

Review Article

Notable Trends of Quality of Spices: Need for Persistence Studies on Residues and Harmonization

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A B S T R A C T

Pesticide residues in foods have always been a cause of concern for regulators as well as policy-makers across the world. Global food trade, these days, is governed by regulations for residues set by Codex which demands for: i) harmonization of standards and ii) fixing limits of various residues, termed as Maximum Residue Limits. Recent trends show that MRLs of pesticides are being made more stringent with time. Fixing of MRLs must be done, on the basis of scientific evidences and reasoning using data from chemical as well as biological dossier of a given pesticide rather than doing it arbitrarily. Some importing countries have lowered MRLs to such levels that look practically unfeasible. Exporting countries keep protesting against this tendency of creating trade barriers and such cases are addressed at WTO. To resolve such matters, one must conduct studies to justify the safety limits for residue. Further, while arriving at the daily intake of a given pesticide in food, it is necessary to know as to how much of the residue has persisted in the food after cooking. Effect of cooking methods on persistence of agrochemical residues plays important role especially for Indian cuisines. It is essential to know as to how much residues remain in foods prepared by different methods. Present paper discusses the notable trends of global trade of spices and presents a path forward for harmonization and persistence studies to ascertain the effect of cooking on residue levels when spices contaminated with high level of residues are used.

Keywords: Pesticides, Residues, Spices, Maximum residue limits (MRLs), Harmonization of Standards

Introduction

One of the key criteria of food safety pertains to the presence of pesticide residues in different types of foods. To produce more food, as per rising demands, use of higher quantities of pesticides was imminent. This helped

in achieving targeted production but at the same time, it resulted in higher residue levels, which posed health-safety concerns. Residues are unavoidable because of the fact that degradation or decomposition of agrochemicals (e.g. pesticides) after they are applied follows a kinetics order

due to which some residues always remain with the crop; no one can guarantee the foods as free from residues. In order to deal with this, permissible limits (also known as Maximum residue limits, MRLs) for various pesticides residues in different food products are fixed by regulators across the world.

Recent trends of global food trade show that the residue limits have been brought down from ppm to ppb to ppt in most of the cases. The manufacturers are supposed to ensure that products meet the quality standards of MRL values set by regulators. It becomes a daunting task for exporters to comply with set quality standards, if importing countries keep reducing the MRL values arbitrarily. For example, countries of EU have fixed the most stringent norms of MRL values. The exporting countries call it unscientific and unreasonable. This results in rising cases of disputes before WTO. Incidents of rejections of lots from India are common and the local food processing industry faces challenges due to this. [1,2,3,4]

Another notable point in this regard relates to the fact that even the pesticides that already banned for use in India find their place in the list of residues as a part of specifications. The reason cited for this anomaly is that pesticides used in the past may continue appearing in future crops, as residues, as it takes years before the banned pesticides degrade fully and vanish. As a result, monitoring of residues of even the banned pesticides must also continue to ensure that consumers get foods meeting criteria of residues below MRL values. [5]

Ministry of Agriculture and Farmers welfare banned 46 pesticides and placed 9 pesticides under restricted use and 8 pesticides registrations were withdrawn as per the records of Oct, 2022 [6]. Banning of pesticides is necessary also to remain in sync with the importing countries. To avoid rejections of lots, it was better to ban all those pesticides, which are not in use in importing countries [7,8].

To fix MRL values, one should consider: a) the biological dossier and b) chemical dossier of each pesticide. However, do all countries follow the same procedure to fix MRLs for a given pesticide in a specific food is the question? In other words, are the standards of food safety with reference to MRL values are harmonized? The present paper highlights these issues taking the example of spices while dealing with the MRL values of spices in general and cumin seeds in particular. Cumin seeds are an integral part of almost every food prepared not just in Indian kitchen but also in cuisines across the globe. The importing countries have been prudent in regulating the lots of cumin's originating from India. Several reports, in this regard, suggest that there exist gap areas responsible for rejection of lots [7,8].

