

# CHLOROPHENOLS IN STARRY FLOUNDER, *Platichthys stellatus*, FROM THE LOWER FRASER RIVER, B.C.

[Data and Summary]

By

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#### **ABSTRACT**

This study was conducted in 1986 to determine the level of chlorophenol contamination in the tissue of starry flounder (*Platichthys stellatus*) and to evaluate the utility of the flounder as an indicator of the presence of these chemicals. Samples were collected from the North Arm of the Fraser River estuary, near sawmills and wood processing plants. The fish were processed (sorted by size and aged) before shipment to the Environment Canada National Water Research Institute Laboratory in Burlington, Ontario, for analysis of a spectrum of 19 chlorophenolic compounds.

Chlorophenol concentrations measured in both composite and individual tissue samples of whole fish, liver and muscle were comparable to previous levels reported for fish from the study area.

Concentrations of individual chlorophenols were highly variable, and ranged from below detection to a high value of 55 ng g<sup>-1</sup> (wet weight) for 2,6-DCP. Apart from occasional high values, measured concentrations of individual chlorophenol congeners were uniformly low, with median levels typically below 5 ng g<sup>-1</sup> wet weight.

Comparison of chlorophenol concentrations between different age groups demonstrated little evidence for bioaccumulation. Analysis of chlorophenol concentrations against size (and weight) showed that, for most of the 19 congeners analyzed, the body burden was inversely related to size. Exceptions were the dichlorophenols, especially 2,4-dichlorophenol and 2,6-dichlorophenol, for which there was a weak relationship between age and contaminant levels.

Life history information and available data concerning bioconcentration of chlorophenols indicate starry flounder should be a good and reliable indicator species. It is recommended that sampling and analysis be restricted to younger age classes until seasonal and age-related movements are better understood. Studies of migration patterns and movement of starry flounder populations are recommended by these results and some work since this study has been conducted (Nelson 1995).

This report presents the contaminant data with minimal interpretation with intent of making this data available for comparison with more recent studies of contaminants in fish in the Lower Fraser River. Data and literature references are those available to 1988. More recent investigations are discussed in Nelson (1995).

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# INTRODUCTION

This project is one of a series of studies examining chlorophenol contamination of the aquatic ecosystem of the lower Fraser River and estuary (e.g. Hall *et al.* 1984, Carey *et al.* 1986, Rogers and Hall 1987). Sawmills and wood processing plants in the lower Fraser River used chlorophenolics, primarily pentachlorophenol, through the 1980s as antifungal agents to protect newly-cut lumber from sapstain fungi. Leaching of preservative from treated wood, inadequate containment during spraying and accidental spills all contributed directly to contamination of the aquatic environment by these chemicals. In addition to the parent chlorophenolics, these anti-sapstain formulations carried a spectrum of related chlorophenol congeners (Jones 1981) and other miscellaneous organochlorines. Pentachlorophenol preservatives, for example, constitute an important environmental source of chlorinated dioxins and furans, either through direct contamination or through incomplete combustion in the burning of PCP-treated woodwaste (Jones 1981). Recognition of the environmental hazard of these formulations, pentachlorophenol was deregistered for routine use as as a wood preservative in 1990.

There has been considerable concern over the presence of chlorophenols in the aquatic environment (Garrett 1980), with consequent potential for accumulation by resident organisms. Searches for suitable biological indicators for chlorophenols in biota have targetted resident fish species for a number of reasons. First, fish are common and large enough to easily provide sufficient tissue mass for low-level organic contaminant analyses. Second, fish are often the highest trophic level in the aquatic ecosystem, integrating and magnifying lower level effects. Third, contaminant levels in fish have direct relevance to the health of humans and other terrestrial consumers.

Starry flounder (*Platichthys stellatus*) is a common, ubiquitous component of the fish community of the Fraser River Estuary. This species reproduces, feeds and grows in the tidal waters of the lower Fraser (Northcote *et al.* 1978), and as such, is exposed to local contaminants in every aspect of its life cycle. Little is known of their movements, but evidence suggests that the flounder are at least seasonally resident in localized areas (Levy *et al.* 1979). In addition, starry flounder are an important food item for piscivorous birds and mammals of the estuary. Man is included amongst the potential consumers, since

a moderate commercial fishery and an increasing recreational fishery for starry flounder.

The objectives of the present study were:

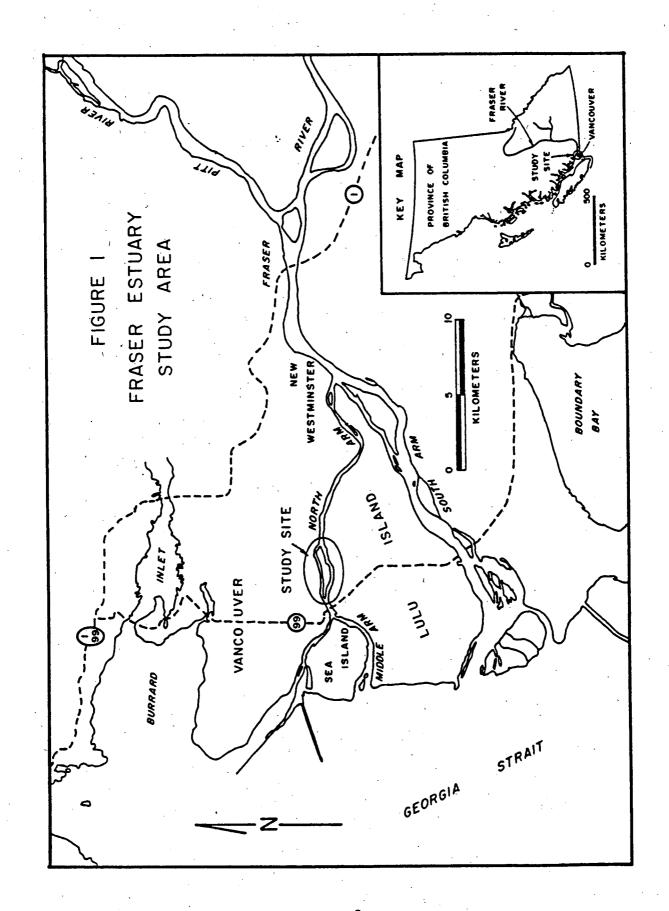
- 1) determine the levels of chlorophenols in the tissue of a representative aquatic organism (starry flounder).
- 2) explore the relationship between chlorophenol concentrations and fish size, fish age and tissue type.
- 3) assess the utility of starry flounder as an indicator of chlorophenol contamination of the ecosystem.

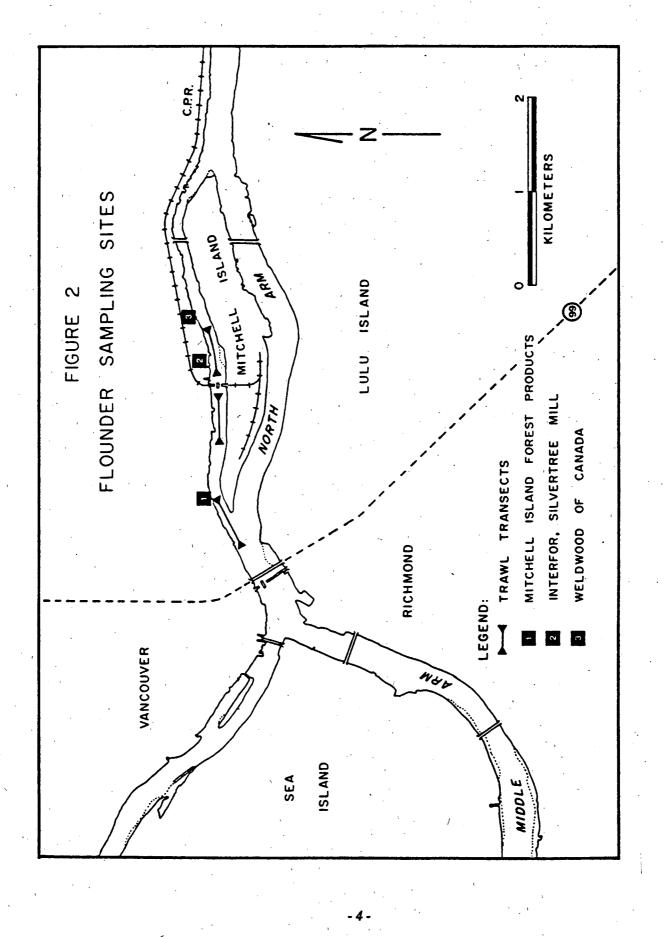
#### **Methods**

This study was conducted during November 1986 in the North Arm of the Fraser River near Mitchell Island (Figure 1). There are numerous sawmills and wood processing mills in this reach of the river, many of which have been identified as sources of chlorophenol-polluted runoff (Jacob 1986). Fish collections were made in the channel north of Mitchell Island at two sites: downstream of the railway bridge alongside the Westcoast Cellufibre Industries yard; and upstream of the railway bridge alongside the Doman Silvertree mill to the downstream end of the Weldwood of Canada mill (Figure 2). Some additional samples were collected at the western end of Mitchell Island, downstream of Mitchell Island Forest Products.

