

PURITY ANALYSIS OF NINE PESTICIDES COLLECTED FROM EIGHT LOCATIONS IN BANGLADESH

AFROZA BEGUM¹, M. W. AKON², M. S. AHMED³ AND S. N. ALAM⁴

Abstract

The study was undertaken to determine the purity of available marketed brands of nine selected pesticide groups viz., chloropyrifos, diazinon, carbofuran, pyrazosulfuranethyle, dimethoate, cypermethrin, carbendazim, mencozeb and quinalphos. These pesticides were collected from local markets of eight locations viz., Rajshahi, Rangpur, Dinajpur, Bogra, Chittagong, Mymensing, Comilla, Norshingdi and Jessoredistricts of Bangladesh where extensive usage of pesticides was recorded. Among the 66 tested pesticides, 66.66 % (44 in number) were found >90% pure in terms of active ingredient (AI). The purity range of about 12% of the total tested brands was 80%--90%. And the remaining 21.34% were less than 80 % pure, of which three pesticide brands contained no active ingredient (AI) at all.

Keywords: Active ingredients, pesticide, purity.

Introduction

Pesticide is an essential concern in crop protection. These are used for the better care of field crops and stored grains against unpredictable losses caused by insect pests and diseases. Their use is also aimed at improving both quantity and quality of food and to decrease the extent of vector borne plant diseases. Thus, pesticides and allied agro-chemicals have become an integral component in sustainable agriculture (Kabir *et al.*, 2008). Over the years, pesticide consumption in Bangladesh has increased manifold from meager 758 metric tons in 1960 and 3028 metric tons in 1980 to over 19000 metric tons in 2000 (Hasanuzzoha, 2004).

The growth rate analysis of pesticide consumption in a period of 24 years shows an average of 9.0% annual increase (Ali, 2004). In the year 2007, over 37,712.20 tons of pesticides were being sold in Bangladesh (BCPA, 2007). The consumption of pesticide throughout the world has increased rapidly over the past fifty years. Starting from 1950s, the consumption increased 10% every year up to 1980s. In 1983, the pesticide consumption was around US\$ 20 billion which went up to 27 billion in 1993 averaging 3% annual increase. There is reason to expect that the growth rate of pesticide consumption is likely to increase by the year 2020, especially in the developing countries (Yudelman *et al.*, 1998).

Survey reports conducted (Kabir *et al.*, 1996; BARC, BARI, 2001, Ahmed *et al.*, 2005) at different locations of Bangladesh indicated that the farmers spray

¹Scientific Officer, ²Senior Scientific Officer, ³Principal Scientific Officer, ⁴Chief Scientific Officer, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur 1701, Bangladesh.

pesticide in their vegetable field irrationally, sometimes every day or in each alternate day. Due to the lack of knowledge and non-availability of sustainable alternatives to pesticide, farmers of Bangladesh become dependent on pesticide for crop production. Excessive and non-judicious use of pesticide has raised several environmental and social issues, as well as, destruction of agricultural ecosystem and development of resistance in insect pest, pathogens and weeds (Handa and Walia, 1996). In Bangladesh, it is assumed that adulteration of pesticide is one of the major causes of such extensive use of pesticide. In the country report originated by FAO (2011) Corporate Document Repository, it is reported that the regulatory scheme for pesticide registration is systematic. But in practice, there are gaps between policies and implementation. While the intent of the ordinance and rules to monitor formulations and residue is commendable, the lack of facilities and trained analysts does not allow proper monitoring. Thus, specification of pesticides on the market may differ from those registered (Aziz, 2006). So, concern on the purity in respect of AI of the marketed brands of pesticides is therefore, likely key factor for repeated use of pesticides in vegetables. Due to absence or little amount of active material in the formulated pesticides, they do not work against insect pests and the farmers use more pesticide for better result (Kabir *et al.*, 2008). Due to impurity of pesticide and low amount of active ingredient, farmers use more than recommended dose which are labeled and pest became resistant to that pesticide rapidly. According to this viewpoint, it has become significant to evaluate the brands of pesticide for quantification of their active ingredient (AI). It will be helpful for pledge the actual, harmless and safe use of pesticide for healthier harvested crops as well as to ensure safer community.

