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## EVALUATION OF MACRORETICULAR RESINS FOR THE DETERMINATION OF LOW CONCENTRATIONS OF CHLORINATED HYDROCARBONS IN SEA WATER AND TAP WATER

NENA PICER and M. PICER

*Centre for Marine Research, "Rudjer Bošković" Institute, Zagreb (Yugoslavia)*

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### SUMMARY

The application of XAD-2, XAD-4 and Tenax macroreticular resins for concentrating chlorinated insecticides and polychlorinated biphenyls from sea and tap water samples was evaluated. The solvents used eluted not only the chlorinated hydrocarbons of interest but also other electron-capture detector sensitive materials, so that the eluates had to be purified. The effects of the adsorbent materials and solvent mixtures on the blank values and the sensitivity and reliability of the procedure investigated for the determination of chlorinated hydrocarbons in sea and tap water are discussed.

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### INTRODUCTION

Since the early 1960s the presence of chlorinated insecticides and, several years later, of polychlorinated biphenyls (PCBs)<sup>1,2</sup> in the environment has received much attention. In spite of this, many questions concerning these compounds and their role in the biosphere and especially in the marine environment are still waiting answers. Some of these problems require very refined and sensitive analytical methods. Little information is available on the concentrations of persistent chlorinated hydrocarbons in sea water, and the published values vary by several orders of magnitude<sup>3,4</sup>. This variation may be due largely to unsatisfactory methods of collection and analysis and to a failure to secure uncontaminated samples. Batch solvent extraction methods for the analysis of chlorinated hydrocarbons in water have a low sensitivity, and the application of continuous extraction methods requires complicated and/or expensive apparatus which is impractical for the manipulation of large sea water samples<sup>5,6</sup>.

Several adsorbent materials for the collection of chlorinated hydrocarbons from fresh and saline waters have been described, including charcoal<sup>7</sup>, specially treated Chromosorb G for reversed-phase liquid-liquid partition<sup>8</sup> and various polymeric materials such as the macroreticular resins XAD<sup>9-13</sup>, Spheron MD<sup>14</sup>, Copolymerisat Y 29/11<sup>15</sup> and Tenax<sup>16</sup>. The use of polyurethane foams as a good adsorbent for the concentration of chlorinated hydrocarbons from water has also been described<sup>17</sup>.

In our investigations on the extent of pollution of eastern Adriatic coastal waters by chlorinated hydrocarbons in biota and sediments<sup>18,19</sup>, we have found very low concentrations of these pollutants in samples which were collected at a distance from the origin of the direct pollution. The routine application of already published analytical methods for such very low concentrations of chlorinated hydrocarbons in sea water did not produce satisfactory results. In this paper we describe our results and experience with the application of XAD-2, XAD-4 and Tenax. The main objective was to find the optimal relationship between minimal blank values using several adsorbents and solvents.

## EXPERIMENTAL

### *Materials and reagents*

All solvents were of analytical-reagent grade (mostly from Merck, Darmstadt, G.F.R.) and were freshly distilled in glass prior to use. A commercial PCB compound containing 54% of chlorine (Aroclor 1254) was obtained from the Monsanto Organic Chemical Division (St. Louis, MO, U.S.A.). Standards of chlorinated insecticides were obtained from Polyscience Corp. (Evanston, IL, U.S.A.).

The macroreticular resins Servachrom XAD-2 and XAD-4 were obtained from Serva (Heidelberg, G.F.R.). Tenax (Enka, developed by AKZO Research Labs., Arnhem, The Netherlands) was purified as described later.

"Pure" water was prepared by passing distilled water through a chromatographic column containing XAD-2 resin.

Anhydrous sodium sulphate was heated for 12 h at 400 °C and stored in a glass container in a desiccator.

Silica gel, porosity 60 Å, 70–230 mesh (ASTM), was obtained from Merck. The activation and deactivation of the silica gel were performed as specified by Picer and Ahel<sup>20</sup>.

### *Apparatus*

The column extraction apparatus is illustrated in Fig. 1. Approximately 15 ml of resin in the form of a methanolic slurry was poured into the brass column, which was plugged at the other end with a brass plug and glass-wool. Finally, another plug of glass-wool was placed at the top of the column to retain the resin in place.

A Hewlett-Packard Series 7620 gas chromatograph equipped with a <sup>63</sup>Ni electron-capture detector and a Varian Model 2700 gas chromatograph also equipped with a <sup>63</sup>Ni electron-capture detector and coupled with a Hewlett-Packard 3380A integrator were used for the quantitative analysis of the extracts.

A 1.8 m × 5 mm I.D. glass column packed with 4% SE-30 + 6% OV-210 on 80–100-mesh Gas-Chrom Q was used in the Hewlett-Packard gas chromatograph, and a column 2.5 m × 2 mm I.D. packed with 4% SE-96 + 8% QF-1 (a mechanical mixture, 1:2) on 100–120-mesh Chromosorb W AW DMCS was used in the Varian gas chromatograph. The flow-rate of the carrier gas was 30 ml/min, the injector and detector temperatures were 250 °C and the column temperature was 210 °C. The organochlorine compounds were quantified by comparison of the peak areas of the sample with standard chromatograms.

