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Groundwater contamination through pesticide usage in vegetable growing areas of Delhi

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Abstract
Groundwater samples were collected from eight tube wells of different vegetable farm fields growing various vegetables like: Tori (*Luffa acutangula*), Ladyfinger (*okra*), Beans (*Phaseolus vulgaris*), Radish (*Raphanus sativus*), Corn (*Zea mays*), Arbi (*Colocasia esculanta*), Spinach (*Basella alba*) and Chilli (*Capsicum Annum*) in Yamuna Khaddar region, Delhi. Residues were estimated by GC-ECD and GC-FPD system equipped with capillary columns for organochlorine, synthetic pyrethroid and organophosphate insecticides. In groundwater, 31.2% samples were found contaminated with organochlorine pesticides. While 19.4% samples were contaminated with organophosphate pesticide. Synthetic pyrethroids were not detected in groundwater samples. Concentration of organochlorine pesticides ranged from 0.293 to 1.462µg/l in groundwater sample. While concentration of organophosphate pesticides ranged from 0.159 to 39.90µg/l. Almost 93% samples were found contaminated with organochlorine pesticides and organophosphate pesticides respectively. According to the analysis, residues of the banned organo chlorine pesticide residues (DDT and BHC) were found above MRL value. It seems that they are present either due to the high persistence of these pesticides or due to their continuous use in the form of adulterated pesticides by farmers. The study reveals that rigorous extension services are required to make the farmers aware about the harmful residues in water and switching to safer molecules like synthetic pyrethroids and Integrated Pest Management techniques for the judicious use of pesticides.

Keywords: Groundwater, Regulatory limits, Gas chromatography, Multiresidues, Monitoring

1. Introduction
India is the largest producer of pesticides in Asia and ranks twelfth in the world for the use of pesticides [1]. A vast majority of the population in India is engaged in agriculture and is therefore exposed to the pesticide used in agriculture [2]. Pesticides are generally recognized as significantly benefiting our ability to meet the world's need for abundant, safe and affordable food and fiber [3, 4]. Due to their wide use, they are detected in various environmental matrices such as soil, water and air [5]. Pesticides may enter the soil environment by missing the target, through runoff from treated plant surfaces or by spillage during application [6]. The main processes potentially affecting the ultimate fate of pesticides in soil are retention by soil materials (involving adsorption/desorption processes), transformation processes (biological and chemical degradation), and transport (through soil, atmosphere, surface water, or groundwater) [7, 8]. Several pesticides including organochlorine, organophosphate, carbamate and synthetic pyrethroid insecticides, fungicides and herbicides are commonly used in vegetables and other crop growing areas to increase the agricultural productivity. Pesticides enter surface and groundwater primarily as runoff from crops and are most prevalent in agricultural areas. Although the use of such synthetic chemicals has led to increased production of food and fiber but their use have also been associated with several concerns, including risks to human health and alteration of local environment [9, 10]. The perseverance of pesticide residues in soil, water and food may deteriorate the environment and its produce. Contamination in groundwater has been reported on a global scale. A study observed that in India organochlorine insecticides such as DDT and HCH constitute more than 70% of the pesticides used at present. The study also reports that Delhi, Bhopal, other cities and some rural areas have indicated presence of significant level of pesticides in fresh water systems as well as bottled drinking mineral water samples [11]. In Farrukhabad region, in India almost all the groundwater samples of rural area were found to be contaminated with residues of Hexa Chloro Cyclo Hexane (HCH) and Dichloro Diphenyl Trichloroethane (DDT). Residues of Aldrin, endosulfan and heptachlor were also detected in a large number of sample [12]. In North- East India, district Dibrugarh and Nagaon of Assam state, 93% groundwater samples of DDT and 90% groundwater samples of HCH were found to be above MRL value [13]. About 80% groundwater samples were found to

