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Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455114>

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To cite this Article Hellou, J. , Hodson, P. V. and Upshall, C.(1995) 'Contaminants in Muscle of Plaice and Halibut Collected From the St. Lawrence Estuary and Northwest Atlantic', *Chemistry and Ecology*, 11: 1, 11 – 24

To link to this Article: DOI: 10.1080/02757549508039061

URL: <http://dx.doi.org/10.1080/02757549508039061>

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CONTAMINANTS IN MUSCLE OF PLAICE AND HALIBUT COLLECTED FROM THE ST. LAWRENCE ESTUARY AND NORTHWEST ATLANTIC

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(Received 10 June 1994)

Levels of aromatic hydrocarbons in muscle of plaice and halibut were determined by fluorescence, using the chrysene standard, as recommended by the International Oceanographic Commission, for the analysis of PAH in environmental extracts. Concentrations were highest in muscle of halibut collected at the most contaminated, nearshore site, in the Saguenay Fjord of the St. Lawrence Estuary, compared to other locations further from shore. Although concentrations of fluorescing compounds were not statistically different in plaice, the saturated hydrocarbons displayed unquestionably more biodegradation, with a decrease of n-alkanes and increase of branched aliphatics, at the less contaminated site. Synchronous fluorescence indicated the presence of benzenoid and biphenyl hydrocarbons in the extracted mixtures, while GC-MS-TIC analysis tentatively identified the presence of a series of benzenoid (alkyl benzenes), chlorinated (PCB and DDE), N (trialkylamines) and O (phenols) hydrocarbons. These anthropogenic compounds could derive from petroleum products, surfactants and common products used in industry and households. This study emphasizes the importance of a multispectroscopic approach when investigating complex environmental mixtures.

KEY WORDS: Fish muscle, halibut, plaice, aromatic hydrocarbons.

INTRODUCTION

A large number of organic contaminants are fluorescent or contain a benzene ring moiety in their structure. The polycyclic aromatic compounds (PAC), with two benzene rings and more, include polycyclic aromatic hydrocarbons (PAH) and heterocyclic aromatic compounds, with N, S and O substituents. Other non-polar organic contaminants, also aromatic and present in the environment, are represented by organochlorines, well known examples being the polychlorinated biphenyls (PCB), the dichlorodiphenyltrichloroethanes (DDT), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF). Other less well known or less characterized contaminants are represented by polychlorinated naphthalenes (PCN; Auger *et al.*,

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1993), polybrominated biphenyls and diphenyl ethers (PBB and PBDE; Zitko, 1977; Jansson and Asphend, 1987) and linear alkylbenzenes (LAB; Vivian, 1986; Eganhouse, 1986). In general, PACs of anthropogenic origin predominate over aromatics from a diagenic or biogenic origin that tend to derive from isoprenoid precursors (Ward-roper *et al.*, 1984; Killops and Howell, 1988).

The analysis of PAC or PAH has been approached using a variety of extraction, purification and quantification techniques (Ehrhardt *et al.*, 1991). The choice of extraction will affect recoveries, purification will determine the type of components present within a mixture, while specific or broad results will be obtained depending on the number and type of analyses performed. The higher sensitivity and somewhat lower selectivity of ultra-violet/fluorescence spectroscopy (uv/f, a semi-quantitative technique) allows preliminary investigations concerning levels of aromatic contaminants in biota. Synchronous fluorescence, a variation of uv/f, allows an overall insight into the carbon skeleton of structures present within mixtures, sometimes difficult to characterize otherwise. The biological and chemical transformation of organic contaminants, the large number and sources of compounds, low concentrations, lack of synthetic standards, all contribute to limit our ability to characterize components fully within complex mixtures in environmental extracts, and ultimately to determine bioavailability, fates and effects.

The present study examined the level of aromatics (uv/f) in muscle of plaice and halibut collected along a pollution gradient in the St. Lawrence Estuary and from offshore Newfoundland, in the northwest Atlantic (Fig. 1). Synchronous fluorescence and gas chromatography-mass spectroscopy (GC-MS) in the selected ion monitoring (SIM) and total ion chromatogram (TIC) modes were used to delineate further the chemical nature of the bioaccumulated compounds. Saturated hydrocarbons were also examined briefly in plaice.

