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ORGANOCHLORINE, ORGANOPHOSPHORUS AND SYNTHETIC PYRETHROID PESTICIDES AFFECTING FOOD CONSTITUTENTS IN COTTON SEEDS AND WHEAT GRAINS DURING STORAGE

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The work has been carried out to evaluate the effects of studied pesticides on food constituents in cotton seeds and wheat grains. The results are assessed using analytical data from trial applications of organochlorine, organophosphorus and synthetic pyrethroid pesticides to the aforesaid food commodities. The studied samples were stored after pesticide treatment at ($30^o \pm 3^oC$) for one month and analyzed for carbohydrates, lipids, phosphorus and trace metals in triplicate alongwith control samples. The data presented herein shows adverse effects on carbohydrates in samples of cotton seeds and wheat grains with pesticidal treatment while SP pesticides caused more adverse effect than OC and OP pesticides and reduced an appreciable amount of lipids in both commodities. It was also observed that phosphorus content decreased in cotton seeds and wheat grains treated with OC and SP pesticides but it increased in case of OP treatment. Lead (toxic element) was totally absent.

Key words: Pesticide affects, Food constituents, Storage.

Introduction

Pesticides are essential inputs of agriculture and are used for crop protection throughout the world. They affect the food constituents of sprayed crop to different extents. The effects of pesticides on food constituents in cotton seeds and wheat grains are briefly reviewed to throw light on information gathered on this aspect. Szymczak and Grajeta (1980) studied the effect of wheat herbicides on lipid levels in the grain. Trace elements are affected by the pesticide application. Szymczak and Bierant (1980) studied the effect of herbicides on calcium and iron levels in the grain of different wheat varieties. Thirteen herbicides decreased Ca and Fe levels, sometimes by 30%, in the Alcedo variety of winter wheat. The Ca level increased and the Fe level decreased by 40% in the Maris Huntsman and Tadorna varieties after herbicide treatment but with opposite effect in the Mironwskaja variety. On 4 other varieties, the herbicides had slight effect on the Ca and Fe levels. Trace elements are affected by the pesticide application. Pal and Sethunathan (1982) applied HCH (hexa-chlorocyclohexane) granules to potted soil at the flooding time in rice plant and noted significant decrease in Fe concentration and to some extent, Mn. Zurawski *et al* (1980) investigated the changes in grain mineral contents as indicators of the effect of herbicides on different winter wheat cultivars. Post-seeding application of terbutryn, triazolex or methabenz-thiazuron, post-emergence methoprotryne, metoxuron, or chloro-toluron or spraying MCPA+mecoprop, MCPA+dicamba or 2,4-D-mecoprop or 2,4-D-dicamba on tillering wheat increased grain N by < 6.5%, tended to increase P and did not affect K. Chlorotoluron tended to decrease grain yield.

Saad *et al* (1984) undertook field experiment to study the effect of synthetic pyrethroids, used for cotton pests control, on constituents of cotton seeds. In seeds, acephate increased the free fatty acids and fat contents. All treatments, especially with acephate and mephospholan, decreased the Ca-contents in the seed meal whereas the P-content was increased. Gautam *et al* (1984) studied the physiological effect in soybean plant after soil treatment with 0.5-10 ppm triadimefon. Total chlorophyll and carbohydrate contents increased. Several other workers have reported effects of different pesticides on food constituents of different commodities (Al-Khalidi *et al* 1984; Fayed *et al* 1981; Faraq *et al* 1986; Ross *et al* 1986; Munshi *et al* 1987).

The knowledge of data presented on the levels of nutrients in cotton seeds and wheat grains, analyzed with the help of different sophisticated techniques and coupled with the

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information on the stability of these food constituents after treatment with some pesticides under simulated and natural environmental conditions, is an important part of this research work. The study also evaluates the intrinsic changes caused in these two agricultural commodities which are not only used as a food and feed but also as a seed for the next crop. The study also includes the assessment of the micro-food constituents and trace elements essential for human health and required for the healthy cotton seeds and wheat grains, since they act as constituents of complex molecule or as enzyme activator. Some of the minerals, which are considered toxic from health point of view, are also determined in the aforesaid food commodities.

