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Determination of Residues of Triclopyr in Fishes of Caspian Sea (Iran)

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In this paper, the remains of chloride organochlorine insecticide sprays such as triclopyr(2,4,5-T), in the four the most consumed kinds of fishes found in Caspian sea were investigated. Four different kinds of fishes (Sefid, Koli, Kilca and Kafal fish) were selected. 100 Samples of fishes were collected from four different hunting regions (Chalous, Babolsar city, Khazar Abad and Miankaleh) in 2004. After cleaning, Hun muscle of the samples were prepared, then after the process of extraction, the fishes were distilled in vacuum by means of organic solvent. The results of insecticides analyzed in four kinds of fishes showed that Kafal in the hunting region of Khazar Abad had greatest amount of 0.037 ppm. Kilca from Chalous had the highest amount of triclopyr(2,4,5-T), 0.029 ppm ($p < 0.05$). In case of Sefid and Koli fishes, significant difference was not seen. It is nesserary to mention that no research has so far been done to be a criterion for comparison in this area, But, fortunately the amounts of the insecticide sprays has not reached to standard level in fishes and it raises the alarm health.

Key Words: Triclopyr(2,4,5-T), Organochlorine pesticides, 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). These compounds are characteristically very stable[1-3].

This characteristic is widely recognized as being a problem in some uses such as pesticides and transformer oils, because the chemicals can be distributed in the environment especially river and sea where they persist long after their original use. They degrade slowly and being fat-soluble, accumulate in the food chain, eventually ending up in the fat of our bodies[4,5].

Key properties of organochlorines, which cause concerns, are persistence and toxicity. While organochlorine pesticides 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. Therefore, the chlorinated organic compounds held an important position in pest control in agriculture for a long time, being versatile and against some pests very effective[1,2,6].

Triclopyr, a chlorinated pyridine, is a selective systemic herbicide used for control of woody and broadleaf plants along rights-of-way in forests, on industrial lands and on grasslands[6]. Unlike a similar product 2,4,5-T, which has been banned in United States, there is no possibility of dioxin impurities occurring in triclopyr. Some or all applications of the product access may be classified as restricted use pesticides (RUP).

The product will either have a Danger or Caution signal word on the label depending on the specific formulation. Products marked Danger include Garlon 3A, Redeem, Turflon Amine. The oral LD_{50} of triclopyr in rats ranges from 630 to 729 mg/kg and from 2,000 to 3,000 mg/kg for various formulated products. Similar differences were noted for skin toxicity in the rabbit The LD_{50} for the technical material was greater than 2,000 mg/kg and greater than 4,000 mg/kg for the formulations. Inhalation of triclopyr (technical) did not affect rats but inhalation of some of the formulations did cause nasal irritations. Other oral LD_{50} values for triclopyr are 550 mg/kg in the rabbit and 310 mg/kg in the guinea pig[7].

Triclopyr was found in higher quantities in the liver and fatty tissue of the rat when compared to the blood plasma. The dog had higher levels in the kidney than in the blood plasma and in monkeys, residues in all tissues were the same as in blood plasma[8,9]. The compound is not expected to concentrate to any significant degree in the tissues of animals.

The compound is practically non-toxic to fish. Triclopyr has a LC_{50} of 117 ppm for rainbow trout and a 96 h LC_{50} of 148 ppm for bluegill sunfish. The compound is practically non-toxic to the aquatic invertebrate *Daphnia magna*, a water flea (LC_{50} for the triclopyr salt of 1170 ppm). The compound is non-toxic to bees[9-11].

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* 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.

It is important to note that the use of almost all the chemicals mentioned above is now banned in Iran and that a nationwide plan is being developed for their overall management[9,10].

The goal of this study was to survey levels of organochlorines (triclopyr) in the four species of the most consumed fishes that have been hunted from four central fishery locations in order to estimate the potential of human exposure[11-13].

EXPERIMENTAL

Four commonly consumed fish (Sefid = *Rutilus frisikutum*, Koli = *Clupeonella delicatula*, Kafal = *Mugila auratus* and Kilka = *Vimba vimba*) were selected to analysis.

All samples were collected from Caspian sea in July and August 2004. 100 Individuals of each fish were collected from four sites (Chalous and Babolsar city and Khazar Abad and Miankaleh region). Dorsal muscle of the samples were removed and frozen at -20 ºC and shipped to central laboratory (Sari city) for analysis and finally concentration of residues of Triclopyr(2,4,5-T), were determined.

Sample preparation and analysis: The sample preparation and analysis protocols are similar to those described previously[14]. Dorsal muscle (*ca.* 5 g) from samples fish was thawed and homogenized 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). OC levels (triclopyr) were measured using the internal standard method in conjunction with the corresponding external standards using selected ion monitoring mode[8,13-16].

RESULTS AND DISCUSSION

The amounts of triclopyr(2,4,5-T) contents in all samples of four examined fishes (Sefid, Kafal, Kilca and Koli) of Caspian sea were measured and represented in Table-1.

According to Table-1, residues of triclopyr(2,4,5-T) in Kafal fish samples had maximum amounts (0.037 ppm) in Khazar Abad region. In Chalus region, Kilca fish presented the greatest quantity of triclopyr(2,4,5-T) (0.029 ppm). In the case of Sefid and Koli fishes significant difference was not seen.

Statistical analysis (One-way ANOVA), indicated a significant difference regarding triclopyr(2,4,5-T) ($p < 0.05$, Sig 0.082) among fishery sites.

The results presented that of poisonous residues is very serious and important and since researches in the case of Caspian sea fishes is very little, to compare with this study, then, there is a requirement to complete survey in Caspian sea (Mazandaran Province) and Southern coasts of Caspian sea[17,18].

Other study in North Atlantic indicated that means of DDT (0.002 ppm), lindane (0.002 ppm), dieldrin (0.006 ppm) and endosulphan (0.007 ppm) in liver samples (in Shirbit fish), that these levels ware lower than quantities proposed by WHO (0.05 ppm)[16,17].

TABLE-1
AVERAGE QUANTITIES OF TRICLOPYR(2,4,5-T) CONTENTS (ppm)
IN FOUR SPECIES OF FISHES UNDER STUDY IN THE CASPIAN SEA

Region	Kind of fish	Mean of triclopyr(2,4,5-T) (ppm)
Chalus	Sefid	0.024
	Koli	0.029
	Kafal	0.025
	Kilca	0.018
Babolsar	Sefid	0.031
	Koli	0.015
	Kafal	0.018
	Kilca	0.018
Khazar abad	Sefid	0.030
	Koli	0.023
	Kafal	0.031
	Kilca	0.022
MianKaleh	Sefid	0.027
	Koli	0.023
	Kafal	0.022
	Kilca	0.026

Quantities of triclopyr(2,4,5-T) in Caspian sea (Table-1) was lower than WHO standard levels (0.05 ppm). 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[18].

There is evidence that the population of seals in the Caspian sea is declining and fertility rates are decreasing. 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 triclopyr(2,4,5-T) insecticides in this population are lexicologically important[19].

Additionally, chemical analysis has demonstrated the presence of highly toxic contaminants such as the triclopyr(2,4,5-T). No long-term monitoring data exist for these compounds, which may affect fish and wildlife at extremely low concentrations[19]. New approaches and technologies, capable of detecting chemical exposure and its effects at all levels of biological organization, will be required to monitor and assess highly toxic chemicals and those that do not accumulate in fish and wildlife before concentrations reach harmful levels[19].

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