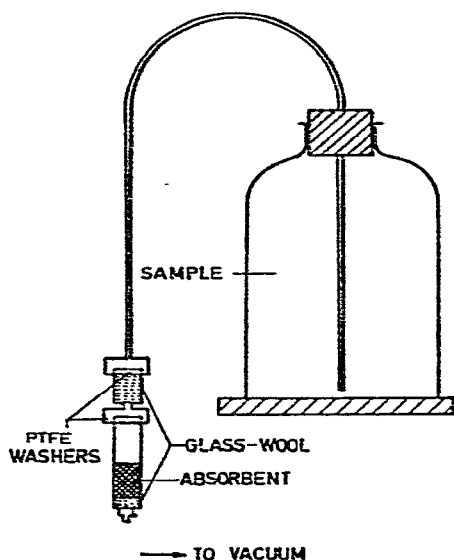


Fig. 1. Adsorption apparatus.

#### Procedures

**Pre-treatment of resins, dishes and adsorbent apparatus.** The XAD-2 and XAD-4 resins were specially pre-cleaned for chromatography. The resins were purified by extraction for 24 h with acetonitrile in a Soxhlet extractor, extraction for 12 h with diethyl ether and extraction for 24 h with methanol. After cleaning, the resins were tested by adding 10 ml of *n*-hexane and then evaporated to 0.1 ml for examination by gas chromatography. Subsequently the resins were placed in methanol in a glass bottle and stored in a refrigerator. Tenax was purified and stored in the same way.

The glassware and dishes and the metal apparatus were specially cleaned and pre-heated at 300 °C overnight. All PTFE gaskets were carefully cleaned with re-distilled solvents and checked for possible bleeding of electron-capture-detector-sensitive substances.

**Column adsorption process.** Prior to use, 200 ml of clean tap water was passed through the column which was packed with the resin under investigation. When a sample had passed through the adsorbent, the walls of the sample reservoir were rinsed with 30 ml of polar solvent (acetone, methanol or acetonitrile). The same amount was passed through the adsorbent to obtain the first eluate. After this first eluate had been collected the adsorbent was washed with a further 30 ml of *n*-pentane to give the second eluate.

The eluates were combined and the non-polar phase was separated from the polar phase in a glass separating funnel. Then the polar phase was extracted twice with *n*-pentane. The *n*-pentane extract was dried over anhydrous sodium sulphate, concentrated to 1 ml and cleaned on an alumina column using a modification of the method described by Holden and Marsden<sup>25</sup>.

The eluates were placed on a silica gel column for the separation of PCBs from DDT, its metabolites and dieldrin. This procedure is a modification of the method of Snyder and Reinert<sup>26</sup> and was described in detail in an earlier paper<sup>20</sup>.

## RESULTS AND DISCUSSION

*Solvents and resin blank*

We carried out very careful investigations in an attempt to keep the blanks as low and reproducible as possible with the laboratory dishes, solvents and reagents used. This part of the blank investigations was performed on XAD-2 resin. The solvents used were acetonitrile, acetone, methanol and diethyl ether as polar solvents and *n*-pentane and light petroleum (b.p. 40–60 °C) as non-polar solvents.

After the elution of chlorinated hydrocarbons from the adsorbent, the solvents had to be re-extracted with *n*-pentane. This step involves the separation of chlorinated hydrocarbons from other organic materials desorbed by the polar solvent from the adsorbent. A 15-ml volume of methanol was re-extracted with two 15-ml volumes of *n*-pentane.

Gas chromatograms obtained from *n*-pentane extracts using electron-capture detection are shown in Fig. 2. Chromatograms of *n*-pentane extracts concentrated to 1 ml before and after alumina clean-up are shown in (a) and (b). Chromatogram (c) was obtained after concentration of the *n*-pentane extract to 0.1 ml. A chromatogram of a pesticide mixture is shown in (c) and of an Aroclor 1254 standards in (d). The standard represents a 100% yield in our analytical procedure with spiked samples: 10 l of water were spiked with 1 ng of DDE, TDE and dieldrin, 3 ng of DDT and 10 ng of Aroclor 1254, the eluates were concentrated to 0.1 ml and an aliquot of 5  $\mu$ l was injected into the gas chromatograph.

A peak due to Mirex (chlorinated pesticide), used as an internal standard, appears in all chromatograms. The amount of Mirex added to the eluates after the desorption process in some experiments was 1 ng, but later we used only 0.2 ng, as this amount was closer to the investigated concentrations of pesticides and PCBs in spiked water samples.

