American-Eurasian J. Agric. & Environ. Sci., 19 (2): 136-142, 2019
ISSN 1818-6769

DOI: 10.5829/idosi.aejaes.2019.136.142

Disappearance of Iprodione Residues In/On Strawberry Fruits and Soil Under Field Conditions

Maher A. Hammad

Plant Protection Department, Faculty of Agriculture,
Ain Shams University, P.O. Box: 68, Hadayek Shoubra 11241, Cairo, Egypt

Abstract: Fruit rots disease of strawberry caused by fungal pathogens (*Botrytis cinerea*, *Colletotrichum* spp., *Phytophthora cactorum* and *Gnomonia comari*) is one of the important problems faced strawberry growers in Egypt. The most common fungicide used to control such disease is iprodione fungicide (Rovral®50%WP). The present study aimed to investigate fate of the fungicide when applied on strawberry plant. The field experiment has been done with 3 rates of application (*i.e.* recommended, recommended + half and double recommended rates of application during the season of 2017/2018, at El-Nobaria district, Abo-Elmatamer, El-Behaira Governorate, Egypt. The fungicide was applied by using snake sprayer fitted with one nozzle on foliage at the blooming stage. Agilent GC Model 6890 equipped with Ni^{63} -electron capture detector was used to determine the residues on fruits and soil. The fruits and soil samples were collected after two hours (initial time), 1, 3, 7, 14 and 21 days after application. The iprodione initial deposits, degradation percentages of residues, residues level 50% (RL_{50}), residues level 90% (RL_{90}) and pre harvest intervals (PHIs) of the fungicide were determined as the criteria of concern. Results revealed that strawberry fruits remained higher initial amounts by 11.24, 16.59, 23.02 mg kg^{-1}. As for RL50, RL90 and PHIs values, iprodione showed (3.93, 4.26, 4.31 days) and (12.2, 15.1, 16.0 days) and (13.37, 19.59, 23.28 days) in/on strawberry fruits at the recommended, recommended + half and double recommended rates of application, in/on strawberry, respectively. The corresponding calculated values on soil at recommended rate were 5.2 and 21.7 days for RL_{50} and $RL_{90,}$ respectively. In general, iprodione residues in/on strawberry fruits and soil had low persistence. In addition, the strawberry fruits could be consumed safely after 13.37 days when treated at recommended rate compared by Maximum Residue Limit (MRL) of Codex Aimentarias Commission value of iprodione residues in/on strawberry fruits (15 mg kg^{-1}).

Key words: Pesticide Residues · Behavior · Degradation · Persistence · Iprodione · Strawberry

INTRODUCTION

In Egypt, strawberry cultivation is widely spread with area of 5, 416.66 hectares and total production about 367818 kg/ha [1]. Consumption appropriate amounts of vegetables increase exposure of pesticide concern but prevent many chronic diseases [2]. Iprodione is a contact fungicide belongs to synthetic dicarboximide group that prevents spores germination and inhibits mycelium growth of various fungi specially that cause fruit rots infection. Excessive use of fungicides resulted in the risk of the residual contamination of strawberry which reduces their commercial value and consumer acceptance. Many factors determine environmental fate of pesticides including chemical and environmental characteristics, *i.e.* soil properties, adsorptive behavior, solubility, moisture, pH, temperature and precipitation, in addition to agricultural practices and risk assessment decisions based on predicted levels of exposure, behavior of the pesticide in the field as mobility and degradation rate. Maximum Residue Limits (MRLs) exceeding indicates over-use of pesticides and links to problems of developmental neurobehavioral of immune cells altered function [3]. According to Grosicka-Maciąg [4], the residues of pesticides, which break down slowly and stay in the environment for a long time, contaminate food and may cause health adverse effects. It is worth noting that the MRLs are different in many countries. For example, in

Corresponding Author: Maher A. Hammad, Plant Protection Department, Faculty of Agriculture, Ain Shams University, Cairo, P.O. Box: 68, Hadayek Shoubra 11241, Cairo, Egypt.

