Bull. Environm. Contam. Toxicol. 27, 397-405 (1981)

Residues of DDT in a Contaminated Norwegian Lake Ecosystem

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Concentrations of DDT in roaches (3 ppm), bottom sediments (25 ppm) and water (3 ppt) from lake Ørsjøen in southern Norway were high in comparison to similar data in fish from other lakes in Norway (KVESETH & BREVIK 1974) Sewage effluent from a nearby nursery school was found to be the source of contamination. Fish collected 5000 m from the sewage effluent contained 0.16 $\pm$ 0.13 ppm Σ DDT and bottom sediments sampled 450 m away 0.01 ppm. The apparent bioconcentration factor for DDT in the fish was calculated to be 1.07×10^6.

The area of lake Ørsjøen is about 6 square kilometers. The population density around the lake is low, and except for the plant nursery school located at the southern end, near to Sagbukta, there are no other known sources of DDT (see Fig.1).

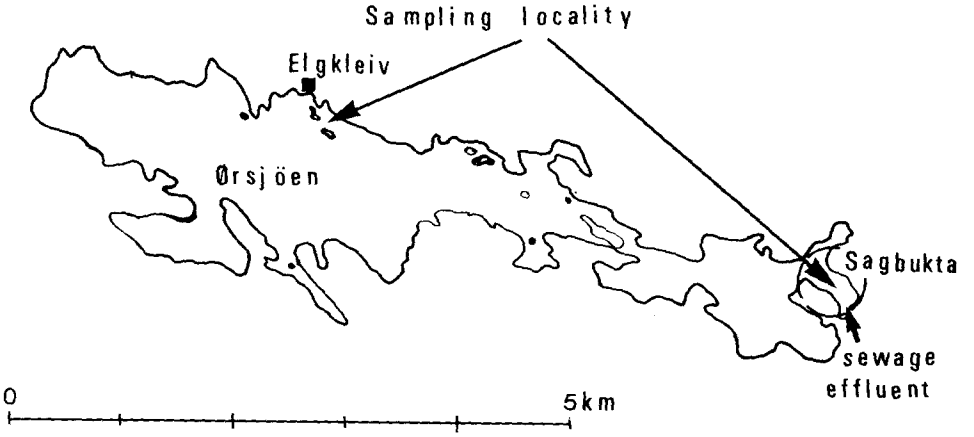

Fig.1.The sampling localities in Ørsjøen, Sagbukta and Elgkleiv.

In the spring of 1975 high values of DDT were detected in some fish from Ørsjøen. The sewage effluent from the nursery school was suspected as source of contamination and the nursery was prohibited from emptying sewage into the lake.

This paper presents the results of a stydy characterizing the contamination source, the geographic distribution of DDT among bottom sediments, water and roaches.

MATERIALS AND METHODS

DDT content was measured in water, bottom sediments and in roaches (Rutilus rutilus) from two sampling sites, one at Sagbukta, around the suspected source of DDT and the other at Elgkleiv about 5000 m away (Fig. 1).

Water samples were taken at 30, 150, 300, 600 and 5000 m (at Elgkleiv)from the effluent point, 0.5 m below the wather surface. Three samples of 2.8 L were sampled at each point and stored at 4^{o} C for 14 days prior to analysis. Five samples of bottom sediments were collected along each of three different lines at distances of 1,4,11,33 and 99 m from the effluent point. Sediments were also sampled at 200, 300, 400, 500 and 5000 m.

Roaches were about 25 cm in length and weighed about 170 g. They were captured using gill nets at Sagbukta and Elgkleiv.

Amberlite XAD-4 (Rohm & Haas, Philadelphia, PA, U.S.A) a synthetic polymeric absorbent was used for the extraction of DDT compounds from water. XAD-4 resin has been used by other to extract organochlorine insecticides from water (MUSTY & NICKLESS 1974). Prior to extraction the resin was exhaustively purified in a Soxhlet extractor with successive portion of acetone, methanol, water and methanol. Recovery tests with lindane, pentachloronitrobenzene, DDE, DDD and DDT added to tap water were made prior to analysis of the water samples. The XAD-4 resin was weighed into glass columns (I.D. 0.60 - 1.10 cm) containing a glass wool plug just above the stopcock. Methanol was rinsed from the resin with ca. 20 bed volumes of distilled water before the column was ready for use. The water were passed through the column

at a flow rate of 15 to 30 mL per min. The adsorbed insecticides were eluted first with acetone (10 mL) and then hexane (100 mL). The elutants were shaken with 50 mL distilled water (two times), the hexane phase was dried over Na_2SO_4 and transferred to a flask and concentrated to 1 mL on a rotary evaporator.

