Drink. Water Eng. Sci., 4, 51–60, 2011
www.drink-water-eng-sci.net/4/51/2011/
doi:10.5194/dwes-4-51-2011

Drinking Water
Engineering and Science
Open Access

Status of organochlorine pesticides in the drinking water well-field located in the Delhi region of the flood plains of river Yamuna

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Received: 18 July 2011 – Published in Drink. Water Eng. Sci. Discuss.: 12 August 2011
Revised: 18 October 2011 – Accepted: 31 October 2011 – Published: 11 November 2011

Abstract. This study presents the occurrence of pesticides in a well-field located in Yamuna flood plain of Delhi region. Ground water sampling campaigns were carried out during pre-monsoon and post-monsoon periods covering 21 borewells and 5 Ranney wells. Major 17 organochlorine pesticides (OCP's) along with other water quality parameters were monitored during this period. Pesticide concentrations were determined using GC-ECD, while GC-MS was used for confirmatory purposes. OCP's groups like ∑HCH, ∑DDT, endosulfan and aldrin were observed in this well-field. Concentration of OCPs from Ranney well exceeded the limit ($1\,\mu g\,l^{-1}$) prescribed by the Bureau of Indian Standards (BIS) in pre-monsoon season, though OCP levels in borewells were within BIS limits. However, these levels were very close to the World Health Organisation (WHO) and European Union (EU) limit of for pesticides ($0.5\,\mu g\,l^{-1}$) in many samples. Borewell produced better quality water compared to the water from Ranney wells. Although, the level of OCP's was slightly lower than prescribed limit of national regulatory agency but such low doses may cause long-term damage to human populations if such water is consumed for longer durations. At low doses OCP's acts as endocrine disrupting agent and cause metabolic disorders in local population.

1 Introduction

Every year hundreds of new molecules are produced by the industry in addition to the production of existing ones. These chemicals either in the original form or as residues enter different components of the ecosystem. Several of these synthetic organics are persistent compounds. Important groups include pesticides, polycyclic aromatic hydrocarbons (PAHs) and pharmaceutical and personal care products (PPCPs). Pesticide contamination in drinking water resources is widely recorded in many parts of the world. Majority of pesticides enter the environment through non-point sources, following normal spraying in agricultural field and further surface run-off systems. Incidences of occurrence of pesticide residues in ground water may be of prime concern because majority of rural and urban populations in the developing world depend upon ground water resources for potable purposes.

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The organochlorine groups of pesticides are non-biodegradable and thereby these compounds can be concentrated through food chains and produce a significant magnification of the original concentration at the end of the chain. Once contaminated, (entered) these pesticides remain there for long. It is also supported by long half life of community like DDT's half life is 30 yr. Other chlorinated pesticides such as aldrin, endosulfan, HCH, lindane, endrin and dieldrin remain stable in water for many years after their use. Due to long residence time of these substances, there is a great interest in examining their presence in the environment. Reports showing their ubiquitous presence have made the situation worse as their residues are found in water (Hassan et al., 1996), ground water (Kaushik et al., 2011; Mudiam et al., 2011), food commodities (Mukherjee and Gopal, 1996), dairy milk (John et al., 2001), bovine milk (Sharma et al., 2007), edible oil (Bajpai et al., 2007), animal feed (Mukherjee and Gopal, 1996), mother's milk (Kumar et al., 2006a), human blood (Waliszewski et al., 2001) and in skin (Dua et al., 1998). Organochlorine pesticides (OCP's) were detected even in the most remote parts of the pristine environment like

ice core from Mt. Everest (Wang et al., 2008), Antarctic marine ecosystem (Geisz et al., 2008), Alpine glaciers (Villa et al., 2003; Bizzotto et al., 2009) and the breast milk of Inuit communities of Canada (Barrie et al., 1992; Blais et al., 2007) where these pesticides have never been used, but reached due to global circulation pattern and cold deposition on mountains. In India, OCP's have been reported in drinking water sources at: Bhopal (Dikshith et al., 1990), Hyderabad (Shukla et al., 2006), Jaipur (Bakore et al., 2004), Kanpur (Sankararamakrishnan et al., 2005) and Ahemedabad (Jani et al., 1991). The total pesticides consumption in Delhi area is continuously decreasing due to conversion of agricultural land to residential and industrial land. The total pesticides consumption in Delhi area was 100 MT 1990 which reduced to 53 MT in 2005 (www.ncipm.org.in). Mukherjee and Gopal (2002) reported higher level ($\mu g\,ml^{-1}$) of OCP's contamination in ground water samples taken from different zones of Delhi. But now we expected to have lower levels of pesticide residues in the ground water due to decreased pesticide consumption. It is evident from the literature that no comprehensive report is available on pesticide residues in Yamuna flood areas of Delhi region which is the main watershed zone for harvesting water for urban supply of Delhi NCT. The present study is focused on the special Palla-Burari well-field. The study area is strategically important because this area is also used by the local water supply organization as a potable water source. It has around 80 borewells and 5 Ranney wells to extract the good quality water from the Yamuna river flood plains to meet the growing water demand of Delhi. About 15 % of the public water supply of Delhi is contributed by this well-field, making the area hotspot as this area contributes a significant fraction of drinking water to 16.8 million people of Delhi. Since, this well-field has both the borewells and Ranney wells, so it is also contemplated to study effect of type of well on the water quality.

