

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDIAN COASTAL WATER USING A MOORED *IN-SITU SAMPLER*

A. SARKAR and R. SEN GUPTA

*Chemical Oceanography Division, National Institute of
Oceanography, Dona Paula, Goa-403 004, India.*

1.0 INTRODUCTION

The problem of environmental contamination by persistent chlorinated pesticides still evokes major concern owing to the presence of their residues in human and animal tissues. In the developing countries organochlorine insecticides especially DDT are extensively used in agriculture and disease vector control programmes. High concentrations of DDT found in the environment has led to a total ban on its use in USA, Europe and Japan with restricted use of the other chlorinated pesticides (Harvey, 1974). Data on their levels of concentration from the seas around India are very few (Jenson *et. al.*, 1972; Tanabe *et. al.*, 1980; Kureishy *et. al.*, 1978; Kannan and Sen Gupta, 1987; Sarkar and Sen Gupta, 1987, 1988 a, b). About 55000 tons of pesticides are used every year in India at present (Sen Gupta and Qasim, 1985). The cumulative effects of the chlorinated pesticides over time on our coastal marine environment can be expected to be considerable. Persistent pesticide residues can be expected to accumulate in marine organisms, like zooplankton (Kureishy *et. al.*, 1978; William and Holden, 1978; Patel, *et. al.*, 1972; Kannan and Sen Gupta, 1987). Considerable amounts of organochlorine pesticides have been detected in the coastal water of the Mediterranean sea (Ei-Dip and Badway, 1985). However, very little data on their presence in Indian coastal water are available mainly due to problems in contamination-free sampling. An attempt has, therefore, been made to determine the concentration of different organochlorine pesticides in the seawater off the central west coast of India using an *in-situ sampler*.

2.0 MATERIALS AND METHODS

Samples were collected at a few stations (Fig. 1) along the central west coast of India at a depth of 20m. Samplings were made

by deployment of a *Seastar*^(R) *in-situ* sampler with the help of a self lubricating hydrographic winch with PVC-coated wire on board, *ORV SAGAR KANYA* during Jan, 87. The *Seastar*^(R) *in-situ* sampler is an instrument which is designed to pump large volumes of water slowly ($50\text{--}200\text{ml. min}^{-1}$) through an extraction column which concentrates chlorinated hydrocarbons from the water. It provides accurate measure of the volume of water extracted. It is a self-contained instrument comprising a small pump, a flow meter, a microprocessor controller and a battery pack of 20D cell batteries (Fig. 2). The top of the sampler houses three switches that allow control of the flow rate, the delay time to start pumping, and the sampling schedule (Fig. 3). A window

