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Agricultural Produce in the Dry Bed of the River Ganga in Kanpur, India—A New Source of Pesticide Contamination in Human Diets*

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Abstract—Vegetables grown in the dry bed field of the River Ganga in Kanpur, an important industrial city of North India, were analysed for the pesticides hexachlorocyclohexane (HCH), dichlorodiphenyl trichloroethane (DDT), their isomers and metabolites at three different sites. Residues of both the pesticides were found in all the samples. Mean levels of 109.35, 136.76 and 145.93 μg HCH/kg and 6.64, 49.3 and 46.70 μg DDT/kg were found in the rural upstream, city and downstream industrial areas, respectively. The mean total HCH and DDT levels were within safe limits as per the Indian Standard but some samples had HCH levels above the WHO/FAO limit. The pesticide residue level in vegetables was several fold higher than their surrounding sandy soil and could pose health problems since these popular vegetables are consumed regularly by the population.

Keywords: vegetables; soil; pesticide; residue; DDT; HCH; dry river bed; biomagnification.

INTRODUCTION

Rivers flowing near cities and industrial areas have turned into big sewer canals. City sewage and industrial wastewater containing many toxic compounds are dumped in the river. Some of the pollutants flow away with the water current and some are deposited slowly in the river bed through out the year. Thus, the river bed is gradually enriched with the pollutants. In summer, farmers cultivate vegetable and fruit crops in the dry river beds. Plants take up these toxic compounds via their roots and they accumulate in the edible portions. Summer vegetable and fruit crops from dry beds contribute to human diets and thus become another source of exposure to these toxic compounds. Kanpur (88°22′E longitude and 26°26′N latitude) is one of the most industrialized cities of the northern India with hundreds of industries (tanneries, textiles, woollens, jute, steel and chemicals) and a large thermal power station (Panki). The River Ganga carries almost all of the city's sewer and effluent water from these industries. As no baseline data were available for such exposure, a survey and collection of vegetable/fruit crops grown in the dry bed of the River Ganga in Kanpur was carried out to assess hazards to the public from such agriculture produce. Soil samples were also collected. Pesticide residues of long half-life organochlorine pesticides such as dichlorodiphenyl trichloroethane (DDT) and hexachlorocyclohexane (HCH) and their isomers and metabolites were estimated.

MATERIALS AND METHODS

Samples of soil and vegetables cultivated in the fields of the dry bed of the River Ganga were collected twice during the summer season (at the beginning and at the end of the season) from the entry point (A), middle point (B) and the exit point (C) of the River Ganga in Kanpur. The entry point was the village Bethore, an old historical and pilgrimage place, about 50 km away from Kanpur

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main city. The middle point was Ganga Ganj, an area at the heart of the city, and Jajmau was the exit point of the river immediately after an industrial area (Fig. 1). Plant samples were collected from different species of vegetable crops available in the fields of the dry river bed. Most of the vegetable crops selected have widespread distribution throughout the country (Table 1). Soil samples were also obtained from the same sites, being collected from the subsurface horizon (2–15 cm) at three different positions and were mixed thoroughly. The composite samples (1000 g) were brought to the laboratory in polythene bags, air-dried and sieved before analysis. The soil of the dry river bed was sandy in nature.

For pesticide analysis of vegetables, representative 100-g samples were cut in small pieces and homogenized in 200 ml solvent mixture of (HPLC grade) *n*-hexane and isopropanol (2:1, v/v) in a waring blender for 2 min at 4000 rpm, filtered and the remains were re-extracted with 75 ml of the same solvent mixture. The two extracts were combined and washed with saturated sodium chloride solution in water (30 ml/100 ml extract) to break the emulsion. The hexane layer was treated with 2 ml conc sulfuric acid (Virirou and Aharondon, 1978). The flasks were allowed to stand for 15 min with occasional shaking. The hexane layer was separated and traces of sulfuric acid were removed by washing with water (equal volume, three times) and the hexane layer was passed through an activated florisil (Fluka, AG, Buchs, Switzerland) column. Thereafter, the *n*-hexane layer was evaporated to dryness and made up to a suitable volume with hexane. The efficiency of extraction ranged from 86.5 to 90.2% in recovery experiments.