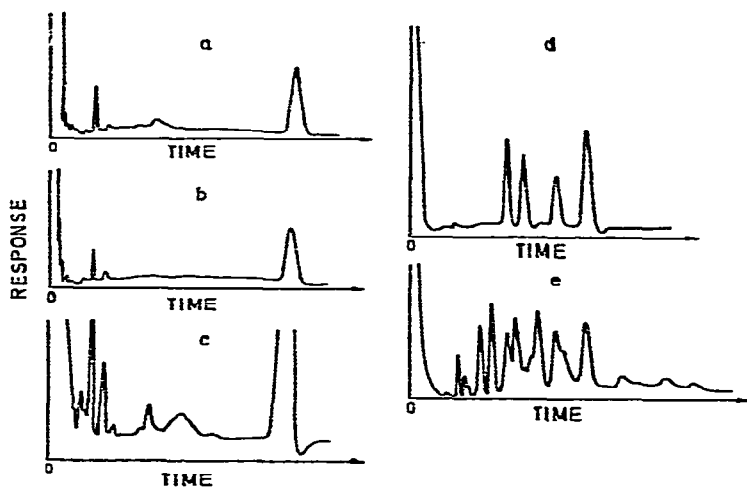


Fig. 2. Electron-capture gas chromatograms of *n*-pentane extract after the re-extraction of methanol eluate. (a) Concentrated to 1 ml prior to alumina clean-up; (b) concentrated to 1 ml after alumina clean-up; (c) concentrated to 0.1 ml after alumina clean-up; (d) pesticide standard, amount injected 25  $\mu$ g of DDE, TDE and dieldrin and 75  $\mu$ g of DDT; (e) Aroclor 1254 standard, amount injected 250  $\mu$ g.

Fig. 3 shows blank chromatograms obtained with XAD-2 resin using the following eluents: methanol [chromatograms (a) and (b)], acetone (c) and acetonitrile (d). *n*-Pentane was used for the re-extraction. After cleaning on an alumina column it was concentrated to 0.1 ml, and 10- $\mu$ l aliquots were injected into the gas chromatograph. Although the shape of the chromatograms was not perfect, it encouraged us to proceed with further investigations with all three solvents.

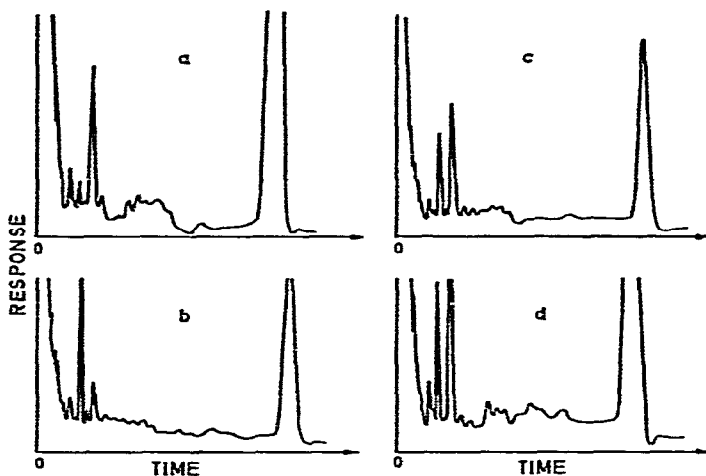


Fig. 3. Electron-capture gas chromatograms of solvent blanks after treatment of the adsorption apparatus. (a) Treatment of the column with methanol; (b) treatment of complete apparatus with methanol after percolation of tap water (0.5 l) through the column; (c) treatment of the column with acetonitrile; (d) treatment of the column with acetone.

Chromatograms (a), (c) and (d) were obtained with percolation of solvents through dry XAD-2 resin in the column. Chromatogram (b) was obtained after the percolation of 0.5 l of tap water through the complete apparatus filled with XAD-2 resin and elution with methanol; hence in this experiment the influence of all parts of the apparatus, resins, solvents and dishes on the blank value was evaluated.

#### *Recoveries and study of natural water*

It is evident from the literature that in investigations of the recovery of pesticides in water analysis most workers spiked the samples with pesticides in the range 0.1–1.0  $\mu$ g/l ( $0.1 \cdot 10^{-6}$  g/l) and only a few tested the range 10–20 ng/l ( $10 \cdot 10^{-9}$ – $20 \cdot 10^{-9}$  g/l). There are few literature data on the concentrations of chlorinated pesticides and PCBs in tap and sea water in the range 0.1–10 ng/l, and we decided to investigate the recovery in the concentration range 1.0–0.1 ng/l for pesticides and 10–1 ng/l for Aroclor 1254. Some workers developed methods for the analysis of 1-l water samples and then applied them to 50-l samples or larger; we investigated the recovery of chlorinated hydrocarbons added to 10-l samples.

