Supporting Information

Urban-Rural Inequality in Microplastic Exposure Exacerbates Health Risks for Rural Residents in Northern China

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Supplementary Text 1-3

Supplementary Table 1-4

Text S1: MP and Plasticizer in $PM_{2.5}$ analysis

MP analysis: Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) was used to analyze common MPs in each sample. As shown in Table S1, these MPs included polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC), as well as natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber originating from tire wear. A clean set of blunt-tipped tweezers was used to fold a filter membrane sample measuring 0.5 cm^2 by using ferromagnetic graphite foil (F670; Japan Analytical Industry, Tokyo, Japan). This foil was then placed in a Curie point pyrolyzer (model JHS-3; Japan Analytical Industry) coupled with a gas chromatography mass spectrometry system (7890GC/5975MS; Agilent Technologies, Santa Clara, CA, USA) and rapidly heated to 670°C within 5 s. The interface between the Curie point and the gas chromatograph inlet was set to 300°C. Thermolyzed compounds were separated using a DB-5ms capillary column (30 m × 0.25 mm × 1 μm; J&W Scientific, Santa Clara, CA, USA). The temperature of the gas chromatograph column oven was initially set to 50°C for 5 min and then increased at a rate of 25°C min^{-1} to 300°C and finally held at 310°C for 10 min. The carrier gas was selected as ultrahigh-purity helium (99.999%). The mass spectrometer detector was set to full scan mode from 30 to 500 amu, operating in electron ionization mode at a voltage of 70 eV and an ion source temperature of 230°C. Peaks were identified on the basis of the known fragments, mass spectra, and retention times of the target compounds. Calibration curves were established using the reference standards of unique pyrolysis compounds (Table S1). While processing each sample, operators wearing cotton laboratory coats and nitrile gloves worked on an aluminum-foil-covered clean bench in a sealed room, and no plastic items were used throughout the experiment to avoid background contamination.

PAE analysis: PAEs were quantified using thermal desorption gas chromatography mass spectrometry. After a filter membrane measuring 1.0–1.5 cm^2 was cut into small pieces, [$^2H_{10}$] phenanthrene and [$^2H_{12}$] and [$^2H_{50}$] *n*-tetradecane prepared by combining benzene and isopropanol at a ratio of 1:1 were added as internal standards to a thermal desorption sample tube. This sample tube was then loaded into

the 7890GC inlet of the gas chromatography mass spectrometry system. Next, the temperature was increased from 50°C to 275°C, and the sample was desorbed in splitless mode. Simultaneously, the gas chromatograph column was maintained at 30°C to focus the desorbed target pollutants on the column head, followed by separation using a DB-5ms capillary column (30 m × 0.25 mm × 0.25 μm) in high-purity helium (99.999%) as the carrier gas (1.0 cm^3 min^{-1}) through temperature programming. Finally, 5975MS was used in full scan mode from 50 to 550 amu, operating in electron ionization mode at a voltage of 70 eV and an ion source temperature of 230°C. Both qualitative and quantitative analyses were conducted by comparing the characteristic ions and retention times of the chromatographic peaks with those of standard substances. Table S2 lists the PAEs detected.

BTs analysis: Briefly, a sample measuring 2 cm^2 was obtained from each filter membrane to identify BTs. After benzothiazole-d_4 was added as an internal standard, the sample was cut and transferred to a test tube containing 10 mL of ultrapure deionized water (18M-OHM) and methanol (high-performance liquid chromatography [HPLC] grade) at a ratio of 5:3 (v/v). Next, the sample was extracted in an ultrasonic water bath at room temperature for 60 min, and the combined extract was concentrated and diluted with ultrapure deionized water containing 0.2% (v/v) formic acid (pH 2.5). Subsequently, the diluted solution was purified using an Oasis HLB vacuum chromatography column (3 mL, 60 mg per column, particle size: 30 μm; Waters, Milford, MA, USA). After the target analytes were eluted with 5 mL of methanol, the eluent was evaporated to 1 mL under a gentle nitrogen stream for analysis. Next, the target analytes were separated using ultrahigh-performance liquid chromatography (ACQUITY; Waters), and qualitative and quantitative analyses were conducted using a triple-quadrupole mass spectrometer (Xevo TQ-S; Waters). The BEH Shield RP18 column (100 mm × 3 mm × 1.7 μm) of the ACQUITY chromatograph was connected in series to a Vanguard column (BEH C18, 5 mm × 2.1 mm × 1.7 μm). The mobile phase for HPLC consisted of 100% methanol (A) and ultrapure deionized water acidified with 0.1% (v/v) formic acid (B), with a flow rate of 450 mL min^{-1}. Separation was performed using a gradient elution program. A tandem mass spectrometry system

was operated in positive ion multiple reaction monitoring mode. Identification was performed by comparing the characteristic ions and retention times of the chromatographic peaks with those of standard substances. Table S2 lists the detected BTs.