Flounder were sampled by beach seine, gill net and trawl. In general, larger (older) fish were collected by trawling in deeper water, while smaller fish were found in shallow areas. Fishing efforts were hampered by bottom debris and considerable time was spent searching for relatively clean trawl transects. Even at the suitable transects (Figure 2), trawl deployment and recovery required a powerful boat and winch.

Standard length of each flounder was measured (±0.5 mm) and grouped in 5 cm size classes until at least 10 individuals in each size class were collected. Fish selected for chlorophenol analyses were then weighed (±0.1 g) and sampled for otoliths. Each fish was then individually wrapped in acetone/hexane-





rinsed foil and kept frozen at -20°C until analysis. Age was determined using otolith ring counts (Campana and Neilsen 1982).

Samples were sorted by age, individually packaged and shipped to the National Water Research Institute (N.W.R.I.) laboratory in Burlington, Ontario for chlorophenol analysis. Where possible, analyses were conducted on whole individual fish. Younger fish (age 0+ to age 2+) were often not large enough to provide the necessary tissue for lab analyses and tissues from comparable sizes within these age groups were pooled. Numbers of fish collected and the final lab sample sizes are listed in Table 1.

Analytical protocols for chlorophenol and lipid determinations were as described by Carey *et al.* (1986, 1988). Samples were ground with sodium sulphate and extracted with dichloromethane using soxhlet for a minimum of 20 cycles. The extract was cleaned up by gel permeation chromatography eluted with a 55:45 mixture of hexane and dichloromethane. Chlorophenol compounds were derivatized to their acetate esters and analyzed by dual-column gas chromatography. In all, 17 identified and 2 unidentified chlorophenol compounds were quantified in each analysis. The analytical parameters of the chlorophenol compounds examined are presented in Table 2. Summaries and results presented for chlorophenols are based on concentrations per gram of wet tissue.

Statistical summaries and graphics were produced using SYSTAT version 5.0 (Wilkinson 1989). For the purpose of calculating summary statistics, measurements below detection limit were replaced with a zero concentration.

Table 1. Numbers of fish collected and number of chlorophenol analyses performed.

Age	Whole	-Body	Musc	le/Liver
(years)	# Caught	#Analyses	# Caught	# Analyses
0+	19	5	0	0
1+	8	6	8	2
2+	10	10	7	4
3+	11	11	5	3
4+	4	4	1	1
5+	4	4	0	0
Total	56	40	21	, 10

Table 2. Analytical parameters of chlorophenolic compounds determined in the Fraser River starry flounder study.

Chlorophenol	RT	RRT	RRF
•	(0.01 min)	(rel to PCP)	(rel to PCP)
2,6-DCP	, 906	0.313	0.191
2,4-DCP	991	0.342	0.194
3,5-DCP	1055	0.365	0.225
2,3-DCP	1093	0.378	0.209
3,4-DCP	1202	0.415	0.155
2,4,6-TCP	1354	0.468	0.577
2,3,6-TCP	1513	0.523	0.493
2,3,5-TCP	1574	.0.544	0.541
2,4,5-TCP	1596	0.551	0.484
2,3,4-TCP	1757	0.607	0.622
3,4,5-TCP	1842	0.636	0.550
2,3,5,6-TeCP	2109	0.729	0.651
2,3,4,6-TeCP	2125	0.734	0.890
2,3,4,5-TeCP	2381	0.823	0.934
3,4,5-TCG	2476	0.856	0.934
unidentified 1	2614	0.903	0.934
unidentified 2	2810	. 0.971	0.934
pentachlorophenol	2894	1.000	1.000
tetrachloroguiacol	3009	1.040	1.000

RT=retention time

RRT= relative retention time

RRF = instrument response factor relative to pentachlorophenol

# **Results and Discussion**

In the course of this study, 77 individual fish were collected from which 60 samples were submitted for chlorophenol analysis (Table 1). Of the fish captured, 40 analyses were conducted on whole-fish (as composite or individual submissions), and 10 separate analyses were conducted on liver and remaining body tissues (here referred to as muscle). Raw data are tabulated in Appendix 1.

Chlorophenol congeners were detected in all tissue samples. Analytical results are summarized by major chlorophenol class in Table 3. The highest contaminant levels were found in liver tissue samples, with total chlorophenols (sum of all congeners) as high as 527.65 ng·g<sup>-1</sup> wet weight. Summaries for each of the 19 individual congeners in whole body, liver and muscle samples are presented in Tables 4, 5 and 6.

Eight of the 19 chlorophenol congeners were detected in more than 80% of the whole-body analyses (Figure 3). The compounds most frequently detected were: 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, PCP, 3,4,5-TCG, TeCG and both of the two unidentified chlorophenols. The pattern of chlorophenol detections in "muscle" analyses mirrored results of the whole-body composite samples, with the exception of an increased frequency of occurrence of 2,3,4-TCP in muscle. The chlorophenol spectrum measured in liver tissues was predominated by the four chlorophenol congeners, 2,4,6-TCP, 2,3,4,6-TeC, PCP and TeCG. The more highly-substituted chlorophenol congeners were also detected in the liver analyses, but with a reduced frequency compared to either the muscle or composite samples.

Concentrations of individual chlorophenols from all analyses range from below detection to a high value of 55 ng·g<sup>-1</sup> for 2,6-DCP (Figure 4). Apart from occasional high values, measured chlorophenol concentrations were uniformly low, with median levels typically below 5 ng·g<sup>-1</sup> wet weight. The highest individual concentration recorded was that of 2,6-DCP, the highest median concentration was that of PCP, at 13.15 ng·g<sup>-1</sup>. Congeners with high median concentrations, in addition to PCP, were 2,4-DCP and 2,3,4,5-TeCP (Fig 4, Table 9) with median concentrations of 6.90 and 5.65 ng·g<sup>-1</sup> respectively.

Table 3. Summary statistics for general classes of chlorophenols measured in starry flounder tissues in the lower Fraser River. Concentrations are expressed as ng/g wet weight, non-detections were assigned a zero value

Liver SD 25.57 9.42 60.21							
SD 25.57 9.42 28.46 60.21				Live			
25.57 9.42 28.46 60.21		c	Mean	SD	Median	Min	Max
9.42 28.46 60.21 127.22	DCP	10	20.25	25.57	12.27	00.0	76.81
28.46 60.21 127.22	TCP	10	19.54	9.42	18.36	5.69	34.49
60.21	TeCP	10	37.16	28.46	29.20	12.25	108.13
127.22	PCP	10	85.47	60.21	64.61	37.77	223.91
	Total CP	10	234.21	127.22	, 201.51	103.80	527.65

			Muscle	e e		,
	u	Mean	OS	Median	Min	Max
DCP	10	15.15	23.21	5.6	00.00	77.24
TCP	10	5.98	2.54	5.35	2.89	11.59
TeCP	10	9.59	10.45	6.73	2.19	38.52
PCP	10	15.63	6.83	17.38	2.71	25.67
Total CP	10	62.54	29.51	55.51	26.35	120.43

,		ţ	Whole	ə		
	u	Mean	SD	Median	Min	Max
DCP	40	15.08	13.63	10.72	0.00	64.16
TCP	40	4.59.	1.98	4.30	0.41	10.42
TeCP	40	7.43	4.33	7.53	1.83	20.71
PCP	40	14.75	6.86	11.88	4.35	29.17
Total CP	40	56.37	19.95	56.27	25.25	109.38

Chlorophenols are, to varying degrees, soluble in body fats. The solubility is related directly to the level of chlorine substitution in the molecule, with DCPs being least soluble (in general) and PCP the most soluble in lipids. This pattern is evident in the plots in Figure 5. Correlation between total dichlorophenols and lipid is not significant ( $\alpha$ =0.05), but the remaining more highly substituted congeners are strongly associated with tissue lipid content. Because of their similar association with tissue lipid concentrations, concentrations of TCP, TeCP and PCP are all highly correlated (Figure 5).

