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Principles and Procedures of Herbicides Residue Estimation in Groundnut Cultivated Soils of *Saurashtra* Region

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ABSTRACT: A research was conducted at Division of Agronomy, JAU, Junagadh on medium black calcareous soil in two *kharif* seasons to judge the bioefficacy of Pre-and PoE herbicides in groundnut and determination of their residues in treated soil. The herbicides residue were analyzed in soil at 30, 60 days crop stage, at harvest and at 30 DAH of the crop. Soil samples were analysed for pendimethalin, oxyfluorfen and quizalofop-ethyl with the help of QuEChERS process in GC-MS and for imazethapyr in LC-MS/MS. The average recovery ranges from 85.60 to 95.50% at three spike levels *viz.,* 0.1, 0.25 and 0.5 µg/g). The lowest detectable limit (BDL) of pendimethalin and quizalofop-ethyl in field soil was 0.01 µg g^{-1}. The value for oxyfluorfen and imazethapyr were 0.015 and 0.008 µg g^{-1}, respectively. The analytical marks revealed that residues of pendimethalin, oxyfluorfen and quizalofop-ethyl in soil were detected up to 30 days crop stage while the remains of imazethapyr in soil samples were not detected till harvest. The farmers are advised to adhere with the recommended dosage of these herbicides application to minimize the soil and water pollution threats.

Keywords: Analysis, extraction, imazethapyr, oxyfluorfen, pendimethalin, quizalofop-ethyl, soil persistence.

INTRODUCTION

Groundnut is grown throughout the year in our country. About >85% groundnut is grown in *kharif* season in rainfed lands having full monsoon vagaries and get low yield. Weed menace is the serious tailbacks in these areas. Herbicides are gaining popularity among the farmers due to increased labour cost, choice of application and quick weed control in crop fields. Spray of PE herbicides like pendimethalin, oxyfluorfen and imazethapyr (Kumar *et al.,* 2013) and quizalofop-ethyl (Samant and Mishra 2014) as POE have been establish very successful in weed management and higher groundnut returns. However, these herbicides did not show any phytotoxic effect on growth and yield of groundnut (Naveen Kumar *et al.,* 2020).

To ensure consumer safety, the USA has set up MRL of pendimethalin and imazethapyr as 0.1 mg/kg in peanut kernel. In European Union (2021), MRL was established for pendimethalin (0.1 mg/kg), oxyfluorfen (0.05 mg/kg) and quizalofop-*p*-ethyl (0.1 mg/kg) in peanut seed (EU, 2014). In India, the MRL for oxyfluorfen (0.05 mg/kg) and imazethapyr (0.1 mg/kg) has been established only in peanut oil (Food Safety and Standards Authority of India, 2011). To analyse the herbicide residues in soil, groundnut fodder and seed this experiment was carry out on *kharif* groundnut on black cotton calcareous soils.

MATERIAL AND METHODS

An agronomic field trial was carried out at Division of Agronomy, Junanagd (Gujarat) on medium black calcareous soil for two consecutive *kharif* seasons. The soil was clayey in texture and slightly alkaline in pH (8.0), low in available N (236.5 kg N ha^{-1}), while medium in available P_2O_5 (22.9 kg ha^{-1}) and K_2O (241.7 kg ha^{-1}). Ten treatments on weed management practices were evaluated in RBD replicated three times. The groundnut (cv. GG-20) was grown with standard PoP. Herbicides were sprayed as per treatments using knapsack sprayer with 500 L water ha^{-1}. The herbicides residue in soil samples were studied at an interval of 30, 60 DAS, at harvest and at 30 DAH. Soil samples were collected at 0-15 cm depth from each treated plot. Randomly five soil samples were taken at each sampling time, mixed and final composite sample (weighing 200 g) was brought to analytical lab. Soil samples were analysed with the help of QuEChERS procedure in GC-MS and LC-MS/MS. The results were inferred from side to side accuracy and validation using average recoveries for pre-and PoE herbicides which ranged from 91.5 to 95.6% at three concentrations (Table 1).

