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Status of organochlorine pesticides in Ganga river basin: anthropogenic or glacial?

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1

Abstract

This study reports the occurrences of organochlorine pesticides (OCPs) in Ganga river basin covering 3 states, i.e. Uttarakhand, Uttar Pradesh and Bihar covering 72 % of total river stretch consisting of 82 sampling points covered through 3 sampling campaigns. Samples were monitored for 16 major OCPs, including HCHs, Endosulfan group, Aldrin group, DDTs and Heptachlor group pesticides.

The results showed the ng l^{-1} levels contamination of OCPs in all the stretches sampled during these campaigns. The results also revealed that different type of OCPs were dominating in different stretches in accordance to the land use practices and agricultural runoff generated from those stretches. HCHs were most frequently detected (detection rate = 75 %) in mountainous stretch; Endosulfans were prominent in UP (detection rate = 75 %) stretch while BR stretch Aldrin group pesticides were paramount (detection rate = 34 %). Source apportionment of the OCP's revealed that in the upper reaches of the Ganges i.e. in the state of Uttarakhand, the glacial melt may be responsible for the presence of OCP's. In the lower reaches, intensive agriculture and industrial activities may be significantly contributing these pesticides. The sample from tributaries of Ganga river were found to contain higher number of pesticides as well as higher concentrations. The maximum total pesticide in an individual sample from these sampling campaigns was found in Son river sample ($0.17 \mu\text{g l}^{-1}$, Location: Koilwar, Bhojpur, Bihar).

1 Introduction

River basin management plans in India have traditionally considered the point sources of water pollution. The non-point sources of pollution have largely missed out. Non-point pollution source is of greater importance than point source pollution particularly in rural catchments, where agricultural run-off is the major pollution contributor, which brings nutrients and pesticides to the rivers (Duda, 1993; Jain, 2002). Similar

2

conditions of agricultural practices and run-off, exists in Ganga basin and thus non point source of pollution to the rivers are of serious concern as mostly pesticides enter river systems via diffuse sources (Holvoet et al., 2007). Trends of high levels of pesticide residues in agricultural runoff leading to river contamination have been reported from different part of the world (Schulz, 2001a, b; Varsa, 2011; Oliver et al., 2011). In the Ganga river basin, where agriculture predominates the land use activities, pesticides used in agriculture could easily find their way into the river via runoff. Organochlorine pesticides (OCPs) have been extensively used in India for agricultural and public health purposes. OCPs in different environmental matrices are a matter of concern as the complete environmental fate of these chemicals is still an unexplored field.

The Indo-Gangetic alluvium plain, due to fertile soils, is the region of high agriculture and industrial activities with high population density, where pesticides may enter the water environment through runoff. As the OCPs are persistent in nature and could easily find their way in runoff after several years of their application (Kreuger, 1998). So, even after the recent ban on the use of these pesticides, monitoring of their residues in the river is required to assess the impact on human health and related ecological risks. The reported OCP levels in river Ganga are either for specific tributaries or for a stretch of the river. There is no single study available which reports the levels of these contaminants across the Ganga basin. ~~The glacial melt could be another source of pesticide contamination in the Ganga basin as glacial melt contributes the major share of Ganga and its tributaries.~~ Source apportionment of OCPs in Ganga river is of high importance. It is yet to be established whether glacial sources or anthropogenic activities contribute pesticides to various rivers in the Ganga river basin. Rivers in the the Ganga basin are the main source of freshwater for half the population of India and Bangladesh. Thus, an understanding of the fate of OCPs in Ganga basin rivers, and identification of their source of origin is warranted. Present study reports the status of OCPs in the Ganga river and its major tributaries passing through three different states in India. The study area covers 1805 km long stretch of river Ganges, covering 72% of its entire length. Sampling campaigns were carried in three states, i.e. Uttarakhand

3

(UK), Uttar Pradesh (UP) and Bihar (BR) which represent major part of the Ganga basin.

2 Materials and methods

2.1 Study area

The Ganga rises at 7010 m in Gangotri, Uttarakhand, India, on the Southern slopes of the Himalayan range. It flows through four different States, Uttarakhand (UK), Uttar Pradesh (UP), Bihar (BR) and West Bengal (WB) covering a distance of 2525 km before it enters the Bay of Bengal. Ganga river and its major tributaries at Uttarakhand (UK), Uttar Pradesh (UP) and Bihar (BR) states represent the study area. The river Ganga was sub-divided into three stretches representing different watershed conditions as the UK, UP and BR stretch. The stretches were divided considering (1) different types of watershed, land-use activities, flow types and (2) state boundaries since states are responsible for managing the discharges to the river. The division of river stretches on the basis of states will help in understanding the health of river in that particular state and their environmental awareness. Details on the sampling campaigns undertaken are presented in Table 1. Water samples were picked from 82 different points during these sampling campaigns from 3 different stretches/regions. The locations of the sampling points are shown in Fig. 1, while Fig. 2 showed the sampling points and flow chart of the rivers covered during each sampling campaign. The UK stretch was the smallest stretch, while UP stretch was the longest stretch of the sampling.

