Jr. of Industrial Pollution Control 29(1)(2013) pp 19-24

www.envirobiotechjournals.com

COMPARISON OF ORGANOCHLORINE PESTICIDES LEVELS IN SOIL AND GROUNDWATER OF AGRA, U.P., INDIA

N. GUPTA [1], V. GUPTA [2], B.S. CHAUHAN [3] AND R.P.SINGH [2]

[1] Faculty of Engineering & Technology, R.B. S. Engineering Technical Campus, Bichpuri, Agra 283 105, U.P., India
[2] School of Chemical Sciences, St. John's College, Agra, U.P., India
[3] Noida Institute of Engineering & Technology, Noida, U.P., India

Key words : Organochlorine pesticides, Aldrin, BHC, Dieldrin, DDT and endrin.

(Received 9 June, 2012; accepted 6 July, 2012)

ABSTRACT

One seventy five soil and one twenty six groundwater samples collected from agricultural, garden, nursery and waste disposal sites were analyzed for organochlorine pesticides (OCPs) to investigate their occurrence, severity and sources, and to compare their levels in soil and groundwater. Soil and groundwater samples were collected from the middle horizon 15-30 cm and tube wells respectively. OCPs determined and comparised BHC, DDT, endosulfan, aldrin, dieldrin & heptachlor and chlordane. Depending on physical and chemical characteristics of OCPs different behaviors were found. In soil DDT had higher concentrations than that of BHC but in groundwater BHC exceeded DDT. In the present case soil is poor in organic matter so DDT metabolites being more stable than BHC could leach down to lower horizons richer in class and aquifers while more soluble BHC and DDT. Biodegradable BHC remained in the upper horizons, retained by organic matter. Aldrin levels were much higher than that of dieldrin both in soil and groundwater samples. Heptachlor was found at only few locations and chlordane was not detected. Further characterization of OCPs in soils and their aged signatures would be useful as to predict their levels on a regimal scale.

INTRODUCTION

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 photo-degraded 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 ground-waters 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,

* **Corresponding authors email :** namrata_g28@ymail.com; (Dr. Namrata Gupta)

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.* 1997). 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 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 fro collecting soil and groundwater samples. The sampling stations were classified as agricultural, nursery, gardening and landfill areas, the first three use OCPs directly for frowning wheat, gram, linseed, mustard, potato, flowers and fruits, but the landfills receive them with solid wastes and agricultural runoffs.

The representing 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 labeling 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 pre-cleaned 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 pre-cleaned 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 one 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 x 0.2 mm i.d. x 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 Gujarat 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. BHC residues were deleted at almost all locations obviously due to its regular use. BHC 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. The results of analysis are given in Table 1 and Table 2. Technical DDT is largely comprised of ρ,ρ'-DDT (~80%), but also of o,p'-DDT (~15%) (Buffin 1998) and is slowly decomposed to the main metabolites -ρ,ρ'-DDE and ρ,ρ'-DDD. In the soil samples ∑DDT ranging from ND-1.82mg/kg, ρ ρ'-DDT was dominant component of the DDT family, accounted for an average of 48% of ∑DDT, whereas ρ,ρ'-DDE and ρ,ρ'-DDD accounted for an average of 28% and 33% respectively. However, in the groundwater ρ,ρ'-DDE was 50% of ∑DDT whereas ρ,ρ'-DDE and ρ,ρ'-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 ?-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 anti-termite 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 and 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 of the 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 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 unfavorable 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.

ACKNOWLEDGEMENTS

We sincerely thanks Dr. A. P. Singh, Director, Faculty of Engineering & Technology, Raja Balwant Singh

Table 1. Range and mean in mg/kg dry soil of organochlorine pesticide residues in soil samples of Agra

Areas	Type of Locations	No. of Samples	ε BHC	ε DDT	Endosulfan	Dieldrin	Aldrin	Heptachlor
Dayalbagh	Agricultural	15	ND-0.31	ND-1.80	ND-0.01	ND-0.30	0.30-0.84	ND-0.98
Sikandara	,,	15	0.21-0.41	0.46-1.81	ND-0.03	ND-0.30	0.20-0.70	ND-1.20
Kitham	,,	10	ND-0.45	0.21-0.83	ND	0.08-0.20	0.10-0.90	ND-0.23
Panwari	,,	15	ND-0.25	ND-0.53	ND	0.03-0.32	0.20-0.94	ND
Mau	,,	10	ND-1.30	0.31-0.63	ND	0.02-0.42	0.23-0.73	ND-0.12
Malpura	,,	10	0.31-0.42	0.41-1.23	ND	0.01-0.52	0.43-1.32	ND
Tehribagia	,,	15	0.21-0.56	0.31-1.80	ND-0.05	0.12-0.71	0.50-2.00	0.11-0.22
Cantt.	,,	12	ND-1.90	0.61-1.62	ND-0.06	0.09-0.12	0.60-1.98	0.12-0.33
Dhanoli	,,	13	ND-0.89	ND-0.92	ND-0.08	ND-0.31	ND-0.89	ND
Rambagh	Nursery	18	0.41-0.88	0.90-3.20	0.03-0.10	0.02-0.14	0.98-2.10	0.13-0.44
St. John's	Gardening	8	ND-0.32	ND-0.94	ND	0.02-0.14	0.18-0.32	ND
MLN Park	,,	9	0.21-0.42	0.12-0.52	ND	ND-0.72	ND-0.82	ND
Shahadra	Landfill	12	0.55-1.62	0.49-1.82	0.08-0.23	0.05-0.92	0.92-2.30	0.24-0.53
Shahganj	,,	8	0.49-0.99	0.32-1.02	0.04-0.08	0.22-0.81	0.82-1.23	0.22-0.43
Lohamandi	,,	5	ND-0.62	0.11-0.92	0.55-0.09	0.21-0.92	0.53-1.29	0.23-0.52

