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RESEARCH ARTICLE

Review of 6PPD-quinone environmental occurrence, fate, and toxicity in stormwater

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Abstract – The antioxidant N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) is widely used to improve the durability of rubber. However, one of its transformation products, 6PPD-quinone (6PPD-Q), was recently found to be toxic. Herein, we aim to provide a comprehensive understanding of 6PPD-Q ecological and human-linked toxicity to facilitate the preparation of robust and specific environmental standards and policies. We reviewed 6PPD-Q environmental occurrence, fate, and toxicity originating from stormwater runoff and summarised its origin and environmental shaping conditions. Stormwater runoff was found to be the main driver in introducing 6PPD-Q into the environment. 6PPD-Q detection in roadside soils and other vehicle-related environments indicates that vehicle tyres are the major source of this compound; its presence in the soil can contaminate plants, thereby entering the food cycle. 6PPD-Q air concentrations were higher at roadside sites than at secluded building sites. Nevertheless, the mechanisms underlying 6PPD-Q toxicity and their relationship to various environmental factors, other contaminants, and removal technologies remain unknown. Addressing these gaps can help raise 6PPD-Q environmental risk awareness and facilitate development innovations to mitigate 6PPD-Q-linked risks.

Keywords – Stormwater; Runoff; Toxicity; Antioxidant; Aquatic; Risk

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1. INTRODUCTION

In the aquatic environment context, tyre wear is one of the major pollution sources. Despite this fact, it remains largely underrepresented in environmental impact assessments. Specifically, pollution stems from tyre and road wear particles (TRWPs) formed by the mechanical abrasion of car tyres against the road during driving and braking (Tamis et al., 2021). Up to 12% of the tyre mass can be released into the environment over its lifetime (Rauert et al., 2021), and estimated annual tyre wear emissions in different countries can range from 0.2–5.5 kg per capita (Baensch-Baltruschat et al., 2020). A recent study identified 214 organic compounds in tyre particle extracts, of which 145 were leachable; 58% of these leachable compounds were found to be mobile, indicating their transportation potential into various environmental compartments (Müller et al., 2022). Despite these alarming values, efforts to assess TRWP's potential ecotoxicological impacts, especially novel ones, are still in their infancy (Halle et al., 2021). Therefore, to facilitate technological and policy-related innovation in the TRWP-linked pollution context, it is necessary to acquire a broad overview of the gaps that currently plague research on these particles.

N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD) is an antioxidant and antiozonant that is used in synthetic rubber production. Specifically, this substance is used to improve rubber durability, thereby reducing chemical and mechanical degradation effects (Varshney et al., 2022).

This compound is found in tyres at mass fractions ranging from 0.4–2.0% (Johannessen et al., 2022a). Tian et al. (2021) recently discovered a 6PPD transformation product, 6PPD-quinone (6PPD-Q), which induces acute mortality in coho salmon (*Oncorhynchus kisutch*) as they return to spawn in urban and suburban streams in the U.S. Pacific Northwest. Owing to the parent compound 6PPD ubiquity in tyres, 6PPD-Q is expected to be widely present on roads and in road runoff globally, although its toxicity to humans and other organisms remains mostly unknown (Tian et al., 2022). Recent reports have revealed the presence of 6PPD-Q in runoff water (Cao et al., 2022; Tian et al., 2021), rivers (Johannessen et al., 2022a; Rauert et al., 2021), wastewater (Seiwert et al., 2022), air particles (Cao et al., 2022; Y. J. Zhang et al., 2022), and roadside soil (Cao et al., 2022). Given that tyre production and usage will continue, investigating 6PPD-Q occurrence and fate in the environment is critical to understand and emphasise its potential ecotoxicological impact.

With the growing interest in 6PPD-Q environmental occurrence, fate, and toxicity, a systematic review of the literature is necessary to critically assess the current state of knowledge and research gaps. This approach will provide a broader understanding of 6PPD-Q ecological and human toxicities; these insights can be used to facilitate the creation of robust environmental policies that are based on insights rooted in scientific understanding. Hence, the current study provides a critical review of published papers on 6PPD-Q to (i) summarise its occurrence and fate in water, soil, and air as influenced by stormwater runoff, (ii) identify the influence of environmental conditions on its levels, (iii) evaluate its toxicity to aquatic organisms and plants, (iv) identify ways to manage its risks, and (v) identify research gaps and future prospects. The implications of the insights revealed through this study are global, as they touch on steps that can be taken to mitigate the toxicity of a ubiquitous and understudied pollutant.

Based on an online database search of peer-reviewed articles using Web of Science, ScienceDirect, and Google Scholar, 17 journal articles that reported 6PPD-Q occurrence in different environmental media were identified. Additionally, 14 journal articles that investigated 6PPD-Q toxicity to aquatic organisms and terrestrial plants were found. The keywords ‘6PPD’ and ‘6PPD-quinone’ were used in finding these articles, which were all published between 2021–2023. While most sections of this paper were heavily based on these 31 articles, other peer-reviewed papers were also cited to elucidate selected article observations.

2. 6PPD-quinone formation

Once TRWPs are released onto a road’s surface, they degrade and transform when exposed to sunlight, heat, ozone, and mechanical shear stress when forced against the road by passing vehicles (Hiki and Yamamoto, 2022a). 6PPD degrades by photooxidation or thermal oxidation (when the road’s surface temperature exceeds 80 °C), and some resultant products have been identified only recently (Hiki and Yamamoto, 2022a; Seiwert et al., 2022). One of the oxidation products is 6PPD-Q, which is formed via three principal steps (amine oxide, side-chain oxidation, and nitroxide radical formation) under ozone action (Y. J. Zhang et al., 2022). Figure 1 illustrates the industrial process of 6PPD synthesis and its transformation into 6PPD-Q.

