

# Method Development and Validation in Water Matrix Employing Tandem Mass Spectrometry: Quantitative Analysis of 76 Multiclass Pesticides in Groundwater Samples Collected From Delhi NCR Region by Quechers Based Liquid-Liquid Extraction Method

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## Abstract

A miniaturized, QuEChERS based, liquid-liquid extraction method followed by tandem gas chromatography-mass spectrometry determination was developed and validated for 76 pesticide residues determination in water using European SANTE/11312/2021 guideline and monitored the 70 ground water samples collected from Delhi NCR, India region for the determination of pesticide residues. The accuracy, precision, specificity, linearity, recovery, repeatability, reproducibility, robustness, limit of detection and limit of quantification of the method were evaluated. Uncertainty measurement was calculated for each analyte. The samples were extracted with dichloromethane using liquid-liquid extraction process. Each Pesticide was optimized in terms of different MS parameters and chromatographic conditions by GC-MS/MS using Multiple Reaction Monitoring (MRM) mode. In linearity regression co-efficient ( $R^2$ ) value of each pesticide was determined in the range of 0.9856-0.9997. The percent average recoveries were found from 87.98—119.99 at 1, 5 and 10 LOQ spiking level. The method performance complied with the regulatory requirements, and thus, can be implemented. LOD and LOQ of the pesticides were found 10 $\mu$ g/L and 30 $\mu$ g/L respectively. Expanded Measurement of uncertainty of all pesticides was below  $\pm 50$  percent of mean recovery value as per SANTE 11312/2021. Organophosphorous, fungicides, and pyrethroids were the group of pesticides most frequently found. In this study, 12 pesticides were found above the MRL (EEC Council Directive 1980/778/EEC). Additionally, dieldrin, which is now banned by law in India, was found in samples of ground water. The method provided a high throughput analysis of multi-class pesticides with satisfactory selectivity, sensitivity, accuracy, and precision.

**Keywords** QuEChERS, European SANTE/11312/2021, GC-MS/MS, MRM, Pesticides, Uncertainty measurement, Groundwater

## 1. Introduction

Pesticides are chemical substances that are frequently used in farming. They are primarily used to plant pathogen from harm that may be brought on by other undesirable plants, creatures, or animals. They are also used to stimulate plant development processes or improve the effects of other chemicals [1]. The usage of pesticides now raises serious concerns for ecological systems, animals, and health impacts [2]. The need for food goods and reliance on chemical pesticides to boost productivity and effectively manage insect populations expanded along with the world population [3]. Pesticide application helps to prevent a loss in food output of 65%. Additionally, it is desirable to cultivate the product more regularly under the right circumstances so that it may be kept fresh for a long time and provide the producer with greater economic profit [4]. Intensive agricultural practices included the use of pesticides to enhance crop yields, which is one of the cause of occurrence and persistence of pesticide residues in water [5]. Only 10% of sprayed pesticides, according to studies, reach their intended targets; the remainder penetrates and contaminates several environmental matrices, such as air, soil, and water [4]. Surface run-off is the main method by which pesticides are transported from agricultural fields to surface waterways [6]. Monitoring and assessment of pesticide contamination in farmland water has become a necessity. Particularly, there is need to determine, quantify and confirm pesticide residues in water for both research and regulatory purposes. The pesticides are analyzed by gas chromatography Mass spectrometry [7, 8, and 9]. The preparation of the sample and the instrumentation analysis are the two fundamental phases in the examination of pesticide residues at the trace level. In the first phase of the analysis, matrix interference is removed, and the analyte is concentrated up to the LOQ of the instrument. The instrument's LOQ level for the second step allows for both qualitative and quantitative assessment of the analyte when utilizing the right analytical strategy.

In this paper, the work has been done on method development, validation and the determination of pesticide residues in ground water samples collected from Delhi NCR, India. Because of the increasing usage of organic pollutants on the Indian subcontinent, which has led to their prevalence in the aquatic environment, 76 pesticides have chosen for this study. Organic solvents are typically evaporated and the solutions are reconstituted with a different solvent when the GC-MS/MS technique is used to identify pesticide residues. Various evaporation techniques exist, such as heating, gas blowing onto the solvent's surface, centrifugal force, rotary vacuum evaporator in present study etc. After applying a high vacuum, the solvents are quickly and easily evaporated from the dried or concentrated extracts in centrifugal tubes [10].

Objectives of this study are to: (1) develop a liquid liquid extraction method employing QuEChERS that would enable the extraction of several classes of pesticides from samples of ground water; and (2) integrate this method with the triple quadrupole mass spectrometry and its validation and MU calculation to assure the competency of the procedures; (3) Applying the developed and validated techniques for the analysis of pesticides in ground water and other water samples.

## Pesticide consumption: Indian scenario

In 1948, DDT, used to treat malaria, and hexachlorocyclohexane (HCH), used to treat locusts, were the first pesticides used in India [11]. India holds 4th position in global pesticide production and supply after

the USA, China, and Japan, with a pesticide production of 93,000 metric tons in 2020 [12]. The use of ineffective pesticides and a lack of knowledge about pesticide use hinder pesticide use in India. According to the Economic Survey 2015-16, India has seen an increase in pesticide residue found in food products as a result of pesticide usage without sufficient controls [13 and 14]. Over the past 30 years, a decline in pesticide usage has been determined to be the national trend. While fungicides and herbicides were used more often over time, insecticide use decreased from 1990 to 2020 (Fig.1) [15].