2 Materials and methods

2.1 Description of sampling site

This site is located along the upstream of urbanised parts of Delhi comprising, North West and North district of Delhi, on the flood plain of the western bank of the river Yamuna. The total sampling area of well-field is around 40 km^2, on the western bank of river Yamuna, starting from outskirts of Delhi (un-urbanised area) to the border of neighbouring state of Haryana. The flood plains have an embankment on both sides at a distance of 500–2000 m from the actual course of river Yamuna to protect the populated rural area from flood events. The flood plain is of younger alluvium and the sediments have been deposited upon a series of several hundreds of meters of older alluvium, which predominately composed of fine sand, silt and clay (Shekhar and Prasad, 2009). The well-field has relatively plain terrain within the embankment and the ground water level is about

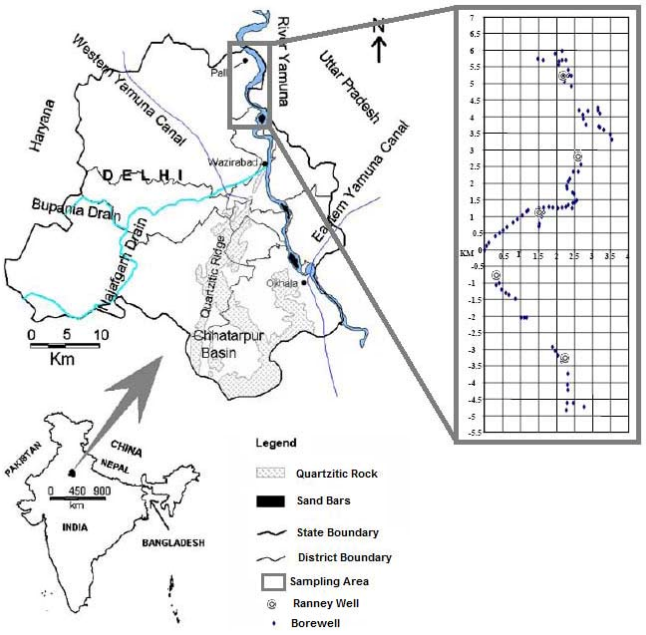

Figure 1. Map showing location of the study area (NCT Delhi) with the grids selected for the OCP analysis (map: modified from Shekhar and Prasad, 2009).

4–6 m b.g.l. (below ground level). The well-field contains two types of wells, Ranney wells and borewells. Ranney wells comprise a central concrete caisson excavated to a target depth (shallow) at which well screens project laterally outward in a radial pattern and are designed to induce infiltration. The site is on the bank of river Yamuna, thus can support Ranney wells by inducing infiltration through riverbank filtration from river Yamuna. The well-field also contains borewells which pumps the water from relatively deeper aquifer. Yield of borewells ranges from 100–280 $m^3\,h^{-1}$ in the area (Kumar et al., 2006b). The distance of wells sampled, from the feeding water source Yamuna river varies from 50–1000 m. The site is strategically important to compare the water quality from shallower and deeper aquifers, as Ranney wells water sample represent ground water quality in shallow aquifer while borewell water sample represent the deep aquifer water quality. Thus water samples were collected from borewells and Ranney wells, which are located between latitude 28°46′56.69″ N, longitude 77°11′58.62″ E and latitude 28°50′34.94″ N, longitude 77°12′34.91″ E. Sampling sites are shown in Fig. 1.

2.2 Water sampling

Sampling area was divided in a grid of 500×500 m, to reduce the total number of samples for OCP's analyses and to make a representative sampling as the sampling points were located in close proximity. Samples were taken from all the functional borewells and Ranney wells. One sample from

each grid was chosen for OCP analysis in order to obtain complete representation of the well-field. Average number of borewells in a grid of 2.5 km^2 was around 5. Thus 21 borewells and all 5 Ranney wells were selected for OCP analysis. The average depth of the Ranney wells ($N = 5$) was 25.56 m while the average depth of the borewells ($N = 80$) was 44.07 m. Samples were collected in high density polyethylene (HDPE) amber coloured bottles with Teflon lined caps. Prior to sampling, pumps were run for at-least 10 min to clear the casing of standing water and to bring in fresh water from the aquifer. The sampling bottles were rinsed with well water and were carefully filled to overflowing, without passing air bubbles through the samples or trapping air bubbles in sealed bottles. Field blanks were prepared with distilled water and were analysed only when pesticide residues were detected in primary samples. Two samples were taken from each site during each sampling campaign. One sample was used to determine physico-chemical parameters while the second sample was used for OCP analysis. The sample collection bottles were transported in cool-box with ice packs and subsequently stored in a refrigerator at 4 °C until further analysis.

2.3 Reagents and standards

Analytical grade (AR) chemicals (Merck, Germany) were used throughout the study without any further purification. To prepare reagents and calibration standards, double glass distilled water was used. The glass-wares were washed with dilute nitric acid (1.15 N) followed by several portions of distilled water. EPA 502 Pesticide Standard Mix (49690-U) was procured from Sigma-Aldrich USA. The working standards of pesticides were prepared by diluting EPA pesticide mixture standard in *n*-hexane and were stored at −20 °C.

2.4 Physico-chemical parameters

Samples were analysed for different physico-chemical parameters: pH, electrical conductivity (EC), alkalinity, hardness, major anions (Cl^-, F^-, NO_3^-, SO_4^{-2}) and major cations (Na^+, K^+, Ca^{+2}, Mg^{+2}) as per APHA (1998). EC and pH were measured using a portable EC and pH meter, respectively.

2.4.1 Extraction of pesticides residues

Method prescribed by APHA (1998) with some modifications was used for the extraction of OCP residues from the water samples. A liquid liquid extraction (LLE) method, using *n*-hexane as solvent, was used for extraction of pesticide residues. The water samples were prefiltered using 0.45 µm glass-fiber filter to remove any suspended impurity and were extracted without any pH adjustment. For extraction, one litre water sample was taken into a separating flask. It was mixed with 30 g of NaCl and 50 ml of *n*-hexane. Sample was shacked properly and hexane layer was separated. This process was repeated thrice with same water sample and hexane portions were pooled and transferred to a Buchi Condenser flask through a column of anhydrous sodium sulfate and florosil mixture to remove any remaining water molecules. The extract was condensed to around 2 ml on Rotavac and further reduced to 1 ml under gentle N_2 stream. The concentrated extract was transferred to air-tight GC vials and stored at −20 °C until analysis.

