PESTICIDE SECTION

CANADIAN WILDLIFE SERVICE

MANUSCRIPT REPORTS

Evidence for aerial fallout of polychlorinated biphenyls (PCB) in the eastern Canadian Arctic.

No. 23

R.W. Risebrough
&
D.D. Berger

1971

CANADIAN WILDLIFE SERVICE

PESTICIDE SECTION

MANUSCRIPT REPORTS

C.W.S. Manuscript Reports are compilations of research data reflecting the activities of Toxic Chemicals (formerly Pesticide) Section personnel and contractors and are not intended for general distribution. Some of the material in this report will eventually appear in published form, and prior right to publication is reserved. Enquiries concerning the content of this report should be addressed to the author; requests for copies should be made to the author or to the Toxic Chemicals Section, Canadian Wildlife Service, 400 Laurier Ave. W., Ottawa, Ontario, K1A 0W1.

EVIDENCE FOR AERIAL FALLOUT OF POLYCHLORINATED BIPHENYLS (PCB) IN THE EASTERN CANADIAN ARCTIC.

Robert W. Risebrough

and

Daniel D. Berger

Submitted to the Canadian Wildlife Service

under contract CWS 7071-052

March 31, 1971

INTRODUCTION

Polychlorinated biphenyls (PCB), like many of the persistent pesticides, are chlorinated hydrocarbons which are relatively resistant to natural degradation processes, but have comparatively low biocidal activity and are used in many industrial applications(1). They are not known to be synthesized by any natural process, but nevertheless polychlorinated biphenyls have been detected in many ecosystems remote from the industrial areas where they are manufactured and used (2,3), including the marine waters of the Canadian Arctic which transmit these pollutants via the food chains to polar bears(4). PCB is known to enter the marine environment as a component of urban sewage (5,6,7) and has been detected in rainwater(8), indicating that aerial fallout and atmospheric transport are dispersal mechanisms. Other possible paths of entry into ecosystems include discharge into the atmosphere from incinerators, the wasting of electrical equipment, paints, plastics and other materials containing them, and wastes from manufacturing plants.

Possible sources of the PCB detected in polar bears include aerial fallout of PCB in global atmospheric circulation, discharge of PCB-containing materials from ships, and products such as hydraulic oils brought to

the Arctic which are eventually released into the environment as waste materials. At present little information is available that might indicate the relative contribution of each source. PCB is potentially significant as a pollutant in the Arctic since like several chlorinated hydrocarbon insecticides it may stimulate the synthesis of microsomal liver enzymes in birds(3,9). The resulting effects upon the concentrations and metabolism of one or more steroid hormones are believed to be the cause of the delayed ovulation observed in birds on chlorinated hydrocarbon diets(10). Arctic populations of birds experiencing a delay in ovulation might not be able to complete the reproductive cycle within the short time period available and would thereby experience reproductive failures.

During a survey of Ungava and adjacent islands of the North-West Territories for breeding Peregrine Falcons(Falco peregrinus) in the summer of 1970, we visited Lake Minto in north-western Quebec, under contract with the Canadian Wildlife Service. Lake Minto, 75° W, 57° 30' N, is approximately 80 kilometers east of Hudson's Bay and is drained by the Leaf River which flows to the north-east to Leaf Bay, an inlet of Ungava Bay. Trees reach their northern limit in this

area, which is mainly flat tundra. Lake Minto is not in fact a single lake, but rather an extensive region consisting of small lakes and inlets.

We flew from Fort Chimo to Lake Minto in a chartered Norseman aircraft on July 30, 1970 and were left in a bay in the eastern part of the lake. After travelling several miles downstream, we made camp at 74° 26' W, 57° 25' N. In this area the lake was barren, with a rock bottom showing no plant growth. The only water birds seen were 4-6 Herring Gulls (Larus argentatus). We saw no evidence of previous human intrusions. The area is evidently too far from existing settlements to be visited by Eskimo hunting parties and white men have little reason to come here. The most likely source of synthetic pollutants is therefore aerial fallout. Comparison of PCB concentrations in the fish from this lake with PCB concentrations in similar fish from Hudson's Bay and other marine waters of the Arctic might therefore indicate how much of the PCB in marine waters derives from aerial fallout.