## 2. Materials and methods

### 2.1 Chemicals

All the pesticides (methomyl, trichlorfon, omethoate, propoxur, trifluralin, sulfotep,  $\alpha$ -BHC, thiometon, dimethoate, atrazine,  $\beta$ -BHC, Propetamphos,  $\gamma$ -BHC, fluchloralin, etrimphos, triallate, iprobenphos, dimethachlor, metribuzin, transfluthrin, metalaxyl, paraoxon methyl, paraoxon ethyl, pirimiphos methyl, malathion, phoratesulfoxide, chlorpyrifos, fenthion, aldrin, fipronil sulfide, pendimethalin, fipronil, chlorfenvinphos, phenthoate, captan, butachlor, cis-chlordane, hexaconazole, isoprothiolane, profenophos, dieldrin, o,p-DDD, buprofezin, kresoxim methyl, chlorfenapyr, fenthionsulfoxide, endosulfan-I,  $\beta$ -endosulfan, ethion, o,p-DDT, benalaxyl-M, parathion methyl, ediphenphos, propiconazole, endosulfan sulfate, p,p-DDT, diclofop methyl, bifenthrin, methoxychlor, fenpropathrin, dicofol, anilofos, pyriproxifen, L-cyhalothrin, permethrin,  $\beta$ -cyfluthrin, cypermethrin, fenvalerate, deltamethrin, chlorpropham, triadimenol, flucythrinate, cinmethylin, oxyflorfen, cyphenothrin and fluvalinate were purchased from Ms. Sigma Aldrich and Dr. Ehrenstorfer. HPLC grade n-hexane, acetone, ethyl acetate and dichloromethane solvents were purchased from Fisher Scientific and Merck. Anhydrous NaCl and Na<sub>2</sub>SO<sub>4</sub> were procured from Fisher Scientific.

### 2.2 Preparation of pesticide standard solutions

Each pesticide was prepared individually as a stock solution at a concentration of 1000 ppm (about 10 mg in 10 ml of volume flask) using diluent hexane and acetone in ratio of 9:1. Stock and working standards were both maintained in a deep freezer at a temperature of -20°C. The use of solvents without distillation was made possible by the absence of contaminants in the GC-MS/MS blank chromatogram.

### 2.3 Sampling Location

The National Capital Region (NCR) is a planning region centered upon the National Capital Territory (NCT) of Delhi in India (NCR Planning Board). The NCR is a rural-urban region, with a population of over 46,069,000 and an urbanization level of 62.6% [16]. Due to extensive groundwater abstraction for household, agricultural, and industrial use, Delhi City now has a restricted supply of surface water resources for drinking. Significant concerns have been expressed concerning the quality and quantity of groundwater as a result of the widespread abstraction of groundwater, which has also upset the resource's demand-supply equilibrium. Water resources in Delhi are currently facing a number of serious problems, such as overuse and groundwater contamination. Delhi has been categorized as over exploited in terms of groundwater development [17].

### 2.4 Water sample collection

Due to their significant populations as well as the anticipated high levels of organic pollutant contamination, Delhi NCR was chosen as the testing sites for this investigation. There were a total of 14

sites for ground water sampling. Each of the sites in Gurugram, Ghaziabad, Noida, and Faridabad had two samples collected, while North West Delhi, North East, West Delhi, New Delhi, South Delhi, and South West Delhi, from each site one sample was collected (Fig.2). Ground water samples were collected in glass bottles and stored at 4°C in dark as per BIS method IS 13969:1994. This study describes an in-house developed analytical procedure that was established and validated for the analysis of 76 multiclass pesticide residues and also detection of residues in 70 ground water samples collected from Delhi NCR region.

## 2.5 Sample Preparation

QuEChERS based liquid liquid extraction method result is being followed in this paper. A total of 500 mL of water sample was transferred into a 1 liter glass-separating funnel. Then, 50 g of NaCl was added to produce a salt out effect. It was thoroughly mixed by inverting the flask three to four times. The sample was extracted thrice with (50:50:50) mL dichloromethane and shaken for 4–5 mins each time with periodic venting. The combined organic phase was dried by passing it through anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic phase was dried in a vacuum rotary evaporator (Buchi make) and further sample was reconstituted in 5 mL of ethyl acetate and evaporated using nitrogen evaporator. Final sample was reconstituted in 1ml of n-hexane and acetone in the ration of 9:1, which was analyzed by GC–MS/MS (Tandem Gas Chromatography-Mass Spectroscopy). 1 LOQ, 5 LOQ, and 10 LOQ were the three replicas of each spiking level that were prepared for the study.

## 2.6 Instrumental conditions

Gas chromatography–tandem mass spectrometry (Shimadzu GCMS-TQ 8040) equipped with auto-sampler. For efficient chromatographic separation and quantification of pesticides HP-5 ms capillary column (J and W Scientific Co., 5% Phenylated methyl siloxane, 30 m length × 0.25 mm i.d. × 0.25 μm film thicknesses) was used. Temperature of injector was set at 250°C splitless. Carrier gas flow was 1.0 ml/min and the ion source temperature was set at 230°C. Better chromatographic separation was observed using an oven programming of initial temperature 50°C for 2 min, followed by a ramp rate of 15°C/min. up to temperature of 190°C with a hold time of 1 min and finally by ramping up to a final temperature of 280°C at a rate of 5°C/min with a hold duration of 10 min. For all weighing requirements, a Mettler Toledo weighing balance was used, with a range of 0.01 mg to 200 g. Both nitrogen and vacuum rotary evaporators from Caliper Life Sciences and Buchi were used for the evaporation process.