2.4.2 Qualitative and quantitative analysis

Analysis of pesticide residue was carried out on a Thermo® Trace GC, microprocessor controlled gas chromatograph, equipped with electron capture detector (ECD), having Nickel (63) foil as the electron source and auto sampler. The column specifications and operating conditions are given in Table 1. Confirmation of the identity of the OCP was done on a Mass Spectrometer (MS), coupled with Trace GC Ultra. The column type, column condition, temperature programming and injector temperature were kept the same for GC-ECD and GC-MS analysis. MS transfer line temperature and ionization source temperature were kept 280 °C and 200 °C, respectively (Table 1). The samples were injected by a Thermo AS 3000 autosampler by setting injection volume of 1 µl in splitless mode for each sample. Analysis was done in full scan mode, range of 50–650 units with 70-eV electron impact (EI) mode and specific ions were monitored for confirmation. The instrument was operated by Xcaliur software from Thermo Finnigan. To ensure the quality of extraction and detection procedure, 5 different concentrations of each OCP standards were mixed with distilled water, extracted by the same method, and recovery was measured. Table 2 presents retention time (RT), recovery efficiency (RE), method detection limit (MDL) and ions monitored for confirmation of different pesticides for this method. Important physico-chemical properties of investigated OCPs are given in Table 3.

3 Result and discussion

Physico-chemical quality of the ground water of the area is presented in Table 4. Water quality of groundwater at selected locations for major parameters: pH, electrical conductivity (EC), alkalinity, hardness, major anions (Cl^-, F^-, NO_3^-, SO_4^{-2}) and major cations (Na^+, K^+, Ca^{+2}, Mg^{+2}) was within BIS limits (IS:10500), except for EC and hardness for Ranney wells (1934.2 µS cm^{-1} and 653.6 mg l^{-1}, respectively) in pre-monsoon season which is slightly higher than prescribed limits. However, the EC and hardness decreased during the post-monsoon season. This could be attributed to the recharge of aquifer by good quality rain water and high flood level in river Yamuna during monsoon season. Lorenzen et al. (2010) reported a steep gradient from surface water

Table 1. Operating conditions used for the operation of GC-ECD and GC-MS.

	GC-ECD	GC-MS
Column used	DB-5, fused silica capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm)	DB-5, fused silica capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm)
Injector temperature	250 °C	250 °C
Oven programming	90 to 150 °C at 15 °C min^{-1}, 150 to 220 °C at 3 °C min^{-1} and 220 to 270 °C at 5 °C min^{-1}	90 to 150 °C at 15 °C min^{-1}, 150 to 220 °C at 3 °C min^{-1} and 220 to 270 °C at 5 °C min^{-1}
Detector temperature	280 °C	–
Carrier gas	Helium at 1.5 ml min^{-1}	Helium at 1.5 ml min^{-1}
Makeup gas	Nitrogen at 40 ml min^{-1}	
MS transfer line temperature	–	280 °C
Ionisation source temperature	–	200 °C

Table 2. Standardisation of OCP's compounds using GC-ECD and GC-MS.

Compound	RT (min)	Recovery (%)	R^2	MDL[a] ($ng\,l^{-1}$)	Selected Ions (m/z)
α-HCH (H1)	12.28	71.28	0.9994	0.01	
β-HCH (H2)	13.52	79.42	0.9984	0.01	
γ-HCH (H3)	13.74	70.99	0.999	0.01	
δ-HCH (H4)	14.97	78.56	0.9985	0.01	**181**, 183, 109, 288*
Heptachlor (He1)	17.22	87.53	0.9956	0.01	**100**, 272, 274, 370*
Aldrin (A1)	18.99	146.78	0.9988	0.01	**66**, 263, 79, 362*
Hepta-Epoxide (He2)	21.21	59.55	0.9987	0.01	**81**, 353, 355, 386*
α-Endo (E1)	23.15	107.97	0.9993	0.01	**195**, 197, 241, 404*
Dieldrin (A2)	24.6	123.87	0.9993	0.01	**79**, 81, 263, 378*
4,4′-DDE (D1)	24.8	86.16	0.999	0.01	**246**, 318, 316*
Endrin (A3)	25.79	87.70	0.9983	0.01	**81**, 79, 263, 378*
β-Endo (E2)	26.4	90.85	0.9978	0.01	**195**, 197, 241, 404*
4,4′-DDD (D2)	27.18	87.47	0.9972	0.01	**235**, 237, 165, 318*
Endrin-aldehyde (A4)	27.47	133.12	0.9951	0.01	**67**, 345, 250, 378*
Endo-Sulfate (E3)	28.81	85.80	0.9948	0.01	272, **387**, 420*
4,4′-DDT (D3)	29.24	99.22	0.9895	0.01	**235**, 237, 352*
Methoxychlor (M1)	32.28	95.48	0.9868	0.01	**227**, 228, 344*

MDL = methods detection limit
The ions were used for confirmation purpose only; the bold ions represent the base peak ion while the ion with a asterisk shows the molecular peak ion.

to groundwater and between shallow and deeper groundwater in this area, which is likely to be a consequence of heavy pumping in the well-field leading to high recharge rates from the river and a strong vertical flow component. Water quality improved in the post-monsoon season for all the parameters (Table 4), except for NO_3, which has slightly increased in the post-monsoon season. It may be due to recharge of water from surface run-off from agricultural field. The borewell water quality was much superior to Ranney well water and was less prone to seasonal change (Table 4).

Both, borewell (TW-1 to TW-21, grid wise) and Ranney well (RW-1 to RW-5) samples were analyzed for the presence of OCP's (Fig. 1, grid). One sample from each grid (500 × 500 m) of the well-field was taken. One sample may represent the whole grid since OCP's contamination may not vary within the grid. In these grids, OCP's are contributed by the anthropogenic activities only. Data revealed the trace levels of OCP's in the ground water. Tables 5 and 6 show levels of OCPs detected. In pre-monsoon, only 2 samples (TW-6, TW-9) out of 21 samples did not contain any of 17

Table 3. Physico-chemical properties of investigated organochlorine pesticides.

