

DETERMINATION OF ORGANOCHLORINATED PESTICIDE AND POLYCHLORINATED BIPHENYL CONGENERS RESIDUES IN CHICKEN EGGS BY GAS CHROMATOGRAPHY

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ABSTRACT

The aim of this study was to determine the concentrations of organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) congeners in chicken eggs obtained from various locations in Turkey by gas chromatography and validation of the results using different detector systems (MS, MS/MS and ECD). In total, eighteen OCP and PCB compounds were analysed in hundred egg samples. Only β -HCH, 4,4-DDE and PCB138 were found in nine egg samples at concentrations of 5.1-7.2 $\mu\text{g}/\text{kg}$, 8.4-30 $\mu\text{g}/\text{kg}$ and 4.2 $\mu\text{g}/\text{kg}$ respectively. The detected concentrations of these compounds were found to be lower than the maximum residue levels (MRLs) set by EU. The recoveries, relative standard deviations (RSD), limit of detection (LOD) and limit of quantification (LOQ) were found in the range of 83-111%, 0.9-14.1%, 1.2-3.5 $\mu\text{g}/\text{kg}$ and 0.3-10.0 $\mu\text{g}/\text{kg}$ respectively.

Keywords: Organochlorinated pesticides, Polychlorinated biphenyls, Chicken egg, Gas chromatography

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Introduction

Environmental contamination of persistent organic compounds (POPs) has been widely reported and documented (Virgínia C Fernandes et al., 2011; Ritter et al., 1995). Polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) are semi volatile, ubiquitous compounds and resistant to biochemical and physical degradation mechanisms (Mansilha et al., 2010; Ritter et al., 1995). They can be accumulated in adipose tissues and fat layers of organisms due to their lipophylic structure (Ritter et al., 1995; Vallack et al., 1998). Exposure to these compounds may lead to cancer formation, neurotoxic disorders, reproductive and behavioral adverse effects (Mansilha et al., 2010). Since these compounds can be accumulated in fat, they can be delivered through foods having certain amount of fat to the human beings (Bernhoft et al., 1997; Polder et al., 2016). They can still be found in the environment and in food materials at levels that may cause harmful effects on human health (such as disruption of hormonal activity) due to their persistent and lipophylic nature despite the production and use of these toxic substances have been banned or restricted in most countries since early 1970s (Virgínia C Fernandes et al., 2011). It has been reported that residual distribution of these pollutants such as dichlorodiphenyltrichloroethane (DDT), PCBs, dieldrin, chlordane, hexachlorobenzene (HCB) and hexachlorohexanes (HCH) are widely found in foods containing fat (Jeong et al., 2014; Liu et al., 2007). Some studies have revealed their occurrence in dairy products such as cheese, milk, butter, yoghurt (Keikotlhaile et al., 2010; Salem et al., 2009) and in human milk (Çok et al., 2011; Nasir et al., 1998) as well. Substances reported to be found in these foods include HCHs, DDTs and endosulfan.

Exposure to OCPs and PCBs and accumulation in the adipose tissues occurs through the food chain contamination and environmental pollution (Ahmad et al., 2010). Pesticide contamination from pesticide containing feeds to chicken meat and egg has been reported (Aulakh et al., 2006; Kilic et al., 2011; Olanca et al., 2014; Tao et al., 2009). OCP residues in feed material ingested by chickens and therefore results in the occurrence in meat tissues and eggs which are then consumed by consumers. Due to their lipophylic structure, they tend to be accumulated in body tissues. According to some researchers, the proportions of intake of DDTs and HCHs into the body through inhalation and dermal contact are 5.1% and 13.5% of the total intakes respectively, Ingestion through diet was reported as around 94.9% of the total (Kilic et al., 2011).

Chicken egg, and chicken meat tend to be the most popular food items in many countries. However, these food materials are reported as main sources of OCPs by researchers

worldwide (Aulakh et al., 2006; Darko & Acquah, 2007; Fontcuberta et al., 2008) due to their significant amount of fat components. Therefore, regular screening of these foodstuffs is necessary to inform both the consumers and traders to increase the level of awareness. Although the contamination and toxicity of OCPs and PCBs have been extensively investigated in many developed countries, very few studies are available in the literature on OCP and PCB levels in foods in Turkey (Kilic et al., 2011). Thus, this work was carried out to investigate the degree of contamination with HCH-isomers, heptachlor, aldrin, dieldrin, heptachlorobenzene, total DDT and polychlorinated biphenyls (PCBs) congener's residues in chicken eggs.

