Tyre Wear Particles and Associated Chemical Pollutants: Contribution to Urban $PM_{2.5}$ in the Pearl River Delta

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Abstract

Tyre wear particles (TWPs) are a global concern due to their large emissions worldwide and potential toxicity, as a vector for tyre wear chemicals (TWCs). However, the contribution of TWPs to urban fine particles remains unknown. This study collected 72 paired gaseous and $PM_{2.5}$ samples in urban air of the Pearl River Delta, China in 2018. Among 54 targeted compounds, 28 TWCs (Σ_{28}TWCs) were detected. Total atmospheric Σ_{28}TWCs concentrations ranged from 3,130 to 317,000 pg/m^3, mainly contributed in the gaseous phase (73 ± 26%). Specifically, 2-OH-BTH (82 ± 21%) dominated in the gas phase, while BTSA (74 ± 18%) dominated in $PM_{2.5}$. The cities of Guangzhou and Foshan were identified as "hot spots" of TWCs. Most TWCs significantly correlated with nearby road length. Measured gas-particle partition coefficients were higher than model predictions, potentially caused by sampling artefacts, particulate burial and re-release from TWPs itself. Importantly, source apportionment combined with characteristic molecular indicators revealed that the TWPs contributed an average of 13 ± 7% to the urban $PM_{2.5}$, highlighting their important contribution to urban air pollution and potential threat to human exposure. These findings emphasize the urgent need for initiatives aimed at reducing tyre wear emissions as part of broader strategies to improve urban air quality.

Keywords

Tyre wear particles, gas-particle partition, fine particles, urban air, source apportionment

Synopsis

Tyre wear particles (TWPs) make an important contribution to urban $PM_{2.5}$ and the load of gas-phase organic compounds in air, highlighting the urgent need for strategies to reduce TWPs emissions.

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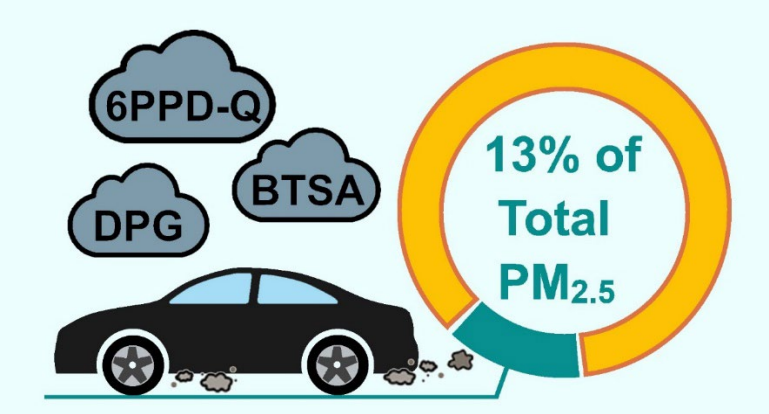

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Introduction

Tyre wear particles (TWPs) generated by the rolling shear of tread against a surface.[1] During the life of tyres, approximately 10-20% of their mass is released into the environment through tyre wear.[2] It is estimated that global annual emissions of TWPs more than 6 million tons, which means about 0.8 kg/capita/year.[2] TWPs was estimated to contribute more than 50% to non-exhaust emissions (NEEs), which constituted 60% of primary $PM_{2.5}$ emissions from road transport.[3-5] Several studies have found that TWPs play a significant role in sources particles,[3, 4, 6, 7] which is estimated that TWPs accounted for 4-10% of $PM_{2.5}$ emissions in tunnels[4] and 12.3% in the roadway.[8] The contribution of TWPs is expected to continue growing and become the major source of vehicular emission under various control measures mainly aimed at controlling automobile exhaust emissions.[9] However, the contribution of TWPs to urban atmospheric $PM_{2.5}$ is still unknown. Urban $PM_{2.5}$ poses one of the greatest global health risks,[10] being associated with various negative health outcome such as lung cancer,[11] cardiovascular disorders[12] and nervous system diseases.[13]

TWPs is also the carrier for tyre wear chemicals (TWCs), which are compounds referred to as tyre additives and compounds emitted from tyre wear. These chemicals typically including benzothiazoles (BTHs), p-phenylenediamines (PPDs), 1,3-diphenylguanidine (DPG), hexa (methoxymethyl) melamine (HMMM) and benzotriazoles (BTRs). PPDs is a “hotspot” of TWCs research due to their potential hazards to the environment and human health. PPDs have widely reported in various environmental media, including water, snow,[14] air,[15, 16] sediment[17] and dust,[18] even in human urine,[19] human milk,[20] human serum[21] and human cerebrospinal fluid.[22] Among them, N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine-quinone (6PPD-Q), a quinone derivative of antioxidant N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD) have the acute mortality in salmon.[23] Moreover, PPDs and PPD-quinones, can induce oxidative stress[24] and hepatotoxicity.[25, 26]

Furthermore, certain TWCs, like 6PPD-Q, have demonstrated to be a promising molecular indicator of TWPs,[17, 27] indicating their potential utility in quantifying the contribution of TWPs to atmospheric $PM_{2.5}$ by source apportionment methods. It is crucial to consider the environmental behavior of TWCs in urban atmosphere when using them as organic molecular markers of TWPs.[28] Hence, it is of great importance

to investigate the gas-particle (G/P) partition affecting the environmental behavior of TWCs. However, a comprehensive understating of their occurrence and fates simultaneously in the gaseous and particulate phases of urban air is still lacking.

The Pearl River Delta (PRD) is an ideal region for studying TWPs and associated TWCs. It is one of the four great Bay Areas in the world and has the largest vehicle inventory in China.[29] It is also the center of China's new energy vehicle (NEV) industry clustering.[30] The aims of this study were threefold: i) to investigate the occurrence and atmospheric behavior, including gas-particle fractions, of typical TWCs in urban air of the PRD region; ii) to quantify the contribution of TWPs to urban $PM_{2.5}$ by characteristic source indicators; and iii) to offer suggestion for reducing TWPs emissions. To our knowledge, this study presents the first comprehensive dataset of TWCs in ambient air, covering both gaseous and particulate phases. Our findings will provide valuable insights into the environmental behavior of TWCs and important information to guide the development of traffic control policies aimed at mitigating pollution in urban air.

