

CS(AR) 7/98-99

POLLUTION POTENTIAL OF THE PESTICIDES IN THE HINDON RIVER



जले श्रेष्ठं पानं

**NATIONAL INSTITUTE OF HYDROLOGY
JALVIGYAN BHAWAN
ROORKEE - 247 667
1998-99**

PREFACE

Water is very important constituent of the ecosystem on the Earth. The importance of water quality preservation and improvement is constantly increasing. Among various organic, inorganic and biological water pollutants, the pesticides are very dangerous and harmful because of their tissue degradation and carcinogenic in nature. The pesticides are bioaccumulative and relatively stable, as well as toxic or carcinogenic, and, therefore, require close monitoring.

Although a considerable work has been carried out on the pesticide analysis in waters in different parts of the world. However, a few reports are available on the pesticides analysis in Indian rivers. Therefore, in this report attempts have been made to find out the pesticides pollution potential in the Hindon river. The Hindon river is selected for this study as it is the most polluted river in Western UP. The importance of the river lies in the fact that it covers a large area of its basin from which the pesticides enter into the river water. Finally, water of the Hindon mixup in the Yamuna river at Delhi which resulted into further increase of pollution of the Yamuna river.

The report has been prepared by Dr. Imran Ali, Scientist 'B' and Dr. C. K. Jain, Scientist 'C' of Environmental Hydrology Division, under the work programme of Environmental Hydrology Division for the year 1998-99.


(S. M. SETH)

DIRECTOR

CONTENTS

	LIST OF FIGURES	i
	LIST OF TABLES	ii
	ABSTRACT	iii
1.0	INTRODUCTION	1
2.0	THE HINDON RIVER	7
3.0	EXPERIMENTAL	10
	3.1 Chemical and reagents	10
	3.2 Equipments and Glasswares	10
	3.3 Samples Collection	10
	3.4 Extraction of Water and Sediment Samples	11
	3.5 Concentration of the Mother Liquors	11
	3.6 Preparation of the Standard Solutions and Calibration of Gas Chromatography Machine	12
	3.7 Analysis of the pesticides By Gas Chromatography	12
	3.8 Calculation	12
4.0	RESULTS AND DISCUSSION	14
	4.1 Concentrations of the Pesticides in the Hindon River Water	18
	4.2 Concentrations of the Pesticides in the Hindon River Sediment	19
	4.3 Concentrations of the Pesticides in the Hindon River Tributaries and Effluent Drains	20
5.0	CONCLUSION	21
	REFERENCES	23

LIST OF FIGURES

Sl. No.	TITLE	PAGE NO.
1.	The Pesticides in Food Chain.	4
2.	The Hindon River Basin with Details of Sampling Locations	8
3.	The Hindon River: Conceptual Linearised Diagram Showing Tributaries and Water Abstraction	9

LIST OF TABLES

Sl. No.	TITLE	PAGE No.
1.	WHO Recommendations of the Pesticides Hazards	2
2.	Properties of the Pesticides Which Indicate Their High Groundwater Contamination Potentia	3
3.	The Concentrations of the Pesticides in the Hindon River Water	15
4.	The Concentrations of the Pesticides in the Hindon River Bed Sediment	16
5.	The Concentrations of the Pesticides in the Hindon River Tributaries and Effluent Drains	17

ABSTRACT

The preservation and improvement of water quality is very important aspect and its demand is increasing continuously. Among various organic, inorganic and biological water pollutants, pesticides are very dangerous and harmful because of their tissue degradation and carcinogenic in nature. The pesticides are bioaccumulative and relatively stable and, therefore, require close monitoring. In view of this, attempts have been made to find out the pesticides pollution potential in the Hindon river which is the most important and polluted river in Wester UP.

The total samples (pre-monsoon) collected were 34 including 13, 13 and 8 samples of the Hindon water, sediments and its tributaries and effluent drains respectively. The same set of the sampling was also collected in post-monsoon season. The total detected pesticides were lindane, malathion, BHC, p,p'-DDD, o,p'-DDT, and methoxychlor. The concentrations of these pesticides were high in sediments comparatively to the Hindon water and its tributaries and effluent drains. The presence of the pesticides in river sediment shows the self purification capacity of the river by adsorption process. The concentrations of these pesticides in water, sediment, tributaries and effluent drains were also higher in comparison to the maximum permissible limits indicating the pesticides pollution of the Hindon river. It has been observed that the agricultural activities are the main source of pesticide pollution (non point). Besides, the presence of the pesticides in the Hindon tributaries and effluent drains indicates that these tributaries and effluent drains are also polluting (point source) the Hindon river.

1.0 INTRODUCTION

Water is very important constituent of the ecosystem on the Earth. The importance of water quality preservation and improvement is constantly increasing. Among various organic, inorganic and biological water pollutants, the pesticides are very dangerous and harmful because of their tissue degradation and carcinogenic in nature (IARC Monographs, 1987). The pesticides are bioaccumulative and relatively stable and, therefore, require close monitoring. The herbicides and nematocides are frequently water pollutants due to their direct application on to the plants. According to Indian standards all the pesticides should be absent in drinking water (ISI, 1991). However, the EEC Directive 80/778 (EEC, 1988) concerning the quality of water for human consumption, established the maximum concentration of each pesticide at 0.1 $\mu\text{g/L}$ and the total pesticides concentration at 0.5 $\mu\text{g/L}$ (Vettorazzi, 1979). The WHO has classified the pesticides into five groups on the basis of their (LD_{50} values) hazardous nature (Table 1). The EPA has (Cova, et al., 1990) also elaborated the lists of the pesticides properties which indicate their groundwater contamination potential (Table 2).

The major sources of the pesticide pollution are agricultural, forestry, industries and domestic activities. However, the pesticides pollution through air has also been reported. The dust particles in air adsorbed the pesticides (due to pesticides spray in agriculture, forestry and domestic use) and then contaminate natural water resources, sediments and soil through rain water (Jain and Ali, 1997). The pesticides from domestic, industrial and agricultural effluents enter into the food chain through ground/surface water. The pesticides from the contaminated water are taken up by plants and animals and enter into the food chain. The detail rout of the pesticides through food chain (Ali and Jain, 1998) is given in Fig. 1.

The study of pesticides in different water resources started in 1950 in USA with multiple detection of various the pesticides. The same issue has been addressed in other countries. It has been reported that the increasing amount of the pesticide residue may be present in the soil and these can ultimately be leached to aquifer levels and contaminate the groundwater or they may be carried away by runoff waters and soil erosion (Raju, et al., 1993, Miliadis, 1994 and Sherma, 1995) in natural water resources including rivers. The leachability of the pesticides are measured in terms of the groundwater ubiquity score (GUS).

