

**MONITORING OF DIOXIN LEVELS IN
SELECTED FISH SPECIES COLLECTED FROM
THE EGYPTIAN COASTAL HARBORS**

By

SHERIF MOHAMED HASSAN EL-SAFY
B.Sc. (International Agriculture), Fac. Agric., Cairo Univ., Egypt, 2002

THESIS

**Submitted in Partial Fulfillment of the
Requirements for the Degree of**

MASTER OF SCIENCE

In

**Agricultural Sciences
(Pesticides)**

**Department of Economic Entomology and Pesticides
Faculty of Agriculture
Cairo University
EGYPT**

2009

SUPERVISION SHEET

**MONITORING OF DIOXIN LEVELS IN
SELECTED FISH SPECIES COLLECTED FROM
THE EGYPTIAN COASTAL HARBORS**

**M.Sc. Thesis
In
Agric. Sci. (Pesticide)**

By

SHERIF MOHAMED HASSAN EL-SAFETY
B.Sc. (International Agriculture), Fac. Agric., Cairo Univ., Egypt, 2002

SUPERVISION COMMITTEE

Dr. Samia Abd Menahim El-Kabbany
Professor of Pesticides, Fac. Agric., Cairo University

Dr. Hamed Khairallah Omar Said
Assistant Professor of Pesticides, Fac. Agric., Cairo University

Dr. Yasser Mohamed Nabil
Senior Researcher of Pesticides, Central Agri. Pesticides Lab. Agri. Res. Center

APPROVAL SHEET

**MONITORING OF DIOXIN LEVELS IN
SELECTED FISH SPECIES COLLECTED FROM
THE EGYPTIAN COASTAL HARBORS**

**M.Sc. Thesis
In
Agric. Sci. (Pesticide)**

By

SHERIF MOHAMED HASSAN EL-SAFETY
B.Sc. (International Agriculture), Fac. Agric., Cairo Univ., Egypt, 2002

Approval Committee

Dr. SOHAIR AHMED GADALLAH
Head Researcher of Pesticides, Central Agri. Pesticides Lab., Agri. Res. Center

Dr. MOHAMED ABDEL-HADDY KANDIL.....
Professor of Pesticides, Fac. Agric., Cairo University

Dr. HAMED KHAIRALLAH OMAR SAID
Associate Professor of Pesticides, Fac. Agric., Cairo University

Dr. SAMIA ABD MENAHIM EL-KABBANY.....
Professor of Pesticides, Fac. Agric., Cairo University

Date: / /

تقصي مستويات الداىوكسين فى عينات سمك جمعت من الموانئ الساحلية
لجمهورية مصر العربية

رسالة مقدمة من

شريف محمد حسن الصفتى

بكالوريوس فى العلوم الزراعية (زراعة دولية) - كلية الزراعة - جامعة القاهرة - ٢٠٠٢

للحصول على

درجة الماجستير

فى

العلوم الزراعية
(مبيدات)

قسم الحشرات الاقتصادية والمبيدات
كلية الزراعة
جامعة القاهرة
مصر

٢٠٠٩

تقصي مستويات الداىوكسين فى عينات سمك جمعت من الموانى الساحلية
لجمهورية مصر العربية

رسالة ماجستير
فى العلوم الزراعية
(مبيدات)

مقدمة من

شريف محمد حسن الصفتى

بكالوريوس فى العلوم الزراعية (زراعة دولية) - كلية الزراعة - جامعة القاهرة - ٢٠٠٢

لجنة الإشراف

دكتور/ سامية محمد عبد المنعم القبانى
أستاذ المبيدات - كلية الزراعة - جامعة القاهرة

دكتور/ حامد خير الله عمر سعد
أستاذ مساعد المبيدات - كلية الزراعة - جامعة القاهرة

دكتور/ ياسر محمد نبيل
باحث أول المبيدات - المعمل المركزى للمتبقيات للمبيدات - مركز البحوث الزراعية

