

Organochlorine Pesticide Residue Analyses in Some Fruit Samples Collected from Konya City Supermarkets

H. NAGEHAN UCAN, SUKRU DURSUN*, KEMAL GUR and ABDURRAHMAN AKTUMSEK†

Engineering and Architecture Faculty, Selçuk University, 42003 Konya, Turkey

E-mail: nagehanucan@selcuk.edu.tr; sdursun@selcuk.edu.tr

Food demand increased with increasing population on the world and this demand required usage of fertilizers and pesticides in agriculture. Extremely and uncontrolled usage of pesticide give numbers of problem on vegetation and human health. In this study, the existence of organochlorine pesticide residues have been investigated in 18 types of fruit specimens consumed in Konya, Turkey. The numbers of investigated residues of organochlorine pesticides were 24. The examined fruit specimens for analysis of pesticide residues were apple, pear, black grape, plum, quince, carrot, white grape, persimmon, orange, pomegranate, banana, tangerine, pumpkin, grapefruit, strawberry, kiwi, jarusalem artichoke and medlar. As a result, it was found that, the levels of orghanochlorine pesticides in the all investigated furit specimens were lower than those of the MRL of European Legislations.

Key Words: Organochlorine pesticides, Fruit, GC, Extraction, Konya, Turkey.

INTRODUCTION

One of the important problems of the world as well as in Turkey is increasing environmental population. The foremost prerequisite for the increasing population to survive is nutrition. To feed mankind fertile agricultural lands have been investigated and studies to increase production of agricultural lands have been carried out¹. With irrigation, fertilization, better cultivation of lands, seed improvement and fertilization is continuously rising. However, a significant amount of yield is destroyed by harmful plants, animals and microorganisms both before and after the harvest. Among the genetic, biotechnical, mechanic and chemical methods used to protect agricultural products from illness and pests not only in-production but also in storing, transporting, processing, marketing and consumption. The chemical methods are the most efficient ones. These methods are easy to implement and fast-resulting. Therefore, the agriculturist who do not want to risk their products, choose to use "chemicals". However, the widespread and intense use of these chemicals leads to such prominent results as environmental pollution, the spoiling of natural stability and the development of the organisms' resistance². These chemicals which mix

†Science and Art Faculty, Selçuk University, 42003 Konya, Turkey.

with surface and ground waters accumulate in the bodies of water organisms and go into the food chain of human beings. These chemical complexes which are called pesticides cannot be completely eradicated in the cleaning processes of wastewaters and in the production of drinking waters.

With the improvement of technology and especially with the latest improvements in chemical industry, the production of chemicals has increased. This is also true in agricultural fight for pests. Since early 1970s, more than 60,000 agricultural pesticides which have 500 active, highly toxic complexes, have been used in the U.S.³ As it is known, in many regions of Turkey (primarily in Mediterranean and Aegean regions), as climate conditions are also convenient, various pesticide chemicals are intensively used in the growing of fruits and vegetables for agricultural struggle. These pesticides can also indirectly pass and accumulate in the fruits and vegetables through water, plants or soil.

Therefore, in this study, the pesticide remains in fruits sold in Konya public bazaar are investigated. Besides, it has also been investigated whether the amount of accumulation in these fruit samples is over concentration of internationally tolerable levels or whether it reached to harmful levels or not.

Pesticide types: Various chemical materials and chemical complexes are used to fight against harmful bugs, weeds, funguses and rodents. The synthetic and organic materials used for pest control are called pesticides. Pesticides are chemicals used to destroy bugs, microorganisms and other pests which harm to plants and spoil foods during production, consumption and storage^{4,5}. World Health Organization (WHO) and United Nations Food and Agriculture Organization (FAO) define plant protection medicine as "substance and complexes of substances used to prevent or control undesired plants and organisms"⁶. Currently 300 different types of organic pesticides are known with different names and formulations. There are over 10,000 commercial pesticides. Eventough there are many formulations of pesticides but they are generally classified in terms of their chemical formulations or their purpose of use.

Pesticides are naturally poisonous. They are not applied to pests directly, but mixed with some supplementary materials in safer, more economical and healthier ways for mankind and environment. This physical mixture is called formulation and pesticides in them are called effective material or active material. These formulations include active substance, supplementary substances, amalgamators and filling materials. The specifications of these formulations are determined by FAO and WHO and some standards methods for these formulations are developed⁷. A poisonous substance can be called pesticide on some certain conditions. For a poisonous substance to be an ideal pesticide, it should have the following features; (1) biologically active, (2) effective, (3) reliable, (4) stable enough, (5) safe for the applicers, (6) safe for consumers, (7) safe for pets, (8) non-hazardous for wild life, (9) non-hazardous for useful organisms and (10) acceptable for the environment⁸.

