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Organochlorine Pesticide Residues in Water and Fish Samples: First Report from Rivers and Streams of Kumaon Himalayan Region, India

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The accumulation of organochlorine pesticides like DDT, BHC in the freshwater aquatic ecosystem is well documented. Several of pesticides are being used in India both in agriculture and public health sectors. Although the uses of pesticides have resulted in increased food production and other benefits, it has raised concerns about potential adverse effects on the environment and human health. The greatest potential for unintended adverse effects of pesticides is through contamination of the hydrologic systems, which supports aquatic life and related food chains and is used for drinking water, irrigation, recreation and many more purposes. The persistence of the organochlorines in aquatic ecosystem has special significance as they are picked up by aquatic organisms like plankton and in the process pesticide residues entered in the food chain.

The organochlorine pesticides are lipophilic, extremely toxic and non-biodegradable. It is reported that DDT and endosulfan at concentration of 16 ppb and 1 ppb respectively, are toxic to freshwater fish (Brown 1979). In streams there is also possibility of pesticide contamination through non-point source pollution and agricultural runoff during wet season. The other possibility is deposition of pesticides originating from plains during snow melting and interference of various physico-chemical processes. The recent reports indicate contamination of United States streams from atmospheric deposition and erosion of soils contaminated from past use. The pathways by which the pesticides are transported from the application areas to other parts of the environment with reference to stream are given in Fig1. Incidence of fish kill due to insecticides had occurred in different streams (Young and Nicholson, 1951; Rudd and Genelly, 1956). However, in India report on occurrence and distribution of organochlorine pesticide in stream environment is very rare and no systematic investigation was done on the pesticide residues in the streams and rivers of Kumaun Himalayas. In view to conserve the fish genetic biodiversity of the Kumaun Himalayan region , it is necessary to determine the level of contamination in stream and aquatic biota since these are important in the food web of terrestrial organisms, with some aquatic biota, such as fish, being consumed by people and wildlife. In the present communication a systematic survey was carried out in nine rivers and streams of Kumaun Himalayas and levels of DDT, BHC and endosulfan in water and fish samples were examined.

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MATERIALS AND METHODS

The water samples were collected from nine rivers and streams of Kumaun Himalayan region during November, December 1999.Samples were collected from different segments of rivers and streams (upstream and downstream) and the altitudinal variations were ranged from 300 to 1750 meters. The data on river type (snowfed/rainfed) altitude, latitude and longitude of the sampling sites were recorded using Magellan make Global Positioning System (Table1). Water samples (n=18) were collected from the sides and midstream. The details of the sampling locations and the details of the water quality parameters of the rivers/streams sampled are given in Fig.2 and Table 2, respectively. Fishes (n=10) were collected using cast net and gill net and

