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TRACE ANALYSIS OF SOME CHLORINATED HYDROCARBONS IN WATERS BY GAS–LIQUID CHROMATOGRAPHY

MANFRED MOHNKE*, KARL-HEINZ ROHDE, LUTZ BRÜGMANN and PETER FRANZ
Forschungsstelle für chemische Toxikologie und Institut für Meereskunde der Akademie der Wissenschaften der DDR, Permoserstrasse 15, 7050 Leipzig (G.D.R.)*

SUMMARY

A composite analytical procedure is proposed for the determination of some chlorinated hydrocarbons (polychlorinated biphenyls, hexachlorobenzene, dichlorodiphenyltrichloroethane (DDT) metabolites, and four hexachlorocyclohexane isomers) in natural waters in the lower ppt range. The procedure includes sampling by 23.5-l balloons, applicable to a depth of 1500 m, and by a microlayer screen sampler; extraction by turbo-stirring, directly in the sampler with *n*-hexane; clean-up with sulphuric acid; and instrumental detection by packed column gas chromatography with electron-capture detection. Cross-checks with the capillary column technique turned out to be successful.

INTRODUCTION

The aquatic environment is increasingly affected by organic chemicals of anthropogenic origin. This is especially true for xenobiotic substances, produced in huge amounts, which are inevitably introduced into the environment in large quantities as a result of their specific applications; they also have considerable persistence. An acute threat to the living aquatic resources is posed if substances accumulate to a significant extent via organisms, if additional enrichment takes place along the food webs and if relatively low contents in water and in organisms cause acute toxic or sub-lethal effects.

Due to these facts, a group of chlorinated hydrocarbons from among the xenobiotics have been investigated extensively for several decades in different media, *e.g.* seawater, surface water, drinking water, etc. This group includes some persistent pesticides such as the dichlorodiphenyltrichloroethane (DDT) metabolites, hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs) (lindane and the other non-insecticidic isomers) and residues of technical formulations of polychlorinated biphenyls (PCBs), terphenyls (PCT) or camphenes (PCC, toxaphene). Studies like these constitute an essential part of environmental programmes on a global scale, *e.g.* governed by U.N. organizations (UNESCO/IOC-GIPME, UNEP-GEMS) or by selected regions (UNEP Regional Seas Programme, Baltic Monitoring Programme, MedPol) and on a national level for coastal and surface waters.

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The accurate and precise determination of the above-mentioned compounds in natural waters is a challenge for the analyst. The concentrations are often at the pg/l level and there are many risks of contamination of the sample and/or of losses of the determinant during the whole analytical procedure, which comprises sampling, extraction, enrichment, storage and clean-up. In the samples prepared for gas chromatography with electron-capture detection (GC–ECD), the target compounds have to be enriched up to 50 000 times and more. In addition, a complex mixture of numerous substances with sometimes very close retention properties has to be dealt with. Therefore, a sophisticated GC technique and much analytical experience is needed to identify and quantify the desired substances. Finally, further errors could be introduced by improper approaches for the computation of the results.

Taking into consideration the above-mentioned analytical problems to be solved, it is not surprising that for media such as sea water, in which these chlorinated hydrocarbons occur close to global background levels, there is only a very limited pool of accepted and reasonable data. Recently, it has been stated that integrated monitoring for organochlorines in ocean waters cannot be carried out before further improvements and intercalibrations of the necessary analytical techniques have taken place[1].

The present paper reports studies aimed at elaborating a relatively simple overall scheme of interim character for the determination of selected organochlorines in natural waters, with special emphasis on seawater. This scheme is to cover the state-of-the-art on the analytical procedure, from sampling to recording of the GC peaks and their computation. The quality of the data obtained should fulfil the needs for baseline studies in the marine environment, followed by contamination assessments and trend monitoring. The main part of this paper will deal with the presentation and discussion of the details of GC measurement. However, it should always be kept in mind that an adequate instrumental technique is only one of the tools necessary to obtain reliable results on the occurrence of the compounds in the environment. The present work is further intended to establish the distribution patterns of some organochlorines declared as "hazardous substances" (PCB, DDT metabolites) or "noxious substances" (*e.g.* HCH isomers, HCB) in the "Baltic Sea Convention", Helsinki, 1974.

EXPERIMENTAL

Sampling

The samples were taken on four cruises of rv "A. v. Humboldt" (Academy of Sciences of the G.D.R.) between 1980 and 1984 into the Baltic Sea and adjacent parts of the north-east Atlantic (Fig. 1). Samples down to a depth of 1500 m were taken with home-made glass samplers, modified from Stadler and Schomaker[2]. Commercially available 23.5-l glass balloons (VEB Jenaer Glaswerk) fastened in a metal frame were covered with a stainless-steel lid without any O-ring. Both parts were fitted together smoothly with their grinded surfaces. By cutting a glass tube using a messenger-operated releaser, the balloon was filled with water at the desired depth and retrieved.

