

Pesticides and Polychlorinated Biphenyls Drained into North Coast of the Mediterranean Sea, Egypt

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Environmental pollution with pesticides and other organic contaminants initiated the interest for many authors to investigate the level and the fate of these compounds in different environmental compartments. Concerning the aquatic environment, many studies were carried out to monitor the occurrence of different types of pesticides and PCBs in surface water (Maguire and Tkacz 1993; Donald and Syrgiannis 1995; Dua et al. 1996; Galiulin and Bashkin 1996). These studies indicated that the major detected compounds in river and drainage waters were in general: DDE, DDD, DDT, PCBs and trace levels of some of triazine herbicides and organophosphorus insecticides.

Concerning the levels of pesticides in the aquatic environment of Egypt, several studies have been reported on the occurrence of these compounds in different aquatic systems (Abu El-Amayem et al. 1979; Macklad et al. 1990; Badawy et al. 1995; Badawy and Wahaab 1997; Osfor et al. 1998). These results showed that the organic chemicals mainly chlorinated pesticides were detected at appreciable levels.

The purpose of the present study is to monitor pesticides and PCBs (resulting from the agricultural practices and industrial runoff) in water that drained into the Mediterranean north coast of Egypt. This study was conducted in a one year from March 1997 to March 1998.

MATERIALS AND METHODS

Water samples (4 liters each) were collected monthly in triplicates from the mouths of Edku lake at El-Madia, north coast of El-Behera governate, El-Amia drain at El-Tabia, north east coast of Alexandria governate, and El-Umum drain and Maruit lake at El-Mex pump station, north west coast of Alexandria governate (Figure 1). Samples were filtered according to the method of Kimbrough and Litke (1996).

All solvents and other chemicals used in the present study (ethyl acetate, n-hexane, acetone, methanol, acetonitrile, dichloromethane, anhydrous sodium sulfate and florisil) were analytical grade AR (BDH). Analytical standards of pesticides and PCBs: chlorinated pesticides (HCB, lindane, aldrin, dieldrin, endrin, p,p'-DDE, p,p'-DDD and p,p'-DDT), PCBs (aroclor 1254 and aroclor 1260) organophosphorus insecticides

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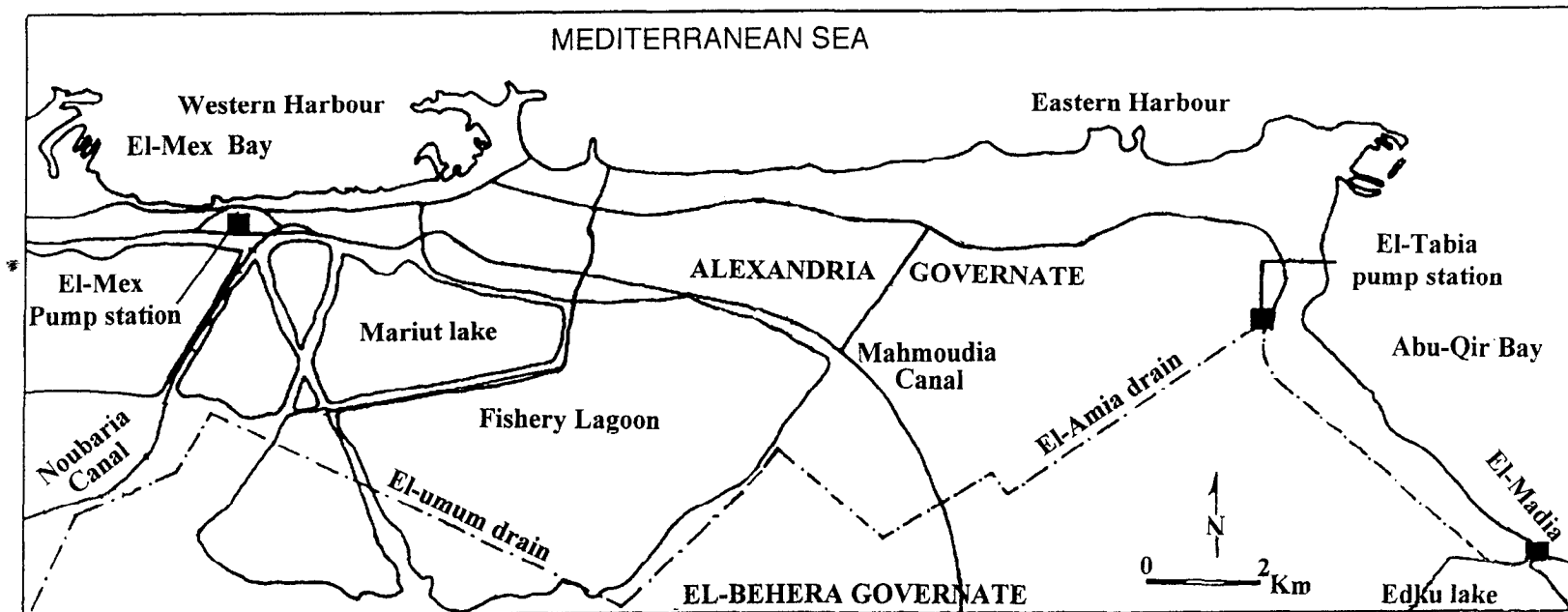