Materials and methods

Sampling Campaign

The details of the sampling campaign were given in a previous study.[31] Briefly, nine prefecture-level cities of PRD, Shenzhen, Foshan, Dongguan, Zhongshan, Jiangmen, Zhuhai, Zhaoqing, Huizhou and Guangzhou, were selected (Table S1 and Figure S1). At each site, gaseous and particulate ($PM_{2.5}$) phases pollutants were captured with polyurethane foam plugs (PUFs, 14 cm in diameter × 7.5 cm in thickness, 0.02 g/cm^3 in density) and quartz fibre filter (QFF, Whatman, 203 mm × 254 mm), respectively, by high-volume active air sampler (Mingya Instruments Co., Guangzhou, China). The 24-hour sampling was conducted continuously for 4 days in both winter (January to February 2018) and summer (July to August 2018). Seventy-two paired gaseous and $PM_{2.5}$ samples were obtained in total. Before sampling, the QFFs were baked at 450 °C overnight, and the PUFs were precleaned successively with acetone and dichloromethane (DCM). All samples were delivered to the laboratory and stored at −20 °C before analysis.

Sample Pretreatment and Instrumental Analysis

The chemicals and reagents information are given in Text S1. After adding 50 ng D5-

6PPD-Q, d6-5-methylbenzotriazole (d6-5-MBTR), PPD-d10, BTR-D4 and 100 ng BTH-D4 as surrogate standards, QFFs and PUFs were ultrasonicated three times for 30 min with methanol (MeOH). The extracts were evaporated to 0.5 mL and filtered with a 0.22 µm syringe filter. The filtrate was concentrated to 100 µL and spiked with 5 ng benzophenone-d10 as internal standard before instrumental analysis.

Samples were analyzed by liquid chromatography and triple quadrupole mass spectrometry (UPLC-MS/MS 8050, Shimadzu, Kyoto, Japan) on an instrument equipped with an electrospray ionization source (ESI). Fifty-four compounds were separated by a Waters X-Bridge BEH C18 column (2.1 mm × 100 mm, 2.5 µm) with three different mobile phases. Details of instrumental analysis were reported in our previous studied[32, 33] and described in Text S2 and Table S3 - S4.

The detailed sample treatment and instrumental analysis for water-soluble ions, trace elements, organic carbon (OC), elemental carbon (EC) and polycyclic aromatic hydrocarbons (PAHs) can be found in our previous studies[34, 35] and described in Text S2.

Quality Assurance and Quality Control (QA/QC)

Solvent, field and procedural blanks were conducted to evaluate possible contamination caused by solvent, sampling and pretreatment. Most compounds were not detected or detected with a low contribution (<6%) in blanks, while benzothiazole (BTH) and 3-cyclohexyl-1,1-dimethylurea (C-DMU) in blanks were detected accounting for ~20% of their concentrations in samples, introduced by the nitrogen blowdown step. The matrix recoveries ranged from 33 to 153% in PUFs and QFFs samples. The average (± standard deviation) recoveries of pretreatment ranged from 51 ± 1 % to 124 ± 2 %, except for benzothiazole-2-sulfonic acid (BTSA, 288 ± 89 %) (Table S5). Further experiments were conducted to justify the abnormally high recoveries of BTSA, as detailed in Text S3. Seven BTHs (2-mercaptobenzothiazole (2-SH-BTH), 2-methylbenzothiazole (2-Me-BTH), 2-methythylthio-benzothiazole (2-Me-S-BTH), 2-chlorobenzothiazole (2-Cl-BTH), 2,5-dimethyl-1H-benzothiazole (XTH), 2-(thiocyanomethythio)benzothiazole (TCMTB) and BTH) were found to convert to BTSA. Six recoveries (D5-6PPD-Q, d6-5-MBTR, PPD-d10, BTR-D4, and BTH-D4) ranged between 55 - 129% in $PM_{2.5}$ samples and 62 - 141% in PUF samples. All reported concentrations have been corrected by the blank and recoveries.

The calibration curve was made over 13 points (0.01–1000 μg/L) with all regression coefficients higher than 0.99. The stability of LC-MS/MS was assessed by injecting two concentrations (10 and 100 μg/L) of calibration standards between every 10 samples. The instrumental detection limits (IDLs) and method detection limits (MDLs) were 0.001−20.5 ng and 0.098−503 pg/m^3, respectively (Table S5).

Backward Trajectories Simulation and PSCF model

Backward particle release simulation and potential source contribution function (PSCF) models have been widely used to identify the history of air masses and possible geophysical pollution source locations, respectively.[31] The PSCF analysis relied on the results of backward trajectory calculated in our previous study using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT 4.0, https://ready.arl.noaa.gov/HYSPLIT.php). Briefly, 72 h backward trajectories were computed at three-hour intervals and at a height of 500 m above ground level.[31] More details can be found in Text S4.

Gas-particle Partitioning

The G/P partition coefficient commonly describes the distribution of organic chemicals between gaseous and particulate phases in the atmosphere.[36] Two widely used G/P partition models, the Harner-Bidleman model[36] and the steady-state Li-Ma-Yang model,[37, 38] which use the octanol-air partition coefficients (Koa), were employed to predict the G/P partition quotients of TWCs, as detailed in Text S5. It should be noted that only compounds with detection frequency > 30% in pairs of gaseous and particulate phase samples were included.

Positive Matrix Factorization (PMF)

PMF is widely used to identify pollution sources and quantify contributions to ambient air pollutants.[39] In this study, three TWCs (BTSA, DPG and 6PPD-Q) were identified as tyre wear markers to quantify the contribution of TWPs. The screening step for tyre wear markers and PMF analysis were detailed in Figure S2 and Text S6, respectively.

