© IWA Publishing 2020
327

Water Practice & Technology Vol 15 No 2
doi: 10.2166/wpt.2020.017

Assessment of the impact of pesticide usage in groundwater aquifer of an agriculturally dominated area in North West India

Jyoti Chaubey*, S. K. Singh, Sukhwant Singh and H. Arora

Department of Civil Engineering, M.B.M. Engineering College, J.N.V. University, Jodhpur 342001, India

*Corresponding author. E-mail: jyotichaubeyy@gmail.com

Abstract

Groundwater pollution due to several anthropogenic activities has been a worldwide problem, one such activity being injudicious pesticide usage in agriculture. Assessment of pesticide impact on groundwater is a prerequisite step towards the formulation of regulatory policies related to the pesticides' application. The present study deals with assessment of the impact of pesticide usage in the groundwater aquifer of an agriculturally dominated area in North West India. The relationship between the pesticide usage and its impact on the quality of groundwater has been established by employing a model named Pesticide Impact Rating Index (PIRI). For illustration, seven farms lying in Nakodar tehsil of Punjab state in India were considered. Based on the frequency of usage of various pesticides in the study area, four pesticides namely atrazine, chlorophyrifos, phorate and monocrotophos were selected for detailed analysis. Groundwater samples were collected and analyzed for observed values of pesticide residues. The observed residues were compared with the PIRI model estimates and results showed that though the observed values were higher corresponding to the estimated values, the ratio seemed to be fluctuating within a consistent range. Therefore multiplicative correction factors were introduced for the model estimates so as to predict realistic pesticide residues in an area.

Key words: groundwater, pesticide usage and residues, PIRI software

INTRODUCTION

Groundwater plays an important role as a decentralized source of drinking water for millions of rural and urban families across the globe. In India, it accounts for nearly 80 percent of the rural domestic water needs and 50 percent of the urban water needs (Kumar & Shah 2004). Although groundwater is less susceptible to contamination compared to surface water resources, several anthropogenic activities such as the improper disposal of municipal and industrial effluents and agricultural leachate, are causing groundwater pollution. Among various sources of groundwater pollution, the extensive and improper utilization of pesticides has also become a source of groundwater pollution.

Development of agriculture is assisted by the usage of pesticides. Pesticide use has helped in preventing the losses caused by pest attack and has improved the net production potential of crops, but the surplus amount unutilized by the crops leaches down to ground water causing its pollution (Zhao & Pei 2012). Pesticide contamination in ground water is related to the persistence of pesticides in soil. The ability of a pesticide to be absorbed by the soil media decides whether it will leach down to ground water or not. The pesticides with poor adsorption or absorption on soil surface will have a higher tendency to leach down to ground water thus leading to its pollution. Groundwater once polluted will take several decades to get cleaned on its own and clean up processes are uneconomic, tedious and cumbersome.

Several studies have been reported showing groundwater pollution due to pesticides usage. Pesticides cause serious health hazards to living systems due to their rapid solubility in fat and thus accumulating in target organisms (Agrawal *et al.* 2010). The vulnerability of groundwater to pesticide pollution is generally governed by the soil properties such as its texture, total organic matter present, and pesticides usage and their degradation products (Kumar & Shah 2004). Aktar *et al.* (2009) have discussed in details the potential effects of pesticides usage viz. advantages and disadvantages, over the surface water and groundwater resources of the corresponding area.

Thakur *et al.* (2015) assessed the groundwater contamination through pesticide usage in the vegetable growing areas in Delhi. Eight groundwater samples from different farms were collected and analyzed for the pesticide residues (Organochlorine) in it. Authors detected the presence of pesticides in groundwater in the area. Kole & Bagchi (1995) conducted a survey by drawing drinking water samples from various hand pumps and wells around Bhopal and found that more than half of the samples were contaminated with Organo Chlorine pesticides above the EPA standards. Chaudhary *et al.* (2002) showed the elevated levels of pesticides in the groundwater aquifer in Howrah district rendering the water unfit for drinking purposes. Sankararamakrishnan *et al.* (2005) conducted the groundwater quality analysis of Kanpur, India and reported the presence of high concentration of organochlorine and organophosphorus pesticides. Kumari *et al.* (2008) collected groundwater samples from the tube wells in farm fields around Hissar and found the pesticide residues (organosulphates, only chloropyriphos) more than the prescribed drinking water limits rendering the groundwater in the area unfit for drinking purposes.

Mohapatra *et al.* (1995) analyzed the ground water samples in rural areas near Farrukhabad (U.P) and concluded that the possible sources of groundwater contamination are the groundwater recharge by contaminated Ganga River and downward movement of pesticide residues along with rain water. Tariq *et al.* (2004) analyzed the groundwater samples in the cotton growing districts of Bahwalanagar, Muzafargarh and Rajanpur and found the presence of pesticide residues in groundwater.

Li *et al.* (2013) reported the presence of organo-chlorine pesticides in the shallow groundwater, samples collected from Taibu basin of China. Goncalves *et al.* (2007) studied the impact of intensive horticultural practices on ground water contamination in Portugal and found the presence of these pesticides in the groundwater – Lindane, Pendimethaline, endosulfan sulphate and endosulfan. Hernández-Romero *et al.* (2004) evaluated the water quality of the Pozuelos–Murillo lagoon system in southern Mexico with particular emphasis on the detection of organochlorine and organophosphate pesticide residues in water and sediments. Residues of organochlorine compounds were detected in the study area. As per a study conducted by Belluck *et al.* (1991), Atrazine and its metabolites have become the main toxic contaminants in the ground water of USA/Canada.

The above mentioned studies are based on the experimental detection of the pesticide residues in groundwater by analyzing the groundwater samples in an area. There have been only a few studies based on prediction of the residues employing computational tools like the Pesticide Root Zone Model (PZRM) (Carsel *et al.* 1985; Trevisan *et al.* 1993; Cogger *et al.* 1998), Pesticide Emission Assessment at Regional and Local scales (PEARL) Model for assessing leaching of pesticide into groundwater or its retention in the soil (Leistra *et al.* 2001; Tiktak *et al.* 2002a, 2002b) and Pesticide Impact Rating Index (PIRI) (Kookana *et al.* 2005; Aravinna *et al.* 2017).

PRZM is a finite difference based model used in simulating the movement of a contaminant (pesticide in the present case) in an unsaturated soil system. The model utilizes the data related to the soil characteristics, climatological data and data related to pesticide application, its degradation rate etc. to predict the movement of the pesticide through soil and ultimately to the groundwater. PEARL is also a finite difference based model which describes the fate of a pesticide and relevant transformation products in the soil-plant system. The model utilizes data related to pesticide application, pesticide transport processes (convective, dispersive and diffusive), pesticide sorption (equilibrium and non-equilibrium) and transformation, uptake of pesticides by plant roots, lateral discharge of pesticide with drainage water, and volatilization of pesticide from soil and plant surfaces.

