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Banned Organochlorine Cyclodiene Pesticide in Ground Water in Varanasi, India

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Many man made chemicals can be found as environmental contaminants but few generate as much controversy and public fear as pesticides. They are considered to be a special case because they are deliberately introduced into the environment and they are, by their very nature, intended to kill or injure some form of life. In fact much of the public fear of pesticides and their environmental residues derives from the discovery in the 1940s that persistent organochlorine insecticides such as DDT, BHC and more particularly the organochlorine cyclodiene insecticides, viz. aldrin, dieldrin, endrin etc. were causing damage to non-target species such as birds of prey (Sen Gupta 1996). These compounds are highly bioaccumulated in the fatty tissues with consequent magnification of (Henry *et al.* 1998) environmental concentrations through the food chain. In addition, they were found in significant quantities in humans and particularly, in breast milk (Petreas *et al.* 1996).

For human and environment safety point of views, several countries have banned such highly persistent organochlorine insecticides, viz., aldrin, endrin, toxaphene, heptachlor, chlordane etc. whose residues persist for long duration in food commodities and different environmental component, such as surface and ground water, soil and atmosphere. For such reasons, the Government of India has banned 24 pesticides and another 7 pesticides have been permitted for restricted use only (Pesticide Statistics 2003). Preliminary survey report revealed that, still now some of the banned pesticides are available in market. Some farmers and local municipality of studied area are also in favour of these few pesticides. Varanasi is densely populated, oldest existing civilized city in the world and heavily pressured by national and international tourists. Moreover, Varanasi is popular Indo Gangetic area for production of vegetables and fruits. Thus, there was a quite long history of the use of long persistence, fat accumulative highly toxic banned cyclodiene organochlorine pesticide in Varanasi and adjoining areas for public health purpose and agriculture. Although few reports concerning the contamination of organochlorine insecticides in ground water in India are available (Jani *et al.* 1991; Raha *et al.* 2003), moderate to high levels of DDT, BHC and endosulfan have been reported from different components of environment in certain areas in India (Nayak *et al.* 1995, Shukla *et al.* 2002; Bansal 2004), but there appears to be no systematic investigations on

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banned cyclodiene organochlorine pesticide residues in ground water in Indo Gangetic plains of India, particularly in Varanasi and its adjoining areas. The dearth of information on the levels of banned pesticide in ground water, a valuable resource of any civilization has prompted the authors to monitor the status of cyclodiene pesticides in ground water, coming mainly through leaching of rain water in Varanasi and adjoining villages.

MATERIALS AND METHODS

The water samples were collected from the wells in Varanasi city and adjoining rural areas of Kashividyapith block of Varanasi district (between 24°43′N to 25°35′N latitude and between 82°11′E to 83°34′E longitude), Uttar Pradesh, India. Location of the sampling are shown as detailed in Figure 1. The water samples were randomly collected on second week of October, 1999 and March, 2000 after south-west (SW) monsoon period (approx. July to September) and north-east (NE) monsoon period (approx. December to February) respectively to obtain maximum possible leaching of pesticides in ground water. According to distribution pattern of rainfall, 80% occur during south west monsoon period. 2.5 litres of water samples from each spot were collected in amber glass bottles, previously cleaned and rinsed with double distilled water and processed within 24 hours in laboratory. Extraction and clean up were curried out according to the method followed by Sarkar *et al.* (1997).

The samples were analysed with a Hewlett Packward 5890A gas chromatograph equipped with a Ni^{63} electron capture detector coupled with a HP 3392A integrator. Instrument parameters and operating conditions for cyclodiene insecticides were as follows : 1.8 m × 2 mm I.D. glass packed with 3% SE 30 W.H.P. (80-100 mesh); oven temperature 140°C for 2 minutes, increased @ 3°C/minute upto 220°C for 10 minutes; injector temperature 200°C; detector temperature 300°C; N_2 flow rate : 70 mL/minute, with ECD. Peaks of the compounds were identified by retention times.

Identification and quantification were accomplished using reference solutions of analytical grade pesticides, supplied by Environmental Protection Agency, USA. 98.7% Aldrin, 99% dieldrin, 99.2% heptachlor, 98.9% heptachlor epoxide and 99% γ-chlordane were used as a external standard. The identification was cross checked with another GLC column packed with OV-101 (3%) on chromosorb W.H.P. (80-120 mesh) through multiresidue analysis. Recoveries of the compounds ranged from 85-92%, but the residue data of the water samples were not adjusted on the basis of these recoveries. Minimum detection limit was 0.01 ng mL^{-1}.

