

1 **Rubber additives and relevant oxidation products in groundwater in**

2 **a central China region: Levels, influencing factors and exposure**

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26 **Abstract:** This study investigated the presence of rubber additives and relevant

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27 oxidation products (RAROPs) in groundwater in central China's aboveground river  
28 region. Seven RAROPs were detected, and their levels in shallow groundwater  
29 showed a mild decreasing trend from the area near the Yellow River (Avg: 8.49 ng·L<sup>-1</sup>)  
30 to the area on the far bank of the Yellow River (Avg: 5.01 ng·L<sup>-1</sup>). In contrast, deep  
31 groundwater's RAROPs contents showed a dramatic decrease to only 0.26 ng·L<sup>-1</sup>. The  
32 dominant contaminant was found to be *N*-(1, 3-dimethylbutyl) -*N'*-phenyl  
33 -*p*-phenylenediamine (6PPD). The vicinity of the garages and car parks was often  
34 characterized as contamination hotspots. Correlation analyses further indicated that  
35 aquaculture was likely to be a potential pathway for shallow groundwater contaminant  
36 inputs. The amount of RAROPs intake by humans through groundwater is nearly 30  
37 times different due to the imbalanced development between urban and rural areas.  
38 Children were the most vulnerable to RAROPs. Therefore, human activities  
39 (transportation, waste tire storage, water resource allocation and utilization patterns,  
40 diversion of Yellow River water to aquaculture ponds) may exacerbate RAROPs  
41 pollution in groundwater by leaching contaminants through the surface soil. These  
42 results are important for developing appropriate utilization and protection strategies  
43 for groundwater resources in developing countries.

44 **Keywords:** Rubber additives, Oxidation products, Groundwater, 6PPD-Q, Exposure  
45 assessment

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## 50 **1. Introduction**

51 In numerous regions of the world, the water resource and water pollution issues  
52 have become more severe due to climate change and rising water demand associated  
53 with socioeconomic growth. Over the decades to come, they are destined to worsen  
54 (Jung et al., 2010; Van Dijk, 2024). Compared with surface water, groundwater is  
55 cleaner, less susceptible to external pollution, more widely distributed, and more  
56 consistent, making it an important supplemental source of water for civil, industrial,  
57 and agricultural production. Groundwater supplies up to 40% of irrigation water and  
58 50% of drinking water throughout the world (Gaston et al., 2019; Kuang et al., 2024).  
59 In China, approximately 70% of the population relies on groundwater as their primary  
60 water source (Zhang et al., 2023b), so it is regarded as an important strategic resource.  
61 Additionally, groundwater is essential to the well-being of numerous ecosystems,  
62 including wetlands, lakes, and rivers (Chen et al., 2024). Thus, the issue of  
63 groundwater pollution deserves increasing attention.

64 Rubber additives are a significant group of synthetic organic compounds utilized  
65 as antioxidants, scorch retardants, or binding agents in the manufacturing of  
66 rubber-related products, especially rubber tires (Alhelou et al., 2019; Tian et al., 2020).  
67 With a year-over-year growth of 0.65%, China's output of rubber auxiliaries reached  
68 1.239 million tons in 2020, making up approximately 75% of the world's total  
69 production (China BaoGao, 2021). Furthermore, the quantity of tire wear that is  
70 released into the environment worldwide varies from 0.2 to 5.5 kg·(capita·year)<sup>-1</sup>,  
71 according to Baensch-Baltruschat et al. (2020). The rubber additive emissions into the  
72 environment are a result of the widespread and extensive use of rubber additives in  
73 tires as well as the ubiquitous tire wear particles (Seiwert et al., 2022). Therefore,  
74 aquatic environments that receive runoffs from roadways are increasingly serving as  
75 both the main route for the transport of these tire wear compounds and significant  
76 sinks for rubber additives from dry and wet atmospheric deposition. However, rubber  
77 additives may pose health and environmental risks. A typical example is 6PPD, which  
78 has a median lethal concentration (LC<sub>50</sub>) of 162 µg·L<sup>-1</sup> and 443 µg·L<sup>-1</sup> for larvae of  
79 the China-specific *Gobiocypris rarus* and zebrafish, respectively (Di et al., 2022;

80 Varshney et al., 2022). The utilization of 6PPD as an anti-ozone agent unintentionally  
81 leads to the creation of the more toxic and mobile  
82 *N*-(1,3-Dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine quinone (6PPD-Q, LC<sub>50</sub>=  
83 0.095 µg·L<sup>-1</sup> for coho salmon) oxidation product (Tian et al., 2022), which  
84 significantly increases the environmental risk and toxicity of roadway dry/wet  
85 atmospheric deposition and runoff.

86 To date, most studies on rubber additives and relevant oxidation products (RAROPs)  
87 have focused on the contamination levels in multiple phases, *e.g.* atmospheric  
88 particles, dust, surface water, runoff, snow, drinking water, and wastewater (Cao et al.,  
89 2023; Challis et al., 2021; Dos Santos and Snyder, 2023; Zhang et al., 2023a; Zhang  
90 et al., 2024; Zhang et al., 2022) and the internal exposure amount of RAROPs among  
91 humans (Du et al., 2022; Mao et al., 2024), while less emphasis has been placed on  
92 groundwater. Understanding the contamination status and distribution of groundwater  
93 RAROPs is crucial for determining the fate and behavior of RAROPs in aquatic  
94 environments, because of the possible long-range transport of these pollutants (Zeng  
95 et al., 2023). In practice, there is a need for guidance and reference for groundwater  
96 water safety.

97 The Yellow River, which is renowned for its high siltation rate, is the second  
98 longest river in China, stretching 5464 km from the Tibetan plateau to the Yellow Sea.  
99 Once the Yellow River rushes out of Mangshan Mountain in Zhengzhou and into the  
100 plains, the river channel's slope abruptly decreases and a significant amount of  
101 sediment is deposited, causing the downstream Kaifeng section of the Yellow River to  
102 have a bed that is around 7 to 8 meters above the ground level of the Kaifeng city. The  
103 highest part of the river bed has risen to be more than 10 meters above the ground  
104 level of Kaifeng city, which is located on the south bank of the Yellow River. The  
105 aboveground overhanging river water is also the main source of groundwater recharge  
106 on both sides of the Yellow River, making the region rich in groundwater resources.  
107 Besides, previous research has shown that fish pond leakage is also an important  
108 source of shallow groundwater in the study area (Li, 2020). Furthermore, the  
109 exploitation of groundwater resources has significantly promoted the local economy

110 and improved the living standard of the local people. Therefore, the Kaifeng area is  
111 chosen in this study, for its abundant shallow groundwater resource, high temperature,  
112 relatively good water quality, and high level of groundwater exploitation. The  
113 objectives of our study include (i) to discover the characteristics of 15 RAROPs  
114 contaminants in the groundwater of Kaifeng City, (ii) to provide important guidance  
115 on water safety by evaluating the daily intake of groundwater RAROPs, and (iii) to  
116 provide new insights into the impact of a specific land use type and physicochemical  
117 properties on the transport and fate of RAROPs in groundwater.

