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A STUDY ON PESTICIDE CONTAMINATION AND ASSESSMENT OF HEALTH EFFECTS USING HEALTH EFFECT MODEL IN SOME VEGETABLES OF DURG DISTRICT, CHHATTISGARH STATE, INDIA

RUCHI TAMRAKAR[1] AND SUMITA NAIR[2*]

Department of Chemistry, Bhilai Institute of Technology, (B.I.T.), Durg, Chhattisgarh, India

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Abstract–This study reveals the presence of five pesticides (Malathion, Chlorpyrifos, Endosulphan, Deltamethrin and Butachlor) in some vegetable samples of Durg district of Chhattisgarh state. Malathion presence accounted for highest proportion with 57.14% samples and Chlorpyrifos was detected in 48.98% samples while 16.33% and 24.49% samples were detected with Deltamethrin and Butachlor respectively while Endosulphan was not detected in any sample. Fifty percent samples exceeded the ADI value of respective pesticides. Study reveals Chlorpyrifos pesticides pose significant health risk toward consumers as their health risk indices was 1.67.The EFSA -PRIMo2.0 reveals the highest percentage of ARfD of Chlorpyrifos and Malathion for acute effect for adults and children was 26%, 54.2% and 9.9%, 20.7% respectively in cauliflower.

INTRODUCTION

The objective of this study is to assess the pesticide contamination in vegetables collected from different farms of Durg district and to evaluate the related health risks. One of the important contents of human diet is vegetable, since vegetables provide many essential nutrients required for human metabolism and growth. A high intake of fruits and vegetables are recommended not only to avert consequences of vitamin deficiency but also to reduce the incidence of major diseases such as cancer, cardiovascular diseases skin rashes, headache, lacrimation, sweating, vomiting, diarrhea, lung edema etc (Azab, *et al*., 2015; Rodrigues, *et al*., 2018). During the cultivation and storage like other crops the vegetables have threat of pest and disease attack (Keikotlhaile and Spanoghe, 2015). In modern agriculture pesticides i.e., herbicides, fungicides, and insecticides are widely used in environmental fields due to its high efficiency to control pest, easy synthesis, and low cost (Das and Das, 2004; Battaglin and Airchild, 2002). Despite of pesticide need to protect vegetables from diseases there will always a chance of entering pesticide residue in human food chain and cause harmful toxic effects on human health. Therefore, the determination of pesticides in such products is of great concern in recent years (Klaassen, 2001). There are different classes of pesticides like insecticides, herbicides, fungicides, rodenticides, and nematicides for a targeted pest (Bhadekar, *et al.*, 2011). The insecticides are further divided into organophosphate, organochlorine, carbamates, pyrethroids, and neonicotinoids; there is a wide and extensive usage of endosulfan in the world (Randhawa, *et al*., 2016). Approximately one million deaths per year are reported due to extensive use of pesticides according to Environ-news Forum-1999. The monitoring and proper investigation of pesticide residues in fruits and vegetables have great importance to consumer health protection, and the development or usage of robust and economical analytical methods is of great interest (Oellig and Schmid, 2019). This study was designed to analyze the level of pesticide residual concentration in some vegetable samples collected from direct vegetable farm. Nowadays the use of pesticide is inevitable in the world due to its largescale impact on yield of crops and vegetables. In addition to commonly used pesticides, the use of banned pesticide in agriculture practice is also an important challenge. In this investigation, a validated multi-residue technique was used for the identification and determination of various pesticide residues in some vegetable samples collected from vegetable farm field of some villages of Durg district. In order to determine the possible adverse effect of pesticides on human health by taking fresh vegetables, the risk should be assessed for each individual pesticide and for their combinations because it is known that two or more substances found together in the body can assume quite different actions than each of them alone (Singh, *et al*., 2017). A combined technique of Gas chromatography and mass spectrometry (GC-MS) was used to determine the presence and level of particular pesticides in selected fresh vegetables. The potential risk for human health was assessed by the use of the EFSA software PRIMO 2.0 model.