2.1.1 UK stretch

The state of Uttarakhand (UK) has three districts which fall in the main-stream of Ganga: Haridwar, Tehri Garhwal and Uttarkashi. Sampling campaigns of this stretch were carried out in December 2010. Sampling was started from upstream

4

of Rudraprayag at Alaknanda and Mandakini rivers, and it went up to downstream of Haridwar (Table 1). This area is the hilly-mountainous zone of the river Ganga with a high bed slope (1:67) and mean flow rate of $856 \text{ m}^3 \text{ s}^{-1}$ (Fig. 2). Domestic sewage is the major source of pollution since there are no other major agricultural or industrial activities in this stretch.

2.1.2 UP stretch

It is the mid-stretch of the river and forms a part of Great Plains of Ganga basin. It constitutes 17 districts of Uttar Pradesh (UP). Sampling campaign was carried out in July 2011. Sampling started from upstream of Bijnor and went ~~downstream~~ up to Ballia, separating a distance of 1131 km (Fig. 2). Samples from Ramganga, Ghaghra, Yamuna, Gomti, Rapti and Aami; the major tributaries of Ganga, were also taken, to quantify the pesticides contamination contributed by the tributaries to river Ganges. Total 36 samples were taken from this stretch (Table 1). Rivers, in this stretch, receive pollution from highly diversified sources, including domestic, industrial and agricultural sources. Downstream to Haridwar, where the Ganga opens to the Gangetic Plains, major share of water is diverted by various barrages for irrigation and other purposes. The Ganga does not receive any major tributary until its tributary, Ramganga river joins at Kannauj, which is 460 km downstream from Haridwar (Fig. 2). River has relatively less flow upto Allahabad, where Yamuna confluences the river Ganges. Downstream to Allahabad, river is joined by Tons and Gomti (Fig. 2). The subsequent upper plain section extends from Rishikesh to Allahabad at a slope of one in 4100 and a mean flow rate range between $850\text{--}1720 \text{ m}^3 \text{ s}^{-1}$ before its confluence with the Yamuna.

2.1.3 BR stretch

There are 12 districts which fall within the Ganga basin in Bihar (BR) where, agriculture and commercial fisheries in river are the two most important source of livelihood for people. The river Ganga receives several major tributaries in this section, namely,

5

Ghaghara, Son, Gandak, and Kosi. The flow in this stretch continually increases since major tributaries to Ganga river join in this stretch. The average annual flow increased to $7626 \text{ m}^3 \text{ s}^{-1}$ at Patna (Fig. 2) from $4126 \text{ m}^3 \text{ s}^{-1}$ at downstream of Allahabad. The sampling campaign was carried up to Kohalgaon, just few km before joining Kosi. The sampling campaign covered 341 km stretch (Fig. 2) of the river Ganges, from Chhapra to Kohalgaon, via Patna, Munger and Bhagalpur (Table 1). The samples were also collected from Son and Gandak River, the major tributaries of Ganga in this stretch. This river stretch receives pollution from domestic, agricultural as well as industrial sectors. Raw sewage flows into the river in this stretch since sewage is not treated in Bihar due to various reasons as reported (CPCB report, 2009) (<http://www.cpcb.nic.in/newitems/8.pdf>).

2.2 Water sampling, collection and storage

During these sampling campaigns, which carried out between December 2010 and August 2011, a total of 82 water samples were collected from different sites (Figs. 1 and 2). Two samples were taken from each site during each sampling campaign. One sample was collected in a 1000 ml HDPE bottles, was used to determine physico-chemical parameters and OCP analysis, while the second sample was taken in 100 ml HDPE bottle and preserved with acid. This acidified sample was used for TOC, NO_3^- -N and NH_4^+ -N analysis. Sampling bottles were rinsed with river water and were carefully filled to overflowing, without trapping air bubbles in sealed bottles. The samples were transported in cool-box with ice packs and subsequently stored in a refrigerator at 4°C until further analysis. All the samples were transported on ice and kept under refrigeration until performance of laboratory analysis.

2.3 Reagents and standards

Analytical grade (AR) chemicals (Merck, Germany) were used throughout the study without any further purification. Reagents and calibration standards for

6

physico-chemical analysis were prepared using double glass distilled water. The glass-ware 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 . The samples were analysed within one week of sampling campaigns.

2.4 Physico-chemical parameters

Samples were analysed for different physico-chemical parameters: pH, electrical conductivity (EC), alkalinity, chloride, hardness, dissolved oxygen (DO), total organic carbon (TOC), nitrate, and ammonia as per APHA (1998). EC, pH, DO and TDS were measured onsite using a portable meters. Alkalinity, chloride and hardness were measured by titration method in the laboratory. Nitrate and ammonia was measured by selective ion electrode (Thermo and HACH, respectively), while TOC was analysed on TOC analyser (Shimadzu).

2.5 Extraction

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. Samples were prefiltered using $0.45\ \mu\text{m}$ glass fiber filter to remove suspended impurity and were extracted without any pH adjustment. Sample containers were shaken and each 500 ml portion of filtered sample was transferred to a separating funnel (1000 ml cap.) fitted with glass-stopper. It was mixed with 30 g of NaCl and 50 ml of *n*-hexane. Sample was shaken properly for 30 min and hexane layer was separated. Two further extractions with 30 ml *n*-hexane were done and the combined hexane extract was treated with 5 g anhydrous Na_2SO_4 to remove traces of water. The water-free extract was rotary vacuum evaporated to a small volume and transferred to a glass-stoppered test tube

7

followed by evaporation of solvent under a mild stream of N_2 to 0.5 ml. The concentrated extracts were transferred to air-tight GC vials and stored at -20°C until their analysis.

