

Journal of Plant Protection and Pathology

Journal homepage: www.jpmp.mans.edu.eg
Available online at: www.jpmp.journals.ekb.eg

Effect of Water pH and Direct Exposure to Sunlight on Chemical Stability of Fungicide Chlorothalonil

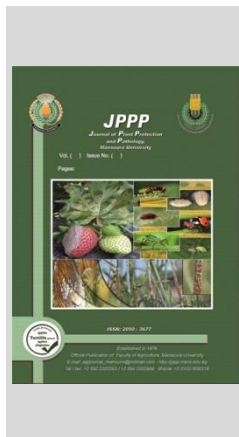
Seloma, A. S. O.^{1*} and A. A. Shalaby²

¹ Pesticides Analysis Res. Dept., Central Agric. Pesticides Lab., Agric. Res. Center, Dokki, Giza, Egypt.

² Plant Prot. Dept., Fac. of Agric., Zigzag, Univ., Egypt.



Cross Mark



ABSTRACT

This project target aim to investigate the hydrolysis of fungicide chlorothalonil at different pH solutions at (pH4, pH7, and pH9), as well as its stability under exposure to different temperature degrees and direct exposure to sunlight, and to estimate the photoproducts degradation of chlorothalonil using GC/MS. The data showed that chlorothalonil dissipation from different pH solutions increased more rapidly with increasing both pH value and temperature when compared to acidic and neutral solutions, and that tested pesticides were hydrolyzed more rapidly in alkaline media (PH9) than the other tested pH values at all tested temperatures. The percentage of pesticides that decompose steadily increases and is positively connected with exposure times, according to the data. The results also demonstrated that after 336 hours of exposure to direct sunlight, no detectable level of the pesticides tested was found. The compound (4-hydroxy-2,5,6-trichloroisophthalonitrile) was identified as a major metabolites in environmental samples after photo-degradation products were investigated using GC/MS following exposure to direct sunlight.

Keywords: Pesticide, Chlorothalonil , Environmental Factors, Temperature degrees, Direct sunlight , pH solutions, GC/MS.

INTRODUCTION

Diamond Shamrock Corp. introduced that, in 1965, fungicide, chlorothalonil, [2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile] CAS1897-45-6, (Fig.1), and it's the first approved to using for turfgrasses in 1966, at United, States. Four years later, an additional registration for usage on potatoes was given, making potatoes the first certified to food-crop-applications, (U.S. EPA, 1999). It comes in a variety of forms, including concentrates, powders, and granules, among others. Bravo, Daconil, and Sweep are some of the well-known products that include chlorothalonil as an active ingredient (U.S. EPA, 1999). Among other crops the celery, beans, peanuts, and peaches, have been treated with these or other chlorothalonil formulations. 34% approximately of chlorothalonil were applied on peanuts and 12% and 10% applied on potatoes and golf-courses respectively, in United, States (U.S. EPA, 1999).

Structure of "Chlorothalonil" is non-systemic-organochlorine "fungicide, and mildewicide" with a broad spectrum of activity. It's mostly used to combat fungal foliar infections on a wide range of ornamentals, turf, vegetables and fruits (U.S. EPA, 1999). The performance for "chlorothalonil" as anti-fouling, paint-additive and wood-protectant efficient to replacing as a biocides organotin, e.g. "tributyltin" nonetheless, which is slowly-released in rivers with possibility to surface-water bodies contaminate once applied, Sakkas, *et. al.* 2002. Despite the fact that, water-surface in marinas at San-Diego C.A., were tested as a anti-fouling-residues, and no found for above-detection-limit of 10 mg/L. Sapozhnikova, *et. al.* 2007.

From 1993 to 2000, chlorothalonil residues in surface and groundwater in California were monitored. Only

one surface water sample [out of (705) totals] from USGS, water-monitoring sites detected "chlorothalonil" at value, 0.29g/L. (USGS, NAWQA, U.S. EPA, 2007).

Table 1. Physiochemical characteristics of chlorothalonil.

Chlorothalonil's physiochemical characteristics

Molecular, Formula.	(C ₈ Cl ₄ N ₂)
Molecular, weight/g/mol.	(265.9)
Density, 20°C g/mL.	(2)
Melting, point/°C.	(252.1)
Octanol-water-partition-coefficient/log Kow	(2.88)
Organic-carbon-normalized-partition-coefficient/Koc.	(5.000)
Vapor-pressure 25°C/torr	(5.72 x 10 ⁻⁷)
Henry-law constant, atm, m ⁻³ /mol	(1.4 x 10 ⁻⁷)
Solubility/g/kg.	(0.81)
Water/mg/L.	(<10)
Kerosene,	(20)
Acetone,	(80)
Chemical-Abstracts-Service, registry-number CAS#	(1897-45-6)

Obtained data according to Tomlin, 2000.