The first use of these chemical substances dates as back as early times. Since Pasteur explored some microbes harmful for plants and animals, some chemical substances have been synthesized and used to fight against these pests. Maroon complex with copper have been started to use just after Pasteur's exploration. Later about the half of 19th century, limestone, sulphur complexes and arsenic were used to fight against illnesses and bugs in apple gardens. Other than these, naturally growing bug killers like rotenone, pyrethrums were used very commonly. In 1939, with the notification of the killing effect of DDT on bugs and of the killing effect of 2,4-D on wild plants, artificial chemical substances were first used in the fighting with pests. With the killing of various harmful animals and plants, the farmers started to earn more from agriculture. The increasing profits of farmers led to more common use of these chemical substances. The use of pesticides not only increased crops but also prevented the illnesses such as yellow fever, brain inflammation, malaria and the like which are brought homes by bugs. Besides, the protection of pets from various illnesses and bugs saved a lot of money. Food could come to our kitchens without negative effects with the use of pesticides. There are 3 prominent problems which limit the use of these seemingly very beneficial pesticides. First is that harmful bugs became resistant to these chemicals substances. In this case more effective chemical substances were used to kill the resistant bugs. Second is that some chemical substances persist in the environment without change its structure. These kinds of chemicals are carried to other environments, accumulate there and affect life in these environments. The third problem in relation with this is that chemical substances are toxic for some harmless plants and animals. These chemicals affect fauna and flora of the soils and fish and other wild animals. As these chemicals accumulate and become very intensive in the tissues of animals and reach up to toxic amounts⁹.

In terms of formulation, they classified in water solutions, emulsion concentrate medicines, granules, aerosols, poisonous bait. In terms of biological period of harmful organisms pesticides are classified as adult killer, larva and egg killer complexes. In terms of the habitat of the harmful organisms they are classified as culture plant pests, forest pests, storeroom pests. In terms of endurance, pesticides are classified as 3 groups as enduring, half enduring and not enduring ones. Endurance indicates the time passes in the removal of 75-100 % of the pesticide remains. Non-enduring pesticides stay in the application field for 1-2 weeks. This is 1-18 months for half enduring pesticides and 2-5 years in long enduring pesticides⁹.

Movements of pesticides: Pesticides generally sprayed and applied to the plants, on the surface or in the soil. Most of the pesticides pass on to the soil. These chemical substances which pass on to soil can (1) Evaporate and mix with the gases in the atmosphere without any chemical change, (2) Be absorbed by the soil, (3) Be washed and diffused as it goes to lower layers in the soil, (4) Be exposed to chemical changes, (5) Be split by microorganisms in the soil and (6) Taken by the plants⁹.

Pesticides application in Turkey: The technical substance needed for agricultural struggle in Turkey is either produced by the factories in Turkey or mostly imported. In Turkey pesticides are intensively applied in the Mediterranean and Egean regions where poly-cultural agriculture is common¹⁰. Table-1 shows usage of pesticides in Turkey, most of them are organic chlorine pesticides. Pesticides usage in Turkey is banned because their harmful effects on the environment and human health. However, the bans on the application of pesticides have mostly been violated. Although the application of DDT was banned in 1985, it was used in the fight against sun pest (*Eurygaster integriseps*) especially in Southeastern Anatolia till early 1990s. Today, endosulfan is the only chlorine insecticide with legal permission¹¹.

TABLE-1
PERCENTAGES OF PESTICIDES APPLIED IN TURKEY

Type of pesticide	Usage percentage
Insecticides	46
Herbicides	23
Fungicides	25
Others	6

Application of pesticides in the fields: Pesticides are mostly used for agricultural struggle. They are used to protect such agricultural products like fruits and vegetables, cereals (wheat, barley *etc.*), rice, maize, cotton, soya beans, sugar-beet, colza. Moreover, in cattle-breeding they are used to eradicate the harmful organisms. Furthermore, pesticides are also used to get rid of harmful organisms in closed places. The sprayed pesticides used to kill mosquitoes in a room can be an example for this type of usage⁶.

Role of pesticides in environmental pollution: The pesticides applied to plants, soil and seeds for agricultural struggle can be assimilated in various organs of the plants or can face transformation in the soil after they have achieved their killing effects. These transformations can be summarized as (1) Getting far away from the soil, (2) Retaining in the soil, (3) Transforming to other plants. There is a dynamic balance between pesticides remains in the soil and water, atmosphere, the medical remains in food and organisms' tissues. The essential component of these remains which physically, chemically and biologically replace is the soil itself. A significant amount of the pesticides applied to soil and plant mix with the atmosphere during application. Pesticides which return back to earth with rains or particles settle into a circulation. It has been determined that pesticide remains which travel through rains, particles and with horizontal profile movements intensify and accumulate in the reservoirs, the lakes and the seas which are all important environmental components. The accumulation of organochlorine pesticide remains in especially the fat tissues of the organisms is through herbal food, water and the air. In this period, pesticide remains are carried directly and indirectly. The researches so far indicated the fact

that plants accumulate pesticide remains- which they take by means of their stems in their stems, bodies, leaves and seeds. Another outstanding way of pollution stems from the plants taking the pesticides evaporating from the soil. Among some polluting waste substances pesticides comes the first and followed by heavy metals and SO₂^{9,12}.

