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Chlorinated Hydrocarbons: Pollutants or Indicators of Fish Stock Structure[†]

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Chlorinated hydrocarbons are used in industry for many purposes. They are ubiquitous in the environment. Being soluble in lipids, they tend to accumulate in living organisms and consequently in the food chain. In an attempt to identify the herring stock units (*Clupea harengus harengus*) present in the St. Lawrence Estuary and the Chaleur Bay, we have measured the degree of contamination by some organochlorinated compounds, of herrings fished in both locations. The purpose of the study is to establish the presence of many discrete stocks units or of only one homogeneous stock brought about by large scale straying of individuals from one group to another. Adult herrings are thought to migrate to spawning areas in spring or autumn depending on whether they were born in spring or autumn. The juveniles are believed to remain close to where they were born for about three years before they join their parent stock migrations. If one area is contaminated by chlorinated pesticides, these products will accumulate in the herring fat and could possibly be used for fingerprinting if straying is negligible. The data obtained indicate that the populations studied are marked by their environment and that they probably have their own life cycle and their own migration pattern. A study of the genetic structure of these herring populations is being concurrently made.

KEY WORDS: St. Lawrence Estuary, Chaleur Bay, herring stocks, chlorinated pesticides.

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INTRODUCTION

The Gulf of St. Lawrence is a major area for both spring-and-fall spawning herring (*Clupea harengus harengus*).¹ Tagging experiments² have confirmed that these herrings emigrate in late fall to overwinter in fjords along the western half of the south coast of Newfoundland. They reenter the Gulf of St. Lawrence in late April-early May to spawn and feed. In 1965, purseseining was initiated and herring landings increased from 40 000 metric tons to nearly 300 000 metric tons in 1970³; in 1973, herring landings were back to less than 50 000 metric tons.⁴ Such a fluctuation in abundance gave a new impetus to better delineate the herring stock complex of the Gulf of St. Lawrence.

We have focused our attention on the herring populations of the St. Lawrence Estuary and the Chaleur Bay (Figure 1). These herrings arrive from the east some time in April; the stock breaks up at Gaspé with a portion entering the Estuary to spawn in the Isle-Verte area in April and May while another part of the stock migrates to spawn during the same period in the Carleton Chaleur Bay area. The group of fall spawners probably stops on the banks in front of Gaspé for feeding purposes where it is apparently joined later by the spring spawners. The fall spawners would only come to the coast for spawning late in August and September.⁵ In October–November, the stock complex emigrates back to southwest Newfoundland.⁶

The identification of different stocks of fish can be made by various methods.⁷ These methods consist mainly in a study of various forms of polymorphism. These polymorphisms can be genetic, biochemical, physiological, meristic or morphometric. A stock can also be marked by an experimental or a natural marker. Recently, Moreau and Barbeau (1982)⁸ introduced the use of pollutants as markers of eel stock origin. By measuring heavy metal contents in eel muscles, they were able to differentiate between eels from different regions of the St. Lawrence basin.

In order to differentiate between the herring stocks of the spawning areas of Isle-Verte and Carleton, we chose the halogenated hydrocarbons, mainly the chlorinated pesticides as possible markers. These pesticides are persistent in the environment with a relatively long half life. We are seeking a chemical or biochemical, a pollutant if any, to provide a fingerprint of a subgroup spawning in a specific