## 2.7 Identification of pesticides

The GC-MS Browser software Lab solution program (Shimadzu, Kyoto, Japan) was used to perform a qualitative evaluation of pesticide residues in water examined by GCMS/MS. Identification was accomplished by comparing the Quantifier ion peak and the Qualifier ion peak for each pesticide on each substrate, comparing the ion ratios of two transitions of samples, matrix-matched standard and confirming the retention time standard deviation.

## 2.8. Method Development and Validation

The following seven fundamental criteria need to be satisfied before a technique could be developed and validated: linearity, accuracy/recovery, repeatability/reproducibility, specificity/selectivity, limit of

detection, limit of quantitation, and robustness/ruggedness. As a result, one blank sample (solvent), one non-spiked sample (matrix only), five spiked samples at 1LOQ, five spiked samples at 5LOQ, and five spiked samples at 10 LOQ were required for the experimental component of the validation. The validation parameters examined were linearity (the value  $R^2 > 0.98$  was established as the internal criteria), sensitivity, LOQ, specificity, accuracy (bias), repeatability-precision, reproducibility-precision, ion ratio, retention duration, and uncertainty.

### 2.8.1 Specificity

Reagent blank and blank control samples were processed and analyzed following the sample preparation procedure as described. The response and quantitative analysis data have been evaluated to find out the specificity. A triple quadrupole mass analyzer is employed in the procedures developed, resulting in exceptional specificity and selectivity due to the two specialized transitions monitored for each pesticide.

### 2.8.2 Linearity

Linearity of GC-MS/MS instrument was assessed at seven points calibration curve of matrix matched standard calibration, prepared by spiking pesticide mixture solution at different concentration levels in blank sample extract. Calibration curves were plotted by plotting an area of individual pesticide against seven different concentration levels of 0.010, 0.025, 0.050, 0.150, 0.250, 0.300, 0.500 mg/Kg. Regression co-efficient less than 0.99 was determined for 10 pesticides and greater than 0.99 was for 66 pesticides. Regression co-efficient ( $R^2$ ) value of each pesticide was determined in the range of 0.9856 to 0.9997. Regression co-efficient ( $R^2$ ) values have been shown in Table 1.

### 2.8.3 Limit of Detection (LOD) and Limit of Quantification (LOQ)

LOD and LOQ were measured as per SANTE 13112/2021 guideline. Limit of Quantification for each molecule was set by default as  $30\mu\text{g/L}$  and the Limit of Detection as  $10\mu\text{g/L}$ . The concentration of each pesticide (in  $\mu\text{g/L}$ ) was estimated from the matrix spiked chromatogram that produced a signal three times that of (Np-p) blank.

### 2.8.4 Trueness/Accuracy/Recovery

Recovery of sample was determined in six replicates at each level by spiking with working standard solution of pesticide CRM to homogenously mixed sample at 1, 5 and 10 LOQ level. Recovery percentage values were in the range of 87.98% to 119.99%. Samples were prepared according to the mentioned procedure and quantitatively analyzed by GC-MS/MS. Average recovery percentage of pesticide has been shown in Table 2. Chromatogram is presented in Fig:

### 2.8.5 Precision/Repeatability

Precision has been evaluated at 5 LOQ ( $150\mu\text{g/L}$ ) spiking level. Based on the findings of independent tests carried out using the same methodology on identical test samples on the same day, precision under repeatability conditions was assessed. The observed recovery values have been statistically analyzed to find out the SD and RSD values. In case of all analytes the %RSD values have been found (1.981-11.666) within the acceptable criteria of  $\leq 20\%$  as per SANTE 11312/2021 guideline.

### 2.8.6 Reproducibility/Ruggedness

Ruggedness was evaluated by analyzing the spiked samples at 150µg/L on a different day. Freshly spiked samples were processed as per the sample preparation procedure and analyzed in instrument. The obtained recovery % values were evaluated and found within the acceptable range of 75.65%-114.5%.

### 2.8.7 Robustness

Recovery experiment at 50µg/L spiking level was performed with minor variation in method parameter. Sample extraction method was modified. 75g Sodium chloride was used for extraction in place of 50mg Sodium chloride as mentioned in the method. The obtained recovery % values were evaluated and found within the acceptable range of 74.14% to 105.19%.

### 2.7.8 Uncertainty Measurement

Uncertainty is quantitative indication of the quality of the result. Expanded Measurement of uncertainty for all pesticides was below ±50 percent of mean recovery value as per SANTE 11312/2021 guideline.

#### MU estimation:

For each pesticide, an estimate of  $u'$  (bias) and  $u'$  (precision) was calculated. Data is represented in Table 3.