These tools give quantitative assessment of the pesticide impact on groundwater, which is based on the pesticide usage in the area. This assessment helps in formulating regulatory policies and practices related to pesticide usage having least detrimental impact on the environment and specifically groundwater, so that proper pesticide usage policies can be developed.

Present study

The present study deals with assessment of the impact of the pesticide usage in terms of its residues/load in groundwater in an area (a few villages) lying in Jalandhar district in the state of Punjab, India. At present, few studies have been carried, out in only limited regions in India, to assess the impact of pesticides and agrochemicals. Although the entire country seems to be affected by the over usage of pesticides, the problem appears to be more acute in the state of Punjab because the state is dominant in agricultural activities. Increased productivity due to modernization of agriculture has been driven by the excessive use of pesticides, which has consequently resulted in accumulation of pesticide residues in the groundwater of the region. Numerous studies on estimating the pesticide residues in groundwater have been performed experimentally, but little information exists on a probable relationship between the quantity of pesticide used and its impact on quality of groundwater. A need to carry out comprehensive monitoring across the country to regulate the usage of pesticides with suitable mathematical models, under corresponding Indian conditions, is required.

Accordingly, certain villages of Jalandhar district were chosen as the study area to assess the relationship between pesticide usage and its impact on quality of groundwater. A software package, Pesticide Impact Rating Index (PIRI), has been used for this purpose (Kookana *et al.* 2005). PIRI is based on pesticide use, the pathways through which the pesticides are expected to migrate to the water resources (the assets), and the value of the asset.

Based on the frequency of usage of various pesticides in the sampling stations, four pesticides, namely atrazine, chlorophyrifos, phorate and monocrotophos, were selected for detailed analysis employing PIRI. PIRI software was evaluated for its suitability under Indian conditions by arriving at suitable correction factors related to local conditions. Correction factor is the ratio of observed pesticide residue values in groundwater and corresponding model-estimated residues.

MATERIAL AND METHODOLOGY

Study area

Three villages, viz. Boparai, Samailpur, and Malwal in Nakodar Tehsil in Jalandhar district, India, were chosen as the study area for the present study. The study area is densely populated and is a part of the prosperous Satluj Beas Doab Region. The region has fertile alluvial deposits and therefore is primarily an agricultural-dominated area. Apart from agriculture, the subsidiary occupations include dairy, followed by poultry, fishery and beekeeping. The major problems being faced by the region are depletion of the water table, poor soil fertility and small land holding, traditional methods of agriculture, improper use of pesticides, over fertilization of crops and improper spray techniques.

Figure 1 depicts seven different farm locations lying in three villages in Nakodar Tehsil, which were identified for sampling. The soil data, groundwater samples and pesticide usage data is collected from the farmers from the seven sampling stations (SS). The details of the sampling stations (SS) are as follows –

(a) Village Boparai – SS-1 (Sugarcane), SS-2 (Rice – Potato-Winter Maize)

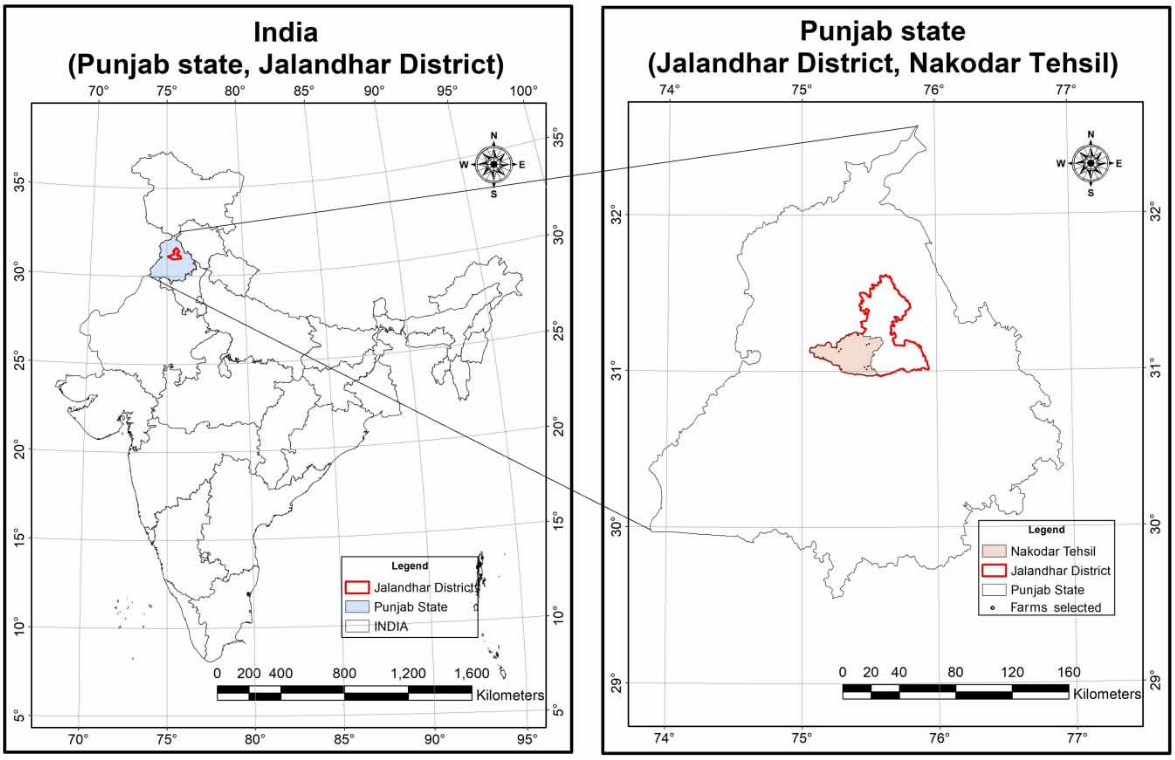

Figure 1 | Study area.

(b) Village Samailpur – SS-3 (Sugarcane), SS-4 (Vegetables), SS-5 (Rice-Wheat)
(c) Village Malwal – SS-6 (Rice – Potato-Winter Maize), SS-7 (Rice – Potato-Winter Maize)

PIRI software

PIRI is a quantitative approach for assessing the potential impact of pesticide on groundwater and surface water and consequently its detriment to living organisms in reach, by employing the data related to pesticide usage, the pathways through which the pesticides are expected to migrate to the water resources (considered as assets), and the value of the corresponding asset (Kookana *et al.* 2005). Each component is quantified using site hydrogeological conditions, viz. type of soil, its organic matter content, soil porosity, land slope, soil loss, recharge rate and water table depth, and corresponding hydro-meteorological conditions, viz. rainfall and temperature of the area.