MATERIALS AND METHODS

Fish were collected by trawling during the Department of Fisheries and Oceans research cruises, that took place in June of 1990, in the St. Lawrence (Site 1), and in October 1990 and November-December of 1991 (two cruises) in the northwest Atlantic. Plaice, *Hippoglossoides platessoides*, and Greenland halibut, sometimes referred to as turbot, *Reinhardtius hippoglossoides*, were sampled. Fish from the northwest Atlantic were caught in the North Atlantic Fisheries Organisation (NAFO) divisions 2J-3K at several different stations. Gill nets were used to collect fish from depths of 100-200 m in the Saguenay Fjord near its source (Site 4) and its mouth (Site 6), while trawls took place in the St. Lawrence Estuary at two sites east of the Fjord (Sites 1 and 2, Fig. 1).

Fish from the Saguenay and St. Lawrence were kept in flowing salt water for several hours before necropsy to remove samples of dorsal white muscle, which was frozen immediately on dry ice and kept at -20°C until analysis. Fish from the northwest Atlantic were frozen on board ship (-30 to -40°C), transported to land, dissected, and samples frozen for a few weeks until needed. Analysis of PAC by fluorescence and GC-MS-TIC has been detailed previously (Hellou *et al.*, 1993). In brief, caustic digestion of tissue (5N KOH, MeOH:H₂O, 1:1, 40°C , 20 hours) is followed by a two

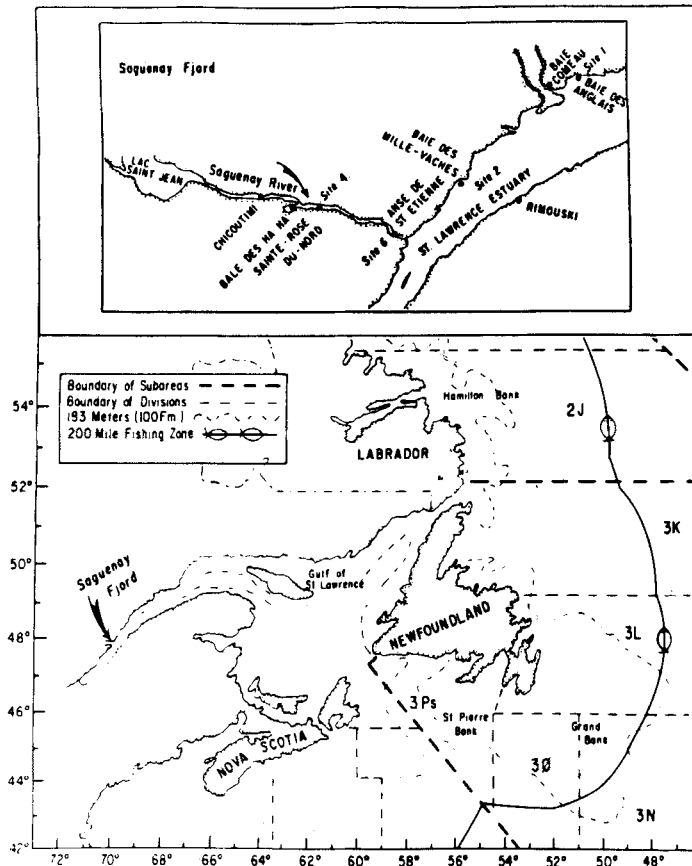


Figure 1 Location of sampling sites on the Saguenay Fjord, St. Lawrence Estuary and northwest Atlantic.

step purification using alumina and silica columns. The first fractionation removes lipids, while the second column separates saturates from unsaturates. The procedure is followed by measurement of fluorescence at the chrysene wavelength pair of 310/360 nm and is validated by the use of a standard PAH solution (NBS 1647, or phenanthrene or chrysene, as standards). Results are reported in terms of chrysene units, as recommended by the International Oceanographic Commission (IOC). Blanks (procedural) and recoveries are processed with every 6 to 9 samples.