Table 1: WHO Recommendations of the Pesticides Hazards

Sl. No.	Class	LD ₅₀ for rat, oral (mg/Kg body mass)	
		Solid	Liquid
I	Extremely Hazardous	≤5	≤20
II	Highly Hazardous	5-50	20-200
III	Moderately Hazardous	50-500	200-2000
IV	Slightly Hazardous	> 500	> 2000
V	Unlike to Present Hazard in Normal Use	>2000	>3000

**Table 2: Properties of the Pesticides Which Indicate
Their High Groundwater Contamination Potential**

Parameters	Values
Water Solubility	> 30 mg L ⁻¹
K _d	< 5, usually < 1
K _{oc}	< 300
Henry's Law Constant	< 10 ⁻² atm. m ³ mol
Speciation	Negatively charged, fully or partially at ambient pH
Hydrolysis Half Time	> 25 weeks
Photolysis Half Life	> 1 week
Field Dissipation Half Life	> 3 weeks

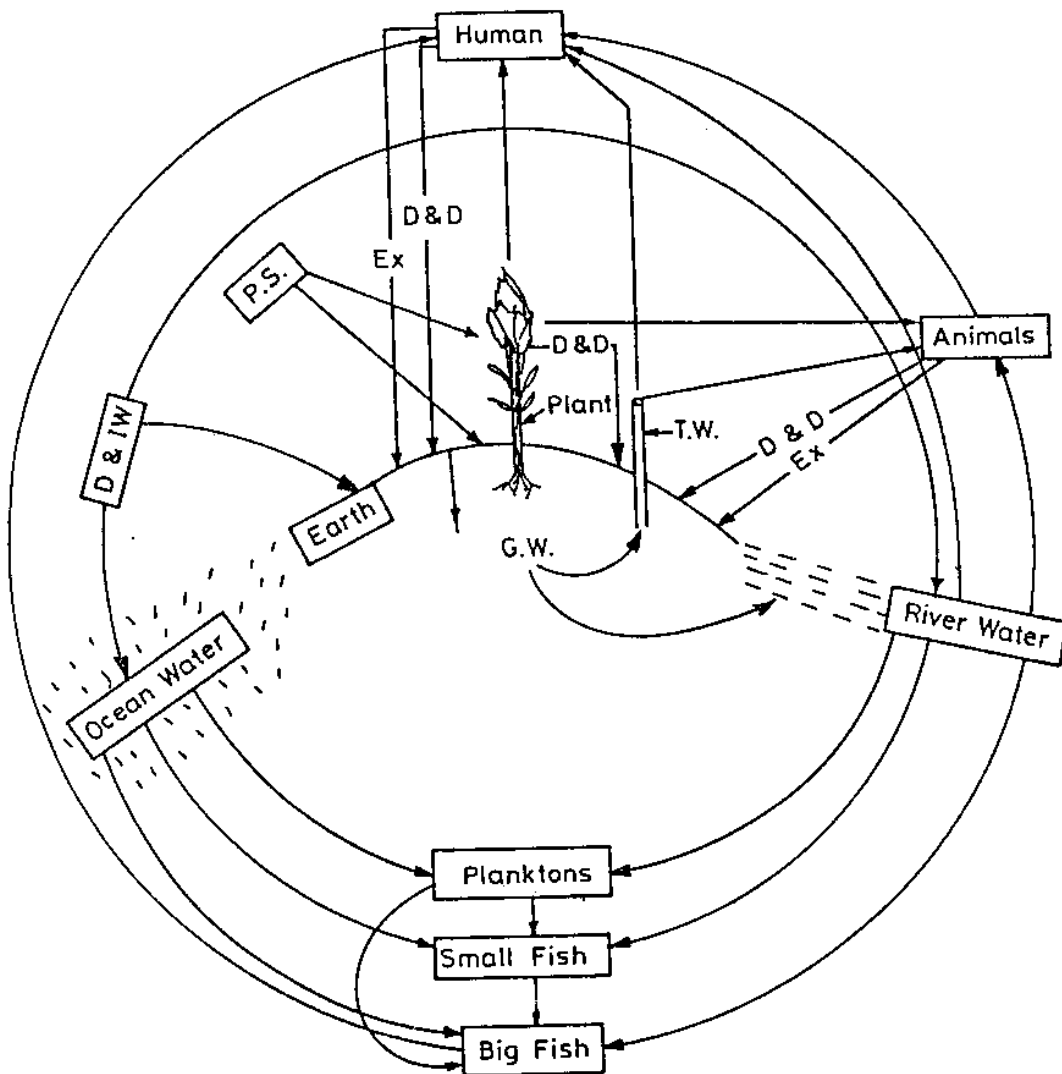


Fig.1: Pesticides in Food Chain.

Abbreviation : D & D: Death & Decay; D & IW: Domestic and Industrial Wastes;
 Ex: Excretion; G W: Ground Water; P S: Pesticides Spray;
 T W: Tube Well.

The persistence and mobility of pesticides are the key parameters responsible for the overall leaching potential of non-ionic compounds. The GUS index (Gustafson, 1989) can be written as

$$\text{GUS} = \log (\text{DT}_{50}) \cdot [4 - \log(\text{K}_{oc})]$$

where,

DT_{50} and K_{oc} are persistence and mobility respectively. Bottoni and Funari (1992) have evaluated the impact of 48 herbicides on groundwater quality. The tendencies of groundwater contamination are (a) non-leacher ($\text{GUS} < 1.8$), (b) transition ($1.8 < \text{GUS} < 2.8$) and (c) leacher ($\text{GUS} > 2.8$).

Various reports on pesticides analysis (by gas chromatography due to its wide applications) in different matrices have been published in last few years all over the world but literature survey indicates that there are only a few reports available on pesticides analysis in Indian rivers (Clement, et. al., 1995, MacCarthy and co-workers 1995, Sherma, 1995, Hartik and Tekel, 1996, Jain and Ali, 1997, Del Pino and Diaz, 1998 and Martin-Esteban and co-workers, 1998). The DDT, DDD, BHC, lindane, malathion, methoxychlor, etc. (Haldar, et al., 1989) are the very common pesticides used in India both in agricultural and domestic activities. It can be concluded from the literature that a little attention has been paid for monitoring the pesticides in natural water resources in India. However, some reports have been published on the presence of organochlorine pesticides in some urban water resources near Calcutta (Thakker and Pande, 1986 and Thakker and Vaidya, 1992) and Indian costal water and sediments (Sarkar and Gupta, 1989 and Sarkar, et al., 1997). The pesticides pollution of some of the Indian rivers of north and north east regions has been reported by Pathak et al. (1992). The groundwater contamination by some arsenic pesticides (Chaterji, 1994) has been reported in some of the districts of West Bengal (Calcutta). The presence of the pesticides in groundwater has also been reported in some areas, nearer to water storage ponds, in Gujrat. In these area the rain water, containing the pesticides from agricultural fields, is stored in ponds and during the course of time water (with pesticides) of these ponds enter into the aquifers leading to the groundwater contamination by pesticides (Ali and Jain, 1998). It is very interesting to note that all the drinking water, obtained from