Pesticides penetration to the food products: The pesticides passing to air, water and soil can directly or indirectly pass to foods with the effects of inner and outer factors. The passage ways can be summarized: (a) The mixing of particle pesticides with the air, (b) The mixing of particle pesticides with the air by means of the winds, (c) The chimney gases of the factories producing pesticides. The passage of pesticides to water: (a) The direct application of chemicals to fight against aquatic plants or bugs in or around the water, (b) Medicated plants or surface or underground drainage waters movements, (c) Washing away by rain, (d) The carriage of plants, insects and soils including medical wastes remains to water ecosystem, (e) The direct or indirect complication of medical or industrial wastes present in river or still waters, (f) The washing of application devices or empty packages. The complication of pesticides with the soil; (a) The accumulation of pesticides applied directly to soil, (b) The complication of the pesticides-applied to plants -with irrigation or rain water and thus accumulating on soil, (c) The concentration of particles pesticides in the air by means of rain water and accumulation in the soil, (d) The disposal of industrial pesticides to soil⁹.

The pesticides which complicates with the air, water and soil can pass to foods and affect to life. Especially, chlorine hydrocarbon insecticides get more concentrated as they are stored in the fat of the body. Species eating an animal with pesticide remains can face some physiological disorders or even death. As the concentration is very high on the last item of food chain, hunter species have higher risks⁵.

Permanency of pesticides: After pesticides applied the permanency of them or their decomposition derivatives in the soil or water highly depend on the molecular structure of pesticides, soil, water or environmental conditions⁴. The prominent processes that affect the permanency of pesticide remains are (a) The decomposition processes of pesticide (b) The physical and chemical features of the soil and the water (c) The physical movements of pesticide remains in the soil and in the water. It is also a known fact that the pesticides which are used effectively against soil pests, are resistant to division and divide in very small amounts and stay very long in the environment -especially in the soil and water- and create very big accumulations⁴.

Pesticide reduces: The level of pesticides in the products depends on the type of the food, various features of pesticides (the type of effect, chemical structure, *etc.*), climate conditions, the period between the last application and harvest. In the reduction of pesticide remains the most effective factor among them is undoubtedly the period between the application of medicine and harvest. Therefore, some countries have adopted a new regulation to define the period before harvest for various plants and thus have taken necessary precautions to keep pesticide remains at least to some extend lower. Even if pesticides are applied in a fully controlled way, our

food will have pesticide remains¹³. Therefore, the reduction of pesticide remains with technological methods seems to be an alternative way ahead¹⁴. Today, many researchers intensively study the effectiveness of technological processes to reduce the harmful effects of pesticides. Currently applicable methods are (a) washing, (b) peeling, (c) heating processes (boiling, cooking, pasteurization, sterilization), (d) protection (storage), (e) radiation, (f) decaying by microorganisms and (g) addition of some solid substances¹³.

Pesticide residue studies: There have been many studies on pesticides which accumulate in the air, water, soil and food and thus affect the whole atmosphere. Aydin *et al.*¹⁵ have collected waste water samples from different parts of the drainage system, especially from the exit of the system and 3 different points of main drainage channel of Konya. These waste waters have been analyzed for organic chlorine pesticides like lindane, mirex, aldrin, heptachlor, methoxychlorine, *o,p*-DDE, *p,p'*-DD, *p,p'*-DDT and dieldrin. In the analysis, solid phase extraction and liquid-liquid extraction methods were used. The organic chlorine pesticides in the samples varied in accordance with the places they were taken. Gaw *et al.*¹⁶ measured the total DDT levels and trace element concentrations in soil sample taken from three different regions of New Zealand. The arsenic, cadmium, copper, lead and total DDT levels were also determined. Total DDT was 0.03-34.5 mg/kg.

Hussain *et al.*¹⁷ carried out a study to find out the remains of commonly used pesticides like cypermethrin, methamedphos, monochlorophos, cyfluthrin, diazinon and methyl parathion in 3 different types of mangoes in Multan region. In the samples, cyclohexane and ethyl acetate were used as organic solvent, gel permeation chromatograph (GPC) was used for cleaning and the samples were analyzed with automatic system gases chromatograph (GC) with electron catcher detector (ECD) were analyzed. In the samples, the pesticides were found at different levels. However, all the values were within the permitted limits defined by FAO/WHO. Ochiai *et al.*¹⁸ were developed by combining GC-MS and thermal desorption which is used in the identification of the 5 groups of the chlorine, carbamate, phosphorus and 85 types of pesticides in vegetables, fruits and green tea. With this method, the level of pesticide remains in vegetables, fruit and green tea were determined as $\mu\text{g}/\text{kg}$.