CA, DPR, Risk-Characterization-Document, 2005.

Obtained data according to Waltz, *et. al.* 2002

Some pesticides' stability is influenced by the pH of the water. Alkaline hydrolysis happens in alkaline conditions, converting, inactive and nontoxic pesticides-forms. The insecticide, especially "carbamates" and "organophosphates" highly sensitive to alkaline-hydrolysis, than herbicide and fungicide, or growth-regulators in general.

As a result, the low active-ingredient is applied and effectiveness pesticides were suffered. Pesticide half-life can be used to determine how quickly it degrades, when a half-

* Corresponding author.

E-mail address: aymansameih@yahoo.com

DOI: 10.21608/jppp.2021.198243

life product has a one hour, for example, reduced of active-component-amount to (50%), at one-hour, (25%), in the next-hour and (12.5%), in next-hour, and so on. Insecticide eventually is ineffective. Impact of (pH) on pesticide differs according to product and influence according to solution of buffering, included pesticide formulations. When different insecticides are mixed in a tank, pH of tank can be changed. The major of pesticides are stable, when, spray-solution-pH is around five. Because, some of water-sources are high-alkaline than, pH of spray-solution may need to be adjusted. The copper based fungicide solutions should not be acidified since, the copper become more-soluble in a lower-pH and possibility is phytotoxic-crops. Furthermore, phosphorous-acid and others of acid based fungicides ought to no-acidified because their pH is already low, and reducing it could result in phytotoxicity. On the other hand, acidifying carbonate-salts of fungicides, e.g., "Armcarb" may render them useless.

The present investigation aimed to throw light on the hydrolysis of the fungicide chlorothalonil at different pH solutions and temperature degrees, chlorothalonil dissipation after exposure to direct sunlight and estimated its photodegradation products were deal with.

MATERIALS AND METHODS

1-Pesticides under test

Daconil 72% SC

Common name: Chlorothalonil

IUPAC, name: (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile).

Chemical Structure:

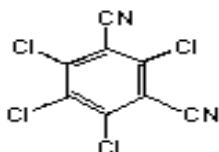


Fig. 1 Chlorothalonil

Registration no: 1335.

2- At pH4, pH7, and pH9, hydrolysis evaluates different pH solutions.

A FRAGILE PH meter with serial number 1557, model 3520, and frequency (50/60) created in the United Kingdom, was used three buffer solutions were used according to Raj and Chiba (1985) as follow:

Buffer solutions:

PH4: 0.1M Citric-acid (159ml), and 0.2M Na₂HPO₄ (41ml)/1L.

PH7: 0.067M Na₂HPO₄ (122ml), and 0.067M K₂PO₄ (78 ml)/1L

PH9: .025M borax, (246ml), and 0.1M NaOH (4 ml) in 1 L. Prior to starting the hydrolysis experiment, all buffer solutions and glass apparatus were autoclaved to guarantee that no microbes were responsible for the observed hydrolytic degradation. The pesticide was added to the buffer to produce 500 ug/ml solutions.

Hydrolysis tests were conducted out in the dark for 14 days at temperatures of 25, 35, and 45 degrees Celsius. (Nakayama *et al*, 1997). Transferred (10ml.) of the buffer solution to a separator-funnel then, extracted of three-times in dichloromethane (10ml.), and mixed "dichloromethane" dried over anhydrous-sodium-sulphate, and then, evaporated

to dry under vacuum by rotary-evaporator, finally analysed using GLC technique.

The rate of disappearance in aqueous solutions was used to evaluate the hydrolysis rates of chlorothalonil. Lee *et al* (1989); Lartiges and Garrigues (1995); Jones and Norris (1998); Hong and Pehkonen (1998); Ramesh and Balasubramanian (1999).

3- Effect of direct sunlight.

500 ug of the test fungicide was placed as evenly as possible on the surface of uncovered petri plates in aliquots of 1 ml ethyleacetate (5 cm i.d.) an ethylacetate that has been allowed to dry at ambient temperature After that, the dishes were left in direct sunlight for 1, 2, 4, 6, 12, 24, 96, 192 and 336 hours. The dominant temperature ranged from 32 to 38 degrees Celsius. (Abu- Zahw *et al*, 1998) and (Khay *et al*, 2008).

