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ORGANOCHLORINE PESTICIDE RESIDUES IN CATTLE DRINKING WATER

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Seventy-nine samples of cattle drinking water drawn from the Karachi Cattle Colony were monitored for organochlorine pesticides in 1984. Nearly 13% of the samples were found to be contaminated with different chlorinated pesticides or their metabolites. Recovery studies of thirteen pesticides at different spiking levels are also included in the paper. It ranged between 76 and 107% for different compounds.

Key words: Chlorinated pesticides, Water samples, Gas chromatography.

INTRODUCTION

Higher agricultural productivity through increased acreage yields can be obtained for most crops with the judicious use of pesticides. These chemicals have been instrumental in greatly reducing crop and livestock damage. However, the use of pesticides to bring greater agricultural productivity is not free from risk, as fatalities have occurred, directly or indirectly, from its usage. The transport of these toxic substances in minute amounts by water and air to locations far removed from the area being treated is of paramount significance. During pesticide application, varying amounts of toxic substances fall in the canal or pond water which is consumed by cattle. Pesticides are also carried in precipitation or in run-off and drainage from land to water. It is unavoidable that during application of pesticides to a crop, a portion of the applied pesticide will settle very slowly and be carried outside of the treated area by wind currents. The transport and deposition of pesticide outside of the intended area is known as drift. If a stream is in the area of drift deposition, the water will be blanketed by the formulation.

Sometimes insecticides are accidentally applied to ponds and rivulets in and adjacent to treated areas. A number of such cases have been observed in the treatment of large areas of forest lands [1]. Nicholson *et. al.* [2] found that one of the causes of pesticide contamination of a farm pond is the deposition of eroded soil containing pesticide in the pond.

The persistence and distribution of DDT, DDD and DDE in a farm and pond were determined by Bridges *et. al.* [3]. These compounds were not detected after three weeks in open water but did persist in the mud, vegetation and fish upto sixteen months. Schulze *et. al.* [4] monitored water streams for some organochlorine pesticides in Western United States for a period of three years at monthly intervals. No pesticides were found at levels in excess of those permitted in public water supplies. Several such studies are reported elsewhere in the literature [5-10].

Contaminated water is a possible pollutant for dairy cattle. Studies presented here have been undertaken with a view to assessing the levels of contamination of cattle drinking water with organochlorine pesticides in the Karachi cattle colony. The entire work was accomplished in three phases. In the first phase, recovery studies were carried out to establish a proper analytical methodology for thirteen organochlorine pesticides or their metabolites spiked with known amount in water. The compounds studied were α-BHC, β-BHC, γ-BHC, δ-BHC, pp′-DDT, pp′-DDE, DDD, dicofol, heptachlor, heptachlor-epoxide, aldrin, dieldrin and endrin. In the second phase, random samples of water were drawn from the cattle colony and stored at -20° until analysis. In the third and final phase, samples were analyzed for residues and the data were interpreted.

EXPERIMENTAL

Reagents and apparatus

(a) *n*-Hexane

(b) Acetone

(c) Sodium sulphate, anhydrous (Merck)

(d) Insecticide standards - A.R. grade procured from the manufactures. Stock solutions and subsequent dilutions were prepared in acetone and *n*-hexane for spiking with water and GLC determination respectively.

All chemicals were AR grade and all solvents were redistilled in glass before use.

(e) Filter paper-Whatman No. 542.

(f) Separatory funnels (250 ml), glass stoppered, Pyrex.

(g) Gas chromatograph: Pye-Pan chromatograph

equipped with a tritium electron capture detector ; two glass columns each 30 cm x 4 mm i.d., packed separately with (i) a mixture of 7.5% QF-1 + 5% DC-200 and (ii) 1% NGS, both supported on 80-100 mesh chromosorb W. Operating conditions: Temperatures, column oven 150°; detector oven 175°; detector voltage, 1 Volt for column (i) and 5 Volts for column (ii) pulsed; attenuator setting, 10^{-10} amp. full scale; carrier gas (nitrogen) flow rate, 65ml min^{-1} Honeywell recorder, 10 milivolts; Chart speed, 8mm min^{-1}. The two columns were conditioned at 175° for 24 hr before use. The above operating parameters were observed for both columns for the present studies.

