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CONGENER-SPECIFIC ANALYSIS OF THE ACCUMULATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY AQUATIC ORGANISMS IN THE MAXIMUM TURBIDITY ZONE OF THE ST. LAWRENCE ESTUARY, QUÉBEC, CANADA*

MONIQUE M. GAGNON and JULIAN J. DODSON**

Département de Biologie, Université Laval, Sainte-Foy, Québec G1K 7P4 (Canada)

MICHAEL E. COMBA and KLAUS L.E. KAISER

Lakes Research Branch, National Water Research Institute, P.O. Box 5050, Burlington, Ontario L7R 4A6 (Canada)

ABSTRACT

The polychlorinated biphenyl (PCB) contamination of the biota of the St. Lawrence estuary maximum turbidity zone (MTZ) was investigated. The species analyzed consist of zooplankton (mostly *Neomysis americana*), larval smelt (*Osmerus mordax*), juvenile smelt, juvenile tomcod (*Microgadus tomcod*) and adult smelt, tomcod and capelin (*Mallotus villosus*). A significant increase in total PCB contamination from zooplankton to all fish developmental stages indicates that the St. Lawrence MTZ is a site of significant PCB contamination. The total PCB contamination of adult smelt and tomcod sampled in the St. Lawrence MTZ was greater than the limit of 0.1 ppm set by the International Joint Commission for the protection of predators. For zooplankton, tomcod and capelin, significant correlations were found between lipid content and PCB contamination. The congener-specific analyses showed that the bioconcentration factor of the individual congeners varied with the species involved and with the molecular structure of the congener. It was found that the chlorine atoms in positions 2, 4 and 5 on at least one phenyl ring of the PCB molecule was a dominant factor causing accumulation of PCBs in aquatic organisms. The pattern of PCB congeners found in beluga (*Delphinapterus leucas*) whale tissues is similar to the PCB pattern found in the St. Lawrence estuary MTZ biota.

INTRODUCTION

The residues of polychlorinated biphenyls (PCBs) are found in biota all over the world. Between 1929 and 1977, North American PCB production totaled 635×10^6 kg, of which ~14% has been released into the environment (Viswanathan, 1986). In aquatic ecosystems, it has been suggested that sediments are the greatest potential source of PCBs to aquatic life (Beeton et al., 1979). Several laboratory studies have shown that aquatic organisms can accumulate

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**Author to whom reprint requests should be sent.

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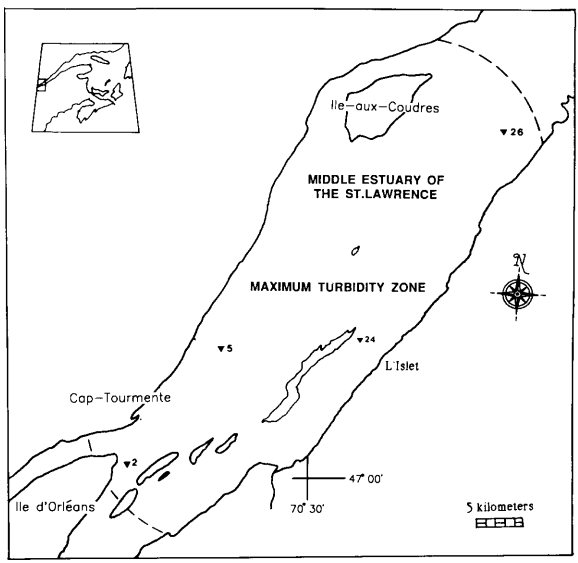

Fig. 1. Middle estuary of the St. Lawrence River and stations sampled in 1987. The approximate summer position of the maximum turbidity zone is indicated by the dashed lines; sampling Stations 2 and 5 were located in the northern channel, while Stations 24 and 26 were located in the southern channel.

chlorinated hydrocarbons from contaminated sediments (Oliver, 1984; Larsson, 1984a,b, 1986). Accumulation can occur through direct uptake from water and through food intake. Adsorption of PCB onto sediments and marine plankton occurs rapidly, whereas desorption is a much slower process (Hiraizumi et al., 1979; Wildish et al., 1980). Macroinvertebrates and fish may take up the compounds by ingesting sediments and/or plankton or directly by equilibrium partitioning between suspended particles, water and lipids of macroinvertebrates and fish (McLeese et al., 1980; Niimi and Oliver, 1983; Larsson, 1984b).

The lower the water solubility of a chemical, the more readily it will partition into fish lipid. Generally, highly chlorinated compounds have a lower water solubility, exhibit higher adsorption to various surfaces and show greater accumulation in biota than lower chlorinated PCBs (Larsson, 1983). It has been suggested that for PCBs, which have a relatively long half-life, the rate of intake exceeds the capacity of fish to eliminate the chemicals and thus they will accumulate through the food chain more readily than through the water (Niimi and Oliver, 1983). Rubinstein et al. (1984) demonstrated the spot

(*Leiostomus xanthurus*), a demersal marine fish, exposed to PCB-contaminated sediments and fed a daily diet of polychaete worms from the same sediment accumulated more than twice the PCB whole-body residues than fish exposed to similar conditions but fed uncontaminated worms. In addition, fish isolated from direct contact with PCB-contaminated sediment did not significantly accumulate PCB residues when compared with fish allowed contact with sediments. Larsson (1986) showed that planktivorous fish accumulated PCBs to high levels at high summer concentrations of the compound in water (total PCB fraction), after which elimination was slow. Levels in benthic fish continuously increased during the 1.5 year study. PCB concentrations in organisms generally increase as trophic level increases (Metcalf et al., 1975).