RESULTS AND DISCUSSION

The levels of contamination of various banned cyclodiene pesticides in ground water in rural areas (Fig. 2) of Varanasi are given in Table 1. Although the percentage

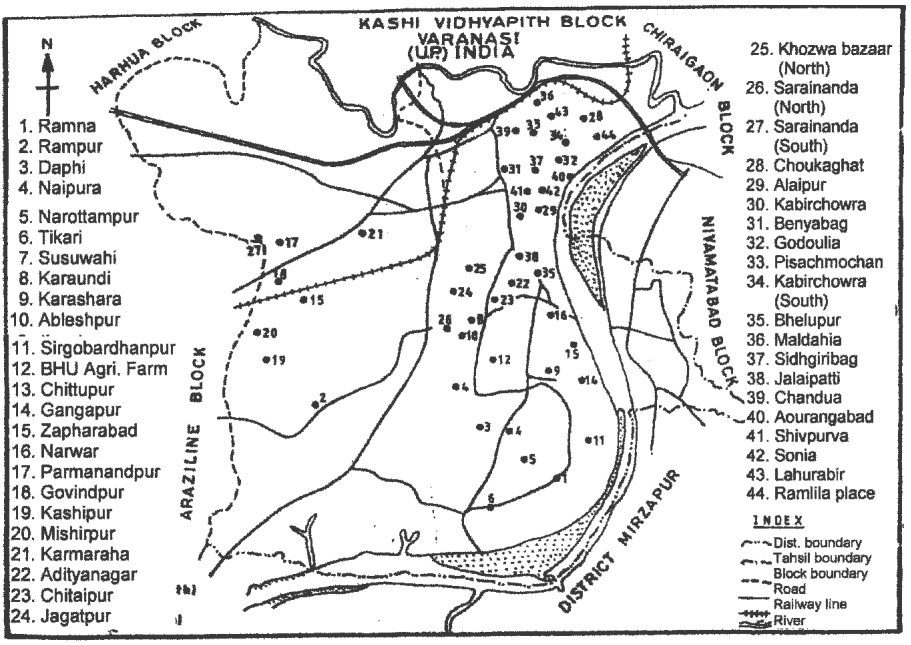

Figure 1. Ground water sampling sites at Varanasi, Uttar Pradesh (U.P.), India.

of locational contamination of aldrin was higher in case of post NE monsoon period (100%), but higher concentration of aldrin in ground water (mean, 3.66 ng mL^{-1}) was detected during post SW monsoon period. The higher amount of aldrin in ground water in rural areas appear to be related to their extensive use in plant protection measure in cereals, vegetables and fruits for the last few decades. Aldrin was similarly detected in sediments from the mouth of almost all the estuaries along the west coast of India (Sarkar *et al.* 1997) and other cyclodienes in river water (Reddy *et al.* 1997).

Table 1. Banned cyclodiene organochlorine pesticide residues in ground water in rural areas of Varanasi.

Period of sample collection (Post monsoon) 24 samples	Banned cyclodiene pesticides					
	Aldrin	Dieldrin	Heptachlor	Heptachlor epoxide	γ-Chlordane	Total (ng mL^{-1})
South West monsoon	3.66 (0.06-20.00) 83.33	0.83 (0.01-20.00) 8.33	0.02 (0.06-0.20) 25.00	0.51 (0.01-4.00) 29.16	2.20 (0.20-10.00) 54.16	7.22
North East monsoon	0.24 (0.05-0.96) 100.00	0.02 (0.01-0.28) 29.16	0.01 (0.01-0.11) 16.66	0.01 (0.04-0.16) 12.50	0.03 (0.02-0.30) 37.50	0.31

Figures show geometric mean in ng mL^{-1}, range in parentheses, percentage occurrence.