The maximum residue levels (MRLs) for pesticide residues in various foodstuff permitted in the EU are given in respective legislations. The MRLs in Turkish legislation are the same as in EU legislation. The MRLs for OCP and PCB compounds investigated in this study were set as varied from 10 to 50 µg/kg for different compounds (Table 1) (EC 2005; 2008; 2011; Turkish Legislation 2011).

Table 1. MRL values set by EU

Compound Name	MRL (µg/kg)	EC regulation No
Aldrin	20	Reg. (EC) No 839/2008
α-HCH	20	Reg. (EC) No 149/2008
β-HCH	10	Reg. (EC) No 149/2008
γ-HCH (lindane)	10	Reg. (EC) No 149/2008
Dieldrin	20	Reg. (EC) No 839/2008
Heptachlor	20	Reg. (EC) No 149/2008
HCB	20	Reg. (EC) No 149/2008
Sum of DDT and DDE	50	Reg. (EC) No 149/2008
Biphenyl	10	Reg. (EU) No 978/2011

The occurrence and level of POPs in various food materials has been studied using different analysis methods (Barriada-Pereira et al., 2005; Bolanos et al., 2007; Cortes-Aguado et al., 2008; Wong et al., 2010). However, little information about comparison of detection capacities and limits of GC system coupled with different detectors for these substances has been found in the literature (Fernandes et al. 2012; Olanca et al. 2014). In this work GC method using ECD, MS and MS/MS detector systems have been used for determination of PCB and OCP residues in hundred egg samples obtained from different regions of Turkey. The results obtained from different detector systems have been elucidated and discussed.

Materials and Methods

Chemicals, Reagents and Standards

OCPs and PCBs standards [Aldrin, dieldrin, hexachlorobenzene (HCB), α -hexachlorocyclohexane (α -HCH), β -heptachlorosikloheksan (β -HCH), γ -heptachlorosikloheksan (γ -HCH), heptachlor, 4,4-dichlorodipenyldichloroethylene (4,4DDE), 2,4-dichlorodipenyldichloroethane (2,4DDT), 4,4-dichlorodipenyldichloroethane (4,4DDD), 4,4 dichlorodipenyldichloroethane (4,4 DDT), 2,4,4'-Trichlorobiphenyl (PCB28), 2,4,6-Trichlorobiphenyl (PCB30), 2,2',5,5'-Tetrachlorobiphenyl (PCB52), 2,2',4,5,5'-Pentachlorobiphenyl (PCB101), 2,2',3,4,4',5'-Hexachlorobiphenyl (PCB138), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB153), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB180), 2,2',3,3',4,5,5',6-Octachlorobiphenyl (PCB198)] were obtained from Dr. Ehrenstrofer GmbH (Ausburg, Germany). Isooctane secondary and working calibration standard solutions of OCPs and PCBs were prepared to spike egg samples to the required concentrations. Working solutions were prepared in isooctane at 1000 mg/L. PCB 198 (1000 mg/L in isooctane) purchased as internal standard (IS).

The solvents used (isooctane, petrol ether, and acetone) were pesticide residue analysis grade, obtained from Merck&Co., Inc. (Kenilworth, N.J., U.S.A). The absorptive materials used in our study were silica gel (60-70 mesh) and alimuna purchased from Merck&Co., Inc. (Kenilworth, N.J., U.S.A). Silica and alumina were activated after drying at 200°C for 15 h prior to use.

Silanized glass wool (research grade), provided by Serva (Heidelberg, Germany) was used to plug the matrix solid-phase dispersion (MSPD) column. Anhydrous sodium sulphate (pro-analysis) were obtained from Merck&Co., Inc. (Kenilworth, N.J., U.S.A).

Eggs

100 egg samples were collected from local shops and supermarkets in different locations of Turkey (Table 2) representing various production areas from various regions.

Instruments

GC-ECD chromatographic analysis of OCPs and PCBs was performed using Shimadzu 14A gas chromatography (Kyoto, Japan) equipped with a ^{63}Ni electron capture detector (ECD). Analytes were separated with Zebron ZB-35 column (30x0.50 μm x0.25mm) containing 5% phenylmethylpolysiloxane with phase thickness of 0.25 μm (Phenomex, U.S.A). The temperature program used for the analysis was: from 50 °C (3 min) to 170 °C (0 min), and to 290°C (3 min) at 4 °C/min. The injector was set to 270 °C in the

split mode. Helium was carrier at 2 mL/min and nitrogen was used at the make-up gas pressure 75 kPa. Identification of peaks was based on comparison of the retention times of compounds in the standard solutions. Quantification of the analyzed compounds was performed using the internal standard and the GC/MS system.