The middle estuary of the St. Lawrence (Fig. 1) is characterized by a maximum turbidity zone (MTZ) in which the concentration of suspended particulate matter is higher than both landward and seaward (D'Anglejan and Smith, 1973). Mechanisms involved in maintaining the MTZ include the net estuarine circulation and resuspension by tidal currents (D'Anglejan and Ingram, 1984), flocculation during early salt mixing (Gobeil et al., 1981) and suspended sediment exchanges between the estuary and the adjacent tidal marshes (Lucotte and D'Anglejan, 1986). The MTZ starts and ends farther upstream in the north channel than in the south channel and thus reflects the general cyclonic circulation in the estuary (Krank, 1979). The intensity and the position of the MTZ fluctuate seasonally, the downstream limit retreating upstream during the summer months (Lucotte and D'Anglejan, 1986).

The maximum turbidity zone is a region of high plankton density (Bousfield et al., 1975) and the principal retention zone of the larvae of several fish species that are found throughout the estuary as juveniles and adults. The spring and summer distribution of smelt *(Osmerus mordax)* larvae in the St. Lawrence estuary is clearly associated with the MTZ, as is the distribution of the macrozooplanktonic species *Neomysis americana, Gamarus* sp. (principally *G. tigrinus), Mysis stenolepis* and *Crangon septemspinosus* (Dodson et al., 1989). In addition, major concentrations of larval tomcod (*Microgadus tomcod*), presumably originating from winter spawning sites located upriver in the vicinity of Trois-Rivières, are found in the MTZ in June and July (Laprise and Dodson, 1989). The adaptive significance of larval fish retention in the MTZ appears to be related in part to feeding. Copepods, freshwater cladocera and the estuarine mysid *N. americana* are major prey items of the larvae and juveniles of smelt and tomcod (Dauvin and Dodson, 1990; R. Laprise and J.J. Dodson, unpublished data). The importance of mysids in the diet increases with fish length. *N. americana* is the most common shallow water mysid found in the western North Atlantic and has long been recognized as a significant prey item for juvenile and adult fish in estuaries (Zagursky and Feller, 1985). Mysids are considered omnivores with the most common food items being detritus, phytoplankton and crustaceans. Zagursky and Feller (1985) have shown that *N. americana* feeds on *Spartina* detritus and have suggested that this mysid may be an efficient trophic link between saltmarsh macrophyte production and higher trophic levels.

The food web of the St. Lawrence estuary is capped by the beluga or white whale (*Delphinapterus leucas*). The St. Lawrence beluga population has been classified as endangered (Béland et al., 1987) and this has been attributed in part to the chemical stress to which the population is subjected, the beluga being highly contaminated by PCBs (Massé et al., 1986). Beluga are opportunistic predators exploiting a wide variety of fish and invertebrates (Vladykov, 1946). Sediments are the greatest potential source of PCBs to aquatic life, and a potentially important part of the whales' fish prey is associated with the MTZ. We, therefore, hypothesized that the turbidity zone is a region contributing significantly to the contamination of the beluga food chain via the accumulation of PCB residues in macroinvertebrates, larval and adult fish. The first objective of this study was to quantify the level of PCB contamination in water, suspended sediments and organisms of the maximum turbidity zone and to determine the concentration of PCB residues in different compartments of the food chain. Specifically, we analyzed PCB residues in zooplankton (composed principally of *Neomysis americana*), the larval, juvenile and adult stages of smelt, juvenile and adult tomcod and adult capelin (*Mallotus villosus*). Although not permanent residents of the MTZ, capelin spawn on beaches within the influence of the MTZ and their larvae are immediately transported downstream and out of the MTZ (Jacquaz et al., 1977). Secondly, we quantified the relative importance of 51 PCB congeners in water, suspended sediments and organisms to determine if there is a specific molecular structure characterizing the contamination of the MTZ community. Although monitoring total PCB gives a good idea of the levels of contaminants in the environment, it is of great importance to monitor different PCB congeners because the chlorine positions on the molecule will greatly influence the fate and toxicity of each congener (Cullen and Kaiser, 1983). The evaluation of individual toxicity for each congener is progressing constantly and may eventually permit us to associate a particular toxicity with a particular molecular pattern.

MATERIALS AND METHODS

Study site and sampling

Macrozooplankton and fish were sampled using a pelagic Tucker trawl (109 × 1.19 m opening) equipped at the cod end with a 0.5 m standard plankton net (0.5 mm mesh). The net was towed against the current at a speed of 2–3 knots by a 21 m vessel (M/V *Rigolet*) until a sample of at least 10 g of each taxa was obtained. Three sampling series were conducted in the summer of 1987, the first during the last week of June, and the second and the third during the first and last week of July, respectively. During each sampling series, four stations were sampled in the maximum turbidity zone; Stations 2 and 5 in the northern part of the estuary, and Stations 24 and 26 in the southern part of the estuary (Fig. 1).

Water and suspended sediments were sampled in the vicinity of the same

four stations in the maximum turbidity zone by the scientific crew of the CSS *Limnos* in early July 1987. Samples were immediately refrigerated and transported for PCB analysis to the National Water Research Institute, Burlington, Ontario.

PCB analyses

The details of the water and suspended sediments PCB analyses are described by Comba et al. (1989b), and may be briefly summarized as follows. Two hundred liters of water were pumped, centrifuged and extracted with dichloromethane; the water extracts were evaporated and transferred to the original amber solvent bottles for storage before the final laboratory analysis. Suspended sediments were also collected with a centrifuge, refrigerated and brought to the laboratory for subsequent extraction and analysis.

One hundred and one biological samples were collected and analyzed. Samples of zooplankton and smelt larvae were composites of hundreds of individuals, while samples of juvenile fish were composites of 10–12 individuals. Adult fish were analyzed separately. Four samples of zooplankton, two samples of smelt larvae, four samples of juvenile smelt and two of juvenile tomcod were replicated to estimate the reproducibility of the chemical analyses.