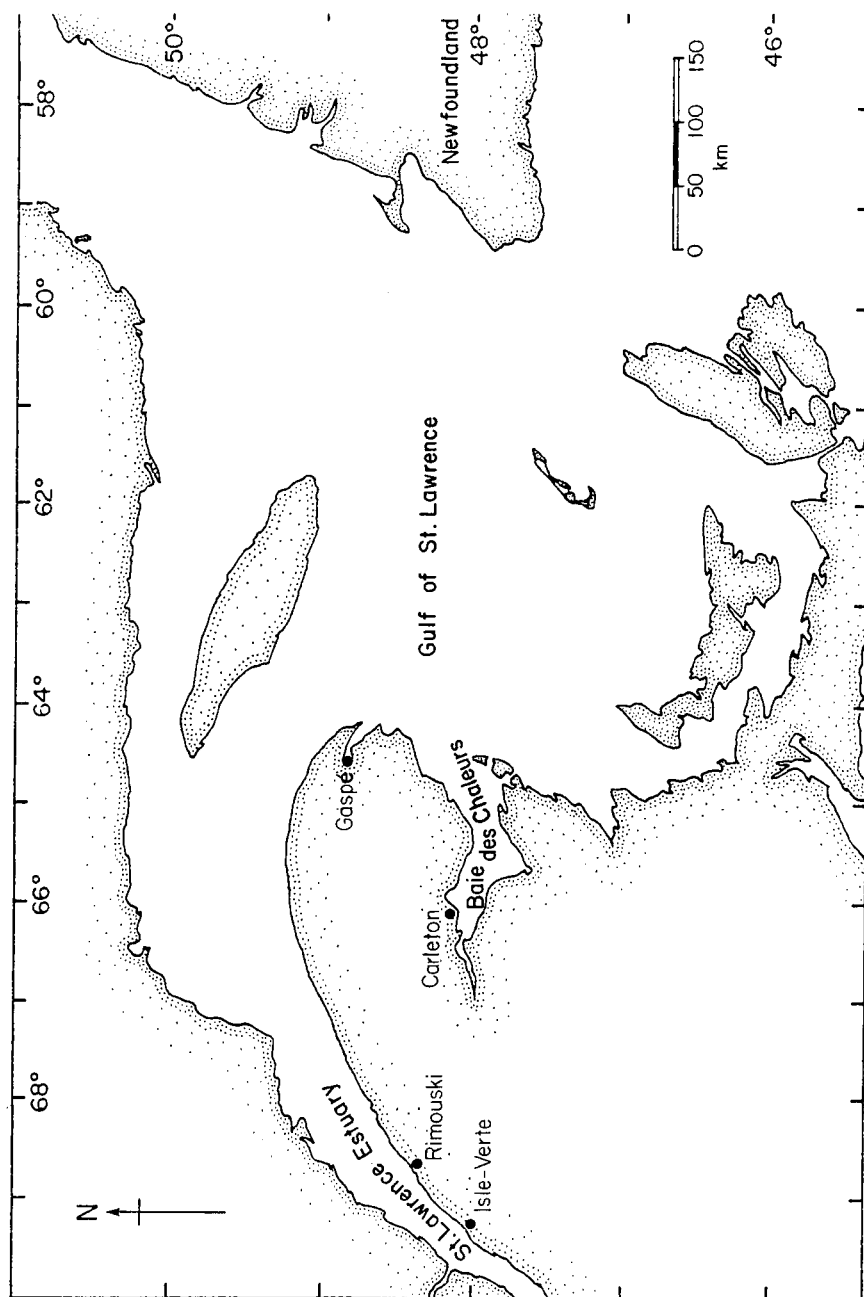


FIGURE 1 The Gulf of St. Lawrence.

area. The various stock units could also be contaminated at different levels by a group of compounds.

Different paths are under investigation: (1) contamination by halogenated hydrocarbons, the subject of this study; (2) contamination by heavy metals namely Cu, Zn, Cd and Pb; (3) electrophoresis of tissue proteins; (4) electrophoresis of specific enzymatic systems.

Herring muscles are rich in lipids. Lipid content was found to vary from 10 to 17%. Halogenated hydrocarbons are soluble in lipids. Adult herrings were found to have age 4 or more while juvenile herrings were of age 3 or less. It is believed that juveniles remain sedentary near or around the spawning location for about three years. We then assume that juveniles feeding and growing in a specific area are in contact with the contaminants present in the water column or in the organisms on which they feed. The juveniles will bioaccumulate chlorinated pesticides if these are present in their environment. We limited this study to DDD, DDE, DDT and total DDT. These chlorinated pesticides have been extensively used during the fifties for agricultural purposes and for forest spraying in eastern Canada.

MATERIALS AND METHODS

Sampling

Herrings at Isle-Verte and Carleton were sampled just before spawning. These spawning sites were visited in spring and autumn of 1982 and 1983. Herrings were kept on ice till their arrival at the laboratory. Their weight and length were determined. The gonads were separated and weighed. The otoliths were used to determine the age of the fish. A sample of 15–50 g of muscle was taken at the same place on each herring. The samples were wrapped in clean aluminium foil, then sealed in polyethylene bags and frozen at -25°C till their analysis. Prior to the analysis, the muscles were thawed and extracted. The young herrings (juveniles) were sampled as a group of ten rather than individually. From each specimen, nearly 5 g were sampled and the 50 g thus collected represent the juveniles of a spawning site.

Extraction

All the samples were extracted according to the scheme presented in

Figure 2. Recuperation with the extraction procedure used varied from 72.5 to 115% with a mean value of 90.2%.

Analysis

The extract was injected in a Perkin Elmer gas chromatograph model Sigma 2000 equipped with a capillary column SE-54 of 30 m length and 0.25 mm I.D. The detector is an electron capture (Ni^{63}). The carrier gas is a mixture of Argon-methane (95–5%) at a speed of 32 cm/s. The gas chromatograph is controlled by a microprocessor model Sigma 15 from Perkin Elmer.

