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THE LACK OF ACCUMULATION OF DDT RESIDUES BY BENTHIC INVERTEBRATES AND DEMERSAL FISH IN ST. MARGARET'S BAY, NOVA SCOTIA

by

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INTRODUCTION

A preliminary survey, started during 1973 in St. Margaret's Bay, N.S., was intended to quantify organochlorine residue concentrations in various organisms, water, sediments and suspended particulate matter. The overall aim of the proposed study was to describe the dynamics of residue transfer through a marine food chain in an area remote from immediate pesticide release. Studies concerning the physical and chemical oceanography of the area, as well as estimates of biomass and production of major producer and consumer organisms within St. Margaret's Bay during the last seven years, provide extensive background information useful for the construction of a budget which would examine biological and physical transfer mechanisms of pesticide residues within an unpolluted coastal ecosystem.

Monitoring of various compartments (freshwater discharge, atmospheric input, water, suspended and sedimented particulate material, plankton, benthic invertebrates and various species of fish) for organochlorine residues began during May 1973. Analytical problems became apparent immediately. No reliable measures of the extremely low concentrations of residues in water, suspended

particulate matter or sediments could be achieved. Even with the largest samples used (4-5 litres of water, 5-10 grams of sediment), estimates of residue concentrations were always equal to or below the limit of reliable detection (1 ng/µl [1 ppb] in an extract volume of 1 ml). Problems of glassware contamination and solvent purity, discussed by Giam and Wong (1972), prevented accurate determination of chlorinated hydrocarbons below this level. Concentration of organochlorine compounds by passage of large volumes of water through Amberlite XAD-2 resin was attempted by Badger (unpublished data) and while the technique appeared promising in laboratory efficiency tests, field samples were badly contaminated. Concurrent studies of fluorescing material in seawater (Gordon *et al.*, 1974) indicated that conventional water bottles, when unrinsed and passed open through the surface film, contaminate samples with material adsorbed to the inner bottle surface. Usual methods of sample collection are thus unsuitable for quantitative estimates of trace amounts of hydrocarbons in sea water and special glass-walled containers which open and close at the desired depth are required.

Organochlorine residues were present in samples of benthic invertebrates and demersal fish taken from St. Margaret's Bay during April and May 1973, in concentrations which could be reliably measured. Data obtained for a variety of these species are summarized here.

METHODS

Samples of benthic invertebrates and demersal fish were obtained from the deep central (60-75 m) and littoral (5-20 m) areas of St. Margaret's Bay during April and May 1973. Van Veen (0.1 m^2) bottom grabs were taken from an anchored boat and fauna collected as described by Peer (1970). A small otter

trawl towed at 2 knots was used to collect demersal fish species. All organisms were frozen within three hours of collection and held at -20 C until analyzed.

Organochlorine residues were extracted from groups of benthic invertebrates sorted to species, from whole fish and from dissected tissues, by homogenizing for two minutes in a blender with a stainless steel chamber. Small invertebrates were grouped to provide a minimal sample size for extraction (at least 1 g wet weight). Duplicate extractions were carried out for each determination using a chloroform:methanol (2:1) solvent mixture described by Folch *et al.* (1957) but used in a slightly modified procedure (Sameoto *et al.* 1975). The chloroform phase of an extract was reduced in volume by gentle rotary evaporation, taken up in *n*-hexane and again reduced to a small volume to remove chloroform. Aliquots of this solution were placed in pre-weighed aluminum foil cups and dried to a constant weight (24 hr) in a desiccator. Weights of material in this extract, taken as equivalent to lipid content, were expressed as a percentage of original wet tissue weight. The presence of *p,p'*-DDT isomer[1] was confirmed through saponification (reflux of residue with 2.5% alcoholic KOH for 15 minutes at 40 C) and conversion to *p,p'*-DDE (Holden and Marsden 1967).

Recovery of ^{3}H-*p,p'*-DDT, 'spiked' into various types of sample material to serve as an internal standard, ranged from 78-90%. No correction for loss during extraction and subsequent analysis by gas-liquid chromatography has been applied to estimates of residue concentrations. The analytical procedure has been described by Addison *et al.* (1972).

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1. Abbreviations used:

   p,p'-DDT, 2,2-bis-*p*-chlorophenyl-1,1,1,1-trichloroethane;
   p,p'-DDE, 2,2,-bis-*p*-chlorophenyl-1,1-di-chloroethylene;
   p,p'-DDD, 2,2-bis-*p*-chlorophenyl-1,1-di-chloroethane.

