Science of the Total Environment 955 (2024) 177023

Contents lists available at ScienceDirect

Science of the Total Environment

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

Occurrence, sources, and human exposure assessment of amine-based rubber additives in dust from various micro-environments in South China

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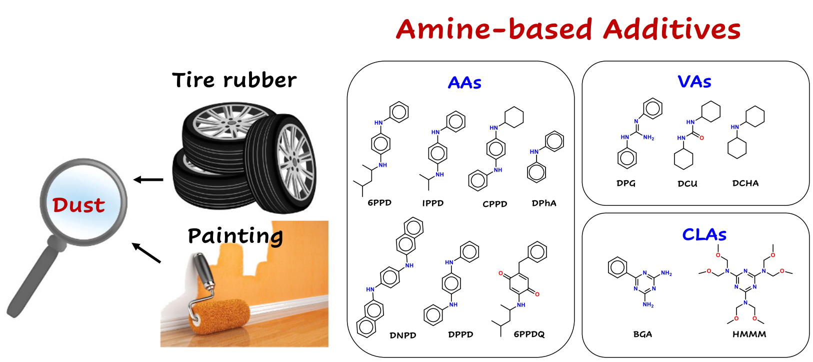
HIGHLIGHTS

- Parking lots exhibited the highest concentration of amine-based rubber additives.
- The composition of AAs, VAs, and CLAs varied greatly in indoor environments.
- Paint particles might be an overlooked contributor to rubber additives indoors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jay Gan

Keywords:
Amine-based rubber additives
PPDs
Indoor environments
Dust
Human exposure

ABSTRACT

Despite the ubiquitous use and potential health effects of amine-based rubber additives, information regarding their occurrences in indoor environments remains scarce and is basically investigated in traffic-related environments. In this study, a total of 140 dust samples collected from eight indoor micro-environments were analyzed for twelve amine-based rubber additives. Overall, 1,3-diphenylguanidine (DPG), dicyclohexylamine (DCHA), N-(1,3-dimethylbutyl)-*N*′-phenyl-p-penylenediamine (6PPD), 6PPD-quinone (6PPDQ), and hexa (methoxymethyl)melamine (HMMM) were frequently detected across all micro-environments with detection frequencies of 97 %, 51 %, 71 %, 99 %, and 77 %, respectively. The highest total concentration of amine-based rubber additives was found in parking lots (median 10,300 ng/g), indicating heavier emission sources of these compounds in vehicle-related indoor environments. Despite this, amine-based rubber additives were also frequently detected in various non-vehicle-related environments, such as markets, cinemas, and hotels, probably due to the widespread use of consumer products and more frequent air exchanges with outdoor environments. Further tracking of tire rubber products and paint particles from flooring materials in parking lots revealed that paint particles might be an overlooked contributor to amine-based rubber additives in indoor environments. Finally, the highest estimated daily intakes (EDIs) of all amine-based rubber additives via dust ingestion at home were observed for toddlers (3.48 ng/kg bw/d). This research provides a comprehensive overview of human exposure to a variety of amine-based rubber additives in various indoor environments.

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https://doi.org/10.1016/j.scitotenv.2024.177023
Received 11 September 2024; Received in revised form 15 October 2024; Accepted 15 October 2024
Available online 17 October 2024

Environmental implication: This study highlights the presence of high concentrations of amine-based additives in indoor dust from both traffic-related and non-traffic-related indoor environments. Additional efforts are needed to identify potential sources of amine-based rubber additives indoors, beyond just tire rubber. This is critical because the widespread presence of rubber products in indoor settings could pose a risk to human health.

1. Introduction

The rubber industry utilizes various amine-based additives to improve the properties of rubber composites, including mixing efficiency, tensile strength, the vulcanization process, mechanical properties, thermal stability, and resistance to aging and oxidative degradation (Alam et al., 2014; Datta Sarma et al., 2021; Longseng and Khaokong, 2020). Amino antioxidants (AAs), the primary amine-based rubber additives, are incorporated into rubber products to extend the service life and reliability by protecting against degradation (Zhao et al., 2023). Among these, *p*-phenylenediamines (PPDs) represent an essential class of AAs widely used in tires. In addition to AAs, vulcanization accelerators (VAs) like 1,3-diphenylguanidine (DPG) are synthetic chemicals used in the vulcanization of rubber to enhance vulcanization speed, enabling the process to occur at lower temperatures with increased efficiency (Kim et al., 2020; Shi et al., 2021; Wang et al., 2019). Cross-linking agents (CLAs), structurally different from AAs and VAs, are another essential group of additives in rubber. These agents help prevent the rubber chains from sliding and tangling under stress (Sperling, 2005). Notably, several amine-based rubber additives, including N-(1,3-dimethylbutyl)-*N*′-phenyl-p-penylenediamine (6PPD) and DPG, are listed as high-production-volume chemicals in the U.S. and Europe (Jin et al., 2024, 2023).

Amine-based additives from rubber products can be readily leached into the environment, including wastewater sludge, surface waters, sediments, and soil, during their production, use, and recycling (Deng et al., 2022; Hiki and Yamamoto, 2022). Besides, researches have indicated that rubber additives, such as 6PPD, can generate toxic transformation products (e.g., 6PPD-quinone [6PPDQ]) that potentially harm environmental organisms, thereby raising concerns about their ecological effects (Page et al., 2022; Roubeau Dumont et al., 2023; Shin et al., 2020; Tian et al., 2021). Recent biomonitoring studies have indicated that certain AAs, such as 6PPD and 6PPDQ, were found to bioaccumulate in the liver in a dose-dependent manner through animal experiments (Fang et al., 2023). Furthermore, the latest research reports that 6PPDQ acts as a RARα agonist and RXRα agonist in vivo, posing a severe risk of developmental abnormalities or birth defects (Zhao et al., 2023c). Additionally, VAs have been reported as the most frequent cause of allergic contact dermatitis resulting from the frequent use of rubber products (Dejonckheere et al., 2019). Moreover, existing data have indicated that human exposure to VAs may pose a significant risk of developing cancers (Loomis et al., 2018). Regarding the toxicity of CLAs, in vitro tests with mammalian cells show that these compounds have genotoxic potentials (Dsikowitzky and Schwarzbauer, 2015). These findings underscore potential concerns regarding the human health impacts of amine-based additives.

