likely due to different compounding strategies used by manufacturers as well as the target product characteristics (i.e., stiffness, durability, performance, adhesiveness). RDCs concentrations in shoe samples were generally lower (DPG and PPDs) or similar (benzothiazoles) to those in tire tread[21,26,27,29] but higher than in other elastomeric consumer products[21]. Finally, shoe powder samples collected on climbing holds were highly representative of the variability found in shoe samples, both in terms of RDCs concentrations and profile (Figures 1, S1).

Inhalable particles (PM < 100 µm) usually deposit in the nose and upper airways and are subsequently swallowed[30,31]. Respirable particles (PM < 10 µm) are of special interest because of their higher probability of deposition within deeper regions of the lung[32,33], and because associations between short- and long-term exposure and adverse health effects have been shown[34–36]. The glass liquid impinger used in this study for air sampling inherently separates inhalable from respirable particles (Section S2). Inhalable PM concentrations in climbing halls 3 and 4 were 1,590 µg/m^3 and 1,000 µg/m^3, respectively, while respirable PM concentrations were 1,040 µg/m^3 and 900 µg/m^3 (Table 1). Despite differences in sampling techniques, the measured respirable particle concentrations correspond well to PM10 concentrations reported for indoor climbing halls (from 509 to 4,028 µg/m^3)[37]. These values exceed WHO guidelines for indoor PM_{10} concentrations of 50 µg/m^3 for 24 hours[38].

All RDCs except for CPPD, DPPD, and their quinones were detected above LOQ in at least one dust or PM sample; most were detected consistently (Table S5). Cumulative RDCs concentrations in dust samples ranged from 16 to 43 µg/g between the three halls where dust samples were collected (Table 1). Variation most likely reflects varying rubber content in dust samples collected in different areas in different halls. Cumulative inhalable RDCs concentrations were 17 and 27 ng/m^3 in halls 3 and 4, respectively, while cumulative respirable RDCs concentrations were 6 and 8 ng/m^3 in halls 3 and 4, respectively. This suggests that both the gastrointestinal tract[30,31] and the respiratory tract[32,33] are relevant exposure routes for these RDCs.

Despite the variations in total RDCs content, all dust and PM samples had remarkably similar RDCs profiles, which differed markedly from the shoe powder samples (Figure 2). The mean fraction of 2SH-BTZ dropped from 69.9% in the shoe powder samples to 2.6% in the dust and PM samples. At the same time, the fractions of BTZ and 2OH-BTZ increased from 8.7% to 41.8% and 5.1% to 19.9%, respectively. A similar pattern emerged for the PPDs. The fraction of 6PPD dropped from 2.8% in the shoe powder samples to 0.8% in the dust and PM samples, while the fraction of 6PPDq increased from 0.0% in the shoe powder samples to 2.1% in the dust and PM samples. Likewise, the fraction of IPPD dropped from 1.3% to 0.5%, while IPPDq increased from 0.0% to 0.1% (Figures 2, S2, Section S7). These shifts are likely due to chemical transformations on the surface of the particles. Transformation of 2SH-BTZ has been mostly studied in the aquatic environment[15], but 2OH-BTZ and BTZ are frequently reported as transformation products of 2SH-BTZ[15,39–43]. Likewise, it is well-documented that PPDs can be oxidized to form their respective quinones[18,21,44].

Concentrations of most RDCs in dust samples (Table 1) were higher than in many other dust samples from indoor environments (house, malls, vehicles)[20,45–48] and of the same order of magnitude as in highly contaminated environments (e-waste recycling factory, parking lot and road dust[49,50]) (Figure S3). Moreover, RDCs concentrations in the collected PM samples were very high as compared to other atmospheric environments. PPDs and PPDqs concentrations in the respirable fraction were higher than measured in Chinese megacities[45,51] and similar to roadside sites and city centres in China during air pollution events[52]. Therefore, PM-bound PPDs and PPDqs could contribute to the oxidative potential of indoor PM as recently demonstrated for outdoor environments[53]. Concentrations of DPG, BTZ, and 2OH-BTZ in PM samples were one or two orders of magnitudes higher than in 18 megacities worldwide[54] and BTZ and 2OH-BTZ were up to 10-fold above concentrations from industrial areas in Spain[55] (Figure S4).