Poland thiram pesticide MRL value is 10 mg kg^{-1} [5], it is 7 mg kg^{-1} in Canada [6], in Egypt, 5 mg kg^{-1} [7] and MRL value in Australia is 3 mg kg^{-1} [8].

Food safety is a main concern of public health all over the world and food consumption is the main pathway for human contaminants exposure. So, food contamination with pollutants is a master issue, with repercussion on human health [9]. Pesticide residues data in food serve to clarify and evaluate final situation of international trade problems and potential human risk to help decision makers risk issues. Such data should be concentrated and to study cumulative risk assessment (cocktail effect), carcinogenicity and endocrine disruption [10]. In Egypt, multi-efforts have been taken to study the behavior of pesticide residues in assessment possible risks in different matrices of environment. Organic pollutants in food increase health risks; all over the worldwide nations including Egypt didn't supply safe hazardous chemical standard ratios.

Reliance on pesticide residues is dif?cult to tolerate because of long-term adverse effects unintended on public health in particular. Reliable pesticide residues status analysis data in foods may be of great value indicating probable risks on international trade and human health of exposure to pesticide residues [11]. Periodically status records of pesticide residues in markets provide data take regulatory actions to ensure excessive residues do not recur [12, 13]. Based on the aforementioned facts, this study aimed to determine the iprodione residues in/ on strawberry fruits and surrounding soil under canopy as well as determination of its initial deposits, degradation percentages of residues RL_{50}, RL_{90} and PHIs.

MATRIALS AND METHODS

Strawberry Plants: Fresh strawberry transplants (*Fragaria×ananassa* cv. Festival) were obtained from Arid Land Agriculture Research Institute, Faculty of Agriculture, Ain Shams University. Transplants were planted on 19th of September 2017/2018 winter season, in the open field of farm located in El-Nobaria district, Abo-Elmatamer, El-Behaira Governorate, Egypt to investigate the effect of foliar spraying with three different doses of iprodione on strawberry plants during the bloom stage, when the fruit rots severity reached to 3%, to control disease.

Tested Fungicide and Application Rates: Iprodione (Rovral® 50%WP), (N- (3, 5- dichlorophenyl) -3- isopropyl- 2, 4- dioxoimidazolidine -1- carboxamidis) was purchased from Agrimatco company, El-neanay Office, Tanta Governorate, Egypt. Rates of iprodione application were chosen on the basis of recommended dose (90 g 100 L^{-1} water), 1½ recommended dose (135g 100 L^{-1} water) and double dose (180g 100 L^{-1} water) on strawberry.

Treatments and Experimental Design: The field experimental area with sandy loam soil was divided into 12 main plots (four treatments with three replicates); each plot covered 42 m^2 with 12 adjacent rows of 6 m in length. The distance between each row was 50 cm. Transplants were cultivated in each row with 30 cm between plants. Fertilization was applied with standard recommendations of the Egyptian Ministry of Agriculture and Land Reclamation. Three doses of iprodione fungicide were sprayed on foliage at the blooming stage, in 15th of January, with the beginning of the fruit rots infection appeared (3% severity) by using snake sprayer fitted with one nozzle and compared with untreated plants as follows: Control (sprayed with tap water), Iprodione 90 g, 135g and 180g /100 L^{-1} water. Each target plot was sprayed with one of the previous treatments separately. Plots were arranged in a complete randomized block design. The experiment was performed in three replicates to determine pesticide residues at initial time (2 hours after application), 1, 3, 7, 14 and 21days after application. Three samples of strawberry fruits (1kg/treatment) were taken randomly and transported immediately in ice box to the laboratory and kept in freezer at -20°C till analyses.