Materials and Method

Six insecticides namely Chloropyriphos, Diazinon, Carbofuran, Quinalphos, Dimethoate and Cypermethrin, two groups of fungicides such as Carbendazim and Mencozeb, and a herbicide group namely pyrazosulfuran ethyl were tested to check the percent active ingredient available.

Pesticide brands of the tested pesticide groups were collected from dealers of Rajshahi, Rangpur, Dinajpur, Bogra, Chittagong, Mymensing, Comilla, Norshingdi and Jessore where extensive usage of pesticides was reported. The brands were selected on the basis of their demand among the farmers. Each formulated product either of granular or liquid was being dissolved in the respective solvent. The solvents were selected on the basis of the criteria described by Lehotay and Mastovska (2004). The solutions of different brands of marketed pesticides were prepared in the pesticide analytical laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipurat 2015 following the procedure compatible with the respective equipment. In case of granular pesticides the solid inert materials were removed by filtration. In case of liquid pesticide the known concentration of the solutions were prepared directly. For the solid or liquid pesticides with color substances, the color was removed by passing it through

florisil column chromatography. Thus known and similar concentrated solutions of each of the standard and formulated pesticides were prepared.

Table 1. The instrument parameters of HPLC-20A prominence set for analysis of Carbofuran

Pesticide group	Solvent	Detector	Pump mode	Mobile phase	Flow rate	Injector	Inj. vol
Carbofuran	Methanol	PDA detector	Binary gradient	Methanol/water =88/12 (v/v)	1ml/min	Auto	10 µl

Table 2. The instrument parameters of GC-2010 set for analysis of different groups of pesticide

Pesticide group	Detector	Solvent	Temperature	Carrier gas	Injector	Inj. vol
Quinalphos	FID	Acetonitrile	Column-200°C, Injection port-220°C, Detector-240°C	Nitrogen	Auto	1 µl
Diazinon	FID	Acetonitrile	Column-185°C, Injection port- 200°C, Detector-220°C	Nitrogen	Auto	1 µl
Dimethoate	FID	Acetonitrile	Column-190°C, Injection port-220°C, Detector-250°C	Nitrogen	Auto	1 µl
Cypermethrin	ECD	Acetonitrile	Column-160°C(1min)-270°C (10°C /min) (6min), Injection port-280°C, Detector-300°C	Nitrogen	Auto	1 µl
Chloropyrifos	ECD	Acetonitrile	Column-160°C(1min)-270°C (10°C /min) (6min), Injection port-280°C, Detector-300°C	Nitrogen	Auto	1 µl
Carbendazim	ECD	Acetonitrile	Column-160°C(1min)-270°C (10°C /min) (6min), Injection port-280°C, Detector-300°C	Nitrogen	Auto	1 µl
Pyrazosulfuran ethyl	ECD	Acetonitrile	Column-160°C(1min)-270°C (10°C /min) (6min), Injection port-280°C, Detector-300°C	Nitrogen	Auto	1 µl
Mencozeb	ECD	Acetonitrile	Column-160°C(1min)-270°C (10°C /min) (6min), Injection port-280°C, Detector-300°C	Nitrogen	Auto	1 µl

Methods for testing different brands with GC-FID, GC-ECD and HPLC were developed by setting the instrument parameters suitable for analyzing concerned group of pesticide selected on the basis of peak sharpness of the chromatogram and retention time for respective compound. The instrument parameters of two equipment sets for analysis of each pesticide are listed in table 1 and 2:

Results and Discussion

Quinalphos: Six marketed brands of Quinalphos were tested with GC (FID). The analysis results for the purity testing of the formulated brands have been summarized in the Table 3.