Results and Discussion

Profile of TWCs in the Air of PRD

Out of the 54 target analytes, 28 TWCs (Σ_{28}TWCs) were detected in total. Except for

BTSA and 2-OH-BTH, the remaining 26 chemicals are referred to as Σ_{26}TWCs. As detailed in Text S7, the Σ_{26}TWCs were classified into five categories, Σ_6BTHs, Σ_4BTRs, Σ_7DPGs, Σ_8PPDs and HMMM, according to their chemical structure. The detection rate of Σ_{26}TWCs ranged between not detected (ND) and 100%, while the detection frequencies of 2-OH-BTH and BTSA were 97%-100% in both gaseous phases and $PM_{2.5}$. Overall, Σ_{28}TWCs concentrations ranged between 3,130 and 317,000 pg/m^3, mainly in the gaseous phase (73 ± 26%). Σ_{28}TWCs concentrations in the gas and particulate phases were 587–312,000 pg/m^3 and 375-18,500 pg/m^3, respectively. Various composition patterns of TWCs were observed in the particulate and gas phases. The gas phase was dominated by 2-OH-BTH (82 ± 21%), whereas $PM_{2.5}$ was dominated by BTSA (74 ± 18%). Specifically, 2-OH-BTH, Σ_6BTHs and Σ_8PPDs prevailed in the gas phase, accounting for 94 ± 17%, 75 ± 15% and 68 ± 33% for the total concentrations, respectively. BTSA, Σ_4BTRs, Σ_7DPGs and HMMM were more prevalent in $PM_{2.5}$, contributing 80 ± 24%, 63 ± 32%, 69 ± 26% and 73 ± 25% to the total concentrations, respectively. The detection rates and concentrations of target compounds are detailed in Table S6 and Figure 1 and the pattern of Σ_{26}TWCs is shown in Figure S3. Only the summed concentrations in the gas and $PM_{2.5}$ phases are discussed further in this section.

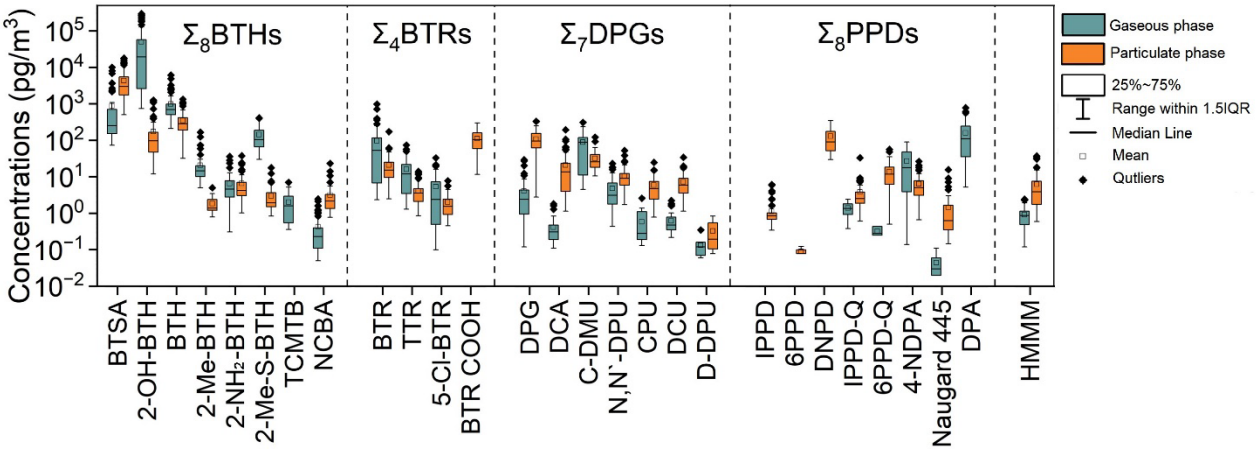


Figure 1. The atmospheric profiles of Σ_8BTHs (the sum of 2-OH-BTH, BTSA and Σ_6BTHs), Σ_4BTRs, Σ_7DPGs, Σ_8PPDs and HMMM from nine cities in PRD (n=72). IQR is the interquartile range. The green and orange box presented the concentration of gaseous and particulate phases, respectively.

Concentrations of BTSA ranged at 100-16,600 pg/m^3 (median 3,170 pg/m^3) in the PRD. Previous studies have reported that BTSA is an oxidative product of 2-SH-BTH.[40] We found it can also be transformed from the other six BTHs, except for 2-SH-BTH.

Although the exact formation pathway of BTSA is unclear, according to their chemical structure (Figure S4), we speculate that sulfur dioxide (SO_2) may enhance the production of BTSA, as SO_2 and SO_4^{2-} positively correlated with the BTSA level in $PM_{2.5}$ (Spearman, r=0.508-0.572, p<0.001). This finding also matched with the high particle-bound fractions of BTSA (80 ± 24%).

Concentrations of 2-OH-BTH measured in this study ranged from 22.6 to 298,000 pg/m^3 (median 17,800 pg/m^3). Significantly, there is a pronounced seasonal difference (Kruskal–Wallis H Test, $p < 0.001$), with a median concentration in summer (57,900 pg/m^3) approximately 20 times higher than that in winter (2,730 pg/m^3). It has been proven that 2-OH-BTH is a product of BTH.[41] A positive correlation was observed between the ratio of 2-OH-BTH/BTH and temperature (Spearman, r=0.633, p<0.001), suggesting that higher temperature promote the conversion of BTH to 2-OH-BTH in summer.[42]

The Σ_{26}TWCs concentrations ranged between 956-8,300 pg/m^3 (median 1,830 pg/m^3) with a significant seasonality (median 2,320 pg/m^3 in summer *vs* 1,340 pg/m^3 in winter, Kruskal–Wallis H Test, p<0.001). Most TWCs concentrations were positively related to temperature (Spearman, r=0.470-0.819, p<0.001), suggesting higher temperatures in summer increase tyre wear rate, leading to more TWCs entering the environment.[43] As can be seen in Figure S3, Σ_{26}TWCs was dominated by Σ_6BTHs accounting for 38-86% (65 ± 10%) and followed by Σ_7DPGs (12 ± 4%), Σ_4BTRs (11 ± 5%) and Σ_8PPDs (11 ± 7%). The concentrations for most compounds were strongly correlated (Table S7), consistent with them having similar sources.