Extraction and Clean Up: Iprodione was extracted and cleaned up from strawberry fruit samples according to the methods adopted by QuEChERS [14] and according to the methods adopted by QuEChERS [15] but soil samples were extracted by using Liquid Extraction (LLC) and clean up according to the method adopted by Zhubo Deng *et al.* [16].

Determination of Iprodione Residues: Gas chromatography, Agilent GC Model 6890 equipped with Ni^{63} -electron capture detector was used in this study. GC conditions: capillary column PAS-5 methyl silicone (30m x 0.32 mm internal diameter (i.d) x 0.25 µm film thickness), carrier gas: A nitrogen gas flow rate was 4 ml min^{-1}; injector and detector temperatures were 280°C and 300°C, respectively. The initial column temperature 200°C for 2 min., raised at 5°C/min then held at 280°C for 10 min. These conditions with good separations and high sensitivity were obtained with retention time 5.1 min for iprodione.

Table 1: Recovery percentages (%) of Iprodione fungicide from spiked samples of strawberry fruits and soil.

Spiked samples	Iprodione			
Fruits	84.12[a]	89.57[b]	92.38[c]	95.26[d]
Soil	81.29[a]	88.79[b]	90.18[c]	93.23[d]

- Values in the table represent the average of three replicates.
- Spiked sample levels (a, b, c and d represent 0.5, 1, 2 and 2.5 µg g^{-1}), respectively.
- Limits of detection (LOD) were 0.01µg g^{-1} for iprodione from spiked samples of strawberry fruits and soil.

Recovery Tests: To estimate the recovery percentages, known quantities of iprodione were added to control samples at four levels (0.5, 1.0, 2.0 and 2.5 µg g^{-1}), extraction and clean-up processes were carried out as described above. The average recovery percentages for the iprodione pesticide were 84.12[a], 89.57[b], 92.38[c] and 95.26[d] % (fruits) and 81.29[a], 88.79[b], 90.18[c] and 93.23[d] % (soil) for the four tested levels, respectively (Table 1). All obtained results were corrected by their mean of recovery percentages. The degradation constant (K) and degradation periods (RL_{50} and RL_{90}) of iprodione level were calculated as follows: rate of degradation K = 2.303 × slope and the half-life period RL_{50}=0.693/K.

RESULTS AND DISCUSSION

Residues Of Iprodione In/on Strawberry Fruits: Residues and degradation percentage of fungicide iprodione in/on strawberry fruits were illustrated in Table (2) and Figures (1, 2 and 3) at the recommended, recommended and half and double recommended rates of application in/on strawberry, respectively. The initial residue deposits, which remained in/on unwashed strawberry fruits two hours after application treatment were found to be 11.24, 16.59, 23.02 mg kg^{-1}. This amounts decreased to 9.21, 13.62, 16.90 mg kg^{-1} one day after the application indicating degradation percentages of 18.06, 17.9, 26.58 %. Residues of iprodione in/on strawberry fruits was gradually decreased to 7.99, 9.01, 15.40 and 2.1, 5.73, 6.89 and 1.7, 1.89, 2.79 and 0.18, 0.91, 1.8 mg kg^{-1}corresponding degradation percentages of 28.91, 45.69, 33.1 and 81.31, 65.46, 70.06 and 84.87, 88.60, 87.88 and 98.39, 94.51, 92.18 % after 3, 7, 14 and 21 days of treatment application, respectively. The total amount dissipated to 84.87, 88.60 and 87.88 % at the end of 2 weeks of application. The pesticide residues dissipation in/on crops depends on application type, plant species, climatic conditions, dosage, PHIs values between application and harvest time [17]. Examination of the considered criteria represented by the established regression lines, *i.e.* slope, degradation constant (K) and RL_{50}, RL_{90} proved significant differences in persistence behavior of the targeted pesticide (Table 2). The iprodione degradation constant (K) values were 0.1763, 0.1627, 0.1611 in/on strawberry fruits. As for RL_{50}, RL_{90} and PHIs values, iprodione showed (3.93, 4.26, 4.31), (12.2, 15.1, 16.0) and (13.37, 19.59, 23.28) days in/on strawberry fruits, respectively. These results indicated the same trend of degradation behavior of iprodione fungicide with the different rates of application in/on strawberry fruits. Data in the same table indicated that low residue half-live for iprodione fungicide in/on strawberry fruits (3.39 days) less than the maximum residue limit (MRL) of iprodione residues in/on strawberry (15 mg kg^{-1}) according of Codex Aimentarias Commission [18] and concerning health aspects. Consequently, strawberry fruits can be consumed safely after 13.37 days of treatment by recommended rate of application.