## 118 **2. Materials and methods**

### 119 2.1. Sample collection and data collection

120 Kaifeng is located on the alluvial plain of the Yellow River's middle and lower  
121 reaches, with a flat and open terrain. As a result of the city's evolution in Chinese  
122 civilization and long-term natural sedimentation, a silt stratum has gradually formed  
123 with inter bedded polymictic and alluvial soils. As a typical wandering streambed, the  
124 strata are composed of silt, fine sand, sand, and light loam, so they are highly  
125 permeable and of low strength. Kaifeng City has a warm continental semi-arid  
126 monsoon climate, with four distinct seasons, the average value of multi-year  
127 temperature ranges from 13.1°C to 14.5°C, and the long-term annual average  
128 precipitation is about 600 mm. June, July, August, and September are the months with  
129 the highest precipitation. The long-term average relative humidity ranges from 65% to  
130 75%, and the ground levels decrease from northwest to southeast. According to the  
131 Kaifeng Statistical Yearbook 2023 (KBS, 2024), Kaifeng had a population of 4.69  
132 million with a population density of 751 per square kilometer in 2023. In the same  
133 year, the total number of automobiles in Kaifeng reached 830,000, representing an  
134 increase of 4.0% from the end of the previous year.

135 As shown in Fig. 1, the study area starts from the south bank of the Yellow River  
136 and is divided from north to south into the “Near-Yellow River suburban areas”  
137 (North area), urban areas, and the “Far-Yellow River suburban areas” (South area).  
138 According to the sampling depth and classification of aquifers (see the Supplemental

139 Material Table S1 and Table S2 for details), groundwater samples could be classified  
140 into four categories: unconfined aquifers (UA, from 1-3 m below the surface to 13-25  
141 m below the surface), shallow confined water (SCW, from 13-25 m below the surface  
142 to 45-80 m below the surface), medium-to-deep confined water (MCW, from 85-110  
143 m below the surface to 350 m below the surface), deep confined low-temperature  
144 thermal water (DCW, from 350 m below surface to 1300 m below surface). A total of  
145 51 groundwater samples were collected from 6 residential communities and 35  
146 villages in the urban and suburban/rural areas of Kaifeng City from 21st August to 4th  
147 September 2023 (Table S1). To compare groundwater contaminant levels at different  
148 depths, samples were collected at two depths in seven villages in the northern region  
149 and three villages in the southern region.

150 Groundwater samples were collected from community geothermal water systems  
151 in urban areas and civil wells, such as private groundwater wells in rural areas. Before  
152 sampling, well water was pumped for 20 min to obtain stable fresh groundwater. Two  
153 liters of groundwater samples were collected at each site, and stored in polyethylene  
154 bottles, which were pre-rinsed with methanol and ultrapure water. Water samples were  
155 transported to the laboratory at 4 °C. All of the collected water samples were analyzed  
156 within two days after collection.

## 157 2.2. Chemical and reagents

158 Standard solutions (GC grade) of these RAROPs include 6PPD, *N*,  
159 *N'*-bis(1,4-dimethylpentyl)-*p*-phenylenediamine (7PPD),  
160 *N*-(1-methylheptyl)-*N'*-phenyl-*p*-phenylenediamine (8PPD),  
161 *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (CPPD), *N*,  
162 *N'*-bis(2-naphthyl)-*p*-phenylenediamine (DNPD), *N,N*-diphenyl-*p*-phenylenediamine  
163 (DPPD), *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD),  
164 *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine quinone (6PPD-Q),  
165 *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine quinone (IPPD-Q),  
166 4,4'-bis( $\alpha,\alpha$ -dimethylbenzyl) diphenylamine (445), 4-aminodiphenylamine (2N),  
167 4-nitrosodiphenylamine (4-NOH), 2-benzimidazolethiol (MB),

168 poly(1,2-dihydro-2,2,4-trimethylquinoline) (TMQ-3), and  
169 2,4,6-tris[bis(methoxymethyl)amino]-1,3,5-triazine (HMMM). These solutions,  
170 surrogate standard (6PPD-Q-d<sub>5</sub>), and internal standard (Benzophenone-d<sub>10</sub>, BP-d<sub>10</sub>)  
171 were obtained from Tokyo Chemical Industry (Tokyo, Japan), AccuStandard, Inc.  
172 (New Haven, CT, USA), Cato Research Chemicals Inc. (Guangzhou, Guangdong,  
173 China), J&K Scientific (Beijing, China). 6PPD-Q-d<sub>5</sub> and BP-d<sub>10</sub> were regarded as the  
174 internal standard and surrogate standard. Table S3 presents their CAS registry  
175 numbers, molecular formulae, and primary physicochemical characteristics.

176 Other reagents, including sodium chloride (NaCl, analytical grade), methanol  
177 (CH<sub>3</sub>OH, GC grade), and acetonitrile (CH<sub>3</sub>CN, analytical grade) were supplied by  
178 ANPEL Laboratory Technologies (Shanghai) Inc., China.

### 179 2.3. Analysis of groundwater physicochemical parameters

180 The physical parameters of groundwater include: total organic carbon (TOC) and  
181 total nitrogen (TN). The total organic carbon (TOC) and total nitrogen (TN) contents  
182 in groundwater samples were determined using a total organic carbon analyzer  
183 (TOC-L CPH, SHIMADZU, Kyoto, Japan), and TOC was calculated based on the  
184 principle that TOC is equal to the total carbon (TC) amount minus the inorganic  
185 carbon (IC) amount.