Dust has long been recognized as both a reservoir and a major human exposure pathway for many environmental contaminants via ingestion, inhalation, and skin contact (Singh et al., 2023; Zheng et al., 2020a, 2020b). The presence of PPDs, often associated with traffic, has been frequently documented in traffic-related settings such as open roadways, where tire wear is common (Jin et al., 2023). A recent study has identified a broad array of emerging VAs, with median total concentrations reaching up to 29,200 ng/g in traffic-related environments (Ge et al., 2024). Crosslinking agents such as melamine-based resins in road dust samples collected from residential areas were measured at 146 ng/g (Zhao et al., 2022). These findings indicate that amine-based rubber additives are commonly found in outdoor environments associated with vehicular traffic. As most people spend around 90 % of their time in non-traffic indoor environments (e.g., homes and offices) (Tran et al., 2020), however, little information is available on the occurrence of amine-based rubber additives in these indoor micro-environments.

Multiple recent studies have revealed that amine-based rubber additives are also utilized in various consumer products beyond tires, including plastic, furniture, and electronic equipment (Liang et al., 2022; Rauert et al., 2022; Singh et al., 2021). The diffusion of these additives across rubber-to-rubber interfaces (Corish, 1985), coupled with their tendency to absorb solid airborne particles/dust, might lead to indoor accumulation. For example, PPD-derived compounds have been consistently found in door mats, sneaker soles, and toy tires with concentrations up to 770 ng/g, highlighting a previously overlooked source of PPD-derived compounds indoors (Huntink et al., 2004; Zhao et al., 2023a). Additionally, studies have identified various PPDs, such as 6PPD and N, N′-di(o-tolyl)-*p*-phenylenediamine (DTPD), in indoor dust samples with concentrations ranging from 1.7 to 223 ng/g (Huang et al., 2021; Zhu et al., 2024). Notably, the concentrations of certain VAs found in household dust were significantly higher than those from roadways, parking lots, and vehicle repair facilities (Ge et al., 2024). These results further support the evidence of the widespread presence of amine-based rubber additives in indoor settings.

Our previous research and other studies have indicated that concentrations of certain contaminants (e.g., quaternary ammonium compounds, per-, and poly-fluoroalkyl substances) vary across different indoor settings, including residential and commercial buildings (Zheng et al., 2021a, 2021b). This variation is likely associated with the application and usage frequency of consumer products in areas of high human activity (Deng et al., 2022). Therefore, further studies are required to explore the environmental occurrence of amine-based rubber additives in traffic and non-traffic areas. In this study, we selected eight common settings, including parking lots, railway stations, hotels, hospitals, markets, cinemas, homes, and offices, to measure the concentrations of twelve typical amine-based rubber additives with high production volumes, including seven AAs, three VAs, and two CLAs. Additionally, we investigated the distribution of these chemicals in different indoor settings and compared the concentrations measured in the current study and those reported previously. Then, we traced the source of these chemicals (e.g., tire rubber products and paint particles from flooring materials) indoors in highly contaminated parking lots. Finally, we evaluated the estimated daily intakes (EDIs) of amine-based rubber additives for humans of different ages via dust ingestion at home.

2. Materials and methods

2.1. Chemicals and reagents

The analytes measured in this study, including 6PPD, N-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD), N-cyclohexyl-*N*′-phenyl-*p*-phenylenediamine (CPPD), *N*, *N*′-diphenyl-*p*-phenylenediamine (DPPD), 6PPDQ, diphenylamine (DPhA), dicyclohexylamine (DCHA), 1,3-dicyclohexylurea (DCU), 1,3-diphenylguanidine (DPG), *N*,*N*′-di-2-naphthyl-*p*-phenylenediamine (DNPD), HMMM, benzoguanamine (BGA). Two labeled standards, benzophenone-d_{10} and coumaphos-d_{10}, were purchased from Toronto Research Chemicals (Canada) and Dr. Ehrenstorfer (Germany), respectively. Detailed information, including formula, CAS numbers, vendors, and purities of native standards, is shown in Table S1. All solvents used in this study were HPLC grade or higher.

2.2. Dust sample collection and pretreatment

A total of 140 dust samples were collected in parking lots ($n = 15$), homes ($n = 31$), railway stations ($n = 12$), hotels ($n = 18$), hospitals (n = 18), markets ($n = 20$), cinemas (n = 12), and offices ($n = 14$) in Shenzhen City, China during July to September 2022. Dust sample collection was performed using a pre-sanitized nylon sock (25 μm pore size) attached to a commercial-grade vacuum cleaner (Dyson, V8 Fluffy Extra). To minimize background contamination, nylon socks were sequentially extracted with ultrapure water and methanol in ultrasonic twice and then air-dried before use. All collected dust samples in nylon socks were wrapped with aluminum foil, sealed in a polypropylene bag. Tire rubber ($n = 8$) from commercial cars and paint particles from flooring materials ($n = 4$) in parking lots have been manually collected and immediately placed into a clean centrifuge tube and tightly capped. All the samples were transported to the laboratory and stored at −20 °C for further chemical analysis. An overview of the housing characteristics, including site volumes, ventilation systems, sampling areas, and flooring types for both public spaces and residential settings is provided in Table S2.