Surface sampling (0.2 m) was performed upwind and ahead of the main vessel aboard a small rubber boat by dipping the glass balloon under water. The surface

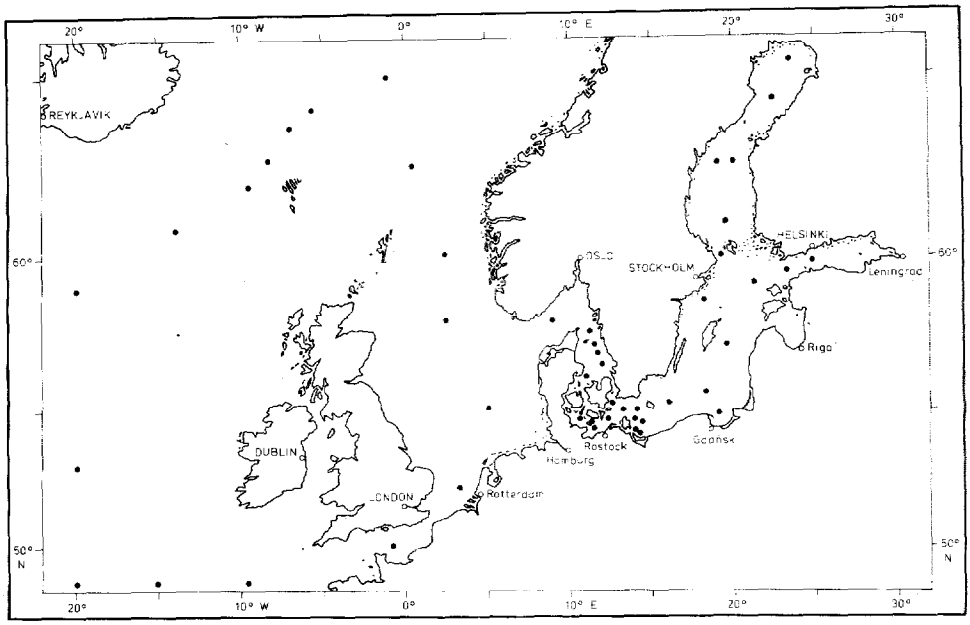

Fig. 1. Sampling stations for studies on chlorinated hydrocarbons in the Baltic Sea and in the adjacent north-east Atlantic.

microlayer of a maximum thickness of *ca.* 0.5 mm was taken with a 0.5-m^2 stainless-steel wire net of 1 mm mesh size[3]. About 2 l of this sample were obtained by 10–13 skimmings. Special attention was paid so that the sample prior to injection of the extracts into the chromatograph was in contact only with glass or metal parts.

Sample preparation

Immediately after sampling, extraction of the organochlorines was performed by 15 min of turbo-stirring[4] with 250 ml of *n*-hexane directly in the glass balloons. The applied hexane was previously twice-distilled following initial purification by treatment with concentrated sulphuric acid and sodium hydroxide–potassium permanganate. The microlayer samples were extracted by shaking them with 100 ml of hexane for 1 h.

After separation of the phases, the organic fraction was displaced from the top of the samples by adding previously extracted water through a glass tube to the bottom. The extracts were sealed in brown-glass bottles and stored in a deep-freeze.

In the land laboratory, the hexane was separated from water residues and treated once or twice with 20–50 ml of sulphuric acid. By this treatment the hexane was dried, the organic matter interfering with the GC analysis was destroyed and any salt residues removed. Thereafter, the extracts were carefully evaporated to near-dryness in a water bath of 75–80°C from 50-ml flasks with a 0.5-ml appendix ("nose") at the lowest part. The flasks were connected to a Vigreux separation column. Residual hexane was evaporated at 20–25°C under a dust protective hood. A 0.45-ml aliquot of carefully purified *n*-heptane was added to rinse the walls of the flask and to redissolve the organochlorines. For final clean-up, the heptane was then under-

layered with some drops of sulphuric acid added into the appendix of the flask. After an additional reaction time of 12 h, the sample was ready for injection into the GC apparatus.

Analysis

Most of the analyses were carried out with a packed column (diameter: 3 mm, length: 2 m, filling: 5% QF 1 on Gas Chrom Q 100–120 mesh, temperature: 185°C, nitrogen flow-rate: 60 ml/min, detector: ^{3}H-ECD) in the isothermal mode. The GCHF 18.3-4 (VEB Chromatron Berlin) chromatograph was run with a home-made constant-current electronics electrometer and a Hewlett-Packard 5880 A data system. The GC patterns of the samples were related to the signals obtained from measurements on mixtures of standard solutions, which were prepared for concentration levels and relations between the different components similar to the original samples. The standard solutions were made up from certified pure substances, obtained, for example, from the E.P.A. In addition, a diluted technical PCB formulation "Clophen 50" was used for comparison.

A 0.2-ml aliquot of the concentrated sample in *n*-heptane was hydrolysed in a microreactor for 90 min at 80°C with a small piece of potassium hydroxide. Thereby, DDT was transformed quantitatively into dichlorodiphenyldichloroethene (DDE), and dichlorodiphenyldichloroethane (DDD) resulted in dichlorodiphenylmonochloroethene (DDMU). The accuracy of the PCB determination increased considerably by this additional chemical treatment, due to reduced overlapping interferences. Taking into consideration the GC output from both types of samples, *i.e.* the untreated and hydrolysed aliquots, the final calculation of the target organochlorines was performed.