4-Determination of chlorothalonil.

The residues of chlorothalonil was analyzed according to the method of Alicia Chaves (2007).with some modification by using (GLC).

A continuous flowing of (8ml/min) of nitrogen was using as a carrier-gas in an Agilent-7890B gas-chromatograph and autosampler-7693 equipped with Flame-Ionization-Detector "FID", capillary-column HP-50+(30mx0.53mmI.D.,1um film-thickness) at 250 0C. The temperature-oven set at (200⁰C) for 1min, then increased to 260 degrees Celsius at a rate of 20 degrees Celsius per minute for 2 minutes. The injector temperature was 250 ⁰C in splitless mode. An injection of one ul was used. The average retention time for chlorothaonil was 3.612 minutes. The results of Chlorothaonil were quantitatively quantified by comparison with known purity standards under identical GLC circumstances.

5- Kinetic study:

The degradation rates of tested active-ingredient and period half-life (t_{0.5}) for the tested pesticides were calculation according to equation Moyer *et al*. 1987.

$$RL t 0.5 = \ln 2 / K = 0.6932 / K$$

$$K = 1 / T_x \cdot \ln a / b_x$$

Where; R=Decomposition rate

a=Initial residue

T_x=Time/days

b_x=Residue/time

6-Analysis using gas chromatography and mass spectrometry (GC/MS)

Ballee, *et al*. 1976; Rouchaud, *et al*. 1988 and Putnam, *et al*. 2003. GC/MS-analysis conducted on an Aglient7890B gas-chromatograph with a direct capillary interface and fused silica capillary column HP-5MS (30mx0.25mmx0.25m film-thickness) and a 5977 A MSD Aglient mass spectrometric detector. Helium-gas used as a carrier-gas in pulsed split mode with split ratio about of 1.0ml/min (10:1). Injection volume was 1µl and solvent delay was 4 minutes. The GC temperature program was set at 500⁰C for 0.5min., and then ramped to 1900⁰C at a rate of 10⁰C /min for 1 min., followed by 10 ⁰C/min ramped to 300⁰C and 2⁰C hold (total run time 29.5 minutes, injector temperature 2800 ⁰C). Wiley mass spectral data base Library was used to identify EI mass spectra.

RESULTES AND DISSCUSSION

At pH 5 and 7, chlorothalonil is resistant to hydrolysis Szalkowski&Stallard, 1977 and U.S. EPA, 1999. According to basic-condition (pH9), compound degradation into product categories; (3- cyano - 2, 4, 5, 6-tetrachlorobenzamid) and (4 - hydroxyl - 2, 5, 6 trichloroisophthalonitrile), Szalkowski, and Stallard, 1977.

The reductive - dechlorination; oxidative-dechlorination / hydrolysis and base-hydrolysis are postulated as pathways for “chlorothalonil” breakdown in aquatic-systems by Kwon and Armbrust (2006). Fig. 2. Chlorothalonil has a half-life hydrolysis “30-60 days” according to the US EPA (1999).

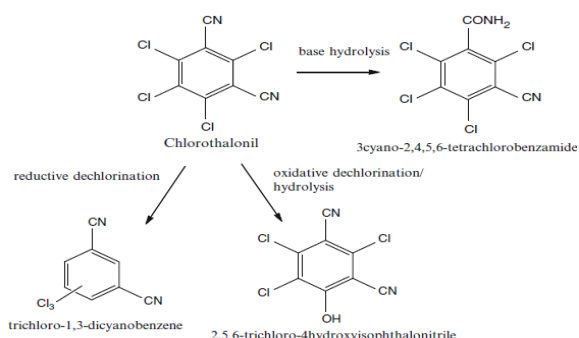


Figure 2. Shows a proposed chlorothalonil breakdown route in the aquatic environment according to Kwon, and Armbrust, 2006.

The majority of pesticides sold as a concentrated-form and suspended or dissolved by waters when treated on crops. Wells, ponds, rivers, and municipal water systems are all possible sources of this water. Dissolved minerals amount, organic-matter and pH of water changes depend on it source. Hydrogen number H⁺ and hydroxyl OH ions in solutions determine pH which the acidity measures or water alkalinity. Lower-pH more solution acidic and higher-pH more solution alkaline. Water-pH (7) is a neutral means equal-quantity of hydroxyl-ions and hydrogen. Water alkaline with high content of mineral/iron can be found in several parts of Michigan. Furthermore, water-pH from natural-sources can be change seasonally (Annemiek Schilder, 2008).