2.6 OCPs analysis

The determination of OCPs was performed on a Thermo Trace GC Ultra gas chromatograph equipped with 63-Ni micro-electron capture detector (GC-ECD) and an auto-sampler. The column specifications and operating conditions are given in Table 2. Analysis was performed by EPA method 508, with slight modification. Identification of individual OCPs was based on comparison of retention time between samples and the standard solution by double column chromatography under similar conditions. DB-5 ($30\ \text{m} \times 0.25\ \text{mm i.d.}$, and $0.25\ \mu\text{m}$ film thickness) and DB-1701 ($30\ \text{m} \times 0.25\ \text{mm i.d.}$, and $0.25\ \mu\text{m}$ film thickness) columns were used in the analysis. Tentative identification of the pesticides were made on the basis of retention time obtained using DB-5. These were subsequently confirmed with second capillary column, DB-1701, having dissimilar liquid phase with different retention properties. The injection volume, column conditions, temperature programming, injector and detector temperature were kept the same for GC-ECD in both analysis. Helium was used as carrier gas at a constant flow of $1.2\ \text{ml min}^{-1}$ and high purity nitrogen was used as make-up gas ($40\ \text{ml min}^{-1}$). Samples were injected using Thermo AS 3000 auto-sampler. Injection volume was $2.5\ \mu\text{l}$ in splitless mode for each sample (Table 2). The instrument was operated by Xcaliur software (Thermo Finnigan). Quality of extraction and detection procedure was ensured by spiking 5 different concentrations of each OCP standards with distilled water, and extracting by the same method. Recovery was determined. Table 3 presents recovery efficiency (RE), retention time (RT) and pattern of compounds eluting on both the columns. The DB-5 column was used for quantification, while DB-1 was used for compound cross confirmation by retention pattern. The important physico-chemical properties of investigated OCPs are expressed elsewhere (Mutiya et al., 2011).

8

3 Result and discussion

3.1 Physico-chemical parameters (general water quality parameters)

Both, the quantity and quality of water get affected as the water from the river is either being diverted for various beneficial uses (canals for irrigation, industrial and drinking purposes) or by the sewage from the cities and agricultural run-off from other areas flowing into the river. The water quality of all the three stretches covered during different sampling campaign is shown in Table 4. Water quality in mountainous stretch (UK stretch) is very good, with high DO levels (DO_{avg} ($mg\ l^{-1}$) = 7.7 ± 0.6), very low EC, TDS and TOC, indicating no significant pollution load in this stretch. The lower organic loading from the small cities of UK and high flow in the river keeps the stretch relatively clean. In this stretch, the major class 1 cities on Ganges are Rishikesh and Haridwar, where 3 STPs are in operation. The STPs remove 61–93 % organic matter present in the sewage (CPCB report, 2009). Domestic sewage is major contributor of pollution in this stretch, which is more significant towards the end of this stretch where the last sampling point is situated, i.e. Haridwar and Rishikesh. Kumar et al. (2010), reported that water quality of UK river stretch is of category A as per CPCB river classification, except for the stretch downstream of Haridwar, the last sampling point of the campaign 1. Results revealed similar situation in this study (Table 4). The UP stretch is the longest stretch of the sampling campaign, including many rivers and the sub-basins of Ramganga, Ghaghra and Gomti river. The total discharge of wastewater from this zone to Ganga Basin is second maximum after Delhi. The water quality in the stretch is affected by domestic and industrial discharges, and agricultural runoff. The DO levels in all the samples were in the range of 1–6.5 $mg\ l^{-1}$ (DO_{avg} ($mg\ l^{-1}$) = 6.5 ± 1.4), however this zone has some of the worst polluted stretches, including Kanpur and Allahabad regions. But due to high monsoonal flow, the river water quality appeared good from the water quality data obtained in this sampling campaign (Table 4). The minimum DO ($1\ mg\ l^{-1}$) was reported from Varuna river, a small tributary of Ganga, at Banaras where this river has very less flow even in monsoon season. The recent report on

9

trends on water quality in Ganga Basin (CPCB, 2009) showed that river water quality of this stretch is fine except maximum BOD_5 levels, in Kannauj – Gazipur segment. In Bihar, no sewage treatment plant was found during the sampling campaigns. The total installed sewage treatment capacity is 84 mld against total discharge of 671 mld in Ganga basin, and none of the STPs is functional in Bihar (CPCB report, 2009). Though, the sewage management in Bihar is very poor, but the water quality continually improved. It may be attributed to the dilution provided by the high flow from the major tributaries in this stretch. The DO levels were high (DO_{avg} ($mg\ l^{-1}$) = 6.9 ± 1.4) and Gangatic dolphins were seen during the sampling at various places, from Patna to Bhagalpur. The water quality was good and the report on trends in water quality in Ganga Basin (CPCB, 2009) supports the data as water quality in Bihar segment was well within permissible limits except for fecal coliforms (FC).

