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Persistent Organochlorine Pesticide Residues in Alluvial Groundwater Aquifers of Gangetic Plains, India

K. P. Singh,[1] A. Malik,[1] D. Mohan,[1] S. Sinha[2]

[1] Environmental Chemistry Section, Industrial Toxicology Research Center, Post Box 80, Mahatma Gandhi Marg, Lucknow 226 001, India
[2] National Botanical Research Institute, Rana Pratap Marg, Lucknow 226 001, India

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Groundwater contamination has aroused a global concern over the last few decades. The problem has become more severe in the countries where groundwater aquifers constitute the main drinking water resources. Groundwater may be contaminated with various types of contaminants released from sources, such as recharge from the polluted freshwater bodies, leakage of chemicals from landfills and lagoons, and leaching from agricultural fields (Ahel, 1991). Extensive use of pesticides in the agricultural fields, due to high leaching potential of many of them, is among the most prominent sources of groundwater contamination. In India, organochlorine pesticides (OCPs) are extensively used due to their low cost and broad-spectrum toxicity. Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, HCB and toxaphene are among the members of the persistent organic pollutants (POPs) group. As the OCPs are lipid soluble in nature, cumulative bioaccumulation of low concentrations of these in the body fat of mammals might pose potential hazards in the long run (Metcalf 1997). Due to their toxic, lipophilic and persistent nature, all the POP-pesticides, except DDT, which is under restricted use, are under complete ban in India. Residues of different OCPs, used earlier have been reported in the water, soil, sediments, vegetables, animal tissues, human blood and breast milk in India (Mohapatra et al 1995, Sharma and Bhatnagar 1996, Hans et al 1999, Dua et al 2001, Sanghi and Sasi 2001, Singh 2002). Hypertension, abdominal pains, diarrhea, respiratory diseases, dysfunctioning of reproductive system, pre/postnatal damage, carcinogenesis and mutagenesis are the main health hazards associated with the exposure to OCPs (UNEP 2003). In northern India, the Gangetic alluvium plain, due to fertile soils, is the region of high agriculture and industrial activities with high population density. The main crops in the study area are paddy, maize, barley, jwar, wheat, potato and oilseeds. The shallow character and high permeability of alluvial aquifers make them highly vulnerable to contamination (Garcia-Hernan et al. 1988). India being a signatory to the Stockholm Convention on POPs requires current state-of-art on residue of the POP-pesticides. The present study basically aimed to assess the residual contamination of groundwater aquifers in the Gangetic alluvium plains with the persistent OCPs currently in use and those used earlier in the region. Since, the groundwater in the region is largely used for domestic and agricultural purposes, the data generated will be of great concern, in order to prevent and avoid human health risks in the region.

