

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

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Abstract—Residues of various organochlorine pesticides were determined in the water off the central west coast of India using an *in-situ* sampler. Y-BHC and the two cyclodiene compounds, Aldrin and Dieldrin were found to be more consistent than the compounds of the DDT family. Y-BHC ranged from 0.26 to 9.4 ng l⁻¹ whereas Aldrin and Dieldrin were from 1.4 to 9.8 and 2.1 to 50.9 ng l⁻¹, respectively. Among the compounds of the DDT family, *pp'*-DDT was found to be more abundant than the others in the southern part of the region, whereas *op'*-DDT was present in a fairly considerable amount off Ratnagiri coast. Among the metabolites of DDT, *pp'*-DDE was found to be present in every alternate station with increasing concentration (2.5–20.39 ng l⁻¹) whereas *op'*-DDE could be detected occasionally in the northern part of the region. Presence of *op'*-DDD was observed only in one sample off the Ratnagiri coast, whereas *pp'*-DDD was not detected at all.

Key words—organochlorine pesticides, coastal water, *in-situ* sampler, XAD-2 resin, column efficiency

INTRODUCTION

The problem of environmental contamination by persistent chlorinated pesticides still evokes major concern due 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 marine environment has led to a total ban on its use in the U.S.A., 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 and Tatsukawa, 1980; Kureishy *et al.*, 1978; Kannan and Sen Gupta, 1987; Sarkar and Sen Gupta, 1987, 1988a, b). About 55,000 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.*, 1977; Kannan and Sen Gupta, 1987). Considerable amounts of organochlorine pesticide have been detected in the coastal waters of the Mediterranean Sea (El-Dib and Badway, 1985). However, very little data on their presence in Indian coastal waters 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.

MATERIALS AND METHODS

Samples were collected at a few stations (Fig. 1) along the central west coast of India at a depth of 20 m. Samplings were made by deployment of a Seastar[®] *in-situ* sampler with the help of a self lubricating hydrographic winch with PVC-coated wire on board, *ORV SAGAR KANYA* (during January 1987). The Seastar[®] *in-situ* sampler is an instrument which is designed to pump large volumes of water slowly (50–200 ml min⁻¹) through an extraction column which concentrates chlorinated hydrocarbons from the water. It provides accurate measurement 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 20 D 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 provides a liquid crystal display for the total volume of water which has passed through the column. Battery power is sufficient for approx. 120 h of continuous operation.

The extraction column is a Teflon cylinder (37 × 2.5 cm o.d.) containing either Amberlite XAD-2 resin or precloned 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

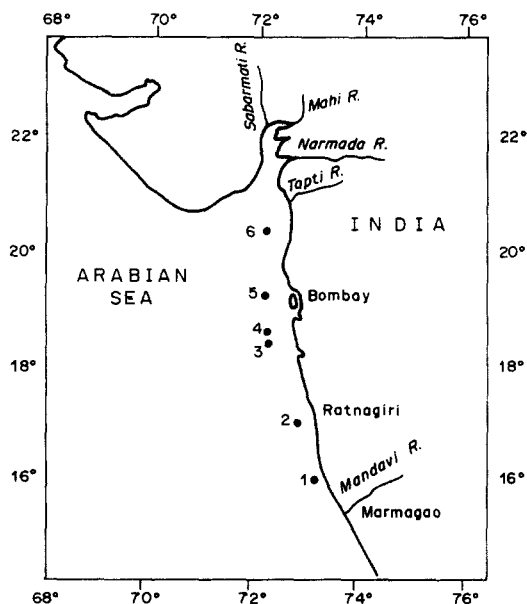


Fig. 1. Location of the sample collection sites.