Sediment samples were air dried and extracted using hexane-2-propanol (3:1) in a Soxhlet extractor for 5 h. The extract was shaken with water in a separatory funnel and the organochlorine compounds paritoned into hexane. The 2-propanol-water solution was reextracted twice with hexane, the combined hexane extracts washed once with water, dried by passage trough a column of Na_2SO_4 and reduced to 2 ml on a rotary evaporator.

Fish liver was ground with anhydrous $MgSO_4$ and seasand and the homogenate transferred to a glass column (I.D.= 1.0 cm) containing a glass wool plug and extracted by eluting with diethyl ether. The diethyl ether extract was evaporated to dryness on an air stream at room temperature.

Prior to the gas chromatographic analysis the concentrated extracts were treated by conc.sulfuric acid and a solution of 10% KOH in methanol. For the mass spectrometric analysis the extracts were cleaned by adsorption chromatography using aluminiumoxide and florisil as adsorbents.The concentrated extracts were added to a glass column (I.D= 0.6 cm) packed with 1 g Al_2O_3, (activated at 800°C for 8 h and deactivated with 5% distilled water) and eluted with 15 mL hexane (fraction I) and then with 15 mL hexane with 10% diethyl ether added (fraction II). For further purification each of the two concentrated fractions were similarly chromatographed using florisil (activated at 130°C for 4 h and deactivated with 5% distilled water) instead of aluminium oxide as adsorbent.

All GLC analyses were performed with a gas chromatograph equipped with dual columns (1.8 m ID = 2 mm) packed with 10% QF-1 and 4% SF-96 on 80/100 mesh Chromosorb W AW-DMCS, and electron capture detectors (Sc^3H). Comined gas chromatography-mass spectrometry studies were performed using a glass column

(2.1 m I.D.=4 mm) packed with 3% SE-30 on 80/100 mesh Chromosorb W AW-DMCS.

RESULTS AND DISCUSSION

The results of the recovery analysis of some organochlorine insecticides in water using the prescribed technique with XAD-4 as an adsorbent are given in Tabel 1. The effect of varying the concentration of lindane, pentachlornitrobenzene, p,p'-DDE, p,p'-DDD, and p,p'-DDT in a water solution showed that with increasing concentrations recoveries decreased, most for DDE and DDT when 2g XAD-4 was packed in a column. (I.D. = 6 mm) and 1 L of the fortified water was passed through the resin at a flow rate of 15 mL/min. Desorption with 10 mL acetone and thereafter 100 mL hexane was used all the time.

Recoveries were improved by using more resin and at the same time increasing the column diameter to 1.1 cm and the flow rate to 30 mL/min. With 8g XAD-4 and 2.8 L fortified water (concentrations of the insecticides between 50-400 ppt) recoveries were 100% or above for all the insecticides except DDE (91%).

Detectable amount of DDE and DDT, i.e. between 1 and 3 ng/L, were found in water samples (2.8 L) collected within a distance of 300 m from the sewage effluent (Table 2)

In fish liver almost extensively DDE (90-93% of ΣDDT (DDE + DDD + DDT)) was found. In 1975 the average ΣDDT of 14 + 12 ppm in fish from Sagbukta decreased to 0.16 ± 0.13 ppm in fish collected 5000 m away, at Elgkleiv. The following year 3.2 + 1.0 ppm ΣDDT was found in fish from Sagbukta (Table 3). The reason for the reduction of DDT residues in fish collected at Sagbukta from 1975 may be that the sewage effluent from the nursery school was closed in April 1975. The DDT-residues in fish from Elgkleiv are equivalent to residues found in fish from uncontamintated lakes in Norway (KVESETH & BREVIK 1974, 1975, 1977).