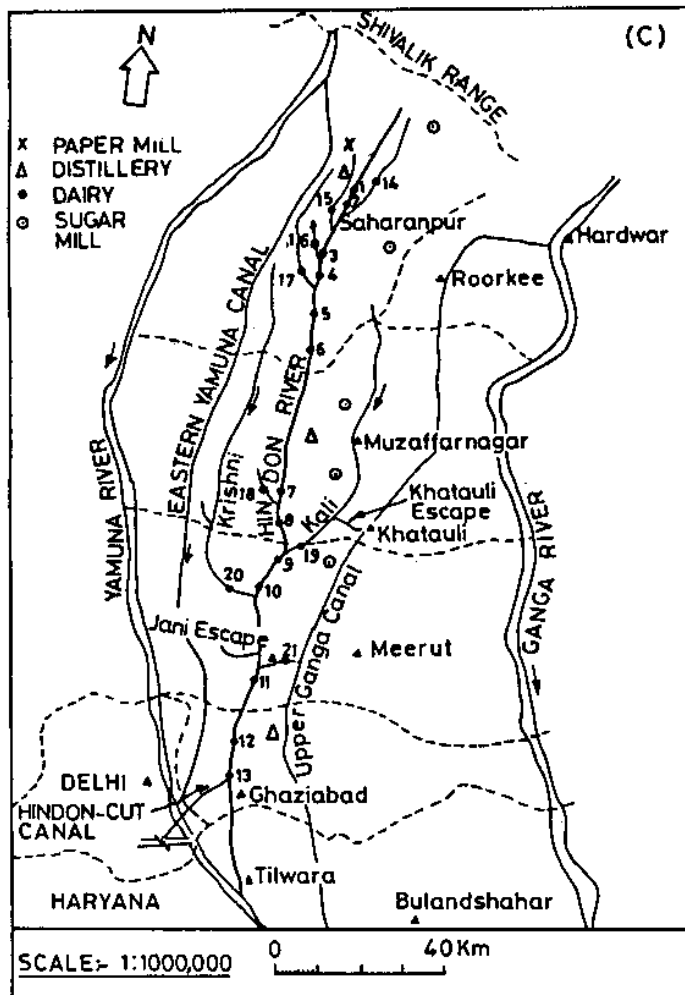
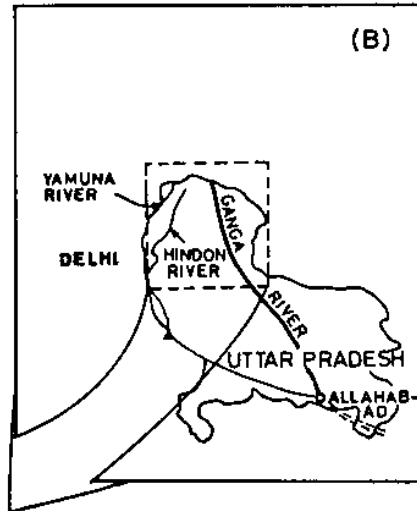
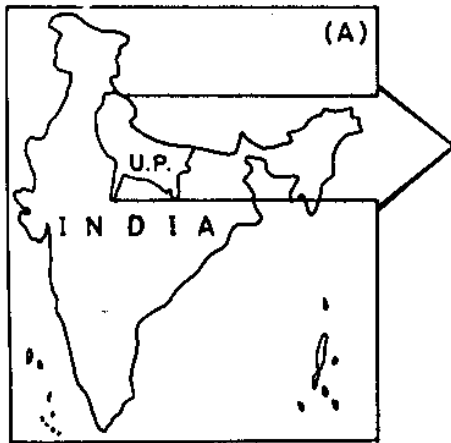
surface and ground, in India is supplied with out pesticides monitoring and, therefore, it is very important to know the purity of water prior to its supply to the public.

In view of the toxic and hazardous nature of pesticides, attempts have been made to find out the pesticides pollution potential in the Hindon river. The farmers of the Hindon basin were contacted and attempts were made to find out the types of the pesticide used by them in agricultural fields. It was found that mostly lindane, malathion, BHC, p,p'-DDD, o,p'-DDT, methoxychlor etc. pesticides are used in the area. The Hindon river is selected for this study as it is the most polluted river in Wester UP. The importance of the river lies in the fact that it covers a large area of its basin from which the pesticides enter into the Hindon water and its sediment. Finally, water of the Hindon mixup in the Yamuna river at Delhi which resulted into further pollution of the Yamuna river. In this study, the pre- and the post-monsoon samples from the Hindon river were collected and the qualitative and quantitative estimation of pesticides was carried out by Gas Chromatography. To find out the self pollution controlling capacity of the river, the concentrations of the pesticides were also determined in the sediment samples of the river. The results obtained are presented and discussed in this report.

2. THE HINDON RIVER

The Hindon river is very important river of western Uttar Pradesh. The river is highly polluted due to industrial, municipal and agricultural activities. The river originates from Upper Shivalik (Lower Himalayas) and lies between the latitude $28^{\circ}4'$ to $35^{\circ}5'$ N and longitude $77^{\circ}8'$ to $77^{\circ}4'$ E. The study area of the river ranged from Saharanpur to Mohan Nagar, Ghaziabad, U.P. The detail of the river with its tributaries is shown in Fig. 2. The conceptual linearised diagram showing the tributaries and water abstraction is given in Fig. 3. The river is purely rainfed but some industrial and municipal effluents also flow (starting from Saharanpur district) continuously through out the year. The river basin is a part of Indo-gangetic Plain (Joshi, 1987) and covers an area of about 7083 sq. km. The climate of the region is semi-arid due to significant diurnal variations in the temperatures. The average rainfall is about 12 cm, the major part of which is received during the monsoon period. The soil texture of the area are loamy to silty loamy.

The river basin is purely the agricultural field containing various villages, towns and cities. The quality and quantity of the river water is effected by municipal effluents and agricultural fields discharge. In addition to this, the river got the maximum percentage of pollution due to various industries situated on its basin. The river Hindon passes through four major industrially important districts of U.P. viz. Saharanpur, Muzaffar Nagar, Meerut and Ghaziabad which consist Pulp and Paper, Steel, Rubber, Ceramic, Plastic, Dairy, Laundry, Sugar, Distillery etc. industries (Fig. 2). These industries effect the water quality of the river by discharging their effluents. In this way, water and sediment of the river got polluted by pesticides from agricultural fields, domestic and industrial effluents.



