SEASONAL LEVELS OF INSECTICIDE RESIDUES IN WATER SOURCES AT BEHERA GOVERNORATE

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To My Husband, Sun and Daughter

قرار لجنة الحكم والمناقشة

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INTRODUCTION

Water is one of our basic natural resources, since the total amount of water on the earth is essentially constant, any wasteful consumption will reduce its small available supply. Consequently the concept of control was introduced and obligatory adopted. Water quality degradation "pollution" is an impairement which does not only create an actual hazard to public health but also adversly and unreasonably affect water utilization.

Water is considered polluted when it is either directly or indirectly altered in composition or condition, as a result of human and livestock activities, so that it becomes less suitable for any purpose. A polluted stream is therefore contains excessive amounts of specific pollutants such as insecticides. Some water insecticide pollutants are persistent and do not change their composition in the aquatic environment, while other compounds are biodegradable producing intermediate residues which may be more toxic than the original insecticides.

Recent insecticides are important examples of the newly developed synthetic organic chemicals which have substantially helped man in his continous struggle for improving his environment.

As would be the case in widespread use of any toxic substance, a through understanding of the hazards as well as the benefits associated with the use of insecticides is necessary. Ideally their injurious action would be highly specific for undesirable target organisms. In fact however, most of the chemical insecticides are not highly selective but are generally toxic to many non target species including man, animals and other desirable forms of life that coinhabit the environment (Hays, 1969). Currently, there is no evidence that the insecticide level in water, present an acute toxicity hazard to man and animals. Little is known however,about the effect of long-term, low level environmental contamination. Moreover, the concept of biological magnification under scores is the need to be aware of less than the lethal concentration of insecticides in drinking water.

Nowadays, the massive use of pesticides for agricultural and domestic purposes, has resulted in an increased occurrence of these toxic organics in natural waters and environment. It has been estimated that approximately 4 billion pounds of pesticides were used worldwide during the year 1975 (Moses, 1980). In Egypt, 617507 metric tons were the total quantity of pesticides used between 1952 to 1984. El-Gharbia exceeded all Egyptian governorates in using 68673 metric tons of pesticides during that period, followed by El-Behera (57771 metric tons) and El-Sherkia (36860 metric tons) (Abdel-Gawaad, 1985).

The increasing use of organic chemicals has become a concern to environmentalists and many research workers. When a pesticide is applied to the soil it may undergo microbial decomposition, photodecomposition, chemical degradation, volatilization, plant up-take, adsorption, transported in surface runoff, sedimented or leached through the soil. Losses of pesticides in surface runoff have been well decumented (Ritter, 1986).

Ground-water contamination by insecticides has only been in recent years of scientific interest which began to emphasize the problem after the detection of some insecticides in ground water in various localities (Cohen, et al., 1984). A comprehensive approach was focussed on the prevention of future contamination as well through its general protection strategy. It has been recently realized that as much as 141 existing pesticides were identified and registered as potential contaminants of ground water. Obligatory restriction has been developed against the use of chlorinated hydrocarbons in many countries, since they are long term acting persistent compounds and become concentrated in the tissues and the upper trophic level of the food chain. D.D.T residues were detected in soft tissues and deposited fat samples collected from slaughtered animal carcasses. On the other hand, the restriction on the use of chlorinated compounds, increased the utilization of other insecticides such as organo-phosphorus and carbamate compounds on account of their lesser persistence although they are highly toxic. (Salah, 1986).

Insecticides reach aquatic systems by direct application, spray dirft, aerial spraying, washing from atmosphere by precipitation, erosion and runoff from agricultural factories and sewage, Moreover, water at the bottom of rivers, streams and lakes are the major reservoirs persistent insecticide residues.

The world-wide use of insecticides make it urgent to know as much as possible about the effect of insecticides and their degradation products on human beings and animals. Immediate toxic effects are relatively readily assessed, but delayed effects are more difficult to detect and yet may be the most important possibly leading to an increased susceptibility to diseases, tissue damage and other affections under investigation (Dandliker, et al., 1980).

The aim of the present work are :

1. Determination of insecticide residues in different water sources during various seasons in Behera Governorate.

2. Effectiveness of water treatment in the removal of

insecticide residues from water in the public water treatment plants, as well as by the experimental use of activated carbon filters.

3. To study the relationship between the presence of some chemicals and the level of insecticide residues in different water sources.

REVIEW OF LITERATURE

1- INSECTICIDE RESIDUES IN SURFACE WATER.

The widespread use of pesticides to destroy plant or animal insects, has resulted in contamination of surface water with insecticide residues. Organic insecticides reach surface water through the direct application for control of aquatic weeds, trash fish, aquatic insects, percolation and runoff from agricultural lands, drift from aerial and land applications as well as discharge of industrial waste water from cleanup of equipments used for insecticide application.

In Egypt, these compounds are used on a large scale and consequently affecting the environment very badly, since insecticides are toxic to animal health and responsible for a pollution of a serious character to man and animal living along the banks of rivers and surface water in general. It is essential therefore to determine these compounds in surface water.

Many organic pesticides were added directly to water for aquatic-insect control. D.D.T. was added to the river water to give a concentration of 0.1 p.p.m. for the control of black-fly larvae (Freeden, 1953).

Many chlorinated hydrocarbon insecticides have been detected from various surface waters in the United States. In 1953, D.D.T. was recovered from raw and treated drinking water in concentrations of 1-20 p.p.b. In 1957, D.D.T. was also detected in river water in concentrations of 1-20 p.p.b. Apparently, rain washed these chlorinated hydrocarbons into the rivers from the soil. Empirical evidence to support this speculation came from an incident in which fish were decimated in stream tributary to the river by chlorinated hydrocarbon insecticides applied to cotton fields (Rosen and Middleton, 1959).

Middleton and Lichtenberg (1960) stated that D.D.T. in several rivers ranged from 1 to 20 p.p.b. Moreover, they concluded that concentrations of Malathion of less than one p.p.m. were investigated in various lakes.

Weidhass, et al. (1960) studied experimentally the pathways of D.D.T. in water when kept above a layer of soil covered with a filter paper. It has been found that after 6 hours, about 56% of the insecticide were retained in the soil and about 22% were further moved into the soil after 24 hours.

The distribution and disappearance of Endrin in water, mud and vegitation of ponds were studied by Bridges (1961). An initial concentration of 0.04 p.p.m. of Endrin was found to disappear from the water within a month. However, most of the insecticide was concentrated in the mud and vegitations, where it persisted for a long period.

As a part of water quality determination, insecticides were identified in 38 samples from ten rivers during a period of 6 months. D.D.t. was identified by infra-red and gas chromatographic analysis of carbon adsorption extracts (Breidenbach and Lichtenberg, 1963).

Faust and Aly (1964) found that many chlorinated hydrocarbons were detected in various surface waters in the United States. Most of these insecticides were identified during the research performed for the purpose of developing the carbon filter technique.

Warnick and Gaufin (1965) stated that the electron-capture system of gas chromatography could be used to obtain reproducible quantiative detection of both organophosphorus and chlorinated hydrocarbon pesticides in concentrations of less than one p.p.b.

The detection of chlorinated hydrocarbons in stream water depended upon the amount applied, the fraction carried to the stream in runoff and the stability of the stream environment. High levels of chlorinated hydrocarbons were generally demonstrated (Weaver, et al., 1965).

On the other hand, D.D.T. was frequently detected in cases of extensive irrigation. Moreover, the authors reported that water contamination by insecticidal soil residues was to a large degree a function of water solubility of the particular insecticide. The degree of water contamination was also dependent on the insecticidal concentration in the soil resulting from the original application dose and the specific dose and the specific properties of a given pesticide in the soil. They recorded that the mean values of Endrin and D.D.T. were found to be 5.5 and 9.3 ng/liter with a maximum of 94.0 and 102.0 ng/liter in U.S. river basins respectively.

Chlorinated hydrocarbon pesticide compounds were reported to contaminate the aquatic environment as a result of their widespread utilization and persistence. Their concentrations were detected in nanograms or micrograms per litre of water in almost all major U.S. rivers and lakes (Croker and Wilson, 1965 and Weaver, et al 1965).

Wheathley and Hardman (1965) indicated the presence of organochlorine insecticides in rain water. The results of their investigation revealed that rain water samples contained -B.H.C (Benzene Hexachloride), Dieldrin and D.D.T. in detectable amounts up to 100,20 and 3 p.p.t. respectively.

Cohen and Pinkerton (1966) recorded that P,P-D.D.T. in rain water was found to range between 7 and 340 p.p.t.

Green, et al. (1966) reported that D.D.T. was detected in large amounts in U.S. rivers, but it was not always the most common organochlorine residue.

Keith and Hunt (1966) stated that a very little amount of D.D.T. was detected in river water however, much more quantities were demonstrated in suspended particulate matter and bottom sediment.

Warnick, et al. (1966) selected 70 areas in Salt Lake County, Utah, U.S.A. in order to determine the pesticide residues, including rivers, creeks, canals, ditches, ponds, drainage areas, springs and wells. All areas were sampled at least monthly throughout the subsequent spring, summer and autumm. The investigation of 48 water samples collected from ditches and ponds draining agricultural areas revealed that Dichlorodiphenyl ethane (D.D.E.) was detected in concentrations varying from 2.0 to 25 p.p.b. in 24 samples, orthopara-D.D.T. in concentrations varying between 1.4 and 4.6 p.p.b. in 14 samples and para-para-D.D.T. in concentrations varying between 0.6 and 2.8 p.p.b. in 8 samples and the remaining two sample were found to be negative. Moreover, the authors noticed that increased concentrations of chlorinated hydrocarbons were detected in the water of some areas that were treated with organic phosphates. An explanation was given to be due to the release of tissue-stored chlorinated hydrocarbons (D.D.T. and D.D.E.) on decomposition of organisms killed by Dursban treatment.

Weibel, (1966) determined pesticides and other contaminants in rainfall and runoff. Detected pesticides included Chlordane, Heptachlor Epoxide, D.D.E., D.D.T. and Dieldrin at concentrations 0.5, 0.04, 0.2, 0.6 and 0.003 p.p.m. respectively.

Brown and Nishioka (1967) examined monthly water suspension samples of a mixture from 11 streams for organochlorine pesticides. All insecticides were detected in quite small amounts ranging from less than 5 parts per trillion of Lindane to 110 parts per trillion of D.D.T.

Breidenbach, et al. (1967) determined chlorinated hydrocarbon pesticides in major river basins. The results of the synoptic pesticide surveys revealed that Dieldrin was dominated in all river basins while Endrin reached a maximum level in the fall and incriminated in a major fish kills. Moreover, D.D.T. and its metabolites were found to be fairly common in the samples examined.

D.D.T. residues were reported to be very persistent in nature, and it has been estimated to remain up to 20 years and perhaps longer under certain circumstances (Nash and Woolson, 1967).

Weatherholtz, et al. (1967) investigated thirty five farm ecosystems for Heptachlor residues D.D.T. was the only chlorinated hydrocarbon that could be detected in addition to Heptachlor and its epoxide.

Rice and Dishburger (1968) determined Dursban residues in water by Gas-liquid chromatography. Extraction was performed by using methyline chloride and cleaned up with an silica gel column. Dursban residues of 0.0001 p.p.m. were recovered from as much as 92% of water samples.

The first suggestion about air-borne transportation of organochlorine residues for long distances was reported by Tarrant and Tatton (1968). A further survey about rain water collected from seven sites scattered over the British isles was performed. It has been found that D.D.T. and Lindane were detected at mean values of 79.57 and 41.66 ng/kg respectively.

U.S. Department of Interior, Federal Water Pollution Control Administration, Water Quality Criteria (1968) reported that the permissible levels of Endrin, D.D.T., Lindane, Chlordane, organophosphates together with carbamates in a water supply were found to be 1.7, 1,42,56,3 and 100 ng/liter respectively. In addition, because of their toxicity to fish, it has been recommended that environmental levels of these substances should not be permitted to rise above 0.050 ug/liter.

Croll (1969) examined the rivers in England through a survey in order to study the pesticide residues in 26 rivers in different parts of the country. The concentrations reported were relatively small (less than 50 ng/liter), particularly when considered that samples were expected to be taken from areas that might receive drainage from an insecticid-treated land. Moreover, nearly similar data were reported by Lowden, et al. (1969) from a survey of 17 British rivers.

Lichtenberg, et al. (1970) summarized the results of five annual synoptic surveys (1964-1968) for chlorinated hydrocarbon pesticides in surface water at 101 sampling stations. The results showed a wide spread occurrence of certain compounds. Dieldrin dominated the pesticide occurrence of 199 positive results out of 529 analysed samples with 0.407 ug/liter as a maximum concentration, while D.D.T. and its metabolites D.D.E. and D.D.D. occured in 183 positive results with a maximum concentration of 0.316, 0.050 and 0.840 ug/liter respectively.

Moreover, Endrin, Lindane and Chlordane were the other chlorinated hydrocarbons detected at maximum concentrations of 0.133, 0.112 and 0.169 ug/liter respectively. On the other hand, the organophosphorus compounds could not be detected in the investigated samples.

Macek and Mcallister (1970) reported that organophosphate insecticides were relatively soluble and those which were not readily hydrolysed might be expected to be taken up by a wide range of aquatic organisms. However, all organophosphates were relatively short-lived in biological systems.

Cowart, et al (1971) reported that about 46.3 percent of Diazinon remained after two weeks in natural aquaeous solutions at room temperature.

Dimond, et al. (1971) showed that D.D.T. persisted in small streams for as long as 10 years after a single application. Such sprays which reached water were responsible for maintaining low levels of pesticide pollution in many lakes, rivers and streams, but usually in amounts insufficient to be toxic to many aquatic organisms.

Eichelberger and Lichtenberg (1971) investigated the efficiency of carbon adsorption method for recovery of chlorinated pesticides from water. They concluded that this method was useful for the isolation and determination of some chlorinated hydrocarbon pesticides. They also stated that this method was not suitable for most of the investigated organophosphorus pesticides.

Data obtained from the Jordan water shed revealed the presence of D.D.T. and its metabolites (D.D.E. and T.D.E.) at variable levels. Detectable levels of D.D.T. in water ranged from 0.019 and 0.500 p.p.b. It has been found that the agricultural use of D.D.T. in valleys was the main source of its presence in water (Jacob, 1971).

Kolipinski, et al. (1971) examined different sites for monitoring environmental concentration of selected insecticides. It has been found that the water in these sites contained D.D.T. and its metabolites D.D.D. and D.D.E. in concentrations up to 0.03 ug/liter. D.D.T. and its metabolites were detected more frequently than other organochlorine insecticides. Residues in these sites were carried by transport mechanisms such as surface water inflow and aerial transport consisting of direct particulate fallout and precipitation.

Miles and Harris (1971) examined water for insecticide residues (P,P-D.D.E., O,P-D.D.T., P,P-D.D.D. and P,P-D.D.T.).

The concentration of P,P-D.D.T. varied betwen 10 and 230 p.p.t. while at house pumps its concentration ranged from < 1 to 50 p.p.t. The concentration of insecticides in drainage system was greater than those in creek water. Moreover, they found that the residues of organochlorine insecticides primarily D.D.T. and its metabolities were present in streams and ditches located in draining agricultural areas.

Woodwell, et al. (1971) concluded that only about 0.1% of the D.D.T. produced annually reached natural waters via run-off from agricultural lands. Although the continual replenishment of natural waters with persistent pesticides was a hazard that could not be ignored however, it did not seem to be of major importance as a source of pollution.

Yule and Tomlin (1971) estimated D.D.T. in river water after application to an forest area. They found that D.D.T. was recorded in the streams during and for a few hours after actual spray application in a concentration exceeded a steady background level of 0.5 p.p.b.

Bevenue, et al. (1972) examined 46 non-potable water samples and reported that P,P-D.D.T., Lindane and Chlordane ranged from 0.2-64, 0.0-3.4 and 3-17.6 p.p.t. respectively.

Moreover, they added that P,P-D.D.T., Lindane and Chlordane were recorded in non-potable water from other areas in 1-7.1, non detectable to 20 and 3-13 p.p.t. respectively.

Bradly, et al. (1972) noticed the movement of D.D.T. in surface run-off from cotton fields and contamination of a farm pond. They found that D.D.T. residues in water of a small pond, ranged from < 0.35 p.p.b. before spraying to 13.4 p.p.b. during the spraying season.

Fay and Newland (1972) determined the presence and distribution of organochlorine insecticide residues in 80 water samples collected monthly. Endrin and P,P-D.D.T. residues were detected in 3 samples where D.D.T. was recorded in trace amounts (less than 0.1 p.p.b.), while Endrin in 4.4 p.p.b. The occurrence or concentration of residues could not be related neither to the salinity nor the water pH.

Herzel (1972) assessed pesticide residues in unfiltered water sampled monthly. Lindane was recorded most frequently and its concentration ranged up to 7100 p.p.t. However D.D.T. and particularly its metabolites D.D.D. and D.D.E. were detected infrequently. The highest concentration of D.D.T. was found to be 170 p.p.t., while D.D.E. and D.D.D. were 85 and 830 p.p.t. respectively.

Lenon, et al. (1972) recorded that samples of cistern water used by local population were analysed for pesticides residues. Chlorinated hydrocarbon pesticides were previously used quite extensively in the investigated areas however, Malathion was commonly used at the same time. Evidence of an unknown Malathion metabolite was detected in all of the water samples analysed, wherease Malathion was found in only two (0.01 and 0.14 p.p.m.). On the other hand, D.D.T. and its metabolites were not commonly recorded in the water samples.

Current agricultural application practices resulted in a contamination of the aquatic environment through atmospheric processes. Those processes which contributed to contamination included volitilized fallout, washout, drift from dusting and spraying operations as well as wind transportation from pesticide-treated soil precipitation and entrained dust seemed to be the major source of pesticides in water (Edwards, 1973).

Methomyl as a water soluble carbamate insecticide which degraded rapidly by microbes with by-product CO_2 and S-methyl N-hydroxythioacetimidate as hydrolysis by-products. Methomyl was generally considered to be a non-leaching and available for uptake and transformation (Harvey and Pease, 1973).

Miles and Harris (1973) examined organochlorine insecticide residues in water systems draining agricultural, urban agricultural and resort areas. The maximum concentration of P,P-D.D.T., Chlordane, Endrin and Lindane were found to be 58,21,7 and 14 p.p.t. (part per 10^{-12}) respectively with a minimum of 4,0,0, and less than 1 p.p.t. respectively. They concluded that the recreational use of insecticides was contributing a greater portion of these residues to the water system. The authors did not attempt to draw any detailed relationships between pesticide use in the drainage areas and their concentrations in water.

In the course of program of U.S. Geological survey for the monitoring of pesticides in streams in the west of United States, water samples were analysed to detect the common chlorinated insecticides. D.D.T. was found to be the most frequent insecticide detected but in small amounts (the maximum concentration was 0.46 ug/liter). Moreover, the highest concentrations were detected in water samples containing appreciable amounts of suspended sediments. On the other hand, residues of other organophosphorus insecticides such as Diazinon could not be detected in any of the samples examined (Schulze, et al., 1973).

Residues of D.D.T. recorded in 341 samples of water averaged 18.5 p.p.t. (parts per U.S. trillion $\{10\}^{12}$) in waste and culinory water, 26-4 in surface water and 43.7 in industrial waste water. The average residues of D.D.T. and some other detected chlorinated hydrocarbons were below the statutory limits. (Southwick, 1973).

Kneip, et al. (1974) studied the occurrence of chlorinated pesticide residues in a river water and found that their concentrations were higher at the upper levels of the food web than in the aquatic medium in which the biota was living, and were higher in animals or tissues having higher fat content. However, a quantitative interpretation of pesticide concentrations in the food web and the relation to water concentration required an understanding of the routes and dynamics of uptake. The pesticide concentrations in sediments were many times higher than those in water. They concluded that pesticide concentrations varied greatly in relation to both season and sampling sites.

It has been reported that high temperatures and relative humidity decreased the toxicity of some insecticides. (Korpela and Tulisolo, 1974).

Water samples were analyzed for Diazinon and detectable concentrations were detected with a maximum of 82 p.p.b. (Ritter, et al., 1974). They added that the highest concentrations of Diazinon were recorded in the runoff samples collected 4-10 days after Diazinon application, with a maximum of 0.1% in the surface runoff. The low concentrations of Diazinon in water were due partly to the rapid degradation and partly to the incorporation of chemicals into the soil.

Schacht (1974) reported that chlorinated hydrocarbon insecticides in Michigan Lake water samples were all below 0.001 p.p.b.

Mattraw (1975) revealed that insecticide residues were more frequently detected in agricultural areas of southern Florida than in other U.S water streams. D.D.T. and its metabolites (D.D.D. and D.D.E.), Dieldrin and Landane were detected in all samples examined. The investigator added that the restrictions applied in using insecticides resulted in a less frequent detection of several chlorinated hydrocarbons.

Richard, et al. (1975) found that the amount of D.D.E. in various surface, subsurface and finished water ranged from 0.5 to 42,000 p.p.t.. They added that every major watershed revealed a degree of pesticide contamination and seasonal variation consistent with agricultural runoff model. Consequently, D.D.E. appeared in substantial quantities, providing a further evidence of the persistence of D.D.T. and its metabolites.

Rosival and Szokolay (1975) found that the content of P,P-D.D.T. in 176 surface water samples varied from 0.00 to 0.83 ug/liter.

Brodtman (1976) stated that the maximum values of Lindane and -Chlordane in river water were found to be 3 and 1.2 ng/liter with a maximum of 1.3, and 0.4 ng/liter respectively. The levels of Endrin and P,P- D.D.T. ranged from 1.4 to 7.4 and 0.0 to 3.5 ng/liter, respectively. He added that these pesticides occured almost continuously near the point of discharge into the river.

Edwards (1976) mentioned that the pesticides reached aquatic systems by direct application, spray drift, aerial spraying, washing from atmosphere by precipitation, erosion and run-off from agricultural land, by dischharge of effluents from factories and in sewage. He concluded that run-off from agricultural land was the main source of gradual pollution, with direct application to water and discharge of effluents into aquatic systems causing more serious, but localised contamination. He added that the pesticides in water became bounded to organic matter in the mud and sediment quite rapidly, and only small amounts remained in solution.

Glooschenko, et al. (1976) analysed samples of water for 15 organochlorine and 17 organophosphorus pesticides. All of the compounds analyzed in water samples were found to be below the quantification limits but traces of Lindane were found in all samples.

Paz (1976) stated that the detectable level of summation D.D.T. in water of rivers and fish ponds varied from 0.019 to 0.500 p.p.b.

The pesticides might be applied directly to water in order to control aquatic pests. The degradation of pesticides in aqueous systems was attributed to both the chemical and biological actions (Walker, 1976).

An investigation of chlorinated hydrocarbon insecticides in raw water of over 3000 samples from 333 locations indicated that approximately 12% of the samples contained D.D.T., while Chlordane was not detected in any of the samples (Environment Canada 1977).

Frank, et al. (1977) reported that since D.D.T. had not an agricultural use, its presence in stream water came from its persistence in the soil. Moreover, they reported that the presence of Chlordane in agricultural soil was below 0.5 ug/g and hence the soil itself could only act as a minor reservoir and source of this compound in water. They concluded that despite of the widespread use of Chlorpyrifos and Diazinon, only 20% of the soil contained detectable residues of Chlorpyrifose, while Diazinon was found in only one sample. The presence of organophosphorus insecticides in stream water would therefore indicate a recent use with introduction into water via storm runoff events or by nearly spills and spray drifts.

Most organophosphorus (O.P) and carbamate insecticides were regarded as being non-persistent. But recent reports have indicated that residues of O.P. insecticides were persisting for extended periods in organic soil used for vegetable production. (Harris, et al., 1977).

Sackmauerova, et al. (1977) stated that the average content of D.D.E. and D.D.T. in surface water samples were found to be 0.050 and 0.125 ug/liter respectively.

Microorganisms, rather than chemical agents were almost exclusively involved in the detoxification of organophosphorous insecticides as Diazinon and Parathions in the environment. Factors generally associated with microbial activity, including temperature, moisture and organic matter, have been implicated in its degradation. Bacteria readily built up in natural ecosystems such as flooded soils in response to repeated additions of Diazinon and Parathion, bringing about rapid inactivation of these organophosphates upon enrichment. Proliferation of these bacteria occured not during the enzymatic hydrolysis of Diazinon and Parathion, but through the utilization of the resultant hydrolysis products as exclusive and energy source. (Sethunathan, et al., 1977).

Degradation of Dimethoate in incubated solutions was examined at 4, 10, 24, and 34C. Gas liquid chromatography (GLC) was used to determine Dimethoate residues. Temperature, pH and type the of medium were important factors affecting the stability of Dimethoate in solutions. Evaporation was a minor factor in determining the loss of Dimethoate from water. With pH of 7-11, Dimethoate degradation depended on the alkalinity of the medium rather than the time of storage. At pH 4.2, degradation was largely dependent on the length of storage time of dimethoate solution. Acid or salt concentration had a little effect on the degree of degradation when the pH was maintained constant. (El-Beit, et al., 1978).

Greichus, et al. (1978) studied the concentration of organochlorine insecticides in a lake in Kenya and found that the water samples had a minimum analytical level (less than 0.0001 p.p.m.). The most prevalent residues was D.D.E. followed by D.D.D. and D.D.T., where the average concentration of each was found to be less than 0.0001 p.p.m.

Greichus, et al. (1978) examined the insecticide residues in a lake water. The average values of D.D.T., D.D.E. and D.D.D. in lake water were found to be less than 0.0001 p.p.m. for each insecticide. Lindane, Chlordane and Endrin were found in concentrations below the minimum values(less than 0.0001 p.p.m).

Kurtz (1978) analysed the community water supplies and open water reservoirs for D.D.T. and its metabolites. Only 4 of 19 streams and 7 of 110 community water supplies were found to contaminated with insecticide residues. However, three open water reservoirs were found to be free from detectable residues of investigated compounds.

Miles and Harris (1978) studied the insecticide residues in the drainage system. Residues of organochlorine and organophosphorous insecticides were present in the drainage system. The rate of insecticide transfer was highest in spring during maximum runoff. Organochlorine insecticides, chiefly D.D.T. and its metabolites predominated during this time. Dieldrin and Endrin were also detected. Organophosphorus insecticides including Diazinon and Parathion were found to be predominant in the water during summer and fall. The concentration of chlorinated and phosphorous insecticides in the river downstream were 3.5 x higher than those found upstream. Insecticide residues were present in bed materials of the drainage system at p.p.m.-levels and comprised mainly of D.D.T. and its metabolites.

In Canada, Pearce, et al. (1978) found that 76 of 101 rain water samples collected during spring and summer contained residues of D.D.T. The dominant residue was P,P-D.D.T. The levels of D.D.T. and its combined metabolites ranged from less than 0.01 to 1.33 ug/kg.

Residues of D.D.T. and Dieldrin were detected in several destricts in Canada. Samples of rain water were collected during the spring and summer. The total D.D.T. ranged from 0.01 to 0.90 ug/kg. The only organochlorine compound detected was Dieldrin in a concentration of 0.01 ug/kg (Peter, et al., 1978).

Rihan, et al. (1978) examined ten sampling sites at north Mississippi which was considered mainly as an agricultural area, to determine the quality and quantity of pesticide residues in the water. They found that the concentration of P,P-D.D.T. ranged from 2.73 to 12.31 and Lindane from 0.02 to 0.16 ng/liter.