تقسي مستويات الذايوكسين فى عينات سمك جمعت من الموانى الساحلية
لجمهورية مصر العربية

رسالة ماجستير
فى العلوم الزراعية
(مبيدات)

مقدمة من

شريف محمد حسن الصفتى
بكالوريوس فى العلوم الزراعية (زراعة دولية) - كلية الزراعة - جامعة القاهرة - ٢٠٠٢

لجنة الحكم

دكتور/ سهير أحمد جاد الله
رئيس بحوث المبيدات - المعمل المركزى للمتبقيات للمبيدات - مركز البحوث الزراعية

دكتور/ محمد عبد الهادي قنديل
أستاذ المبيدات - كلية الزراعة - جامعة القاهرة

دكتور/ حامد خير الله عمر سعد
أستاذ مساعد المبيدات - كلية الزراعة - جامعة القاهرة

دكتور/ سامية محمد عبد المنعم القبانى
أستاذ المبيدات - كلية الزراعة - جامعة القاهرة

التاريخ / ٢٠٠٩

Name of Candidate: Sherif Mohamed Hassan El-Safty **Degree:** M.Sc.
Title of Thesis: Monitoring of dioxin levels in selected fish species collected from the
Egyptian coastal harbors
Supervisors: Dr. Samia Abd Menahim El-Kabbany
Dr. Hamed Khairallah Omar Said
Dr. Yasser Mohamed Nabil
Department: Economic Entomology and Pesticides
Branch: Pesticides **Approval:** / /2009

ABSTRACT

Seventeen WHO toxic congeners of PCDD/Fs in the muscles of four fish species (Tilapia, grey mullet, sardine and brush tooth lizard fish) from two sites in the Mediterranean Sea and two sites in the Red Sea were quantitatively determined by high resolution Gas chromatography/ high resolution mass spectrometry. Dioxin survey aim to determine the distribution and levels of PCDD/Fs in the major Egyptian harbors environment. A total number of 50 fish samples that represent different types; Tilapia (*Tilapia zilli*), grey mullet (*Mugil cephalus*), sardine (*Sardinella spp.*) and brush tooth lizard (*Saurida undosquamis*) samples were collected during 2006 from fourteen locations along the coastal borders for Egyptian governorates. The results demonstrated that the concentration of dioxins didn't exceed the maximum level proposed by the Egyptian Organization for Standardization which is the same as the European Community which has set a limit of 4 pg WHO-TEQ/g of PCDD/Fs for fish and fish products on a wet weight basis. The results obtained from the analysis of seventeen 2,3,7,8-substituted congeners of PCDD/Fs in the four species of fish from fourteen areas along the Mediterranean and Red Sea were found to be lower than the maximum permissible limits.

The results obtained from the analysis of the seventeen 2,3,7,8-substituted congeners (pg WHO-TEQ/g) of PCDD/Fs showed that the highest average concentration was found in grey mullet followed by tilapia, sardine and brush tooth lizard fish. Average concentration of total PCDD/Fs in tilapia, grey mullet, sardine and brush tooth lizard fish from Egypt ranged from 0.22 to 2.9 pg WHO-TEQ/g fw, 0.26 to 2.0 pg WHO-TEQ/g fw, 0.13 to 1.3 pg WHO-TEQ/g fw, and 0.3 to 0.87 pg WHO-TEQ/g fw, respectively. The concentration of the PCDD/Fs in the Red Sea was higher than the concentration in the Mediterranean Sea due to its high lipoplicity of PCDD/Fs and their persistence in the environment. The data show that the \sum PCDD/Fs varied among different locations e.g. \sum PCDD/Fs levels detected in Port Said was the highest concentration in tilapia followed by Alexandria. These results reflect the contamination levels in the fish samples where Ismailia was much higher than those determined in Suez in grey mullet. A significant contribution from the lower PCDD/Fs to the total PCDD/Fs has been observed in grey mullet from Alexandria and Port Said where a PCDD constitutes average concentration of 76% was higher than those PCDFs which were 24% from \sum PCDD/Fs. All results showed that the total PCDD were higher in grey mullet fish than in brush tooth lizard fish either collected from Mediterranean Sea or Red Sea.