The major of pesticides formulations e.g. emulsifiable concentrations, dry, flowables and wetttable powders are designed to diluted/water. Some pesticides can be degraded or chemically broken down when the pH of the water exceeds 7 (creating alkaline conditions). This process is known as hydrolysis. Insecticides, in comparison to fungicides, herbicides, defoliant, or growth regulators, are far more vulnerable to hydrolysis. Insecticides containing organophosphates and carbamates are more vulnerable than those containing chlorinated hydrocarbons. Some pesticides degrade quite quickly. In the pH range of 8 to 9, the rate of hydrolysis can be quite rapid. Hydrolysis rate increases around 10-times for every pH point increase. Alkalinity degree of water, pesticides susceptibility and pesticide time contact of water and temperature degree of mixture all influence severity of losses caused by alkaline hydrolysis. The problem can be solved by reducing water-pH to recommended-range 4-7 before adding of pesticides. These

done using appropriate-amounts of acidifying substance or buffering. It should be emphasized that the buffering has no effect on the pesticide's residual action. The buffering effect begins during mixing, persists through storage in tank and doesn't end until water in spray-droplet has evaporated. The fixed-copper-fungicides, such as basic-copper-sulphate, copper-oxide and Bordeaux-mixes shouldn't buffer since acid-solution may be makes metals-soluble, causing phytotoxicity when sprayed on plants. Straight acidifying agents, as well as surfactants and nutritious components like as trace elements, may be used to acidify tank solutions. The most accurate determine method water-pH using of pH-meter. The use of tested materials, such as litmus paper, is unreliable and can result in errors of up to two pH points. Their air-liquid-color-indicators “for example” Bromothymol Blue can be detecting pH to within half-point. The (pH) of water-sources for both surface and ground does fluctuating throughout time. In most cases, the pH changes to more of alkaline-state. Generally, it's critical understand water-pH using with pesticides, also susceptibility of pesticides to hydrolysis. It's preferable to combine pesticide right before applying them, and only in quantity, that will be utilized in shortest amount of the time. If conditions dictate, the water-pH should be adjusted to optimum-level. (Howard, 2001).

The results of chlorothalonil residues occurring in different pH through different hours are illustrated in Tables, 2, 3 and 4, and showed that, the pH degrees, temperatures and exposure period influenced the persistence of chlorothalonil.

It is clearly evident that chlorothalonil was hydrolyzed more rapidly in the alkaline media (pH9) than the other tested pH degrees at all tested temperatures.

The percent loss of chlorothalonil at pH9 and 25 °C was 2.6 percent after six hours, whereas the loss percentage of chlorothalonil in acidic pH4 and neutral solutions pH7 at the same temperature and time were 1.4 percent and 1.6 percent, in acidic and neutral solutions, respectively. 6.4 and 6.8 degradation percentage from the starting concentration (500 ug) were recorded after 336 hours (14 days). After 336 hours, the amount of chlorothalonil in the alkaline media at 25 °C had fallen to 468 ug, a loss of 6.4 percent.

Furthermore, after six hours of exposure to pH4, pH7, and pH9 at 35 °C, the percent losses of chlorothalonil were 1.6, 2 and 6.8%, respectively. The total losses of chlorothalonil at 35 °C after 336 hours from exposure to varied pH solutions were 6.8, 7.2, and 70% at pH4, pH7, and pH9, respectively.

Data in Tables (2, 3& 4) cleared that after six hours of exposure to pH4, pH7, and pH9, the loss percentages of chlorothalonil were 2.2, 2.4, and 10.4 %, respectively, at 45 °C, whereas after 96 hours of exposure to the different pH solution, the loss percentage of chlorothalonil were 5, 5.4, and 40 percent, respectively, at the previously mentioned temperature (45 °C). However, after 336 hours at 45 °C, the amount of chlorothalonil in the acidic and neutral mediums reduced to 310 ug and 300 ug, respectively, with a percent loss of 38 and 40%. The amount of chlorothalonil in the solution reduced to 7 ug after 336 hours of exposure to pH9 at 45 °C, with a percent loss of 98.6%.

In general, the data demonstrated that chlorothalonil is slowly hydrolyzed in acidic solutions, as shown

previously. In comparison to acidic and neutral solutions, hydrolysis occurs more quickly in basic solutions, and the dissipation of chlorothalonil from different pH solutions occurs more quickly as both pH and temperature rise.