# Age/Size Relationships

If chlorophenols were being sequestered in the body tissues of starry flounder, then increases in concentration with either age or size would be expected. Plots of chlorophenol concentration against age class show few such trends (Figures 6-9). Tissue concentrations of 2,4-DCP and 2,6-DCP show some increase with age, but the trend is weak and the pattern is not evident in any of the other chlorophenols studied. Declining chlorophenol burden with age was more commonly observed, as seen in plots of 2,3,4,6-TeCP, PCP and TCG (Figures 8, 9). Clearance rates of chlorophenols are known to be high (Carey et al. 1986), and it would appear that the present data would support this conclusion. Declining concentrations of chlorophenols with age/size might reflect the decreasing surface to volume ratio with consequent changes in available area for passive absorption of the contaminants. The pattern may also reflect the effects of age-related habitat selection and exposure hazard. Younger fish, resident in shallow water may be more directly exposed to runoff from wood treatment facilities and thus accumulate relatively higher levels of chlorophenol. Results presented here probably represent a point observation of a dynamic system of exchange between the tissue pool and the ambient environment.

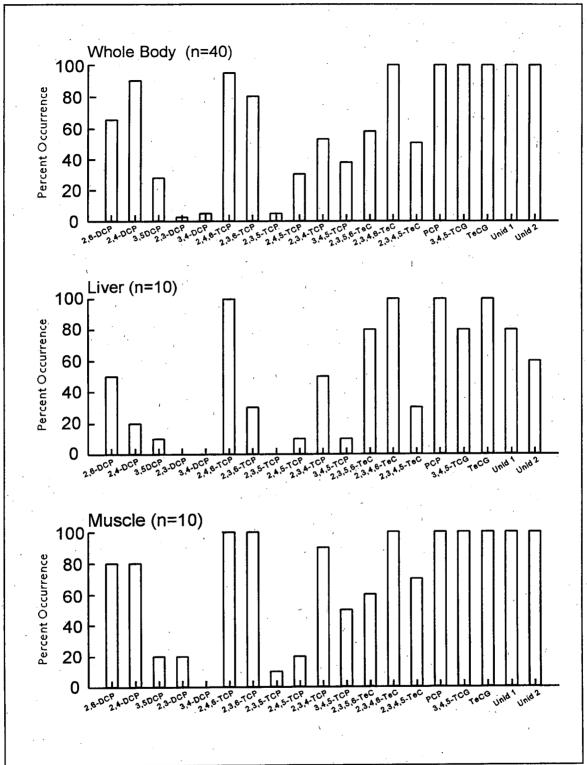


Figure 3. Frequency of occurrence of each of the 19 chlorophenol congeners in the three tissue types from starry flounder from the Fraser River Estuary.

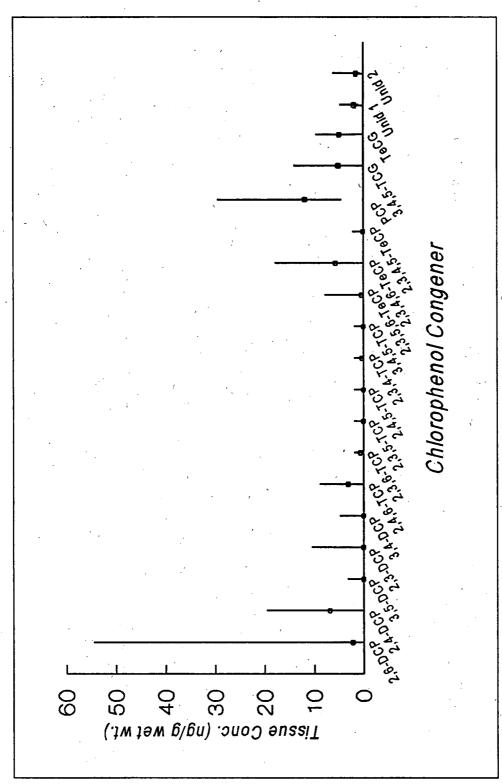


Figure 4. Summary plot showing the occurrence and concentrations of chlorophenol congeners analyzed in starry flounder from the lower Fraser River. Data include all analyses (whole-body and separate tissues). Lines indicate median, upper and lower concentrations.

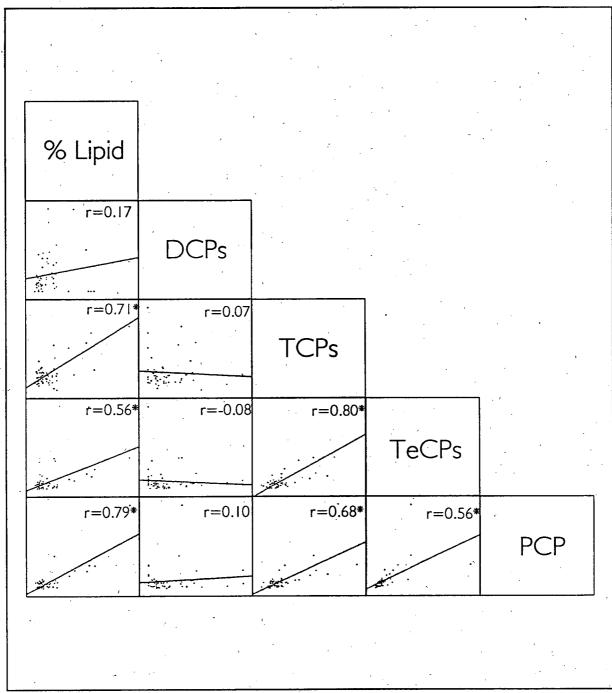


Figure 5. Casement plot showing relationship of major chlorophenol congeners to one another and to the tissue lipid content. Shown in each plot are the least-squares line-of-best-fit and the correlation coefficient. Significant relationships ( $\alpha$ =0.05) are indicated with an asterisk. Axes are arithmetic and n in all cases is 58.

Table 4. Summary results of whole-body analyses of starry flounder tissues collected from the lower Fraser River.

Chlorophenol	z	MEAN	SD	MEDIAN	Min	Max
•		ng/g wet wt.				
2,6-DCP	40	6.39	10.85	2.22	00:0	54.55
2,4-DCP	40	7.96	5.71	6.90	00.00	19.66
3,5-DCP	40	0.34	0.77	0.00	0.00	3.26
2,3-DCP	40	0.26	1.66	0.00	00.00	10.50
3,4-DCP	40	0.13	0.77	0.00	0.00	4.83
2,4,6-TCP	40	3.24	1.68	3.16	0.00	8.90
2,3,6-TCP	40	0.63	0.45	0.65	00.00	1.78
2,3,5-TCP	40	0.01	0.04	0.00	0.00	0.26
2,4,5-TCP	40	0.14	0.25	0.00	00.0	0.89
2,3,4-TCP	40	0.38	0.42	0.35	0.00	1.38
3,4,5-TCP	40	0.18	0.29	0.00	0.00	1.09
2,3,5,6-TeCP	40	96.0	1.65	0.39	0.00	7.82
2,3,4,6-TeCP	40	6.23	4.02	5.67	1.70	17.86
2,3,4,5-TeCP	40	0.25	0.42	0.06	0.00	2.24
3,4,5-TCG	40	5.38	2.50	4.91	1.51	14.19
unidentified 1	40	2.08	0.93	1.88	0.77	4.61
unidentified 2	40	1.99	1.33	1.38	0.50	6.13
Pentachlorophenol	40	14.75	98.9	11.88	4.35	29.17
Tetrachloroguaicol	40	5.08	1.88	4.88	1.66	9.63

Table 5. Summary results of analyses of starry flounder liver tissue samples collected from the lower Fraser River.

