Environ Monit Assess (2018) 190: 315
https://doi.org/10.1007/s10661-018-6694-3

Background biomonitoring of residue levels of 137 pesticides in the blood plasma of the general population in Beijing

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Received: 30 December 2017 / Accepted: 16 April 2018 / Published online: 29 April 2018

Abstract Due to the widespread use of pesticides, human exposure to pesticides is possible and can potentially cause adverse impacts on public health. We measured 137 pesticides including organophosphorus, organochlorine, pyrethroid and carbamate pesticides together with various herbicides in 100 human blood samples collected from the general population in Beijing. The samples were analysed by triple quadrupole tandem gas chromatography-mass spectrometry. In total, 24 organochlorine pesticides, 5 pyrethroid pesticides and 6 organophosphorus pesticides were detected. The detection rates of HCB, α-HCH, β-HCH, γ-HCH, p,p′-DDE and quintozene were 99, 96, 74, 72, 96 and 95%, respectively. No statistically significant gender difference in the blood concentrations of the pesticides was found. Consistent with the trend of the increasing β-HCH, p,p′-DDE and quintozene concentrations with age, a strong positive correlation between the age and concentrations of β-BHC, p,p′-DDE and quintozene was observed.

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Keywords Human blood · Pesticide · General population · GC-MS/MS

Abbreviations

OCP	Organochlorine pesticide
OPP	Organophosphorus pesticide
PP	Pyrethroid pesticide
GC	Gas chromatography
MS	Mass spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification

Introduction

Synthetic pesticides have been widely used in agricultural production. Many public benefits have been gained from the use of synthetic pesticides, such as eradication of various diseases and pests in the fields, increase of agriculture yields and prevention of the propagation of carriers transmitting deadly diseases to humans. But despite the obvious advantages, the potential adverse effects on public health and the environment could be significant. Human beings are exposed to artificial chemicals from various environmental sources. The general human population is predominantly exposed to a range of pesticides through dietary intake, inhalation and drinking water (Margni et al. 2002). Because some pesticides are lipophilic and metabolically resistant, concerns have increased in the last few years regarding the toxicological and human health implications of these chemicals. Low-dose, long-term exposure and uptake of pesticides accumulatively among the general population can lead to chronic health issues, such as cancer, birth defects, reproductive disorders and Parkinson's disease (Alavanja et al., 2013; Mostafalou and Abdollahi, 2013). A useful and common means of detecting human pesticide exposure is biological monitoring. Over the past few decades, methods have been established for the detection of various pesticides in human biological samples, such as blood, breast milk and urine, to assess exposure. Numerous analytical techniques, like chromatography and mass spectrometry, have been used as a part of these detection methods to precisely measure pesticides (Yusa et al., 2015). The applications of biological monitoring data are broad. These data record the universality of exposure to pesticides and can help us better understand the possible risks to humans. Meanwhile, the data can help us understand the main indicators of pesticide exposure in a particular population and identify potential pesticide exposure pathways. Furthermore, toxicological, epidemiological and molecular biological evidence can be obtained to confirm the relationship between specific pesticides and several diseases (Koureas et al., 2012). The very first step is to investigate the background biomonitoring data reflecting the internal exposure and body burden of the general population. Recently, several publications have appeared in which specific pesticide congeners have been identified and quantified in human milk in a Beijing population (Yu et al., 2006; Fujii et al., 2011; Song et al., 2013a; Song et al., 2013b). However, reports specific to the blood concentrations of pesticides, which can reflect exposure from all pathways, are few.

In this study, we developed a rapid screening GC-MS/MS method for a pesticide analysis of human blood plasma. We evaluated various pesticides including forbidden and restricted organochlorine pesticides which were proposed by the ministry of agriculture of the People's Republic of China, early and modern organophosphorus pesticides, commonly used pyrethroid and carbamate pesticides, as well as multifarious herbicides. The aims of this study were to measure the background level of pesticides in the general population living in Beijing and to examine possible associations between pesticide levels and age and gender.

Materials and methods

Sample collection

The Ethics Committee of the Peking Union Medical College (PUMC) approved the study of contaminants in human blood. Briefly, blood from 52 female donors and 48 male donors was collected by the Peking Union Medical College Hospital (PUMCH). All the participants were from the Han nationality. The eligibility of the blood donors was based on the screening performed by nurses during the recruitment of the donors. And all the 100 donors were from ordinary physical examination population in hospital. The age of the blood donors ranged from 17 to 79. Children were excluded from participating. The donors were divided into six age groups: 17–29 ($n = 17$), 30–39 ($n = 21$), 40–49 ($n = 26$), 50–59 ($n = 24$), 60–69 ($n = 8$) and ≥ 70 ($n = 4$). Samples of human blood were gathered in heparinized tubes, stored at 4 °C, and then centrifuged for 10 min at 4000 rpm. The plasma supernatant was aspirated out and placed in a 2-mL glass vial kept at − 20 °C until extraction.

Reagents and apparatus

The individual standard stock solutions of 137 pesticides (concentration 100 μg/mL, > 98.8% purity) were obtained from the Agriculture Environmental Protection of Institute (China). N-hexane (HPLC grade) was purchased from Sigma (USA). Acetonitrile (AR), cyclohexane (AR), ethyl acetate (AR) and anhydrous sodium sulfate (AR) were all purchased from Beijing Chemical Works (China).

The gas chromatography-mass spectrometer system consisted of a Varian 450 GC and a 300 triple quadrupole MS (Bruker Daltonics Inc., USA). The chromatographic separation was accomplished using a Varian capillary column VF-5 MS (60 m × 0.25 mm × 0.25 μm) with 5% phenyl polysiloxane as the non-polar stationary phase (Bruker Daltonics Inc., USA). Meanwhile, the electronic balance (PL203/01, Mettler Toledo Inc., Switzerland), the vortex mixer (WH-1, Shanghai huxi analytical instruments, China), the vacuum pump (SHB-B, Zhengzhou greatwall scientific company, China), the rotary evaporator (Laborota 4000/4, Heidolph instruments, Germany) and the centrifuge (80–2, Jintan medical-equipment company, China) were used.

Sample preparation technique

The procedures for the sample preparation, including the extraction and clean-up, were based on a liquid solvent extraction method. A mixture of ethyl acetate and cyclohexane was a common solvent applied in a multi-residue pesticide analysis using QuEChERS methodology (Steiniger et al., 2010; Wilkowska and Biziuk, 2011). Briefly, the plasma was thawed at 4 °C, and then, a precise 0.5 mL plasma sample was mixed with 1 mL acetonitrile in a 5 mL stoppered test tube, vibrated and centrifuged. The supernatant was transferred to another test tube and extracted with 3 × 1 mL ethyl acetate/cyclohexane (*v*/*v*, 3:1). The organic phase was desiccated using an appropriate amount of anhydrous sodium sulfate and concentrated to 0.5 mL with mild nitrogen blowing.

Instrumental analysis

The conditions for the GC analysis were as follows. The injector temperature was maintained at 250 °C in splitless injection mode, and the volume of the injection was 1 μL. Pure helium (99.999%) was used as the carrier gas with a constant flow of 1 mL/min. The column temperature was 120 °C at the start, held for 1 min, increased to 150 °C at a rate of 8 °C/min, held for 2 min, then increased to 205 °C at 2 °C/min, held for 6 min, increased to 270 °C at 5 °C/min and finally increased to 280 °C at 1 °C/min and maintained for 30 min.