The analysis of 27 PAC by GC–MC–SIM was performed on pooled samples, in described by Hellou *et al.* (1993). Lipids were analysed by the well-established Bligh and Dyer method (1959), while PCBs were identified by GC–MS as outlined in Wittlinger and Ballschmiter (1987), using two ions per series of isomers. The Wiley/NBS registry of mass spectral data (McLafferty and Stauffer, 1989) and the important peak index of the registry of mass spectral data (McLafferty and Stauffer, 1991) were used to search for structures that could correspond to the molecular formulas proposed in Tables II and III.

RESULTS AND DISCUSSION

Concentration of Aromatics

Levels of aromatics in muscle of plaice and halibut collected from different locations of the St. Lawrence Estuary and from the northwest Atlantic, near the island of Newfoundland, are presented in Table I. Results obtained by uv/f analysis are listed by species, moving from offshore to nearshore locations. Detailed concentrations relative to locations in the Estuary are depicted in Figure 2. As can be observed in the case of plaice, concentrations for all locations ranged from ND to $0.39 \mu\text{g g}^{-1}$ (dry weight, chrysene units, Table 1). An analysis of variance performed on log transformed data, followed by comparison of means (Scheffe test), showed no significant pair-wise differences (5% level) among the St. Lawrence plaice. However, it should be noted that a higher median associated with a higher variability has been observed in tissues of biota collected at contaminated sites (e.g. Jackson *et al.*, 1994).

Concentrations in muscle of halibut from the St. Lawrence were higher than in other fish. The Scheffe test indicated the presence of two statistically different (5% level) groups in the St. Lawrence halibut: H4 being one and H2 and H6, the other.

Studies have demonstrated that a variety of contaminants: metals, PCDD, PCDF and PAH are present in the St. Lawrence (Allan, 1990; Tremblay *et al.*, 1992; Brochu *et al.*, 1993; Gearing *et al.*, 1993). Martel *et al.* (1986) showed that the sum of 13 PAHs in sediments of the Saguenay follow a gradient of decreasing concentrations away from the Chicoutimi area (Fig. 1). In the present sampling area, site 4 is near aluminium smelters and pulp and paper mills, where the Saguenay Fjord acts as a settling basin. Site 1 receives waste from an aluminium smelter and a paper mill, but is on the open coast of the St. Lawrence. Site 6 is also on the Saguenay, but more remote from industry than site 4, where sedimentation is limited by strong currents. Site 2 in the St. Lawrence Estuary is more pristine and sampling in the northwest Atlantic is more remote from shore and can be viewed as a control site.

Table I Concentration of aromatics ($\mu\text{g/g}^{-1}$, dry weight) in muscle tissue.

	Site	N	H_2O (%) mean (range) SD	Chrysene units mean (range) SD
Plaice:				
	Sea	NWA	13	82 (80–86) 2
P1	↓	1	5	79 (77–83) 2
P2		2	4	76 (72–80) 4
P6	Land	6	7	81 (76–86) 4
Halibut:				
	Sea	NWA	6	73 (53–82) 10
H2	↓	2	4	73 (67–77) 4
H6		6	9	74 (60–80) 4
H4	Land	4	10	69 (56–78) 7

-NWA: Northwest Atlantic, ND: not detected. P1, P2 and P6 refer to plaice at sites 1, 2 and 6, while H2, H6 and H4 refer to halibut at sites 2, 6 and 4, respectively.

We have previously analysed the level of aromatics in cod from the St. Lawrence and northwest Atlantic and observed scarcely detectable amounts (uv/f; Hellou *et al.*, 1994). Plaice appear to bioaccumulate contaminants at levels that are slightly higher than in cod, while halibut display much higher concentrations of fluorescing compounds in muscle (uv/f, chrysene units). Although the geographical distribution of cod, plaice and halibut in the St. Lawrence is not well documented, it is the halibut, with a higher overall lipids content, which displays a gradient of contamination. The particular diet, age, sex or activity of mixed-function oxygenase enzymes of fish could also contribute to the observed difference in the concentration of aromatics.

Lipids

Lipids were analysed in muscle of fish from the northwest Atlantic, where means in cod (Hellou *et al.*, 1994), plaice and halibut were 0.33, 3.5 and 19%, respectively. Assuming that lipid content is relatively similar in the St. Lawrence species, lipid means can be compared to mean aromatic concentrations of 0.03, 0.07 and 1.7 $\mu\text{g g}^{-1}$ (dry weight). Lipid content could have played a role in the bioaccumulation of contaminants, not on an individual sample basis, but in terms of the general tissue distribution of aromatics. Different distributions of organic contaminants in tissues have been observed previously in fish and ducks (e.g. Albaiges *et al.*, 1987; Llorente *et al.*, 1987).