The pretreatment method of dust samples was adopted from previous studies (Cheng et al., 2024; Jin et al., 2023). Briefly, approximately 100 mg of dust, filtered through a 500 μm mesh sieve, was weighted into a 15 mL centrifuge tube, spiked with 50 ng benzophenone-$d_{10,}$ and subjected to a 30-min extraction in 4 mL of methanol via sonication at ambient temperature. The extraction procedure was repeated twice. The combined extracts were concentrated to 1 mL of methanol and spiked with 50 ng coumaphos-d_{10} before instrumental analysis. The pretreatment method of tire rubber products and paint particles from flooring materials was cut into small particles (around 30–60 μm in diameter) and stored in a clean centrifuge tube. These samples were washed with Milli-Q water to remove particles of soil or dust and dried overnight at room temperature. The extraction procedures were basically consistent with dust samples, as mentioned above.

2.3. Instrumental analysis

The amine-based rubber additives were analyzed by an ultra-performance liquid chromatograph coupled with a triple-quadrupole mass spectrometer (Agilent 1290 Infinity II UPLC, 6470 QQQ-MS) in the positive electrospray ionization (ESI+) mode. The separation was conducted by an Acquity UPLC C18 column (100 × 2.1 mm i.d., 1.7 μm; Waters, US) at 30 °C. The mobile phases for analysis were water (A) and acetonitrile (B), both containing 0.1 % formic acid (v/v). The flow rate of the mobile phase was 0.3 mL/min, and the injection volume was 5 μL. Initially, the gradient was 10 % B, ramped to 100 % B at 5 min, kept for 10 min, and then returned to 10 % B at 15.1–18 min. The optimized MRM transitions, fragmentors, and collision energies for target compounds analytes, surrogate, and internal standards analyzed under ESI (+) mode were shown in Table S3.

2.4. Quality assurance and quality control

One procedural blank and one matrix spike sample were included in each batch of 15 samples, and 2 field blanks were collected using pre-cleaned nylon socks briefly opened during sampling. Procedure blanks ($n = 6$) and matrix spike (n = 6) recovery samples were analyzed across the pretreatment progress. Absolute matrix spike recoveries ranged from 57 to 140 % for all target analytes, with the exception of DPPD (47 %) (Table S4). The recovery of the surrogate standard (benzophenone-d_{10}) was 70 ± 17 %. Blanks constituted <0.1 % of the sample levels. For compounds detected in blanks, method detection limits (MDLs) were set at three times the standard deviation of the target analyte levels detected in blanks. For compounds not detected in blanks, MDLs were based on a signal-to-noise ratio of three (Table S5). All data were blank corrected by subtracting blank levels from sample levels. The influence of instrument drift on compound detection was minimized by incorporating internal standards in the samples and adding a quality control (QC) sample after every ten samples.

2.5. Data analysis

This study used estimated daily intake (EDI) of amine-based rubber additives via dust ingestion for risk assessment. The current study did not account for dermal dust absorption, as the EDI through this pathway is up to two orders of magnitude lower than that through dust ingestion (Zhang et al., 2024; Zheng et al., 2020a). The non-dietary exposure of analytes via dust ingestion was estimated by EDI (ng/kg bw/day) with the following equation:

$$EDI = \frac{C \times DIR \times IEF}{BW}$$

where EDI is the estimated daily intake (ng/kg body weight [bw]/day), and C is the median concentration of the analytes measured in indoor dust (ng/g). DIR is the daily dust ingestion rate, which was reported to be 20, 100, 50, 50, and 50 mg/day for infants (<1 y), toddlers (1–5 y), children (6–11 y), teenagers (12–19 y), and adults (≥20 y), respectively, BW is the body weight (kg), which was reported to be 5, 19, 29, 53, and 63 kg for infants, toddlers, children, teenagers, and adults from Asian countries (Li and Kannan, 2023a; U.S. EPA, 2011). Since we did not have specific data on the duration of human presence in public spaces, only samples collected from homes were included in this calculation. IEF refers to the indoor exposure fraction (in this study, the time spent indoors is primarily represented by the time spent at home), which was reported to be 88 %, 79 %, 79 %, 88 %, and 88 % for infants, toddlers, children, teenagers, and adults, respectively (U.S. EPA, 2011).

2.6. Statistical analysis

Only those analytes with detection frequencies (DF) >50 % were included in statistical analyses. For the statistical analyses, concentrations below MDLs were imputed with MDL/2 according to previous studies (Overdahl et al., 2023; Tian et al., 2022). The normality of data was tested using the Shapiro-Wilk test. The concentrations of the targeted chemicals across micro-environments were compared using a nonparametric test. Spearman's rank correlation was applied to assess the correlations between analytes. Statistical significance was set as 0.05. Consequently, the log-transformed data set was verified through the skewness-kurtosis normality. Plotting and statistical tests, including analysis of variance (ANOVA) with Turkey's post hoc test for mean comparison and linear regression, were performed using Prism 9.0. Source analysis was performed using the positive matrix factorization (PMF) 5.0 model published by the United States Environmental Protection Agency (US EPA) (Brown et al., 2015; Patton et al., 2009).