The triple quadrupole tandem MS system was manipulated using the ionisation mode of electron impact (EI), and the electron energy was 70 eV. The SIM width was 0.7 amu. The temperature of the transfer line was set at 250 °C, while the ion source and manifold were 220 and 40 °C, respectively. The collision gas was high-purity argon (99.999%), and the pressure was kept at 2.0 mTorr.

Table 1 lists the determination parameters used in this paper, including the time segments, retention times, qualification and quantification ions and the collision energies for each pesticide. The determination of the concentrations of the pesticide residues was performed using an external standard method. The concentration of the standard solution of the matrix-matched pesticide was 10 ng/mL. The peak area of the quantitative ion for each pesticide was determined using the standards and then applied to measure the pesticides in the unknown samples.

Quality assurance/quality control

A solvent blank (ethyl acetate: cyclohexane *v*/v, 3:1) was periodically processed through the full analytic procedure to detect any background interference. Meanwhile, the 12 samples of each set contained a method blank sample to monitor the background pollution. To assure the proper recognition and quantification of the object compounds, some quality control specifications were employed. First, the retention times for the determination of the reference compounds should match. Second, the proportions of two typical ions should be no more than 15% of the theoretical values. Finally, the signal to noise ratio of the selected ions should be greater than 3. The congener was excluded if all of these conditions were not met.

Statistical analysis

The statistical software package SPSS 17.0 was used to analyse the data. If the detected concentrations of the compounds were lower than the LODs, the values applied to the statistical analysis were equal to one-half of the LODs of the analytical method, and the computations of the median, mean and sum were set at zero. P-P plots were used to test the normality of the variables, and the Kolmogorov-Smirnov test was used to validate the normality. The result of a chi-squared test was used to determine the relationship among categorical variables. A non-parametric u-test was used to compare the continuous variables with non-normal distributions, while the Spearmen-rho coefficient was used to measure the correlation of two continuous variables.

Results and discussion

Method validation

The results suggest that the separation of all 137 pesticides was successful because of the high selectivity and sensitivity of the detection. The calibration curve of each compound was calculated using the concentration peak area obtained through the injection of matrix-matched pesticide standard solutions in GC-MS/MS. The results from a method validation study are shown in Table 1. The linear relationships of the calibration curves were well within the correlation coefficients (r^2), ranging from 0.9002 to 0.9998 in the study of serial

Table 1 The parameters for the determination of 137 pesticides (including isomers) by GC-MS/MS and validation study results for pesticides in a blank plasma matrix

No.	Compound	Retention time (RT, min)	Segment	Transitions in GC-MS/MS [$Q_1 \rightarrow Q_3$(CE), m/z → m/z(V)]		Calibration range (ng/ml)	r^{2a}	LOD (S/N = 3) (ng/mL)	LOQ (S/N = 10) (ng/mL)	Recovery and precision (n = 6)[b] Recovery% (RSD%)		
				Quantification	Qualification					10 ng/ml	50 ng/ml	200 ng/ml
1	Methamidophos	12.89	1	141 → 95(8)	94 → 79(14)	5~500	0.9969	1.1	3.6	98.6 (13.2)	95.6 (14.7)	105.8 (11.4)
2	Dichlorvos	13.19	1	109 → 79(5)	79 → 65(5)	5~500	0.9917	0.9	3.0	106.3 (8.9)	108.9 (7.7)	118.2 (12.3)
3	Trichlorfon	13.91	1	109 → 79(8)	185 → 108(19)	5~500	0.9953	0.6	1.9	105.3 (9.6)	118.6 (6.7)	112.4 (5.2)
4	Mevinphos	17.75	1	192 → 127(10)	127 → 109(10)	5~500	0.9961	0.7	2.5	106.2 (13.5)	116.6 (5.7)	112.1 (10.7)
5	Methacrifos	19.79	1	208 → 180(7)	180 → 93(10)	1~500	0.9987	0.5	1.8	107.5 (7.5)	111.1 (18.9)	112.9 (17.3)
6	Pentachlorobenzene	21.26	1	250 → 179(25)	179 → 109(15)	1~500	0.9926	0.9	3.1	108.7 (13.7)	115.1 (9.1)	116.0 (10.2)
7	Molinate	21.72	1	126 → 98(5)	126 → 106(5)	5~500	0.9904	0.9	3.0	90.3 (13.3)	98.7 (12.4)	109.2 (13.0)
8	Fenobucarb	23.23	1	150 → 121(10)	121 → 77(20)	1~500	0.9973	0.5	1.6	98.1 (12.9)	117.0 (6.4)	120.3 (12.8)
9	Hexaflumuron	23.58	1	277 → 176(15)	176 → 148(11)	10~500	0.9857	0.9	3.0	97.4 (8.0)	106.5 (2.1)	114.0 (0.6)
10	Ethoprophos	24.23	2	158 → 97(20)	200 → 158(8)	5~500	0.9972	1.0	3.2	104.9 (4.1)	106.5 (5.5)	110.2 (6.8)
11	Trifluralin	24.66	2	306 → 264(10)	264 → 206(10)	5~500	0.9964	0.9	2.9	105.5 (12.5)	110.1 (6.2)	105.1 (4.6)
12	chlorpropham	24.92	2	213 → 171(10)	171 → 127(10)	5~500	0.9948	0.8	2.8	95.4 (13.8)	117.8 (11.8)	120.8 (7.0)
13	Sulfotep	25.26	2	322 → 174(20)	322 → 202(20)	10~500	0.9964	0.7	2.5	92.4 (6.0)	111.1 (7.6)	113.0 (14.6)
14	Phorate	26.46	2	260 → 75(10)	260 → 231(5)	5~500	0.9956	0.9	3.1	120.5 (12.9)	120.4 (9.4)	120.7 (14.6)
15	α-BHC	27.37	2	219 → 181(10)	181 → 145(15)	5~500	0.9998	1.0	3.3	117.1 (8.4)	111.5 (7.5)	98.2 (5.3)
16	Thiometon	27.51	3	88 → 60(10)	246 → 88(10)	1~500	0.9977	0.8	2.8	104.3 (13.2)	109.7 (11.3)	112.1 (6.8)
17	Hexachlorobenzene	27.72	3	284 → 177(50)	284 → 214(20)	10~500	0.9995	1.7	5.6	80.9 (6.3)	85.7 (10.3)	99.3 (11.9)
18	Dicloran	28.18	3	206 → 176(25)	206 → 124(14)	100~500	0.9942	2.0	6.7	98.4 (11.3)	99.6 (13.2)	101.6 (12.6)
19	Simazine	28.18	3	201 → 158(10)	201 → 173(10)	50~500	0.9015	0.8	2.8	80.0 (15.4)	81.3 (8.1)	99.8 (4.6)
20	Atrazine-desethyl	28.44	3	187 → 172(10)	187 → 145(20)	50~500	0.9847	3.2	10.5	–[c]	85.6 (9.4)	78.3 (13.3)
21	β-BHC	29.00	4	219 → 181(10)	181 → 145(15)	5~500	0.9905	1.0	3.4	102.5 (7.2)	107.9 (10.5)	91.4 (9.2)
22	Propetamphos	29.03	4	236 → 194(10)	194 → 94(25)	50~500	0.9970	1.0	3.2	113.4 (9.5)	115.0 (6.1)	103.6 (15.3)
23	Quintozene	29.37	4	295 → 237(20)	237 → 143(25)	5~500	0.9993	0.9	3.1	83.2 (13.6)	93.4 (10.6)	103.9 (9.6)
24	Terbufos	29.44	4	231 → 129(25)	231 → 175(10)	5~500	0.9935	0.8	2.7	104.3 (8.6)	108.7 (13.1)	116.0 (10.4)
25	Diazinorl	29.53	4	304 → 137(35)	304 → 179(15)	50~500	0.9921	1.4	4.7	104.3 (11.5)	105.9 (7.3)	97.4 (11.8)
26	Cyanophos	29.56	4	243 → 109(10)	243 → 127(5)	1~500	0.9939	0.9	2.8	113.7 (15.5)	116.1 (5.1)	102.2 (9.0)
27	γ-BHC	29.72	5	181 → 109(20)	183 → 147(15)	5~500	0.9949	1.3	4.4	88.3 (10.9)	85.1 (9.2)	96.3 (12.4)
28	Fonofos	29.99	5	246 → 137(10)	246 → 109(20)	5~500	0.9928	0.8	2.7	102.8 (6.7)	107.2 (5.9)	93.6 (7.5)
29	Paraoxonmethyl	29.99	5	109 → 79(5)	247 → 109(10)	10~500	0.9926	0.9	2.9	91.7 (12.5)	91.5 (12.0)	124.7 (5.6)
30	Paraoxon-ethyl	30.17	5	109 → 81(5)	109 → 79(5)	10~500	0.9919	0.9	2.9	70.5 (14.5)	79.3 (15.6)	78.2 (13.8)