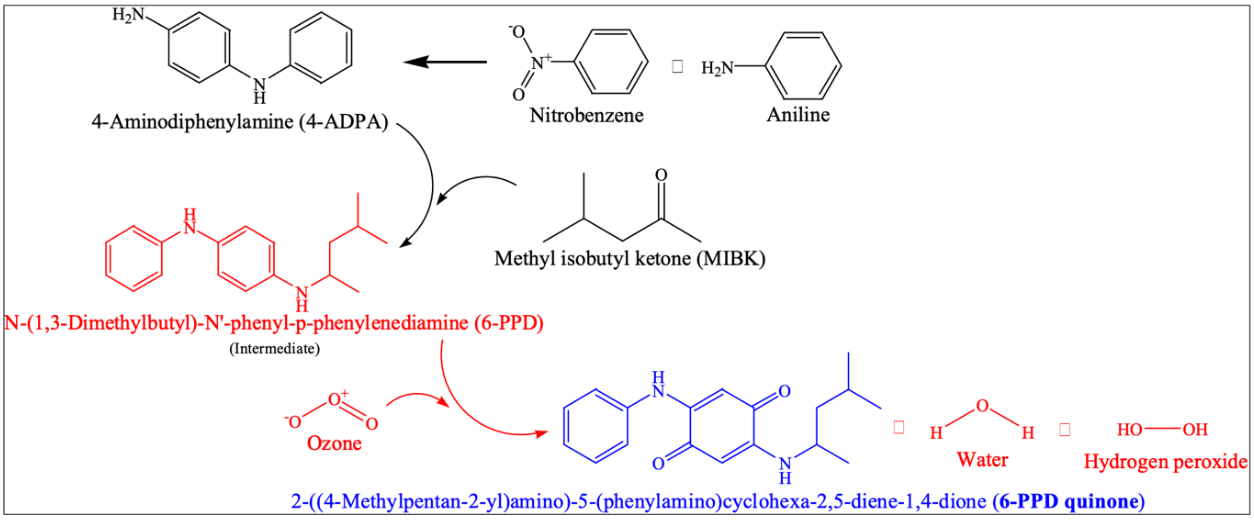

Fig. 1 Technological synthesis of 6PPD and its transformation to 6PPD-quinone (source: Zhang et al. (2022))

Although it has been established that 6PPD-Q is formed by the reaction of 6PPD and ozone, the specific pathways by which this process advances in road environments remain unelucidated. Tian et al. (2021) proposed two possible ozonation pathways for 6PPD conversion to 6PPD-Q (Figure 2). Both pathways involve an initial 6PPD attack by ozone at either C7 or C10 to yield (i) intermediate phenols and singlet oxygen molecules ($^1O_2$) via heterolytic O–O scission or (ii) semiquinone hydroperoxyl ($HO_2^\bullet$) radicals via homolytic O–O scission. The intermediate phenols and semiquinone radicals then form 6PPD-Q through an ozone reaction followed by heterolytic O–O scission, yielding quinone and hydroperoxide, and an $HO_2^\bullet$ reaction followed by H_2O release.

A recent study showed that 6PPD-Q bound to fine particulate matter ($PM_{2.5}$) was positively correlated with ozone concentration (Y. Zhang et al., 2022). This suggests that 6PPD-Q formation is enhanced in areas with higher ozone levels. The uncertainty of how 6PPD-Q is formed in the actual environment calls for more studies investigating the factors that shape 6PPD transformation. Focusing on the correlations between 6PPD-Q concentrations and different environmental conditions, such as ozone levels and temperature, could narrow down potential 6PPD-Q reaction pathways.

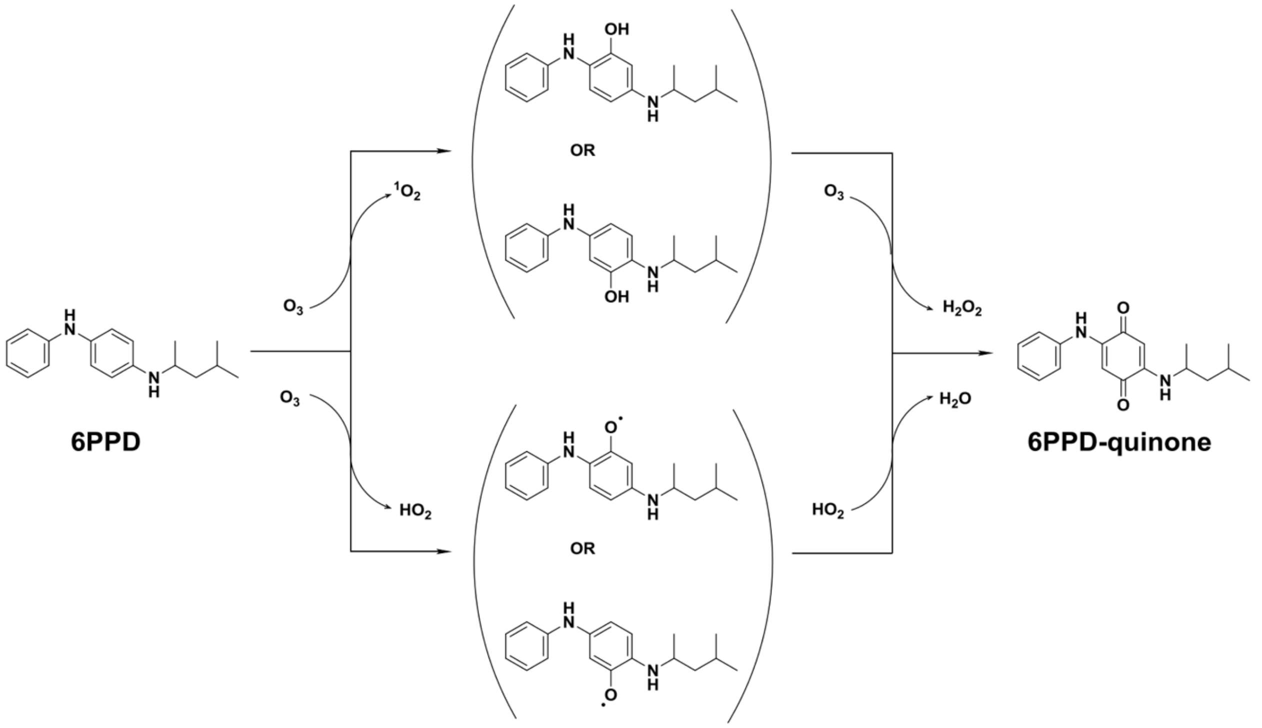

Fig. 2 Possible ozonation reaction pathways for the production of 6PPD-quinone from 6PPD (source: Tian et al. (2021))

3. 6PPD-QUINONE OCCURRENCE AND FATE

Since the discovery of 6PPD transformation into 6PPD-Q, several researchers have reported 6PPD-Q occurrence in different environmental compartments, including surface water, wastewater treatment plant effluents, soils, dust, and air (Cao et al., 2022; Tian et al., 2021; Y. J. Zhang et al., 2022). Figure 3 shows 6PPD-Q environmental pathways as influenced by stormwater runoff. In the following sections, we present an overview of findings on the contamination of the abovementioned environmental compartments by 6PPD-Q.