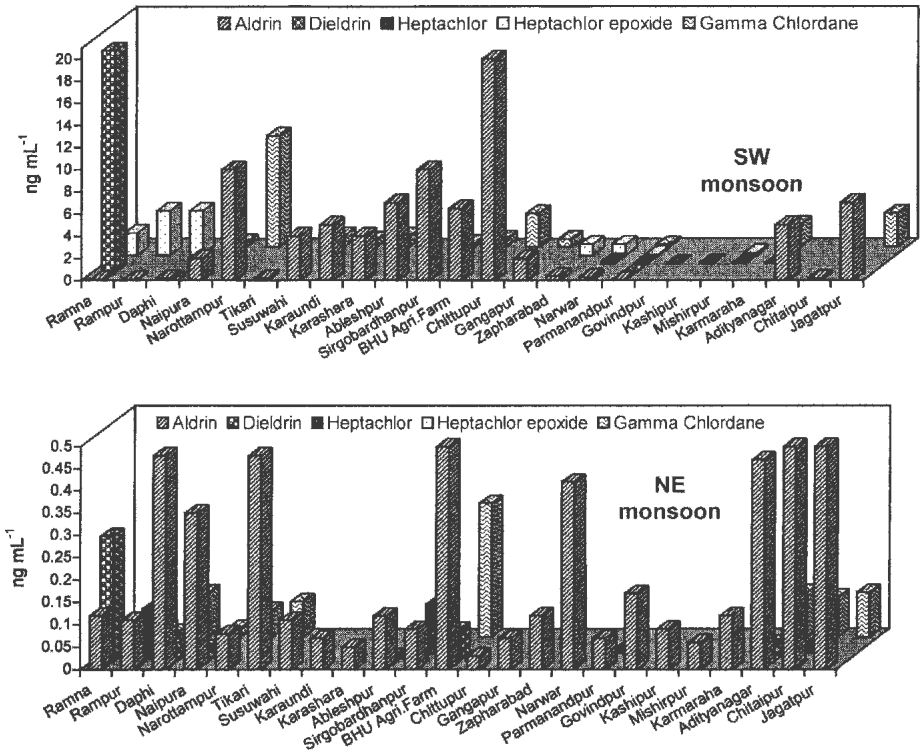

Figure 2. Banned organochlorine cyclodiene pesticide residues in ground water in rural areas of Varanasi.

Considering both the periods of sampling the relative concentration of cyclodiene organochlorine pesticides in ground water were in the following order : aldrin > chlordane > dieldrin > heptachlor and its epoxide. The γ-chlordane was found in a significant amount in 13 ground water samples in SW monsoon samples and 9 samples, collected in NE monsoon period. Relative proportions of aldrin, dieldrin, heptachlor, heptachlor epoxide and γ-chlordane in total banned cyclodiene pesticide concentrations in ground water in the rural areas of Varanasi were 50.7, 11.5, 0.3, 7.0 and 30.5% respectively (Fig. 4) during post SW monsoon and 77.5, 6.5, 3.2, 3.2 and 9.6% (Fig. 4) respectively during post NW monsoon period. Thus, the contribution of aldrin in contamination of banned cyclodiene pesticides was more than 50% followed by chlordane.

The banned organochlorine cyclodiene pesticide residues in ground water collected after SW and NE monsoon period in urban areas of Varanasi (Fig. 3) are given in Table 2. The higher amount of aldrin in ground water in urban area appeared to be related to their extensive use in house hold purpose and plant protection measure in vegetables in kitchen garden as well as public health

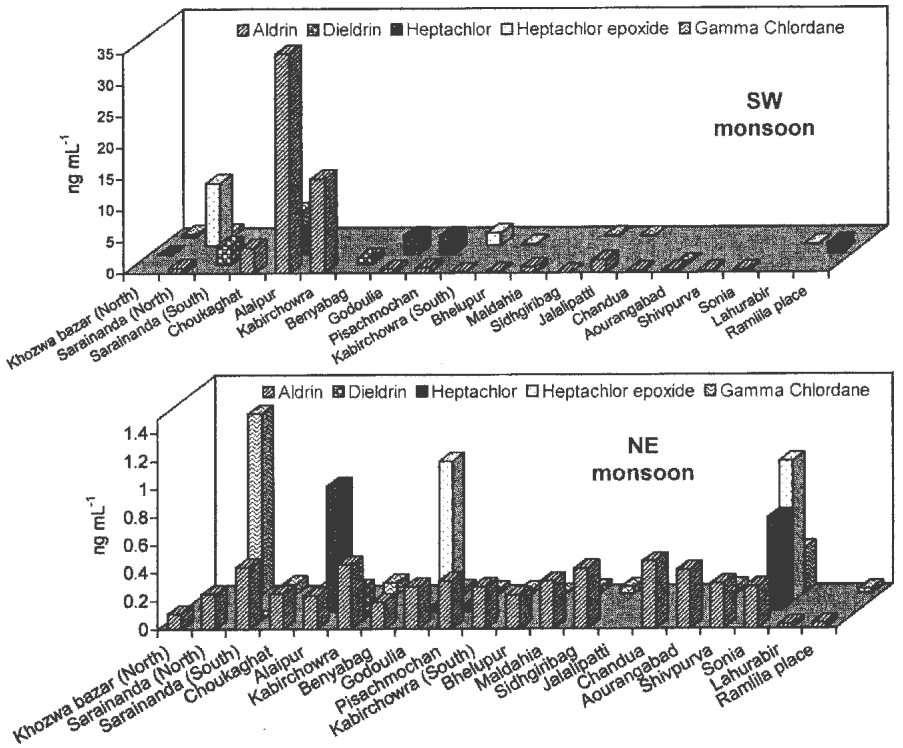

Figure 3. Banned organochlorine cyclodiene pesticide residues in ground water in urban areas of Varanasi.