SAMPLING LOCATION:

1 TO 13 : HINDON WATER AND SEDIMENT
 14 TO 21 : HINDON TRIBUTARIES AND EFFLUENT WATER SAMPLES

1. BEHREKI
2. GHOGREKI
3. SANTAGARH
4. NANDI
5. SADHAULI HARIYA
6. MAHESHPUR
7. BUDHANA
8. CHANDERI
9. ATALI
10. BARNAWA
11. DALUHERA
12. SURANA
13. HINDON CUT, MOHAN NAGAR
14. NAGDEO NALA
15. STAR PAPER MILL EFFLUENT
16. DISTILLERY EFFLUENT
17. DHAMOLA NALA
18. BUDHANA DRAIN
19. KALI RIVER
20. KRISHNI RIVER
21. GANGA CANAL

FIG.2: HINDON RIVER BASIN WITH DETAILS OF SAMPLING LOCATIONS

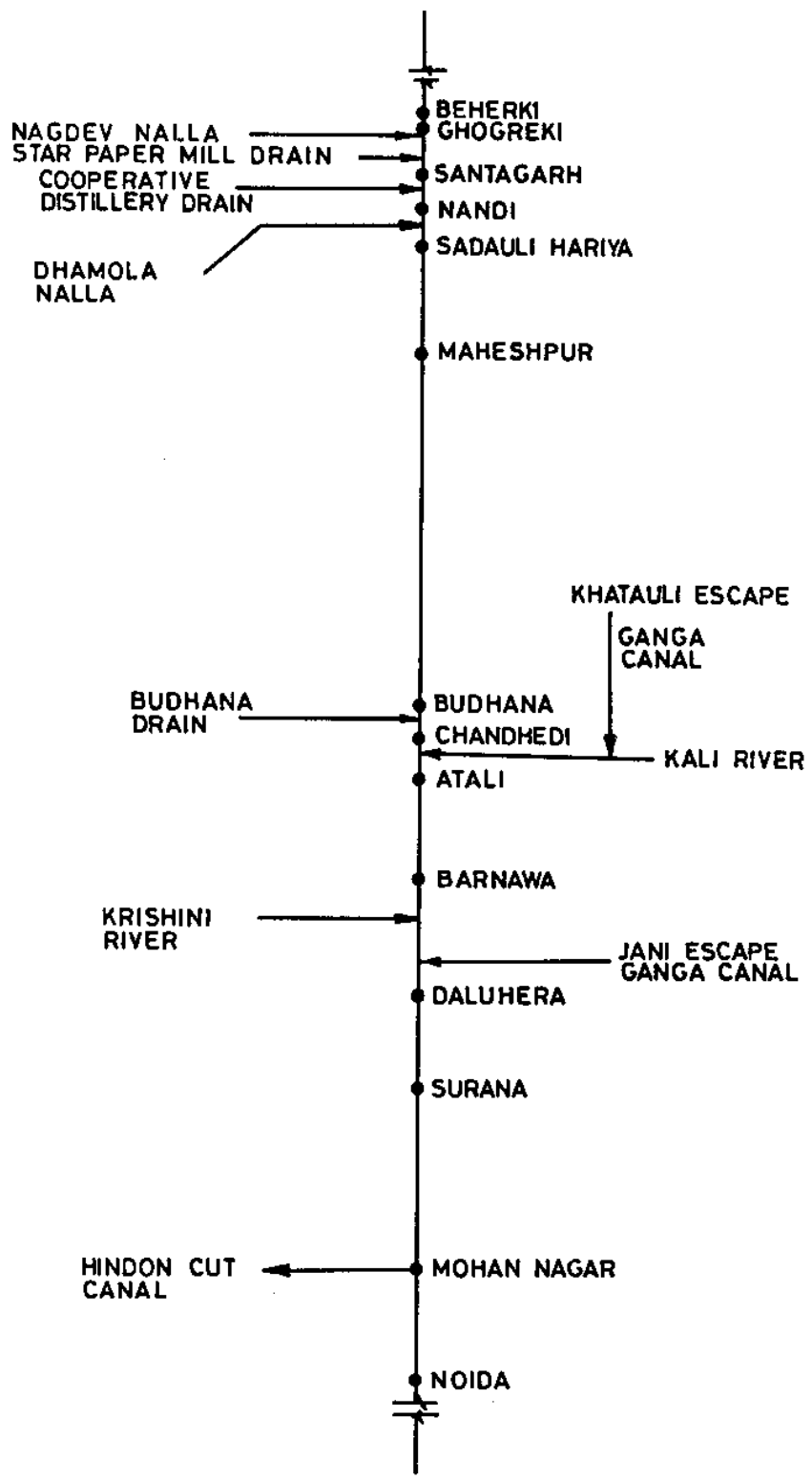


FIG.3: HINDON RIVER: CONCEPTUAL LINEARISED DIAGRAM SHOWING TRIBUTARIES AND WATER ABSTRACTION

3. EXPERIMENTAL

3.1 Chemical and reagents

All the pesticides of chromatography grade were purchased from E. Merck, Germany. The other solvents and reagents such as n-hexane (LC grade), anhydrous sodium sulphate (A.R. grade) etc. were obtained from E. Merck, India. The carrier gas nitrogen was of gas chromatography grade and were obtained from Mittal Gases, Ghaziabad, India.

3.2 Equipments and Glasswares

The qualitative and quantitative analysis of the pesticides was carried out by gas chromatography (model Nucon, 5700, India). The extraction of pesticides from water samples was done in 500 mL capacity separating funnels while the extraction of pesticides from sediment was carried out in 100 mL capacity air tight conical flask. The extracted n-hexane was concentrated with the help of Kuderna-Danish assembly and rotary evaporation apparatus. The other glasswares and equipments used were measuring cylinders, graduated pipettes, beakers, Hamilton syringes, boiling chips, water bath, balance etc.

3.3 Samples Collection

The points of samples collection at the Hindon river are shown in Fig. 2 and are also given in Table 3, 4 and 5. The total samples collected in pre-monsoon season were 34 including 13, 13 and 8 of the Hindon water, sediment and the Hindon tributaries and effluent drains respectively. The same set of the sampling was also collected in post-monsoon season. The sampling locations at the Hindon were selected by considering certain criteria. The important criteria for the site selection based on the easy approachability by road in all seasons, confluence of tributaries, industrial drains, water abstractions and impact of pollutional load from important town and industries in the river basin.

The grab sampling was done for pesticides analysis. Water samples were collected in the pesticide grade solvent prewashed glass containers closed with teflon lined caps while the sediment samples were collected in clean and properly labelled polythene bags. Water and sediment samples were collected with the help of water and sediment samplers respectively. To find out the possible source of pesticides pollution, sampling of the municipal and industrial discharges and the Hindon tributaries mixing into the Hindon at different points were also done. The first set of sampling was carried out in May 1998 (pre-monsoon) while the second set of sampling was done in October 1998 (post-monsoon). These water and sediment samples collected were kept at 4°C in the laboratory till their extraction.