### 186 2.4. Sample extraction and instrumental analysis

187 Each 300 mL of groundwater sample was filtered through pre-cleaned 0.7 μm GF  
188 (glass microfiber filter)/F membranes (Hangzhou Special Paper Industry Corp., Ltd.,  
189 Hangzhou, China). Then, filtrates were extracted by high flux automatic solid-phase  
190 extractor (Fotector Plus, RayKol Group Corp., Ltd., Xiamen, China) with Oasis  
191 hydrophilic lipophilic balanced (HLB) solid-phase extraction (SPE) cartridges (500  
192 mg·6 mL<sup>-1</sup>, Waters, Milford, MA, USA), following the procedure described below.

193 Each cartridge was sequentially pre-conditioned with 10 mL of methanol and 10  
194 mL of deionized water. After that, the filtrates were loaded onto the cartridge at a flow  
195 rate of approximately 1.5 mL·min<sup>-1</sup>. The cartridge was then rinsed with 10 mL of  
196 mixed solvent (equal amount of methanol and deionized water by volume) and dried

197 under nitrogen gas for 30 min. After drying, the analytes were eluted from the HLB  
198 cartridge using 15 mL methanol and 10 mL acetonitrile. The elution was finally  
199 evaporated to 0.5 mL, before being diluted to a final amount of 1 mL using deionized  
200 water for analysis using ultra-high-performance liquid chromatography and mass  
201 spectrometry (UHPLC-MS/MS).

202 Seven *p*-phenylenediamine antioxidants (PPDs), *i.e.* 6PPD, 7PPD, 8PPD, CPPD,  
203 DNPD, DPPD, and IPPD, five Non-*p*-phenylenediamine antioxidants (NON-PPDs),  
204 *i.e.* 445, 2N, 4-NOH, MB, and TMQ-3, one binding agent (BA), *i.e.* HMMM, and two  
205 *p*-phenylenediamine quinones (PPD-Qs), *i.e.* 6PPD-Q and IPPD-Q, were analyzed  
206 using an Agilent 1290 Infinity II ultra-high-performance liquid chromatography  
207 equipped with a ZORBAX Eclipse Plus C18 column (Rapid Resolution HD 2.1 × 100  
208 mm, 1.8-Micron) and coupled with an Agilent 6470 triple quadrupole mass  
209 spectrometer (UHPLC-MS/MS, Agilent Technologies Inc., California, USA) with an  
210 injection volume of 2 μL. The mass spectrometer was equipped with an Agilent jet  
211 stream electrospray ionization (AJS ESI) probe in positive ion mode for the  
212 determination of all targets. The mobile phase was made up of (A) methanol and (B)  
213 0.1% formic acid in water, pumped at a rate of 0.3 mL·min<sup>-1</sup> and with the following  
214 gradient variation: 0 min, 50% A; 3 min, 98% A; 8 min, 98% A; 8.1 min, 50% A; and  
215 10 min, 50% A. All the analytes were identified and quantified using the multiple  
216 reaction monitoring (MRM) mode. All MS method details, including  
217 precursor/product ions, retention time, collision energy, fragmentor, detection limits,  
218 and calibration curve linearity, could be found in Table S4 and S5.

## 219 2.5. Quality control /quality assurance (QC/QA)

220 To minimize the background errors for QC/QA, standard addition in blanks and  
221 matrices, sample parallels, method blanks, and field blanks were regularly checked.  
222 For these analytes, satisfactory recoveries ranged from 51.6 to 109%. For every set of  
223 twenty samples, blank samples were evaluated in duplicate for the extraction and  
224 analytical procedures. The duplicate samples had a relative variation of less than 9.8%  
225 on every batch treatment.

## 226 2.6. Land use type (aquaculture pond) characterization

227 To give a general idea of the potential impact of fish pond leakage on the transport  
228 and fate of groundwater RAROPs, the correlation between characteristic of fish ponds  
229 and RAROPs concentration was assessed.

230 The remote sensing image, with a resolution of 2 m, of the Gaofen-1 satellite in  
231 September 2023 is downloaded from the Natural Resources Satellite Remote Sensing  
232 Cloud Service Platform (<http://www.sasclouds.com/chinese/home/>). Images with less  
233 than 10% cloudiness were screened. Preprocessing efforts, such as multi-band  
234 information fusion, mosaicking, geometric rectification, and clipping, were performed  
235 to obtain orthophotos of the study area. Following the establishment of the fish pond  
236 interpretation symbols, the distribution of fish ponds in the study area was obtained  
237 through supervised classification combined with manual visual interpretation. A  
238 random sample of 20% of the interpretation results was then field-verified, and the  
239 accuracy of the interpretation exceeded 90%. Three geospatial buffers (*i.e.*, radii: 500  
240 m, 1000 m, 1500 m) were used to conduct a correlation analysis to assess how the  
241 land use characterization influenced the groundwater RAROPs pollution.

## 242 2.7. Exposure assessment of chronic daily intakes (*CDIs*)

243 To describe the exposure of RAROPs (PPDs, NON-PPDs, BA, and IPPD-Q), the  
244 *CDIs* assessment of RAROPs in groundwater samples was performed following the  
245 models recommended by U.S. Environmental Protection Agency (US EPA) (Liu et al.,  
246 2009). This study emphasized the assessment of *CDIs* for RAROPs in groundwater  
247 through direct ingestion ( $CDI_{ing}$ ), dermal contact ( $CDI_{dem}$ ), and total chronic daily  
248 intake (*TCDI*) (equations are given in SI).

## 249 **3. Results and discussion**

### 250 3.1. RAROPs in the groundwater of the Kaifeng area

251 Spatial distributions and descriptive statistics for the concentrations of RAROPs  
252 in groundwater samples are shown in Fig. 2 and Table S7. For the study area, 8 of the  
253 15 analytes were not detected (ND) (7PPD, 8PPD, DNPD, DPPD, 445, 2N, 4-NOH,  
254 and MB), and 4 were detected in no more than 10% of the samples (CPPD, IPPD,

255 IPPD-Q, and TMQ-3), with the range of 6%-10%. In over 10% of groundwater  
256 samples, 3 targets were found, with 6PPD identified as the most dominant congener,  
257 with the highest detection frequency of 55%, followed by its relevant oxidation  
258 products, 6PPD-Q (16%) and binding agent HMMM (12%). For PPDs antioxidants,  
259 the concentrations of 6PPD (Avg: 4.05 ng·L<sup>-1</sup>, range: ND - 43.0 ng·L<sup>-1</sup>) followed by  
260 IPPD (Avg: 0.20 ng·L<sup>-1</sup>, range: ND - 3.86 ng·L<sup>-1</sup>) and CPPD (Avg: 0.17 ng·L<sup>-1</sup>, range:  
261 ND - 4.45 ng·L<sup>-1</sup>) were among the highest, while binding agent HMMM ranged from  
262 ND to 11.0 ng·L<sup>-1</sup>. When compared with BA, PPD-Qs, and NON-PPDs, the  
263 concentrations of PPDs were nearly an order of magnitude greater (Table S7).

