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SURVEY AND MEASUREMENT OF RESIDUES OF DIELDRIN AND ENDOSULPHAN IN FOUR SPECIES OF FISHES IN CASPIAN SEA, IRAN

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ABSRACT

Pesticides are compounds that used by human being, especially farmers for controlling biotical factors for a long time and bring a lot of environmental problems. Among these compounds clorine insecticide sprays have high half-life, the property of maintaining for a long time and high lipophilicity characteristic. Due to having chronic consequences, it is necessary to evaluate and analysis in environment especially in foods and also in fishes which have high fat and may carry this kind of insecticides. In the present studies we have investigated the residues of chloride organo-insecticides such as Dieldrin and Endosulphan in the four kinds of fishes in the Caspian sea. In this investigation we have selected 4 different kinds of fishes, i.e., sefid - koli- kilca - kafal and 4 different hunting region i.e., Chalous, Babolsar city, Khazarabad and Miankaleh region in 2004. After cleaning, we prepared hun muscle of the fished. Then. after the process of extraction, we distilled them in vacuum by means of organic solvent and determined residues of insecticide by Gas Chromatography(GC) with ECD detector. The results of insecticides analyzed in four kinds of fishes showed that Sefid in the hunting region of Babolsar had an amount of 0.03 ppm. Kilca from Chalousand, Kafal from Babolsar and Khazarabad had the highest amount of Dieldrin (0.017 ppm), Kafal from Khazarabad region with 0.057 ppm had the highest amount of Endosulphan ($P<0.05$).

Key words: Dieldrin, endosulphan, organochlorine residues, Caspian sea, fish

INTRODUCTION

The term organochlorine refers to a wide range of organic chemicals, which contain chlorine and sometimes several other elements. A range of organochlorine compounds have been used in Iran, including herbicides, insecticides, fungicides and industrial chemicals such as polychlorinated biphenyls (PCBs). The compounds are characteristically very stable (Ware, 1986; Shereif and Mancy, 1995). They degrade slowly and being fat-soluble, accumulate in the food chain, eventually ending up in the fat of our bodies. Organochlorine pesticides (OCP) were manufactured for their toxicity, the fact that they were also persistent, had advantages in that they remained effective against target pests for prolonged periods. Chlorinated organic compounds held an important position in pest control in agriculture for a long time, being versatile and very effective against some pests (Ware, 1986; Shereif and Mancy, 1995). Some commonly used OCP insecticides are DDT, lindane, chlordane, dieldrin, aldrin and heptachlor (Shereif and Mancy, 1995; Joan, 2002).

Dieldrin was widely used against locusts and argentine ants; in the protection of electricity and telephone cable; soil treatment in farm and industrial premises for control of termites; and control of termites in buildings, fences and similar structures (Joan, 2002; Smith, 1991). Between 1967 and 1977 both aldrin and dieldrin were used extensively in the production of tobacco crops in Mazandaranm province (Iran). Aldrin was used to control wire worm/black beetle and dieldrin to control grasshoppers. In 1976-77 there were 3600 hectares devoted to tobacco farming in Victoria, of which 3000 hectares could have been regularly treated with aldrin and/or dieldrin. Cattle grazing land that had been used for tobacco growing retained the OCPs, which reached detectable levels in the animals' flesh. So serious was the impact that between 1987 and 1991 a total of 35 herds grazing on ex-tobacco properties were quarantined because of concerns over the levels of organochlorine residues in export cattle (Anonymous, 1990; Kidd and James, 1991; Anonymous, 1995).

Aldrin and dieldrin are common names for two closely related chemicals that have been widely used for controlling soil insects and certain insect vectors of disease. Aldrin, which readily breaks down to dieldrin in living systems, is used to control soil pests (namely termites) on corn and potato crops. Dieldrin is also an insecticide used on fruit, soil and seed, and has been used to control flies and other vectors of tropical diseases. Because the chemicals are intended for use on insects in soil. Aldrin and dieldrin readily bind to sediment and are rarely leached to groundwater. Dieldrin, for example, persists in soils with a half-life of five years (Anonymous, 1990; Vidar *et al*., 1998) at temperate latitudes, while it disappeared up to 90% in one month in tropical areas (WHO, 1989). Both may be volatilised from sediment and redistributed by air currents, contaminating areas far from their sources. (Hall, 1999; Stephanson *et al*., 1995). Another route of transfer appears to be surface run off. (Gudrun *et al.*, 1998).