3.4 Extraction of Water and Sediment Samples

The extraction of pesticides from water and sediment samples was carried out by n-hexane. 250 mL of water sample was shaken with 30 mL of n-hexane in separating funnel for 30 minutes. n-Hexane layer was allowed to separate from water for about 10 minutes. The n-hexane layer was separated and the same procedure was repeated for three times. The three fractions of extracted n-hexane were mixed together and a total volume of extracted n-hexane (mother the liquor) obtained was 90 mL. For the extraction of pesticides from sediment, 10 g of sediment was extracted with 30 mL of n-hexane three time and the three fractions of n-hexane were mixed together and a total volume of extracted n-hexane i.e. 90 mL was obtained.

3.5 Concentration of the Mother Liquors

The combined n-hexane (90 mL) extracts obtained from water and sediment samples respectively were concentrated to 10 mL. The 90 mL extracted n-hexane was reduced to 10 mL by Kuderna-Danish assembly and rotary evaporation apparatus. The extraction was carried out by using water bath at 40°C temperature. The moisture in concentrated n-hexane (10 mL) was removed by adding anhydrous sodium sulphate (1.0 g) in each extracted n-hexane (10 mL) fractions and keeping them over night. All the extracted n-hexane fractions (from the Hindon water, its tributaries, effluent drains and sediment samples) were already clean and clear and, therefore, no further clean up was carried out.

3.6 Preparation of the Standard Solutions and Calibration of Gas Chromatography Machine

The standard solutions (5 mg/L) of lindane, malathion, BHC, p,p'-DDD, o,p'-DDT and methoxychlor were prepared in n-hexane. The instrument was calibrated with these pesticides. The chromatograms of the standard individual and their mixture were recorded. The values of the retention times obtained were used for the identification of pesticides present in the Hindon river water, sediments, its tributaries and effluent drains. The surface areas of the peaks obtained by the standard pesticides were used to determine the concentration of the pesticides present in the Hindon river water, sediments, its tributaries and effluent drains.

3.7 Analysis of the Pesticides By Gas Chromatography

The qualitative and quantitative analysis of the pesticides was carried out by gas chromatography (model Nucon, 5700, India). The electron capture detector (ECD) was used to detect the pesticides. The column used was made of glass, Ch. W.H.P., OV-17 (3%), mesh size 80-100 (120 cm x 3 mm). The temperatures of the column, injector and detector were 240, 250 and 275°C respectively. The flow of carrier gas (nitrogen) was kept constant at 60 mL/minute. The extracted fractions (containing pesticides) of n-hexane was analyzed by gas chromatography under the chromatographic conditions mentioned above. 2.0 μ L of extracted hexane was injected with the help of Hamilton syringe. The chromatograms of the standard required pesticides (2 μ g/L of 5 mg/L) were recorded under the identical gas chromatographic conditions. The confirmation of the pesticides was also carried out by the internal standard addition method.

3.8 Calculation

The method of the calculation of the concentrations of the pesticides was already described (Jain and Ali, 1997 and Ali and Jain, 1997). However, the concentration of each pesticides is determined by the comparison of peak area or height of the samples with those of standards. This can be done by using the following equation.

$$X_{sam} = \frac{H_{sam}}{H_{std}} \times \frac{V_{inj\ std}}{V_{inj\ sam}} \times X_{std} \times \frac{V_{ext}}{V_{sam}}$$

where,

X_{sam} = concentration of pesticide in original water sample (mg/L)

H_{sam} = peak height (or area) of sample

H_{std} = peak height (or area) of standard

$V_{inj\ std}$ = volume of standard injected (μ L)

$V_{inj\ sam}$ = volume of sample injected (μ L)

X_{std} = concentration of pesticide in standard solution (mg/L)

V_{ext} = final volume of sample extract (mL) and

V_{sam} = volume of original water sample extracted (mL).

4.0 RESULTS AND DISCUSSION

It is clear from Table 3, 4 and 5 that lindane, malathion, BHC, p,p'-DDD, o,p'-DDT and methoxychlor were detected as the pesticides present in the Hindon river water, sediments and its tributaries and effluent drains. The values of the retention times were 1.00, 1.64, 3.65, 4.12, 4.97 and 7.48 minutes for lindane, malathion, BHC, p,p'-DDD, o,p'-DDT and methoxychlor respectively under the reported gas chromatographic conditions. The concentrations of these pesticides ($\mu\text{g/L}$) are also given in Table 3, 4 and 5 in the Hindon water, sediment and effluent drains and tributaries respectively. The presence of these reported pesticides was identified by the comparison method i.e. the retention times of the standard pesticides were used to identify the unknown pesticides present in the samples. The presence of these pesticides was further confirmed by the addition of known amount of known pesticides in unknown samples (n-hexane extracted samples from the Hindon water, sediment and the tributaries and effluent drains). It has been observed that by the addition of known pesticide in the unknown samples the peak area and height of the corresponding pesticide increased and the increase in the peak area and height was in directly proportional to the concentration of the additive pesticide. This addition method is supposed as the best method for the identification of pesticides in unknown samples. The concentrations of the pesticides present in the unknown samples were calculated by using the area and height of the peaks of chromatograms obtained from standard pesticides. The detail of the calculation is given in the experimental section.

In order to optimize the separation conditions of the reported pesticides in unknown samples, various combinations of the gas chromatographic conditions were tried. The different columns such as Supelcoport with SP, Fused Silica, GasChrom Q, CP Sil, etc. were tried with the different types of mobile phases i.e. nitrogen, helium, methane, argon as pure and their mixtures. The variation in the flow rate of the mobile phases and the temperature was also made. The isocratic and gradient temperature programmes were also used. In addition to this, the detector sensitivity by attenuation was also varied and the best sensitivity was adjusted. As a result of extensive experimentation, the best gas chromatographic conditions in terms of stationary (type only) and mobile (type and flow both) phases and temperature values (for column, injector and detector) were selected, used and reported herein.