Wegman and Greve (1978) analysed 1492 water samples for organochlorine pesticides and their metabolites in aquatic environments. The highest concentration of organochlorine pesticides were detected in the river and its tributaries which decreased downstream.

Boethling and Alexander (1979) during their study about the effect of concentration of organic chemicals on their biodegradation by natural microbial communities, reported that the microflora of stream water mineralized the 1-naphthyl 1-N methylcarbamate (Sevin) or nephthol formed from Sevin, at concentrations of 2 to 3 ng/ml or less, but it mineralized 60% or more of the compounds in 6 days when they were provided at higher levels.

After spraying of D.D.T. to control insects, the water was found to contain only 0.02 parts per million (p.p.m) of D.D.T. This very low concentration of D.D.T. appeared quite safe, and indeed after two weeks, no D.D.T. could be detected within the water. However, later studies showed that organochlorine compounds were extremely dangerous in an aquatic environment because, owing to their greater chemical stability, low aqueous solubility (D.D.T. 1.2 p.p.b., Dieldrin 186 p.p.m), and high lipohicity, they became concentrated in the living components of the river's ecosystem. the disappearance of D.D.T. from the water after two weeks was therefore, not due to its degradation, but rather arose from its transport into living organisms e.g., (Plankton, plants, fish, frogs, etc.). (Cremlyn, 1979).

Insecticide residues in the drainage system were studied by Miles and Harris (1979). Water contamination in the drainage ditches occured through surface erosion of contaminated soil by wind, and drift occuring as a result of insecticide spray programs. High insecticide and sediment levels in the drainage ditch and canal system during spring runoff indicated that surface erosion of soil by water was of major importance. To determine if leaching through the soil into the tile drains, four farms were monitored, which showed from 16-59 p.p.m. of D.D.T. in the soil. however, submerged water concentrations. of D.D.T. ranged from 26 to 100 ng/liter.

Some of the results were presented of an investigation to study under laboratory conditions, the adsorption of P,P-D.D.T., Diazinon and Chlorpyrifos in soil and their persistence in water. In order to use these results to explain the presence and fate of insecticides detected in an agricultural watershed, the field study indicated that the persistent organochlorine compounds were detectable in the drainage ditches and canals. (Sharom, et al., 1979).

Wang, et al. (1979) reported that the surface river water did not show any detectable D.D.T. residues.

The persistence and biological impact of the organophosphorus insecticides, Abate, Reldan and Dursban, were studied following the application of 10 p.p.b. to a series of artifical polyethlenelined ponds and a single natural pond inoculated with leafy litter. Disappearance of the insecticides from water was in 2 phases direcly post-treatment, in which rapid partitioning took place, and a variable time period characterized by a slowly decreasing residues pollutant perisistence in a decreasing order was Dursban, Reldan and Abate. The rapid initial pesticide disappearance from water was primarily attributed to adsorption on the bottom sediments and polyethylene. Polyethylene apparently had a greater affinity for the pesticides than the sediments. However, desorption from polyethylene contributed to residual concentrations in the water of artifical ponds for prolonged periods (Boyer, et al., 1980).

As a part of the comprehensive study about the effect of agricultural land activities on the quality of water stream water samples from agricultural watersheds were collected and analyzed for organochlorine and organophosphorus insecticide residues which were currently used in those watersheds. Detectable residues of Chlordane was found in 1.6% of the samples. Sixteen organophosphorus insecticdes were known to be used in the watersheds but only Chlorpyrifos, Diazinon and Malathion were detected. No other organophosphorus insecticides were found to exceed the proposed water quality objectives.

(Braun and Frank, 1980). They also reported that routes of entry of insecticides into water were postulated. Base flow, storm runoff, spills and spray drift were conditions assumed to prevail when ambient seasonal base flow and insecticide concentrations in water showed a significant coincidental increase. Spills and drifts were associated with conditions where the base flow remained steady but the concentration of the insecticides showed a significant increase. Moreover, soil erosion might be regarded as a major factor in the transport of insecticides into water systems.

Periodic sampling and analysis were carried out for pesticide immediately before and following application to the soil. The water and sediment of the pond, and the water of the river and three irrigation channels emptying into the pond were analyzed. The results showed that D.D.T. was detected in water in very low levels (Mestres, et al., 1980).

The relative importance of chemical and biological processes in degradation of some insecticides in water was studied by comparing their persistence in different types of water (natural, distilled, sterilized , natural and sterilized distilled). Some organochlorine such as D.D.T. disappeared fairly quickly in the natural water, but was very persistent in the other types, indicating the importance of microbial action in their degradation. There was a little indication of chemical degradation. Generally the other organophosphorus such as (Chlorpyrifos, Diazinon and some carbamates) disappeared from all types of water, demonstrating that chemical processes played a major role in their degradation, with biological processes having a secondary role. (Sharom, et al., 1980).

Sonzogni (1980), stated that pesticides including herbicides, insecticides and fungicides were applied in varying quantities to almost all types of land. Pesticides, if persistent (not rapidly degradable), could be carried off the land and into receiving waters. Pesticide residues could continue to contaminate drainage water for long periods after the use of the pesticide was discontinued. D.D.T. and Dieldrin residues in water were derived from past use in the basin. Little could be done to change this slow release to water. D.D.T. therefore explained how small amounts of certain pesticides could create long-term problems, but it was expected that the persistence or carry over associated with pesticides would soon be eliminated.

Among the pesticides detected in their study were Lindane, Endrin, D.D.T. and its derivatives (Eisenreich, et al., 1981). Organophosphorus group was frequently identified in water samples since it degraded rapidly in the environment.

Agricultural watersheds ranging in size between 19 and 79 km^2 were studied for residues of persistent organochlorine insecticides. Stream and rain water were analysed for the presence of D.D.T. and its metabolites that have been removed from field application. Summation D.D.T. was found to be present in 93% of stream water samples of which 40.6% excceded 3 ng/liter (Frank and Braun, 1981).

Kveseth (1981) found that summation D.D.T. residues in contaminated lakes, ranged from 1 to 3 ng/liter in water samples collected within a distance of 300 meter from a sewage effluent.

Persistence of Aldicarb was generally felt to be short term, its conversion to metabolites was rapid and complete. Rapid oxidation of Aldicarb to sulfoxide with a slower conversion to the sulfone has been reported and its break down by bacteria and fungi resulted in the eventual formation of CO_2 and H_2O (Leistra and Smelt, 1981).

The relative solubility of organophosphate insecticides in water and those which were not readily hydrolyzed might be expected to be taken up by a wide range of aquatic organisms. However, all the evidence was that organophosphates were relatively short-lived in biological systems and their toxicity to animals (Macek, 1981).

Disposal costal areas were treated with controlled-release pellets of Chlorpyrifos at the recommended rate, and the water and underlying soil were analysed to determine the Chlorpyrifos residues before and after treatment. Residues were found to be usually much lower in the soil than in warer (Merriam, et al., 1981).

Schnoor (1981) calibrated a model for the fate and transport of pesticide with field data. He found that approximately 50% of the pesticide load was exported from reservoir in outflow, 40% undergone sedimentation and 10% entered fish.

In Egypt, Riskallah, et al. (1981) investigated the fate of Chlorpyrifos in different types of water. After a storage period of 32 weeks in different types of water at room temperature ($25\underline{+}2^oC$), they found that less than 1% of initial Chlorpyrifos degradation was faster in distilled water than in river Nile, irrigating canals and drainage water.

Badawy (1982) examined natural water sources in selected agricultural areas in Egypt. He reported that the maximum concentrations of Lindane, Endrin, D.D.T. and Chlordane were found to be 12.4, 18.6, 17.0 and 7.4 ng/liter respectively, with minimum values of 1.3 and 1.6 ng/liter for the first two compounds respectively while the minimum values for D.D.T. and

Chlordane could not be detected. The concentration of Dursban ranged from 1.0 to 42.3 ng/liter.

Stream water draining 11 agricultural watersheds in Ontario was analyzed for 61 parent pesticidal compounds (plus four isomers), 13 metabolites and two industrial organic pollutants. Forty-one pesticides were common in the list of compounds used in watersheds, which accounted about 73% of the weight of pesticides used. Eighteen parent compounds (plus three isomers), three metabolites, and one industrial organic pollutant were found in drainage waters. In addition, three pesticides (D.D.T., T.D.E. and H.E.O.D.) were identified in water which did not recorded in current use for several years. However, the entrance of pesticides into stream water was determined to occur in main ways namely the storm runoff water (about 60%) internal soil drainage (about 18%) and from carelessness in operating equipment adjacent to streams (about 22%) Frank, et al., 1982).

Dimethoate residues were found to be decomposed in plants but not in water; which presented a hazard of a serious character in the field of seepage or persistently toxic residues from treated crops into water bodies containing non-target aquatic organisms. (Purohit, et al., 1982).

In Egypt, Ramadan (1982) studied the contamination of surface water following an aerial spraying of cotton fields with Chlorpyrifos. He reported that the initial deposit in water (9.33 p.p.b.) was determined one hour after application. After 24 hours, the residues dropped to 3.99 p.p.b. indicating 57.23% loss of initial deposits. After 7 days of spraying the residue of Chlorpyrifos reached 0.17 p.p.b., indicating 98.18 loss of the initial deposit.

All Chlorinated hydrocarbon pesticides such as D.D.T. and Lindane were detected in surface water samples collected in every investigated location. The most interesting finding was their presence in measurable concentrations. (Tanabe, et al., 1982).

Studies of the behavior of trace organic pollutants as D.D.T. and others have shown that the atmosphere and sediment inputs of D.D.T. decreased their hydrospheric burdens. However, seasonally driven processes of mixing and sediment resuspension might increase residence times of such compounds in water column. Episodic fluctuations in contaminant concentrations due specially to sediment resuspension might also had an important short-term consequences such as exposure of contaminants to spowning fish. The response time of fish, water and atmosphere to diminished inputs was remarkably fast however, with residene times on the order of few years. (Eadie, et al., 1983; Eisenreich and Johnson, 1983 and Eisenreich, et al., 1983).

Macalady and Wolfe (1983) reported that Chlorpyrifose, a model compound representive of the organophosphorathioate insecticides, was studied in aquatic ecosystems because of its potential hydrolysis not only in water but also in sediment. Chloropyrifos has undergone a pH-independent hydrolysis reaction over the environmentally relevant pH range of 4-7.5 and above pH 8, alkaline hydrolysis dominated.

Nadia E.H. (1983) found that hydrocarbon insecticides (Lindane, D.D.E. and D.D.T.) in the water of El-Mahmoudia canal at Khourshid averaged concentrations of 0.91, 2.32 and 1.97 p.p.b. Lindane and D.D.T. were found to be more frequent in spring and summer seasons. The highest concentration of summation D.D.T. was recorded in summer. She added that the average concentrations of Lindane, D.D.E., D.D.T. and summation D.D.T. in Mahmoudia canal at the up stream of Mountazah canal were found to be 0.73, 4.22, 1.81 and 6.51 p.p.b. respectively.

Some chlorinated hydrocarbon pesticides were analyzed monthly to evaluate their residues in water for irrigation purposes. High concentrations of these insecticides were detected which were attributed to their new application (Polemio, et al., 1983).

The photodecomposition of pesticides and other man made pollutants in the aquatic environment occured in both direct and indirect photochemical processes. Hydrogen peroxide promoted photoxidations occuring naturally in agricultural irrigation water and other surface water (Draper and Grosby, 1984).

To determine the means of decreasing organophosphrous pesticide levels by the effect of heat, 14 pesticides were tested for thermal decomposition in water (T.D.W.) and stream distillation (S.D.) behaviour. It has been found that Dimethoate related to the stable T.D.W. category of insecticides (Ishikura, et al., 1984).

The concentration of some organophosphate insecticides in almost all of the samples of drain water was below the detectable limit. However, in samples from water courses, pesticide residues were found regularly, sometimes at fairly high concentrations. Therefore, contamination of water courses would seem to be produced not by leaching of pesticides through the soil but by other pathways. (Leistra, et al., 1984).

Organochlorine and organophosphorus pesticide concentrations were monitored in the river water. Chromatographic analysis performed indicated that Parathion and Lindane were the most ubiquitous species with mean concentrations of 22 and 9 ng/liter respectively. The dissoolved-in water pesticides did not show a clear association with discharges with the exception of Lindane, which was adsorbed on the sediment (Lenardon, et al., 1984).

A method for the determination of trace amounts of Dimethoate; an organophosphorus insecticide, in waste water was described by Kjolholt (1985). Separation of Dimethoate from other compounds was carried out by using gel permeation chromatography with Bio-Beads SX-3. Dimethoate was determined by capillary gas chromatography with a nitrogen-phosphorus detector. Detection limits were 10 and 130 p.p.t. for surface and waste water respectively. Recovery of the respective insecticide was found to vary between 70.6-75.2% with standard deviations between 5.4 and 9.2%.

Larsen (1985) concluded that contaminated sediments of lakes and oceans acted as sources of chlorinated hydrocarbons to be released in water and atmosphere. Atmospheric transport was a major route for entery of chlorinated hydrocarbons into aquatic ecosystems. Once in the water, the compounds were readily taken up by the biota and distributed in the food webs. Major fractions of the compounds were deposited in the sediment. It has been thought that the most persistent contaminant was inactivated in that way as a consequence of their lipophilic properties. However, the results from recent laboratory studies raised the possibility that aquatic sediment might not be the final sink for the substances but might rather act as a source through re-distribution of compounds to water and atmosphere.

Lindane (B.H.C.) as an immobile, long-lived organochlorine insecticide was reported by Wagenet, et al. (1985) to be adosped by organic matter constituting an important factor in increasing both its persistence and solubility with a consequent increase in its mobility. The degradation of Lindane resulted in the formation of alpha, beta, delta and gamma isomers of B.H.C.

Aref (1986) examined water samples used for human and poultry consumption after treatment processes for several times and D.D.T. residues were found to vary from 0.010 to 0.017 p.p.m.

Water solubilities of organic pollutants and pesticides were reported to be among the most important physical properties controlling the transport and fate of the chemicals in aquatic systems. Moreover, water solubility enhancement was accomplished by dissolved humic and fulvic acids in the soil and aquatic organisms (Chiou, et al., 1986).

Abd El-Kader (1987) examined 72 water samples from agricultural streams and drains, and found that Lindane residues ranged from 0.3755 to 85.1403 ng/liter. Autumn and summer samples exhibited the highest Lindane concentrations. On the other hand, Chlordane varied between 2.8368 and 338.888 ng/liter. The highest concentrations of Chlordane were detected in autumn. Endrin residues ranged from 1.8518 to 73.8461 ng/liter and higher levels were also determined in autumn. P,P-D.D.T. residues varied between 2.5641 to 109.3750 ng/liter and its levels were comparatively higher in samples collected in summer and autumn. Moreover, Diazinon residues could be detected only in summer and autumn with values ranged from 0.7936 to 297.0880 ng/liter. In addition, Chlorpyrifos residues were only detected in autumn, and varied from 13.2569 to 183.4324 ng/liter.

2. INSECTICIDE RESIDUES IN GROUND WATER

Organic insecticides, along with many other types of synthetic organic materials, contribute substantially to the ever-increasing problem of pollution of water supplies. Ground water is a critical resources and in some parts of Egypt is the only source of drinking water. Ground water contamination is one of the major environmental problems in recent years particularly the numerous reports of insecticide contamination.

Achari, et al. (1975) analysed 27 water samples of different wells in order to detect the migration of pesticides from surface soil to ground water. They found that the amount of D.D.T. and Lindane in ground water samples ranged from 6.4 to 161 and up to 12.1 p.p.t. for D.D.T. and Lindane respectively.

In order to understand where particular groups of toxics were found in the environment, ten well water samples were found to be very contaminated with chlorinated hydrocarbons from a total of 408 well samples examined. (Greenberg, et al., 1982).

Rothschild, et al. (1982) monitored the ground water below 5 fields, and sampled 25 private wells and 7 irrigation wells for Aldicarb in the centeral sand plain. The highest Aldicarb concentrations were detected in shallow monitoring wells located immediately below the ground water table. Concentrations from 190-200 ug/liter were detected in several wells but the average concentration was found to be 80/liter. On the other hand, Aldicarb could not be detected in monitoring wells located 18 meters below the water table but was detected in some irrigation wells. The downward hydraulic gradient created during irrigation probably responsible for the presence of Aldicarb into irrigation wells. Most of the Aldicarb residues found in the ground water were in the form of degradation products sulforide and sulfone.

Cohen, et al. (1984) discussed the pesticide characteristics and field conditions under which the potential for ground water contamination might occur. When both the chemical characteristics and field conditions occured in combination, the potential for ground water contamination was consequently high.

Aldicarb as a carbamate insecticide had a water solubility of 6000 mg/liter. Its sulfoxide and sulfone degradation products having water solubilities of 43000 and 7800 mg/L respectively. (Cohen, et al., 1984). They added that Aldicarb residues have been found in ground water in the range of 1.50 ug/liter. Twenty seven percent of 8408 sampled wells showed detectable amounts (> ug/L) of total Aldicarb residues (parent + sulfoxide + sulfone).

Mass, et al. (1984) have reviewed the best management practices available for pesticide pollution control. The four general categories were :

1. Soil and water conservation practices.
2. Increasing the efficacy of pesticide application technology.
3. Integrated pest management system (I.P.M.) which minimized the amounts of pesticides needed (I.P.M. was defined as interdisciplinary approach to pest control incorporating the judicious application of ecological principles).
4. Substitution of less biotoxic and less persistent pesticides where effective alternative existed.

Terhy, et al. (1984) reported that Aldicarb slowly hydrolyzed to Aldicarb oxime in sterile anaerobic ground water at pH 8.2, in the presence of a high concentration of anaerobic microorganisms, Aldicarb rapidly degraded to Aldicarb nitrile.

Soren and Stelz (1985) reported that Aldicarb was used on 9700 hectare of potatoes. Aldicarb concentrations as high as 515 ug/L were detected in the ground water which indicated the maximum depth of penetration below the ground water table. Seventy-six percent of the samples collected from depths of 2-12 meters below the water table had Aldicarb concentrations above 7 ug/L. From depths of 12-45 meters below the water table, 16% of the wells at 25 sites had Aldicarb concentrations greater than 7 ug/L. All samples exceeding 7 ug/L were from irrigation wells that produced large drawdowns. The highest Aldicarb concentrations and highest frequency of positives (94.4%) were found within 300 meters of the application sites.

Halberg (1985) reported the detection of 8 pesticides in well water. Ground-water contamination has occured in the vicinity of chemical supply dealers. Moreover, pesticide contamination was detected in water pools or soil in the loading areas and areas where equipments were rinsed. Pesticide concentrations in the ground water were much higher than local back ground levels. Farm chemical suppliers might be sources of serious pesticide contamination in localized areas.

Aldicarb as a carbamate insecticide and nematocide was used extensively untill it has been discovered in ground water in leached soils and found to move laterally from the point of application (Wagenet, et al., 1985).

Ritter (1986) concluded that over 20 pesticides have been found in ground water. Most of the concentrations detected were below the toxic levels however, organophosphorus (Atrazine) concentrations in ground water were correlated with nitrate contamination. The annual amount of recharge, soil type, aquifer depth from the surface, nitrate contamination and soil pH were important field conditions in determining the potential of ground-water pesticide contamination. The soil water partition coefficient, water solubility, pesticide half-life, the ratio of the soil water partition coefficient to soil organic carbon content, and hydrolysis half-life were important pesticide characteristics for determining the potential pesticide contamination of ground water.

Investigations were conducted in 311 events of suspected contamination of wells with pesticides. This involved water analysis from 359 wells where the suspected contamination orginated from spills, spray drift or surface run-off waters carrying pesticides into wells. Investigations covered 83 spill events involving 104 rural wells, revealed that 79 of them became contaminated. The contamination was caused by spills of pesticide concentrates, back-siphoning of spray solutions or spill from overfilling, emptying or rinsing spray equipment. The pesticides either entered directly into the wells or contaminated the area in their vicinity. In spite of cleanup attempts, difficulty was experienced in decontaminating most well waters and some had to be abandoned. The longest period monitoring a contaminated well was 117 days; during that time the decline in residue was slow (Frank, et al., 1987). Moreover, they concluded the need for care and safe handling around these wells when drawing water for pesticide spraying. Anti-back flow devices should be mandatory when loading spray equipment. They recommended that mixing of pesticide concentrations should be done away from the water supply. Well heads should be protected against surface runoof waters and should be covered to prevent spray drift gaining entrance, elevated heads were recommended and well sites should be selected to be away from sprayed areas or crops. Decontamination of a well water could be lengthy and costly, especially of other supplies must be sought. Accidental spills around the well should be cleaned up promptly by removing contaminated soil. Pumping off of contaminated water was recommended but care must be taken when disposing of contaminated water, to ensure that it was deposited away from water sources. Moreover, they stated that during a survey of farm wells for pesticide residues, water samples from 11 wells located in an area of intensive vegetable production of an organic soil were collected and analyzed for pesticide residues. Residues of Diazinon and Malthion were identified in four of the wells. The authours concluded that the above contaminations resulted from introduction of chemicals from the surface while mixing and loading of pesticides into spray equipments and not from ground or surface protection and were situated on elevated land and hence it was unlikely that surface runoff waters could have entered the wells. Among six dug wells, three were used to draw water for spraying purposes and three were used for drinking only. The authors suggested that the contamination had been either present in the well for many months, surface water had carried the aged residues into the well or internal soil drainage had leached the residues into the ground water and then into the wells. Among the six contaminated deep wells, five were being used to draw water for spraying purposes and could become contaminated through these practices.

3. WATER TREATMENT

The ever-increasing production of synthetic organic chemicals, the multiplicity of the sources of trace organic contaminants in raw water and the wide diversity of these contaminants all contribute to the problem of water pollution by organic chemicals. Pollution of water supplies with these contaminants can however, become significant if it increases.

Hence, if insecticides do gain entry to water resources inspite of all reasonable precautions taken, water treatment officials must have the knowledge and plant facilities to remove them. Concentrations of these chemicals in drinking water should be minimized.

In 1945, Carollo reported a laboratory study on the removal of D.D.T. from water supplies with various combinations of carbon and chemical coagulation with iron and aluminum salts. The coagulation, sedimentation and filteration will remove 80-98 percent of 0.1-10.0 p.p.m. of D.D.T. Complete removal of D.D.T. was suggested if activated carbon was provided for 15 minutes contact time after coagulation and sedimentation but before filteration.

In 1960, Cohen reported the removal of several chlorinated hydrocarbons from water by treatment with carbon, chlorine dioxide. In general activated-carbon treatment was recorded as the most effective process for removing fish poisons and their associated odour from a water supply. Chlorine and chlorine dioxide were effective against chlorinated hydrocarbon compounds, but these oxidizing agents carried the disadvantages of long contact times, high residuals and the need for subsequent dechlorination.

Weber and Morris (1963) reported that D.D.T. was adsorbed at a rate of approximately 150 Umo (micro-moles)/9 hours on activated carbon.

The results obtained by Faust and Aly (1964) revealed that there were more than 500 organic pesticides in some 54,000 formulations. These pesticides were found in water supplies in very low concentrations as a result of accidental or deliberate discharge of waste waters and direct application. Potable water supplies were affected through impairement of the taste and odour quality. Some of these organic pesticides could persist for long periods in the ground, surface waters and soils where they were resisting biologic decomposition. In general, activated carbon appeared to be the most effective method of reducing the most organic pesticide levels in water supplies. Chemical coagulation and oxidation were inefficient or impractical. Moreover, some of the chemical and biological factors affecting the persistance of organic pesticides in surface waters has been investigated. They suggested that clay could be added to surface waters in order to adsorb organic pesticides that could subsequent be removed by chemical coagulation. They added that considerable quantities of clay would be required for adsorption of organic pesticides.

Booth, et al. (1965) confirmed that activated carbon columns, even with the greatest practical contact times, did not adsorb all the organic matter that was present in stream waters. At the same time, it has been shown that lower sampling rates and volumes were significantly required for maximum utilization of the carbon adsorbition method as a gross monitoring technique. In this respect, a rate of not more than 120 milliliters per minute (contact time of 5 minutes) and volume of not more than 400 gallon were suggested.

Hager and Flentze (1965) reported that granular activated carbon has long been used for the removal of organic contaminants from water. The results indicated that the particle size of carbon, in addition to the contact time should be considered carefully as a design factor. Reduction of the particle size for a given set of flow conditions was recognized to be a means of increasing adsorption rates and thereby, improving adsorption performance. The utilization of granular-carbon filtration was a relatively simple and economical procedure for removing taste and odour pollutants such as pesticides. The granular carbon beds would provide the margin of safety for treatment of water containing unknown and varying pesticide residues.

Robeck, et al. (1965) studied the effectiveness of water treatment processes in pesticide removal. They found that D.D.T.

was easily removed by setlling and coagulation followed by filtration while Lindane and Parathion could not be removed. On the other hand, chlorine and potassium permenganate at 1-5 p.p.m. could convert parathion to a different but more toxic compound. At relatively large and impractical concentrations, ozone could reduce chlorinated hydrocarbons somewhat, but again the byproducts formed and their toxicity were unknown. When the authors used activated carbon they found that 20 p.p.m. of activated carbon were sufficient to remove D.D.T., Lindane, Parathion, Dieldrin and Endrin at 100,80,90,92, and 94% respectively.

Sigworth (1965) made an attempt to remove Lindane and D.D.T. by coagulation, sedimentation and filtration. Although 10 p.p.b. of D.D.T. could not be removed.

Nicholson, et al. (1966) reported that activated carbon infilteration system was used to remove D.D.T. from water successfully.

King, et al. (1969) summarized the pesticide distribution data that have been obtained from a number of studies, utilizing a variety of adsorbing media that represented both natural environments and potential treatment processe. They found that the data for adsorption of pesticides by using coal and activated carbon illustrated the possible means of removing these pesticides from solutions. Coal was found to be 2-2.5 order of magnitude superior to soil in adsorbing Parathion however, it was relatively ineffective when compaired with activated carbon. Activated carbon on the other hand, was found to be about 4 orders or magnitude greater in the ability to adsorb Parathion than the soil. They reported that the coal used as one component in a multimedium filter might however, significantly increase pesticide removal, especially if the grade of the coal was selected that would result in a maximum uptake. In general, they concluded that activated carbon remained as a superior adsorbant of pesticides.

Eichelberger and Lichtenberg (1971) studied the efficiency of standard carbon adsorption method (C.A.M.) for recovery of eleven organochlorine insecticides and ten organophosphorous pesticides from water. They found that the C.A.M. was a useful procedure for the isolation and determination of certain chlorinated hydrocarbon pesticides in water, namely methoxychlor, Lindane, Endrin, Dieldrin and Heptachlor epoxide. Although it might be used efficiently for recovery of Chlordane, D.D.T. and endosulphan however, it did not appear to be useful to all for isolating Heptachlor or Aldrin. The C.A.M. was found to be unsuitable for recovery of six organophosphorous pesticides (fenthion, methylparathion, malathion, ethion, trithion and methyl trithion). It was fairly efficient for bidrin, but considerably less efficient for azodrin, parathion and D.E.F. The compounds were recovered with good reproducibility indicating that the efficiency of data were not significantly influenced by analytical errors.

Hyndshow (1972) used activated carbon to remove organic contaminants from water. He found that 10 p.p.m. of activated carbon were sufficient to remove 60 and 70 percent of Lindane and Dieldrin respectively.