Experimental condition

Initial temperature 50°C for 2 min followed by temperature programming successively of 5°C/min, 4°C/min, 4°C/min till 275°C with plateaux of 10, 5 and 5 min at 180°C, 210°C and finally at 275°C.

Injection temperature: 250°C

Detector temperature: 320°C

Splitless injection : 2 μL

All the solvents used are residue free. They have been freshly distilled in glass before use. Blanks were run on all the materials used. Internal standards were used for qualitative and quantitative determinations. Confirmation of the identity of the chlorinated pesticides was performed by the use of a second gas chromatograph containing a column packed with 1.5% OV₁₇ and 1.95% QF₁ on Chromosorb WH (80–100 mesh). This column of 180 cm length and 0.64 mm I.D. is on a Perkin–Elmer gas chromatograph model 900 with an electron capture detector (Ni^{63}). When further confirmation of the results was needed, the GC/MS was used.

RESULTS AND DISCUSSION

The concentrations of the chlorinated pesticides studied are given in Table I for the juveniles living at Isle-Verte and Carleton. At Isle-Verte, we found juveniles in spring and autumn while at Carleton it was not possible to find juveniles in autumn. The juveniles living at

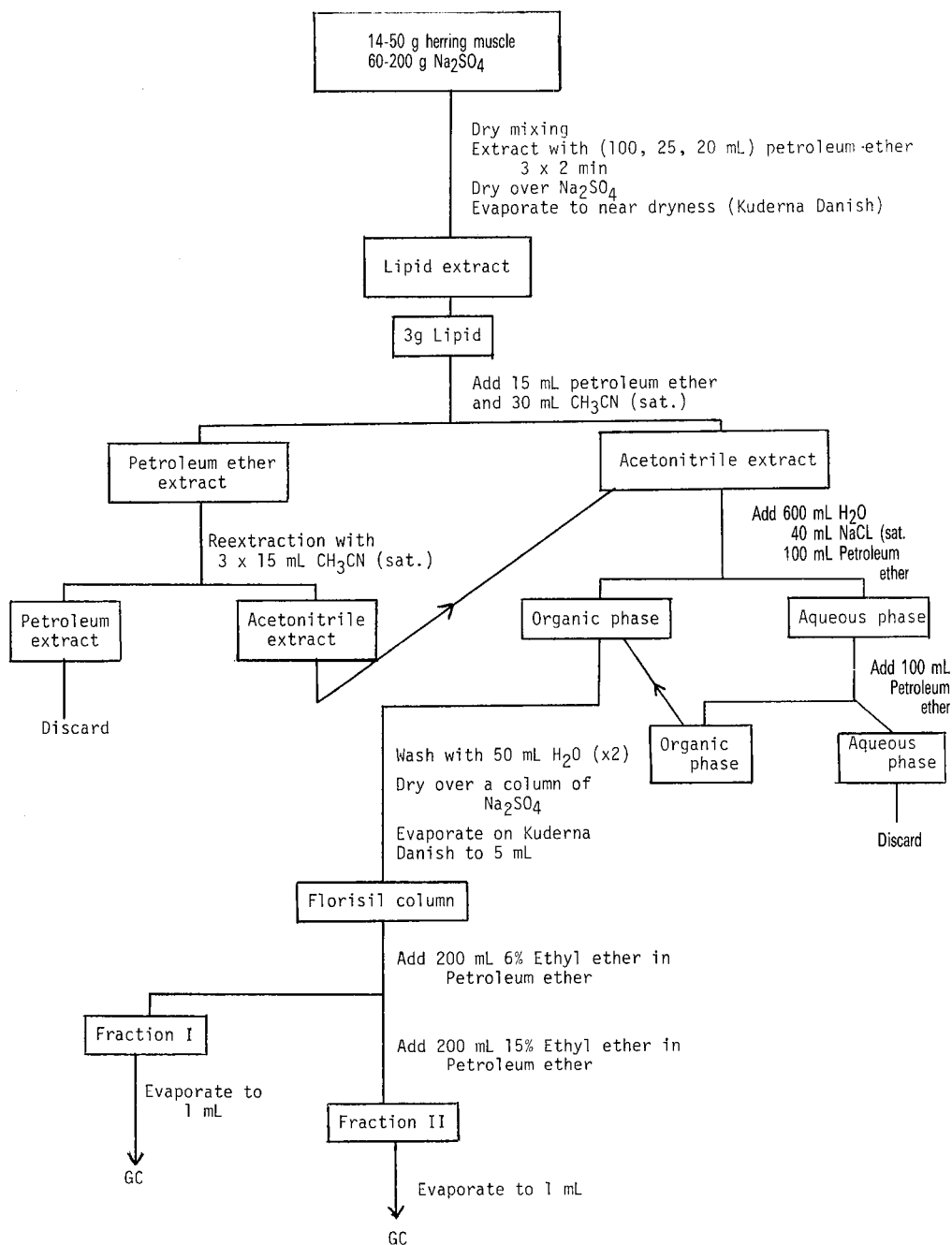


FIGURE 2 Extracting scheme for organochlorinated compounds from herring muscle.