Figure 1. Sampling sites (■) at the outputs of Edku lake at El -Madia, El-Amia drain at El-Tabia, and El-Umum drain and Mariut lake at El-Mex.

(dichlorvos, sulfotep, diazinon, monocrotophos, ethion, methyl-chlorpyrifos, dimethoate, chlorpyrifos, methyl-parathion, fenthion, malathion, fenitrothion, parathion, chlorthion, tetrachlorvinphos, methidathion, leptophos, EPN, azinphos-methyl, azinphos-ethyl, and coumaphos), nitrogen-containing halogenated fungicides (chlorothalonil, vinclozolin, metalaxyl, folpet, captan, and captafol) and triazine herbicides (simazine, prometon, atrazine, propazine, desmetryne, symetryne, ametryne, prometryne, and terbutryne). All these pesticides and PCBs were kindly provided by Dr. J.P. Villeneuve, International Atomic Energy Agency (IAEA), Monaco.

Filtered water sample was extracted by passing it through extraction cartridge of 4.7 cm containing 500 mg of C-18 bonded silica (Interchir BP 1140-03 103 Montlucon, France). The analyte was then eluted from the cartridge by using methylene chloride-acetone (9+1 v/v), acetonitrile and ethyl acetate (10 ml each). The three eluents were combined and concentrated for gas chromatographic analysis or for further cleanup and fractionation procedures (Sherma and Bretschneider 1990; Barcelo et al. 1993; Tolosa et al. 1996). Many of a multiresidue analysis studies were carried out to assess the efficiency of C-18 bonded silica for extraction and isolation of PCBs and chlorinated, organophosphorus, and triazine pesticides from water (Sherma and Bretschneider 1990; Johnson et al. 1991; Tan 1992; Balinova 1993; Tolosa et al. 1996). Average recoveries of the tested pesticides and PCBs obtained were ranged between 76 and 93%. In the present study, the average recoveries from triplicate of one liter of deionized water (pre-extracted with n-hexane) spiked with a 0.1-0.7 µg/l range of the analyzed compounds were ranged from 62 to 94%. Reported concentrations have not been adjusted on the basis of percent recoveries. The method detection limits were ranged between 0.009 to 0.07 µg/l based on the response factor of the detector used to the tested compounds.

Determination of Pesticides and PCBs was performed with gas chromatograph (GC) HP- 5890 fitted with tritium-electron capture detector (³H-ECD) for detection of chlorinated pesticides and PCBs, and nitrogen phosphorus detector (NPD) for detection of organophosphorus insecticides, fungicides and triazine herbicides. Megbore column HP-608 proprietary polysiloxane (30 m X 0.53 mm id X 0.5 µm film thickness) was used. Gas chromatographic conditions applied were: Split/splitless injection (0.8 min. hold) with split ratio 1:60, temperature 220°C and the carrier gas used was helium at a flow rate 2.5 ml/min.. Nitrogen was used as a makeup gas and anode purge for ECD at flow rates 35 and 4 ml/ min., respectively, detector temperature 280° C The initial oven temperature was 80°C (1 min. hold), ramps: 30°C /min. to 170°C (0.0 min. hold), 10°C /min. to 300°C, final temperature 300°C (10 min. hold). For NPD mode: hydrogen, air and helium (makeup gas) flow rates were at 4, 100 and 30 ml/min., respectively, detector temperature 225 °C Initial oven temperature 80 °C (1 min. hold), ramps: 25 °C /min. to 190 °C (0.0 min. hold), 2 °C /min. to 225 °C (0.0 min. hold), 5 °C /min. to 280°C , final temperature 280°C (20 min. hold).