BPA analysis: BPA is a key monomer used in the synthesis of epoxy resins and polycarbonate plastics. In this study, HPLC-based fluorescence detection was used to quantitatively measure BPA in different filter membrane samples [错误!未找到引用源。]. Briefly, one-quarter of a quartz filter membrane sample was cut into pieces and placed in a 20 mL screw-capped colorimetric tube. Next, 4 mL of 0.1% hydrochloric acid and methanol was added to fully immerse the sample for 2 h, followed by ultrasonic extraction at 50°C for 30 min. After the extracted solution was transferred, 6 mL of 0.1% hydrochloric acid and methanol was added to the colorimetric tube for repeat extraction. Subsequently, the extracted solutions obtained from the two extraction steps were mixed and filtered through a 0.45 μm filter membrane. These solutions were then separated using a PerkinElmer Brownlee HRes Biphenyl chromatographic column (50 mm × 2.1 mm × 1.9 μm; PerkinElmer, Waltham, MA, USA). An isocratic elution program was initiated at a water-to-acetonitrile volume ratio of 6:4 and a flow rate of 0.5 mL min^{-1} for 4 min. Finally, the target analytes were quantified using a fluorescence detector with excitation and emission wavelengths of 275 and 313 nm, respectively. All solvents and diluents used in this method were of HPLC grade.

All analyses of MPs and plasticizers were subjected to duplicate testing every five samples to ensure data reliability, with a duplicate testing deviation of ≤5%. Table S2 presents the minimum detection limits for the target analytes.

Text S2: Reliability of the PMF Method

A comprehensive set of diagnostic metrics was employed to assess the stability and uncertainty of the obtained PMF solution. This included evaluating element collinearity prior to modeling, examining Q-values and residual distributions to determine the optimal number of factors and assess model fit, and analyzing signal-to-noise ratios to ensure data quality. Additionally, the coefficient of determination (R^2) was used to quantify the goodness-of-fit between measured and predicted values. We initially explored 3-5 factors in this study. The 3-factor model did not meet the criterion that the ratio of Q(Robust) to Q(True) should be closer to 1 for higher fitting degree, and the Bootstrap analysis result for the 5-factor model was far below 80%. After comprehensively considering the reliability of the model, only 4 factors proved to be the most suitable. The source apportionment results were validated through Bootstrap analysis, with detailed findings presented in Supplementary Information Table S4.

Text S3: Calculation of Non-Carcinogenic Risks and Carcinogenic Risks

To evaluate the risks posed by MPs and plasticizers to human health, the average daily dose (ADD) of personal inhalation exposure was calculated using the first health risk assessment model established by the United States Environmental Protection Agency (EPA, 1989). For certain substances, personal exposure concentration (EC) was calculated using the second model:

$$ADD = \frac{C \times IR \times EF \times ED \times ET}{AT \times BW} \quad (1)$$

$$EC = \frac{C \times EF \times ED \times ET}{AT} \quad (2)$$

where ADD is the average daily exposure dose (mg kg^{-1} d^{-1}); EC is the personal exposure concentration (μg m^{-3}); *C* is the concentration of MPs and plasticizers in $PM_{2.5}$ (mg m^{-3}), obtained from sampling data; IR is the inhalation rate (20 m^3 d^{-1}); EF is the frequency of exposure, assumed to be 350 d a^{-1}; ED is the period of exposure, obtained from the average age of the sampled population of 58 years; ET is the exposure time, measured as 20.5 h d^{-1} for indoor environments and 3.5 h d^{-1} for outdoor environments; and AT is the average time, measured as ED × 365 d y^{-1} for noncarcinogens and 70 y × 365 d y^{-1} for carcinogens.

The hazard quotient (HQ) is a ratio used to describe noncarcinogenic risk and determine whether a specific risk is significant. It is calculated as the ratio of the ADD to the reference dose (RfD, mg kg^{-1} d^{-1}). The hazard index (HI) is the sum of the HQ values for various chemicals. An HQ of ≤1 or an HI of ≤1 indicates that the level of exposure has not exceeded the threshold for adverse effects and that the noncarcinogenic risk is low. By contrast, an HQ of >1 or an HI of >1 indicates that the level of exposure has exceeded the threshold for adverse effects and that the noncarcinogenic risk is high, warranting attention.

The incremental lifetime cancer risk (ILCR) is calculated as the product of the ADD for a specific substance and the slope factor (SF, kg d mg^{-1}) or as the product of the EC and the inhalation unit risk (IUR, m^3 μg^{-1}). According to the EPA (1989), an ILCR value less than 1×10^{-6} is considered acceptable, an ILCR value between 1.0×10^{-6} and 1.0×10^{-4} indicates potential harm to human health and a certain carcinogenic

risk that warrants attention, and an ILCR value above 1×10^{-4} indicates a high carcinogenic risk that necessitates immediate attention.