In a study carried out by Kaihara *et al.*¹⁹, SFE method was used and later on finished with HPLC to identify the 27 types pesticides fresh fruit and vegetables. It has been found out that semi-automatic analyses are good for SFE studies. In this study, SFE and HPLC were used in the determination of pesticides and other metabolites. The suggested method was found out to be inconvenient for juiced fruits and vegetables and therefore, it is suggested that the juices in the samples are to be taken away by using absorbing polymers. The 27 types of pesticides values were found out to be between 5 and 10 ng/kg

Chen *et al.*²⁰ have studied the contents, dispersion and possible sources of polycyclic aromatic hydrocarbons (PAHs) and organic chlorine pesticides in the 43 different surface and underground soils in Guangzhou on which various vegetables

are grown. The results indicated that polycyclic aromatic hydrocarbons levels were between 42 and 3077 $\mu\text{g}/\text{kg}$ and that pollution levels was at reasonable levels compared to other studies and with regard to soil quality. Correlation analyses have indicated that polycyclic aromatic hydrocarbons complexes include organic carbon and they are related to black carbons. Besides, DDT concentrations varied between 3580 and 8310 ng/kg and the DDT/(DDD + DDE) proportion was above 2. In this study, it was also found out that HCHS concentrations were between 1900 and 4230 ng/kg .

Goto *et al.*²¹ studied carbamated 9 N-methyl in fruits and vegetables by using ESI LC/MS/MS methods with short column direct sample injection. After the extractions of ethyl acetate pesticides were evaporated to solve in pure water and to achieve dryness. It has been found out that average elimination was between 0.2 % and 7.6 % in the day and among the days it was at level of 10 ng/kg between 56.0 % and 119.1 % with the deviation coefficient between 0.8 and 18.4 %. It has been claimed that this method is good enough to watch the remains of charbamat pesticides in vegetables and fruits and that it can also be used for other foods.

Blasco *et al.*²² used liquid chromatography atmospheric pressure chemical ionization mass spectrometer method to identify imidaclopryd, carbendazim, methiocarb and hexythiazox pesticides present in peaches and nectarine. The cores of the samples were gathered by using ethyl acetate and sodium sulphate without water. It has been found out that the elimination for carbendaizm was between 64 ± 9 % and for hexythiazox it was between 108 ± 14 %. It has been found out that this method is applicable in the identification and for the numbering of imidaclopride, carbendasim, methiocarb and hexythiazox found in 159 peach and nectarine samples taken from agriculture cooperatives.

In a study, Zohair *et al.*²³ studied PAHs, PCBs and OCPs remains in 4 different kinds of potatoes and 3 kinds of carrots organically grown in Britain and in the soils they were grown. The soils, husks and the core of the products were extracted in 3 samples, completely cleaned by open column chromatography and analyzed with analytic method in which gase chromatography with sensitive detector was used. The PAHs, PCBs and OCPs concentrations in the soil were $590 \pm 43 - 2.301 \pm 146$ $\mu\text{g}/\text{kg}$ for PAHs, $3.56 \pm 0.73 - 9.61 \pm 1.98$ $\mu\text{g}/\text{kg}$ for PCBs and $52.2 \pm 4.9 - 478 \pm 111$ $\mu\text{g}/\text{kg}$ for OCPs. It has been found out that all of kinds of Desiree potatoes and Nairobi carrots are sensitive to PAH pollution and PCBs and OCPs pollutions can resist to potato kinds. It has been found out that there is an important correlation between the PCB and OCP concentrations in the soil and the carrots; however the same correlation was not valid between the soil and the potatoes. The peeling of the carrots and potatoes eliminated the pesticides between 52 and 100 %.

Colume *et al.*²⁴ have investigated 25 types of pesticides permitted in European Union countries by using gas chromatography with electron catching detector. The identification limits for all pesticides other than lindane and captan are seen to be *ca.* 1-10 ng/g . This method is also used to identify the existence of these pesticides in 100 vegetables kinds.

EXPERIMENTAL

Samples for fruits: In this study, samples are used containing 18 varieties of fruits (apple, pear, black grapes, plum, quince, carrot, white grapes, date, orange, pomegranate, banana, tangerine, old buffer, grapefruit, strawberry, kiwi fruit, yam, medlar) which are sold to public at different supermarkets at the city center of Konya. Only the edible parts of the fruits used as sample are studied on. In the study, the preparation of the samples of fruits for the analysis, the determination of pesticide remains in the mentioned samples and all the proceeds of analysis and determinations are performed at the laboratory of the Department of Biology in Science-Art Faculty of Seluck University, Konya, Turkey.