Confirmatory test was carried out by using 2,4,5-trichlorobiphenyl and chlorthion as internal standards added to the water samples for qualitative (relative retention time) and quantitative (recovery percentage) measurements. Also, GC test column; HP-1 cross-linked methyl silicone (5 m X 0.53 mm id X 2.65 μ m film thickness) was used to confirm the detected compounds under the same GC conditions as mentioned before.

RESULTS AND DISCUSSION

The results showed in Figure 2 indicated that pesticides and PCBs; HCB, lindane, p,p'-DDT and its degradates (p,p'-DDD and p,p'-DDE), aroclor 1254 and aroclor 1260 were detected in all water samples collected from the output of Edku lake at El-Madia during the study period. The levels of HCB, lindane, aroclor 1254 and aroclor 1260 were at about 10 fold higher than the levels of p,p'-DDE, p,p'-DDD and p,p'-DDT. The levels of aldrin, dieldrin and endrin were below the detection limits (0.009-0.01 μ g/l) in all samples collected during the study period. Concerning the occurrence of organophosphorus insecticides, fungicides and triazine herbicides; dimethoate was detected in all water samples except those collected during January and February 1998. Malathion was detected in water samples collected from June monthly to November 1997. Triazine herbicides were below the detection limits (0.06-0.07 μ g/l) in water samples collected during the period of this study. Only captan from 6 selected fungicides analyzed was detected in water samples collected from June monthly to October 1997 and was at below the detection limit (0.07 μ g/l) in the other collected samples. In respect of the detection of dimethoate, malathion insecticides and captan fungicide, they might be correlated to the extensive use of these compounds at the vicinity of the study area especially during summer and autumn seasons. On the other hand, the spatial detection of organochlorine compounds referred to their persistence in the environment, therefore, they are reached to drainage water mainly due to the leaching (runoff) processes from sediment to the water body. Also, direct spillage of industrial wastes into drainage system contribute PCBs (Macklad et al. 1990).

Chlorinated compounds; HCB, lindane, p,p'-DDE, p,p'-DDD, p,p'-DDT, aroclor 1254 and aroclor 1260 were detected at the same manner as in water of El-Madia drain in all water samples collected from El-Amia drain at El-Tabia during the study period (Figure 3). Aldrin, dieldrin and endrin were below the detection limits in all collected water samples. The detected levels of aroclor 1254 and aroclor 1260 were higher than those levels in water samples of El-Madia drain. These results are correlated with the urbanization activities (e.g. industrial wastes) of El-Tabia region that contribute the PCBs compared with the El-Madia. From 36 organophosphorus insecticides, fungicides and triazine herbicides analyzed, dimethoate and malathion were detected in water samples of El-Amia drain from March to December and from May to November 1997, respectively. The high levels of both insecticides were detected in August 1997. No fungicides were detected in water samples of El-Amia drain during the study period. Ametryne herbicide was detected at months from August to December 1997, and the highest level (0.076 μ g/l) was detected in September 1997 and the lowest one (0.071 μ g/l) was detected in November 1997. Temporal detection