Max	ng/g wet wt	70.88	11.35	5.93	0.00	0.00	22.15	. 3.91	0.00	4.34	17.12	24.00	20.25	89.62	7.05	71.10	141.50	7.52	223.91	44.78
Min	ng/g wet wt	0.00	0.00	0.00	00:00	0.00	5.15	0.00	00.00	0.00	0.00	0.00	0.00	11.71	0.00	0.00	0.00	0.00	37.77	7.76
MEDIAN	ng/g wet wt	09.9	0.00	0.00	0.00	0.00	12.39	0.00	0.00	0.00	0.94	0.00	4.57	16.21	0.00	20.20	8.96	1.32	. 64.61	17.19
SD	ng/g wet wt	23.44	4.42	1.88	00.0	00.0	5.53	1.65	00.0	1.37	5.25	7.59	7.45	24.31	2.40	20.69	47.69	2.67	60.21	.11.37
MEAN	ng/g wet wt	17.57	2.09	0.59	0.00	0.00	12.83	0.98	0.00	0.43	2.90	2.40	7.78	28.14	1.24	21.76	28.49	2.18	85.47	19.36
z		10	10	10	10	10	10	10	10	10	10	10	10	10	10	40	10	10	10	10
Chlorophenol	3	2,6-DCP	2,4-DCP	3,5-DCP	2,3-DCP	3,4-DCP	2,4,6-TCP	2,3,6-TCP	2,3,5-TCP	2,4,5-TCP	2,3,4-TCP	3,4,5-TCP	2,3,5,6-TeCP	2,3,4,6-TeCP	2,3,4,5-TeCP	3,4,5-TCG	unidentified 1	unidentified 2	Pentachlorophenol	Tetrachloroguiacol

Table 6. Summary results of analyses of starry flounder "residue" samples (whole body less liver tissue) collected from the lower Fraser River.

Chlorophenol	z	MEAN	SD	MEDIAN	Min	Max
	,	ng/g wet wt.				
2,6-DCP	10	11.03	16.64	4.09	0.00	53.70
2,4-DCP	10	3.57	6.38	1.33	0.00	21.35
3,5-DCP	10	0.33	0.75	0.00	0.00	2.19
2,3-DCP	10	0.21	0.44	0.00	0.00	1.09
3,4-DCP	10	0.00	0.00	0.00	0.00	0.00
2,4,6-TCP	10	3.30	1.37	3.14	1.72	6.39
2,3,6-TCP	10	1.05	0.38	0.93	0.58	1.57
2,3,5-TCP	. 10	90.0	0.17	0.00	0.00	0.55
2,4,5-TCP	. 10	0.25	0.64	0.00	0.00	2.02
2,3,4-TCP	10	0.86	0.56	0.79	0.00	2.07
3,4,5-TCP	10	0.47	0.58	0.21	0.00	1.46
2,3,5,6-TeCP	10	0.73	1.24	0.51	0.00	4.14
2,3,4,6-TeCP	10	8.30	8.40	6.20	2.19	31.48
2,3,4,5-TeCP	10	0.57	0.86	0.38	0.00	2.90
3,4,5-TCG	10	5.57	2.07	4.95	3.35	9.80
unidentified 1	10	2.92	1.61	3.02	1.04	6.27
unidentified 2	10	2.32	0.99	2.12	0.84	3.50
Pentachlorophenol	10	15.63	6.83	17.38	2.71	25.67
Tetrachloroguaicol	10	5.38	2.12	4.97	2.86	10.66

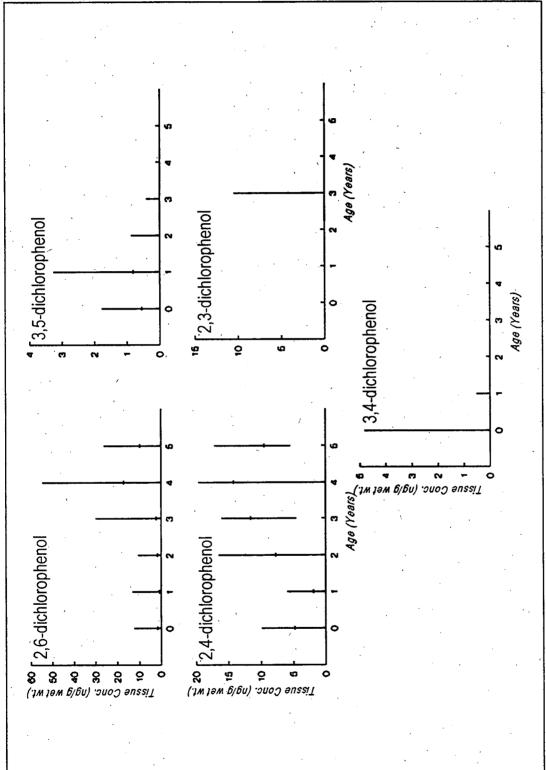


Figure 6. Concentrations of individual dichlorophenol congeners in each age class of starry flounder collected from the lower Fraser River. Data shown are from analyses of whole-body samples. Plots show median, upper and lower concentration limits.

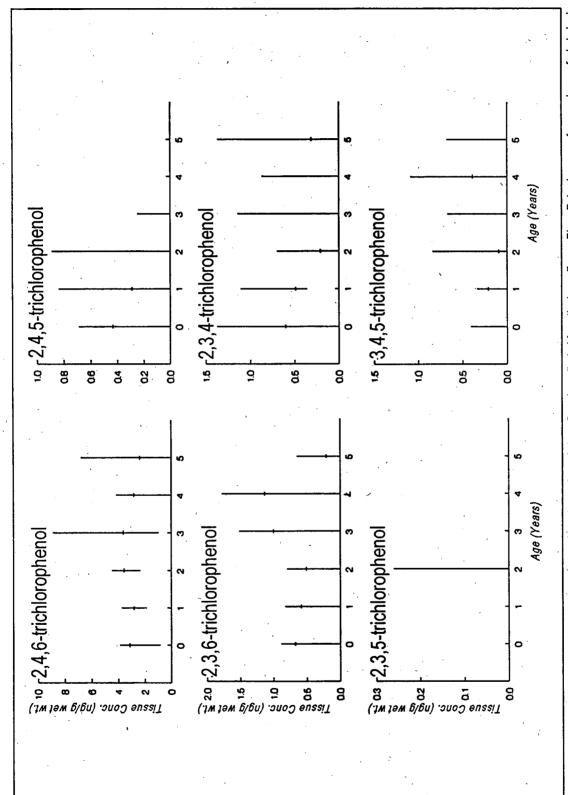


Figure 7. Concentrations of individual trichlorophenol congeners in each age class of starry flounder collected from the lower Fraser River. Data shown are from analyses of whole-body samples. Plots show median, upper and lower concentration limits.

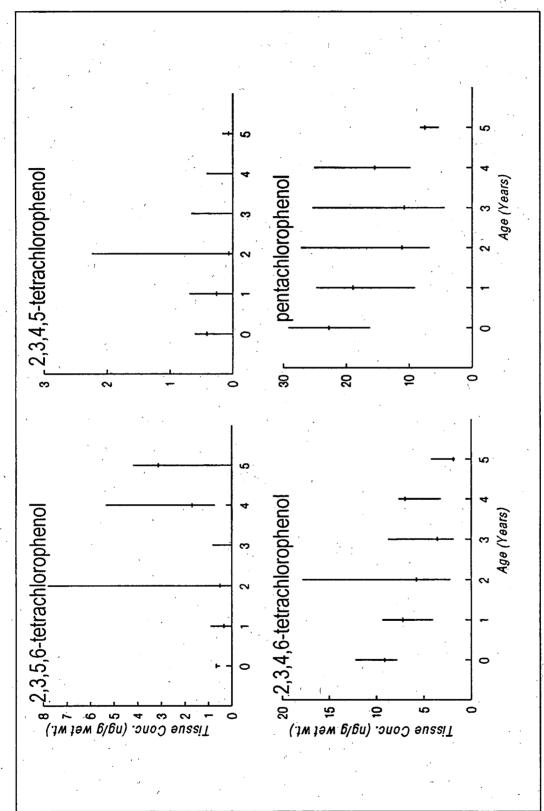


Figure 8. Concentrations of tetra- and pentachlorophenol congeners in each age class of starry flounder collected from the lower Fraser River. Data shown are from analyses of whole-body samples. Plots show median, upper and lower concentrations.