It is obvious that the solvent has a large influence on the blank value. Therefore, we investigated elution profiles with several solvents and the results are presented in Fig. 4. Although most chlorinated hydrocarbons are eluted in the first eluate (5 ml of

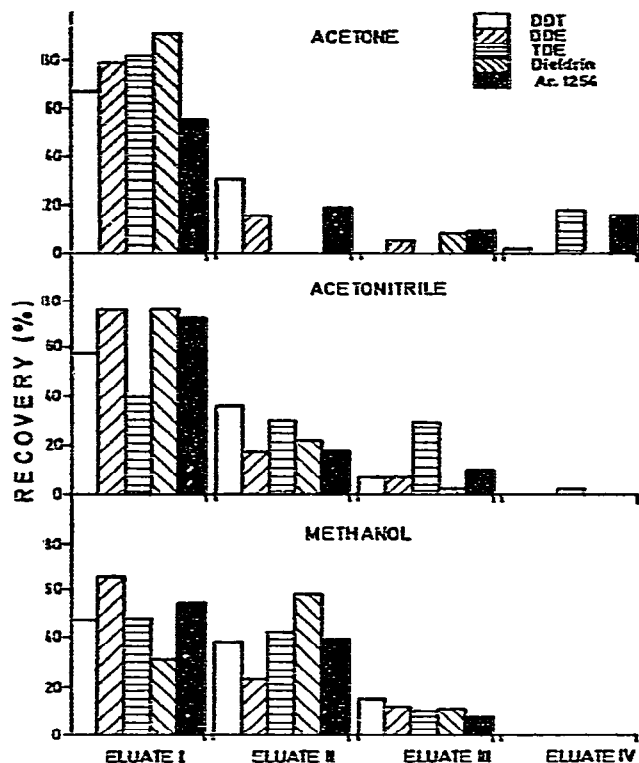


Fig. 4. Recovery of chlorinated hydrocarbons from 10 l of tap water spiked with 10 ng of pesticides and 100 ng of Aroclor 1254, percolated through XAD-2 resin. Solvents for elution: acetone, acetonitrile methanol. Eluates: I, 5 ml; II, 5 ml; III, 5 ml; IV, 10 ml.

solvent), for a quantitative recovery we need 15 ml of methanol and acetonitrile and 25 ml of acetone. As was explained under Experimental, we used silica gel separation prior to the determination of pesticides and Aroclor 1254 in the eluates. However, we must stress that even in recovery tests at the concentration levels of 1 ng/l for pesticides and 10 ng/l for Aroclor 1254 we never obtained a peak shape for Aroclor 1254 identical with that in a pure standard. Therefore, we performed an experiment in which tap water samples were separately spiked with pesticides and Aroclor 1254, and the results are presented in Fig. 5. It is interesting that the elution profile is not the same as that in the previously described experiment. We do not know if the differences are the consequence of the better recognition of PCBs than the pesticides, or if there exists a real influence of PCBs on all chlorinated hydrocarbons and their behaviour during the analytical process. However, in all other experiments we spiked water samples with both pesticides and Aroclor 1254 because they usually occur together in the marine environment.

The results of the recovery tests on sea water samples are presented in Fig. 6. It is interesting that for the elution of all chlorinated hydrocarbons 25 ml of solvent were required. In all further investigations we used 25 ml of polar solvents and 50 ml of *n*-pentane as the re-extractant.

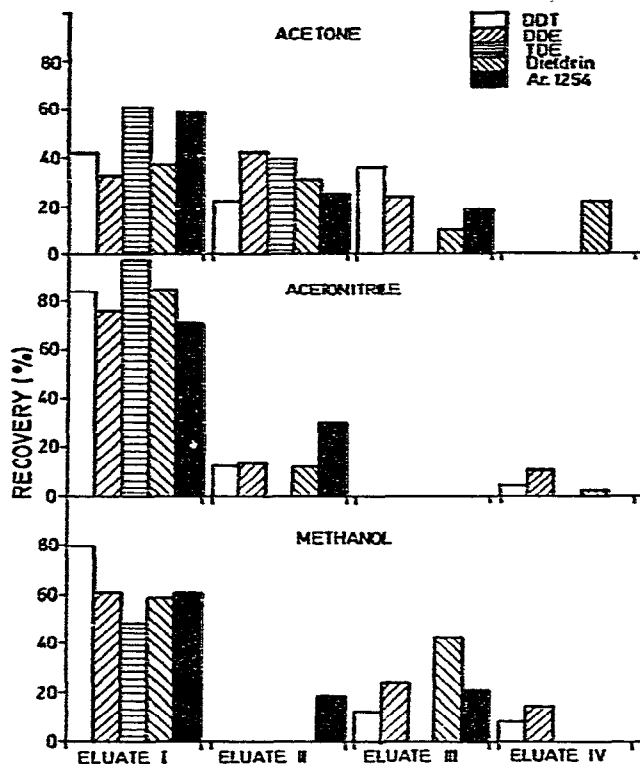


Fig. 5. Recovery of chlorinated hydrocarbons from 10 l of tap water percolated through XAD-2 resin. Tap water samples were spiked separately with 10 ng of pesticides and 100 ng of Aroclor 1254. Solvents for elution and eluates as in Fig. 4.