3. Results and discussion

3.1. Concentrations of amine-derived chemicals in indoor dust

Table 1 and Table S6 show detection frequencies (DF), the median concentrations, and the concentration ranges for the twelve amine-based rubber additives, including seven AAs, three VAs, and two CLAs detected in dust collected from various micro-environments. The structures of selected amine-based rubber additives are shown in Fig. 1. DPG, DCHA, 6PPD, 6PPDQ, and HMMM were frequently detected in all micro-environments with detection frequencies of 97 %, 51 %, 71 %, 99 %, and 77 %, respectively, while other amine-based rubber additives were detected at <21 %. CPPD was not detected in any dust samples and is not included in the further discussion. The median total concentration of these additives reached 1200 ng/g, and the highest concentration was found for VAs with a median concentration of 650 ng/g, followed by AAs

Table 1
Detection frequencies (DF, %) and median concentrations of amine-based rubber additives in dust samples (ng/g, n = 140) from eight sampling sites.

Cpds	Total		Parking lots		Markets		Railway stations		Hotels		Homes		Cinemas		Hospitals		Offices	
	DF	Median	DF	Median	DF	Median	DF	Median	DF	Median	DF	Median	DF	Median	DF	Median	DF	Median
AAs																		
6PPD	71	194	100	3590	55	150	100	322	100	240	39	<MDL	42	<MDL	100	221	57	179
CPPD	0	<MDL	0	<MDL	0	<MDL	0	<MDL	0	<MDL	0	<MDL	0	<MDL	0	<MDL	0	<MDL
DPPD	19	<MDL	100	60.9	15	<MDL	17	<MDL	11	<MDL	0	<MDL	17	<MDL	6	<MDL	14	<MDL
IPPD	14	<MDL	100	216	5	<MDL	17	<MDL	0	<MDL	0	<MDL	0	<0.730	6	<MDL	0	<MDL
6PPDQ	99	65.4	100	868	100	90.6	100	39.1	100	116	94	31.3	100	65.9	100	50.8	100	59.2
DPhA	15	<MDL	100	89.0	5	<MDL	0	<MDL	6	<MDL	6	<MDL	8	<8.60	0	<MDL	7	<MDL
DNPD	12	<MDL	100	0.704	0	<MDL	17	<MDL	0	<MDL	0	<MDL	0	<0.0100	0	<MDL	0	<MDL
ΣAAs	100	282	100	4750	100	247	100	464	100	337	100	65.5	100	183	100	268	100	226
VAs																		
DPG	97	463	100	3560	100	477	67	107	100	295	100	583	100	529	100	375	100	361
DCHA	51	11.6	100	38.5	55	11.8	58	57.9	72	70.5	26	<MDL	42	<MDL	50	3.44	29	<MDL
DCU	21	<MDL	100	239	15	<MDL	33	<MDL	11	<MDL	3	<MDL	0	<MDL	11	<MDL	14	<MDL
ΣVAs	98	650	100	3940	100	748	75	233	100	689	100	583	100	529	100	390	100	360
CLAs																		
BGA	9	<MDL	53	1.72	0	<MDL	0	<MDL	0	<MDL	10	<MDL	0	<MDL	0	<MDL	14	<MDL
HMMM	77	106	100	1430	65	199	100	137	89	81.1	48	<MDL	83	113	94	148	71	31.7
ΣCLAs	78	106	100	1430	65	199	100	137	89	81.1	48	0.0900	83	113	94	148	79	31.7
Sum	100	1200	100	10,300	100	1620	100	1170	100	1080	100	970	100	927	100	894	100	763

and CLAs (282 and 106 ng/g, respectively).

Among the analytes, DPG, a VA in rubber products (e.g., tires, furniture, and shoes) (ECHA, 2023), was measured as the predominant compound with the highest median concentration of 463 ng/g across various micro-environments. The DPG level determined in the current study was 2–18 times higher than those from India (median 26 ng/g), Pakistan (33 ng/g), Colombia (100 ng/g), and the USA (250 ng/g), comparable to those collected from Saudi Arabia (440 ng/g). This may be related to the consumption of rubber products (e.g., tires) per capita in these countries. For example, China consumes about 33 % of global rubber, three times more than the US (Jumpasut, 2016), which is consistent with DPG levels in dust from China and the US. Further studies with larger sample sizes are needed to confirm the findings. Besides, dust concentrations of another VA, DCHA, were considerably lower with a median concentration of 11.6 ng/g compared to those from Australia (4090 ng/g, respectively) (Sherman et al., 2023). The significant difference in concentrations of VAs among different studies indicates regional differences originating from different usage patterns or release mechanisms of these compounds in the environment (Li and Kannan, 2023a).

6PPD emerged as the second most abundant compound in our study, with a median concentration of 194 ng/g. This level was higher than those recorded in Australian dust samples (median 101 ng/g) but lower than in Japan (323–356 ng/g) (Hiki and Yamamoto, 2022). 6PPDQ, the transformation product of 6PPD, was detected at a relatively low median concentration of 65.4 ng/g in the dust samples in the current study. This concentration was seven times higher than that in the road dust from Hangzhou, China (median 9.80 ng/g) (Jin et al., 2023) and comparable to that in the residential dust from Guangzhou, China (range 42–81 ng/g) (Huang et al., 2021). Other AAs, including DPhA, IPPD, DPPD, and DNPD, were detected with relatively low detection frequencies (15, 14, 19, and 12 %, respectively) compared to 6PPD (71 %). This discrepancy can be attributed to the predominant usage of 6PPD in China, which accounts for approximately 54 % of the antioxidants used (Zeng et al., 2023). Besides, HMMM, the primary CLA, was consistently detected in dust samples with a median concentration of 106 ng/g, two times higher than that determined in dust from indoor environments (mean 58 ng/g) in Australia (Sherman et al., 2023). BGA, structurally similar to HMMM, was rarely found in all samples (DF 9 %).