Table 2. The regions where the egg samples collected

Region	City	Number of samples collected
Black Sea Region	Samsun	5
Central Anatolia	Karaman	10
Central Anatolia	Ankara	5
Central Anatolia	Çorum	5
Central Anatolia	Kayseri	10
Central Anatolia	Yozgat	3
Egean Region	Afyon	9
Egean Region	Denizli	7
Egean Region	İzmir	8
Egean Region	Manisa	5
Marmara Region	Balikesir	10
Marmara Region	Bursa	7
Marmara Region	İstanbul	10
Marmara Region	Kırklareli	3
Marmara Region	Sakarya	3

GC/MS chromatographic analysis of OCPs and PCBs was done using Thermo DSQ GC/MS instrument (Austin, Texas, U.S.A), equipped with ZB-35 column. Helium was used as the carrier at 1.5 mL/min. The ion source and transfer were kept 280 °C respectively. Electron impact ionization mode with 70 eV electron energy was selected. The screening analysis was performed in the selected-ion monitoring (SIM) mode monitoring at least two characteristic ion for each compound. In some experiments and for confirmation purpose, scan acquisition mode (m/z 50-450) was used. The oven programme was the same as applied for GC-ECD analysis.

GC-MS/MS analysis was done using Thermo Finnigan Polaris Q Ion Trap instrument (San Jose, CA, USA). The oven programme was the same as applied for GC-ECD analysis. Ion source temperature was set to 250 °C, and transfer line temperature to 280 °C. Emission current was 250 μA at SIM mode, and multiplier voltage was 1500 V.

Solid Phase Preperation for Clean-up

100 parts by weight of alumina to 8.8 parts of water was added and shaken until the clumpings disappeared. It was kept for 24 hours in the dark at room temperature to equilibrate the final water content at 9 % (Hogendoom and Goewie, 1998). 5.1 grams of silica gel (70-230 mesh) (Merck, Kenilworth, N.J., U.S.A) was weighed and held at 200 °C for about 15 hours (overnight) in an oven. Then it was placed in the desiccator until cooling to the room temperature.

Sample Preparation

Sample preparation was done according to the method given elsewhere (Valsamaki et al., 2006). The samples were taken to the laboratory and homogenized using a blender. 20g of homogenized sample was taken into a centrifuge tube before adding 30 mL diethylether. Then the mixture was vortexed for 30 seconds. The tube containing mixture was centrifuged at 4000 rpm for 10 minutes. Diethylether phase was separated and dried under nitrogen gas flow at 40°C. The remaining oil part was then passed through alumina and silica gel columns for cleaning-up.

Extraction and Clean-up

10 µg/kg of standart solution which was prepared using selected OCPs and PCBs was spiked into 1 g of oil extracted from egg sample. 2 mL of petroleum ether was added and vortexed for 30 seconds before transferring into the columns

containing varied amounts of alumina/silica and alumina/florisil mixes (4 g alumina/5 g silica, 4 g alumina/5 g florisil, 8 g alumina/10 g silica, 8 g alumina/10 g florisil). The elutions were mixed with 1 mL of hexane and analysed using GC-ECD and GC-MS.

Validation

The analytical method developed for determination of PCBs and OCPs in chicken egg samples was validated according to the EU Decision 2002/657/EC by using GC-ECD and GC-MS. For this purpose, selectivity, specificity, linearity, precision (intra-day and inter-day reproducibility) accuracy were determined. Also in GC-MS/MS recovery was studied for confirmation of three instruments RSDs.

Results and Discussion

The tests were conducted using GC-ECD and GC-MS in three replicates and % recoveries were calculated as given in Table 3. According to the results obtained from GC-ECD analysis, it can be stated that using 8 g alumina/10 g silica and 8 g alumina/10 g florisil columns resulted in lower % recoveries compared to 4 g alumina/5 g silica and 4 g alumina/5 g florisil columns especially for 2,4-DDT and PCBs 138, 153 and 180. The best % recoveries were obtained from both GC-ECD and GC-MS when combination of 4 g alumina/5 g silica was used in extraction and clean-up step for 24DDT, PCB153 and PCB180.