During our investigations we always used Mirex as an internal standard, added to the eluate after the percolation of the polar solvent through the resin column. Hence this internal standard shows only the loss of chlorinated hydrocarbons during the re-extraction, alumina clean-up and silica gel separation. The recovery of Mirex during these steps varied between 80 and 90%. Losses of the investigated chlorinated hydrocarbons during these steps were 10–30% for about 10 ng of pesticides.

Fig. 7 shows gas chromatograms obtained after the percolation of a 10-l sea water sample through XAD-2 resin and elution with 25 ml of methanol; 10 ng of a pesticide mixture and 100 ng of Aroclor 1254 were added to the eluate, then eluate re-extraction with *n*-pentane and clean-up on an alumina column were performed. A chromatogram was also obtained without the addition of chlorinated hydrocarbons to the eluate. It is obvious that our experimental set-up is capable of determining chlorinated hydrocarbons in a 10-l sea water sample at levels far below 1.0 ng/l for pesticides and 10 ng/l for PCBs.

In sea water it is reasonable to expect pesticides at a level of 0.1 ng/l and PCBs at a level of 1 ng/l<sup>3,21</sup>. For this reason we percolated 50-l sea water samples through an XAD-2 column, and the chromatograms of such samples were compared with those for samples for which we added chlorinated hydrocarbons to the eluate (Fig. 8).

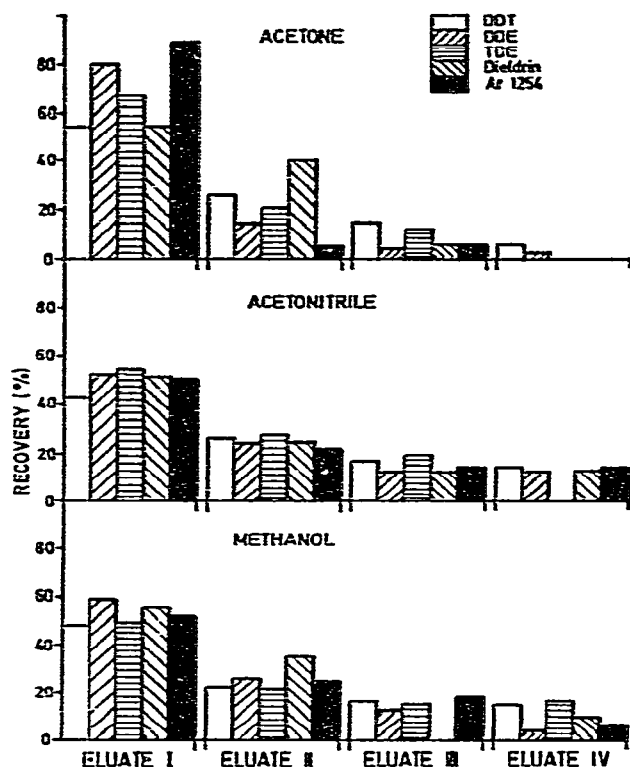


Fig. 6. Recovery of chlorinated hydrocarbons from 10 l of sea water percolated through XAD-2 resin. Sea water samples were spiked with 10 ng of pesticides and 100 ng of Aroclor 1254. Solvents for elution and eluates as in Fig. 4.

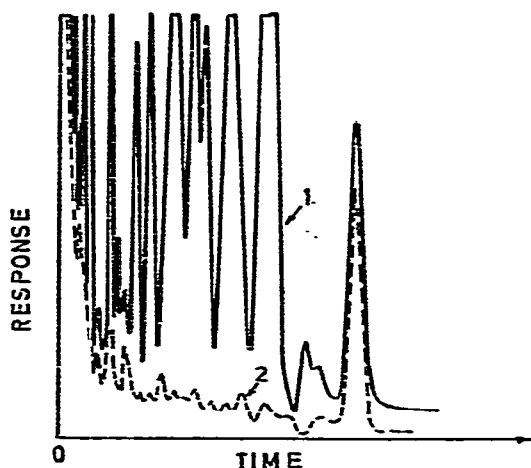


Fig. 7. Comparison of chromatograms obtained after the percolation of 10 l of sea water through XAD-2 resin column. 1, Eluate to which 10 ng of pesticides and 100 ng of Aroclor 1254 were added; 2, eluate with no addition of chlorinated hydrocarbons.