the retained chlorinated hydrocarbons from the column via the elution process and the column efficiency (retention \times recovery) have been examined. This was accomplished using a 20 l. sample of seawater spiked with a standard solution of different chlorinated pesticides to create dissolved concentrations in the range 10–100 ng l⁻¹ per compound. Four liters of this spiked water were then pumped through the XAD-2 column at a flow rate of 200 ml 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 (nine compounds \times three replicate experiments) of $94 \pm 14\%$. The results of this experiment are reproduced in Table 1. The instrument was deployed at each station at a depth of 20 m for about 15 h and around 140–145 l. of seawater was passed through the column. Organochlorine pesticides were determined by solvent elution of the XAD-2 column using 250 ml of methanol (about 2–3 ml min⁻¹) followed by 300 ml of dichloromethane. Volumes were reduced to 5 ml 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 sulphate, activated copper powder and finally by passage through a Florisil column. The extracts were then concentrated and injected into a gas chromatograph (Perkin–Elmer 3920 B) equipped with a Ni⁶³ electron capture detector and a glass column (3.6 m \times 0.63 cm i.d.) packed with 2.5% OV-17 + 2.5% QF-1 on chromosorb 80/100 mesh. The column, injector and detector temperature were 200, 225 and 250°C respectively. Argon with 5% methane was used as the carrier gas at a flow rate of 75 ml min⁻¹. The accuracy and prediction of the measurement was within the limit ± 0.01 ng l⁻¹.

RESULTS

The results of the extraction of various organochlorine compounds from seawater by XAD-2 resin column in the laboratory using the Seastar[®] *in-situ*

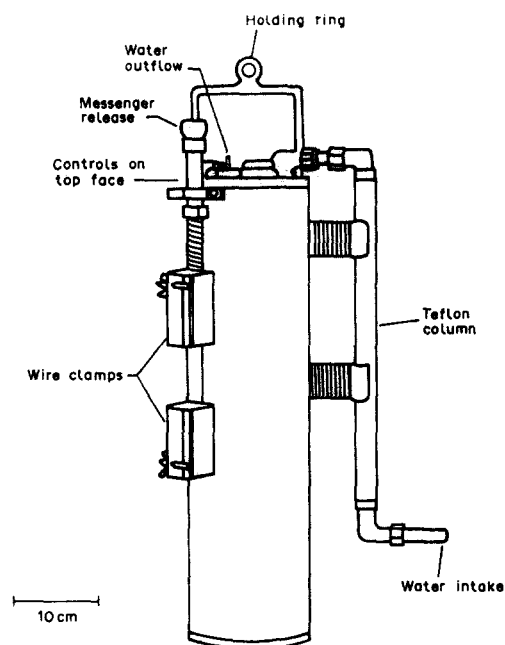


Fig. 2. Diagram of the Seastar[®] *in-situ* water sampler. (The Teflon column on the right-hand side contains polyurethane foam or XAD-2 resin.)

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 Y-BHC, 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 has been found that

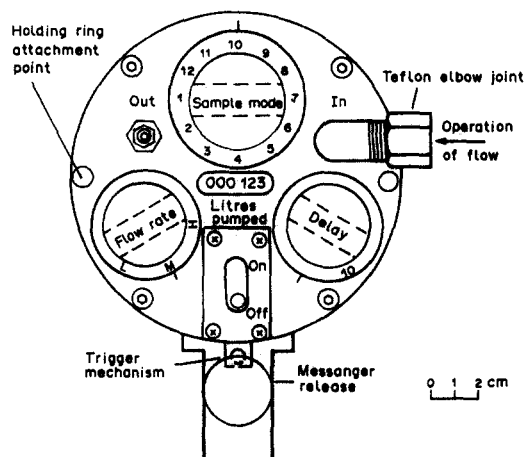


Fig. 3. Diagram of the top-plate of the sampler showing controls and volume read-out. (Microprocessor control allows the selection of flow rate, delay time, and sampling interval and duration. The flow meter read-out records the total volume of water passed through the column in litres.)