Correspondence to: K. P. Singh

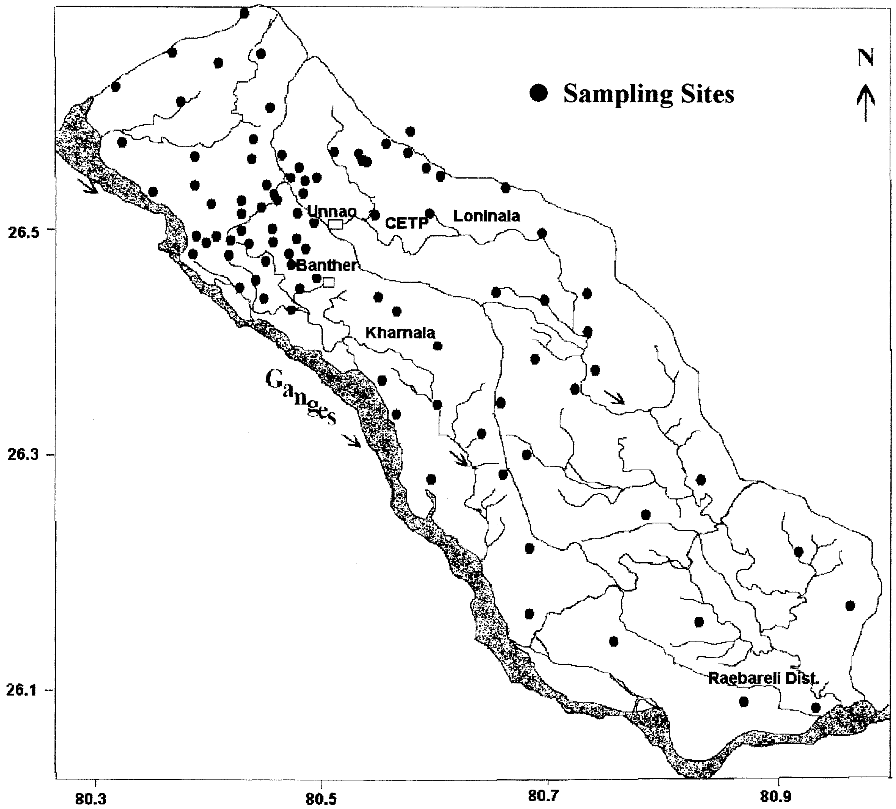

Figure 1. Map of the study region showing sampling locations.

MATERIALS AND METHODS

The study region (about 2150 km^2) is located in the Unnao district (26° 05' & 27° 02' N latitude and 80° 03' & 81° 03' E longitude) in the Gangetic alluvium plains in northern part of India (Fig. 1). It lies between the two giant cities, Kanpur and Lucknow with the Ganga and Sai rivers forming the hydrological boundaries. The dug well, tube well, bore well and hand-pump constitute the groundwater sources in the study area. The groundwater in this region occurs at shallow depth as phreatic aquifers with water level depth of less than 10 m below ground level (bgl). Total 96 samples of groundwater (42 from dug wells and 54 from bore wells) were collected in the months of October-November, 2003, using high quality brown glass bottles. Samples from bore wells (tube well, bore well and hand-pumps) were collected from the outlets after flushing water for 10-15 minutes in order to remove the stagnant water. Samples from the dug wells were collected using water sampler. All the water samples (unfiltered) were processed for selected OCPs analysis following the standard method (AOAC 1995). All the water samples were analysed for aldrin, dieldrin, endrin, HCB, HCH isomers, DDT isomers/metabolites, endosulfan isomers (α and β), endosulfan sulfate, heptachlor and its metabolites, α-chlordane, γ-chlordane and methoxychlor on Varian CP-3800 Gas Chromatograph equipped with fused silica CP-Sil 19 CB capillary column (30mx0.32mm i.d.x0.25μm film thickness) and Ni^{63} ECD. For all extractions GC grade methylene chloride (Spectrochem, India; 99%) was used. The instrumental analyses were made employing nitrogen (IOLAR) as carrier gas (2ml/min) and operating temperatures were: 300°C for the injector port and detector and 220°C for column. The split ratio of 1:2 was used. The pesticides standards (99.9% purity) were supplied by Sigma-Aldrich, USA. The minimum detection limit for aldrin, α-chlordane, γ-chlordane, dieldrin, op-DDT, pp-DDT, pp-DDE, pp-DDD, endrin, α-endosulfan, β-endosulfan, endosulfan sulfate, HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor epoxide-A, heptachlor epoxide-B and methoxychlor was found to be 0.1, 0.1, 0.1, 0.05, 0.1, 0.1, 0.03, 0.06, 0.05, 0.04, 0.07, 0.05, 0.01, 0.05, 0.1, 0.1, 0.05, 0.06, 0.02, 0.02 and 0.1 ugL^{-1}, respectively. A further lower detection of these was achieved through 1000-fold concentration of the samples. All analyses were carried out in duplicate and the recoveries of individual pesticides were determined through spiked sample method, which were found between 91-104%. Recovery correction factors were applied to the final results.