contain organochlorine pesticide residues above the regulatory limits were reported in study of Hisar, Haryana [14]. The study reported that in Bhagalpur, India the concentration level of organochlorine and organophosphate pesticide were found above MRL value in Ganga River [15]. The residue levels of persistent chlorinated pesticides such as HCH (hexachlorocyclo-hexane) isomers and DDT (dichlorodiphenyltrichloroethane) compounds were quantified in water samples collected from the River Kaveri and its distributor River Coleroon [16]. In Brazil, 23 pesticides were monitored from which λ -cyhalothrin, p, p′-DDT, deltamethrin and permethrin compound were identified in sediment samples from 25 sites in 17 rivers of the Pantanal [17]. In an agricultural catchment area in Germany, seven inflow events were analysed for 20 pesticide agents. All three entry routes were remarkably contaminated [18]. The study reported that agricultural chemicals used in vegetable production in Arizona, Florida, Michigan and Texas are potential contaminants of groundwater and surface water, which, in turn, pose risks to human health [19]. The groundwater samples collected from Lawad, Hapur Bypass, and Lohia Nagar Mandi showed the presence of POPs. Heptachlor Epoxide, Fipronil, Aldrin, Heptachlor, β− B.H.C., λ− B.H.C were detected in the drinking water and the water used for irrigation. This indicates that over a period of time these pesticides have leached down to the groundwater level. The *Doab* area of Muzaffarnagar district is witnessing ground water getting poisonous due to the widespread presence of POPs in the samples collected from this district. All six water samples contained more than one toxic pesticide. The ground water of district Ghaziabad is also contaminated with POPs. Five of the six samples contained more than one type of pesticide. The samples collected from hand pump at Ghaziabad contained Heptachlor (25 times higher than EU limit) [20]. Water samples collected from Syrian costal area reported that the residue level DDE was the highest among the rest of the detected organochlorine residues and it ranged from 8.54 to 22.50 μgl^{-1}. However the range of residues concentration of the other detected organochlorine pesticides were as follow; $_{4,4}$DDD from 3.81 to 14.37 μgl^{-1}, $_{4,4}$DDT from 2.22 to 12.38 μgl^{-1}, $_{2,4}$DDT from 2.94 to 5.28 μgl^{-1}, HCH from 3.18 to 571 μgl^{-1}, $_{2,4}$DDD from 0.87 to 4.28 μgl^{-1} and the combination of Endosulfan and Endosulfan sulfate ranged from 0.05 to 9.18 μgl^{-1}[21]. A study conducted by School of Chemical sciences, India, reported that pesticide residues concentrations were exceeded above the allowable levels in drinking water samples of river water and groundwater in Hyderabad [22]. A study was reported by civil engineering department of IIT-Delhi on the groundwater quality in the Palla-Burari region which has made some alarming revelations. The water samples tested from this area contain moderately high levels of pesticides; along with some residues of the banned pesticides like DDT. This region has nearly 80 borewells and five Ranney wells that meet about 15% of Delhi's water needs. The same team also conducted a larger study of the entire Ganga basin covering Uttarakhand, UP and Bihar. The results showed that different types of OCPs predominate in different regions depending upon land-use pattern. HCH, a byproduct of insecticide lindane, was detected mostly in the mountainous stretch (Uttarakhand), the water in UP contained more of endosulfan residues and the Bihar region contained more of the aldrin group of pesticides [23]. In the present study, monitoring of multiresidues i.e organochlorine, organophosphate and synthetic pyrethroids in groundwater from tubewells was conducted to access the contamination level due to leaching of pesticides used in vegetables.

2. Material and method

2.1 Study area

The present study covers the entire suburban region of Mayur Vihar Phase-I in Delhi (28°35'42"N and 77° 18' 5" E). A survey was carried out to collect information from farmers regarding usage of pesticides in vegetable growing fields (Table 1).

Table 1: Survey of vegetables grown and pesticide usage

Crop Names	Pesticides
Tori- *Luffa acutangula*	malathion, cypermethrin
Ladyfinger (*okra*)	Cypermethrin, endosulfan
Beans(*Phaseolus vulgaris*)	Profenophos, endosulfan
Radish (*Raphanus sativus*)	Cypermethrin
Corn(*Zea mays*)	Endosulfan
Arbi(*Colocasia esculanta*)	Chlorpyrifos
Spinach(*Basella alba*)	Profenophos, Cypermethrin
Chilli(*Capsicum Annum*)	Ethion, Cypermethrin

A total of eight different vegetable farms were identified for sampling in Yamuna khaddar area (part of Chilla village) located opposite to Mayur Vihar Phase- I for groundwater samples from agricultural area. To study the impact of pesticide residues on the groundwater aquifers, groundwater samples were collected from various tubewells, which were located in different vegetable farms of East Delhi area as shown in Figure 1.