Residues of Iprodione on Soil: Residues and degradation percentage of fungicide iprodione on soil were illustrated in Table (3) and Figure (4) at the recommended rate of application on soil. The initial residue deposits, which remained on soil, two hours after treatment, was 24.02 mg kg^{-1}. This amount decreased to 21.60 mg kg^{-1} one day after the application indicating degradation percentages of 10.07 %. Residues of iprodione on soil were gradually decreased to13.72, 6.86, 5.85, 3.20 mg kg^{-1} corresponding degradation percentages of 42.88, 71.44, 75.64, 86.67 % after 3, 7, 14 and 21 days of application, respectively. Examination of the considered criteria represented by the established regression lines, *i.e.* slope, degradation constant (K) and RL_{50}, RL_{90} proved significant differences in persistence behavior of the targeted pesticide. The iprodione degradation constant (K) value was 0.133 on soil. As for RL_{50} and RL_{90} values, iprodione showed 5.2 and 21.7 days in soil. These results showed low residue half-life which mean high degradation behavior of iprodione fungicide on soil. Depends on Environmental Fate Assessment, the main routes of the dissipation were hydrolysis in neutral and alkaline environments (half-life pH 7 = 4.7 days; pH 9 = 27 minutes) and under microbial degradation conditions. All results of the mechanisms of dissipation referred that iprodione had low persistence to intermediate in the environment. In fact iprodione is highly mobile to intermediate in some soils, it is rapid and highly degradable in the environment thus, unlikely leaching into ground water. Furthermore, because iprodione as a foliar treatment application, absorbed by plants and/or degradation/metabolism on the

Table 2: Residues, degradation (%) and persistence (%) of iprodione in/on strawberry fruits.

	Recommended rate of application (90 g 100 L^{-1} water)			Recommended and half rate of application (135 g 100 L^{-1} water)			Double Recommended rate of application (180 g 100 L^{-1} water)		
Days after treatment	Residues mg kg^{-1}	Degradation %	Persistence %	Residues mg kg^{-1}	Degradation %	Persistence %	Residues mg kg^{-1}	Degradation %	Persistence %
Initial (2 hours.)	11.24	□	100	16.59	?	100	23.02	?	100
1	9.21	18.06	81.93	13.62	17.9	82.09	16.90	26.58	73.41
3	7.99	28.91	71.09	9.01	45.69	54.30	15.40	33.1	66.89
7	2.1	81.31	18.68	5.73	65.46	34.53	6.89	70.06	39.93
14	1.7	84.87	15.12	1.89	88.60	11.39	2.79	87.88	12.11
21	0.18	98.39	1.61	0.91	94.51	5.48	1.8	92.18	7.81
K	0.1763			0.1627			0.1611		
RL_{50} ($t_{1/2}$)	3.93			4.26			4.31		
RL_{90}	12.2			15.1			16		
PHI	13.37			19.59			23.28		