Lipids were not analysed in muscle of the St. Lawrence fish, although the water content of muscle was determined in order to express concentrations on a dry weight basis (Table I). The water content in halibut (mean = 72%) was lower than in plaice (mean = 80%, Fig. 2). However, Spearman rank correlations between concentrations of aromatics and water content (also log transformed data) in each species of fish, analysed by site or species, were not statistically different, except for log transformed data of plaice at site 6.

Synchronous fluorescence

To determine the aromatic carbon skeleton of the fluorescing compounds present in tissues, synchronous fluorescence with an offset of 10 and 25 nm was used (Wakeham, 1977; Baudot *et al.*, 1991). This analysis indicated that two maxima were present in tissue extracts. The excitation/emission wavelength pairs were of 280/290, 305/315 nm and 285/310, 295/320 nm, with slightly different relative ratios (varying between 1:1 to 1:2, the first compared to second maxima). These wavelength pairs are representative of benzene and biphenyl type aromatics (Baudot *et al.*, 1991). A third minor maximum was apparent in plaice at 325/335 nm (not with the 25 nm offset) and this was of lower intensity (0.25%) than the other two peaks. This third maximum is indicative of naphthalene type derivatives.

The fluorescence of aromatic compounds increases with the number of rings, while it decreases with the presence of heavy metals (and is also lowered with increasing number of substituents, such as chlorine atoms) (Wehry, 1973). Therefore, the relative intensity of the maxima is not related directly to the level of the different aromatic species in a mixture.

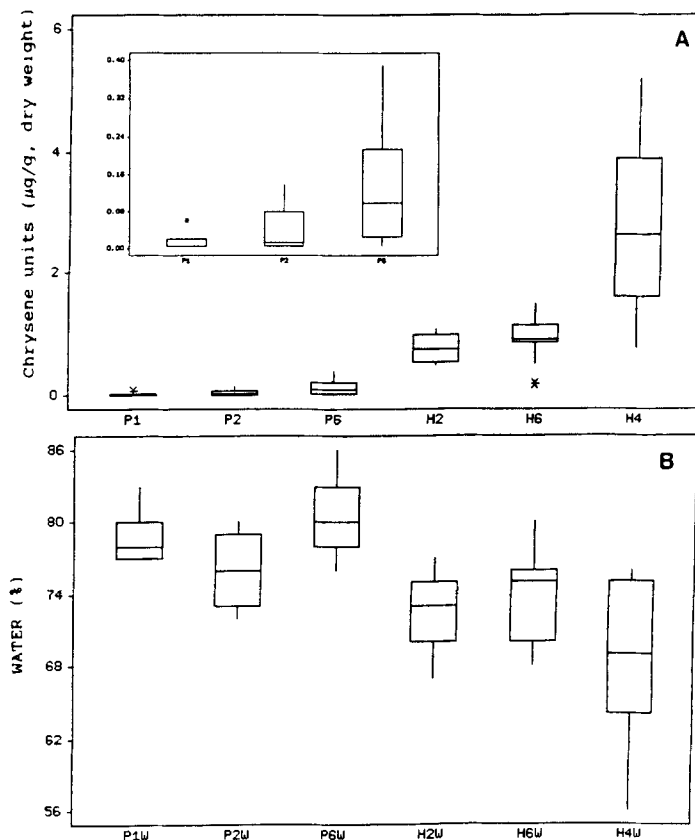


Figure 2 Concentration of aromatics in plaice (P) and halibut (H), at various sampling sites (number following P and H) measured in terms of chrysene units. Percent (%) water (W) in corresponding muscle samples. Boxes enclose the middle half of the data, the horizontal line within the box represents the median and the whiskers display the range of the data.