MATERIALS AND METHODS

Fish were obtained with a gill net. This was first set on the evening of July 30. High winds prevented recovery until 1600 hrs the following day. It was set again and recovered the following morning. Nine fish

were obtained, which were later identified by Charles Gruchy, Assistant Curator of Fishes, National Museum of Canada. Two were Arctic char, Salvelinus alpinus, and the remainder were lake trout, Salvelinus namaycush.

Other specimens obtained for PCB analysis in other regions of Ungava include:

- liver and gonads of an Arctic char from the Koksoak River,
- liver and gonads of an Atlantic salmon, Salmo salar, from the Koksoak River,
- an Atlantic Salmon from the Leaf River,
- livers of 10 Arctic char from Leaf Bay,
- land birds, including White-crowned Sparrows (Zonotrichia leucophrys), Horned Larks (Eremophila alpestris), and Common Redpoll (Acanthis flammea),
- two Semipalmated Plovers, Charadrius semipalmatus,
- lemmings, from nests of Rough-legged Hawks (Buteo lagopus),

-seven addled or unhatched eggs of Peregrine Falcons

In this report are the results of the analyses of five of the lake trout from Lake Minto and of the gonads and liver of the Arctic char from the Koksoak River. When completed, the results of the remaining analyses will be combined with those reported here for publication. Several of the Peregrine eggs have been analysed for total mercury. These results are presented in a separate report.

In collecting the samples, all precautions were taken to prevent contamination. They were preserved in 5% formalin in plastic bags. To eliminate the possibility that the plastic bags employed contained PCB, petroleum ether had been stored in the bags overnight, concentrated to a smaller volume and aliquots injected into the gas chromatograph. Plastics subjected to this treatment frequently produce peaks in gas chromatograms that interfere with the determination of chlorinated hydrocarbons, but no peaks that would interfere with the determination of PCB were found in these samples.

The entire fish were digested in commercial BFM solution, a mixture of perchloric and acetic acids(11). This technique permits the extraction of large amounts

of tissue, without damage to the DDT compounds or to PCB. The extracted lipids were passed through a sintered glass filter, the organic solvents removed by evaporation, dried from six hours to overnight at 65°, weighed, and aliquots were passed through a modified Davidow column(11). This cleanup procedure is superior to florisil for the present purposes since relatively small amounts of chlorinated hydrocarbons and large amounts of lipids are involved.

The DDT compounds p,p'-DDE, p,p'-DDT, o,p'-DDT and p,p'-DDD produced prominent peaks on chromatograms of these extracts, but these and peaks of unknown compounds prevented the detection of PCB. Saponification, which converts p,p'-DDT, p,p'-DDD, and o,p'-DDT to their respective ethylene derivatives with smaller retention times, usually permits PCB to be detected in such extracts(12). The unknown compounds, however, persisted. Preparations were therefore subjected to further clean-up by passage through the Armour-Burke procedure(13). Initially imperfect separation between PCB and DDE was obtained, but upon drying all of the column materials according to the methods described by these authors, satisfactory separation was achieved. This procedure separated out the unknowns from the PCB. Figure 1 shows a chromatogram of the PCB peaks in the extract from

