# PRESENCE OF ORGANOCHLORINE PESTICIDES IN HAKE FILLETS

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## ZASTUPLJENOST OGANOHLORNIH PESTICIDA U FILETIMA OSLIĆA

*Apstrakt*

Organohlorni pesticidi (OCP) su grupa jedinjenja široko zastupljena u prirodi a samim tim i u hrani koju konzumiramo. Da bismo za proizvod rekli da je bezbedan za upotrebu neophodno je da sadržaj OCP-a u njemu bude manji od maksimalno dozvoljenih vrednosti koje su propisane važećim Pravilnikom. Identifikacija ove grupe jedinjenja se vrši gasnom hromatografijom sa masenim detektorom. Priprema uzoraka za analizu sa brzom QuECHERS metodom obezbeđuje da za kratko vreme, pouzdano ekstrahujemo analite od interesa. U našoj studiji ispitivali smo sadžaj 19 organohlornih pesticida u filetima oslića, ribljem proizvodu popularnom u našoj zemlji. Ispitivanja su pokazala da se koncentracija OCP-ova u ovim proizvodima nalazi znatno ispod maksimalno dozvoljenih koncentracija. Organohlorni pesticidi se akumuliraju u hrani i okruženju što izaziva zabrinutost zbog potencijalnih rizika po ljudsko zdravlje kao i zbog narušavanja ekološke ravnoteže (Kartalovic et al, 2015). U predhodnim decenijama organohlorni pesticidi su se koristili širom sveta kako bi unapredili poljoprivrednu proizvodnju. Globalna upotreba ove grupe jedinjenja je od 1950. godine dovela je do povećanja njihove potrošnje i do pedeset puta, paralelno sa rastom stanovništva (Nath, 2013). U našoj studiji ispitivali smo slučajno izabrane uzorke iz marketa. Uzorci su do ispitivanja čuvani u orginalnom pakovanju u skladu sa preporukom proizvođača. Na osnovu ispitivanja 18 uzoraka zaključeno je da je sadržaj organohlornih pesticida znatno niži od maksimalno dozvoljenih koncentracija u ribi, koje su propisane važećim Pravilnikom Republike Srbije. Opseg koncentracija OCP-a se kretao od 0.0065-0.0097 mg/kg.

Generalno, svi pesticidi su toksične supstance dizajnirane da ubiju štetočine sa svojim otrovnim ili štetnim efektima. Direktno ili indirektno pesticidi mogu ući u ljudsko telo kroz lanac ishrane i konačno, mogu prouzrokovati različite efekte na ljudsko zdravlje, poput alergijskih reakcija uključujući i sterilitet i kancer. Zagađivanje hrane sa ovim supstancama se smatra jednim od najopasnijih aspekata u poslednjih nekoliko godina. Riba i riblji proizvodi mogu biti kontaminirani sa hloriovanim ostacima kroz različite izvore. Ovi kvaliteti ih čine najopasnijom grupom hemikalija kojima prirodni sistemi mogu biti izloženi i funkcionišu kao hemijski indikatori antropogenog pritiska i zagađenja (Baiarri i dr., 2001; Storelli et al.,2004). Zbog činjenice da su OCP ipak prisutni u ovim proizodima neophodno je iste izloziti stalnom monitoringu s ciljem obezbeđivanja plasmana samo bezbednih proizvoda na naše trzište.

*Ključne reci: fileti oslica, organohlorni pesticidi, gasna hromatografija*
*Keywords: hake fillets, organochlorine pesticides, gas mass chromatography*

## INTRODUCTION

Due to accumulation of residues in food and in the environment, the concern was raised regarding potential risks to human health and also because of potential harm to the ecological balance (Kartalović et al, 2015). In previous decades, organochlorine pesticides have been used around the world with the aim to improve the agricultural production. However, global usage of these chemicals since 1950 increased their use 50 times, in parallel with the growth of the human population (Nath, 2013). The main sources of OCPs are food and soil contaminated by them (Snelson, 1979, Valiszevski 1997). Organochlorine pesticides are chemical substances and they contain a lot of combined chlorine and carbon atoms. They can be classified into three general groups: dichlorodipheniletans (DDT, DDD, dicofol, etc.), chlorinated ciclodines (Aldrin, dieldrin, heptachlor, etc.), hekachlorociclohekanes (lindane). These compounds differ considerably between and within the group in terms of the toxic dose, the skin absorption, fat storage, metabolism and elimination. Signs and symptoms of toxicity in humans however, are very similar except for DDT (Abdel-Wahab, 2004). OCP were widely used throughout the world, until the restrictions on their usage were imposed in the late seventies, both in Europe and in the United States, initially only for DDT (Fontcuberta, 2008). Generally, all pesticides are toxic substances designed to kill pests with its poisonous or harmful effects. Directly or indirectly pesticides can enter human body through the food chain and eventually, cause a variety of effects on human health, such as allergic reactions to deadly effects, even including sterility and cancer. Contamination of food with these substances is considered as one of the most dangerous aspects in recent years. Fish and fish products may be contaminated with chlorinated remnants through various sources. Organochlorine pesticides persist and tend to bioaccumulate in the environment. These qualities make them the most dangerous group of chemicals to which natural systems can be exposed and function as chemical indicators of anthropogenic pressure and pollution (Bayarri et al., 2001; Storelli et al., 2004). Analysis of organochlorine compounds are carried out because of their potential health hazardous effect on humans. In this study, hake fillets were monitored using GCMS, for 19 organochlorine pesticides to determine the degree of contamination with them.