Table 1 (continued)

No.	Compound	Retention time (RT, min)	Segment	Transitions in GC-MS/MS [$Q_1 \rightarrow Q_3$(CE), m/z → m/z(V)]		Calibration range (ng/ml)	r^{2a}	LOD (S/N = 3) (ng/mL)	LOQ (S/N = 10) (ng/mL)	Recovery and precision (n = 6)[b] Recovery% (RSD%)		
				Quantification	Qualification					10 ng/ml	50 ng/ml	200 ng/ml
31	Pyrimethanil	30.32	5	198 → 158(25)	198 → 183(15)	10~500	0.9920	0.5	1.6	118.8 (13.2)	110.5 (9.9)	118.0 (5.3)
32	Isazofos	30.50	5	161 → 119(10)	257 → 119(10)	10~500	0.9947	0.8	2.8	102.0 (8.5)	95.6 (9.0)	108.7 (12.5)
33	Etrimfos	30.76	6	292 → 181(10)	292 → 125(20)	5~500	0.9966	0.4	1.4	108.2 (14.6)	99.6 (11.2)	110.6 (13.6)
34	Flufenoxuron	31.32	6	305 → 126(15)	126 → 98(10)	10~500	0.9988	0.8	2.8	76.1 (9.4)	77.3 (8.3)	96.9 (1.5)
35	δ-BHC	31.46	6	181 → 145(15)	217 → 145(15)	5~500	0.9971	1.1	3.6	92.3 (11.2)	87.0 (7.7)	90.0 (15.3)
36	Dichlofenthion	32.57	6	279 → 251(10)	251 → 223(10)	50~500	0.9968	0.8	2.7	88.2 (13.2)	106.7 (5.6)	120.0 (8.5)
37	Propanil	32.82	6	217 → 161(10)	161 → 125(15)	10~500	0.9945	0.9	3.1	113.4 (16.6)	103.1 (5.8)	101.8 (10.7)
38	Chlorpyrifos-methyl	33.09	6	286 → 93(20)	286 → 271(15)	5~500	0.9969	0.8	2.8	106.3 (7.4)	101.0 (6.0)	102.3 (12.0)
39	Vinclozolin	33.23	6	285 → 212(10)	285 → 198(30)	50~500	0.9895	0.8	2.6	81.9 (3.4)	88.6 (5.7)	96.3 (0.6)
40	Methyl-parathion	33.52	7	263 → 109(15)	263 → 125(15)	50~500	0.9979	0.9	3.1	94.3 (7.2)	118.5 (11.3)	120.6 (10.3)
41	Tolclofosmethyl	33.60	7	265 → 93(20)	266 → 93(25)	10~500	0.9944	1.1	3.6	92.4 (9.9)	101.5 (13.9)	99.5 (11.0)
42	Metalaxyl	33.84	7	206 → 132(20)	206 → 104(40)	10~500	0.9948	1.0	3.2	93.2 (9.8)	99.3 (14.2)	101.3 (13.9)
43	Prometryne	33.93	7	241 → 184(20)	241 → 226(10)	100~500	0.9955	0.9	2.9	110.0 (4.3)	109.9 (5.4)	106.6 (13.0)
44	Fenchlorphos	34.15	7	285 → 93(30)	320 → 285(10)	50~500	0.9949	0.8	2.8	110.5 (9.3)	111.1 (8.3)	132.2 (3.0)
45	Heptachlor	34.38	7	277 → 237(15)	337 → 266(16)	50~500	0.9968	1.3	4.3	79.2 (15.0)	80.8 (8.1)	108.6 (7.6)
46	Fenitrothion	34.91	7	277 → 260(8)	260 → 125(15)	50~500	0.9970	0.8	2.8	94.1(5.6)	102.7 (4.5)	114.1 (6.7)
47	Malathion	35.16	7	173 → 99(17)	173 → 127(8)	10~500	0.9977	0.8	2.7	123.3 (3.4)	120.7 (5.3)	106.9 (14.2)
48	Diethofencarb	35.54	8	196 → 96(15)	168 → 96(10)	10~450	0.9964	0.6	2.1	88.5 (9.6)	82.9 (7.5)	104.8 (10.5)
49	Metolachlor	35.73	8	238 → 162(10)	162 → 133(10)	10~450	0.9977	0.8	2.7	92.0 (13.9)	106.4 (4.5)	135.5 (13.1)
50	Etpfenprox	35.73	8	163 → 135(10)	163 → 107(15)	10~450	0.9966	1.1	3.7	79.5 (15.3)	78.2 (12.6)	99.7 (9.6)
51	Chlorpyriphos	35.76	8	314 → 286(10)	314 → 258(15)	10~450	0.9962	0.8	2.8	68.6 (14.7)	99.0 (7.5)	98.4 (6.8)
52	Fenthion	36.04	8	278 → 109(20)	278 → 125(20)	10~500	0.9957	0.5	1.8	110.0 (7.9)	112.1 (9.4)	109.6 (2.1)
53	Parathion-ethyl	36.22	8	291 → 137(10)	291 → 109(10)	10~500	0.9966	0.4	1.5	118.0 (11.2)	114.9 (9.8)	101.3 (8.7)
54	Aldrin	36.50	9	291 → 221(20)	291 → 185(50)	5~500	0.9994	1.0	3.3	108.2 (12.1)	106.5 (11.2)	116.3 (12.7)
55	Pirimiphos-ethyl	36.67	9	318 → 182(5)	333 → 180(10)	5~500	0.9549	0.8	2.8	91.0 (13.2)	100.4 (6.9)	113.2 (8.0)
56	Dicofol	36.92	9	251 → 111(35)	251 → 139(15)	5~500	0.9946	1.2	4.0	114.3 (13.2)	118.2 (6.9)	115.1 (6.1)
57	Bromophos	37.16	9	329 → 314(18)	331 → 316(18)	1~500	0.9960	0.8	2.7	80.3 (6.1)	96.5 (5.6)	97.3 (5.6)
58	Pendimethalin	37.61	9	252 → 162(20)	252 → 191(10)	5~500	0.9991	1.0	3.2	83.4 (13.2)	94.9 (9.3)	109.3 (7.5)
59	Isocarbophos	37.88	9	121 → 65(25)	136 → 108(20)	50~500	0.9990	1.1	3.7	109.6 (11.2)	111.6 (8.4)	109.8 (1.7)
60	Isofenphos	37.89	9	255 → 213(15)	213 → 185(15)	5~500	0.9977	1.0	3.2	82.3 (11.7)	81.1 (7.9)	124.3 (6.4)