Prior to extraction, samples of zooplankton were freeze-dried, while all other samples were ground until homogenous, and a sub-sample of 10 g was obtained. Anhydrous sodium sulfate previously fired at 500° C overnight was added to the homogenous sub-sample to produce a dry pourable mixture. This mixture was then poured into a glass thimble inserted in a Soxhlet extractor. Extraction with dichloromethane (pesticide grade) was conducted for at least 3 h or 20 cycles. Extracts were passed through a funnel containing fired sodium sulfate to remove any water remaining after the Soxhlet extraction. The extract was then reduced to 1–2 ml and stored at − 20° C.

The next step involved separating lipophilic contaminants from all lipids using a gel permeation chromotography column. A mixture of hexane: dichloromethane (50:50, by volume, pesticide grade) was used as the eluting solvent. A glass column of 50 × 2 cm was filled with preswelled Bio-Beads SX-3 (200–400 mesh), which is a spherical styrene–divinylbenzene copolymer with 4% cross-linkage. A 250 ml solvent flask was maintained full on the top of the column to give a constant flow rate of 1.5 ml min^{-1} through the column. The first fraction of 100 ml contained the lipids. This first fraction was evaporated to dryness to give the lipid weight of the sample. The second 100 ml fraction contained the lipophilic contaminants. This last fraction was concentrated to an approximate volume of 5 ml; 10 ml of hexane were then added and the extract was reduced to a volume of 2–4 ml on a rotary evaporator. The sample was allowed to air-evaporate in a test tube to a final volume of 1 ml. This fractionation procedure was determined prior to sample separation using an external PCB standard.

The third step, which serves to fractionate the PCBs from other lipophilic contaminants present in the extracts, consisted of chromatography on an activated silica gel column. Glass columns 300 × 1 cm prewashed with acetone, toluene and hexane were prepared by gravity settling through hexane to a height of 20 cm with activated silica gel. An acid silica gel column was prepared by placing a Teflon wool plug into a 5 × 0.2 cm column with a 24/40 female ground-glass fitting reservoir. The Teflon plug was prewashed with toluene and hexane before the column portion was filled with 4 cm of 40% (by weight H_2SO_4) acid silica gel and rinsed with 25 ml of hexane. The acid silica gel column was placed in a 250 ml round-bottom flask and positioned beneath the silica gel column, which previously had the hexane layer drained to the top of the silica gel bed.

The prepared sample was added to the top of the silica gel column and eluted to the top of the bed. The sample container was rinsed twice with 2 ml of hexane and the above procedure repeated for each addition. Another 46 ml of hexane was then added to the column and the eluant allowed to chromatograph through the acid silica gel column beneath the silica gel column. The flask was removed and the acid reservoir rinsed with 10 ml of hexane and labelled.

To each fraction, 0.5 ml of toluene was added and the fraction concentrated to between 2 and 3 ml on a rotary evaporator. The sample was transferred to a centrifuge tube with two 1-ml hexane rinses. The sample was allowed to evaporate to 1 ml and, when required, quantitatively adjusted to 1 ml with toluene, transferred to autosampler vials, capped with an aluminium foil liner and autosampler crimp cap and the liquid level recorded on the vial.

All extracts of water, suspended sediment and biota were analyzed by capillary column gas chromatography with a HP 5880-A gas chromatograph equipped with a ^{63}Ni electron capture detector. The column types used were a 30-m OV-1 and a 30-m OV-17 (Hewlett-Packard). Aliquots of 1 μl were injected by autosampler with an acceptance window of 0.03 min used for component identification by retention time comparison, according to the method described by Mullin et al. (1984). The injection port temperature was 250° C, while the detector was maintained at 350° C. The hydrogen carrier gas flow rate was 1 ml min^{-1}. The temperature regime was held at 90° C for 2 min, and then increased at a rate of 4° C min^{-1} to a final temperature of 280° C.

Quantitation of total PCB was determined by relative responses on two columns to a United States EPA standard reference mixture of Aroclors 1221, 1016, 1254, and 1262 in proportions of 10, 5, 3.5, and 3, respectively. Sixteen congener signals [18(15), 31, 52, 44, 101, 66(98), 110, 118(149), 153, 138, 174, 187, 180, 201, 203(196), and 194] were assigned quantitative values proportional to the total PCB content in the standard (coeluting congeners are noted in parentheses). Validation and quality assurance procedures for this method are described by Comba et al. (1989a).

Individual congeners quantitation and assignments were based on averaged dual column responses (OV-1 and OV-17) to 51 congeners in the National Research Council of Canada, Marine Analytical PCB Reference Standard.

Four standard mixtures contained the following congeners: IUPAC Nos 15, 18, 31, 40, 44, 49, 52, 54, 60, 77, 86, 87, 101, 103, 105, 114, 118, 121, 128, 129, 137, 138, 141, 143, 151, 153, 154, 156, 159, 170, 171, 173, 180, 182, 183, 185, 187, 189, 191, 194, 195, 196, 200, 201, 202, 203, 205, 206, 207, 208, and 209. Additional qualitative congener assignments were made from the data supplied by Mullin (1985). Average recovery for standard was between 90 and 100% such that PCB concentrations were not corrected.

Statistical analysis

A total of 16 samples of zooplankton, 14 samples of smelt larvae, 16 samples of juvenile smelt, 14 samples of juvenile tomcod, 26 samples of adult smelt, nine samples of adult tomcod and six samples of adult capelin were compared for significant differences in total PCB (TPCB). The natural (Naperian) logarithm of the variable TPCB was used so that the residues of this variable were normally distributed. Normality of the residues was confirmed using the Kolomogorov D statistic ($D > 15$). The homogeneity of the variance of the transformed data was confirmed graphically. The general linear model (GLM) procedure was first used to evaluate the contribution of each independent variable to the variability of the dependent variable. The GLM procedure implements a linear regression analysis which relates the behavior of the dependent variable TPCB to a linear function of the set of independent variables: taxa, station and time (Freund and Littell, 1981). Considering the results of the GLM procedure, the classification variable "taxa" was submitted to the least-squares mean analysis. This option produces the least-squares estimates of classification variables (in this case, "taxa") for the tests of equality of all pairs of variables (Freund and Littell, 1981). The seven taxa were subsequently compared for significant differences at $\alpha = 0.05$ using Duncan's multiple range test.