Sampling. The choice of sampling depends on the concentration of pesticides in water, the amount of water sample available, and the sensitivity of the analytical method or methods used [1]. There are three methods in current use: direct collection of a water sample, centrifugal liquid - liquid extraction and adsorption on activated carbon. The latter two methods can be used for sampling over a prolonged period of time and with waters containing picogram or greater quantities of pesticides, whereas the direct collection method is frequently used when instantaneous sampling is desired. This method was adopted in the present investigations and involves collecting a known volume (1 to 20 litres) of water in glass or Teflon container with glass or Teflon-lined cap. Seventy nine samples were drawn from Karachi Cattle Colony in accordance with this procedure. Random sampling of water was done from reservoirs meant for cattle consumption from every sixth dairy farm. Three samples (1 litre each) were drawn from different reserviors at each sampling location, composited by mixing in clean and dry Teflon bottles, properly sealed, labelled and frozen at-20° in the laboratory until analysis.

Extraction. Each sample was processed in triplicate for the extraction of pesticides in order to check reproducibility of results. 10 g of each water sample was vigorously shaken with 25 ml *n*-hexane in a 250 ml Erlenmeyer flask by means of an electric shaker for 15 min. and processed exactly according to the described procedure [11]. The extract was then concentrated down to approx. 0.5 ml in a rotary vacuum evaporator at 40° and taken up in a graduated 5 ml test tube for EC/GLC. A control sample was processed in a similar manner. No cleanup was considered necessary for these samples.

The efficiency of extraction was evaluated in model experiments with tap water available in the laboratory. 25 g of tap water were taken in triplicate for each experiment and spiked separately with calculated amounts of each pesticide standard at different levels. Each spiked sample was then processed for extraction by the above method and the recovery evaluated by EC/GLC ranged between 76 and 107%. Recovery data are presented in Table 1.

Table 1. Recovery of studied pesticides from spiked water on two different GLC column

Sl. No.	Pesticides	Added μgkg^{-1} (ppb)	Recovery* (%) 7.5% QF1 + 5% DC-200	Recovery* (%) 1% NGS
1.	α-BHC	1	100.97 ±1.76	101.46 ± 1.12
2.	β-BHC	10	91.91 ±1.24	92.18 ± 0.68
3.	γ-BHC	1	98.39 ±2.05	98.29 ± 1.87
4.	δ-BHC	10	92.43 ±2.61	94.07 ± 2.76
5.	pp′-DDT	50	102.88 ±2.32	102.03 ± 1.64
6.	pp′-DDE	50	95.03 ±0.15	95.87 ± 1.11
7.	DDD (TDE)	50	88.17 ±1.29	88.01 ± 2.34
8.	Dicofol	50	76.54 ±1.44	76.33 ± 1.80
9.	Heptachlor	2	99.84 ±0.33	102.35 ± 0.85
10.	Heptachlor epoxide	2	100.63 ±0.83	103.29 ± 0.33
11.	Aldrin	1	91.22 ±0.97	90.88 ± 1.13
12.	Dieldrin	20	107.0 ±1.56	105.72 ± 1.48
13.	Endrin	10	92.94 ±0.95	93.73 ± 1.20

*Mean and standard error of three analyses.

GLC Determination. 1-5 μl aliquots of extracts were injected into the gas chromatograph using a 10 μl syringe along with the relevant pesticide standards. Two different columns (see section 2.1) were used for identification and quantification. Pesticides were qualitatively identified by comparison with standard pesticides with the help of GLC retention time and quantified by comparing the peak heights of samples with those of the relevant standards. The control sample gave a clear gas chromatogram and did not respond to any interferring peak. Typical gas chromatograms of a water sample as well as a control are depicted in Fig. 1.