The calculated half-life times for chlorothalonil in pH4, pH7 and pH9 were 722, 481, and 121 hours at 25 °C while, at 35 °C the half- life were 482, 368, and 86 hours in pH4, pH7 and pH9, respectively. These values reached to 325, 251 and 51 hours at 45 °C from exposure to pH4, pH7 and pH9, respectively.

Table 2. Effect of pH4 on chlorothalonil stability.

Time/h	Chlorothalonil at 25 °C		Chlorothalonil at 35 °C		Chlorothalonil at 45 °C	
	ug	Loss %	ug	Loss %	ug	Loss %
	initial	500	0	500	0	500
1	499	0.2	498	0.4	497	0.6
2	497	0.6	495	1	493	1.4
6	493	1.4	491	1.6	489	2.2
24	490	2	487	2.6	485	3
48	486	2.8	483	3.4	480	4
72	482	3.6	479	4.2	477	4.6
96	479	4.2	477	4.6	475	5
120	476	4.8	474	5.2	472	5.6
192	473	5.4	470	6	370	26
336	468	6.4	466	6.8	310	38
DT 50/h	722		482		325	

Initial = one hour before exposure

Table 3. Effect of pH7 on chlorothalonil stability.

Time/h	Chlorothalonil at 25 °C		Chlorothalonil at 35 °C		Chlorothalonil at 45 °C	
	ug	Loss %	ug	Loss %	ug	Loss %
	initial	500	0	500	0	500
1	498	0.4	497	0.6	495	1
2	495	1	493	1.4	491	1.6
6	491	1.6	490	2	488	2.4
24	487	2.6	485	3	484	3.2
48	484	3.2	481	3.8	479	4.2
72	480	4	477	4.6	475	5
96	477	4.6	475	5	473	5.4
120	473	5.4	471	5.8	469	6.2
192	470	6	468	6.4	364	27.2
336	466	6.8	464	7.2	300	40
DT 50/h	481		368		251	

Initial = one hour before exposure

Table 4. Effect of pH9 on chlorothalonil stability.

Time/h	Chlorothalonil at 25 °C		Chlorothalonil at 35 °C		Chlorothalonil at 45 °C	
	ug	Loss %	ug	Loss %	ug	Loss %
	initial	500	0	500	0	500
1	490	2	485	3	480	4
2	485	3	478	4.4	460	8
6	477	2.6	466	6.8	448	10.4
24	461	7.8	451	9.8	440	12
48	450	10	442	11.6	420	16
72	440	12	422	15.6	370	26
96	400	20	380	24	300	40
120	315	37	290	42	180	64
192	275	45	250	50	91	81.8
336	175	65	150	70	7	98.6
DT 50/h	121		86		51	

Initial = one hour before exposure

Effect of direct sunlight on chlorothalonil.

Table 5 shows that after being exposed to direct sunlight, the proportion of chlorothalonil breakdown increased progressively. It is known that photodecomposition is inversely proportional to the

exposure time. It was discovered that when chlorothalonil residues exposed to directly sunlight, especially the lengthy periods of time, they deteriorated significantly. Time of half-life was calculated to be 18.84 hours. After 1, 2, 4, 6, 12, 24, 48, 96,192 and 336 hours. The loss percentages for chlorothalonil were 6, 12, 19.8, 34, 40, 51.4, 59.8, 73.4, 90 and 100 % respectively. After 336 hours of direct sun exposure, undetectable amount of chlorothalonil was found.

Table 5. Effect of sunlight on the stability of chlorothalonil

Period /hours	ug	Loss %
Initial	500	0
1	470	6
2	440	12
4	401	19.8
6	330	34
12	300	40
24	243	51.4
48	201	59.8
96	133	73.4
192	50	90
336	UND	100
DT 50 /h	18.84	

Initial = one hour before exposure

UND = undetectable.

Aqueous-chlorothalonil dissolves the concentrations absorbed sunlight's in wavelength range about, (300 to 340nm), and the direct-photolysis is highly degradations pathways of this fungicides Leistra, and Van Den Berg, 2007.

Photolytically, the "chlorothalonil" destroyed more quickly in natural-waters [DT50=0.21-0.76 days] than, in aqueous buffered solution [pH7;DT50=1.1 days] when directly exposure to lights 300-400nm, Wallace *et al.* 2010.