Materials and Methods

The analytical methods for the determination of carbohydrates, lipids, phosphorus and trace metals in cotton seeds and wheat grain were adapted from a book written by Osborne and Voogt (1978). Each sample of cotton seeds was taken in three replicates for pesticide treatment and transferred to galss jars. Calculated amount of monocrotphos, pp'-DDT and cyhalothrin (2 ppm each) were separately added and shaken for 3 h. Samples of wheat grain were also treated separately with three grain protectants namely chlorpyriphos-methyl (10 ppm), pirimiphos-methyl (4 ppm) and permethrin (2 ppm) at recommended dosages. The fortified samples of aforesaid food commodities were allowed to stand in the sealed glass jars for one month at the room temperature ($30^o \pm 3^oC$).Each fortified sample was analyzed along with control samples for macro and micro food constituents according to above referred procedures which are briefly described hereunder:

Carbohydrates. For carbohydrates, the material is digested with perchloric acid. Hydrolyzed starches, together with soluble sugars are determined colorimetrically by Anthrone Method and expressed as glucose. A spectrophotometer (Spectronic 20A Shimadzu and Bausch and Lomb) was used to measure the absorbance at selected wavelength (630 nm) to determine the concentration of glucose of each solution of the samples and standards (Table 1).

Total lipid. For the determination of total lipids, constituents present in above mentioned food commodities. Chloroform-Methanol Extraction process was applied. The total percentage of lipids in the cotton seeds and wheat grains samples are presented in Table 2.

Phosphorus. For the quantification of phosphorus in cotton seeds and wheat grain (control and fortified) samples (5g each) were digested by Ash Digestion Method. The phosphorus content in each sample was determined by the described formula (Table 3).

Trace metals. Atomic absorption spectroscopic technique was used for the determination of trace metals i.e. Ca, Co, Cu, Fe, Pb, Mg, Mn, Ni and Zn in cotton seeds and wheat grains samples. Employing the procedure "Wet Digestion" of food products for the investigation of trace metals, the homogenised cotton seeds and wheat grain samples (2 g) were digested in mineral acids until all organic matter was destroyed. The measured values (Table 4) of each sample were determined by atomic absorption spectrophotometer (Perkin-Elmer 2380).

From the digested samples, sodium and potassium contents were measured flame photometrically. The measured values of cotton seeds, wheat grains and blank samples were calculated from the prepared calibration graph and presented in (Table 5).

Results and Discussion

Carbohydrates. Great progress has been made in the past in the analyses of carbohydrates in cotton seeds and wheat grains but not much reaearch is being carried out to evaluate the effects of different pesticides on this essential food constituent in the aforesaid commodities in storage. During the storage of wheat, a number of biochemical changes occur, including a decrease in non-reducing sugars and in total sugars. Under natural storage conditions, these changes are associated with the growth of moulds. It has also been observed that marked changes in non-reducing and reducing sugars did take place in an atmosphere of nitrogen, even if mould growth had been prevented (Milner and Geddes 1954).

In the present study, an effort has been made to evaluate the effects of pp'-DDT (OC), monocrotophos (OP) and cyhalothrin (SP) on carbohydrate component of cotton seeds and results obtained, are presented in Tables 1 & 6. The carbohydrate level in samples decreased significantly when treated with OC and SP pesticides, i.e. 6.76 and 3.86% respectively, while it was minimum (i.e. 1.24%) in case of OP pesticide.

The samples of wheat grains were treated with chlorpyriphos-methyl and pirimiphos-methyl (OP) and also with permethrin (SP) to determine the effects of these chemicals. Alarming decrease (21.06%) was caused by chlorpyriphos-methyl while the influence of pirimiphos methyl was comparatively less as shown in Table-6. The effect of the SP grain protectant was also significant as the reduction is observed to be at the level of 9.19%.

Lipids. Wheat is adopted to production in widely different agro-ecological environment around the world but unusual variability does not appear in its total lipid contents. Wheat grain obtained from different varieties differs more in lipid content than wheat of the same variety grown in different locations (Garcia *et al* 1968; Shollenberger *et al* 1949; Sullivan and Near 1927)). In a study of breakdown of lipid constituent of wheat, stored at high moisture content (22%), Daftary and Pomeranz (1965) reported that polar lipids degraded more rapidly than triglycerides. The degradation was attributed to enzyme from micro-organisms rather than wheat enzymes. In the present investigations, the effects of two OPs, chlorpyriphos-methyl, pirimiphos-methyl and one SP, permethrin were studied on samples of wheat grains in Table 2. Insignificant deficiency in lipid content was observed in samples treated with OP pesticide while adverse effect of SP pesticide was also noted to be negligible (Table 6). An effort was also made to evaluate the effect of OC, OP and SP pesticides on lipids in the samples of cotton seeds (Table 2). The influence of pp'-DDT and monocrotophos was observed to be negligible. As it is evident from Table 6 cyhalothrin was found to have more adverse effect than the other two on this essential food constituent.