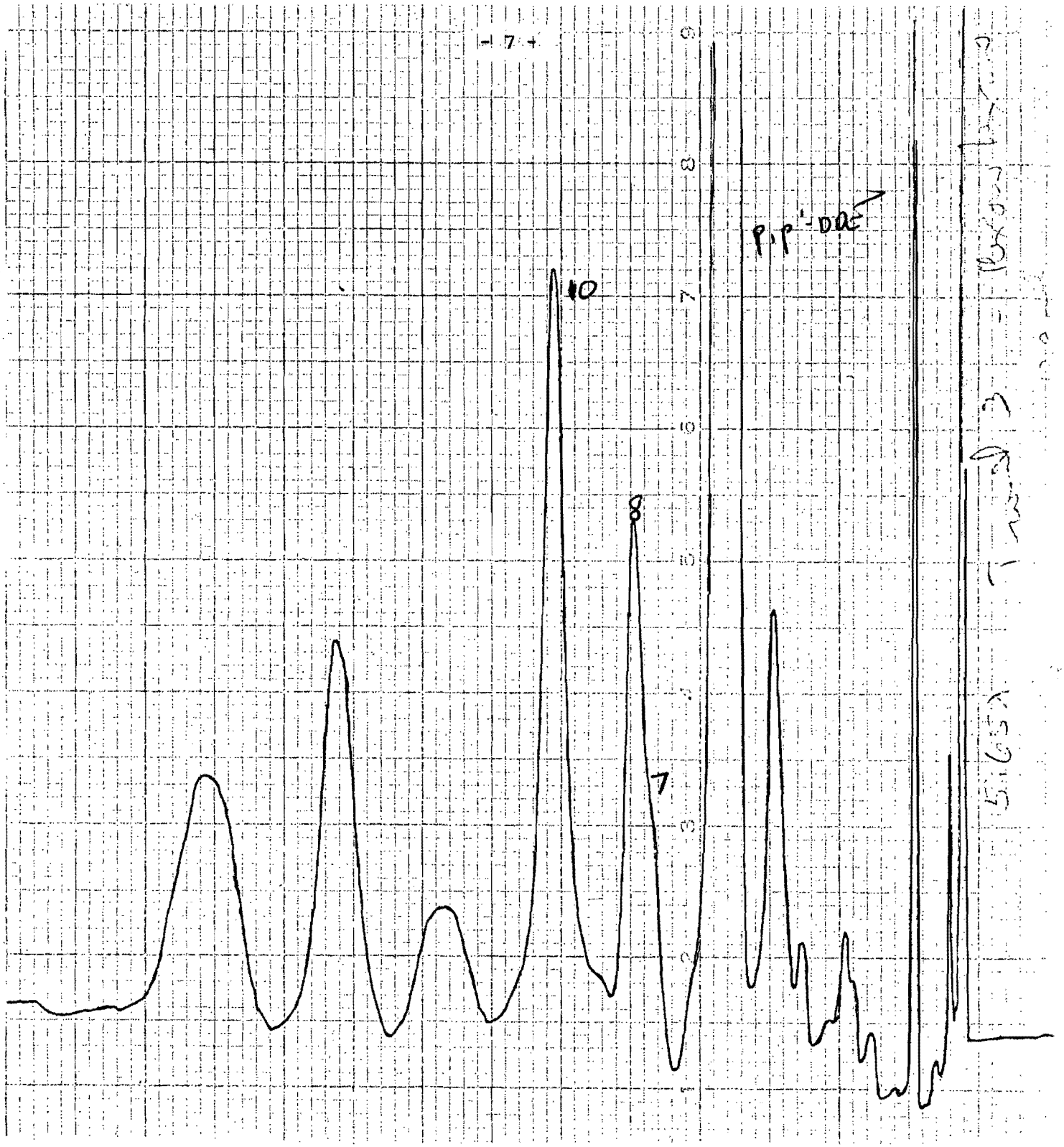

Figure 1. Chromatogram of the hexane fraction of the extract of trout 3. Separation of DDE and PCB in this instance is imperfect. Operating conditiona are described in the text.

lake trout 3, and Figure 2 shows a chromatogram of the commercial PCB preparation Aroclor 1254. In this extract, separation of PCB and DDE is incomplete, but the presence of DDE does not interfere with the quantification procedure employed. The column employed was a 2% QF-1, 2% NPGS, on Chromosorb W, 80-100 mesh, HMDS treated. Other operating conditions and methodologies were equivalent to those previously described (14). The PCB in these extracts was quantified on the basis of a comparison between the areas of peaks emerging after p,p'-DDE and the areas of the same peaks on chromatograms of Aroclor 1254. Areas were determined by weighing peaks cut out from xerox copies. This procedure is time-consuming but was used in the present instance as a test of other methods(15).

The presence of chlorine in the compound identified as p,p'-DDE was confirmed by microcoulometric analysis through the kindness of Paul Reiche. Additional confirmatory tests will be carried out and reported in the publication of these results.