In addition to DDE, DDD and DDT (called ΣDDT) in bottom sediments, the following DDT-components were identified by gas chromatography - mass spectrometry, 1-chloro-2, 2-bis (p-chlorophenyl) ethane (DDMS),4,4-dichlorobenzophenone (DBP), 1-chloro-2,2-bis(p-chlorophenyl) ethene (DDMu) and bis(p-chlorophenyl) acetonitrile (DDCN).

TABLE 1. Recovery tests for lindane (HCH), pentachloronitrobenzene (PCNB), DDE, DDD and DDT added to tap water at 8 - 5000 ppt. The effects of varying concentration of the compounds, the amount of water and resin, and column diameter are shown. Water flow rate was held between 0.5 and 2.0 L/min. Eluting solvent was 10 mL acetone and 100 mL hexane.

amount XAD-4,	conc range,	amount of water,	column i.d.,	Recovery (mean and range of values in per cent)				
g	ppt	L	cm	HCH	PCNB	DDE	DDD	DDT
2	2-80	1	0.6	-	111 86-130	108 106-113	115 105-120	112 98-108
2	50-400	1	0.6	-	116 99-146	89 67-112	116 104-126	72 51-90
2	125-5000	1	0.6	-	-	41 30-48	74 59-90	42 39-45
6	50-400	2.8	1.1	90 62-120	88 84-92	66 58-73	104 96-110	89 78-102
8	50-400	2.8	1.1	117 95-137	104 89-124	91 86-100	101 87-116	101 75-105

TABLE 2

DDT-residues in water samples (mean values of three samples of 2.8 L) from Ørsjøen (ppt). 8g XAD-4 and a glass column (I.D.=1.1 cm) is used, flow rate 0.5 L/min. and desorption with 10 mL acetone and 100 mL hexane.

Distance from effluent point, m	DDT	DDT	ΣDDT
30	0.26	2.8	3.1
150	0.13	1.4	1.5
300	0.13	2	2.2
600	-	t	-

t = trace, less than 0.1 ppt.

Masspectra of DDMS and DDCN are shown (Fig.2, Fig.3). DDD and DBP are reported as major metabolites after adding DDT to microbial communities of sewage and freshwater containing sediments while small amount of DDMS and DDMu was also formed (PFANDER & ALEXANDER 1972). Some of the compounds formed are strikingly similar to those formed by the bacteria Hydrogenomonas under anaerobic conditions and those previously reported to be products of the metabolism of DDT by Aerobacter aerogenes (WEDEMEYER 1967).

ΣDDT in bottom sediments at the sawage effluent point was 25 ppm, but concentrations decreased rapidly with increasing distance from the point. At 100, 300 and 450 m 0.1 ppm was found and at 5000 m the DDT was undetectable (below 0.005 ppm). In sediments sampled along three different directions all originating at the effluent point differing by 45^{o} (samples taken at 1, 11,33 and 99 m) the DDT residues decreased rapidly in all directions with increasing distance. The results from this investigation all demonstrate that the sewage effluent must be the contamination source, and that the contamination is limited to a relatively small area around the sewage effluent. The fact that insecticides virtually disappear from water into bottom mud is reported by several other workers who reported much higher residues in mud than in water above it (ROWE et al. 1971, MILES & HARRIS 1971).

TABLE 3. DDT-residues in liver of roach (Rutilus rutilus) (ppm)

Locality	Year	No	Fat(%)	S.D.	DDT (wet wt. basis)	Std. dev.	DDT (fat wt. basis)	S.D.
Sagbukta	1975	9	7.4 1.6-16.4	4.7	13.8 1.1-36	12.3	166 22-387	124
Elgkleiv	1975	10	2.2 0.9-3.5	0.9	0.16 0.05-0.5	0.13	8.1 2.1-23	6.8
Sagbukta	1976	10	4.9 2.8-10.0	2.9	3.2 1.7 -4.9	1.00	52 30-93	23
Sagbukta	1976	11	6.3 2.8-10	2.6	5.1 1.7-24.6	6.5	105 30-424	142