OCP	CAS No	Molecular weight	Molecular formula	Density ($g\,cm^{-3}$)	Melting Point (°C)	Boiling Point (°C)	Water Solubility ($mg\,l^{-1}$)	Log K_{OC}	Log K_{OW}
α-HCH	319-84-6	290.8	$C_6H_6Cl_6$	1.87	159	288	0.02–2	3.3–3.6	3.8–5.8
β-HCH	319-85-7	290.8	$C_6H_6Cl_6$	1.89	314	60	0.05–0.2	3.6	3.78
γ-HCH	58-89-9	290.8	$C_6H_6Cl_6$	1.85	112.5	323.4	0.7–5.59	3.57	3.6–3.7
δ-HCH	319-86-8	290.8	$C_6H_6Cl_6$	NA	141.5	60	0.2–259	3.8	4.14
Heptachlor	76-44-8	373.3	$C_{10}H_5Cl_7$	1.58	135–145	95-96	0.002–0.18	4.4	5.2–6.1
Aldrin	309-00-2	364.9	$C_{12}H_8Cl_6$	1.7	105	385	0.002–0.078	4.68	5.7–7.4
Hepta-Epoxide	1024-57-3	389.3	$C_{10}H_5Cl_7O$	1.58	161	425	0.02–0.275	4.48	4.6–5.4
α-Endo	959-98-8	406.9	$C_9H_6Cl_6O_3S$	1.94	108	NA	0.05–1.73	4.2	3.8–4.9
Dieldrin	60-57-1	380.9	$C_{12}H_8Cl_6O$	1.75	176	385	0.002–0.19	5.28	4.5–6.2
DDE	72-55-9	318	$C_{14}H_8Cl_4$	1.51	89	316	0.065	5.04	5.9–6.9
Endrin	72-20-8	380.9	$C_{12}H_8Cl_6O$	1.7	240	416	0.026–0.25	3.97	4.7–5.2
β-Endo	33213-65-9	406.9	$C_9H_6Cl_6O_3S$	1.7	106	NA	0.2–1.6	4.2	3.6–4.8
DDD	72-54-8	321	$C_{14}H_{10}Cl_4$	1.385	59.8	376	0.016–0.09	4.9	4.7–6.3
Endrin Aldehyde	7421-93-4	382.9	$C_{12}H_8Cl_6O$	NA	163	340	0.016–0.26	6.33	6.44
Endo-Sulfate	1031-07-8	422.9	$C_9H_6Cl_6O_4S$	NA	181	481	0.001–0.1	5.9	6.1
DDT	50-29-3	354.4	$C_{14}H_9Cl_5$	1.6	109	260	0.003	5.2	5.4–6.9
Methoxychlor	72-43-5	345.6	$C_{16}H_{15}Cl_3O_2$	1.39	86–96	436	0.001–0.045	4.89	5.66

NA = Not available

Table 4. Water quality of ground water of the Palla well field.

Parameters	Pre-monsoon Season						Post-monsoon season						IS Standards
	Borewell			Ranney Well			Borewell			Ranney Well			
	Ranges	Avg.	SD	Ranges	Avg.	SD	Ranges	Avg.	SD	Ranges	Avg.	SD	
pH	6.7–7.5	7.1	0.2	6.7–7.3	6.9	0.2	7.2–7.9	7.5	0.2	7.2–7.4	7.3	0.1	6.5–8.5
EC ($\mu S\,cm^{-1}$)	87–1770	725.3	309.4	825–4030	1934.2	1451.7	440–1570	728.6	248.5	847–2330	1210.6	470	1500
Sulfate ($mg\,l^{-1}$)	43.6–187.7	83.8	42.4	59.7–255.8	160.5	80.8	7–199.8	54.	43.9	39.2–255.7	93.9	94.7	200–400
Cl^- ($mg\,l^{-1}$)	38–232.3	86.4	38.3	72.8–1063.5	369.3	425.7	32–503	129.2	113.5	64–950	292.6	414.3	250–1000
Nitrate ($mg\,l^{-1}$)	0.4–0.9	0.6	0.1	0.4–7.9	2.2	3.2	2.1–30	6.9	5.4	3.6–7.9	3.5	1.6	<45
F^- ($mg\,l^{-1}$)	0.3–1.8	0.8	0.4	0.2–0.6	0.4	0.2	0.1–1.7	0.6	0.3	0.2–0.4	0.3	0.1	1–1.5
Na^+ ($mg\,l^{-1}$)	28–122	54.1	20.3	44–491.5	223.1	227.0	7–199.8	70.7	43.9	35.4–491.5	119.6	192.2	–
K^+ ($mg\,l^{-1}$)	2–31	3.7	4.8	3–8.1	5.0	2.0	1.5–8.4	7.3	1.2	4.7–8.1	9.6	1.3	–
Hardness ($mg\,l^{-1}$)	184–792	353.7	178.8	252–960	653.6	308.5	180–584	260.1	73	337–484	400	53.3	300–600
Alkalinity ($mg\,l^{-1}$)	176–356	241.8	51.0	244–320	290.4	34.6	180–388	259.2	56.8	284–336	300	21.8	200–600

targeted OCP's (Fig. 2). Rest of the samples contained 2 or more pesticides. Residues of all 17 targeted OCP's were found in 3 samples only. The most frequently occurring pesticides in this sampling campaign were aldrin, followed by $\sum$HCH, endosulfan and degradation product of DDT. The total numbers of pesticide occurrences were more in Ranney well, with an average of 11 OCP's per sample compared to the 7 OCP's in the borewell. None of the Ranney well sample was free from all the pesticides (Fig. 3). Concentrations of $\sum$HCH in the borewell water varied from not detected (ND) to $0.269\,\mu g\,l^{-1}$, with maximum of β-HCH being $0.201\,\mu g\,l^{-1}$ as individual HCH. The aldrin residues were detected in the range of ND to $0.047\,\mu g\,l^{-1}$, while dieldrin, endrin and endrin aldehyde were found in same range ND to $0.094\,\mu g\,l^{-1}$ but the frequency of occurrences was 27 % as compare to aldrin showing 76 % occurrences. During the sampling, it was noticed that the area has problem of mites and root worms. High occurrence of aldrin could be due to the use of pesticide to control the mites in the past. In case of Ranney wells, the most frequently occurring contaminants were $\sum$HCH, aldrin, DDE (frequency = 100 %), followed by β-endosulfan and methoxychlore with 80 % occurrence frequency. The maximum residue of single pesticide detected were similar to borewell water i.e. β-HCH, ($0.206\,\mu g\,l^{-1}$). The maximum concentration of endosulfan was $0.095\,\mu g\,l^{-1}$ for β-endosulfan in all the samples. During post-monsoon sampling campaign, more grids reported no pesticides (Fig. 4) and lower occurrences frequency where only 1 sample showed the presences of all the targeted OCP (Table 7) while in pre-monsoon periods 3 samples showed presence of all OCP's (Table 5). All the banned pesticides, viz $\sum$HCH, aldrin, heptachlor, DDT, DDD and DDE

Table 5. Organochlorine residues ($\mu g\,l^{-1}$) in ground water (bore well) of Palla area during pre-monsoon seasons.

