Electronic Supplementary Material (ESI) for Analytical Methods.

Human Biomonitoring of Serum Polycyclic Aromatic Hydrocarbons and Oxygenated Derivatives by Gas Chromatography Coupled with Tandem Mass Spectrometry

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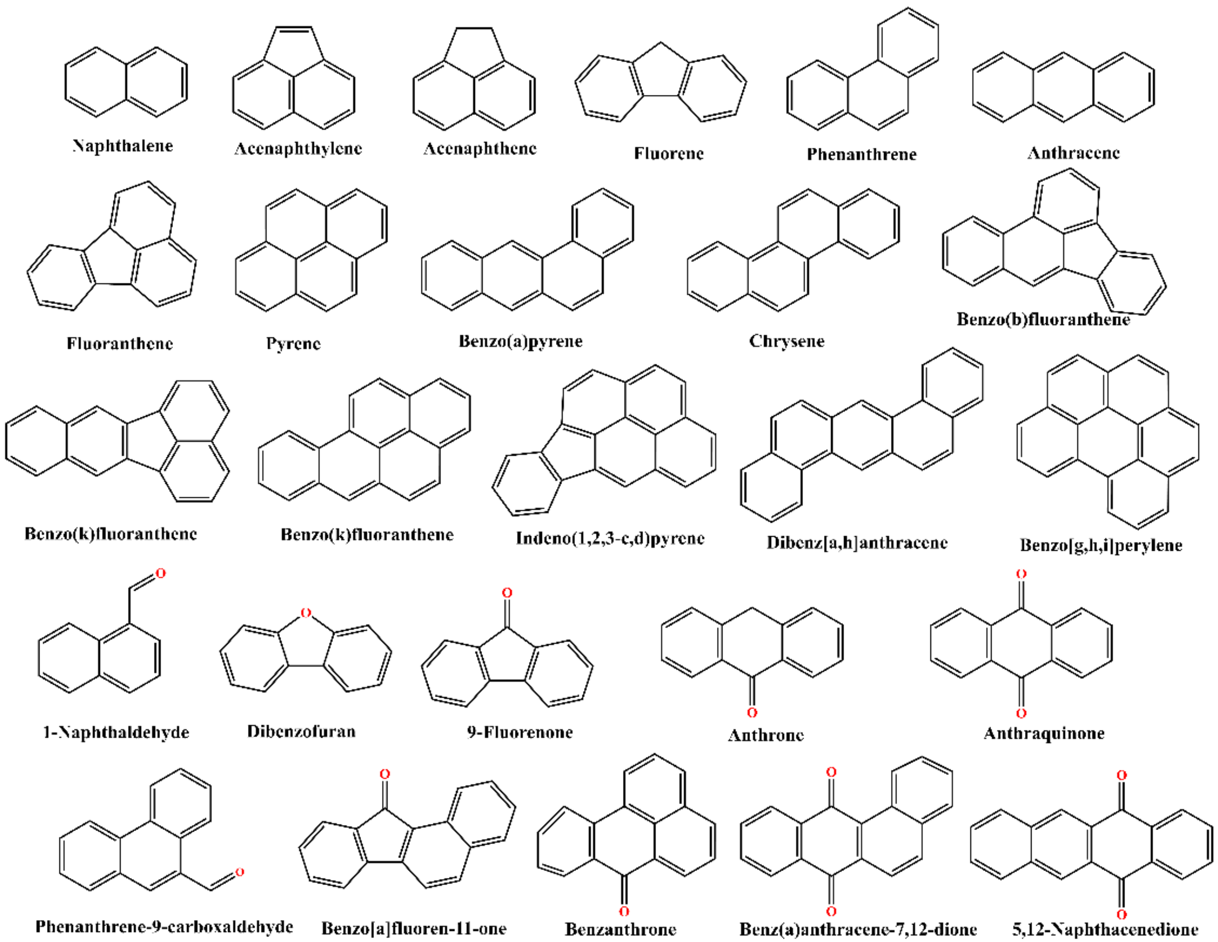

Figure S1. Chemical structures of the PAHs and OPAHs in the study.