Principles of Analytical Procedure, Extraction and Clean-Up: The soil samples were analysed for pendimethalin, oxyfluorfen and quizalofop-ethyl with the help of QuEChERS process in GC-MS and for imazethapyr in LC-MS/MS described by Sharma (2007).

Table 1: GC-MS / LC-MS/MS herbicide minimum detectable limits and recoveries in groundnut soil.

Particulars	GC-MS						LC-MS/MS					
	Pendimethalin			Oxyfluorfen			Quizalofop-ethyl			Imazethapyr		
Spike levels (mg/kg)	0.100	0.250	0.500	0.100	0.250	0.500	0.100	0.250	0.500	0.100	0.250	0.500
Recovery (mg/kg)	0.084	0.234	0.485	0.092	0.225	0.478	0.089	0.241	0.507	0.093	0.239	0.472
Mean % recovery	91.53			92.53			95.60			94.33		
Lowest detectable level (mg kg^{-1})	0.01			0.015			0.01			0.008		

Principle of analytical procedure. The QuEChERS method describes multi-residue analysis of important pesticide residues from soil as most pesticide residues are extracted by soxhlet extraction (Anastassiades *et al.*, 2003). This method eliminates the possibility of losing the heat labial pesticides. In this method soil samples were extracted with acetonitrile along with $MgSO_4$ and sodium citrate-sodium hydrogen citrate sesquihydrate. After salting out, the representative aliquot was subjected to d-SPE (dispersive solid phase extraction) where the clean-up was easily performed by shaking and centrifugation. The final aliquot was analyzed by GC-MS. The LC-MS/MS is used for separation of pesticides for imazethapyr due to instant polarity of its analyte.

Extraction and estimation. The extraction of pendimethalin, oxyfluorfen and quizalofop-ethyl were carried out as per the QuEChERS procedure. At first soil was extracted with acetonitrile followed by clean-up by using d-SPE with PSA (Primary Secondary Amine). The extraction was later divided with solvent cyclohexane. In some cases NaCl was added to increase the recovery efficiency. The soil analysis procedures flow diagram (Fig. 1) is outlined below:

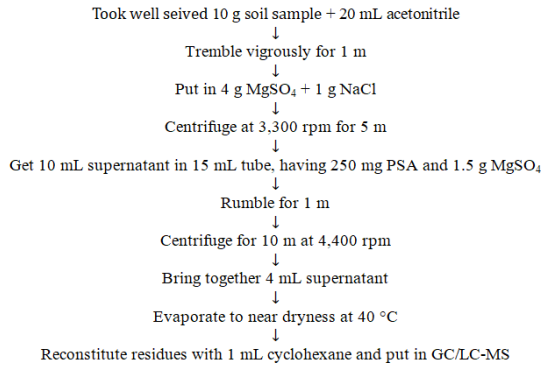

Fig. 1. Flow diagram of QuEChERS method used for soil residue analysis.

Clean-up. As per the specific analytical quality of QuEChERS method, no precise clean-up process was adopted for soil residue analysis because analytical chemicals help in clean-up at the same time. A proper clean-up procedure was used for samples containing colour and pigments like fruits and vegetables. The herbicide residue in soil sample was calculated with the next formula.

$$\text{Residue } (\mu g\ g^{-1}) = \frac{\text{Peak area (sample)} \times \text{Conc std. (ppm)} \times \mu L \text{ std. injected} \times \text{Final volume of the sample (1 mL)}}{\text{Peak area (std.)} \times \text{Weight of the sample (2 g)} \times \mu L \text{ of sample injected}}$$

RESULTS AND DISCUSSION

Persistence of herbicides in soil samples. Level of herbicide residues may be very low or high in soil and its estimation involves lengthy procedures of extraction and clean-up. Herbicide organization and soil and climatic conditions between the time of spraying and sampling may also affect the status of herbicide persistence.