Residual chlorine from the chlorination of waste water treatment plant effluents and other waters was found to pocess biotoxic properties (Brungs, 1973).

The adsorption and desorption of pesticides by organic matter and clay minerals were important factors affecting the fate of pesticides in the environment. Organic pesticides adsorbed on both organic and inorganic surfaces were found to depend on the chemical properties of the adsorbants and adsorbates involved. Basic pesticides were strongly adsorbed by organic matter while acidic pesticides were adsorbed in moderate amounts of organic matter and in relatively low amounts on clay minerals and hydrous metalic oxides. Moreover, nonionic pesticides were adsorbed in the greatest amounts by organic matter but adsorption by clay minerals was also important for organophosphates and several other pesticide families. In addition, it has been reported that carbamate and organophosphate insecticides were adsorbed by organic matter (Carringer, et al., 1975).

Jolley (1975) studied the effect of chlorination on organics contained in domestic sewage and textatively identified 17 chlorinated compounds including chlorinated hydrocarbons, phenols, purines and pyrimidines. He found that approximately one percent of chlorine used in the treatment of domestic sewage was associated with stable chlorine-containing organic compounds at the end of the chlorination reaction period.

It has been shown that chlorination of natural waters containing humic substances producing chloroform and given the obiquitous occurrence of this and other trihalomethanes in chlorinated U.S. drinking waters (Stevens, et al., 1975).

A slurry system to deliver buoyant activated carbon to a static body of water to remove organic hazardous material from the water, was designed and built. In a field demonstration of the slurry system, organophosphous pesticides Diazinon was spilled into a 10 million-gallon water storage basin. A total of 260 Kg of activated carbon to diazinon-was used to treat the spill. Post treatment samples were analyzed for phosphates and total organic compounds which revealed a removal of 76 and 84% respectively. (Dawson and NcNeese, 1978).

Rook (1979) stated that chlorine used to disinfect drinking water might combine with synthetic organic compounds, and result in elevated levels of a variety of chlorinated compounds.

Saleh, et al. (1980) investigated that transformations and removal of chlorinated hydrocarbon pesticides from waste water by activated sludge treatment under nitrifying conditions effected the limited removal of these organic residues as detected on chromatograms.

The toxicological effects of chlorine which almost did not receive sufficient studies constituting the major gap in the present available research. There is only one long-term investigation of chlorine toxicity, Bean, et al. (1982) reported that no harmful effects from drinking water containing as much as 100 mg/L of chlorine provided to rats over several generations. They added that in a study of the mutagenicity of 30 chlorinated water supplies, it has been found that at least one from each four samples taken from every water treatment plant was mutagenic. In addition, they reported that the byproducts of chlorination trihalomethanes "T.H.Ms.", did not seem to be correlated with mutagenicity. T.H.Ms. were found to be promoters of cancers. Besides T.H.Ms., other byproducts were produced by chlorination. The formation of chlorinated phenols having a direct mutagenic activity was known to be produced during chlorination of waste waters. The treatment of waste water was reported to be important because advanced treatment was realized as a potential source for replenishment of ground water supplies. Waste water was found to be weakly mutagenic before chlorination but strongly mutagenic after treatment. They noted that bromination occured during chlorination and suspected a connection between bromination and increased mutagenicity.

Powdered activated carbon (P.A.C.) was used without harmful effects for more than 50 years to remove taste and odour from public water supplies but granular activated carbon (G.A.C.) might become more common because of the new information of limiting the concentration of trihalomethanes (byproducts of chlorination) and the occurrence of trace organic matter in public water supplies and the possibility of requirements for granular activated carbon treatment (Club and Clark, 1983).

Nadia E.H. (1983) studied the quality of Alexandria public water supply through determination of pesticide concentrations in the inffluents and effluents of water treatment plants. She reported that the water treatment plants

(El-Seouf, Bab-Sharky and Forn El-Geraia) had an effeciency in reducing Lindane and D.D.T., but El-Manshia and El-Gidida water treatment plants were not efficient in removing them which might be due to lake of periodic washing of the sand filter beds.

Abd El-Kader (1987) reported that water treatment with chlorin in El-Abbasa station of drinking water. A total of 10 water samples before and after water purification were examined. The obtained results revealed that the mean value of Lindane residues in raw surface water was 3.6882 ± 1.6201 ng/liter, but after purification the mean value of residues increased (5.4926 + 1.4939 ng/liter). Chlordane residues were undetectable in water samples of El-Abbasa station. The mean values of Endrin in raw surface water was 3.5069 ± 1.4467 ng/liter, while in treated water it was 1.8447 ± 1.2863 ng/liter. P,P-D.D.T. residues could be detected in raw surface water before and after purification of drinking water with a mean of 15.4117 ± 8.4176 and 5.4160 + 2.3066 ng/liter respectively. Non of the organophosphorus compounds were detected in water samples of El-Abbasa station. The drinking water filter containing activated carbon could be applied with success in minimizing the concentration of pesticide residues in water.

4. SIGNIFICANCE OF INSECTICIDE RESIDUES TO HUMAN AND ANIMAL HEALTH

It is always desirable to control human environment that created the use of certain chemicals, among which the insecticides are intensively used for insect control. When it is necessary to use these insecticides for control of aquatic weeds, trash fish and aquatic insects, complete information must be available such as the conditions under which residues disappear, the effeciency of water treatment and the permissible limits of insecticide residues.

Radeleff, et al. (1955) concluded that the use of Chlordane on or around livestock was not free from the risk, although under regular usage in accordance with the recommended procedures there should be no harm to any species. However, any condition which would increase the rate of deposition on the skin could produce poisoning. They suggested that the deaths in calves following dipping in Chlordane were recorded and attributed to increased deposition on the coat.

It has been suspected that a substantial quantity of stable, chlorinated hydrocarbon insecticides applied to farm crops washed from the soil surface into streams and lakes, where serious damage might result to aquatic life. The effects of D.D.T. on human beings and animals have been evaluated thoroughly. Generally speaking however, it might be concluded that if the insecticides were not present in streams or lakes in sufficient quantites to kill fish, there would be no known significant public health hazard due to their presence in drinking water from these sources (Nicholson, 1959).

Dimethoate was used occasionally as a systemic insecticide for livestock (Meleny and Peterson, 1964). Its toxicity was reported to vary with purity and chronic cases of poisoning in sheep was characterized by depression, anorexia, salivation and diarrhoea.

Carbaryl which has found some application in the control of ectoparasites in both large and small animals, was the most widly used. It has been found that the carbaryl was of low toxicity in warm blooded animals (Bukin and Filatov, 1965).

Warnick, et al. (1966) reported that the presence of detected levels of chlorinated hydrocarbons in drinking water even after ceasing of its large scale of application indicated the danger of continous release of these persistent chemicals in the environment, because most of these chemicals were reported to be carcinogenic.

The relationship between tissue D.D.T. levels and chronic diseases in man and animals have not been established (Hoffman, et al., 1967) however, other reports indicated a statistical association between levels of storage D.D.T. and certain types of chronic disease in man and animals (Cassarett, et al., 1968).

Canadian drinking water standards and objectives (1968) stated that the maximum permissible level of Chlordane D.D.T., Endrin and Lindane for raw as well as treated water were found to be 0.003, 0.042, 0.001 and 0.056 ug/L respectively.

Malathion was one of the least toxic organophosphorus insecticides. Poisoning in dog was characterized by malaisa, salivation, anorexia and vomition (McCurnin, 1969).

According to the recommendations of the U.S. Secretory of the Interior, Nicholson (1969) suggested that the permissible limit of pesticide residues in public water supplies should be 0.003, 0.042, 0.001 and 0.056 ug (p.p.m)/liter for Chlordane, D.D.T., Endrin and Lindane respectively. He added that the permissible limits for each pesticide was absent in water samples.

Schafer, et al. (1969) assayed 500 samples of raw and purified drinking water. Only Endrin and Chlordane were found in concentrations that exceeded the suggested maximum permissible amounts of Endrin (0.001 ug/liter) and Chlordane (0.003 ug/liter).

The high toxicity of the organophosphorus compounds was offset to some extent by the fact that their residues disappeared rapidly because of the hydrolytic destruction with a consequent loss of their potential danger to domestic livestock. Although chlorinated hydrocarbon insecticides were much less toxic however, they were yet still dangerous to domestic livestock because of their persistence. Cummulative poisoning from these compounds was a hazard that should not be entirely ignored (Cox, 1970).

Bevenue, et al. (1972) examined 45 drinking water samples including wells, shafts, tunnels and springs for organochlorine pesticide residues. They reported that D.D.T. was the predominant pesticide appearing in 87% of the samples in concentrations ranging from 0.6 to 2.2 p.p.t. Chlordane and Lindane were detected in variable quantities from 0.5 to 5 and from 0.06 to 0.4 p.p.t. respectively.

The toxicity of Diazinon was very variable, on account of its hydrolysis in the presence of water to the highly poisonous tetraethyl monothiopyrrophosphate which was incriminated at times in serious accidents to livestock (Mello, et al., 1972).

The U.S.A. Water Quality Criteria (1972) recorded that the maximum permissible level of Chlordane, D.D.T., Endrin and Lindane in drinking water were found to be 0.003, 0.05, 0.0005 and 0.005 ug/liter (p.p.m.) respectively.

Robeck (1973) reported that the standards of Lindane and D.D.T. recommended in the drinking water were 5.0 and 50.0 p.p.b. respectively.

Hurley (1974) indicated that the water supplies investigated had only trace amounts of chlorinated hydrocarbon pesticides. They were in the very low parts pertrillion range. Many single pesticides were present in concentrations of less than 1 p.p.t., which was considerably below the proposed U.S. Environmental Protection Agency (E.P.A.) drinking water standards.

Rosival and Szokolay (1975) examined ground water samples intended for human consumption and found that P,P-D.D.T. varied from 0.00 to 0.32 ug/liter.

Brodtman (1975) analysed potable water for chlorinated hydrocarbon pesticides. The results indicated that only a trace amount (> 0.1 p.p.t.) of D.D.T. was detected.

It has been reported in the International Joint Commission

(I.J.C) (1977) that the water quality objectives for Diazinon, Chlordane and Chlorpyriphos were 80,60 and 130 ng/liter respectively.

Mcneil, et al. (1977) determined the pesticide residues in potable water by using electron capture gas chromatography. They found that the level detected were 1.3 p.p.t. of Lindane, less than 0.05 p.p.t. for each of Endrin, Chlordane and D.D.T.

Sackmauerova, et al. (1977) analysed 92 drinking water samples and reported that the average content of D.D.E. in drinking water was found to be 0.022 ug/liter and 0.042 ug/liter for D.D.T.

Hameza et al. (1978) indicated the presence of some pesticides in concentrations ranging from 0.1 to 0.95 p.p.b. in water at Alexandria Poultry Process Plant (A.P.P.P.). The initial source of these pollutants was reported to be the Mahmoudia Canal raw water containing relatively higher concentrations than treated water at El-Seouf Plant. The results indicated the presence of pesticidal pollutants in A.P.P.-tap-water. The chlorinated hydrocarbon pesticides detected were Lindane and its isomers (-B.H.C., B-B.H.C.), D.D.T. and its metabolites (D.D.D., D.D.E.) as well as Heptachlor epoxide. In addition, they found that the chlorine dosage of tap-water had no effect on the chlorinated hydrocarbon pesticides.

William's et al. (1978) analyzed monthly duplicate samples of drinking water, for organochlorine pesticides. Endrine and O,P-D.D.T. were detected and their mean concentrations were found to be 4 and 3 p.p.t. respectively.

A screening method was developed for determining organophosphorus pesticides at ng/liter levels in drinking water. Diazinon, Dimethoate, Chlorpyrifose and other organophosphorus pesticides were extracted by Amberlite XAD-2 resin from 100 and 200 liters of drinking water previous spiked with these insecticides. The insecticides were eluted from the XAD-2 resin with acetone : hexan (15:85). The analysis of 300 liters of tap water showed no detectable amounts (> 1 ng/liter) of any of those organophosphorus insecticides (Lebel, et al., 1979).

During the two years sampling period no samples of stream water were found to contain Chlordane and Chlorpyrifose above the adopted standards (60 and 130 ng/L respectively). Moreover, the authors reported that only one sample was found to contain Diazinon in excess of the objective of 80 ng/L (Braun and Frank, 1980).

Micheal (1980) reported the presence of some organochlorine pesticides and their residues at Alexandria poultry process plant (A.P.P.P.) water supply during the period of the study (one year). The results indicated the average concentrations of Lindane and its isomer which ranged from 0.39 to 6.26 p.p.b. Average concentrations of D.D.T. and its residues and metabolites were found to range from 1.20 to 30.80 p.p.b.

U.S. Environmental Protection Agency (E.P.A.) (1980) recorded that the level of D.D.T. (0.24 ng/L) might result in incremental increased risk of cancer through contaminated drinking water.

Frank, et al. (1982) reported that during two years of sampling period D.D.T. and D.D.E. were detected in water samples in concentrations exceeded the Water Quality Criteria established by the International Joint Commission (I.J.C.) for Lake and stream waters.

The effects of Aldicarb (a carbamate insecticide) on selected immune and non-immune parameters of mice were examined. The primary objective was to determine whether exposure to low levels of Aldicarb through drinking water could affect selected immune functions. Aldicarb was administered via drinking water either at 10,100 and 1000 p.p.b. for 14 days or at 1,10,100 and

1000 p.p.b. for 34 days. The 34-day experiment was reported twice with minor variation. Aldicarb significantly suppressed the splenic plaque forming cell response to sheep red blood cells at the lowest concentrations tested (Olson, et al. 1987).

MATERIAL AND METHODS

1. DETERMINATION OF INSECTICIDE RESIDUES :

The residual properties and fate of chemicals used in agricultural pest control and veterinary practice have been the cause of considerable concern in recent years. The environmental massive use of these chemicals has resulted in an increased occurrence of these toxic agents in natural water sources with a consequent creation of a critically urgent problem in connection with hygienic water supply.

1.1- Collection of samples

A) From different natural water sources :

A total of 108 duplicate water samples were collected from different water sources of Behera Governorate including 72 samples from localities along the Rosetta Branch of the River Nile, Mahmoudia Canal as well as drains illustrated in Figure (1) and Table (1). In addition, 36 ground water samples were collected from Damanhour, Mahmoudia and Edfina.

The sampling localities were visited at monthly intervals along the investigation period from October, 1987 to September, 1988.

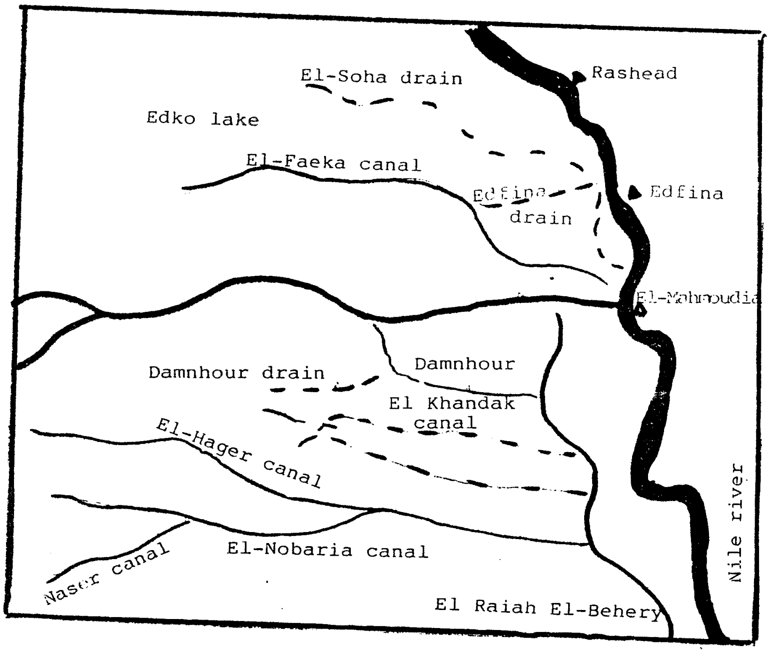


Figure (1) : Location sites for sampling surface water in Behera Governorate.

▬ Nile river
— canals
••• Drain

Table (1) : The distribution and localities of investigated water samples.

	Number of Samples			
Locality	Surface		Ground	Water treatment plant.
El-Mahmoudia	River Nile	(12)	(12)	
	Mahmoudia Canal	(12)		
Edfina	River Nile	(12)	(12)	
	Edfina drain	(12)		
Damanhour	Damnhour drain	(12)	(12)	(12)
Rashied	River Nile	(12)		
Total		72	36	12

Two transparent stoppered glass bottles of one liter capacity were used for each sample. The bottle was immersed in an inverted position and at the most possible depth the stopper was removed. Ground water samples were taken directly from the pump orifice. Each sample was labelled to indicate the date, source and locality. The samples were transfered directly in an ice box to the laboratory without delay.

B) From water treatment plants :

Twelve water samples were collected from Damanhour water treatment plant, at the points (A) and (B) as illustrated in Figure (2).

C) After experimental treatment with an activated carbon filter :

A drinking water filter made in England & model number PWF5. was used, which consisted of a water filter with an external hight 318 mm, external width 147 mm and cartridge height 254 mm. The filter containing 10 Cartridges of activated carbon surrounded by polyester (Figure 3).

1.2- INSECTICIDES USED AND THEIR CHEMICAL STRUCTURE (THOMSON, 1983).

A) CHLORINATED HYDROCARBON INSECTICIDES.

A.1- D.D.T (Dichlorodiphenyl trichloroethane).

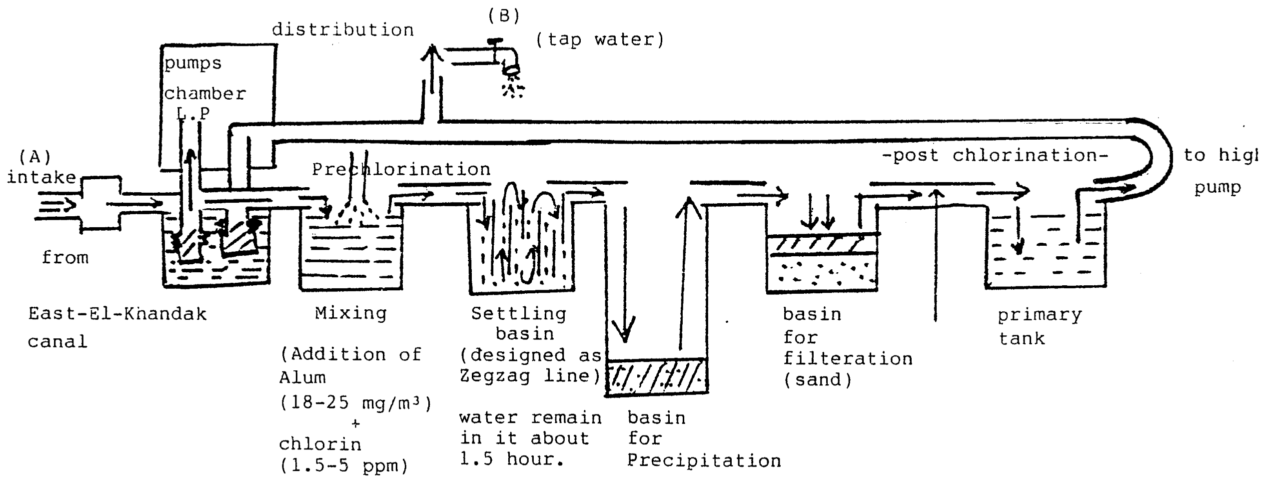


Figure (2) : Damnhour Water Treatment Plant

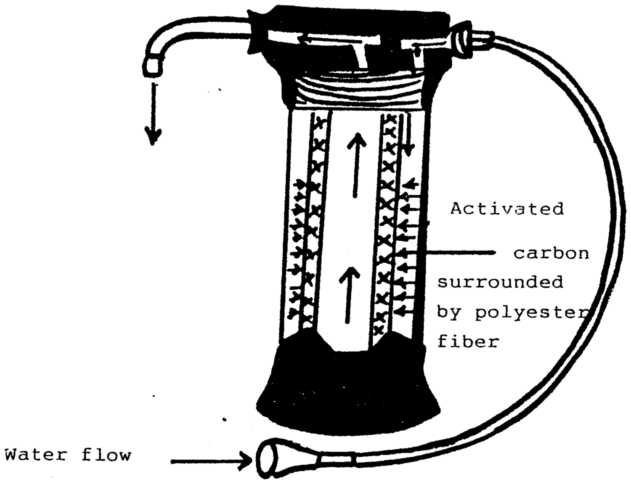
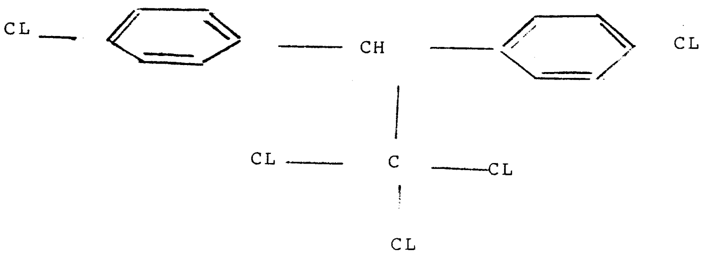
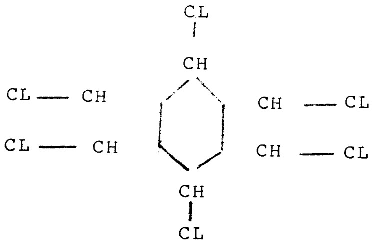


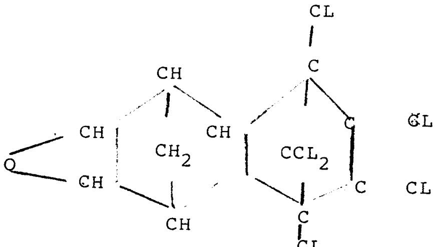
Figure (3) : Drinking water filter with Ca 10 Cartridge (Polyester fiber and activated carbon).



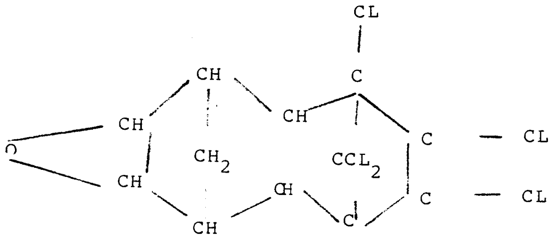
A.2- Lindane (Gamma-1,2,3,4,5,6-Hexachlorocyclohexane-at least 99% of the gamma isomer of BHC (Benzene Hexachloride).



A.3- Chlordane (Octachloro-4-7-methanotetrahydroindane)

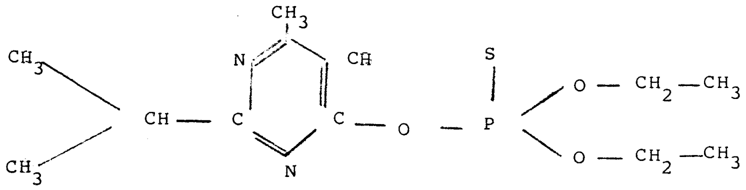


A.4- Endrin (Hexachloroepoxyoctahydro-endo,endo-dimethanonaphthalene).

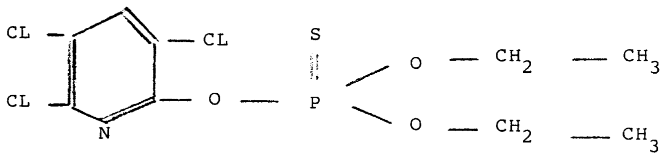


B) ORGANOPHOSPHORUS INSECTICIDES.

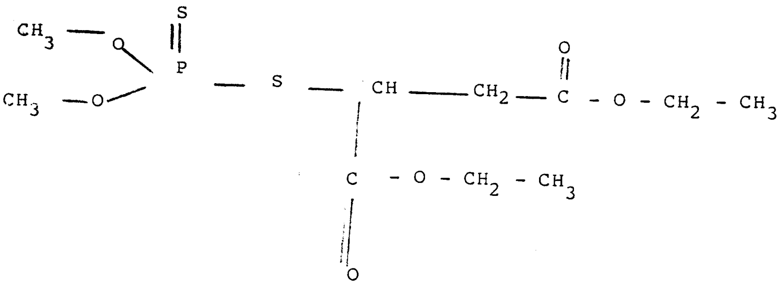
B.1- Diazinon [0-0-Diethyl-0(2-isopropyl-6-methyl-5-pyrimidinyl)phosphorothioate].



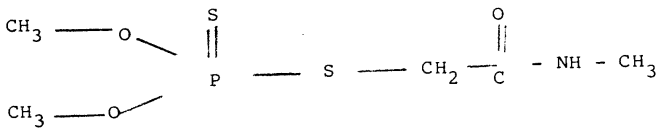
B.2- Chlorpyrifos, (Dursban) 0,0 Diethyl-0 [3,5,b-trichloro-2-pyridyl] phosphorothioate



B.3- Malathion [0,0-dimethyl phosphorodithioate ester of diethyl mercaptosuccinate].

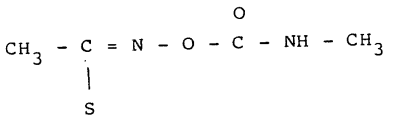


B.4- Dimethoate [0,0-Dimethyl-S-(N-methyl carbamoyl-methyl) phosphorodithioate]



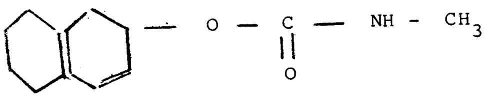
C) CARBAMATE INSECTICIDES.

C.1- Lannate, Methomyl [S-Methyl-N-(methyl carbamoyl oxy) thioacetimidate].

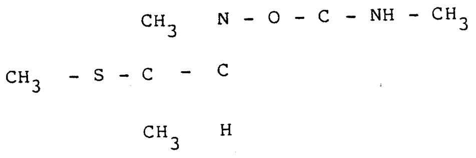


$$CH_3-\underset{\underset{S}{|}}{C}=N-O-\overset{O}{C}-NH-CH_3$$

C.2- Carbaryl, Sevin (1-Naphthyl methyl carbamate).



C.3- Aldicarb, Temik [2-methyl-2 (methylthio) propionaldehyde 0-(methyl carbamoyl) oxime].



$$CH_3-S-\overset{CH_3}{\underset{CH_3}{C}}-\overset{N-O-C-NH-CH_3}{\underset{H}{C}}$$

PROCEDURE :

A mixture of each group of insecticides of a known weight (10 ug of each compound) were transfered to a glass cylinder containing 10 liters of distilled water proved against insecticide (pH 6.8) and 2ml of acetone was added as a solvent.

The treated distilled water was mixed thoroughly, and passed through the drinking water filter with a flow rate of one-liter per minute. Five samples were taken successively, each sample of one liter capacity, then subjected to the insecticide residue determination.

1.3- THE GENERAL METHOD FOR DETERMINATION OF INSECTICIDE RESIDUES.

According to Ambrus, et al. (1981), the general method has been developed in recent years and used as an official method for the control of insecticide residues.

A) EXTRACTION OF WATER SAMPLES.

