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"STUDIES ON CONTAMINATION LEVEL OF PESTICIDES RESIDUES ON GRAPE GROWING SOILS IN NASHIK DISTRICT"

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Abstract—Nashik is well known as "Grape City" in the Maharashtra state. Soil samples were collected from different villages of leading grape growing areas of Nashik district and analyzed for its pesticides residue using multiresidue pesticide analysis technique by LCMS/MS and GCMS/MS instruments. Pesticides were detected in 73.33% of the soil samples collected. Concentration and percent contamination of pesticides residues were determined. In the tested soil samples residues of various pesticides were found, the pesticides which are found in notable amount are: Azoxystorbin (1.2-3 ppb, 53.33%), Carbendazim (2.2-9.2 ppb, 13.33%), Dimethomorph (2-17.3 ppb, 66.66%), Clothianidin (1.6-2.5 ppb, 26.66%), Imidacloprid (1.9-27.2 ppb, 40%) etc. Apart from this during our study to our great surprise in two soil samples we have found the residues of pp-DDE, an isomer of DDT (3-17 ppb) which is already banned. The presence of banned pesticide residues in soil sample is a matter of concern for future food chain accumulation and human health also. The right awareness about the use of pesticides will thus be useful for sustainable farming.

Keywords- *Multiresidue pesticide analysis, LCMS/MS, Sustainable development.*

I. INTRODUCTION

Soil is a dynamic living system. The overdose of chemical pesticides retains the residue in soil.[1,2] Pesticides may reach the soil through direct application to soil surface, incorporation in the top few inches of soil or during application to crops. Excessive use of chemicals has put forth question mark on sustainability of agriculture by contaminating the soil and declining food quality.[3] Pesticide consumption in Grape farms is on higher side. A plant retains only half of this applied spray as the leaf creates a non-wetting interface for the pesticide. The remaining pesticide runs off and contaminates soil and water and affects terrestrial and aquatic life. [4]

Out of total geographical area of Nashik district 8, 65,000 ha are under grape cultivation. About 60-70% of total production of seedless grapes are produced in Nasik district .Out of 15 talukas from Nasik district, 90% of grape production are from Nasik, Niphad and Dindori. These are leading growers of grapes. Percentage of pesticides consumption for grapes in these areas are on higher side. Out of 10-12 metric tonnes of grapes produced every year, the export rate tunes to only 1% due to excess application of pesticides which, declines quality of grapes. [5].A survey about pesticide use-practices was conducted at the same time of sample collection with the help of structural questionnaire. Survey results indicated that farmers with low education level used highly toxic pesticides. Farmers reported that they did not always use pesticides in an appropriate manner. These improper practices may result in the contamination of the environment by pesticides. For the present study not much work has been found in Nasik district and its outskirts. Therefore, the need of present proposed study is felt. As well as it is urgent need to promote the farmers about judicious use of pesticides as per recommended Protocol.

II. MATERIALS AND METHODS

A. Study area:

Three major grape growing talukas from Nasik district as, Niphad, Dindori, and Nasik was selected. Grape farm of five progressive farmers were selected from each talukas for proposed study.

B. Soil sampling:

Sampling equipment (soil auger, bucket, plastic sheet, plastic bags) Soil samples were collected from the study areas in August to September 2012 by proper soil sampling methods.[6] The composite soil samples were drawn from 0-15 cms. 2 depth Samples were collected from the vine row where most of the vine roots are located using stainless steel auger. The subsamples were placed into a 16-liter bucket, 4-5 samples from each location were thoroughly mixed on a plastic sheet to ensure that the soil collected was truly representative of each location, then air-dried, grounded and sieved through a mesh with a grain size of 2 mm. samples are packed in air tight plastic bags, codes are given as, A to O for 15 samples and then samples are transported ice preserved to the laboratory until further chemical processing. 5 soil samples from different villages of each taluka were collected by proper sampling method in such a way that, 2 samples from export quality grape growing field and 3 samples from random field.

Figure 1. Soil sampling procedure

C. Sample Extraction Procedure:

Weigh 1g soil sample, add 5 ml water, 10 ml ethyl acetate and 10 g sodium sulphate anhydrous and homogenize it for 2 min at high speed and centrifuge for 5 minutes at 50000 rpm. Draw 3 ml of the ethyl acetate phase into a centrifuge tube containing 25 mg primary secondary amine shake vortex for 1 min. Centrifuge at around 5000 rpm for five minutes. Take 2 ml cleaned supernatant and add 0.2 ml 10% diethylene glycol in methanol to it. Evaporate it under gentle stream of nitrogen using low volume concentrator at 35 °C. Reconstitute into 1 ml methanol and 1 ml 0.1% acetic acid in water. Centrifuge at 10000 rpm for 5 min and filter through 0.2 µm PVDF/nylon membrane filter. Inject 10 µl into LCMS/MS.

D. Instrumental analysis:

Chemicals

Methanol & Water (HPLC Grade) of J T Backer as a mobile phase. Chilled distilled water to maintain the temp. of matrix as increase in temp cause degradation of residues like, captan, captafol and dicofol and Ethyl Acetate to prevent degradation of some pesticide residues in Extraction Primary secondary amine for cleaning of matrix interference in sample, Activated Sodium sulphate to remove water traces, formic acid to acidify extraction solvent,Ammonium formate as a buffer for mobile phase. 10% Di ethylene glycol in methanol as analytes keeper & protector in MS. roethylene. Filter of 0.22 µm used to filter final injection volume before going to fill vial. All these were purchased from Merk.