	α-HCH	β-HCH	γ-HCH	δ-HCH	Hepta chlor	Aldrin	Hepta-Epoxide	α-Endo	Di-eldrin	DDE	Endrin	β-Endo	DDD	Endrin-aldehyde	Endo-Sulfate	DDT	Methoxy Chlor
TW-1	ND	0.004	ND	ND	ND	0.012	ND	0.024	ND	0.017	ND	ND	ND	ND	ND	0.008	ND
TW-2	0.017	0.045	0.057	0.018	0.018	0.047	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.035	ND
TW-3	0.011	0.024	0.036	0.007	0.007	0.029	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.015	ND
TW-4	ND	ND	0.012	ND	ND	0.010	ND	ND	ND	ND	ND	0.013	ND	ND	ND	ND	ND
TW-5	ND	ND	ND	ND	ND	0.022	ND	ND	ND	ND	ND	0.009	ND	ND	ND	ND	0.041
TW-6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-7	0.014	0.079	0.055	0.078	0.022	0.009	0.019	0.020	0.066	0.066	0.041	0.024	0.064	0.052	0.074	0.082	0.089
TW-8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.058	ND	0.030	ND	ND	ND	ND
TW-9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-10	0.012	0.018	0.028	0.012	ND	0.033	ND	ND	0.009	0.009	ND	ND	ND	0.044	ND	ND	ND
TW-11	0.015	0.089	0.055	0.078	0.017	0.009	0.021	0.020	0.075	0.033	0.048	0.045	0.033	0.047	0.044	0.052	0.066
TW-12	0.005	0.014	0.013	ND	ND	0.015	ND	ND	ND	0.009	ND	ND	0.011	ND	ND	ND	ND
TW-13	0.004	0.008	0.013	0.005	0.022	0.016	0.012	ND	ND	0.014	ND	0.030	0.007	ND	ND	0.018	0.050
TW-14	0.015	0.201	0.041	0.012	0.017	0.015	0.009	0.015	ND	0.010	ND	0.020	0.013	0.059	ND	ND	0.034
TW-15	0.018	0.033	0.061	0.022	0.019	0.042	ND	ND	ND	0.010	0.018	0.050	0.012	0.069	ND	ND	ND
TW-16	ND	0.009	ND	ND	ND	ND	ND	ND	ND	0.024	ND	ND	ND	ND	ND	0.014	ND
TW-17	ND	ND	ND	ND	ND	ND	ND	0.012	ND	ND	ND	0.017	ND	ND	ND	ND	ND
TW-18	0.007	0.017	ND	0.012	0.022	0.013	0.012	ND	ND	0.008	ND	0.029	ND	ND	ND	ND	0.075
TW-19	0.008	0.016	0.025	0.010	0.016	0.016	0.008	ND	ND	0.011	ND	ND	0.014	ND	ND	0.037	0.034
TW-20	ND	ND	ND	ND	ND	0.014	ND	ND	0.015	ND	0.021	0.016	ND	ND	ND	ND	ND
TW-21	0.012	0.034	0.048	0.015	0.018	0.030	0.009	0.019	0.018	0.013	0.021	0.094	0.016	0.053	0.020	0.035	0.035

Table 6. Organochlorine residues ($\mu g\,l^{-1}$) in ground water (Ranny well) of Palla area during pre-monsoon seasons.

	α-HCH	β-HCH	γ-HCH	δ-HCH	Hepta chlor	Aldrin	Hepta-Epoxide	α-Endo	Di-eldrin	DDE	Endrin	β-Endo	DDD	Endrin-aldehyde	Endo-Sulfate	DDT	Methoxy Chlor
RW-1	0.003	0.012	0.016	0.008	ND	0.013	ND	ND	ND	0.009	ND	0.015	ND	ND	ND	ND	ND
RW-2	0.006	0.017	0.027	0.011	ND	0.030	ND	ND	0.010	0.009	ND	0.020	ND	0.035	ND	ND	0.033
RW-3	0.012	0.022	0.035	0.015	0.015	0.021	0.008	ND	ND	0.009	ND	0.022	0.012	ND	ND	ND	0.034
RW-4	0.014	0.206	0.032	0.012	0.017	0.015	0.009	0.015	ND	0.011	ND	ND	0.014	ND	ND	0.037	0.035
RW-5	0.016	0.099	0.069	0.100	0.027	0.030	0.041	0.067	0.115	0.073	0.083	0.095	0.073	0.087	0.066	0.072	0.070