PROCEDURE :

One liter of the respective water sample to which 50 ml of saturated sodium chloride solution (665 g/L) were added for the removal of any floating material or mud. The mixture was then transfered into a 2-liters separatory funnel. 100,50 and 50 ml quantities of methylene chloride were added successively to the mixture during the occurrence of extraction in each addition. The extracts were filtered through 30 g anhydrous sodium sulphate for elimination or lessening the formation of emulsions. Sodium sulphate layer was rinsed with 20 ml methylene chloride. The volume of combined mehthylene extracts was reduced to 2 ml with vacum rotary evaporator to 2-3 ml. This step was repeated twice (for complete removal of methylene chloride). The concentrated extract was transfered to a conical glass test tube with a Pasteur pipet 2 ml quantities of acetone were repeatidly added to the extract which by gentle shaking excess solvent was evaporated until the final volume was adjusted to one ml. The extract was dried at room temperature, then one ml of benzene was added for removal of the remaining acetone. The extract was evaporated to 0.5-0.8 ml, then the final volume was adjusted to 5 ml with benzen addition.

B) THIN LAYER CHROMATOGRAPHY (T.L.C.)

1. PREPARATION OF T.L.C. PLATES (SILICA GEL.G.).

30 g of silica gel G. were dissolved in 60 ml water to which few drops of acetone were added. The suspension was uniformly spread on glass plates (20 x 20 cm, 3 mm thickness). A thin layer of silica gel G (about 0.5 mm) was spready on the glass plate, then dried at room temperature.

2. TREATMENT OF THE SAMPLE ON CHROMATOGRAPHIC PLATE

According to Ambrus, et al. (1981).

Known concentrations of ethanolic solutions were prepared from the active principle of different insecticides which obtained from Kafr El-Zayat Pesticides and Chemicals Company.

These solutions were spotted on a chromatographic plate at a distance of about 2 cm from the bottom. The sample was applied in an area about 0.2 cm diameter on the plate. The samples were separated from each other by a distance of about 2 cm.

Suitable eluents were poured into the chromatographic jar and covered tightly. The eluent was ascending to a certain height from the starting line which differ according to chemical structure of the insecticide.

The plate was dried and then sprayed by different spot locating agents (Ammoniacal silver nitrate solution, palladium chloride solution and Furfuraldehyde /HCl). The resulting colour was detected under an ultra violet lamp (Ggllenkamp 254 mu) and Retention factor (R_f value) of each spot was recorded.

The above mentioned steps were repeated with each extracted water sample as in Figures (4,5 & 6). The suitable elunet, spot locating agent, colour and R_f value of each studied insecticide were listed in table (2).

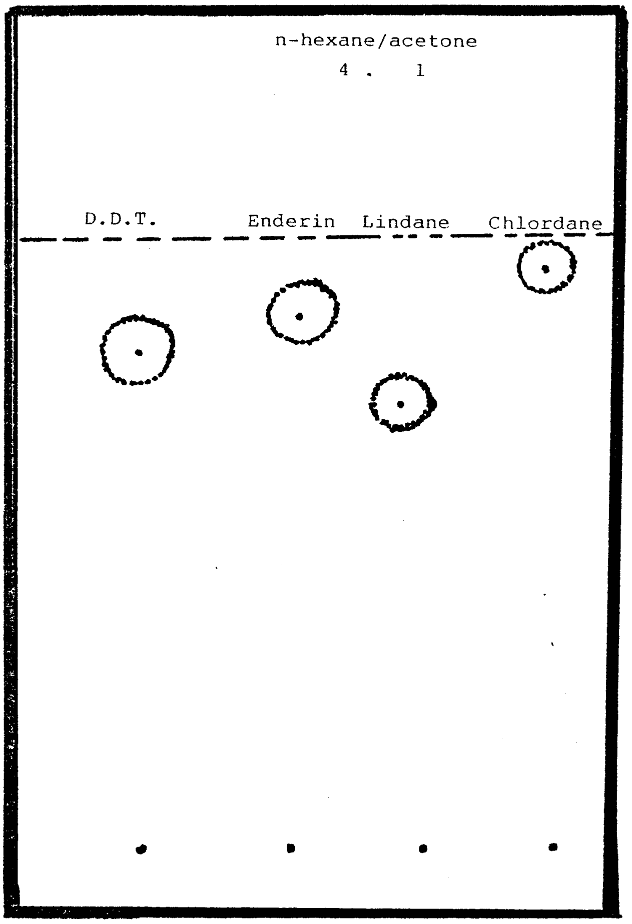


Figure (4) : Thin Layer Chromatogram of Organochlorine Insecticides on Silica Gel. G,

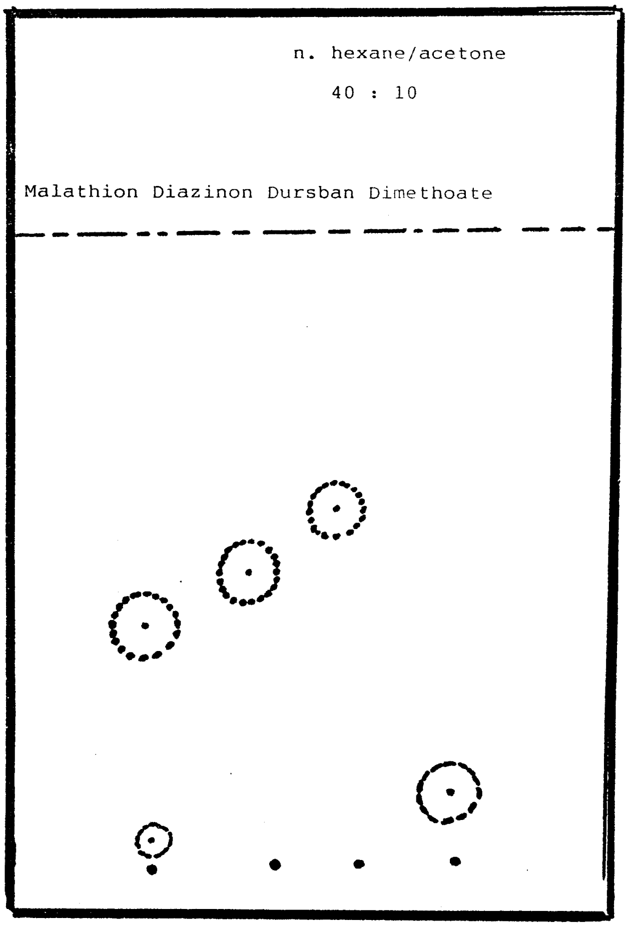


Figure (5) : Thin Layer Chromatogram of Organophosphorus Insecticides on Silica Gel G.

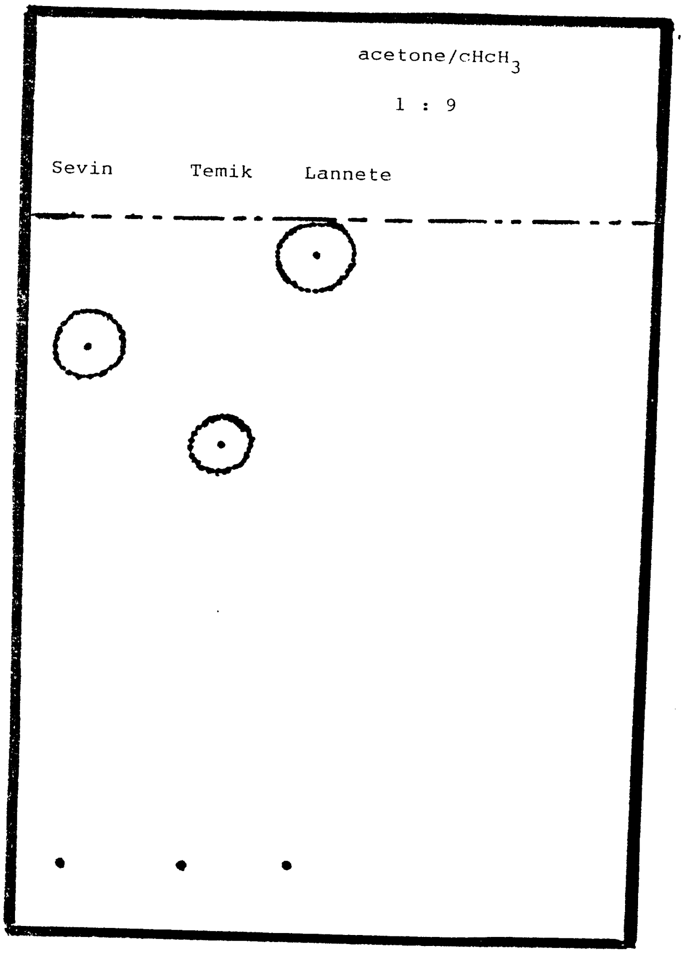


Figure (6) : Thin Layer Chromatogram of Carbamate Insecticides on Silica Gel. G.

Table (2) : The suitable eluent, spot locating agent, colour and R_f value of each studied insecticide.

Insecticide	Elluent	Spot Locating agent	Colour	R_f
I) <u>ORGANOCHLORINES</u>				
1. D.D.T.	n.hexane/	Ammoniacal	Gray	0.63
2. Lindane	acetone	Silver nitrate	Spots	0.54
3. Chlordane	(40 + 10)	Solution		0.72
4. Endrin				0.66
II) <u>ORGANOPHOSPHORUS</u>				
1. Diazinon	Hexane/	Palladium	Orange	0.58
2. Malathion	acetone	chloride	spots	0.46
3. Dursban	(80 + 20)	solution		0.70
4. Dimethoate				
III) <u>CARBAMATE</u>				
1. Lannet	n. hexane/	Furfuraldhyde/	violet	0.90
2. Sevin	acetone	HCL	to pink	0.78
3. Temik	(90 + 10)		spots	0.65

Where :

The Retention factor (R_f) =

$$\frac{\text{The distance travelled by center of = the solute spot.}}{\text{The distance travelled by the front of the mobile phase}}$$

Under suitable conditions the different rates of flow could bring about a complete separation of substances. The rate of flow (R_f value) depends on the following three factors according to Fifield and Kearly (1975).

1. Activity of the layer.
2. Saturation of the area in which insecticide was applied.
3. The uniform thickness of the layer.

C) SPECTROPHOTOMETERIC DETERMINATION :

An ultraviolet Unicam S.P 1800 automatic recording as used. The sensitivity of spectrophotometer in the range of ± 1 A°. A hydrogen lamp was used as the source of light in the ultra violet region.

Stock solutions of pure insecticides were prepared by dissolving an accurate weight of each insecticide into 100 ml of absolute alcohol. Further dilutions were made into volumetric flasks. The absorption spectra were recorded against a blank and the spectrum of each insecticide was recorded (Figure 7-17).

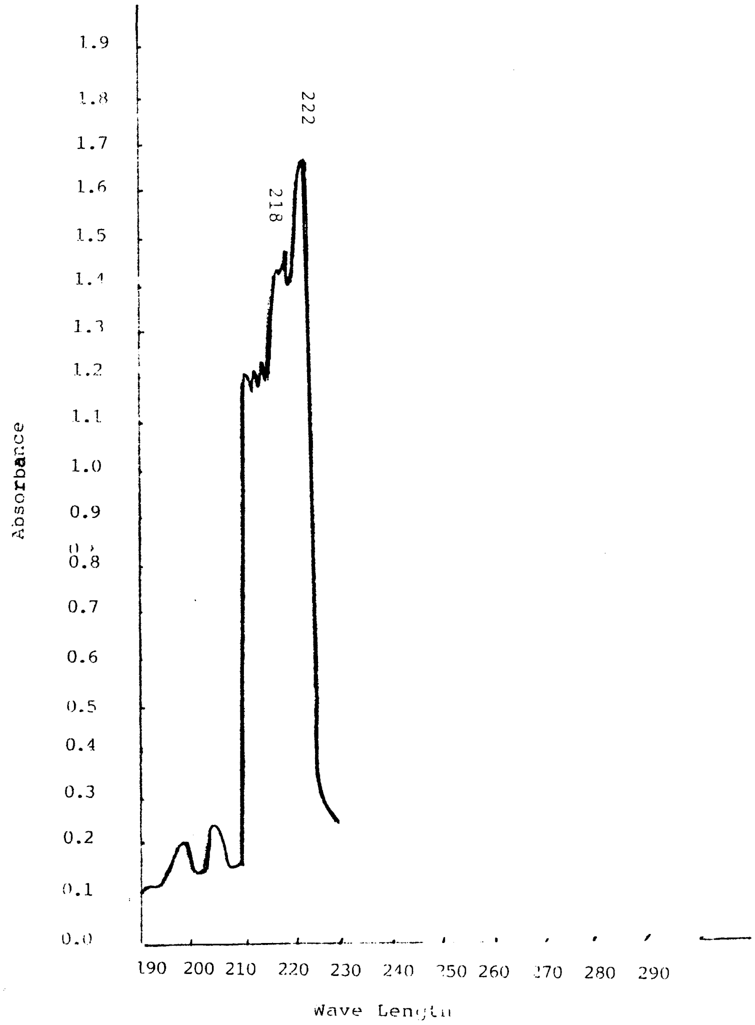


Figure (7) : The Absorption Spectrum of D.D.T. in

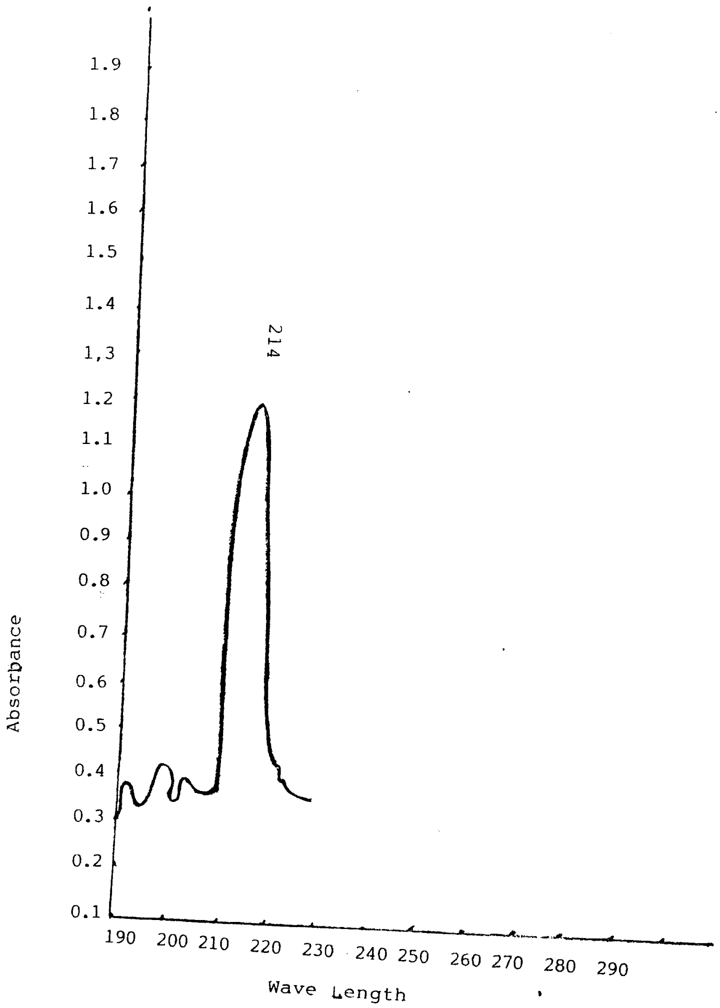


Figure (8) : The Absorption Spectrum of Lindane in Ethanol.

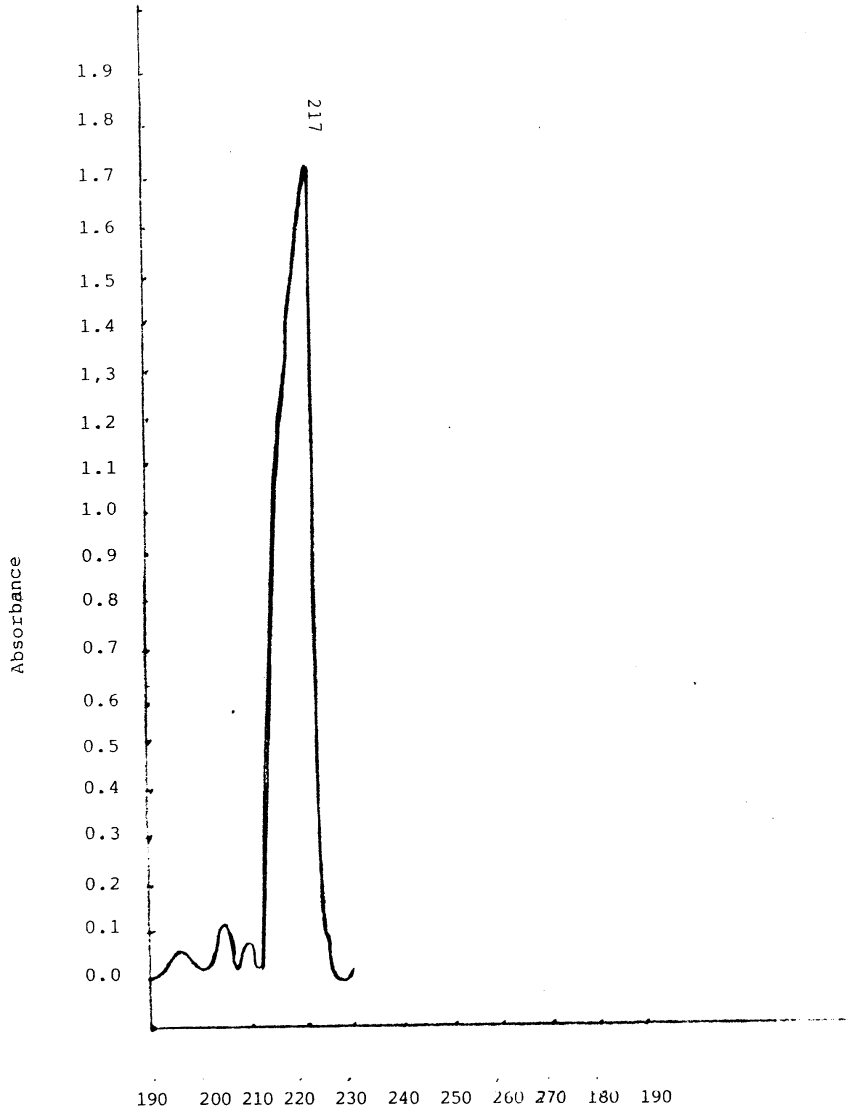


Figure (9) : The Absorption Spectrum of Chlordane in Ethanol.

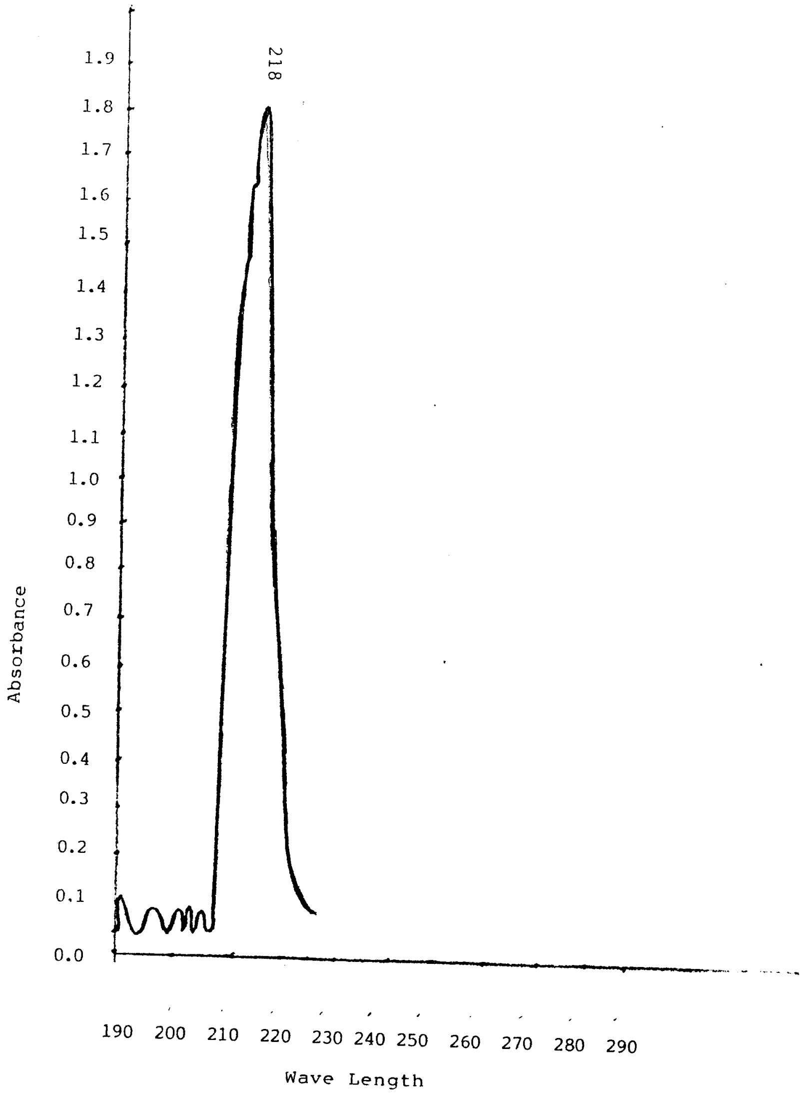


Figure (10) : The Absorption Spectrum of Endrin in Ethanol.

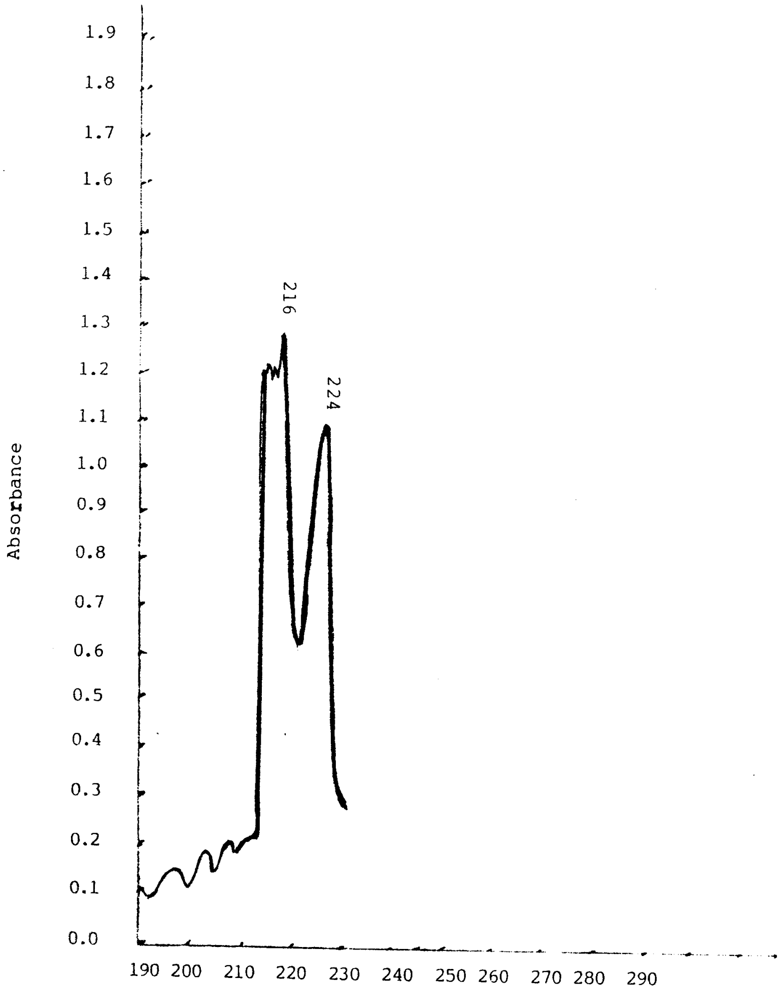


Figure (11) : The Absorption Spectrum of Diazinon in Ethanol.

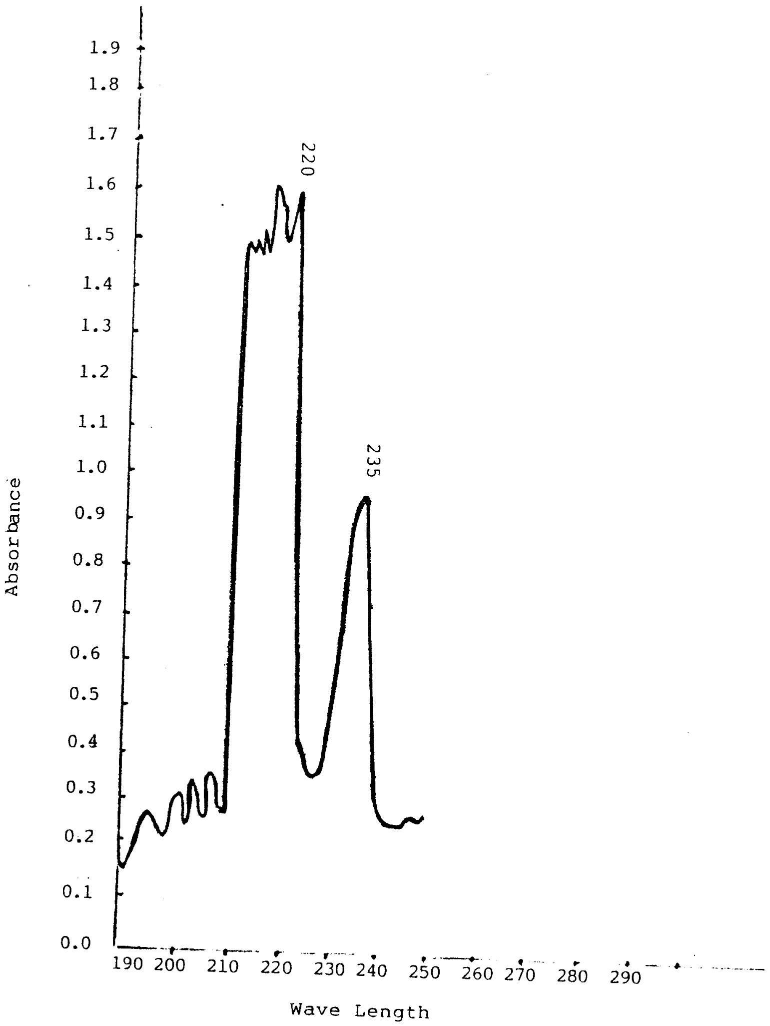


Figure (12) : The Absorption Spectrum of Dursban in Ethanol.