Table 3: The Concentrations of the Pesticides in the Hindon River Water

Sl.No.	Name of Sites	Lindane		Malathion		BHC		p,p'-DDD		o,p'-DDT		Methoxychlor	
		a	b	a	b	a	b	a	b	a	b	a	b
1.	Behreki	ND	2.18	ND	ND	0.15	1.64	ND	ND	0.10	ND	ND	ND
2.	Ghogreki	ND	1.46	ND	ND	ND	0.10	ND	ND	ND	ND	ND	ND
3.	Santagarh	0.52	1.09	0.09	0.13	ND	ND	ND	ND	ND	ND	ND	ND
4.	Nandi	ND	0.19	1.52	ND	ND	ND	2.38	ND	ND	0.38	ND	ND
5.	Sadhauli	ND	ND	1.00	1.50	0.11	ND	ND	0.95	ND	0.10	ND	ND
6.	Hariya	ND	2.06	0.95	1.62	0.21	0.10	ND	ND	ND	0.17	ND	ND
7.	Maheshpur	ND	0.24	0.33	0.83	ND	0.05	ND	ND	ND	2.28	ND	0.60
8.	Budhana	ND	0.12	0.12	0.86	ND	0.10	ND	ND	ND	ND	ND	0.71
9.	Chandheri	ND	0.19	0.52	ND	0.11	0.36	ND	ND	ND	1.03	ND	0.60
10.	Atali	ND	0.20	0.50	0.06	0.10	0.58	ND	ND	ND	0.60	ND	0.50
11.	Barnawa	ND	0.42	0.48	0.44	0.05	5.61	ND	ND	ND	0.86	ND	1.50
12.	Dahuhara	ND	ND	ND	0.52	ND	0.72	0.15	ND	ND	2.00	0.15	0.93
13.	Surana	ND	0.49	ND	1.51	0.11	0.81	0.15	ND	ND	0.46	0.11	ND
	Mohan Nagar												

Pesticides concentration: $\mu\text{g/L}$

a: pre-monsoon samples, b: post-monsoon samples, BHC: 1,2,3,4,5,6-a,a,e,e,e-hexachloro cyclohexane, p,p'-DDD: 2,2-bis(p-chlorophenyl)-1,1-dicloroethane, o,p'-DDT: 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane and ND: Not detected.

Table 4: The Concentrations of the Pesticides in the Hindon River Bed Sediment

Sl.No. Name of Sites	Lindane		Malathion		BHC		p,p'-DDD		o,p'-DDT		Methoxychlor	
	a	b	a	b	a	b	a	b	a	b	a	b
1. Behreki	ND	ND	5.22	22.95	3.89	14.0	ND	ND	ND	9.5	ND	ND
2. Ghogreki	1.50	ND	ND	19.27	2.96	8.06	ND	13.6	ND	ND	ND	ND
3. Santagarh	0.52	ND	ND	15.00	2.21	50.20	ND	ND	ND	10.43	ND	ND
4. Nandi	0.50	21.0	ND	27.25	2.00	ND	ND	7.50	ND	ND	ND	ND
5. Sadhauri Hariya	0.50	7.28	ND	33.17	2.00	10.50	ND	ND	ND	ND	ND	56.67
6. Maheshpur	0.48	ND	0.50	32.53	1.86	15.86	ND	ND	ND	ND	ND	32.20
7. Budhana	0.47	ND	0.40	ND	1.80	95.89	ND	ND	ND	7.56	ND	8.90
8. Chandheri	0.43	1.81	0.31	ND	1.70	27.46	ND	20.94	ND	ND	ND	12.43
9. Atali	0.40	3.40	0.15	9.95	1.61	ND	ND	35.65	ND	ND	ND	16.35
10. Barnawa	0.21	1.90	0.11	4.11	1.42	ND	ND	ND	ND	7.41	ND	ND
11. Daluhera	ND	7.31	0.10	45.50	2.52	16.81	0.52	ND	ND	ND	ND	ND
12. Surana	ND	1.50	ND	ND	1.51	ND	ND	8.92	ND	ND	ND	11.29
13. Mohan Nagar	0.30	34.31	0.10	10.10	0.21	ND	0.05	12.68	ND	2.60	ND	17.34

Pesticides concentration: $\mu\text{g/Kg}$

a: pre-monsoon samples, b: post-monsoon samples, BHC: 1,2,3,4,5,6-a,a,e,e,e-hexachloro cyclohexane, p,p'-DDD: 2,2-bis(p-chlorophenyl)-1,1-dichloroethane, o,p'-DDT: 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane and ND: Not detected.

Table 5: The Concentrations of the Pesticides in the Hindon River Tributaries

Sl.No.	Name of Sites	Lindane		Malathion		BHC		p,p'-DDD		o,p'-DDT		Methoxychlor	
		a	b	a	b	a	b	a	b	a	b	a	b
1.	Nagdeo Nalla	ND	0.54	ND	ND	ND	ND	ND	ND	ND	0.65	ND	ND
2.	Saharanpur Star Paper Mill Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3.	Saharanpur Distillery Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4.	Dhamola Nalla	ND	ND	0.51	1.00	0.15	ND	ND	ND	ND	ND	ND	0.76
5.	Budhana Drain	2.15	8.30	1.81	3.50	0.54	ND	ND	ND	ND	11.46	ND	0.54
6.	Kali River	ND	0.10	1.12	5.01	1.51	ND	ND	1.88	ND	ND	ND	ND
7.	Krishni River	ND	ND	1.53	0.66	1.00	ND	ND	0.61	ND	0.49	ND	2.31
8.	Ganga Canal	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Pesticides concentration: $\mu\text{g/L}$

a: pre-monsoon samples, b: post-monsoon samples, BHC: 1,2,3,4,5,6-a,a,e,e,e-hexachloro cyclohexane, p,p'-DDD: 2,2-bis(p-chlorophenyl)-1,1-dichloroethane, o,p'-DDT: 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane and ND: Not detected.

The concentrations of the pesticides in the Hindon water, sediment and its tributaries and effluent drains in pre- and post-monsoon seasons have been determined separately. The values of the pesticides with their variation are discussed below.

4.1 Concentrations of the Pesticides in the Hindon River Water

To determine the pesticides pollution in the Hindon river water, the concentrations of the pesticides in river water were determined. The effect of rainy season on pesticide pollution in the Hindon river water was studied by the qualitative and quantitative estimation of the pesticides in the post-monsoon season.

In the pre-monsoon samples, the lindane was found 0.52 $\mu\text{g/L}$ only at Santagarh. The concentrations of malathion varied from 0.09 to 1.52 $\mu\text{g/L}$ while it has not been detected at Behreki, Ghagreki, Surana, and Mohan Nagar. The concentrations of BHC ranged from 0.05 to 0.21 $\mu\text{g/L}$ and it has not been detected at Ghogreki, Santagarh, Nandi, Budhana, Chandheri and Surana. The concentrations of p,p'-DDD were found 2.38, 0.15 and 0.15 $\mu\text{g/L}$ at Nandi, Surana and Mohan Nagar respectively while it was not found at other sampling sites. The o,p'-DDT was detected only at Behreki with the concentration of 0.10 $\mu\text{g/L}$. The methoxychlor was absent except at Surana and Mohan Nagar with the concentrations of 0.15 and 0.11 $\mu\text{g/L}$ respectively. In case of post-monsoon season, the concentrations of lindane varied from 0.12 to 2.18 $\mu\text{g/L}$ except at Sadhauri Hariya where it was absent. The malathion was absent at Behreki, Ghogreki, Nandi and Atali and the concentrations found were ranged from 0.53 to 1.62 $\mu\text{g/L}$ at other sampling sites. The concentrations of BHC ranged from 0.05 to 1.64 $\mu\text{g/L}$ with the exception at Santagarh, Nandi and Sadhauri Hariya where it was absent. The p,p'-DDD was absent at all the sampling sites except at Sadhauri Hariya where the concentration of it was 0.05 $\mu\text{g/L}$. The o,p'-DDT was absent at Behreki, Ghogreki, Santagarh and Chandheri while its concentrations ranged from 0.10 to 2.28 $\mu\text{g/L}$ at other places. The concentrations of methoxychlor detected were 0.60, 0.71, 0.60, 0.50 and 0.93 $\mu\text{g/L}$ at Budhana, Chandheri, Atali, Barnawa, Daluhera and Surana respectively while it was absent at other sampling sites. It is clear from these results that the reported pesticides detected at most of the sampling sites in post-monsoon season.