Analysis of samples for the quantification of organochlorine pesticides was carried out on gas–liquid chromatograph (Varian Aerograph, series 6000) equipped with an electron capture detector (63-Ni) under the following operational condition.

Column. Glass column (length 6 ft, internal diameter 4 mm) packed with Chromosorb-W 80/100 mesh coated with 1.5% OV-17 + 1.95% OV-210 by weight.

Carrier gas. Nitrogen IOLAR (99.9% Indian Oxygen Ltd, A.R. Grade) passing through silica gel and a molecular sieve to remove moisture and oxygen, respectively.

α, β, γ and δ isomers of HCH and *o,p′*-DDT, *p,p′*-DDT isomers of DDT and *p,p′*-DDE, *p,p′*-DDD metabolites of *p,p′*-DDT were calculated from the chromatogram. Peaks were identified by comparing relative retention time with that of standards (EPA reference standards). Total HCH (ϵ-HCH) and total DDT (ϵ-DDT) were the sum of the

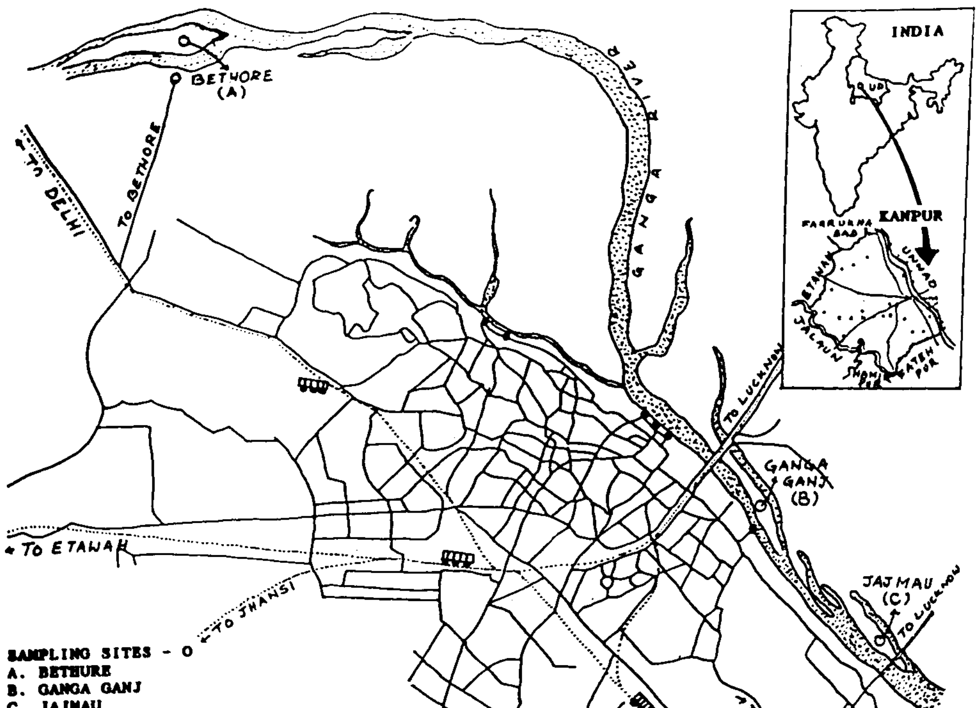

Fig. 1. Map showing location of sampling sites in the dry bed of River Ganga in Kanpur, India.

Table 1. List of vegetable crops with their botanical, common and local names* and number of samples collected from different sites

Vegetable/fruit crops uses	No. of samples A	B	C	Total
Lagenaria siceraria (Bottle gourd, Luoki)	5	5	3	13
Memordica Charantia Linn (Bitter gourd, Karela)	2	2	4	8
Luffa cylindrica Linn (Sponge gourd, Torai)	5	2	4	11
Citrullus varifistulosus (Tinda Punjab, Tinda)	2	NA	3	5
Spinacia oleracea Linn (Garden spinach, palak)	NA	3	1	4
Total number of vegetable samples	(14)	(12)	(15)	(41)
Soil	6	6	6	18

*In parentheses.
NA = not available.

isomers of HCH and DDT, respectively. The residue data of a site was pooled in view of non-availability of different vegetable samples in sufficient numbers. The data was analysed statistically; to calculate, mean, range and standard error. The data of city site (B) and industrial site (C) was compared with the data of village site (A). The significance was calculated by Student's *t*-test (Baily, 1959).