3.1. Stormwater runoff

Stormwater runoff is a significant transportation pathway of contaminants to surface waters which, in turn, substantially degrades water quality. The extent of this degradation has been attributed to the complex structure of stormwater matrices (Tian et al., 2022; Werbowski et al., 2021). Given that 6PPD in tyres is released onto road surfaces through mechanical abrasion, the contamination of stormwater runoff with 6PPD-Q can occur extensively. Table 1 summarises previously reported 6PPD-Q concentrations in stormwater and other streams. 6PPD-Q concentrations ranging 0.8–19 μg/L and 4.1–6.1 μg/L were reported for roadway runoff in Seattle and Los Angeles, respectively (Tian et al., 2021). While these concentrations could be diluted upon reaching surface waters, the reported concentrations exceed 0.095 μg/L, which has been linked to a 50% mortality rate in coho salmon; this concentration is technically referred to as the lethal concentration 50 (LC_{50}) (Tian et al., 2022). These results highlight the importance of understanding the occurrence and fate of 6PPD-Q in stormwater runoff.

Cao et al. (2022) investigated rubber-derived quinones from *p*-phenylenediamine (PPD) antioxidants, including 6PPD. They found that 6PPD-Q levels (0.21–2.43 μg/L) in the runoff water samples from Hong Kong were lower than those reported by Tian et al. (2021); nevertheless, this range exceeded the LC_{50} for coho salmon, indicating a potential risk to aquatic organisms. The reported 6PPD concentrations are similar to those of 6PPD-Q, with values ranging from 0.21–2.71 µg/L. Similarly, Challis et al. (2021) reported lower 6PPD-Q concentrations in stormwater runoff from Saskatoon (0.086–1.4 µg/L) across all sites and sampling events. In a recent study, Kryuchkov et al. (2023) found tunnel-wash runoff samples in Norway containing 6PPD-Q at 0.11–0.14 µg/L. Runoff samples from artificial turf pitch, which is usually made of rubber granules from discarded car tyres, also contained 6PPD-Q at 0.16 µg/L. These studies highlight the geographic variability in the amounts of 6PPD-Q, suggestive of the possibility that 6PPD-Q levels could be influenced by several factors, i.e., land utilisation, infrastructure, population, weather conditions, study sampling design, and chemical transportation dynamics (Challis et al., 2021). In future studies, experiments should be designed to consider the effects of these factors on the occurrence and fate of 6PPD-Q.

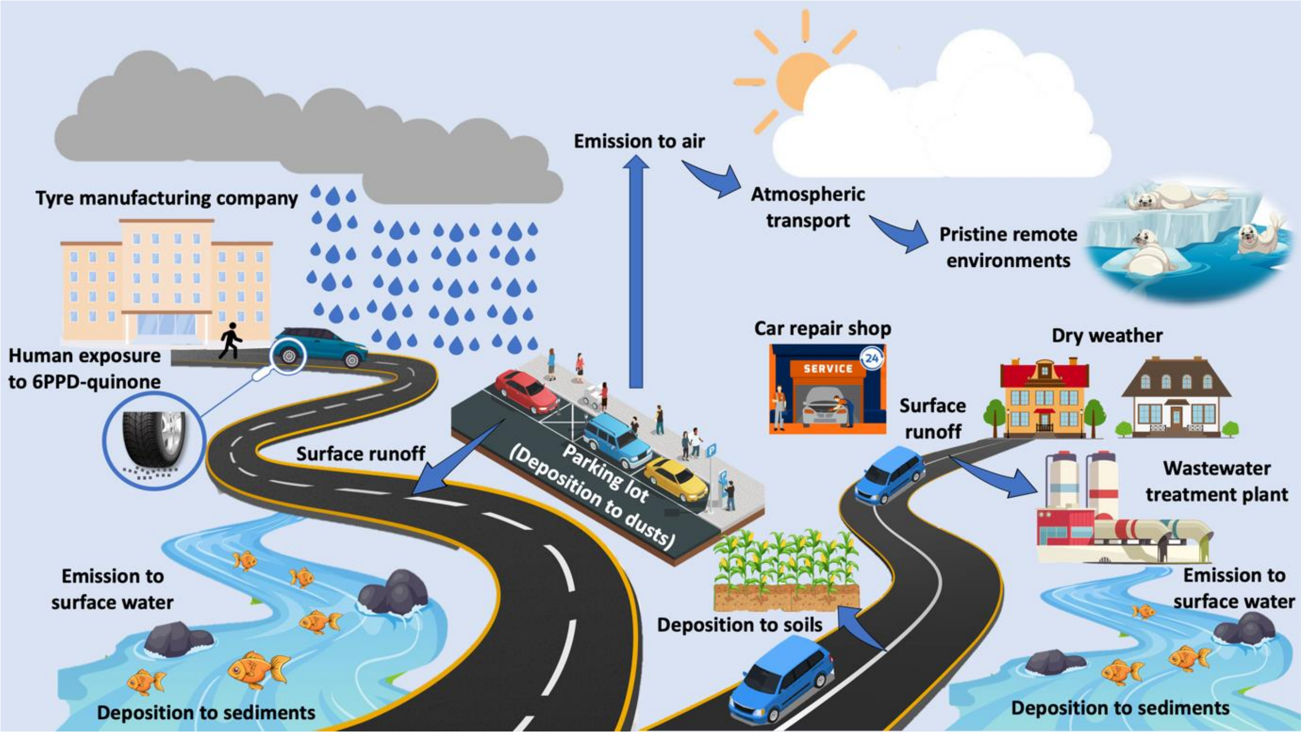

Fig. 3 Environmental pathways of 6PPD-quinone from tyres as influenced by stormwater runoff