Monadjemi, *et al.* 2011, mentioned that, the photo-degradation chlorothalonil on simulate plant-surface was investigate by paraffin-wax irradiated between 300 and 800nm wavelengths, and the results obtained indicated that, the chlorothalonil was sensitivity to direct-photolysis "as well as" surface-penetration at half-life 5.3 days. Additionally, he cleared that, major degradation action represented in dechlorination reductive. Waltz *et al.* 2002, investigated photo-degradations of "hydroxychlorothalonil" HC, metabolites of major chlorothalonil-hydrolytic, and result obtained cleared that, "HC" in samples of waters were expose to simulate sunlights [via using lamps] radiation was absorbed and this substance was "photolyzed" with (t_{1/2} of 33-37min).

Identification of photodegradation products of chlorothalonil, using GC/MS after exposure to direct sunlight.

The chlorothalonil samples were analyze after storage in sunlight of 14-days use (GC-MS) to identifying of products degradations Table 6.

Some of researches in degradations were published of "chlorothalonil" Sato, and Tanaka 1987, Rouchaud, *et al.* 1988, Katayama, *et al.* 1992, Motonaga *et al.* 1996, Katayama *et al.* 1997, Regitano, *et al.* 2001, Sakkas, *et al.* 2002 and Kwon&Armbrust 2006. Compound (4-hydroxy-2,5,6-trichloroisophthalonitrile) "metabolite II" was reported as a predominant-metabolites in samples environments Ballee *et al.* 1976, Rouchaud, *et al.* 1988 and Ukai, *et al.*

2003. The metabolites showed that, high persistent; mobile; and toxic, than parent compound, recording on suppression of soil-microorganisms, Van Doorn, *et. al.* 1995, Hamish, and Jones, 1997, Ukai, *et. al.* 2003. The others of metabolites product cited in literature, the results of reaction

lead to substitutions of “Cl” in chlorothalonil atoms and diversion of “CN” function-groups to amides; thiazoles, and acidic-groups Rouchaud, *et. al.* 1988, Regitano *et. al.* 2001, Putnam, *et. al.* 2003 and Kwon, and Armbrust 2006.

Table 6. GC/MS-derived mass-ions (m/z) and percent relative-abundances of chlorothalonil and degradation products.

Analyte	Primary ions m/z (% relative abundance)	Chemical structure
Chlorothalonil (2,4,5,6-tetrachloro isophthalonitrile)	266 (100), 264 (78), 268 (48), 270 (10.4)	
Pentachloronitrobenzene (1,2,3,4,5-pentachloro-6-nitrobenzene)	295 (100), 297 (64), 293 (62)	
Metabolite II (methyl ester) (4-hydroxy-2,5,6-trichloro isophthalonitrile)	260 (100), 262 (90), 264 (40), 232 (90)	
Metabolite VI (2,4,5-trichloro isophthalonitrile).	230 (100), 232 (96), 234 (31)	
Metabolite IV (2,5,6-trichloro-4-methoxy isophthalonitrile)	260 (100), 262 (96), 232 (90), 234 (85)	
Metabolite VII 2,5,6-trichloro-4-(methylthio isophthalonitrile)	278 (100), 276 (99), 280 (35), 243 (90)	
Metabolite V (methyl ester) (1-Carbamoyl-3-cyano-4-hydroxy-2,5,6-trichlorobenzene).	264 (100), 266 (95), 278 (50), 280 (60)	
1,3-dicyanobenzene (isophthalonitrile)	128 (100), 129 (9.8)	

REFERENCES

Abu-Zahw. M. M; M. E. A. Hegazy; S. M. Doghiem; M. M. Almaz and A. Shahin (1988): Thermal and photo decomposition of fonitrothion and fenvalerate: Insecticides Bull. ENT. SOC. Egypt, Econ. Ser, 17:193-198.

Alicia Chaves (2007): Analysis of chlorothalonil and degradation products in soil and water by GC/MS and LC/MS. Chemosphere 71 (2008) 629–638.

Annemiek Schilder (2008): Effect of water pH on the stability of pesticides, Michigan State University Extension, Department of Plant Pathology - March 18, 2008.

Ballee, D.L., Duane, W.C., Stallard, D.E., Wolfe, A.L., (1976): Chlorothalonil. Analytical Methods of Pesticide and Plant Growth Regulators. Academic Press, pp.263–274.

CDPR, California department of Pesticide Regulation (2005): Chlorothalonil: risk characterization document for dietary exposure <http://www.cdpr.ca.gov/docs/risk/rcd/chlorothalonil.pdf>.

Hamish, K., Jones, D., 1997. The Agrochemicals Handbook. Royal Society of Chemistry, England.