In addition to the packed column technique, for several samples gas chromatography with capillary columns was applied. The column itself was a home-made 50 m × 0.26 mm I.D. glass capillary tube coated with SE 54. The column was prepared by high-temperature silylation[5,6] and statically coated with a 0.25-μm layer of SE 54. To avoid splitting and distortion of the peaks, the column was connected, dead-volume free with silver chloride–polyimide, at the entrance with a 2 m × 0.3 mm I.D. deactivated fused-silica capillary tube[7,8]. Aliquots of the solution (2 μl) were injected into this retention gap by the on-column injection technique. Analysis was performed with a temperature programme between 40 and 250°C. A HP 5880A (Hewlett-Packard) chromatograph with a ^{63}Ni electron-capture detector was used. Additional sample chemistry, which has to be used with the packed column, was made unnecessary by the high peak resolution power (Fig. 2).

RESULTS AND DISCUSSION

Reproducibility of results obtained

The reproducibility of the measurements of consecutive samples from selected depths proved to be satisfactory. The relative standard deviation, depending on the type and concentration of the selected organochlorines, was between ±2 and ±20% (mean ±12%). No memory effects for the sampling step were observed when applying PCB, HCB or HCH isomer concentrations differing from one sample to another by one order of magnitude. In contrast, in the case of DDT, the samples were slightly

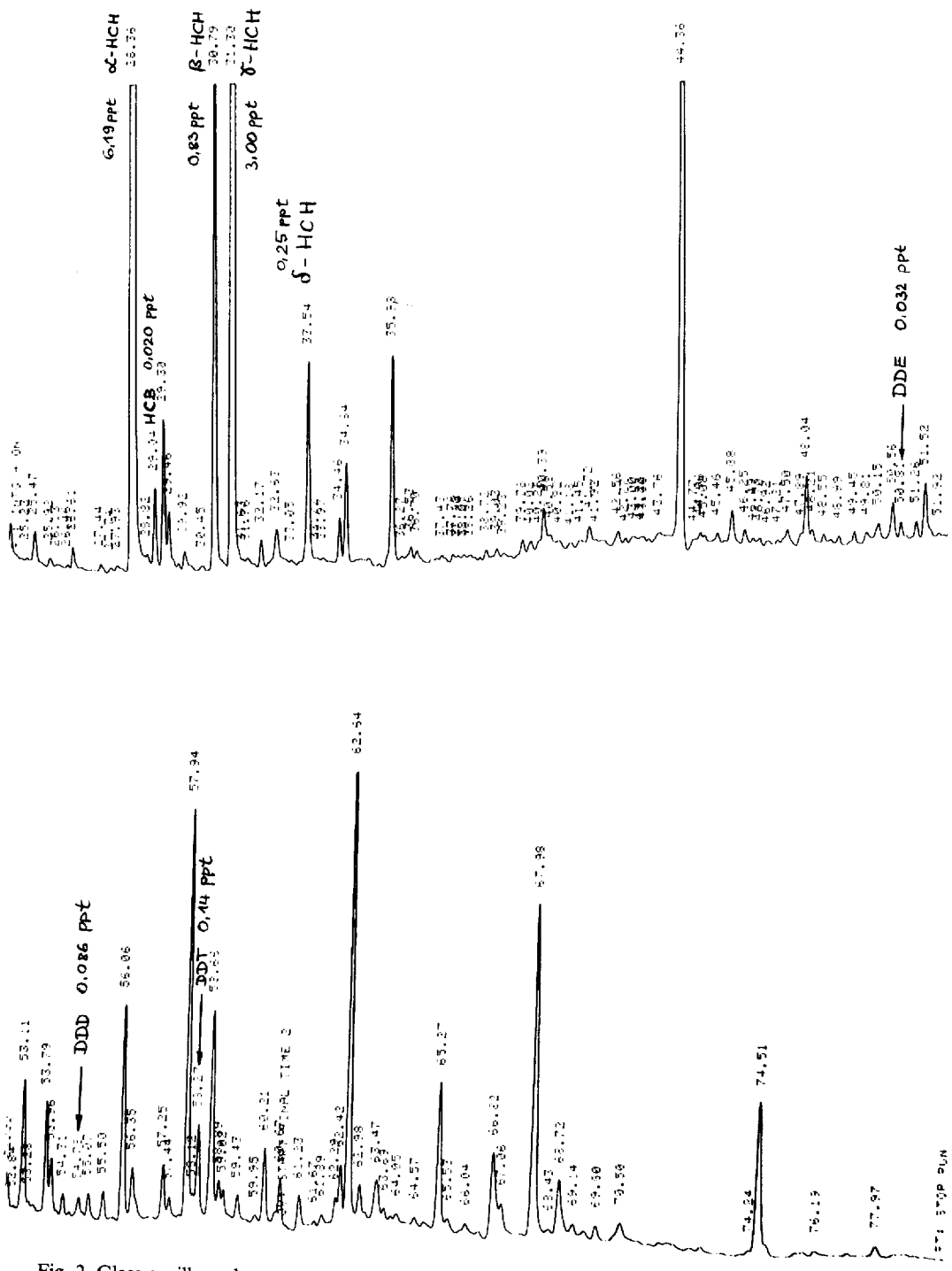

Fig. 2. Glass capillary chromatogram of an extract from a typical seawater sample. For GC conditions, see Experimental.

contaminated if the glass balloons had previously contained water with DDT levels ten times higher. This was consistent with the results of recovery tests, which reflected again the extraordinary role of DDT in this respect with only about 75% recovery, whereas the other chlorinated hydrocarbons were found more or less quantitatively.