3.2. Comparison of typical additives in different micro-environments

Overall, the highest concentrations of amine-based rubber additives were observed in parking lots, with a median concentration reaching 10,300 ng/g (Fig. 2). This high level of tire-derived contaminants in parking lots underscores their predominant usage in vehicle-related industries. This finding also aligns with prior research, which reported higher abundances of amine-based rubber additives in dust from roads, inside cars, and parking lots than those from homes (Jin et al., 2023). The accumulation of amine-based rubber additives in parking lots can also be attributed to the infrequent cleaning activities in these areas compared to other micro-environments (Drake and Bradford, 2013). Despite this, amine-based rubber additives were frequently detected in various non-vehicle-related environments, such as markets, railway stations, and hotels, but with significantly lower concentrations of total amine-based rubber additives (medians 1620 ng/g, 1170 ng/g and 1080 ng/g, respectively). Indoor sources of rubber additives may include building materials, furniture, and household appliances (Jin et al., 2023). Additionally, it is hypothesized that the presence of these additives in indoor environments occurs through the transport of traffic emissions (Enroth et al., 2016; Hiller et al., 2021). No significant difference was found for the total concentration of these additives across these non-vehicle locations, however, it was noteworthy that significantly higher total concentrations of these compounds were observed in samples from more well-ventilated than those from less well-ventilated (Fig. S1). Typically, markets with more frequent air exchanges with

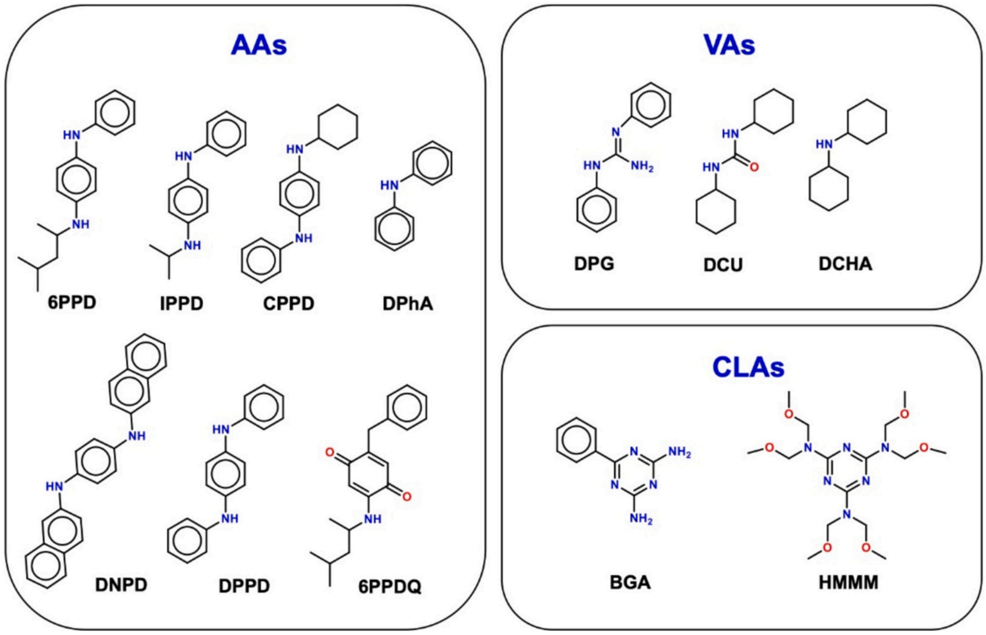

Fig. 1. The structures of selected chemicals of amino antioxidants (AAs), vulcanization accelerators (VAs), and crosslinking agent (CLAs).

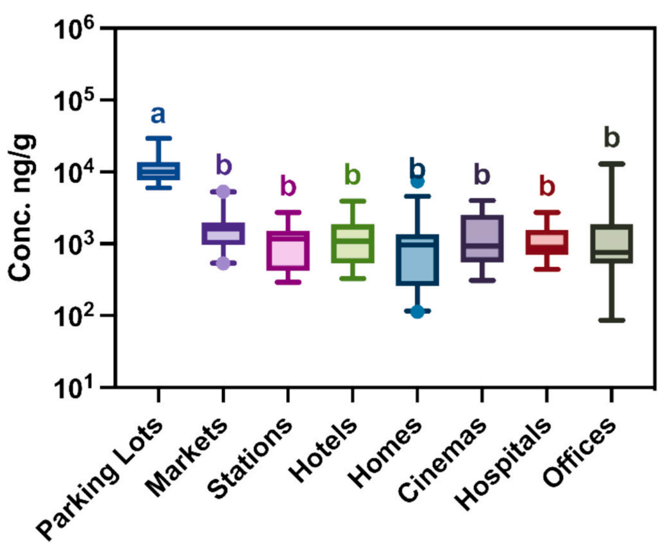

Fig. 2. The total concentration of amine-based rubber additives in the dust samples collected from various micro-environments (ng/g). Concentrations are shown as box plots, representing the 25th and 75th percentiles; lines in the box represent the median, the whiskers represent the 10th and 90th percentiles, and the dots represent the 5th and 95th percentiles. The letters represent the results of the one-way analysis of variance (ANOVA); the concentrations are ranked from the highest to lowest in alphabetic order, and concentrations sharing the same letter are not statistically different at $p < 0.05$.

outdoor environments exhibited higher dust concentrations of amine-based rubber additives than other non-vehicle indoor environments. Further studies should investigate whether higher indoor exposures are found in close proximity to roads, as previous studies have shown that other traffic-related compounds increase dramatically with road proximity (Huang et al., 2018).