MATERIALS AND METHODS

Study area

Durg is a city in Indian state Chhattisgarh, situated in east side of the Shivanath river and is a part of the Durg –Bhilai urban agglomeration. The latitude of the Durg, C.G., India is 81.28" and the longitude is 81.28".Bhilai is a city in the district of Durg, C.G in eastern central India. The latitude of the Bhilai, C.G., India is 21.13" and the longitude is 21.13". Vegetable samples were collected from S1-Khedamara, S-2 Kachandur, S-3 Anjora, S-4 Durg and S-5 Kuthrel area (Figure 1). Analysis of pesticide was carried out by applying GC/MS method.

Sample Collection and Analysis

A total of 53 samples of vegetables (Cauliflower, Spinach, Kundaroo, Egg Plant, and Barbatti) were collected from October 2019 - August 2021 at agricultural field from each of the 5 villages of Durg district, Chhattisgarh. The sampling was done according to guidelines on sampling for official control of pesticide residues. Samples were analyzed within 24 hr and stored at 4 ^{o}C until the moment of extraction. 500 g. Samples were collected from the different vegetable farms of Durg Bhilai region. 200 g of samples were taken for further procedure and analyzed for pesticide and to assess their health safety. The samples were analyzed by GC-MS for pesticide residue.

Extraction of samples

The sample was extracted and dissolved with MS grade ethyl acetate and filtered with 0.45 micron. The particle-free extracts were taken in a syringe and injected into GC-MS instrument.

Sample analysis

Gas chromatograph with a mass spectrometer (GC-MS/MS) instrument (Make-Bruker Scion, Model-TQ MS System) was used for the analysis of different vegetable extract sample by attempting following conditions: Column DB-5MS Agilent (30m x 0.25 mm1D), composed of 100% dimethyl polysiloxane). For GC-MS detection, electron ionization system with ionization energy of 70eV was used. Helium gas (99.99%) was used as the carrier gas at constant flow rate 1.0 ml/min with a split ratio of 10:1. The oven temperature was operated according to the following oven temperature: 40 °C held for 1 min, raising at the rate

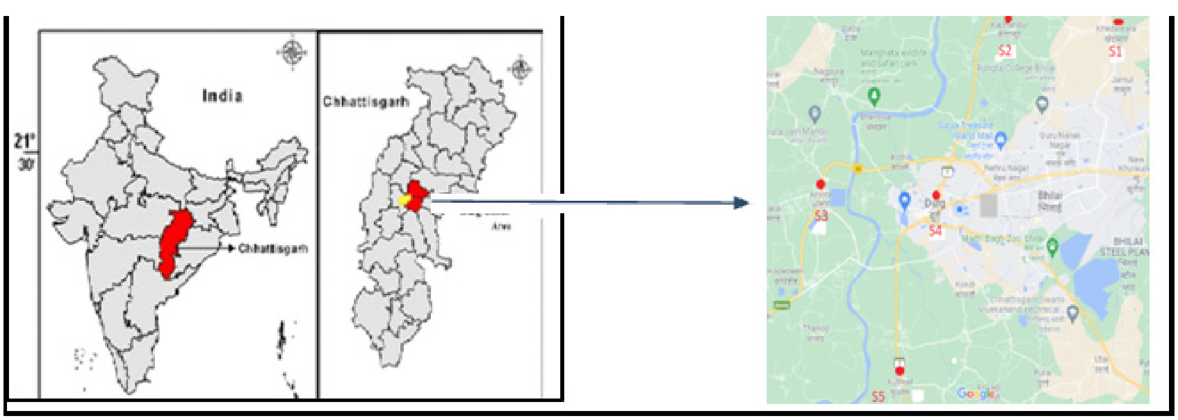

Fig. 1. Study area Durg district showing sampling locations.

of 20 °C min-1 up to 150 °C then, raising at the rate of 3 °C min-1, hold for 0 min and raising at the rate of 20 °C min-1 up to 300 °C with 10 min held, injector temperature and volume 250 °C and 2ìL, respectively. The total GC running time was about 45 min. The MS operating conditions were ionization voltage 70 eV, source temperature of 250 °C, inlet line temperature 280 °C, mass scan (m/z)-30-500, solvent delay: 4.0 min, total MS running time 40 min. The mass spectra of compounds were identified by comparing the mass spectra obtained from their related chromatographic peaks with NIST mass spectral libraries.