#### Measurement of the $u'$ (bias) component

The discrepancy between the measured value and the real value is known as bias. Without CRM, the bias is the difference between the spiked and measured concentrations, and the actual value is the concentration that has been injected. Relative bias is determined by:

$$relative\ bias = \frac{measured\ concentration - spiked\ concentration}{spiked\ concentration} \times 100$$

The equation below can be used to calculate  $u'$ (bias):

$$u'(bias\ \%) = \sqrt{RMS'(bias)^2 + u'(Cref)^2}$$

RMS'(bias) = root mean square of the relative bias =

$$\frac{\sqrt{\sum bias^2}}{N} = \sqrt{mean^2\ bias + SD.P^2\ bias}$$

Mean bias = the mean of the relative bias

SD.Pbias = the population standard deviation of the relative bias

$u'(Cref)$  = uncertainty of the spiked concentration

It may be considered that the amount of uncertainty associated with the spiking is insignificant when the spiked samples are prepared using certified analytical standards and calibrated/verified volumetric material/balances. Then, the equation is reduced to:

$$u'(bias\ \%) = \sqrt{mean^2\ bias + SD.P^2\ bias}$$

#### Measurement of the $u'$ (precision) component

The pesticide's RSDrW (within-lab reproducibility) is employed as a precision component.

$u'$  (precision %) = RSDrW

### Measurement of the combined measurement uncertainty

The total measurement uncertainty is calculated by combining the aforementioned formulae.

$$u'(\text{combined } \%) = \sqrt{\text{mean}^2 \text{ bias} + \text{SD} \cdot P^2 \text{ bias} + \sqrt{\text{RSD}r_w^2}}$$

### Measurement of the expanded measurement uncertainty Coverage factor $k$

In general, the value of the coverage factor  $k$  is chosen on the basis of the desired level of confidence to be associated with the interval. Typically,  $k$  is in the range 2 to 3.

$$U' = k \times u'$$

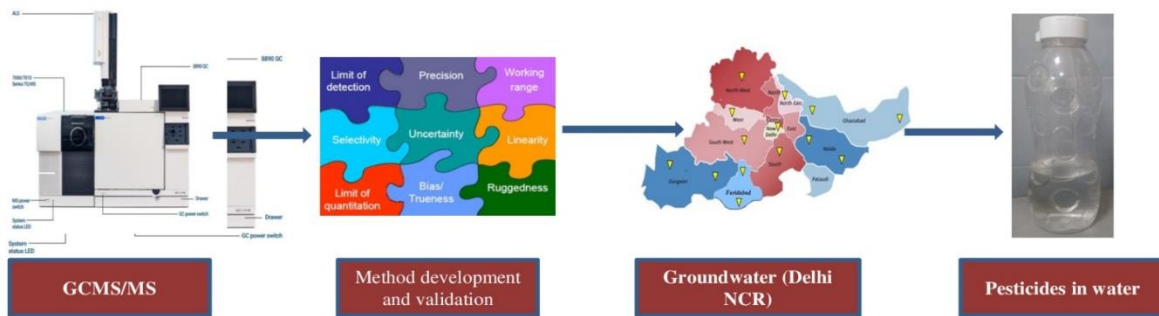
## 3. Results and discussion

The validation in accordance with SANTE/11312/2021 instructions showed the techniques capacity to detect pesticide residues in a number of different commodities. In this study, we presented a large-scale multi-residue method for the determination pesticide residues in groundwater. Delhi NCR was chosen as the testing sites for this investigation. There were a total of 14 sites for ground water sampling. QuEChERS based liquid liquid extraction method resulted is being followed in this study followed by analysis using GCMS/MS. The method offered high throughput residue analysis for a large number of pesticides (76 in total). As the method performance complied with the requirements of SANTE 11312/2021 analytical quality control criteria, the current method is recommended for regulatory testing of water for the residues of pesticides. The seven point calibration curve of the matrix matched standard calibration, which was created by spiking a pesticide combination solution at various concentration levels. Regression co-efficient ( $R^2$ ) value of each pesticide was determined in the range of 0.9856-0.9997. Limit of Quantification for each molecule was set by default as 30 $\mu\text{g/L}$  and the Limit of Detection as 10 $\mu\text{g/L}$ . Recovery percentage values are in the range of 87.98%—119.99% at 1, 5 and 10 LOQ spiking level. At a spiking level of 5 LOQ (150  $\mu\text{g/L}$ ), precision has been assessed. Percent RSD have been observed (1.981%-11.666%) that fall within the permitted range of 20%. The resulting recovery percent values of ruggedness were assessed from 75.65 to 114.5% and found within the acceptable range. The obtained recovery percent values of robustness were evaluated from 74.14 to 105.19% and found within the permissible range. According to SANTE 11312/2021 guidelines, the expanded measurement of uncertainty for all pesticides was less than 50% of the mean recovery value. We examined 70 samples of ground water and discovered that all of them were pesticide-contaminated. Organophosphorous, fungicides, and pyrethroids were the group of pesticides most frequently found (Table 4). According to European Economic Commission standards (EEC Council Directive 1980/778/EEC), the total amount of different pesticides in water should not be more than 0.50 $\mu\text{g/l}$ , and the level of each pesticide should not be higher than 0.10 $\mu\text{g/l}$ . In this study 12 pesticides were found above the MRL. Additionally, dieldrin, which is now banned by law in India, was found in samples of ground water.

## 4. Conclusion

In this paper we discussed the application of GC-MS/MS analysis with a liquid extraction approach based on QuEChERS for the detection of pesticides. In ground water samples taken from the Delhi NCR region, several multi-class pesticides were identified. The used technique enables the detection of the targeted analytes while obtaining LOD at  $\mu\text{g/L}$  levels with great precision, accuracy, and recovery.