Three components – Pesticide load factor (L), transport factor (T) and asset value factor (V) are estimated first and then the detriment is calculated as the product of these three components.

$$\text{Detriment} = LT\,V \tag{1}$$

Pesticide load factor

The pesticide load factor is based on the quantity of a pesticide applied to how great a fraction of the land in the study area. The load factor (L_i) of the i$^{\text{th}}$ pesticide applied in an area is determined from its frequency of application (f_i), dosage (d_i), active ingredient fraction (a_i) in the product and the proportion of the area (p_i) receiving the pesticide

$$L_i = f_i \times d_i \times a_i \times p_i \tag{2}$$

Pesticide transport factor

This factor is applicable to both surface water and groundwater, but here only transport to groundwater is considered, which is in line with the objectives of the present study.

Transport to groundwater

The movement of pesticides through soil is generally slower compared to the water movement due to the sorption of pesticides to soil organic matter (K_{oc}). This retardation of movement is proportional to K_{oc} and the retardation factor (*RF*) is given as

$$RF = 1 + \frac{\rho f_{oc} K_{oc}}{\theta_{FC}} \tag{3}$$

where, ρ = soil bulk density (kg/m^3), f_{oc} = organic carbon content (kg/kg soil), and θ_{FC} = volumetric moisture content of the soil at field capacity (m/m^3).

The degradation of a pesticide during its transport through the vadose zone and residence time in the vadose zone (*t*) can be represented by the *AF* for the groundwater, as

$$AF_{GW} = \exp\left[\frac{-0.693 D \theta_{FC} RF}{q t_{1/2}}\right] = \exp\left[-t \frac{(\ln 2)}{t_{1/2}}\right] \tag{4}$$

$$t = \frac{D \theta_{FC} RF}{q} \tag{5}$$

where, $t_{1/2}$ = half-life of pesticide in soil, D = water table depth, q = rate of water entering the soil (m/d). Incorporating the fact that organic carbon content and microbial population density change significantly with changing depth of the soil, *AF* mentioned above is modified and is given as (Kookana *et al.* 2005).

$$AF_{GW} = AF_{SZ} \times AF_{TZ} \times AF_{RZ} \tag{6}$$

where, $AF_{SZ} = AF$ at surface zone (extending up to 0.1 m depth of soil profile), calculated by employing Equation (5); $AF_{TZ} = AF$ at the transitional zone (extending from 0.1 to 1.0 m depth of soil profile), calculated by estimating the organic content of the soil at 0.4 m depth and applying this to Equation (5); $AF_{RZ} = AF$ at the residual zone (extending from 1.0 to D m depth of soil profile), calculated by Equation (5) with f_{oc} and rate of degradation of pesticide ($=\ln 2/t_{1/2}$) as 1/10th of those of the surface zone.

The attenuation factor gives an indirect measure of the pesticide mobility in groundwater. The higher the attenuation factor, the greater would be the pesticide mobility in groundwater. Total pesticide load likely to reach the groundwater at a particular site is

$$\text{Groundwater Load} = L_{GW} = \sum L_i AF_{GW_i} = \sum L_i T_i \tag{7}$$

The pesticide residue in groundwater is considered to be the result of the mixing of the residue in a certain aquifer thickness and soil porosity (θ_s). Considering the top 1.0 m to be the aquifer mixing zone, the predicted pesticide residue (C_{GWi} in kg/m^3) is given as

$$C_{GW_i} = L_i \times AF_{GW_i} \times \frac{1}{\theta_s} \tag{8}$$

This residue is compared to the acceptable pesticide residue in groundwater in order to calculate the groundwater risk index.

$$\text{Groundwater Risk Index} = C_{GW}/\text{Detectable or Acceptable residue} \tag{9}$$

Asset value factor

This factor is important when risks associated with pesticides to water bodies located in different regions are compared. This value is insignificant when pesticides threatening the same asset are compared with each other.

Data collection

Pesticide data

A survey was carried out to collect information from farmers regarding usage of pesticides in specific fields along with the cropping pattern over the last two years (2015–2017). It was observed that the farmers used a variety of pesticides for the same crop due to proliferation of the various brands and types of pesticides, different recommendations by the shopkeepers/company representatives and resistance developed by the target pests to certain pesticides. A total of 21 different pesticides were used in four cropping patterns that were prominent in the study area (Table 1).

Based on the frequency of usage of various pesticides in the sampling stations, out of the above 21 pesticides, a total of four pesticides, namely **Atrazine, Chlorophyrifos, Phorate and Monocrotophos**, were selected for detailed analysis to PIRI. Table 2 depicts the pesticide properties and application data relevant to the study (rate at which the pesticides are applied and the nozzle size for the spray application), at all seven sampling stations (SS). Environmental persistence (half-life, $t_{1/2}$) and the soil sorption coefficient (K_{oc}) of the four pesticides were obtained from the available literature.

Table 1 | List of pesticides used in the study area

S. No	Chemical name	Formulae	Class
1.	Atrazine	$C_8H_{14}ClN_5$	Herbicide
2.	Bifenthrin	$C_{23}H_{22}ClF_3O_2$	Insecticide
3.	Butachlor	$C_{17}H_{26}ClNO_2$	Herbicide
4.	Carbendazim 50% WP	$C_9H_9N_3O_2$	Fungicide
5.	Carbofuran	$C_{12}H_{15}NO_3$	Insecticide
6.	Cartap Hydrochloride	$C_7H_{15}N_3O_2S_2$	Insecticide
7.	Chlorantraniliprole 0.4% GR	$C_{18}H_{14}BrCl_2N_5O_2$	Insecticide
8.	Chlorophyriphos 20% EC	$C_9H_{11}Cl_3NO_3PS$	Insecticide
9.	Cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	Insecticide
10.	Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	Insecticide
11.	Dimethoate	$C_5H_{12}NO_3PS_2$	Insecticide
12.	Fipronil 5% SC	$C_{12}H_4Cl_2F_6N_4OS$	Insecticide
13.	Imidacloprid	$C_9H_{10}ClN_5O_2$	Insecticide
14.	Metalaxyl 35% WS	$C_{15}H_{21}NO_4$	Fungicide
15.	Monocrotophos 36% SL	$C_7H_{14}NO_5P$	Insecticide
16.	Parquat Dichloride 24% SL	$C_{12}H_{14}Cl_2N_2$	Herbicide
17.	Pendimethalin 30% EC	$C_{13}H_{19}N_3O_4$	Herbicide
18.	Phorate 10% CG	$C_7H_{17}O_2PS_3$	Insecticide
19.	Propiconazole 25% EC	$C_{15}H_{17}Cl_2N_3O_2$	Fungicide
20.	Propineb 70% WP	$C_5H_8N_2S_4Zn$	Fungicide
21.	Thiamethoxan 25% WG	$C_8H_{10}ClN_5O_3S$	Insecticide