Table 1 (continued)

No.	Compound	Retention time (RT, min)	Segment	Transitions in GC-MS/MS [$Q_1 \rightarrow Q_3$(CE), m/z → m/z(V)] Quantification	Qualification	Calibration range (ng/ml)	r^{2a}	LOD (S/N = 3) (ng/mL)	LOQ (S/N = 10) (ng/mL)	Recovery and precision (n = 6)[b] Recovery% (RSD%) 10 ng/ml	50 ng/ml	200 ng/ml
61	Bioallethrin I	38.03	10	123 → 81(5)	136 → 93(11)	10~500	0.9974	1.2	4.1	92.6 (13.2)	118.3 (20.0)	119.3 (7.3)
62	Chlorfenvinphos	38.04	10	323 → 267(10)	267 → 159(20)	10~500	0.9967	0.8	2.7	70.6 (14.3)	77.6 (14.6)	79.7 (13.3)
63	Isodrin	38.16	10	193 → 158(15)	141 → 95(9)	10~500	0.9986	0.9	3.1	84.6 (14.3)	89.6 (8.6)	102.7 (7.8)
64	Phenthoate	38.30	10	274 → 125(25)	274 → 246(10)	10~500	0.9916	1.1	3.7	98.6 (5.6)	110.2 (8.6)	125.3 (4.1)
65	Quinalphos	38.49	10	146 → 118(20)	146 → 90(45)	10~500	0.9942	1.4	4.6	92.1 (8.1)	111.6 (9.5)	108.8 (1.0)
66	Procymidone	38.73	10	283 → 96(15)	283 → 145(50)	50~500	0.9947	0.8	2.8	94.4 (7.0)	104.0 (4.8)	112.3 (12.0)
67	Bromophosethyl	39.20	10	359 → 331(10)	359 → 303(30)	50~500	0.9956	0.9	2.9	82.0 (6.2)	92.1 (9.0)	114.3 (10.7)
68	Methidathion	39.38	11	145 → 85(11)	85 → 58(8)	50~500	0.9986	1.1	3.6	70.9 (19.9)	71.6 (8.6)	77.3 (3.8)
69	Tetrachlorvinphos	39.49	11	329 → 109(15)	331 → 109(15)	10~500	0.9944	0.8	2.8	114.6 (6.3)	116.7 (6.5)	98.2 (9.9)
70	o,p′-DDE	39.63	11	248 → 176(30)	318 → 248(20)	5~500	0.9961	0.9	3.2	74.7 (8.8)	86.6 (6.3)	118.3 (12.3)
71	Hexythiazox	39.67	11	156 → 112(15)	109 → 81(5)	10~500	0.9915	2.1	7.0	98.5 (5.9)	90.5 (5.9)	100.3 (11.1)
72	cis-Chlordane	39.72	11	373 → 337(10)	272 → 237(15)	10~500	0.9905	1.6	5.4	102.0 (6.5)	94.6 (14.5)	107.6 (11.8)
73	Paclobutrazol	39.73	11	236 → 125(10)	236 → 167(10)	10~500	0.9965	0.7	2.2	74.2 (8.7)	108.1 (4.4)	117.3 (6.7)
74	Chlorfluazuron	39.98	11	321 → 304(17)	356 → 321(10)	50~500	0.9987	0.8	2.8	92.7 (12.3)	119.3 (11.0)	105.5 (13.6)
75	Fenamiphos	40.08	11	303 → 154(10)	303 → 217(20)	50~500	0.9960	0.8	2.7	109.5 (10.8)	113.9 (6.8)	120.0 (1.6)
76	Flutolanil	40.23	12	323 → 281(10)	281 → 173(10)	10~500	0.9928	1.3	4.4	107.6 (10.4)	105.6 (8.6)	112.7 (6.3)
77	trans-Chlordane	40.42	12	272 → 237(25)	373 → 337(10)	10~500	0.9052	1.2	4.1	101.9 (12.0)	103.6 (14.3)	120.5 (9.1)
78	Napropamide	40.47	12	271 → 128(10)	271 → 72(15)	10~500	0.9919	0.8	2.8	82.0 (11.4)	107.7 (9.6)	106.1 (8.2)
79	α-Endosulfan	40.48	12	195 → 159(15)	241 → 170(25)	50~500	0.9996	1.0	3.4	86.1 (8.4)	100.0 (6.8)	114.6 (4.6)
80	Dieldrin	40.48	12	277 → 206(20)	277 → 241(10)	5~500	0.9911	1.0	3.5	92.3 (13.2)	109.6 (7.6)	112.4 (6.6)
81	Iodofenphos	40.67	12	377 → 362(15)	377 → 250(20)	10~500	0.9962	0.8	2.7	118.1 (5.6)	91.1 (5.5)	104.6 (7.8)
82	Hexaconazole	40.73	13	175 → 111(10)	214 → 175(15)	51~500	0.9988	0.9	2.9	72.5 (11.5)	81.1 (12.5)	79.7 (13.7)
83	Chlorfenson	40.76	13	302 → 175(10)	175 → 111(10)	1~500	0.9921	1.0	3.3	84.6 (10.2)	79.6 (10.6)	89.3 (9.6)
84	Oxadiazone	40.84	13	302 → 258(10)	258 → 175(10)	10~500	0.9956	0.8	2.7	101.3 (12.6)	100.8 (12.0)	111.7 (4.1)
85	Profenofos	41.15	13	372 → 337(5)	337 → 295(10)	100~500	0.9052	10.2	33.8	–	75.9 (10.3)	79.7 (5.0)
86	Uniconazole	41.23	13	234 → 137(15)	137 → 95(5)	50~500	0.9970	1.6	5.3	118.2 (5.5)	109.9 (5.5)	116.0 (13.0)
87	p,p′-DDE	41.23	13	318 → 248(25)	246 → 176(20)	10~500	0.9959	1.0	3.4	100.7 (13.0)	109.4 (7.0)	118.6 (7.4)
88	Flusilazole	41.32	13	233 → 152(12)	233 → 165(12)	10~500	0.9932	0.9	3.1	114.7 (13.6)	112.7 (6.0)	127.4 (7.1)
89	Endrin	41.91	14	263 → 193(20)	263 → 227(15)	50~500	0.9085	1.0	3.4	118.4 (3.2)	120.5 (9.5)	121.3 (9.7)
90	Nitrofen	42.62	14	283 → 162(20)	202 → 139(25)	10~500	0.9958	0.9	3.0	105.8 (6.6)	115.6 (7.6)	110.7 (9.4)

Table 1 (continued)