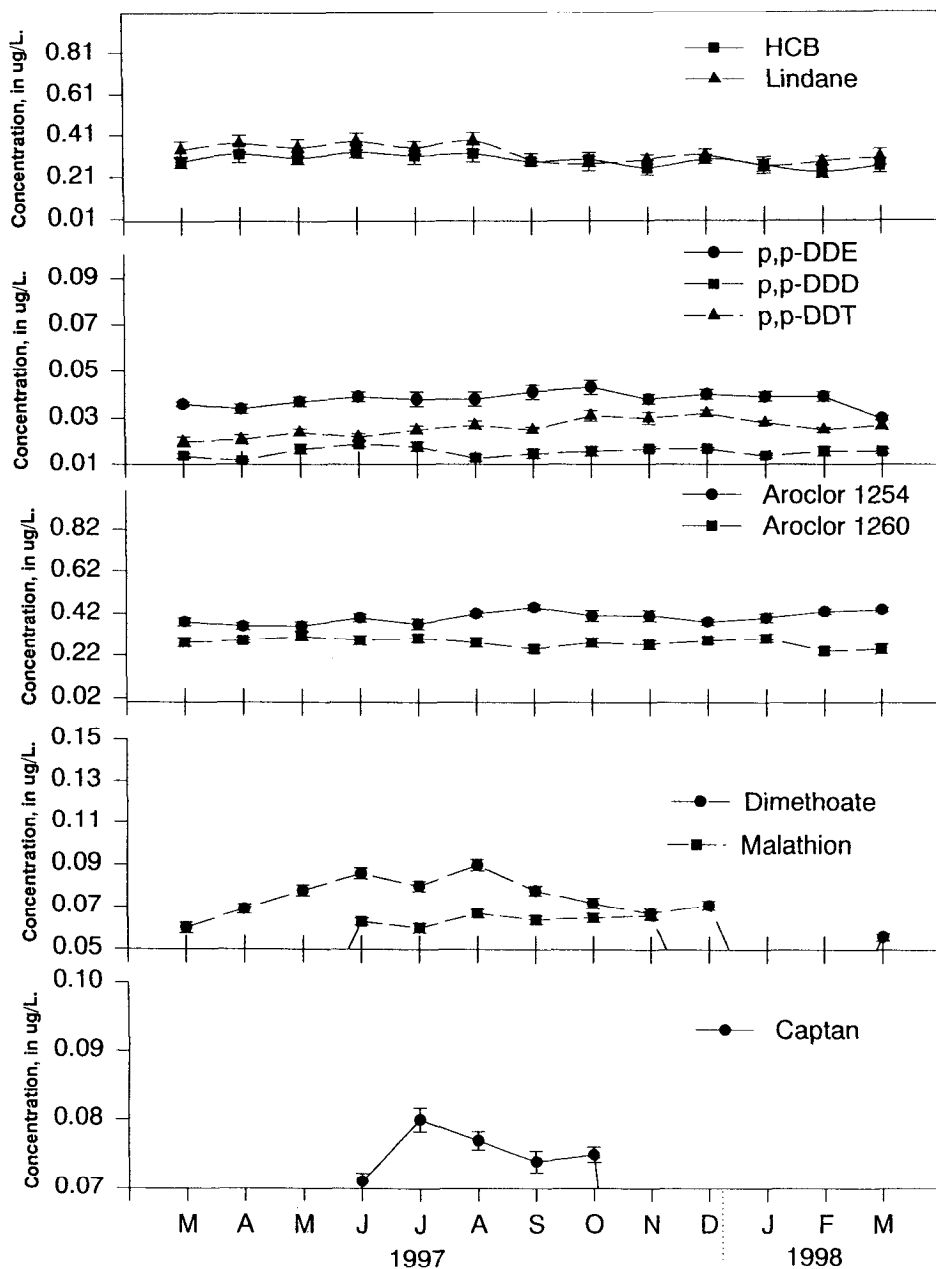


Figure 2. Selected compound data for Edku lake output at El-Madia, March 1997-March 1998. Concentrations below the X-axis are less than the method detection limit