2.2 Sample collection

Groundwater samples were collected in 1litre precleaned glass bottle with Teflon lined caps from each wells and immediately transported to the laboratory. For the groundwater samples, around 30–40 l of water was flushed out of the tubewells before the collection. Duplicate samples for pesticide measurement were collected from each sampling location. The bottles were carefully filled just to overflowing, without passing air bubbles through sample. After transportation to the laboratory, samples were stored at 20.8°C and extraction was normally done within 48 h.

2.3 Chemicals and instrumentations

Water extracts were analyzed using Agilent 7820A Gas Chromatograph equipped with a Ni^{63} Micro–Electron capture detector (ECD). The GC was fitted with capillary column (DB-1, 30 m x o.25µm x 0.25µm). Helium was the carrier gas at aconstant column flow rate of 1.0 ml/min. The detector make up gas was nitrogen at flow rate of 1.160 ml/min. Samples were injected in the split less mode, the injector`s temperature was 250ºC, the detector temperature was 300ºC. The temperature program used for DB-1 capillary column was 180ºC for 2 minutes, 10ºC/min. to 220ºC held for 30 min.

High performance liquid chromatography analysis

The pesticide residue analyses were carried out by using high performance liquid chromatography (Agilent) attached with Class 10 A software. The column used was Zorbas Eclipse x DB –C-18, 4.6cmx150mm, 5 µm,; pressure at isocratic system, 59 kg/cm^2; flow rate, 0.800 mL/min; wavelength,205 nm; oven temperature, 40ºC and acetonitrile: water(60:40 v/v) HPLC grade was used in mobile phase.

2.4 Analytical Procedure

Liquid–liquid extraction followed by gas chromatographic (K.K. Sharma, 2007) was used for the determination of pesticide residues. 500 ml of groundwater sample taken in a well rinsed 1litre separatory funnel and 10g of NaCl was added to it. The funnel was shaken to dissolve NaCl completely. The residues were extracted thrice with dichloromethane (50:25:25 ml) shaking vigorously for 2-3 minutes with intermittent pressure release. The separatory funnel was kept undisturbed to separate the two layers. The lower aqueous layer was drawn from 1 litre separatory funnel. The 3 extracts were combined and dried by passing through an adsorbent (2.5 cm ID and 15 cm long) containing anhydrous Na_2So_4 over a small pad of glass wool at the bottom and collected in a well rinsed 250 ml flat bottom flask. The extracts were concentrated upto 1 ml with vacuum rotary evaporator (Buchi Rota vapor R-215) and 10 ml of n-hexane was added to the combined extract and concentrated to 1 ml again. The final volume was made up to 2 ml with n-Hexane solvent and with acetonitrile solvent**.** Concentrated 2 ml sample was analyzed with the help of Gas Chromatograph (GC).

For quality assurance, blank and laboratory control samples were run with each set of samples. Both were subjected to the same analytical procedure as those used on the study samples. Recoveries < 70% or >130% for laboratory control samples were promptly investigated and if necessary reanalyzed. Mixed standards were injected before and after the sample run. Appropriate quality assurance and quality control was performed including analysis of procedural blank (analyte concentrations were <MDL, method detection limit), random duplicate samples (standard deviation <5), and calibration curves with r^2 value of 0.999.

The instrument detection limits were established by using 3:1 signal to noise ratio to determine a peak as a valid quantifiable peak. Each sample was analyzed in duplicate and the average was used in analytical calculations. Calculated concentrations were reported as less than the limit of detection if the peak area did not exceed the specified threshold (three times the noise). Concentrations below the limit of detection were assigned zero values for the statistical analysis. Method detection limits were established by processing eight aliquots of the sample spiked with a quantity sufficient to produce a detectable response (s/n > 3) and multiplying the standard deviation by 3 (the $t_{student}$ value for eight replicates). MDL for organochlorine pesticides were 0.004µg/L, organophosphorous pesticides were 0.02µg/L but for phosphamedion and dimethoate MDL were 0.05µg/L, while for synthetic pyrethroids the MDL were 0.04µg/L respectively.