$K = \ln(2)/t_{1/2}$

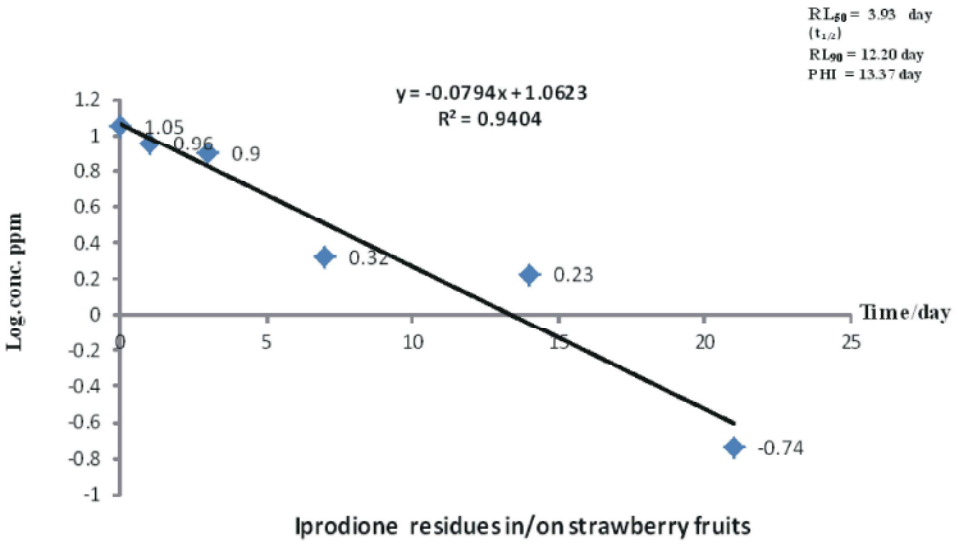

Fig. 1: Degradation line of iprodione applied at 1RD detected in/on strawberry fruits

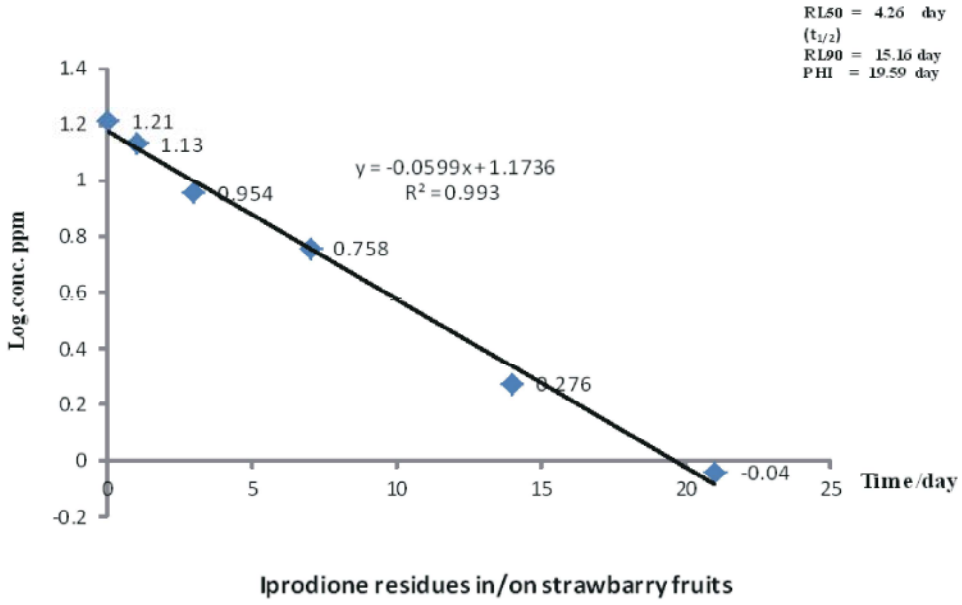

Fig. 2: Degradation line of iprodione applied at 1½ RD detected in/on strawberry fruits