RESULTS AND DISCUSSION

GLC analysis of seventy nine samples of cattle drinking water revealed contamination of ten samples with different chlorinated pesticides or their metabolites. The results of such samples are presented in Table 2. Each figure in columns No. 4 and 5 is the mean value of three replicates and is presented with standard error. It is evident from the

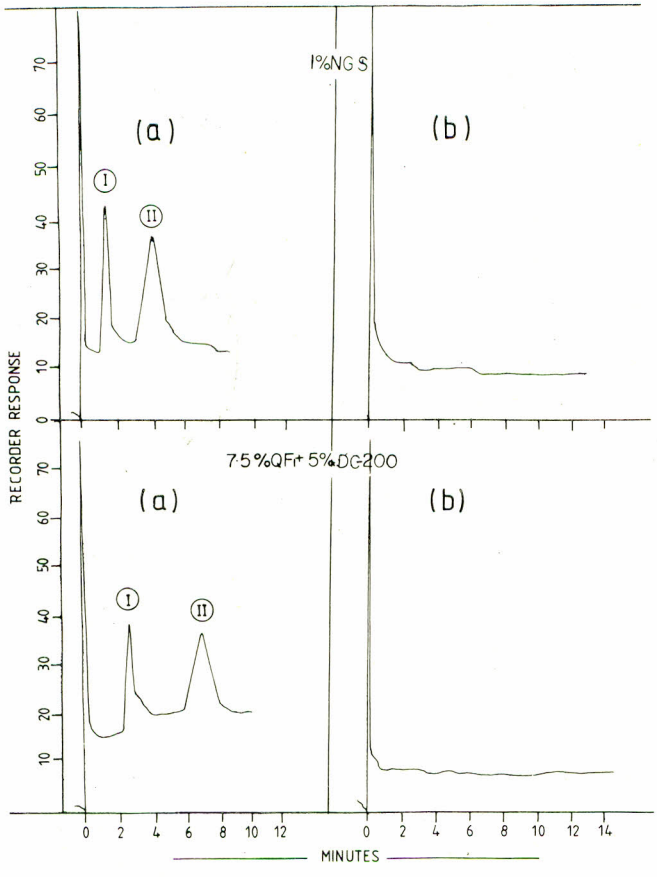

Fig. 1 Gas chromatograms of water samples for organochlorine pesticide residues on two different GLC columns. (a) Sample from plot no. 464 peak identification (a) Dieldrin and (b) control

table that six samples were found to contain γ-BHC in the range of 1.0 to 16.4 ppb, one contained pp′-DDT in traces while pp′-DDE was found to be present in trace amounts in two samples only. Aldrin and dieldrin were present in one sample in quantities of 2.0 and 31.5 ppb respectively.

n-Hexane has been employed as an extractant for pesticide residues from water. The suitability of this solvent was earlier established in recovery studies with spiked samples of tap water. The extract obtained by this method does not require any partitioning or cleanup. The concentrated extract was subjected directly to GLC determination. The procedure is not only economical but also efficient and may be reliably used for the monitoring of organochlorine pesticides in water.

CONCLUSION

The above described monitoring studies, carried out as part of our programme to monitor organochlorine pesticides contamination in milk, feed and cattle drinking water shows that pesticide may be transferred to cattle through contaminated water and appear in milk as residues

Table 2. Organochlorine pesticide residues in ppb (μgkg^{-1}) found in water samples on two different GLC columns.

Sl. No.	Plot No.	Pesticide detected	Mean residue (μgkg^{-1}) with standard error *	
			7.5% QF$_1$+5% DC-200	1% NGS
1.	13	pp′-DDE	Traces	Traces
2.	25	γ-BHC	1.3 ±0.00	1.4 ± 0.09
3.	49	pp′-DDT	Traces	Traces
4.	61	pp′-DDE	”	”
5.	187	γ-BHC	1.0 ±0.05	1.3 ± 0.05
6.	230	γ-BHC	2.9 ±0.08	2.8 ± 0.08
7.	284	γ-BHC	16.4 ±0.24	16.7 ± 0.05
8.	428	γ-BHC	8.0 ±0.05	7.9 ± 0.00
9.	440	γ-BHC	3.8 ±0.05	3.6 ± 0.12
10.	464	Aldrin	2.0 ±0.05	2.1 ± 0.05
		Dieldrin	31.5 ±0.12	31.8 ± 0.09

Traces = Numerical values can not be calculated.
* = Mean and standard error of three analyses.

which ultimately pose a potential health hazard. Monitoring of pesticides in milk and cattle feed are being reported separately. It is, therefore, suggested that wide publicity be given to educate the common man about benefits which can be derived if pesticides are used properly in accordance with established practices. If misused, these compounds can cause disasters.

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