were below their regulatory concentrations in the borewells. α-endosulfan was present only in one sample ($0.034\,\mu g\,l^{-1}$), which shows the wise use of highly controversial pesticide, endosulfan in Yamuna catchment area. In case of Ranney well samples, the trends of occurrences were similar to the pre-monsoon sampling campaign; but the levels were lower (Table 8, Fig. 5). The student's t-test was carried out for pre-monsoon and post-monsoon samples taking all the samples as independent variables. It showed that there was no significant difference in total pesticide concentration in both the season ($P > 0.05$). Thus, it can be inferred that during whole year people receiving water supply from this wellfield are at high risk of pesticide exposure. Though, levels in post-monsoon season were lower than safe limit, but were not statistically different from pre-monsoon season. However, concentration of individual pesticides for both the seasons was statistically different ($P < 0.01$) for borewells and Ranney wells. This indicates that concentrations of individual pesticides decreased in post-monsoon season. It can be attributed to the dilution due to recharge of the aquifer during monsoon. Figures 6 and 7 indicate the total pesticides concentration in individual samples. The water quality of borewells was superior to the Ranney well as none of the borewell sample was found to contain the OCP residues level more than BIS permissible limit (Figs. 6 and 7). As per BIS drinking water standard, the water should be free from all pesticides, but in case of non availability of other sources, the limit is $1\,\mu g\,l^{-1}$ of total pesticides. Water, other than packaged mineral water, is not an important commodity in international trade, so there is no initiative in place to harmonize these limits at the international level. It varies from place to place, depending on the awareness level and economy of the country. The safe limit for pesticide residues are different in different parts of the world: WHO and EU have a safe limit of $0.5\,\mu g\,l^{-1}$ as compare to BIS limit of $1\,\mu g\,l^{-1}$. Recent reports on the total OCP levels in groundwater of neighbouring areas of Palla (Delhi) have reported much higher concentrations, $2.184\,\mu g\,l^{-1}$ in Haryana (Kaushik et al., 2011) and up to $4\,\mu g\,l^{-1}$ in Lucknow city (Mudiam et al., 2011). This wellfield is being recharged with the bank filtrate of river Yamuna (Lorenzen et al., 2010). Both external flux through bank filtrate and local use of pesticides can contribute to the pesti-

Table 7. Organochlorine residues ($\mu g\,l^{-1}$) in ground water (bore well) of Palla area during post-monsoon season.

	α-HCH	β-HCH	γ-HCH	δ-HCH	Hepta chlor	Aldrin	Hepta-Epoxide	α-Endo	Di-eldrin	DDE	Endrin	β-Endo	DDD	Endrin-aldehyde	Endo-Sulfate	DDT	Methoxy Chlor
TW-1	0.004	0.009	ND	ND	ND	0.024	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.040	ND	ND	ND
TW-3	ND	ND	ND	ND	ND	0.017	ND	ND	ND	ND	ND	ND	ND	0.039	ND	ND	ND
TW-4	ND	ND	0.007	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-5	ND	ND	ND	ND	ND	0.019	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-7	0.005	0.037	0.012	0.039	0.032	0.034	0.026	0.034	0.058	0.046	0.046	0.041	0.055	0.069	0.057	0.093	0.094
TW-8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.054	ND	0.024	ND	ND	ND	ND
TW-9	ND	ND	ND	ND	ND	0.024	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-10	0.003	ND	ND	ND	ND	0.011	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-11	ND	ND	ND	ND	ND	0.014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-12	ND	ND	ND	ND	ND	ND	ND	ND	0.009	0.018	ND	ND	ND	ND	ND	ND	ND
TW-13	ND	ND	ND	ND	ND	0.018	ND	ND	ND	0.018	ND	ND	0.022	ND	ND	ND	0.066
TW-14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.029	ND	ND	0.083	ND	ND	ND
TW-15	ND	0.013	0.009	0.014	0.028	0.025	0.017	ND	0.016	0.021	ND	ND	0.025	ND	0.038	0.069	0.069
TW-16	ND	0.008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TW-17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.031	ND	ND	ND	ND	ND
TW-18	ND	ND	ND	ND	0.028	0.016	0.016	ND	ND	0.018	ND	0.060	ND	ND	ND	ND	0.066
TW-19	0.005	ND	0.014	0.013	ND	0.018	0.016	ND	0.030	0.019	ND	ND	0.024	ND	0.036	0.068	0.068
TW-20	ND	ND	ND	ND	ND	ND	ND	ND	0.010	ND	0.042	ND	ND	ND	ND	ND	ND
TW-21	ND	ND	ND	ND	ND	0.028	ND	ND	ND	ND	ND	0.031	ND	ND	ND	ND	ND

Table 8. Organochlorine residues ($\mu g\,l^{-1}$) in ground water (Ranny well) of Palla area during post-monsoon seasons.

	α-HCH	β-HCH	γ-HCH	δ-HCH	Hepta chlor	Aldrin	Hepta-Epoxide	α-Endo	Di-eldrin	DDE	Endrin	β-Endo	DDD	Endrin-aldehyde	Endo-Sulfate	DDT	Methoxy Chlor
RW-1	0.006	ND	ND	0.013	ND	0.018	0.016	ND	0.010	0.019	ND	0.018	0.024	ND	0.036	0.068	0.068
RW-2	0.005	0.011	0.037	0.022	ND	0.018	ND	ND	ND	ND	ND	0.023	ND	0.015	ND	ND	ND
RW-3	0.005	ND	0.024	ND	ND	0.021	ND	0.024	ND	ND	ND	0.022	0.022	ND	ND	ND	ND
RW-4	0.009	0.015	0.019	ND	ND	ND	ND	ND	ND	0.013	ND	ND	ND	ND	ND	ND	0.068
RW-5	0.008	0.015	0.018	0.017	ND	0.018	0.019	0.044	0.021	0.023	0.030	0.032	0.031	0.018	0.038	0.074	0.070

cides in the aquifer. The presence of α-HCH and γ-HCH reveals the use of technical HCH (55–80 % α-HCH and 8–15 % γ-HCH plus other compounds) and lindane (more than 99 % γ-HCH) in the Yamuna catchment area. Most of the developed countries have banned the use of technical HCH in the 1980s, but in India, it is still under production for export and restricted use, other than agriculture. The α-HCH/γ-HCH ratio within the technical formulation ranges from 4–15 and 0.2–1 in lindane (Ridal et al., 1996). The low ratios of α-HCH/γ-HCH (Table 9) in the ground water samples indicate that lindane may also be an important source of HCHs in Yamuna river watershed. Among the DDTs, 4, 4-DDD and DDE were found to be the predominant compound (Tables 5, 6, 7 and 8). The DDE/DDTs and DDD/DDTs ratios can be used to assess whether the DDT input is of recent origin or from the past (Kannan et al., 1997). Since DDE/DDTs and DDD/DDTs ratios in all the samples were much lower than unity (Table 9), it appears DDT inputs is of recent origin from the Yamuna river catchment area. Total annual production of DDT in India is still more than 3000 t. (UNEP/POPS, 2008). It is used for export and malaria control programme in India, which supports the findings of recent inputs of DDT.