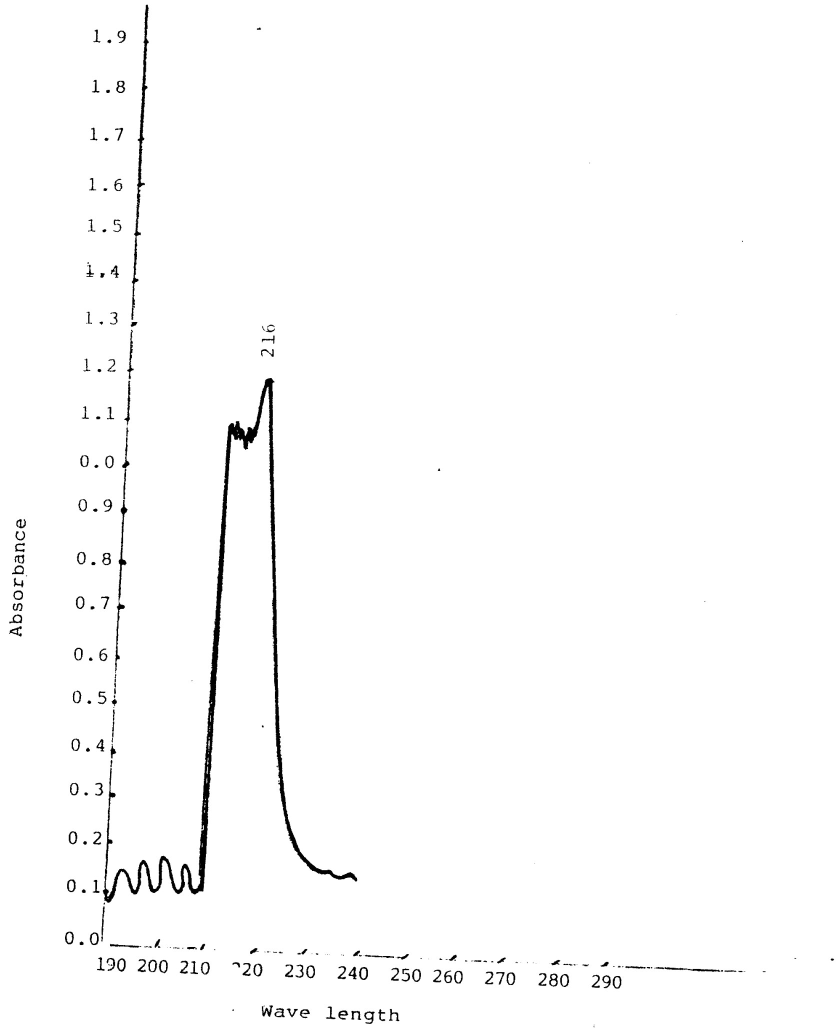


Figure (13) : The Absorption Spectrum of Malathion in Ethanol.

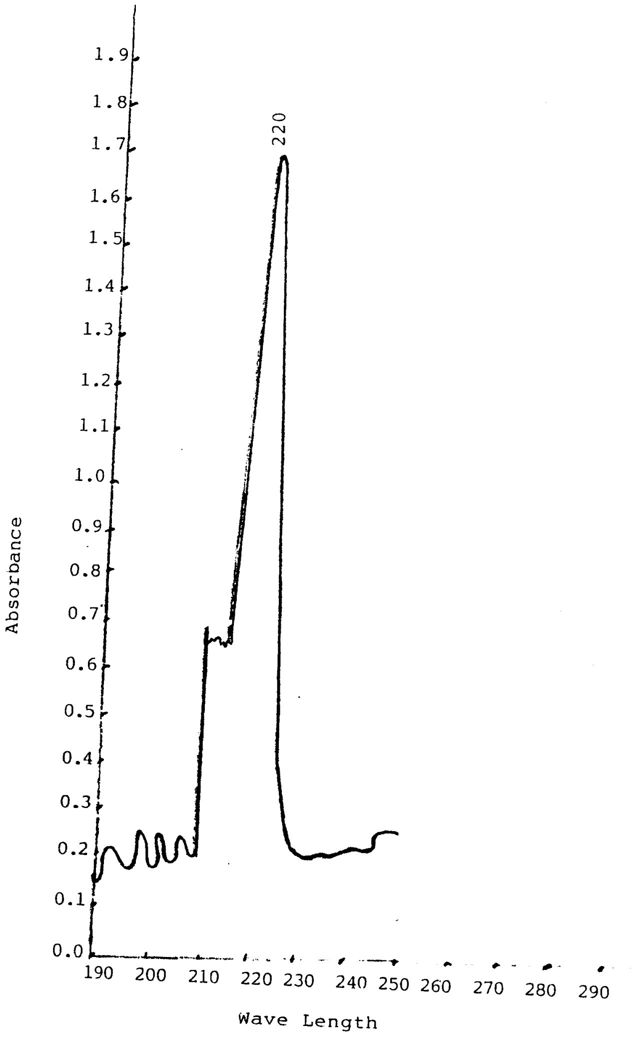
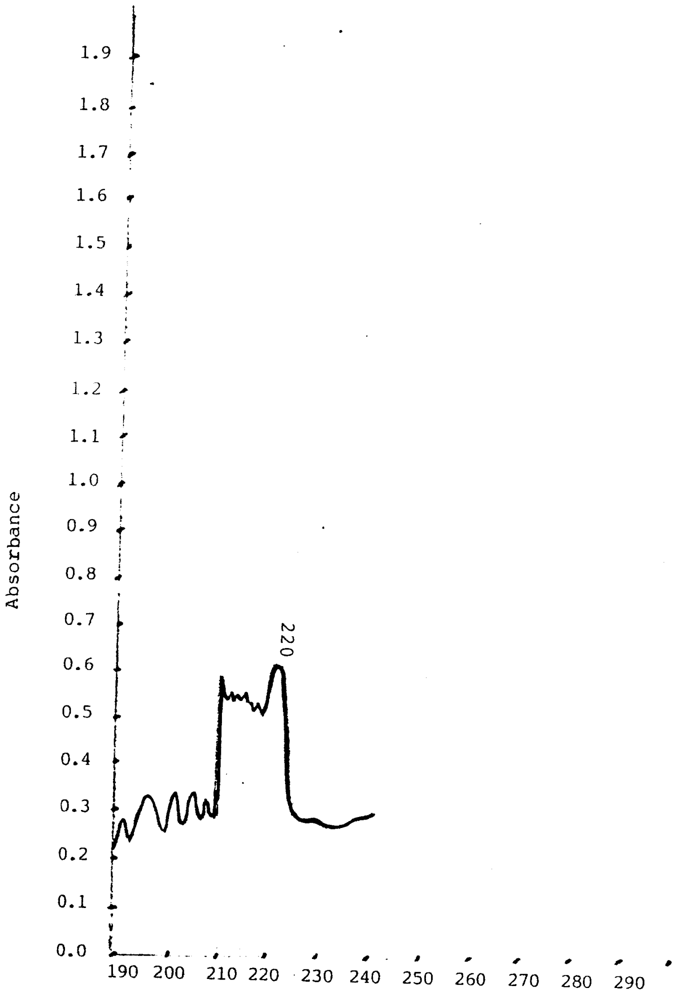


Figure (14) : The Absorption Spectrum of Dimethoate in Ethanol.



Wave Length

Figure (15) : The Absorption Spectrum of Lannate in Ethanol.

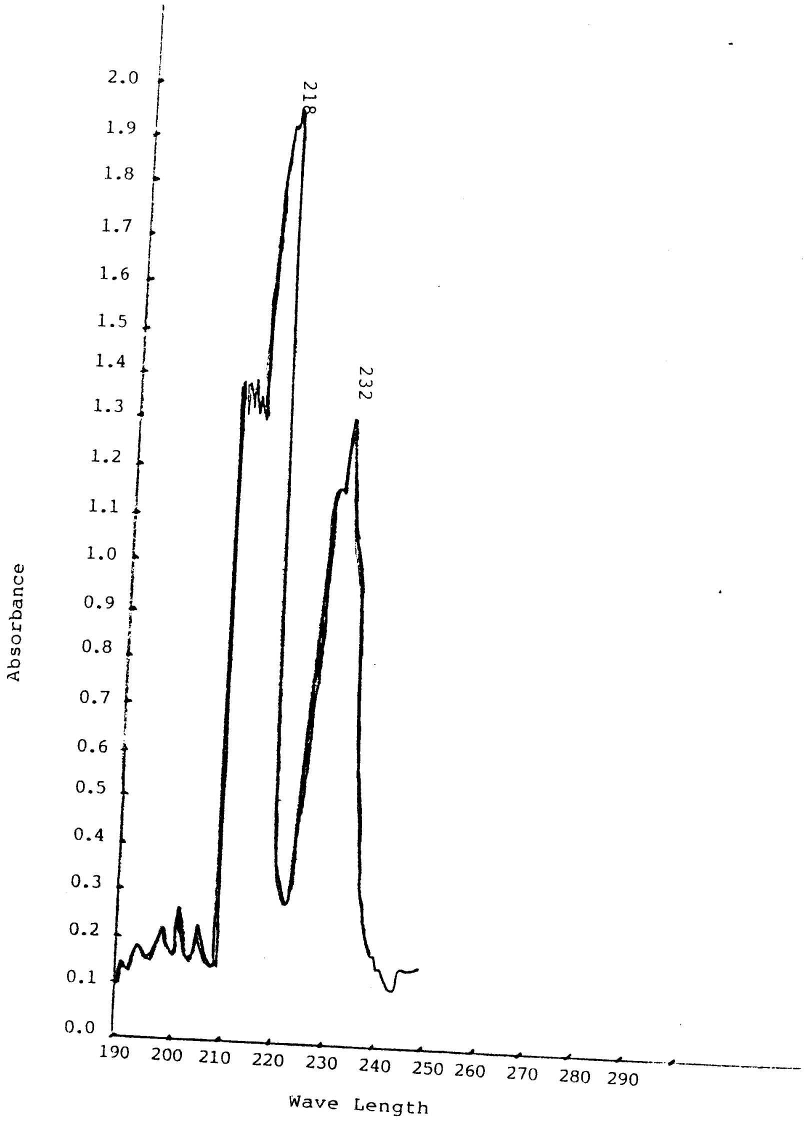


Figure (16) : Absorption Spectrum of Sevin in Ethanol.

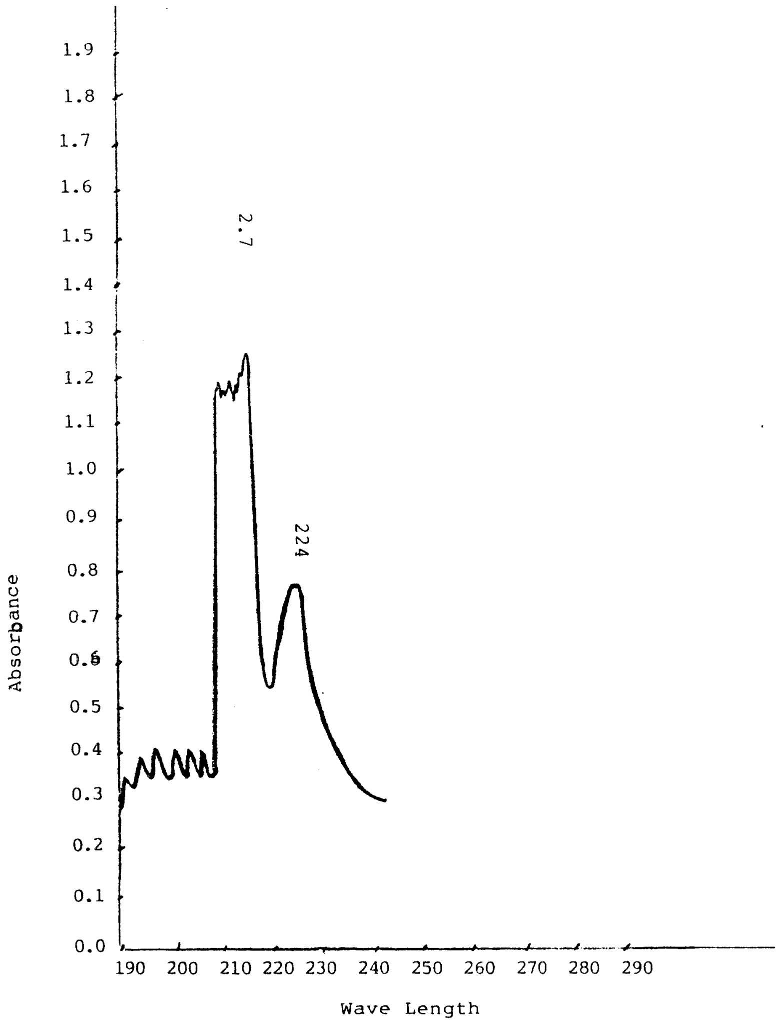


Figure (17) : The Absorption Spectrum of Aldicarb
in Ethanol.

"Bear-Lambert Law" was the base of any quantitative spectrophotometric determination.

$$\text{Log } I_o/I = EBC = A$$

Where :

I_o = Intensity of incident radiation.

I = Intensity of incident transmitted radiation.

E = Molr extention coefficient.

B = Ligh path (in cm).

C = Molar concentration.

A = Absorbance.

As the law predicts, a linear relation between absorbance and concentration was drawn. To a very good extent this relation was found to hold many systems whether in the visible or ultra violet region.

The concentration of studied insecticides in water samples were calculated from standard curves which prepared from appropriate concentrations of insecticides used carried out in an identical procedure including the standard calibration curves (Figure 18-28).

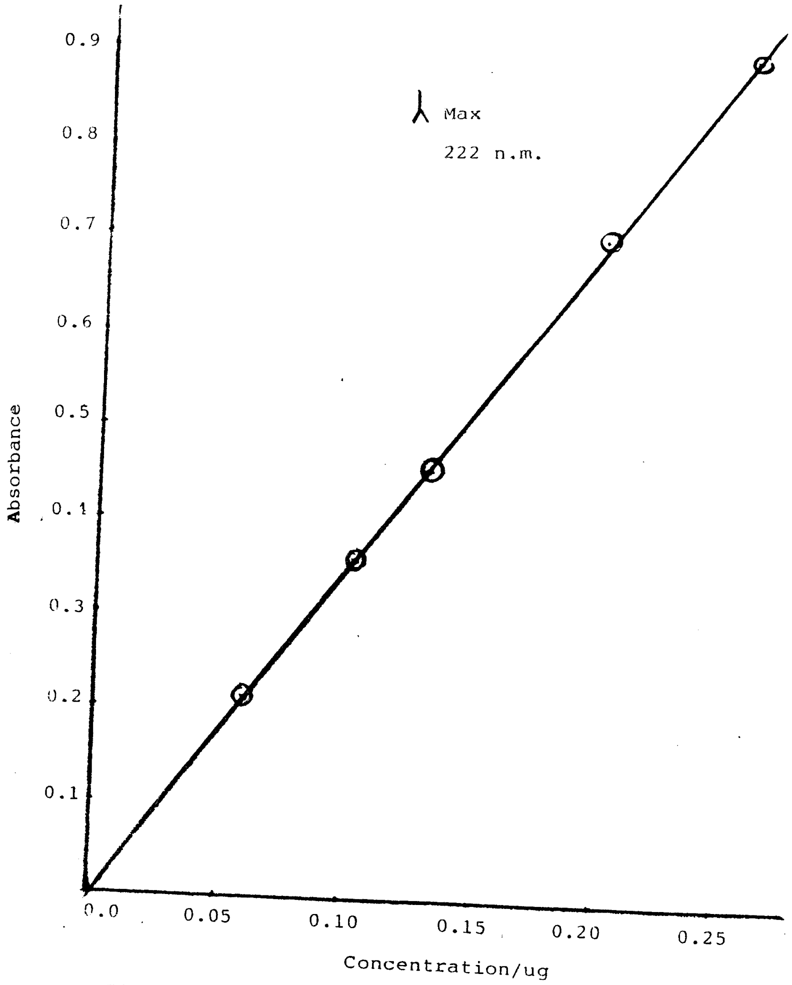


Fig. (18) : The Caliberation Curve of D.D.T. in Ethanol at Wave Length 222 nm.

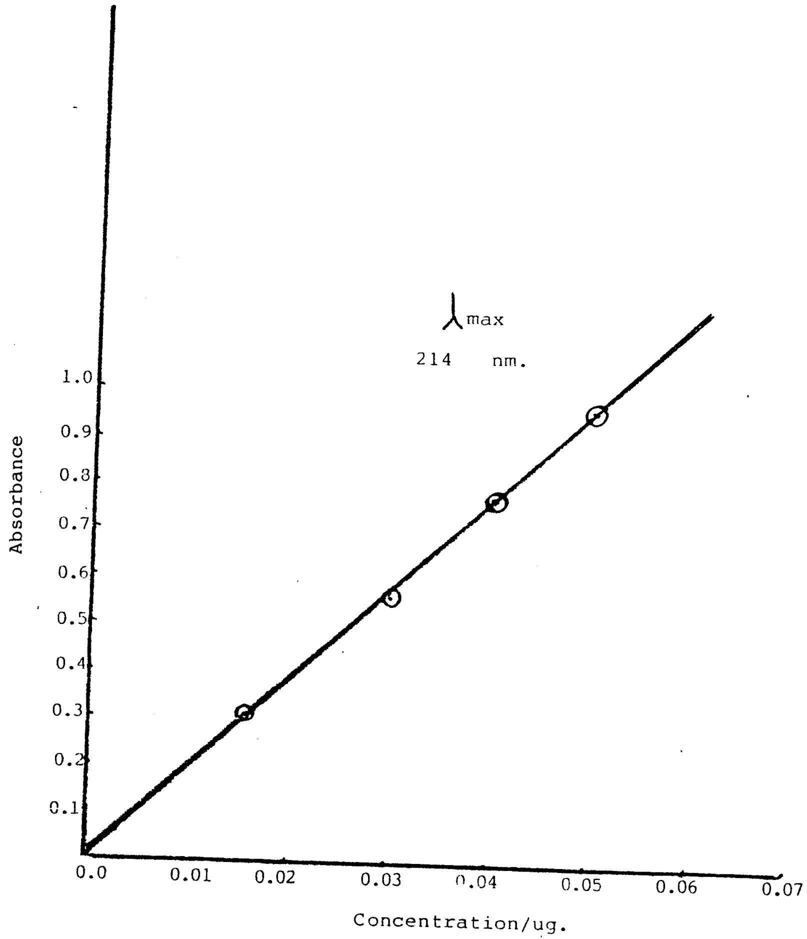


Fig. (19) : The Caliberation Curve of Lindane in Ethanol at Wave Length 214 nm.

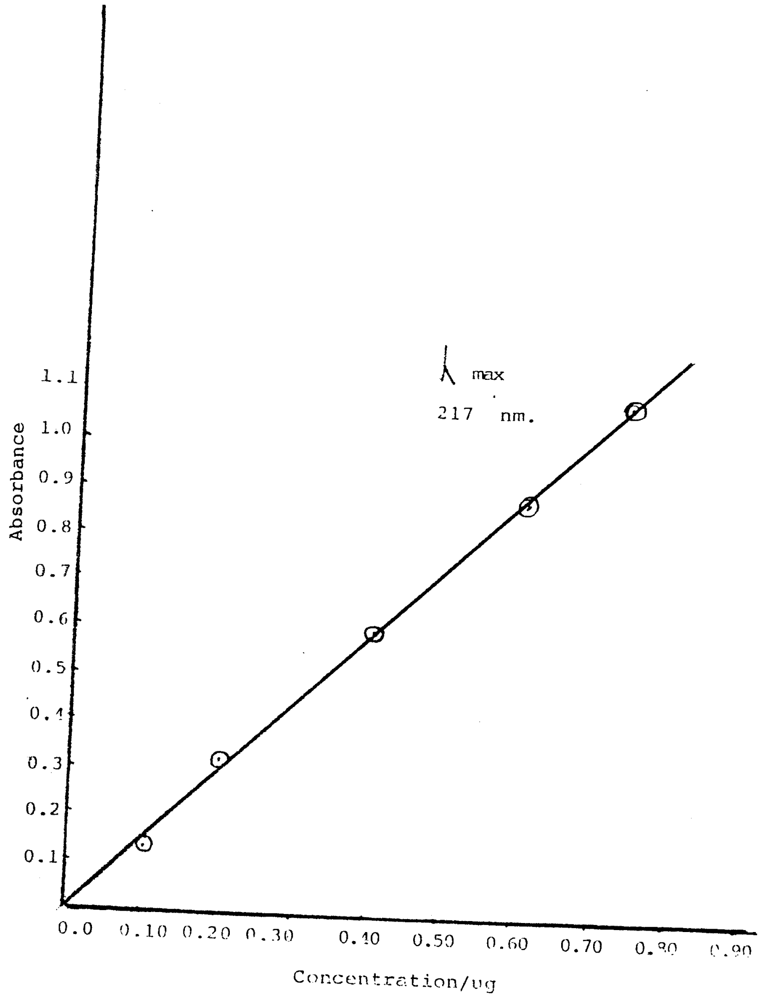


Fig. (20) : The Caliberation Curve of Chlordane in Ethanol at Wave Length 217 nm.

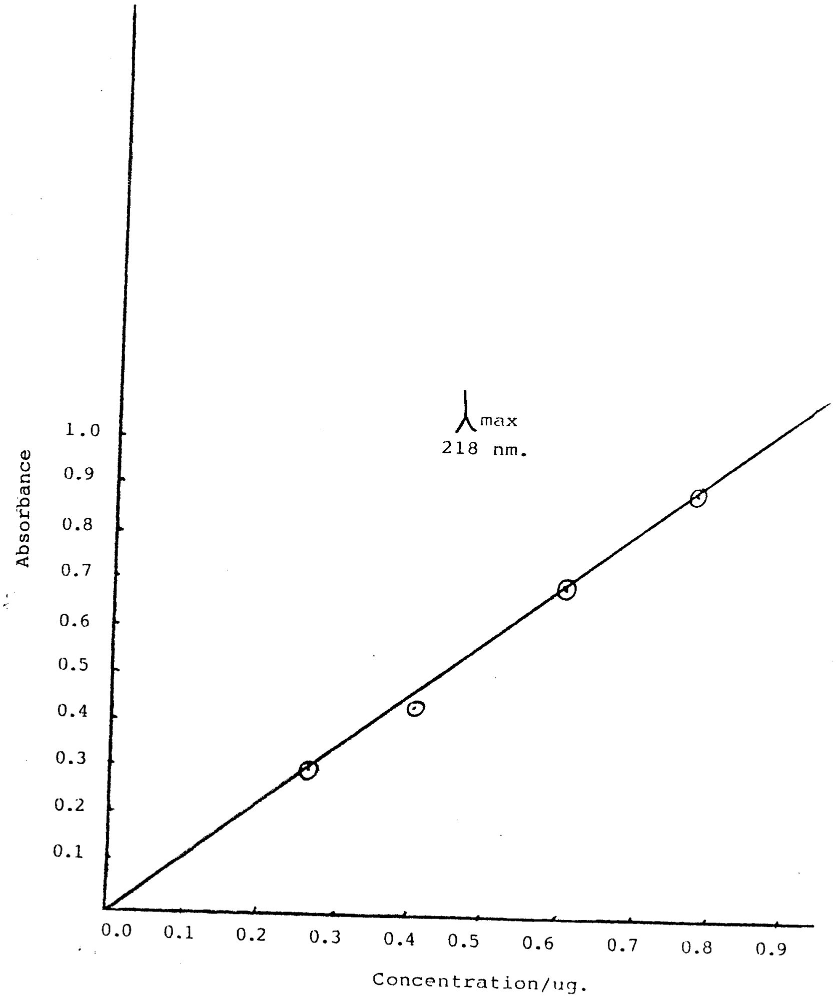


Fig. (21) : The Caliberation Curve of Endrin in Ethanol at Wave Length 218 nm.

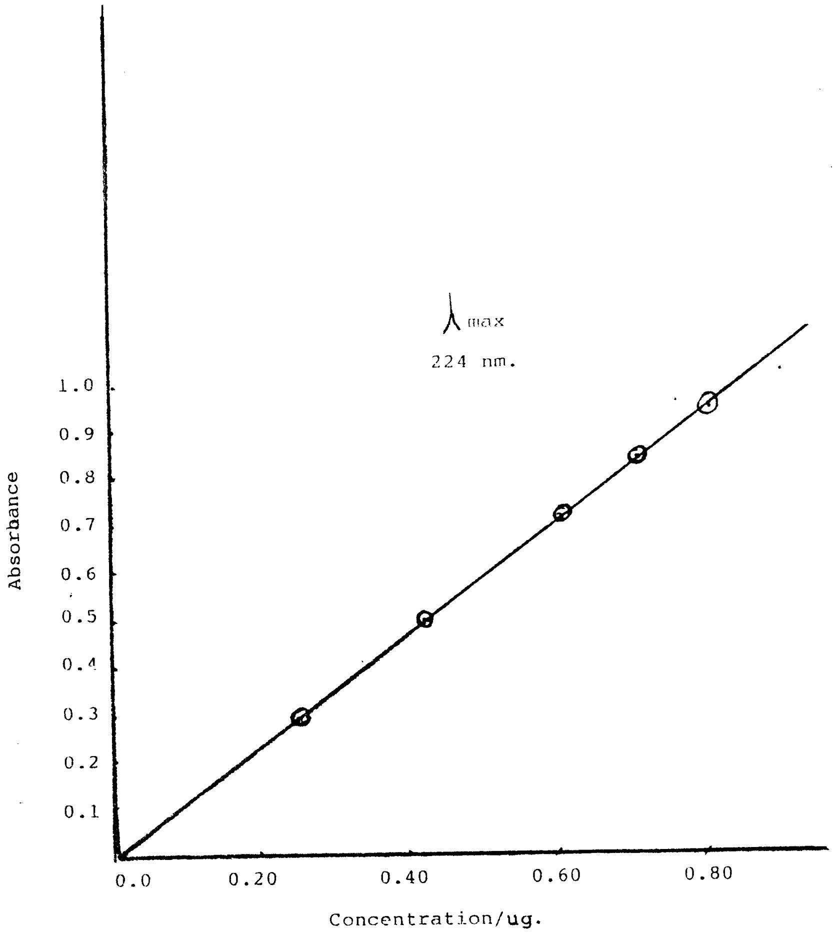


Fig. (22) : The Calibration Curve of Diazinon in Ethanol at Wave Length 224 nm.

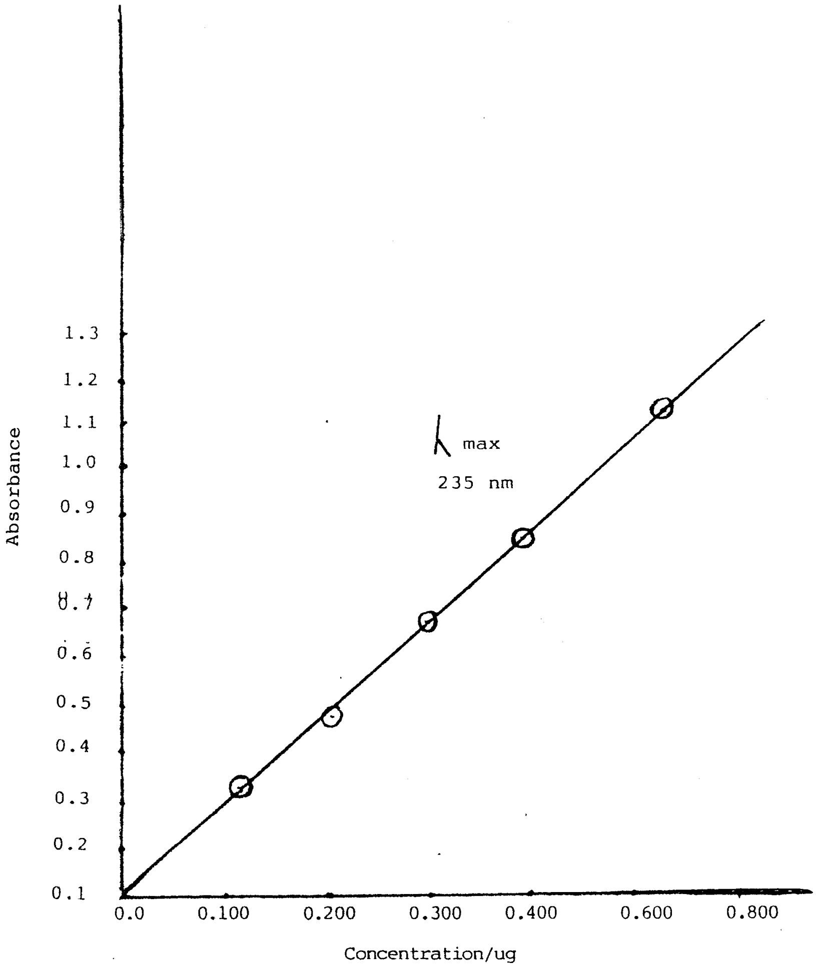


Figure (23) : The Caliberation Curve of Dursban in Ethanol at Wave Length 235/nm.