Examined the uncertainty measurement of the existing analytical method in order to provide reliability. As the method performance complied with the requirements of SANTE 11312/2021 analytical quality control criteria, the current method is recommended for regulatory testing of water for the residues of pesticides. Throughout water from various sources, pesticide residues that are still widely utilized in the nation have been discovered. Pesticides even at low concentrations pose a serious threat to the environment and human health; thereby pesticides are toxic not only to those who work in agriculture and horticulture fields but also to the general populace [18]. It is possible to limit pesticide residue in the environment by using pesticides wisely and providing end users with the necessary knowledge on how to use them in agriculture and the home. To control excessive usage, farmers need to be made more aware of their responsibilities. Implementing integrated pest management approaches and taking strict action against vendors of outlawed or fake pesticides are two potential strategies for reducing future pesticide usage.



Figures and Tables

Graphical Abstract

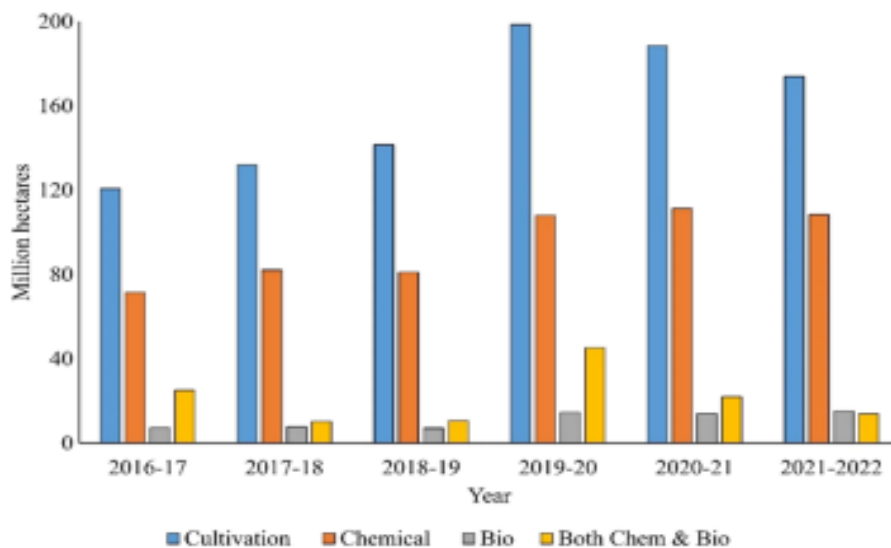


Fig: 1

Fig. 1: Cultivation area and the use of chemical and bio-pesticides in India Source: PPQS, (2021)



Fig: 2

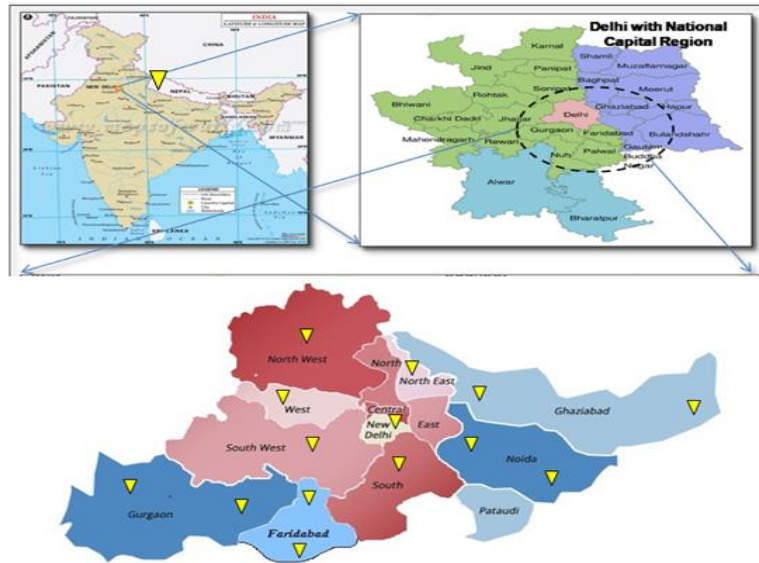


Fig 2: Map of sampling locations in Delhi NCR in India

Fig: 3

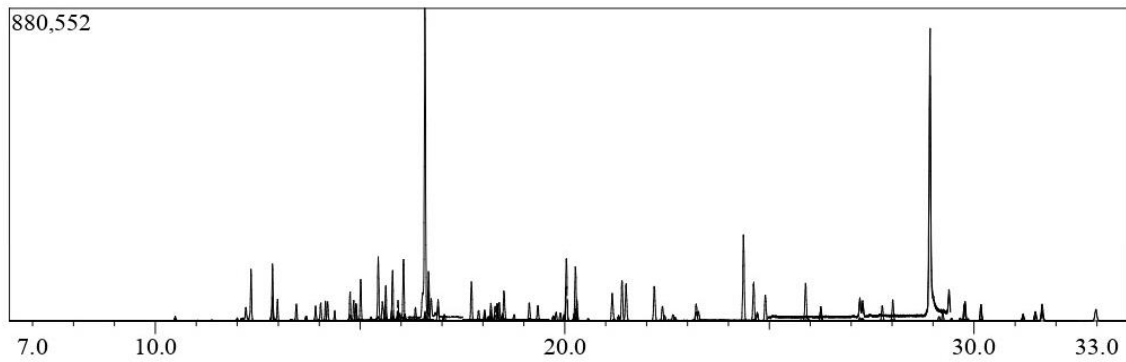


Fig. 3 Chromatogram of 1LOQ Recovery

Table: 1 Regression co-efficient ( $R^2$ ) value

S.No.	Compound Name	Regression co-efficient ( $R^2$ )
1	Methomyl	0.9926
2	Trichlorfon	0.9957
3	Omethoate	0.9980
4	Propoxur	0.9989
5	Trifluralin	0.9897
6	Sulfotep	0.9990
7	alpha-BHC	0.9990
8	Thiometon	0.9987
9	Dimethoate	0.9983
10	Atrazine	0.9968
11	beta-BHC	0.9988