264 There is a horizontal reduction in the concentration of RAROPs in shallow  
265 groundwater (Fig. 2 and Table S8) from north to south. Approximately 1.7 times as  
266 much  $\sum$ RAROPs (Avg: 8.49 ng·L<sup>-1</sup>) was found in shallow groundwater (UA and  
267 SCW) in the northern region as in the southern region (Avg: 5.01 ng·L<sup>-1</sup>). In terms of  
268 depth,  $\sum$ RAROPs in different aquifers showed a clear decreasing trend from shallow  
269 to deep groundwater (MCW and DCW, average 4.41 ng·L<sup>-1</sup> in the northern region and  
270 1.40 ng·L<sup>-1</sup> in the southern region) (Table S8), with the lowest RAROPs (Avg: 0.26  
271 ng·L<sup>-1</sup>) seen in the urban areas due to the centrally mined deep geothermal water wells.  
272 At the same sampling sites (Fig. S1), the concentrations of RAROPs in shallow  
273 groundwater were much higher than those in deep groundwater.

274 There have been a few reports on the RAROPs concentrations in groundwater.  
275 Table S9 reviews contents of 6PPD, IPPD, and 6PPD-Q detected in various water  
276 samples in China (Zhang et al., 2023a) and elsewhere (Challis et al., 2021;  
277 Johannessen et al., 2021a; Johannessen et al., 2021b; Monaghan et al., 2021; Seiwert  
278 et al., 2022; Tian et al., 2020). The concentrations of 6PPD in groundwater were  
279 higher in Kaifeng (ND-43.0 ng·L<sup>-1</sup>, Avg: 4.05 ng·L<sup>-1</sup>) than in the surface/groundwater  
280 of Guangzhou, China (Liuxi River, China) and the surface water during storm events  
281 in Don River and Highland Creek, Canada, but were evidently lower than the  
282 concentrations of the runoff in Saskatoon (Canadian, 86 - 1400 ng·L<sup>-1</sup>) and of the  
283 wastewater treatment plants water in City of Leipzig (Germany, ND - 105 ng·L<sup>-1</sup>).  
284 The individual IPPD contents were ND - 3.86 ng·L<sup>-1</sup> (Avg: 0.20 ng·L<sup>-1</sup>), which were

285 comparable to the surface water of Liuxi River, China (ND - 2.14 ng·L<sup>-1</sup>), but were  
286 lower than the groundwater in Liuxi River area, China (ND - 25.7 ng·L<sup>-1</sup>). The  
287 content of 6PPD-Q in the groundwater in Kaifeng was slightly higher than that of  
288 groundwater in the Liuxi River region, China, was comparable to that of surface water  
289 in the Liuxi River region, China, and was much lower than those in various waters  
290 reported elsewhere.

291 Compared with the general pollutants in groundwater reported in previous research,  
292 the pollutant levels of RAROPs were higher than those of polybrominated diphenyl  
293 ethers (a few to dozens of ng·L<sup>-1</sup>) (Levison et al., 2012; Trinh et al., 2019), and were  
294 comparable to those of short-chain chlorinated paraffins and perfluoroalkyl  
295 substances (several dozens of ng·L<sup>-1</sup>) (Harrad et al., 2020; Wu et al., 2021), but lower  
296 than those of polycyclic aromatic hydrocarbons (hundreds of ng·L<sup>-1</sup>) (Qiao et al.,  
297 2021; Wu et al., 2016), antibiotics (dozens to thousands of ng·L<sup>-1</sup>) (Chen et al., 2018a;  
298 Liu et al., 2024), and heavy metals (up to tens of thousands of ng·L<sup>-1</sup>) (Sarath et al.,  
299 2023; Sheng et al., 2022).

300 The yearly worldwide consumption amounts of rubber additives (vulcanizing agent,  
301 antioxidant, scorching resistant agent, accelerator, activator, light stabilizer, filler, and  
302 anti-mold agent, etc.) are around 1500,000 tons and 40% of them are antioxidants  
303 (about 600,000 tons). This makes antioxidants the most consumed type of rubber  
304 additive around the globe, with PPDs (representative products: 6PPD) making up  
305 56-60% of the total. The Organization for Economic Co-operation and Development  
306 (OECD) has classified 6PPD, the most widely used tire antioxidant among PPDs, as a  
307 high production volume (HPV) chemical (OECD, 2022). Wang et al. (2022) and Cao  
308 et al. (2022) reported that 6PPD was the most abundant congener of RAROPs in  
309 water, fine air particles, and soil. This is approximately in line with the RAROPs  
310 composition pattern seen in this research, where 6PPD turns out to be the most  
311 dominant congener of groundwater in the study area, accounting for approximately 82%  
312 of PPDs and 65% of RAROPs.

313 Compared with its precursor chemicals, 6PPD-Q, a significant hazardous oxidation  
314 product of 6PPD, is more chemically persistent and stable in the environment

315 (Klößner et al., 2021). Thus, linear regressions between log-transformed  
316 concentrations of 6PPD (dominant component among RAROPs) and 6PPD-Q were  
317 performed to delve into the form of occurrence for the 6PPD-Q. As shown in Fig. S2,  
318 no convergence was observed in groundwater samples ( $p > 0.05$ ). A similar result was  
319 observed in deep-sea sediments (Zeng et al., 2023). Moreover, it is also reported that,  
320 with the inducement of sunlight, 6PPD-Q could be transformed from 6PPD in aquatic  
321 environments and no degradation of 6PPD was detected under dark conditions (Zhou  
322 et al., 2023). This partially explained the relatively low detection frequency and  
323 content of PPD-Qs in groundwater samples (dark and reducing environments) in this  
324 study. Since there is currently insufficient proof of 6PPD and 6PPD-Q transition  
325 (oxidation or degradation) in groundwater environments, more studies based on field  
326 measurements are required to validate this occurrence.