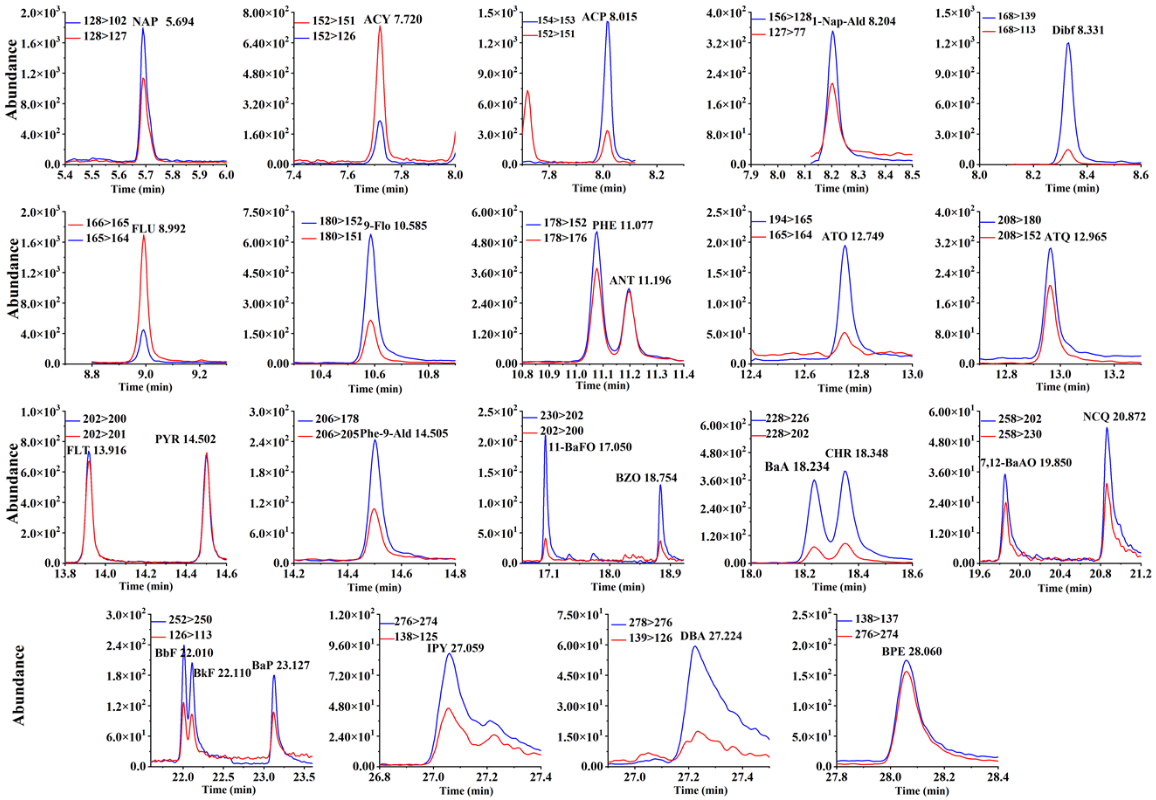

Figure S2. Multiple reaction monitoring of extracted chromatograms of the PAHs and OPAHs with an external standard concentration of 1.0 μg/L.

Table S1. Chemical characteristics of PAHs and OPAHs and their optimized MS/MS parameters