12	Propetamphos	0.9982
13	gamma-BHC (Lindane)	0.9927
14	Fluchloralin	0.9868
15	Etrimfos	0.9996
16	Tri-allate	0.9973
17	Iprobenfos	0.9970
18	Dimethachlor	0.9941
19	Metribuzin	0.9875
20	Transfluthrin	0.9948
21	Metalaxyl	0.9892
22	Paraoxon Methyl	0.9856
23	Paraoxon-ethyl	0.9893
24	Pirimiphos-methyl	0.9990
25	Malathion	0.9985
26	Phoratesulfoxide	0.9992
27	Chlorpyrifos	0.9989
28	Fenthion	0.9968
29	Aldrin	0.9988
30	Fipronil sulfide	0.9978
31	Pendimethalin	0.9880
32	Fipronil	0.9894
33	(E)-Chlorfenvinphos	0.9995
34	Phenthoate	0.9988
35	Captan	0.9965
36	Butachlor	0.9983
37	cis-Chlordane	0.9979
38	Hexaconazole	0.9997
39	Isoprothiolane	0.9968
40	Profenofos	0.9984
41	Dieldrin	0.9995
42	o,p'-DDD	0.9962
43	Buprofezin	0.9992
44	Kresoxim-methyl	0.9988
45	Chlorfenapyr	0.9901
46	FenthionSulfoxide	0.9930
47	Endosulfan-I	0.9980
48	beta-Endosulfan	0.9980
49	Ethion	0.9984
50	o,p'-DDT	0.9985
51	Benalaxyl-M	0.9966
52	Parathion-methyl	0.9935
53	Edifenphos	0.9962

54	Propiconazole	0.9986
55	Endosulfan sulfate	0.9983
56	p,p'-DDT	0.9975
57	Diclofop-methyl	0.9936
58	Bifenthrin	0.9875
59	Methoxychlor	0.9916
60	Fenpropathrin	0.9985
61	Dicofol	0.9977
62	Anilofos	0.9948
63	Pyriproxyfen	0.9996
64	L-Cyhalothrin	0.9908
65	Permethrin	0.9972
66	beta-Cyfluthrin	0.9947
67	α-Cypermethrin	0.9969
68	Fenvalerate	0.9963
69	Deltamethrin	0.9906
70	Chlorpropham	0.9988
71	Triadimenol	0.9962
72	Flucythrinate	0.9935
73	Cinmethylin	0.9907
74	Oxyfluorfen	0.9888
75	Cyphenothrin	0.9978
76	Fluvalinate	0.9927

**Table: 2 Recoveries at 1, 5 and 10 LOQ (30,150,300µg/L) Level**

S.No	Name	Spiking Concentration (µg/L)	Mean Recovery % 1LOQ	Mean Recovery % 5LOQ	Mean Recovery % 10LOQ
1	Methomyl	30, 150, 300	117.8672	96.9656	103.8376
2	Trichlorfon	30, 150, 300	117.6228	109.2067	119.4474
3	Omethoate	30, 150, 300	115.8789	98.9249	113.1357
4	Propoxur	30, 150, 300	110.1922	104.8248	108.2363
5	Trifluralin	30, 150, 300	119.6761	114.1760	116.6342
6	Sulfotep	30, 150, 300	113.8194	104.8928	103.3147
7	alpha-BHC	30, 150, 300	116.8433	105.1052	104.7936
8	Thiometon	30, 150, 300	111.0022	99.2232	97.9402
9	Dimethoate	30, 150, 300	119.9939	104.6027	100.6567
10	Atrazine	30, 150, 300	119.0489	110.4712	108.8628
11	beta-BHC	30, 150, 300	118.3322	103.7527	99.3929
12	Propetamphos	30, 150, 300	111.5806	102.3178	101.0488
13	gamma-BHC (Lindane)	30, 150, 300	119.5161	107.4251	107.1943
14	Fluchloralin	30, 150, 300	111.8517	98.6983	97.5485