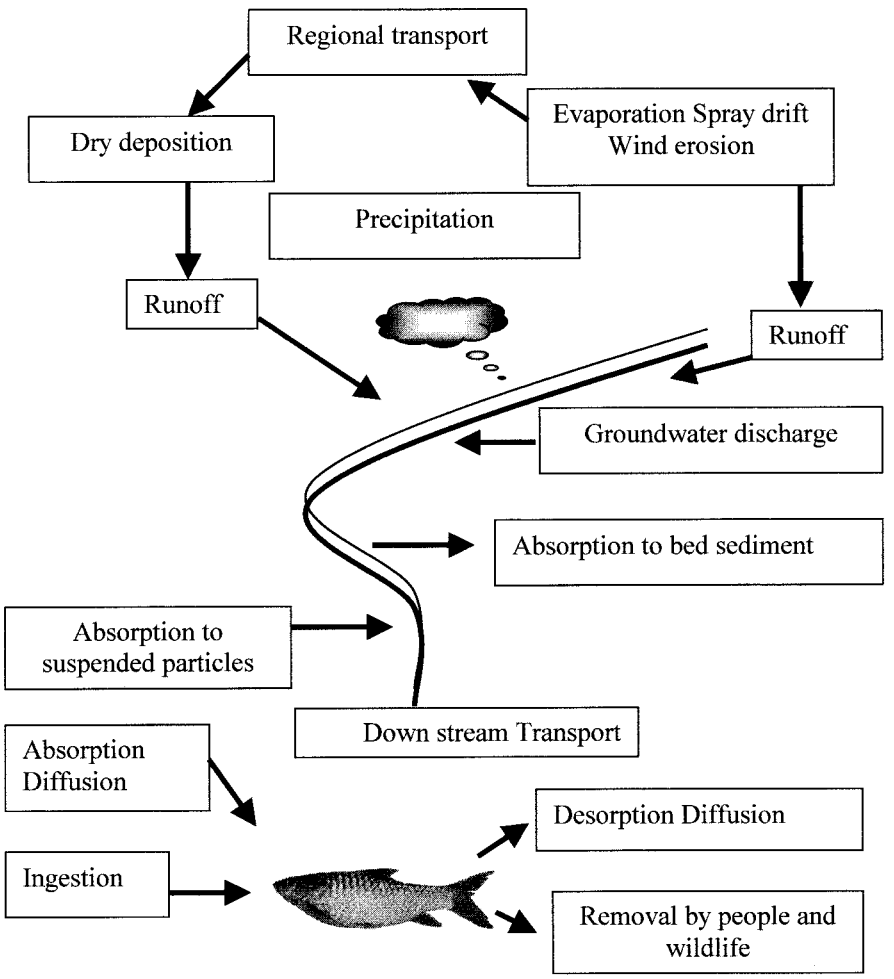

Figure 1. Pathways of Pesticides in streams. (Modified from Majewski and Capel, 1995)

preserved in crushed ice till analysis. The sample processing, extraction, cleanup and gas chromatography was done by the pesticide laboratory of Industrial Toxicology Research Center (ITRC) Lucknow, Uttar Pradesh, India as per standard methods (Singh *et al.* 1987). Physico-chemical parameters of the water were analysed as per standard methods (APHA, 1992).