3.2. Surface water

Since 6PPD-Q was shown to induce mortality in coho salmon found in urban streams (Tian et al., 2021), several researchers have investigated its occurrence in different surface waters that could have been impacted by roadway runoff. For example, Johannessen et al. (2021) analysed surface water samples from two rivers near transportation corridors in the Greater Toronto Area for 6PPD-Q, together with two tyre additives and other transformation products. The mean 6PPD-Q concentrations in the grab and composite samples collected during the rain events were 0.72 ± 0.05 and 0.21 ± 0.02 µg/L, respectively. In another study by Johannessen et al. (2022), a peak 6PPD-Q concentration of 2.30 ± 0.05 µg/L was recorded in Don River in Toronto during storm events. These values are considerably higher than those observed by Rauert et al. (2021, 2022) in their study on the quantification of TRWPs and tyre additive chemicals in Australian surface waters during extreme storms. Tyre additive concentrations increased more than 40 times during storm events, with a 0.088 µg/L 6PPD-Q maximum concentration (Rauert et al., 2021). However, lower 6PPD-Q levels (<0.00005–0.024 µg/L) were detected at 18 of the 21 sampled sites (Rauert et al., 2022), with the highest concentration approximately four times lower than 0.095 µg/L, the LC_{50} for coho salmon (Tian et al., 2022). Conversely, Tian et al. (2021) reported higher 6PPD-Q levels ranging from <0.30–3.20 µg/L in three Seattle-region watersheds during storm events, whereas 1.00–3.50 µg/L concentrations were detected in San Francisco regional creeks affected by urban runoff.

These findings indicate that hydrological events can mobilise tyre-derived chemicals such as 6PPD-Q from stormwater runoff to surface waters. In some instances, tyre additives maintain elevated levels despite the water depth being at baseflow levels between storms (Rauert et al., 2022). Thus, methods geared towards effectively and sustainably treating stormwater in urban environments will need to be developed; such methods would be especially important near multilane roads, where most tyre-derived compounds found in roadway runoff originate.

Table 1. Range of 6PPD-Q concentrations in stormwater, surface water, and wastewater.

Type of sample	Range of 6PPD-Q concentrations (μg/L)	Reference
Stormwater runoff		
Seattle, USA	0.80–19.00	Tian et al. (2021)
Los Angeles, USA	4.10–6.10	Tian et al. (2021)
Hong Kong	0.21–2.43	Cao et al. (2022)
Saskatoon, Canada	0.086–1.40	Challis et al. (2021)
Trondelag, Norway	0.11–0.14	Kryuchkov et al. (2023)
Surface water		
Toronto, Canada	0.21–0.72	Johannessen et al. (2021)
Toronto, Canada	2.30	Johannessen et al. (2022)
Brisbane, Australia	<0.00005–0.088	Rauert et al. (2021; 2022)
Seattle, USA	<0.30–3.20	Tian et al. (2021)
San Francisco, USA	1.00–3.50	Tian et al. (2021)
Wastewater		
Leipzig, Germany	0.05–0.11	Seiwert et al. (2022)
Ontario, Canada	<LOD[a]–0.15[b]	Johannessen and Metcalfe (2022)

[a]: LOD, limit of detection; [b]: 6PPD-quinone mass in μg

3.3. Wastewater

Stormwater flowing into sewer systems carries TRWPs that accumulate in municipal wastewater treatment plants (WWTPs). These treatment plants act as sinks, which gradually release TRWPs into receiving waters (Johannessen and Metcalfe, 2022). This is alarming because water sources impacted by human activity and wastewater discharge now constitute a significant source of drinking water, and the contaminants therein can interact with disinfectants to form carcinogenic byproducts (Jin et al., 2023). Thus, more studies are required to examine wastewater matrices for residual contaminants and explore subsequent treatment methods to remove these pollutants.

Seiwert et al. (2022) detected 6PPD and 13 transformation products, including 6PPD-Q, in WWTP influent and effluent during snowmelt, rainfall, and dry weather in Germany. The 6PPD-Q concentrations were generally below the quantification limit except in the influents during snowmelt (0.11 ± 0.04 μg/L) and rainfall events (0.05 ± 0.02 μg/L). These values were lower than those detected for road runoff (Cao et al., 2022; Challis et al., 2021; Tian et al., 2021), which could be due to runoff dilution with wastewater from households and industry in combined sewer systems (Seiwert et al., 2022).

Johannessen and Metcalfe (2022) studied four wastewater treatment plants (WWTPs) in Canada to investigate tyre-linked wear compounds and their transformation products, including 6PPD-Q. In two of the WWTPs studied, 6PPD-Q accumulated in the sampler deployed in the influents to mean masses of 0.14 and 0.15 μg, while the amounts in the effluents were below the detection limit. This suggests that the treatment processes employed in these WWTPs could remove or transform 6PPD-Q. In contrast, 6PPD-Q was detected in both the influent and effluent of the other two WWTPs; interestingly, the 6PPD-Q mass increased by two and seven times in the effluents relative to the amounts measured in the influents for both the plants. Air plug flow reactors, which could have generated 6PPD-Q via 6PPD oxidation within the WWTP, were utilised in both cases. Zhang et al. (2023) also found 6PPD-Q traces in the influents (0.01–0.07 μg/L) and effluents (<detection limit–0.002 μg/L) of three WWTPs in China. The 6PPD-Q removal rate corresponded to 85.3–100.0%, indicating that the treatment process was effective for removing or transforming 6PPD-Q. This was necessary to avoid potential 6PPD-Q release from WWTPs, as this compound has been shown to be highly toxic to some aquatic organisms (Brinkmann et al., 2022; Tian et al., 2021). Hence, investigating 6PPD-Q transformation products and their potential toxicity to aquatic organisms is equally crucial.

3.4. Soils, sediments, and dusts

Soil is a crucial ecological system element and the foundation for human survival and development (Jia et al., 2020); yet it is one of the most contaminated environmental media. TRWPs released into soils, for instance, can be harmful to humans and other organisms via different routes such as soil ingestion, root uptake by edible plants, and contaminated soil transportation and deposition in surface waters (Castan et al., 2023). Similarly, dust is a contaminant exposure source for humans via ingestion, inhalation, or dermal contact (Huang et al., 2021), whereas TRWPs are major dust components in different vehicle-related microenvironments, including roads and parking lots (Deng et al., 2022). Soils, sediments, and dust have been increasingly used as target matrices to determine the occurrence and abundance of organic compounds, including 6PPD-Q, in various environments (Table 2). Similar to that in water bodies, 6PPD-Q soil contamination was highly influenced by stormwater during infiltration.