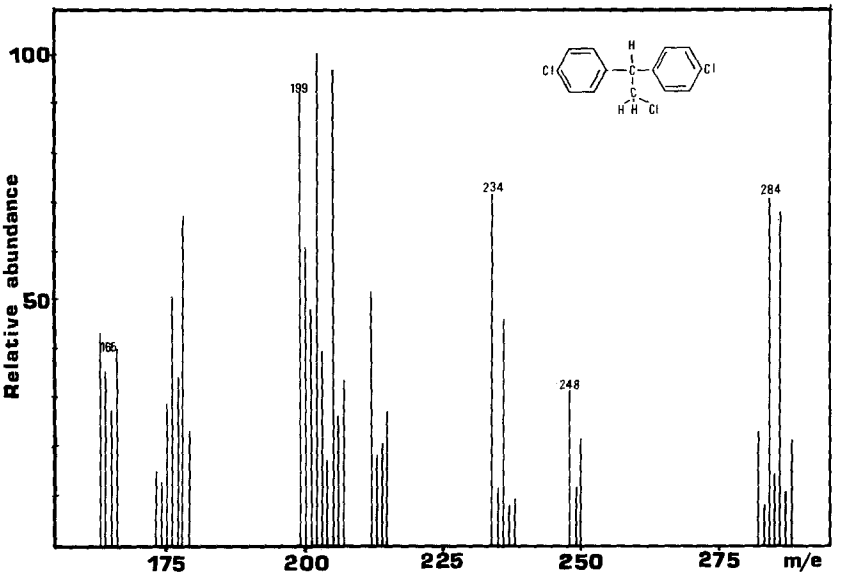

Fig.2 . Mass spectrum of 1-chloro-2,2-bis(p-chlorophenyl) ethane (DDMS).

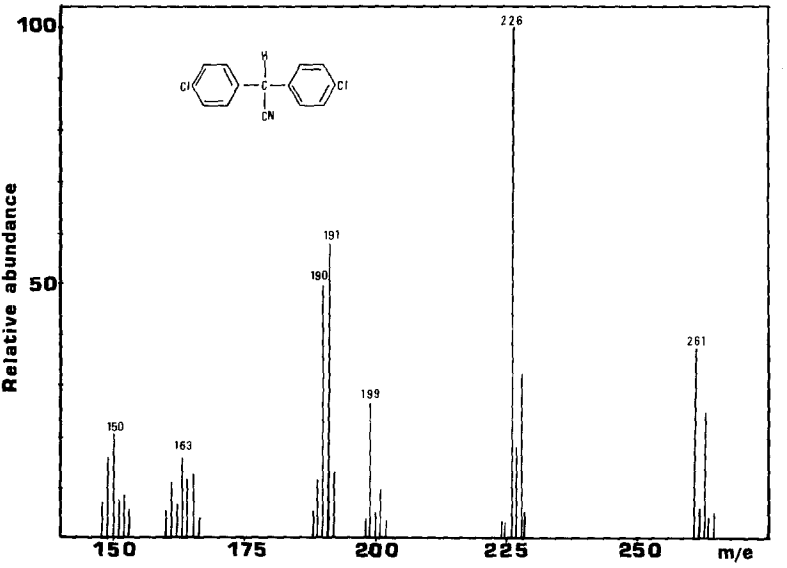

Fig.3 . Mass spectrum of bis(p-chlorophenyl)acetonitrile (DDCN).

The bioconcentration factor - ratio of DDT-residues in fish liver to water - is calculated to 2 x 10^6. Results from a similar study in lake Michigan were 2 ppt in water, 0.0014 ppm in sediments and 3-6 ppm in fish (HENDERSON 1972).

In an attempt to quantity the different DDT components, 0.78 ppm DDT, 22 ppm DDD, 0.29 ppm DDE, 0.70 ppm DBP, 1.3 ppm DDCN (used response one fourth of DDDs) and 2.9 ppm o,p'-DDD were found in a sediment sample taken 1 m from the sewage effluent point. The relative amount of DDT-components varied from place to place, DDD dominated near effluent point (96% of ΣDDT) while the distribution was 39% DDT, 26% DDD and 35% DDE 100 m away.

Acknowledgements. Investigation was supported by the Norwegian Agricultural Council. I thank I. Røken for assisting in analysis and J. Uthne Skaare for consultation during the mass spectrometric analysis.

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Accepted June 24, 1981