Screening of Organochlorine Pesticide Residues in Chicken Eggs in and around Mumbai City


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ABSTRACT

A multiresidue method was standardized using Gas Chromatography (GC) equipped with Electron Capture Detector (GC-ECD) for simultaneous detection and quantification of selected pesticide residues viz., DDT isomers, HCH isomers and α-endosulphan in chicken egg samples. Method validation revealed average recoveries ranging between 68.64% to 115.62% with percent RSD below 10% for all the analytes under study. Among all the 120 chicken egg samples analysed from five different sources, 76 (63.33%), 17 (14.16%) and 8 (6.66%) samples showed presence of DDT isomers, HCH isomers and α-endosulphan, respectively. Highest prevalence of pesticide residues was noted for DDT isomers (70.83% each) in eggs collected from northern Maharashtra and Andhra Pradesh followed by HCH isomers from western Maharashtra (25%) and for α-endosulphan from Karnataka and Tamil Nadu (12.5%). On the other hand, lowest prevalence was observed for DDT isomers (54.16%) in eggs from Western Maharashtra, followed by HCH isomers from Andhra Pradesh (8.33%) and nil for α-endosulphan from northern and western Maharashtra. Although the eggs marketed in the Mumbai city were containing organochlorine pesticide residues, none of the egg sample showed presence of residue levels in excess of permissible levels prescribed by PFA and Codex.

Keywords: Chicken egg, gas chromatography, organochlorine pesticide residues

Introduction

Indiscriminate and irrational use of pesticides in the agriculture sector has posed a serious environmental and public health problem. Uncontrolled and unscrupulous use of these pesticides may lead to their accumulation in or on the crops and ultimately in animals and their products such as milk, meat and eggs. Many techniques are available for analysis of the residues but GC with ECD is most widely used analytical technique for detection and quantitation of organochlorines as it provides high resolution of peaks, high sensitivity and specificity of detection of organochlorines. Moreover, using capillary column large number of organochlorine pesticides can be detected in single run (Hoff and Zoonen, 1999). The present study was undertaken with broad objective of screening selected organochlorine pesticide residues in chicken eggs sold at retail markets in and around Mumbai city by employing a multi-residue method.

Materials and Methods

Sampling

A total of 120 chicken egg samples (pooled samples) were collected from wholesale shops in and around Mumbai city, which receive the eggs from five different sources viz., Western Maharashtra, Northern Maharashtra, Karnataka, Andhra Pradesh and Tamil Nadu 24 pooled samples from each source as per Codex guidelines.

Chemicals and standards

All the chemicals used during study were of HPLC grade and were procured from M/s. sd Fine - Chem Ltd., Mumbai and M/s. Merck Specialities Pvt. Ltd., Mumbai.

Extraction and clean-up

Extraction and clean-up procedure for detection of selected organochlorine pesticide residues in chicken egg samples was standardized as per AOAC Official Method...
970.52 for organochlorine and organophosphate pesticide residues - General Multiresidue Method (AOAC, 2000) in the whole egg content with slight modifications. The florisil column clean-up was carried and the final elute was analysed by GC-ECD.

Gas chromatographic analysis

Gas chromatography system (Shimadzu model GC 2010) equipped with $^{63}$Ni Electron Capture Detector, fused silica capillary column (30 m x 0.25 mm i.d.) were used. Nitrogen was used as carrier as well as make up gas with flow rate of 2 ml and 30 ml/min, respectively. The detector and injector temperatures were set as 320°C and 250°C, respectively. The column oven temperature was programmed as starting with 60°C to 280°C, for a total run time of 24.87 min. GC-MS System (Shimadzu model GCMS-QP 2010 plus) equipped with MS detector was used for confirmation of organochlorine pesticide residues. Amongst various organochlorine pesticide residues, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD and p,p'-DDT among DDT isomers; $\alpha$-HCH, $\beta$-HCH, $\gamma$-HCH and $\delta$-HCH among HCH isomers and $\alpha$-endosulphan were evaluated in the present study.

Results and Discussion

Chromatographic analysis of elution pattern of all the analytes under study revealed that $\alpha$-HCH eluted earlier followed by $\beta$-HCH, $\gamma$-HCH, $\delta$-HCH, o,p'-DDE, $\alpha$-endosulphan, p,p'-DDE, o,p'-DDD, p,p'-DDD and p,p'-DDT (Fig 1). Linearity for the standard showed a good regression with coefficient of regression ($r^2$) as 0.998 for all the analytes.