Aldrin and dieldrin have been banned in most developed countries but, aldrin is still used as termiticide in some others. However, aldrin and dieldrin have also been identified in organisms in Arctic waters and in sediments in the Great Lakes basin, suggesting long range transport from southern agricultural regions. (Stephanson *et al.*, 1995; Gudrun *et al.*, 1998; Hall, 1999). Dieldrin has been isolated in the amniotic fluid in tissues of developing human foetuses, confirming its capacity for placental transfer. The half-life of the residues in humans is approximately nine to twelve months, and the rates of excretion of dieldrin are roughly equal to the average daily intake for most people. (Hall, 1999; Falandysz *et al.*, 1999). Aldrin and dieldrin produce adverse enzymatic and hormonal change in fish that lead to impaired reproductive ability. Aldrin bioconcentrates in molluscs and fish, and high levels of dieldrin have been found concentrated in fish, sculpins, snails, and lake trout. (Kidd, 1991; Anonymous, 1995; Hall, 1999).

Endosulphan is a chlorinated hydrocarbon insecticide and acaricide of the cyclodiene subgroup which acts as a poison to a wide variety of insects and mites on contact. Although it may also be used as a wood preservative, it is used primarily on a wide variety of food crops including tea, coffee, fruits, and vegetables, as well as on rice, cereals, maize, sorghum, or other grains. Formulations of endosulphan include emsulsifiable concentrate, wettable powder, ultra-low volume (ULV) liquid, and smoke tablets. It is compatible with many other pesticides and may be found in formulations with dimethoate, malathion, methomyl, monocrotophos, pirimicarb, triazophos, fenoprop, parathion, petroleum oils, and oxine-copper. It is not compatible with alkaline materials. Technical endosulphan is made up of a mixture of two molecular forms (isomers) of endosulphan, the alpha- and beta-isomers. Information presented in this profile refers to this technical product unless otherwise stated.Endosulphan is highly toxic via the oral route, with reported oral LD50 values ranging from 18 to 160 mg/kg in rats, 7.36 mg/kg in mice, and 77 mg/kg in dogs(Joan, 2002;Smith, 1991; Kidd and James, 1991; Anonymous, 1995). It is also highly toxic via the dermal route, with reported dermal LD50 values in rats ranging from 78 to 359 mg/kg (Joan, 2002; Smith, 1991). Endosulphan may be only slightly toxic via inhalation, with a reported inhalation LC50 of 21 mg/L for 1 hour, and 8.0 mg/L for 4 hours(Shereif and Mancy, 1995). It is reported not to cause skin or eye irritation in animals (Kidd and James, 1991). The alpha-isomer is considered to be more toxic than the beta-isomer (Joan, 2002; Kidd and James, 1991). Animal data indicate that toxicity may also be influenced by species and by level of protein in the diet; rats which have been deprived of protein are nearly twice as susceptible to the toxic effects of endosulphan (Smith, 1991). Solvents and/or emulsifiers used with endosulphan in formulated products may influence its absorption into the system via all routes; technical endosulphan is slowly and incompletely absorbed into the body whereas absorption is more rapid in the presence of alcohols, oils, and emulsifiers (Kidd and James, 1991). Stimulation of the central nervous system is the major characteristic of endosulphan poisoning (Anonymous, 1990). Symptoms noted in acutely exposed humans include those common to the other cyclodienes, e.g., incoordination, imbalance, difficulty breathing, gagging, vomiting, diarrhea, agitation, convulsions, and loss of consciousness (Smith, 1991). Reversible blindness has been documented for cows that grazed in a field sprayed with the compound. The animals completely recovered after a month following the exposure (Smith, 1991). In an accidental exposure, sheep and pigs grazing on a sprayed field suffered a lack of muscle coordination and blindness (Smith, 1991).

Endosulphan is very highly toxic to four fish species and both of the aquatic invertebrates studied; in fish species, the reported 96 h LC50 values were (in µg/l): rainbow trout, 1.5; fathead minnow, 1.4; channel catfish, 1.5; and bluegill sunfish, 1.2. In two aquatic invertebrates, scuds (G. lacustris) and stoneflies (Pteronarcys), the reported 96-h LC50 values were, respectively, 5.8 µg/l and 3.3 µg/l (Anonymous, 1990; Anonymous, 1995). The bioaccumulation for the compound may be significant; in the mussel (*Mytelus edulis*) the compound accumulated to 600 times the ambient water concentration (Anonymous, 1995).

The Caspian sea, the largest inland sea in the world, is bordered by five countries: Iran, Azerbaijan, Turkmenistan, Kazakhstan and Russia. It has no outlets and acts as a reservoir for water in the region . Environmental pollutants found in the sea probably arrive via the Mazandaran and Gillan rivers. Industrial complexes along the coast particularly in Mazandaran and Gillan provinces, in Iran, also discharge waste directly into the Caspian sea (Hall, 1999) .

It is important to note that the use of almost all the chemicals mentioned above are now banned in Australia, and that a nationwide plan is being developed for their overall management (Vidar *et al.*, 1998; Hall, 1999). The aim of .this study was to survey levels of organochlorines (Dieldrin and Endosulphan) in the 4 fish species available from the local market.