TABLE I
Organochlorinated compounds in juvenile herring muscles.

Location and season	Age	Number of individuals	DDE ←	DDD — μg/Kg fresh weight	DDT — μg/Kg fresh weight	ΣDDT →	ΣDDT μg/Kg lipid
Isle-Verte captured in spring	2	30	6.1 ± 1.4	8.7 ± 1.9	7.3 ± 2.4	22 ± 4.9	273.4 ± 55.6
Isle-Verte captured in autumn	3	60	8.7 ± 2.2	10.5 ± 3	9.1 ± 2.6	28.4 ± 7.8	226 ± 58.1
Carleton	2	30	4.5 ± 0.8	6.1 ± 1.9	3.3 ± 1.1	13.9 ± 3.7	156.4 ± 73.1

Carleton are to a certain degree less contaminated than those living in the Isle-Verte area. While it is relatively easy to determine that an adult herring is a spring or a fall spawner, it is not possible to determine that a juvenile was born in spring or fall. In this light, it is interesting to note that there is no significant difference between the juveniles captured in spring or autumn at Isle-Verte. In Table I, we report the total DDT as $\mu\text{g/kg}$ fresh weight and as $\mu\text{g/kg}$ lipid.

In Table II, we report the concentrations of chlorinated hydrocarbons for the four groups of adult herrings. It is seen that spring spawners are more contaminated than autumn spawners; herrings at Isle-Verte, taking into account the spawning season, are more contaminated than at Carleton. The Isle-Verte spring spawners are the most contaminated, followed by the Carleton spring spawners, the Isle-Verte autumn spawners and the Carleton autumn spawners. The differences observed are not statistically significant but strong trends are indicated. Herrings analysed were mainly 4 and 5 years old; a few were older. As expected, older herrings were found to be more contaminated than younger ones.

The high level of contamination found in spring spawners particularly at Isle-Verte has led us to consider the following points as possible explanations:

- 1) The Isle-Verte area receives during May of each year the highest freshwater flow. This water comes from the highly industrialized area of the Great Lakes. These waters may contain levels of chlorinated hydrocarbons higher than during the rest of the year. The spawning period of Isle-Verte herrings coincide with this maximum flow of freshwater.

- 2) The St. Lawrence estuary during the spring period has a turbidity maximum. Buried sediments are resuspended in the water column. Desorption of associated halogenated hydrocarbons from these sediments may be a source of a periodical input during the spring period.

- 3) Spring spawners probably stay and feed in the St. Lawrence Estuary for a longer period than was thought. Tagging studies made by Côté and Powles⁹ tend to corroborate this point of view. The waters of the Estuary are certainly more contaminated than the waters of the Gulf. As to fall spawners, it is thought that they spend most of the feeding season far from the coast. This would explain

TABLE II
Organochlorinated compounds in adult herrings muscles.

Location and season of capture	No. of sample	DDE ←—————	DDD ————— μg/Kg fresh weight	DDT —————→	ΣDDT —————→	ΣDDT μg/Kg lipid
Carleton spring	25	17 ± 7.7	14.6 ± 5.5	13.6 ± 6	45.2 ± 19	624 ± 354
Carleton autumn	25	8.8 ± 2.6	8.6 ± 2.5	8.4 ± 2.4	25.8 ± 7.5	145 ± 39
Isle-Verte spring	27	78 ± 25	55.7 ± 17	44 ± 18	178 ± 60	1214 ± 285
Isle-Verte autumn	28	15.4 ± 5.3	13.8 ± 4.3	13.4 ± 4	42.5 ± 13.6	286 ± 117

their low level of contamination. The same arguments on a relatively smaller scale can explain the higher level of contamination of the spring spawners of the Carleton area compared to the autumn spawners at the same location.

CONCLUSION

The differences in contamination by chlorinated pesticides may probably be used as an indicator of herring origin. It would be interesting to analyse for pesticide contents, herring samples fished in winter time when all the stocks from different spawning areas are supposedly mixed. Work is in progress to test this hypothesis.

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