Pesticide standards

The certified Pesticides standards were purchased from Dr. Ehrenstorfer GmbH, Germany. The purity of all pesticide standards were greater than 95%.

Preparation of standards

Weight around 5.0 mg of pesticide standards makeup with ethyl acetate for GCMS/MS compounds and methanol for LCMS/MS compounds in to 5 ml volumetric flask. The solution concentration is around 1000 mg/ litre Preparation of the working standard (mix standard) concentration 1.0 mg/litre and do the subsequent dilution with respective solvent was done. Theses individual standard stock solutions were mixed appropriately to obtain desire concentration of Pesticides and then stock solution of std mix was serially diluted with methanol to 1 µg/ ml. Separation and quantification of organochlorine pesticides was carried out using GCMS(Perkin Elmer,Clarus500) with auto sampler equipped with an Electron Capture Detector,while Quantification of other pesticides was carried out using LCMS/MS(Abscex, 4000 Q TRAP) [7] .

III. RESULTS AND DISCUSSION

Calibration was done by Linear regression method. Concentrations of analyte were determined by comparing the peak area of the samples and five level calibration curves of the standards. The correlation coefficient of calibration curves were ranged from 0.9980 to 0.9990. The peak identification was conducted by the accurate retention time of each standard on chromatogram. Concentration and percent contamination of pesticides residues were determined. In the tested soil samples residues of various pesticides were found shown in a given table I.

TABLE I: Concentration of pesticides residues in soil samples all values are in **ppb (ng/ml)**

Soil sample	*Azoxystrobin*	*Carbendazim*	*Dimethomorph*	*Chlothianidin*	*Imidacloprid*	*pp-DDE*
A	3.42	-	2.8	-	1.9	-
B	1.03	9.2	3.7	-	10.2	-
C	-	-	5.6	1.6	-	3
D	-	-	26.3	-	-	-
E	-	2.2	3.8	2.2	-	-
F	-	-	-	-	-	-
G	2.03	-	-	2.5	-	-
H	-	-	-	-	-	-
I	7.2	-	9.5	2.1	3.8	-
J	-	-	2.9	-	-	-
K	1.2	-	3.2	-	27.2	-
L	-	-	-	-	-	-
M	11.		17.		14.	-
N	5.	-	2.	-	17.	17
O	-	-	-	-	-	-

The residues of pp-DDE, an isomer of DDT were detected in soil samples which were already banned.[8,9] The presence of banned pesticide residues in soil samples is matter of concern for future food accumulation and human health also. So we need to find out an alternative solution [10,11] and stronger regulations. Therefore, the avoidance of these pesticides can reduce the contamination in soil and also can help to prevent the financial loss of farmers and exporter too.

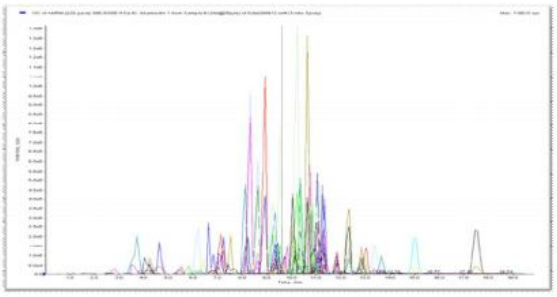

Figure 2. Chromatogram of all PR in soil on LCMS by multiresidue pesticide analysis

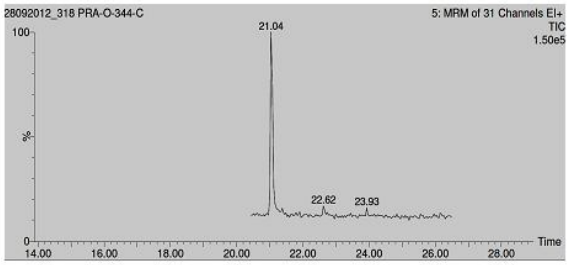

Figure 3. Chromatogram of pp-DDE pesticide in soil sample-C on GCMS/MS.

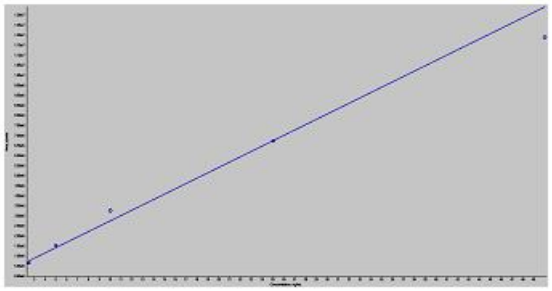

Figure 4. Linear Regression curve of standard of concentration vs. peak area.

IV. CONCLUSION

LCMS/MS and GCMS/MS are the best techniques for analysis of soil samples for it's pesticide residues. Organochlorine pesticides which have low molecular weight and volatile can be analyzed on GCMS while, other pesticides are analyzed with the help of LCMS. Limit of Detection (LOD) for LCMS is 1ppb and for GCMS it's 10ppb. Therefore, LCMS is more sensitive than GCMS. Out of 15 soil samples 12 samples are found contaminated by pesticides. Thus, it is urgent need to promote the farmers about judicious use of pesticides as per recommended protocol and adopting safe and effective system that are capable of maintaining their productivity commercially competitive and environmental sound.

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