Pilot trials to study the linearity and recovery of the known concentrations of organochlorines after spiking in blank egg samples revealed the average recovery percentage ranging between 68.64% to 115.62% for inter day assay, while for intraday assay it was reported between 53.26% to 104.39%.

For DDT and its isomers, out of 120 samples, 76 chicken egg samples were found positive with an overall incidence of 63.33%. Maximum residue prevalence was observed in egg samples procured from northern Maharashtra and Andhra Pradesh (14.10% each), followed by Karnataka (12.50%), Tamil Nadu (11.66%) and western Maharashtra (10.83%). Amongst the DDT isomers, highest prevalence was noted for p,p'-DDE (44.16%), followed by p,p'-DDT (26.66%), o,p'-DDE (25.00%), o,p'-DDD (4.16%) and p,p'-DDD (0.83%). The mean concentration of DDT and its isomers was reported to be 2.33 ng/g for all the samples irrespective of the source. Over all 40 samples were found positive for presence of single DDT analyte, followed by 27 samples positive for two DDT analytes and nine samples were containing three or more analytes. The results of the DDT contamination observed in the present study are in agreement with the Furusawa and Morita (2000) who reported maximum prevalence of DDE in egg samples. The highest prevalence of DDE among all the DDT isomers could be due to metabolism of DDT to DDE in the hen's body and their rapid transmission to the egg-forming tissues and egg yolk content (Furusawa, 2002). The residue levels in the present study are found to be less than the residue levels observed by Aulakh et al. (2006) probably due to restricted and judicious use of DDT only in public health programmes.

For HCH isomers, maximum egg samples were positive for $\gamma$-HCH, followed by $\beta$-HCH, $\delta$-HCH and least

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of analyte</th>
<th>Western Maharashtra</th>
<th>Northern Maharashtra</th>
<th>Karnataka</th>
<th>Andhra Pradesh</th>
<th>Tamil Nadu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o,p'-DDE</td>
<td>6 (1.74-20.46)</td>
<td>4 (1.74-35.14)</td>
<td>3 (4.21 – 6.38)</td>
<td>10 (1.96 – 47.63)</td>
<td>7 (1.60 – 50.80)</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>p,p'-DDE</td>
<td>9 (1.89-7.12)</td>
<td>14 (1.58-6.52)</td>
<td>8 (3.48 – 8.22)</td>
<td>11 (1.47 – 4.43)</td>
<td>7 (1.71 – 21.24)</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>o,p'-DDD</td>
<td>2 (1.21-3.55)</td>
<td>-</td>
<td>1(6.96)</td>
<td>2 (3.75 – 4.50)</td>
<td>-</td>
<td>05</td>
</tr>
<tr>
<td>4</td>
<td>p,p'-DDD</td>
<td>-</td>
<td>1(1.08)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>01</td>
</tr>
<tr>
<td>5</td>
<td>p,p'-DDT</td>
<td>7 (1.47-9.05)</td>
<td>9 (1.22 – 7.10)</td>
<td>6 (2.16 – 5.81)</td>
<td>5 (1.39 – 3.17)</td>
<td>3 (1.07 – 3.86)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>24</strong></td>
<td><strong>28</strong></td>
<td><strong>18</strong></td>
<td><strong>28</strong></td>
<td><strong>17</strong></td>
<td><strong>115</strong></td>
</tr>
<tr>
<td>6</td>
<td>$\alpha$-endosulphan</td>
<td>-</td>
<td>-</td>
<td>03 (1.22 – 2)</td>
<td>02 (1.91 – 2.47)</td>
<td>03 (1.03 – 14.47)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td>-</td>
<td>-</td>
<td><strong>03</strong></td>
<td><strong>02</strong></td>
<td><strong>03</strong></td>
<td><strong>08</strong></td>
</tr>
<tr>
<td>7</td>
<td>$\alpha$ HCH</td>
<td>-</td>
<td>-</td>
<td>01 (1.12)</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>$\beta$ HCH</td>
<td>03 (1.14-1.83)</td>
<td>-</td>
<td>01 (1.87)</td>
<td>01 (23.43)</td>
<td>02 (1.42 – 1.71)</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>$\gamma$ HCH</td>
<td>03 (1.07 – 4.38)</td>
<td>02 (2.41 – 2.49)</td>
<td>02 (1.85 – 5.07)</td>
<td>01 (1.31)</td>
<td>01 (2.32)</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>$\delta$ HCH</td>
<td>-</td>
<td>01 (11.05)</td>
<td>-</td>
<td>01 (19.58)</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>6</strong></td>
<td><strong>3</strong></td>
<td><strong>4</strong></td>
<td><strong>3</strong></td>
<td><strong>3</strong></td>
<td><strong>19</strong></td>
<td></td>
</tr>
</tbody>
</table>