3.2 Organochlorine pesticides

Various types of pesticides are widely used in agricultural sector all over the Ganga basin and have been frequently reported in the water matrices from basin (Rehana et al., 1995; Nayak et al., 1995; Sankararamkrishnan et al., 2005; Semwal and Akolkar, 2006; Malik et al., 2009; Singh et al., 2011). Beside the runoff from agricultural fields, the agriculture practices in the dry bed of the rivers, which are common in India (Hans et al., 1999) also, add pesticides to the river during monsoon. The OCPs levels in UK stretch are shown in Fig. 3. In this stretch concentration of all the targeted OCPs varies from ND to $7.07\ ng\ l^{-1}$. Water sample from Rishikesh showed the maximum number of OCPs, i.e. 14 out of targeted 16, while Ganga main river at Haridwar showed presence of least number, only 2 out of 16 were present. The occurrence frequency for the OCPs in this stretch varied from 0 to 100 %, as heptachlor and DDT were not detected in any of the samples (detection rate, 0 %), while β -HCH and γ -HCH were found in all the samples (detection rate, 100 %). The endosulfan sulfate and endrin were detected in one sample (detection rate, 13 %) while aldrin, endrin, dieldrin, heptapoxide, α -Endo, β -Endo, DDE and DDD showed 75 % occurrence. The Σ HCH group

was more predominant in this stretch, accounting 75 % of relative abundance (Fig. 4). The low ratios of α HCH/ γ HCH (0.15) indicate that lindane may be an important source of HCHs in this stretch as technical HCH sources have high α HCH/ γ HCH (Ridal et al., 1996). The lindane has been used extensively in the Indo-Gangtic plains for agriculture. Wang et al. (2008), reported that the OCPs used in Indo-Gangtic plains could reach the snow of Mount Everest via global circulation and cool deposition. Similar trends of deposition of OCPs in glacier via cold trap have also been reported by Valsechhi et al. (1999) and Kang et al. (2002). Blais et al. (2001) explained that melting glaciers supply up to 97 % of OCPs input while contributes 73 % of input water. In UK zone, the major share comes from melting ice from glaciers, thus high share of HCHs in glacial stream is expected. Σ Endo group's relative abundance was 10 % of the total, but high occurring frequency (54 %) in the total samples, indicate that this pesticide has limited use for agricultural purposes. Very limited farming is done in this part of the Ganga basin, so trace levels of endosulfan residues could find their way into the river water from agricultural application via run-off. The heptachlor group formed 2 % of the total abundance, with no heptachlor being detected in any of the sample. Only heptachlor epoxide was detected in the samples suggested that this pesticide has been used in past in the basin.

The occurrence of OCPs in UP stretch is shown in Fig. 5. The trend of detection rate of OCPs was different in UP stretch as the detection rate varies from 6–94 % (Fig. 6). All the samples were found to contain one or more pesticides. The minimum number OCPs detected in any sample were 3, while maximum of 14 OCPs were present in one of the sample. The β -Endo OCP was frequently detected in many of the samples in relatively high concentration as the maximum concentration of β -Endo was 133.10 ng l^{-1} (Fig. 5). Σ Endo group pesticides contributed maximum (75 %), while aldrin, DDT and HCH group contributed 11, 9 and 5 %, respectively (Fig. 6). The use of endosulfan is now banned in more than 60 countries but India has been the world's largest producer and consumer of endosulfan with a total use of 113 000 tonnes from 1958 to 2000 (NGBRA, 2011). Recently, the supreme court of India has put a temporary ban

on agricultural use of pesticides (Writ petition 213, 2011), but the impacts of this ban could only be noticed after a number of decades. The high concentration of Endo group pesticides is in conformity with its wide use in this area. The endosulfan was most widely used pesticide in Indo-Gangtic plains for agricultural purposes. Most studies suggest that α -endosulfan has a faster degradation than β -endosulfan, and that endosulfan sulfate is much more persistent (INIA, 1999–2004). Similar trends were observed for Endo group pesticides in UP stretch. β -endosulfan and endosulfan sulfate were more frequently detected in the water samples as compared to α -endosulfan. Endosulfan sulfate is the most persistent, but its reported concentrations are lower than its other isomers. It may be due to its lower share (<1 %) in technical endosulfan. As pesticides are used more sporadically, there are different reports on their occurrences in rive Ganga. Higher levels of endosulfan (750 ng l^{-1}) have been previously reported in the Ganges river at Kannauj (Rehana et al., 1996) to the present level of 31.61 ng l^{-1} but no other study has reported residues of endosulfan in Ganges at Kanpur (Sankararamkrishnan et al., 2005).

The occurrences of OCPs in Bihar stretch is shown in Fig. 7. The levels for OCPs varied from ND to 38.80 ng l^{-1} for aldrin in Son river, a major tributary of the river Ganga in Bihar. δ -HCH was not detected in any of the samples, while α -HCH was present in all the samples (Fig. 7). Frequency of appearance of the OCPs was for samples from tributaries of Ganga, than the parent river (Fig. 7). Samples from storm water drain near Ara which carried agricultural runoff was contain 15 out of 16 targeted compounds. Sultanganj and downstream to Bhagalpur city area are located in the most downward stretch of the studied stretches. These stretches were found to contain 15 OCPs. Besides, the average concentration of monitored OCPs continually increased from UK to BR stretch (upstream to downstream) (Fig. 1). It may be due to continual increase of contribution from the agriculture in the downstream stretches. In BR stretch, the occurrence patterns of OCPs were different from UK and UP stretch. In UK stretch, HCHs group was more frequently detected, while in UP stretch the same was observed for Endo groups. High glacial water in UK stretch may be possible reason for this,

