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The Study and Measurement of Residues of Heptachlor (Organochlorine Pesticides) in the Four Fish Species in Caspian Sea

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Abstract: This study investigated the chloride oregano insecticide sprays such as heptachlor in the four of the most consumed kinds of fishes in the Caspian Sea. This investigation prepared four different kinds of fishes, which arc highly used and available in the Caspian Sea (Sefid, Koli, Kilca and Kafal fish) that we selected 100 samples of fish from the four different hunting region (Chalous and Babolsar city and Khazar Abad and Miankaleh regions) in 2004. After cleaning, we prepared Hun muscle of the samples, then after the process of extraction, we distilled them in vacuum by means of organic solvent and at last we evaluated the remaining and reported based on ppm by Gas Chromatography (GC) with ECD detector. The results of insecticides analyzed in four kinds of fishes and showed that Kafal in the hunting region of Khazar abad had greatest amount of 0.037 ppm. Kilca from Miankaleh had the highest amount of heptachlor, 0.026 ppm ($p<0.05$) in the case of Sefid and Koli fishes in regions, significant difference was not seen. It is necessary to mention that no research has sofar 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: Heptachlor, 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) and These compounds are characteristically very stable[1-3].

This characteristic (stability) is widely recognised 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].

Heptachlor is an organochlorine (cyclodiene) insecticide which was first isolated from technical chlordane in 1946. During the 1960s and 1970s, it was used primarily by farmers to kill insects in seed grains and on crops, as well as by exterminators and home owners to kill termites[1]. Before heptachlor was banned, formulations available included dusts, wettable powders, emulsifiable concentrates and oil solutions. It acts as a non-systemic stomach and contact insecticide[2,7].

Heptachlor is highly toxic to humans and can be absorbed through the skin, lungs and gastrointestinal tract. It causes hyperexcitation of the central nervous system and damage to the liver. Poisoning symptoms observed in laboratory animals include lethargy, incoordination, tremors, convulsions, stomach cramps or pain and coma. In humans exposed to chlordane, a closely related organochlorine insecticide which usually contains 10% heptachlor, signs of neurotoxicity such as irritability, salivation, lethargy, dizziness, labored respiration, muscle tremors and convulsions have been observed. In severe cases, death may occur due to respiratory failure. Persons with convulsive disorders or liver damage are at increased risk from exposure[8].

Heptachlor appears to be fairly low in toxicity to birds such as mallards[4]. It decreases the survivability of chicken eggs[9].

Heptachlor is toxic to freshwater fish and aquatic invertebrates (like snails, worms, crayfish, etc.). Both heptachlor and heptachlor epoxide have been shown to

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bioconcentrate in aquatic organisms, especially fish and mollusks[1,7].

Heptachlor has been found in the fat of fish and birds. They have also been found in the liver, brain, muscle and eggs of birds. Heptachlor, like all organochlorines, has a strong tendency to bioaccumulate. Fish, insects, plankton and algae accumulate heptachlor. It has been found in several fish and other aquatic species at concentrations of 200 to 37, 000 times the concentration of heptachlor in the surrounding waters[10].

Fish get PCBs in their bodies from living in contaminated water or near contaminated sediment and by eating contaminated food. PCBs are a group of more than 200 similar man made chemicals that were used widely in electrical equipment like capacitors and transformers. More than 1 billion pounds of PCBs were manufactured in the United States Because of the health effects associated with exposure, commercial production of PCBs ended in 1977. In 1979, the US Environmental Protection Agency (USEPA) banned all use of PCBs.

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[7].

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[9,11].

The goal of this study was to survey the levels of organochlorines (Heptachlor) 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[8,12,13].

MATERIALS AND METHODS

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

All samples were collected from Caspian Sea in July and August 2004. One hundred 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°C and shipped to central laboratory (Sari city) for analysis and finally concentration of residues of heptachlor, were determined.

The sample preparation and analysis protocols are similar to those described in Vidar and Anuschka, 1998. Briefly, 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). OC levels (Heptachlor) were measured using the internal standard method in conjunction with the corresponding external standards using selected ion monitoring mode[8, 13-15].

RESULTS AND DISCUSSION

According to Table 1, residues of heptachlor in Kafal fish samples had maximum amounts (0.031 ppm) in Khazar abad Region. In Miankaleh Region, Kilca fish presented the greatest quantity of heptachlor (0.026 ppm). In the case of Sefid and Koli fishes significant difference was not seen.

Statistical analysis (One-way ANOVA), indicatad a significant difference regarding heptachlor ($p < 0.05$, sig. 0.082) among fishery sites.

The results presented that difficulty 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[9,10].

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)[6].

Quantities of heptachlor in Caspian Sea was lower than WHO standard levels (0.05 ppm) Table 1. 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[7,8].

There is evidence that the population of seals in the Caspian Sea is declining and fertility rates are decreasing.

Table 1: The average quantities of heptachlor levels (ppm) in four species of fishes in the Caspian Sea

	Regions			
	Miankaleh	Khazar Abad	Babolsar	Chalus
Kilka	0.026	0.022	0.018	0.018
Kafal	0.022	0.031	0.018	0.025
Koli	0.023	0.023	0.015	0.029
Sefid	0.027	0.030	0.031	0.024

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 heptachlor insecticides in this population are lexicologically important[9-13].

When properly prepared, fish provide a diet high in protein and low in saturated fats. Many doctors suggest that eating a half pound of fish each week is helpful in preventing heart disease. Almost any kind fish may have health benefits when it replaces a high-fat source of protein in the diet.

Steps can be taken to reduce risks from eating contaminated fish. The fat of the fish is where most of the contaminants, except mercury, are stored. Size does matter. As fish grow older, they tend to develop a higher overall body fat content. By choosing to eat smaller fish, exposure to contaminants is reduced. Smaller fish have less fat and have retained fewer contaminants. By following the cooking and cleaning advice in the advisory, exposure to contaminants in fish will be reduced.

Laboratory tests in animals have shown that long-term exposure to high doses of some PCBs and chlordane cause adverse health effects including cancer, liver damage, reproductive damage and developmental damage. Health effects associated with long-term mercury exposure may include damage to the brain, kidney, lungs and the developing fetus.

Heptachlor is almost insoluble in water and is therefore unlikely to contaminate groundwater. In sunlit water, it will remain active for about 1 day, otherwise it may last from 2-10 days[8,14]. After one week, 75% of the heptachlor entering the Little Miami River in Ohio disappeared. After 2 weeks, the heptachlor was 100% degraded. Chemical hydrolysis is expected to be the main fate of heptachlor in water, with half-lives of 233.1 h in buffered water and 4.48 days at pH 7 in 99:1 water: ethanol. After hydrolysis, volatilization, adsorption to sediments and photodegradation may be significant routes for disappearance of heptachlor from aquatic environments.

Additionally, chemical analysis has demonstrated the presence of highly toxic contaminants such as the heptachlor. No long-term monitoring data exist for these compounds, which may affect fish and wildlife at extremely low concentrations[10-15]. 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[10-16].

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