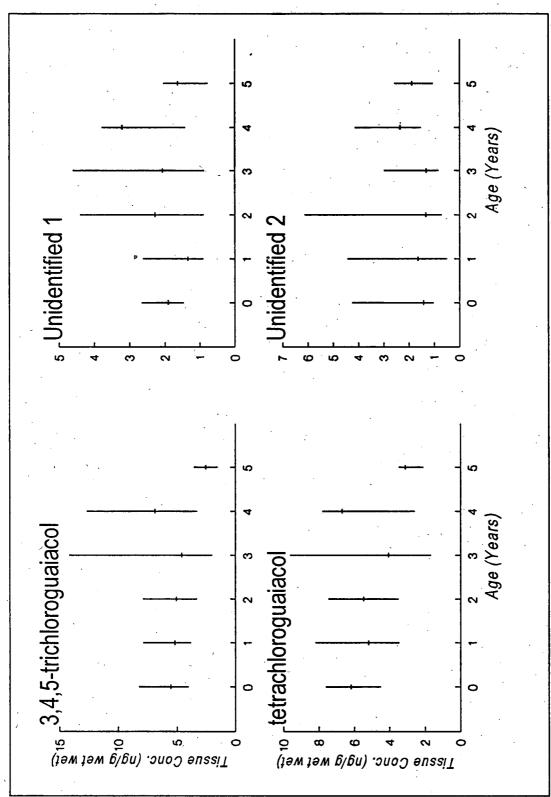


Figure 9. Concentrations of guaiacols and unidentified chlorophenols in each age class of starry flounder collected from the lower Fraser. Data shown are from analyses of whole-body samples. Plots show median, upper and lower concentrations.

# **Comparison with Previous Studies**

The chlorophenol concentrations observed in the flounder collected for this study were comparable to previous work on flounder in the same area of the Fraser system (Carey *et al.* 1986, Rogers and Hall 1987). A comparative summary of past and present studies of chlorophenols in starry

Table 7. Comparison of chlorophenol concentrations in starry flounder from this and other studies in the Lower Fraser River.

TISSUE	TeCP (ng/g wet)	PCP (ng/g wet)	Reference
Residue	<b>4.7</b> (ND - 47.8)	<b>6.1</b> (0.8 - 15.8)	Rogers and Hall (1987)
Residue	<b>6.3</b> (2.2 - 38.5)	<b>17.9</b> (7.3 - 25.7)	This study (1988)
Whole Fish	13 -15	18 - 22	Carey <i>et al.</i> 1986
Whole Fish	<b>6.3</b> (1.8 - 20.7)	<b>13.2</b> (4.4 - 29.2)	This study (1988)
Liver	<b>26</b> (ND -118.9)	<b>114</b> (14.7 - 496.6)	Rogers and Hall (1987)
Liver	<b>26.4</b> (10.6 -108.1)	<b>68.9</b> (37.8 - 223.9)	This study (1988)

flounder is presented in Table 7. The similarity in results is encouraging in that it demonstrates that with equivalent collection and analytical methods, comparable results might be obtained. While this may seem a trivial observation, this is not always the case with biological collections and should serve to strengthen the use of flounder in following trends in contaminant levels in biota.

# **Starry Flounder as Contaminant Sentinel**

The question of whether the starry flounder is a reliable indicator of chlorophenol contamination can be addressed by examining the criteria for a biological monitor discussed by Jacob (1986). Starry flounder are resident throughout the area of interest. They appear to be relatively sedentary (at least seasonally), are sufficiently long-lived to allow sampling of more than one year class, tolerate brackish water and are hardy enough to survive laboratory conditions. At age 3+, flounder are often large enough

to provide adequate tissue samples for analysis of individual fish, and the younger age classes are sufficiently abundant to allow pooling of representative size classes.

Starry flounder appear to be able to concentrate chlorophenols to quite high levels without being killed. Rogers and Hall (1987), did suggest that the levels of PCBs, DDT and chlorophenols observed in Fraser estuary flatfishes are sufficient to cause reproductive losses and possibly increased mortality of 0-and 1-yr age groups. Carey *et al.* (1986) found good correlation between 2,3,4,6-TeCP (*r*=0.91) and PCP (*r*=0.81) concentrations in starry flounder tissue and the water column, suggesting that the chlorophenol content of the flounder is indeed reflective of ambient conditions. Combined with the ability of starry flounder to bioconcentrate chlorophenols (100x for 2,3,4,6-TeCP, 380x for PCP; Carey *et al.* 1986), the above attributes suggest starry flounder would be a valuable indicator of chlorophenol contamination of the ecosystem.

The only evident problem with using starry flounder as an indicator species is the wide range of chlorophenol concentrations observed in the population. This variability, as well as the higher concentrations observed in younger fish, may be the product of two processes. Direct absorption of chlorophenols from water combined with high clearance rates (Carey *et al.* 1986) could result in a highly variable contaminant body-burdens. The range in concentrations may also be the result of exposure histories and different age-specific migration patterns. The high concentrations in smaller flounder may, in addition to surface/volume relationships, reflect a higher exposure to wood-yard runoff in near-shore areas. Until the seasonal and life history and migration patterns of starry flounder are better understood, it may be best to standardize and concentrate indicator sampling on the more abundant and more clearly resident younger fish (up to age 3). [Studies on starry flounder migration patterns in the Lower Fraser River were presented by Nelson (1995)]

#### **Conclusions**

1) There was little evidence of increasing bioaccumulation of chlorophenols with age or size in starry flounder. The possible exceptions were 2,4-DCP and 2,6-DCP. In most cases, the higher concentrations of chlorophenol were found in smaller individuals.

2) Studies of migration patterns and movements of starry flounder populations should be undertaken. [Studies on this aspect were undertaken by Nelson (1995)]

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#### LITERATURE CITED

- Campana, S.E, and J.D. Neilsen. 1982. Daily growth increments in otoliths of starry flounder (*Platichthys stellatus*) and the influence of some environmental variables in their production. Can. J. Fish. Aguat. Sci. 39: 937-942.
- Carey, J.H., M.E. Fox, and J.H.Hart. 1986. The distribution of chlorinated phenols in the North Arm of the Fraser River estuary. Env. Cont. Div., Nat. Wat. Res. Inst., Env. Can., NWRI Contribution No. 86-45
  - -.1988. Identity and distribution of chlorophenols in the north arm of the Fraser River estuary. Water Pollution Research Journal of Canada 23:31-44
- Garrett, C.L. 1980. Toxic organic contaminants. Water Quality, Fraser River Estuary Study, Min. Env., Victoria, B.C., 125 p.
- Hall, K.J., V.K. Gujral, P. Parkinson, and F.T.S. Mah. 1984. Selected organic contaminants in sediment and fish from the Fraser River estuary. In Proceedings of the 11th Annual Aquatic Toxiciology Workshop: Nov. 13-14, 1984, Ed. G.H. Geen, Can. Tech. Rep. Fish. Aquat. Sci. 1480: 312 p.
- Jacob, C. 1986. Use of the bioconcentration capability of leeches to evaluate chlorophenol pollution. M.Sc. thesis, U.B.C., 182 p.
- Jones, J.A. 1981. Chlorophenols and their impurities in the Canadian environment, Env. Prot. Serv., Env. Canada, Econ. Tech. Rev. Rep. EPS 3-EC-81-2: 434 p.
- Levy, D.A, T.G. Northcote, and G.J. Birch. 1979. Juvenile salmonid utilization of tidal channels in the Fraser River estuary, British Columbia. Westwater Research Centre, Tech. Rep. 23
- Nelson, T.C. (Ed). 1995. Studies of the starry flounder in the Fraser River 1992-1994. Fraser River Estuary Management Program, Technical Report WQM 95-02. 69pp+append.
- Northcote, T.G., N.T. Johnston, and K. Tsumura. 1978. A regional comparison of species distribution, abundance, size and other characteristics of Lower Fraser River fishes. Westwater Research Centre, Tech. Rep. 14: 38 p.
- Rogers, I.H., and K.J. Hall. 1987. Chlorophenols and chlorinated hydrocarbons in starry flounder (*Platichthys stellatus*) and contaminants in estuarine sediments near a large municipal outfall. Water Poll. Res. J. Canada 22(2): 197-210.
- Wilkinson, L. 1989. SYSTAT: The system for statistics. SYSTAT, Inc., Illinois, USA

Max
ng/g wet wt.
53.70
21.35
2.19
1.09
0.00
6.39
1.57
0.55
2.02
2.02
2.07
1.46
4.14
31.48
31.48
2.90
9.80
6.27
3.50
25.67

Appendix 1. Raw data from Chlorophenol Analyses of Starry Flounder from the Fraser River Estuary.

Appendix 1. Table 1a. Chlorophenol analysis raw data: biological characteristics and dichlorophenols.

