RESIDUES AND TRACE ELEMENTS

# Organochlorine and Organophosphorus Pesticide Residues in Food from Egyptian Local Markets

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**A market basket survey was conducted to monitor organochlorine and organophosphorus pesticide residues in potatoes, citrus fruits, and fish collected from local Egyptian markets. Maximum Residue Limits (MRLs) of the Codex Committee on Pesticide Residues for γ-hexachlorocyclohexane (HCH) in potatoes were exceeded in 8 samples and for DDT in 2 samples. The aging of HCH and DDT indicated a recent use of both pesticides during the potato storage period between cultivation seasons. However, such use is illegal because HCH mixture isomers (gammaxane) and DDT have been officially prohibited from agricultural use in Egypt since 1980. The highest residue levels of fenitrothion (3.8 ppm) in potatoes may be due to its repeated use before and after harvest. No organochlorine pesticide residues were found in citrus fruits. None of the detected organophosphorus pesticides exceeded their MRLs. HCH and DDT residue limits were exceeded in 5 and 7 fish samples, respectively, collected from 12 markets throughout the country. The heptachlor MRL was violated in only one fish sample (3.9 ppm).**

Organochlorine pesticides were used extensively in Egypt since the early 1950s. However, their use was officially banned in 1980. These compounds are characterized by persistence, high absorbance on sediments and soil, and high accumulation in fatty animal tissues. Organophosphorus compounds that have low persistence and are readily decomposed were used extensively during those years for pest control throughout the country.

The monitoring program for pesticide residues should be conducted routinely on a large scale to evaluate actual food contamination. The present study is one in a series dealing with detection of organochlorine and organophosphorus pesticide residues in Egyptian foods (1–4).

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Three foods that are most common in the Egyptian diet, potatoes, citrus fruits, and fish, were selected for this investigation.

The objective of this work was to accumulate data on the contamination of food with pesticide residues. Such data would help in assessing the risk of human exposure to pesticides and in following up the implementation of the Good Agricultural Practices recommended for agricultural fields (Egypt).

## Experimental

### *Sampling*

Fifty-four potato samples and 53 orange samples were collected from 6 local markets; 12 boltifish (*Tilapia nilotica*) samples were collected from the same markets and from 6 other markets from November 1990 to April 1992. Both organochlorine and organophosphorus pesticides were found in potatoes, orange peel, and orange pulp. Only organochlorine compounds were found in fish. A 1 kg sample of each commodity was prepared according to the general sample preparation steps described in the U.S. Food and Drug Administration's *Pesticide Analytical Manual* (PAM) section 141 (5).

### *Extraction and Cleanup*

The method used for extraction of organochlorine compounds depends upon the water and fat content of the sample (5). Fish samples (adjusted weight) were extracted according to PAM section 211.31(f-1) (5) for >10% fat. The whole volume of petroleum ether obtained was used for petroleum ether-acetonitrile partitioning as in section 211.14a (5). Cleanup on Florisil adsorbent was performed as in the method (6) previously used (1). Extraction with ethyl acetate was used for determination of organophosphorus residues (7).

### *Apparatus*

(a) *Gas chromatograph.*—PYE Unicam 104 equipped with $^{63}$Ni dc 10 V electron capture detector with the following columns: 9 ft × 4 mm id glass packed with (A) 1.5% OV-17 + 1.95% OV-210 on Gas Chrom Q (80–100 mesh); (B) 10% DC-200 on Gas Chrom Q (80–100 mesh). Operating conditions: nitrogen carrier gas set at 120 and 130 mL/min for columns A and B, respectively; column 210°C, injector 225°C, and detector 220°C (column A); column 202°C, injector 225°C, and de-

**Table 1. Organochlorine pesticide residues found in potato samples collected from local Egyptian markets (March 1991 to January 1992)[a]**