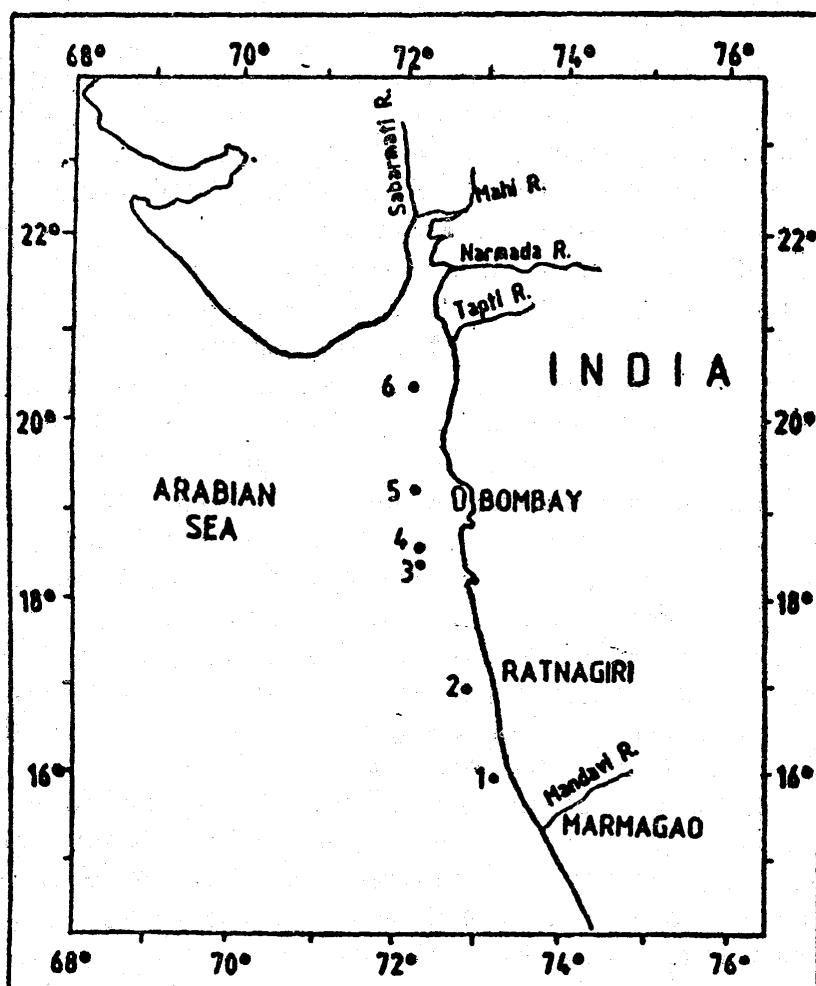


Fig. 1 Location of the sample collections sites

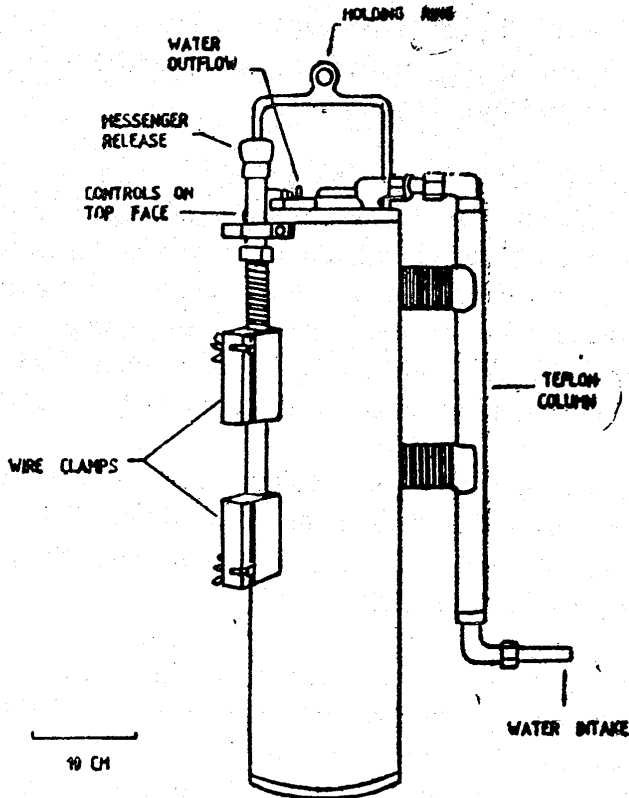


Fig. 2 Diagram of the Seastar in situ water sampler. (The teflon column at right contains the polyurethane foam or XAD-2 resin.)

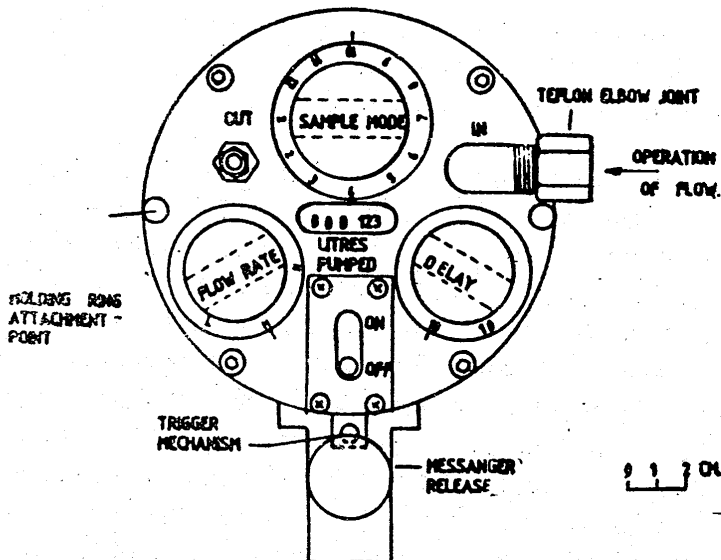


Fig. 3 Diagram of the top-plate of the sampler showing controls and volume read-out. (Microprocessor control allows the selection of flow rate, delay time, and sampling interval and duration. The flow meter read-out records the total value of water passed through the column in litres.)

provides a liquid crystal display for the total volume of water which has passed through the column. Battery power is sufficient for approximately 120 hrs. of continuous operation.