DPG is used as a catalyst in tyre production to accelerate the cross-linking of rubber materials with sulfur.[44] The German Environment Agency has identified DPG as a potential persistent, mobile, and toxic (PMT) substance and very persistent and very mobile (vPvM) substance,[45] indicating that DPG could pose environmental and human health risks. The concentration of DPG varied from 3.45 to 300 pg/m^3 (median 91.9 pg/m^3), with a significant seasonal difference (Kruskal–Wallis H test, p=0.002). DPG has been frequently detected at high concentrations in various environmental media such as human urine, water and dust,[46-48] which is attracting attention. However, there is only one report of DPG in ambient air at a global scale from a passive sampler study.[49]

6PPD-Q and N-isopropyl-N'-phenyl-1,4-phenylenediamine-quinone (IPPD-Q) are

ozonation products of 6PPD and N-isopropyl-N'-phenyl-1,4-phenylenediamine (IPPD), respectively. In this study, the level of 6PPD-Q ranged from ND to 50.5 pg/m^3 with a seasonal variation (Kruskal–Wallis H test, $p < 0.001$). Concentrations in winter (median 13.5 pg/m^3) were higher than in summer (median 8.16 pg/m^3). The concentration of IPPD-Q varied between ND-31.1 pg/m^3 (median 1.84 pg/m^3). The detection frequency of IPPD-Q was 100% in winter, while only 31% in summer.

Spatial Distribution

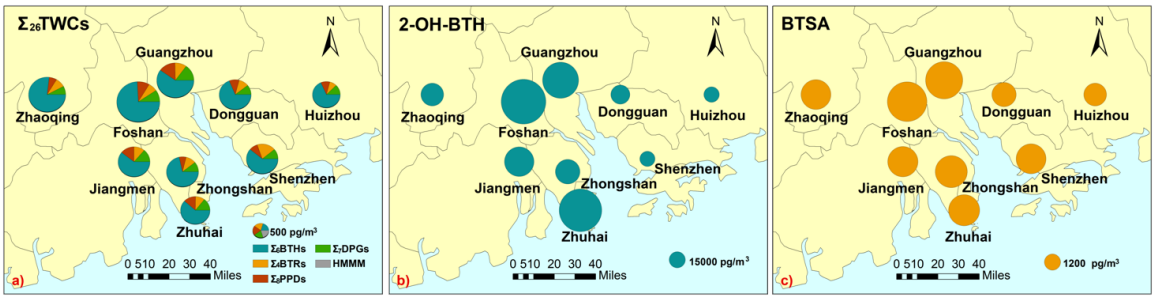


Figure 2. The spatial distributions of Σ_{26}TWCs, 2-OH-BTH and BTSA in nine cities of the PRD, presented as average summed concentration of gaseous and particulate phases (pg/m^3) including winter and summer. This figure was modified from outputs of ArcGIS 10.4.1 software, and the base map of China was from http://www.arcgisonline.cn.

Figure 2 presents the spatial distribution of Σ_{26}TWCs, 2-OH-BTH and BTSA, showing varied patterns in the PRD. The "hotspot" of Σ_{26}TWCs, 2-OH-BTH and BTSA was identified as Guangzhou (2,630 ± 782 pg/m^3, 71,900 ± 52,100 pg/m^3 and 6,580 ± 5,220 pg/m^3, respectively) and Foshan (3,540 ± 2,490 pg/m^3, 110,000 ± 128,000 pg/m^3 and 7,440 ± 6,220 pg/m^3, respectively). As depicted in Figure 2, Σ_6BTHs emerged as the most abundant compound among the Σ_{26}TWCs, with 2-OH-BTH and BTSA also belonging to BTHs. Notably, BTHs not only serve as tyre additives but also act as essential precursors for certain pharmaceuticals.[50] Moreover, high concentrations of BTHs and BTRs have been found in textiles.[51] Considering Guangzhou and Foshan are important manufacturing centers for medicine and clothing in China,[52] these industries may contribute significantly to the presence of BTHs in the PRD. Additionally, the sampling point in Guangzhou was located approximately 300 meters from a major express intersection, where vehicles frequently brake and decelerate when passing through the high-speed toll station, generating a large number of TWPs associated with increased concentration of TWCs. Notably, the concentration of 2-OH-BTH (101,000 ± 121,000 pg/m^3) was second highest in Zhuhai, which may be associated

with a point source near the sampling site. Within one kilometer of sampling point in Zhuhai, three driving schools, one karting club, and four high-speed toll stations were identified, all potentially contributing significant amount of TWPs.

Comparison with Other Studies

The comparison of gas and particulate phase concentration with literature is detailed in Table S8. Only two studies have reported the occurrence of four BTHs[53] and five BTRs[54] in indoor gaseous phase. Compared with indoor air,[53] the BTHs concentrations in the urban atmosphere gas phase show different profiles. The median gas phase concentration of BTH in urban air was 700 pg/m^3, which was 20 times lower than observed in indoor air (14,200 pg/m^3). Conversely, 2-OH-BTH measured in urban atmospheric gaseous phase was 17,700 pg/m^3, which was 20 times higher than that in indoor air (860 pg/m^3). One explanation could be that higher temperatures and stronger UV radiation outdoors favor the degradation of BTH into 2-OH-BTH.[40, 41] For BTRs, our median level in urban gaseous phase, ranging from 2.34 pg/m^3 to 53.3 pg/m^3, was 10 to 35 times higher than that in indoor air.[54] BTRs are widely used to inhibit the corrosion of metal alloys in vehicles or are added to aircraft de-icing agents and fluids, making them more prevalent outdoors than indoors.[32]

As illustrated in Figure S7, the levels of 2-OH-BTH in this study exhibit a broader range (ND-1,130 pg/m^3) with a lower median concentration (84.4 pg/m^3) compared to previous reports in Taiyuan, Shanghai, and Guangzhou (range 66.8-557 pg/m^3 with median 152-455 pg/m^3) in $PM_{2.5}$.[42] This variation could be attributed to the point sources near the sampling points in Guangzhou and Zhuhai, as mentioned earlier. Our BTH concentrations (median 256 pg/m^3) were an order of magnitude higher than that in Taiyuan, Shanghai, and Guangzhou (median 32.6-55.9 pg/m^3) in $PM_{2.5}$.[42] In contrast, the levels of 2-Me-S-BTH and 2-aminobenzothiazole (2-NH_2-BTH) in $PM_{2.5}$ (median 1.52 and 3.65 pg/m^3) were an order of magnitude lower than those reported in other studies.[42, 55] Overall, the concentration of BTHs in our study is notably higher than reported in previous literature.