Relationships between total PCB concentrations and lipid content of organisms sampled in the maximum turbidity zone of the St. Lawrence estuary were also tested with the general linear model procedure of SAS (1985a,b). For tomcod, the PCB concentration was transformed into the common logarithm (log to the base 10) so that the residues of this relation were normally distributed ($n = 23, p < 0.05$). The residues of the three other relationships were all normally distributed ($p < 0.41$ and $n = 16$ for zooplankton, $p < 0.15$ and $n = 56$ for smelt, and $p < 1.00$ and $n = 6$ for capelin). Homogeneity of variance was graphically confirmed for each species.

RESULTS

Total PCBs

The reproducibility of chemical analyses was tested by replication of 12 samples. The variation of the replicated samples was below 8% of total PCB,

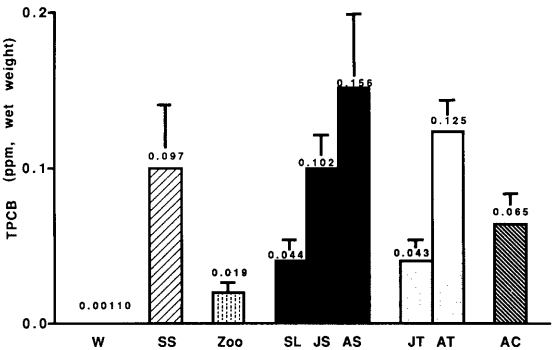

Fig. 2. Total PCB contamination of the water (W), suspended sediments (SS), zooplankton (Zoo), smelt larvae (SL), juvenile smelt (JS), adult smelt (AS), juvenile tomcod (JT), adult tomcod (AT) and adult capelin (AC) sampled in the St. Lawrence estuary maximum turbidity zone. The PCB concentration is expressed as micrograms per litre for water, on a dry weight basis for suspended sediments, and on a whole-body wet weight basis for biota. Error bars represent the standard deviations of the data.

indicating reproducibility comparable to that reported for other studies (Japenga et al., 1987; Martineau et al., 1987; Duinker et al., 1988).

Dissolved TPCB in 1987 water samples was uniformly distributed throughout the maximum turbidity zone, being on average $1.1 \pm 0.1\,\mathrm{ng\,l^{-1}}$. In the simultaneously sampled suspended sediments, PCB concentrations averaged $0.10 \pm 0.04\,\mu\mathrm{g\,g^{-1}}$, which is nearly 10^5 more concentrated than in the surrounding water (Fig. 2). TPCB also varied both with the concentration of suspended sediments and with the distance downstream from Ile d'Orléans. For example, near Station 2 (Fig. 1), PCB in suspended sediments in surface waters (5 m depth) averaged $8\,\mu\mathrm{g\,m^{-3}}$ water, while downstream at Station 5 (in the

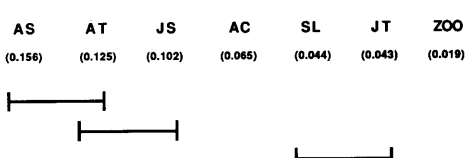

Fig. 3. Contamination of the different biotic groups studied in the St. Lawrence estuary maximum turbidity zone presented in decreasing order from adult smelt (AS) to zooplankton (Zoo). PCB concentrations (in parentheses) are expressed as ppm on a whole-body wet weight basis. Groups joined by a line are not significantly different at $\alpha = 0.05$ (Duncan's multiple range test). Abbreviations are the same as in Fig. 2.

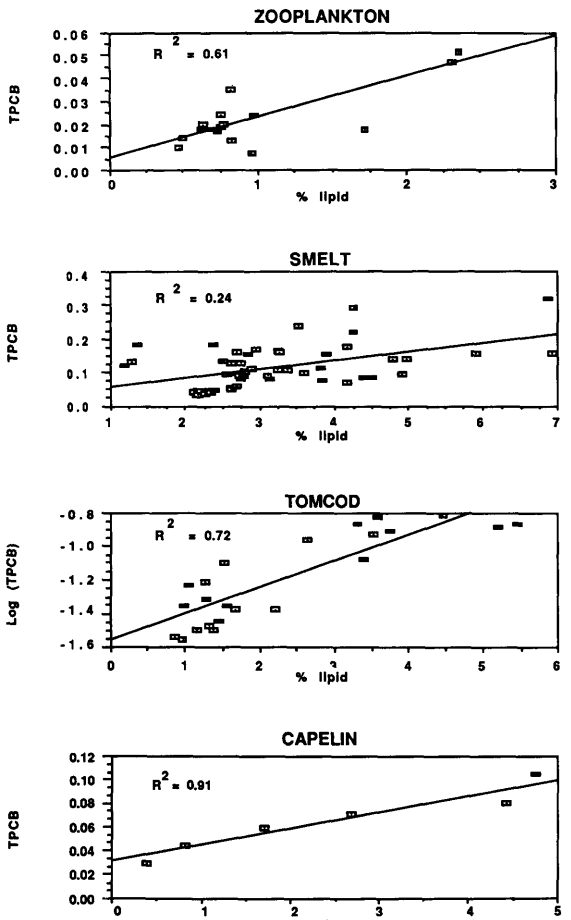

Fig. 4. Relationship between total PCB concentration (ppm) and lipid content of organisms for each species sampled in the maximum turbidity zone of the St. Lawrence estuary. All the relations are statistically significant at $p < 0.05$. $N = 16$ for zooplankton, 56 for smelt, 23 for tomcod and 6 for capelin.