The extraction column is a Teflon cylinder (37cm. x 2.5cm. o.d) containing either Amberlite XAD-2 resin or precleaned polyurethane foam which extracts the chlorinated hydrocarbons from the water passing through it. The columns were packed under controlled conditions and stored sealed until mounted on the sampler. On completion of the sampling the instrument was retrieved and the column was removed, sealed, stored on board and returned to the laboratory for analysis.

An XAD-2, macroreticular resin column was used particularly for the extraction of chlorinated hydrocarbons from water. This has been used extensively for this specific purpose (Moody and Thomas, 1982; Osterroht, 1974; Le Bel and Williams, 1980).

Prior to deployment of the instrument in water, retention of chlorinated hydrocarbons on the column, the recovery of the retained chlorinated hydrocarbons from the column via the elution process and the column efficiency (retention x recovery) have been examined. This was accomplished using a 20 litre sample of seawater spiked with a standard solution of different chlorinated pesticides to create dissolved concentrations in the range 10—100ng. L⁻¹ per compound. Four litres of this spiked water were then pumped through the XAD-2 column at a flow rate of 200ml. min⁻¹. Recovery, work up and analysis procedure are described in the following paragraph.

For the XAD-2 resin column, retention of chlorinated hydrocarbons averaged $97.5 \pm 3.5\%$ and recovery from the column averaged $95 \pm 12\%$ giving average column efficiency (9 compounds x 3 replicate experiments) of $94 \pm 14\%$ (Table 1). The instrument was deployed at each station at a depth of 20m. for about 15hrs. and around 140-145 litres of seawater was passed through the column. Organochlorine pesticides were determined by solvent elution of the XAD-2 column using 250ml. of methanol (about 2 3ml. min⁻¹) followed by 300ml. of dichloromethane. Volumes were reduced to 5ml. in a Kuderna-Danish concentrator. The solvent was exchanged for hexane. The extracts were purified by stepwise treatment with conc. sulphuric acid, 1% sodium bicarbonate solution, anhydrous sodium sulfate, activated copper powder and finally by passage through a Florisil column. All the chemicals used were suprapure quality. The extracts were then concentrated and injected

TABLE - 1

Documentation of the extraction of chlorinated hydrocarbons from seawater by XAD-2 resin columns in the laboratory using *Seaster*^(R) *in-situ* sampler at a flow of 200 ml min⁻¹.

Compound	Retention %	Recovery %	Column Efficiency %
	X ± s. d. (n = 3)	X ± s. d. (n = 3)	X ± s. d. (n = 3)
pp' - DDT	95.5 ± 0.6	80.3 ± 11.8	76.7 ± 11.3
op' - DDT	96.5 ± 0.5	79.5 ± 10.5	76.7 ± 10.5
pp' - DDE	93.9 ± 0.2	89.8 ± 2.6	84.3 ± 2.4
op' - DDE	92.5 ± 0.3	88.5 ± 2.4	81.9 ± 2.3
pp' - DDD	100 ± 0.1	110 ± 5	110 ± 5
op' - DDD	100 ± 1.5	108 ± 6	108 ± 6
aldrin	98 ± 1	91 ± 9.4	89.2 ± 9.2
dieldrin	100 ± 1	100 ± 6	100 ± 6
Y-HCH	100 ± 2	100 ± 5	100 ± 5

into a gas chromatograph (Perkin Elmer 3920B) equipped with a Ni⁶³ electron capture detector and a glass column (3.6m. × 0.63cm.id. packed with 2.5% OV-17+2.5% QF-1 on chromosorb 80/100 mesh. The column, injector and detector temperatures were 200°C, 225°C and 250°C respectively. Argon with 5% methane was used as the carrier gas at a flow rate of 75ml. min⁻¹. The accuracy and precision of the measurement was within the limit ± 0.01ng. L.⁻¹.

