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Comparison of Organochlorine Pesticide Levels in Soil and Groundwater of Agra, India

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Organochlorine pesticides (OCPs) have been dispersed ubiquitously in the environment (Yi-Fan Li et al., 1996). When applied on a field, they can meet a variety of fates : some may be lost to the atmosphere through volatilization and transported long distances from their sites of application; others are carried away by surface runoff or photodegraded by sunlight. When entering into the soil, pesticides may be taken up by plants or degraded; but they may also be transported through the unsaturated zone to groundwaters or via drains, reach surface water bodies. Consequently, considerable levels of OCPs have been detected in different components of human environment such as air, water, soil, plants and animals (Patton et al. 1991, Kolpin et al. 1996, Miglioranza et al. 1999). Differences in physicochemical properties of insecticides (K_{OC}, half-life, etc.) and that of soil system (amounts and types of clay materials, hydrous oxides and organic matter, redox status and pH), climate, and biology can highly affect the eventual fate of a pesticide in the soil environment (Cheng 1990).

Several types of invertebrates in the soil. Beetles are considered beneficial arthropods in agriculture because they are natural enemies of cereal pests and they represent a food source for species at other trophic levels. Arthropods and earthworms contribute with their burrowing activities to maintain soil fertility. These organisms (non-target) as well as insect pests (target) can bioconcentrate OCPs from soils in these tissues due to their basic physiological similarities (Huusela-Veistola 1996). This accumulation limits the growth rate and maintains the population of most invertebrates (target & non-target) at low densities. Also, it might imply a risk for many vertebrate species feeding on these invertebrates. Furthermore, soil pollutants can be taken up by plants by partitioning to the root and translocation to the plant through xylem that can be passed through the food chains (via herbivores, omnivores and carnivores) to humans (Simonich and Hites 1995, Trapp and Matthies 1995).

Pesticides reach aquatic or soil ecosystems by direct application, spray drift, aerial spraying, erosion and run off from agricultural land, by discharging of effluents from factories and sewage. OCPs are now less widely used than previously because of a number of disadvantages including environmental persistence, bioaccumulation and their toxic action upon the nervous systems (Hellwell 1988). Also their entry into an ecosystem adversely affects many non-target organisms including fish and birds (Ayas et al. 1996). Their effects may be acute, resulting in mass mortality or chronic, involving changes in survival growth and reproduction (Kocan and Landolt 1989). They and their degradation products are more toxic for animals (Barlas 1997), and play important role in the population declines of waterbirds (Fox et al. 1991). Usage of OCPs have been prohibited in most of countries, but 70% of banned pesticides are still used in India because of their low cost. In India

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DDT was banned for use in agriculture in 1985, but still 7500 metric tons per year is used here.

The present work was carried out to determine some organochlorine pesticide residues in soil and groundwater samples from Agra.

MATERIALS AND METHODS

The present study covers the entire urban and suburban region of Agra city (27°10' N and 78°5' E, 120 km^2, 1.5 million population). After the initial survey of the city and nearby agricultural fields, 15 stations were selected for collecting soil and groundwater samples. The sampling stations were classified as agricultural, nursery, gardening and landfills areas, the first three use OCPs directly for growing wheat, gram, linseed, mustard, potato, flowers & fruits, but the landfills receive them with solid wastes and agricultural runoffs.

The soil samples from middle horizon (15-30 cm) were taken in zig-zag along different sections of the area until the whole area was covered. A representative composite sample from agricultural was made up of 10 sub-samples from a uniform field, for Shahadra landfill (30 acres solid wastes being filled for 30 years) 15 sub-samples and for other landfills 5 sub-samples were taken with a soil auger after cleaning ground lightly with wooden pestle in a wooden mortar. The composite sample was spread to be air dried and extraneous materials such as leaves, twigs, rocks, etc. were removed. The whole of composite sample was spread in a uniform way and went on quartering and taking diagonal quarters rejecting the other two till approximately 600 g soil sample was obtained. The sample was filtered through a 2-mm plastic sieve. About 0.5 kg filtered soil sample was stored in a clean polythene bag with proper labelling for analysis. In all 105 soil samples were analyzed.