#### Whole Body Analyses

Sample	Fish	Age	Wt	%Lipid	2,6-DCP	2,4-DCP	3,5-DCP	2,3-DCP	3,4-DCP
Number	Number (s)	(years)	(gr.)		ng/g. wet wt				
. 1	49,100,45	0+	2.96	1.1	•	9.90	-	•	· .
2	54,101,42	0+	7.80	2.0	•	6.24	-		-
	102,103,105,106,10		,						
3	7,121	0+	3.32	1.5	12.29	3.30	1.78		
4	50,108,111	0+	4.31	1.3	3.25		1.12		-
6	55,104,119,120	0+	5.66	1.5	3.87	1.45	0.88	•	
6	51,53,36	1+	6.48	1.3	0.64	4.41			•
7	109	1+	10.41	0.8	3.59	6.93	3.26	•	•
8	47	1+	14.70	0.3	-	•		-	
9	52	1+	23.44	0.6	13.06	1.90			-
10	26	1+-	30.55	1.3	0.41	0.75	0.82		0.51
11	46	1+	49.20	0.6	-	3.13	3.06	•	•.
14	44	2+	13.10	0.8	•	7.41	-		•
16	31	2+	30.18	0.6	0.68	2.83	0.25		•
17	41	2+	43.24	0.6	•	8.00			•
18	28	2+	56.00	2.1	2.30	8.04	0.87	•	•
19	24	2+	77.68	1.3	2.42	•	-		•
20	70	2+	88.15	1.2	0.90	6.24	•		•
21	71	2+	96.78	3.0	3.37	13.11	0.36	-	-
22	40	2+	111.30	2.1	•	12.84			•
23	22	2+	144.35	. 2.2	10.59	16.51		•	•
28	60	3+	58.95	2.0	•	6.34	•		
29	58	3+	76.15	1.3	-	11.57		•	· · ·
30	23	3+	99.56	1.5	•	14.57		•	
31	89	3+	149.60	0.9	•	8.48	-	•	-
32	87	3+	154.80	3.7	10.58	16.06	•	•	-
33	97	3+	173.42	3.2	2.81	8.64	0.41		-
34	96	3+	173.85	3.2	2.33	5.28		-	-
35	79	3+	214.68	3.0	•	13.29	•	· •	-
36	91	3+	241.02	0.9	29.87	4.49	-	•	-
38	37	3+	101.48	3.0	2.13	15.14	<u> </u>	•	
40	39	3+	.131.64	1.5	7.87	12.20	<u> </u>	10.50	-
44	92	4+	397.48	1.6	16.09	19.66	•	· ·	-
46	82	4+	218.11	1.5	•	• .	•	•	•
46	66	4+	223.02	2.5	54.55	9.61	•		•
47	94	4+	228.70	2.6	18.03	18.78	•	<u> </u>	-
49	68	6+	205.91	0.6	1.06	5.37	•	-	
50	98	5+	228.75	2.3	18.13	12.65	•		
51	90	5+	304.74	0.5	•	6.38_	•	•	
52	99	6+	643.02	3.7	26.01	17.16		-	-
79	33	2+	14.40	1.0	8.64	0.83	0.76		•

#### Liver Tissue Analyses

Sample	Fish	Age	Wt	%Lipid	2,6-DCP	2,4-DCP	3,5-DCP	2,3-DCP	3,4-DCP
Number	Number (s)	(years)	(gr.)	· ·	ng/g. wet wt				
12	110,112,113,117,11	1+	17.98	14.8	27.10	-	-	•	•
13	114,115,116	1+	23.48	n/a	35,19	• .	•	•	
24	35,74,29	2+	31.00	3.2	13.19	11.36	-	•	· ·
26	75,38	2+	49.62	8.2	29.30	9.52	-		-
26	30	2+	64.02	n/a	•	•	-	•	
27	86	2+	86.14	8.9	•	•	-	•	-
37	67	3+	83.52	8.5	•	•	•		•
39	43	3+	112.28	6.3	70.88	-	5.93		•
41	96	3+	168.05	5.5	-	-	-	I	•
48	93	4+	157.45	9.4	•		-		-

#### Muscle Tissue Analyses

Sample	Fish	Age	Wt	%Lipid	2,6-DCP	2,4-DCP	3,5-DCP	2,3-DCP	3,4-DCP
Number	Number (s)	(years)	(gr.)		ng/g. wet wt				
12	110,112,113,117,11	1+	17.98	1.3	5.15	1.06	•	٠ .	-
13	114,115,116	1+	23.48	1.2	8.10	4.38		-	
24	35,74,29	2+	31.00	0.9	•	•	•	-	•
25	76,38	2+	49.62	2.4	63.70	21.35	2.19	•	-
26	30 -	2+	64.02	0.9	•	1.26	•	•	
27	. 86	2+	86.14	3.6	12.63	2.59	•	1.00	-
37	67	3+	83.52	3.4	1.72	1.15	• •	•	•
39	43	3+	112.28	2.4	23.57	•	1.15	1.09	•
41	96	3+	168.05	0.9	2,45	2.54	•	•	
48	93	4+	167.46	3.7	3.02	1.39		-	

# Whole Body Analyses

Sample	2,4,6-TCP	2,3,6-TCP	2,3,5-TCP	2,4,5-TCP	2,3,4-TCP	3,4,5-TCP
Number	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt
1	3.35	0.71	-		•	
- 2	2.95	0.64	-	0.38	0.33	•
						,
3	4.83	0.85	•	0.49	1.38	0.41
4	3.91	0.89	• • • • • • • • • • • • • • • • • • • •	0.69	0.88 /	<u>-</u>
5	3.77	0.70	•	0.84	1.11	0.23
6	3.59	0.58	•	0.38	0.57	0.27
7	2.44	•	•	•	0.46	•
8	1.86	0.66	•	•	0.48	•
9	2.84	0.59	•	0.29	0.71	0.34
10	2.11	0.47	·	0.37	0.36	0.21
11	3.40	0.83	•		0.49	• .
14	2.97	0.71		-	-	-
16	4.50	0.65	0.09	0.28	0.65	0.19
17	3.54	-		•	-	-
18	4.16	0.25	0.26	0.60	0.70	0.48
19	3,66	• ;	-	-		-
20	4.07	0.52	•	0.18	-	0.24
21	2.34	0.31		-	0.42	
22	2.86	0.63			-	
23	2.55	0.80	-	-	0.51	0.44
28	3.76	0.85	•	•	-	•
29	6.46	1.16	• ,		0.64	
30	2.44	0.45	•		<u>.</u> '	
31	1.47	0.47	•	_	-	<u>.</u> ,
32	2.74	1.00				
33	5.05	1.15		0.25	0.85	0.42
34	0.96	. ,-	•		•	- ,
35	3.64	1.37		•		-
36	8.90	1.52	. •		_	
38	4.43	1.04		•	•	-
40	2.99	0.75	<b>.</b> .		1.14	0.67
44	4.19	1.44				0.77
45	3.32	0.83	-			
46	2.35	0.03	•			
47	2.33	1.78	•		0,87	1.09
49	1.93	0.42	•		0.21	•
50	2.86	0.65		<u> </u>	1.37	0.68
51	6.82	0.05			1.57	0.00
52	- 0.02	<del></del>			0.41	
79	3.68	0.50	•	0.89	0.58	0.84

# Liver Tissue Analyses

Sample Number	2,4,6-TCP ng/g. wet wt	2,3,6-TCP ng/g. wet wt	2,3,5-TCP ng/g. wet wt	2,4,5-TCP ng/g. wet wt	2,3,4-TCP ng/g. wet wt	3,4,5-TCP ng/g. wet wt
12.	22.15	-	•	•	•	-
13	10.49	•	•		· -	24.00
24	15.92	•	•	-	•	-
25	12.33	•	-	-	4.32	-
26	12.44	•	•	•	17.12	_ •
27	18.18	•	-	•	1.88	• ,
37	17.14.	3.91	•	4.34	3.29	•
. 39	5.69	•	•	•	•	
41	8.81	3.73	-	-	2.34	•
48	5.15	2.20	-	-	-	•

#### Muscle Tissue Analyses

Sample Number	2,4,6-TCP ng/g. wet wt	2,3,6-TCP ng/g. wet wt	2,3,5-TCP ng/g. wet wt	2,4,5-TCP ng/g. wet wt	2,3,4-TCP ng/g. wet wt	3,4,5-TCP ng/g. wet wt
12	3.26	0.95	•		1.16	-
13	3.38	1.37	•	•	2.07	1.01
24	3.02	0.58		0.47	0.84	
25	1.93	1.45		-	0.65	1.23
26	2.25	0.64		-	-	-
27	2.74	0.71	•	-	0.42	1.46
37	6.39	0.91	0.55	2.02	1.10	0.62
39	1.72	0.82		-	0.49	, <u>'</u>
41	4.32	1.57	-	-	1.17	0.41
48	3.96	1.45	•	-	0.74	-

Appendix 1. Table 1c. Chlorophenol analysis raw data: tetra and pentachlorophenols, guaicols, totals.