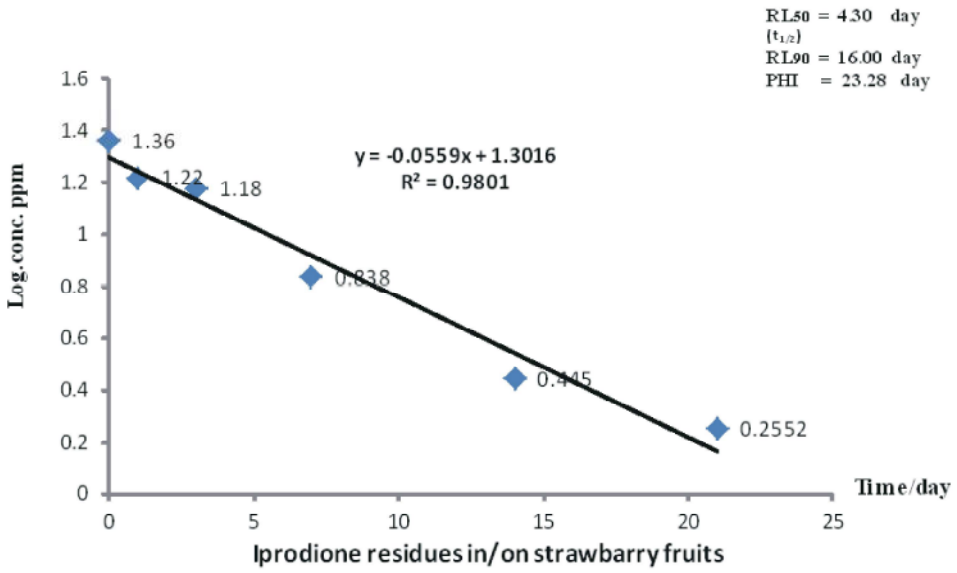

Fig. 3: Degradation line of iprodione applied at 2RD detected in/on strawberry fruits

Table 3: Residues of iprodione on soil using the recommended rate of application.

	Recommended rate of application (90g 100 L^{-1} water)		
Days after treatment	Residues mg kg^{-1}	Degradation %	Persistence %
Initial time (2 hours)	24.02	-	100
1	21.60	10.07	89.92
3	13.72	42.88	57.11
7	6.86	71.44	28.55
14	5.85	75.64	24.35
21	3.20	86.67	13.32
K		0.133	
RL_{50} (DT_{50})		5.2	
RL_{90}		21.7	

K= ln(2)/ DT_{50}

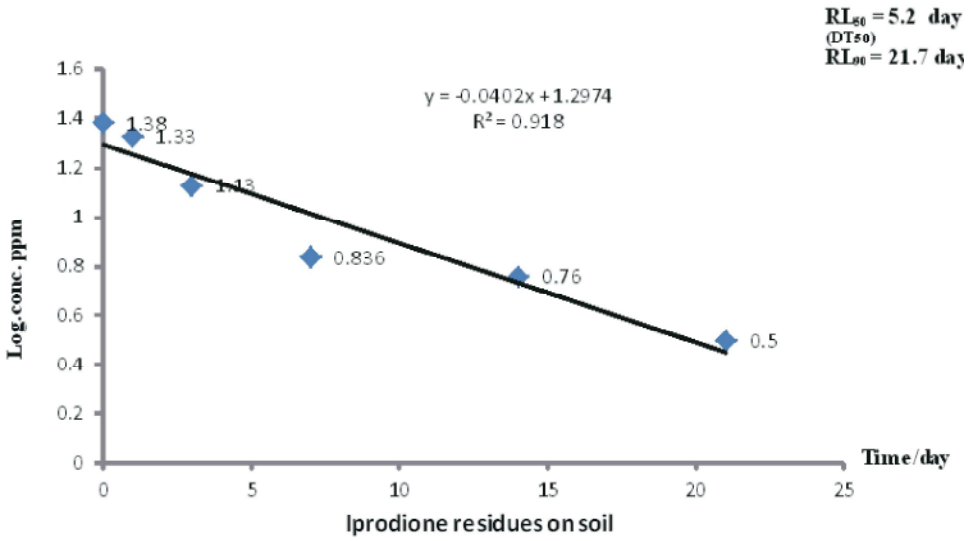

Fig. 4: Degradation line of iprodione applied at 1RD detected on soil.