Groundwater samples were collected from tube wells at eight different locations amidst and around each site in the study area. Tube wells were selected away from the dwelling units in such a way as to represent the entire site used for a particular activity. The distance between any two tube wells chosen for study was at least 0.8 km. In all 75 samples were analyzed.

Soil samples were thawed and mixed. Approximately 15 g of the wet soil was mixed with anhydrous granular sodium sulfate and soxhlet extracted with dichloromethane overnight in precleaned cellulose thimbles. Extracts were reduced and transferred into 1-2 mL isooctane by rotary evaporation and blown down with a gentle stream of nitrogen. Samples were cleaned up using 2 g of alumina (6 % added water) capped with sodium sulfate and eluted with 20 mL of 5 % dichloromethane/petroleum ether. The cleaned extracts were reduced, and the solvent was exchanged into isooctane by nitrogen blowdown, given further cleanup by shaking with 0.5 mL of 18 M sulfuric acid (omitted for dieldrin), and adjusted to a volume of 2 mL for analysis.

One litre of groundwater sample was collected in a precleaned glass bottle with teflon lined caps from the each wells. Samples were kept under refrigeration until analysis. All analyses on a sample were completed within one week of sampling. 500 mL of water sample was taken in 1-litre separatory funnel and 10 g NaCl was added to it. The funnel was shaken to dissolve NaCl completely. Then 50 mL of 15 % dichloromethane in n-hexane was added and the funnel was shaken vigorously for 2-3 minutes with intermittent pressure release. The separatory funnel was kept undisturbed to separate the two layers. The lower aqueous layer was drawn into 1-litre separatory funnel. The process of partitioning was reported two more times using fresh 50-mL portions of 15 % dichloromethane in n-hexane. The 3 extracts were combined and dried by passing through an adsorbent (2.5 cm ID and 15 cm long) containing 5-cm layer of anhydrous Na_2SO_4 over a small pad of glass wool at the bottom. The extracts were concentrated to about 0.5 mL with Kuderna Danish evaporator containing a 3 ball Suyder column. 3 mL of n-hexane was added to the combined extract and concentrated to 0.5 mL again. The process was repeated one more time to remove the final traces of dichloromethane. The residues were finally taken up in n-hexane for GLC analysis.

Organochlorine pesticides were analyzed with a chromatograph equipped with a HP PC, a capillary column HP 101 (25 m × 0.2 mm i.d. × 0.2 μm film thickness) with splitting ratio 1 : 100, an autosampler and a Ni electron capture detector (^{63}Ni). The operating parameters were : Carrier gas nitrogen with flow rate 1 mL/min, operating temperatures – injection port 250°C, column 195°C and detector 300°C. The OCPs were quantified by comparing the samples chromatograms with standards obtained from Alltech Sigma.

RESULTS AND DISCUSSION

OCPs were the first synthetic insecticides to be developed and of these DDT and BHC are probably the best known. Their advent in 1940s revolutionized global agriculture and it was thought that the war with the insects was over once for all. But, as per United States National Research Council and FAO experts, over 650 species of weeds, insects and fungi have become resistant. 17 of insects have assumed the status of 'super bugs' and are immune to all poisons. Therefore every year the requirement of pesticides in India increases by 20-25 %. Andhra Pradesh tops list with 33.6 % followed by Karnataka at 16.2 % and Gujrat 15.0 %. The widespread and sometimes indiscriminate use of OCPs to destroy disease vectors and to protect crops leads to what proved to be serious environment problems.

Technical BHC is largely comprised of 55-70 % α, 5-14 % β, 10-13 % γ, 6-8 % δ and 3-4 % ε forms. γ-BHC is a very strong insecticides and is called gammaxene, gammane, lindane or 666. Here BHC refers the sum of mainly α, β & γ forms and is better indicated in Table 1 & 2 by Σ BHC. BHC residues were deleted at almost all locations obviously due to its regular use. Alfa was the predominant isomer, followed by gamma and beta isomers. The beta isomer invariably had the lowest concentration. However, it was more than its normal percentage in technical BHC, indicating its accumulation in the environment. γ-BHC concentrations were well below the limit (3000 ng/l) specified by the WHO for drinking water quality. Although there is no specified limit for β-HCH, accumulation of this carcinogenic isomer is a cause for concern. The mean total HCH concentration was, however, less than that found in earlier reports on groundwater from urban areas.