Hong, F. and S. Pehkonen (1998): Hydrolysis of phorate using simulated Environmental conditions, rates, mechanism and product analysis .j. Agric. food chem. 46, 1192-1199.

Howard M. Deer (2001): EFFECT OF WATER PH ON THE CHEMICAL STABILITY OF PESTICIDES, Extension Pesticide Specialist Richard Beard, Extension Equipment and Machinery Specialist Utah State University, Logan UT 84322-4620.

Jones, R. L and F. A. Norris (1998): Factors affecting degradation of aldicarb and ethoprop. J. of Nematology 30(1):45-55.

Katayama, A., Itou, T., Ukai, T., (1997). Ubiquitous capability to substitute chlorine atoms of chlorothalonil in bacteria. J. Pest. Sci. 22, 12–16.

Katayama, A., Ukai, T., Nomura, K., Kuwatsuka, S., (1992) .Formation of a methylthiolated metabolite from the fungicide chlorothalonil by soil bacteria. Biosci. Biotech. Biochem. 56, 1520 -1521.

- Khay, S; A. M. A. El-Aty; C SoonKil; C Jeong Heui; M. I.R. Mamun; A. Goudah; S. HoChul and S. JaeHan, (2008): Development of extraction procedures for the determination of imidacloprid: application to residue analysis and dynamics of two formulations in Chinese cabbage. *Biomedical Chromatography*. 2008. 22: 6, pp 581-589.
- Kwon JW, Armbrust KL (2006): Degradation of chlorothalonil in irradiated water/sediment systems. *J Agric Food Chem* 54:3651-3657.
- Lartiges. S. B and P. P Garrigues (1995): Degradation kinetics of organo phosphorus and organ nitrogen pesticides in different waters, under various environmental conditions. *Environ. Sci. Technol.* 29, 1246-1254.
- Lee, P. W; S. M. Stearns; H. Hernandez; W. R. Powell and M. V. Naidu (1989): Fate of dictotophos in the soil environment. *J. Agric, food chemistry*. 27, 1169-1174.
- Leistra M, Van Den Berg F (2007): Volatilization of parathion and chlorothalonil from a potato crop simulated by the PEARL model. *Environ Sci Technol* 41:2243-2248.
- Monadjemi S, El Roz M, Richard C, Ter Halle A (2011): Photoreduction of chlorothalonil fungicide on plant leaf models. *Environ Sci Technol* 45:9582-9589.
- Motonaga, K., Takagi, K., Matumoto, S., (1996): Biodegradation of chlorothalonil in soil after suppression of degradation. *Biol. Fert. Soils* 23, 340-345.
- Moye, H.A; Y Malagodi.; G. L Leibe and P.G Wislocki, (1987): Residues of avermectin B1a potato crop and soils following soil treatment with (C14) Avermectin B1a. *J Agric. Food chem.* 35, 859-864.
- Nakayama, A; M. Sukekawa and Y. Eguchi, (1997): Stereochemistry and active conformation of a novel insecticide, acetamiprid. *Pesticide Science*. 1997. 51: 2, 157-164. 19 refs.
- Putnam, R.A., Nelson, J.O., Clark, J.M., (2003): The persistence and degradation of chlorothalonil and chlorpyrifos in a cranberry bog. *J.Agric. Food Chem.* 51, 170-176.
- Raj. P. S and M. Chiba; (1985): Solubility of Benzomyl in water and different P^H., and its conversion to methyl, 2-Benzimidazole carbamate, 3-butyl -2,4-dioxi [1, 2-a]-5-triazinobenzimidazole, and 1-2-benzimidazolyl 3-n-butyl urea. *J. Agric Food. Chemistry*, 33, 63-67.
- Ramesh, A and M. Balasubramanian (1999): Kinetics and hydrolysis of fenamiphos, fipronil and trifluralin in aqueous buffer solutions, *journal of agricultural and food chemistry*, 47 (8): 3367-3371.
- Regitano, J.B., Tornisiello, V.L., Lavorenti, A., Pacovsky, R.S., (2001). Transformation pathways of C-14-chlorothalonil in tropical soils. *Arch. Environ. Con. Tox.* 40, 295-302.
- Rouchaud, J., Roucourt, P., Vanachter, A., Benoit, F., Ceustermans, N; (1988). Hydrolytic biodegradation of chlorothalonil in the soil and in cabbage crops. *Toxicol. Environ. Chem.* 17, 59-68.
- Sakkas VA, Lambropoulou DA, Albanis TA (2002): Study of chlorothalonil photodegradation in natural waters and in the presence of humic substances. *Chemosphere* 48(9):939-945.
- Sapozhnikova Y, Wirth E, Schiff K, Brown J, Fulton M (2007): Antifouling pesticides in the coastal waters of Southern California. *Mar Pollut Bull* 54:1972-1978.
- Sato, K., Tanaka, H., (1987). Degradation and metabolism of a fungicide, 2, 4, 5, 6 tetra-chloroisophthalonitrile (TPN) in soil. *Biol. Fert. Soils* 3, 205-209.
- Szalkowski MB, Stallard DE (1977): Effect of pH on the hydrolysis of chlorothalonil. *J Agric Food Chem* 25(1):208-210.
- Tomlin CDS (2000): The pesticide manual, 12th edn. The British Crop Protection Council, Surre, UK, pp 620-621.
- Ukai, T., Itou, T., Katayama, A., (2003): Degradation of chlorothalonil in soils treated repeatedly with chlorothalonil. *J. Pest. Sci.* 28, 208-211.
- United States Environmental Protection Agency (2007): Office of Pesticide Programs. Potential risks of labeled chlorothalonil uses to the federally listed California red legged frog. 2007, US Environmental Protection Agency Office of Pesticide Programs Environmental Fate and Effects Division: Washington, D.C.
- United States Environmental Protection Agency (1999): Office of Pesticide Programs. Special Review and Reregistration Division., Reregistration eligibility decision: chlorothalonil (1999) US Environmental Protection Agency Office of Pesticide Programs Special Review and Reregistration Division :Washington, D.C.
- USGS National Water Quality Assessment Data Warehouse 2007.
<http://web1.er.usgs.gov/NAWQAMapTheme/index.jsp>
- van Doorn, C., Vink, M., van der Poll, J.M., 1995. Gas Chromatographic determination of chlorothalonil and its metabolite 4 - hydroxyl - 2, 5, 6-trichloroisophthalonitrile (HTI) in water. *Chromatographia* 40, 458 - 462.
- Wallace DF, Hand LH, Oliver RG (2010): The role of indirect photolysis in limiting the persistence of crop protection products in surface waters. *Environ Toxicol Chem* 29(3):575-581
- Waltz C, Armbrust K, Landry G (2002): Chlorpyrifos and chlorothalonil in golf course leachate .
<http://www2.gcsaa.org/gcm/2002/sept02/pdfs/09chlorpyrifos.pdf>