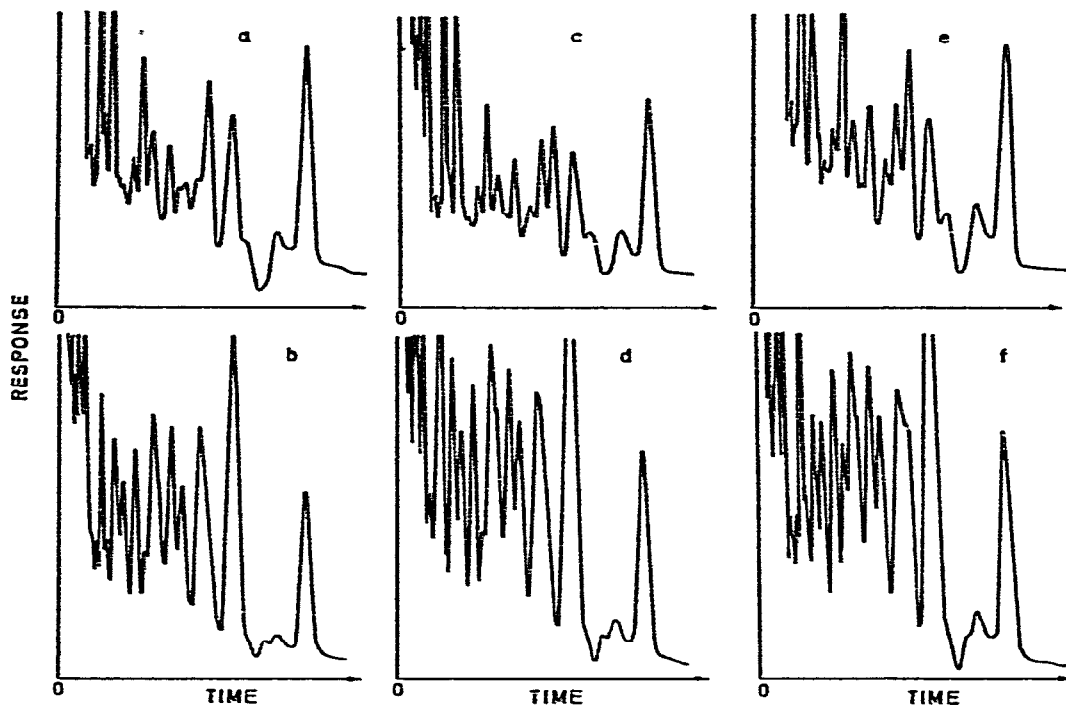


Fig. 8. Comparison of chromatograms obtained after the percolation of 50 l of sea water through XAD-2 column: (a), (c) and (e), with no addition of pollutants; (b), (d) and (f), after addition of 5 ng of pesticides and 50 ng of Aroclor 1254 to eluates. Solvents: (a) and (b), acetone; (c) and (d), acetonitrile; (e) and (f), methanol.

Acetone, methanol and acetonitrile were used for the elution. It is interesting that the shapes of the chromatograms for natural water samples are different for these three eluents. When chromatograms were obtained after the addition of pollutants to the eluate, there was a similarity between the results obtained with acetone and acetonitrile but a significant difference between these and the results obtained with methanol as eluent. Because some workers used hot solvents for the elution<sup>10</sup>, we investigated whether there are differences between using hot and cold solvents (Fig. 9). We used 10-l tap water samples spiked with pesticides at 1 ng/l concentration and Aroclor 1254 at 10 ng/l concentration.

The histograms show the recovery obtained when the loss of the pollutants during the process of re-extraction, clean-up and separation were taken into account by measuring the loss of internal standard. It can be seen that there is no significant difference between the results obtained when using hot and cold solvents for the elution. Large differences in the recoveries and low recoveries for some pollutants were especially surprising. Because we were dissatisfied with the poor recoveries we examined other similar resins, *i.e.*, XAD-4 and Tenax<sup>16,22</sup>. This investigation was performed on 50-l sea water and tap water samples that were spiked to obtain concentrations of 0.1 ng/l of pesticides and 1.0 ng/l of Aroclor 1254. The results are presented in Fig. 10. The recoveries obtained were even lower than those in the previous experiments. The best results were obtained with XAD-2 resin and methanol as the solvent.

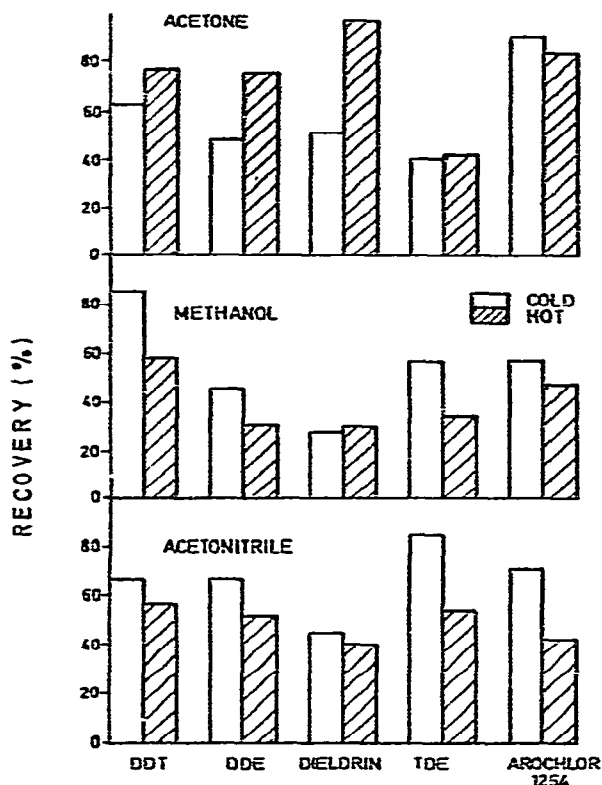


Fig. 9. Recovery of chlorinated hydrocarbons from 10 l of tap water spiked with 10 ng of pesticides and 100 ng of Arochlor 1254 percolated through XAD-2 column and eluted with hot and cold solvents.