Table S1 List of pyrolyzed products and selection of quantified markers for MPs analysis.

Polymer	Abbreviation	Pyrolysis Product	Potential Qualification Marker
Polyethylene	PE	C20 alkane C20 α-alkane C20 α,ω-alkane	C20 alkane C20 α-alkane C20 α,ω-alkane
Polypropylene	PP	2,4-dimethylhept-1-ene 2,4,6,8-tetramethyl-1-undecene	2,4-dimethylhept-1-ene 2,4,6,8-tetramethyl-1-undecene
Polystyrene	PS	3-butene-1,3-diydibenzene 5-hexane-1,3,5-trytribenzene	3-butene-1,3-diydibenzene 5-hexane-1,3,5-trytribenzene
Polyvinyl Chloride	PVC	1-chloroindan dihydronaphthaleneazelene	1-chloroindan dihydronaphthaleneazelene
Natural Rubber	NR	1-methyl-4-(1-methylethenyl)-cyclohexane dipentene	1-methyl-4-(1-methylethenyl)-cyclohexane dipentene
Butadiene Rubber	BR	4-vinylcyclohexene (dimer)	4-vinylcyclohexane*
Styrene-Butadiene Rubber	SBR	4-vinylcyclohexene	4-vinylcyclohexane*

*4-vinylcyclohexane is selected for the marker, and only a sum of BR and SBR are reported.

155 **Table S2** LOD and background of the analytes.

Analytes	Abbreviation	LOD (ng cm^{-2})	Background (ng cm^{-2})
MPs			
Polyethylene	PE	1.2×10^{-2}	bd*
Polypropylene	PP	7.6×10^{-3}	bd
Polystyrene	PS	1.5×10^{-2}	bd
Polyvinyl Chloride	PET	9.2×10^{-2}	bd
Polymethyl Methacrylate	PMMA	6.5×10^{-3}	bd
Polyethylene Terephthalate	PVC	4.8×10^{-3}	bd
Natural Rubber	NR	4.6×10^{-3}	bd
Butadiene Rubber + Styrene-Butadiene Rubber	BR+SBR	3.3×0^{-2}	bd
PAEs			
dimethylphthalate	DMP	0.01	0.05
diethyl phthalate	DEP	0.01	0.08
di-n-butyl phthalate	DBP	0.05	0.05
butyl benzyl phthalate	BBP	0.03	0.16
bis(2-ethylhexyl)phthalate	DEHP	0.42	0.23
di-n-octyl phthalate	DNOP	0.29	0.43
BTs			
benzothiazole	BT	1.0×10^{-4}	bd
2-aminobenzothiazole	2-NH_2-BT	1.0×10^{-3}	bd
2-hydroxy benzothiazole	HOBT	5.7×10^{-3}	bd
2-mercaptobenzothiazole	MBT	1.5×10^{-3}	bd
2-(methylthio)benzothiazole	MTBT	7.0×10^{-4}	bd
2-(4-morpholinyl)benzothiazole	24MoBT	6.1×10^{-3}	bd
N-cyclohexyl-2-benzothiazolamine	NCBA	1.3×10^{-3}	bd
2-benzothiazolyl-N-morpholinosulfide	OBS	1.9×10^{-3}	bd
N-cyclohexyl-2-benzothiazolesulfenamide	CBS	7.8×10^{-4}	bd
BPA		0.07	bd

156 *bd stands for below detection limit

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158 **Table S3** Comprehensive evaluation of rural and urban family environment survey
159 indicators

	Questionnaire	Min value	Max value	Average value	Standard deviation	Variance
Rural	Sampling location and surrounding environment	1.00	2.00	1.53	0.28	0.08
	Daily living habits	1.00	2.00	1.50	0.41	0.17
	Exposure to plastic products	1.57	1.86	1.80	0.10	0.01
Urban	Sampling location and surrounding environment	1.00	2.00	1.45	0.27	0.07
	Daily living habits	1.50	2.25	1.73	0.26	0.07
	Exposure to plastic products	1.36	1.93	1.54	0.15	0.02

160 *Daily living habits include： use of air purification equipment, ventilation frequency, and cleaning
161 practices

Table S4 Bootstrap analysis results in the PMF model (4 factors, run 100 times)

	Factor	Mapping Rate	Conclusion
Rural	Factor 1	87%	Stable
	Factor 2	86%	Stable
	Factor 3	76%	Basically stable
	Factor 4	82%	Stable
Urban	Factor 1	84%	Stable
	Factor 2	95%	Stable
	Factor 3	92%	Stable
	Factor 4	92%	Stable