Various studies have used chemical markers to estimate TRWP concentrations in the air[3,4,8,56]. DPG was used here as a chemical marker to estimate respirable shoe particle concentrations. Respirable shoe particle concentrations were estimated at 10 µg/m^3 in hall 3 and 24 µg/m^3 in hall 4, which are an order of magnitude higher than any TRWP concentration measured in a global study[6]. Considering that TRWP contain approximately 50% rubber[57], the calculated concentrations are close to the proposed human no-observed-adverse-effect-concentration of 55 µg/m^3 for respirable TRWP[8]. Although DPG

appeared fairly unreactive in our specific indoor environment (Figure 2, S2), using RDCs as markers for rubber particles should be treated with caution.

Mean EDI_{inh} values estimated for two sub-groups (adult climbers and employees) showed that employees would be more exposed than climbers due to their longer average exposure time and despite their lower inhalation rate (Tables S4, S6). EDI_{inh} for benzothiazoles ranged from 6.7 to 30 ng/kg/day and exceeded EDI_{inh} for ∑PPDs (0.2 to 0.8 ng/kg/day) which were similar to EDI_{inh} for ∑PPDqs (0.4 to 1.6 ng/kg/day). The EDI_{inh} derived for BTZs in this study were two orders of magnitude above those estimated for employees near industrial sites in Spain[55]. EDI_{inh} for PPDs and PPDqs were up to 3.1 and 7.8-fold higher than EDI_{inh} for near-roadside workers in Chinese megacities and two orders of magnitudes higher than the EDI_{inh} for the adult population in Hong-Kong[51]. EDI_{inh} for DPG ranged from 4.9 – 8.7 ng/kg/day exceeding EDI via household dust ingestion in 11 countries (0.0 – 0.9 ng/kg/day)[46].

Overall, the contribution of climbing halls to the total daily intake of RDCs is significant for individuals visiting these facilities. The findings of this study support a recent review calling for a need to understand atmospheric transformations of organic RDCs in TRWP[56], and point out that transformations of organic RDCs could also occur in indoor environments. Future research should address the leaching and bioavailability of RDCs within the human body, including in epithelial lung fluid, as well as the toxicological risk that RDCs pose in the respiratory and gastrointestinal tracts. To reduce human exposure to RDCs, rubber producers should develop alternatives to toxic RDCs for climbing shoes. Potential strategies to minimize exposure in climbing halls should also be investigated.

Figures:

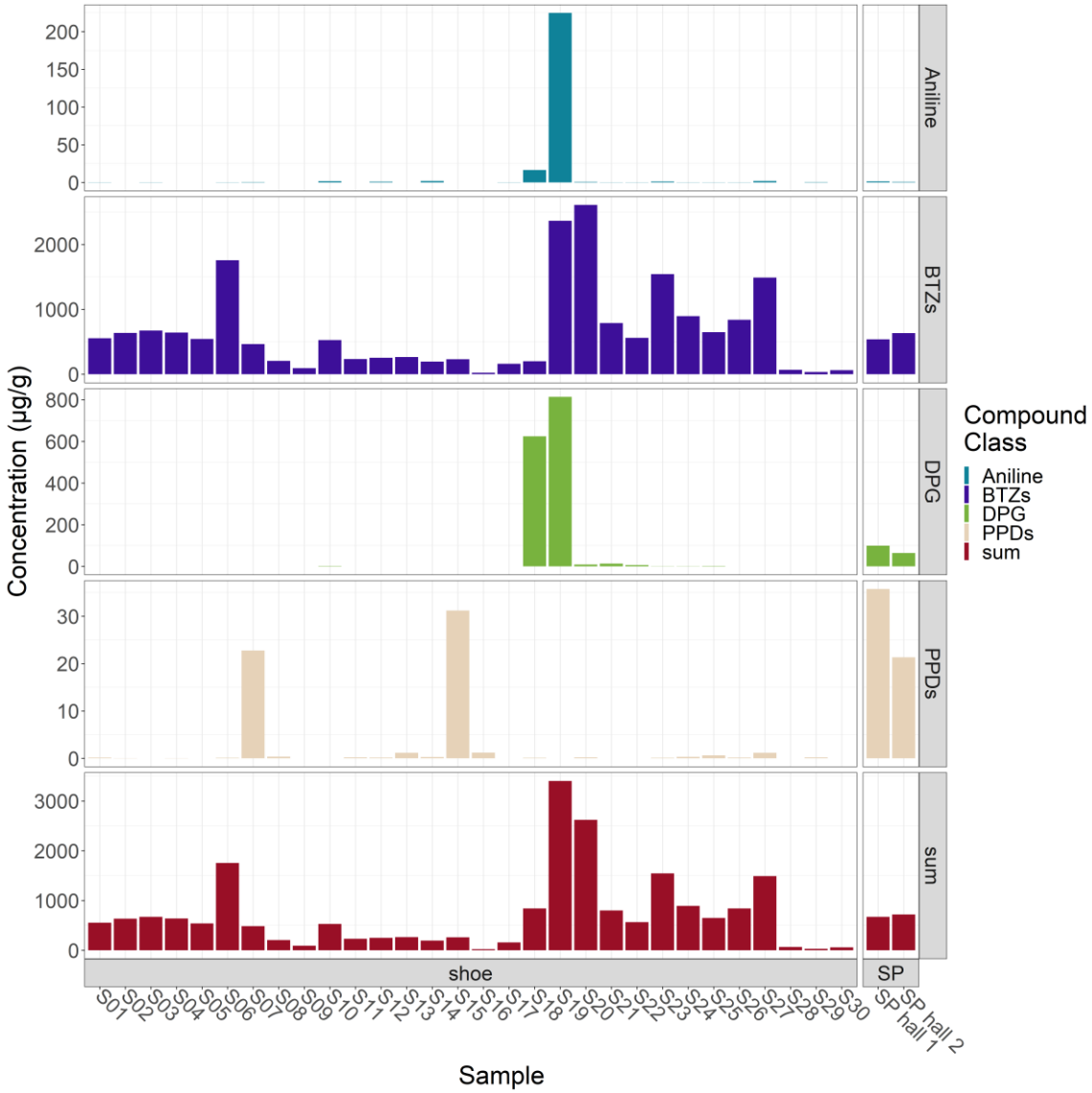


Figure 1: RDCs content in 30 shoe soles, and two shoe powder samples by compound class. BTZs include BTZ, 2OH-BTZ, 2SH-BTZ, and 2amino-BTZ. PPDs include 6PPD, IPPD, CPPD, DPPD, and their respective quinones. Note the difference in y-axis scales between panels. Individual concentrations for each compound and sample can be found in Table S5.

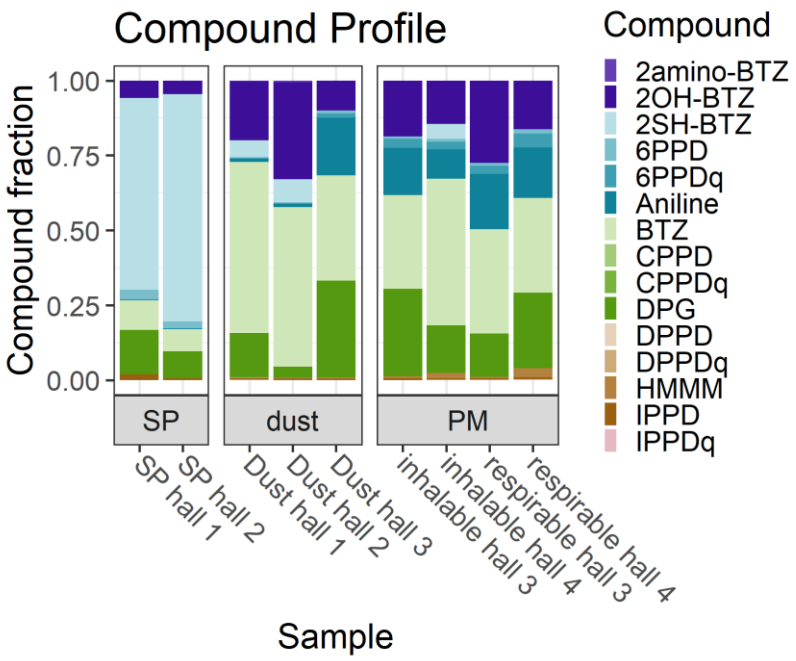


Figure 2: RDCs profile in shoe powder, dust, and PM samples. Compound fraction was calculated as [compound$_i$]/$\sum_{15}$compounds. Dust and PM samples display similar profiles, which differ from the profiles of shoe powder samples. The RDCs profile of freshly generated shoe powder samples reflect the composition of climbing shoes. This profile shifts in PM samples, likely due to chemical transformations at the surface of airborne rubber particles. The similarity between dust and PM sample chemical profiles show that the rubber particles found in dust samples are chemically similar to airborne rubber particles.

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

	Respirable PM ng/m^3		**Inhalable PM ng/m^3**		**total PM ng/m^3**		**dust (*n* = 5) mean (SD) ng/g**
	Hall 3	*Hall 4*	*Hall 3*	*Hall 4*	*Hall 3*	*Hall 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)

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