In general, it can be concluded that the type of sampler and sampling technique proved satisfactory for the envisaged aim. Obviously, the extraction in the sampler reduced adsorption losses and contamination risks, and the application of the intensive turbo-stirring technique enabled more frequent sampling due to the rapid throughput. International intercalibrations have shown that the transfer of water from the sampler to the extraction system, *e.g.* continuous liquid–liquid extraction[9] or adsorption during passage of columns filled with XAD-2 resin[10], was time consuming and resulted in problems due to contamination by the degrading resin ("ghost peaks") or by losses. A limitation for further studies could possibly be the maximum volume of 23.5 l of sample obtainable. However, this could be solved by parallel sampling with several glass balloons. The so-called "airlift system" for continuous sampling of large volumes is applicable only to relatively shallow depths. Larger stainless-steel samplers for greater depths ("Bodega-Bodman sampler") are very expensive and more complicated to use.

The microlayer sampling technique with stainless-steel screens, which has been used by us successfully since 1980, has now become a widely accepted means for investigating exchange phenomena of organic substances between the sea and the atmosphere. The results of a recent intercalibration exercise, carried out at the Bermuda Biological Station and focused mainly on petroleum hydrocarbon collection, confirmed in principle entirely the approach applied by us for the organochlorines[11]. The reproducibility in terms of the thickness of the skimmed layer (0.26–0.44 mm) and of the measured organochlorine concentrations was found to be sufficient. In addition, sampling time and volume of the samples were well in accordance with the demands for monitoring purposes, because a great number of samples could be taken without losses in sensitivity or accuracy.

In all cases, unfiltered samples were used. It is often argued that with the lipophilic character increasing from the HCH isomers and HCB, which are dissolved in seawater reasonably well, to DDT metabolites and PCB, whose solubility is several orders of magnitude lower, a remarkable percentage of the latter compounds could be expected to exist in suspended forms. In turbid waters, the truly dissolved fraction should be entirely controlled by the quantity and quality of the particles. As an example, about one third of the total PCB content in a North Sea water sample was found to be combined with the suspended matter load of 0.8 mg/l (ref. 9). Comparable data for the Baltic Sea are still lacking.

With the increasing access of the laboratories working in the field of trace organic chemistry to sophisticated capillary column gas chromatography equipment, which is often connected to mass spectrometers, the less expensive and faster-working packed column technique is frequently condemned and classified as having no further value for studies on organochlorines in the environment. This is only partially true. Certainly, it is well accepted that for investigations on the origin, fate, biogeochemical cycle, degradation, metabolism, pathways, or toxicity assessment of substances that are composed of a mixture of hundreds of isomers/congeners, as, for example, PCB, PCT or PCC, time-consuming high resolution techniques including pre-separation

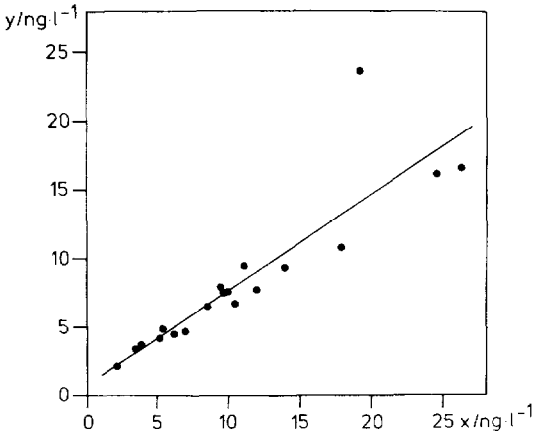

Fig. 3. Regression curve for PCB concentrations determined in nineteen extracts from seawater samples by packed and glass capillary column GC. For details, see Table I.

procedures by HPLC or simple adsorption chromatography and a positive identification through their masses are unavoidable prerequisites. For example, of the 209 theoretically possible PCB isomers, about 120 are significant constituents of technical products whose identification and quantitation demands the full resolution power of advanced capillary GC[12,13]. However, the preliminary step of environmental studies consists in the collection of baseline data with a wide diversity in space and time, to detect and predict trends and spatial differences. The necessarily high number of samples can be managed better with the relatively fast-working packed column technique, which generates valuable results if run properly. This can be demonstrated by Table I and Fig. 3, presenting the results of analyses carried out on nineteen samples from the Baltic Sea using two different techniques in parallel. Both the packed and the capillary column technique produced well-correlated data for most of the organochlorines, including PCB (Fig. 3). This, again, is in contradiction to statements from the literature, which declared the capillary column approach as the only applicable

TABLE I

CORRELATION BETWEEN ORGANOCHLORINE CONCENTRATIONS DETERMINED IN 19 EXTRACTS FROM SEAWATER SAMPLES, TAKEN IN 1981 FROM 10 STATIONS AT THE SURFACE AND CLOSE TO THE BOTTOM, BY TWO DIFFERENT GC TECHNIQUES

$y = A + Bx$, with x = analysis performed by capillary column gas chromatography ("HP 5880 A"), and y = analysis performed by packed column gas chromatography ("GCHF 18.3-4").