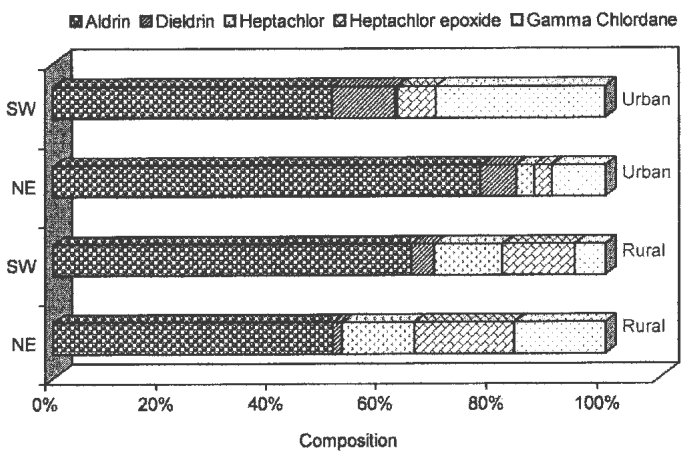

Figure 4. Relative proportions (%) of cyclodiene pesticide residues in ground water in Varanasi.

programme through local municipality. Thus, quite a good number of foreign and national tourists have visited this city throughout the year. For this reason, the local authority of city, the municipality, used the aldrin extensively for quite long period.

All the occurrence of other banned cyclodienes insecticides were confined in some limited sampling locations, but the residues in few places (Fig. 3) were quite high. Considering both periods of sample collection, the relative concentration of cyclodiene organochlorine pesticides in ground water were in the following order: aldrin > heptachlor and its epoxide > γ-chlordane > dieldrin. Relative proportions of aldrin, dieldrin, heptachlor, heptachlor epoxide and γ-chlordane in total banned cyclodiene pesticide concentrations in ground water samples of Varanasi city were 65.0, 4.2, 12.2, 13.1 and 5.5% respectively (Fig. 4) during post SW monsoon and 50.8, 1.7, 13.1, 18.0 and 16.4% respectively (Fig. 4) during post NE monsoon period. Thus, the contribution of aldrin in contamination of banned cyclodiene pesticides in city was more than 50% followed by heptachlor and its epoxide.

Table 2. Banned cyclodiene organochlorine pesticide residues in ground water in urban areas of Varanasi.

Period of sample collection (Post monsoon) 20 samples	Banned cyclodiene pesticides					
	Aldrin	Dieldrin	Heptachlor	Heptachlor epoxide	γ-Chlordane	Total (ng mL^{-1})
South West monsoon	3.04 (0.10-35.00) 75.0	0.20 (0.02-3.00) 15.0	0.57 (0.06-4.00) 25.0	0.61 (0.20-10.00) 20.0	2.26 (0.03-4.00) 25.0	4.68
North East monsoon	0.31 (0.03-0.48) 95.0	0.01 (0.01-0.23) 10.0	0.08 (0.02-0.90) 20.0	0.11 (0.03-1.10) 20.0	0.10 (0.01-1.29) 70.0	0.61

Figures show geometric mean in ng mL^{-1}, range in parentheses, percentage occurrence.

Since, the major portion of annual rainfall in Varanasi occurs in SW monsoon period (80%), the samples during post SW monsoon contained higher amounts of banned cyclodiene pesticide residues, while the post NE monsoon samples had less amount in both rural (approx. 23 fold higher) and urban (approx. 8 fold) areas. This clearly indicates that heavy shower during SW monsoon period leached down the high persistence cyclodiene to the ground water from surface and subsurface soil. According FAO/WHO (1985) the safe limit for aldrin, dieldrin, chlordane, heptachlor and its epoxide in drinking water are 0.003, 0.003, 0.002, 0.004 and 0.002 ng mL^{-1} respectively. The present study indicated that the banned cyclodiene pesticids so far analysed both in rural and urban areas have crossed the FAO/WHO limit of water quality and contamination of these cyclodiene pesticides are in alarming stage for human and livestock consumption and the possibility of their accumulation in food chain can not be ignored. The annual load of banned use cyclodiene pesticides in ground water was 7.53 and 5.29 ng mL^{-1} in rural and urban areas respectively of Varanasi during the period 1999-2000; the ground water in rural areas was 1.4 times more contaminated than urban areas. The contribution of contamination in ground water of Varanasi was more than 50 per cent (50.7-77.5%) through aldrin. Moreover, contamination of total cyclodiene pesticides through leaching of rain water from soil were maximum through south-west monsoon period (95.9% in rural areas and 88.5% in

urban areas). Despite the fact that aldrin, chlordane heptachlor and its epoxide were banned at least 10-15 years ago in India and dieldrin has been recently banned by Govt. of India but they were still present in a very significant amount in ground water.

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