Table 3. GC-ECD and GC-MS % recoveries after clean-up process

Pesticides	GC-ECD				GC-MS	
	Recovery (%)				Recovery (%)	
	A	B	C	D	A	B
HCB	109.75	102.60	107.19	114.90	97.23	97.73
Dieldrin	106.15	89.07	83.90	102.70	92.53	114.70
24DDT	84.05	88.43	64.28	73.00	110.73	73.23
PCB28	113.35	101.50	169.80	144.63	107.70	112.40
PCB52	106.10	106.17	112.13	119.33	99.33	115.40
PCB101	98.75	95.70	91.17	94.80	101.10	113.83
PCB118	113.03	105.63	89.53	93.30	101.77	126.33
PCB138	81.53	84.30	70.00	72.03	96.87	106.63
PCB153	91.85	85.90	55.75	74.80	96.67	81.90
PCB180	118.10	106.02	73.83	100.00	91.13	59.35

A: 4 g alumina/5 g silica. B: 4 g alumina/5 g florisil. C: 8 g alumina/10 g silica. D: 8 g alumina/10 g florisil

The selectivity of the methods used was assessed by the analysis of six blank samples. No peaks of interfering compounds were observed within the intervals of the retention time of the analytes in any of these samples. Additionally, spiked samples with mix of standarts prepared at concentration of 5 µg/kg in isooctane were analysed using GC-MS. A typical chromatogram of spiked egg oil sample obtained from GC-MS is given in Figure 1.

Linearity was obtained from the triplicate injections matrix-matched calibration standard solutions at 5 levels (0.5, 10, 15 and 20 µg/kg) by using internal standard method. The correlation coefficients (r^2) were calculated in the range of 0.9564-0.9999 for GC-ECD and in the range of =0.9701-0.9994 for GC-MS.

The accuracy was evaluated by recovery tests; analyzing fortified blank samples at the same concentration levels used in the precision tests (5, 10 and 15 µg/kg in oil) for egg samples for GC-ECD and GC-MS. The accuracy and precision of the results of the method (Table 4) confirm to the values given in Decision 2002/657/EC. Thus, the mean accuracy values obtained in the recovery tests were between 86 and 116% and for intra-day (n=6) study, RSDs were obtained in the range of 1.10-15.31% and for inter-day study RSDs were obtained in the range of 2.73- 17.51% from validation results obtained using GC-ECD as given in Table 4.

The mean accuracy values obtained in the recovery tests were between 81 and 116 % and for intra-day (n=6), RSDs were obtained in the range of 0.30-7.20 and for inter-day study RSDs were obtained in the range of 1.20-10.10% from validation results obtained using GC-MS (Table 4). The precision of the method was determined in two stages: repeatability (intra-day) and intermediate precision (inter-day). Repeatability was expressed by the RSD of the results from six replicates analysed on the same day by the same analyst using the same instrument. The intermediate precision was expressed by the RSD of the results of eighteen analyses performed on three different days (n=3), six analyses/day, by the same analyst using the same instrument.

Recovery tests at 10 µg/kg concentration (n=10) was done in GC-ECD, GC-MS and GC-MS/MS systems. The mean recoveries and RSDs were given at Table 5. Recovery was obtained in the range of 70-120% and RSDs were obtained below at 20%.

GC-ECD, GC-MS and GC-MS/MS methods have been applied to hundred egg samples and the analyses of OCP and

PCB congener's residues were determined. As a result of an efficient clean-up step, the interfering substances and background noise have been eliminated. Thus, the determination of each compound has been succeeded in high accuracy and precision. Nine egg samples showed the presence of β-HCH, 4,4-DDE and PCB138. Quantification of the substances was carried out through the matrix-matched calibration curves by GC-ECD, obtained in terms of µg/kg of sample according to the recovery values given in Table 5. The highest concentration found was 30 µg/kg of 4,4-DDE in a sample obtained from Karaman. Other regions that OCP and PCB residues found in samples were Kayseri, Balikesir, and Yozgat. Other than nine egg samples, the other results were always lower than the LOD values given in Table 6. The detected amounts of β-HCH, 4,4-DDE and PCB 138 in nine egg samples were in the range of 5.1-7.2 µg/kg, 8.4-30 µg/kg and 4.2 µg/kg respectively.