4.2 Concentrations of the Pesticides in the Hindon River Sediment

The sediment of the rivers has been supposed as the good adsorbent for a variety of compounds. It is supposed that some of the pesticides would have been adsorbed by the river sediment in due course of time. Therefore, to find out the self pollution controlling capacity of the river by adsorption process, the concentrations of the pesticides in river sediment were determined in pre- and post-monsoon seasons.

In the pre-monsoon season, lindane was absent at Behreki, Daluhera and Surana while at other places the concentrations ranged from 0.21 to 1.50 $\mu\text{g/L}$. The concentrations of malathion varied from 0.10 to 5.22 $\mu\text{g/L}$ at all the sampling sites except at Ghogreki, Santagarh, Nandi, Sadhauri Hariya and Surana where it was absent. The BHC has been detected at all the places and the concentrations ranged from 0.21 to 3.89 $\mu\text{g/L}$. The p,p'-DDD was absent at all the places except at Daluhera and Mohan Nagar where the concentrations found were 0.52 and 0.05 $\mu\text{g/L}$ respectively. The o,p'-DDT has not been detected at any sampling site. The methoxychlor was also absent at all the places. In the post-monsoon season, lindane was absent at Behreki, Ghogreki, Santagarh, Maheshpur and Budhana while at other sampling sites the concentrations of it varied from 1.50 to 34.31 $\mu\text{g/L}$. The malathion was absent only at Budhana, Chandheri and Surana while at other places the concentrations were in the range of 10.10 to 45.50 $\mu\text{g/L}$. The BHC was not detected at Nandi, Atali, Barnawa, Surana and Mohan Nagar while the concentrations at other sampling sites were in the range of 10.50 to 95.89 $\mu\text{g/L}$. The concentrations of p,p'-DDD were determined in the range of 7.50 to 35.65 $\mu\text{g/L}$ at Ghogreki, Nandi, Atali, Surana and Mohan Nagar while it was not detected at other places. The Behreki, Santagarh, Budhana, Barnawa and Mohan Nagar only show the presence of o,p'-DDT with concentrations ranging from 2.60 to 10.43 $\mu\text{g/L}$. The concentrations of methoxychlor ranged from 8.90 to 56.67 $\mu\text{g/L}$ and it was not detected at Behreki, Ghogreki, Santagarh, Nandi, Barnawa and Daluhera sampling points. It has been observed again that these pesticides were not detected at most of the places in pre-monsoon season.

4.3 Concentrations of the Pesticides in the Hindon River Tributaries and Effluent Drains

To find out the maximum possible pesticides pollution sources, attempts have been made to determine the pesticides concentrations in the Hindon tributaries and effluent drains. The concentrations of the reported pesticides in these tributaries and drains were determined in pre- and post-monsoon seasons.

In the pre-monsoon season, it is clear from Table 5 that the lindane was determined at only Budhana drain with the concentration of 2.15 $\mu\text{g/L}$. The malathion was absent at Nagdeo Nalla, Star Paper Mill effluent, Saharanpur Distillery effluent and Ganga canal while it has been detected in the range of 0.51 to 1.81 $\mu\text{g/L}$ at other sampling points. The BHC was absent at Nagdeo Nalla, Star Paper Mill effluent, Saharanpur Distillery effluent and Ganga canal while at other sampling sites the concentrations ranged from 0.15 to 1.51 $\mu\text{g/L}$. The p,p'-DDD, o,p'-DDT and methoxychlor were absent at all the sampling sites. In the post-monsoon season, lindane was detected only at Nagdeo Nalla, Budhana drain and Kali river with the concentrations of 0.54, 8.30 and 0.10 $\mu\text{g/L}$ respectively. The malathion was absent at Nagdeo Nalla, Star Paper Mill effluent, Saharanpur Distillery effluent and Ganga canal while the concentrations at other places varied from 0.66 to 5.01 $\mu\text{g/L}$. The BHC was absent at all the sampling points. The p,p'-DDD was detected only at Kali river and Krishna river with the concentrations of 1.88 and 0.61 $\mu\text{g/L}$ respectively. The o,p'-DDT has been determined at Nagdeo Nalla, Budhana drain and Krishna river with the concentrations of 0.65, 11.46 and 0.49 $\mu\text{g/L}$ respectively while it was absent at other sampling points. The concentrations of methoxychlor were 0.76, 0.54 and 2.31 $\mu\text{g/L}$ at Dhamola Nalla, Budhana drain and Krishna river respectively while it was absent at other sampling points. It is clear from these results that there is no marked effect of monsoon on the qualitative and quantitative nature of the pesticides in tributaries and effluent drains. It is also interesting to observe from table 5 that no pesticide has been detected in Star Paper Mill effluent, Saharanpur Distillery effluent and Ganga canal either in pre- or post-monsoon seasons.

5.0 CONCLUSION

The qualitative and quantitative analysis of the pesticides in different natural water resources is very important part of water quality because of the carcinogenic and hazardous nature of the pesticides. The complete analysis of the pesticides by gas chromatography has indicated the presence of lindane, malathion, BHC, p,p'-DDD, o,p'-DDT and methoxychlor in the Hindon water, sediment and its tributaries and effluent drains. The analysis of the samples of the pre- and post-monsoon seasons indicates that the most of the pesticides have been detected at maximum sampling points in post-monsoon season while these pesticides were found at a few sampling points in pre-monsoon season. This type of pesticides presence indicates that the pesticides pollution in the the Hindon river has increased in the monsoon season. It has also been observed that the concentrations of all the reported pesticides were higher in post-monsoon season in comparison to the pre-monsoon season which is due to the increase of these pesticides in the river in monsoon season. The concentrations of all the detected pesticides were also higher than the maximum permissible values which shows that water of the Hindon river is not safe by the pesticides point of view. It is very interesting to observe that the concentrations of the reported pesticides were higher in all the sediment samples than the water samples. The higher concentrations of these pesticides may be due to the adsorption of pesticides on bed sediment as in adsorption process the concentration of the adsorbate increases on the adsorbent from the solution.