*Egg samples positive for one or more than one analyte of the respective isomer

Table 1. Details of positive samples with concentrations (ng/g)
for α-HCH. Amongst the HCH isomers analysed in chicken egg samples collected from different sources, only one egg sample was found positive for (0.83%) α-HCH belonging to Karnataka. Prevalence of β-HCH was more in western Maharashtra (12.5%), followed by Tamil Nadu (8.33%), Karnataka and Andhra Pradesh (4.16%) with overall prevalence of 5.83%, while none of the sample from northern Maharashtra was found positive. Out of total nine (7.5%) γ-HCH positive samples, three egg samples (12.5%) were procured from western Maharashtra, two each from western Maharashtra and Karnataka (8.33%), while one each from Tamil Nadu and Andhra Pradesh (4.16%). Out of two (1.66%) positive samples for δ-HCH, one egg each was equally procured from western Maharashtra and Andhra Pradesh (4.16%). Overall, 17 (14.16%) samples showed the presence of HCH and its isomers. Highest number of positive samples belonged to western Maharashtra (5.0%), followed by northern Maharashtra, Karnataka and Tamil Nadu (2.5%), while lowest samples were from Andhra Pradesh (1.66%) (Table 1). The concentration of HCH and its isomers ranged between 1.07-23.43 ng/g with mean concentration of 4.42 ng/g for all the samples irrespective of the source. The range of concentration of HCH and its isomers was found to be lower than the respective values reported by other workers. Ehrenberg et al. (1976) observed prevalence of β-HCH and γ-HCH as 58% and 11% in egg samples with the concentration levels of 0.45 mg/kg. Khandekar et al. (1981) reported 59.45% and 75.67% prevalence of γ-HCH and other HCH isomers in egg samples collected from various markets in Mumbai city, which was far above than the percent prevalence observed in the present study. Over all, 15 samples were found positive for presence of single HCH analyte, followed by 15 samples positive for two HCH analytes and no sample was possessing three or more analytes. The poultry feed through various ingredients from agricultural sector might have contributed to presence of HCH residues in the chicken egg samples analysed in the study. The lowest prevalence of α-HCH may be because this isomer of HCH is banned for agricultural use (Aulakh et al., 2006). The use of unpurified technical β-HCH may contribute to contamination of animal origin foods along with other HCH isomers (Ehrenberg et al., 1976). The highest prevalence of HCH isomers observed in western Maharashtra could be due to use of more pesticides containing technical HCH for agricultural use since western Maharashtra is well irrigated and agriculturally well developed region of Maharashtra.

Individual analysis of the residues revealed presence of α-endosulphan in 8 samples (three samples each from Karnataka and Tamil Nadu and two from Andhra Pradesh) giving overall prevalence of 6.66%. None of the samples from northern as well as western Maharashtra was found positive (Table 1). The α-endosulphan concentration ranged between 1.03–14.47 ng/g with mean concentration of 2.88 ng/g. Singh (2005) reported much higher mean residual concentration of 0.1754 µg/g with moreover similar prevalence (4.36%) in comparison with
the present study, while the prevalence observed in this study is a lot less than 46.15% as reported by Mishra (2001).

The organochlorine residue concentration in the positive samples was compared with permissible levels of 0.5 mg/kg and 0.1 mg/kg (PFA, 2006) and 0.1 mg/kg and 0.1 mg/kg (Codex, 2006) for DDT and its isomers and γ HCH, respectively. There is no prescribed limit for α-endosulphan by PFA and Codex. Although, high prevalence of organochlorine analytes was recorded in the present study, the residual concentration levels are far below that is 2.33, 4.42 and 2.88 ng/g for DDT and its isomers, HCH and its isomers and α-endosulphan, respectively, than the tolerance levels prescribed by these regulatory agencies.

Consumption of egg and egg products in all strata of the society is increasing considerably owing its nutritive value and culinary benefits. On perusal of the results of the present study, it is clear that people of all age groups from all the community are exposed to residual levels of organochlorine pesticides through consumption of eggs in different forms, although the residue levels do not pose any significant risk to the consumers. Therefore, it is essential to carry out proper scientific surveillance of egg samples from large geographical area covering major egg producing states in the country to consistently monitor the prevalence of residual levels of organochlorine pesticides. This will also be helpful to trace back the source of contamination, adoption of proper control measures, judicious use of pesticides and most importantly to safeguard the public health.

References