Devices and tools: Sensitive scale (GEC AVERY, VA304-1AAZM13AAE), Ultra-Turrax (Janke&kunkel IKA-Labortechnik), Rotary evaporator (Heidolph, Laborota 4000-efficient), Gas chromatography (GC), HP Agilent 6890, EC (Electron Capture) Detector, Gas chromatography colon Agilent HP-5 kapillar colon; length: 30 m, inner diameter (id): 0.25 mm, film thickness 0.25 μm .

Chemicals and the testing reagents: The chemicals and the testing reagents used are at the chromatographic in analytic grade, lens, granular sodium sulphate (Na_2SO_4), lens, flouricil, 60-10 mesh, lens, flouricil was activated by keeping it pasteurization oven at 200 °C for 12 h, oil ether, lens, dietile ether, lens, filter paper, Whatmann no. 4, glass cotton. Reference pesticide standards used in this study are obtained from Dr. Ehrenstorfer firm in 10 ppm standart solutions. Pesticide standards are given to GC after dilution in different concentrations²⁵.

Conditions of chromatographic analysis of pesticide remains: Samples were analyzed with the column held initially at 80 °C for 1 min. It was then increased to 180 °C, with 30 °C/min heating ramp and then increased to 205 °C with a 3 °C/min heating ramp and kept there for 4 min. Finally, temperature was increased to 290 °C with a 20 °C/min heating ramp and the temperature was kept there for 2 min. Injection temperature was 270 °C and detector temperature 320 °C. Carrier gas used was helium with a flow rate of 2 mL min⁻¹.

Pesticide remains extraction: In analytical examples, acetone was determined by Luke *et al.*²⁶ as the best solvent for pesticide types and metabolites is used as an extraction solvent. A method has been developed by making use of the studies of Luke *et al.*²⁶. In this study, firstly a sample of 100 g fruits was taken for the extraction. The sample was chopped into little pieces by using a knife and 100 mL acetone was added. It was homogenized in a blender in high cycle. It was infiltrated into extraction funnel (250 mL) with filter paper. And on the filter, 40 mL oil ether and 40 mL diethyl ether were added and it was mixed for 10 min. Water phase (lower phase) was taken to a second separator funnel. Upper phase (organic phase) was taken to retort joje by filtering with 20 g Na_2SO_4 . The phase on the other separator funnel was mixed with 40 mL of diethyl ether. The phase at the bottom was again taken to a separator funnel. The upper phase was taken to balloon joje by filtering in Na_2SO_4

again. The lower phase which was taken to separator funnel was mixed with 30 mL of diethyl ether. The lower phase has been deleted. The upper phase was taken to balloon joje by filtering in Na_2SO_4 . The upper phases gathered in the balloon joje were evaporated in rotary evaporator until it remains 0.5 mL. 2 mL of acetone was added and forwarded to clean up phase.

Purification of the pesticide remains in the extraction (clean-up method):

The flouriscile technique was used for dispelling the existing pollution in the obtained extract. For the elusion of the pesticides, oil ether and diethyl ether are used as elusion solvent²⁷. While preparing the glass chromatography column, the proportion of floricile and sodium sulphate is very important for the regaining of pesticides. Luke *et al.*²⁶ suggest the proportion of floricile and sodium sulphate as 8:1.

For fining down the pesticide remains in the extraction, firstly glass cotton was placed under the glass chromatography column. And 7 g of floriciel was added on the glass cotton and then 2 g of dehydrated sodium sulphate was added on. Pre-wash was carried out with 15 mL of acetone. After filtering the acetone in the column, it was evaporated in rotary evaporator and it was collected into an experiment tube *via* directing it into an eluate column on which we add 2 mL of acetone. The sample collected into the experiment tube was completely evaporated in nitrogen atmosphere. This was added on *via* oozing out 0.25 mL of hexane from the edge of experiment tube and it was transferred into mili vial and taken to GC. The analyses were carried out as three recurrences with 1 μL of the last eluate solution. As a result the average of three analyses was noted down.

RESULTS AND DISCUSSION

It was found that, the levels of organochlorine pesticides in the all investigated fruit specimens were lower than those of the MRL of European Commission Directives (Tables 1-3, Fig. 1).

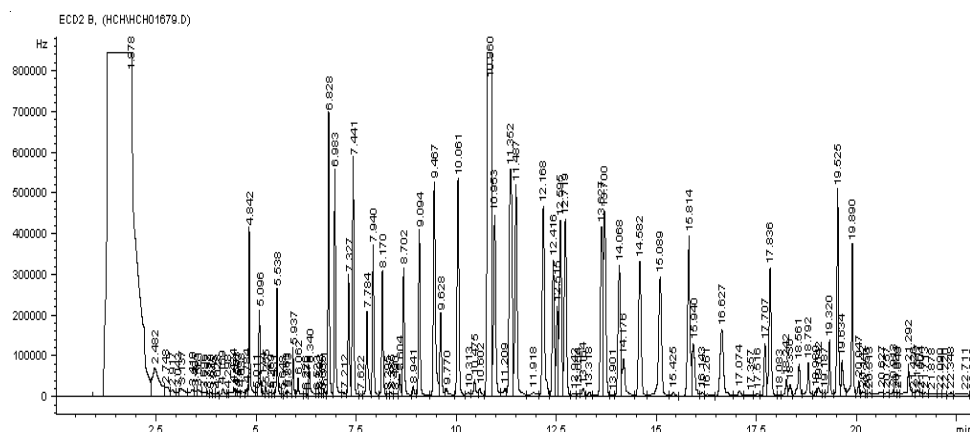


Fig. 1. Chromatogram of the pesticide standards

TABLE-2
PESTICIDE REMAINS DETECTED IN FRUIT SAMPLES (ng/kg)