RESULTS AND DISCUSSION

The concentration range, mean, and standard deviation for different OCPs in the groundwater samples collected from the dugwells and borewells are given in Table 1. In general, concentration levels as well as detection frequency of aldrin were higher than those of dieldrin and endrin in both of the groundwater sources (Fig 2 and 3). Relatively lower residues of dieldrin and endrin indicate their earlier use, as both of these are now banned for manufacture and use in India. The aldrin residues in the studied area (BDL-1355.2 ngL^{-1}) are higher than those found in the groundwater of different regions in India (Kumar et al 1995, Mohapatra et al 1995 and Singh 2001). Use of aldrin as an anti-termite agent in the potato crop may explain for its high residue levels, as potato is one of the major crops grown in the area. Higher residue levels of aldrin also show high persistency of the chemical in environment, since, it is under complete ban. Mean concentration of HCB was higher in borewells water (ranging BDL-118.9 ngL^{-1}) as compared to the dugwells. Use of HCB has been reported in India till 1997 (UNEP 2003). Among the chlordane isomers, γ-chlordane dominated over the α-chlordane both in terms of frequency of detection and residue levels (Fig. 2). The γ-isomer is more persistent in nature, which may lead to its higher residue levels in groundwater after several years of its ban for use. α-endosulfan predominated among the isomers/metabolites of endosulfan (α-endosulfan, β-endosulfan and endosulfan sulfate) in both the shallow and deeper ground water aquifers. The residues of α-endosulfan, β-endosulfan and endosulfan sulfate ranged between BDL-81.6, BDL-28.4 and BDL-33.7 ngL^{-1}, respectively in the groundwater samples collected from the study area. These current residue levels are lower than the concentration range for α-endosulfan (ND-127 ngL^{-1}), β-endosulfan (ND-105

Table 1. Concentration range (ngL^{-1}), mean and SD for OCPs in groundwater of the Unnao district.

Pesticide	**Dugwells (n=42)**		**Borewells (n=54)**	
	Range	Mean±SD	Range	Mean±SD
Aldrin	BDL-1355.2	33.1±208.9	BDL-24.8	2.7±5.8
α-Chlordane	BDL -2.5	0.1±0.5	BDL-15.7	0.3±2.1
γ-Chlordane	BDL -7.2	0.8±1.6	BDL-11.5	1.4±11.5
Total Chlordane	BDL-7.2	0.9±1.7	BDL-27.2	1.7±4.2
op-DDT	BDL -58.5	3.5±9.5	BDL- 46.6	2.8±7.4
pp-DDT	BDL -5.4	0.4±1.2	BDL-13.6	0.6±2.3
pp-DDE	BDL -47.5	4.9±9.1	BDL- 73.9	8.9±15.9
pp-DDD	BDL -240.8	6.4±37.0	BDL-9.2	0.7±1.96
∑ DDT	BDL -266.2	16.5±43.7	BDL-96.8	14.1±22.9
Dieldrin	BDL -5.5	0.3±0.9	BDL-6.4	0.4±1.2
Endrin	BDL -4.6	0.3±1.0	BDL-6.4	0.4±1.1
α -Endosulfan	BDL -53.4	7.9±12.9	BDL-81.6	8.4±15.6
β-Endosulfan	BDL -29.6	5.5±9.5	BDL-28.4	3.0±7.0
Endosulfan sulfate	BDL -6.2	0.2±1.0	BDL-33.7	0.6±4.6
Total Endosulfan	BDL-54.4	13.6±14.8	BDL-95.8	12.0±17.9
HCB	BDL -20.1	1.7±4.1	BDL-118.9	3.4±16.2
α -HCH	BDL -383.6	24.8±66.8	BDL-909.6	29.4±129.6
β -HCH	BDL -744.4	67.2±130.5	1.06-372.9	46.1±72.7
γ -HCH	BDL -247.7	19.6±49.8	BDL-743.1	30.4±116.7
δ-HCH	BDL-2813.8	97.4±435.6	BDL-439.7	38.6±73.4
∑ HCH	0.56-2920.9	208.9±497.5	2.14-1856.6	144.6±295.5
Heptachlor	BDL -291.3	8.7±44.8	BDL-94.8	4.6±13.2
Heptachlor epoxide-A	BDL -12.4	1.2±2.9	BDL-66.2	4.1±11.2
Heptachlor epoxide-B	BDL -7.6	0.4±1.5	BDL-44.5	2.3±8.7
Total Heptachlor	BDL-303.6	10.3±46.7	BDL-138.1	11.0±25.5
Methoxychlor	BDL -3.5	0.2±0.7	BDL-19.9	0.8±3.4
∑ OCPs	3.30-2976.2	285.7±615.5	2.14-2173.4	191.2±350.1