RESULTS AND DISCUSSION

Level of residual pesticide concentration in studied vegetable samples

The level of pesticide residues (Malathion, Chlorpyrifos, Butachlor, Deltamethrin and Endosulphan) found in the analyzed vegetable samples during the present study is outlined in Table 1.

Total 53 samples were collected from the study area. The residual pesticide concentration of Malathion, Chlorpyrifos, Endosulphan, Deltamethrin and Butachlor were analyzed. Malathion presence accounted for highest proportion with 57.14% (30 samples) samples and Chlorpyrifos was detected in 48.98% samples (26 samples) while 16.33 % and 24.49% samples (9 and 13 samples) were detected with Deltamethrin and Butachlor respectively while Endosulphan was not detected in any sample. Average residual pesticide concentration in vegetable samples of study area is shown in Table 1.

Health risk assessment

The first attempts at such a risk assessment were reported as early as the 1970s and referred to vinyl chloride, published by the Environmental Protection Agency (EPA), entitled "Quantitative Risk Assessment Community Exposure to Vinyl Chloride" (Kuzmack and McGaughy, 1975). Over the years, risk assessment has become increasingly important and various tools for risk assessment have been developed and used by researchers (Stephenson and Harris, 2016; Benbrook, *et al.*, 2002). The risk was assessed separately for each pesticide detected positive. Risk assessment was calculated according to the EFSA-PRIMo 2.0 model for acute and chronic exposure to pesticides for which the Acute Reference Dose (ARfD) has been established. Risk assessment was performed separately for adults and for children under 6 years of age. The results are shown in Table 2.

Malathion and Chlorpyrifos pesticide were the most frequently detected pesticide in ours study.

Table 1. Average residual pesticide concentration in vegetable samples collected from study area (Results are in mg kg^{-1})

Site	Commodity	Malathion	Chlorpyrifos	Endosulphan	Deltamethrin	Butachlor
Khedamara	Egg Plant	0.04	0.07	BDL	BDL	BDL
Khedamara	Barbatti	0.05	BDL	BDL	BDL	BDL
Kachandur	Kundaroo	0.08	0.04	BDL	BDL	BDL
Anjora	Egg Plant	0.28	0.84	BDL	0.17	0.41
Durg	Cauliflower	0.94	0.82	BDL	BDL	BDL
Durg	Spinach	0.19	0.87	BDL	BDL	0.41
Kuthrel	Egg Plant	0.37	0.91	BDL	0.12	0.55

Table 2. % ARfD value for Acute overview Children and Adult for Malathion and Chlorpyrifos pesticide for vegetable samples calculated using EFSA model 2.0.

Commodity	% ARfD Acute Overview Children		% ARfD Acute Overview Adult	
	Malathion	Chlorpyrifos	Malathion	Chlorpyrifos
Cauliflower	20.7	54.2	9.9	26
Egg Plant	3.1	22.8	3.1	22.6
Kundaroo	1.6	2.3	0.7	0.8
Spinach	1.4	19.7	0.6	7.8
Barbatti	1.2	1.9	0.5	1.1