Analysis of components within extracts

The presence of 27 PAC, parental and alkylated, two to six ring structures, was examined by GC-MS-SIM in pooled samples. Scarcely detectable levels were obtained for all PACs, except for phenanthrene, C-1 and C-2 phenanthrene, present in trace amounts. To gain more information on the specific components present in the extracted plaice and halibut mixtures, analysis by GC-MS-TIC was undertaken. An unresolved complex mixture (UCM) was present in all pooled samples, with resolved peaks of low intensity. This UCM is characteristic of petroleum oil contamination. A series of structure could be proposed from the fragmentation pattern of resolved peaks. These can be divided into three groups of chemicals, mono-aromatic hydrocarbons, chlorinated and hetero-atomic N and O hydrocarbons.

Unsaturated hydrocarbons, represented by alkyl and alkene benzenes (AB), were detected in plaice and halibut (Table II). These derivatives were characterized by the

presence of major fragment ions in the MS at $m/z = 91, 105, 119$ and 133 a. m. u., due to C-1 to C-4 benzenoid moieties within larger molecules. The molecular ion and two abundant fragments are listed along with the proposed molecular formula (Table II); the benzenoid derivatives ranged from unsaturated C-13 to C-17 compounds (Table II).

The chlorinated hydrocarbons identified in halibut tissue ranged from tetra to hepta-chlorobiphenyls (Fig. 3). These were detected initially as resolved peaks in the TIC, displaying characteristic isotopic ions due to multi-chlorinated fragments. This was followed by the extraction of ions, representative of the degree of PCB chlorination, from the chromatogram (TIC), as outlined in Wittlinger and Ballschmiter (1987). The general retention time fingerprint of the hexa and hepta congeners was almost identical to Aroclor 1260 (Fig. 3). The penta-chlorinated isomers appear as a combination of Aroclor 1254 and 1260, while the tetra derivatives are similar to Aroclor 1254. Interestingly, using the present procedure, PCB could not be detected in the pooled unsaturated fractions of plaice or in the previously eluting fraction (saturates).

One chlorinated hydrocarbon of $RI = 2120$ ($RI =$ Relative Kovat Index) was detected in plaice. The fragmentation was indicative of a tetra-chlorinated $C_{14}H_8Cl_4$ structure and corresponded to a DDE standard. After saponification, DDE would be expected as the major DDT representative (Albaiges *et al.*, 1987). Scanning the chromatograms for tetra- to octa-chloronaphthalenes and for C-5 mono- to tetra-chlorobiphenyls, as outlined in Koistinen (1992), gave negative results in both species. Different nitrogen and oxygen containing compounds were identified tentatively (Table III). Alkylphenols have been identified in fish on some other occasions (Heil and Lindsay, 1990; Shirashi *et al.*, 1989). Trialkylamines (TAM) were identified mainly in plaice, but no standards are available to confirm the structure of the proposed molecular formula (Table III). The lowest molecular weight TAM, detected in samples from site 6, was 50-100 times more abundant than the other TAM listed. The rest of the resolved contaminants identified in plaice were present in relatively similar abundance.

Source of contaminants

Contaminants similar to some of the above aromatics have been identified in at least two other studies: sewage effluents and sediments from the Santa Monica basin and

Table II Alkyl and alkene benzenes identified in muscle extracts.

Chemical	MF ^a	MW ^b and fragmentation (% abundance)			RI ^c	Species ^d
A-C13 AB	C ₁₉ H ₃₂	260 (38)	133 (50)	119 (100)	1756	H
B-C13 LAB	C ₁₉ H ₃₂	260 (50)	133 (40)	119 (100)	1803	P and H
C-C13 LAB	C ₁₉ H ₃₂	260 (13)	119 (68)	91 (100)	1854	H
D-C14:1 AB	C ₂₀ H ₃₂	272 (20)	148 (100)	133 (98)	1930	H
E-C14:1 AB	C ₂₀ H ₃₂	272 (58)	159 (47)	119 (100)	1940	H
F-C13:2 AB	C ₁₉ H ₂₈	256 (35)	241 (100)	159 (90)	1945	H
G-C16:3 AB	C ₂₂ H ₃₂	296 (11)	252 (100)	185 (66)	2040	P
H-C17 AB	C ₂₃ H ₄₀	316 (16)	133 (79)	119 (100)	2333	P

a-Proposed molecular formula; b-Proposed molecular weight and two m/z fragments; c-Relative Kovat indices; d-H: halibut, P: plaice;