Export of Spices (including Cumin seeds) from India

India is the largest exporter of spices. Amongst the spices, Cumin is the one used in most of the cuisines not just Indian but also global. India is also the largest exporter of cumin seeds supplying it to several countries. Almost 75% of global market share is with India. There are certain market forces due to which the growth of exports is getting difficult. Here, it is worth mentioning that of the total production of cumin export is only 20% while rest is for domestic consumption. Why cumin is so important and in demand is because it falls in the category of a functional food as it renders several health benefits: resolving digestion issues, improving immunity, keeping blood sugar under check and many more [9,10]

The biggest importer of cumin is China with a share of 19% of total export of Cumin seeds from India. The exports to China started rising from 2018 with a share of 0.1% to 2019 with a share of 19% [11]. What is notable in this case is the fact that China started value-adding of cumin seeds and re-exported them. The increased seafood consumption (using cumin seeds) in China is also perhaps the reason of rising imports [12-15].

Cases of Warning about quality of Cumin

Recently, there are cases of warning by importers about quality of cumin from India. Malta's health directorate issued a warning on cumin from India due to elevated levels of pesticides. They did a risk assessment study using Acceptable Daily Intake (ADI). Lately, exports of cumin to China, the largest buyer, declined because of the regulator wanted the shipments to be free of nine pesticide residues, including malathion and carbosulfan. Further, other importing countries including European countries, Saudi Arabia, Morocco and Egypt also want pesticide-free cumin [16, 17].

Effect of processing and cooking method on persistence of Pesticide residues in foods

Before proceeding further on this subject, let us look at some of the prominent studies [18, 19, 20] already published dealing with this. Reduction of risk due to residues seems possible with processing and method of cooking. Chafing dish and soup methods reduce the risks. Salads retain almost all of residues and in chafing dish and soup; there is dispersion of pesticide residues in the media resulting in low risks. A study [21] reported reduction in the level of certain residues in shrimps from 0.917 µg/kg for raw form to 0.514 µg/kg for the one cooked by microwave. The order of reduction registered the following order: Raw < Processed < Boiled (48.8%) < Grilled (51.3%) < Fried (59.4) < Microwave (60.4%) cooking. This recommended frying and microwave processing as better methods for minimizing residues in seafood compared to boiling or grilling.

Shoeibi [22] attributed the percent reduction in residues of carbaryl, propoxur and pirimicarb were 78%, 55% and 35% respectively for vapor pressure, boiling point, and tendency of hydrolysis of these pesticides. One study [23] reported considerable reduction of amphenicols and metabolites residues in meat by boiling and frying processes but authors cautioned about the reliability of these methods for removal of such residues.

Shoeibi [22] demonstrated reduction in residues in rice by washing and soaking in water ranged from 0.40 to 4.28%. When cooked, reduction of residues ranged: from 20.73% to 57.72% for simple washing, from 32.74% to 70.39% for excess washing and from 68.87% to 87.50% for pre-soaking. Based on this trend, it would be wise to carry out studies on the effect of method of cooking on persistence of residues of pesticides.

Phopin [24] reported reduction of residues of nitrates and nitrites on peeling, washing and rinsing with water. Further, on boiling, steaming and frying there was remarkable reduction. Literature is full of diversified information related to the effect of methods of preparation, processing and cooking of foods on pesticide residues. One must take care in using them for purpose of food safety. Extent of reduction in residues of pesticides on cooking will depend upon the nature of pesticide, method of processing or cooking and the time given for any process. All processes like pasteurization, blanching, boiling, cooking, steaming, canning, scrambling etc. cause degradation of pesticides. Refining, fermentation and curing can also reduce residues. However, it is important to note that drying or dehydration may increase residue levels mainly due to concentration effect. But one must remember that it is impossible to remove residues completely by cooking methods. Only a reduction in amounts is possible.

Several reports [25-27] in literature suggest that significant reductions in pesticide residues is possible during processing and cooking of food. However, there are also reports indicating that processing can either concentrate residues or convert them into metabolites, which may be more toxic. Thus, it is important to envisage whether consumers eat the agricultural products fresh or cooked.