The concentrations of the pesticides have also been detected in the Hindon tributaries and effluent drains except in Saharanpur Star Paper Mill Effluent, Saharanpur Distillery Effluent and Ganga canal. The concentrations of these pesticides in tributaries and effluent drains were not as much high as in the Hindon water and sediment. Moreover, some of the pesticides present in the Hindon water and sediment have not been detected in the Hindon tributaries and effluent drains. Therefore, the higher concentrations of all the pesticides and the presence of the pesticides in the river, which have not been detected in the Hindon tributaries and effluent drains, at various sampling points indicate the possibility of non point source pollution of pesticides. The non point source pollution of pesticides may be due to the agricultural activities where the farmers use different types of pesticides. This non point source pollution of the Hindon river due to pesticides may be supported by the fact that the

reported pesticides are being used in the agricultural fields of the Hindon basin (told by farmers). The pesticides pollution in natural water resources due to agricultural activities has been reported by Lap, et al. (1998). Therefore, it may be concluded that the major pollution source of pesticides is agricultural field from where the pesticides transported into the Hindon river during monsoon season. Finally, it may be concluded that the pesticides pollution is present in the Hindon river. In view of all these points, it is advisable that water of all the effluent drains should be treated properly for the pesticides prior to their discharge into the river. The farmers should use the newly developed low toxic pesticides. The other methods of pest control may be used in place of pesticides (Ali and Jain, 1998).

REFERENCES

- Ali, I. and Jain, C.K. (1997) 'Trace Analysis of Pesticides by Gas Chromatography,' NIH, Roorkee, Report - In Press.
- Ali, I. and Jain, C.K. (1998) 'Groundwater Contamination and Health Hazards by Some of the Most Commonly Used Pesticides,' *Current Science*, **75(10)**, 1011-1014.
- Bottoni, P. and Funari, E. (1992) 'Effect of Herbicides on Groundwater Quality,' *Sci. Total Environ.*, **123**, 581.
- Chaterji, A., (1994) 'Groundwater Arsenic Contamination in Residential Area and Surroundings of P.N. Mitra Lane, Behala, Calcutta, due to Industrial Effluent Discharge,' Ph.D. Thesis, p.10.
- Clement, R.E., Eiceman, G.A. and Koester, G.J. (1995) 'Environmental Analysis,' *Anal. Chem.*, **67**, 221R-255R.
- Cova, D., Molinari, G.P. and Rossini, L. (1990) 'The Properties of the Pesticides of Their High Groundwater Contamination Potential,' *Toxicol. Environ. Safety*, **20**, 234.
- Del Pino, J.N. and Diaz, R.D. (1998) 'Pesticides Distribution and Movement,' *Biotherapy*, **11**, 69.
- EEC (1988) 'Drinking Water Directive Official Journal N 229/11, Directive 80/778/EEC.
- Guidelines for Drinking Water Quality (1996) Geneva, WHO, IInd Ed., 1996, Vol. **2**, p. 944.
- Gustafson, D.I. (1989) 'Groundwater Ubiquity Score: A Simple Method for Assessing Pesticides,' *Environ. Toxicol. Chem.*, **8**, 339.

Haldar, P., Raha, P. and Bhattacharya, P. (1989) 'Studies on the Residues of DDT and Endosulfan Occuring in Ganga Water,' Indian. J. Environ. Health, **31**, 156.

Hartik, S. and Tekel, J. (1996) 'Extraction Methodology and Chromatography for the Determination of Residual Pesticides in Water,' J. Chromatogr., **733**, 217-233.

IARC Monographs (1987) Suppl. 7, IARC, Lyon, Vol. **54**, 40.

Indian Standard: (1991) 'Drinking Water Specification' (First revision), IS 10500.

Jain, C.K. and Ali, I. (1997) 'Determination of Pesticides in Water, Sediment and Soils by Gas Chromatography,' Int. J. Environ. Anal. Chem., **68**, 83.

Joshi, S.B. (1987) 'Hydrochemical Studies of Upper the Hindon Basin, UP., M.E. Thesis, Department of Hydrology, University of Roorkee,

Lap, P., Madramootoo, C.A., Enright, P., Papineau, F. and Perrone, J. (1998) 'Water Quality of an Intense Agricultural Watershed in Quebec,' J. Am. Resour. Assoc., **34**, 427.

MacCarthy, P., Klusman, R.W., Cowling, S.W. and Rice, J.A. (1995) 'Water Analysis,' Anal Chem., **67**, 525R-582R.

Martin-Esteban, A., Fernandez, P., Fernandez-Alba, A. and Camara, C. (1998) 'Analysis of Polar Pesticides in Environmental Water,' Quim. Anal., **17(2)**, 51.

Miliadis, G.E. (1994) 'Determination of Pesticides Residues in Natural Waters of Greece by Solid Phase Extraction and Gas Chromatography,' Bull. Environ. Contam. Toxicol., **52**, 25.

Pathak, S.P., Kumar, S., Ramteke, P.W., Murthy, R.C., Singh, K.P., Bhattacharjee, J.W. and Ray, P.K. (1992) 'Riverine Pollution in Some Northern and North Eastern States of India', Environ. Monit. Assess., **22(3)**, 227 (1992).

Raju, G.S., Jacques, A. and Khan, S.U. (1993) 'Pollution Potential of Pesticides in Soils,' *Chemosphere*, **26**, 1442.

Sarkar, A., Nagarajan, R., Chaphadkar, S. and Singbal, S.Y.S. (1997) 'Detrmination of Organochlorine Pesticides in Sediments from the Arabian Sea along the West Coast of India,' *Water Res.*, **31**, 195.

Sarkar, A. and Gupta, S. (1989) 'Determination of Organochlorine Pesticides in Indian Costal Water Using a Moored In-Situ Sampler,' *Water Res.*, **23**, 975.

Sherma, J. (1995) 'Pesticides,' *Anal. Chem.*, **67**, 1R.

Thakker, N. P. and Pande, S.P. (1986) 'Study of Organochloro Pesticides in Some Urban Water Resources,' *J. Indian Water Works Asson.*, **XVIII**, 313.

Thakker, N.P. and Vaidya, M.V. (1992) 'Determination of 1,2-dichloro benzene, 1,2,4-trichloro benzene and hexachloro benzene in Surface Water,' *J. Indian Water Works Asson.*, **XXIV**, 343.

Vettorazzi, G. (1979) 'International Regulatory Aspects for Pesticide Chemicals,' *CRC Press Inc.*, Vol. 1 p.141.

DIRECTOR S M SETH

DIVISIONAL HEAD K K S BHATIA

STUDY GROUP

IMRAN ALI, Sc 'B'

C K JAIN, Sc 'C'

SUPPORTING STAFF

Mr. T.R. SAPRA, R.A.

Mr. RAKESH GOEL, Tech. II

Mr. DAYANAD. Tech. II