Table 9. Concentration ratios of selected OCP's compounds in the ground water according to the sampling source and seasons.

Sampling sites		α-HCH/γ-HCH	DDE/DDTs	DDD/DDTs	DDE/DDD
Borewell	Pre-monsoon	0.245	0.518	0.269	0.931
	Post-monsoon	0.347	0.692	0.327	1.334
Ranney well	Pre-monsoon	0.292	0.319	0.319	1.137
	Post-monsoon	0.329	0.274	0.2	0.709

The DDE/DDD ratio is indicative of the prevalent redox conditions in the area. While, in oxic conditions, DDE is the main metabolite of DDT (Wolfe et al., 1977), in anoxic conditions, DDD is the major degradation product (Zoro et al., 1974). Here, the DDE/DDD ratio varies from 0.709–1.334, more than unity is indicative of the less reducing conditions or an extended degradation during the long- range transport of DDT. As the major share of the ground water is replenished by river Yamuna and the river is in losing condition (Lorenzen et al., 2010) in this area, the background level of OCP present in river water could also reach into

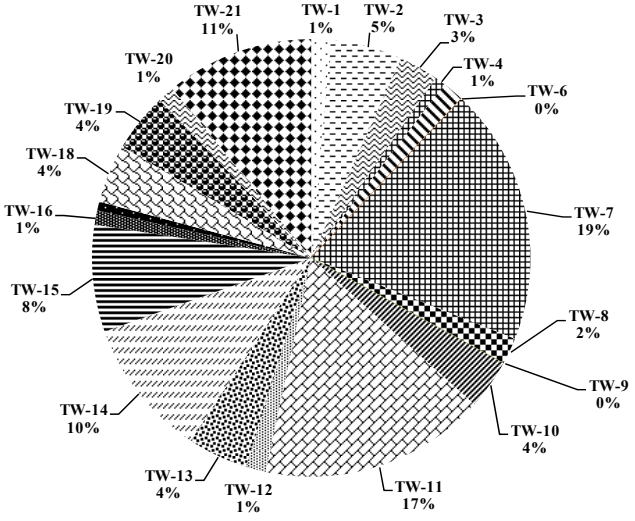

Figure 2. Relative abundance of OCP in different borewell samples (Pre-monsoon).

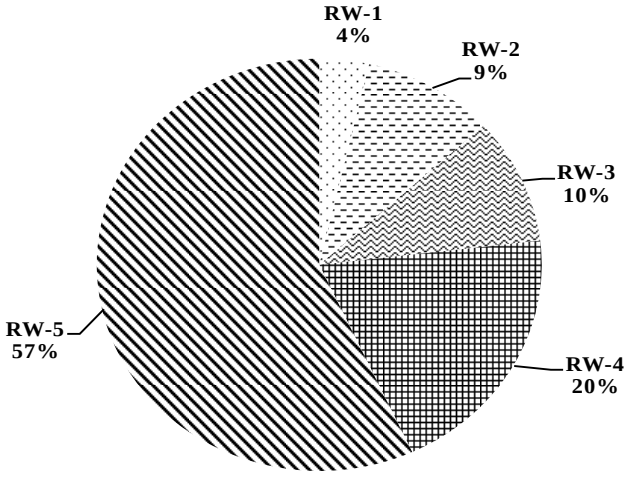

Figure 3. Relative abundance of OCP in different Ranney well samples (Pre-monsoon).

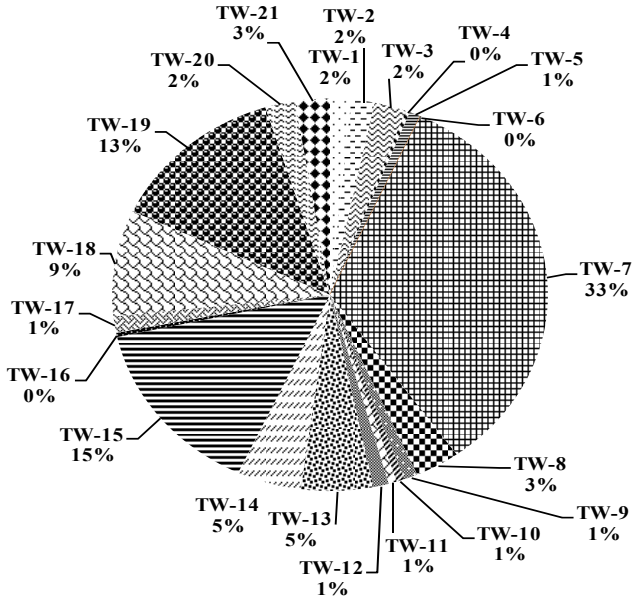

Figure 4. Relative abundance of OCP in different borewell samples (Post-monsoon).

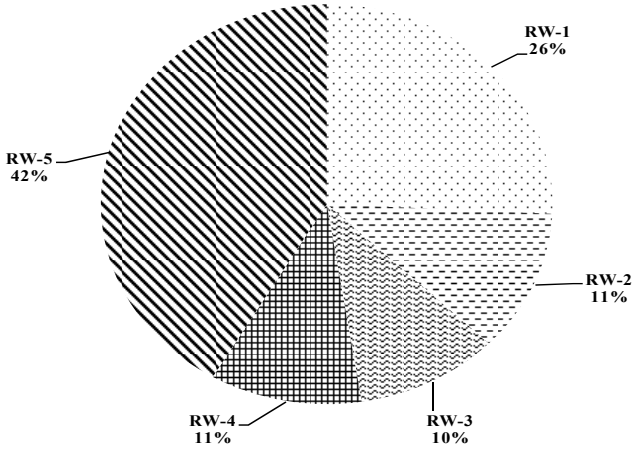

Figure 5. Relative abundance of OCP in different Ranney well samples (Post-monsoon).

the aquifers. Kaushik et al. (2008), monitored the levels of OCP's in the river Yamuna and reported $\sum$HCH 0.012–0.593 $\mu g\,l^{-1}$, and $\sum$DDT = 0.066–0.723 $\mu g\,l^{-1}$ in surface water of river Yamuna, in upstream of this well-field. Levels of these pesticides in the aquifer of this well-field were much lesser. It may be because of dilution or adsorption of organic compounds by soil strata during recharge. The high affinity to soil organic matter (high K_{OC}) make these pesticides strongly bound to soil organic matter and thus they are less leached in the aquifer while recharging the well-field. The levels of OCP residues were higher for Ranney wells than borewells (Tables 5, 6, 7 and 8) in all the cases. Ranney well have much higher hydraulic gradient as compared to borewells. Thus, higher gradient may result in higher desorption of pesticides from solid phase to aquifer or lower transfer of pesticides from aquifer to soil particles.