# Whole Body Analyses

Sample	2,3,5,6-TeCP	2,3,4,6-TeCP	2,3,4,5-TeCP	3,4,5-TCG	unid 1	unid 2	PCP	TeCG	Sum	SUM	SUM	Total
Number	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	ng/g. wet wt	DCPs	TCPs	TeCP.	Cps
1	0.51	12.23	•	4.02	1.47	1.24	22.12	5.19	9.90	4.06	12.74	62.74
2	0.68	7.93	· 0.36	5.05	1.46	1.03	16.17	4.51	6.24	4.30	8.97	51.73
<del></del>												
3	0.65	10.36	0.47	8.26	2.34	4.25	23.36	7.61	25.20	3.13	11.48	88.63
4 .	0.69	7.81	0.61	6.08	2.66	1.60	29.17	7.20	4.37	6.37	9.11	74.56
5	0.26	8.49	0.33	7.90	2.62	2.52	24.69	8.20	6.20	6.65	9.08	77.86
6	0.34	8.46	0.57	4.65	1.34	1.06	10.66	4.40	5.05	5.39	9.37	53.92
7	-	4.03	-	4.74	1.06	1.64	9.34	3.60	12.78	2.90	4.03	54.09
8		6.18	0.26	5.56	1.82	3.44	19.85	6.29	0.00	3.00	6.44	62.40
9	0.41	7.22	0.17	5.18	1.54	4.43	18.90	5.19	14.96	4.77	7.80	80.77
10	0.51	6.09	0.69	3.81	0.90	0.50	9.04	3.47	2.49	3.52	7.29	51.02
11	0.92	9.39	0.24	6.27	1.28	1.18	21.04	6,56	6.19	4.72	10.55	79.79
14	-	8.27	•	5.38	2.47	1.09	17.26	6.17	7.41	3.68	8.27	79.73
16	0.36	4.74	0.36	5.79	1,69	2.82	9.37	4.60	3.76	6.36	5.46	71.85
17	1.43	6.86	•	6.07	2.28	5.42	21.50	7.46	8.00	3.54	8.29	96.56
18	1.23	13.22	1.21	4.40	1.31	6.13	11.44	5.45	11.21	6.45	15.66	98.05
19	1.07	17.86	•	5.94	4.40	0.70	27.13	6.97	2.42	3.66	18.93	108.15
20	-	2.61	0,26	7.91	2.79	1.31	6.77	5.48	7.14	5.01	2.87	79.28
21	-	2.74	0.12	3.89	2.43	1.84	8.75	3.94	16.84	3.07	2.86	85.62
22	-	2.19	-	3.27	2.28	0.97	10.84	3.49	12.84	3.49	2.19	<b>83.37</b>
23	7.82	2.65	•	4.76	0.89	0.73	9.19	3.57	27.10	4.30	10.47	107.01
28	, . <del>-</del>	1.95	•	3.92	1.30	0.93	10.59	3.09	6.34	4.61	1.95	88.73
29	-	4.05	•	6.24	2.09	1.32	16.60	6.13	11.57	8.26	4.05	114.26
30	•	1.83		4.58	2.34	1.35	4.35	3.78	14.57	2.89	1.83	95.69
31	-	3.46		2.44	0.87	0.93	6.10	1.66	8.48	1.94	3.46	87.88
32	-	, 7.77	•	4.10	, 1.94	1.30	20.38	3.31	26.64	3.74	7.77	133.18
- 33	-	5.25	0.36	5.84	2.07	0.83	18.28	4.06	11.86	7.72	5.61	122.27
34	-	4.73	. •	2.00	1.44	1.29	19.21	6.92	7.61	0.96	4.73	112.16
35	· · ·	3,56	•	6.52	1.81	1.70	10.26	3.42	13.29	5.01	3.56	115,57
36	-	8.77	0.66	14.19 ~	4.61	1.41	25.33	9,63	34.36	10.42 .	9.43	181.38
. 38	-	3.07	-	4.44	2.77	2.99	10.74	4.93	17.27	5.47	3.07	127.68
40	0.83	3.01	0.27	7.62	3.43	2.41	9.30	4.82	30.57	5.55	4.11	147.81
44	1.06	6.86	-,	7.01	3.79	4.14	25.05	7.80	35.75	6.40	7.92	185.86
45	5.34	3.18	<u> </u>	6.80	3.11	1.73	12.32	5.90	0.00	4.15	8.52	132.53
46	2.32	7.13	-	3.29	1,41	2.96	9.75	2.58	64.16	2.35	9.45	187.95
• • 47	0.72	7.68	0.42	12.67	3.30	1.53	18.51	7.45	36.81	3.74	8.82	186.83
49	-	2.01	0.16	2.84	1.79	1.05	5.24	3.17	6.43	2.56	2.17	123.25
50	3.38	1.71	0.13	3.55	1.47	2.50	8.26	3.06	30.78	5.56	5.22	160.40
51	2.87	4.20	-	1.51	0.77	1.28	7.43	2.11	6.38	6.82	7.07	135.37
52	4.20	1.70	-	2.23	2.05	2.57	7.50	3.48	43.16	0.41	5.90	171.30
79	0.66	17.81	2.24	4.60	1.59	1.35	18.12	6.40	10.22	6.49	20.71	227.48

### Liver Tissue Analyses

Sample	2,3,5,6-TeCP	2,3,4,6-TeCP	2,3,4,5-TeCP	3,4,5-TCG	unid 16	unid 17	PCP	TeCG	Sum	SUM	SUM	Total
Number	ng/g. wet wt	ng/g. wet wt_	ng/g. wet wt	ng/g. wet wt	DCPs	TCPs	TeCP	Cps				
12	-	41.92	•	71.10	89.17	7.52	223.91	44.78	27.10	22.15	41.92	551.65
13	20.25	35.00	-	-	-	-	161.17	17.22	35.19	34.49	55.25	329.32
24	4.98	32.74	3.94	21.04	16.97	5.11	88.64	17.16	24.54	15.92	41.66	279.04
25	4.15	17.60		-	- ,	•	50.70	19.90	38.82	16.65	21.75	197.82
26	16.30	14,82	- ,	25.38	141.50	-	71.04	13.56	0.00	29.56	31.12	364.16
27	3.11	13.24	1.45	32.54	10.13	1.29	40.61	20.44	0.00	20.06	17.80	196.87
37	11.46	89.62	7.05	28.52	7.78		65.08	32.43	0.00	28.68	108.13	344.62
39	-	12.25	-	7.97	2.78	4.71	51.69	10.08	76.81	5.69	12.25	249.98
41	1.96	12.45	-	19.36	5.30	1.78	37.77	10.30	0.00	14.88	14.41	185.80
48	15.56	11.71	-	11.70	11.29	1.35	64.13	7.76	0.00	7.35	27.27	226.85

# Residue Tissue Analyses

Sample Number	2,3,5,6-TeCP ng/g. wet wt	2,3,4,6-TeCP ng/g. wet wt	2,3,4,5-TeCP ng/g. wet wt	3,4,5-TCG ng/g. wet wt	unid 16 ng/g. wet wt	unid 17 ng/g. wet wt	PCP ng/g. wet wt	TeCG ng/g. wet wt	Sum DCPs	SUM TCPs	SUM TeCP	Total Cps
12		6.31	0.29	6.20	2.82	3.38	22.71	5.21	6.21	5.37	6.60	82.50
13	0.84	7.39	0.40	5.01	1.46	3.50	19.95	4.61	12.48	7.83	8.63	89.47
24	0.66	9.33	0.85	4.89	3.22	0,84	18.73	5.40	0.00	4.91	10.84	96.83
25	-	6.14	0.36	4.80	1.99	3.38	16.54	4.72	77.24	5.26	6.50	170.43
26	-	2.19		3.35	1.19	0.99	10.66	3.82	1.26	2.89	2.19	78.35
27	0.62	2.90	-	3.39	1.04	1.85	7.28	2.86	16.22	5.33	3.52	95.49
37	4.14	31.48	2.90	9.80	3.46	2.12	25.67	10,60	2.87	11.59	38.52	178.63
39	0.61	6.25	-	4.04	6.27	2.11	16.28	6.24	25.81	3.03	6.86	148.64
41	0.40	6.07	0.45	8.16	4.23	3.17	18.22	6.08	4.99	7.47	6.92	141.24
48		4.92	0.42	6.04	3.56	1.82	20.27	4.19	4.41	6.15	5.34	147.78

# **Appendix 2. Quality Control Analyses**

#### Methods

The accuracy of the chlorophenol analysis was tested by analysis of spiked tissue samples.