since the glacial water streams reportedly have higher concentrations (1 log) of HCHs as compared to endosulfan and dieldrin pesticides in Bow lake in Canada (Blais et al., 2001) and Himalayan glaciers (Kang et al., 2009). Bizzotto et al. (2009) compared the HCHs concentration in glacial and non-glacial streams from Alpine glaciers and found that glacial streams were always having high concentration (200–400%) than non-glacial streams. Thus high frequencies of HCHs in mountainous zone of Ganga were on the expected lines. The UP stretch was predominant with the Endosulfan group pesticides in connection to high previous use of this group of pesticides in the Indo-Gangtic plains for agriculture use (NGBRA, 2011). In Bihar stretch, none of these groups were dominant in occurrences. The maximum detection frequency was for aldrin group (34%), followed by HCHs (21%), Endo group (20%), heptachlor group (13%) and DDTs group (12%) (Fig. 8). It showed the mixed flow of glacial, domestic, agricultural and industrial discharge to the river. The high concentration of heptachlor group in this stretch could be because of high previous use of this pesticide in parts of Bihar and Western Bengal for termite control. As this stretch of the river receive flow from different river basins, having different agricultural practices and different pesticide uses. So the mixture of all OCPs was expected (Fig. 8). Table 5 presents the relative contamination levels of OCPs in 2011 along with the values reported in the literature. It shows lower levels of OCPs in the Ganga water.

4 Conclusions

OCPs, 16 in number were monitored from 82 sampling sites in the Ganga river basin. These included mountainous and the great plains of the Ganga basin. The results revealed that different types of OCPs predominate in different regions depending upon land use pattern and differential past use of the OCPs for agricultural and public health programme. Since, there is not even a single report on the levels of OCPs representing the entire Ganga stretch; the present findings could be effectively used in understanding the present status of the river. The comparative analysis of present study to the

13

previous reports, showed the decline trend in OCPs contamination in the river water, which is a good sign at environmental and ecological front. The ban on the use of various OCPs has shown a positive sign for river health, but as these compounds are highly lipophilic, thus it becomes quite necessary to monitor these compounds continuously in the river stretch. There is a wide gap in the time line of the continuous reporting of OCPs levels and thus, it is recommend to frequently monitor the river quality for OCPs contamination with changing land-use pattern, pesticide formulation, climatic conditions and ecological and environmental sense of the society. Decreasing trends in the OCPs contamination levels in Ganges water was also confirmed. The banned or restricted use of OCPs and increasing environmental awareness regarding pesticide application in farmers may be the possible contributor for this declining trend. The maximum total pesticide concentration in individual sample ($0.17 \mu\text{g l}^{-1}$, Son river sample from Koilwar) was less than $0.2 \mu\text{g l}^{-1}$ for all the samples against a safe drinking water limit of $0.5 \mu\text{g l}^{-1}$ by European Union (EU) and $1 \mu\text{g l}^{-1}$ of Bureau of Indian Standards (BIS). The low (ng l^{-1}) concentration in river indicates the wise use of pesticide in the area but the higher detection rate of endosulfan group pesticide in the UP stretch which receive agricultural runoff from Indo-Gangtic plains is of significant concern. The recent temporary ban on use of endosulfan for agricultural use by Supreme Court of India (Writ petition 213, 2011), is a precautionary and appreciable step towards conserving the water resources from the further POP contamination.

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Table 1. Various river stretches and the major rivers covered during the sampling campaigns.

Stretches	Uttarakhand (UK)	Uttar Pradesh (UP)	Bihar (BR)
Sampling months	Dec–Jan 2011	Jun–Jul 2011	Jul–Aug 2011
Distance (km)	193	1131	341
1st Sampling Point	Rudraprayag	Bijnor	Chhapra
Last Sampling Point	Haridwar	Ballia	Kohalgaon
No of sampling points	20	36	26
Major rivers covered during sampling campaign	Mandakini, Alaknanda, Bhagirathi, Ganga	Ramganga, Ghaghra, Yamuna, Varuna, Gomti, Rapti, Aami, Ganga	Son, Gandak, Ganga

Table 2. Operating conditions used for the operation of GC-ECD (Double column confirmation.

GC-ECD		
Column	DB-5, fused silica capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm)	DB-1701, fused silica capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm)
Purpose	Screening and Quantification	Cross confirmation by Retention Pattern
Injector Temperature	250 °C	
Injection Volume	2.5 μl (Splitless mode)	
Oven Programming	90 to 150 °C @ 15 °C min ⁻¹ , 150 to 220 °C @ 3 °C min ⁻¹ and 220 to 270 °C @ 5 °C min ⁻¹	
Detector Temperature	280 °C	
Carrier gas	Helium @ 1.2 ml min ⁻¹	
Makeup gas	Nitrogen @ 40 ml min ⁻¹	

Table 3. Standardisation of OCP's compounds using GC-ECD.