DPG and HMMM in the atmosphere were only reported on the global scale by passive sampling.[49] The global median level of DPG was comparable to our study (93.9 pg/m^3 *vs* 91.9 pg/m^3), while the HMMM concentration was considerably lower in the global survey (0.11–0.22 pg/m^3 *vs* 0.65-34.4 pg/m^3) than our observations.[49] Different from

other studies, N-(1,4-dimethylpentyl)-N'-phenylbenzene-1,4-diamine (7PPD), N-(1,4-dimethylpentyl)-N-phenylbenzene-1,4-diamine (77PD), N,N′-diphenyl-p-phenylenediamine (DPPD), N,N′-di-(p-tolyl)-phenylenediamine (DTPD), N-phenyl-N′-cyclohexyl-p-phenylenediamine (CPPD), 77PD-quinone (77PD-Q), DPPD-quinone (DPPD-Q) and CPPD-quinone (CPPD-Q) were not detected in this study.[15, 16, 18, 24, 56] Additionally, the detected IPPD and IPPD-Q in $PM_{2.5}$ were present at lower concentrations (median 0.74 pg/m^3 and 1.64 pg/m^3 for IPPD and IPPD-Q, respectively) than those reported in Guangzhou, Taiyuan, Zhengzhou, Shanghai, Nanjing and Hangzhou (median 1.1-230 pg/m^3 and 2.00-65.5 pg/m^3 for IPPD and IPPD-Q, respectively).[15, 16, 18, 24] Additionally, compared with literature (median 1.18-25.5 pg/m^3), [16, 18, 24] the 6PPD-Q level was at a median range in this study (median 10.4 pg/m^3).

Influencing Factors

Socio-economic Parameters

The concentration of most TWCs shows a significant correlation with road length within a two-kilometer radius of the sampling sites (Spearman, r=0.242-0.525, p<0.001-0.041) and the production volume of rubber tyres in the PRD (Spearman, r=0.542-0.773, p<0.001-0.021), as detailed in Table S9. This suggests that TWCs are not solely emitted by TWPs but are also released during tyre production processes. Additionally, it is noteworthy that the level of most BTHs were positively related to the length of dyed fabrics (Spearman, r=0.369-0.495, p<0.001-0.002), implying potential sources of BTHs in textiles.[51]

Interestingly, the concentration of HMMM was positively correlated with human activities, including the residential land area within a one/two/five/ten/twenty-kilometer radius of the sampling sites, permanent population density and automobile population (Spearman, r=0.269-0.389, p=0.001-0.028). HMMM, added to tyres as an organic vulcanizer to enhance durability and strength,[57] has been widely detected in various environmental media.[49, 58] The observed positive correlation of HMMM levels with human activities, coupled with its widespread detection in various environmental media, suggests that HMMM may serve as a suitable indicator for assessing human activity.

Meteorological Parameters

A significantly negative correlation was found between the concentrations of most

directly emitted TWCs (e.g., 4-methyl-1H-benzotriazole and 5-methyl-1H-benzotriazole, TTR) and $PM_{2.5}$. Conversely, a positive correlation was observed between the concentrations of most product TWCs (e.g., 6PPD-Q) and $PM_{2.5}$. This implies that the product TWCs achieved a co-benefit reduction with $PM_{2.5}$.

Furthermore, the concentrations of most TWCs exhibited a positive correlation with relative humidity (RH) (Spearman, r=0.327-0.794, p<0.001-0.007), while demonstrating a negative correlation with wind speed (Spearman, r=-0.308~-0.605, p<0.001-0.037). This suggests that higher RH and lower wind speeds are disadvantageous for pollution diffusion,[59] resulting in elevated concentrations of TWCs in the atmosphere.

The Influence of Monsoons

To comprehend the influence of monsoons and regional sources on TWCs, PSCF model results and 24 h distribution of air mass concentrations was drawn and presented in Figure S5. During the sampling period, summer air masses were predominantly from the South China Sea. Winter air masses mainly originated from the East China Sea and South China Sea in Guangzhou, while from northern inland regions in other sites.

The PSCF results (Figure S5-S6) indicated that only the TWCs of Guangzhou during summer were influenced by air masses from the South China Sea, while other sites were primarily affected by local sources in both winter and summer. As TWCs are compounds associated with tyre wear, they may enter the environment via TWPs. Numerous studies have demonstrated that the ocean is an important sink for MPs, which included TWPs.[60-62] Tyre dust contributes 34% to the amounts entering the aquatic environment in mainland China in 2015.[60] However, recent studies suggest that TWPs in the ocean may be re-emitted into the marine atmosphere through sea spray and bubble bursting, transforming the ocean from a sink into an important source of atmospheric TWPs.[61] The South China Sea is one of the most polluted areas of MPs in China.[62] Therefore, the summer monsoon may carry TWCs from marine atmosphere of South China Sea into Guangzhou. The percentage difference of Σ_{28}TWCs concentration between winter and summer in Guangzhou was the smallest among all sampling sites (1.03 *vs* 1.20-1.83), which could be attributed to the marine source by summer monsoon in Guangzhou.