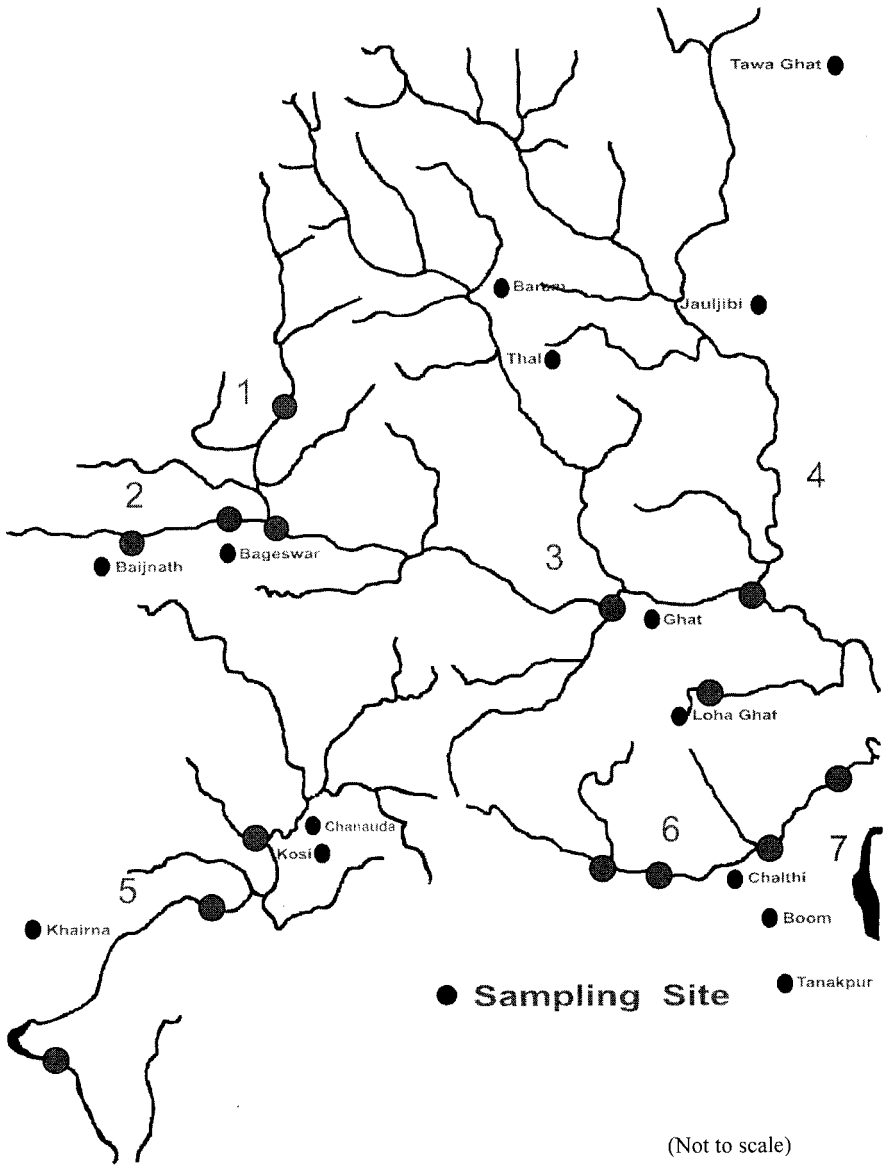

Figure 2. Drainage map of Kumaun Himalayas showing sampling sites
1. Saryu river 2. Gomti seam 3. Saryu stream 4. Sharda river 5. Kosi river 6. Ladhiya stream 7. Sharda river

Table 1. Details of the sampling stations in Kumaon Himalayas.

River / stream	Place of sampling	Altitude (m)	Longitude	Latitude
Snowfed				
Sharda(Kali)	Boom bangla.	300	80.03	29.14
Sharda (Kali)	**Sharda barrage**	300	**80.04**	29.12
Saryu	**Ghat**	**1100**	**80.07**	**29.51**
Saryu	Bageswar	930	79.77	29.83
Ramganga East	Thal	710	80.37	29.82
Dhauli	Tawaghat	920	80.56	29.90
Sharda(Kali)	Tawaghat	920	80.56	29.90
Sharda(Kali)	Jauljibi	720	80.37	29.74
Gori	Baram	735	80.36	29.73
Gori	Jauljibi	720	80.37	29.74
Rainfed				
Gomti	Bageswar	930	79.77	29.83
Gomti	Kameri	980	79.76	29.82
Gomti	Baijnath	1120	79.61	29.90
Ladhiya	Chalthi	605	80.16	29.20
Lohawati	Lohaghat	1750	80.08	29.39
Kosi	Channoda	1215	79.52	29.54
Kosi	Kosi	1315	79.43	29.55
Kosi	Khairna	790	79.52	29.54

Table 2. Mean values of physico-chemical parameters of rivers/streams studied.

Parameters	**Snow fed rivers**	**Rain fed rivers**
Turbidity (mg/l)	3.75±3.06	1.62±0.08
Conductivity (μ mhos/cm)	223.47±6.85	92.75±3.18
Total Solid (mg/l)	186.25±15.95	98.0±14.14
Total Dissolved Solid (mg/l)	155.81±12.98	75.5±12.02
Total Suspended Solid (mg/l)	30.43±12.48	22.5±2.12
pH	8.3±0.05	7.95±0.21
Total alkalinity (mg/l)	110.0±41.8	53±12.71
Hardness (mg/l)	125.75±8.8	37.5±0.70
Calcium (mg/l)	82.5±3.1	31.0±0
Magnesium (mg/l)	43.25±10.87	6.5±0.70
Chloride (mg/l)	1.75±0.64	3.5±1.41
Fluoride (mg/l)	1.3±0.21	0.91±0.12
BOD (mg/l)	2.33±0.66	3.57±0.95
COD (mg/l)	5.45±1.98	7.65±0.21
Sulphate (mg/l)	**18.48±15.7**	**2.0±2.8**
Total Nitrogen (mg/l)	**8.05±5.84**	**4.16±1.02**

RESULTS AND DISCUSSION

The physicochemical analysis of the water samples collected from snowfed and rainfed rivers / streams of Kumaon Himalayas are given in Table 2. The results of the physicochemical parameters of snowfed and rainfed rivers / streams indicate that the mean value of all the parameters were on the higher side except chloride, COD and BOD in snowfed rivers. Highly significant differences ($p<0.001$) were recorded for conductivity and hardness. The other parameters where significant ($p<0.05$) variation was observed includes turbidity, total solids, total dissolved solids, pH, total nitrogen calcium and magnesium. The values for total suspended solids, total alkalinity, chloride, fluoride, BOD, COD, sulphate and total nitrogen were not significantly differed.