| Pesticide | Minimum, ppm | Maximum, ppm | Mean, ppm | 90th Percentile | Frequency |
|---|---|---|---|---|---|
| α-HCH | <0.0005 | 0.099 | 0.008 | 0.017 | 50 |
| β-HCH | <0.0005 | 0.798 | 0.037 | 0.055 | 52 |
| γ-HCH | <0.0005 | 0.104 | 0.006 | 0.011 | 43 |
| δ-HCH | <0.0005 | 0.053 | 0.006 | 0.017 | 18 |
| Total HCH | 0.0007 | 1.13 | 0.053 | 0.113 | 52 |
| Aldrin | 0.014 | 0.014 | 0.014 | — | 1 |
| Dieldrin | <0.001 | 0.007 | 0.004 | — | 6 |
| Aldrin and dieldrin | <0.001 | 0.021 | 0.001 | — | 6 |
| Heptachlor | <0.001 | 0.063 | 0.005 | 0.001 | 13 |
| Heptachlor epoxide | <0.001 | 0.121 | 0.006 | 0.004 | 25 |
| Heptachlor and heptachlor epoxide | <0.001 | 0.139 | 0.005 | 0.002 | 32 |
| Endrin | <0.001 | 0.003 | 0.001 | 0.002 | 13 |
| DDT, *o,p'*- | <0.001 | 0.763 | 0.019 | 0.009 | 46 |
| DDT, *p,p'*- | <0.001 | 1.21 | 0.032 | 0.038 | 49 |
| DDE, *p,p'*- | <0.001 | 0.109 | 0.004 | 0.006 | 52 |
| DDD, *p,p'*- | <0.001 | 0.197 | 0.02 | 0.005 | 11 |
| Total DDT | <0.001 | 2.28 | 0.054 | 0.05 | 54 |

[a] Number of samples analyzed = 54.

tector 207°C (column B). Detector attenuation was set to give ca 1/2 FSD for 0.1 ng heptachlor epoxide (columns A and B).

(**b**) *Gas chromatograph.*—Philips 4500 flame photometric detector in P mode with column 7 ft × 2 mm id packed with 4% SE-30 + 60% OV-210 on Gas Chrom Q (80–100 mesh). Operating conditions: column 210°C, injector 225°C, and detector 220°C; gas flow rates, 30, 60, and 30 mL/min for nitrogen, air, and hydrogen, respectively.

Detector attenuation was set to give ca 1/2 FSD for 0.4 ng chlorpyrifos. The approximate limits of quantitation (minimum quantitative levels) were 0.0005 ppm for HCH isomers and 0.001 ppm for all other organochlorine pesticides measured.

The approximate limit of quantitation for organophosphorus compounds was 0.01 ppm.

### Reagents

(**a**) *Solvents.*—Acetonitrile, petroleum ether, *n*-hexane, ethyl acetate, benzene. All solvents were distilled from all glass apparatus and subjected to a general purity test as in sections 121.1 and 121.2 (5).

(**b**) *Adsorbent.*—Florisil, PR grade, 60–100 mesh; handled and tested as in section 121.3 (5).

(**c**) *Pesticide reference standards.*—Organochlorine compounds, DDT complex (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE), hexachlorocyclohexane (HCH) isomers (alpha, beta, gamma [lindane], and delta), heptachlor and heptachlor epoxide, aldrin and dieldrin, and endrin. Reference materials were kindly provided by the National Food Administration, Food Research Department, Uppsala, Sweden. Standard solutions of reference materials were prepared in *n*-hexane.

(**d**) *Organophosphorus compounds.*—Malathion, prothiophos, pirimiphos-methyl, fenitrothion, profenofos, methamidophos, dimethoate, chlorpyrifos, chorpyrifos-methyl, parathion-methyl, and pirimiphos-ethyl. Standard solutions of reference materials were prepared in ethyl acetate. Pesticide standards were obtained from the Division of Pesticide

**Table 2. Organophosphorus pesticide residues found in potato samples collected from local Egyptian markets (March 1991 to January 1992)[a]**

| Pesticide | Minimum, ppm | Maximum, ppm | Mean, ppm | 90th Percentile | Frequency |
|---|---|---|---|---|---|
| Chlorpyrifos | <0.01 | 0.100 | 0.028 | — | 9 |
| Dimethoate | <0.01 | 0.013 | 0.011 | — | 2 |
| Malathion | 0.02 | 0.285 | 0.212 | — | 5 |
| Pirimiphos-ethyl | <0.01 | 1.248 | 0.507 | — | 4 |
| Fenitrothion | 0.668 | 3.815 | 2.220 | — | 5 |
| Parathion-methyl | 0.389 | 0.540 | 0.465 | — | 2 |
| Profenofos | 0.033 | 0.954 | 0.508 | — | 3 |

[a] Number of samples analyzed = 54.

**Table 3. EMRL and MRL values of organochlorine organophosphorus pesticide residues in potatoes**

| Pesticide | EMRL or MRL, mg/kg[a] | No. of violations |
|---|---|---|
| Organochlorine | | |
| HCH[b] | — | — |
| Lindane | 0.05 | 8 |
| Aldrin and dieldrin | 0.1 | — |
| Heptachlor and heptachlor-epoxide | 0.02 | 1 |
| Endrin | 0.02 | — |
| DDT | 0.1 | 2 |
| Organophosphorus | | |
| Chlorpyrifos | 0.05 | 0 |
| Dimethoate | 0.05 | 0 |
| Pirimiphos-methyl | 0.05 | 3 |
| Malathion | 0.50 | 2 |
| Fenitrothion | 0.05 | 5 |
| Parathion-methyl | 0.05 | 2 |
| Profenofos | 0.05 | 2 |

[a] EMRL (Extraneous Maximum Residue Limits) and MRL (Maximum Residue Limits) were established by the Codex Committee on Pesticide Residues (FAO/WHO) in 1992.
[b] EMRL for HCH withdrawn by CCPR.