Gas-particle Fractions

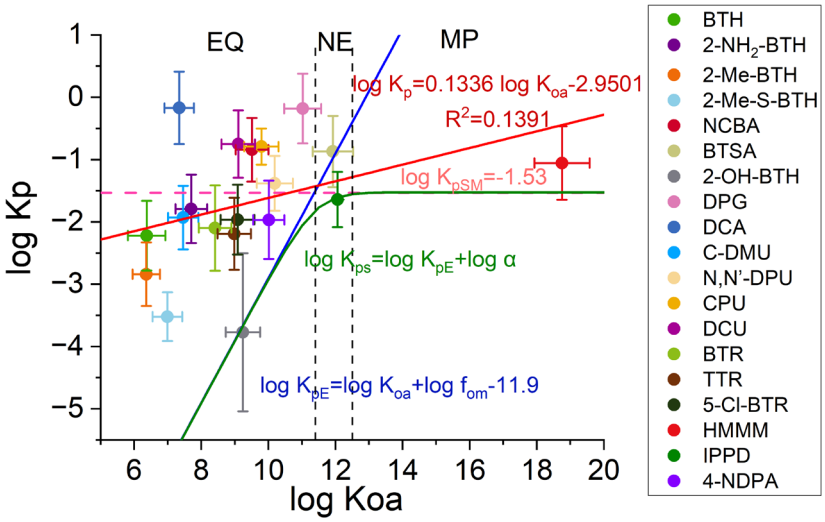
The gas-particle fraction largely varied among TWCs in this study (Figure S8). The particle-bound partition of BTHs ranged from 2-Me-S-BTH at 2 ± 2% to BTSA at 80 ± 24%, DPGs ranged from C-DMU at 42 ± 36% to *N,N*-dicyclohexylmethylamine (DCA) at 96 ± 4%. BTRs varied from TTR at 23 ± 24% to BTR COOH 100% and PPDs ranged from diphenylamine (DPA) at 0% to IPPD at 99 ± 12%. HMMM played a dominant role in particulate phase, accounting for 73 ± 25%. Compared with indoors,[53, 54] the G/P partitioning of most BTHs and benzotriazole (BTR) compounds have a similar trend, but 2-OH-BTH and TTR have a higher fraction in the particles in this study. Most BTHs and BTRs, especially the dominant 2-OH-BTR and BTH, were primarily enriched in gaseous phase, underscoring the significance of TWCs in gaseous phase for environmental and human health impact.

The G/P partitioning is affected by various factors such as the sources of particles, temperature and physicochemical properties.[63] As listed in Table S10, a significant positive correlation was found between particle-bound fraction of most TWCs and $PM_{2.5}$ concentrations (Spearman, r=0.244-0.676, p<0.001-0.042), which may indicate the particle level would affect the particle-bound fraction. Additionally, particle-bound partition of most TWCs and aerosol liquid water content (ALWC, detailed calculations in Text S8) also showed a positive correlation (Spearman, r=0.239-0.595, p<0.001-0.046), implying that an increased ALWC in particles leads to a greater number of dissolved targets due to their hydrophily. Meanwhile, a strong negative correlation was observed between temperature and particle-bound partition of most target compounds (Spearman, r=-0.247~-0.792, p<0.001-0.037), suggesting that chemicals are more prone to enter gaseous phase in higher temperature.[63]

The most measured G/P coefficient (log Kp) and log Koa of TWCs were positively associated (Spearman, r=0.417-0.760, p<0.001, Table S11), suggesting that the log Kp of TWCs could be predicted by log Koa.[64] Two widely used G/P partitioning models, Harner-Bidleman model[36] and steady-state Li-Ma-Yang model,[37, 38] were employed to predict the G/P partition quotient of TWCs. The slopes of measured log Kp and log Koa were below unity among TWCs, which implies nonequilibrium G/P partitioning of targets. Two threshold log Koa values (log K_{oa1}= 11.4 and log K_{oa2}=12.5, detailed as Text S5) divided partitioning map into three domains by steady-state Li-Ma-Yang model.[65]

As depicted in Figure 3, HMMM exhibited the highest log Koa (>12.5) and the measured log Kp was closer to the steady-state Li-Ma-Yang model, suggesting that the steady-state model might offer a better fit for predicting the G/P fractions of HMMM. In the non-equilibrium domain (NE, 11.4<log Koa<12.5), measured log Kp of BTSA worked well by Harner-Bidleman model, while measured log Kp of IPPD was well-fitted by Li-Ma-Yang model. For compounds including HMMM, BTSA, IPPD, characterized by higher log Koa (>11.4), a closer fit between detected and predicted log Kp was observed. This suggested that the particle fraction of these compounds might be primarily driven by Koa rather than molecular interactions between compounds and particles.[66]

Compared with measured log Kp, except for 2-OH-BTH, HMMM, BTSA and IPPD, predicted log Kp by two models were underestimated in the equilibrium domain (EQ, log Koa<11.4) as depicted in Figure 3. The underestimation of predicted log Kp may be attributed to three possible reasons. Firstly, the QFFs may absorb gaseous chemicals into particles, a sampling artifact, leading to an overestimation of their concentrations in $PM_{2.5}$.[67] Secondly, for compounds with strong hydrophilicity, residing on the particle surface for sufficient time may result in a portion of these compounds being "buried" into $PM_{2.5}$ and not readily diffuse back to the particle surface and into the gaseous phase. This can lead to elevated levels of these substances in particles.[68, 69] Lastly, TWPs entering the atmosphere might become part of $PM_{2.5}$ without releasing additives, causing these additives to be "buried" into $PM_{2.5}$ along with TWPs. Conversely, the higher vapor pressure of 2-OH-BTH (4.4 Pa at 25 °C) makes it more prone to volatilization from the tyre and $PM_{2.5}$. This explains why the predicted G/P fraction of log Kp of 2-OH-BTH can be fitted by the model even with low log Koa. Furthermore, various hydrophilic substances, such as organophosphate flame retardants (OPFRs),[70] were also found to underestimated log Kp by models, warranting further investigation.



409

410 Figure 3. Log-log plots of K_P, K_{PE}, log K_{PS} and log Koa for TWCs. Log K_P, the regression of
411 measured log K_P, was presented as red solid line. Log K_{PE} (blue solid line) and log Kps (green
412 solid line) were calculated using Harner-Bidleman model and Li-Ma-Yang model,
413 respectively. For Log $K_{oa,}$ the left vertical black dashed line is the first log K_{oa} threshold (log
414 K_{oa1}= 11.4) dividing it into equilibrium domain (EQ) and non-equilibrium domain (NE), while
415 the right vertical black dash is the second log K_{oa} threshold (log K_{oa2}=12.5) starting the
416 maximum portioning (MP) domain as detailed in Text S5. Log K_{PSM}=-1.53 (the horizontal pink
417 dashed line) is the maximum constant value of calculated by steady-state Li-Ma-Yang
418 model.[37]

419 ## Contribution of TWPs to $PM_{2.5}$

420 In this study, TWCs were used as markers of TWPs to more accurately quantify the
421 contribution of TWPs to $PM_{2.5}$ by PMF. The utilization of TWCs in the PMF analysis
422 followed four essential criteria, as illustrated in Figure S2. Briefly, firstly, TWCs were
423 widely detected (detection rate >80%) in this study. Secondly, TWCs were primarily
424 enriched in $PM_{2.5}$ (with their concentration in $PM_{2.5}$ exceeding 50% of the total gaseous
425 and particle phases concentrations), as indicated by the results of G/P partitioning.
426 This suggests that TWCs are closely linked to $PM_{2.5}$ and exhibit limited partitioning into
427 the gas phase. Thirdly, TWPs were identified as unique sources of TWCs. Lastly, the
428 correlation coefficient (r^2) exceeded 0.7, and factor profile results were interpretable
429 in PMF results. Subsequently, three TWCs (BTSA, DPG and 6PPD-Q) were finally
430 identified. In PMF analysis, three-eight factors were performed in PMF model and five
431 factors were determined as the optimal number of sources based on considerations of
432 Q/Qexp value, repeatability and model interpretability (Figure S9). The specific details
433 of PMF analysis and factor profile are provided in Text S6 and Figure 4, respectively.