Table 2. Range of 6PPD-Q concentrations in soils, sediments, and dusts.

Type of sample	Location	Range of 6PPD-Q concentrations (μg/kg)	Reference
Roadside soils	Hong Kong	9.50–936	Cao et al. (2022)
Freshwater sediment	China	1.87–18.20	Zeng et al. (2023)
Marine sediment	China	0.43–3.02	Zeng et al. (2023)
Road dust	China	3.0–88.10	Huang et al. (2021)
Parking lot dust	China	5.7–277	Huang et al. (2021)
Vehicle dust	China	17.9–146	Huang et al. (2021)
House dust	China	<LOD[a]–0.40	Huang et al. (2021)
Road dust	Japan	116–1238	Hiki & Yamamoto (2022)
Road dust	China	10.5–509	Deng et al. (2022)
Indoor parking lot dust	China	4.02–2369	Deng et al. (2022)
Electronic waste dust	China	87.1–2850	Liang et al. (2022)
Indoor dust	China	0.62–106	Zhang et al. (2022)

[a]: LOD, limit of detection.

Cao et al. (2022) also investigated rubber-derived quinone PPD antioxidant formation such as 6PPD in roadside soils in Hong Kong. The 6PPD-Q ranged from 9.5–936 μg/kg; interestingly, the 6PPD to 6PPD-Q ratio was >1, whereas the opposite was observed for the other PPDs studied. These findings indicate that PPD quinone distribution and concentration patterns are distinct and should be considered when assessing their toxicity in various ecosystems. Zeng et al. (2023) observed significantly lower 6PPD-Q concentrations in freshwater (1.9–18.2 μg/kg) and marine (0.4–3.0 μg/kg) sediments in China. This study demonstrated that 6PPD-Q long-range transportation can occur across urban rivers, estuaries, and coastal and deep-sea regions. This highlights the need to investigate the environmental behaviour of different parent compounds and their transformation products, especially given their substantial use in the production of rubber products.

TRWPs constitute a large fraction of traffic-related dust. Hiki and Yamamoto (2022) reported 6PPD-Q concentrations ranging from 116 mg/kg to 1238 μg/kg in road dust from Japan. These values were considerably higher than those found in road dusts from China, with concentration ranges of 3.0–88.1 μg/kg (Huang et al., 2021) and 10.5–509 μg/kg (Deng et al., 2022). Similar to road dust, parking lot dust contains 6PPD-Q at concentrations of 5.7–277 μg/kg (Huang et al., 2021) and 4.0–2369 μg/kg (Deng et al., 2022). Both Huang et al. (2021) and Deng et al. (2022) observed a higher 6PPD-Q content in parking lot dust than in road dust, possibly because of the location and surrounding environment, as the conditions in parking lots are relatively more stable compared to those of roads. Additionally, road dust contains soil minerals, particles from road construction materials, and atmospheric deposition that could have diluted the 6PPD-Q concentrations (Deng et al., 2022).

Other than outdoor environments, 6PPD-Q has been detected in dust samples from different indoor compartments such as vehicles, shopping malls, residential air conditioners, bedrooms, and dormitory rooms (Huang et al., 2021; Y. J. Zhang et al., 2022). Remarkably, 6PPD-Q levels in vehicle dust (17.9–146 μg/kg) were higher than those found in house dust (<detection limit –0.4 μg/kg) (Huang et al., 2021) and dusts from other indoor compartments (0.6–106 μg/kg) (Y. J. Zhang et al., 2022), suggesting that sunlight irradiation and increased temperature inside vehicles could facilitate 6PPD-Q formation (Huang et al., 2021). Additionally, dust from electronic waste has been reported to contain 6PPD-Q with values ranging from 87.1–2850 μg/kg, which were higher than those of the parent compound 6PPD (13.8–1020 μg/kg) (Liang et al., 2022). This proves that electronic waste, aside from rubber products, can also serve as a source of 6PPD-Q, which is an emerging issue of concern considering the worldwide promotion of electronic waste recycling.

3.5. Air

Compared to exposure from other environmental matrices, the inhalation of fine particulate matter ($PM_{2.5}$) is a more frequent contact route (Y. Zhang et al., 2022). Despite this, studies investigating the occurrence of PPD antioxidants and their transformation products in $PM_{2.5}$, as in the case of 6PPD-Q, are still limited (Table 3). Cao et al. (2022) reported the presence of 6PPD and 6PPD-Q in air particles at concentrations ranging from 0.8–6.3 pg/m^3 and 0.5–13.8 pg/m^3, respectively. The higher 6PPD-Q levels may be attributed to high-frequency contact with atmospheric ozone, as 6PPD-Q formation is associated with the presence of environmental oxidants. Zhang et al. (2022) also investigated the atmospheric contamination levels of $PM_{2.5}$-bound PPDs in six major Chinese cities. A total detection rate of 81% has been reported for 6PPD-Q in urban $PM_{2.5}$, demonstrating its broad existence. Its concentration ranged from 0.1–84 pg/m^3, which is of the same order of magnitude as that previously reported. In contrast, low 6PPD-Q concentrations were detected by Johannessen et al. (2022), with a mean estimated concentration of 0.847 pg/m^3 and the highest reported concentration of 1.75 pg/m^3, whereas Wang et al. (2022) observed considerably higher concentrations reaching up to 7250 pg/m^3 in $PM_{2.5}$ samples from two megacities in China. In the latter study, both 6PPD and 6PPD-Q levels were determined at a roadside and campus building site far from heavy traffic jams to evaluate the influence of traffic intensity on the sample concentrations. The roadside site values were significantly higher ($p < 0.001$) than those at the campus building site. Given the frequent detection of airborne contaminants from tyres, there is an urgent need to comprehensively analyse human exposure and test the toxicity of these novel contaminants to assess their effects on human health (Johannessen et al., 2022).

Table 3. Range of 6PPD-Q concentrations in air samples.