327 With the rapid urbanization over the past decades, most of the natural rivers in the  
328 study area have been channelized, thus, pollutants in groundwater come primarily  
329 from leaching of contaminants through the surface soil and from input of recharge  
330 water. Given that there are no managed artificial recharges of partially treated  
331 wastewater or surface water, RAROPs that diffuse into surface soils through dry and  
332 wet atmospheric deposition could migrate from the soil surface to deeper soils and  
333 ultimately to groundwater as a result of leaching effects. This results in higher levels  
334 of RAROPs in shallow groundwater than in deeper groundwater.

335 The northern region of the study area is traversed by the Lianyungang-Horgos  
336 Expressway (G30 National Highway), which connects eastern, central, and western  
337 China. The Kaifeng section of the Lianyungang-Horgos Expressway is one of the  
338 busiest expressways in Henan Province (CRC, 2023). Large amounts of RAROPs  
339 could be introduced into the roadside environment, especially in soil, along with tire  
340 wear particles. Furthermore, Li (2020) found that shallow groundwater in the study  
341 area could also be supplied by the manmade fish pond leakage. This partly explains  
342 why groundwater RAROP levels are higher in the northern region, where more fish  
343 ponds are constructed than in the southern region, as the northern area is relatively  
344 rich in water resources due to its proximity to the Yellow River. It is common for

345 villagers to divert water from the Yellow River for farming edible and ornamental fish.  
346 This will be further discussed in Section 3.2.

347 Besides, Ge et al. (2024) concluded that there were 6-16 times higher rubber  
348 additives in the dust from car repair plants than those from other places. Their  
349 findings are consistent with our results that relatively high concentrations of RAROPs  
350 ( $40.8 \text{ ng}\cdot\text{L}^{-1}$  and  $45.0 \text{ ng}\cdot\text{L}^{-1}$ ) were measured in groundwater in the vicinity of the car  
351 repair shop (S3-2) and car parks (N5S). This may be attributed to the leaching of  
352 RAROPs-containing material from the waste tire storage pits at these locations.

### 353 3.2. Factors controlling pollution patterns in groundwater RAROPs

354 Table S10 displays the Spearman's correlations between RAROPs pollutants and  
355 TOC and TN. Throughout the research region, no significant relationships were  
356 observed between the contents of RAROPs and TOC ( $r = -0.14$ ,  $p = 0.32$ ) or TN ( $r =$   
357  $-0.23$ ,  $p = 0.10$ ), indicating that the presence of nutrient elements TN did not  
358 significantly enhance the accumulation of highly toxic RAROPs. Previous studies  
359 indicated that TOC has essential implications in controlling the fate and behaviors of  
360 PAHs in soils and sediments (Chen et al., 2018b; Wang et al., 2014). Nevertheless, the  
361 amount of RAROPs in the groundwater of the study area was not primarily  
362 determined by TOC. This supports the earlier research (Zeng et al., 2023) that found  
363 no correlation between TOC and the contents of sediment PPDs. As a result, one  
364 potential mechanism impacting RAROPs distribution could be the transformation of  
365 RAROPs in natural environmental conditions.

366 To corroborate the relationships between the specific land use type (fish pond) and  
367 groundwater RAROPs contents, circular buffer zones with radii ranging from 500 m  
368 to 1500 m were drawn centered at each sampling site, and the number of fish ponds  
369 within each buffer zone were counted and measured (Table S11). Then, Spearman's  
370 correlation coefficients were calculated (Fig. 3). RAROPs were positively correlated  
371 with the number of fish ponds within a 500 m radius buffer area (R500NO.) ( $r = 0.44$ ,  
372  $p = 0.005$ ). The results of correlation analysis indicated that the number of fish ponds  
373 may, to a certain extent, influence the groundwater RAROPs pollution if they were

374 located within 500 m (radii for which  $r$ -values were greater). Besides, Gaston et  
375 al.(2019) concluded that contaminants in groundwater could be leached through  
376 subsoils, and high water content of the fish pond area may have contributed to this.  
377 Thus, ponds may be a potential pathway for shallow groundwater contamination.

### 378 3.3. Exposure assessment (Chronic daily intakes, $CDIs$ )

379 For the local populations, including adults and children, the chronic daily intakes  
380 ( $CDI_{ing}$ ,  $CDI_{derm}$ , and  $TCDI$ ) of all RAROPs (PPDs, PPD-Qs, NON-PPDs, and BA)  
381 via two paths of exposure were calculated using Eqs. S1-4 (Fig. 4). The results of the  
382  $CDIs$  assessments were consistent with the distribution pattern of RAROP pollutants  
383 in groundwater samples, which was roughly in the following order: North area  
384 ( $1.01 \times 10^{-1} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ) > South area ( $6.24 \times 10^{-2} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ) > Urban areas ( $3.53 \times 10^{-3}$   
385  $\text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ). More PPDs ( $2.96 \times 10^{-3}$  -  $7.82 \times 10^{-2} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ , avg:  $4.70 \times 10^{-2} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ )  
386 were exposed to the residents in the study area than PPD-Qs ( $0.00$  -  $4.01 \times 10^{-3}$   
387  $\text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ , avg:  $1.95 \times 10^{-3} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ), NON-PPDs ( $0.00$  -  $6.48 \times 10^{-3} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ , avg:  
388  $2.17 \times 10^{-3} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ), and BA ( $5.68 \times 10^{-4}$  -  $1.20 \times 10^{-2} \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ , avg:  $4.41 \times 10^{-3}$   
389  $\text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ). In addition, for the individual RAROPs,  $CDI_{6PPD}$  contributed 65.1% of  
390 the  $TCDI$  values, followed by  $CDI_{HMMM}$  (11.4%) and  $CDI_{IPPD}$  (9.2%). Moreover, of  
391 the two exposure pathways, chronic daily intake caused by ingestion ( $CDI_{ing}$ ) was  
392 almost equal to the  $TCDI$  (avg: 98.9%), and the  $CDI_{ing}$  ( $10^{-3}$ -  $10^{-2}$  level) was about two  
393 orders of magnitude higher than the  $CDIs$  via skin intake ( $CDI_{derm}$ ,  $10^{-5}$  -  $10^{-3}$  level)  
394 (Fig. 5).