Table 2 | Pesticide properties and application data at all sampling stations

S. No	Pesticide	K_{oc} (L/kg)	$t_{1/2}$ (d)	Sampling location	Application rate (L/ha)	Fraction active ingredient	Frequency of use	Percentage area	Class	Spray Type
1	Atrazine	100	75	SS1	5.25	0.50 WP	1	100	Herbicide	320 ± 20 μm
				SS2	5.18	0.50 WP	2	100	Herbicide	320 ± 20 μm
				SS3	3.4	0.50 WP	2	100	Insecticide	240 ± 20 μm
				SS4	NIL	NA	NA	NA	NA	NA
				SS5	NIL	NA	NA	NA	NA	NA
				SS6	NIL	NA	NA	NA	NA	NA
				SS7	1.35	0.50 WP	1	100	Herbicide	Ground spray
2	Chlorophyriphos	8,151	50	SS1	2.49	0.20 EC	1	100	Insecticide	160 ± 20 μm
				SS2	0.5	0.50 EC	1	100	Insecticide	160 ± 20 μm
				SS3	2.94	0.2 EC	1	100	Insecticide	160 ± 20 μm
				SS4	1.24	0.50 EC	2	100	Insecticide	160 ± 20 μm
				SS5	NIL	NA	NA	NA	NA	NA
				SS6	1.24	0.20 EC	1	100	Insecticide	320 ± 20 μm
				SS7	1.24	0.20 EC	1	100	Insecticide	320 ± 20 μm
3	Phorate	1,660	63	SS1	8.38	0.10 CG	2	100	Insecticide	Granular
				SS2	8.38	0.10 CG	2	100	Insecticide	320 ± 20 μm
				SS3	8.25	0.10 CG	2	100	Insecticide	Granular
				SS4	3.22	0.10 CG	1	100	Insecticide	Granular
				SS5	NIL	NA	NA	NA	NA	NA
				SS6	3.22	0.10 CG	1	100	Insecticide	Granular
				SS7	3.22	0.10 CG	1	100	Insecticide	Granular
4	Monocrotophos	19	7	SS1	NIL	NA	NA	NA	Insecticide	NA
				SS2	4.27	0.36 SL	2	100	Insecticide	Granular
				SS3	NIL	NA	NA	NA	NA	NA
				SS4	0.74	0.36 SL	3	100	Insecticide	Ground spray
				SS5	NIL	NA	NA	NA	NA	NA
				SS6	0.97	0.36 SL	2	100	Insecticide	Ground spray
				SS7	5.34	0.36 SL	2	100	Insecticide	Ground spray

Note: EC, Emulsified liquid; CG, Capsule granule; WP, Wettable powder; SL, Soluble liquid, 320 ± 20 μm, Nozzle size for spray of pesticide.

Water sampling

Groundwater samples were collected from various tube wells located in the seven farms for pesticide residue analysis. Tube wells tapped the aquifer between 20 m and 50 m below ground level. Samples were collected after flushing for 5 minutes in the case of bore wells, in order to obtain fresh aquifer water. Sampling bottles made up of high quality dark glass with Teflon stoppers were used. Plastic or polyethylene containers were used initially but later water samples were transferred to glass bottles to avoid the pesticides present in water samples being adsorbed on the inner walls of the bottles.

Liquid–liquid extraction followed by gas chromatography was used for the determination of pesticide residues. A 500 ml groundwater sample was taken in a well-rinsed 1 litre separator funnel and 10 g of NaCl was added to it. The funnel was shaken to dissolve the NaCl completely. The residues were extracted thrice with dichloromethane (50:25:25 ml), shaking vigorously for 2–3 minutes with intermittent pressure release. The separator funnel was kept undisturbed to separate the two layers. The lower aqueous layer was drawn from a 1 litre separator funnel. Three 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 up to 1.0 ml with a vacuum rotary evaporator and 10 ml of n-hexane was added to the combined extract and concentrated to 1.0 ml again. The final volume was made up to 2.0 ml with n-hexane solvent and with acetonitrile solvent. A concentrated 2.0 ml sample was analyzed with the help of a gas chromatograph (GC). 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. Concentrations below the limit of detection were assigned zero values for the statistical analysis. The results obtained are given in Table 3.

Table 3 | Observed pesticide residues in groundwater samples

	Pesticide concentration (μg/L)			
Sample No.	**Atrazine**	**Chloropyrifos**	**Phorate**	**Monocrotophos**
Sample 1	0.06	0.01	0.01	0.00
Sample 2	0.09	0.00	0.01	0.14
Sample 3	0.09	0.03	0.03	0.11
Sample 4	0.01	0.01	0.01	0.03
Sample 5	0.00	0.00	0.01	0.00
Sample 6	0.00	0.00	0.02	0.01
Sample 7	0.01	0.01	0.01	0.06

Soil sampling

The study area was divided into different homogenous units based on the visual observation and farmer's experience, in order to collect the soil samples representing the soil condition of the study area. Surface litter at the sampling spot was removed. At least five samples from each sampling unit were collected. A 'V' shaped cut was made up to a depth of 15 cm at the sampling spot and thick soil slices from top to bottom of the exposed face of the 'V' shaped cut were removed and placed in a clean container for soil analysis (Figure 2).

After this, the samples were mixed thoroughly and foreign materials (like roots, stones, pebbles and gravels) were removed. A representative soil sample was obtained by applying a well-known quartering and coning method. The results of the parameters for soil have been tabulated (Table 4).

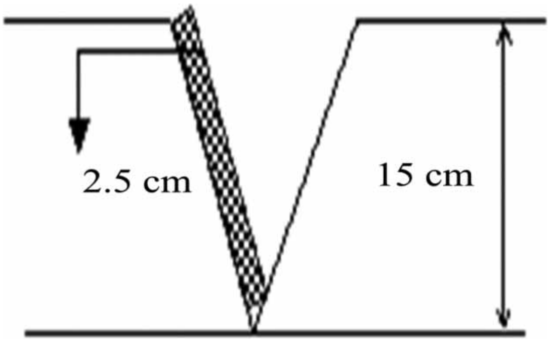

Figure 2 | Figure showing method of soil sample collection.