Location	Range of 6PPD-Q concentrations (pg/m^3)	Reference
Hong Kong	0.5–13.8	Cao et al. (2022)
China	0.1–84	Zhang et al. (2022)
Brazil	1.75*	Johannessen et al. (2022)
China	7250*	Wang et al. (2022)

*highest reported concentration

4. INFLUENCE OF ENVIRONMENTAL FACTORS ON 6PPD-QUINONE LEVELS

To fully understand 6PPD-Q formation and distribution, environmental factors such as ozone, humidity, temperature, and irradiation should be evaluated. Previous studies have suggested that 6PPD transforms into 6PPD-Q under ozone action (Cao et al., 2022; Y. J. Zhang et al., 2022). In line with these reports, the highest 6PPD-Q concentrations were recorded from May to June, when atmospheric ozone concentrations were the highest in Japan (Hiki and Yamamoto, 2022). This was corroborated by the positive correlation between 6PPD-Q and atmospheric photochemical oxidant concentrations, which were used as alternatives to ozone. Zhang et al. (2022) also found a positive correlation between $PM_{2.5}$-bound 6PPD-Q and ozone, suggesting that 6PPD-Q generation in $PM_{2.5}$ was likely enhanced in areas with high ozone levels. Nevertheless, the specific action of ozone on 6PPD-Q formation, particularly in road environments, remains unknown.

Solar radiation and high temperatures have also been hypothesised to drive 6PPD-Q transformation from non-tyre rubber materials inside vehicles (Y. J. Zhang et al., 2022). In this study, automobile interior environments showed the highest mean 6PPD-Q concentrations among other non-occupational indoor environments, including shopping malls, household air conditioners, bedrooms, and dormitory rooms, from April to August. Ozone in cars can initiate ultrafine particle and secondary hazardous substance formation, particularly at elevated temperatures and ozone levels. These results suggest that confined spaces that are characterised by strong solar radiation or high temperatures may promote 6PPD-Q formation.

Storm events have also been shown to increase 6PPD-Q levels in Australian urban tributaries (Rauert et al., 2022). The pre-storm sample collection provided a background 6PPD-Q concentration of 3.9×10^{-4} μg/L, which increased up to 225 times during storm events. Furthermore, post-storm measurements have shown elevated 6PPD-Q levels, suggesting an extended exposure time for aquatic organisms. Xu et al. (2023) also found that anaerobic flooded soil conditions were favourable for 6PPD-Q formation, resulting in a 3.8-fold increase in 6PPD-Q accumulation compared to wet soils after 60-day ageing. In the first 30 days, microbial Fe(III) to Fe(II) reduction coupled with 6PPD oxidation enhanced 6PPD-Q formation in flooded soils, whereas superoxide radical formation induced by environmentally persistent free radicals under anaerobic flooded conditions, facilitated 6PPD-Q formation during the subsequent 30 days. This could explain why 6PPD-Q occurs in anaerobic environments, such as sediments and natural waters.

Previous studies have suggested that soil or dust particle size distributions and 6PPD-Q contaminant concentrations are also correlated (Cao et al., 2019; Lu et al., 2018). Particle size is not an environmental condition but a parameter that is relatively dependent on certain climatic conditions (e.g. temperature and wind speed). Deng et al. (2022) reported that the 6PPD-Q concentrations in road dust samples decreased from 0.27–0.061 μg/g as the dust size fraction increased from < 20 to 500–1000 μm, possibly because of the fine fraction larger surface area. This is consistent with the findings of Hiki and Yamamoto (2022), in which 6PPD-Q concentrations in road dust samples showed an increasing trend with the proportion of fine particles (< 75 μm), and with those of Klöckner et al. (2021), who showed higher 6PPD-Q levels in fine tunnel dust particles (< 100 μm) than in coarse particles. In addition, road dust organic carbon content exhibited an increasing trend with 6PPD-Q concentration (Hiki and Yamamoto, 2022a). Because research on 6PPD-Q is still in its infancy, studies investigating the influence of environmental factors on 6PPD-Q concentrations are limited. Therefore, future studies should evaluate the correlation between environmental factors and 6PPD-Q levels in different media to better understand 6PPD-Q environmental impacts.

5. ENVIRONMENTAL RISKS ASSOCIATED WITH 6PPD-QUINONE

The deleterious effects of 6PPD-Q on the environment and human health have raised widespread concern for several reasons. First, 6PPD-Q is speculated to be continuously present in receiving water bodies on a global scale. This is because of the ubiquitous use of its parent compound, 6PPD, in the production of a wide array of rubber products (Hiki et al., 2021). Second, 6PPD-Q effects on aquatic organisms include mortality, cardiotoxicity, oxidative stress, and developmental and behavioural toxicity (Tian et al., 2021; Varshney et al., 2022). Third, 6PPD-Q exhibits moderate environmental stability (Hu et al., 2023), which may influence its persistence in the environment. The following sections summarise the recent findings on 6PPD-Q toxicity to aquatic organisms and plants.

5.1. 6PPD-quinone toxicity to aquatic organisms

Tian et al. (2021) discovered 6PPD-Q as the cause of acute mortality in coho salmon during their migration to urban freshwater streams for breeding. Identification of 6PPD-Q as the root cause of 'urban runoff mortality syndrome' has triggered a global concern not only about its potential impact on other aquatic organisms but also the potential impact of other PPD-derived quinones (Zeng et al., 2023). Subsequent studies have focused on 6PPD-Q acute toxicity to other ecologically important fishes and aquatic organisms. In particular, the 6PPD-Q levels found in most environmental matrices were elevated relative to the LC_{50} for coho salmon (Tian et al., 2022).

Brinkmann et al. (2022) reported mortality in brook and rainbow trout with LC_{50} values of 0.59 and 1 μg/L, respectively. Brook trout death was observed as early as 1–2 h after exposure, whereas in rainbow trout, the first mortality occurred only after 7 h. Shortly before death, both fish species exhibited recognisable mortality signs, including increased ventilation, breathing difficulties, spinning movements, and equilibrium loss. Species with a shorter time to death may have increased vulnerability to mortality before stormwater dilution in receiving waters over time following rain events. This corresponds to the findings of Di et al. (2022) where 6PPD-Q was found to be 'very highly toxic' to rainbow trout exhibiting 96 h LC_{50} values that ranged from 1.66–4.31 μg/L depending on the 6PPD-Q enantiomer used.