The main analytical problem in chromatographic analysis of foods has been reported as the complexity of the matrix (Fugel et al., 2005) together with interfering co-extractive substances. These substances may deteriorate the chromatographic column (Garrido Frenich et al., 2006). Therefore, the analysis of OCPs and PCBs in egg samples involved a sample preparation step including a clean-up steps prior to extraction process.

The multi-residue methodology for the determination of 11 OCP and 7 PCB substances in egg samples by GC-ECD, GC-MS and GC-MS/MS using a clean-up process has been applied. Using matrix matched calibration procedure avoided matrix interference effects. Recoveries were found to be between 83% and 111%. The LOQs of substances analysed were lower than the MRL established for eggs in the European Union. In agreement with the findings of Olanca et al. (2014), the detected amounts of OCP and BCB substances found in nine egg samples were found to be lower than MRLs set by EC (EC 2005, 2008, 2011).

Chan et al. (1996) analysed 51 PBC and 17 OCP in *Tha-leichthys pacificus* oil using GC-MS and they found β-HCH, 4-4 DDE and PCB138 at the range of 5-10, 30-70, and 2-6 ng/g lipid respectively depending on the location where samples were collected. The amount of residues they have detected in fish oil samples seems lower when compared with the results of this study (from 4.2 to 30 µg/kg egg sample). The reason might be the differences in the concentration of these residues in feeding material of chicken and fish.

Table 4. Method performance of GC-ECD and GC-MS (spike levels: 5,10 and 15 µg/kg)

Analyte	5 µg/kg						10 µg/kg						15 µg/kg					
	Average recovery (%)		Intra-Day precision (RSD %, n=6)		Inter-Day precision (RSD %, n=18)		Average recovery (%)		Intra-Day precision (RSD %, n=6)		Inter-Day precision (RSD %, n=18)		Average recovery (%)		Intra-Day precision (RSD%, n=6)		Inter-Day precision (RSD %, n=18)	
	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD
Aldrin	86	94	4,10	3,40	4,20	8,79	98	93	3,10	1,40	4,93	4,05	109	93	7,20	2,20	9,60	4,33
α-HCH	100	104	2,60	7,90	4,13	10,00	99	90	4,00	9,30	5,20	11,00	116	98	6,00	2,70	10,00	2,73
β-HCH	108	98	4,80	15,31	7,90	15,67	97	90	6,10	4,90	7,90	6,95	104	96	2,40	4,00	9,50	8,87
γ-HCH (lindane)	116	102	3,10	7,90	3,80	14,26	99	107	2,10	3,90	3,57	4,75	105	100	5,73	4,00	8,20	4,50
Dieldrin	102	104	4,63	1,10	8,30	7,93	85	107	2,60	8,90	4,00	10,05	94	102	6,60	3,50	9,67	4,17
Heptachlor	100	116	2,73	14,57	3,00	17,51	97	90	3,10	6,70	4,07	12,80	105	96	7,10	2,60	8,00	4,13
Heptachlorepoxide	96	98	1,70	8,45	2,17	10,81	93	97	1,10	1,80	3,13	3,05	111	100	1,30	4,50	3,47	4,97
HCB	106	96	1,50	4,40	3,50	5,76	100	103	2,10	5,70	4,37	7,00	108	98	6,00	3,70	7,40	4,13
2,4-DDT	100	94	2,70	1,80	3,00	6,05	79	110	2,30	4,10	2,63	4,20	86	100	5,00	4,50	7,57	6,20
44-DDT	100	96	3,77	3,80	4,30	7,50	75	105	5,00	4,05	5,07	8,20	95	100	6,20	4,50	7,10	8,45
44-DDD	110	86	1,90	8,45	1,90	14,28	90	103	1,40	1,10	1,97	5,70	95	102	6,50	2,40	8,47	3,73
44-DDE	102	102	0,80	6,18	1,30	8,44	94	103	2,00	4,70	2,37	7,80	94	96	5,70	2,75	7,53	3,27
PCB 28	102	95	2,23	7,66	2,30	11,51	96	109	1,90	1,60	2,23	3,70	97	100	5,77	3,60	6,80	6,60
PCB 30	106	92	2,00	4,02	3,37	9,82	101	104	2,20	1,50	3,47	2,95	116	101	6,80	3,20	10,10	4,53
PCB 52	104	94	0,60	5,00	1,93	7,67	96	100	2,20	1,90	2,40	4,05	97	101	5,20	2,10	5,97	5,47
PCB 101	100	99	1,50	6,32	1,60	8,60	93	105	1,70	0,90	2,07	7,20	92	100	4,20	3,80	5,83	5,93
PCB 118	106	96	2,30	5,34	4,40	10,57	93	105	0,30	1,30	1,43	2,55	91	99	3,30	1,30	5,60	3,40
PCB 138	108	94	1,30	3,20	1,73	6,62	96	105	1,40	0,20	2,67	3,50	95	94	6,10	3,50	7,27	3,60
PCB 153	104	93	1,13	4,15	1,30	5,45	81	100	2,30	0,40	3,03	4,85	91	101	5,20	1,70	6,07	5,87
PCB 180	106	94	0,83	5,20	1,20	6,76	84	97	1,77	0,50	2,20	2,50	88	94	0,70	2,10	6,77	3,10