In general, insecticide adsorption to the soil or sediment was inversely related to the water solubility of that compound. For example, DDT has very low solubility, thereby being more strongly adsorbed than dieldrin. The greater the water solubility, the greater is the mobility. For instance, lindane, which has a high solubility, is more mobile than many other OCPs. Also, endrin, aldrin and dieldrin are slightly more mobile than DDT as they are more soluble than DDT. Due to more solubility of BHC, it was expected to be much higher than DDT in groundwater, but concentrations of DDT residues were higher than those of other pesticides analysed in the groundwater samples.

Technical DDT is largely comprised of *p,p'*-DDT (~80%), but also of *o,p'*-DDT (~15%) (Buffin 1998), and is slowly decomposed to the main metabolites – *p,p'*-DDE and *p,p'*-DDD. In the soil samples Σ DDT ranging from ND-1.82 mg/kg, *p,p'*-DDT

Table 1. Average in mg/kg dry soil of organochlorine pesticide residues in soil samples of Agra

Areas*	No. of Samples	Σ BHC	Σ DDT	Endosulfan	Dieldrin	Aldrin	Heptachlor
Dayalbagh	15	0.21	1.31	ND	0.66	0.23	0.69
Sikandara	15	0.29	1.22	ND	0.58	0.18	0.73
Kitham	10	0.32	0.61	ND	0.71	0.12	0.10
Panwari	15	0.16	0.42	ND	0.75	0.24	ND
Mau	10	0.82	0.47	ND	0.56	0.28	0.07
Malpura	10	0.36	0.92	ND	0.98	0.40	ND
Tehribagia	15	0.39	1.35	0.02	1.23	0.52	0.17
Cantt.	12	1.23	1.03	0.02	1.12	0.10	0.25
Dhanoli	13	0.61	0.72	0.05	0.61	0.22	ND
Rambagh	18	0.63	1.78	0.08	1.34	0.29	0.32
St. John's	8	0.19	0.75	ND	0.25	0.09	ND
MLN Park	9	0.27	0.32	ND	0.58	0.52	ND
Shahadra	12	1.02	1.58	0.16	1.39	0.68	0.38
Shahganj	8	0.57	0.86	0.06	0.96	0.65	0.36
Lohamandi	5	0.46	0.67	0.06	0.93	0.72	0.41

Table 2. Average in ng/l of organochlorine pesticide residues in groundwater samples of Agra

Areas*	No. of Samples	Σ BHC	Σ DDT	Endosulfan	Dieldrin	Aldrin	Heptachlor
Dayalbagh	12	132	302	15	181	43	92
Sikandara	10	212	331	8	156	40	112
Kitham	8	161	259	ND	186	22	13
Panwari	10	46	202	ND	251	40	ND
Mau	5	681	204	ND	106	62	8
Malpura	8	153	252	ND	301	74	ND
Tehribagia	10	302	603	12	407	81	11
Cantt.	8	733	577	20	321	12	23
Dhanoli	10	321	309	16	142	22	ND
Rambagh	12	292	401	25	471	25	41
St. John's	5	143	212	ND	91	15	ND
MLN Park	7	201	218	ND	151	71	ND
Shahadra	10	702	812	56	412	104	46
Shahganj	5	506	686	11	382	102	42
Lohamandi	5	286	381	21	259	86	53

ND = Not detectable

**Areas Dayalbagh to Dhanoli are agricultural, Rambagh is nursery, St. John.s & MLN Park are gardening and Shahadra to Lohamandi are landfills areas.*

Table 3. Frequency, Mean, Standard deviation of the organochlorine pesticide residues in soil (mg/kg) & in groundwater (ng/l) samples of Agra

Parameter	Soil			Groundwater		
	Frequency	Mean ± SD*	Average	Frequency	Mean ± SD	Average
Σ BHC	94.8%	0.50 ± 0.31	0.50	89.6%	310.25 ± 212.18	324.73
Σ DDT	97.7%	1.01 ± 0.45	0.93	97.6%	389.21 ± 186.10	383.27
Endosulfan	60.0%	0.03 ± 0.04	0.03	43.2%	13.76 ± 15.11	12.27
Aldrin	98.3%	0.87 ± 0.32	0.84	96.0%	265.72 ± 120.21	254.47
Dieldrin	93.1%	0.33 ± 0.19	0.35	78.4%	50.82 ± 29.24	53.13
Heptachlor	63.4%	0.25 ± 0.25	0.23	54.4%	32.71 ± 36.28	29.40