Table 2. Range and mean in ng/l of organochlorine pesticide residues in groundwater samples of Agra

Areas	Type of Locations	No. of Samples	??BHC	??DDT	Endosulfan	Dieldrin	Aldrin	Heptachlor
Dayalbagh	Agricultural	12	63-203	ND-732	ND-36	ND-92	48-330	ND-184
Sikandara	,,	10	42-302	54-836	ND-19	ND-81	21-280	ND-206
Kitham	,,	8	ND-289	48-638	ND	ND-49	12-363	ND-34
Panwari	,,	10	ND-102	28-492	ND	ND-63	22-412	ND
Mau	,,	5	76-876	36-430	ND	ND-95	26-285	ND-14
Malpura	,,	8	112-231	42-696	ND	ND-119	44-631	ND
Tehribagia	,,	10	85-429	46-932	ND-28	ND-122	63-718	ND-26
Cantt.	,,	8	99-1299	38-867	ND-42	ND-24	81-708	ND-70
Dhanoli	,,	10	ND-632	62-502	ND-32	ND-62	ND-338	ND
Rambagh	Nursery	12	42-603	76-857	ND-46	ND-76	122-743	ND-84
St. John's	Gardening	5	ND-186	ND-339	ND	ND-36	ND-189	ND
MLN Park	,,	7	69-322	35-386	ND	ND-140	ND-326	ND
Shahadra	Landfill	10	112-1191	64-1232	28-104	12-282	251-783	11-92
Shahganj	,,	5	72-826	31-921	8-26	10-178	213-611	08-83
Lohamandi	,,	5	46-588	26-644	ND-45	ND-177	46-623	ND-98

ND= Not detected

Table 3. Frequency, mean, standard deviation & average of the organochlorine pesticide residues in soil (mg/kg) & in groundwater (ng/L) samples of Agra

Parameter	Frequency	Soil Mean ± SD	Average	Frequency	Groundwater Mean ± SD	Average
∑ BHC	94.8%	0.50 ± 0.31	0.50	89.6%	310.25 ± 212.18	324.73
∑ 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

College, Bichpuri, Agra to provide basic requirement to carry on the research work.

REFERENCES

Ayas, Z., Barlas, N. and Kolankaya, D. 1997. Determination of organochlorine pesticide residues in various environments and organisms in Goksu Delta, Turkiye. *Aquatic Toxicol.* 39 : 171-181

Barlas, N.E. 1997. Toxicological assessment of biodegraded malathion in albino mice. *Bull. Environ Contam Toxicol.* 57 : 705-712

Buffin, D. 1988. Fact sheet DDT. *Pesticide News.* 40 : 18-20

Cheng, H.H. 1990. Pesticides in the soil environmental: Processes, Impacts and Modeling. Soil Society of America, Madison, Wisconsin

Fox, G.A. *et al.* 1991. Reproduction outcomes in colonial fish eating birds: A bioindicator for development toxicants in Great Lakes food chains. *J. Great Lakes Res.* 17 : 158-167

Hellwell, M.J. 1988. Toxic substances in rivers and streams. *Environ Poll.* 61-85

Hussela-Veistola, E. 1996. Effects of pesticide use and cultivation techniques on ground bettles (Col. Carabidae) in cereal fields. *Ann. Zool. Fennici.* 33: 197-205.

Kocan, R.M. and Landolt, M.L. 1989. Survival and growth to reproductive maturity of Coho salmon following embronic exposure to a model toxicant. *Mar Environ Res.* 27 : 177-193.

Kolpin, D.W., Thurman, E.M. and Goolsby, D.A. 1996. Occurrence of selected pesticides and their metabolites in near-surface aquifers of the mid-western United States. *Environ Sci and Techno.* 30 : 335-340.

Miglioranza, K.S.B., Aizpun de Moreno, J.E., Moreno, V.J., Osterrieth, M.L. and Escalante, A.H. 1999. Fate of organochlorine pesticides in soils and terrestrial biota of "Los Padres" pond watershed, Argentina. *Environ Poll.* 105 : 91-99.

Patton, G.W., Walla, M.D., Bidleman, T.F. and Barrie, L.A. 1991. Polycyclic aromatic and organochlorine compounds in the atmosphere of northern Ellesmere Island, Canada. *J Geophysical Research.* 96 : 10867-10877

Simonich, S.L. and Hites, R.A. 1995. Organic pollutants accumulation in vegetation. *Environ. Sci. and Technol.* 29 : 2905-2914

Trapp, S. and Matthies, M. 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. *Environ. Sci. and Technol.* 29 : 2333-2338

Yi-Fan Li, Mc Millan, A. and Trevor Scholtz, M. 1996. Global HCH usage in 1o ??1o longitude-latitude resolution. *Environ. Sci. Technol.* 30 : 3525-3533