MATERIALS AND METHODS

Four commonly consumed fish (Table 1) were purchased from a local fish market in February 2003 *(n* = 10).

All samples were collected from Caspian sea in July and August 2003. Five individuals of each fish were collected from four sites i.e., Chalous and Babolsar city and Khazar Abad and Miankaleh region. Dorsal muscle of the samples were removed and frozen at -20°C and shipped to central laboratory (Sari city) for analysis. concentrations of DDT and DDE, were determined.

Table 1.Four commonly consumed fish in thids study .

Common name	Sciemtific name
Sefid fish	Rutilus frisiKutum
Koli fish	Clupeonella delicatula
Kafal fish	Mugil auratns
Kilca fish	Vimba vimba

Sample preparation and analysis

The sample preparation and analysis protocols followed by Vidar and Anuschka (1998). Approximately 5 g of dorsal muscle from samples fish was thawed and homogenised with 60 g of anhydrous sodium sulphate in a mortar until a free-flowing powder was obtained. The sample was extracted with 225 ml of 1: 1 methylene chloride/hexane. Extracted sample was injected to Gas chromatography in electron capture detector (ECD). The OC levels (DDT and DDE) were measured using the internal standard method in conjunction with the corresponding external standards using selected ion monitoring mode(Vida *et al*., 1998; Hall, 1999; Falandysz *et al.*, 1999; Joan and Grimalt, 2002).

RESULT AND DISCUSSION

The Amounts of Dieldrin and Endosulphan contents in all samples of four examined fishes such as Sefid, Kafal, Kilca and Koli of Caspian sea were measured and showed in Table 2. Dieldrin contents were found in the order of Sefid (Babolsar , 0.021 ppm) > Kafal (Babolsar and Khazar abade , 0.017) = Kilca (Chalus , 0.017) > Koli (Chalus and Babolsar , 0.013). Endosulphan residues regarding Sefid fish samples had maximum amounts (0.035 ppm) in Khazarabad Region. In Chalus Region, Koli fish had the greatest quantity of Endosulphan (0.029 ppm). The samples of Kafal fish in Khazarabad showed higher amounts of this Poison (0.037 ppm) and Kilca samples, had the maximum quantities of Endosulphan in Chalus fishery region.

Table **2.** The average quantities of of Dielrin and Endosulphan contents (ppm) in four species of fishes in Caspian sea.

Region	Kind of fish	Mean of Dieldrin (ppm)	Mean Endo sulphan (ppm)
Chalus	Sefid	0.015	0.028
	Koli	0.013	0.025
	Kafal	0.014	0.022
	Kilca	0.017	0.029
Babolsar	Sefid	0.021	0.024
	Koli	0.013	0.020
	Kafal	0.017	0.027
	Kilca	0.013	0.023
Khazar abad	Sefid	0.013	0.035
	Koli	0.013	0.022
	Kafal	0.017	0.037
	Kilca	0.012	0.023
MianKaleh	Sefid	0.070	0.020
	Koli	0.012	0.024
	Kafal	0.011	0.030
	Kilca	0.011	0.019

Statistical analysis (one–way ANOVA), indicatad a significant difference regarding Dieldrin ($P< 0.05$) and Endosulphan ($P< 0.05$) among fishery sites. Other study in North Atlantic indicated that means of DDT (0.002 ppm), DDE(0.002 ppm), Dieldrin (0.006 ppm) and Endosulphan (0.007 ppm) in liver samples (in Shirbit fish), that these levels were lower than quantities proposed by WHO (0.05 ppm) (Shailaja and Nair, 1997; Juhler *et al.*, 1999; Joan and Gilmralt, 2002). Quantities of DDT and DDE in Caspian sea (Table 2.) was lower than WHO standard levels (0.05ppm), but in comparison to all regions and other poisons, presented higher quantities for great use by farmers in

Northern Province in Iran (Southern coasts of Caspian sea) and great distribution by agriculture center in Mazandaran among Farmers (Morion, 1989; Dogheim *et al.,* 1996; Chan *et al.*, 1996)

There is evidence that the population of seals in the Caspian Sea is declining and fertility rates are decreasing due to residual effect of pesticides. Further studies on contaminants in live animals and biomarker responses that may indicate reproductive interference are needed before we can conclude that the high levels of Dieldrin and Endosulphan insecticides in this population are lexicologically important (Wolf *et al.,* 1984; Morion, 1986; Muir *et al.*, 1990; Vida and Anuschka, 1998). The results revealed that the presence of poisonous residues in most consumed fishes is very serious and important. Since researches in the case of Caspian sea fishes are scanty, there is a need for an extensive survey in Caspian sea (Mazandaran Province) and Southern Coasts of Caspian sea (Shailaja and Nair, 1997; Juhler *et al.*, 1999).

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