Compound	RT (min) (DB-5)	Recovery (%)	R^2 (ng l ⁻¹)	MQL (DB-1701)	Retention Pattern
α -HCH (H1)	12.00	71.28	0.999	0.01	α -HCH (H1)
β -HCH (H2)	13.42	79.42	0.998	0.01	γ -HCH (H3)
γ -HCH (H3)	14.76	70.99	0.999	0.01	Heptachlor (He1)
δ -HCH (H4)	15.02	78.56	0.999	0.01	Aldrin (A1)
Heptachlor (He1)	16.70	87.53	0.996	0.01	β -HCH (H2)
Aldrin (A1)	18.41	146.78	0.999	0.01	δ -HCH (H4)
Hepta-Epoxyde (He2)	20.56	59.55	0.999	0.01	Hepta-Epoxyde (He2)
α -Endo (E1)	22.45	107.97	0.999	0.01	α -Endo (E1)
4,4'-DDE (D1)	23.87	123.87	0.999	0.01	4,4'-DDE (D1)
Dieldrin (A2)	24.09	86.16	0.999	0.01	Dieldrin (A2)
Endrin (A3)	25.01	87.70	0.998	0.01	Endrin (A3)
β -Endo (E2)	25.75	90.85	0.998	0.01	4,4'-DDD (D2)
4,4'-DDD (D2)	26.40	87.47	0.997	0.01	β -Endo (E2)
Endrin-aldehyde (A4)	28.05	133.12	0.995	0.01	4,4'-DDT (D3)
Endo-Sulfate (E3)	28.44	85.80	0.995	0.01	Endrin-aldehyde (A4)
4,4'-DDT (D3)	31.53	99.22	0.990	0.01	Endo-Sulfate (E3)

MQL = methods quantification limit

Table 4. River Water Quality of Ganga Basin covered during sampling campaigns (December 2010–August 2011).

	UK			UP			Bihar		
	Range	Avg	SD	Range	Avg	SD	Range	Avg	SD
pH	7.7–8.1	7.9	0.1	7.2–8.6	7.9	0.4	7.1–8.8	8.4	0.4
EC ($\mu\text{S cm}^{-1}$)	19.5–42.9	32.2	7.4	118.8–381.0	214.2	75.5	186.7–452	345	74
TOC (mg l^{-1})	0.050–0.664	0.261	0.274	0.1–4.6	2.5	1.1	0.1–18.6	2.3	3.5
Nitrate (mg l^{-1})	NM			0.7–2.8	1.8	0.6	1.5–5.1	2.9	0.9
Ammonia (mg l^{-1})	NM			0.5–7.9	3.4	1.9	0–0.5	0.1	0.1
Chloride (mg l^{-1})	20–40	29.5	6.9	13.0–32.1	23.3	4.8	29–149	49.4	24
Hardness (mg l^{-1})	NM			65.2–143.2	98.9	18.6	100–603	190.3	95.5
Alkalinity (mg l^{-1})	50–110	83.5	15.7	71.2–164.4	109.4	21.4	102–401	178.4	89.6
TDS (mg l^{-1})	12.5–27.5	20.6	4.7	114.8–286	175.9	40.6	119.5–289.3	220	47.4
DO (mg l^{-1})	6.7–9.2	7.7	0.6	1–6.5	5.6	1.4	4.0–9.4	6.9	1.4

NM = not measured

Table 5. Comparison of reported OCPs levels in rivers of Ganga Basin to the present study at different locations.

River	Sampling Site	Compound Reported (ng l^{-1})										Reference
		ΣHCH		ΣDDT		ΣEndo		ΣAldrin		ΣHepta		
		Literature Levels*	Present Levels (2011)	Literature Levels*	Present Levels (2011)	Literature Levels*	Present Levels (2011)	Literature Levels*	Present Levels (2011)	Literature Levels*	Present Levels (2011)	
Ganga	Devprayag	ND (2006)	7.24	ND–365 (2006)	ND	ND–66 (2006)	ND	ND–46 (2006)	2.3	NM	0.07	Semwal and Akolkar (2006)
	Rishikesh	6–124 (1992)	5.5	4–98 (1992)	1.01	0.92		1.89		0.32		ITRC annual report (1992)
	Haridwar	4–153 (1992)	5.2	2–113 (1992)	0.19	0.16		0.12		0.06		ITRC annual report (1992)
	Kannauj	3010 (1995), 8–154 (1992)	0.1–1.0	7740 (1995), 3–150 (1992)	0.05–0.12	750 (1995)	0.8–31.6	3340 (1995)	1.2–1.3	NM	0.14–0.2	Rehana et al. (1995) ITRC annual report (1992)
	Kanpur	450 (2005), 14–359 (1992)	0.1–0.36	ND (2005), 8–174 (1992)	0.2	ND (2005)	9.7–11.6	ND (2005)	ND–1.1	NM	ND–0.08	Sankaramakrishnan et al. (2005) ITRC annual report (1992)
	Allahabad	7–270 (1992)	1.23–3.5	2–136 (1992)	0.08–2.21		ND–0.15		ND–0.4		ND	ITRC annual report (1992)
	Varanasi	9–156 (1992), 105–99 517 (1995)	0.2–0.7	3–84 (1992), 64–143 226 (1995)	0.1–1.9	83–66 516 (1995)	ND–85.4	NM	0.5–2.2		ND–0.1	ITRC annual report (1992) Nayak et al. (1995)
	Patna	11–131 (1992)	0.3–5.0	5–385 (1992)	ND		ND–5.03		ND–1.17		ND	ITRC annual report (1992)
	Bhagalpur	ND–74.04 (2011)	12.4–17.6	NM (2011)	11.6–12.3	ND–208 (2011)	13.8–17.9	ND–489 (2011)	8.8–16.4	NM (2011)	3.2–11.8	Singh et al. (2011)
Gomti	Lucknow	ND–507 (2009)	0.72	ND–108 (2009)	2.75	ND–186 (2009)	1.16	ND–82 (2009)	0.6	ND–91 (2009)	ND	Malik et al. (2009)

* Reported values are from the literature cited in the last column of the table, References.