BDL = Below Detection Limit

ngL^{-1}) and endosulfan sulfate (ND) reported by Mohapatra et al (1995) in the groundwater of Farrukhabad (Indogangetic Plain, India). Relatively higher residue levels of α- and β-endosulfan and absence of endosulfan sulfate suggest for fresh input of the pesticide, while, relatively lower levels of endosulfan isomers and presence of endosulfan sulfate indicates the earlier use of endosulfan in the studied region. Total heptachlor residue (sum of heptachlor and heptachlor epoxides) in dugwell and borewell water ranged between BDL-303.6 and BDL-138.1 ngL^{-1}, respectively. Heptachlor is metabolised to heptachlor epoxides in the soils, plants and animals, which is more stable in biological systems. Heptachlor epoxide-A occurred more frequently (Fig 2, ranging between BDL-12.4 and BDL-66.2 ngL^{-1} in the dugwells and borewells, respectively) as compared to the heptachlor epoxide-B (BDL-7.6 and BDL-44.5 ngL^{-1}, respectively in the dugwells

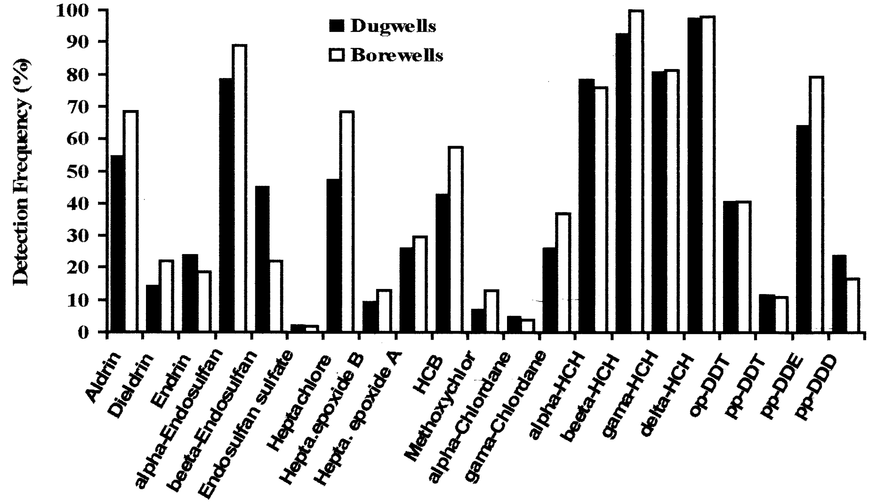

Figure 2. Detection frequency (%) of different organochlorine pesticides in the dugwells and borewells of the study area.

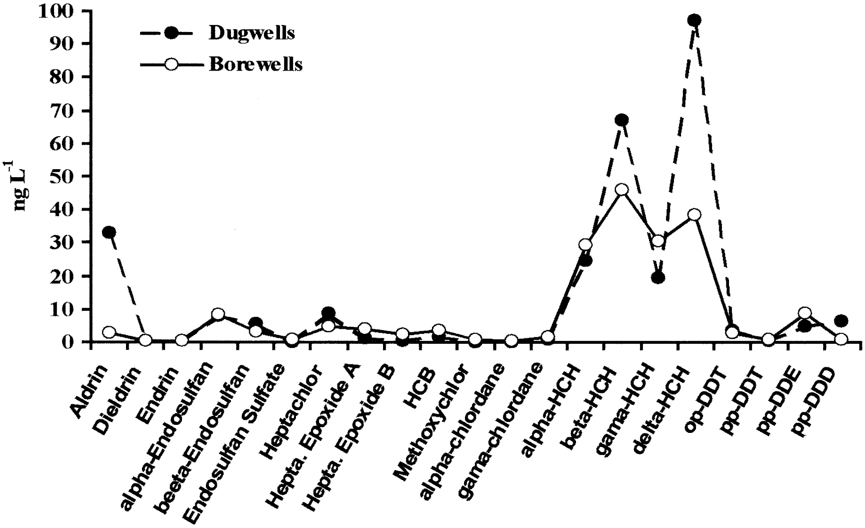

Figure 3. Mean concentration (ngL^{-1}) of different organochlorine pesticides in the dugwells and borewells of the study area.

and borewells). Further, the mean concentration of heptachlor was higher (Fig 3) in the dugwell water whereas, in borewell water, the concentration of heptachlor epoxides was higher. It may be attributed to the relatively high stability of the heptachlor epoxides. Mohapatra et al (1995) and Singh (2001) reported relatively lower residue level of heptachlor in groundwater samples of Farrukhabad (ND-

Table 2. Comparison of OCPs residues (ngL^{-1}) in groundwater of different parts of India.