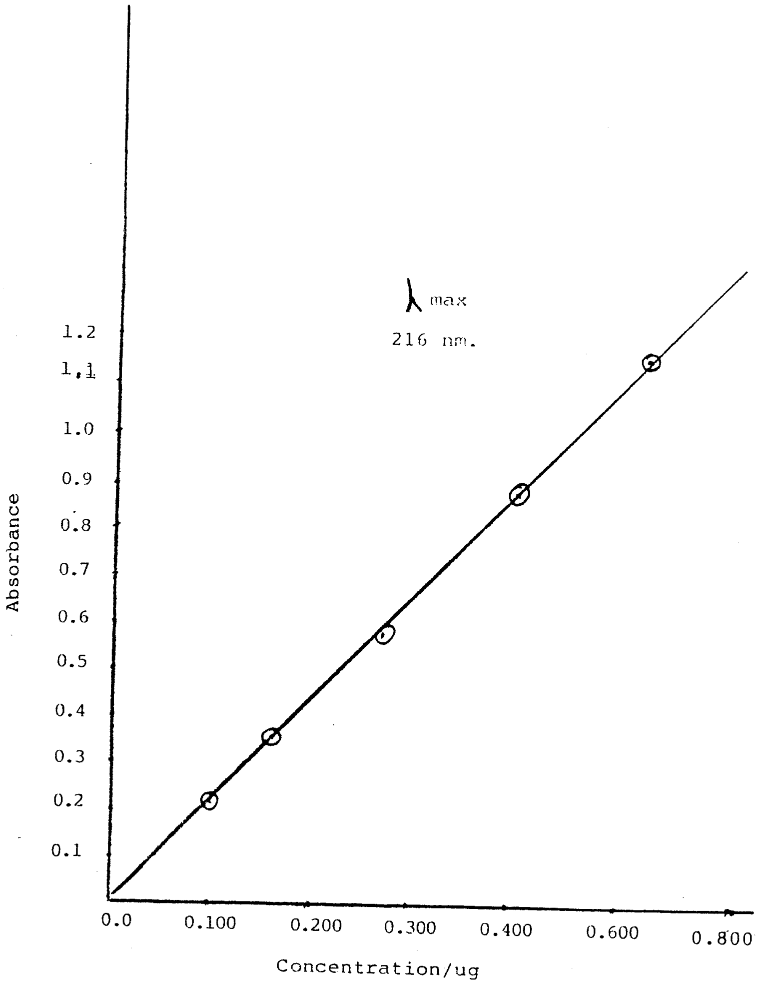


Fig. (24) : The Caliberation Curve of Malathion in Ethanol at Wave Length 216 nm.

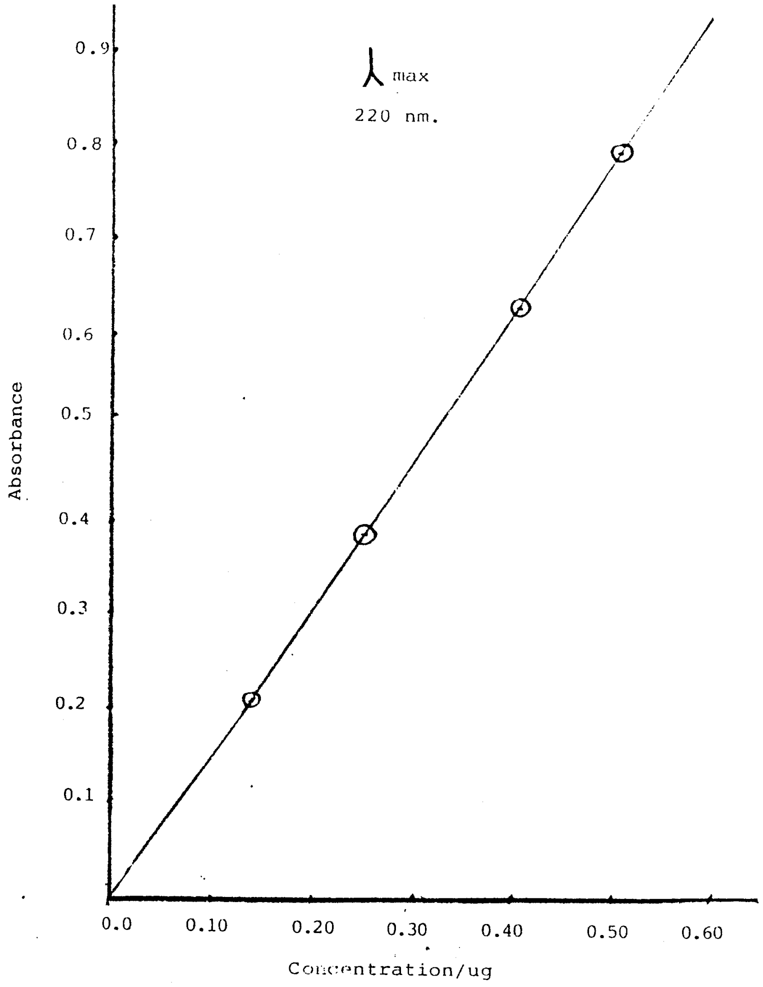


Fig. (25) : The Calibration Curve of Dimethoate in Ethanol at Wave Length 220 nm.

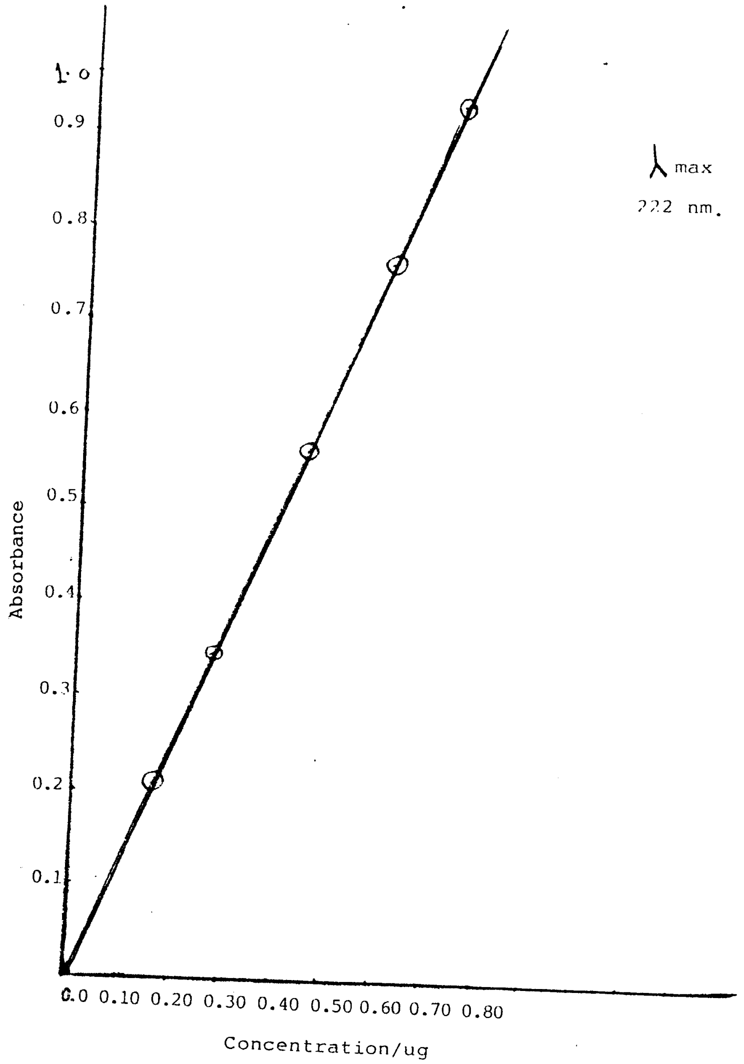


Figure (26) : The caliberation curve of Lannate in Ethanol at Wave Length 222 nm.

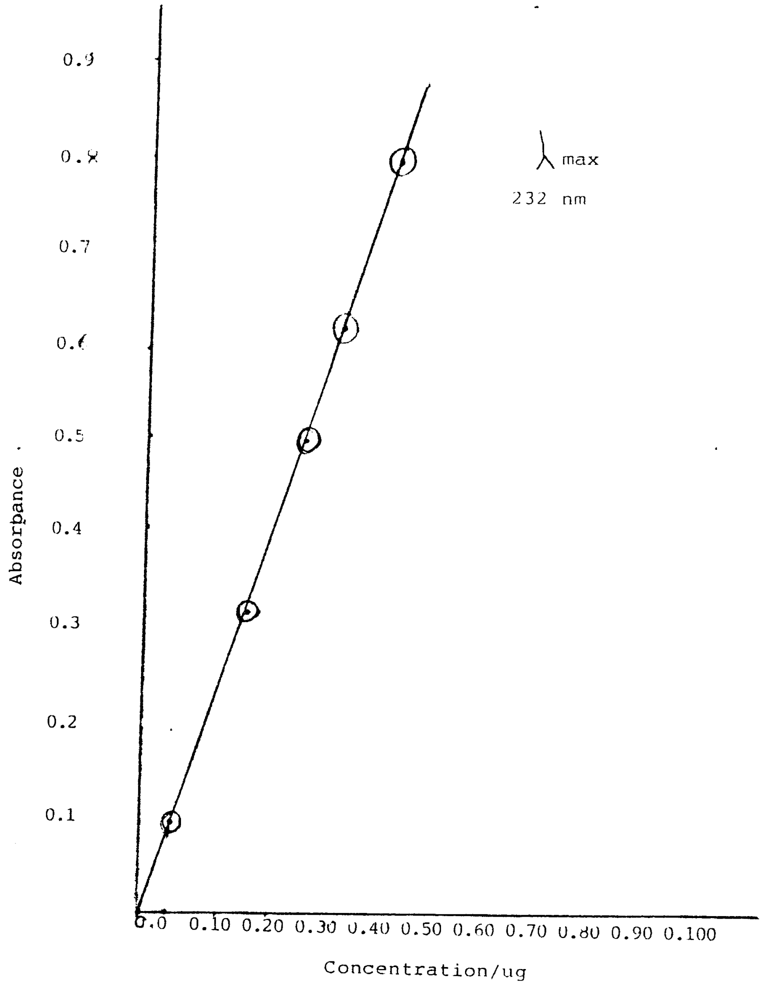


Fig. (27) : The Caliberation curve of Sevin in Ethanol at Wave Length 232 nm.

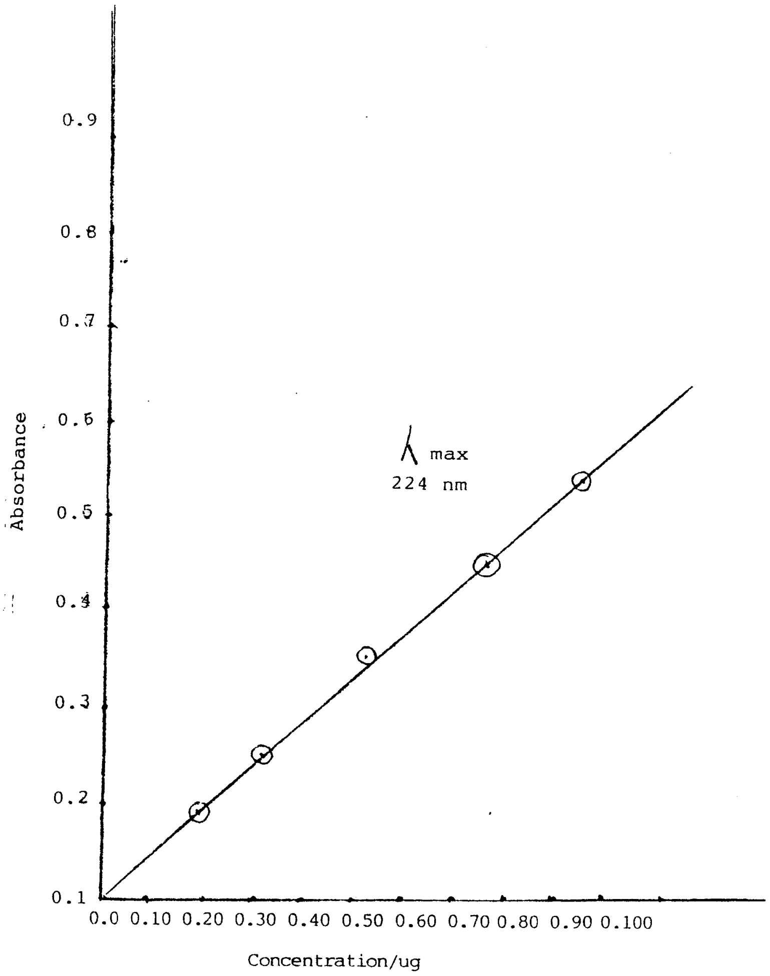


Fig. (28) : The Caliberation Curve of Aldicarb in Ethanol at Wave length 224 nm.

2. CHEMICAL ANALYSIS.

The intensified concern with water quality and the development of criteria and standards for various classes of natural water are reflected in an increased request for more laboratory analysis.

Full chemical reports including insecticide residues are therefore required in order to investigate the suitability of water supply and the relationship between some chemicals and insecticide residues in water which have been reported by Keith and Hunt (1966), Edwards (1976), and Cohen, et al. (1984).

A total of 54 water samples were collected from different water sources in Behera Governorate including 30,18 and 6 samples from surface, ground and tap water respectively. The samples were subjected to the following analytical procedures :

2.1- ORGANIC MATTER

The amount of organic matter was estimated according to Attia (1964).

REAGENTS :

i) Dilute sulphuric acid :

- One part of conc. sulphuric acid was added to 4 parts of distilled water.

ii) Standard ammonium oxalate solution :

- 0.888 gm of ammonium oxalate was dissolved in one liter of distilled water, (one ml of this solution # 0.1 mg of oxygen).

iii) Potassium permenganate solution :

- 0.4 gm of potassium permenganate was dissolved in one liter of distilled water.

The concentration of this solution was adjusted so that every one ml of which should exactly correspond to one ml of the standard ammonium oxalate solution = 0.1 mg 0f oxygen.

PROCEDURE :

- To 100 ml of the water sample, 10 ml of the standardized potassium permenganate solution and 10 ml of dilute sulphuric acid were added.

- The mixture was digested in a boiling water bath for 30 minutes after which 10 ml of the standard ammonium oxalate solution were added.

- The mixture was titrated against the standard potassium permenganate solution untile the appearance of faint pink colour and the quality consumed to bring out such an end point was recorded (R_1). On the other hand, the procedure was carried out again by using 100 ml of distilled water instead of the water sample (R_2).

- The total quantity of organic matter in milligrams per 100 ml of the samples was calculated according to the following equation :

$$(R_1-R_2) \times 0.1/\text{ml of the sample} \times 1000$$

Where :

R_1 = ml of the standard potassium permenganate solution used for the sample.

R_2 = ml of the standard potassium permenganate solution used for the blank.

2.2. CHLORIDES :

The total residue was determined according to A.P.H.A. (1971).

- 100 ml of the water sample were transfered to a previously weighed porceline dish, then placed in a boiling water bath untill complete evaporation.

- The sample was then dried for one hour at a temperature ranged from 103 to 105°C in a thermostatically controlled hot air oven. The end result was determined by obtaining two successive constant weights. The total residue in mg/liter was calculated according to the following equation :

Total residue = (A-B) x 100/ml of the sample.

Where :

A = weight of the dish containing the dried residue.

B = Weight of the dish alone.

2.3- PHOSPHATES :

The phosphate content was determined according to Gomorri (1942).

Reagents :

i) Ascorbic acid reagents :

- 2% pure ascorbic acid in 20% trichloroacetic acid solution, was kept in a dark glass stoppered bottle which could remain stable for at least two months in the refrigerator.

ii) Acid molybdate solution :

- 10 gm of pure ammonium molybdate were dissolved in 120 ml of distilled water.

- Conc. sulphuric acid (30 ml) were carefully added to about 40 ml of distilled water, allowed to cool, and added to the ammonium molybdate solution and completed with distilled water up to 200 ml.

iii) Standard phosphate solution :

- 43.9 mg of pure acid potassium phosphate (KH_2PO_4) were dissolved in distilled water and the volume was completed to 500 ml.

The solution was saturated with chloroform as a preservative and kept as a standard phosphate solution containing 0.004 mg phosphates per 0.2 ml.

PROCEDURE :

- 0.2 ml of the sample was added to 4 ml of distilled water, to which 0.8 ml of ascorbic acid reagent was gradually added with a continuous thoroughly shaking.

- The mixture was left for one minute, and filtered through a small filter paper.

A- The test: 2.5 ml of the filtrate (equivalent to 0.1 ml of the water sample).

B- The standard : 0.2 ml of the standard phosphate solution (equivalent to 0.004 mg phosphate) was added to 1.5 ml of distilled water 0.8 ml of ascorbic acid.

C- The blank : 0.8 ml of ascorbic acid was added to 1.7 ml of distilled water.

- To the test, standard and blank 0.5 ml of acid molybdate solution was added, mixed well and left for 10 minutes and the colours at 70 Um were matched.

Calculation :

$$\frac{\text{R eading of the tes}}{\text{Reading of the standard}} \times 0.004 \times \frac{1000}{0.1}$$

$$= \frac{\text{Reading of the test}}{\text{Reading of the standard}} \times 40$$

= mg/L. of phosphate.

2.4- SULPHATES

The amount of sulphates were determined by the gravimetric method with ignition of residue after A.P.H.A. (1976).

REAGENTS :

i) Methyl red indicator solution:

100 mg of methyl red-sodium salt were dissolved in a small quantity of distilled water and diluted to 100 ml.

ii) Diluted hydrochloric acid :

One part of distilled water was added to one part of conc. hydrochloric acid.

iii) Barium chloride solution :

100 gm of barium chloride were dissolved in one liter of distilled water.

iv) Silver nitrate-nitric acid reagent :

8.5 gm of silver nitrate were dissolved in 500 ml distilled water and 0.5 ml of conc. nitric acid.

PROCEDURE :

- Hydrochloric acid was added to 250 ml of the water sample in order to adjust the pH value at 4.5 to 5 by using a pH meter.

- The adjusted water sample was boiled untile precipitation appeared to be complete, and the precipitate was digested at 80°C over night.

- The solution was filtered through ashless filter paper, then the precipitate was dried and ignited at 800°C for one hour.

- Repeated dessication and weighting several times were performed, untill two successive constant weights were obtained, the weight of the precipitate was calculated according to the following equation :

- The amount of sulphates (mg/L) =

$$\frac{\text{mg of barium sulphate}}{\text{volume of water sample used (250 ml).}} \times 411.5$$

2.5- NITRATES :

Nitrates in water samples were estimated by "Brucine method" according to A.P.H.A. (1960).

REAGENTS :

Sulphuric acid solution 64% by volume (64 ml Conc. H_2SO_4 mixed with 36 ml distilled water).

- Brucine solution : 5 gm. brucine were dissolved in 100 ml of acetic acid.
- Conc. hydrochloric acid (HCl) Stock nitrate solution: 07218 gm of anhydrous potassium nitrate was dissolved in 1000 ml

distilled water (the solution contained 100 mg/LN).

- Standard nitrate solution : 100 ml of the stock nitrate solution were added to one liter of distilled water.
  (1 ml = 0.01 mg N = 0.0443 mg nitrate ions).

PROCEDURE :

In a flask of 100 ml capacity 1 ml of the filtered water sample was added to 10 ml of 64% by volume H_2SO_4 reagent than 0.1 ml of brucine solution and finally one drop of conc. HCl were added to the mixture.

The mixture was heated in a boiling water bath for 10 minutes till the appearance of a yellow colour. The blank was set and the sample was tested at 100 percent transmittance at wave length 410 mu in a spectrophotometer. The concentration of nitrates was determined mathimatically by the following formula.

$$\text{mg/L nitrate N} = \frac{\text{mg nitrate N} \times 1{,}000}{\text{ml of sample}}$$

$$\text{mg/L } NO_3 = \text{mg/L nitrate N} \times 4.43.$$

Table (3) : Seasonal levels of organochlorine insecticide residues (ng/L) detected in surface water.

Season	AUTUMN				WINTER				SPRING				SUMMER			
Source. / Insecticide	D.D.T.	Lindane	Chlordane	Endrin	D.D.T	Lindane	Chlordane	Endrin	D.D.T	Lindane	Chlordane	Endrin	D.D.T	Lindane	Chlordane	Endrin
setta Branch of the ver Nile at :																
1. Rasheid	53.3	5	7	23,3	16.7	35	21	10	6.7	31.7	4.7	6.7	10	58.3	28	3.3
2. Edfina	-	40	60.7	20	-	6.7	23.3	20	-	36.7	21	20	-	46.7	4.7	10
3. Mahmoudia.	-	40	-	20	-	26.7	7	20	-	26.7	14	20	-	-	7	33
Mahmoudia Canal	16.7	23.3	4.7	10	20	31.7	11.7	20	20	38.3	25.7	20	10	26.7	-	10
1. Damanhour Drain	13,3	26.7	-	-	10	23.3	-	10	16.7	31.7	-	10	16.7	26.7	-	10
2. Edfina drain	6.7	31.7	-	-	6.7	35	-	10	20	20	-	10	30	6.7	-	-
Min	6.7	5	4.7	10	6.7	6.7	7	10	6.7	20	4.7	6.7	10	6.7	7	3.3
Max	53.3	40	60.7	23.3	16.7	35	23.3	20	20	38.3	25.7	20	30	58.3	28	33
Mean	15	27.8	12.1	12.2	8.9	26.4	10.5	15	10.6	30.9	10.9	14.5	11.1	31.8	10.1	12.7
S.E.	6.95	8.7	2.8	1.4	2.3	7.7	3.1	5.5	6.5	5.7	4.3	3.4	2.5	6.7	2.9	3.8

Table (4) : Seasonal levels of organophos insecticide residues (ng/L) in surface water.

Season	AUTUMN				WINTER				SPRING				SUMMER			
Insecticide / Source	Diazinon	Dursban	Malathion	Dimethoat	Diazinon	Dursban	Malathion	Dimethoat	Diazinon	Dursban	Malation	Dimethoat	Diazinon	Dursban	Malation	Dimethoat
Rosetta Branch of the River Nile at :																
1. Rasheid	-	183.3	-	13.3								-	4.4		200	38.3
2. Edfina	119.7	-	-	96.7								-	13.3		216.7	-
3. Mahmoudia.	4.4	-	-	106.7								-	4.4		33.3	-
Mahmoudia Canal	186.2	16.7	83.3	23.3								10	93.1		33.3	263.3
1. Damanhour Drain	13.3	33.3	50	-								6.7	-		-	96.7
2. Edfina drain	26.6	-	33.3	-								-	-		-	23.3
Min	4.4	16.7	33.3	13.3								6.7	4.4		33.3	23.3
Max	186.2	183.3	83.3	106.7								10	93.1		216.7	263.3
Mean	58.4	38.9	27,8	40								2.8	19.2		80.5	70.3
S.E.	9.8	7.3	2.9	7.9								1.1	4.3		13.9	14.1

Table (5) : Seasonal levels of carbamate insecticide residues (ng/L) in surface water.

Season	AUTUMN			WINTER			SPRING			SUMMER		
Source / Insecticide	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb
Rosetta Branch of River Nile at :												
1. Rasheid	16.7									30		
2. Edfina	-									66.6		
3. Mahmoudia	56.7									46.7		
El Mahmoudia Canal	-	10									16.7	36.7
1. Damnhour drain	-	46.7					20				33.3	16.7
2. Efinda drain	-	16.7					56.7				20	-
Min.	16.7	10					20			30	16.7	16.7
Max	56.7	46.7					56.7			66.7	33.3	36.7
Mean	12.2	12.2					12.8			23.9	11.7	8.9
S.E.	3.8	1.2					2.3			4.2	3.3	1.6

Table (6) : Levels of chlorinated hydrocarbon residues (ng/L) detected in ground water during different seasons.

Season	AUTUMN				WINTER				SPRING				SUMMER			
Insecticide / Source	D.D.T	Lindane	Chlordane	Endrin	D.D.T.	Lindane	Chlordane	Endrin	D.D.T.	Lindane	Chlordane	Endrin	D.D.T.	Lindane	Chlordane	Endrin
1. Damnhour	66.6	28.3			56.7	26.7			46.7	23.3			56.7	31.6		
2. El-Mahmoudia																
3. Edfina	6.6	3.3			6.7	5			3.3	8.3			6.7	3.3		
Min.	6.6	3.3			6.7	5			3.3	8.3			6.7	3.3		
Max.	66.6	28.3			56.7	26.7			46.7	23.3			56.7	31.6		
Mean.	24.4	10.5			21.1	10.6			16.7	10.5			21.1	11.6		
S.E.	8.3	1.9			3.6	4.8			3.9	4.1			5.1	5.4		

Table (7) : Levels of organophosphorus residues (ng/L) detected in ground water during different seasons.

Season	AUTUMN				WINTER				SPRING				SUMMER			
Source / Insecticide	Diazinon	Dursban	Malation	Dimethoate	Diazinon	Dursban	Malathion	Dimethoate	Diazinon	Dursban	Malathion	Dimethoate	Diazinon	Dursban	Malation	Dimethoate
Damanhour	146.3														16.7	
El-Mahmoudia													119.7		83.3	
Edfina	8.9															
Min.	8.9												119.7		16.7	
Max.	146.3												119.7		83.3	
Mean.	51.7												39.9		33.3	
S.E.	6.9												2.9		8.6	

Table (8) : Carbamate residues (ng/L) detected in ground water during different seasons.

Season	AUTUMN			WINTER			SPRING			SUMMER		
Source / Insecticide	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb	Lannate	Sevin	Aldicarb
1. Damnhour			106.7									96.7
2. El-Mahmoudia												
3. Edfina			100									283.3
Min			100									96.7
Max.			106.7									283.3
Mean			68.9									126.7
S.E.			7.7									17.8

Table (9) : Frequency distribution of insecticide residues in total of 108 water samples.

Insecticide	Not detected		0.1-50 mg/L		Over 50 mg/L	
	No of samples	%	No of samples	%	No of samples	%
I. Organochlorine						
1. D.D.T.	64	59.26	35	32.41	9	8.33
2. Lindane	52	48.13	53	49.07	3	2.8
3. Chlordane	74	68.52	31	28,7	3	2.8
4. Endrin	76	70.37	32	29.63	-	-
II. Organophosphorus						
1. Diazinon	82	75.93	19	17.59	7	6.48
2. Dursban	99	91.67	-	-	9	8.3
3. Malathion	94	87.04	-	-	14	12.9
4. Dimethoate	92	85.19	12	11.11	4	3.70
III. Carbamate						
1. Lannate	93	86.11	11	10.19	4	3.70
2. Sevin	92	85.19	18	16.67	-	-
3. Aldicarb	95	87.9	8	7.8	5	4.6

Table (10) : Mean values of insecticide residues (ng/L) in inffluent and effulent of Damnhour water treatment plant.