3. RESULTS

The results of the extraction of various organochlorine compounds from seawater by XAD-2 resin column in the laboratory using the *Seaster*^(R) *in-situ* sampler is reproduced in Table 1. The results show that the retention of both the isomers of DDT by XAD-2 resin is around 96% whereas that of DDE is around 93%. However, with respect to pp'-DDD, op'-DDD, Dieldrin and γ-HCH, the retention is 100% and that of Aldrin is 98%. The recovery percentage of the chlorinated

hydrocarbons from the XAD-2 column averaged $95 \pm 12\%$ giving an average column efficiency of $94 \pm 14\%$. It was found that the column efficiency is minimum with respect to pp'-DDT and op'-DDT (76%)

The results of the residue level of different chlorinated pesticides in seawater off the central west coast of India are reproduced in Table-2 which reveals that the concentration of the organochlorine compounds identified, so far, are reasonably quite high in regard to the values in the open ocean in view of the fact that the area can be expected to be contaminated due to the river run off and industrial wastes into the ocean.

4.0 DISCUSSION

Results reproduced in Table 2 show that among all the chlorinated compounds detected so far, the concentration of Y-HCH was found to be highly consistent all along the central west coast of India. The two cyclodiene compounds, aldrin and dieldrin were also detected in the water column of almost all the sampling stations which indicated the prolonged use of these pesticides in the peripheral land region. Among the isomers of DDT, pp'-DDT was present in the first three sampling stations whereas op'-DDT could be detected only at the second sampling station near Ratnagiri coast. It is interesting to point out here that among the metabolites of DDT detected so far, pp'-DDE was present at every alternate station whereas op'-DDE was present at the 3rd, 4th and 5th stations only. Unlike pp'-DDE, and op'-DDE op'-DDD could be detected in considerable amounts in the water column at the second sampling station near Ratnagiri coast. But pp'-DDD was not at all present in any of the sampling stations which may be attributed to the fact that the conversion of pp'-DDD from pp'-DDT is not favourable in the marine environment (Sarkar and Sen Gupta, 1987). The concentration of total DDT present in the water column of the central west coast of India ranged from 15.81 — 44.4 ng/l¹ which is fairly low compared to their concentrations in sediments (7.38 — 179.1 ng.g⁻¹) of the same region (Sarkar and Sen Gupta, 1987)

5.0 CONCLUSION

From the point of view of extraction, it was observed that XAD-2 is a highly effective and efficient resin for the isolation of organochlorine pesticides from seawater. With respect to the residue levels of different chlorinated pesticides so far detected from the seawater along the

TABLE - 2

Chlorinated pesticide residues in the seawater of the central west coast of India

St. No.	Concentrations of chlorinated pesticides in the seawater (ng. l ⁻¹)									
	Y-BHC	aldrin	dieldrin	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	o,p'-DDD	t-DDT	
	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)	$\bar{x} \pm \text{s.d.}$ (n = 3)		
1.	2.3 ± 0.25	N.D	50.98 ± 1.5	13.3 ± 1.2	N.D	2.51 ± 0.8	N.D	N.D	15.81	
2.	2.7 ± 0.5	9.8 ± 1.2	N.D	56.0 ± 1.5	251.0 ± 5.6	N.D	N.D	137.0 ± 9.5	444.0	
3.	9.4 ± 0.5	6.72 ± 1.1	N.D	2.05 ± 0.2	N.D	6.34 ± 1.2	18.5 ± 2.1	N.D	26.89	
4.	1.15 ± 0.12	2.57 ± 0.35	N.D	N.D	N.D	N.D	N.D	N.D	—	
5.	0.26 ± 0.05	1.62 ± 0.15	9.18 ± 2.5	N.D	N.D	N.D	64.5 ± 1.5	N.D	64.5	
6.	0.52 ± 0.02	1.42 ± 0.02	2.10 ± 0.5	N.D	N.D	20.34 ± 5.6	4.33 ± 0.71	N.D	24.72	

ND - Non detectable.

central west coast of India, Y-HCH and aldrin concentrations were highly consistent whereas op'-DDD and op'-DDT were not. The order of distribution of different chlorinated compounds along the central west coast of India are as follows: op'-DDD < op'-DDT < op'-DDT < pp'-DDE < dieldrin < pp'-DDE < aldrin < Y-HCH.

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