RSD: Relative standard deviation

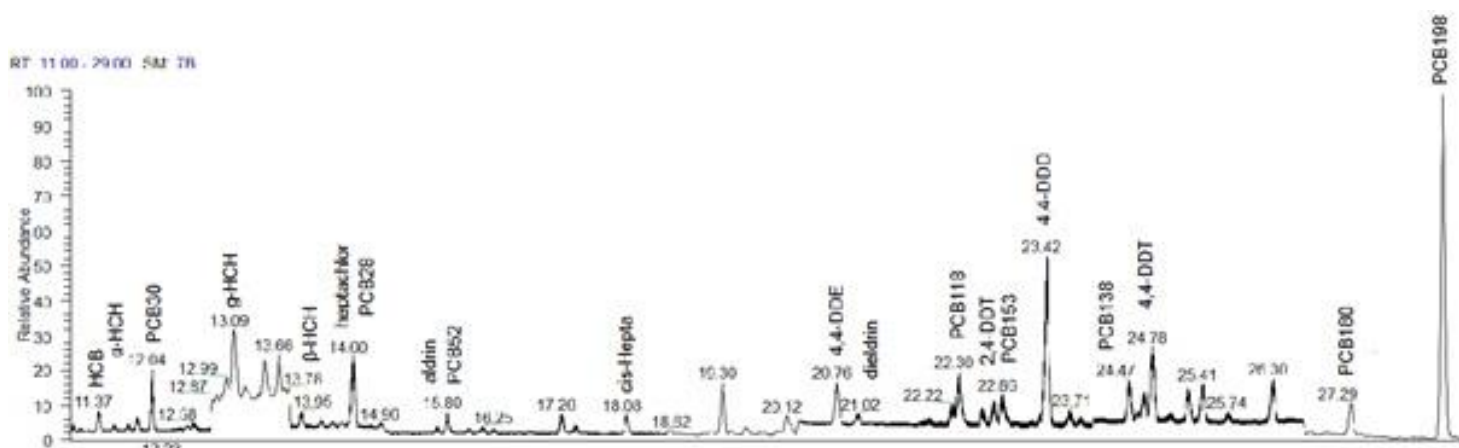


Figure 1. GC-MS chromatogram of mixture of OCPs and PCBs (5 $\mu\text{g}/\text{kg}$)

Table 5. Recovery efficiencies of methods (spike level: 10 $\mu\text{g}/\text{kg}$)

Compound Name	Recovery (%)			RSD (%)		
	ECD	MS	MS/MS	ECD	MS	MS/MS
Aldrin	94	98	95	7.2	3.8	7.1
α -HCH	90	97	104	10.4	4.9	14.1
β -HCH	89	98	102	8.5	5.6	7.7
γ -HCH (lindane)	104	99	111	4.1	2.8	9
Dieldrin	108	86	101	7.4	2.5	4.9
Heptachlor	91	99	96	7.1	2.9	7.3
HCB	102	97	95	7.0	5.0	7.9
2,4-DDT	110	84	99	5.7	2.4	8.2
4,4-DDT	103	83	94	7.5	5.4	11.3
4,4-DDD	101	92	102	6.5	0.9	7.6
4,4-DDE	103	94	96	5.4	1.8	7.2
PCB 28	109	97	104	5.5	2.0	8.4
PCB 30	103	99	111	4.1	2.9	6.6
PCB 52	100	96	101	5.4	1.7	5.7
PCB 101	105	94	101	8.9	1.6	9.7
PCB 138	103	95	89	8.6	1.3	8.8
PCB 153	99	85	92	8.7	2.4	8.5
PCB 180	100	84	96	9.0	1.6	8.1