Chromatograms obtained with 10-l sea water sample after elution through XAD-4 and Tenax resins with cold and hot methanol are presented in Fig. 11. There is no significant difference between chromatograms obtained with hot and cold methanol using XAD resin, but there is a very significant difference with Tenax resin. Also, there is a considerable difference in the shape and amount of electron-capture detector-sensitive materials that were eluted from XAD resins in comparison with Tenax resin. The especially large amounts obtained with the use of hot solvent for the elution indicate that there is a high probability that these substances are eluted from the Tenax resin itself.

Our results support the possible bleeding effect of Tenax when used as a concentrator for organic pollutants in air<sup>23</sup>. Hence the use of Tenax for the concentration of small amounts of chlorinated hydrocarbons from sea water is not satisfactory because the influence of the resin blank is too great. We must stress that in our experiments the Tenax resins were cleaned in the same manner as the XAD resins, but we could not obtain satisfactory blanks. It is also interesting that solvent blanks with Tenax resin, obtained after the percolation of the solvent through the resin (but without the percolation of a sea water sample), were not significantly higher than other resins blanks. At first it was thought that Tenax resin is better than XAD resins for the recovery of electron-capture detector-sensitive organic materials from

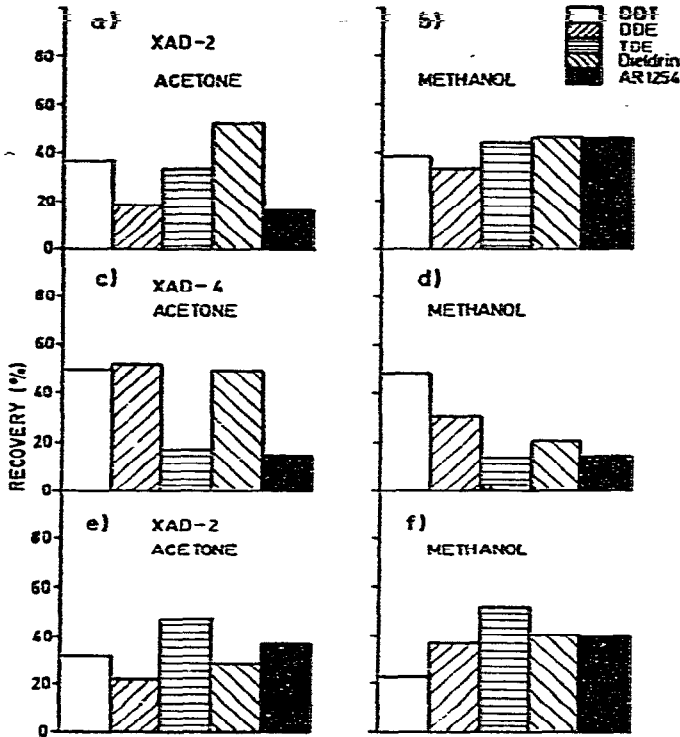


Fig. 10. Recovery of chlorinated hydrocarbons from 50 l water samples spiked with 5 ng of pesticides and 50 ng of Aroclor 1254 percolated through XAD-2 and XAD-4 resins with acetone and methanol: (a), (b), (c) and (d) sea water samples; (e) and (f) tap water samples.

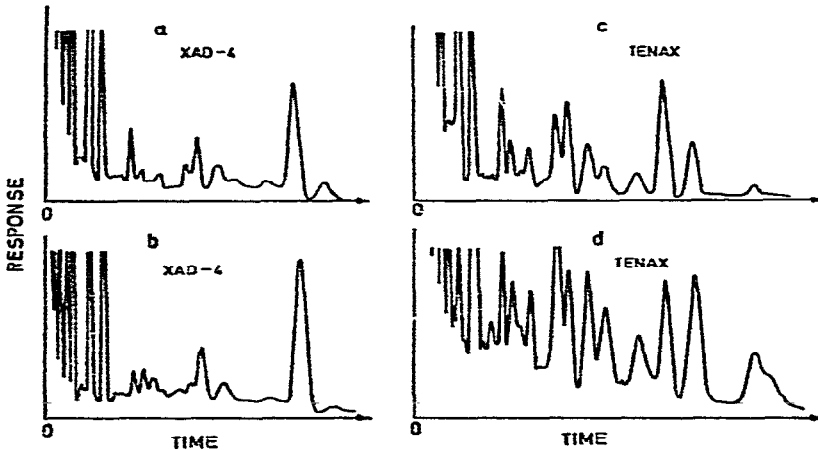


Fig. 11. Comparison of chromatograms obtained after the percolation of 10-l sea water samples through XAD-4 and Tenax resins and eluted with cold [(a) and (c)] and hot [(b) and (d)] methanol.

sea water<sup>23</sup>, but investigations with several times larger sea water samples gave approximately the same response.