Keywords: Fish, dioxin, Egypt, Sea, GC-HRMS

ACKNOWLEDGMENT

I wish to express my deep gratitude to Dr. Samia El-Kabbany, Professor of Pesticides, Department of Economic Entomology and Pesticides, Faculty of Agriculture, Cairo University for his Supervision, guidance, useful criticism and his efforts to fulfill this work.

Many thanks to Dr. Hamed Khairallah Assistant Professor of Pesticide, Department of Economic Entomology and Pesticides, Faculty of Agriculture, Cairo University for his sharing in supervision, kind unfailing help throughout this work.

My Sincere appreciation and deep gratitude and thanks to Dr. Sohair Gadallah, Senior Researcher of Pesticides, Agriculture Research Center for her supervision constructive criticism, valuable advice, continuous encouragement, cooperation, and kind assistance.

I wish to express my appreciation and deep thanks to Dr. Mohamed El sayed, Dr. Yasser Nabil, Dr. Emad Attallah , Dr. Mohamed Amr and Mr. Mustapha Nabil Researcher of Pesticides, Agriculture Research Center for their guidance, advice, encouragement, and kind assistance in completing this work.

اسم الطالب: شريف محمد حسن الصفتى
عنوان الرسالة: تقصى مستويات الداىوكسين فى عينات السمك جمعت من الموانئ الساحلية لجمهورية مصر العربية
المشرفون: دكتور: سامية محمد عبد المنعم القباني
دكتور: حامد خير الله عمر سعد
دكتور: ياسر محمد نبيل
قسم: الحشرات الاقتصادية والمبيدات
تاريخ منح الدرجة: ٢٠٠٩/ /
الدرجة: ماجستير
فرع: المبيدات

المستخلص العربى

لتقصى مستوى الداىوكسين بموانئ مصر الساحلية تم جمع خمسون عينة تمثل أربعة أنواع مختلفة من السمك (بلطى - بورى - سردين - مكرونة) فى عام ٢٠٠٦ من أربعة عشر موقع مختلف (من منطقتين فى البحر المتوسط ومنطقتين فى البحر الأحمر) على طول السواحل المصرية للتقدير الكمي للمركبات السبعة عشر الأكثر سمية من مركبات الداىوكسين (PCDD/Fs) طبقاً لمنظمة الصحة العالمية على جهاز التحليل الكروماتوجرافي الغازي مطياف الكتلة.

تشير النتائج المتحصل عليها إلى ان مستوى الداىوكسينات لا تتعدى الحدود المصرية القصوى المسموح بها والتي تتشابه مع الحدود الأوروبية وهى أربعة بيكوجرام كذلك أوضحت النتائج من تحليل السبعة عشر مركب للداىوكسين إلى أن أعلى معدل تركيز للداىوكسين وجد فى عينات سمك البورى، البلطى، السردين ثم المكرونة و كان إجمالى معدل تركيز للداىوكسين فى عينات سمك البلطى - البورى - السردين - المكرونة يتراوح ما بين ٠.٢٢ إلى ٢.٩ بيكوجرام، ٠.٢٦ إلى ٢.٠ بيكوجرام، ٠.١٣ إلى ١.٣ بيكوجرام، ٠.٣ إلى ٠.٨٧ بيكوجرام أن تركيز الداىوكسين فى عينات السمك التي جمعت من البحر الأحمر كان أعلى من تركيز الداىوكسين فى عينات السمك التي جمعت من البحر المتوسط نتيجة لسرعة ذوبانه العالية فى الدهون وثباته لفترات طويلة فى البيئة.