Table 1

Total available carbohydrates (% as glucose) in cotton seeds/wheat grains

S.No.	Sample	% Recovery			Mean±SE
01.	Cotton seed control	10.19	10.30	11.00	10.59±0.26
02.	Cotton seed+cyhalothrin	6.23	6.91	6.75	6.63±0.21
03.	Cotton seed+pp'-DDT	3.88	3.31	4.01	3.73±0.22
04.	Cotton seed+monocrotophos	9.15	9.57	9.02	9.25±0.17
05.	Wheat grain control	43.86	42.92	43.12	43.30±0.29
06.	Wheat grain+chlorpyriphosmethyl	22.32	21.89	22.52	22.24±0.19
07.	Wheat grain+pirimiphosmethyl	37.32	38.11	37.69	37.71±0.23
08.	Wheat grain+permethrin	34.30	33.99	34.04	34.11±0.10

Table 2

Total extracted lipids from cotton seeds/wheat grains

S.No.	Sample	% Recovery			Mean±SE
01.	Cotton seed control	13.75	13.79	13.71	13.75±0.02
02.	Cotton seed+cyhalothrin	7.79	7.77	7.74	7.77±0.01
03.	Cotton seed+pp'-DDT	13.07	13.15	13.09	13.10±0.02
04.	Cotton seed+monocrotophos	13.86	13.80	13.90	13.85±0.03
05.	Wheat grain control	1.92	1.95	1.91	1.93±0.01
06.	Wheat grain+chlorpyriphosmethyl	1.86	1.89	1.91	1.88±0.01
07.	Wheat grain+pirimiphosmethyl	1.94	1.93	1.96	1.94±0.01
08.	Wheat grain+permethrin	1.12	1.07	1.13	1.11±0.02

Table 3

Phosphorus-content in cotton seed/wheat grains

S.No.	Sample	Recovery mg g^{-1}			Mean±SE
01.	Cotton seed control	358.0	351.0	359.0	356.0±2.56
02.	Cotton seed+cyhalothrin	330.0	326.0	323.0	326.33±10.26
03.	Cotton seed+pp'-DDT	312.0	308.0	311.0	310.33±3.60
04.	Cotton seed+monocrotophos	380.0	384.0	378.0	380.67±1.79
05.	Wheat grain control	210.0	215.0	209.0	211.33±1.89
06.	Wheat grain+ Chlorpyriphos-methyl	225.0	219.0	222.0	222.00±1.76
07.	Wheat grain+pirimiphosmethyl	281.0	277.0	274.0	277.33±2.06
08.	Wheat grain+permethrin	202.0	200.0	207.0	203.00±2.12

Table 4
Working conditions for trace metals analysis

S. No.	Element	Wave-length	Atomic Absorption (AA) or flame filter photometer (FFP)	Limit of detection (ug/metal/ml) (ppm)	Working range (ug/metal/ml) (ppm)
01.	Calcium (+0.5% LaC1)	422.7	AA	0.001	0.01-0.5
02.	Cobalt	240.7	-do-	0.01	0.25-5
03.	Copper	324.8	-do-	0.01	0.1-1.5
04.	Iron	248.3	-do-	0.20	1-10
05.	Lead	283.3	-do-	0.50	1-15
06.	Magnesium	285.2	-do-	0.001	0.01-0.5
07.	Manganese	279.5	-do-	0.10	1-10
08.	Nickel	232.0	-do-	0.01	5-20
09.	Potassium	Filter	FFP	0.01	5-20
10.	Sodium	Filter	-do-	0.01	5-20
11.	Zinc	213.9	AA	0.005	0.02-0.5