In contrast to the high toxicity observed in the aforementioned species, 6PPD-Q did not cause acute mortality in other fish species at environmentally relevant concentrations (i.e. 1.3–54 μg/L), including arctic char and white sturgeon (Brinkmann et al., 2022), chum salmon (McIntyre et al., 2021), masu salmon and southern Asian Dolly Varden (Hiki and Yamamoto, 2022b), zebrafish and Japanese rice fish (Hiki et al., 2021), Atlantic salmon and brown trout (Foldvik et al., 2022) and fathead minnow (Anderson-Bain et al., 2023). Chinook salmon was found to have intermediate 6PPD-Q sensitivity, with the lowest concentration inducing mortality and the projected LC_{50} values being 27.3 μg/L and 80 μg/L, respectively. Remarkably, salmonid species had different 6PPD-Q sensitivities, which could also be the same for other species. Further investigations are required to gain insight into 6PPD-Q toxic mechanisms.

Acute mortality due to 6PPD-Q toxicity has also been reported in other aquatic species. *Caenorhabditis elegans* (roundworm) lethality was observed after exposure to 100 μg/L of 6PPD-Q (Hua et al., 2023a). Lower concentrations (0.1–10 μg/L) did not affect intestinal morphology but enhanced intestinal permeability and decreased intestinal fatty acid-transported ACS-22 expression. Exposure to 1 and 10 μg/L 6PPD-Q also reduced the reproductive capacity of *C. elegans* (Hua et al., 2023b). The planktonic crustacean *Daphnia magna* and amphipod crustacean *Hyalella Azteca* did not exhibit acute mortality, even at 6PPD-Q maximum water solubility (< 100 μg/L) (Hiki et al., 2021). Acute toxicity was not observed in the rotifer *Brachionus koreanus*, although its population growth rate moderately decreased with increasing exposure time (Maji et al., 2023). *B. koreanus* fertility was also not affected. However, the decreased population growth rate may have adverse transgenerational effects on offspring generation with long-term exposure. Similarly, freshwater rotifer *Brachionus calyciflorus* population growth was barely affected by 1000 μg/L 6PPD-Q, indicating the low toxicity of this compound to rotifers (Klauschies and Isanta-Navarro, 2022).

In addition to mortality, other 6PPD-Q toxicity signs in aquatic organisms have been reported (Figure 4). For example, Varshney et al. (2022) found that exposure to 1 μg/L 6PPD-Q did not influence zebrafish embryo behaviour; however, it induced developmental, behavioural, and cardiotoxicity at higher concentrations (10 and 25 μg/L). Specifically, developmental toxicity and morphological abnormalities were exhibited by intestinal reddening, physical deformities (e.g. lordosis and kyphosis), and reduced eye size in a concentration-dependent manner. Cardiotoxicity was demonstrated by reduced heartbeat per minute, while behavioural toxicity showed reduced total distance travelled, velocity, and larval heading. These toxicity results correspond to those of Zhang et al. (2023) in which 6PPD-Q exposed zebrafish embryos showed an enlarged intestine and blood-coagulated gut, activated neutrophils, and overexpressed enteric neurones. Ji et al. (2022) also reported that 6PPD-Q exposure reduced velocity and increased meandering in adult zebrafish.

However, limited information is available on the mechanisms underlying 6PPD-Q toxicity in aquatic organisms. Brinkmann et al. (2022) observed an increase in blood glucose concentration in brook and rainbow trout, indicating that 6PPD-Q exposure affected their energy metabolism, although the cause of this increase remains unclear. In the same study, an increase in brook trout haematocrit levels was observed. This corresponds to the findings of Blair et al. (2021), who observed a distinct increase in coho salmon haematocrit levels after exposure to urban runoff. This severe haematocrit increase was accompanied by the accumulation of Evans blue dye complexed with bovine serum albumin in coho salmon brains, which suggests that blood–brain barrier disruption was the driver of symptom development and acute mortality. Ji et al. (2022) observed increased neurotransmitter dopamine levels in adult zebrafish, suggesting that the abnormal behaviour of this species induced by 6PPD-Q could be attributed to dopamine metabolic disorders in the striatum substantia niagra pathway. Varshney et al. (2022) suggested that oxidative stress is a probable cause of the 6PPD-Q-induced inflammatory response in zebrafish larvae. Given these uncertainties, further investigations should be performed at different life stages of the species and different environmental chemistries. Therefore, it is necessary to gain a better understanding of the 6PPD-Q toxicity mechanisms, which could be useful for evaluating its environmental risks.