Table 4 | Results of soil testing

S. No	Sampling station	Type of soil	Soil pH	% Organic content
1	SS – 1	Silt	8.1	0.75
2	SS – 2	Clayey silt	8.3	0.90
3	SS – 3	Clayey silt	7.9	0.60
4	SS – 4	Clayey silt	8.2	0.75
5	SS – 5	Silt	8.4	0.60
6	SS – 6	Sandy silt	8.1	0.45
7	SS – 7	Silt	8.2	0.60

Rainfall, irrigation and weather details

Average annual rainfall in the study area for a period of one year (01 April 2016–31 May 2017) was taken as 551.3 mm (MoEIT 2017). Details of the water supplied to farms by tube wells (total irrigation), depth of borewells (given in Table 5) were ascertained from the farmers, which may not be very accurate, but can be presumed to be reasonably good. These have been tabulated below. The average maximum temperature during this year was 29.93 °C and average minimum temperature during this period was 17.27 °C.

Table 5 | Details of tube well depth and total irrigation provided in the farms (SS)

S. No	Sampling station	Tube well depth (m)	Tube well Irrigation (mm)
1	SS – 1	40	2,700
2	SS – 2	40	1,650
3	SS – 3	25	2,050
4	SS – 4	20	2,100
5	SS – 5	30	1,850
6	SS – 6	45	1,850
7	SS – 7	45	1,850

Employment of PIRI software

The software package as received from Commonwealth Scientific and Industrial Research Organisation (CISRO), Australia, relates to PIRI version 6. The input parameters necessary for the software run for the assessment of pesticides leaching into the groundwater are organic carbon partition coefficient (Koc), environmental persistence ($t_{1/2}$) of pesticide, water table depth (D), total rainfall, total irrigation, soil type, percentage organic content in soil (f_{oc}). The soil bulk density and moisture content can be given manually and if not, like in the present case, the software uses the suitable values according to the given soil type. The recharge rate (q) is also calculated by the software (if not provided manually) on the basis of the soil type, total rainfall and total irrigation for flat terrain.

For benchmarking of the guideline value for drinking water, a thorough study of the existing guidelines for drinking water for various pesticides was carried out including Draft Indian Standard Drinking Water – Specification (Second Revision of IS 10500), WHO Guidelines for Drinking-water Quality Third Edition, 2008 and USEPA guidelines. The adopted acceptable values for the present study are 35 ppb, 20 ppb and 1 ppb for atrazine, chlorophyrifos and monocrotophos respectively (USEPA 2000). For phorate the limiting values was assumed to be 25 ppb.

Applying the data, model was run to assess the groundwater pollution potential for a period of one year (01 April 2016–31 May 2017) and the results obtained are given in the following section.

RESULTS AND DISCUSSION

PIRI estimates of pesticide residues/load and mobility in groundwater

The model (PIRI) estimated the pesticide residue/load and its mobility in the groundwater. The model assigns the risk categories to each pesticide and category names were given according to the scoring system based on the application of Equation (9). The groundwater pesticide load risk rating and mobility for each sampling station as assigned by model are shown in Figures 3–9. The attenuation factor and the groundwater pollution potential in terms of pesticide residue/loads obtained for each sampling station are given in Table 6.

The pesticide residues/loads estimated by PIRI are further compared with the observed pesticide residues of the four pesticides under consideration (atrazine, chloropyrifos, monocrotophos and phorate) in all the seven water samples in order to compare the actual risk with PIRI prediction.

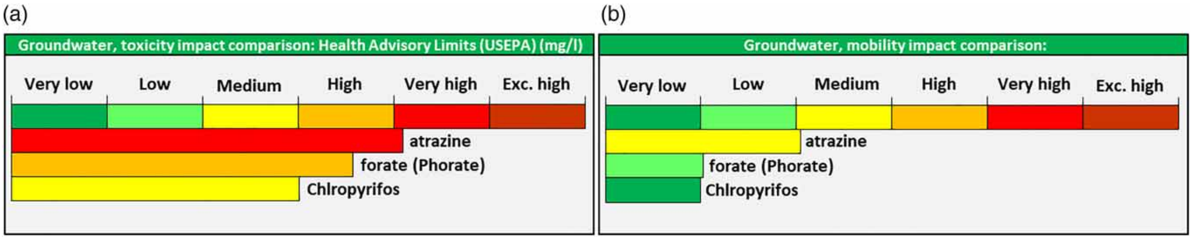

Figure 3 | Groundwater pesticide (a) load and (b) mobility in case of sample 1.

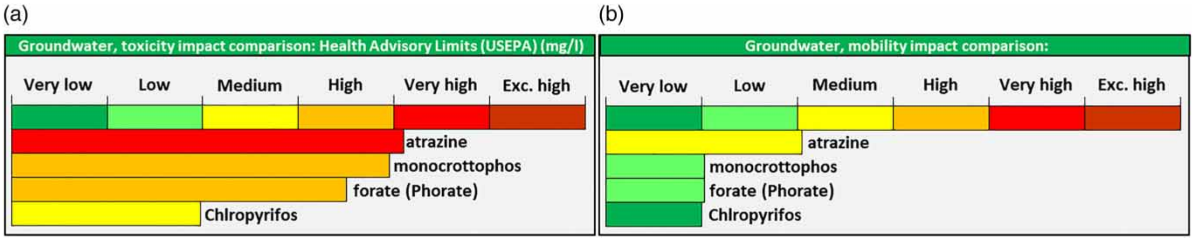

Figure 4 | Groundwater pesticide (a) load and (b) mobility in case of sample 2.

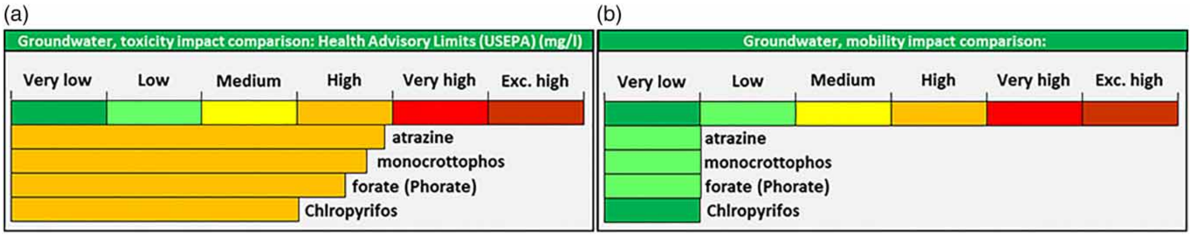

Figure 5 | Groundwater pesticide (a) load and (b) mobility in case of sample 3.