Persistence of pendimethalin in soil. Pendimethalin is very frequently used PE herbicide for grassy weed species control in legumes and cereals A perusal of data (Table 2) tell that PE application of pendimethalin persisted in soil up to 30 days after application. The maximum residue (0.032 µg g^{-1}) in soil was detected with the treatment T_6 (Pendimethalin 0.9 kg ha^{-1} PE fb imazethapyr 75 g ha^{-1} POE at 25-30 DAS) followed by T_1 and T_5 with residue level of 0.031 and 0.030 µg g^{-1} soil, respectively which were upper than the BDL (0.01 µg g^{-1}) at 30 DAS. At 60 DAS, harvest and 30 DAH of the peanut crop, pendimithalin residue was noted below the exposure limit.

At 60 days crop stage, harvest and at 30 DAH of the crop, not a single herbicide residues were detected above the limits of quantification (0.01 µg g^{-1}) as ascribed due to that pendimethalin have half-life periods ranged from 12.8 to 13.2 days in red soils and 28.3 to 91.8 days in vertisol owing to rapid microbial degradation and dissipation due to more rapid increase in soil temperature and moisture levels (Sireesha *et al.*, 2011), hence found safe for the environment and rotational crops.

Table 2: Persistence of pendimethalin herbicide residues in soil.

Treatments		Pendimethalin residues in soil (µg g^{-1} soil)			
		30 DAS	60 DAS	At harvest	30 DAH
T_1:	Pendimethalin 0.9 kg ha^{-1} PE *fb* IC & HW at 40-45 DAS	0.031	BDL	BDL	BDL
T_5:	Pendimethalin 0.9 kg ha^{-1} PE *fb* Quizalofop-ethyl 40 g ha^{-1} POE at 20-25 DAS	0.030	BDL	BDL	BDL
T_6:	Pendimethalin 0.9 kg ha^{-1} PE *fb* Imazethapyr 75 g ha^{-1} POE at 25-30 DAS	0.032	BDL	BDL	BDL

Persistence of oxyfluorfen herbicide in soil. As per data (Table 3) indicated that residue of PE applied oxyfluorfen was carry on in the soil up to 30 days after its application. The maximum residue detection level (0.04382 µg g^{-1}) was recorded with the treatment T_8 (Oxyfluorfen 0.18 kg ha^{-1} PE *fb* imazethapyr 75 g ha^{-1} POE at 25-30 DAS), followed by treatment T_7 and T_2 (Table 3) with the residue levels of 0.04248 and 0.04009 µg g^{-1} soil, respectively which were higher than the minimum limit (0.015 µg g^{-1}) at 30 DAS. At 60 DAS, harvest and at 30 DAH of the crop, soil persistence of oxyfluorfen was subsisted to some extent, but remains below the standard minimum detection limit. The findings were to the tune reported earlier by Saini *et al.* (2010).

Persistence of quizalofop-ethyl in soil. Quizalofop-ethyl is widely used as PoE weedicide to control weeds in groundnut. Residue of quizalofop-ethyl was persisted in the soil up to 60 days crop stage. At 30 DAS, the quizalofop-ethyl residue of 0.09413 µg g^{-1} was detected in soil with the treatment T_5 (Pendimethalin 0.9 kg ha^{-1} PE *fb* quizalofop-ethyl 40 g ha^{-1} POE at 20-25 DAS), which was higher than the lowest detectable limit. Residues of herbicide quizalofop-ethyl in the same treatment (T_5) at 60 DAS, harvest and at 30 DAH of the crop was observed below the detection limit (Table 4).

Table 3: Persistence of oxyfluorfen herbicide residues in soil.

Treatments		Oxyfluorfen residues in soil (µg g^{-1} soil) at 30 days crop
T_2:	Oxyfluorfen 0.18 kg ha^{-1} PE *fb* IC & HW at 40-45 DAS	0.04009
T_7:	Oxyfluorfen 0.18 kg ha^{-1} PE *fb* Quizalofop-ethyl 40 g ha^{-1} POE at 25-30 DAS	0.04248
T_8:	Oxyfluorfen 0.18 kg ha^{-1} PE *fb* Imazethapyr 75 g ha^{-1} POE at 25-30 DAS	0.04382

Table 4: Persistence of quizalofop-ethyl herbicide residues in soil.