Specifically, 6PPD was the most abundant compound in dust collected from parking lots, followed by DPG, HMMM, and 6PPDQ (Fig. 3). These tire rubber-related compounds in parking lots were 1–2 orders of magnitude higher than those in other places ($p < 0.05$, Fig. S2). Interestingly, concentrations of 6PPD and 6PPDQ were significantly correlated in parking lots ($r^2 = 0.75$, $p < 0.001$, Fig. S3a). However, no significant linear correlation was observed between 6PPD and 6PPDQ in other micro-environments (Fig. S3b). Moreover, 6PPD held a dominant proportion in parking lots, stations, hotels, hospitals, and offices, with contributions ranging from 27 % to 48 %, but this was not observed in cinemas and homes. In contrast, the contribution of 6PPDQ showed minor fluctuations across different micro-environments (5 %–14 %). This phenomenon can be explained by the significantly higher ozone concentrations in residential homes (4.3–5.2 ppb) compared to parking lots (<0.01 ppb) (Hwang and Park, 2019; Kiyoung et al., 2002), as elevated ozone concentrations can accelerate the degradation of PPDs in rubber particles, leading to the formation of oxidative transformation products (Zhao et al., 2024; Zhao et al., 2023b). In addition, the disparity between 6PPD and 6PPDQ concentrations could be due to the stability and persistence of 6PPDQ in the environments compared to 6PPD (Klöckner et al., 2021).

It is interesting to note that the contribution of DPG in homes was as high as 93 %, higher than that in public settings (16–74 %), despite the relatively lower concentration (583 ng/g) than that in parking lots (3560 ng/g). The abundance of DPG in households may be attributed to its widespread use in various consumer products, including gloves, shoes, toys, and household furniture (Aizawa et al., 2018; ECHA, 2023; Tang et al., 2015). This is further supported by elevated dust concentrations of DPG in certain micro-environments with more furniture and electronic products (Aizawa et al., 2018; Dahlin et al., 2014; Li and Kannan, 2023a). Furthermore, the composition of CLAs across various micro-environments ranged from 0.01 % to 20.5 %, with the lowest proportion observed in homes (0.01 %), which was lower than in other micro-environments. Thermosetting polyester coatings crosslinked with HMMM are commonly used for pre-painted metal sheets in white goods and architectural cladding, as well as for waterproof surfaces (Rahman and Shaikh, 2014; Sorce et al., 2020). This suggests that the higher contribution of CLAs in environments such as hospitals, hotels, and markets may result from the specific waterproofing and thermal insulation requirements of the applied coatings.

3.3. Concentration correlations

To further investigate the sources of amine-based rubber additives in dust, heatmaps and cluster analyses were conducted using Pearson

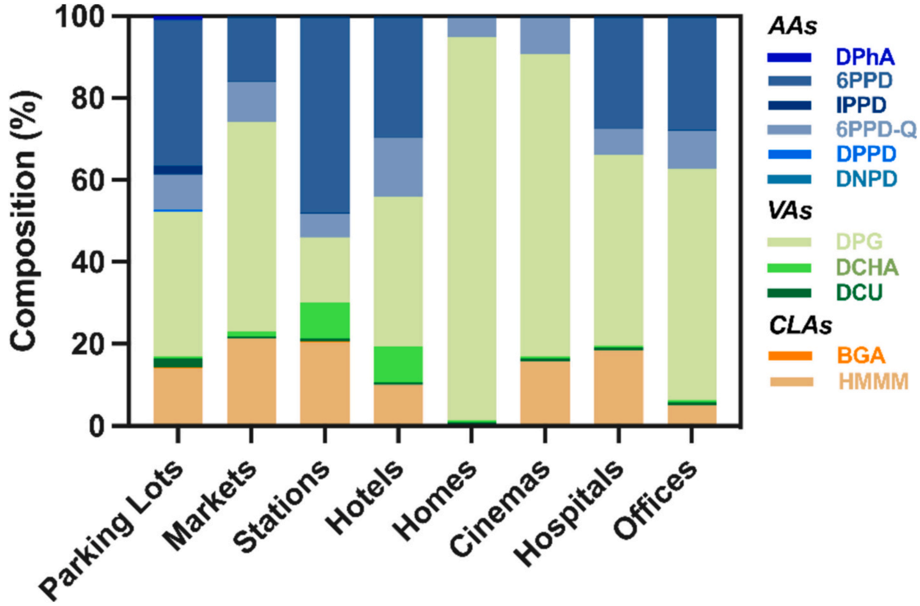

Fig. 3. Composition of amine-based rubber additives in different indoor environments (%).

correlation coefficients of logarithmically transformed concentration correlations for compounds detected in more than half of the dust samples. Significant concentration correlations were observed among targeted analytes in parking lots (Fig. 4), but no significant correlations were found in other micro-environments, likely due to the negligible traffic emissions in these areas. 6PPD was significantly correlated with DPPD, IPPD, and 6PPDQ ($r = 0.7$–0.8, $p < 0.002$), suggesting common sources for these compounds. Among these analytes, 6PPD has the highest production worldwide, accounting for >55 % of the total amine antioxidants. DPPD and IPPD are reportedly integrated with 6PPD to improve performance and ensure an antiaging effect in rubber products (Xu et al., 2022). In addition, 6PPDQ, known as a typical transformation product of 6PPD during aging, is always found alongside 6PPD in traffic-related areas (Wang et al., 2022; Zeng et al., 2023). Besides, DCU was significantly correlated with DCHA ($r = 0.6$, $p < 0.05$), attributing to their typical industrial applications (Table S7), similar emission sources, and environmental behaviors. For example, DCU and DCHA are known to be applied as accelerators to improve rubber products' overall performance and longevity. Moreover, DCU is a known reaction byproduct during surface-grafting of polymers with DCHA (Peter et al., 2018). HMMM, distinguished by its triazine structure, was found to correlate distinctly with other amine-based rubber compounds, likely due to their differing functions in rubber materials. For example, AAs and VAs tend to migrate between rubber surfaces, while HMMM, serving as a cross-linking agent, contributes to the formation of a more stable skeletal framework (Su et al., 2021). Interestingly, DPG, considered a marker of rubber additives (Li and Kannan, 2023b), was consistently found in parking lots. However, it showed a distinct source compared to 6PPD, which primarily originates from tires (Fig. 4). This result implies that there are different sources of amine-based rubber additives in parking lots.