The physicochemical parameters of snowfed and rainfed rivers and streams of Kumaon Himalayas showed significant variation in turbidity, conductivity, total solids, total dissolved solid, total alkalinity, hardness, magnesium, calcium and sulphate. This variation may be due to interference of various physical / chemical process, source of origin of river, type of river basin, catchment type and other unknown factors. This was also reflected in the results of pesticide analysis in snowfed and rainfed rivers.

In the present investigation, γ-BHC, total BHC and total DDT were detected in all water and fish samples (Table 3) collected from both snowfed and rainfed rivers and streams, whereas endosulfan was detected only in one water sample collected from Gomti which is a rainfed stream. The concentration of γ-BHC, total BHC and total DDT in the snowfed rivers/stream was ranged from 0.008 μg/l to 0.034 μg/l, 0.008 to 0.034 μg/l and 0.016 to 0.055 μg/l, respectively. In the samples of rainfed river/stream the concentration of γ-BHC, total BHC, and total DDT ranged from 0.002 to 0.032 μg/l, 0.002 to 0.042μg/l and 0.002 to 0.055μg/l, respectively. While comparing the concentrations, it appears that no remarkable differences were observed for γ- BHC and total BHC but for total DDT the concentration was much higher (0.033μg/l) in the snowfed rivers than rainfed rivers/streams (0.018 μg/l). In water the total DDT showed minimum accumulation of 0.002 μg/l and maximum of 0.072 μg/l. The average value for total DDT was 0.024 ± 0.018μg/l). The maximum concentration of total DDT was noticed in the water samples collected from river Ramganga (East), which is a snowfed river.

The pesticide analysis of the fish samples of endangered *Tor putitora* (n=5) and *Schizothorax richardsonii* (n=5) indicated presence of γ-BHC (0.001-0.003 μg/g), total BHC (0.001-0.006 μg/g) and total DDT (0.013-0.055 μg/g), respectively. The mean values recorded were 0.002 ± 0.001μg/g for γ-BHC, 0.003 ± 0.002μg/g for total BHC and 0.035 ± 0.22μg/g for total DDT. No endosulfan residues were detected in fish samples collected from snowfed and rainfed rivers of Kumaun Himalayas. The maximum concentration of total DDT was

Table 3. Mean values of organochlorine pesticides in water (μg/l) and fish (μg/g) samples.

Water samples	**Streams**								
	Snowfed					**Rainfed**			
	Sharda (Kali)	Saryu	Gori	Ram Ganga	Dhuali	Kosi	Gomti	Ladhiya	Lohawati
γ-BHC	0.01	0.013	0.015	0.012	0.01 0	0.004	0.023	0.007	0.01
Total BHC	0.01	0.015	0.015	0.018	0.01	0.004	0.026	0.007	0.01
Total DDT	0.02	0.033	0.04	0.072	0.021	0.009	0.025	0.019	0.021
Endosulfan	ND	ND	ND	ND	ND	ND	0.002	ND	ND
Fish samples	Snow fed					Rain fed			
γ-BHC	N.D.	0.001	0.002	0.001	0.003	0.001	0.002	N.D.	N.D.
Total BHC	N.D.	0.001	0.004	0.001	0.006	0.004	0.004	N.D.	N.D.
Total DDT	N.D.	0.048	0.013	0.055	0.055	0.019	0.006	N.D.	N.D.

Tot-BHC=Sum of αβχδ isomers of BHC;
Tot-DDT=Sum of pp-DDT; op-DD, pp-DDD; ND-Not detected.

recorded in fish collected from snow fed rivers (0.013 - 0.055 μg/g) as compared to rain fed rivers (0.006- 0.019 μg/g).This indicates higher persistency of pesticides in snow fed waters.

The present study revealed occurrence of organochlorine pesticide (γ-BHC, total BHC and total DDT) in the water and fish samples of both snowfed and rainfed rivers / streams of the Kumaon Himalayas. While comparing the total DDT concentration with the EPA-water quality criteria for freshwater aquatic life, it appears that all the values of water and fish samples exceed the standards laid down by USEPA (1979,1995), which is 0.001 μg/l. In the present study the mean values of total DDT were on the higher side in water and fish samples of snowfed rivers like Ramganga, Saryu and Gori. Comparatively lower values of total DDT were recorded for the water and fish samples collected from rainfed rivers. The higher values of total DDT in water and fish samples in snowfed waters might be due to contamination of pesticides originating from plains during snow melting period coupled with other physical process. The t-test (two sample assuming unequal variance) between pesticide concentrations in snowfed and rainfed rivers indicated that concentration of γ- BHC and total DDT of water samples were significantly higher in ($p<0.05$, $p<0.01$) while it was nonsignificant for total BHC ($p=0.108$). On the other hand, the correlation coefficient between altitudinal