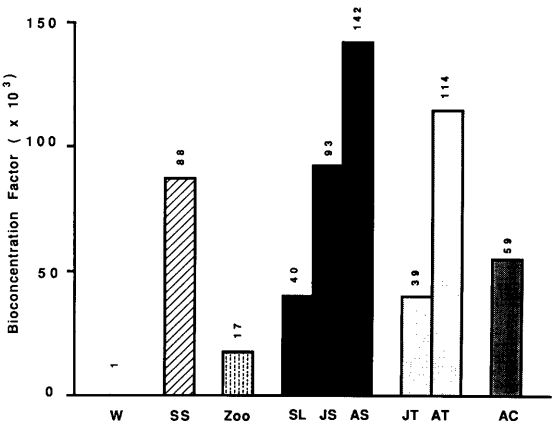

Fig. 5. Bioconcentration factors of total PCB residues for the different levels studied. Abbreviations are the same as in Fig. 2.

north channel) and at Station 24 (in the south channel) these values dropped to $\sim 2\,\mu g\,m^{-3}$ water. Although suspended sediment levels also vary between channels, the PCB levels in these sediments ($\sim 2\,\mu g\,m^{-3}$ water) appear not to vary either across or along the stream when calculated on a water volume basis. The observed PCB loads of $2\,\mu g\,m^{-3}$ water in suspended matter were similar to those observed further upstream at locations near Québec City (Kaiser et al., 1990) and indicate a relatively uniform distribution of dissolved and adsorbed PCB in the estuary over a 3-year period (K.L.E. Kaiser and M.E. Comba, unpublished data).

The general linear model procedure revealed that among the independent variables "taxa", "time" and "station", only the variable "taxa" contributed significantly to the variability of TPCB ($p < 0.0001$, $r^2 = 0.85$). The variables "time", "space", or the interaction between them and with the "taxa" variable were not significant at $\alpha = 0.05$. Testing for significant differences among taxa, the least-squares means analysis and the Duncan's multiple range test are in accordance (Fig. 3). Adult smelt contamination was not significantly different than that of adult tomcod, which in turn was not significantly different than that of juvenile smelt. In addition, the contamination of smelt larvae was not significantly different than that of juvenile tomcod. The contamination of all the other groups was statistically different among themselves.

Total PCB concentration varied with the lipid content of organisms (Fig. 4). In the case of zooplankton, tomcod and capelin, respectively 61, 72 and 91% of the variation in total PCB concentration was explained by variation in the lipid content of organisms. In the case of smelt, the lipid content of organisms explained only 24% of the variation in TPCB concentration.

Figure 5 illustrates the bioconcentration factors, defined as the averaged amount of pollutant in the organisms divided by the amount of the same pollutant in the water. The bioconcentration factor increases from zooplankton to adult smelt, the concentration of TPCBs in adult smelt being 1.42×10^5 times higher than in water, while the concentrations in adult tomcod and adult capelin were respectively 1.14×10^5 and 5.9×10^4 times higher than in water.

Congener-specific analysis

Fifty-one PCB congeners were monitored in this study, but only the most abundant will be discussed. Quantitated congeners were classified, for ease of analysis, into two different groups based on their molecular structure (Fig. 6). Group A, including congeners 138, 101, 153, 118(149), 137, 180, 182, 183, 187 and 203(196), corresponds to molecules with chlorine substitution at positions 2, 4 and 5 on at least one phenyl ring. Group B, including congeners 44, 49 and 87, corresponds to the congeners without this substitution pattern (Fig. 6). The absolute amounts of the different congeners are presented in Fig. 7 (Group A) and Fig. 8 (Group B). The percentage of total PCB represented by these two groups is presented in Fig. 9, and the relative amounts of these two same groups are illustrated in Fig. 10.

Of the 51 PCB congeners monitored in this study, 31 possess chlorine atoms in positions 2, 4 and 5 on at least one phenyl ring. We report here the results of the 10 most abundant congeners bearing this chlorine pattern. Of the 20 remaining congeners monitored and having a 2, 4, 5 chlorine substitution

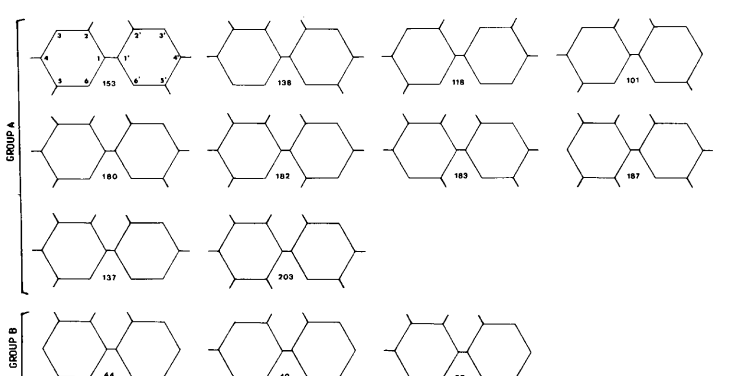

Fig. 6. Molecular structure of 13 PCB congeners discussed in this study. Group A includes congeners with chlorine substitution in positions 2, 4 and 5, while Group B congeners do not bear this chlorine pattern.