Malathion showed the highest ARfD percentage of adults (max% ARfD- 9.9%) in cauliflower commodity, and these values were also high in risk assessment for children, where they amounted up to max% ARfD20.7%. In Chlorpyrifos analysis the highest ARfD percentage of adults was 26.0%and for children the value was 54.2 %. 12 samples (40%) of 30 samples for malathion pesticide residue and 15 samples (57.69) of 26 samples for Chlorpyrifos pesticide residues exceeded the Acute Reference Dose of 0.3 and 0.1 respectively (ARfD) and were labeled as unsafe for human use. However, the EFSA PRIMo model 2.0 suggests the estimated Theoretical Maximum Daily Intakes (TMDI), based on pTMRLs were below the ADI (Acceptable Daily Intake). Hence a long-term intake of residues of Chlorpyrifos and Malathion are unlikely to present a public health concern. The degree of risk associated with the consumption of each pesticide detected was monitored by evaluating the results of pesticide residues detected in samples. The health risk index was found by using EDI (Estimated Daily Intake) and ADI. ADI was used from literature studies. The EDI was calculated by multiplying the average consumption of a person per day (Kg/day) and residual concentration of pesticide (Mg/Kg) and dividing by the average weight of an Asian (60 Kg). The average consumption of fruit and vegetables for adults was considered 0.43 and 0.345 Kg/person/day according to the field survey (Hossain *et al.*, 2015). The health risk index for each pesticide was calculated using the following formula, (EFSA, 2013) Equation 1.

$$\text{Health Risk Index} = \text{EDI}/\text{ADI} \qquad .. (1)$$

where EDI is estimated daily intake, ADI is acceptable daily intake. HRI value more than 1 is considered as not safe for human health (Darko and Akoto, 2008). Recently risk assessment studies have focused on simultaneous exposure to multiple pesticides instead of only on a single pesticide (Van, *et al.*, 200).

The calculated values of Health Risk Index for vegetable samples detected positive pesticide concentration values are presented in Table 3. The calculated values of HRI suggest that in studied five sampling sites the two commodities (Cauliflower and Spinach) in Site-4 and one commodity (Egg Plant) in Site-3 are having HRI > 1 for Chlorpyrifos pesticide suggesting that the use of this pesticide in mentioned sites are associated with human health risk and may affect the health of human consuming those commodities in long run.

CONCLUSION

Long term accumulation of pesticide residues in the human body via dietary intake of vegetables and other food commodities is a severe problem, as indiscriminate amounts of such pesticides are used in many countries. The present research was aimed to evaluate the possible health risk of pesticide residues via dietary intake of vegetables in Durg Bhilai city, Chhattisgarh. LC-MS was applied to determine five pesticides Malathion, Chlorpyrifos, Endosulphan, Deltamethrin and Butachlor in different vegetable samples. The maximum level of pesticide residues was 0.94 Mg/Kg of Malathion. Only one commodity (Eggplant) in two sites contained Malathion, Chlorpyrifos, Deltamethrin and Butachlor pesticide. HRI of Chlorpyrifos in three commodities (cauliflower, spinach, egg plant)

Table 3. Health Risk Index of studied vegetable samples.

Site	Commodity	Pesticide	ADI	EDI	HRI	Health Risk Associated
S-4	Cauliflower	Malathion	0.03	0.005405	0.18	N
		Chlorpyrifos	0.003	0.004715	1.57	**Y**
	Spinach	Malathion	0.03	0.0010925	0.04	N
S-4		Chlorpyrifos	0.003	0.0050025	1.67	**Y**
		Butachlor	0.1	0.0023575	0.02	N
S-3	Egg Plant	Malathion	0.03	0.00161	0.05	N
		Chlorpyrifos	0.003	0.00483	1.61	**Y**
		Butachlor	0.1	0.0009775	0.01	N
		Deltamethrin	0.1	0.0023575	0.02	N
S-2	Kundaroo	Malathion	0.03	0.00046	0.02	N
		Chlorpyrifos	0.003	0.00023	0.08	N
S-1	Barbatti	Malathion	0.03	0.0002875	0.01	N

made the vegetable risky for human health while others were found not to be a health risk. As pesticide residues can bio-accumulate and bio-magnify several folds in a food chain over time, continuous and strict monitoring programs should be enforced to check and limit these residual levels in food items. In developing countries like India, some legal measures should be taken in order to monitor the pesticide residues in vegetables because of potential health risks and to accomplish the standards and to make the products safely consumable by the consumers. It is also recommended that in future studies the risk for child and expecting mothers can be calculated.

Conflict of Interest: The authors declare no conflict of interest.

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