RESULTS

Residues of HCH and DDT and their isomers in vegetables and soils of dry river bed are reported in Table 2. All of the vegetable (41) and soil (18) samples showed the presence of both the HCH and DDT residues although some of the metabolites were not detected. At site "A", the mean HCH level was 109.35 with the range of 28 to 341 μg/kg. γ-HCH was the predominant isomer with about two-thirds quantity followed by α- and β-isomer. Five samples (35%) and the mean level were above the maximum residue limit of 0.1 mg/kg (100 μg/kg) laid down by FAO/WHO (1986). At site "B", the mean value was increased to 136.76 with the range 53 to 446 μg/kg. At this site, both the lower and upper values of the range were higher than site "A". Among the various isomers of HCH, α-HCH was the predominant (approx. 66%) of the total quantity, followed by the γ-HCH isomer. The mean and the residue levels in seven samples (54%) were above the FAO/WHO limit. At site "C", the total HCH content was higher than site "A" and even higher than site "B". The mean value was 145.93, with a range of 36 to 348 μg/kg. The α-HCH isomer was dominant, with making up about 50% of the total HCH followed by γ-HCH isomer. 11 samples (73.3%) were above the FAO/WHO limit. In view of the 3 mg/kg as maximum residue limit of γ-HCH as set by Ministry of Health, Government of India, all the samples had the level within the safe limit (Parmar and Dureja, 1990).

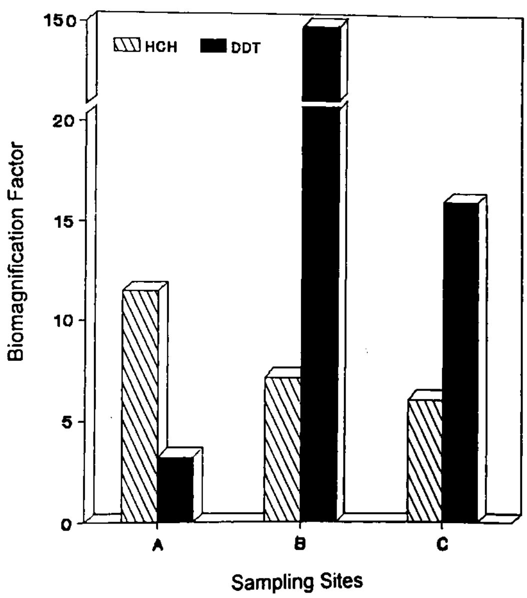

Fig. 2. Biomagnification of pesticides residues in vegetables grown in different sites (A = Bethore, B = Ganga Ganj, C = Jajmau) of dry bed of River Ganga in Kanpur.

Table 2. Pesticides residue and their range† in vegetables crops and soils of dry bed of river Ganga in Kanpur