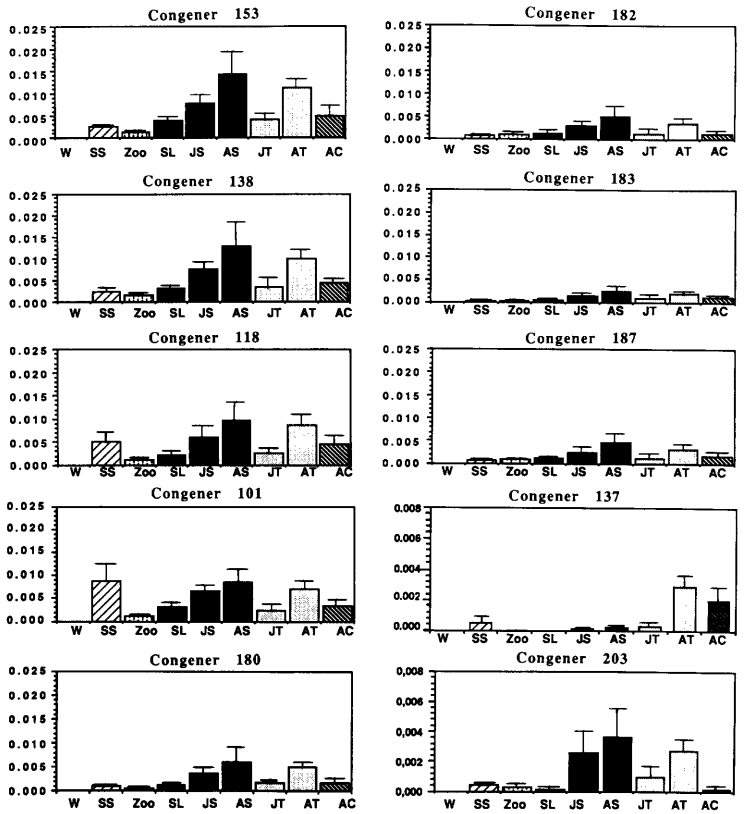

Fig. 7. Means and standard deviations of congeners from Group A (each having chlorine atoms in positions 2, 4 and 5 on at least one phenyl ring of the PCB molecule) assayed in organisms of the St. Lawrence estuary maximum turbidity zone. Concentrations are in ppm, dry weight basis for suspended sediments, and on a whole-body wet weight basis for biota. Abbreviations are the same as in Fig. 2.

pattern (congeners 86, 114, 129, 141, 154, 156, 159, 170, 173, 185, 189, 194, 195, 201, 205, 206, 207, 208 and 209), we found only non-quantifiable traces. The low concentration of these congeners in aquatic organisms may be in part due to their very low concentrations in the original Aroclor mixtures. We also monitored in this study 20 congeners without chlorine atoms in positions 2, 4

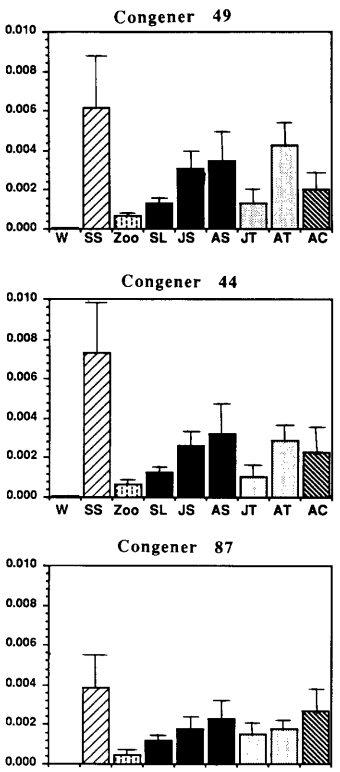

Fig. 8. Means and standard deviations of each congener from Group B (without chlorine substitution in positions 2, 4 and 5) assayed in organisms of the St. Lawrence estuary maximum turbidity zone. Concentrations are in ppm, dry weight basis for suspended sediments, and on a whole-body wet weight basis for biota. Abbreviations are the same as in Fig. 2.

and 5 on at least one phenyl ring. The results for three of these congeners are described here, while the remaining 17 without the chlorine atoms in positions 2, 4 and 5 (congeners 15, 18, 31, 40, 52, 54, 60, 77, 103, 105, 121, 128, 151, 171, 191, 200 and 202) were rarely found.

Congeners 99, 110 and 66 (coeluting with 98 on OV-1) are congeners often reported in the literature, but for which we had no standards. Given the fact that these congeners have similar response factors to congener 101 (Mullin,

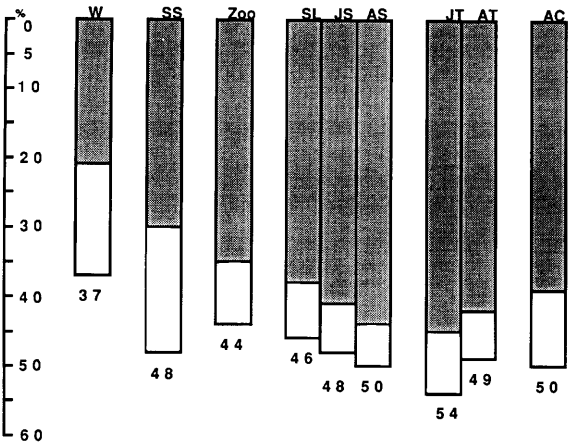

Fig. 9. Percentages of total PCBs represented by Group A and Group B congeners for each component assayed in the St. Lawrence Estuary maximum turbidity zone. (■) Group A congeners, and (□) Group B congeners. Abbreviations are the same as in Fig. 2.

1985), we calculated approximate concentrations of these three congeners by comparison of their chromatogram peak areas with that of congener 101. Congeners 66(98), 99 and 110 represented ~8.1, 8.7 and 11.7% of TPCB in the biota, respectively.

Table 1 presents the 13 most abundant quantitated congeners present in water, suspended sediments and the biota of the St. Lawrence estuary maximum turbidity zone. Group B congeners (44, 49 and 87) were relatively more abundant in water and sediments (16 and 18% of TPCB, respectively) than in the food chain (6% of TPCB for adult smelt and 7% of TPCB for adult tomcod). By contrast, Group A congeners were relatively less abundant in water and suspended sediments (21 and 30% of TPCB, respectively), than in the food chain (44 and 41% of TPCB for adult smelt and tomcod, respectively). The most abundant congeners in biota were, in decreasing order, 153 (8.3% of TPCB), 138 (7.0%), 118 (149) (6.3%), 101 (5.9%) and 180 (3.4%).