Compound	*Corr. coeff. (r)*	*Constant (A)*	*Slope (B)*
PCB	0.88	0.71	0.70
DDT	0.84	0.026	0.77
α-HCH	0.96	1.1	0.67
β-HCH	0.69	0.53	0.53
γ-HCH	0.94	0.51	0.73
δ-HCH	0.88	0.091	0.63
HCB	0.46	0.015	1.6

one for PCB analyses[9]. For HCB, the differences observed were significantly greater, but still in the 5% uncertainty range. This could be explained by the reduction in accuracy when carrying out measurements closer to the detection limit.

Spatial and temporal distribution of organochlorines in the Baltic Sea

Tables II–VI present a statistical survey of the results on the vertical and temporal distribution of some organochlorines in the Baltic Sea, based on 411 samples taken from the microlayer (84) and the water column (327) during four expeditions between 1980 and 1984. As a further example, the frequency distribution for the cruise in 1984 is given in Fig. 4. The number of comparable data from other sources for the area under investigation is very poor and actually zero for microlayer con-

TABLE II

CHLORINATED HYDROCARBONS IN BALTIC WATERS IN 1980 ("POLEX '80")

Compound	*Samples**	*n*	*Mean (ng/l)*	*Range (ng/l)*	*R.S.D.** (±%)*
PCB	Total	156	4.14	0.38 –13.94	65
	Surface	34	5.15	0.38 –13.94	69
	Subsurface	84	3.32	0.64 –11.78	59
	Bottom	38	5.05	0.72 –12.94	53
DDT	Total	156	0.18	0.03 – 0.99	71
	Surface	34	0.17	0.03 – 0.4	47
	Subsurface	84	0.17	0.03 – 0.76	77
	Bottom	38	0.19	0.1 – 0.99	74
α-HCH	Total	156	3.15	0.22 –19.11	71
	Surface	34	3.26	0.54 –19.11	97
	Subsurface	84	3.21	0.22 –16.72	66
	Bottom	38	2.89	1.15 – 6.35	44
β-HCH	Total	147	0.60	0.1 – 3.65	66
	Surface	34	0.63	0.16 – 3.65	91
	Subsurface	79	0.59	0.11 – 2.59	56
	Bottom	34	0.58	0.1 – 1.51	53
γ-HCH	Total	156	2.20	0.29 –12.45	69
	Surface	34	2.42	0.38 –12.45	88
	Subsurface	84	3.91	0.29 –12.21	412
	Bottom	38	2.12	0.85 – 5.15	41
δ-HCH	Total	146	0.17	0.03 – 0.96	63
	Surface	34	0.16	0.03 – 0.96	94
	Subsurface	78	0.17	0.04 – 0.54	51
	Bottom	34	0.17	0.03 – 0.45	53
HCB	Total	142	0.10	0.004– 0.78	86
	Surface	34	0.12	0.3 – 0.78	113
	Subsurface	77	0.09	0.004– 0.48	71
	Bottom	31	0.09	0.03 – 0.19	46

* Surface: 0.2 m; subsurface: 8–445 m; bottom: 1.5–5 m above sea floor.

** R.S.D.: relative standard deviation.

TABLE III

CHLORINATED HYDROCARBONS IN BALTIC WATERS IN 1981 ("POLEX '81")

Compound	*Samples**	*n*	*Mean (ng/l)*	*Range (ng/l)*	*R.S.D.*** *(±%)*
PCB	Total	92	7.0	1.16–41	93
	Surface	24	8.3	2.41–27	88
	Subsurface	44	5.8	1.16–21	66
	Bottom	24	7.9	1.18–41	114
DDT	Total	86	0.15	0.04– 1.20	120
	Surface	23	0.17	0.04– 0.56	74
	Subsurface	40	0.13	0.04– 0.48	133
	Bottom	23	0.15	0.04– 1.20	154
α-HCH	Total	92	4.6	0.89– 8.18	37
	Surface	24	4.9	2.55– 6.26	22
	Subsurfacce	44	4.9	0.89– 8.18	40
	Bottom	24	3.9	1.11– 6.4	41
β-HCH	Total	92	0.6	0.07– 1.02	38
	Surface	24	0.6	0.35– 1.02	27
	Subsurface	44	0.6	0.07– 0.85	37
	Bottom	24	0.5	0.08– 0.91	50
γ-HCH	Total	92	2.3	0.59– 4.08	36
	Surface	24	2.7	1.43– 4.08	21
	Subsurface	44	2.2	0.67– 5.00	37
	Bottom	24	2.0	0.59– 3.28	44
δ-HCH	Total	92	0.2	0.04– 0.39	36
	Surface	24	0.2	0.10– 0.39	34
	Subsurface	44	0.2	0.04– 0.32	35
	Bottom	24	0.2	0.05– 0.27	40
HCB	Total	91	0.07	0.01– 0.24	46
	Surface	24	0.08	0.05– 0.15	37
	Subsurface	44	0.07	0.02– 0.24	51
	Bottom	23	0.06	0.01– 0.12	47