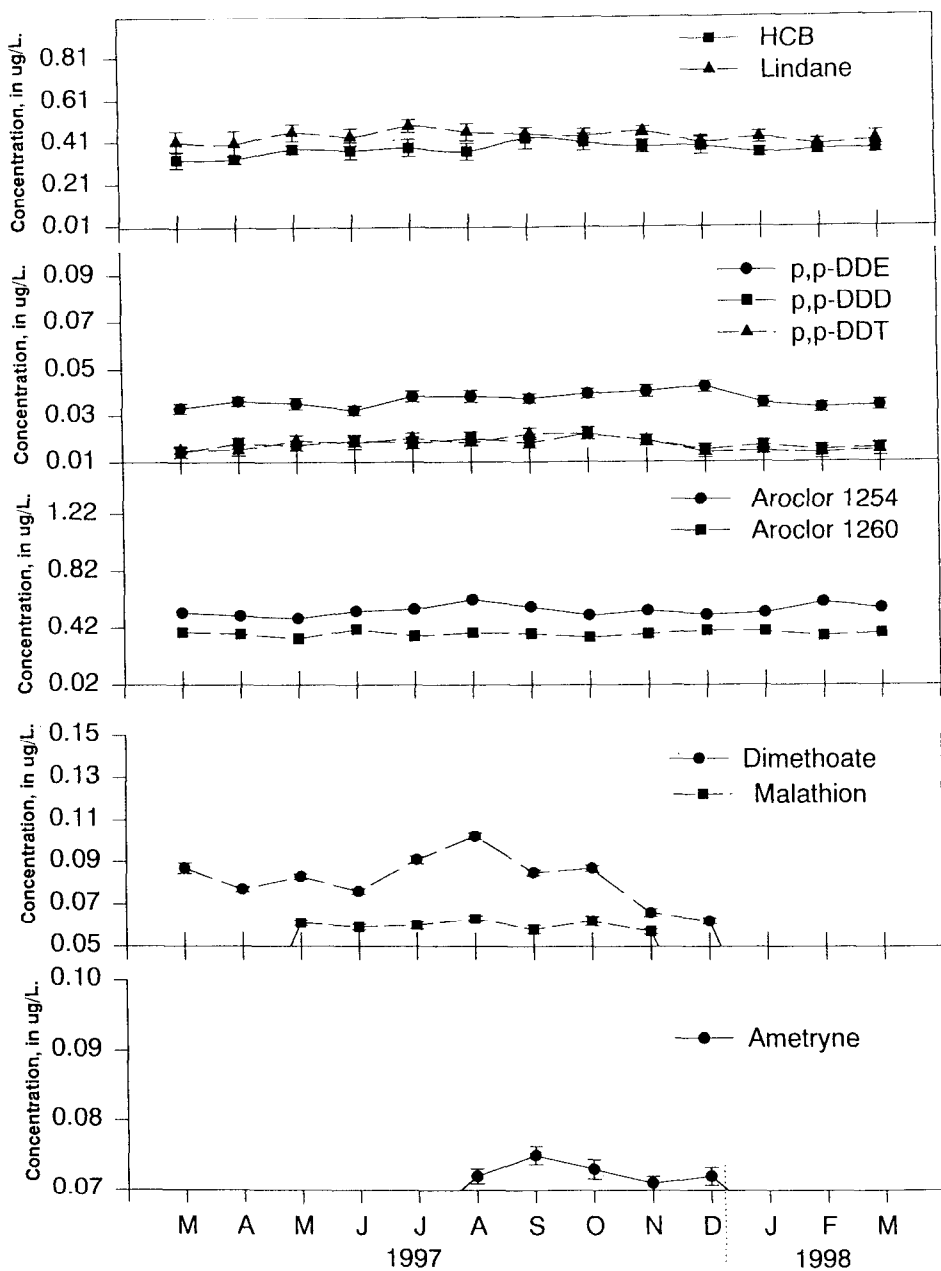


Figure 3. Selected compound data for El-Amia drain at El-Tabia, March 1997-March 1998. Concentrations below the X-axis are less than the method detection limit.