variation and pesticide occurrence showed insignificant negative correlation for γ-BHC(r=-0.02), total BHC(r=-0.009) and total DDT(r=-0.195). This clearly reflects higher persistency and absorption of pesticides in snowfed waters. The higher pesticide concentrations also observed in the locations having agricultural and urban areas. Gilliom *et al.*, (1999) reported occurrence of highest levels of pesticides as seasonal pulses-usually during spring and summer lasting from a few weeks to several months during and following high-use periods. They also indicated that pesticide concentration in streams draining urban areas were generally lower than in agricultural areas. These indicate certain level of pesticide pollution by DDT and its metabolites in the Kumaun Himalayan waters and show a high probability of adverse effects on aquatic life. EPA- recommended screening values were exceeded for total DDT in 50 percent studies in streams of United States as reported by Nowell *et al* 1999. He stated that pesticides in general were found to have the potential to accumulate in sediment and aquatic biota if they had (a) a water solubility less than 1 mg/l or an octanol-water partition coefficient greater than 1000 and (b) a soil half-life greater than 30 days. Occurrence of pesticide in a stream also depends on the sources of that pesticide in the drainage basin, the characteristics of the stream (such as water flow), and chemical properties of the pesticide (such as water solubility).

The wealth of information on pesticides in bed sediment and aquatic biota in the scientific literature has provided a national perspective on organochlorine pesticides in United States rivers (Nowell *et al*, 1999, Majewski and Capel, 1995). The review of literature indicates that no studies have been done earlier in Indian streams. However, a considerable works on the occurrence of pesticide accumulation in Ganga waters had been done earlier by several investigators (Haldar *et al.* 1989; ITRC, 1992; Nayak *et al.*, 1995; Kannan, 1995). Recently, Senthilkumar *et al.*, (1999) have recorded high accumulation (3700 ng/g) of DDT in dolphin samples collected from Ganga river at Haridwar. It is surprising from their observation that much lower values of DDT (60-1300 ng/g) were recorded in samples collected from plain areas of river Ganga at Kanpur, Allahabad, Patna and Farrakka as compared to 3700 ng/g of DDT at Haridwar, which is located in the foothills of Garhwal Himalayas. The results of the recent studies of the United States Geological Survey (USGS) programmes showed detection of a large number of organochlorine pesticides in stream sediment and aquatic biota in which forty four percent of the pesticides targeted were detected in sediment, and 64 percent were detected in aquatic biota, even though their agricultural uses in the United States were discontinued during the 1970s (Nowell *et al.*, 1999). This reflects the hydrophobicity and persistence of these compounds in coldwater ecosystem.

Studies in natural waters reveal a persistence of pesticides over a long period of time. The Yellow stone river system contained the following residues after spraying of spruce budworm with DDT: water with 0.03 ppm; vegetation 2.3 ppm; fish 14.0 ppm DDT and 6.53 DDE (total body analysis). It has been observed that trout 85 miles downstream two years latter from an isolated untreated area also had residues of approximately 0.45 ppm (Cope, 1961). Changes in species composition of stream fish was recorded by Graham and Scott (1958) and they reported 79-80% reduction in game fish in two streams the first

year after a DDT timber spraying operation and complete elimination of Sculpins (*Cottus spp.*) from one river. Hynes (1964) stated that change in fauna may involve species composition, but more commonly it affect that relative abundance and size distribution. The detection of organochlorine pesticide in the present study rivers and streams might be due to their environmental persistence and their extensive use in the past.

The findings emerged from the present study will provide baseline information for making effective conservation programmes in the cold water habitats of endangered fishes. The present observation suggests a need for more studies of organochlorine pesticide occurrence in the snowfed and rainfed drainage systems of Kumaon Himalayas where fishes are getting endangered. Also, researches should look for currently used pesticides with the potential to accumulate in sediment and aquatic biota, and toxic and long- term effects of pesticide mixtures on people and wildlife. Studies are also required to investigate the mechanisms and pathways of pesticide contamination in coldwater migratory fishes in the up streams.

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