* Surface: 0.2 m; subsurface: 8–445 m above sea floor.
** R.S.D.: relative standard deviation.

tents. Due to the different analytical techniques in use, the number of comparable results is further diminished. Comparison is only possible with a set of data from one other laboratory, concerning 55 samples taken in May/June 1983 in the Baltic Sea[14]. The author used a similar sampling (10 l) and extraction system, but different clean-up and GC procedures[15]. The reported limits of detection are nearly identical to ours (0.03 ng/l for DDT metabolites, 0.01 ng/l for the HCH isomers and 0.005 ng/l for HCB), taking into consideration the different sample volumes applied.

Due to the variability of the results (see Tables II–VI), no statistically significant regional distribution patterns were found for any of the investigated substances. However, saline water penetrating the deeper parts of the Baltic Sea from the North

TABLE IV

CHLORINATED HYDROCARBONS IN BALTIC WATERS IN 1983 ("POLEX '83")

Compound	*Samples**	*n*	*Mean (ng/l)*	*Range (ng/l)*	*R.S.D.** (±%)*
PCB	Total	24	12.04	3.46–36.20	77
	Surface	6	13.47	7.45–19.54	36
	Subsurface	12	12.34	4.15–31.20	77
	Bottom	6	10.00	3.46–36.20	129
DDT	Total	26	0.48	0.14– 1.20	68
	Surface	8	0.62	0.26– 1.20	57
	Subsurface	12	0.40	0.14– 1.01	74
	Bottom	6	0.45	0.16– 0.98	77
α-HCH	Total	24	6.19	1.41–19.40	62
	Surface	8	7.17	4.90–19.40	70
	Subsurface	11	5.90	1.41–14.29	59
	Bottom	5	5.29	1.56– 8.81	50
β-HCH	Total	24	0.82	0.09– 2.24	48
	Surface	8	0.84	0.52– 1.04	18
	Subsurface	11	0.84	0.09– 2.24	65
	Bottom	5	0.73	0.22– 0.89	39
γ-HCH	Total	24	4.01	1.71– 8.02	44
	Surface	8	4.46	2.80– 7.19	37
	Subsurface	11	3.73	2.02– 7.58	44
	Bottom	5	3.90	1.71– 8.02	62
δ-HCH	Total	24	0.17	0.04– 0.53	53
	Surface	8	0.16	0.10– 0.22	23
	Subsurface	11	0.18	0.06– 0.53	69
	Bottom	5	0.16	0.04– 0.20	43
HCB	Total	24	0.12	0.01– 0.72	115
	Surface	8	0.11	0.08– 0.16	22
	Subsurface	11	0.16	0.03– 0.72	128
	Bottom	6	0.06	0.01– 0.10	57

* Surface: 0.2 m; subsurface: 8–445 m; bottom: 1.5–5 m above sea floor.
** R.S.D.: relative standard deviation.

Sea obviously has a distinctly lower content of organochlorines. This fact is expressed by the lower mean values for these compounds in the bottom waters and a negative correlation with salinity. The vertical distribution peculiarities with maxima in the surface layer reflect the influence of recent atmospheric and land-derived inputs. The concentrations of some HCH isomers seem surprisingly high. This is in accordance with the findings of Gaul[14]. Only γ-HCH ("lindane", which partly replaced DDT due to its lower bioaccumulation potential) has an insecticidic effect. However, undesired by-products of technical formulations, *e.g.* α-HCH with up to 60–75%, the most persistent β-HCH (7–10%) or δ-HCH (7%), are proportionally enriched in the marine environment. In recent years, many countries have applied products, which

TABLE V

CHLORINATED HYDROCARBONS IN BALTIC WATERS IN 1984 ("POLEX '84")

Compound	*Samples**	*n*	*Mean (ng/l)*	*Range (ng/l)*	*R.S.D.** (±%)*
PCB	Total	54	4.80	0.90–46.21	128
	Surface	17	3.59	0.90– 6.78	47
	Subsurface	30	8.86	1.57–46.21	137
	Bottom	7	3.16	1.82– 5.62	42
DDT	Total	55	0.51	0.03– 5.33	138
	Surface	17	0.36	0.03– 0.92	51
	Subsurface	30	0.45	0.04– 1.19	52
	Bottom	8	1.02	0.22– 5.33	172
α-HCH	Total	55	3.19	1.10– 4.84	28
	Surface	17	3.00	1.10– 4.29	34
	Subsurface	30	3.3	1.27– 4.84	28
	Bottom	8	3.18	2.39– 4.04	20
β-HCH	Total	55	0.74	0.09– 3.62	60
	Surface	17	0.65	0.21– 1.07	35
	Subsurface	30	0.72	0.09– 1.04	29
	Bottom	8	1.03	0.53– 3.62	102
γ-HCH	Total	55	2.22	0.75– 3.13	22
	Surface	17	2.17	0.75– 3.13	33
	Subsurface	30	2.23	1.3 – 2.88	17
	Bottom	8	2.31	1.49– 2.67	18
δ-HCH	Total	55	0.11	0.01– 0.21	39
	Surface	17	0.09	0.02– 0.14	36
	Subsurface	30	0.12	0.02– 0.21	36
	Bottom	8	0.08	0.01– 0.13	45
HCB	Total	55	0.09	0.03– 0.19	33
	Surface	17	0.09	0.03– 0.13	36
	Subsurface	30	0.13	0.05– 0.13	103
	Bottom	8	0.11	0.07– 0.19	37