Table 3. Percentage of Active Ingredient presents in some marketed brands of Quinalphos 25 EC

Code no.	Formulation type	Amount of AI (EC) present	% purity
ChiQKL	25 EC	25.00	100
MyQAGQ	25 EC	12.42	49.66
RjQKRL	25 EC	25.00	100
RjQKL	25 EC	25.00	100
BQKRL	25 EC	25.00	100
JQDBG	25 EC	21.09	84.39

Out of six tested marketed brands of Quinalphos, four contained 100% of the required amount of AI, which is considered as pure in terms of AI present. But another one is below 90%. There was one quinalphos brand contained below 50% A.I. On the other hand, Quinalphos 25 EC were reported with purity ranged from 68% to 76% (Kabir *et al.*, 2008)

Table 4. Percentage of Active Ingredient present in some marketed brands of Dimethoate 40 EC

Code No	Formulation type	Amount of AI present (%)	% purity
RDtDT	40 EC	40	100
DiDtSST	40 EC	40	100
ChiDtTF	40 EC	40	100
CDtDT	40 EC	40	100
RjDtSNG	40 EC	40	100
RjDtSST	40 EC	40	100
BDtSST	40 EC	40	100
JDtDMT	40 EC	40	100
NDtDT	40 EC	40	100

Dimethoate: Nine brands of Dimethoate collected from different local markets were tested with the GC-FID. The percent Dimethoate present in the formulated pesticides along with their purity percentage were shown in the Table 4.

The analysis results revealed that all of the nine tested brands of Dimethoate contained 100% active ingredient. So, all brands of Dimethoate are pure in term of AI presence. But in from Kabir *et al.*, 2008, it were found with very poor purity which was <20%.

Chloropyrifos: Eleven brands of Chloropyrifos 20 EC and 50EC were tested using GC-ECD for determination of actual AI contained. The results were presented in Table 5.

Table 5. Active Ingredient Percentage presents in some marketed brands of Chloropyrifos 20EC

Code no.	Formulation type	Amount of AI present (%)	% purity
RChMB	20EC	15.28	76.42
ChiChBP	50EC	50	100
CChCPF	50EC	36.81	73.63
CChSF	20EC	20	100
CChSVA	20EC	17.38	86.84
MyChCC	20EC	20	100
RjChMR	20EC	20	100
RjChHLX	20EC	15.26	76.3
BChMST	20EC	20	100
JChFLK	20EC	4.42	22.1
NChCRS	20EC	0.0	00.00

Results reveal that five of the eleven tested brands were 100% pure in term of AI present. Among the other six tested brand, one contained below 90% AI. Three brands contained below 80% of required AI. One contained below 50% AI while no AI was found in the other. Eighty five to hundred percent (85%-100%) Purity of Chloropyrifos 20EC were reported by Kabir *et al.* (2008).

Diazinon: Eight brands of Diazinon 60 EC and 10G were tested with GC-FID. The purity percentages of different marketed brands of Diazinon were shown in the Table 6.

Table 6. Percentage of Active Ingredient present in some marketed brands of Diazinon 60 EC.

Code No	Formulation type	Amount of AI present (%)	% purity
DiDDT	60EC	60EC	100
ChiDDZ	60EC	60EC	100
MyDAG	60EC	60EC	100
BDTR	60EC	39 EC	65
NDDZN	60EC	00 EC	0.0
NDSON	60EC	60 EC	100
RjDBGN	10G	10G	100
RjBFR	10G	10G	100

Analysis results of Diazinon shows that six of eight tested brands were 100 % pure in term of AI present, and one contained 65% active ingredient. The remaining one contained no AI at all.

Cypermethrin: Eleven collected marketed brands were analyzed and the following results were obtained (Table 7).

Results for cypermethrin revealed that out of eleven tested brands one was 100 % pure in term of AI present, and the other one contained no AI at all. Among the nine brands, two had > 90% purity. The remaining other brand had below 90% purity. On the other hand, Kabir *et al.*, 2008 had been reported ten to ninety three percent (10%-93%) AI present in different brands of Cypermethrin (Table 7).

Table 7. Percentage of Active Ingredient present in some marketed brands of Cypermethrin 10EC

Code no.	Formulation type	Amount of AI present (%)	% purity
DiCyMP	10 EC	8.2	82
RCyACP	10 EC	7.59	75.9
ChiCyAMT	10 EC	0.0	0.0
CCyRV	10 EC	8.6	86
CCySC	10 EC	8.42	84.2
MyCyCPK	10 EC	9.45	94.5
RjCyBMT	10 EC	8.49	84.9
RjCyPSK	10 EC	10	100
BCyST	10 EC	8.42	84.2
JCyCPD	10 EC	9.17	91.7
NCyTND	10 EC	4.28	42.8

Carbofuran: Nine brands of Carbofuran 5G were tested using HPLC- PDA for determination of actual AI contained. The results were shown in Table 8.