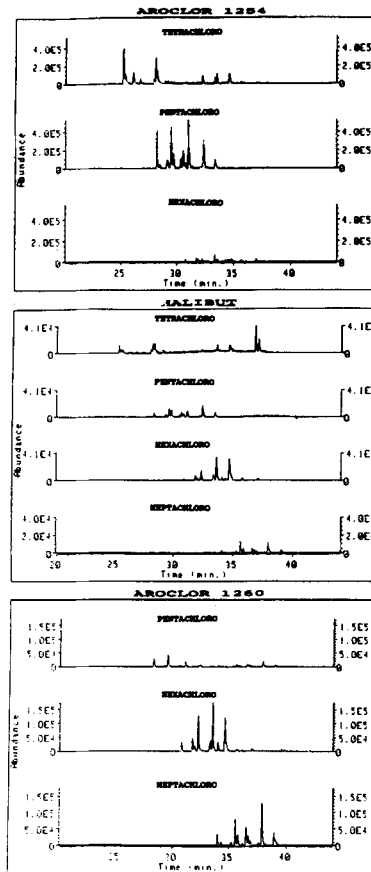


Figure 3 Extracted ion chromatograms representing different groups of PCB congeners.

Table III N and O derivatives identified in muscle extracts.

Chemical	MF ^a	MW ^b and fragmentation (% abundance)	RI ^c	Species ^d
A-BHT ^e	C ₁₅ H ₂₄ O	220 (25) 205 (100) 177 (10)	1492	H
B-phenol	C ₁₆ H ₂₆ O	234 (30) 219 (100) 191 (8)	1546	H
C-N aromatic	C ₁₆ H ₁₅ N	221 (100) 143 (53) 128 (20)	1675	H
D-TAM	C ₁₆ H ₃₅ N	241 (18) 227 (18) 141 (100)	1792	H and P
E-TAM	C ₁₇ H ₃₇ N	255 (16) 227 (16) 155 (55)	1852	P
F-TAM	C ₁₈ H ₃₉ N	269 (3) 241 (6) 155 (100)	1910	P
G-TAM	C ₁₈ H ₃₉ N	269 (8) 238 (20) 155 (100)	1924	P

a-Proposed molecular formula; b-Proposed molecular weight and two m/z fragments; c-Relative Kovat indices; d-H represents halibut, P represents plaice; e-BHT: 2, 6-di-tert-butyl-4-methylphenol, the second phenol could correspond to di-t-butyl-ethyl-phenol, TAM: trialkylamines.

two polluted rivers in Barcelona (Chaloux *et al.*, 1992; Gomez-Belichon *et al.*, 1991). The source of these contaminants is varied and includes commercial products, surface active agents, combustion products from incinerator emissions and petroleum oils (Fangmark *et al.*, 1993).

Linear alkylbenzenes (LAB) are anionic surfactants produced as side-products during the synthesis of linear alkylbenzene sulphonates (LABS). LABS are used in detergents and in pesticide formulations (Schreuder and Martijn, 1988), while alkyl benzenes (AB) can also originate from petroleum oil (Upshall *et al.*, 1993). In addition, volatile AB have been associated with off-flavour and smell in fish (Berg, 1983). Dialkyltetralin sulphonate surfactants and petroleum sulphonates are used as emulsifiers in lubricating oils and could also represent the source of these aromatic compounds (Schmitt, 1992).

Polychlorinated biphenyls have become ubiquitous environmental contaminants, due to their resistance to biodegradation. They have been used in a variety of products, such as transformers, paints, inks and pesticides. PCBs are believed to represent the precursors of the more toxic series of PCDD and PCDF (Fangmark *et al.*, 1993).

Trialkylamines (TAM) are cationic surfactants also used as fabric softeners (anti-static agents) and in hair products; they have been identified previously in sewage effluents and biota (Valls *et al.*, 1989a and b; Chaloux *et al.*, 1992).

The phenolic compound BHT is an anti-oxidant, widely used commercially in food, paints and oils. It is a hydrophobic and lipophilic chemical, a potent inhibitor of lipid-containing viruses (Snipes *et al.*, 1975) and has been observed to induce metamorphosis in polychaete larvae (Jensen and Morse, 1990).