Compound	Abbreviation	CAS	Molecular Formula	Molecular Weight	RT (min)	MRM Parameter	Collision Energy (ev)	IARC)Carcinogen Classification Schemes
Analytes								
Naphthalene	NAP	91-20-3	C10H8	128.17	5.694	128>102, 128>127	20, 20	2B (Vol. 82) 2002
Acenaphthylene	ACY	208-96-8	C12H8	152.19	7.720	152>151, 152>126	25, 25	
Acenaphthene	ACP	83-32-9	C12H10	154.21	8.015	154>153, 152>151	20, 25	3 (Vol. 92) 2010
1-Naphthaldehyde	1-Nap-Ald	66-77-3	C11H8O	156.18	8.204	156>128, 127>77	15, 20	
Dibenzofuran	Dibf	132-64-9	C12H8O	168.19	8.331	168>139, 168>113	25, 45	
Fluorene	FLU	86-73-7	C13H10	166.22	8.992	166>165, 165>164	20, 25	3 (Vol. Sup 7, 92) 2010
9-Fluorenone	9-Flo	486-25-9	C13H8O	180.2	10.585	180>152, 180>151	20, 30	
Phenanthrene	PHE	85-01-8	C14H10	178.23	11.077	178>152, 178>176	25, 35	3 (Vol. Sup 7, 92) 2010
Anthracene	ANT	120-12-7	C14H10	178.23	11.196	178>152, 178>176	25, 35	3 (Vol. 92, Sup 7) 2010
Anthrone	ATO	90-44-8	C14H10O	194.23	12.749	194>165, 165>164	25, 25	
Anthraquinone	ATQ	84-65-1	C14H8O2	208.21	12.965	208>180, 208>152	10, 25	
Fluoranthene	FLT	206-44-0	C16H10	202.25	13.916	202>200, 202>201	40, 25	3 (Vol. Sup 7, 92) 2010
Pyrene	PYR	129-00-0	C16H10	202.25	14.502	202>200, 202>201	40, 25	3 (Vol. Sup 7, 92) 2010
Phenanthrene-9-carboxaldehyde	Phe-9-Ald	4707-71-5	C15H10O	206.24	14.505	206>178, 206>205	15, 15	
11H-Benzo[a]fluoren-11-one	11-BaFO	479-79-8	C17H10O	230.26	17.050	230>202, 230>200	20, 50	
Benzo(a)anthracene	BaA	56-55-3	C18H12	228.29	18.234	228>226, 228>202	35, 30	2B (Vol. 92, Sup 7) 2010
Chrysene	CHR	218-01-9	C18H12	228.29	18.348	228>226, 228>202	35, 30	2B (Vol. 92) 2010
Benzanthrone	BZO	82-05-3	C17H10O	230.26	18.754	230>202, 202>200	25, 40	
Benz(a)anthracene-7,12-dione	7,12-BaAO	2498-66-0	C18H10O2	258.27	19.850	258>202, 258>230	25, 20	
5,12-Naphthacenedione	NCQ	1090-13-7	C18H10O2	258.27	20.872	258>202, 258>230	25, 20	
Benzo(b)fluoranthene	BbF	205-99-2	C20H12	252.31	22.010	252>250, 126>113	30, 10	2B (Vol. 92) 2010

Benzo(k)fluoranthene	BkF	207-08-9	C20H12	252.31	22.110	252>250, 126>113	30, 10	2B (Vol. 92) 2010
Benzo(a)pyrene	BaP	50-32-8	C20H12	252.31	23.127	252>250, 126>113	40, 10	1 (Vol. Sup 7, 92, 100F) 2012
Indeno(1,2,3-c,d)pyrene	IPY	193-39-5	C22H12	276.33	27.059	276>274, 138>125	45, 15	2B (Vol. Sup 7, 92) 2010
Dibenzo(a,h)anthracene	DBA	53-70-3	C22H14	278.35	27.224	278>276, 139>126	35, 10	2A (Vol. Sup 7, 92) 2010
Benzo(g,h,i)perylene	BPE	191-24-2	C22H12	276.33	28.060	138>137, 276>274	15, 50	3 (Vol. 92, Sup 7) 2010
Internal Standards								
Naphthalene-D8	NAP-D8	1146-65-2	C10D8	136.22	5.673	136>108, 136>84	25, 25	
Acenaphthene-D10	ACP-D10	15067-26-2	C12D10	164.27	7.958	164>162, 164>160	20, 35	
9-Fluorenone-D8	9-Flo-D8	137219-34-2	C13D8O	188.25	10.542	188>160, 188>158	20, 30	
Phenanthrene-D10	PHE-D10	1517-22-2	C14D10	188.29	11.022	188>160, 188>186	25, 25	
Anthraquinone-D8	ATQ-D8	10439-39-1	C14D8O2	216.26	12.909	216>188, 188>160	10, 15	
Chrysene-D12	CHR-D12	1719-03-5	C18D12	240.36	18.259	240>236, 240>212	40, 35	
Perylene-D12	PER-D12	1520-96-3	C20D12	264.38	23.319	264>260, 132>118	40, 20	

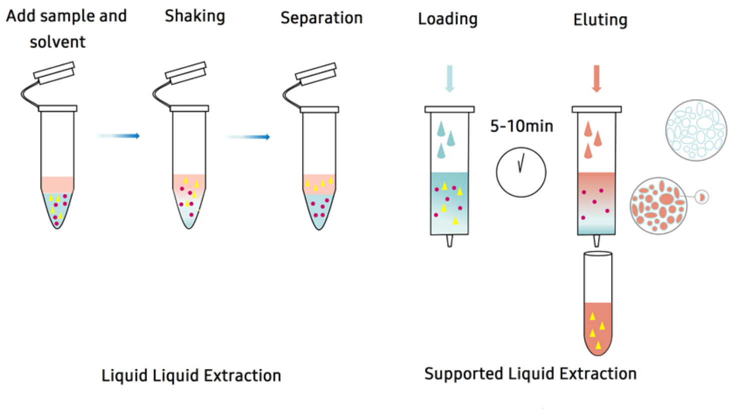

Figure S3. Schematic illustration of the experiment procedures for liquid-liquid extraction, supported liquid extraction and solid-phase extraction.