No.	Compound	Retention time (RT, min)	Segment	Transitions in GC-MS/MS [$Q_1 \rightarrow Q_3$(CE), m/z → m/z(V)] Quantification	Qualification	Calibration range (ng/ml)	r^{2a}	LOD (S/N = 3) (ng/mL)	LOQ (S/N = 10) (ng/mL)	Recovery and precision (n = 6)[b] Recovery% (RSD%) 10 ng/ml	50 ng/ml	200 ng/ml
91	Chlorobenzilate	42.82	14	253 → 139(15)	139 → 111(10)	5~500	0.9940	1.3	4.5	113.8 (4.9)	111.8 (6.7)	101.3 (4.3)
92	Fensulfothion	42.93	14	293 → 141(25)	293 → 125(10)	10~500	0.9964	2.1	7.2	103.9 (9.7)	107.4 (7.5)	110.4 (4.1)
93	Ethion	43.13	14	231 → 129(30)	231 → 185(10)	5~500	0.9955	1.2	4.1	106.0 (11.8)	113.5 (6.6)	115.5 (3.3)
94	Diniconazole	43.23	14	268 → 232(10)	270 → 232(15)	10~500	0.9978	1.1	3.7	82.8 (6.0)	113.2 (6.4)	92.4 (4.4)
95	Chlorthiophos	43.32	15	325 → 269(15)	360 → 269(15)	5~500	0.9944	0.9	3.0	72.5 (9.6)	72.6 (11.2)	73.0 (7.7)
96	Oxadixyl	43.36	15	163 → 132(20)	163 → 117(40)	10~500	0.9938	1.0	3.2	77.1 (10.2)	90.5 (19.3)	78.7 (4.7)
97	o,p′-DDT	43.51	15	235 → 200(16)	235 → 165(21)	50~500	0.9950	1.5	4.9	90.2 (8.2)	93.7 (9.1)	115.8 (3.4)
98	β-Endosulfan	43.64	15	195 → 159(10)	241 → 170(25)	50~500	0.9978	1.1	3.8	118.5 (8.3)	114.6 (8.9)	124.1 (8.0)
99	p,p′-DDD	43.68	15	235 → 165(20)	235 → 200(15)	1~500	0.9955	1.1	3.5	120.4 (14.6)	103.1 (4.8)	121.9 (3.2)
100	Triazophos	44.00	15	161 → 77(20)	161 → 134(16)	50~500	0.9970	1.3	4.2	116.3 (6.9)	109.5 (7.2)	109.5 (4.9)
101	Carbophenothion	44.84	16	342 → 157(15)	342 → 143(15)	50~500	0.9981	0.9	3.0	104.8 (4.2)	112.2 (4.1)	100.0 (9.2)
102	Edifenphos	45.18	16	310 → 173(10)	173 → 109(10)	50~500	0.9947	0.9	3.0	96.5 (7.6)	112.7 (5.0)	111.4 (9.3)
103	Acetamiprid	45.44	16	152 → 90(10)	152 → 99(20)	100~500	0.9084	21.6	71.9	–	–	98.7 (10.3)
104	p,p′-DDT	45.66	16	235 → 200(14)	235 → 165(19)	50~500	0.9984	1.0	3.2	107.3 (8.5)	83.0 (5.2)	111.8 (4.5)
105	Endosulfan sulfate	45.75	16	272 → 237(15)	241 → 206(10)	10~500	0.9967	1.1	3.6	94.8 (8.3)	91.6 (6.6)	94.0 (12.9)
106	Propargite	46.07	16	135 → 107(10)	150 → 135(15)	50~500	0.9548	0.9	2.8	81.5 (6.8)	77.1 (11.5)	80.3 (13.7)
107	Sethoxydim	46.25	16	178 → 81(15)	109 → 81(10)	50~500	0.9945	1.2	3.9	98.7 (9.4)	118.7 (8.1)	116.2 (8.6)
108	Tebuconazole	46.79	17	250 → 153(35)	227 → 169(30)	50~500	0.9846	0.8	2.8	104.0 (3.4)	116.6 (6.9)	117.8 (7.1)
109	Pyridaphenthion	47.65	17	340 → 125(20)	199 → 77(25)	50~500	0.9932	10.7	35.8	–	109.6 (12.0)	112.7 (10.3)
110	Bifenthrin	47.83	17	181 → 141(20)	181 → 165(25)	10~500	0.9951	0.9	3.0	66.7 (12.7)	84.8 (8.2)	119.5 (5.6)
111	Tetramethrin	48.17	17	164 → 135(10)	164 → 93(10)	10~500	0.9956	1.0	3.4	85.3 (13.0)	88.5 (12.1)	89.7 (14.8)
112	EPN	48.53	17	185 → 157(10)	157 → 110(15)	50~500	0.9986	2.5	8.2	106.5 (9.6)	107.1 (5.8)	93.1 (12.9)
113	Bromopropylate	48.58	17	341 → 155(50)	341 → 183(30)	10~500	0.9925	1.0	3.3	119.7 (9.5)	114.0 (6.6)	102.8 (4.0)
114	Phosmet	48.58	17	160 → 77(25)	160 → 104(20)	10~500	0.9974	1.2	4.1	93.0 (17.9)	82.8 (8.5)	96.5 (2.2)
115	Fenpropathrin	48.67	17	181 → 152(25)	209 → 181(10)	10~500	0.9962	1.0	3.2	109.7 (8.5)	114.5 (4.0)	111.5 (8.5)
116	Methoxychlor	48.84	18	227 → 153(35)	227 → 169(30)	50~500	0.9919	1.1	3.6	78.6 (2.6)	85.3 (11.3)	78.7 (12.4)
117	Tetradifon	50.63	18	356 → 229(10)	229 → 201(15)	10~500	0.9990	1.0	3.2	90.5 (8.9)	107.7 (9.0)	118.6 (5.5)
118	Phosalone	50.88	18	367 → 182(10)	182 → 111(15)	50~500	0.9925	0.9	3.1	94.1 (8.9)	116.0 (7.8)	123.2 (2.1)
119	Cyhalothrin	51.44	18	197 → 141(5)	208 → 181(10)	50~500	0.9925	0.8	2.8	110.3 (5.5)	105.9 (7.5)	103.4 (4.1)
120	Azinphos-methyl	51.45	18	160 → 132(9)	132 → 77(9)	50~500	0.9922	1.5	5.1	109.6 (2.6)	114.6 (6.5)	116.4 (15.4)

Table 1 (continued)

No.	Compound	Retention time (RT, min)	Segment	Transitions in GC-MS/MS [$Q_1 \rightarrow Q_3$(CE), m/z → m/z(V)]		Calibration range (ng/ml)	r^{2a}	LOD (S/N = 3) (ng/mL)	LOQ (S/N = 10) (ng/mL)	Recovery and precision (n = 6)[b] Recovery% (RSD%)		
				Quantification	Qualification					10 ng/ml	50 ng/ml	200 ng/ml
121	Sulprofos	51.93	19	322 → 156(10)	322 → 139(15)	10~500	0.9915	1.4	4.7	113.8 (10.6)	110.2 (5.7)	108.1 (8.5)
122	Mefenacet	52.00	19	192 → 136(15)	148 → 120(10)	10~500	0.9956	1.1	3.6	108.5 (10.3)	119.6 (5.0)	117.6 (5.8)
123	Fenarimol	53.47	19	139 → 111(15)	219 → 107(15)	50~500	0.9969	0.9	2.9	70.4 (5.7)	92.9 (7.4)	90.2 (4.9)
124	Mirex	53.66	19	272 → 237(20)	272 → 167(40)	5~500	0.9951	1.1	3.5	75.3 (7.5)	87.2 (6.1)	87.1 (5.2)
125	Azinphos-ethyl	53.85	19	160 → 132(8)	132 → 77(10)	50~500	0.9965	1.8	5.9	104.3 (7.9)	109.5 (8.3)	113.3 (5.6)
126	Coumaphos	56.63	19	362 → 109(20)	263 → 210(16)	1~500	0.9986	1.0	3.3	86.9 (3.4)	109.2 (7.4)	118.3 (9.0)
127	Pyridaben	56.78	19	147 → 105(10)	147 → 132(10)	10~500	0.9956	0.8	2.7	96.6 (9.6)	88.5 (9.5)	95.4 (8.6)
128	Baytroid	61.59	20	199 → 157(10)	157 → 107(10)	10~500	0.9949	0.8	2.8	93.1 (9.5)	102.3 (6.8)	99.3 (1.4)
129	Cyfluthrin	61.72	20	208 → 181(10)	181 → 152(20)	5~500	0.9984	2.1	7.1	70.6 (11.7)	77.3 (9.6)	79.6 (5.7)
130	Cypermethrin	61.74	20	181 → 152(25)	163 → 127(5)	5~500	0.9971	0.9	2.9	78.6 (9.6)	86.3 (11.0)	76.8 (5.0)
131	cis-Permethrin	61.80	20	163 → 127(5)	183 → 153(15)	5~500	0.9925	1.5	5.1	112.2 (9.6)	94.4 (12.0)	107.0 (13.5)
132	trans-Permethrin	63.00	20	163 → 127(5)	183 → 153(15)	1~500	0.9916	1.5	5.1	112.2 (9.6)	94.4 (12.0)	107.0 (13.5)
133	Fluvalinate	67.73	20	181 → 152(19)	208 → 181(20)	50~500	0.9515	0.9	3.1	89.0 (8.6)	95.3 (9.6)	97.1 (8.4)
134	Fenvalerate	68.40	20	157 → 107(10)	419 → 167(10)	5~500	0.9934	1.4	4.6	110.7 (6.1)	96.5 (9.7)	112.6 (12.6)
135	Flumioxazin	67.75	20	354 → 312(12)	354 → 326(10)	50~500	0.9992	1.2	4.1	107.7 (9.3)	109.4 (11.2)	116.7 (9.3)
136	Difenoconazole	72.41	21	265 → 139(25)	325 → 265(15)	50~500	0.9922	1.7	5.8	108.6 (9.6)	103.9 (9.8)	114.8 (5.2)
137	Deltamethrin	73.08	21	253 → 93(15)	253 → 172(10)	20~500	0.9002	1.0	3.3	85.3 (10.6)	91.0 (11.8)	87.9 (7.1)