plant surface will further mitigate the potential for water contamination [19]. The fate of fungicides and their transformation products (TPs) on the soil depends on the properties of its active ingredients and the degree of interaction with the soil particles or adsorption. The parameters such as the soil-sorption constant (Koc), adsorption, water solubility, the half-life and octanol/water partition coefficient (Kow) of insecticides in soil (DT_{50}) as well as the properties such as charge distribution, chemical functions, polarity and polarizability of both soil and fungicides molecules are all the characteristics that measure the persistence and movement of fungicides and their TPs in the soil [20]. In this study, fungicide residues with highly polar characteristics were found to be existent in the soil samples as iprodione. The persistence and mobility of iprodione in soil are also controlled by several processes such as (a) - chemical degradation (*i.e.* photolysis, hydrolysis, oxidation and reduction), (b) - microbial degradation with the aid of soil microorganisms [20]; the degradation process ranges from the formation of (TPs) the transformation products to decomposition of inorganic products, (c) - pesticides mobility includes volatilization, sorption, run-off, wind erosion, plant uptake and leaching . Furthermore, the fate of pesticides varies depending on the type of soil, agricultural practices and climate [20]. Half-life, which is the typical measurement for persistence, has ranged between 10 to 100 days for modern pesticides. Iprodione has low leach ability, moderately persistent in soil and volatile. These properties of the compound can be most likely explained why it was found positive in soil samples. Iprodione persistent and volatile in soil based on Henry's Law of Concentration. The soil serves as a purifying filter and as such contamination of groundwater is unlikely to happen.

However, Hamilton *et al.* [6] found that pesticide compounds were detected in water in different depth. Due to modernization, pesticides being developed are more water-soluble, thermo labil and more polar and have longer persistence to enable effective pest control [20]. Perhaps, this serves as inkling to the possibility of pesticide contamination in water. For underground water contamination, soil profile plays a very important role in determining the potential of pesticides to leach to underground water, the more organic content of soil, the greater persistence of the pesticide in the soil and the low leaching potential to underground water. Studies reported that bound residues present in the soil could be taken up by vegetation [21]. Pesticides behavior in soil depend on their persistence, leach ability, mobility and volatility. Nearly all of the pesticide residues detected in soil have low leaching potential according to the high (Koc). The compound's movement is therefore limited throughout and over the soil profile, such that there is less potential for groundwater contamination [22].

REFERENCES

1. FAOSTAT, 2017. http://www.fao.org/faostat/en/#data/QC.
2. Drouillet-Pinard, P., M. Boisset, A. Périquet, J.M. Lecerf, F. Casse, M. Catteau and S. Barnat, 2011. Realistic approach of pesticide residues and French consumer exposure within fruit & vegetable intake. Journal of Environmental Science and Health, Part B, 46(1): 84-91.
3. Cecchi, A., G.M. Sabino and G. Magnarelli, 2012. Environmental exposure to organophosphate pesticides: Assessment of endocrine disruption and hepatotoxicity in pregnant women. Ecotoxicol. Environ. Saf., 80: 280-287.
4. Grosicka-Maciąg, E., 2011. Biological consequences of oxidative stress induced by pesticides. Post. Hig.Med. Doœw., 65: 357-366.
5. Regulation of Agriculture and Rural Development Minister, 2008. Available online at file: ///C:/Users/Admin/Downloads/D20080201.pdf; cited on 17 Sept 2014.
6. Hamilton, D.J., A. Ambrus, R.M. Dieterle, A.S. Felsot, C.A. Harriss, P.T. Holland, A. Katayama, N. Kurihara, J. Linder, J. Unsworth and S.S. Wong, 2003. Regulatory Limits for Pesticide Residues in Water (IUPAC Technical Report). Pure. Appl. Chem., 75(8): 1123-1155. http://prrp.hc-sc.gc.ca/mrl-lrm/results-eng.php
7. Dogheim, S.M., S.A. Gad Alla and A.M. El-Marsafy, 2001. Monitoring of pesticide residues in Egyptian fruits and vegetables during 1996. Journal of AOAC International, 84(2): 519-531.
8. Keats, A., 2013. Thiram strawberry residue study. Horticulturae Australia. Available online at http://www.horticulture.com.au/reports/search_final_reports_result.asp?src=&orgid=0&projid=62&strSearch=&strProjectNo=BS12024&strIndustry=0.
9 Randhawa, M.A., S.W. Rehman, F.M. Anjum and J.A. Awan, 2014. Pesticide Residues in Food: Health Implications for Children and Women. Practical Food Safety: Contemporary Issues and Future Directions, 1st ed. John Wiley & Sons Ltd Chichester, UK. doi: 10.1002/9781118474563.ch9.