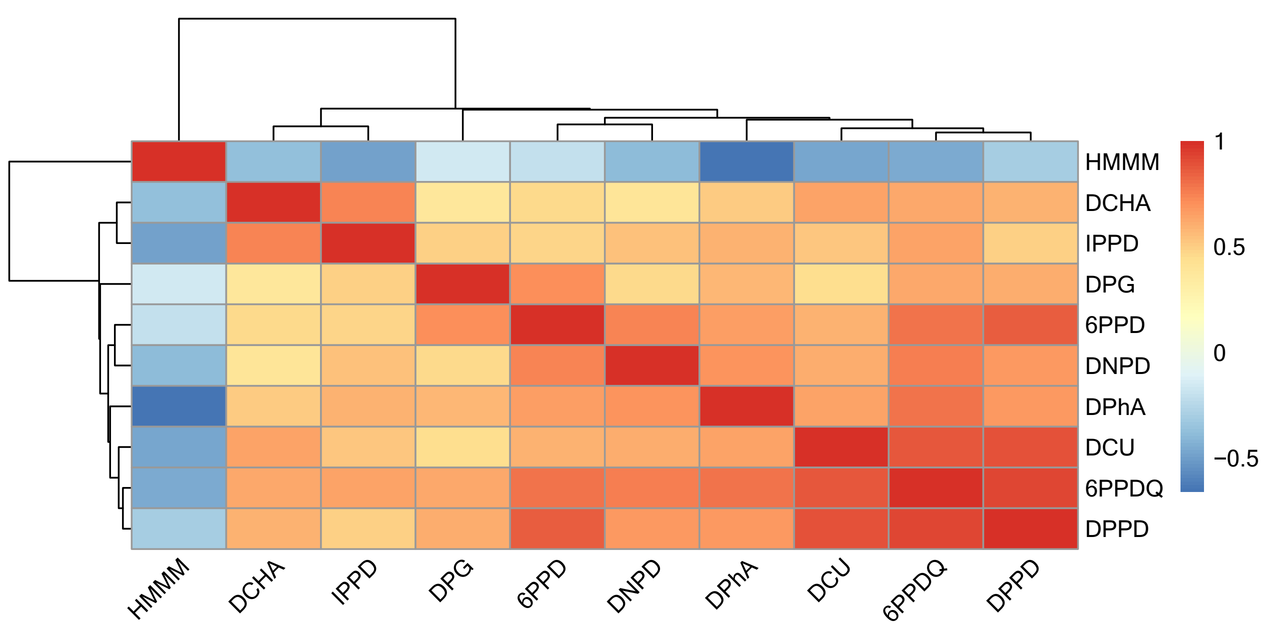

Fig. 4. Correlation heatmaps and hierarchical clustering of individual amine-based rubber additives in dust samples collected from parking lots.

3.4. Source identification of amine-based rubber additives in parking lots

Consequently, two typical related rubber products, including tire rubber (TR) products and paint particles (PP) from flooring materials, were analyzed to further unveil the sources of amine-based rubber additives in parking lots. Fig. 5 shows the contributions of AAs, VAs, and CLAs to the total amine-based rubber additives in parking lot dust and twelve materials (TR and PP) collected from the parking lots. All these additives were detected in the analyzed products but at widely varying concentrations (6.6–75 mg/g). 6PPD was the most abundant compound at concentrations up to 12.5 mg/g in TR products, supporting the fact that this compound was the predominant congener in parking lot dust. Overall, AAs were the predominant compounds in all the TR and PP samples, implying that both were vital sources of AAs in dust from parking lots.

In contrast to tire rubber products, lower concentrations of amine-based rubber additives (up to 1.35 mg/g) were observed in paint particles from flooring materials, while these paint particles had a higher contribution of VAs than tire rubber products, accounting for 25 %–49 %. Concentrations of DPG, DCHA and DCU in paint particles reached up to 10,900, 592 and 25,100 ng/g, respectively, further supporting the fact that these compounds are ubiquitously detected in parking lot dust. Previous studies have found that paint particles contain a variety of toxic compounds and are considered to be an important source of indoor pollutants due to their wide application in buildings (Weiss, 1997). Although several recent studies found that certain semivolatile organic compounds were found in the extract of paint particle products (Fan et al., 2024; Kim et al., 2023), this is the first study measuring amine-based rubber additives in paint particles, which might be an overlooked contributor to these compounds in indoor settings with interior paints on ceilings and walls. The sources of amine-based rubber additives in environmental dust samples were characterized using the PMF model (Fig. S4). Factor 1, displaying significant loadings of 6PPD, IPPD, and other antioxidants typically employed in tire manufacturing, was attributed to vehicular tire wear (Mao et al., 2024). Factor 2, with a predominant loading of DCHA, suggests that rubber products such as gloves and hoses may be potential environmental sources of amine-based rubber additives. However, further investigations, including a comprehensive sampling of various rubber products, are required to substantiate these findings.

