CONCENTRATIONS OF ORGANOCHLORINE PESTICIDES IN MALE SERUM FROM KOREA

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Abstract
Concentrations of 22 organochlorine pesticides (OCPs) were measured in the human serum samples taken from 40 males in Korea. The serum samples were obtained in 2005-2006 and ages of donor ranged between 27 years and 69 years. OCPs were determined using isotope dilution method with GC/HRMS to provide more reliable serum concentrations. Out of 22 OCPs, β-HCH, HCB, heptachlor expoxide, oxychlordane, and *p,p'*-DDE were detected in all serum samples. General trend of increasing concentration with age for the *p,p'*-DDE, heptachlor expoxide, and oxychlordane which are metabolites of parent pesticides was found. Serum concentrations of organochlorine pesticide in Korea were similar to the concentration from US and UK, but were lower than some other studies.

Introduction
Organochlorine pesticides (OCPs) have been widely used all over the world as agricultural and domestic pesticides. Most of OCPs are listed as United Nations Environment Programme (UNEP) priority compound due to their ubiquity and persistence in the environment. Consequently, they are considered to be persistent organic pollutants (POPs). Nine of the OC pesticides, as well as PCBs and PCDD/Fs, were the subjects of the Stockholm convention on POPs.
In Korea most of organochlorine pesticides have been prohibited in 1970s, but they are still detected in the environment as well as human body. As a result of their ubiquity and bioaccumulation, measurable levels of organochlorine pesticides are found in large proportion of the general population[1]. The general population is exposed through diet of contaminated foods, as POPs accumulate up the food chain. However, exposure may also occur through dermal contact or inhalation of indoor and outdoor air. Some organochlorine pesticides are considered as endocrine disrupters and as carcinogens. Previous studies have shown organochlorine compounds to be related to breast cancer and diabetes.
The purpose of this study was to determine the levels of 22 organochlorine pesticides in the serum of 40 adult men living in Korea and to provide useful data on contamination in population of Korea that has not been yet studied. In order to provide precise analytical data, 22 organochlorine pesticides were measured with isotope dilution GC-HRMS using the isotope-labeled pesticides standard.

Materials and Methods
Samples
The serum samples were colleted in 2005 and 2006 from forty male volunteers whose ages were between 27 and 69 years.

Standards
All standard solutions were purchased from Cambridge Isotope Laboratories (Andover, MA). The 6-points calibration standard, ES 5348 POPs Pesticide, contained a mixture of 23 native POPs pesticides with the concentration ranging from 0.4 to 800 ng/mL and 21 ^{13}C-labeled POPs pesticides at a concentration of 20 ng/mL in nonane. The ES 5349 cleanup spike internal standard contained a mixture of the same 21 ^{13}C-labeled POPs pesticides at a concentration of 100 ng/mL in nonane. The EC 5350 syringe spike internal standard contained the ^{13}C-labeled CB-15 and CB-70 at a concentration of 100 ng/mL in nonane.

Sample preparations
Serum samples were prepared according to the procedure reported by the Centers for Disease Control and Prevention (Method No. 28)[2] with some modification. Briefly, serum samples were spiked with isotopically labeled POPs pesticides cleanup spike standard and were allowed to equilibrate. The serum samples were

denatured and diluted with an equal amount of formic acid and water. The mixtures were vortexed to ensure complete homogeneity. Samples were then extracted on the C18 SPE, where the analytes were then eluted with 16 mL of hexane. Extracts were concentrated to 1 mL and applied to a silica gel/florisil column, then eluted with hexane followed by dichloromethane/hexane (1:1 v/v). The extracts were further purified using gel permeation chromatography where a distinct fraction of elute was collected. The final purified extracts were concentrated for GC-HRMS quantification[3].

Instrumental analysis

GC-HRMS measurements were performed on a JMS-800D instrument (JEOL, Japan) interfaced with a 6890N gas chromatograph (Agilent Technologies, USA). Measurements of OCPs were carried out using a 60 m * 0.25 mm i.d. * 0.25 um film thickness DB-5MS capillary column (Agilent). The oven was programmed from 100℃ (1.0 min) to 220℃ with a ramp rate of 20℃ /min for 4.0 min and then to 300℃ with a ramp rate of 8℃ /min for 3.0 min. Splitless injections were carried out with an injector temperature of 260℃. The source temperature was 280℃ in the electron impact mode using a filament bias of 38 eV. Data were acquired in the single ion monitoring (SIM) with a resolution of more than 10,000.

Results and Discussion

OCP concentrations

Distribution of OCP levels in serum samples obtained from 40 men is shown in Table 1. The *p,p'*-DDE, HCB, β-HCH, heptachlore epoxide, and oxychlordane were detected in all serum samples. *trans*-Chlordane, *cis*-Chlordane, α-HCH, γ-HCH, δ-HCH, and aldrin were not detected in any of the samples analyzed. The *p,p'*-DDE was the predominant residue in serum. Our observations are consistent with the results reported by UK[4] and US[1]. The most persistent or metabolized form of pesticides was detected in human serum. The median concentration of *p,p'*-DDE was 244 ng/g lipid which was between the median concentration found in serum taken from UK and from US. However, the *p,p'*-DDE concentrations were approximately four-fold lower than the concentrations found in the New Zealand[5]. Among four HCH isomers, only β-HCH was detected in serum samples of this study because of its longer half-life of 7 years in blood.

Relationship between donor age and OCPs concentrations

The *p,p'*-DDE, heptachlor epoxide, and oxychlordane showed a tendency to increase concentration with age, but age related increase was not observed with HCB and β-HCH.