أوضحت البيانات المتحصل عليها من أماكن مختلفة أن محافظة بورسعيد وجد بها أعلى تركيز للداىوكسين من محافظة الإسكندرية فى البحر المتوسط، أما فى البحر الأحمر وجد أن أعلى تركيز للداىوكسين فى عينات سمك البورى من محافظة الإسماعيلية ثم محافظة السويس. من الملاحظ أن البحر الأحمر أعلى تركيز من البحر المتوسط. أن الـPCDD أعلى من الـPCDF فى عينات سمك البورى من الإسكندرية إلى بورسعيد والتي تتمثل بنسبة تركيز ٧٦% للـPCDD عن الـPCDF والتي تتمثل بنسبة تركيز ٢٤%.

الكلمات المفتاحية: السمك، الداىوكسين، مصر، بحر، الكروماتوجرافي الغازي مطياف الكتلة

CONTENTS

	page
INTRODUCTION	1
REVIEW OF LITERATURE	5
1. Persistent organic pollutants (POPs)	5
2. Sources of dioxin	7
a. Physical and chemical properties	8
b. Occurrence in air and aerial transport	10
c. Dioxin exposure pathway	11
3. Monitoring and Daily intake of dioxin in fish	13
a. European studies.....	13
b. North American studies.....	19
c. Asian studies.....	21
d. African studies.....	23
4. Methods of analysis	24
a. Toxic Equivalency Factors	25
5. Toxicological side effect of dioxin	27
6. Carcinogenic effects	31
7. Reduction of dioxin exposure	35
MATERIALS AND METHODS	38
RESULTS AND DISCUSSION	59
1. Validation of analytical method for PCDD/Fs in fish samples	60
2. Monitoring ΣPCDD/Fs in different fish type from different sites (local fish)	69
a. Σ PCDD/Fs, Pg/g fw (fresh weight)	69
b. Σ PCDD/Fs, Pg WHO-TEQ/g fw (fresh weight).....	82
c. Σ PCDD/Fs, Pg WHO-TEQ/g lw (lipid weight).....	97
3. Monitoring of ΣPCDD/Fs, Pg WHO-TEQ/g fw (fresh weight) in imported fish	109
4. Estimated Dietary Intake of ΣPCDD/Fs	111
CONCLUSION	114
SUMMARY	116
REFERENCES	123
ARABIC SUMMARY	

LIST OF TABLES

No	Title	Page
1.	Accidents make dioxin interest pollution	28
2.	Classification of polychlorinated dibenzo-p-dioxin/ Furan.....	38
3.	POPs (Persistence Organic Pollutants) properties and criteria set by the United National Economic Commission of Europe.....	40
4.	Locations, numbers and varieties of collected local fish samples during years 2005 and 2006.	42
5.	Numbers and varieties of collected imported fish samples from Egyptian ports during 2006.....	43
6.	Comparative concentration of (PCDD/Fs) between Finnish and Egyptian laboratories.....	63
7.	Relative standard uncertainty calculations of fish samples.....	66
8.	Average concentration (pg/g) fw of PCDD/Fs in four local fish species in (Tilapia(T),Grey mullet(G), Sardine(S), Brush tooth lizard fish (B) and Mean (M) concentration in four locations in Alexandria (Mediterranean Sea).....	70
9.	Average concentration (pg/g) fw of PCDD/Fs in four local fish species in (Tilapia(T),Grey mullet(G), Sardine(S), Brush tooth lizard fish (B) and Mean (M) concentration in three locations in Port Said (Mediterranean Sea).	71
10.	Average concentration of (pg/g) fw of PCDD/Fs in Alexandria &Port Said (Mediterranean Sea).....	73
11.	Average concentration (pg/g) fw of PCDD/Fs in four local fish species in three locations in Ismailia (Red Sea).	74
12.	Average concentration (pg/g) fw of PCDD/Fs in four local fish species in three locations in Suez (Red Sea).....	75
13.	Average concentration (pg/g) fw of PCDD/Fs in Ismailia & Suez (Red Sea).....	77
14.	Average concentration (pg/g) fw of PCDD/Fs in Mediterranean & Red Sea (Egypt).....	78
15.	Toxic equivalency factor (TEF) for PCDD/Fs	83
16.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in four local fish species in (Tilapia(T), Grey mullet(G), Sardine (S), Brush tooth lizard fish (B) and Mean (M) concentration in four locations in Alexandria (Mediterranean Sea).....	85
17.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in four local fish species in (Tilapia(T),Grey mullet(G), Sardine (S), Brush tooth lizard fish (B) and Mean (M) concentration in three locations in Port Said (Mediterranean Sea).....	86