* Surface: 0.2 m; subsurface: 8–445 m; bottom: 1.5–5 m above sea floor (only from Western Baltic).
** R.S.D.: relative standard deviation.

consist mainly of the insecticide component γ-HCH. However, this change in application is not yet expressed in the change of the ratios between the HCH isomers during the period of investigation.

In spite of the restrictions for the use and production of PCB and DDT, which have been introduced in several countries bordering the Baltic Sea, both substances showed no trend for a decrease in the period under investigation. One possible interpretation is that the concentrations in the water column are effectively controlled by the contents of these substances in the sediments, which represent a long-term and large pool for them. Under laboratory conditions, the experiments of Södergren and Larsson[16] have shown the reflux of PCB from sediments to the water column by

TABLE VI

CHLORINATED HYDROCARBONS IN THE SURFACE MICROLAYER OF THE BALTIC SEA IN 1980–1984 (ng/l)

Compound	*1980 Sept./Oct. (n = 26)*		*1981 May/June (n = 25)*		*1983 June/July (n = 22)*		*1984 Nov./Dec. (n = 16)*	
	Mean ± S.D. (Range)	*EF* Range*	*Mean ± S.D. (Range)*	*EF* Range*	*Mean ± S.D. (Range)*	*EF* Range*	*Mean ± S.D. (Range)*	*EF* Range*
PCB	20.2 ± 5.6	6.7	20.0 ± 10.2	2.0	19.8 ± 7.7	0.3	8.6 ± 3.9	1.6
	(10.6–31.5)	0–59	(7.2–46.0)	1–6	(10.0–38.9)	0–1	(5.5–20.0)	0–4
DDT	1.46 ± 0.43	10.8	1.08 ± 0.55	8.0	3.08 ± 3.90	3.5	1.6 ± 0.8	2.9
	(0.58–2.40)	2–44	(0.41–2.71)	0–22	(0.82–17.9)	1–14	(0.22–3.50)	0–6
α-HCH	1.43 ± 0.44	1.2	6.50 ± 1.63	0.4	5.31 ± 0.96	0	3.1 ± 1.1	0.3
	(1.9–7.3)	0–8	(2.7–11.9)	0–2	(3.2–7.1)		(1.1–5.4)	0–2
β-HCH	0.55 ± 0.21	0.6	1.10 ± 0.23	0.8	1.28 ± 0.56	0.3	1.1 ± 0.6	1.3
	(0.16–1.11)	0–3	(0.55–1.62)	0–2	(0.69–3.46)	0–1	(0.20–2.70)	0–7
γ-HCH	4.73 ± 1.42	2.6	5.60 ± 1.40	1.0	8.55 ± 5.90	0.6	3.1 ± 1.1	0.7
	(2.40–6.60)	0–13	(2.95–25.2)	0–8	(4.08–32.4)	0–2	(1.4–5.7)	0–4
δ-HCH	0.14 ± 0.06	0.4	0.30 ± 0.12	0.5	0.26 ± 0.14	0.5	0.10 ± 0.03	0.5
	(0.06–0.30)	0–3	(0.15–0.66)	0–2	(0.10–0.68)	0–2	(0.06–0.20)	0–4
HCB	0.26 ± 0.10	2.8	2.00 ± 1.36	27	0.33 ± 0.27	2.4	0.18 ± 0.08	1.3
	(0.12–0.46)	0–15	(0.12–6.38)	0–127	(0.06–1.01)	0–12	(0.04–0.31)	0–4

* EF (enrichment factor) $= \frac{c\ (\text{microlayer})}{c\ (0.2\ \text{m depth})} - 1.$