Analysis (CAPL, Cairo, Egypt), Agricultural Research Centre, Aldrin and chlorpyrifos were used as external standards for organochlorine and organophosphorus pesticides, respectively.

## Results and Discussion

### *Potato Samples*

Organochlorine pesticide residues were the main contaminants in potato samples (Table 1). Almost all samples were contaminated with DDT and HCH isomers; heptachlors, endrin, and dieldrin were found less frequently. Potato tubers may have been contaminated as a result of their direct contact with soil contaminated with such pollutants. The higher concentrations of DDT and HCH detected and the pattern of the different metabolite and isomer distribution may indicate recent use of such pesticides.

The highest residue levels were found in samples collected during July and August, the storage period between cultivation seasons when potatoes might be subjected to illegal post-harvest treatments with DDT and HCH, which are prohibited from agricultural use in Egypt.

Table 2 demonstrates the presence of 7 organophosphorus pesticides found in potato samples. The highest levels were for fenitrothion; the 5 samples in which the chemical was detected (Tables 2 and 3) violated the Codex MRL. Such violation might be attributed to repeated use of fenitrothion in the field and in stores before and after harvest. This requires implementation of Good Agricultural Practices for potato crops. Pirimiphos-methyl, malathion, parathion-methyl, and profenofos were found at lower levels and had fewer violations.

Of 54 samples investigated, 11 exceeded the Extraneous Maximum Residue Limits or Maximum Residue Limits (MRLs) established by the Codex Committee on Pesticide Residues (CCPR, 1993; Table 3).

### *Citrus Samples*

The frequent presence of chlorpyrifos (Table 4) in 45 out of 53 citrus samples reveals misuse of the pesticide. Its use is restricted to cotton pest control from June to August and from November to March (when it was detected in citrus) because of possible drift contamination. Dimethoate was detected in 29 samples.

No organochlorine pesticides were found in citrus samples, probably because of their prohibition from use since 1980. None of the organophosphorus pesticides found exceeded their MRLs (Table 5).

### *Fish Samples*

As shown in Table 5, the mean value of total HCH isomers found in fish samples was due mainly to the beta isomer, which might correspond to the concept of possible isomerization of alpha and gamma isomers to the beta isomer (8, 9). Total HCH (mainly beta isomer) was found less frequently but in much higher concentrations than in the previous monitoring of fish during 1985 and 1986 (1, 2).

Heptachlor epoxide was found in only one sample at a concentration of 0.4 ppm, which exceeded its MRL (Table 6). This contaminant gradually decreased from 0.267 ppm in 1985 to 0.140 ppm in 1986 (1, 2).

**Table 4. Organophosphorus pesticide residues in citrus samples collected from local Egyptian markets (March 1991 to January 1992)[a]**

| Pesticide | Minimum, ppm | Maximum, ppm | Mean, ppm | 90th Percentile | Frequency | MRL, mg/kg[b] |
|---|---|---|---|---|---|---|
| Chlorpyrifos | <0.01 | 0.301 | 0.026 | 0.048 | 45 | 0.3 |
| Dimethoate | <0.01 | 1.22 | 0.132 | 0.28 | 29 | 2 |
| Malathion | 0.01 | 0.033 | 0.024 | — | 3 | 4 |
| Pirimiphos-methyl | 0.036 | 0.036 | 0.036 | — | 1 | 2 |
| Fenitrothion | 0.023 | 0.681 | 0.332 | — | 4 | 2 |
| Profenofos | 0.038 | 0.038 | 0.038 | — | 1 | 1 |

[a] Number of samples analyzed = 53.
[b] MRL = Maximum Residue Limit established by the Codex Committee on Pesticide Residues (FAO/WHO) in 1992.