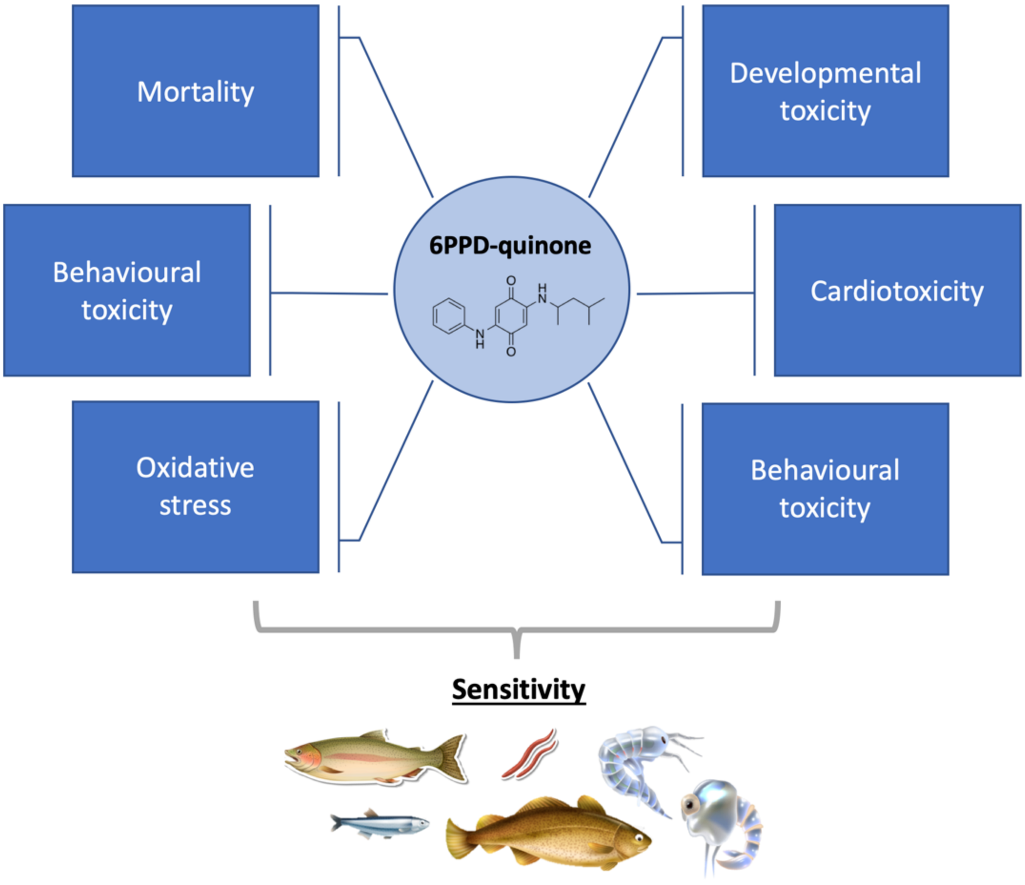

Fig. 4 Types of toxicity caused by 6PPD-quinone to aquatic organisms

5.2. 6PPD-quinone toxicity to plants

Highly toxic compounds, such as 6PPD-Q, may also be a concern to consumers, as they occur in edible plant root zones. Castan et al. (2023) exposed lettuce plants to TRWP-derived compounds including 6PPD-Q. As shown by the recorded biomass and the absence of growth inhibition, lettuce plants did not exhibit phytotoxicity signs. However, 6PPD-Q was siphoned by lettuce roots and translocated to their leaves. The compound concentration (i.e. 6PPD-Q) then continued to increase in the leaves over two weeks, with values reaching 2.19 µg/g. 6PPD-Q accumulation in lettuce roots may be more alarming for root vegetables such as carrots and radishes. Generally, this could become a critical issue if the regulatory limits are based only on the original compound concentrations without considering the sum of the parent compound and transformation products, which have unknown toxicities at present.

6. RISK MANAGEMENT

Stormwater runoff is a toxicant mixture that poses risks to aquatic organisms, suggesting that runoff treatment technologies are essential for protecting receiving water bodies from contaminant toxicity, especially TRWPs. However, these contaminant levels have not been systematically monitored, and their synergistic toxic effects are poorly defined and sometimes underestimated (Lapointe et al., 2022). Thus, to locate sites where mitigation strategies are required, a detailed assessment of contaminant loading and toxicity is required. New and strategically placed treatment processes (e.g. physicochemical filtration and adsorption systems) that are flexible for expansion can help mitigate contaminant load, especially during rainfall and snowmelt events (Lapointe et al., 2022). Considering 6PPD-Q, however, runoff treatment technologies targeting their removal are still in their infancy. McIntyre et al. (2023) investigated the ability of bioretention filtration to prevent acute mortality and reduce chronic toxicity for early life stage coho salmon exposed to stormwater runoff with 6PPD-Q. Although bioretention filtration did not prevent all effects for coho embryos (i.e. partial prevention only of smaller length and eye area), this technique resulted in water quality improvement and increased coho alevin survival.

New regulations regarding changes in tyre-rubber composition could also be necessary to reduce TRWP-associated risks, which are primary 6PPD-Q sources in stormwater and surface waters. Without an antidegradant, such as the parent compound 6PPD, tyres may fail after 100–1000 driving miles (UMass, 2023). Hence, 6PPD prevents tyre failures or blowouts, which could endanger motorist and passenger safety; its function and ubiquitous use makes it a difficult compound to replace. However, a recent study introduced an eco-friendly amine-functionalised lignin incorporated into rubber as a 6PPD alternative (Chung et al., 2023). This material exhibits excellent anti-ageing properties, such as thermal stability and fatigue resistance, comparable to those of 6PPD. Further research is needed to investigate whether this replacement generates toxic transformation products and has a lower environmental impact than that of 6PPD.

7. CONCLUSIONS

6PPD-Q occurrence, fate, and toxicity were reviewed in this study. All environmental components, including water, soil, sediment, dust, and air, contain 6PPD-Q at levels that pose risks to living organisms. Aquatic environment effects are mainly related to stormwater runoff, highlighting the need for runoff treatment to protect receiving water bodies from 6PPD-Q toxicity. Regarding the terrestrial environment, previous studies have mostly focused on 6PPD-Q occurrence on roadsides and parking lots, minimising the fact that the parent compound 6PPD could also leach from non-tyre rubber materials. Finally, 6PPD-Q occurrence and fate in air is a much less explored area, despite $PM_{2.5}$ inhalation, which is a frequent contact route. However, the health effects associated with 6PPD-Q inhalation are largely unknown. Furthermore, despite the surge in interest in 6PPD-Q due to coho salmon mortality, studies on 6PPD-Q toxicity in living organisms are still scarce; nevertheless, they are required to fully understand 6PPD-Q toxicity mechanisms and the resulting ecological impacts. For future studies, the following 6PPD-Q research aspects require further investigation.

- 6PPD-Q suspect screening should be performed to cover more environmental matrices and biota. This will give a broader perspective of the environmental occurrence and fate of this compound.

- A deeper understanding of the correlation between environmental factors (e.g. ozone, humidity, temperature, and irradiation) and 6PPD-Q concentrations in environmental media is needed to identify 6PPD-Q formation mechanisms, especially under road conditions.

- Detailed characterisations and quantification of adducts formed by 6PPD-Q and organism macromolecules are necessary to explore 6PPD-Q exposure biological consequences. The potential biomarkers should be identified to obtain additional insights into 6PPD-Q toxicity mechanisms.

-The role of 6PPD-Q in possible bioavailability, bioaccumulation, and biomagnification alteration of other contaminants, such as metals and other TRWPs, should also be investigated.

- 6PPD-Q treatment technologies are still lacking and should be developed together with the approach to strategically locate sites where 6PPD-Q is likely to accumulate (e.g. sediments). However, substituting the chemical additive 6PPD in tyre composition is still an important action required to address 6PPD-Q environmental and human health impacts. Thus, more research on 6PPD alternatives should be prioritised.

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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.

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AUTHOR CONTRIBUTIONS

Nina Ricci Nicomel contributed to the conception and design of the study; compiled the data from the literature for the analysis; wrote the first draft of the manuscript; reviewed and edited the previous versions of the manuscript; and read and approved the final version of the manuscript. **Loretta Y. Li** contributed to the conception and design of the study;

supervised the study; obtained the funding; reviewed and edited the previous versions of the manuscript; and read and approved the final version of the manuscript.

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