تأثير درجة حموضة الماء والتعرض المباشر لأشعة الشمس على الثبات الكيميائي للمبيد الفطري الكلوروثالونيل أيمن سميح عربي سلومه¹ و علي عطا شلبي²

¹ قسم بحوث تحليل المبيدات - المعمل المركزي للمبيدات - مركز البحوث الزراعيه - الدقي - الجيزه - مصر.

² قسم وقايه نباتات - كلية الزراعه - جامعه الزقازيق - مصر.

الهدف من هذا البحث هو دراسة التحلل المائي لمحاليل الأس الهيدروجيني المختلفة عند الأس الهيدروجيني 4 و 7 و 9 بالإضافة إلى ثبات المبيد المستخدم (كلوروثالونيل) في ظل بعض العوامل البيئية المصرية، مثل ضوء الشمس المباشر وتقدير المنتجات الضوئية بعد تحلل الكلوروثالونيل باستخدام GC / MS. تُظهر البيانات أن تحطم الكلوروثالونيل من محاليل الأس الهيدروجيني المختلفة زاد بسرعة أكبر مع زيادة قيمة الأس الهيدروجيني ودرجة الحرارة و مدة التعرض عند مقارنتها بالمحاليل الحمضية والمتعادلة، وأن المبيد تم تحلله بالماء بسرعة أكبر في الوسط القلوي (pH9) مقارنة بقيم الأس الهيدروجيني المختبرة الأخرى وفقاً للبيانات. أظهرت النتائج أيضاً أنه بعد 336 ساعة من التعرض لأشعة الشمس المباشرة، لم يتم العثور على مستوى يمكن اكتشافه من المبيد تحت الدراسة. تم تحديد المركب 4-hydroxy-2,5,6-trichloroisophthalonitrile باعتباره ناتج التحطم الرئيسي في العينات البيئية بعد فحص منتجات التحلل الضوئي باستخدام GC / MS بعد التعرض لأشعة الشمس المباشرة.