395 A thorough comprehension of the exposure dose of RAROPs to the general  
396 population was obtained by comparing the daily excretion ( $DE$ ) and chronic daily  
397 intake of PPDs in human urine. In a previous study conducted in 2019 in eastern  
398 China, the  $DE$  of the population was  $87.2 \text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$  (Mao et al., 2024), while the  
399 average  $CDI$  attributed to PPDs in groundwater in the study area was  $4.70 \times 10^{-2}$   
400  $\text{ ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ , which was 0.05% of the population's  $DE$ . Therefore, ingestion of  
401 groundwater may not be the primary route of chronic daily intake for the population,  
402 and more attention should be paid to chronic intake associated with exposure to

403 RAROPs in other media (*e.g.*, atmospheric particles, dust, or food) in daily life.

404 The Monte Carlo simulation was operated 10,000 times to reveal the cumulative  
405 probability distributions of the computed TCDI for each group of the population at  
406 different sites (Table S12). Different chronic daily intake characteristics were revealed  
407 by subgroup analysis, and *TCDI* values showed a decreasing trend: girl (50<sup>th</sup>:  
408  $3.71 \times 10^{-2} \text{ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ) > boy (50<sup>th</sup>:  $3.30 \times 10^{-2} \text{ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ) > male adult (50<sup>th</sup>:  
409  $3.27 \times 10^{-2} \text{ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ) > female adult (50<sup>th</sup>:  $3.00 \times 10^{-2} \text{ng} \cdot (\text{kg} \cdot \text{d})^{-1}$ ). For an adult, local  
410 resident with an average bodyweight of 38.0 kg (boy), 34.9 kg (girl), 66.6 kg (male),  
411 and 57.9 kg (female) (Wang and Duan, 2016; Zhao and Duan, 2016a; Zhao and Duan,  
412 2016b; Duan et al., 2013), the daily RAROPs intakes were 1.25, 2.18, 1.29, and 1.74  
413  $\text{ng} \cdot \text{d}^{-1}$  in CTE (50<sup>th</sup>) scenario and 183, 318, 190, and 254  $\text{ng} \cdot \text{d}^{-1}$  in reasonable  
414 maximum exposure (RME, 90<sup>th</sup>) scenarios, respectively.

415 In the study area, the chronic daily intake values of RAROPs in groundwater were  
416 greater than the *CDI* values of PAHs *via* groundwater that have been reported  
417 (Ambade et al., 2021). Given the relatively minimal  $\text{LC}_{50}$  of some RAROPs, such as  
418 6PPD-Q ( $0.79 \mu\text{g} \cdot \text{L}^{-1}$  for 6PPD-Q and tens to thousands of  $\mu\text{g} \cdot \text{L}^{-1}$  for individual PAH  
419 compounds), ingestion of groundwater in the study area poses potential health risks to  
420 the local population. Unfortunately, a risk assessment for human health was not  
421 possible in this study due to the lack of parameters for the corresponding slope factor  
422 (*SF*) or carcinogenic reference dose (*RfD*). Thus, risk thresholds should be conducted  
423 in future studies, developing a thorough understanding of the health risk generated by  
424 water RAROPs pollution.

425 There are growing studies reporting the race, gender, or social status-specific  
426 differences in pollution exposure, despite some controversy over their exact biological  
427 roles (Cheeseman, 2020; Pan et al., 2023; Zanobetti and Schwartz, 2000). The study  
428 area includes both urban, suburban, and rural areas. There is a difference in income  
429 between urban and rural areas, with a per capita disposable income of 31,868 RMB  
430 for urban residents and a per capita rural net income of 15,370 RMB for rural  
431 residents (KBS, 2022). There are also differences in groundwater abstraction policies  
432 between urban and rural areas, with rural abstractions less regulated. Differences in

433 policies and incomes lead to differences in living conditions. Rural residents primarily  
434 dig shallow wells in their own homes (mainly unconfined aquifers, shallow confined  
435 water, and medium-to-deep confined water), which contain significant amounts of  
436 contaminants, and they consume more groundwater in their everyday lives to save  
437 money. In urban residential areas, geothermal water is obtained from deep wells that  
438 are centrally dug (*i.e.*, deep confined water). The geothermal water that is used for  
439 daily drinking and bathing contains minimal pollution. In addition, a growing number  
440 of Chinese people are now inclined to drink filtered tap water (*i.e.*, tap water that is  
441 purified on-site through a multi-stage filter installed in a drinking fountain) and  
442 bottled/barreled water (Ben et al., 2020; Chen et al., 2023). The imbalance between  
443 urban and rural development has led to a significant disparity (nearly 30 times) in the  
444 population's intake of RAROPs pollutants induced through groundwater.

445 Moreover, previous studies indicated that children are the sensitive group to  
446 environmental pollution (*i.e.*, heavy metals, PAHs, and disinfection by-products  
447 (DBPs) in drinking water, food, suspended particles, dust, and soil) (Chen et al.,  
448 2018b; Du et al., 2021; Jiang et al., 2020; Xia et al., 2010; Zheng et al., 2010).  
449 Furthermore, Chen et al. (2023) reported that throughout childhood, females were  
450 more vulnerable to the harmful effects of DBPs in tap water than males, but as they  
451 grew older, the risk decreased. Their conclusions supported our findings, which  
452 indicated that there was a declining tendency for the *CDI* values among the following  
453 subgroups: girl > boy > male adult > female adult. The chronic daily intakes of  
454 groundwater RAROPs for children are higher than that of adults for both genders.  
455 Consequently, both water intake rates per kilogram of body weight and individual  
456 weight may have a major impact on the chronic daily intake characteristic among  
457 subgroups. As a result, children's (especially girls') potential health risks from  
458 groundwater RAROPs exposure require more attention.