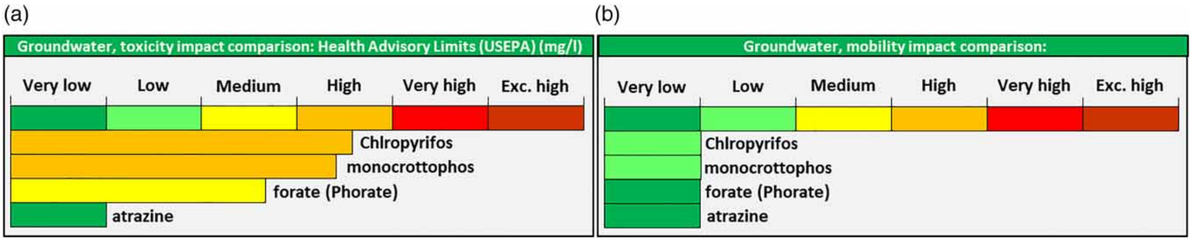

Figure 6 | Groundwater pesticide (a) load and (b) mobility in case of sample 4.

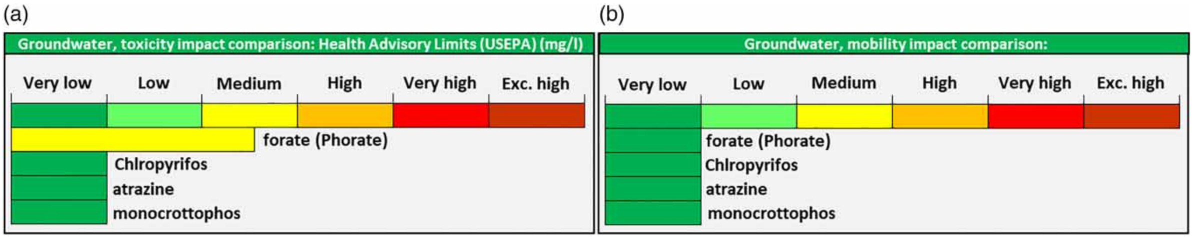

Figure 7 | Groundwater pesticide (a) load and (b) mobility in case of sample 5.

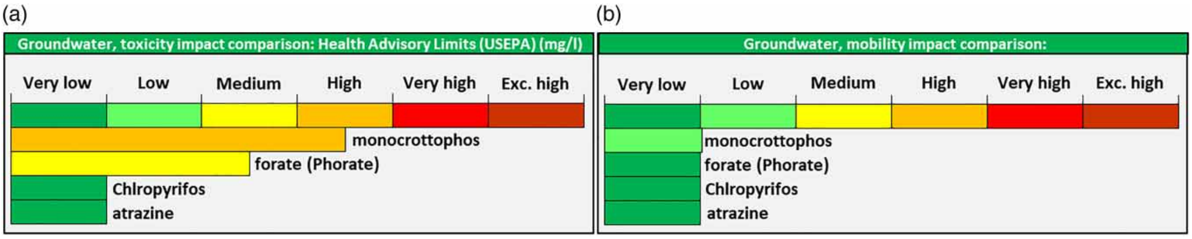

Figure 8 | Groundwater pesticide (a) load and (b) mobility in case of sample 6.

Sample 1

The risk rating in terms of total groundwater load was 'Very high' for atrazine, 'High' for phorate and 'Medium' for chloropyriphos. As monocrotophos was not applied in field 1, its risk was classified as 'Very low' by the software. With the type of soil being 'Silt' and borewell depth 40 m, the mobility was calculated as 'Medium' for atrazine, and 'Low' for phorate, whereas chloropyrifos and monocrotophos were classified as 'Very low' (Figure 3).

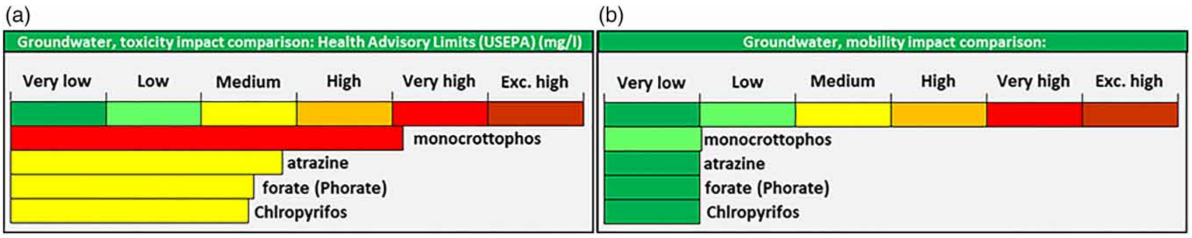

Figure 9 | Groundwater pesticide (a) load and (b) mobility in case of sample 7.

Table 6 | PIRI estimates for groundwater pollution potential and risk rating for all samples

		PIRI estimates			
			Groundwater pollution potential		
Sample	**Pesticide**	**Attenuation factor**	**(kg/ha)**	**(ppb)**	**Groundwater risk rating**
1	Atrazine	0.002	0.30	30.00	Very high
	Chloropyriphos	0.002	0.05	4.98	Medium
	Phorate	0.002	0.13	13.40	High
	Monochrotopos	0.000	0.00	0.00	Very low
2	Atrazine	0.002	0.29	29.60	Very high
	Chloropyriphos	0.002	0.01	1.00	Low
	Phorate	0.002	0.11	11.98	High
	Monochrotopos	0.002	0.24	24.59	High
3	Atrazine	0.002	0.20	20.68	High
	Chloropyriphos	0.002	0.05	5.88	High
	Phorate	0.002	0.13	13.20	High
	Monochrotopos	0.002	0.17	17.56	High
4	Atrazine	0.002	0.00	0.00	Very low
	Chloropyriphos	0.002	0.12	12.40	High
	Phorate	0.002	0.02	2.36	Medium
	Monochrotopos	0.002	0.08	8.78	High
5	Atrazine	0.002	0.00	0.00	Very low
	Chloropyriphos	0.002	0.00	0.00	Very low
	Phorate	0.002	0.03	2.57	Medium
	Monochrotopos	0.002	0.00	0.00	Very low
6	Atrazine	0.002	0.00	0.00	Very low
	Chloropyriphos	0.002	0.00	0.00	Very low
	Phorate	0.002	0.03	2.85	Medium
	Monochrotopos	0.002	0.11	10.65	High
7	Atrazine	0.002	0.04	3.85	Medium
	Chloropyriphos	0.002	0.02	2.24	Medium
	Phorate	0.002	0.03	2.65	Medium
	Monochrotopos	0.002	0.31	30.75	Very high

Sample 2

The risk rating in terms of total groundwater load was ‘Very high’ for atrazine, ‘High’ for monocrotophos and phorate and ‘Low’ for chloropyriphos. Chloropyrifos, although applied in minor dosage, was not observed. With the type of soil being ‘Silty clay’ and borewell depth 40 m, the mobility was calculated as ‘Medium’ for atrazine, ‘Low’ for phorate and monocrotophos, whereas chloropyrifos was classified as ‘Very low’ (Figure 4).