Pesticide	Apple	Pear	B. grapes	W. grapes	Plum	Quince	Carrot	Date	Orange
Aldrin	0.0019	0.4707	0.0180	0.0290	0.2625	0.0067	0.0095	0.0069	0.0137
<i>cis</i> -Chlordane	0.0094	0.0238	0.0271	0.0637	0.3418	0.0150	0.0215	0.0057	0.0327
<i>trans</i> -Chlordane	0.0073	0.0027	0.0137	0.0203	0.3571	0.0181	0.0104	0.0020	0.0191
Oxy-Chlordane	0.0886	1.1129	0.2240	0.2814	0.8269	0.2852	0.3404	0.0832	3.6987
2,4'-DDD	0.3558	0.3727	0.0144	0.0960	0.3168	0.0074	0.0808	0.0592	0.0742
4,4'-DDD	0.0026	0.1652	0.0600	0.0222	0.0861	0.0109	0.0055	0.0170	0.0196
2,4'-DDE	0.0044	0.0409	0.1133	0.0217	0.4149	0.0069	0.0075	0.0119	0.0134
4,4'-DDE	0.0014	0.1264	0.5315	0.0104	0.1439	0.0060	0.0030	0.0128	0.0062
2,4'-DDT	0.0005	0.0288	0.0025	0.0088	0.0248	0.0027	0.0012	0.0117	0.0004
4,4'-DDT	0.0003	0.3429	0.0028	0.0165	0.0414	0.0022	0.0039	0.0051	0.0005
Dieldrin	0.0002	0.0129	0.0079	0.0022	0.0163	0.0022	0.0017	0.0005	0.0005
α -Endosulfan	0.0004	0.0026	0.0253	0.0043	0.0230	0.0042	0.0030	0.0004	0.0011
β -Endosulfan	0.0020	0.0208	0.1390	0.0047	0.0080	0.0029	0.0047	0.0002	0.0003
Endrin	0.0002	0.0020	0.0040	0.0288	1.3094	0.0077	0.0081	0.0019	0.0025
α -HCH	0.0041	0.0000	0.0025	0.0132	0.0086	0.0025	0.0028	0.0005	0.0007
β -HCH	0.0021	0.0000	0.0028	0.0052	0.2018	0.0047	0.0057	0.0014	0.0015
γ -HCH	0.0006	0.0000	0.0009	0.0115	0.2730	0.0028	0.0018	0.0003	0.0003
δ -HCH	0.0160	0.0000	0.0021	0.0147	0.1676	0.0058	0.0037	0.0007	0.0003
ϵ -HCH	0.0039	0.0000	0.0032	0.0046	0.0019	0.0059	0.0069	0.0008	0.0004
Heptachlor	0.0004	0.0000	0.0156	0.0042	0.0010	0.0045	0.0045	0.0003	0.0002
<i>cis</i> -H.epoxide	0.0003	0.0000	0.3320	0.0052	0.0000	0.0054	0.0025	0.0002	0.0000
<i>trans</i> -H.epoxide	0.0030	0.0000	0.0603	0.0051	0.0000	0.0208	0.0199	0.0006	0.0005
Hexachlorobenzene	0.0012	0.0000	0.0114	0.0808	0.0101	0.0096	0.0067	0.0006	0.0005
Methoxychlor	0.0104	0.1416	0.0479	0.1305	0.2624	0.0260	0.0163	0.0057	0.0298

TABLE-3
PESTICIDE REMAINS DETECTED IN FRUITS (ng/kg)