3. Results and Discussion

All the groundwater samples were analyzed in triplicate. The groundwater quality at the studied sites has already been discussed by [24]. The level (range and arithmetic mean ± SE values) of pesticides detected in groundwater samples of vegetable growing area are discussed here. Table 2 presents the levels of pesticide residues in 8 samples collected from different farm fields of vegetable growing area. As evident from the data, all samples were found contaminated with organochlorine and organophosphate pesticides used in vegetables, while synthetic pyrethroids were found Below Detectable Limit (BDL). Concentration of organochlorine and organophosphate pesticides (Lindane, Endosulfan and its isomers, DDT and its metabolites and Dicofol) in water of different tubewells of different vegetable farm fields of Yamuna khaddar, Delhi area growing various vegetable crops are summarized in Table 2 and Figure 2. Among HCH, α-HCH**,** β-HCH, γ-HCH and δ-HCH were found in detectable amounts in groundwater samples whereas one sample did not show residues of any isomers of HCH. ∑- HCH varied from 0.048 to 1.462 µgl^{-1}. Among DDT analogues, *p,p'*-DDT (0.075 to 0.095 µgl-1) was detected in 2nd and 7th samples and *p,p'*-DDE (0.322 to 0.990 µgl^{-1}) in 2nd, 4th and 6th samples of groundwater respectively. ∑- DDT ranged from 0.332 to 0.095 µgl^{-1}. Residues of ∑- endosulfan ranged from 0.055 to 0.074 µgl^{-1}. Endosulfan-II and endosulfan sulfate was not detected in any of the samples whereas endosulfan-I was found in 4th and 7th samples of groundwater. dicofol (0.191 to 0.293 µgl^{-1}) was detected in 2nd and 7th samples. Maximum contamination was observed due to HCH, followed by DDT and Dicofol. Observations of the present studies clearly indicate that OCPs particularly HCH and DDT are still persisting in the environment even after their restricted use in agricultural and public sectors. All the synthetic pyrethroids (beta cyfluthrin, fenpropathrin, lemda cyhalothrin, alpha cypermethrin, deltamethrin, fenvelerate) were found below the BDL as shown in Table 3 and Figure 3. Residues of malathion (0.130-0.159 µgl^{-1}) was detected in 1st, 4th and 6th samples, chlorpyriphos (0.104 to 0.623 µgl^{-1}) were found in 1st, 2nd, 4th and 6th samples, quinalaphos (0.400 to 0.517 µgl^{-1}) in 4th and 6th samples, profenophos ranged from (14.15 to 39.90 µgl^{-1}) in 2nd, 4th and 6th samples and ethion (0.400 to 0.517 µgl^{-1}) in 7th and 8th samples of groundwater. As the range of profenophos and ethion in groundwater samples was found higher than below detectable limits, therefore the samples may be contaminated. None of the samples contained other analysed organophosphate pesticides like Phorate, Dimethoate, Phosphamedion and Methyl Parathion was Below Detectable Limit (Table 4). On adopting the European Union (EU) permissible limit of individual pesticide in drinking water 0.1 and 0.5 µgl^{-1} for total pesticides which has currently been enforced in India [25], residues in about 35.8% (organochlorine pesticides) and 21.29% (organophosphate pesticides) of the samples exceeded the safe limits. Therefore the results are alarming and show that either the use of banned pesticides is still continued or they are present in water samples as they are very persistent. On the contrary, synthetic pyrethroids, owing to their biodegradable property, were found Below Detectable Limit and hence can be considered as safe pesticides.

4. Conclusion

Groundwater samples collected from eight tubewells of different vegetable farm fields of Yamuna khaddar, Delhi area growing various vegetable crops have shown contamination with different groups of pesticides which is a matter of concern. Regular monitoring of pesticide residues in water is required in order to have a check on contamination level of water systems in order to plan the future strategies for the use of pesticides.

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