Table 1. Documentation of the extraction of chlorinated hydrocarbons from seawater by XAD-2 resin columns in the laboratory using Seastar® *in-situ* sampler at a flow of 200 ml min⁻¹

| Compound | Retention (%) | Recovery (%) | Column efficiency (%) |
|-----------------|--------------------------|--------------------------|--------------------------|
| | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) |
| <i>pp'</i> -DDT | 95.5 ± 0.6 | 80.3 ± 11.8 | 76.7 ± 11.3 |
| <i>op'</i> -DDT | 96.5 ± 0.5 | 79.5 ± 10.5 | 76.7 ± 10.5 |
| <i>pp'</i> -DDE | 93.9 ± 0.2 | 89.8 ± 2.6 | 84.3 ± 2.4 |
| <i>op'</i> -DDE | 92.5 ± 0.3 | 88.5 ± 2.4 | 81.9 ± 2.3 |
| <i>pp'</i> -DDD | 100 ± 1.0 | 110 ± 5.0 | 110 ± 5.0 |
| <i>op'</i> -DDD | 100 ± 1.5 | 108 ± 6.0 | 108 ± 6.0 |
| Aldrin | 98 ± 0.1 | 91 ± 9.4 | 89.2 ± 9.2 |
| Dieldrin | 100 ± 1.0 | 100 ± 6.0 | 100 ± 6.0 |
| Y-BHC | 100 ± 2.0 | 100 ± 5.0 | 100 ± 5.0 |

the column efficiency is maximum 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 high with 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.

DISCUSSION

Results reproduced in Table 2 show that among all the chlorinated compounds detected so far, the concentration of Y-BHC was found to be highly consistent all along the central west coast of India as well as 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. This might be attributed to the fact that DDT is being biodegraded to its metabolite, DDE in the marine environment for

its variable physico-chemical properties such as pH, salinity, dissolved oxygen, nutrient concentrations, high concentrations of various elements (such as Cu, Mn, Fe, Co, Ni etc.), clay mineral concentrations (such as montmorillonite, illite, kaolinite etc.) and above all various kinds of microorganisms (Sarkar and Sen Gupta, 1987). Moreover, unlike *pp'*-DDE and *op'*-DDE, *op'*-DDD could be detected in considerable amounts in the water column at the second sampling station near the 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 to 444 ng l⁻¹ which was fairly low compared to their concentrations in sediments (7.38–179.1 ng g⁻¹) of the same region (Sarkar and Sen Gupta, 1987).

CONCLUSIONS

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 central west coast of India, Y-BHC and Aldrin concentrations were highly consistent whereas *op'*-DDT and *op'*-DDD were not. The order of distribution of different chlorinated

Table 2. Chlorinated pesticide residues in the seawater off the central west coast of India

| Sta. No. | Concentrations of chlorinated pesticides in the seawater (ng l ⁻¹) | | | | | | | | |
|----------|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| | Y-BHC | Aldrin | Dieldrin | <i>pp'</i> -DDT | <i>op'</i> -DDT | <i>pp'</i> -DDE | <i>op'</i> -DDE | <i>op'</i> -DDD | <i>t</i> -DDT |
| | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) | $\bar{X} \pm SD$ (n = 3) |
| 1 | 2.3 ± 0.25 | ND | 50.98 ± 1.5 | 13.3 ± 1.2 | ND | 2.51 ± 0.8 | ND | ND | 15.81 |
| 2 | 2.7 ± 0.5 | 9.8 ± 1.2 | ND | 56.0 ± 1.5 | 251.0 ± 5.6 | ND | ND | 137.0 ± 9.5 | 444.0 |
| 3 | 9.4 ± 0.5 | 6.72 ± 1.1 | ND | 2.05 ± 0.2 | ND | 6.34 ± 1.2 | 18.5 ± 2.1 | ND | 26.89 |
| 4 | 1.15 ± 0.12 | 2.57 ± 0.35 | ND | ND | ND | ND | ND | ND | ND |
| 5 | 0.26 ± 0.05 | 1.62 ± 0.15 | 9.18 ± 2.5 | ND | ND | ND | 64.5 ± 1.5 | ND | 64.5 |
| 6 | 0.52 ± 0.02 | 1.42 ± 0.02 | 2.10 ± 0.5 | ND | ND | 20.34 ± 5.6 | 4.33 ± 0.71 | ND | 24.72 |

ND = Not detected.

compounds along the central west coast of India are as follows: *op'*-DDD < *op'*-DDD < *pp'*-DDT < *op'*-DDE < Dieldrin < *pp'*-DDE < Aldrin < Y-BHC.

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