The first factor, characterized by high fractions of p-phthalic acid, levoglucosan (levo.), K^+, NH_4^+, NO_3^-, SO_4^{2-}, fluoranthene (FLA) and pyrene (PYR), is identified as a mixed source associated with secondary formation, vehicle exhaust, biomass burning and plastic waste combustion. Specifically, p-phthalic acids are indicators of plastic burning.[71] Levo. and K^+ are acknowledged markers indicative of biomass burning. [72, 73] The presence of NH_4^+, NO_3^- and SO_4^{2-} is associated with secondary aerosols.[74] FLA and PYR have a high level in motor vehicle exhaust.[75] Moreover, vehicle exhaust and biomass burning are recognized as important contributors to secondary formation of NOx^- and SO_4.[76] This mixed source had the highest contribution to $PM_{2.5}$ at 38 ± 7%.

The second factor was dominated by Mg^{2+} and Ca^{2+}, which are typical tracers of resuspended soil and road dust.[77, 78] It is higher in winter (17 ± 8%) than summer (11 ± 6%) with seasonal variation (Kruskal−Wallis H test, p =0.005). Previous studies found that RH and wind speed significantly influence the generation and resuspension of dust.[78] The contribution of soil and road dust was negatively correlated with RH (Spearman, r=-0.604, p<0.001), while positively correlated with wind speed (Spearman, r=0.378, p=0.008) in this study. These correlations support to the reasonableness of PMF results.

The third factor was characterized by Na^+ and Cl^-, representing the source of sea salt.[79] Its contribution was slightly higher in winter (14 ± 5%) than summer (16 ± 13%) with seasonality (Kruskal−Wallis H test, p =0.018). The summer monsoon (Figure S5) could carry the sea salt from the coastal region into the PRD, resulting in the seasonality.

The fourth factor was attributed to industrial emissions, primarily from metals such as Cu, Zn, Cr, Mn, Cd, and As, which exhibited substantial loading (19%). Industrial emissions, particularly from iron and steel industries as well as non-ferrous industries, emerged as the predominant sources of these metals.[80] Industrial emissions contributed 19 ± 7% to $PM_{2.5}$ in the PRD.

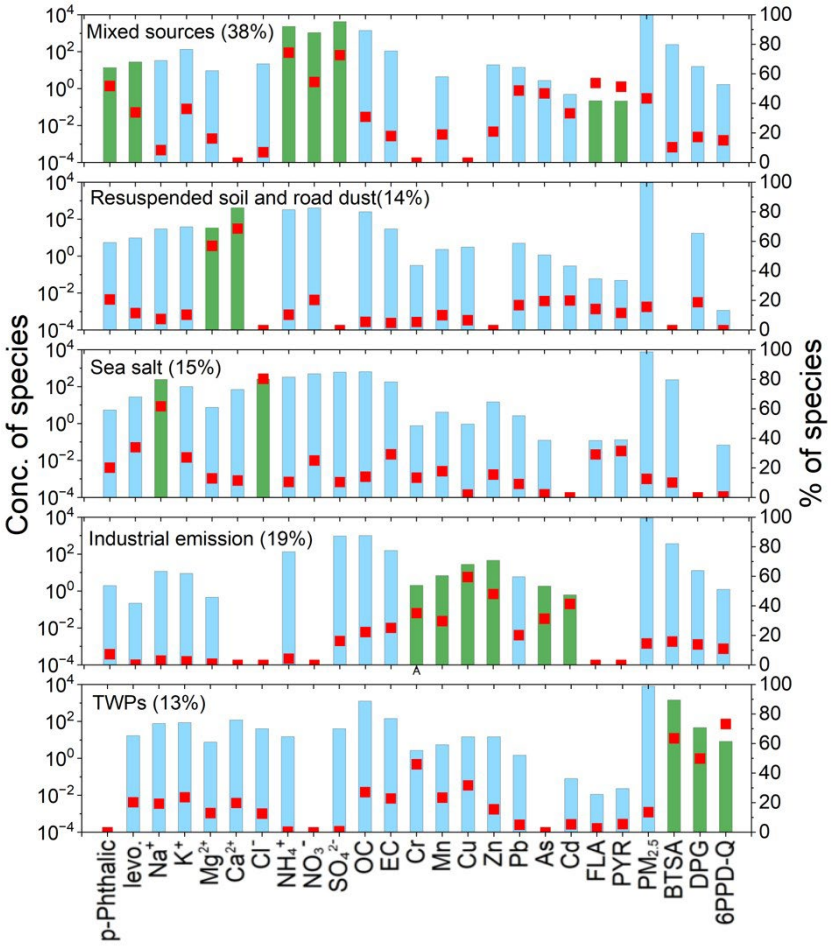


Figure 4. Source profiles gained from PMF analysis of $PM_{2.5}$. Bars represent concentration of selected species and red squares represent contribution (%) of selected specie.

The fifth factor shows a high loading of BTSA, DPG and 6PPD-Q, which are identified as TWPs. BTSA, DPG and 6PPD-Q serve as tracers of TWPs in this study (detailed in Figure S2). Recent studies have proposed 6PPD-Q as a promising marker for tyre wear.[17, 27] Additionally, BTSA is set as the total variable in the PMF model to quantify its source composition, as the details of Text S6 and Figure S10. The results showed that the contribution of TWPs to BTSA is 55 ± 17%, which indicates that TWPs are the main source of BTSA. This suggests the rationality of BTSA as TWPs indicator. The contribution of TWPs to $PM_{2.5}$ ranged from 6% (Zhaoqing) to 25% (Guangzhou) without

seasonality (Figure S11). As shown in Figure S12, Guangzhou, where sampling near the highway intersection toll station, showed the highest contribution of TWPs at 25% to $PM_{2.5}$.