RSD(%) = relative standard deviation, (standard deviation/mean) × 100%

Segment time segment, *Q1* the precursor ion of each analyte, *Q3* the corresponding product ion of each analyte, *CE* collision energy, *LOD* limit of detection, *LOQ* limit of quantitation

[a] Correlation coefficient of linear eq. (X = concentration of the respective compounds; Y = peak area)

[b] Intra-lab recovery and precision of three spiked concentrations. The results are mean values of six replicate recoveries at each concentration

[c] Less than LOQ

Table 2 Concentrations of pesticides in the blood plasma of humans from Beijing (ng/mL)

Type	No.	Name	Gender	LOD	*N* > LOD	DR(%)	Mean ± SD	Median	Range	P (gender difference)	Spearman's rho coefficient	Spearman's P
OCPs	1	Pentachlorobenzene	Female	0.9	8	15.4	0.26 ± 0.62	<LOD	1.43–2.25	0.256	0.163	0.105
			Male		4	8.3	0.13 ± 0.44	<LOD	1.43–1.73			
	2	Hexachlorobenzene	Female	1.7	52	100.0	2.22 ± 0.64	2.06	1.74–6.01	0.102	−0.104	0.305
			Male		47	97.9	2.24 ± 0.55	2.19	1.84–3.83			
	3	Quintozene	Female	0.9	51	98.1	3.39 ± 1.34	2.92	2.67–10.56	0.111	*0.200*	*0.046*
			Male		44	91.7	3.92 ± 7.81	2.87	2.66–56.48			
	4	α-BHC	Female	1.0	50	96.2	3.70 ± 0.84	3.74	3.37–5.03	0.091	0.079	0.436
			Male		46	95.8	3.59 ± 0.83	3.64	3.35–5.36			
	5	β-BHC	Female	1.0	39	75.0	3.23 ± 2.84	2.85	2.46–14.19	0.189	*0.277*	*0.005*
			Male		35	72.9	2.40 ± 1.64	2.65	2.45–5.11			
	6	γ-BHC	Female	1.3	34	65.4	2.34 ± 1.74	3.38	3.25–6.59	0.983	0.167	0.098
			Male		38	79.2	2.84 ± 1.57	3.37	3.28–6.59			
	7	δ-BHC	Female	1.1	6	11.5	0.64 ± 1.78	<LOD	5.09–7.65	0.296	−0.030	0.768
			Male		9	18.8	1.07 ± 2.27	<LOD	5.09–7.65			
	8	p,p′-DDE	Female	1.0	51	98.1	5.19 ± 2.34	4.41	2.85–13.36	0.664	*0.211*	*0.035*
			Male		45	93.8	4.57 ± 1.78	4.35	2.85–8.49			
	9	p,p′-DDD	Female	1.1	9	17.3	0.73 ± 1.72	<LOD	3.29–24.37	0.160	0.021	0.832
			Male		14	29.2	1.45 ± 3.72	<LOD	3.29–24.37			
	10	p,p′-DDT	Female	1.0	7	13.5	2.52 ± 7.37	<LOD	9.55–82.14	0.257	0.075	0.456
			Male		3	6.3	2.53 ± 12.45	<LOD	14.91–82.14			
	11	o,p′-DDE	Female	0.9	4	7.7	0.24 ± 0.87	<LOD	2.40–4.64	0.930	0.066	0.512
			Male		4	8.3	0.22 ± 0.73	<LOD	2.40–2.69			
	12	o,p′-DDT	Female	1.5	1	1.9	0.14 ± 1.02	<LOD	7.36–7.36	0.377	−0.164	0.104
			Male		0	0.0	0.00 ± 0.00	<LOD	0.00			
	13	Isodrin	Female	0.9	8	15.4	0.49 ± 1.30	<LOD	2.44–6.99	0.628	0.105	0.300
			Male		9	18.8	0.54 ± 1.15	<LOD	2.47–3.90			
	14	Heptachlor	Female	1.3	14	26.9	0.73 ± 1.24	<LOD	2.12–3.82	0.767	−0.014	0.888
			Male		14	29.2	0.80 ± 1.27	<LOD	2.18–3.82			
	15	α-Endosulfan	Female	1.0	16	30.8	0.79 ± 1.20	<LOD	2.43–7.43	0.572	0.034	0.738
			Male		11	22.9	0.72 ± 1.50	<LOD	2.46–7.43			
	16	β-Endosulfan	Female	1.1	3	5.8	0.24 ± 1.07	<LOD	2.96–6.62	0.640	0.066	0.515
			Male		4	8.3	0.25 ± 0.84	<LOD	2.96–3.18			
	17	cis-Chlordane	Female	1.6	16	30.8	1.17 ± 1.78	<LOD	3.34–6.78	0.499	−0.079	0.434
			Male		17	35.4	1.43 ± 2.01	<LOD	3.40–6.78			
	18	trans-Chlordane	Female	1.2	3	5.8	0.26 ± 1.07	<LOD	3.67–5.44	0.640	0.040	0.690
			Male		4	8.3	0.36 ± 1.23	<LOD	3.76–5.09			
	19	Propanil	Female	0.9	3	5.8	0.50 ± 2.34	<LOD	3.67–15.09	0.674	−0.086	0.396

Table 2 (continued)