10. PAN (Pesticide Action Network), 2002. Cocktail of denial, Pesticide News 58, pp: 18. Downloaded from http:// www.pan-uk.org
11. DAF (Department of Agriculture and Food's) under the terms of a service contract with FSAI (the Food Safety Authority of Ireland), 2006. Pesticide residues in food 2005. Pesticide control service, Back Weston Campus, young's cross, celbridge, co Kildare, Ireland.
12. Dogheim, S.M., S.A. Gad Alla and A.M. El-Marsafy, 1999. Monitoring pesticide residues in Egyptian fruits and vegetables. Journal of AOAC International, 82(4): 948-955.
13. Eissa, F.I., 2005. Pesticide residues study as environmental pollutants on some vegetable crops and their removal. Ph. D. Dissertation, Fac. Agric., Al-Azhar Univ., Cairo, Egypt.
14. European Union Reference Laboratory in pesticide Residue in Fruits and Vegetables, 2013. Activity Programme.
15. Anastassiades, M., S.J. Lehotay, D. Stajnbaher and F.J. Schenck, 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and ''dispersive solid-phase extraction'' for the determination of pesticide residues in produce. J. AOAC. Int., 86: 412-431.
16. Zhubo D., H. Jiye, Q. Dongmei and L. Hui, 2010. Simultaneous Analysis of Hexaconazole, Myclobutanil and Tebuconazole Residues in Apples and Soil by SPE Clean-Up and GC with Nitrogen-Phosphorus Detection. Chromatographia., 71: 7-8.
17. Khay, S., J.H. Choi and M.A. Abd El-Aty, 2008. Dissipation Behavior of Lufenuron, Benzoylphenylurea Insecticide, in/on Chinese Cabbage Applied by Foliar Spraying under Greenhouse Conditions. Bull. Environ. Contam. Toxicol., 81: 369-372.
18. Codex Alimentarius Commission for Pesticides residues, 2013. List of maximum residue limits for pesticides in food and animal feeds, Part-1. Joint FAO/WHO Food Standards Program.
19. United States Prevention, Pesticides EPA-738-F-98-017, 1998. Environmental Protection And Toxic Substances NOVEMBER 1998 Agency (7508C) R.E.D. FACTS IPRODIONE).
20. Andreu, V. and Y. Pico, 2004. Determination of pesticides and their degradation products in soil: critical review and comparison of methods. Trends in Analytical Chemistry, 23(10.11): 772-789.
21. Gevao, B., K.T. Semple and K.C. Jones, 2000. Bound pesticide residues in soils: a review. Environmental Pollution, 108: 3-14.
22. Fernandes, V.C., V.F. Domingues, N. Mateus and C. Delerue-Matos, 2012. Pesticide residues in Portuguese strawberries grown in 2009–2010 using integrated pest management and organic farming. Environmental Science & Pollution Research, 19: 4184-4192.