**Table 5. Organochlorine pesticide residues in fish samples collected from local Egyptian markets (December 1991 to April 1992)[a]**

| Pesticide | Minimum, ppm | Maximum, ppm | Mean, ppm | 90th Percentile | Frequency |
|---|---|---|---|---|---|
| Total HCH (mainly β-HCH) | 0.211 | 8.708 | 2.795 | — | 5 |
| DDT, *o,p'* | 0.051 | 1.494 | 0.443 | 1.410 | 11 |
| DDT, *p,p'* | 0.018 | 1.896 | 0.524 | 0.814 | 12 |
| DDD, *p,p'* | 0.149 | 0.694 | 0.296 | — | 7 |
| DDE, *p,p'* | 0.044 | 12.832 | 4.448 | 11.369 | 12 |
| Total DDTs | 0.172 | 14.127 | 5.866 | 13.129 | 12 |
| Heptachlor and heptachlor epoxide | 0.398 | 0.398 | 0.398 | — | 1 |
| Endrin | 0.164 | 0.274 | 0.219 | — | 2 |

[a] Number of samples analyzed = 12.

**Table 6. Range of FAO limits for organochlorine pesticide residues in fish compared with levels detected in samples collected from 12 local Egyptian markets (December 1991 to April 1992)**

| Pesticide | Range of limits,[a] mg/kg | No. of samples exceeding max. range limits[b] |
|---|---|---|
| HCH isomers | 0.2–0.5 | 5–5 |
| DDT complex (DDT, *p,p'*- ; DDD, *p,p'*-; DDE, *p,p'*-; DDT, *o,p'*-) | 2.0–5.0 | 9–4 |
| Heptachlor and heptachlor epoxide | 0.01–0.3 | 1–1 |
| Aldrin and dieldrin | 0.1–0.5 | 0–0 |
| Endrin | 0.02[c] | — |

[a] Range of limits used in Canada, Germany, Denmark, Sweden, United States, and Thailand.
[b] First value = number of samples exceeding lowest maximum limit; second value = number of samples exceeding highest maximum limit.
[c] MRL of high starch content commodities such as rice and potatoes.

The concentration of endrin was also lower than that (0.7 ppm) detected in 1986.

DDTs were detected in all the analyzed samples. *p,p'*-DDE was the main metabolite present with the highest residue levels (Table 5). The increase in total DDT residues from 4.17 ppm in 1986 to 5.866 ppm in 1992 might be attributed to biomagnification and bioaccumulation of fat-soluble residues and direct contact of fish with contaminated river water even at the low concentrations that are within permissible limits in water (10).

The lowest MRL values show that 5, 9, and 1 samples are violatives for total HCH isomers, DDTs, and heptachlor, respectively (Table 6). However, the highest MRL in 5, 4, and 1 samples exceeded the levels for total HCH, DDTs, and heptachlor, respectively.

## Conclusions

In general, the data obtained in this investigation show that organochlorine pesticides still contribute to the problem of human exposure to their residues through certain foods. Corrective action must be taken in the Good Agricultural Practice for potato crops, particularly during the pre- and post-harvest treatments with fenitrothion to maintain residues of that substance below the permissible limits.

The data also emphasize the importance of the pesticide residue monitoring program. Sustainability of the program and its expansion to include more foods and other markets throughout the country are essential.

## References

(1) Dogheim, S.M., Almaz, M.M., Kostandi, S.N., & Hegazy, M.E. (1988) *J. Assoc. Off. Anal. Chem.* **71**, 872–874

(2) Dogheim, S.M., Nasr, E.N., Almaz, M.M., & El-Tohamy, M.M. (1990) *J. Assoc. Off. Anal. Chem.* **73**, 19–21

(3) Dogheim, S.M., El-Shafeey, M., Afifi, A.M., & Abdel-Aleem, F. (1991) *J. Assoc. Off. Anal. Chem.* **74**, 89–91

(4) Dogheim, S.M., El-Zarka, M., Gad Alla, S.A., El-Saied, S., Salama, E.Y., Ayoub, M.M., & Fahmy, S.M. (1996) *J. AOAC Int.* **79**, 111–116

(5) *Pesticide Analytical Manual* (1990) Vol. 1, U.S. Food and Drug Adminstration, Washington, DC

(6) Suzuki, T., Ishikawa, K., Sato, N., & Sakai, K. (1979) *J. Assoc. Off. Anal. Chem.* **62**, 681–684

(7) *Analytical Method for Residues of Pesticides* (1988) 5th Ed., Ministry of Welfare, Health and Cultural Affairs, Rijswijk, The Netherlands

(8) IPCS (1991) *International Programme on Chemical Safety*, Environmental Health Criteria 123, World Health Organization, Geneva, Switzerland

(9) IPCS (1992) *International Programme on Chemical Safety*, Environmental Health Criteria 124, World Health Organization, Geneva, Switzerland

(10) Dogheim, S.M., El-Moattassem, M., Mackland, F., Shaker, N., & Hassan, S. (1992) *International Conference on Protection Development of the Nile and Other Major Rivers*, Vol. 212, February 1992, Cairo, Egypt