**Standard deviation*

was dominant component of the DDT family, accounted for an average of 48% of Σ DDT, whereas *p,p'*-DDE and *p,p'*-DDD accounted for an average of 28% and 33% respectively. However, in the groundwater *p,p'*-DDE was 50% of Σ DDT whereas *p,p'*-DDD and *p,p'*-DDT constituted 10% and 40% respectively. The DDT residues were detected at almost all the locations. At many places DDT concentration was quite high and even exceeded the WHO limit (100 ng/l).

Endosulfan residues were detected at many locations throughout the year. α-Endosulfan was found in higher concentrations than its β-form. Endosulfan sulfate was not detected in any sample.

Aldrin was detected in almost all the samples. Its concentrations were very much higher than that of dieldrin. The aldrin residues in groundwater were found to exceed the WHO limit (30 ng/l) by many times for drinking water.

Heptachlor was found at only few locations and no regular trend was noticed with respect to its concentration in groundwater samples.

The high concentrations of pesticides are obviously due to their extensive use in agricultural. It is estimated that 20,000 kg of pesticides is used in the region per annum of which organochlorines comprise more than 60%. The major crops grown in the area are potato, wheat and vegetables. The use of aldrin as antitermite agent in potato crop could account for such high concentration of aldrin in groundwater. Although DDT is banned for use in agricultural, it continues to be used for public health. Despite ban some farmers still use DDT because of its low cost. This has resulted in a high concentration of DDT in groundwater. In addition the Yamuna river is also an important source of pesticide pollution of soil and groundwater because the Yamuna water is heavily burdened with pesticide residues. According to the Central Pollution Control Board the Yamuna water at Agra contains 1733.2 ng/l of BHC & 1802.58 ng/l of DDT.

A large amount of water is pumped out from the tubewells during each cropping season. When water evaporates, non-degradable pesticides remain on the surface. With rains they get incorporated into the subsoil and eventually infiltrate into the groundwater. Although most organochlorine pesticides are sparingly soluble in water, they leach to the lower soil profiles under the influence of water moving towards the sub-soil. The rapid leaching of pesticides may be attributed to the texture of the soil which is either silt, loam or sandy loam with the organic matter content as low as 0.5%.

The wells with pesticide residues detected did not cluster together in a single geographic region of the city. This indicates that the pesticides found may not have a single large scale source of contamination of the groundwater. The region is having multiple aquifers. The unsaturated zone and shallow aquifers are 20-30 meters deep mostly composed of silty or sandy loam and are more contaminated than deeper aquifers. Some of the wells contaminated with pesticides were drilled into bedrock and most wells were 5-10 years old. The bedrock in this area is a fractured metamorphic rock. Several hypotheses for the source of these pesticides may be advanced. There could be faults in the well parapets allowing surface water into the wells. There could be large fractures in the bedrock which result in relatively fast flow of groundwater and recharge from surface. It is also possible that the long term usage of these pesticides has allowed the pesticides to leach into the groundwater source despite their unfavourable physical characteristics. The scope of this study did not allow us to determine the mechanism by which these wells are being contaminated.

These results show the presence of pesticides in groundwater wells from a residential areas around agricultural, horticultural, waste disposal and roadside sites. Although only a small percentage of the wells were found to have pesticides residues, and the concentrations found below levels of concern, these findings do indicate that pesticides can potentially contaminate the groundwater used by home owners. To illuminate fully the scope of the contamination, further research is necessary. Firstly, a more widespread region wide set of samples would allow us to determine how typical these results are for a community. Secondly, a smaller subset of wells should be monitored on a regular basis. This would allow us to determine if there is a seasonal aspect to the pesticide occurrences. In any case, this research shows the potential for contamination of drinking water and therefore supports the idea to reduce pesticide use when possible.

It is concluded from this work that the level of OCPs in Agra soil and groundwater is relatively high and is expected to be much higher in food chains including plants, predators and humans. The illegal use of OCPs must be immediately stopped. The level of contamination should be regularly monitored at different levels and appropriate measures, must be taken to control pesticide in Agra.

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