Area	Unnao	Kolleru Lake Area	North and NE India	Farrukhabad	Agra
Aldrin	BDL -1355.2	–	ND-40	ND-876	15-104
Dieldrin	BDL -6.4	BDL-17.8		ND-88	91-471
α-HCH	BDL -909.6	2.1-48.2	0.3-29	ND-486	–
β-HCH	BDL -744.4	–	ND-55	ND-261	–
γ-HCH	BDL -743.1	3.8-34.5	ND-54	ND-859	–
δ-HCH	BDL -2813.8	–	–	–	–
α-Endosulfan	BDL -81.6	–	–	ND-127	–
β-Endosulfan	BDL -29.6	–	–	ND-105	–
Endosulfan Sulfate	BDL -33.7	–	–	ND	–
op-DDT	BDL -58.5	–	ND-30.5	ND-540	–
pp-DDT	BDL -13.6	BDL-67.3	ND-700.8	ND-1070	–
pp-DDE	BDL - 73.9	–	ND-54	ND-82	–
pp-DDD	BDL -240.2	–	ND-234	ND	–
Heptachlor	BDL -291.3	–	–	ND-129	ND-112
Reference	Present Study	Rao and Rao (1999)	Kumar et al (1995)	Mohapatra et al (1995)	Singh (2001)

BDL= Below Detection Limit, ND= Not Detected

129 ngL^{-1}) and Agra (ND-112 ngL^{-1}), respectively as compared to the levels (BDL-291.3 ngL^{-1}) in Unnao district under the current study. Among the HCH isomers β- and δ-HCH were detected most frequently. The observed trend is contrary to the findings of Mohapatra et al (1995), who have reported predominance of α-, γ- and β-isomer in the ground water of Farrukhabad (Gangetic plain). In our case, both the high frequency of detection and residue levels of β-isomer, which is more persistent as compared to other isomers, suggest for earlier usage of the pesticide. Moreover, high levels of δ-isomer may be attributed to its relatively higher aqueous solubility then other isomers. pp-DDE was predominant among the isomers/metabolites of DDT, followed by op-DDT, both in the dugwells and borewells. Residues of isomers/metabolites of HCH and DDT are, generally, lower than the other reports (Table 2). Due to high bio-accumulation/bio-concentration potential lower levels of DDT are of great concern, further, it is notable that there have been found residues of these pesticides in vegetables grown in the dry-bed of the river Ganga in Kanpur (Hans et al 1999). Total OCPs residues were found higher in the dugwell water (mean value 285.7 ngL^{-1}) as compared to the borewell waters (191.2 ngL^{-1}). This may be attributed to the shallow depth of the dugwells with open tops. Due to long range transport potential of OCPs dugwell water is more prone to contamination than the borewell water. It was also observed that residues of POPs pesticides viz. aldrin, chlordane, DDT, dieldrin, endrin, heptachlor and HCB, except aldrin and DDT, are higher in the deeper aquifers (borewells) than shallow aquifers (dugwells). This indicates the declined use of these pesticides in the region due to ban and migration of persistent metabolites to the deeper aquifers through the sub-

soil mass. Further, there was observed significant inverse correlation ($r=-0.56$, $p<0.05$) between log K_{oc} values and detection frequencies of pesticides in the dugwells, however, in case of borewells, the correlation was non-significant. As the dugwells being shallow, retain water from the upper aquifers and the borewells draw water from the deeper aquifers, thus, high detection frequency of pesticide residues in the samples collected from the borewells may be due to the movement of pesticide residues from the upper aquifers to the deeper aquifers. Further, we presume that the infiltration of Ganga River water is also an important source of pesticide pollution of ground water in this region, as the water table is rather shallow and is dependent on the level of Ganga river water already burdened with pesticide residues (Agnihotri et al 1994). During each cropping season large amount of pesticides is used. While water evaporates, non-degradable residues remain on the surface. With rains, they get incorporated into the subsoil and eventually infiltrate into the groundwater. Although most OCPs have low water solubility, they leach to the lower soil profiles under the influence of water moving downward (Mohapatra et al 1995).

The present study suggests that the residues of the OCPs, which constitute the POP-pesticides group and are now banned for last several years for manufacture and use in the country, are still present in the groundwater in this region. Their presence along with residues of pesticide still used poses health risk to the local population using these water resources.

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