Sample 3

The risk rating in terms of total groundwater load was 'High' for all the four pesticides. With the type of soil being 'Silty clay' and borewell depth as 25 m, the mobility was estimated to be 'Low' for atrazine, phorate and monocrotophos. Chloropyrifos was classified as 'Very low' (Figure 5).

Sample 4

Monocrotophos and chloropyrifos were rated as 'High', phorate was rated as 'Medium' and atrazine was rated as 'Low' groundwater pollution risk. With the type of soil being 'Silty clay' and borewell depth 20 m, the mobility was calculated as 'Low' for monocrotophos and chloropyrifos, whereas atrazine and phorate were classified as 'Very low' (Figure 6).

Sample 5

Phorate was rated as 'Medium' and for the rest pesticides it was rated 'Very low' as they were not applied in the field. With the type of soil being 'Silt' and borewell depth as 30 m, the mobility was calculated as 'Low' for phorate (Figure 7).

Sample 6

Monocrotophos was rated as 'High', phorate was rated as 'Medium', whereas chloropyrifos was rated as 'Very low' groundwater pollution risk as they were not applied in the field. With the type of soil being 'Sandy silt' and borewell depth 45 m, the mobility was calculated as 'Low' for monocrotophos, whereas chloropyrifos and phorate were classified as 'Very low' (Figure 8).

Sample 7

In Sample 7, monocrotophos was rated as 'Very high', phorate, atrazine, chloropyrifos were rated as 'Medium' groundwater pollution risk. With the type of soil being 'Silt' and bore well depth 45 m, the mobility was calculated as 'Low' for monocrotophos, whereas atrazine, chloropyrifos and phorate were classified as 'Very low' (Figure 9).

Comparison of observed and model estimates of pesticide residues/load

From the results of observed residues of the four pesticides (atrazine, chloropyrifos, monocrotophos and phorate) in the groundwater samples and the pesticide residues/load estimated by the model (PIRI software), it can be inferred that the observed values were comparatively higher than the model estimated values for most of the cases. The higher observed pesticide load in groundwater could be due to accumulation of pesticide residues despite degradation by various processes, because of the prolonged use of these pesticides over the years. PIRI software has been evaluated only for one year time period and therefore the estimated values are reflecting the residues during a limited time period.

Although the absolute values of observed and model estimated residues did not match, they seemed to bear consistent ratios fluctuating between reasonable ranges. Therefore the correction factor can be applied to the results of the model estimates, which may comply with the Indian scenarios for the chosen study area. This correction factor was estimated by dividing the observed values by the model estimated values, as shown in Table 7. The spatially averaged correction factors along with the range for each pesticide are shown in Figure 10. Multiplicative correction factors have to be imposed to the model estimates so as to predict the realistic pesticide residues in an area.

Table 7 | Correction factors for each pesticide at all the sampling stations

	Pesticide residues (ppb)											
	Atrazine			**Chloropyrifos**			**Phorate**			**Monocrotophos**		
Sample No	**Estimated value (a1)**	**Observed value (b1)**	**CF (b1/a1)**	**Estimated value (a2)**	**Observed value (b2)**	**CF (b2/a2)**	**Estimated value (a3)**	**Observed value (b3)**	**CF(b3/a3)**	**Estimated value (a4)**	**Observed value (b4)**	**CF (b4/a4)**
Sample 1	30.0	60.0	2.0	5.0	10.0	2.0	13.4	10.0	0.8	0.0	0.0	–
Sample 2	29.6	90.0	3.0	1.0	0.0	–	12.0	10.0	0.8	24.6	140.0	5.7
Sample 3	20.7	90.0	4.4	5.9	30.0	5.1	13.2	30.0	2.3	17.6	110.0	6.3
Sample 4	0.0	10.0	–	12.4	10.0	0.8	2.4	10.0	4.2	8.8	30.0	3.4
Sample 5	0.0	0.0	–	0.0	0.0	–	2.6	10.0	3.9	0.0	0.0	–
Sample 6	0.0	0.0	–	0.0	0.0	–	2.9	20.0	7.0	10.7	10.0	0.9
Sample 7	3.9	10.0	2.6	2.2	10.0	4.5	2.7	10.0	3.8	30.8	60.0	2.0
Average correction factor			**3.0**			**3.1**			**3.3**			**3.7**

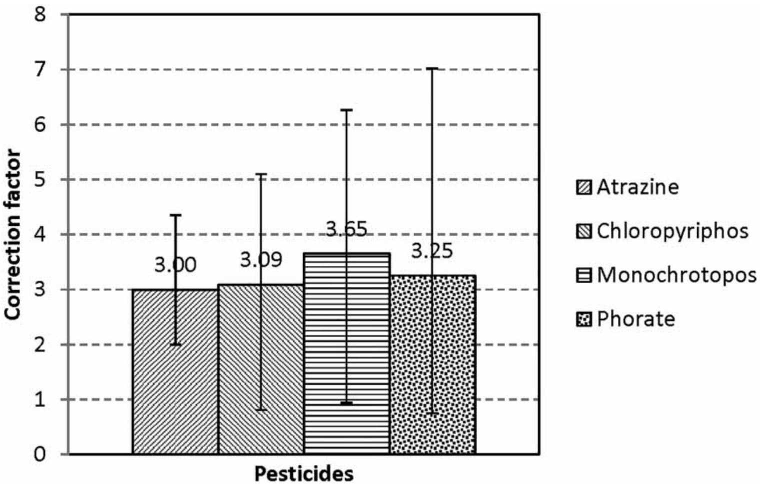

Figure 10 | Correction factors for different pesticides.

CONCLUSION

Pesticide usage has become an inseparable part of modern agriculture. If only the potential impacts of its usage over groundwater resources can be determined, thorough monitoring policies can be made for regulating pesticide application and also the local farmers can be made aware of the problems of improper pesticide usage. This will lead to conservation of ground water quality for various uses as well as future generations.

Based on the results of the study, it is recommended that PIRI software can be introduced for assessment of residues and mobility potential of various pesticides being used in India. For this, the suitable correction factors have to be incorporated based on corresponding local conditions and considered time frame of analysis.