DDT/DDE ratio

In all samples, the *p,p'*-DDE concentration exceeded the *p,p'*-DDT concentration, indicating that exposure to the DDT pesticides was either indirect or historical. The DDT/DDE ratio in this study was low ranging from 0.008 to 0.172, even though the mean DDT/DDE ratio in this study was higher than the value from UK and US. When the DDT/DDE ratio was analyzed by age, higher levels were found in the group below 55 than the group aged above 55.

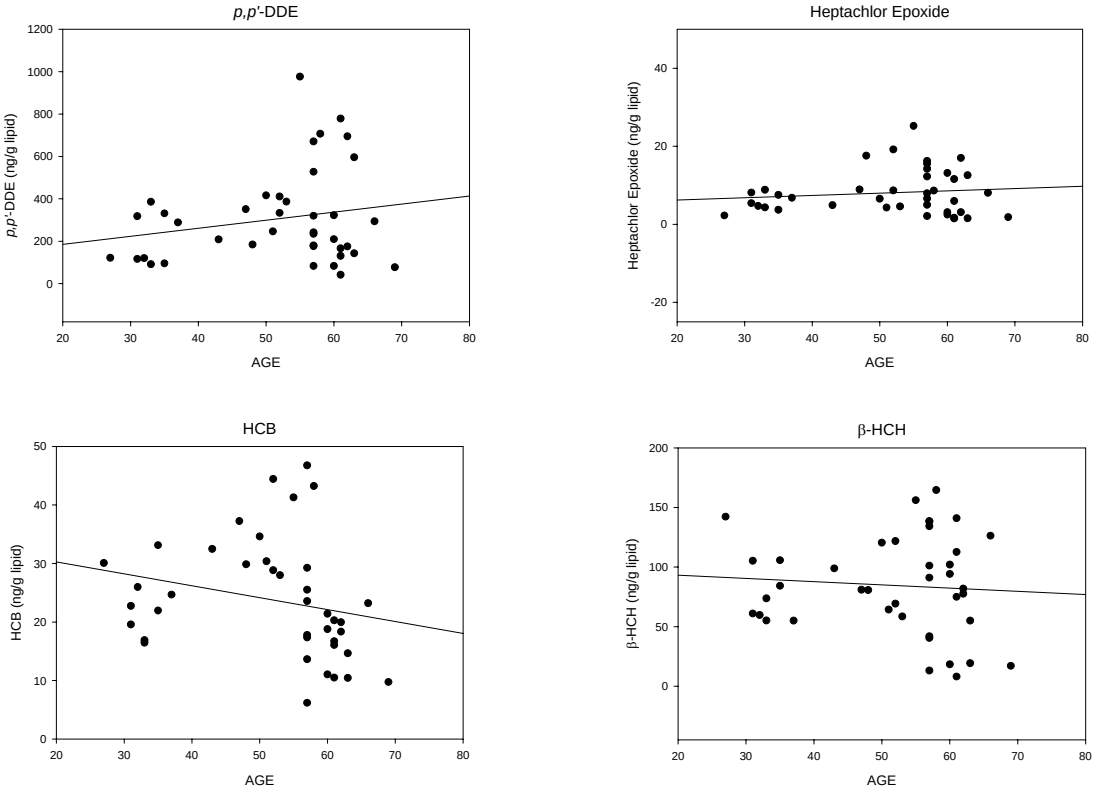
In conclusion, this study provides the concentrations of UNEP priority OCPs in 40 males in Korea. The OCP concentrations were determined using isotope dilution GC/HRMS method. The data provide a baseline for investigation of trends and for international comparisons. We also consider this data will be applied to other research for human diseases related to OCPs levels.

Table 1. Mean, Median, Min and Max concentrations of OCPs in serum. (ng/g lipid)

Compound	Mean	Median	Min	Max	N[a]	Frequency (%)
α-HCH	ND	ND	0	0	0	0
β-HCH	84.6	81.4	8.07	165	40	100
δ-HCH	ND	ND	0	0	0	0
γ-HCH	ND	ND	0	0	0	0
HCB	23.8	22.4	6.18	46.8	40	100
Heptachlor	ND	ND	0	0	0	0
Heptachlor Epoxide	8.08	6.68	1.47	25.2	40	100
Aldrin	ND	ND	0	0	0	0
Dieldrin	3.56	2.60	1.67	8.4	11	27.5
Endrin	ND	ND	0	0	0	0
Oxychlordane	6.67	5.59	1.72	17.4	40	100
t-Chlordane	ND	ND	0	0	0	0
c-Chlordane	ND	ND	0	0	0	0
t-Nonachlor	12.05	10.02	3.24	37.0	33	82.5
c-Nonachlor	2.51	1.18	0.508	9.18	14	35
o,p'-DDE	1.96	1.53	0.436	8.76	31	77.5
p,p'-DDE	306	244	41.9	976	40	100
o,p'-DDD	0.567	0.411	0.254	1.43	10	25
p,p'-DDD	4.31	3.20	1.19	18.5	31	77.5
o,p'-DDT	4.00	3.35	0.692	12.7	29	72.5
p,p'-DDT	21.2	16.5	6.25	52.5	32	80
Mirex	2.16	1.65	0.644	5.60	13	32.5

[a] Number of samples with concentration above LOD (out of 40)
ND = not detected (concentrations below LOD)

Fig. 1. Concentration of selected chemicals plotted against age.



Acknowledgements
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