Table S2. Detailed calibration characteristics, quantification limits, and reproducibility data for the analysis of PAHs and OPAHs in serum samples.

Compound	r2	Linear equation	Linear range (ug/L)	LOD (ug/L)	Inter-day (n=6) Recovery (%)	Inter-day (n=6) RSD (%)	Intra-day (n=6) Recovery (%)	Intra-day (n=6) RSD (%)	Matrix effects (%)	Internal standard
PAHS										
NAP	0.998	y=0.939x+0.187	0.10-5.0	0.02	115.3	8.9	107.8	5.6	99.4	NAP-D8
ACY	0.999	y=0.786x	0.10-5.0	0.02	102.0	7.4	106.4	6.2	99.5	ACP-D10
ACP	0.999	y=1.43x	0.10-5.0	0.02	102.6	6.1	110.8	4.4	93.7	ACP-D10
FLU	0.997	y=1.94x+0.0257	0.10-5.0	0.02	105.1	6.5	107.3	5.9	96.8	PHE-D10
PHE	0.999	y=0.693x+0.0413	0.10-5.0	0.02	110.9	6.8	99.5	4.6	94.8	PHE-D10
ANT	0.997	y=0.532x	0.10-5.0	0.05	102.4	7.6	104.3	5.4	92.6	PHE-D10
FLT	0.997	y=1.36x	0.10-5.0	0.02	107.5	6.2	100.2	8.3	102	PHE-D10
PYR	0.997	y=1.29x	0.10-5.0	0.02	103.2	8.8	102.3	4.5	101	PHE-D10
BaA	0.999	y=.0.887x	0.10-5.0	0.03	104.2	9.0	110.8	8.4	129	CHR-D12
CHR	0.999	y=1.35x	0.10-5.0	0.03	112.0	10.2	99.4	8.6	102	CHR-D12
BbF	0.999	y=0.915x	0.10-5.0	0.05	82.5	9.7	98.1	7.6	130	CHR-D12
BkF	0.998	y=1.03x	0.10-5.0	0.05	85.4	6.3	89.4	5.3	108	CHR-D12
BaP	0.999	y=0.859x	0.10-5.0	0.05	90.3	5.5	107.3	8.0	91.2	PER-D12
IPY	0.998	y=0.613x	0.10-5.0	0.05	93.7	8.6	103.2	7.4	92.8	PER-D12
DBA	0.998	y=0.645x	0.10-5.0	0.05	89.1	7.4	93.4	6.9	95.1	PER-D12
BPE	0.999	y=1.30x	0.10-5.0	0.05	85.4	7.1	109.6	7.6	104	PER-D12
OPAHS										
1-Nap-Ald	0.996	y=0.463x	0.10-5.0	0.02	101.2	10.6	92.6	7.6	98.0	9-Flo-D8
Dibf	0.997	y=1.64x+0.0422	0.10-5.0	0.02	98.6	10.1	97.7	8.6	116	9-Flo-D8

9-Flo	0.999	y=0.506x+0.0400	0.10-5.0	0.02	104.5	11.2	108.9	8.8	90.2	9-Flo-D8
ATO	0.997	y=0.680x	0.10-5.0	0.05	82.4	11.2	85.1	6.2	134	ATQ-D8
ATQ	0.999	y=0.747x	0.10-5.0	0.02	106.5	5.6	114.2	6.6	98.8	ATQ-D8
Phe-9-Ald	0.999	y=1.03x	0.10-5.0	0.02	102.4	9.8	105.4	6.7	96.5	ATQ-D8
11-BaFO	0.999	y=1.23x	0.10-5.0	0.02	102.4	8.4	107.3	5.3	105	ATQ-D8
BZO	0.999	y=0.925x	0.10-5.0	0.05	94.1	7.6	101.6	7.1	127	ATQ-D8
7,12-BaAO	0.995	y=0.277x	0.10-5.0	0.05	91.7	10.6	105.7	7.9	132	ATQ-D8
NCQ	0.996	y=0.258x	0.10-5.0	0.05	90.6	6.5	114.2	6.7	123	ATQ-D8

Table S3. Basic characteristics of the volunteers in the study (N = 240).