Insecticide	Inffluent	Effulent	Percent of increasing (I) or decreasing (D)
I- Organochlorine			
1. D.D.T.	25	12.5	50% (D)
2. Lindane	7.5	11.5	53% (I)
3. Chlordane	19	8	58% (D)
II- Organophosphorus			
1. Diazinon	26.6	19.5	27% (D)
III- Carbamate	not detected	not detected	not detected

Table (11) : Effect of activated carbon drinking water filter on insecticides removal.

Insecticide	Concentration (ng/L)		Reduction
	Infflue nt	Effluent	%
I- Organochlorine			
1. D.D.T.	1000	60	94
2. Lindane	1000	55	95
3. Chlordane	1000	88	91
4. Endrin	1000	N.D	100
II- Organophosphorus			
1. Diazinon	1000	199	80.1
2. Dursban	1000	150	85
3. Malathion	1000	250	75
4, Dimethoate	1000	180	82
III- Carbamate			
1. Lannate	1000	140	85
2. Sevin	1000	180	82
3. Aldicarb	1000	190	81

Table (12) : The relationship between the presence of some chemicals and the level of insecticide residues in water sources.

Variable		Max.	Min.	Mean	Organic matter (mg/L)			R	Chloride			R	Phosphate (mg/L)			R	Sulpate (mg/L)			R	Nitrate (mg/L)			R
					Max.	Min.	Mean		Max.	Min.	Mean		Max.	Min.	Mean		Max.	Min.	Mean		Max.	Min.	Mean	
Insecticide residues (ng/L)	G1	263.3	3.3	71.3 ± 0.6	7.5	1.1	6.1 ± 3.2	* 0.18	97.5	68.9	88.23 ± 2.97	** 0.33	0.7	0.02	0.41 ± 0.03	** 0.67	160	55	110 ± 12.1	**** 0.85	23.8	0.5	9.1 ± 1.3	** 0.44
	G2	119.7	3.3	61.8 ± 1.2	6.7	1.54	4.4 ± 2.31	** 0.22	65.4	21.2	49.55 ± 5.81	** 0.57	0.4	0.03	0.29 ± 0.02	** 0.59	115	37.1	85.3 ± 8.6	**** 0.78	17.1	0.2	6.3 ± 2.1	** 0.65
	G3	19.5	8	8.58 ± 0.2	3.1	1	1.46 ± 0.9	** 0.33	17.36	4	9.46 ± 3.41	** 0.19	0.2	0.01	0.09 ± 0.02	**** 0.78	9.22	9.1	9 ± .02	**** 0.84	3.9	0.1	2.9 ± 0.1	** 0.28

Where G_1 = Surface

G_2 = Ground Water

G_3 = Drinking water

R = Correlation coefficient

* = Significant at (0.05) level

** = Highly significant at (0.01) level

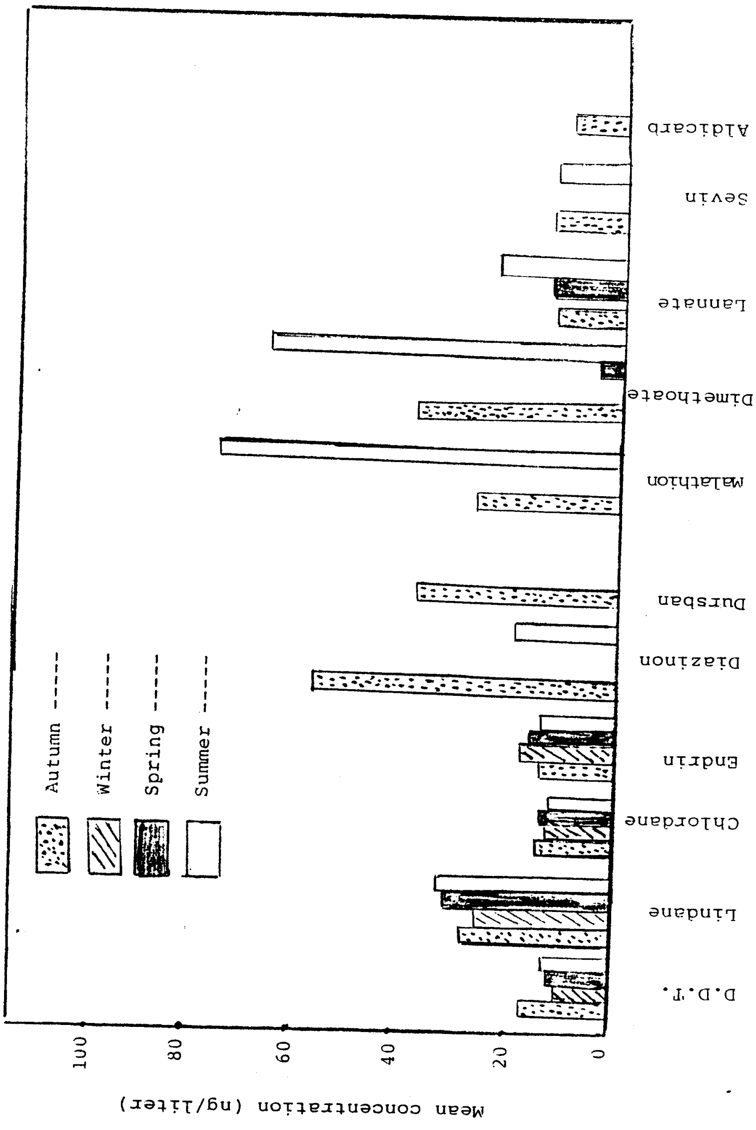


Fig. (29) : Insecticidfe residues in surface water.

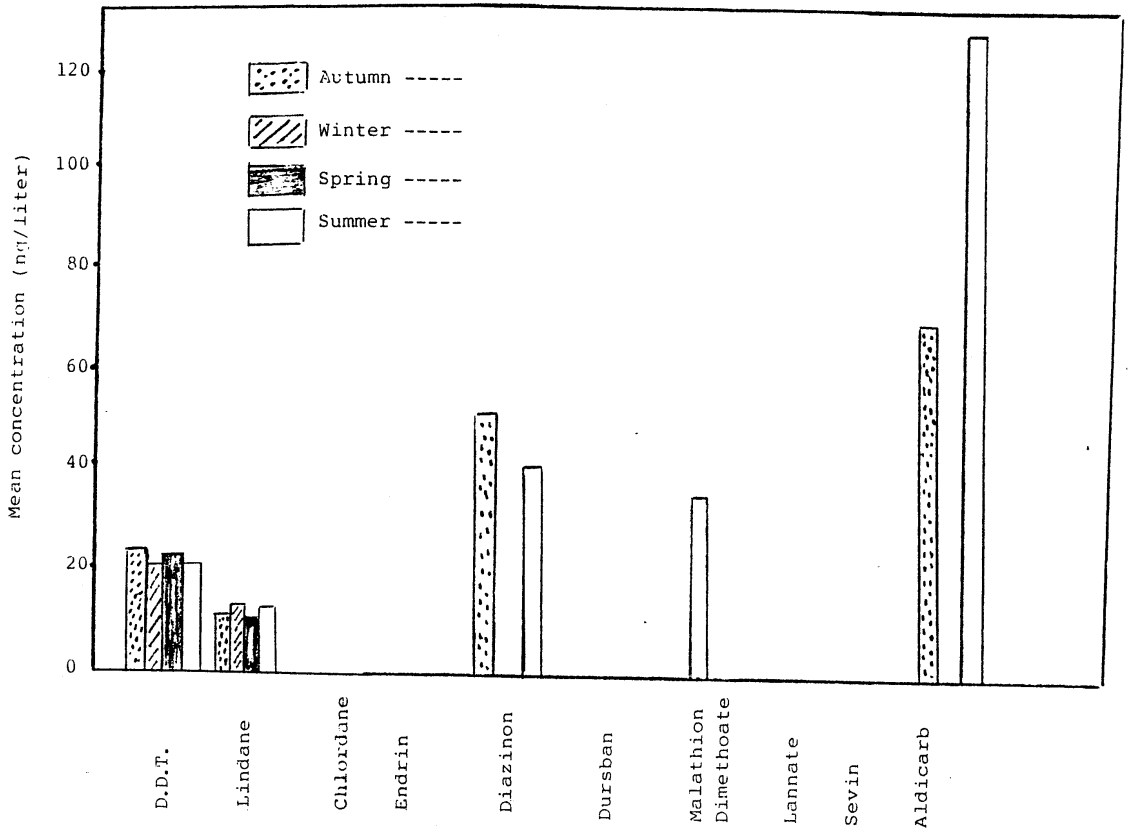


Fig. (30) : Insecticide residues in Ground Water

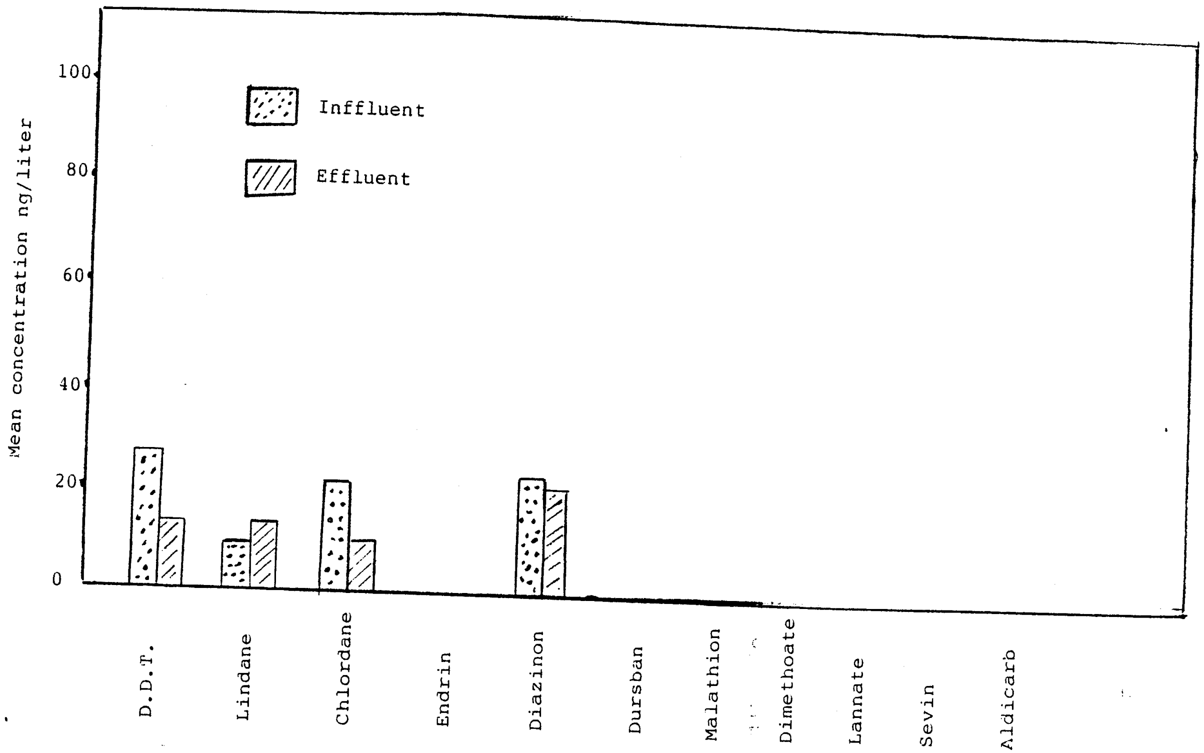


Fig. (31) : Insecticide Residues in Water Samples from Damanhour Water Treatment Plant

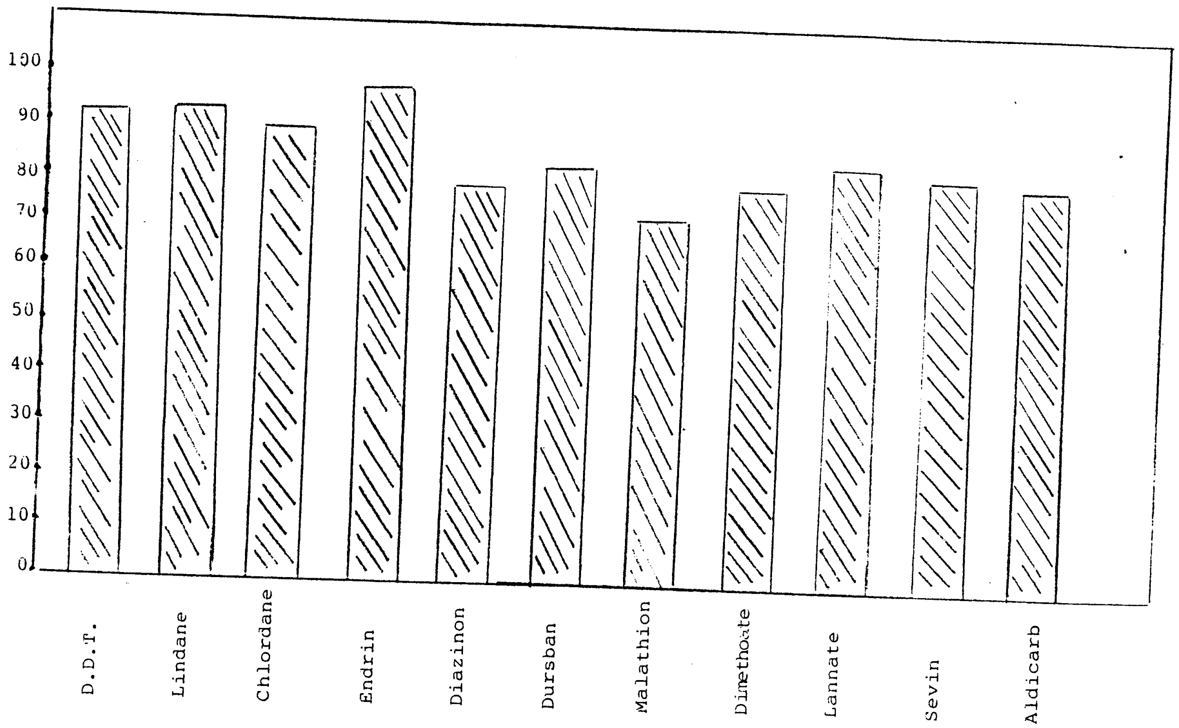


Fig. (32): Effectiveness of Drinking Water Filter (Acivated Carbon) on removal of Insecticide Residues.

DISCUSSION

The main important problems in environmental health are observed in water pollution with insecticides and their toxicological hazard. In Behera Governorate these compounds are used on a large scale, affecting water quality very badly. Therefore, the determination of insecticides in different water sources is essential.

1. OCCURRENCE OF INSECTICIDE RESIDUES IN SURFACE WATER :

a) Chlorinated hydrocarbons.

The values of chlorinated insecticides detected in surface water of different sources in Behera Governorate during the period from October, 1987 to September, 1988 are presented in table (3). It can be observed that the detected insecticides were D.D.T, Lindane, Chlordane annd Endrin, which constitute a major insecticides application in Egypt during the past years.

The results recorded in table (3) revealed that D.D.T residues in autumn varied from 6.7 to 53.3 with a mean of 15+6.95 ng/liter. The concentrations of D.D.T in winter lied between 6.7 to 16.7 (with a mean of 8.9 ± 2.3 ng/liter. although its quantities in spring ranged from 6.7 to 20 (with a mean of 1o.0±6.5 ng/liter) however in summer, an average of 11.1 ± 2.5 ng/liter with a maximum of 30 and a minimum of 10 ng/liiter. The comparison of D.D.T levels in different seasons revealed a comparatively higher concentration in water samples collected during autumn.

In general, it has been found that the concentrations of D.D.T residues in various sources during the different seasons, ranged from 6.7 to 53.3 ng/liter. The above mentioned results are in agreement with those recorded by Wheathley and Hardman (1965), Brodtman (1976) and Kveseth (1981). However, higher levels were reported by Weaver, et al. (1965), Cohen and Pinkerton (1966), Brown and Nishioka (1967), Yule and Tomlin (1971), Bevenue, et al. (1972), Fay and Newland (1972), Miles and Hairris (1973), Achari, et al. (1975). Rosival and Szokolary (1975). Rihan, et al (1978) and Abed El-Kader (1987).

In connection with Lindane analysis in water samples collected during the investigation period, the data recorded in table (3) show that its residue in autumn varied from 5 to 40 with a mean of 27.8 ± 8.7 ng/liter while in winter, Lindane levels ranged from 6.7 to 35 with a mean of 26.4 ± 7.7 ng/liter. On the other hand, its concentration in spring varied from 20 to 38.3 with an average of 30.9 ± 5.7 ng/liter while in summer an average of 31.8 ± 6.7 was detected with a minimum of 6.7 and maximum 58.3 ng/liter. It can be noticed that there was not any seasonal variation in concentrations of Lindane.

It has been found that the residues of Lindane in all water samples lied between 5 to 58.3 ng/liter. Similar findings of Lindane residues were determined by Bevenue, et al. (1972), Brodtman (1976) and Rihan, et al (1978), while Whethley and Hardman (1965), COhen and Pinkerton (1966), Brown and Nishioka (1967), Lichtenberg, et al. (1970), Miles and Hairrs (1973), Sackmuerova, et al. (1977) detected higher levels of Lindane than those obtained in the present investigation. On the other hand, a lower level of Lindane was reported by Lenardon, et al. (1984).

The data presented in table (3) revealed that Chlordane residues in surface water did not exhibit marked seasonal variations where the mean values of Chlordane were 12.1±1.4, 10.5±3.1, 10.9±4..3 and 10.1±2.9 ng/liter in autumn, winter, spring and summer respectively.

Determination of Chlordane residues in investigated water samples exhibited a range varying from 4.7 to 60.7 ng/liter. The obtained results are considered higher than the data recorded by Brodtman (1976) however, lower than the concentrations reported by Lichtenberg, et al (1970), Bevenue, et al. (1972) and Miles and Hairrs (1973).

Regarding the results recorded in table (3) it has been found that the samples collected during autumn showed an Endrin concentration from 10 to 23.3 with a mean of 12.2±1.4 ng/liter. In winter, the detectable concentrations ranged from 10 to 20 with a mean value of 15±5.5 ng/liter. However in spring varying values from 6.7 to 20 were determined with a mean value of 14.5±3.4 ng/liter while in summer an average Endrin value of 12.7±3.8 ng/liter was detected. An overall mean value of Endrin residues in all investigated water samples varied from 3.3 to 33 ng/liter which are considered lower than the concentrations reported by Weaver, et al. (1965), Brawn and Nishioka (1967), Fay and Newland (1970), Lichtenberg, et al. (1970), Miles and Hairrs (1973), Brodtman (1976) and Wegman and Greve (1978).

The presence of chlorinated hydrocarbons in streams depends on the insecticide fractions carried to them in runoff and their stability in stream environment (Weaver, et al., 1965).

The relatively low levels of chlorinated hydrocarbon insecticides in surface water are in good agreement with the explanation given by Dimond, et al. (1971), Miles and Hairrs (1976) who reported that organochlorine residues are unlikely to occure in large quantities in water, because they are relatively insoluble and only the turbulence of moving water can keep the particulate matter in suspension. During rise of the river, some of the deposited residues on the bottom mud may be taken up into the main body of water again. In the same time, it seems that the mud at the bottom of many surface water sources is heavily contaminated with organochlorine insecticides and will continue to be a reservoir for periodic future contamination of the water. On the other hand, such low levels might be due to the prevention of large scale application this group of insecticides in Egypt since 1971 and therefore, the presence of detected levels of contamination may explained to be due to soil erosion, (Lichtenstein, et al., 1966).

The contamination of water by insecticidal soil residues is to a large degree a function of water solubility of a particular insecticide. In addition, the degree to which water is contaminated depends on the insecticidal concentration in the soil resulting from the original application dose and the specific properties of a given toxicant in the soil. (Brawn and Frank, 1980). Therefore, contaminated river sediments can be considered as the main source for release of chlorinated hydrocarbon insecticides to water (Larsson, 1985). Moreover, the presence of organochlorine insecticides may be explained on the fact of the release of tissue-stored chlorinated hydrocarbons upon decomposition of the organisms killed by Dursban treatment Such an explanation was supported by Warnick, et al. (1966).

The presence of detected levels of chlorinated hydrocarbon insecticides indicates the danger of continous release of the persistent chemicals in the environment, because most of these chemicals are carcinogenic and their tolerances are almost zero. (Warnick, et al., 1966).

The data illustrated in table (3) revealed the occurrence of chlorinated hydrocarbon insecticides in surface water of various localities in Behera Governorate including D.D.T, Lindane, Chlordane and Endrin in values ranging from 6.7-53.3, 5-51.7, 4.7-60.7 and 3.3-33 ng/liter respectively. However, D.D.T. could not be detected at Edfina and Mahmoudia sites of Rosetta branch of the Nile River. On the other hand, D.D.T., Lindane, Chlordane and Endrin were the Chlorinated insecticides detected in the water of El-Mahmoudia Canal during the investigation period (Table 3) which are nearly similar to the results obtained by Nadia EL-Haridy (1983).

b- Oranophosphorus insecticide residues.

The data presented in table (4) show that Diazinon could not be detected in winter and spring, while an average values of 58.4±9.8 and 19.2±4.3 ng/liter were determined during autum and summer respectively. Such higher levels of Diazinon in autumn than in summer are in agreament with the results reported by Miles and Harris (1978) and Brown and Frank (1980). On the other hand, low concentrations of Diazinon met with in the present study may be explained to be due in part to its rapid degradation and in another part to the incorporation of chemicals into the soil (Ritter, et al., 1974).

The detection of Diazinon residues in surface water in autumn and summer can be correlated directly with eradication programs for the control of external parasites in livestock practice during these seasons of the year. However, the toxicity of Diazinon was recorded to be very variable. In water it is hydrolysed to the highly poisonous tetraethyl monothiopyrrophosphate which was responsible for serious troubles for livestock (Mello, et al., 1972).

Dursban (Chlorpyrifos) could be detected only in autumn, where its residues were determined in the Nile River at Rashead, Mahmoudia Canal and Damnhour drains, ranging from 16.7 to 183.3 with a mean of 38.9+7.3 ng/liter. These values are lower than those reported by Brown and Frank (1980) and Abed-El-Kader (1987). Such rapid initial disappearance of Dursban from water can be explained to be primarily attributed to adsorption on bottom sediments (Boyer, et al., 1980). Moreover, the slow appearance of little concentrations of Dursban (Chlorpyrifos) residues reported by Riskalla, et al. (1981) and their rapid loss from surface water detected by Ramadan (1982) can be mentioned for further confirmation of the low levels of Dursban residues met with in the present study.

Generally, the low incidence of Diazinon and Dursban in surface water has a relation with their persistence in soils (Frank, et al., 1977) and their disappearance from water may be attributed to the chemical processes playing a major role in their degradation, while the biological processes having a secondary role (Sharom, et al.,, 1980).

The obtained results revealed that Malathion could be detected during autumn in a concentration of 83.3 ng/liter in Mahmodia Canal, 50 ng/liter in Damanhour drain and 33.3 ng/liter in Edfina drain with a mean of 27.8±2.9 ng/liter. Moreover, in summer a mean value of 80.5±13.9 ng/liter was recorded. However, Malathion could not be detected in winter and spring (Table 4).

Determination of Malathion residues in different water sources revealed that its values ranged from 33.3 up to 216.7 ng/liter which are considered lower than those recorded by Brawn and Frank (1980).

Concerning Dimethoate, it has been noticed that its residues in summer were detected at the highest values rather than in both autumn and spring but it could not be detected in winter (Table 4). The values in summer ranged from 23.3 to 263.3 ng/liter with a mean of 70.3±14.1 ng/liter. Dimethoate could not be detected in drain during autumn while in other water sources its concentration ranged from 13.3 to 106.7 ng/liter with a mean value of 40±7.9 ng/liter. In spring, a noticable decrease of residues was detected which ranged from 6.7 to 10 ng/liter with a mean value of 2.8±1.1 ng/liter.

In general estimation of Dimethoate residues in different water sources revealed that its concentrations varied from 13.3 to 263.3 ng/liter which are higher than those reported by Kjolholt (1985).

Such high levels of Dimethoate in water met with in the present investigation may be explained on the basis that its degradation depends on many factors such as the prevailing temperature, pH and type of medium (El-Beil, et al., 1978). At the same time, Dimethoate resists thermal decomposition in water (Ishikura, et al., 1984). Moreover, Dimethoate residues were found to be decomposed in plants but not in water (Purohit, et al., 1982).

Generally, it can be concluded that organophosphorus insecticides are less persistent in water than chlorinated hydrocarbons and it has been assumed that their use will not result in an extensive environmental pollution (Miles and Harris, 1978). However, organophosphorus insecticides are relatively soluble in water and those compounds which are not readily hydrolyzed might be expected to be taken up by a wide range of aquatic organisms, since all the evidence is that organophosphorus are relatively short lived in biological systems and consequently they are quite toxic to ecosystem, human beings and animals. (Macek, 1981). However, the high toxicity of organophosphorus compounds is offset to some extent by the fact that their residues disappear rapidly because of their destruction through hydrolysis lossing therefore their potential danger to domestic livestock (Cox, 1970).

It can be concluded that organophosphorus insecticides (except Dimethoate) were detected only in autumn and summer seasons (table 4) which can be directly correlated to spraying programs for control of different pests in agricultural and veterinary practices.

c- Carbamate insecticides :

Seasonal levels of carbamate insecticide residues detected in surface water from various sources at Behera Governorate are presented in table (5). The detected insecticides were Lannate (Methomyl), Sevin (Carbaryl) and Temik (Aldicarb).

Analysis of water samples in different seasons showed that the residue of Lannate in autumn varied from 16.7 to 56.7 ng/liter with a mean value of 12.2+3.8 ng/liter while in spring it ranged from 20.0 to 56.7 ng/liter with a mean of 12.8±2.3 ng/liter.

However, in summer relatively higher levels ranging from 30 to 66.7 ng/liter were recorded with a mean value of 23.9±4.2 ng/liter, while in winter Lannate residues could not be detected.

Determination of Lannate residues in all examined water samples exhibited a range from 16.7 to 66.7 ng/liter. The obtained results are lower than those reported by Medy (1985).

Low levels of Lannate in surface water may be explained to be due to its solubility in water and consequently rapidly degraded by microbes with the production of Co_2 and S-methyl-N-hydroxythioacetimidate as hydrolysis by products (Harvey and Pease, 1973).

In connection with Sevin (Carbaryl), it could not be detected in spring and winter, while in summer and autumn it was detected in Mahmoudia Canal, Edfina and Damanhour drains. In autumn, an average value of 12.2±1.2 ng/liter was recorded with a minimum of 10 and a maximum of 46.7 ng/liter. However, in summer, the levels of sevin ranged from 16.7 to 33.3 ng/liter with a mean value of 11.7±3.3 ng/liter.

It has been found that residues of Sevin in all examined water samples Lie between 10 to 46.7 ng/liter.

Such low level of Sevin in different water sources may be attributed to the natural microbial communities, where the microflora of stream water mineralize Sevin at rate of 2 to 3 ng/ml or less (Boethling and Alexander, 1979).

The appearance of Sevin in surface water during autumn and summer only can be directly correlated to its application in eradication of livestock ectoparasites as well as for control of different agricultural pests (Clark and Clarke, 1975).