Pesticide	Tangerine	Grape fruit	Pomegranate	Banana	Old Buffer	Strawberry	Kiwi	Yam	Medlar
Aldrin	0.0072	0.0121	0.0090	0.0085	0.0029	0.1061	0.0061	0.0002	0.0198
<i>cis</i> -Chlordane	0.0169	0.0269	0.0288	0.0258	0.0166	0.1942	0.0204	0.0000	0.0258
<i>trans</i> -Chlordane	0.0080	0.0452	0.0154	0.0197	0.0261	0.0715	0.0168	0.0078	0.0000
Oxy-Chlordane	0.0629	0.2666	0.4477	0.3996	0.2175	1.6127	0.3195	0.0605	0.4182
2,4'-DDD	0.0867	0.0203	0.5709	0.0568	0.0447	1.8122	0.0383	0.0442	0.0563
4,4'-DDD	0.0198	0.0157	0.0140	0.0060	0.0128	0.2137	0.0139	0.0084	0.0284
2,4'-DDE	0.0245	0.0189	0.0133	0.0125	0.0071	0.1058	0.0073	0.0176	0.0698
4,4'-DDE	0.0043	0.0049	0.0008	0.0050	0.0029	0.0599	0.0044	0.0082	0.0188
2,4'-DDT	0.0000	0.0011	0.0003	0.0018	0.0012	0.0764	0.0026	0.0000	0.0298
4,4'-DDT	0.0000	0.0025	0.0058	0.0071	0.0025	0.0842	0.0025	0.0107	0.0000
Dieldrin	0.0000	0.0010	0.0004	0.0039	0.0007	0.0577	0.0026	0.0099	0.0000
α -Endosulfan	0.0000	0.0055	0.0003	0.0049	0.0033	0.0402	0.0039	0.0000	0.0000
β -Endosulfan	0.0000	0.0026	0.0004	0.0095	0.0018	0.5664	0.0045	0.0000	0.0000
Endrin	0.0000	0.0050	0.0012	0.0254	0.0025	0.0567	0.0058	0.0000	0.0000
α -HCH	0.0002	0.0214	0.0000	0.0048	0.0024	0.0286	0.0025	0.0011	0.0000
β -HCH	0.0012	0.0107	0.0004	0.0169	0.0043	0.0717	0.0089	0.0041	0.0000
γ -HCH	0.0002	0.0043	0.0410	0.0068	0.0022	0.0302	0.0027	0.0000	0.0410
δ -HCH	0.0001	0.0097	0.0000	0.0264	0.0047	0.0891	0.0095	0.0000	0.0000
ϵ -HCH	0.0000	0.0154	0.0000	0.0085	0.0018	0.0982	0.0053	0.0000	0.0000
Heptachlor	0.0000	0.0077	0.0000	0.0125	0.0027	3.0119	0.0057	0.0000	0.2226
<i>cis</i> -H.epoxide	0.0000	0.0060	0.0083	0.0199	0.0010	0.1177	0.0075	0.0000	0.0282
<i>trans</i> -H.epoxide	0.0000	0.0155	0.0000	0.0280	0.0089	2.0797	0.0346	0.0000	0.0000
Hexachlorobenzene	0.0000	0.0091	0.0000	0.0316	0.0055	0.0202	0.0099	0.0146	0.0000
Methoxychlor	0.0087	0.0268	0.0016	0.0368	0.0138	0.1327	0.0641	0.0445	0.2341

TABLE-4
MAXIMUM REMAIN LIMITS IN THE FRUITS ACCORDING TO EUROPEAN UNION INSTRUCTIONS (ng/kg)

Fruits	Aldrin	<i>cis</i> -Chlordane	<i>trans</i> -Chlordane	Oxy-Chlordane	<i>o,p'</i> -DD	<i>p,p'</i> -DD	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Dieldrin	α -Endosulfan	β -Endosulfan	Endrin	α -HCH	β -HCH	γ -HCH	δ -HCH	ϵ -HCH	Hephtaklor	H-Epoksid A	H-Epoksid B	Hexachlorobenzene	Methoksiklor	
Apple	0.01*	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.3	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pear	0.01	0.01	0.10	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.3	0.30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
B. Grapes	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
W. Grapes	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Plum	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Quince	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.3	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Carrot	0.02	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Date	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Orange	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Tangerine	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Grapefruit	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.5	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pomegranate	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Banana	0.10	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.10	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Old Buffer	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Strawberry	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Kiwi	0.02	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.02	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Yam	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Medlar	0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.01	0.1	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

*Entries in blue are the latest EC MRLs set in Directives 2006/53, 2006/59, 2006/60, 2006/61 and 2006/62.

Conclusion

As a conclusion, many adverse consequences of pesticide remains are at issue. To minimize or eliminate these adverse consequences, the following topics should be taken put into practice.

(1) The tolerance limits of the used pesticides for the health of people and environment should be taken into consideration. After the analysis, if vitally dangerous ones may emerge, it will be indispensable to withdraw them from the market or limit the usage of them. Nevertheless, before doing these processes, the alternative struggle methods should have been determined and put into the service for the producers beforehand. (2) It shows us itself as an important factor that the producers suppose that their struggle against the diseases and pests consists only of the use of chemicals and it is an important issue to get comprehensive knowledge. However, before the chemical control, the effective control of the diseases and pests can be carried out by taking cultural and physical precautions requiring no cost. In other words, a strategy of all the convenient methods and techniques should be aimed at. (3) The period between the usage of the pesticide and harvest, namely harvest intervals should be determined and the producers should exactly be informed about this issue. (4) Within the shortest possible time, the tolerance tables for each pesticides according to the standards of Turkey should be prepared. Although the studies on this topic gained acceleration, a healthy report for a pesticide has not been introduced yet. (5) It is possible with the remain monitoring method to solve the possible problems rapidly which may occur because of pesticide remains, to determine such problems in advance and to take the necessary precautions. And to accomplish this purpose, the related institutions need fully developed laboratories having the capacity to carry out such kind of analysis. For this purpose, modern computer supported laboratories which have competence in both the technical staff and equipments should go into operation. (6) It should keep in mind that the support for the technologic enterprises aiming to eliminate the harmful effects of the pesticide remains and the findings of the studies will reap lasting benefits for both the economy of our country and health of people and environment.