Table 5
Studied trace metals of cotton seed/wheat grains

S. No.	Element	Cotton seed		Wheat grain	
		Recovery (mg g^{-1})	Mean $\pm$SE (mg g^{-1})	Recovery (mg g^{-1})	Mean$\pm$SE (mg g^{-1})
01.	Calcium	4.42, 4.47, 4.40	4.3±0.02	1.87, 1.80, 1.85	1.85±0.02
02.	Cobalt	0.011, 0.014, 0.011	0.012±0.1	0.007, 0.007, 0.009	0.008±0.001
03.	Copper	0.005, 0.008, 0.006	0.006±001	0.005, 0.009, 0.006	0.007±0.001
04.	Iron	0.107, 0.111, 0.109	0.10±0.001	0.078, 0.075, 0.079	0.079±0.001
05.	Lead	-NIL-	—	-NIL-	—
06.	Magnesium	2.59, 2.63, 2.54	2.59±0.03	2.69, 2.96, 2.13	2.59±0.25
07.	Manganese	0.013, 0.015, 0.014	0.014±0.001	0.198, 0.189, 0.194	0.194±0.003
08.	Nickel	0.014, 0.017, 0.011	0.014±0.001	0.014, 0.015, 0.012	0.014±0.001
09.	Potassium	26.78, 25.86, 26.01	26.22±0.029	13.69, 12.15, 12.82	12.89±0.49
10.	Sodium	3.70, 3/68, 3.73	3.70±0.01	2.67, 2.61, 2.69	2.66±0.02
11.	Zinc	0.033, 0.036, 0.031	0.033±0.001	0.027, 0.024, 0.026	0.026±0.001

Phosphorus and trace metals. The essentiality of these elements is due either to their importance as constituents of complex molecules or to their role as enzyme activators. In this relation, it is an important factor to evaluate the mineral contents required for the healthy cotton seeds and wheat grains. Some of the minerals which are considered essential or toxic from health point of view, are quantified in the aforesaid commodities and given in Table 5. No significant decrease or increase of minerals in analytical data is observed in the studied samples of cotton seeds and wheat grains. In particular, phosphorus is regarded as the most important element in general metabolism and its deficiency is considered to cause an adverse effect in fruiting index (Joham 1974). Treated seeds with OP pesticides showed phosphorus contents at higher levels in the samples of both the food commodities (Table 3). Most probably, this increase has occurred due to the presence of this element in the molecules of OP pesticides while OC and SP pesticides caused an adverse effect by reducing it marginally.

Trace metals are of great interest and extreme importance to crops. Certain metals are toxic, some are of nutrient importance while others may affect the shelf-life or appearance of a food product. Lead is an element of particular interest to the food scientists for its reportedly high toxic effects. The

Table 6

Percentage variation of studied macro-food constituents of cotton seed/wheat grains

			Carbohydrates (as glucose)		Lipids	
S. No.	Sample	Fortification level (ppm)	Mean Recovery ±SE	Remarks	Mean Recovery ±SE	Remarks
01.	Cotton seed	Control	10.49±0.26	—	13.75±0.02	—
02.	Cotton seed+ cyhalothrin	2 ppm	6.63±0.21	3.86% decrease	7.77±0.01	5.98% decrease
03.	Cotton seed+ pp'-DDT	2 ppm	3.73±0.22	6.76% decrease	13.10±0.02	0.65% decrease
04.	Cotton seed+ monocrotophos	2 ppm	9.25±0.17	1.24% decrease	13.85±0.03	0.10% increase
05.	Wheat	Control	43.30±0.29	—	1.93±0.01	—
06.	Wheat+ chlorpyriphos-methyl	10 ppm	22.24±0.19	21.06% decrease	1.88±0.01	0.05% decrease
07.	Wheat+ pirimiphos-methyl	4 ppm	37.71±0.23	5.59% decrease	1.94±0.01	0.01% decrease
08.	Wheat+ permethrin	2 ppm	34.11±0.10	9.19% decrease	1.11±0.02	0.82% decrease

general maximum permissible level is 2 ppm (Cowley 1978). On analysis of samples of both the commodities lead was found to be totally absent (Table 5). High levels of copper are also considered to be toxic (Cowley 1978). Its level in the present investigations as shown in Table 5, is much lower than the amount determined in wheat by El-Grindy *et al* (1957). Joham (1974) reported that severe deficiency of zinc delays flowering and fruiting and its excess supply proved to be toxic and reduced the yield of cotton (Joham 1974). He further stated that high range of manganese concentration also showed adverse effects on yield. In the present investigation, both the elements, zinc and manganese, were found at normal levels. In addition, iron and cobalt which are essential elements of human diet were also found within the permissible range.

Sodium, potassium, calcium and magnesium were determined and found to be in normal range (Table 5), while their deficiency decreases relative fruitfulness and fruiting index (El-Grindy *et al* 1957). Deficiency of magnesium also causes adverse effect as it delays flowering process in cotton (Joham 1978). It was further reported that if calcium supply was drastically restricted during the flowering period, flowering and fruiting was almost completely stopped and fruiting index fell to considerable lower levels.