## MATERIAL AND METHODS

Samples were collected from local markets and shops in region of Vojvodina during the period from 1 January to 1 May 2015. In this study we have collected 20 samples of hake fillets in original packing. All samples were stored in room temperature before analysis in accordance with declaration. All chemicals and reagents used were of analytical grade with high purity. The OCP stock standard solution (1000 μg/ml of 20 organochorine congeners) was diluted in n-hexaneto yield spiking solutions 0.005 to 0.5 μg/ml. The spiking solution was used to prepare the calibration curves in the matrix blank extract by appropriate dilutions. First of all, portion of the samples were homogenized. For extraction we took 3g of homogenized sample portion and added 3ml of water and 6ml of ACN. then we added 3g MgSO4 and 1g sodium acetate in the tube of 50ml and mixed it well. The tube was then centrifuged on 4000 rpm for the period 10 min. After that, we took 1 ml of aliquot and transferred it in tube of 5 ml which contained 150 mg MgSO4, 50 mg PSA, 50 mg C18, and vortexed it for 1 minute. The dSPE tube was then centrifuged on 4000 rpm for period of 5 min. Finally, the liquid from the tube, was traversed to a GC vial and analyzed by SIM GCMS. The identification of OCP was based on comparison of the retention times of the peaks and target ions, with those obtained from standard mixture of OCP (standards supplied by instrument manufacturer). Quantification was based on external calibrations curves prepared from the standard solution of each of the pesticides congener. The coefficients of determination (r2) for the OCP standard calibration plots were in the range of 0.99675 to 0.99982. The gas - mass chromatography was Agilent 7890B/5977A MSD, with fused silica column [30m*0.25μmfilmof HP-5M (thickness)]; injection temperature was set at 280 °C using splitless mode and volume injected was 4 μL.

## RESULTS AND DISCUSSION

Humans take up POPs through skin absorption, respiration and ingestion of contaminated food. Skin absorption and respiration are not the main route. Some researchers have confirmed that more than 90% of contaminants come from food (Furst, Furst, & Groebel, 1990). In our study we shows that hake filet have OCP in concentration less than MDK. OCP range of 20 investigated fillets was in range of 0.0065-0.0097 mg/kg.

Among all foods, fish is one of the main sources of contaminants although fish products account only for about 10% of diet (Alcock, Behnisch, Jones, & Hagenmaier, 1998; Harrisonet al., 1998) or less. POPs in fish from some areas were detected to assess the risk for human health (Binelli &Provini, 2004; Jiang et al., 2005; Yang, Matsuda, Kawano, & Wakimoto, 2006). With the banning of massive usage and production of the compounds, the residual levels in foodstuffs have decreased significantly (Xuemei Li, 2008). Toxic effects of pesticides vary in different organs of the fish. Liver, gill, kidney are tissues that can accumulate high level of pollutants as well as other factors, such as salinity temperature, hardness, etc (Mukesh Kumar Napit, 2013). The earliest study was done by Lincer et al., (1981) on the lake Naivasha he reported undetectable to very low levels of DDE in fish from Lake Naivasha in a study conducted to investigate organochlorine pesticide residue levels in Kenya’s rift valley lakes. A predatory fish from Lake Baringo showed the highest level 2.13mg/kg of DDE in the study. Forty fish samples were analyzed from Lake Naivasha and no individual sample had detectable levels of pesticide residues. A composite fillet sample of 10 fish had α -HCH at a concentration of 0.014mg/kg. The single value compares very well with the concentrations in the present study where the mean concentration of α -HCH was 0.118mg/kg. Other organochlorines pesticides residues studies mostly in other countries have reported higher concentrations.

## CONCLUSION

According to the presented investigation of hake fillets from Serbian retail it can be concluded: the present GCMS analytical method was developed for the simultaneous determination of 18 pesticides of hake fillets. The concentrations detected were lower than recommended values in some countries but since there is a possible health risk, it is important to monitor the presence and concentrations of OCP in these products. It could be concluded that OCP pesticide residues were detected in hake fillets, as they were persistent in nature due to their slow decomposition rate, long half - life and high stability in the environment. Chemical analysis showed that the product complies with the Regulations of Republic Serbia.

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