Characteristics	All participants	Males	Females
No. of participants	240	121	119
Age, years (mean ± SD)	35.2±22.6	36.0±23.5	34.5±22.2
Age categories(years) (N, %)			
Youths (<18 y)	92 (38.33)	45 (37.19)	47 (39.50)
Adults (18-59 y)	100 (41.67)	51 (42.15)	49 (41.18)
Elders (≥60 y)	48 (20.00)	25 20.66)	23 (19.33)
BMI, kg/m^2 (mean ± SD)	21.4±5.1	21.7±5.5	21.1±4.6
BMI categories(kg/m^2) (N, %)			
Normal (<25)	185 (77.08)	91 (75.21)	94 (78.99)
Overweight(25 to 29.9)	48 (20.00)	26 (21.49)	22 (18.49)
Obese (>30)	7 (2.92)	4 (3.31)	3 (2.52)

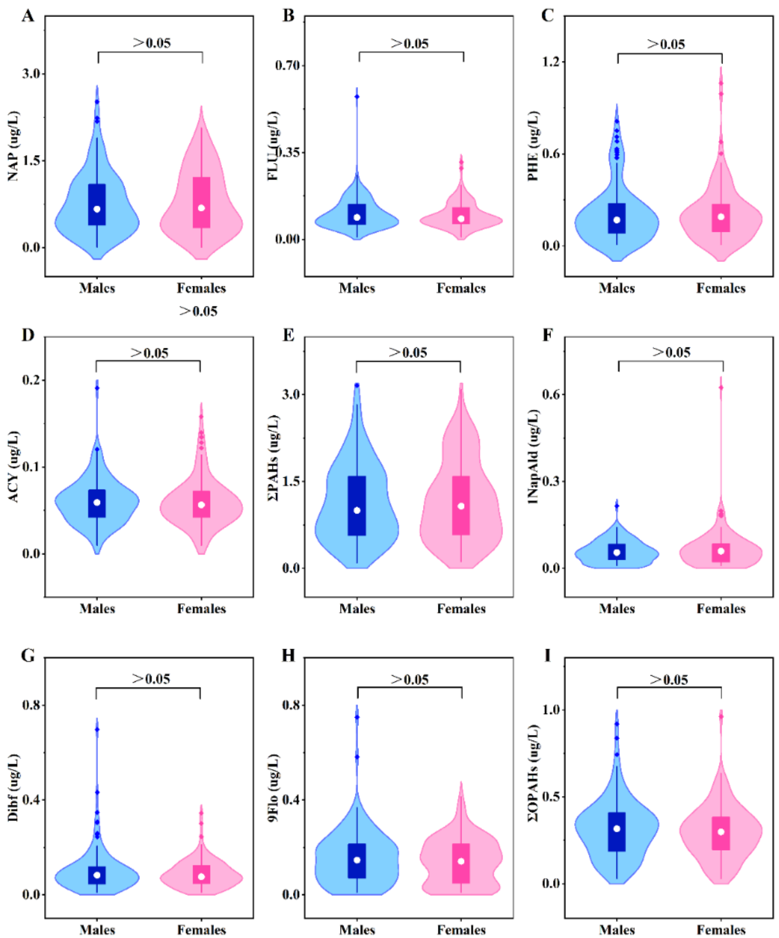

Figure S4. A box plot analysis of gender differences in the concentrations of selected OH-PAHs and PAHs.