Table 8. Percentage of Active Ingredient presents in some marketed brands of Carbofuran 5G

Code no.	Formulation type	Amount of AI present (%)	% purity
DiCrSR	5G	5 G	100
RCrCT	5G	5 G	100
ChiCrVF	5G	5 G	100
CCrVF	5 G	5 G	100
MyCrRF	5 G	4.97	99.4
RjCrBFR	5 G	5G	100
BCrAFR	5 G	5G	100
NCrKFN	5 G	4.91	98.2
NCrSDN	5 G	4.95	99

Results showed that all samples contained >99 % of required AI except one which was 98.2% pure. The purity of Carbofuran was ranged from 0.00% to 100% as reported by Kabir *et al.* (2008).

Carbendazim: Ten different marketed Carbendazim brands were analyzed and following was the result (table 9).

Table 9. Percentage of Active Ingredient present in some marketed brands of Carbendazim 50 WP

Code no.	Formulation type	Amount of AI present (%)	% purity
NCbAGN	50 WP	50 WP	100
CCbACZ	50 WP	50 WP	100
DiCbVC	50 WP	50 WP	100
ChiCbBST	50 WP	50 WP	100
RjCbBZ	50 WP	50 WP	100
RCbEZ	50 WP	50 WP	100
CCbTN	50 WP	50 WP	100
BCbNYE	50 WP	50 WP	100
MyCbADZ	50 WP	50 WP	100
RjCbSDZ	50 WP	50 WP	100

Results for cypermethrin showed that all the tested brands were 100 % pure in term of AI present.

Mencozeb: Eight samples of Mencozeb 80 WP were tested using GC-ECD for determination of actual AI contained. The results were shown in Table 10.

Table 10. Active Ingredient percentage present in some marketed brands of Mencozeb 80 WP

Code no.	Formulation type	Amount of AI present (%)	% purity
DiMzIF	80 WP	80 WP	100
RMzASZ	80 WP	80 WP	100
ChiMzTZ	80 WP	80 WP	100
CMzMSS	80 WP	80 WP	100
CMzOT	80 WP	80 WP	100
CMzGD	80 WP	80 WP	100
MyMzDTH	80 WP	80 WP	100
BMzZAZ	80 WP	80 WP	100

Results revealed that eight of the eight tested brands were 100% pure in term of AI present.

Pyrazosulfuran ethyl: Seven different marketed Pyrazosulfuran ethyl brands were analyzed and the following was the result (Table 11).

Table 11. Percentage of Active Ingredient presents in some marketed brands of Pyrazosulfuran ethyl 10 WP

Code no.	Formulation type	Amount of AI present (%)	% purity
MyPyPL	10 WP	8.25 WP	82.5
BPyNRN	10 WP	10 WP	100
CPyLK	10 WP	10 WP	100
RPyTR	10 WP	6.61 WP	66.1
CPyLZ	10 WP	8.14 WP	81.39
DiPySP	10 WP	6.25 WP	62.5
ChiPyHK	10 WP	4.3 WP	43

Analysis results for Pyrazosulfuran ethyl shows that two tested brands were 100% pure in term of AI present. But other five brands were below 85% pure. However, the location based comparison was shown in table 12.

Table 12. Location based comparison of nine locations of Bangladesh:

Location	Total no. of pesticide brands tested	>90% pure	80%-90% pure	<80% pure	<50% pure	Comment
Rajshahi	11	9	1	1	-	-
Rangpur	6	3	-	3	-	-
Bogra	7	5	1	1	-	-
Dinajpur	6	4	1	1	-	-
Mymensing	7	5	1	-	1	-
Jessore	4	2	1	-	1	-
Chittagong	8	6	-	-	2	One brand contained no AI
Comilla	10	6	3	1	-	-
Narsingdi	7	4	-	-	3	Two brand contained no AI
Total	66	44	8	7	7	

Conclusion

The present results confirmed that 34% of the marketed pesticides in Bangladesh contained less active ingredient (AI). Three of 66 brands contained no AI at all, which supports the claim of overusing pesticides due to impurities.

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