Fewer detected compounds are biogenic or diagenic in origin (compared to anthropogenic) and these are not aromatic but unsaturated hydrocarbons. As expected, the major unsaturated hydrocarbon is squalene, the biosynthetic precursor of cholesterol. Octahydrosqualene was also detected in halibut. This C-30:2 (carbons: unsaturations) hydrocarbon has been reported previously in methane-containing sediments and fine particles ($< 53 \mu\text{m}$) collected in anoxic sampling areas (Wakeham, 1990). Several double bond isomers of this isoprenoid exist. The saturated hydrocarbon pristane is also biogenic in origin.

Fluorescence of LAB and PCB

Since a wide variety of non-PAHs were identified in the muscle extracts displaying fluorescence, it was of interest to determine the response of LAB and PCB mixtures to uv/f at the chrysene wavelength. Therefore, LAB 225 (Monsanto standard of C-10 to C-14 LAB isomers) and Aroclor 1254, 1260 (mixture of PCB congeners) were used to prepare calibration curves expressed in terms of chrysene units and diesel oil. The diesel oil was chosen to report concentrations, because it displays a maximum at 285/310 nm, in synchronous fluorescence, similar to one observed in the extracted mixtures. The degree of uv/f response of LAB 225 is presented in Figure 4, while PCBs were undetectable at the chrysene or diesel wavelength, up to a total concentration of 50–500 ng/ml (in hexane). This result is different from the detection limits of 2.5 and 4 ng/ml determined by Khasawneh and Winefordner (1988), at the wavelength pairs of 260/329 and 230/332 nm, for Aroclor 1254 and 1260, respectively (solvent unspecified).

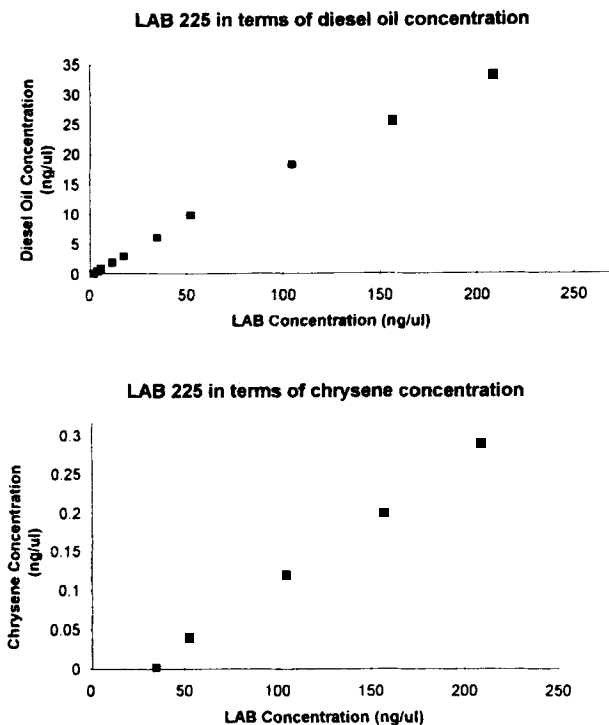


Figure 4 Concentration of alkylbenzenes expressed in terms of diesel oil and chrysene.

The difficulty in detecting PCB compounds by *uv/f* has prompted more research into the enhancement of the sensitivity of that technique (Al-Hadad *et al.*, 1989). Our investigation confirms the higher sensitivity of *uv/f* to aromatics, especially PAC, rather than to chlorinated aromatic compounds. However, since monocyclic and chlorinated aromatics represented a large portion of the bioaccumulated compounds first detected by *uv/f*, more caution is warranted in the interpretation of *uv/f* results as due to PAH.