Type	No.	Name	Gender	LOD	$N>$ LOD	DR(%)	Mean ± SD	Median	Range	P (gender difference)	Spearman's rho coefficient	Spearman's P
			Male		4	8.3	0.36 ± 1.21	<LOD	3.67–5.50			
	20	Vinclozolin	Female	0.8	18	34.6	1.62 ± 2.63	<LOD	3.27–13.51	0.569	0.101	0.317
			Male		18	37.5	1.67 ± 2.24	<LOD	3.39–6.31			
	21	Dicofol	Female	1.2	0	0.0	0.00 ± 0.00	<LOD	0.00	0.298	−0.127	0.207
			Male		1	2.1	0.04 ± 0.26	<LOD	1.82			
	22	Methoxychlor	Female	1.1	0	0.0	0.00 ± 0.00	<LOD	0.00	0.298	−0.169	0.093
			Male		1	2.1	0.14 ± 0.96	<LOD	6.66			
	23	Dieldrin	Female	1.0	3	5.8	0.46 ± 1.88	<LOD	5.57–12.04	0.900	0.041	0.688
			Male		3	6.3	0.57 ± 2.31	<LOD	5.57–12.04			
	24	Endrin	Female	1.0	14	26.9	1.57 ± 2.69	<LOD	4.69–8.20	0.788	−0.095	0.349
			Male		12	25.0	1.40 ± 2.50	<LOD	4.77–7.51			
PPs	25	Bifenthrin	Female	0.9	5	9.6	0.22 ± 0.71	<LOD	0.93–3.39	0.770	0.071	0.481
			Male		6	12.5	0.15 ± 0.42	<LOD	0.93–1.59			
	26	Tetramethrin	Female	1.0	3	5.8	0.78 ± 3.72	<LOD	2.68–23.36	0.366	0.044	0.665
			Male		1	2.1	0.49 ± 3.37	<LOD	23.36			
	27	Fenpropathrin	Female	1.0	2	3.8	0.04 ± 0.22	<LOD	1.07–1.16	0.172	−0.033	0.741
			Male		0	0.0	0.00 ± 0.00	<LOD	0.00			
	28	Cyfluthrin	Female	2.1	1	1.9	0.09 ± 0.67	<LOD	2.48–4.86	0.513	0.015	0.881
			Male		3	6.3	0.08 ± 0.42	<LOD	2.48–3.55			
	29	Deltamethrin	Female	1.0	0	0.0	0.00 ± 0.00	<LOD	0.00	0.139	0.074	0.465
			Male		2	4.2	0.63 ± 3.07	<LOD	12.75–17.34			
OPPs	30	Terbufos	Female	0.8	0	0.0	0.07 ± 0.02	<LOD	0.00	0.214	−0.087	0.389
			Male		1	2.1	0.28 ± 1.91	<LOD	0.00			
	31	Methyl-parathion	Female	0.9	2	3.8	0.42 ± 2.13	<LOD	6.04–11.81	0.968	0.082	0.420
			Male		2	4.2	0.32 ± 1.56	<LOD	6.04–9.10			
	32	Parathion-ethyl	Female	0.4	1	1.9	0.03 ± 0.22	<LOD	1.61–2.28	0.943	0.096	0.343
			Male		1	2.1	0.05 ± 0.33	<LOD	2.28			
	33	Methidathion	Female	1.1	3	5.8	0.96 ± 3.70	<LOD	5.13–23.25	0.278	0.000	0.995
			Male		2	4.2	0.34 ± 1.75	<LOD	5.13–11.07			
	34	Phosalone	Female	0.9	1	1.9	0.04 ± 0.30	<LOD	2.13–2.13	0.337	0.152	0.132
			Male		0	0.0	0.00 ± 0.00	<LOD	0.00			
	35	Coumaphos	Female	1.0	1	1.9	0.03 ± 1.99	<LOD	1.39–2.61	0.286	−0.010	0.919
			Male		2	4.2	0.18 ± 0.71	<LOD	1.39–2.61			

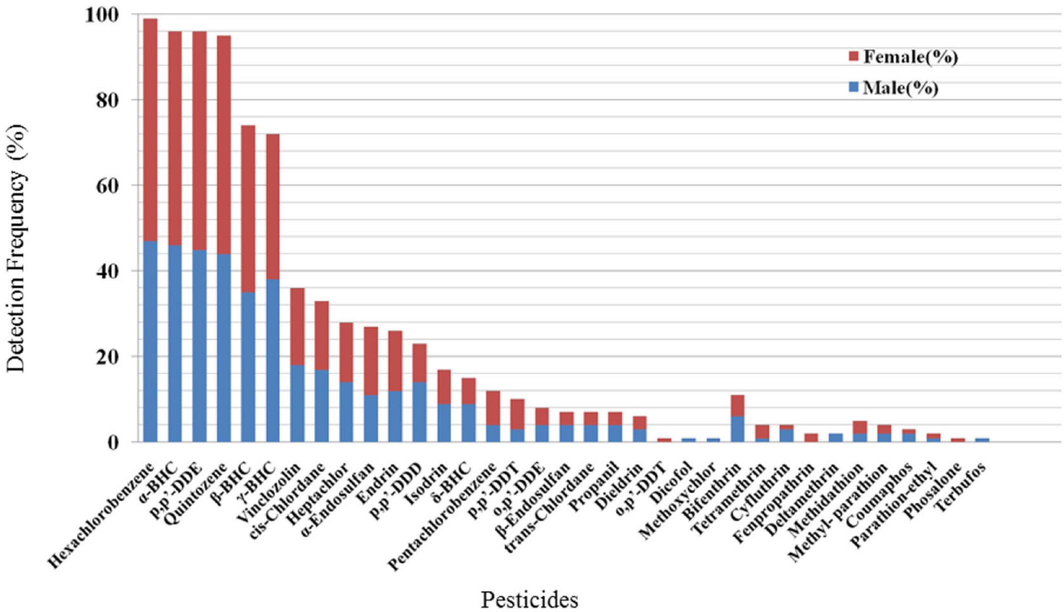

Fig. 1 Gender comparisons of the detection frequency of 35 positive pesticides in 100 plasma samples of a general population

concentrations. The limits of detection (LODs) were calculated using an S/N of 3, and the results were between 0.4 and 21.6 ng/mL. The limits of quantification (LOQs) were calculated using an S/N of 10, and the results were between 1.4 and 71.9 ng/mL. The accuracy of the full methodology was evaluated by recovery experiments, which were implemented using additive concentrations at three levels: 10, 50 and 200 ng/mL. Meanwhile, the precision of the method was determined using six replicates at each concentration and expressed using the relative standard deviations (*RSDs*). As shown in Table 1, the recovery results of most pesticides ranged from 70 to 120%, and the RSD results ranged from 0.6 to 20.0%. Because of the acceptable method validation results, it is clear that the method established in this paper is exact and reliable based on the European Council, Document No.SANCO 825/00 (European Commission, 2010).

Concentrations of pesticides in blood plasma

The 100 plasma samples were analysed with GC-MS/MS for the residues of organochlorine pesticides and organophosphorus, carbamate, and pyrethroid insecticides. The results are shown in Table 2. In total, 24 organochlorine pesticides, 5 pyrethroid pesticides and 6 organophosphorus pesticides were detected with detection rates between 1.0 and 99.0%. The detection frequency of 35 positive pesticides is shown in Fig. 1. Most of the positive OCPs were persistent organic pollutants. HCB, α-HCH, β-HCH, γ-HCH, p,p′-DDE and quintozene were measured at ratios of 99, 96, 74, 72, 96 and 95%, respectively. In the present study, the concentrations of HCB ranged from 1.74 to 6.01 ng/mL. The plasma levels of α-HCH, β-HCH, γ-HCH and δ-HCH ranged from 3.35 to 5.36, from 2.45 to 14.19, from 3.25 to 6.59 and from 5.09 to 7.65 with a mean of 3.65, 2.83, 2.58 and 0.84 ng/mL, respectively. Among the four analysed HCH isomers (α-, β-, γ- and δ-HCH), it was obvious that α-HCH was the most common isomer, and this finding was inconsistent with a former study (Zamir et al., 2009; Freire et al., 2014; Caba et al., 2015). For the DDT isomers (p,p′-DDT, o,p′-DDT, p,p′-DDE, o,p′-DDE and p,p′-DDD), p,p′-DDE was the most abundant, which was consistent with previous results (Bedi et al., 2015; Koureas et al., 2016). The concentrations of p,p′-DDE ranged from 2.85 to 13.36 ng/mL with a mean of 4.89 ng/mL. The concentrations of quintozene and aldrin were in the range of 3.35 to 5.36 and 2.66 to 56.48 ng/mL, respectively. Compared with organochlorine pesticides, the detection rates of organophosphorus and pyrethroid pesticides were much lower. Bifenthrin, tetramethrin, fenpropathrin, cyfluthrin and deltamethrin were detected at rates of 11, 4, 2, 4 and 2%, respectively. The concentrations of bifenthrin ranged from 0.93 to 3.39 ng/mL. Positive OPPs included terbufos, methyl-