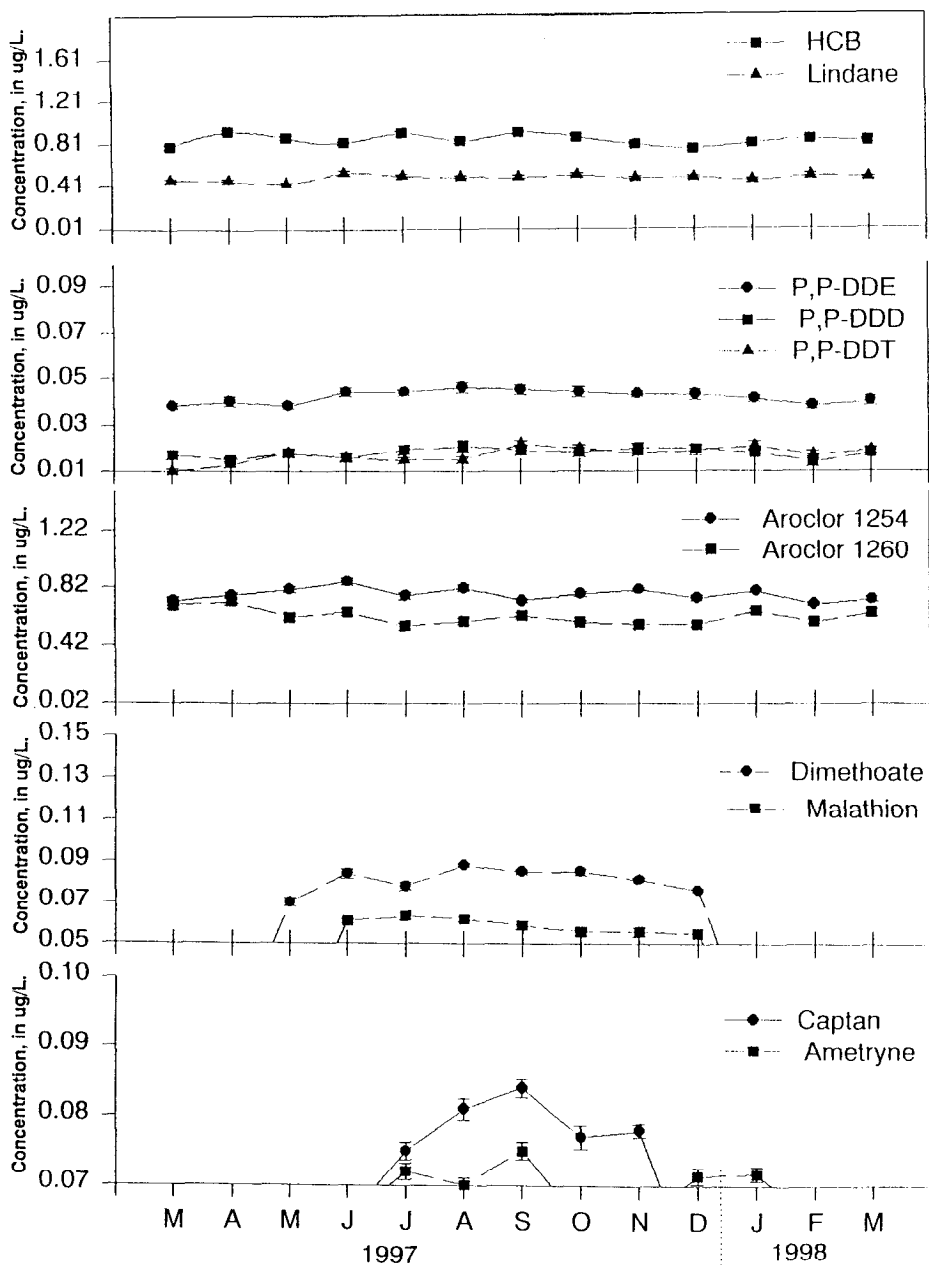


Figure 4. Selected compound data for the output of El-Umum drain and Lake Mariut at El-Mex pump station, March 1997-March 1998. Concentrations below the X-axis are less than the method detection limit.

of capton in water samples of El-Madia and ametryne at El-Tabia region may refer to the variation of the agricultural practices and types of crops between the two regions.

Figure 4 shows that the chlorinated compounds; HCB, lindane, p,p' -DDE, p,p' -DDD, p,p' -DDT, aroclor 1254 and aroclor 1260 were detected in all water samples collected from El-Mex pump station. Aldrin, dieldrin and endrin were not detected in all samples during the period of this study. The levels of detected chlorinated compounds in general, were higher than those levels in samples collected from El-Amia drain at El-Tabia and Edku lake output at El-Madia. These variations might be due to the extensive wastes discharged into the stream of drainage water at Mariut lake and El-Mex region. The detected levels of HCB, lindane, aroclor 1254 and aroclor 1260 were higher than the levels of p,p' -DDE, p,p' -DDD and p,p' -DDT in all samples collected during the study period. From 21 organophosphorus insecticides analyzed, dimethoate and malathion were only detected monthly in water samples collected during the period from May to December and from June to December 1997, respectively. The detected levels of dimethoate were higher than those of malathion. Concerning the detection of fungicides and triazine herbicides in water samples of El-Mex, only captan was detected from July to November 1997, while ametryne was detected in July, August, September, December 1997 and January 1998. Results showed that levels of captan exceeded the levels of ametryne.

In agreement with the present study, it has been previously reported that chlorinated pesticides especially DDT and its degradates; DDD and DDE were still detected in surface water in Egypt inspite of its banning since many years ago because of their persistence against degradation and the result is an accumulation in the environment. On the other hand, organophosphorus insecticides, fungicides and triazine herbicides have rapidly replaced the persistent organochlorines for most pest control purposes. Only four pesticides (dimethaote, malathion, captan and ametryne) from 36 compounds analyzed were detected mainly during summer, autumn and early months of winter. This might be due to application of these pesticides extensively in Egypt during these seasons. Several investigators monitored some of organophosphorus and triazine pesticides beside the predominant detection of organochlorines in river and drainage waters (Kimbrough and Litke 1996; Gotz et al. 1998; Osfor et al. 1998; Abbassy et al. 1999). The levels of pesticide residues detected in these studies were in general ranged from 0.01 to 3.0 µg/l .

It was recommended that more attention need to be focused on contamination of food and water with pesticides and other organic pollutants, and their effect on human health and environment.

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