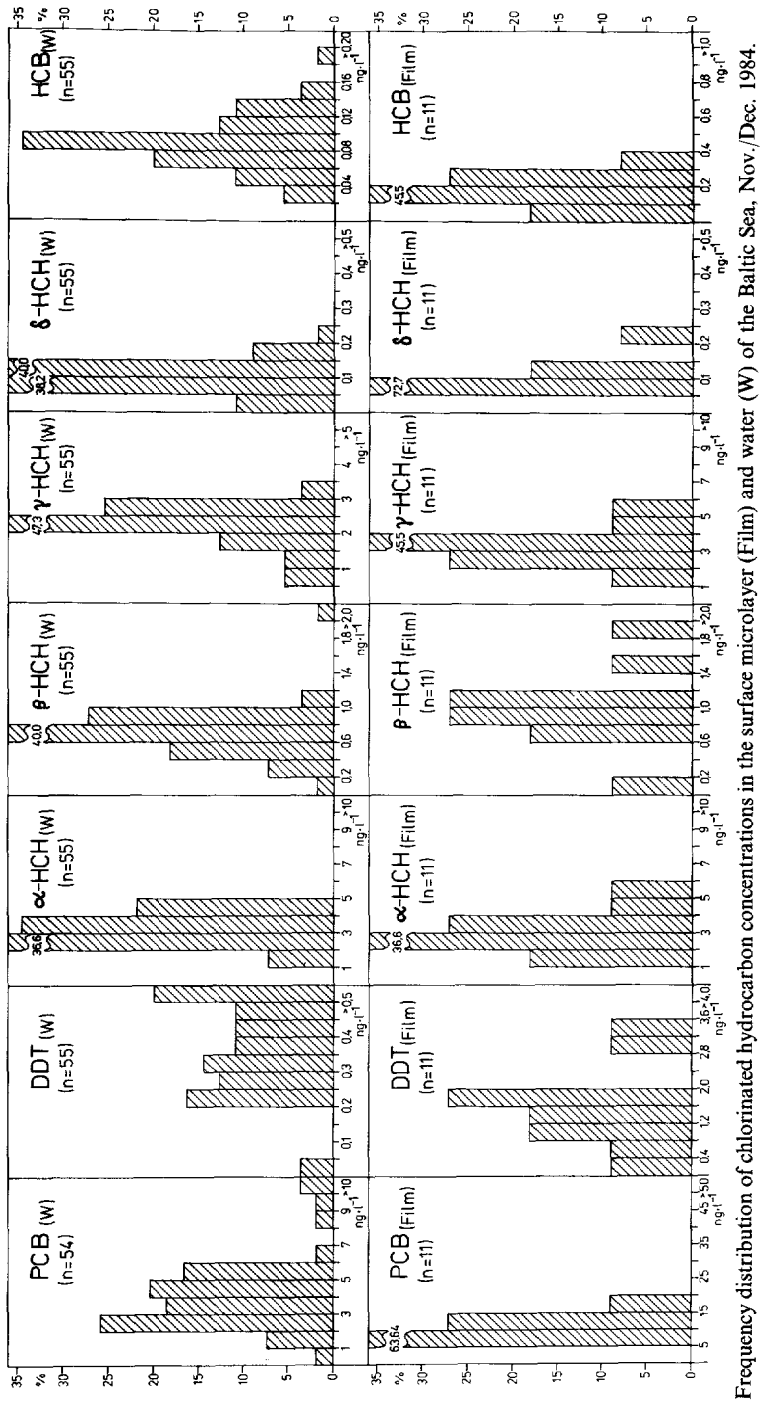

Fig. 4. Frequency distribution of chlorinated hydrocarbon concentrations in the surface microlayer (Film) and water (W) of the Baltic Sea, Nov./Dec. 1984.

transport processes with gas bubbles or conducted by bioturbation. Evidence for the importance of that kind of mechanism for the Baltic Sea could be related from studies on the ratios of different PCB congeners. If the fresh input of these organochlorines decreased significantly, this should be reflected by a relative increase of the most persistent isomers. At least two of the PCB isomers, IUPAC nos. 153 and 138 (2,4,5,2′,4′,5′- and 2,3,4,2′,4′,5′-hexachlorobiphenyl, respectively), could possibly serve as indicators for such studies[13,14].

The accumulation of organochlorines in the sea-surface microlayer is, in several cases, quite high (Table VI) and should exhibit a potential threat for the neuston organisms living close to the sea–atmosphere interface. The enrichment characteristics depend on the state of the sea surface (mixing by wind-induced waves) and from the composition of the total organic matter enriched together with the organochlorines in the microlayer. Petroleum hydrocarbons, for example, seem to act as effective "extracting agents" for some organochlorines[17].

CONCLUSIONS

The proposed analytical procedure for the determination of selected organochlorines in the lower ppt range in natural waters has proved successful in terms of accuracy, precision and simplicity. The values obtained from four expeditions between 1980 and 1984 by packed column gas chromatography with an electron-capture detector are of sufficient quality for use in baseline studies in the Baltic Sea and adjacent areas. The data were reasonably comparable with those received from glass capillary column GC.

Further studies should be focused on broadening the spectra of investigated compounds and should deal first of all with questions of the degradation, metabolism, persistence and potential toxicity of single isomers, *e.g.* of the PCB group. Therefore, a more sophisticated analytical approach including glass capillary column chromatography is needed. In addition, a full set of the predominant PCB congeners should be made available to the laboratories concerned with these studies.

Another important problem is the determination of the speciation of organochlorines. There is still a need for reliable analytical tools for splitting up the total concentrations of the water samples into different fractions, including the truly dissolved, suspended and those parts that are fixed intimately by dissolved/colloidal macromolecules as humic substances, carbohydrates or peptides.

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