RESULTS

The numbering of PCB peaks on Figures 1 and 2 follows that of Jensen(5). Peak 7 is usually present in relatively small amounts in samples from "remote" areas (15) and is also more subject to degradation by ultra-

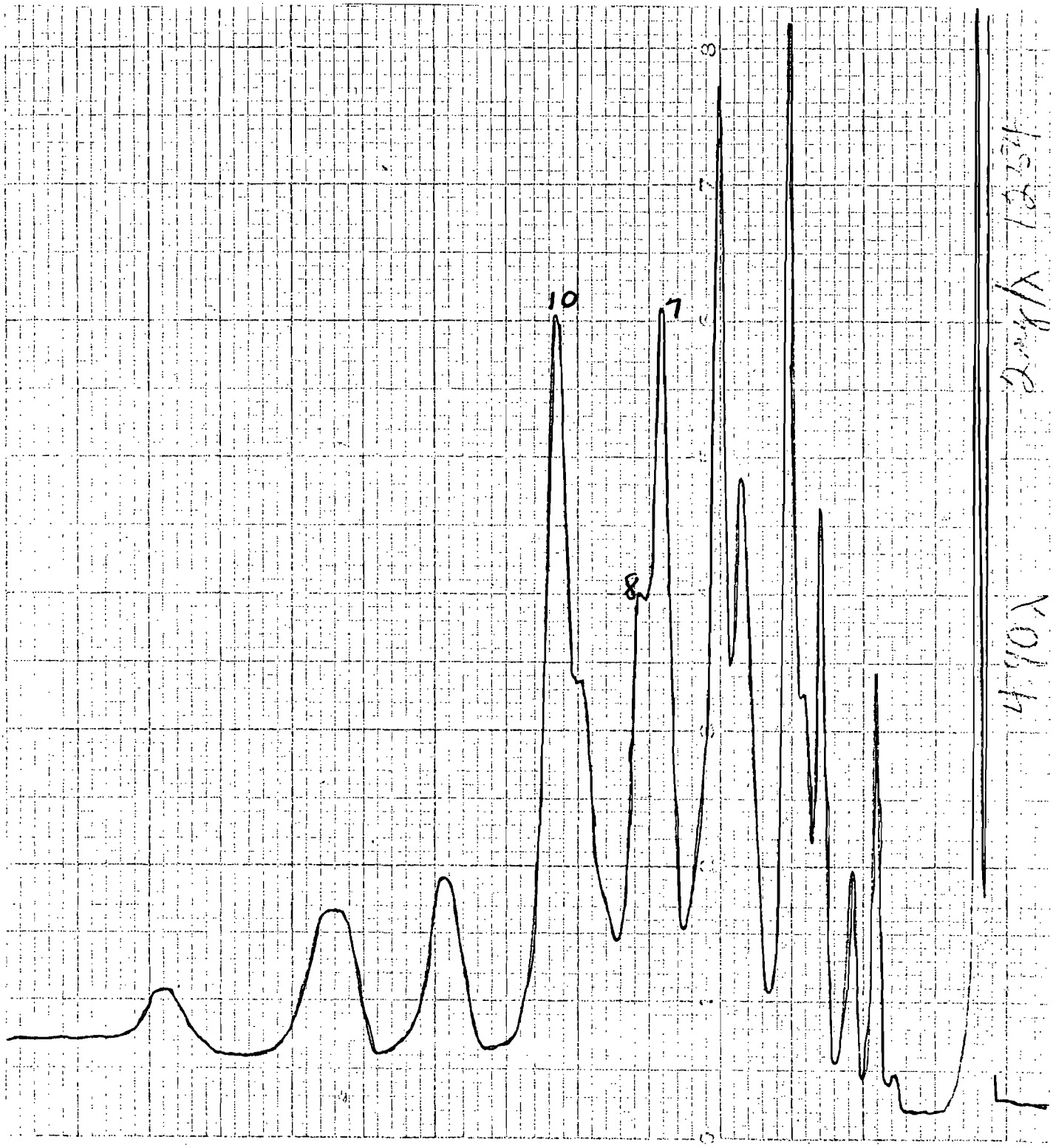

Figure 2. Chromatogram of Aroclor 1254, under operating conditions identical to those of Figure 1.

violet(12).

The results are presented in Table 1. Trout 3 was an exceptionally large fish, 35.5 inches long. Its digestive tract contained the undigested remains of a smaller fish 21 inches long. Only the head and foreparts, weighing 2100 grams, were analysed.

Residue concentrations are in the order of concentrations reported for marine fish from the Pacific and it will be of interest to compare these values with those in comparable fish from Hudson's Bay. Higher concentrations in the fat of trout 3 suggest trophic concentrations of residues. Another large lake trout, 30 inches long, remains to be analysed. This fish had been feeding on aquatic insects.