Chinese traditional cooking involves blanching, frying and "stir-frying" while ensuring that the natural colour and flavour of the raw food is intact and vegetables become crispy losing little moisture and nutrients [28, 29.]. Indian cooking involves many spices; emphasis is on several processing methods, and multiple steps to ensure that it has a unique taste (mouth-watering), flavour, aroma, functionality etc. Elsewhere in the world, consumers prefer to eat agricultural products either as fresh, processed or boiled [30-31.]. Let us elaborate this point a little, here. Chinese consume a lot (10% of the daily food intake) of

vegetables but after thermal processing including stir-frying whereas, Europeans and Americans eat fresh vegetables as salad [32-33]. The risk of intake of residues will vary as per the consumption pattern of vegetables. Indian cuisines involve the frying of spices in oil or ghee as an essential and first step of cooking. Mixing of fried spices to the composition is the next step i.e. boiling. Thus, for spices contaminated with pesticide residues beyond their MRL, will the residue persist in the final product is the question? There are not many studies seen, by the authors of this paper, in the literature to answer this question.

Huan [34] reported that washing and blanching could reduce residues with low K_{ow} while stir-frying and frying were more effective to residues with high K_{ow} ; stir-frying and frying could concentrate residues with low K_{ow} ; the residue levels in oil increased following increasing frying time and frequency especially the residues with high K_{ow} ; Blanching (5 min) followed by stir-frying (3 min) was the most effective combined operation.

Based on the above reported cases setting the trend for pesticide residue free food, it is imminent to carry out studies on the effect of method of cooking on persistence of residues of pesticides. Also, for fixing the MRL values, one must take the data of persistence studies of pesticides residues into consideration [34-37].

Fixing MRL values:

For fixing MRL values, it is essential to determine firstly, the Maximum Permissible Intake (MPI) for human beings. MPI will determine the permissible limit, for any pesticide, from point of view of criterion for declaring the food being good for human consumption. Determine MPI using following equation:

$$ADI \times \text{Average Body Weight} = MPI$$

Then, estimate the value of ADI (Admissible Daily Intake), by using the following equation:

$$ADI = \text{NOAEL} / 100 \text{ to } 1000, \text{ where } 100 \text{ to } 1000 \text{ is the safety factor.}$$

NOAEL is the amount of substance (for which the MRL is being fixed) consumed on daily basis during entire life span without any adverse health effect (mg/Kg body wt. /day)

Finally, ascertain the Theoretical maximum residue concentration (TMRC) using following equation:

$$TMRC = \text{Daily consumption of Food Commodity} \times \text{Residues in ppm.}$$

This procedure looks straight forward and simple but it has several intricacies associated with it. If one goes theoretically, one can calculate the amount of residues consumed by a consumer over entire lifetime, based on the amount of spices consumed daily and level of residues of that pesticide present in it. Practically speaking, it is not

correct approach because of the reason that during the process of cooking certain amount of pesticide residues is lost at different stages of cooking e.g. washing, drying, boiling, baking, frying etc., depending upon the way the food is cooked. At each stage, therefore, there will be loss of pesticides from the food system. Let us take the case of process of frying which involves spices fried in oil or ghee at high temperature. The question is whether there will be any residues of pesticides left in the food cooked with even the highly contaminated spices [34-37].

Harmonization of standards

The other key challenge relevant to food safety pertains to the harmonization of standards. It is evident from several reports and research papers that there exist gaps related to the harmonization of standards of various agro-products including spices. Following notable findings from the literature are worth mentioning here regarding the MRL values fixed by regulators of India and different countries:

- (a) MRLs of most of the pesticides in dried chilli as per FSSAI are much higher than MRLs specified by countries

of EU. However, for deltamethrin, difenoconazole, Hexythiazox, Indoxacarb, Milbemectin, Pyraclostrobin, Pyriproxyfen, Spinosad, Thiachlopid, Thiodicarb. MRL values set by FSSAI are lower than those set by countries of EU are. This is the cause of difficulties in exporting chillies to EU.