REFERENCES

Agrawal, A., Pandey, R. & Sharma, B. 2010 Water pollution with special reference to pesticide contamination in India. *Journal of Water Resource and Protection* **2**(5), 432–448. doi:10.4236/jwarp.2010.25050.

Aktar, M. W., Sengupta, D. & Chowdhury, A. 2009 Impact of pesticides use in agriculture: their benefits and hazards. *Interdisciplinary Toxicology* **2**(1), 1–12. https://doi.org/10.2478/v10102-009-0001-7.

Aravinna, P., Priyantha, N., Pitawala, A. & Yatigammana, S. K. 2017 Use pattern of pesticides and their predicted mobility into shallow groundwater and surface water bodies of paddy lands in Mahaweli river basin in Sri Lanka. *Journal of Environmental Science and Health, Part B* **52**(1), 37–47. doi:10.1080/03601234.2016.1229445.

Belluck, D. A., Benjamin, S. L. & Dawson, T. 1991 Groundwater contamination by atrazine and its metabolites; risk assessment, policy and legal implications. In: *Pesticide Transformation Products, ACS Symposium Series*, Vol. 459. Minnesota Pollution Control Agency, USA, pp. 254–273. doi:10.1021/bk-1991-0459.ch018.

Carsel, R. F., Mulkey, L. A., Lorber, M. N. & Baskin, L. B. 1985 The pesticide root zone model (PRZM): a procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling* **30**, 49–69.

Chaudhary, V., Jacks, G. & Gustafsson, J. E. 2002 An analysis of groundwater vulnerability and water policy reform in India. *Environmental Management and Health* **13**(2), 175–193. https://doi.org/10.1108/09566160210424608.

Cogger, C. G., Bristow, P. R., Stark, J. D., Getzin, L. W. & Montgomery, M. 1998 Transport and persistence of pesticides in alluvial soils: I. Simazine. *Journal of Environmental Quality* **27**, 543–550.

Goncalves, C. M., Silva, J. C. & Alpendurada, M. F. 2007 Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. *Journal of Agricultural and Food Chemistry* **55**(15), 6227–6235. doi:10.1021/jf063663u.

Hernández-Romero, A. H., Tovilla-Hernández, C., Malo, E. A. & Bello-Mendoza, R. 2004 Water quality and presence of pesticides in a tropical coastal wetland in southern Mexico. *Marine Pollution Bulletin* **48**(11–12), 1130–1141. https://doi.org/10.1016/j.marpolbul.2004.01.003.

Kole, R. K. & Bagchi, M. M. 1995 Pesticide residues in the aquatic environment and their possible ecological hazards. *Journal of Inland Fisheries Society of India* **27**(2), 79–89.

Kookana, R. S., Correll, R. L. & Miller, R. B. 2005 Pesticide rating index – a pesticide risk indicator for water quality. *Water, Air and Soil Pollution* **5**(1–2), 45–65. https://doi.org/10.1007/s11267-005-7397-7.

Kumar, M. D. & Shah, T. 2004 *Groundwater pollution and contamination in India*. Available from: https://www.indiawaterportal.org/sites/indiawaterportal.org/files/ground-pollute4_FULL_.pdf (accessed 4 February 2019).

Kumari, B., Madan, V. K. & Kathpal, T. S. 2008 Status of insecticide contamination of soil and water in Haryana, India. *Environmental Monitoring and Assessment* **136**(1–3), 239–244. doi:10.1007/s10661-007-9679-1.

Leistra, M., van der Linden, A. M. A., Boesten, J. J. T. I., Tiktak, A. & van den Berg, F. 2001 *PEARL Model for Pesticide Behaviour and Emissions in Soil-Plant Systems, Description of Processes*. Alterra report 13. Alterra, Wageningen.

Li, Y. Z., Jia, X. F., Xu, C. Y., Wang, Q. S. & Li, Q. Z. 2013 A study on the source tracing of ground water nitrate in Shandong province. *Ecology and Environmental Science* **22**(8), 1401–1407.

MoEIT 2017 *Ministry of Electronics & Information Technology, Government of India*. Available from: https://jalandhar.nic.in/climatic-conditions/ (accessed 21 March 2017).

Mohapatra, S. P., Kumar, M., Gajbhiye, V. T. & Agnihotri, N. P. 1995 Groundwater contamination by organochlorine insecticide residues in a rural area in the Indo Gangetic plain. *Environmental Monitoring and Assessment* **35**(2), 155–164. https://doi.org/10.1007/BF00633712.

Sankararamakrishnan, N., Sharma, A. K. & Sanghi, R. 2005 Organochlorine and organophosphorous pesticide residues in groundwater and surface waters of Kanpur, Uttar Pradesh, India. *Environment International* **31**(1), 113–120. https://doi.org/10.1016/j.envint.2004.08.001.

Tariq, M. I., Afzal, S. & Hussain, I. 2004 Pesticides in shallow groundwater of Bahawalnagar, Muzafargarh, DG Khan and Rajanpur districts of Punjab, Pakistan. *Environment International* **30**(4), 471–479. doi:10.1016/j.envint.2003.09.008.

Thakur, S., Gulati, K. & Jindal, T. 2015 Groundwater contamination through pesticide usage in vegetable growing areas in Delhi. *International Journal of Multidisciplinary Research and Development* **2**(8), 394–397.

Tiktak, A., de Nie, D., van der Linden, A. M. A. & Kruijne, R. 2002a Modelling the leaching and drainage of pesticides in the Netherlands: the GeoPEARL model. *Agronomie* **22**, 373–387.

Tiktak, A., Boesten, J. J. T. I. & van der Linden, A. M. A. 2002b Nationwide assessments of non-point source pollution with field-scale developed models: the pesticide case. In: *Proceedings of the 5th International Symposium on Spatial Accuracy Assessment* (Accuracy 2002) (Hunter, G. J. & Lowell, K., eds). Melbourne, pp. 17–30.

Trevisan, M., Capri, E. & Del Re, A. A. M. 1993 Pesticide soil transport models: model comparisons and field evaluation. *Toxicological & Environmental Chemistry* **40**(1–4), 71–81. doi:10.1080/02772249309357932.

USEPA 2000 *Drinking Water Standards and Health Advisories*. Office of Water, U.S. Environmental Protection Agency, Washington, DC, EPA 822-B-00-001, Summer 2000.

Zhao, Y. Y. & Pei, Y. S. 2012 Risk evaluation of groundwater pollution by pesticides in China: a short review. *Procedia Environmental Sciences* **13**, 1739–1747. https://doi.org/10.1016/j.proenv.2012.01.167.