Treatments		Quizalofop-ethyl residues in soil (µg g^{-1} soil) at 30 days crop
T_3:	Quizalofop-ethyl 40 g ha^{-1} POE at 25-30 DAS *fb* IC & HW at 40-45 DAS	BDL
T_5:	Pendimethalin 0.9 kg ha^{-1} PE *fb* Quizalofop-ethyl 40 g ha^{-1} POE at 20-25 DAS	0.09413
T_7:	Oxyfluorfen 0.18 kg ha^{-1} PE *fb* Quizalofop-ethyl 40 g ha^{-1} POE at 25-30 DAS	BDL

ND = Not dected

No detectable residue of quizalofop-ethyl was noticed in soil at 30 DAS when treated with application of quizalofop-ethyl 40 gha^{-1} POE at 25-30 DAS *fb* IC & HW at 40-45 DAS (T_3) and oxyfluorfen 0.18 kg ha^{-1} PE *fb* quizalofop-ethyl 40 g ha^{-1} POE at 25-30 DAS (T_7). At 60 DAS, harvest and 30 DAH of the crop, no residues were detected above the lowest allowable determination limit (0.01 µg g^{-1}) as ascribed due to that quizalofop-ethylrapidly degraded by soil microbes. The findings are closer to those reported by Sahoo *et al.* (2013) in onion fields.

Persistence of imazethapyr in soil. A close look of the data (Table 5) indicated that residues of herbicide imazethapyr applied at 75 g *a.i.* ha^{-1} as POE in the soil was observed but it was recorded below the detectable limit of 0.008 µg g^{-1} at 30 DAS, 60 DAS, harvest and at 30 DAH of the crop. The poor persistence of imazethapyr in soil might be ascribed due to its moderately persistence nature, highly soluble in water (Wauchope *et al.,* 1992) and might increased adsorption with clay and organic micelle.

Table 5: Persistence of imazethapyr herbicide residues in soil.

Treatments		Imazethapyr residues in soil (µg g^{-1} soil)			
		30 DAS	60 DAS	At harvest	30 DAH
T_4:	Imazethapyr 75 g ha^{-1} POE at 20-25 DAS *fb* IC & HW at 40-45 DAS	BDL	BDL	BDL	BDL
T_6:	Pendimethalin 0.9 kg ha^{-1} PE *fb* Imazethapyr 75 g ha^{-1} POE at 25-30 DAS	BDL	BDL	BDL	BDL
T_8:	Oxyfluorfen 0.18 kg ha^{-1} PE *fb* Imazethapyr 75 g ha^{-1} POE at 25-30 DAS	BDL	BDL	BDL	BDL

CONCLUSIONS

On two-year field experimentation (2013-2014), it is summarised that higher groundnut production with efficient weed control in *kharif* groundnut under South *Saurashtra* region can be achieved by treating the crop with pendimethalin 0.9 kg ha^{-1} PE *fb* IC & HW at 40-45 DAS or pendimethalin 0.9 kg ha^{-1} PE *fb* quizalofop-ethyl 40 g ha^{-1} POE at 20-25 DAS without any herbicidal residues risk to human beings as well as to the environment and rotational crops. These herbicides were found safe for rotational crops in groundnut based cropping system (Mehriya *et al.,* 2020). Persistence of pendimethalin, oxyfluorfen and quizalofop-ethyl in soil detected up to 30 days crop growth. At other sampling stages the applied herbicides residue were found below the hazardous limits (BDL).

FUTURE SCOPE

Use of pre-and PoE herbicides for weed control in *kharif* groundnut with recommended dosage and their persistence would be checked in current changed climatic scenario and their interaction with microbial study. This will gave a better scope to reduce the pesticide residues in leachable soils which may pose a great threat to the all water users. Their residual effect on rotational crops needs the further study.

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