RESULTS

Only residues of three isomers of DDT (*p,p'*-DDE, *p,p'*-DDT and *p,p'*-DDD were present in sufficient quantities for reliable determination (Table 1). No peak corresponding to *o,p'*-DDT, its isomers or dieldrin (detected in a 15% ether-hexane eludate from Florisil, Addison *et al.* 1972) was observed in any sample. Also, peaks attributable to PCBs, some of which have a column retention time similar to that of *p,p'*-DDD and *p,p'*-DDT (Addison *et al.* 1972) were absent.

Residues of *p,p'*-DDE, present in all tissues and organisms examined, ranged in concentration from 1 ppb wet weight in mussels and amphipods to over 1000 ppb wet weight in liver samples from the skate *Raja radiata*. Residues of the *p,p'*-DDT isomer were not found in every sample and when present concentrations were usually equal to or less than those of *p,p'*-DDE. Exceptions to this trend, however, included various infaunal species and the mussel *(Mytilus)*. *p,p'*-DDD isomer was only observed in *Mytilus*, in cod and skate liver samples and in the carcass of one large plaice. Peaks which chromatographically corresponded to *p,p'*-DDD were observed in some other samples but peaks were too small for reliable measurement.

The ratio of the three *p,p'* isomers of the DDT complex may be regarded as an index of metabolism of *p,p'*-DDT by organisms. *p,p'*-DDE is the principal storage metabolite of the DDT group in several mammals and its concentration, relative to total DDT present, may serve to indicate metabolic degradation which has occurred. Levels of *p,p'*-DDE expressed as a percentage of total DDT present varied considerably in different organisms but the values tend to fall into two broad groups. Benthic invertebrates (snails, holothurians, cumaceans, mussels, and four species in infauna) contained less than 50% of total

DDT which they carried in the *p,p'*-DDE isomeric configuration. In all species of demersal fish, predatory starfish and gasteropods *(Thias)*, over 60%, and generally in excess of 75% of the DDT present, was in the *p,p'*-DDE form. One exception to this division was the amphipod, *Ampelisca* spp. Only *p,p'*-DDE was detected in these organisms and concentrations were the lowest observed (Table 1). Since the limit of reliable detection was 1 ppb other isomers of DDT could have been present in lower concentrations which would not have been detected.

Total DDT levels in whole organisms, excluding lipid-rich tissues, grouped as benthic epifauna, infauna or demersal fish (Table 1) were not significantly different (means: 9.8, 13.8, 10.8 ppb wet weight respectively) by a modified Duncan's multiple range test for group means with unequal numbers (Kramer 1956). Thus, on a wet tissue basis, no accumulation of DDT occurs in demersal fish feeding on benthic invertebrates in St. Margarte's Bay. Also, although some individual samples contained concentrations of total DDT significantly higher (snails, lobsters, Lumbrinerid polychaetes and plaice) and lower (amphipods and mussels) than mean levels, the differences were not great and they were unrelated to feeding habits or body size.

The hydrophobic nature of organochlorine compounds tends to concentrate residues in fatty tissues. Expression of residue levels on the basis of concentration per unit lipid weight thus provides a standardized basis for comparison. Storage organs rich in lipids contain the highest levels of DDT residues observed in samples from St. Margaret's Bay. Concentrations in lobster hepatopancreas (9-13 ppm) were an order-of-magnitude higher than those present in cod liver (0.7-2.8 ppm) and more than twice those in skate liver (4.6 ppm). Lipids in all other organisms contained between 0.05 and 2.5 ppm total DDT residues.

Maximum concentrations of total DDT on a lipid basis for whole organisms were found in lobster, cod and plaice muscle and in benthic Lumbrinerid polychaetes and molluscs *(Crenella)* (Table 1). Other benthic invertebrates (amphipods, *Mytilus, Littorina*) contained the lowest concentrations observed. Concentrations in flounder and haddock tissues were only slightly higher than those in these invertebrates. Additional evidence for lack of DDT residue accumulation in this benthic food chain exists in the low concentrations in invertebrate species known to be carnivorous. The gasteropod *Thias* and the polychaete *Glycera* contained concentrations equal to or less than their probable prey (other benthic infauna). In addition, large carnivorous fish (skate and wolfish) contained relatively low residue levels despite their supposedly high trophic position.

No consistent trend in lipid concentration, excluding storage organs, existed between faunal groups, although large organisms of a single species (snails, mussels, plaice) tended to have slightly higher lipid content. The tendency for some organisms to have higher DDT residue levels on a lipid basis, however, was not directly related to enhanced lipid content. Similarly, samples (lobster muscle, *Crenella*) with a low lipid content did not contain correspondingly low DDT residue concentrations.