The congeners concentrated throughout the fish's lifetime, some at a faster rate than others. For example, congener 44 was 46 times more concentrated in adult smelt than in water, while congener 203(196) was 1900 times more concentrated in this fish than it was in water. A similar phenomenon was observed in tomcod and capelin.

DISCUSSION

The significant increase in total PCB contamination from zooplankton to all

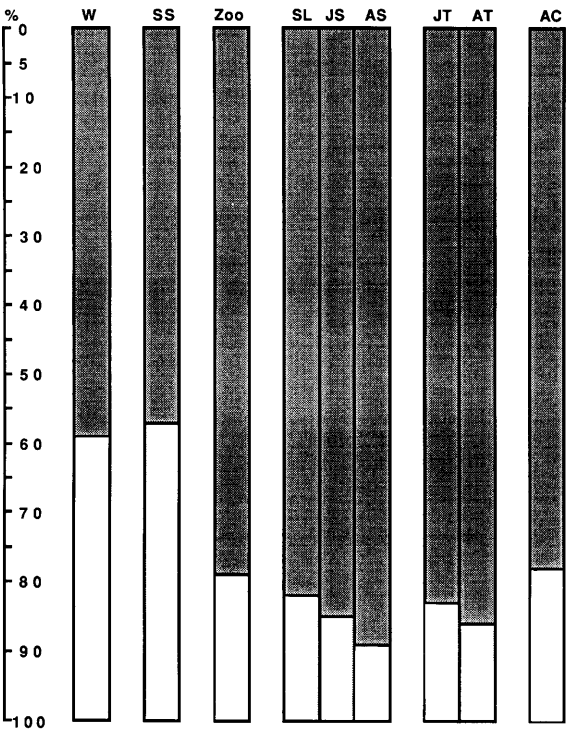

Fig. 10. Relative percentages of Group A and Group B congeners in the different components assayed in the St. Lawrence Estuary maximum turbidity zone. (▩) Group A congeners, (□) Group B congeners. Abbreviations are the same as in Fig. 2.

fish developmental stages, and as smelt and tomcod grow from the early life-history stages to adults, indicates that the St. Lawrence maximum turbidity zone is a site of significant PCB bioconcentration. However, TPCB values reported here indicate that the St. Lawrence estuary MTZ fauna is not as badly contaminated as that found in certain other regions. Adult rainbow smelt collected in Lake Ontario are about nine times more contaminated by PCBs than adult smelt from the St. Lawrence estuary MTZ [$\sim$ 1.4 versus 0.16 ppm, whole-body wet weight basis, for Lake Ontario (Oliver and Niimi, 1988) and St. Lawrence rainbow smelt, respectively]. Atlantic tomcod from the St. Lawrence estuary were slightly less contaminated than the 1977–78 tomcod spawning

TABLE 1

Concentrations (pbb) of the 13 most abundant PCB congeners monitored in this study (standard deviation in parentheses). The PCB concentration is expressed as nanograms per litre for water, on a dry weight basis for suspended sediments, and a whole-body wet weight basis for biota. Abbreviations are the same as in Fig. 2

Isomer	Water ($\times 10^{-3}$)	SS	Zoo	SL	JS	AS	JT	AT	AC
153	22	2.6	1.2	3.7	7.9	14.6	4.1	11.2	5.0
	(3.0)	(0.6)	(0.4)	(1.7)	(2.0)	(4.7)	(1.8)	(2.0)	(2.4)
138	27	2.4	1.2	3.1	7.6	12.0	3.4	7.5	4.5
	(5.0)	(0.9)	(0.5)	(0.5)	(1.3)	(4.8)	(1.7)	(2.8)	(1.4)
118	40	5.1	1.0	2.3	6.1	10.0	2.7	8.7	5.7
(149)	(3.0)	(2.2)	(0.4)	(0.6)	(1.5)	(3.6)	(1.3)	(2.3)	(1.9)
101	48	8.9	1.2	3.1	6.6	8.8	2.4	7.3	3.0
	(4.0)	(3.7)	(0.4)	(0.8)	(1.4)	(2.8)	(1.2)	(1.3)	(1.4)
180	11	1.0	0.4	1.3	3.6	6.2	1.8	5.0	2.0
	(4.0)	(0.3)	(0.2)	(0.2)	(1.4)	(2.9)	(0.8)	(0.9)	(0.7)
182	14	0.8	0.6	1.4	3.0	5.2	1.4	3.4	1.0
	(3.0)	(0.2)	(0.2)	(0.6)	(0.9)	(2.2)	(1.1)	(0.8)	(0.4)
183	2.0	0.3	0.3	0.7	1.6	2.6	1.0	2.0	1.0
	(0.2)	(0.2)	(0.1)	(0.1)	(0.7)	(1.3)	(0.4)	(0.4)	(0.4)
187	14	0.8	0.5	1.1	2.6	4.6	1.2	2.9	2.0
	(3.0)	(0.2)	(0.3)	(0.5)	(0.8)	(1.9)	(1.0)	(0.6)	(0.8)
137	6.0	0.5	ND	ND	0.1	0.3	0.3	2.9	2.0
	(1.0)	(0.2)			(0.1)	(0.1)	(0.3)	(0.8)	(1.0)
203	2.0	0.4	0.1	0.1	2.6	3.8	0.1	2.6	ND
	(1.0)	(0.2)	(0.1)	(0.1)	(1.4)	(1.8)	(0.6)	(0.6)	
49	35	6.1	0.6	1.3	3.0	3.5	1.3	4.0	2.0
	(7.0)	(2.8)	(0.2)	(0.4)	(0.9)	(1.3)	(0.6)	(1.6)	(0.9)
44	72	7.3	0.6	1.2	2.6	3.3	1.1	2.7	2.0
	(12)	(3.0)	(0.2)	(0.2)	(0.8)	(1.4)	(0.5)	(0.9)	(1.0)
87	22	3.8	0.5	1.2	1.8	2.3	1.6	1.8	3.0
	(1.0)	(1.5)	(0.2)	(0.2)	(0.6)	(0.8)	(0.9)	(0.3)	(1.2)
N	8	8	16	14	16	26	14	9	6
% of TPCB	28.6	41.2	43.2	46.6	48.1	49.5	54.2	49.6	50.0

