Science of the Total Environment 466–467 (2014) 306–314

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Multi pesticide and PCB residues in Nile tilapia and catfish in Assiut city, Egypt

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HIGHLIGHTS

- Detection of multiple pesticides in tilapia and cat fish in Assiut city, Egypt.
- Pesticides residues detected using GC/MS.
- OPs, OCs, PCBs congeners, HCB and trifluralin pesticides detected in Elwasta and Mankbad, Assiut city, Egypt.
- Pesticide residue levels in the area 2 (Mankbad) higher than area 1 (Elwasta).
- Higher values were detected of pesticide residues in cat fish than tilapia.

ARTICLE INFO

Article history:
Received 14 April 2013
Received in revised form 29 June 2013
Accepted 1 July 2013
Available online 31 July 2013

Editor: Eddy Y. Zeng

Keywords:
Multi pesticide residues
Trifluralin
Tilapia
Cat fish
GC–MS/MS

ABSTRACT

The current study investigated the levels of multi pesticide residues in the highly consumed types of Nile fish in Egypt: tilapia and cat fish. A total of 50 Nile tilapia (*Oreochromis niloticus*) and 50 African catfish (*Clarias gariepinus*) were collected from two areas in Assiut city, where most industries are situated and where agricultural activities and raising of farm animals are the main activities. In the first area, Elwasta, there is an electrical power station, and the second area, Mankbad, there is a cement factory. Fish samples were analyzed by High Resolution Gas Chromatography/Mass Spectrometry. Average pesticide residue concentrations $\pm$ SE in muscle of tilapia and catfish ($n = 10$ pooled samples with five fish each) were determined. The results indicated the presence of different types of organophosphorous (OPs), organochlorine (OC), polychlorinated biphenyles (PCBs), hexachlorobenzene (HCB) and trifluralin pesticides in Elwasta and Mankbad in varying degrees. Diazenon was the only OP pesticide which exceeded the permissible limit in both investigated areas with the two types of fish. On the other hand, OCs, PCBs, HCB and trifluralin pesticide residue levels have not exceeded the maximum allowable concentration limit. In general, a higher pesticide residue level was obtained in Mankbad than Elwasta. In addition, higher values are realized for the detected pesticide residues in cat fish than tilapia. The results of the study have shown the extensive and recent use of these types of pesticides in the present time in Egypt.

1. Introduction

Pesticides play a key role in pest management and protecting human beings and domestic animals from infectious diseases. However, it is important to remember that any pesticide should be considered as an active poison (Hogsette et al., 2006). Use of pesticides varies greatly among different parts of the world in types and quantities. Consequently, many international organizations such as the Codex Alimentarius Commission (CAC), WHO/FAO, and European Union (EU) as well as different countries have issued their own pesticide maximum residual limits (MRLs) in the international trade (Lin, 2002).

Pesticides reach aquatic ecosystems by direct application, spray drift, aerial spraying, and erosion and runoff from factories and sewage. The contamination of water sources is a major source of concern since it is the habitat of fish and other aquatic organisms such as mussels, oysters, prawns and lobsters. Pesticides end up in the tissue of aquatic organisms and bio-accumulates with time (Jiries et al., 2002). Fish consumption could be therefore considered as one of the major sources of human exposure to all environmental contaminants (EFSA, 2005; Storelli, 2008).

Tilapia is the most popular freshwater fish species in Egypt. It plays an important role in fish consumption in Egypt and around the world. The Nile catfish is highly consumed in Egypt because it is cheap and available in most localities. The African catfish tend to live in turbid and cloudy waters. It is more exposed to different types of environmental contaminants than other fish types. Because

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http://dx.doi.org/10.1016/j.scitotenv.2013.07.002

of the relatively high fat content of catfish meat, the fat soluble environmental pollutants such as organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) are the more probable pollutants present in catfish meat (Holtan, 1998). Furthermore, the organophosphorus pesticides (OPs) could pollute the tilapia and catfish meat via the recent agricultural application.

OC pesticides are ubiquitous anthropogenic contaminants that are persistent in the environment, accumulate in fatty tissues and increase in concentration as they move up the food chain (WHO, 1999). Due to their lipophilic nature they accumulate along trophic levels and induce multiple adverse effects in many organisms (Fleming et al., 2006). Although the production and use of many types of OCs have been severely limited in many countries including Egypt, they are, nevertheless, still being used unofficially in large quantities in many parts of the world, and in other developing countries because of their effectiveness as pesticides and their relatively low cost (Ntow et al., 2006). Since 1980 DDT and lindane have been officially prohibited from agricultural use in Egypt, and in 1996 a Ministerial Decree prohibited the import and use of 80 pesticides including aldrin, dieldrin, endrin, chlordane, heptachlor, DDT, toxaphene, mirex, lindane, endosulfan, pentachlorophenol, and heptachlor epoxide. Due to the great concern in protecting the human health and environment from POPs, Egypt signed the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2002 and ratified it in 2003 (Baraka et al., 2013). OCs were detected in fresh water fish in previous studies in Egypt by Salah El-Dien and Nasr (2004). The probable sources of this pesticide group originated from previous or illegal use.