15	Etrimfos	30, 150, 300	114.0950	112.3968	116.7214
16	Tri-allate	30, 150, 300	119.7861	103.5558	102.2433
17	Iprobenfos	30, 150, 300	100.1100	107.1028	108.0298
18	Dimethachlor	30, 150, 300	115.7733	106.3749	109.6964
19	Metribuzin	30, 150, 300	117.6194	104.8821	101.9081
20	Transfluthrin	30, 150, 300	118.7506	94.1248	94.5554
21	Metalaxyl	30, 150, 300	102.7839	102.1517	98.8612
22	Paraoxon Methyl	30, 150, 300	119.6178	108.7218	113.1918
23	Paraoxon-ethyl	30, 150, 300	112.2161	102.4088	98.7736
24	Pirimiphos-methyl	30, 150, 300	97.4383	87.9764	88.3241
25	Malathion	30, 150, 300	116.2106	108.3419	109.0809
26	Phoratesulfoxide	30, 150, 300	118.1089	113.0679	109.1685
27	Chlorpyrifos	30, 150, 300	112.8194	103.5286	100.5927
28	Fenthion	30, 150, 300	119.7778	107.6872	108.1959
29	Aldrin	30, 150, 300	112.6300	103.7327	98.2168
30	Fipronil sulfide	30, 150, 300	110.7839	103.5509	102.8651
31	Pendimethalin	30, 150, 300	89.3206	116.1821	104.3804
32	Fipronil	30, 150, 300	103.2844	99.2381	97.6487
33	(E)-Chlorfenvinphos	30, 150, 300	113.3067	102.8413	103.2541
34	Phenthoate	30, 150, 300	119.5533	116.5033	124.2803
35	Captan	30, 150, 300	116.3500	105.8761	111.2462
36	Butachlor	30, 150, 300	119.0267	105.6361	108.2837
37	cis-Chlordane	30, 150, 300	115.9983	104.2142	104.7779
38	Hexaconazole	30, 150, 300	119.3900	107.9640	108.2176
39	Isoprothiolane	30, 150, 300	119.4539	114.5098	114.7614
40	Profenofos	30, 150, 300	119.2994	106.2168	108.4205
41	Dieldrin	30, 150, 300	104.9111	99.1360	95.3272
42	o,p'-DDD	30, 150, 300	118.9056	112.8103	111.7491
43	Buprofezin	30, 150, 300	118.4556	103.9529	110.4635
44	Kresoxim-methyl	30, 150, 300	117.7417	108.1774	109.6786
45	Chlorfenapyr	30, 150, 300	111.3500	104.3937	104.0752
46	FenthionSulfoxide	30, 150, 300	115.9411	106.9543	110.5034
47	Endosulfan-I	30, 150, 300	114.2356	102.6621	100.3596
48	beta-Endosulfan	30, 150, 300	114.3322	107.1940	103.3411
49	Ethion	30, 150, 300	118.2383	107.8812	108.6364
50	o,p'-DDT	30, 150, 300	107.8044	104.0160	101.7890
51	Benalaxyl-M	30, 150, 300	102.5144	89.5652	98.1123
52	Parathion-methyl	30, 150, 300	110.1050	101.8114	102.2522
53	Edifenphos	30, 150, 300	107.6272	101.7376	102.2484
54	Propiconazole	30, 150, 300	119.0894	107.9134	108.2521
55	Endosulfan sulfate	30, 150, 300	118.5628	110.5891	108.8037
56	p,p'-DDT	30, 150, 300	119.3339	110.0170	113.9401

57	Diclofop-methyl	30, 150, 300	119.5628	117.1976	115.0550
58	Bifenthrin	30, 150, 300	110.6406	105.3008	102.1957
59	Methoxychlor	30, 150, 300	116.5244	101.0786	107.4681
60	Fenpropathrin	30, 150, 300	117.0156	113.7294	116.4113
61	Dicofol	30, 150, 300	109.5233	106.5310	106.9503
62	Anilofos	30, 150, 300	113.5517	110.6374	113.8362
63	Pyriproxyfen	30, 150, 300	115.1094	113.9781	114.9656
64	L-Cyhalothrin	30, 150, 300	114.4022	104.4497	110.3518
65	Permethrin	30, 150, 300	111.6800	99.4396	102.0436
66	beta-Cyfluthrin	30, 150, 300	117.5500	106.8811	110.8119
67	α-Cypermethrin	30, 150, 300	115.5706	110.8690	114.1193
68	Fenvalerate	30, 150, 300	115.9839	115.3251	115.1367
69	Deltamethrin	30, 150, 300	117.6167	116.1582	117.5068
70	Chlorpropham	30, 150, 300	111.7822	118.6446	119.4589
71	Triadimenol	30, 150, 300	118.6750	108.7411	108.2754
72	Flucythrinate	30, 150, 300	117.8861	116.1203	119.0198
73	Cinmethylin	30, 150, 300	118.7300	123.4072	107.8054
74	Oxyfluorfen	30, 150, 300	118.7839	117.9082	119.3480
75	Cyphenothrin	30, 150, 300	118.3217	108.9213	110.7294
76	Fluvalinate	30, 150, 300	114.6900	113.8567	118.8686

**Table: 3 Expanded measurement uncertainties at 30µg/kg spike level**

S.No	Name	Expanded measurement uncertainty %
1	Methomyl	37.010
2	Trichlorfon	49.08
3	Omethoate	42.49
4	Propoxur	43.83
5	Trifluralin	43.93
6	Sulfotep	37.79
7	alpha-BHC	42.03
8	Thiometon	33.55
9	Dimethoate	44.04
10	Atrazine	40.81
11	beta-BHC	37.13
12	Propetamphos	34.52
13	gamma-BHC (Lindane)	39.56
14	Fluchloralin	33.31
15	Etrimfos	34.52
16	Tri-allate	40.8
17	Iprobenfos	28.69
18	Dimethachlor	30.43
19	Metribuzin	44.77