3.5. Human exposure assessment

Table S8 summarizes the estimated daily intakes (EDIs) of amine-based rubber additives for infants, toddlers, children, teenagers, and adults via dust ingestion at home. The highest EDIs of all these chemicals were observed for toddlers, followed by infants, children, teenagers, and adults (medians 3.48, 2.95, 1.14, 0.697 and 0.586 ng/kg bw/d, respectively), probably due to their variations in dust ingestion rate and body weight (Braun, 2017). This result indicates that infants and toddlers are generally more sensitive and vulnerable to amine-based rubber additives. DPG is the major contributor to the total amine-based rubber additives intake (1.92 ng/kg bw/d), while relatively lower EDIs were observed for DCHA (0.00965–0.0484 ng/kg bw/d). The EDI of 6PPDQ (0.0457–0.272 ng/kg bw/d) is similar to that reported in previous studies, ranging from 0.008 to 0.48 ng/kg bw/d (Marques dos Santos and Snyder, 2023; Wang et al., 2022). Although EDI via dust ingestion for 6PPDQ is lower than that for 6PPD determined in the current study, however, considering the potential early-life health effects of 6PPDQ (Zhao et al., 2023c), more attention should be paid to biomonitoring this compound in infants and toddlers. However, EDIs estimated for amine-based rubber additives were at least four orders of magnitude lower than the toxicity reference doses (RfD) established for DPhA (25,000 ng/kg bw/d) (EPA, 2022), structurally similar to these compounds, since the targeted analytes' RfD are unavailable. Overall, these results suggest that dust ingestion alone is a minor contributor to the health risks of these chemicals.

It should be noted that several uncertainties exist in our exposure assessment of the targeted compounds through dust ingestion. For instance, apart from age, the dust ingestion rate can be affected by factors such as personal habits and living environments. Moreover, the current study's EDI analysis only included homes; thus, the contribution of exposure intakes from other micro-environments needs clarification. This is critical because dust concentrations of some amine-based rubber additives measured from certain micro-environments (e.g., parking lots) were higher than those from residential living rooms or bedrooms, which may augment exposures. Finally, reference doses for amine-based rubber additives are currently unavailable; however, evidence of the toxicity of these compounds is increasing. For example, a recent investigation suggested that both PPD-Qs and PPDs may pose a potential exposure risk of hepatotoxicity (Guo et al., 2024). DPG has potential genotoxic effects in vitro, as shown in a previous study (dos Santos et al., 2022). Therefore, establishing evidence-based human toxicity reference values is essential to assess the risks of amine-based rubber additives in

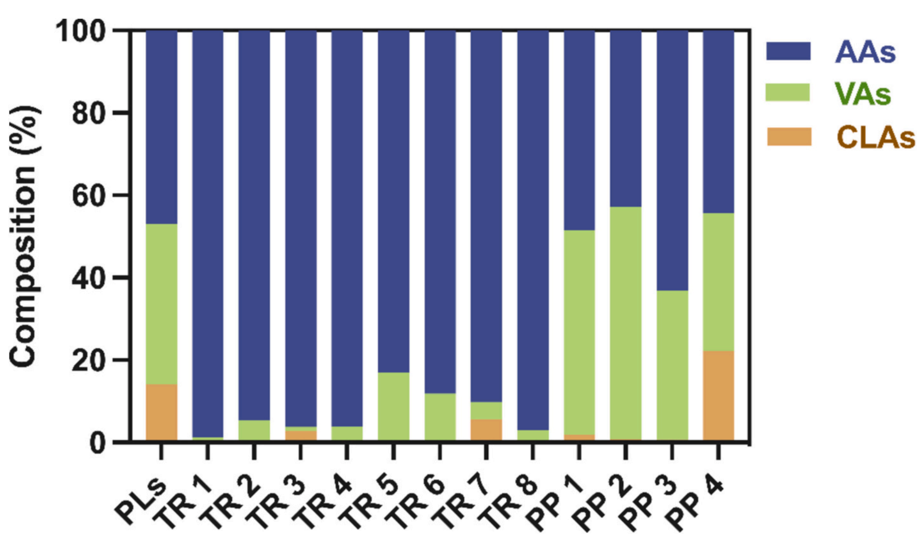

Fig. 5. The compositions (%) of three groups of amine-based rubber additives in parking lots dust (PLs), tire rubber (TR) and paint particles from flooring materials (PP).

the future.

4. Conclusions

This study has several limitations. The sample size was small and covered a limited geographical area, therefore, the differences in concentrations of amine-based rubber additives in various microenvironments should be considered cautiously. In addition, this study notes a lack of specific information regarding other potential sources of these compounds in indoor environments. Nonetheless, the findings underscore parking lots as crucial exposure locations, particularly for compounds like 6PPD, 6PPDQ, DPG and HMMM, which exhibited higher concentrations in these areas compared to other micro-environments. Further investigation into the sources of amine-based rubber additives within parking lots revealed that tire rubber products and paint particles from flooring materials significantly contribute to emissions in indoor environments. Our findings also highlight the urgent need for future research on amine-based additives in indoor environments to elucidate their sources, exposure pathways and health risks.

CRediT authorship contribution statement

Chenglin Liu: Writing – original draft, Investigation, Formal analysis, Data curation. **Sheng Wan:** Formal analysis. **Yao Cheng:** Formal analysis. **Zhong Lv:** Investigation. **Shusheng Luo:** Resources. **Yuge Liang:** Investigation. **Yichun Xie:** Investigation. **Xinrui Leng:** Investigation. **Min Hu:** Investigation. **Bintian Zhang:** Supervision, Resources, Funding acquisition. **Xin Yang:** Validation, Supervision, Resources, Funding acquisition. **Guomao Zheng:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Acknowledgments

This study was financially supported by the Shenzhen Key Laboratory of Precision Measurement and Early Warning Technology for Urban Environmental Health Risks (ZDSYS20220606100604008) and the National Natural Science Foundation of China (22206071).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177023.

Data availability

Data will be made available on request.

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