On the other aspect, OP pesticides are regarded as being low persistent compared with OCs, but some reports have indicated that residues of OPs are persisting for extended periods in organic soil and surrounding drainage systems in Egypt by Abdel-Halim et al. (2006). Due to their low price and effective ability to control pests, weeds and diseases (He et al., 2009), they had been widely used and became more and more important in agricultural production after OCs were forbidden. OP residues can concentrate and diffuse by the effect of biological enrichment and food chains; therefore, it might appear in food products and pose a potential risk for human health (Sun et al., 2011).

Polychlorinated biphenyls (PCBs) were commercially produced as complex mixtures containing multiple isomers at different degrees of chlorination. Today PCBs can still be released into the environment from poorly maintained hazardous waste sites that contain PCBs; illegal or improper dumping of PCB wastes; leaks or releases from electrical transformers containing PCBs (ATSDR, 2002). Some PCB congeners elicit a divers spectrum of toxic and biochemical responses including body weight loss, immunotoxicity (Sormo et al., 2009) and induction of gene expression (El Nemr et al., 2003).

Hexachlorobenzene (HCB) was widely used as a pesticide (ATSDR, 2002), and it is still widely distributed in the environment (Barber et al., 2005). Long term oral exposure to HCB in humans results in liver disease with associated skin lesions. For the general population exposure to HCB occurs primarily from eating low levels of this organic compound in contaminated food (ATSDR, 2002).

Trifluralin is a selective, preemergence herbicide used to control a wide range of annual grasses and broadleaf weeds. It is toxic to aquatic fish and invertebrates, is typically soil incorporated, is highly absorbent to soil, and essentially non-soluble in water. The potential for bioaccumulation under environment conditions depends largely on the elimination rates in biota and the environment (Han et al., 2007).

In fact, dietary intake is considered to be the most important source of pesticides in humans (Tsukino et al., 2006). Fish consumption is a possible source of pesticide accumulation in humans. It is possible that the accumulation of these contaminants reduces fish quality in the hatchery and undermines their survival after release, resulting in financial costs to aquacultures (Botaro et al., 2011). Therefore, the aim of the present study was to investigate the levels of multi pesticide residues in fish samples including the most famous and highly consumed types of Nile fish in Egypt; to compare the levels of pesticide residues between the two different types of Nile fish (tilapia and catfish) and to compare these levels with the recommended international permissible limits.

2. Material and methods

2.1. Sampling

The sampling sites involve two areas in Assiut city, where agricultural activities and raising of farm animals are the main activities, and where the most industries are situated. In the first area, Elwasta, there is an electrical power station, and the second area, Mankbad, there is a cement factory. The study included a total of 50 Nile tilapia (*Oreochromis niloticus*) and 50 African catfish (*Clarias gariepinus*) collected from the two previous mentioned areas (Elwasta and Mankbad) in Assiut city, Egypt. The two types of fish were investigated for detection and determination of multi-pesticide residues. Fish size is on average about (500 ± 60 g) for individual fish. Approximately 200 g from each fish samples was obtained and put into an ice chest. The fish samples were immediately transported to the laboratory in an ice chest with ice and stored at −4 °C in a refrigerator for two days before extraction and analysis. The fish samples were obtained in a composite manner and placed in clean wide-mouth glassy containers and covered immediately after sampling. Average pesticide residue concentrations ± SE in muscle of tilapia (n = 10 pooled samples with five fish each) and catfish (n = 10 pooled samples with five fish each) from two different areas in Assiut city, Upper Egypt were calculated.

2.2. Standards and reagents

The analytical pesticide standards of the organochlorine pesticides included alachlor, p,p0-DDE, lindane, aldrin, heptachlor, dieldrin and hexachlorobenzene (HCB). The organophosphorous compounds analyzed in this study were malathion, parathion, methyl parathion, ethion, chlorpyrifos and diazenon, and the herbicide standard, triflurin. Pesticide standards were purchased from Sigma (Poole, UK). The polychlorinated biphenyls (IUPAC Nos. 28, 52, 118 and 138) were from LGC Standards (Teddington, UK).

Individual stock standard solutions of pesticide were prepared by dissolving 10 mg of each compound in 10 mL hexane and stored in amber bottles. A mixed standard solution was prepared from the individual stock solutions with a concentration of 100 mg/L. A series of calibration standards were prepared by diluting 100 mg/L of the mixed standard solution to produce final concentrations of 0.1, 0.2, 0.5, 1.0, and 2.0 mg/L in hexane. Stock and working solutions were stored at 4 °C and used for no longer than 3 months and 1 week, respectively.

The solvents used were acetone, n-hexane, methylene chloride, toluene and acetonitrile. Anhydrous sodium sulphate and sodium chloride were also used. All the reagents were of analytical (HPLC) grade supplied by BDH, London, UK. Before use; sodium sulphate was heated at 650 °C for 4 h and kept in a desiccator. Distilled water was obtained with a Milli-Q system (Millipore, Bedford, MA, USA). For SPE, an aminopropyl (NH2) cartridge was purchased from Waters.

2.3. Sample extraction

Ten grams of a previously minced fish sample was placed into a 50 mL centrifuge tube and mixed with 3.0 mL of water. The mixture was vortexed for 1 min. A 20 mL aliquot of acetonitrile was added as an extraction solvent. The resulting mixture was stirred for 15 min. 5 g of sodium chloride was added to the mixture and it was vortexed for another 2 min, then centrifuged for 5 min at 4000 rpm. 10 mL of the extraction solution was collected in a 100 mL round flask, which