population from the Hudson River estuary, New York (0.17 ppm for fish from the Hudson River estuary; Klauda et al., 1981). Nevertheless, the total PCB contamination of adult smelt and tomcod sampled in the St. Lawrence MTZ was greater than the limit of 0.1 ppm wet weight set by the International Joint Commission for the protection of predators (International Joint Commission, 1978). The significantly lower total PCB contamination of capelin as compared with adult smelt and tomcod may be a result of the fact that capelin do not spend their entire lifetime in the maximum turbidity zone (Jacquaz et al., 1977). We conclude that the turbidity zone is a region that may contribute significantly to the contamination of beluga whales, with the degree of contamination depending upon the whales' feeding intensity in the region.

We have shown that for zooplankton, tomcod and capelin, respectively 61, 72 and 91% of the variation in TPCB concentration was explained by variation in the lipid content of the organisms. In the case of smelt, only 24% of the variation in TPCB was explained by the variation in lipid content. We propose that much of the remaining variation may be due to active processes such as biological concentration of the pollutant, or a species-specific capacity to metabolize PCBs. The different water/lipid partition coefficients of the congeners involved may be responsible for variation in TPCB. Different lipid composition between species and between development stages may also contribute to the variation observed. These factors may be more important for smelt than for the other species studied, but much more research is required to investigate the validity of these hypotheses.

The bioconcentration factor of the individual congeners varied with the species involved. Comparing adult fish, two interesting congeners are 137 and 203(196). In adult smelt, congener 137 did not accumulate to a great extent, being 50 times higher than in water, while in tomcod and capelin, the concentration of this congener was respectively 483 and 333 times higher than in water. The concentration of congener 203(196) was 1900 and 1300 times higher in smelt and tomcod, respectively, than in water, while it was below the detectable limit in capelin. This phenomenon suggests an interaction of exposure patterns and different patterns of transformation in the different fish species.

The biological accumulation of the different PCB congeners did not follow the same pattern, despite the fact that all fish were caught in the maximum turbidity zone. This process is greatly dependent on the molecular structure of each congener (Fig. 5). Residues of Group A congeners were among the most abundant throughout the food chain, all being characterized by chlorine substitution in positions 2, 4 and 5 on at least one phenyl ring. In contrast, the three congeners (44, 49 and 87, Group B) which are not substituted at positions 2, 4 and 5 possess two adjacent unsubstituted carbon atoms, and decreased in abundance throughout the food chain. This observation supports the conclusion of Safe et al. (1985), who suggsted that PCBs which are readily metabolized possess at least two unsubstituted carbon atoms of which at least one is in *para* position. However, since some of the most abundant congeners, such as 138 and 101, possess chlorine at positions 2, 4 and 5, and two adjacent unsubstituted carbon atoms, the chlorine substitution seems to be the dominant factor for the metabolic fate of PCB congeners. It is also interesting to note that two of the most abundant congeners, 153 and 180, possess chlorine-substitution carbon atoms in positions 2, 4 and 5 on both phenyl rings. The same situation occurs with congener 203(196), which has a very low concentration in the PCB commercial mixture, as well as in water and suspended sediments. However, this congener is relatively abundant in adult fish, indicating strong biological accumulation. Therefore, chlorine substitution in positions 2, 4 and 5 appears to determine the accumulation of PCBs in zooplankton, smelt, tomcod and capelin.

Although studies generally agree that congeners 101, 138, 153 and 180 are present in the highest concentrations in fish (Ballschmiter et al., 1981) and in beluga whale tissues (Massé et al., 1986), different chlorine substitution patterns have been held responsible for biological accumulation of PCBs. It has been suggested that chlorine substitution patterns 2,3,4, 2,3,4,5, and 2,3,4,5,6 are dominant factors for PCB accumulation in biota (Safe et al., 1985; Massé et al., 1986). However, the molecular structure of the 11 most abundant congeners in beluga whale tissues (153, 138, 101, 180, 185, 187, 99, 106, 149, 173, 170; Massé et al., 1986) indicates that all of them bear chlorine atoms in positions 2, 4 and 5 on at least one phenyl ring, in agreement with the chlorine substitution pattern observed in the MTZ food chain of the St. Lawrence estuary. In addition, congeners 153, 138 149 (coeluting with 118), 180, 187 and 101 were among the most abundant detected in the MTZ biota. Congener 99 was also estimated to be among the most abundant. Congeners 185, 173 and 170 were detected in trace amounts in the MTZ biota, whereas 106 was not detected. However, congener 106 is not present in pure Aroclor mixtures (i.e. Aroclors 1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262 and 1268; Mullin, 1985), and its detection in beluga whale tissues may be a case of misidentification.

Although total PCB contamination of adult smelt and tomcod sampled in the St. Lawrence MTZ was greater than the limit of 0.1 ppm wet weight set by the International Joint Commission for the protection of predators, there is evidence that much smaller PCB concentrations in the diet of fish may be harmful to fish predators. For example, Reijnders (1986) showed that reproduction in American mink (*Mustela vision*) was inhibited at a daily intake of only 25 μg of a PCB commercial mixture. In addition, the relative proportions of PCB congeners in tissues of fish documented in this study are quite different from those of commercial mixtures. Assuming that the International Joint Commissions set permissible limits based on data from experiments using whole industrial mixtures of PCBs (International Joint Commission, 1978), these limits may be too lenient in terms of protecting predators and public health. A revision of the limits, based on the congener mixtures actually found in nature, new knowledge about the toxicity of individual congeners and their biomagnification in the food-chain, seems to be in order.

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