ACKNOWLEDGEMENT

The authors would like to thank Selcuk University (BAB) for the financial support of this study.

REFERENCES

1. M.F. Makhdoum, *Int. J. Environ. Appl. Sci.*, **3**, 142 (2008).
2. M. Karatas and S. Dursun, *Int. J. Environ. Appl. Sci.*, **1**, 54 (2006).
3. O. Zeren, H. Kumbur, G. Baydar and K. Yilmaz, *Türkiye' de Çevre Kirlenmesi Öncelikleri Semp. II Bildirileri*, pp. 973-983 (1997).
4. T. Gündüz, *Çevre Sorunları*, Bilge Yayıncılık, Ankara (1994).
5. K. Gür, H.N. Uçan and S. Dursun, June 12-16, 2006 Albena Resort, Bulgaria, p. 453 (2006).
6. M.N. Sisli, *Çevre Biyolojisi L Hacettepe U. Fen Fak. Biyoloji Böl. Ekoloji Ana Bilim Dalı*, Beytepe-Ankara (1994).

7. S. Kaya, H. Yavuz, Özel Toksikoloji, Medisan Yayınevi, Ankara, p. 375 (1995).
8. W. Durham, Pesticides and Human Health, Bioscience Publication, London (1994).
9. M.T. Topbas, A.R. Brohi and M.R. Karaman, Çevre Kirliliği, T.C. Çevre Bakanlığı Yayınları Ankara, p. 339 (1998).
10. S. Dag, V.T. Aykaç, A. Gündüz, M. Kantarci and N. Sisman, Türkiye Ziraat Mühendisliği V. Teknik Kongresi, p. 933 (2000).
11. A. Kelle, *Dicle Üniversitesi Tıp Fakültesi Dergisi*, **16**, 27 (1989).
12. M.A. Khan, R.R.A. Khan and A. Mohammad, *J. Hazard. Mater.*, **122**, 177 (2005).
13. Y. Hisil, Türkiye 3. Gıda Kongresi. Gıda Tek. Derneği Yayınları, Ankara (1982).
14. Y. Hisil and G. Tufan, E.Ü. Mühendislik Fakültesi Dergisi, B, 2, 29 (1992).
15. M. E. Aydın, K. Gür, S. Özcan and S. Sari, *Fresenius Environ. Bull.*, **13**, 1303 (2004).
16. S.K. Gaw, A.L. Wilkins, N.D. Kim, G.T. Palmer and P. Robinson, *Sci. Total Environ.*, **355**, 31 (2006).
17. S. Hussain, T. Masud and K. Ahad, *Pak. J. Nutr.*, **1**, 41 (2002).
18. N. Ochiai, K. Sasamoto, H. Kanda, T. Yamagami, D. Frank and S. Pat, Multi-Residue Method For Determination of 85 Pesticides in Vegetables, Fruits and Green Tea By Stir Bar Sorptive Extraction and Thermal Desorption GC-MS, Global Analytical Solutions (GERSTEL), AN/2004/04-3 (2004).
19. A. Kaihara, K. Yoshii and Y. Tsumura, *J. Health Sci.*, **46**, 336 (2000).
20. L. Chen, Y. Ran and B. Xing, *Chemosphere*, **60**, 879
21. T. Goto, I. Yuko and Y. Sadaji, *Anal. Chim. Acta*, **555**, 225 (2006).
22. C. Blasco, M. Fernandez, Y. Pico, G. Font and J. Manes, *Anal. Chim. Acta*, **461**, 109 (2002).
23. A. Zohair, A. Salim, A.A. Soyibo and A.J. Beck, *Chemosphere*, **63**, 541 (2006).
24. A. Colume, S. Cardenas, M. Gallego and M. Valcarcel, *Anal. Chim. Acta*, **436**, 153 (2001).
25. C. Ozdemir, N. Sen and S. Dursun, *Int. J. Environ. Appl. Sci.*, **2**, 33 (2007).
26. M.A. Luke and J.E. Froberg, *J. Assoc. Off. Anal. Chem.*, **58**, 1020 (1975).
27. M. Shyre, G. Hanschmann and R. Heber, *J. AOAC*, **81**, 513 (1998).