459 The exposure assessment in this study was still subject to some limitations and  
460 uncertainties. Chinese people are used to drinking boiled water for health reasons. It's  
461 been reported that drinking raw water carries a comparatively larger health risk than  
462 drinking boiled water (Wang et al., 2007). Besides, as mentioned above, Chinese

463 people are shifting to drinking filtered tap water and bottled/barreled water. The level  
464 of exposure to RAROPs may vary depending on the type of drinking water consumed.  
465 Therefore, there may be a certain degree of uncertainty in the assessment results.  
466 Based on the above, a quantitative sensitivity analysis was performed to assess the  
467 degree of variability and uncertainty associated with the exposure pathways of the  
468 groundwater RAROPs that had the greatest impact on the estimations of chronic daily  
469 intake. The percentile contribution to variance represents the results of the sensitivity  
470 analysis for the  $CDI_{ing}$  and  $CDI_{derm}$  (Fig. S3). The contents of RAROPs in  
471 groundwater ( $C_w$ ) and body weight ( $BW$ ) were the two most significant variables,  
472 contributing the most to the total variance of  $CDI_{ing}$  for both genders in the direct  
473 ingestion pathway. In contrast to the ingestion rate ( $IR$ ), which contributed just 6% on  
474 average, the average contributions of  $C_w$  and  $IR$  were approximately 99% and -8%,  
475 respectively. In terms of the dermal absorption pathway,  $C_w$  and  $BW$  were the two  
476 most significant variables that made the greatest contribution to the total variance of  
477  $CDI_{derm}$  for both genders. The average contributions from the exposed skin area ( $SA$ )  
478 were just 3%, whereas the average contributions from the  $C_w$  and  $BW$  were  
479 approximately 99% and -6%, respectively. According to the sensitivity results, the  
480 accuracy of the exposure assessment could be increased by improving the accuracy of  
481  $C_w$  and  $BW$ , particularly the accuracy of  $C_w$ , so it is crucial to collect precise data on  
482 the concentration of groundwater RAROPs.

#### 483 **4. Conclusion**

484 For the first time, a comprehensive study about the presence of hazardous  
485 RAROPs in groundwater was conducted across a major city adjacent to the Yellow  
486 River, where the riverbed is above the surrounding ground elevations. In line with the  
487 current practice of the production and utilization of rubber additives, 6PPD is the  
488 predominant contaminant detected in regional groundwater. Human activities,  
489 including transportation and waste tire storage, water resource allocation and  
490 utilization patterns may exacerbate RAROPs pollution in groundwater. A particularly  
491 important mechanism is the diversion of the Yellow River water to create aquaculture

492 ponds, which encourages the leaching of contaminants through surface soil. Therefore,  
493 the area near the Yellow River shows the highest levels of RAROPs, and the  
494 concentration of RAROPs is higher in the shallow groundwater than in the deep  
495 groundwater. In the study area, the population's intake of RAROPs due to  
496 groundwater pollution demonstrates a 30-fold difference as a result of the imbalanced  
497 development between urban and rural areas. Children are the most vulnerable  
498 population to RAROPs exposure. Our study extends the existing research on RAROPs  
499 pollution by characterizing their fate and transport in groundwater. However, there is  
500 a lack of comprehensive research on the general health risks attributed to RAROPs  
501 residue exposure. More research is required to better understand the population's  
502 exposure to these unregulated RAROPs and their carcinogenic and non-carcinogenic  
503 health risks.

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## Figure captions

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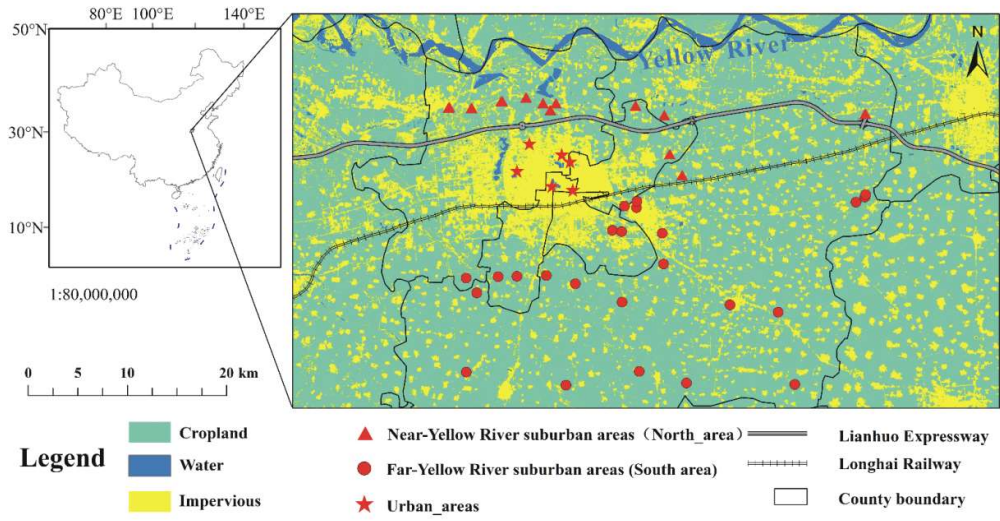
**Fig. 1.** Schematic map of the study area and locations of the sampling sites in Kaifeng, China.

**Fig. 2.** Box plots showing the concentrations of RAROPs in groundwater from all sampling locations (NASG: north area shallow groundwater, NADG: north area deep groundwater, SASG: south area shallow groundwater, SADG: south area deep groundwater, UAG: urban area groundwater).

**Fig. 3.** Spearman's correlations of RAROPs concentration to the number of fish ponds within a 500-meter (R500NO.), 1000-meter (R1000NO.), and 1500-meter (R1500NO.) buffer radius areas.

**Fig. 4.** Chronic daily intakes (CDIs) of local residents exposed to RAROPs from groundwater in the study area (A: North area; B: Urban area; C: South area).