References

Al Khalidi M S, Akel A M, Abas A S 1984 The Effect of some fungicides and storage conditions on chemical and physical characteristics of (Golden delicious) apples. *J Agric Water Resour Res* **4** (2) 163-181.

Cowley K M 1978 *Developments in Food Analysis Techniques-1 Atomic Absorption Spectroscopy in Food Analysis,* ed King R D. Applied Science Publishers Ltd. London, UK pp 293-314.

Daftary R D and Pomeranz Y 1965 Changes in lipid composition of wheat during storage deterioration. *J Agr Food Chem* **13** (3) 442.

El-Grindy M M, Lamb C A and Burrell R C 1957 Influence of variety, fertilizer treatment and soil on the protein content and mineral composition of wheat flour and flour fractions. *Cereal Chem* **34** 185.

Faraq R S, Abdel Magid M M, Abo-Raya S H, Salim A A 1986 Herbicidal effect on soybean oil. *Fette Selfen Anstrichm* **88** (5) 165-167.

Fayed M T, El-Bogoury, Offat H, Al-Marsafy H T 1981 (Pub. 1985). The effectiveness of numerous herbicides in soybean. *Egypt J Agron* **6** (2) 169-179.

Garcia-Faure R, Garcia-Olmedo F, Vallejo-Acenedo J M 1968 Estimation of *Triticum aestivum* in pasta flours. Interspecific limits for sitosteryl palmitate content. *J Sci Food Agr* **19** 322.

Gautam S R, Thapliyal P N, Tripathi R K 1984 Effect of fungicides on physiology of plants. Effect of triadimelon on physiology of soybean plants. *Indian Phytopathol* **37**(4) 600-604.

Joham H E 1974 Effects of Nutrient Elements on Fruiting Efficiency. *Cotton Physiology,* Number one, The Cotton Foundation Reference Book Series. eds Mauney J R and Stewart J McD pp 79-90.

Milner M and Geddes W F 1954 Respiration and heating: In: *Storage of Cereal Grains and their Products, eds* Anderson J A and Alcock A W, Monograph series Vol 2 pp 152-220.

Munshi S K, Kumar A, Sanadi S, Bokhetta D R C, Sukhija P S 1987 Influence of systemic insecticide on lipid biosynthesis in seeds of Indian mustard *(Brassica junceal)* *Plant Sci* **53** (3) 201-208.

Osborne D R and Voogt P 1978 *The analysis of Nutrients in Foods Chemistry & Biological Role of Macro-nutrients Methods for the Analysis of Nutrients in Food.* United States Edition, Published by Academic Press Inc. New York.

Pal S S, Sethunathan N 1982 Concentration of iron & manganese in rice plants as influenced by hexachlorocyclohexane applied to soil. From C A **97** p.256, Ref. No. 140264n.

Ross Lynne F, Chapital, Dorselyn C, Kvein Graigs 1986 Carbohydrates and organic acid in peanut seeds after treatment with a plant growth regulator. *Proc Plant Growth Regul Soc Am* (13), 174-176.

Saad A F S A, Elewa M A, Havwila T, Ibrahim M M 1984 Synthetic pyrethroids used for cotton pests control as a factor affecting constituents of cotton seeds. *Meded Fac Landbovwet Rijksuniv Gent* **49** (3b), 995-1004.

Shollenberger J H, Curlis J J, Jaeger C M, Earle F R, Bayles B B 1949. The chemical composition of various wheats and factors influencing their composition. *U S Dept Agr Tech Bull* No.995.

Sullivan B, Near C 1927 Relation of magnesium in the ash and the lipoid protein ratio to the quality of wheats. *J Am Chem Soc* **49** 467.

Szymczak J, Grajeta H 1980 Effect of herbicides used in wheat cultivation on lipid levels in the grain. C A **93** No.21. Ref.No.198791v.

Szymczak J, Bierant J 1980 Effect of herbicides on calcium and iron levels in the grain of different wheat varities. C A **93** No.23, Ref.No.216302t.

Zurawski H, Jablonski W, Runowska-Hrynzuk Bogdana, Gabinska Krystyna 1980 Changes in grain mineral contents as indicators of the effects of herbicides on different winter wheat cultivars. *Bioindyk Skazen Przem Roln Mater Pokonf* 383-392.