Site	Pesticide content (μg/kg)									
	HCH					DDT				
	α-HCH	β-HCH	γ-HCH	δ-HCH	ϵ-HCH	*p,p′*-DDE	*p,p′*-DDT	*o,p′*-DDT	*p,p′*-DDD	ϵ-DDT
Vegetables										
A	29.85 ± 7.73 (10-126)	10.71 ± 7.27 (ND*-8)	67.68 ± 20.09 (5-262)	5.57 ± 1.47 (1-23)	109.35 ± 21.61 (28-341)	3.00 ± 1.96 (ND-28)	2.36 ± 0.77 (ND-9)	0.97 ± 0.92 (ND-13)	1.07 ± 0.73 (ND-8)	6.64 ± 2.76 (ND-40)
B	82.77 ± 38.75 (11-416)	3.54 ± 1.01 (ND-11)	45.77 ± 12.69 (5-124)	8.15 ± 3.04 (ND-38)	136.76 ± 38.56 (53-446)	18.92 ± 9.26 (ND-107)	19.83 ± 11.92 (ND-151)	2.65 ± 1.14 (ND-12)	4.15 ± 3.13 (ND-41)	49.3 ± 24.50 (2-311)
C	71.93 ± 18.58 (14-251)	6.96 ± 3.38 (ND-38)	47.33 ± 13.66 (6-184)	18.20 ± 5.74 (2-66)	145.93 ± 22.27 (36-348)	19.70 ± 11.33 (ND-88)	10.06 ± 3.18 (ND-81)	8.82 ± 8.68 (ND-87)	6.20 ± 5.65 (ND-56)	46.70 ± 30.56 (ND-312)
Soil										
A	2.20 ± 0.47 (1.0-3.6)	3.33 ± 1.11 (ND*-6)	3.63 ± 0.55 (2-5)	0.87 ± 0.06 (0.7-1.0)	9.53 ± 0.69 (8.0-11.7)	0.1 ± 0.06 (ND-0.3)	0.66 ± 0.42 (ND-2.0)	ND ND	1.26 ± 0.23 (0.9-2.0)	2.06 ± 0.43 (0.9-3.2)
B	1.80 ± 0.35 (0.8-2.7)	5.73 ± 3.56 (ND-17.0)	10.23 ± 3.35 (0.7-19.0)	1.33 ± 0.42 (ND-2.0)	19.10 ± 1.69[b] (14.0-23.70)	ND ND	ND ND	ND ND	0.33 ± 0.21 (ND-1.0)	0.33 ± 0.21[a] (ND-1.0)
C	1.87 ± 0.06 (1.7-2.0)	17.60 ± 4.82 (9.0-32.8)	1.43 ± 0.50 (0.4-3.0)	1.93 ± 0.40 (0.8-3.0)	23.83 ± 4.76[a] (14.4-38.5)	0.06 ± 0.04 (ND-2.0)	0.66 ± 0.21 (ND-1.0)	0.50 ± 0.16 (ND-0.8)	1.66 ± 0.55 (ND-3.0)	2.90 ± 0.41 (1.7-4.0)

†In parentheses.
*ND = not detectable.
The values are the mean ± SE. Number of vegetable samples at site "A" = 14, at site "B" = 12, at site "C" = 15. There were six soil samples at each site. Significance [a] = $P < 0.1$; [b] = $P < 0.05$ (Student's *t*-test).

The mean DDT residue level in vegetables of the dry bed of the River Ganga in Kanpur at site "A" was 6.64, with a range of non-detectable (ND) to 40 μg/kg. Among the various isomers, *p,p′*-DDE and *p,p′*-DDT were predominant. Both *o,p′*-DDT and *p,p′*-DDD were also present in good quantities. At site "B", the total DDT content in vegetable increased several fold with respect to site "A", the mean value being 49.30 with a range of 2 to 311 μg/kg. Among the various isomers, *p,p′*-DDE and *p,p′*-DDT account for more than 60% of the total quantity. *o,p′*-DDT and *p,p′*-DDD were also present in significant quantities. At site "C", the mean DDT residue level was 46.40 with a range of ND to 312 μg/kg. This was slightly less than site "B", and the *p,p′*-DDE level was nearly half of the total DDT residue. The DDT isomers and *p,p′*-DDD were also present.

The mean HCH level in soil at site "A" was 9.53, with a range of 8.0 to 11.7 μg/kg. The main isomers were α, β and γ-HCH. At site "B", the average value was 19.10 μg/kg with a range of 14.0 to 23.70 μg/kg—significantly higher than at site "A". The increase in HCH value was due to increase in β, γ and δ isomers. At site "C", the mean residue value was 23. 83 with a range of 14.4 to 38.5 μg/kg, even higher than the Ganga Ganj site. The HCH was mainly in the form of β-isomer.

The total DDT levels in the same soil samples were much lower than the HCH level. At site "A", mean total DDT residue level was 2.06 with a range of 0.9 to 3.2 μg/kg. The main contributor was *p,p′*-DDD. At site "B", only *p,p′*-DDD was found. At site "C" the mean total DDT residue level was 2.90 μg/kg with a range of 1.7 to 4.0 μg/kg. The main compound found was *p,p′*-DDD, although *o,p′*-DDT and *p,p′*-DDT were also present in good quantities.