Table 6. Limit of detections (LOD), limit of quantitations (LOQ) and correlation coefficients (R^2) of GC-MS and GC-ECD

Compound Name	Linearity (R^2)		LOD ($\mu\text{g/kg}$)		LOQ ($\mu\text{g/kg}$)	
	GC-ECD	GC-MS	GC-ECD	GC-MS	GC-ECD	GC-MS
Aldrin	0.9862	0.9930	1.5	2.4	5.2	8.1
α -HCH	0.9933	0.9973	2.5	1.7	5.2	5.8
β -HCH	0.9564	0.9854	2.5	1.5	7.5	4.9
γ -HCH (lindane)	0.9848	0.9982	2.5	1.2	8.4	4.0
Dieldrin	0.9873	0.9837	1.5	1.0	5.2	3.3
Heptachlor	0.9934	0.9897	2.2	1.9	7.5	6.3
HCB	0.9882	0.9935	1.5	0.9	5.2	3.0
2.4 DDT	0.9827	0.9753	3.1	1.0	10.0	3.5
4.4 DDT	0.9932	0.9701	3.5	1.6	7.2	5.2
4.4 DDD	0.9991	0.9829	2.5	0.9	5.1	3.0
4.4 DDE	0.9873	0.9900	1.5	1.2	5.2	4.0
PCB 28	0.9939	0.9943	2.2	1.1	7.5	3.6
PCB 30	0.9981	0.9994	2.3	0.9	7.2	3.1
PCB 52	0.9956	0.9904	2.4	1.0	8.2	3.3
PCB 101	0.9922	0.9909	1.9	1.2	6.3	3.9
PCB 138	0.9949	0.9864	1.5	0.7	5.1	2.3
PCB 153	0.9956	0.9881	1.2	0.6	4.1	2.1
PCB 180	1.0000	0.9877	3.0	0.3	9.8	1.1

Ahmad et al. (2010) analysed Organochlorine pesticide (OCP) residues in eggs and meat samples from Jordan using GC-ECD. They found that 28% (38/134) of the examined eggs were contaminated with OCP residues and according to their study, mainly HCHs and DDTs were the most prominently noticed compounds. Percentage recovery in eggs after fortification at 100 $\mu\text{g/kg}$ were in the range of 80-99% and LOD values were reported as 4-5 $\mu\text{g/kg}$ which are slightly higher than LOD values obtained in this work. They detected HCH substances in 15 egg samples out of 134 at concentrations ranging from 6 $\mu\text{g/kg}$ to 1.3 mg/kg egg. They have also reported DDE and DDT residues at 5 $\mu\text{g/kg}$ -0.6 mg/kg concentrations. Some egg samples they analysed had higher residue concentrations than the samples analysed in this study which might be explained as the effect of geographic location where the samples collected.

Valsamaki et al. (2006) analysed 20 OCP and 8 PCB in chicken eggs using GC-ECD and GC-MS. The average recoveries they reported are ranging from 82 to 110 % which are in a good agreement with the recoveries obtained in this study. They have reported the LOD and LOQ values as in the range of 0.3-0.7 $\mu\text{g/kg}$ and 1.0-2.3 $\mu\text{g/kg}$ respectively. In this study the LOD and LOQ values were found to be almost three fold of these values. The reason might be the difference in techniques used in sample preparation and clean-up procedures.

Conclusions

According to the data obtained by using GC-ECD, GC-MS and GC-MS/MS methods, it can be stated that the best repeatability and recovery were provided by GC-MS technique. The clean-up procedure using 4 g alumina and 5 g silica columns gave best recoveries. Consequently, the best performance was obtained from clean-up process using alumina and silica combined columns prior to GC-MS method.

In this study, β -HCH, 4,4-DDE and PCB138 were detected in nine egg samples out of hundred samples ranging from 4.2 to 30 $\mu\text{g/kg}$. Although the detected amounts of residues were below the maximum residue levels (MRLs) permitted in foods, they have been banned for several years in countries of the European Union. Some of them are still present in the environment because of their persistent nature. The health risk of POP exposure through egg consumption was discussed elsewhere (Polder et al., 2016). Therefore, continuous monitoring of OCPs and PCBs residues in food materials is necessary and the monitoring procedures has been well established in many developed countries.

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