CONCLUSIONS

Concentrations of DDT residues in St. Margaret's Bay fauna are among the lowest recorded for species of marine fish and invertebrates. For example, concentrations of 10-20 ppb of DDT in oyster tissue are considered as background levels of 'negligible significance' (Butler 1966) and they approach minimum levels which can be reliably determined. Sprague and Duffy (1971) observed

100 ppb or less as an average concentration in whole body or muscle of lobsters, and various molluscs and fish from the Gulf of St. Lawrence and they consider these to be low relative to previous studies. Concentrations in benthic invertebrates and demersal fish in St. Margaret's Bay are an order of magnitude below this level (overall mean 10.5 ±8.8 ppb, wet tissue) and although the levels are higher than those observed in mixed zooplankton samples from the North and South Atlantic shelf and open ocean (Risebrough *et al.* 1972) they are similar to those found in euphausiid populations in the upper estuary of the Gulf of St. Lawrence (Sameoto *et al.* 1975).

The presence of *p,p'*-DDE in samples from St. Margaret's Bay indicates that degradation of *p,p'*-DDT has occurred either externally before incorporation or within the tissues of organisms. While the site of metabolic conversion cannot be identified, it is significant that filter-feeding molluscs and snails feeding on attached epiphytic material and seaweed debris contained proportionately higher amounts of *p,p'*-DDT than did other organisms. If the degraded isomer (*p,p'*-DDE) is being recycled within the food chain of St. Margaret's Bay, as accumulation in all fish species and benthic invertebrates would indicate, the presence of *p,p'*-DDT in molluscs might indicate that the food supply (suspended and sedimented particulate material) of these organisms serves as a pathway for input of *p,p'*-DDT to the food chain. The absence of detectable amounts of *p,p'*-DDE and *p,p'*-DDD and the presence of *p,p'*-DDT (< 1 ppb fresh weight, 10 ppm, lipid weight) in zooplankton in St. Margaret's Bay (Darrow and Harding 1975) supports the idea that the undegraded isomer is present in suspended particulate matter presumably supplied by atmospheric input.

The apparent lack of food chain accumulation in the present data set may be attributable to the organisms considered and the low residue levels

involved. Low concentrations may represent steady-state conditions resulting from a small chronic atmospheric supply of *p,p'*-DDT with constant recycling. Excretion by organisms, adsorption on particulate matter and subsequent re-ingestion by filter feeding and detritus feeding invertebrates and predators, would equalize concentrations within various feeding types. A slow continual accumulation in storage organs of the largest and longest-lived organisms as observed would be expected.

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Table 1 - Organochlorine residue concentrations and lipid content of invertebrates and demersal fish from St. Margaret's Bay collected April - May 1973. Each value is the mean of at least two replicate analyses of one sample. Lipid concentration is expressed as a percentage of wet weight. Minimum level of reliable detection equivalent to 1 ppb = 1 ng/g

Sample	Size (mm)	# of Animals	% Lipid	Wet Tissue (ppb)				Lipid Fraction (ppb)			
				p,p'-DDE	*p,p'*-DDT	*p,p'*-DDD	ΣDDT	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	ΣDDT
Epibenthos											
Littorina littorea (Gasteropoda)	27	1	8.87	9.6	10.8	-	20.4	108.2	121.7	-	230
	18-19	6	5.29	9.9	-	-	9.9	187.1	-	-	187
	15-17	9	5.89	6.3	-	-	6.3	107.0	-	-	107
	12-14	19	4.40	4.2	-	-	4.2	95.5	-	-	96
	12-14	17	4.58	5.3	-	-	5.3	115.7	-	-	116
	9-11	12	10.17	13.0	-	-	13.0	127.8	-	-	128
	5-8	10	3.48	29.3	-	-	29.3	842.0	-	-	842
Thias lapillus (Gasteropoda)	17-20	23	3.78	9.3	-	-	9.3	246.0	-	-	246
	21-24	11	3.14	12.6	-	-	12.6	401.3	-	-	401
Ampelisca spp. (Amphipoda)	2-5	35	2.28	1.2	-	-	1.2	52.6	-	-	53
Psolus phantapus (Holothuria)	100	1	1.59	1.5	1.6	-	3.1	94.3	100.6	-	195
Asterias vulgaris (Echinodermata)	100	5 (gonads)	3.60	9.6	2.9	-	13.0	266.7	80.6	-	347
Eudorella spp. (Cumacea)	2	30	2.31	8.0	9.0	-	17.0	346.3	389.6	-	736
Homarus americanus (Decapoda)											
Muscle	400	1	0.76	24.0	-	-	24.0	3157.9	-	-	3158
	250	2	0.70	11.0	-	-	11.0	1571.4	-	-	1571
Hepatopancreas	400	1	7.13	940	-	-	940	13183	-	-	13183
	250	2	4.22	400	-	-	400	9479	-	-	9479

Table 1 - (Continued)