PCB concentrations approximate those of DDE. The ratio of DDE to PCB is frequently characteristic of ecosystems and was found to be considerable less than unity in the fat of young Peregrines migrating from the Arctic. An examination of the ratio of DDE to PCB in adjacent marine ecosystems will be of interest.

The only likely source of chlorinated hydrocarbon contamination in Lake Minto is aerial fallout. These values are therefore assumed to reflect the background contamination levels from this source at this latitude.

Table 1. PCB and DDT residues in Arctic fish, concentrations in parts per million. DDT residues consist of the sum of p,p'-DDE(DDE), p,p'-DDD(DDD), p,p'-DDT, and o,p'-DDT

Species, tissue	Wet weight grams	% lipid	ppm, wet weight		ppm, lipid weight				
			PCB	Total DDT	PCB	DDE	o,p'-DDT	p,p'-DDT	DDD
Lake trout 1 whole fish	455	4.0	0.045	0.045	1.14	0.86	0.12	0.15	0.00
Lake trout 2 whole fish	492	3.1	0.041	0.076	1.29	1.93	0.16	0.33	0.00
Lake trout 3 head, foreparts	2,100	5.3	0.640	0.597	12.0	10.0	0.31	0.38	0.62
Lake trout 4 whole fish	568	3.3	0.091	0.126	2.74	2.30	0.64	0.63	0.21
Lake trout 5 whole fish	503	3.1	0.091	0.150	2.94	2.94	0.90	0.82	0.19
Arctic char gonads	19.2	0.32	0.130	0.108	7.9	4.46	1.10	0.75	0.30
liver	119	6.3	0.031	0.047	0.59	0.61	0.14	0.07	0.07

Acknowledgments

The analytical work was supported by NSF grant GB 11649 to the Institute of Marine Resources, University of California, H.S. Olcott, principal investigator. Field work was supported by Canadian Wildlife Service contract CWS 7071-052.

Literature cited

1. Monsanto Chemical Company, St. Louis, Mo., Technical Bulletin 0-FF/1
2. Jensen, S., A.G. Johnels, M. Olsson and G. Otterlind. 1969. DDT and PCB in marine animals from Swedish waters. Nature 224:247-250.
3. Risebrough, R.W., P. Reiche, D.B. Peakall, S.G. Herman and M.N. Kirven. 1968. Polychlorinated biphenyls in the global ecosystem. Nature 220: 1098-1102
4. Canadian Wildlife Service; personal communication from C. Jonkel.
5. Ahling, B. and S. Jensen. 1970. Reversed liquid-liquid partition in determination of polychlorinated biphenyl (PCB) and chlorinated pesticides in water. Anal. Chem. 42: 1483-1486.
6. Holden, A.V. 1970. Source of polychlorinated biphenyl contamination in the marine environment. Nature 228:

1220.

7. Schmidt, T., R.W. Risebrough, and F. Gress. 1971. Input of polychlorinated biphenyls into California coastal waters from urban sewage outfalls. Bull. Environ. Contam. Toxicol. 6:235-243.

8. Tarrant, K.R. and J.O'G. Tatton. 1968. Organochlorine pesticides in rainwater in the British Isles. Nature 219:725-727.

9. Lincer, J.L. and D.B. Peakall, 1970. Metabolic effects of polychlorinated biphenyls in the American Kestrel. Nature 228: 783.

10. Peakall, D.B. 1970. p,p'-DDT: Effect on calcium metabolism and concentration of estradiol in the blood. Science 168: 592-594.

11. Stanley, R.L. and H.T. LeFavoure. 1965. Rapid digestion and clean-up of animal tissues for pesticide residue analysis. J. Ass. Offic. Anal. Chem. 48: 666-667.

12. Risebrough, R.W., P. Reiche, and H.S. Olcott. 1969. Current progress in the determination of the polychlorinated biphenyls. Bull. Environ. Contam. Toxicol. 4:192-201.

13. Armour, J.A. and J.A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. J. Ass. Offic. Anal. Chem. 53: 761-768.

14. Risebrough, R.W., G.L. Florant and D.D. Berger. 1970. Organochlorine pollutants in Peregrines and Merlins migrating through Wisconsin. Can. Field-Natur. 84:247-253.

15. Risebrough, R.W. 1971. Determination of polychlorinated biphenyls in environmental samples. International Symposium on Identification and Measurement of Environmental Pollutants. Ottawa, June.