Fig. 12 shows chromatograms obtained after the percolation of 25-l sea water samples through XAD-2, XAD-4 and Tenax resins with acetonitrile and acetone as eluents. The eluates were re-extracted with *n*-pentane and cleaned up on an alumina column. As before, the chromatograms obtained with Tenax are significantly larger than those obtained with XAD resins. However, it is also interesting that the shape of the chromatograms obtained with XAD-2 resin resembles more closely that of a standard PCB mixture than those obtained with XAD-4 resin.

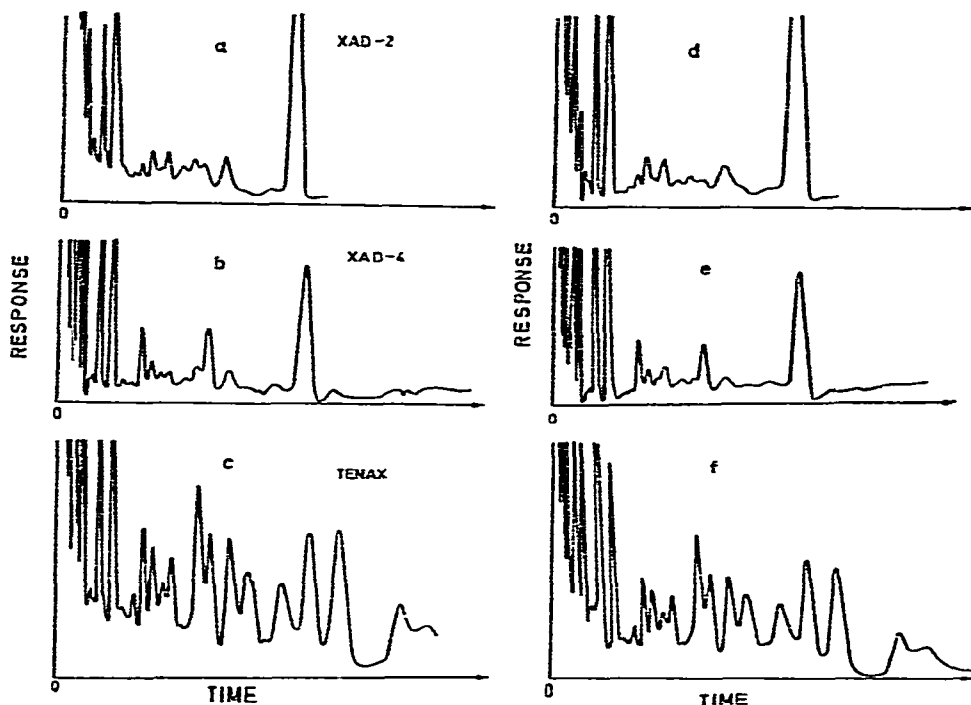


Fig. 12. Comparison of chromatograms obtained after the percolation of 25-l sea water samples through resins and eluted with acetone and methanol: (a) XAD-2, acetone; (b) XAD-4, acetone; (c) Tenax, acetone; (d) XAD-2, acetonitrile; (e) XAD-4, acetonitrile; (f) Tenax, acetonitrile.

## CONCLUSION

The application of macroreticular resins for the adsorption of chlorinated hydrocarbons from water samples and their determination after elution with different solvents has revealed several limitations. When water samples were spiked at levels close to the reported concentrations in sea water, the recovery of the investigated chlorinated hydrocarbons was low and unpredictable.

The problem of blank values is especially critical for Tenax resin, even after its thorough clean-up with several solvents.

Natural sea and tap water samples, although collected at the same time and at the same location, gave different chromatograms with electron-capture detection after re-extraction of the eluate and alumina column clean-up. These differences appeared to be due to the use of different resins and solvents. Hence the procedure for the determination of low concentrations of chlorinated hydrocarbons in sea and tap water by using macroreticular resins is not reproducible.

This explains why during inter-calibration of the method for the determination of chlorinated hydrocarbons in sea water the results between some of the laboratories varied by two orders of magnitude<sup>24</sup>. Such results were obtained in spite of the fact that the adsorption of chlorinated hydrocarbons on XAD-2 resin was performed in only one laboratory, while the desorption, clean-up and determination were performed separately by several independent laboratories.

In conclusion, it is clear that the use of macroreticular resins for the determination of low concentrations of chlorinated hydrocarbons in sea and tap water is not completely satisfactory. Much care is necessary and various uncertainties must be taken into consideration when evaluating the results obtained for the concentration of chlorinated hydrocarbons in sea water by means of this method.

#### ACKNOWLEDGEMENT

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