Sample	Size (mm)	# of Animals	% Lipid	Wet Tissue (ppb)				Lipid Fraction (ppb)			
				p,p'-DDE	*p,p'*-DDT	*p,p'*-DDD	ΣDDT	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	ΣDDT
Mytilus edulis (Pelecypoda)	10	4	1.05	-	-	0.4	0.4	-	-	38.1	38
	25	3	1.14	1.3	7.3	8.6	-	114.0	640.4	-	754
	40	2	2.90	3.0	3.8	3.3	10.1	103.4	131.0	113.8	348
	60	3	2.39	1.8	2.4	2.1	6.3	75.3	100.4	87.9	264
	70	4	2.45	2.5	3.2	2.8	8.5	102.0	130.6	114.3	347
	96	1	2.67	2.7	3.8	2.9	9.4	101.7	142.3	108.6	353
	99	1	1.85	2.2	3.0	2.3	7.5	118.9	162.2	124.3	405
Modiolus modiolus (Pelecypoda)	90	2	1.49	3.0	-	-	3.0	201.3	-	-	201
	125	1	1.80	1.0	1.4	-	2.4	55.5	77.8	-	133
Benthic infauna											
Glycera capitata	55	4	3.12	5.0	6.0	-	11.0	160.3	192.3	-	353
Lumbrineris spp.	35	10	2.17	5.0	19.0	-	24.0	230.4	875.6	-	1106
Clymenalla torquata	40	16	1.47	3.0	5.0	-	8.0	204.1	340.1	-	544
Crenella glandula	3	25	0.63	4.0	8.0	-	12.0	634.9	1269.8	-	1905
Demersal Fish											
Gadus morhua (Atlantic Cod)	carcass	2	1.51	5.0	-	-	5.0	331.1	-	-	331
			0.55	8.0	3.0	-	11.0	1454.5	545.5	-	2000
	muscle	2	0.67	4.0	5.0	-	9.0	597.0	746.3	-	1343
			1.33								
	350										
	liver	3	31.8	830.0	22.0	33.0	885.0	2610.1	69.2	103.8	2783
			32.8	600.0	30.0	-	630.0	1829.3	91.5	-	1921
			40.8	299.0	-	-	299.0	732.8	-	-	733

Continued

Table 1 - (Continued)

Sample	Size (mm)	# of Animals	% Lipid	Wet Tissue (ppb) p,p'-DDE	p,p'-DDT	p,p'-DDD	ΣDDT	Lipid Fraction (ppb) p,p'-DDE	p,p'-DDT	p,p'-DDD	ΣDDT
Pseudopleuronectes americanus (Winter Flounder)	muscle		1.37	2.0	-	-	2.0	146.0	-	-	146
	carcass 230	4	2.41	4.0	-	-	4.0	166.0	-	-	166
	gonad		5.13	9.0	-	-	9.0	175.4	-	-	175
Hippoglossoides platessoides (American plaice)	150 (90 g)	Whole	1.31	23.3/11.1	7.0/5.0	-	23.2	1771/847.3	5344/381.7	-	1767
	165 (120 g)	Whole	1.76	14.0	-	-	14.0	795.5	-	-	796
	200 (150 g)	Whole	1.78	40.1/27.2	16.1/11.5	-	47.5	2253/1528	904.5/646.1	-	2666
	320 (500 g)	Muscle	.72	10.0/2.1	2.0/1.0	-	7.5	1388.9/ 291.7	277.8/138.9	-	1153
	320 (500 g)	Carcass	.95	10.5/10.0	3.1/2.1	3.0	15.9	1105.3/ 1052.6	326.3/221.1	315.8	1669
Melanogrammus aeglefins (Haddock)	350	Muscle	.96	6.5	-	-	6.5	677.1	-	-	677
		Carcass	1.23	0.8	-	-	0.8	65.0	-	-	65
		Liver	29.2	72.3	-	-	72.3	247.6	-	-	248
Raja radiata (Thorny Skate)	675	Muscle	.76	2.2	3.1	-	5.3	289.5	407.9	-	697
		Liver	51.8	1850/ 1090	580/ 620	330/ 390	2430	3560/ 2020	1120/ 1140	640/ 730	4605
Anarhichas lupus (Atlantic Wolffish)	450	1 Muscle	1.10	6.3	-	-	6.3	572.7	-	-	573
		1 Muscle	2.33	13.7	-	-	13.7	588.0	-	-	588

ppb Lipid Weight

Antarctic plankton/fish (Giam *et al* 1973)

Mixed zooplankton, S. Atlantic (Risebrough *et al* 1972)

Mixed zooplankton, N.W. Atlantic (Risebrough *et al* 1972

Zooplankton, N.E. Atlantic (Williams and Holden 1973)

Euphausiids, Gulf of St. Lawrence (Sameoto *et al* 1975)

Demersal fish/benthic invertebrates St. Margaret's Bay (present study)