Sevin is of low toxicity for warm blooded animals and has a teratogenic effect in the dog (Bukin and Filatov, 1965).

In regard to the residues of Aldicarb, they could be detected only in summer in Mahmoudia Canal and Damanhour drain, ranging from 16.7 to 36.7 ng/liter with a mean value of 8.9+1.6 ng/liter. The low levels of Aldicarb may be attributed to its short term persistence, its rapid and complete conversion to metabolites, its rapid oxidation to sulfoxide together with a slower conversion to sulfone and its break down by bacteria and fungi resulting of Co_2 and H_2o (Leistra and Smelt, 1981).

2. OCCURRENCE OF INSECTICIDE RESIDUES IN GROUND WATER.

a- Chlorinated hydrocarbon insecticides.

D.D.T. and Lindane were the only chlorinated hydrocarbon insecticides detected in ground water samples (table 6).

Analysis of water samples collected during the different seasons revealed that the lowest concentration of D.D.T. was recorded in spring rather than in other seasons. In general, determination of D.D.T. in investigated ground water samples exhibite that its residues ranged from 3.3 to 66.6 ng/liter which are considered lower than the data reported by Achari, et al., (1976).

Concerning Lindane residues, a seasonal variation was noticed (Table 6). Where in autumn they varied from 3.3 to 28.3 ng/liter with a mean of 10.5±1.9 ng/liter. While in winter, the average concentration was 10.6±4.8 ng/liter with a minimum of 5 and a maximum of 26.7 ng/liter. In spring, the values lie between 8.3 and 23.3 with a mean of 10.5±4.1 ng/liter however, in summer the values ranged from 3.3 to 31.6 with an average value of 11.6±5.4 ng/liter.

In connection with Lindane residues in ground water samples during the different seasons, it has been found that their concentration ranged from 3.3 to 31.6 ng/liter, which are higher than those reported by Achari, et al. (1975).

b- Organophosphorus.

The values of organophosphorus insecticides in ground water samples are presented in table (7). Diazinon and Malathion were only detected among the members of this group of insecticides. On the other hand, Diazinon could not be detected in winter and spring, while in summer and autumn it was present in certain sampling localities.

Estimation of Diazinon residues in ground water samples, revealed that the values ranged from 8.9 to 146.3 ng/liter (table 7), which are considered lower than those reported by Frank, et al. (1987).

Concerning Malathion, it could be detected only in summer, where its residues were found in Damanhour and Edfina in values ranging from 16.7 to 83.3 ng/liter which are lower than those reported by Frank, et al (1987).

c- Carbamate insecticides.

Aldicarb was the only carbamate insecticide demonstrated in ground water samples (table 8) collected during autumn and summer, with an average values of 68.9±7.7 and 126.7±17.8 ng/liter respectively. The obtained results are lower than those reported by Rothschild, et al. (1982) and Soren and Stelz (1985).

In the present study, it has been found that eleven insecticide compounds relating to different groups of insecticides were detected in surface water samples including the River Nile, Mahmoudia Canal and drains. (Tables 3,4,5 and Figure 29)>

The relatively high levels of insecticide contamination of surface water samples at Behera Governorate may be attributed to certain factors :

a) The intensive insecticide spraying programmes for eradication of agricultural and animal pests.

b) The use of aeroplanes in spraying programmes which facilitates the dissimination of insecticides around including water surfaces.

c) The use of insecticides by Farmers without any precautions enhancing the contamination of the surrounding environment including surface water.

d) The opend drainage system which was constructed in Behera Governorate in the last few years may play a role in this respect.

It is evident that 5 out of 11 insecticide compounds were detected in ground water samples (tables 6,7,8 and figure 30). Such low number of insecticide contamination of ground water in comparison with surface water, possibly because of many factors such as depth of the ground water source (Rothschild, et al., 1982), water solubility, levels of nitrates (Chohen, et al., 1984) and the leaching character of the compound as for example Methomyl (Lannate) which is generally considered to be a non-Leachable compound and available for uptake and transformation (Wagenet, et al., 1985), which may explain the failure to be detected in investigated ground water samples.

The data recorded in table (9) show the frequency distribution of various types of insecticide residues in all of the 108 water samples. Regarding the organochlorine insecticides, it is evident that 9 (8.33%), 3 (2.8%) and 3 (2.8%) contained D.D.T, Lindane and Chlordane residues respectively above the environmental limit (50 ng/liter) recommended by Federal Water Pollution Control, Administration Water Quality Criteria (1968). However, Endrin residues could not be detected in any of the water samples above this limit.

Concerning Organophosphorus insecticides, 9 (8.3%) and 14 (12.9%) of the examined water samples were found to contain Dursban and Malathion residues over 50 ng/liter (the environmental limit), while 7 samples (6.48%) showed Diazinon above this limit and 4 samples (3.7%) contained Dimethoate over 50 ng/liter.

In connection with carbamate residues it has been found that Lannate could not be detected in 93 (86.11% of the samples) and its content in 11 samples (10.19%) did not exceed the environmental limit recommended by Federal Comittee of water Quality Criteria (1968).

The remaining 4 (3.70%) of the samples) were found to contain above this limit. On the other hand, as much as 87.9% of the samples examined were found to be free from Aldicarb residues, while only 4.6% of the samples contained above the environmental level (50 ng/liter). Sevin residues could not be detected in any of the water samples in values above 50 ng/liter.

It can be indicated that the variations in the environmental content and limit of insecticide residues, may be due to an excessive use of some compounds than others or the attributed to persistence of certain insecticide residues in different aquatic environments especially chlorinated hydrocarbons.

3. INSECTICIDE RESIDUES INFFLUENT AND EFFLUENT WATER TREATMENT PLANTS

Organochlorine insecticide residues in El-Khandak Canal water which provides Damanhour water treatment plant were detected in inffluent water samples with mean values of 25, 7.5 and 19 ng/liter of D.D.T, Lindane and Chlordane respectively (table 10 and Figure 31). However, Endrin could not be detected neither in influent nor effluent water samples. The above mentioned results are nearly similar to those reported by Weaver, et al. (1965). Croll (1969), Miles and Harris (1973), Brodtman (1976) and Nadia El-Haridy (1983).

The average concentrations of D.D.T, Lindane and Chlordane in effluent water samples of Damanhour water treatment plant were found to be 12.5, 11.5 and 8 ng/liter respectively (table 10). In general, the results obtained in connection with organochlorine residues in water samples after treatment are in agreement with those reported by Schafer, et al. (1969), Bevenue, et al. (1972). Brodtman (1976), Mcneil, et al. (1978) and Micheal (1980).

It is evident from the data illstrated in table (10) that the mean value of Lindane is comparatively higher in effluent (water after treatment) than influent samples (raw water). These results may be attributed to the chemical combination of chlorine used as a disinfectant with organic compounds in water resulting in an elevated level of a variety of chlorinated hydrocarbon compounds (Rook, 1979). On the other hand, the mean values of D.D.T and Chlordane were lower after treatment than in raw water samples which confirm the results reported by Cohen (1960). Chlorine and chlorine dioxide are effective against chlorinated hydrocarbon compounds, but these oxidizing agents carry the disadvantages of long contact times, high residuals and the need for subsequent dechlorination (Cohen, 1960).

The decreasing levels in insecticide residues after treatment may be attributed to coagulation, sedimentation and filteration of water which remove 80-98% of 0.1-10.0 p.p.m of D.D.T (Carollo, 1945).

The data presented in table (10) reveal that drinking water contains concentrations of organochlorine residues below the maximum permissible level recommended by Canadian Drinking Water Standard (1968), Water Quality Criteria (1972) and International Joint Commission (I.J.C) (1977). However, higher concentrations of D.D.T. than the maximum permissible limit were reported by Frank, et al. (1982) in 41% of the water samples examined.

For the maximum protection of human health from the potential effect of exposure to D.D.T, Lindane, Chlordane through drinking water U.S Environmental Protection Agency (1980) reported that the ambient water concentration of the above mentioned insecticides should be zero. However, zero level may not be attainable at the present time therefore, the levels which may result in an incremental increase of cancer risk over the life time for D.D.T was found to be 0.24 ng/liter.

In addition, there are statistical associations between the level of storage of D.D.T. in different tissues and certain types of chronic diseases in man and animals (Casareit, et al., 1968). Therefore, it can be concluded that organochlorine compounds in water are extremely dangerous because owing to their greater chemical stability, low water solubility and high lipophicity, they become concentrated in living components of the ecosystem (Cremlyn, 1979). However, they are much less toxic than organophosphorus compounds but yet still dangerous to domestic and wild livestock because of their persistence and cummulative poisoning effect that should not be neglected (Cox, 1970).

The detection of organophosphorus residues in Damanhour water treatment plant revealed that the mean values of Diazinon in water samples before and after treatment were found to be 26.6 and 19.5 ng/liter respectively (table 10).

It can be noticed that comparatively lower concentrations of Diazinon were detected in drinking water than in surface raw water (El-Khandak Canal) There is no reference from the available literatures dealing with the action of chlorine on Diazinon, while some other organophosphorus insecticides such as Parathion is somewhat altered by chlorine, through the conversion of Parathion by oxidants to Paraoxon, which is more toxic to insects and mammals than the original compound and could not be detected by the utilized instruments. In addition, chlorine was found of no apparent value in reducing its toxicity (Robeck, et al., 1965).

The results obtained from the present investigation (table 10) indicate that drinking water contain through residues below the maximum permissible level (50 ng/liter) recommended by Water Quality Criteria (1972) and International Joint Commission (130 ng/liter).

The high level of organophosphorus insecticides in water have been responsible for more deaths than any other group of compounds. The toxicity in man and animals manifested by nausea, vometing excess sweating, salivation, abdominal pain, diarrhea, flaccid paralysis, pulmonary oedema and convulsions (Moses 1980)

Carbamate insecticide residues could not be detected in all samples of Damanhour water treatment plant neither before nor after treatment. (Table 10).

4. EFFECTIVENESS OF DRINKING WATER FILTER CONTAINING ACTIVATED CARBON IN INSECTICIDAL REMOVAL.

Organic insecticides, along with many other types of synthetic organic chemicals, contribute substantially to the ever-increasing problem of pollution of water supplies. Some of these insecticides, specially the chlorinated hydrocarbon variety, are extremely persistent and being only partially removed by treatment, reaching the consumer and domestic livestock in their drinking water. As little as 1 ug/liter of an insecticide could conceivably has an undesirable effect on health and interferes with water quality (Eichelberger and Lichtenberg, 1971) therefore, these compounds must be removed or at least minimized to the permissible limit in potable water.

The removal percentage of filteration of experimentally contaminated distilled water through activated carbon at a flow rate of one liter per minute is illustrated in table (11). The reduction percentage of D.D.T. was found to be 94% which support the work performed by Carollo (1945), Nichlson, et al. (1966) and Eichelberger and Lichtenberg (1971). On the other hand, removal percentage of Lindane was found to be 95% which are higher than that mentioned by Robeck, et al. (1965) and Hyndshow (1972).

Endrin residues were removed at a percentage of 100% which is nearly similar to that reported by Robeck, et al. (1965), who recorded that 20 p.p.m. of activated carbon were sufficient to remove 94% of Endrin. The reduction percentage of Chlordane was found to be 91% (table 11 and Figure 32).

With respect to organophosphorus insecticides, the removal percentage of Diazinon, Dursban, Malathion and Dimethoate were found to be 80.1%, 85%, 75% and 82% respectively.

A contradictory opinion was given by Eichelberger and Lichtenberg (1971) which may be due to the difference in contact time or concentration of activated carbon.

In connection with carbamate insecticides, the reduction percentage of Lannate, Sevin and Aldicarb were found to be 85%, 82% and 81% respectively.

Generally, the results obtained about the efficiency of activated carbon in the removal of insecticidal compounds of their residues are coincided with those reported by Faust and Aly (1964) who indicated that activated carbon is the most effective method of reducing the levels of most organic insecticides in water supplies.

5. CHEMICAL ANALYSIS

The relationship between the presence of some chemicals and the level of insecticide residues in water sources was studied in the present investigation. It was been found that a parallel relationship between the amount of organic matter and the insecticide residues in water (table 12) which is confirm the results reported by Edwards (1976).

Moreover, a parallel relationship was observed between the chlorides, phosphates and sulphates content of water samples and their insecticide residues (Table 12).

From the statistical analysis a parallel relationship between the nitrate content in water samples and their insecticidal residues (table 12). These relationships confirm the conclusions reported by Cohen, et al. (1984) and Ritter (1986).

CONCLUSION AND RECOMMENDATIONS

The results obtained from the present investigation revealed contamination of both surface and ground water samples with various insecticide residues in different concentrations. The probable sources of insecticidal contamination of water include direct application for control of aquatic insects, runoff from agricultural lands, drift from aerial and land application, discharge of industrial wastes and discharge of waste water from cleaning up of equipments used for insecticidal application.

Although the use of organochlorine insecticides is forbidden in Egypt and world since 1971 however, these compounds were detected in reasonable amounts in natural water supplies which necessitate a particular attention about their distribution and destruction of their residues in nature. Recently, there is a gradual increase in the use of the more readily degradable organophosphate and carbamate insecticides instead of chlorinated hydrocarbons.

From the health point of view, water pollution with insecticide residues is undoubtedly injurious and harmful to human and animal health that requires a particular concern. One of the main tasks of hygiene necessitating the presence of urgent scientific solution of insecticide pollution. The regulation within the fram work of governmental planning, for sanitary protection againest pollution of water sources supplying both human and livestock collections.

It can be concluded that the removal of organic insecticides by chlorination seems to be inefficient, and the use of activated carbon filter appears to be the most effective and safe method for reducing most of the insecticide residues in water supplies.

In the light of the results obtained from the present investigation, the following recommendations can be suggested :

1. A continous monitoring for insecticidal application.
2. A special attention should be paid by authorities and organizations to the point source of water pollution.

This control process requires joint efforts of both water supply and surveillance authorities.

3. It is recommended that when it is necessary to use a specific insecticide for control of aquatic life, complete information must be available so that the risk to water quality from residues can be directly evaluated.

4. The conditions under which residues disappear from water

sources, the efficiency of water treatment, the level of the daily intake and the body accumulation level as well as the permissible limit of insecticide residues in drinking water must be known before its proposal.

5. Using different clarifying designs, different filter media and adjustment of the operational conditions for improving insecticidal removal.

SUMMARY

The importance of synthetic organic insecticides to the national economy and the potential hazards to public health associated with their widespread use for agricultural purposes and veterinary practice as well as other purposes of preventive medicine require an early control of polluted water.

The present study was carried out to evaluate the seasonal levels of insecticide residues in different water sources distributed in Behera Governorate. On hundred and eight water samples were analysed for insecticide residues and the following results were revealed :

I- Surface water

1. ORGANOCHLORINE RESIDUES :

D.D.T. residues in streams and drains ranged from 6.7 to 53.3 ng/liter and higher concentrations were recorded in water samples collected in autumn. Lindane residues of the examined samples varied rom 5 to 58.3 ng/liter, Chlordane residues lies between 4.7 and 60.7 ng/liter and Endrin residues varied from 3.3 to 33 ng/liter. It has been noticed that there were no seasonal variations for lindane, Chlordane and Endrin concentrations.

2. ORGANOPHOSPHORUS RESIDUES

Dursban residues were only detected in surface water samples

collected in autumn varying from 16.7 to 183.3 ng/liter. Diazinon, Malathion and Dimethoate residues could be detected only in autumn and summer. Diazinon residues varied from 4.4 to 186.2 ng/liter, Malathion residues lies between 33.3 to 216.7 ng/liter while Dimethoate residues ranged from 13.3 to 263.3 ng/liter.

3. CARBAMATE RESIDUES

Lannate residues in surface water samples ranged from 16.7 to 66.7 ng/liter. The highest concentrations were met with in water samples collected in summer could not be detected in winter. Sevin could be detected only in autumn and summer with a value ranged from 10 to 46.7 ng/liter. Aldicarb residues were only detected in summer, varying from 16.7 to 36.7 ng/liter.

II- Ground water

1- D.D.T. and Lindane were the only chlorinated hydrocarbon insecticides detected in ground water samples.

D.D.T residues ranged from 3.3 to 66.6 ng/liter. The lowest value was detected in spring rather than other seasons. Lindane residues of examined ground water samples varied from 3.3 to 31.6 ng/liter.

2 ORGANOPHOSPHORUS RESIDUES

Diazinon residues could be detected in ground water samples collected in autumn and summer with values ranged from 8.9 to 146.3 ng/liter while Malathion residues were only detected in summer, varying from 16.7 to 83.3 ng/liter.

3. Aldicarb was the only carbamate insecticides detected in ground water samples.

It could be detected only in summer and autumn where the residues ranged from 96.7 to 283.3 ng/liter with a mean values of 126.7±17.8 and 68.9±7.7 ng/liter in summer and autumn respectively.

III. The effectiveness of water treatment on the insecticidal content was investigated.

It has been found that the mean values of D.D.T, Lindane and Chlordane in inffluent water were 25, 7.5 and 19 ng/liter respectively while in effluent water were 12.5, 11.5 and 8 ng/liter respectively.

Diazinon residues could be detected in raw surface and treated water with a mean of 26.6 and 19.5 ng/liter respectively. Non of the carbamate insecticides could be detected in water samples of Damanhour water treatment plant.

IV- It has been found that drinking water filter containing activated carbon has a high efficiency in removing the insecticide residues from water. The reduction percentage were found to be 94,95,91 and 100% for D.D.T, Lindane, Chlordane and Endrin respectively. In case of organophosphorus insecticides, the removal percentage of Diazinon, Dursban, Malathion and Dimethoate were found to be 80.1, 85, 75 and 82 respectively. Moreover, a reduction of 86,82 and 81% in concentrations of Lannate, Sevin and Aldicarb respectively was detected.

Consequently this filter could be applied with success in minimizing the insecticidal residues in water.

V- It has been found that a significant relationship between the presence of some chemicals and the level of insecticide residues in water.

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الملخص العربى

ان استخدام المبيدات الحشرية على نطاق واسع فى الاغراض الزراعية والاغراض الاخرى فى التطهير والوقاية من بعض الامراض فى مجال الطب البيطرى دون وجود قوانين علمية تحد او تنظم من هذا الاستخدام وخاصة فى مصر قد ادى الى تلوث المياة السطحية والجوفية وكذلك مياه الشرب وحيث ان هذه المبيدات ضارة بالصحة العامة وكذلك صحة الحيوان فمن ثم كان من الضرورى فحص المياة بصفة دورية حتى يمكن تجنب اضرار هذه المبيدات.

ولقد كان من الضرورى اجراء هذه الدراسة لاستبيان مدى تواجد بقايا المبيدات الحشرية خاصة الهيدروكلورنية والفوسفورية والكربماتية فى بعض مصادر المياة السطحية والجوفية بمحافظة البحيرة وكذلك استبيان مدى تاثير معاملات التنقية فى محطة دمنهور لمياة الشرب عن طريق تقدير متبقيات هذه المبيدات قبل وبعد هذه المعاملات وبالاضافة لذلك تحديد مدى تاثير مرشح مياة الشرب المحتوى على الكربون النشط لتقليل او ازالة متبقيات هذه المبيدات من المياة. وقد شملت الدراسة ١٠٨ عينة ٧٢ منها من المياة السطحية و ٣٦ عينة مياة جوفية وقد اخذت هذه العينات على مدار فصول السنة المختلفة. وقد اسفرت الدراسة عن النتائج الاتية:-

اولا: المياة السطحية

أ- المبيدات الحشرية الهيدروكلورينية

١- د.د.ت :

تراوحت بقايا د.د.ت بين ٧ر٦ و ٣ر٥٣ نانو جرام / اللتر وقد لوحظ ارتفاع نسبة المتبقيات فى فصل الخريف.

٢- اللندين :

بالكشف عن بقايا اللندين فى مياة ترعة المحمودية ونهر النيل فرع رشيد والمصارف كان تواجده متراوح بين ٥ و ٣ر٥٨ نانو جرام / لتر.

٣- الكلوردين:

تراوحت نسبته بين ٧ر٤ و ٧ر٦٠ نانوجرام / لتر.

٤- الاندرين :

بالكشف عن هذا المركب فى العينات المختلفة للمياة وجدت بقايا هذا المركب تتراوح مابين ٣ر٣ و ٣٣ نانو جرام /لتر.

ب- المبيدات الحشرية الفوسفورية :

١- الديازينون :

تراوحت نسبته بين ٤ر٤ و ٢ر١٨٦ نانو جرام / لتر. وقد وجدت بقايا هذا المبيد فى فصل الصيف والخريف فقط.

٢- الدورسبان (كلوربيريفوس)

تراوحت نسبته بين ٧ر١٦ و ٣ر١٨٣ نانو جرام / لتر مع تواجده فقط فى فصل الخريف.

٣- ملاثيون :

تراوحت بقايا الملاثيون بين ٣ر٣٣ و ٧ر٢١٦ نانوجرام / لتر وقد لوحظ ان بقايا هذا المبيد لاتوجد الا فى فصل الخريف والصيف.

٤- الدايمثويت :

وجدت بقايا هذا المبيد فى فصل الخريف والصيف بنسبة تراوحت بين ٣ر١٣ و ٣ر٢٦٤ نانو جرام / لتر.

ج - المبيدات الحشرية الكربماتية :

١- لانيت :

بالكشف عن هذا المركب فى المياة السطحية وجدت بقاياه تتراوح مابين ٧ر١٦ و

٦٦ر٧ نانو جرام / لتر وقد وجد اعلى تركيز له فى فصل الصيف.

٢- السيفين :

تراوحت نسبته مابين ١٠ و ٤٦ر٧ نانو جرام / لتر وقد لوحظ ان بقاياه فى المياه السطحية لاتوجد الا فى فصل الخريف والصيف.

٣- التميك (الدكارب)

وجدت بقايا هذا المبيد فى فصل الصيف فقط بنسبة تراوحت بين ١٦ر٧ و ٣٦ر٧ نانو جرام/ لتر.

ثانيا : المياة الجوفية

١- المركبات الهيدروكلورنية :

قد وجدت بقايا مبيد ال د.د.ت واللندين فى المياه الجوفية بنسبة تتراوح بين ٣ر٣ و ٦٦ر٦ للاول و ٣ر٣ و ٣١ر٦ نانو جرام / لتر للثانى ولم يستدل على مركبى الكلوردان والاندرين فى هذه المياة.

٢- المركبات الفوسفورية :

لم يستدل من هذه المركبات الا على بقايا مبيد الديازينون والملاثيون بنسبة تتراوح بين ٨ر٩ و ١٤٦ر٣ و ١٦ر٧ و ٨٣ر٣ نانو جرام / لتر على التوالى. كما لوحظ ايضا ان مركب الديازينون لم يستدل عليه فى فصل الشتاء والربيع. كما ان الملاثيون لايوجد الا فى فصل الصيف فقط.

٣- المركبات الكربماتية :

التمك هو المركب الوحيد من هذه المجموعة الذى وجدت بقاياه فى المياة الجوفية فى فصل الصيف والخريف بنسبة تتراوح مابين ٩٦ر٣ و ٢٨٣ر٣ نانوجرام/ لتر .

ثالثا : مياة الشرب

لدراسة نوعية مياة الشرب فى محطة دمنهور للتنقية ولتحديد مدى تاثير معاملات التنقية المختلفة على بقايا المبيدات الحشرية. قد تم تقدير تركيزات هذه المبيدات فى مدخل ومخرج هذه المحطة وقد اتضح من هذه الدراسة النتائج التالية :-

١- المركبات الهيدروكلورينية :

قد تم التعرف وتقدير بقايا المبيدات الاتية: د.د.ت و اللندين والكلوردان فى المياه عند مدخل المحطة وذلك بتركيزات ٢٥ و ٥ر٧ و ١٩ نانو جرام/ لتر على التوالى وقد قلت نسبة تركيزات د.د.ت فى مخرج المحطة الى ٥ر١٢ وكذلك الكلوردان قل الى 8 بينما قد ارتفع تركيز اللندين حيث وصل تركيزه الى ١١ نانوجرام / لتر وبذلك يتضح كفاءة محطة دمنهور للتنقية فى إزالة متبقيات مبيد د.د.ت بنسبة ٥٠٪ ومبيد الكلوردان بنسبة ٥٨٪ كما يتضح ايضا عدم كفاءتها فى ازالة متبقيات اللندان قد زادت تركيزاتها بنسبة ٥٣٪.

٢- المركبات الفوسفورية :

الديازينون هو المركب الوحيد من مجموعة المركبات الفوسفورية الذى قد تم التعرف عليه وتقدير بقاياه فى مدخل مياة محطة دمنهور للتنقية حيث كان متوسطه ٦ر٢٦ بينما فى مياه الشرب بعد التنقية كانت نسبته ١٩ نانو جرام/ لتر.

٣- المركبات الكربماتية :

لم يستدل على اى مركب منها فى مدخل او مخرج محطة التنقية التى تحت الدراسة.

رابعا :

لتجنب اضرار بقايا هذه المبيدات فى المياه وذلك للمحافظة على صحة الانسان والحيوان قد استخدم مرشح الكربون النشط لتحديد مدى تاثيره لازالة او تقليل نسبة متبقيات هذه المبيدات فى مياة الشرب ولقد استنتجنا من هذه الدراسة ان استعمال مرشح الكربون النشط له اهمية قصوى فى ازالة معظم المبيدات الحشرية حيث وصلت نسبة ازالتها الى ١٠٠٪ و ٩٥٪ و

٩٤٪ و ٩١٪ لمركبات الاندرين واللندين والـ د.د.ت والكلوردان على التوالى بينما فى المركبات الفوسفورية وهى الديازينون والدورسبان والملاثيون والديمثويت وكانت نسبة الازالة ١ر٨٠٪ و ٨٥٪ و ٧٥٪ و٨٢٪ على التوالى اما بالنسبة للمركبات الكربماتية فكانت نسبة الازالة ٨٦٪ و ٨٢٪ و ٨١٪ كمركبات اللانيت والسيفين والالدكارب على التوالى.

من هذه النتائج يتضح كفاءة هذا المرشح فى ازالة متبقيات المبيدات من المياه وبالتالى يجب تطبيقه وتعميمه فى مجال مياه الشرب وذلك للحصول على مياه ذات مواصفات قياسية صحية.

خامسا:

وقد اتضح من التحليل الكيميائى لبعض عينات الماء ان هناك علاقة بين وجود بعض المركبات العضوية ومستوى متبقيات المبيدات فى الماء.

قرار لجنة الحكم والمناقشة

توصي لجنة الحكم والمناقشة بمنح ط.ب/ سامية محمد علي الحوشي درجة الدكتوراة في العلوم الطبية البيطرية (صحة الحيوان) جامعة الاسكندرية

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الأستاذ الدكتور / سمية حموده
وكيل وزارة العدل لشئون المعامل الكيماوية
بمصلحة الطب الشرعى
وزارة العدل

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بمصلحة الطب الشرعى
وزارة العدل

المعدلات الموسمية لتواجد بقايا المبيدات الحشرية فى مصادر المياه بمحافظة البحيرة

رسالة مقدمة من
سامية محمد علي الحوشي
ماجستير فى العلوم الطبية البيطرية
جامعة الاسكندرية

للحصول على
درجة الدكتوراه فى العلوم الطبية البيطرية
صحة الحيوان

إلى
كلية الطب البيطرى
جامعة الاسكندرية

١٩٨٩