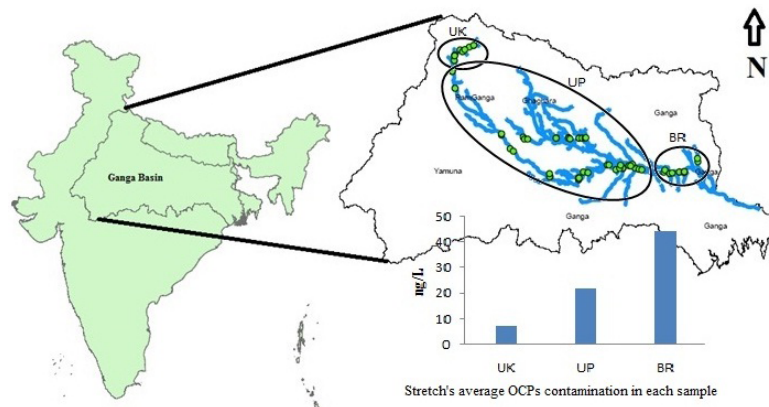


Fig. 1. Sampling location of the river Ganga.

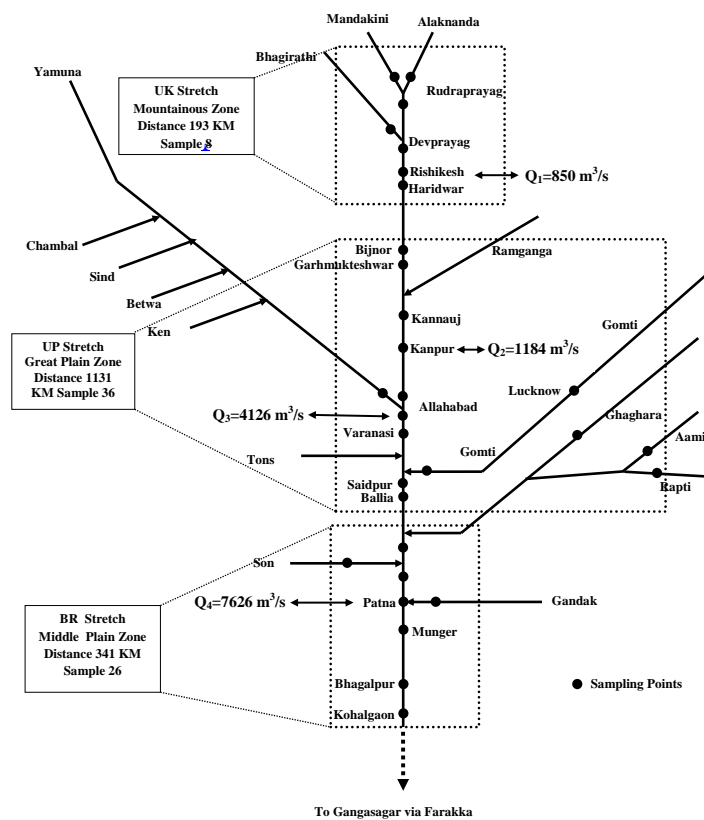


Fig. 2. Sampling locations and space boundary of each sampling campaign along river Ganga (flow data were of CWC, Delhi taken from NGBRA (2011) report as cross reference).

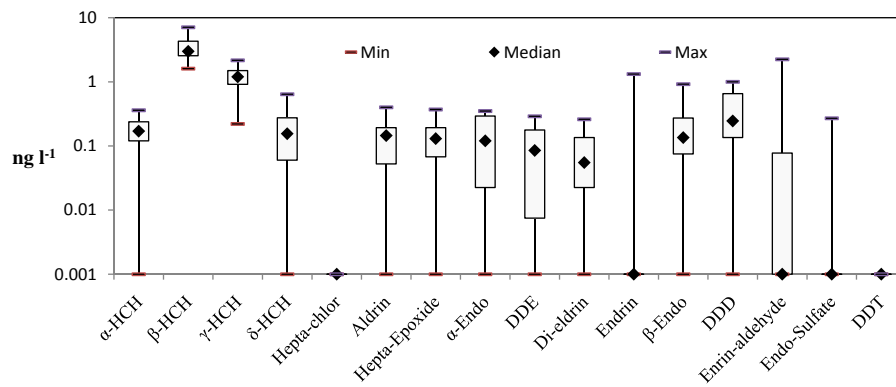


Fig. 3. Organochlorine residues (ng l⁻¹) in river water samples of Uttarakhand (UK) area.

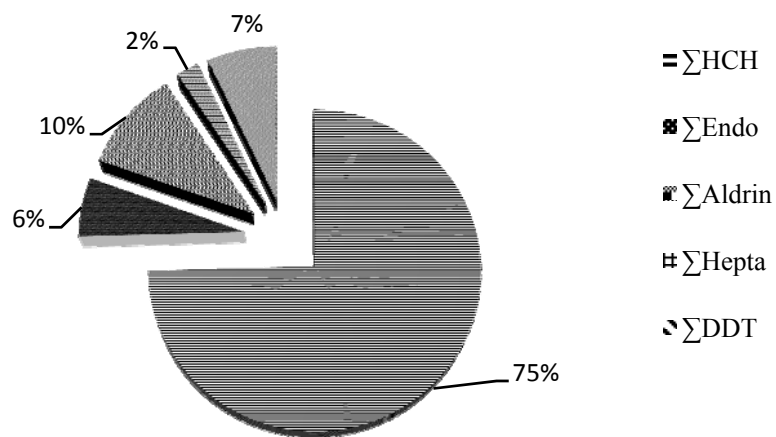


Fig. 4. Detection frequency of individual OCPs across UK stretch of Ganga river.