20	Transfluthrin	45.83
21	Metalaxyl	28.44
22	Paraoxon Methyl	43.77
23	Paraoxon-ethyl	31.68
24	Pirimiphos-methyl	23.18
25	Malathion	35.46
26	Phoratesulfoxide	49.7
27	Chlorpyrifos	39.45
28	Fenthion	45.56
29	Aldrin	35.82
30	Fipronil sulfide	28.21
31	Pendimethalin	40.72
32	Fipronil	23.15
33	(E)-Chlorfenvinphos	33.56
34	Phenthoate	40.89
35	Captan	38.35
36	Butachlor	46.31
37	cis-Chlordane	43.81
38	Hexaconazole	39.96
39	Isoprothiolane	42.35
40	Profenofos	43.41
41	Dieldrin	21.66
42	o,p'-DDD	44.75
43	Buprofezin	38.83
44	Kresoxim-methyl	40.04
45	Chlorfenapyr	37.18
46	FenthionSulfoxide	39.16
47	Endosulfan-I	35.43
48	beta-Endosulfan	41.13
49	Ethion	45.14
50	o,p'-DDT	27.33
51	Benalaxyl-M	48.67
52	Parathion-methyl	39.9
53	Edifenphos	37.4
54	Propiconazole	48.49
55	Endosulfan sulfate	46.99
56	p,p'-DDT	40.74
57	Diclofop-methyl	41.26
58	Bifenthrin	35.93
59	Methoxychlor	41.68
60	Fenpropathrin	40.16
61	Dicofol	31.91

62	Anilofos	29.57
63	Pyriproxyfen	40.87
64	L-Cyhalothrin	38.19
65	Permethrin	27.52
66	beta-Cyfluthrin	41.63
67	$\alpha$ -Cypermethrin	43.08
68	Fenvalerate	44.58
69	Deltamethrin	36.57
70	Chlorpropham	36.84
71	Triadimenol	42.63
72	Flucythrinate	41.83
73	Cinmethylin	39.13
74	Oxyfluorfen	40.68
75	Cyphenothrin	39.51
76	Fluvalinate	45.3

**Table: 4 Results of pesticides detected in groundwater samples collected from Delhi NCR**

S . N .	Sample Location	Phase I	Concentration of pesticide detected $\mu\text{g/L}$	Phase II	Concentration of pesticide detected $\mu\text{g/L}$	Phase III	Concentration of pesticide detected $\mu\text{g/L}$	Phase IV	Concentration of pesticide detected $\mu\text{g/L}$	Phase V	Concentration of pesticide detected $\mu\text{g/L}$
1	North West Delhi(5)	$\alpha$ -Cypermethrin	0.06	$\alpha$ -Cypermethrin	0.22	$\alpha$ -Cypermethrin	0.14	$\alpha$ -Cypermethrin	0.12	$\alpha$ -Cypermethrin	0.14
		Buprofezin	0.08	Buprofezin	0.14	Buprofezin	65.87				
		Buprofezin	0.08	Buprofezin	0.14	Buprofezin	0.13				
2	North East Delhi(5)	Dieldrin	0.14	BQL	BQL	Ethion	0.05	Dieldrin	0.08	Ethion	0.04
3	West Delhi (5)	$\alpha$ -Cypermethrin	0.03	$\alpha$ -Cypermethrin	0.07	BQL	BQL	$\alpha$ -Cypermethrin	0.05	BQL	BQL
4	New	BQL	BQL	Propic	0.07	Hexac	0.06	BQL	BQL	Hexac	0.06

	Delhi (5)			onazole		onazole				onazole	
5	South Delhi (5)	BQL	BQL	Delta methrin	0.07	Delta methrin	0.06	Bifenthrin	0.09	BQL	BQL
6	South West Delhi (5)	Chlorpyrifos	0.03	Ethion	0.09	Chlorpyrifos	0.23	Ethion	0.08	Ethion	0.08
7	Faridabad (5)	Bifenthrin	0.07	BQL	BQL	Chlorpyrifos	0.09	Chlorpyrifos	0.10	BQL	BQL
		Chlorpyrifos	0.04								
8	Faridabad (5)	Delta methrin	0.08	Delta methrin	0.07	BQL	BQL	Chlorpyrifos	0.08	Delta methrin	0.09
		Chlorpyrifos	0.02								
9	Gurugram (5)	Iprobenphos	0.05	Iprobenphos	0.04	Iprobenphos	0.07	Iprobenphos	0.06	Iprobenphos	0.06
10	Gurugram (5)	Iprobenphos	0.05	Pendi methalin	0.06	Iprobenphos	0.06	Iprobenphos	0.08	Pendi methalin	0.07
		Pendi methalin	0.06								
11	Noida (5)	Chlorpyrifos	0.08	BQL	BQL	Bifenthrin	0.03	Chlorpyrifos	0.05	BQL	BQL
12	Noida (5)	Bifenthrin	0.04	Bifenthrin	0.08	BQL	BQL	Chlorpyrifos	0.08	Bifenthrin	0.07
13	Ghaziabad (5)	Iprobenphos	0.05	Hexaconazole	0.06	Iprobenphos	0.06	Iprobenphos	0.06	Iprobenphos	0.06
		Chlorpyrifos	0.25	Chlorpyrifos	0.30			Chlorpyrifos	0.13		
14	Ghaziabad (5)	Bifenthrin	0.06	BQL	BQL	Chlorpyrifos	0.13	Ethion	0.04	Bifenthrin	0.06



Note: Data is represented with dilution factor (0.002)

\*European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water: the total pesticide level should not exceed 0.50 µg/l, and individual pesticide should not be greater than 0.10 µg/l

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