Table 3 The concentrations of DDTs, HCHs and hexachlorobenzene in human blood from different countries or regions (ng/g lw or ng/mL)

Region	Samples	Sample size	∑HCHs			∑DDTs			HCB			Reference
			Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	
Beijing	Plasma	100	3.58–22.12	9.79	9.9	2.85–112.2	4.85	8.79	1.74–6.01	2.12	2.24	The present study
Hong Kong	Plasma	117	115–1616	574	578	177–8842	901	1290	–	–	–	Wang et al.(2013)
Korea	Serum	1904	–	–	–	6.61–2800.75	–	32.04	2.10–99.80	–	1.74	Kim et al.(2013)
Sweden	Serum	246	–	–	–	–	–	–	0.015–0.780	0.170	0.136	Bjermo et al.(2013)
Tunisia	Serum	113	–	22.7	40.4	59.7–994.6	166.1	213.1	–	39.3	49.1	Hassine et al. (2014)
Mexico	Serum	150	200-27,400	3100	4900	1.4–155.2	10.7	18.2	–	–	–	Waliszewski et al.(2012)
Spain	Umbilical cord serum	318	–	–	–	–	–	–	–	2.24	2.93	Mariscal-Arcas et al. (2010)
Spain	Serum	953	–	–	–	–	–	–	–	462.5	379	Jakszyn et al.(2009)
Poland	Maternal serum	18	–	–	–	32–1004	364	401	4.2–40.7	15.1	18.8	Jaraczewska et al.(2006)
	Umbilical cord serum	17	–	–	–	45.5–93.4	341	385	6.7–45.9	18.4	21.0	
UK	Serum	154	1.3–2600	100	–	–	/	/	5.4–72	14	–	Thomas et al.(2006)
India	Blood	18	22.55-91.06	37.77	41.23	21.17–54.47	29.63	32.61	0.13–0.27	0.21	0.2	Bhatnagar et al.(2004)
Romania	Serum	142	177-12,180	1114	–	446–36,930	2420	–	2.0–107	30	–	Dirtu et al.(2006)
French	Serum	386	–	–	–	–	–	–	–	22.8	24.3	Saoudi et al.(2014)
Western and Central African countries	Serum	575	–	1	–	–	294	–	–	–	–	Luzardo et al.(2014)
China	Maternal serum	81	–	–	–	1.54–3234.94	266.75	245.82	0.09–642.94	74.84	70.62	Guo et al.(2014)
Spain	Serum	135	132-9071	957	1291	–	3166	4896	–	–	–	Porta et al.(2008)

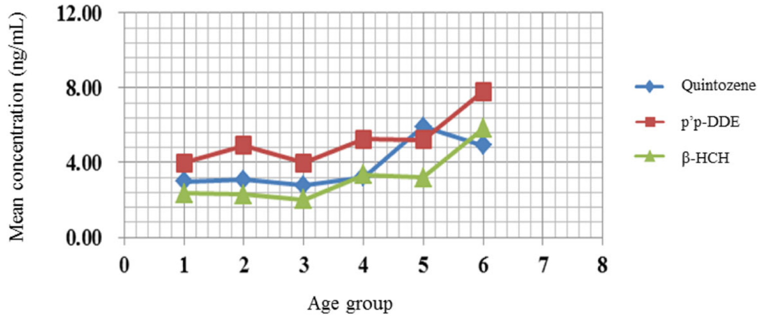

Fig. 2 Increasing trends of quintozene, p,p′-DDE and β-HCH concentrations with age in human plasma from a general population. Age groups: 1.17–29 ($n = 17$), 2.30–39 ($n = 21$), 3.40–49 ($n = 26$),4.50–59 ($n = 24$), 5.60–69 ($n = 8$), 6. ≥ 70 ($n = 4$)

parathion, parathion-ethyl, methidathion, phosalone and coumaphos with detection rates lower than 5%. The concentrations of parathion-ethyl (1.61–2.28 ng/mL) were much lower than those reported in previous studies with a mean of 2900 ng/mL (Park et al., 2009), which represented acute fatality cases. The observed trends for the total DDT, HCH and HCB were comparatively lower than those from earlier reports; see Table 3.

– no detail information mentioned

Pesticide distribution by gender and age

On the basis of the gender and age groups, the results of 100 plasma samples were categorised and interpreted. According to the determined frequency and concentration, a comparison of the results for a total of 35 pesticides was performed. The gender comparisons of the detection frequency of 35 pesticides are illustrated in Fig. 1 and Table 2. Previous research indicated that the concentrations of several OCPs, such as α-HCH, β-HCH, γ-HCH, aldrin, heptachlor, o,p′-DDE and p,p′-DDE, were observably higher in males than those in females (Wang et al., 2013). However, the present study found no statistically significant difference between men and women with regard to the pesticide concentration ($p > 0.05$) based on the Mann-Whitney tests.

The correlations between age and pesticide concentration were evaluated using the Spearman chi-squared test. Spearman rho coefficients and p values are shown in Table 2. Consistent with the trend of increasing β-HCH, p,p′-DDE and quintozene concentrations with age (Fig. 2), strong correlations between age and the concentrations of β-BHC, p,p′-DDE and quintozene were observed. Plasma quintozene concentration and age were positively correlated (Spearman' rho = 0.200, $p < 0.05$). Plasma β-HCH concentration and age were positively correlated (Spearman' rho = 0.277, $p < 0.05$). Plasma p,p′-DDE concentration and age were positively correlated (Spearman' rho = 0.211, $p < 0.05$). These results indicated that plasma β-HCH, p,p′-DDE and quintozene concentrations increased with age, which was consistent with previous results (Jakszyn et al. 2009). The reason of this phenomenon might be that the older had a greater chance for high levels of exposure to these persistent chemicals, whereas they also had a longer time to accumulate these chemicals in their body.

Conclusion

The data presented in this study indicated low exposure of the general population in Beijing to pesticides in comparison to human populations in other countries. No statistically significant difference in the gender-related concentrations was found. Consistent with the trend of the increasing β-HCH, p,p′-DDE and quintozene concentrations with age, strong correlations between age and concentrations of β-BHC, p,p′-DDE and quintozene were observed. A limitation associated with this study was the small sample size. Further research into the specific sources and routes of exposure is warranted.

Acknowledgements We thank Dr. Wu Wei who works at the Peking Union Medical College Hospital for providing us with the blood samples. Gratitude is also expressed to all the donors who collaborated with the study and provided blood samples.

Funding This study was funded by the China Food and Drug Administration; the Item Number was ZG2016–2.

Compliance with ethical standards

Ethics approval for this study was granted by The Ethics Committee of the Peking Union Medical College (PUMC).

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