4 Conclusions

There is wide prevalence of OCPs throughout the well-field though at low concentrations. During monsoon high flood levels results in recharge of the well-field. But, there is no statistical difference between pre-monsoon and post-monsoon periods. The borewell water quality was superior to the Ranney well. So it is advantageous to develop a well-field with borewells rather using Ranney wells. Although the levels of pesticides were lower than the local regulatory

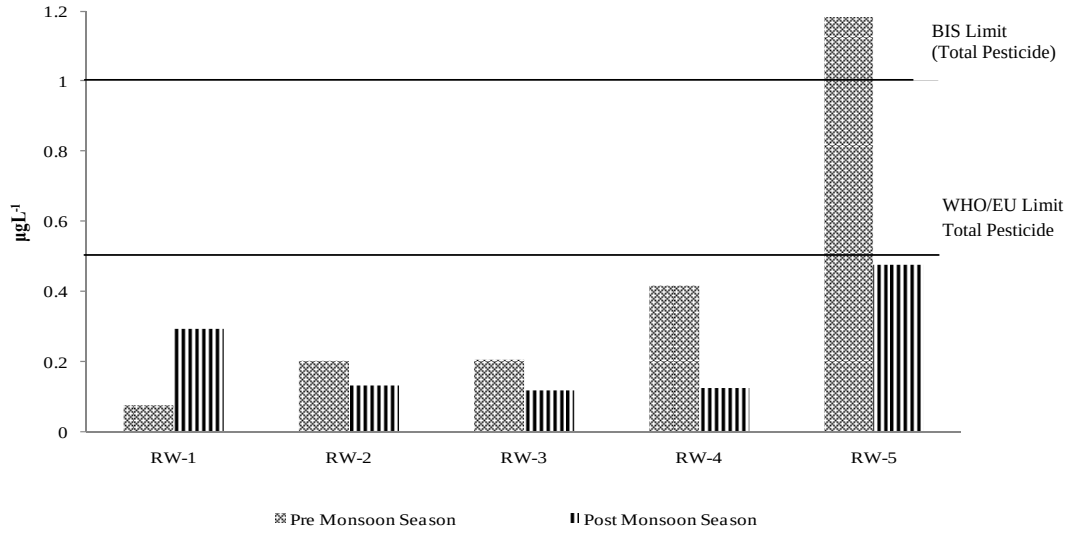

Figure 6. Comparison of Ranney well water quality with respect to various limits.

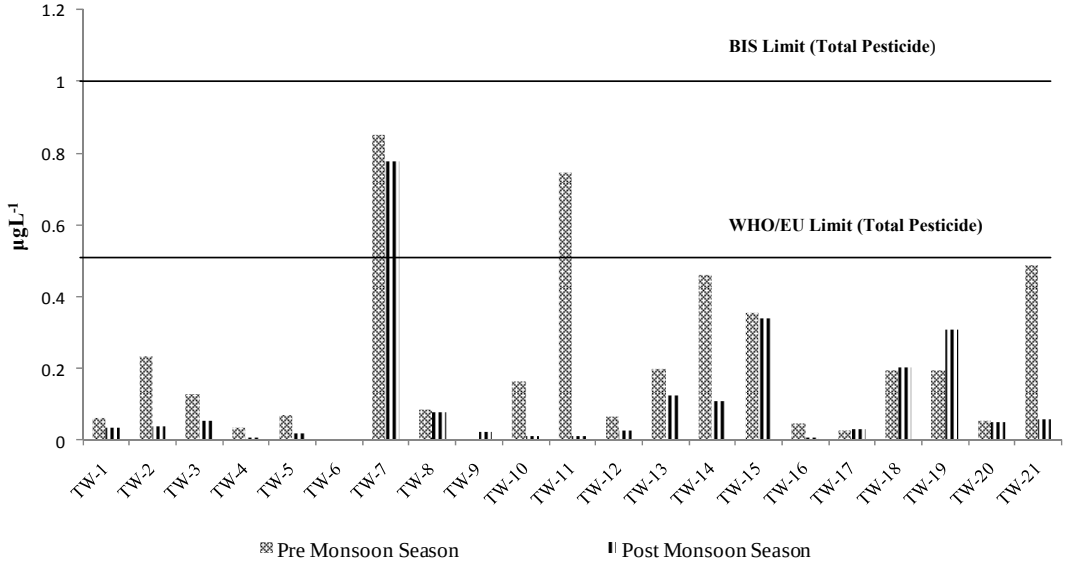

Figure 7. Comparison of borewell water quality with respect to various limits.

limits but regular consumption of such contaminated water may pose serious health hazard to the people who depend for the water on this well-field. In order to rule out any possibility of health risk by OCPs, regular monitoring of pesticide residues in river water and ground water is required. Delhi is a rapid growing urban centre, so there is a great political and social pressure to utilize this well-field to supply water for the city of Delhi since this well-field produces 60–76 million m^3 day^{-1} potable water in all the seasons. There is need for comprehensive investigations to monitor the breakdown products of the pesticides in order to get better idea of the overall risk due to well contamination (since breakdown products are often toxic), and the mechanism causing wells to be contaminated.

Acknowledgements. One of the authors (Pravin K. Mutiyar) is thankful to University Grants Commission (UGC), New Delhi (India) for providing financial assistance in the form of Junior Research Fellowship (JRF) to conduct this work.

Edited by: J. Cho

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