Saturates

To obtain further information on bioavailable contaminants, the saturated hydrocarbon fractions obtained from plaice at sites 2 and 6 were pooled and analysed by GC-MS-TIC (Fig. 5). Non-volatile saturates displayed peaks due to *n*-alkanes ranging predominantly from C-18 to C-31, with no odd carbon preference. The biogenic hydrocarbon pristane was 21 and 6 times more abundant than the most predominant *n*-alkane at sites 2 and 6, respectively. In the case of sediment extracts, a pristane: phytane (isoprenoid hydrocarbon, but diagenic in origin, RI = 1908) ratio much higher than 1 (> 3–5) is indicative of a “clean” environment (Steinhauer and Boehm, 1992). In the present case, pristane derives from the muscle extract and the ratio is nearly as

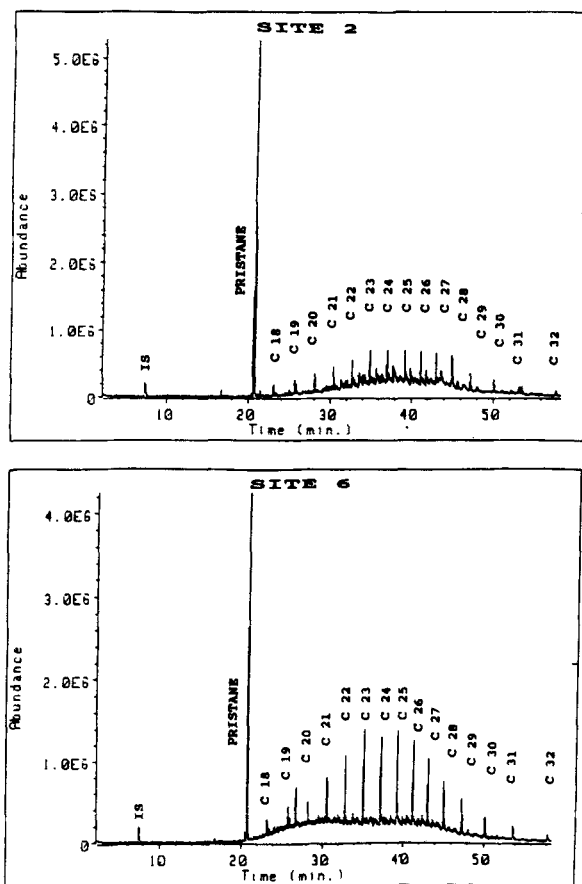


Figure 5 Saturates fraction obtained from pooled extracts of plaice muscle. The carbon number of n-alkanes is indicated (IS: internal standard).

great at both sites (50–100) and cannot be used to discriminate between the quality of the environments. Other isoprenoids of RI 2200 to 2900 were well resolved and represented nearly half and one tenth the concentration of the n-alkanes from sites 2 and 6, respectively. An abundant hydrocarbon of RI = 1940 was present in pooled extracts from site 6 (Fig. 5). The fragmentation of $m/z = 262$ (76%), 191 (53%) and 109 (100%) points to a molecular formula of $C_{19}H_{34}$, where a tricyclic structure deriving from the decarboxylation and hydrogenation of abietic acid would fit the MS fragmentation. The RI reported for dehydroabietane is close to the present $C_{19}H_{34}$ compound (Yamaoka, 1979). This hydrocarbon was barely detectable at site 2 and less abundant than other isoprenoids (Fig. 5). The UCM extended from RI 1700 to 3100 and represented 3.5 and 2.5 times the area of the n-alkanes from site 2 and 6, respectively. All this information points to more biodegradation of saturates at site 2 than at site 6 (Steinhauer and Boehm, 1992). Nevertheless, the bioaccumulation of saturated hydrocarbons was evident in muscle of plaice collected from both locations.

CONCLUSION

In the present study, fluorescence was used to investigate and quantify the bioaccumulation of aromatic compounds in muscle of plaice and halibut. After preliminary assessment of contamination, analysis of pooled extracts by GC-MS identified tentatively the presence of alkyl and alkene benzenes, chlorinated hydrocarbons and trialkylamines as resolved components within the mixtures. The variety of non-PAH contaminants identified in muscle of a fatty flatfish, halibut, and in the bottom dwelling fish, plaice, justify the need for a multispectroscopic approach when studying bioaccumulated organic contaminants.

ACKNOWLEDGEMENTS

The authors would like to thank the staff involved in the collection of the fish during the Department of Fisheries and Oceans research cruises in the St. Lawrence estuary and northwest Atlantic. Without their help, this work would not have been possible. Funding from the Green Plan Program for Toxic Chemicals and the Program for Energy Resource and Development is also acknowledged, as well as Dr. J. F. Payne's role in obtaining funding.

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