No	Title	Page
18.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in Alexandria &Port Said (Mediterranean Sea).....	88
19.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in four local fish species in three locations in Ismailia (Red Sea)...	89
20.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in four local fish species in three locations in Suez (Red Sea).....	91
21.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in Ismailia & Suez (Red Sea).....	92
22.	Average concentration (pg WHO-TEQ/g) fw of PCDD/Fs in Mediterranean & Red Sea (Egypt).....	93
23.	The average mean length, weight and fat per each fish type.....	98
24.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in four local fish species in (Tilapia(T),Grey mullet(G), Sardine (S), Brush tooth lizard fish (B) and Mean (M) concentration in four locations in Alexandria (Mediterranean Sea).....	99
25.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in four local fish species in (Tilapia(T),Grey mullet(G), Sardine(S), Brush tooth lizard fish (B) and Mean (M) concentration in four locations in Port Said (Mediterranean Sea).....	100
26.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in Alexandria &Port Said.....	101
27.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in four local fish species in three locations in Ismailia (Red Sea).....	102
28.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in four local fish species in three locations in Suez (Red Sea).....	105
29.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in Ismailia & Suez (Red Sea).....	106
30.	Average concentration (pg WHO-TEQ/g) lw of PCDD/Fs in Mediterranean Sea & Red Sea (Egypt).....	107
31.	Concentration Pg WHO-TEQ/g fw of total PCDD/Fs in imported fish species.....	109
32.	Estimated Egyptian daily intake of Σ PCDD/Fs from fish.....	113

LIST OF FIGURES

No	Title	Page
1.	(PCDD/Fs) are two related families of planar, tricyclic, organic substances.....	39
2.	Profile (pg/g) fw of total PCDD/Fs in Mediterranean Sea and Red Sea.....	79
3.	Profile (pg WHO-TEQ/g) fw of total PCDD/Fs in Mediterranean Sea and Red Sea.....	94
4.	Profile (pg WHO-TEQ/g) lw of total PCDD/Fs in Mediterranean Sea and Red Sea.....	108

LIST OF ABBREVIATIONS

No	Abbreviations	Synonyms
1.	AHH	Aryl hydrocarbon hydroxylase.
2.	Ah receptor	Aryl hydrocarbon receptor, also known as the dioxin receptor.
3.	Congener	An individual PCDD or PCDF.
4.	DRE	Dioxin responsive element.
5.	EDI	Estimated daily intake.
6.	IPCS	International Programme on Chemical Safety.
7.	fw	fresh weight
8.	GC	Gas chromatography.
9.	GEMS/FOOD	Global Environment Monitoring System/Food.
10.	HRMS	High resolution mass spectrometer.
11.	JECFA	Joint FAO/WHO Expert Committee on Food Additives (JECFA).
12.	LOEAL	lowest-observed-adverse-effect-level.
13.	lw	lipid weight
14.	ng	Nano-gram, 10^{-9} g.
15.	PCBs	Polychlorinated biphenyls.
16.	PCDDs	Polychlorinated dibenzo-p-dioxins.
17.	PCDFs	Polychlorinated dibenzofurans.
18.	pg	Picogram, 10^{-12} g.
19.	POPs	Persistence organic pollutants.
20.	PCBs	Polychlorinated biphenyls.
21.	PCDDs	Polychlorinated dibenzo-p-dioxins.
22.	PCDFs	Polychlorinated dibenzofurans.
23.	TEF	Toxic equivalency factor.
24.	TEQ	Toxic equivalency.
25.	WHO	World Health Organization.