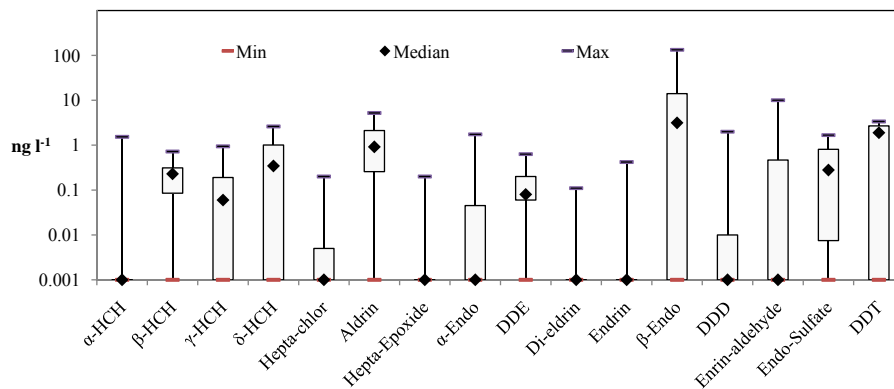


Fig. 5. Organochlorine residues (ng l⁻¹) in water matrices of rivers of Uttar Pradesh (UP).

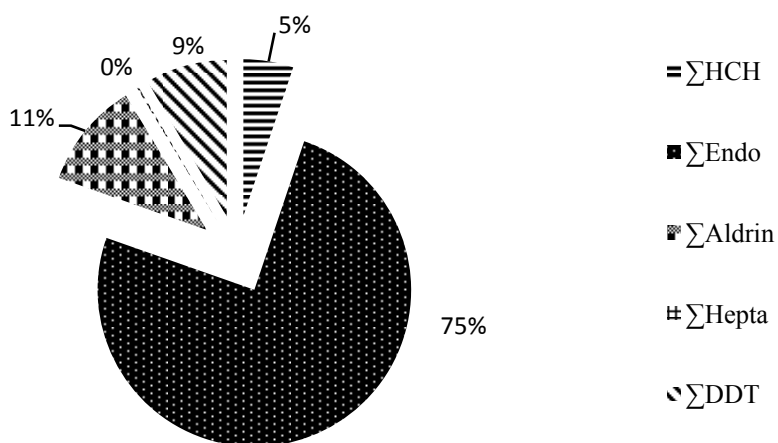


Fig. 6. Detection frequency of individual OCPs across UP stretch of Ganga river.

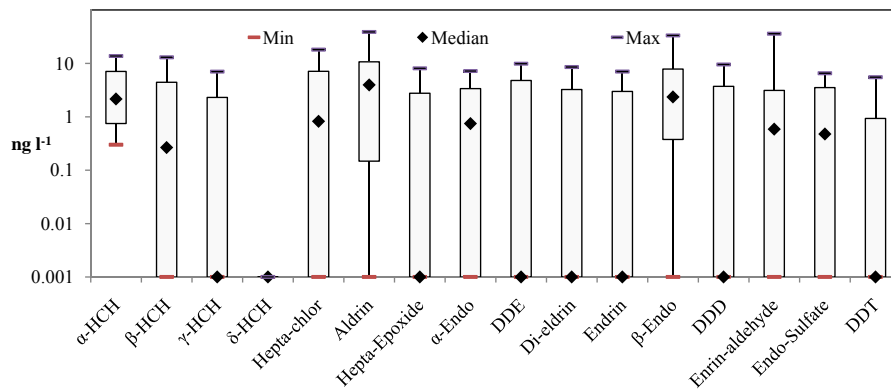


Fig. 7. Organochlorine residues (ng l⁻¹) in water matrices of rivers of Bihar (BR) Area.

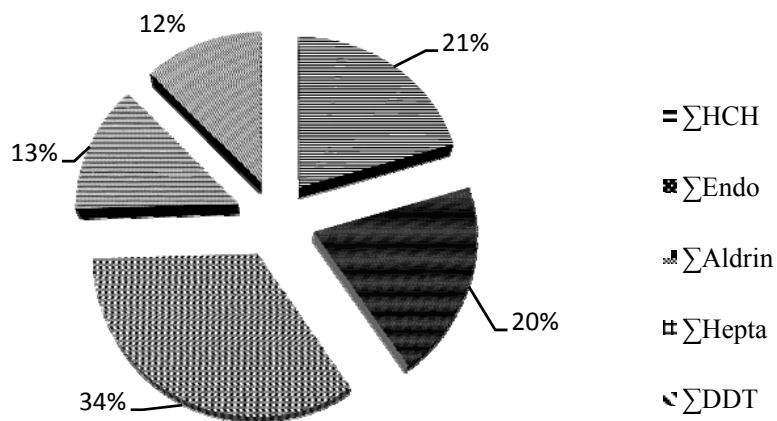


Fig. 8. Detection frequency of individual OCPs across BR stretch of Ganga river.