**Fig. 5.** Relative contribution of individual RAROPs and exposure pathways to TCDI values for local residents



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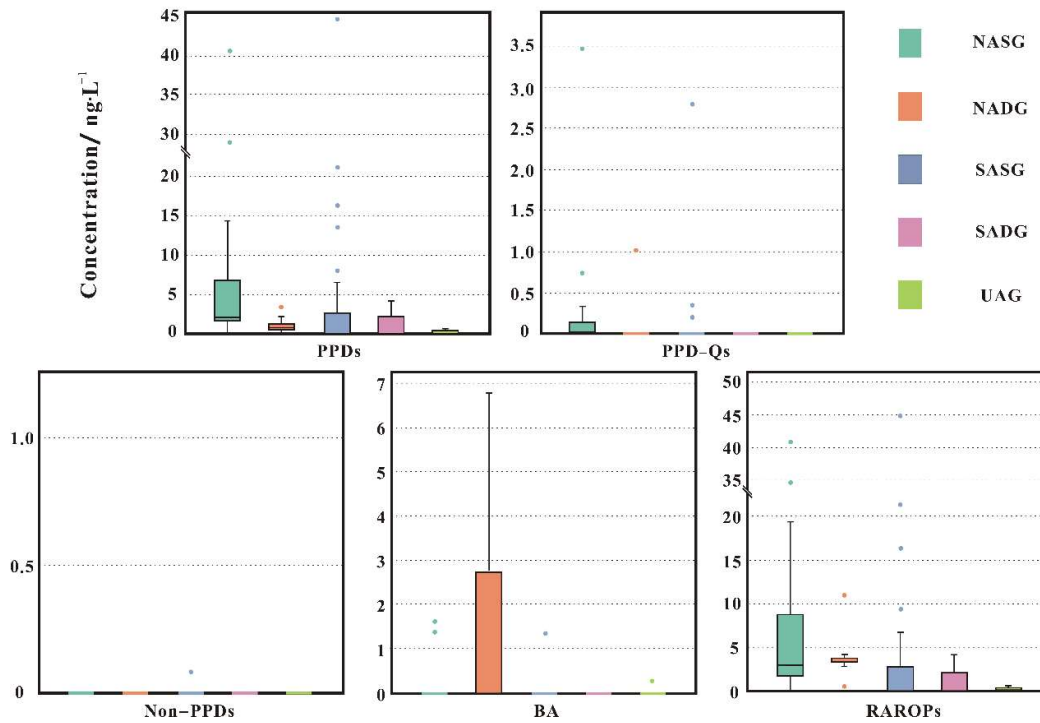
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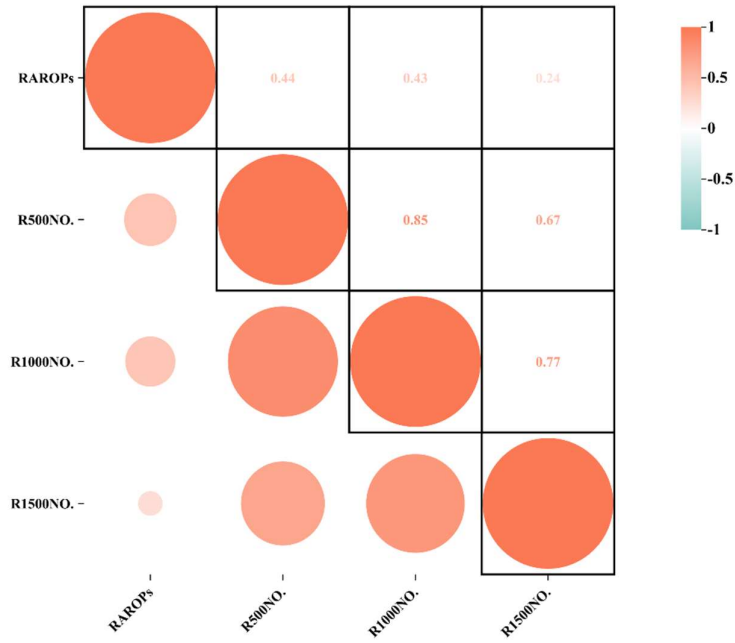
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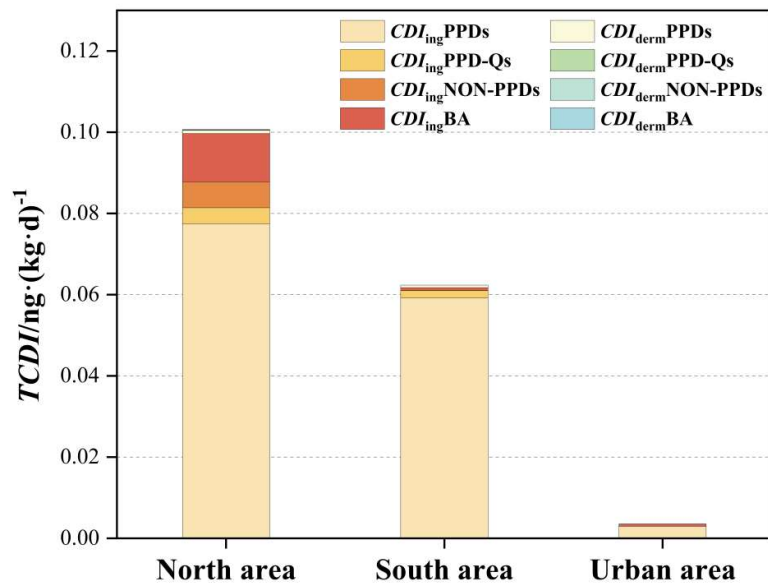


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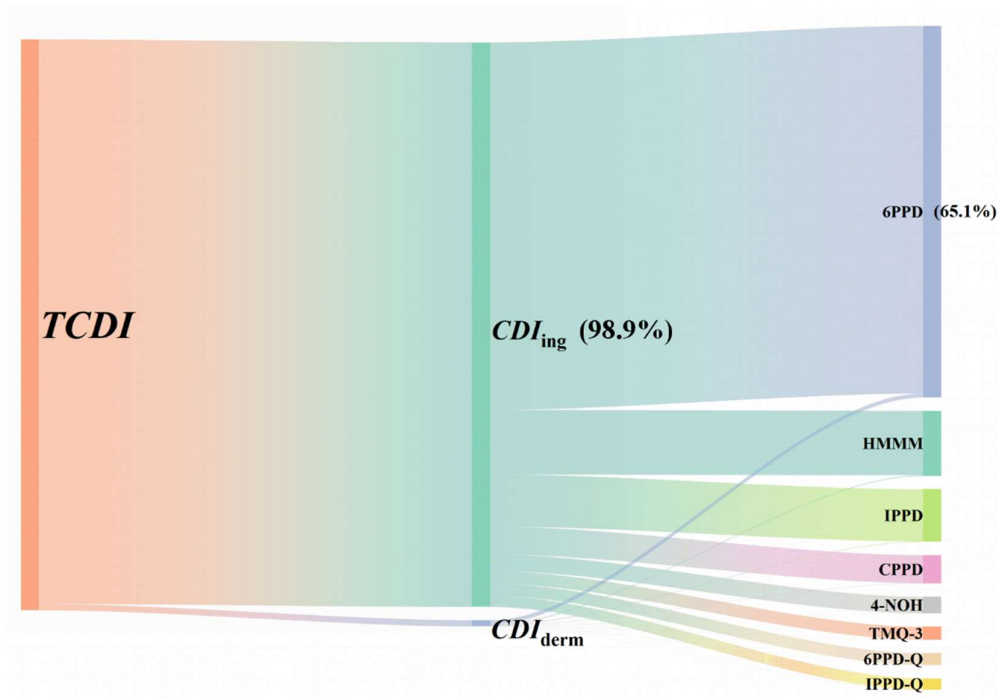


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