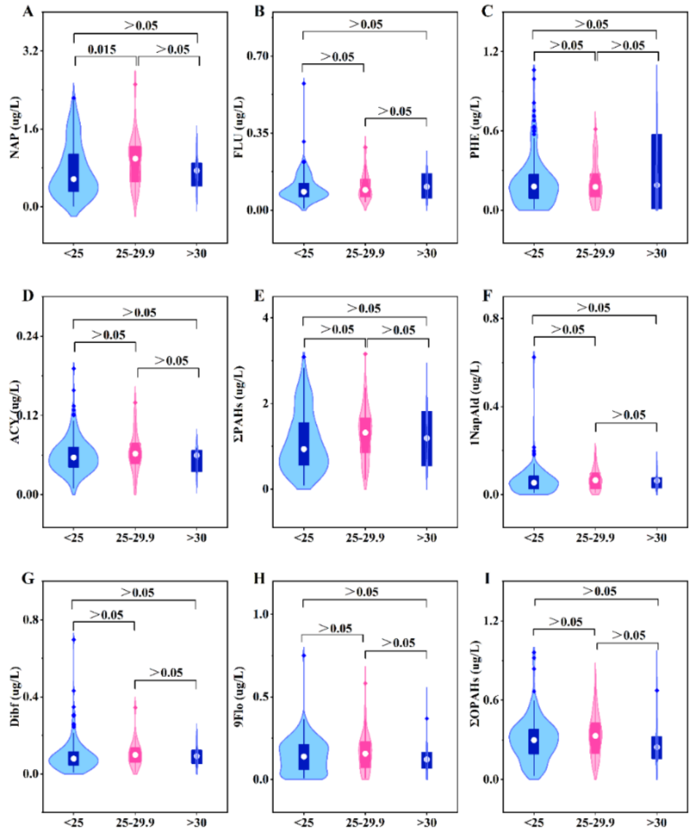

Figure S5. Body mass index differences in concentrations of the target PAHs and OPAHs: A box plot analysis.

Table S4. Comparison of concentrations of PAHs (Median/Mean, μg/L) form different countries and districts.

Country	Sampling year	Mattrixes	NAP	ACY	ACP	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IPY	DBA	BPE	Ref
Guangzhou, China	2022	Serum	0.771	0.0598	/	0.101	0.21	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	This work
Hongkong, China	2005	Maternal serum	331ng/g	35ng/g	94ng/g	155ng/g	144ng/g	48ng/g	128ng/g	154ng/g	63ng/g	68ng/g	16ng/g[a]		＜LOD	＜LOD	＜LOD	＜LOD	1
United States	2010	Plasma	1.459	0.021	0.029	0.046	0.075	0.01	0.027	0.054	0.003	0.003	0.011	0.019	0.021	0.033	0.023	0.04	2
Canada	2003-2004	Serum (smokers)	0.99	—	—	—	5.45	—	—	0.3	—	0.2	—	0.98	—	—	—	—	3
		Serum (non-smokers)	0.44	—	—	—	5.9	—	—	0.27	—	0.4	—	0.22	—	—	—	—	
China	2008	Serum (Exposed group)	0.63	0.07	0.18	0.81	1.42	0.09	0.07	0.11	0.26	0.35	1.78[a]		0.04	58	0.08	4.06	4
		Serum (Reference group)	0.51	0.5	0.11	0.45	0.49	0.02	0.06	0.21	0.15	0.2	1.12[a]		0.02	19.49	0.07	2.27	
Shengsi Islands, China	2011-2012	umbilical cord serum	31.6ng/g	1.46ng/g	0.297ng/g	2.53ng/g	8.13ng/g	6.12ng/g	14ng/g	98ng/g	7.21ng/g	9.49ng/g	6.05ng/g	2.12ng/g	10.6ng/g	6.16ng/g	4.39ng/g	28.9ng/g	5
Spain	2007-2009	Serum (Bladder cancer cases)	0	＜LOD	＜LOD	＜LOD	0.5	0	＜LOD	0	0	0	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	＜LOD	6
		Serum (Controls)	0	0	0	＜LOD	0.9	0	＜LOD	0	0	0	＜LOD	＜LOD	0	＜LOD	＜LOD	＜LOD	
Greece	2017	Serum (Leukemia cases)	11.1	0.39	19.1	23.8	62.2	2.95	9.92	5.03	3.28	0.001	5.48[a]		3.49	1.13	2.85	1.95	7
		Serum (Controls)	9.55	0.39	18.3	18.8	48.6	2.82	6.42	3.97	2.9	0.001	5[a]		3.29	1.47	1.26	1.95	
Beijing, China	2017	serum	—	1.82	—	—	2.43	—	3.09	8.48	—	—	—	—	0.07	—	—	—	8
Poland	2014	maternal blood	57.5	2.1	1.7	3.9	71	79	34	26.5	4.7	7.5	2.2	1.2	0.75	1.65	1.85	2.2	9
		cord blood	45.5	1.45	0.9	6.25	37.95	58.1	50.5	33	16.25	5.05	2.3	2.45	1.6	4.7	5.15	5.05	
Shanxi, China	2010-2013	NTDs serum	—	236ng/g	303ng/g	814ng/g	1820ng/g	142ng/g	345ng/g	441ng/g	137ng/g	188ng/g	103ng/g	32.2ng/g	54.7ng/g	/	/	/	10
		Controls	—	93.8ng/g	99.1ng/g	412ng/g	796ng/g	54.4ng/g	134ng/g	186ng/g	56.9ng/g	65.3ng/g	46.5ng/g	11.3ng/g	21.4ng/g	/	/	/	

"/" Not listed in the paper, "—" Not sdtudied, "a"The sum of BbF and BkF

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