- (b) In the case of cumin, MRLs for Azoxystrobin, Epoxyconazole, Oxadiargyl and Pyraclostrobin set by FSSAI are lower than the limits fixed by countries of EU.
- (c) In case of cardamom, for Monocrotophos FSSAI has ten times higher limits than those set by countries of EU. However, for Quinalphos MRL values set by FSSAI are lower than those set by the countries of EU. [34-42]

Like this, there are discrepancies in almost all the spices. There is an urgent need for harmonization of standards, ensuring that MRL values of different pesticides in all spices are same. The data presented in Table 1 for cumin are enough to demonstrate the need for harmonization of standards.

Table 1. MRL values (in ppm) of residues of pesticides in cumin as set by regulators of India, USA, Canada, Australia/New Zealand and Codex Alimentarius [34-42]

USA MRLs, ppm			Canada MRLs, ppm		
S.No	Pesticides	Cumin seed	S.No	Pesticides	Cumin seed
1	Abamectin	0.01	1	Azoxystrobin	38
2	Acephate	0.02	2	Clethodim	3
3	Acetamiprid	0.01	3	Ethylene Oxide	7
4	Alpha-Cypermethrin	0.05	4	Fludioxonil	0.02
5	Azoxystrobin	38	5	Metalaxyl	0.05
6	Bifenthrin	0.05	6	Propylene oxide	300
7	Carfentrazone-ethyl	2	Australia New Zealand, MRLs, ppm		
8	Chlorantraniliprole	90	1	Alpha-Cypermethrin	0.5
9	Chlorfenapyr	0.01	2	Cypermethrin, sum of isomers	0.5
10	Chlorpyrifos	0.1	3	Lambda Cyhalothrin	0.5
11	Cyfluthrin	0.05	4	Methomyl	0.07
12	Cypermethrin	Zeta; 0.05	FSSAI, MRLs, ppm		
13	Deltamethrin	0.05	1	Azoxystrobin	0.03*
14	Esfenvalerate	0.05	2	Dithiocarbamates a) Mancozeb	10
15	Ethylene chlorohydrin	940		(b) Metiram as CS2	10
16	Ethylene oxide	7		(c) Zineb as CS2	10
17	Etofenprox	5	3	Epoxyconazole	0.01*
18	Fludioxonil	0.02	4	Oxadiargyl	0.01
19	Fluoride	70	5	Picoxystrobin	0.05*
20	Gamma Cyhalothrin	0.01	6	Pyraclostrobin	0.02*

21	Glyphosate	7	9	Thiamethoxam	0.01
22	MGK 264	5	CODEX, MRLs, ppm		
23	Naled	0.5	1	Dithiocarbamates	10
24	Novaluron	0.01	2	Profenofos	5
25	Phosphine	0.01	EU, MRLs, ppm		
26	Piperonyl Butoxide	10	1	Azoxystrobin	0.3
27	Prallethrin	1	2	Epoxyconazole	0.1
28	Pyrethrins	1	3	Oxadiazyl	0.05
29	Pyriproxyfen	0.1	4	Picoxystrobin	0.05
30	Resmethrin	3	5	Pyraclostrobin	0.1
31	Spinetoram	1.7	6	Thiamethoxam	0.05
32	Spinosad	1.7	7	Chlorpyrifos	0.01
33	Thiamethoxam	0.02	8	Aldrin and Dieldrin	0.1
34	Dichlorvos	0.5	9	Deltamethrin	0.1
35	Methyl bromide	125	10	Ethion	3
36	Sulphuryl fluoride	2	11	Cypermethrin	0.1

Conclusion

From the above discussion, it is clear that harmonization of standards for residues of pesticides particularly the MRL values for residues of different pesticides in foods especially spices is a must to avoid disputes resulting from global food trade. All countries should fix MRL values based on scientific principles. While fixing the MRL values, it is imminent to consider studying the effect of cooking on persistence of different residues in foods. As a case study, it will be better to carry out persistence studies on cumin to demonstrate this point.

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