Muscle fillets were collected from 2+ (n=10) and 3+ (n=9) fish and pooled by age. Livers were removed from each of the fish and pooled over all fish from both age classes. These tissues were ground using a pharmaceutical mortar and pestle, homogenized, and divided into four 2 - 3 g. subsamples. Subsamples were spiked with four levels (Low, Moderate, High and Very High: Appendix 2, Table 1) of ten chlorophenol standards at the Inland Waters Directorate Laboratory in Vancouver and forwarded to N.W.R.I. for analysis.

Analytical precision was tested using replicate submissions from a single large (2.33 kg, age 5+) flounder which was purchased from local commercial supplier for the purpose. Five separate samples of epaxial muscle and liver tissue were submitted for analysis.

#### Results

Results of analysis of spikes are shown in Appendix 2, Figures 1 and 2, and Table 2. The figures show little difference between spiked and measured chlorophenol levels in either muscle or liver tissue. Comparison of spiked and measured concentrations by ANOVA showed no significant difference between spiked and measured levels within each tissue type. Consistent deviations were, however, observed for several isomers. In muscle tissue analyses, concentrations of several isomers (eg. 2,4-DCP, 2,3,5-TCP and PCP) were consistently overestimated, while others (eg. 3,5-DCP, 2,3,5,6-TeCP and 2,3,4,6-TeCP) were consistently underestimated.

Measurable levels of 2,3,4-TCP were found in the spiked muscle samples and analyses of spiked liver tissues showed unexpected levels of 2,6-DCP, 2,3,4-TCP and 3,4,5-TCP (Table 2). These congeners were not part of the "spike cocktail" (Table 1) and not found in the blanks, so their presence suggests breakdown of other chlorophenols occurred during sample storage or analytical treatment. Various TCPs can be products of anaerobic degradation of PCP (NRCC 1981, Carey et al. 1986).

Results and summary of replicate analyses of chlorophenols of liver and muscle from a single starry flounder are presented in Appendix 2, Table 3. Values of the coefficient of variation (Mean / SD \*

100) are particularly informative in evaluating the precision of the analysis, but require some care in interpretation. Observations near an analytical detection limit are notoriously unreliable (Crummett 1979). Recognizing this fact, proper assessment of analytical precision should only be made for concentrations well above the detection limit.

The results allow a subjective appraisal of the relative deviation for each chlorophenol type. The methods provided good precision for PCP measurements in both liver and muscle tissue, but relatively poor precision for the lower chlorinated phenols such as 2,4-DCP.

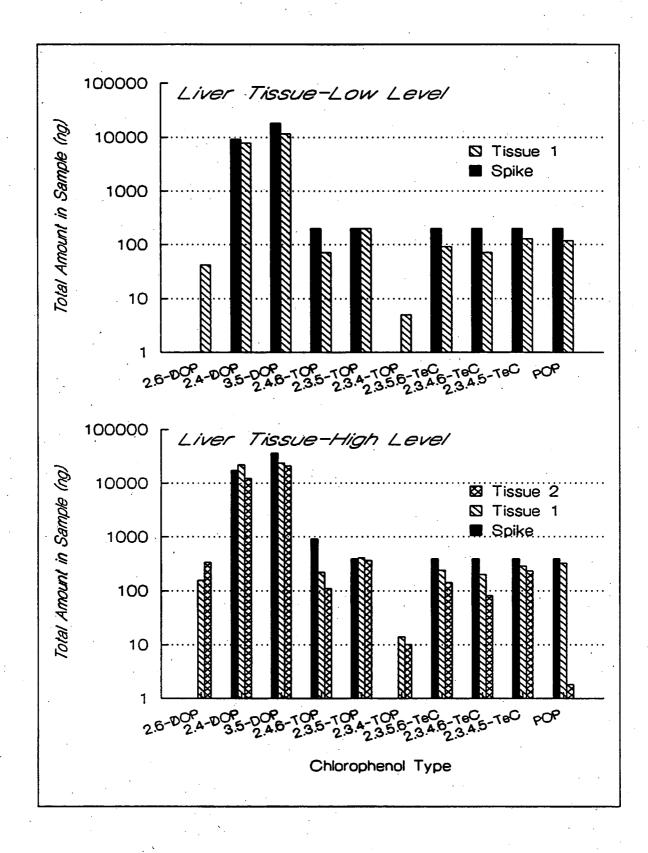
# **Literature Cited**

- Carey, J.H., M.E. Fox, and J.H.Hart. 1986. The distribution of chlorinated phenols in the North Arm of the Fraser River estuary. Env. Cont. Div., Nat. Wat. Res. Inst., Env. Can., NWRI Contribution No. 86-45
- Crummett, W.B. 1979. The problem of measurements near the limit of detection. Annals of the New York

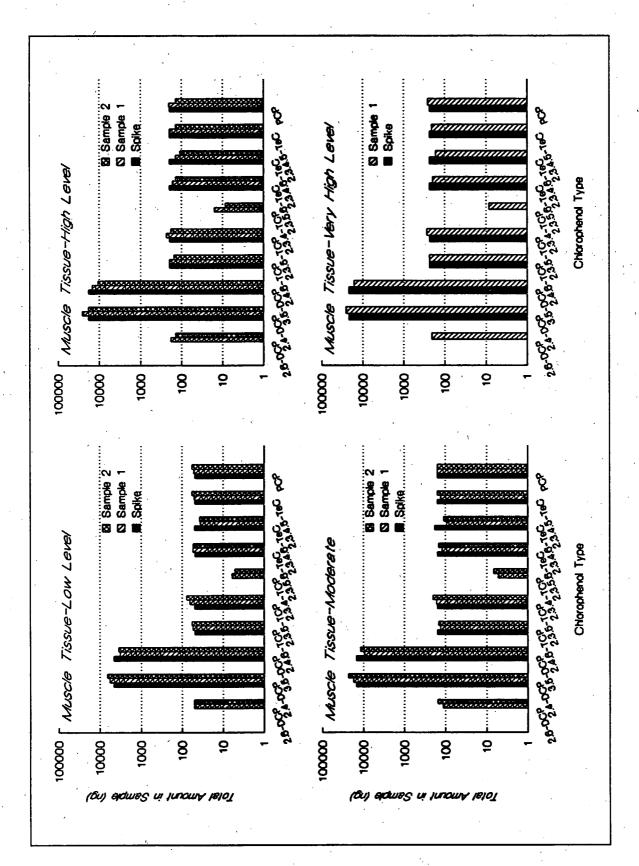
  Academy of Science 320:43-46
- NRCC (National Research Council of Canada). 1981. Chlorinated phenols: Criteria for environmental quality. NRCC No. 18578. 191pp.

Appendix 2. Table 1. Total mass of each chlorophenol congener (ng) in spike mixture.

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Congener		MUSCIE	בֿם			
	Low	Moderate	High	Very High	Low	High
2,4-DCP	5,000	15,000	20,000	25,000	10,000	20,000
3,5-DCP	5,000	15,000	20,000	25,000	20,000	40,000
2,4,6-TCP	50	150	200	250	200	400
2,3,5-TCP	50	150	200	250	200	400
2,3,5,6-TeCP	50	150	200	250	200	400
2,3,4,6-TeCP	50	150	200	250	200	400
2,3,4,5-TeCP	20	150	200	250	200	400
PCP	50	150	200	250	200	400



Appendix 2. Figure 1. Comparison of measured and spiked content of chlorophenols in starry flounder liver tissue.



Appendix 2, Figure 2. Comparison of measured and spiked content of chlorophenols in starry flounder muscle samples. Total amount was calculated as concentration (ng/g) \* sample weight.