The biomagnification factor as reported in Fig. 2 showed that the mean HCH content in plants increased by 11.42, 7.16 and 6.12 times at site "A", "B" and "C", respectively over their surrounding soil, whereas the increase in DDT level was 3.22, 149.42 and 16.0 times at the same sites. The highest accumulation of DDT from soil to vegetable material was at sites "B" followed by site "C" and "A".

DISCUSSION

Food contamination surveys have been conducted in India since 1960. The results of the earlier surveys reviewed by Kalra and Chawla (1981a,b) indicated the predominance of DDT and HCH in produce. DDT and HCH were found in 89% of the vegetables collected in Delhi during 1984–86 (Lal *et al.*, 1989). Average concentrations in vegetables ranged from 0.01 to 0.70 μg/g for DDT, and from 0.01 to 0.32 μg/g for HCH. Concentrations of DDT and HCH in vegetables and fruits collected in Uttar

Pradesh in 1983 were less than 0.06 μg/g (Kaphalia *et al*., 1990). Periodic monitoring of market vegetable samples in Bangalore (India) showed widespread contamination with isomers of HCH and traces of DDT metabolites. However, the levels were within the safe limits prescribed by the Ministry of Health, Government of India (Awasthi and Ahuja, 1997). The data presented in Table 2 showed HCH residues varying from 28 to 446 μg/kg at all the sites. Site "C" was the area where the highest HCH concentrations were recorded; this may be due to industrial effluent wastewater. High HCH concentrations found at site "B" may be due to run-off of city sewage water where organochlorine insecticides are used in public health programmes. Lindane is still used mostly extensively for human disease vector control because of its high insecticidal property and long-lasting effects. In India, even though agricultural use is being phased out, the annual production of lindane in 1996–97 was 40 MT with a forecost of 50 MT in 1997–98 (Mathur, 1998). Although the use of DDT has been banned in almost all the developing countries owing to its enduring persistance, it is still used in limited quantities in agriculture, forestry and public health because of its low cost, and this is responsible for the presence of residues in soil and plants. A survey carried out in Punjab indicated traces to less than 1.0 ppm DDT in soil (Anonymous, 1979).

Distribution of HCH and DDT and their isomers in a selected group of Indian foodstuffs was reported by Kannan *et al*. (1992). α-HCH dominated in all products; in the case of DDT, *p,p′*-DDT was the major constituent. In the present study, α-HCH and γ-HCH isomers were found in vegetables, whereas β-HCH and γ-HCH dominated in soil samples. *p,p′*-DDE and *p,p′*-DDT were the main DDT components found in vegetables.

The mean levels of ϵ-HCH and ϵ-DDT in vegetables were much higher in the city and industrial areas in comparison to the village area. The pesticide residue levels in vegetables was several fold higher than in the surrounding soil. The mean residue levels were above the maximum residue limit of 0.1 mg/kg (100 μg/kg) for γ-HCH and 1.0 ppm (1000 μg/kg) for DDT (FAO/WHO, 1986). Several vegetable samples showed much higher values. Moreover, α-HCH, the major isomer in vegetable samples, is a known carcinogen and a non-insecticidal component of technical HCH (Ito *et al*., 1973). Uptake of residual HCH from soil into crops and migration to the edible parts could lead to cumulative toxic effects in the consumer. Contamination of edible portions by soil contact is unlikely since the samples were washed thoroughly before analysis, but lipid-rich tissues can take up from soil also. Studies conducted at ITRC under the Central Ganga Action Plan over 6 years have shown that the water and sediment at Kanpur continued to build up organochlorine residues (Ray, 1993). Agricultural run-off, domestic effluents and settling of aerosols could account for this, in particular some of the agrochemicals which are used for decreasing vector control.

The dry river bed production is limited and not even adequate for local consumption. However, the study signifies the importance of dry river bed farming in relation to consumers health wherever it is used for agricultural production. These areas should be under surveillance and monitored routinely for chemical contaminants.

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