It`s noteworthy that previous studies have reported several organic compounds as tyre wear markers, such as N-cyclohexyl-1,3-benzothiazol-2-amine (NCBA) and 2-(4-Morpholinyl) benzothiazole (24MoBT).[81] However, in this study, these markers exhibited low detection frequencies, with 24MoBT not being detected in all samples. This could be attributed to the change of predominant vulcanization accelerator of tyre rubber,[82] suggesting that they may no longer suitable as molecular markers of tyre wear.

Previous studies have assessed the contribution of tyre wear by metal markers such as Zn, Mn and Cu. For instance, Zhang *et al*. reported that tyre wear contributed 4 ± 2 % to $PM_{2.5}$ in Beijing, Tianjin, Zhengzhou and Qingdao based on tunnel measurements.[4] Similarly, tyre wear in road air contribute 6.6% to fine particles in Tianjin,[3] 5.2 % to $PM_{2.5}$ in Shanghai[6] and 10.7 ± 2.3 % to $PM_{0.9\text{-}11.5}$.[7] However, it is important to note that metals do not only solely originate from tyre wear but are also emitted by activities such as coal combustion, steel industry, metallurgy.[83] Consequently, the complexity of metal sources may lead to larger uncertainty in quantifying the contribution of TWPs to fine particles. In our study, the contribution of TWPs to $PM_{2.5}$ and the road length within a five-kilometer radius of the sampling sites was positively correlated (r^2=0.67) as in Figure S13. This supports the rationality of using BTSA, DPG and 6PPD-Q as markers to quantify the contribution of TWPs to $PM_{2.5}$.

Limitations and Environmental Implications

In this study, the concentrations of 77PD, DTPD, DNPD, 6PPD and DPPD decreased in MeOH solvent ranging from 17% (6PPD) to 100% (77PD) during a 132-hour chemical stability test (Table S11). Although a significant decline in the concentrations of PPDs, no noticeable increase observed in the concentration of PPDQs. Moreover, in our previous study,[32] the levels of 6PPD, DPPD, IPPD, DNPD, CPPD and 77PD in a MeOH: water solvent mixture (1:9 ,v/v) decreased by 42% (IPPD) to 100% (77PD) in three days. This suggests increased instability of PPDs when exposed to aqueous conditions.[23] As a result, the instability of PPDs could be responsible for the low detection rate in air samples and their underestimated measured level in air. During field work, it is

challenging to pretreat and analyze samples immediately. Despite this, field observations still serve as a valuable reference for understanding their occurrence and fates in the environment.

Our study is the first to report ultra-high concentrations of BTSA (ranged at 0.1-166 ng/m^3, median 3.17 ng/m^3) with 100 % detection frequency in the atmosphere. Although seven BTHs may convert to BTSA during pretreatment, the converted BTSA only accounted for 2.19 ± 3.07% (median 1.52%) of the total BTSA concentration (Text S3), which can be considered negligible. To our knowledge, BTSA has been reported as a transformation product of 2-SH-BTH, without record of its direct use. Previous research observed that BTSA was dominant (332 μg/g) in extracted solution of tyre and road wear particles (TRWPs), whereas only 74.8 μg/g was found in the cryo-milled tire tread (CMTT) extraction. However, the content of extractables in TRWP was higher than that in CMTT by five-eight-fold.[84] The disparity in the composition of BTSA between TRWP and CMTT implies that tire wear is a significant process in BTSA formation. So far, the transformation pathway, environmental behavior and potential biological toxicity of BTSA are rarely studied, thus further research is urgently needed.

China has implemented various control measures, including improvement in exhaust emissions and fuel standards, as well as encouraging the development of NEV, to control automobile exhaust pollution.[9] As a result, the contribution of motor vehicle exhaust emissions (VEE) has decreased, while the contribution of NEE has increased with the rise in car ownership. In UK, particles emitted by NEE contribute 60% to primary $PM_{2.5}$ emissions from road transport and constitute 7.4% of all UK primary $PM_{2.5}$.[5] This suggested that NEEs have become a dominant source of traffic pollution in UK. We attempted to parse VEE source as independent factors when conducting source apportionment by PMF model. Unfortunately, VEE could not be separated from secondary nitrates in this study. Alternatively, the contribution of VEE to $PM_{2.5}$ from the PRD in the literature is used to compare with the contribution of TWPs to $PM_{2.5}$.[85, 86] In our study, TWPs account for 13 ± 7% of $PM_{2.5}$ in PRD, comparable with VEE (13% - 14%) of $PM_{2.5}$ in the PRD region.[85, 86] However, it can be seen that the contribution of TWPs will keep growing, owing to the phasing-out of fossil-fueled cars and the increasing popularity of NEVs. Besides, NEVs, having relatively high weight, accelerating the particle emissions of TWPs.[87]

China, being the largest consumption market for NEVs, has witnessed a significant

increase in NEV sales, with annual growth rates 166% from 2011 to 2022.[88] In 2020, China's automobile sales volume was 25.31 million of which 1.37 million were NEV, accounting for 5.4% of automobile sales.[88] In 2035, NEVs are expected to achieve a market share of 50% and become the mainstream.[89] Additionally, to 2050 if the world avoids the worst global climate change scenarios, globally new vehicles will be almost entirely electric vehicles.[89] The rapid development of NEVs implies that NEEs will become a major contributor to traffic pollution in the near future. Currently, there is no released legislation, restrictions to control/reduce NEEs in any country and region of the world. Reducing NEE to minimize environmental pollution can be approached from three aspects: regulations, technology, and management. On one hand, efforts should be made to enhance the development of technologies such as reducing the weight of NEE, accompanied by the supporting facilities of NEE treatment for vehicles, such as the Tyre Collective developed by a clean-tech company in the UK, (http://thetyrecollective.com). On the other hand, the government should optimize road-related policies, and regulations regarding NEE. Simultaneously, road management should be optimized to reduce traffic congestion, as it plays a crucial role in minimizing NEE.

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