DETERMINATION OF NON-ORTHO SUBSTITUTED POLYCHLORINATED BIPHENYLS: METHOD DEVELOPMENT AND LEVELS IN CANADIAN BIOTA

BY

Catherine A. Ford

A Thesis Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

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Abstract

An automated method was developed to separate trace levels of non-ortho substituted polychlorinated biphenyls (PCBs) from the ortho substituted congeners using an activated carbon column. An automated pumping system was used to load samples onto carbon. Sample preparation included Soxhlet or ball mill extraction, followed by gel permeation and silica gel column chromatography for lipid and pigment removal. Quantification and confirmation of the non-ortho PCB congeners was performed by gas chromatography-mass spectrometry. Congener detection limits in samples ranged from 10 to 100 pg/g. Good accuracy was obtained for internal standard recoveries between samples analysed at different times; precision decreased at the lower congener detection limits.

The method was applied to determine non-ortho PCBs in samples from the Canadian Arctic (whole charr, marine mammal blubber), and the West and East coasts of Canada (cod liver oil, whale blubber). Arctic samples contained non-ortho PCB levels in the low parts-per-trillion range (0.4 to 2 μg/kg). Higher levels (0.5 to 33 μg/kg) were observed in the fish and marine mammal samples from the West and East Coasts of Canada. These samples also contained higher ΣPCB levels and toxic equivalent concentrations (TECs) than the Arctic marine samples. Levels increased from fish to marine mammals, on a lipid weight basis. A difference in non-ortho PCB levels existed between male and female marine mammals, a trend also observed in ΣPCB concentrations. Marine mammals contained higher proportions of PCB 126 and 169 than PCB 77. Fish had a higher proportion of non-ortho PCBs to ΣPCBs than the marine

mammals. Beluga and narwhal contained the lowest proportion of non-ortho PCBs to ΣPCBs of any species, including the other cetaceans.

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Abbreviations

1. Technical

Ah receptor	aryl hydrocarbon receptor, a soluble binding protein
AHH	aryl hydrocarbon hydroxylase
CI	confidence interval
Cl	chlorine
CWS	Canadian Wildlife Service
5% DCM/hex	5% DCM in hexane, by volume
15% DCM/hex	15% DCM in hexane, by volume
50% DCM/hex	50% DCM in hexane, by volume
DCM	dichloromethane
ECD	electron capture detector
EC_{50}	is the concentration level of the chemical at which 50% of the target species have induction of the Ah receptor
ED_{50}	is the concentration level of the chemical at which 50% of the target species demonstrate the response
EROD	ethoxyresorufin *O*-deethylase
FMS	Fluid Management Systems, Watertown, MA, U.S.A.
GC	gas chromatograph
GC-ECD	gas chromatography with an electron capture detector
GC-MS	gas chromatography with mass spectrometry
GLG	growth layer group; technique to age beluga
GPC	gel permeation chromatography
HP	Hewlett-Packard Instrument Co.
HPLC	high pressure liquid chromatograph
HRMS	high resolution mass spectrometry
3-MC	3-methylcholanthrene
MeOH	methanol
MSD	mass selective detector
msec	millisecond
N.A.	not applicable
N.D.	not detectable (i.e. indistinguishable from baseline; signal to noise <3:1)
non-orthos	non-ortho substituted PCBs
PB	phenobarbital
PFTBA	perfluorotributylamine
PYE	2-(1-pyrenyl)ethyldimethylsilylated silica gel HPLC column
RBF	round or flat-bottomed flask, either 250 ml or 500 mL
SIM	selected ion monitoring (used in mass spectrometry)
std	standard
TEC	Toxic Equivalent Concentrations
TEF	Toxic Equivalency Factors
TMP	trimethylpentane
UHP	ultra-high pure
wt	weight

2. Organochlorine Compounds

o,p-DDD	[1,1-dichloro-2-(*o*-chlorophenyl)-2'-(*p*-chlorophenyl)] ethane
p,p'-DDD	[1,1-dichloro-2,2-bis(*p*-chlorophenyl)] ethane
p,p'-DDE	[1,1-dichloro-2,2-bis(*p*-chlorophenyl)] ethylene
p,p'-DDT	[1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)] ethane
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane (alpha, gamma, beta isomers)
MeOCl	methoxychlor
OCN	octachloronaphthalene
OC's	organochlorine compounds; includes toxaphene, chlordane, DDE, HCH's, HCB
PCA	pentachloroanisole
PCBs	polychlorinated biphenyls
ΣPCBs	total concentration of ortho substituted PCBs
PCBz	pentachlorobenzene
PCDD	polychlorinated dibenzo-*p*-dioxins
PCDF	polychlorinated dibenzofuran
2,3,4,7,8-P_5CDF	2,3,4,7,8-pentachlorodibenzofuran
1234-TCB	1,2,3,4-Tetrachlorobenzene
1245-TCB	1,2,4,5-Tetrachlorobenzene
2378-T_4CDD, TCDD	2,3,7,8-Tetrachloro-*p*-dioxin
t-NON	*trans*-Nonachlor

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Introduction

Since 1966, polychlorinated biphenyls (PCBs) have been recognized as persistent environmental contaminants with potential toxicological effects in terrestrial and aquatic food chains (Jensen, 1966; Safe 1984). Early researchers assumed the toxicity of PCB oils came from co-contaminants such as polychlorinated dibenzofurans (PCDFs), in the commercial mixtures, rather than from one or more of the possible 209 PCB congeners (Kannan *et al.*, 1987; Tanabe, 1988). However, in the last 10 to 15 years, this toxic potential has been linked to a small number of congeners that are non-ortho or mono-ortho substituted on the biphenyl ring. Detection of the non-ortho substituted congeners in environmental samples has raised concerns that the toxic effects of these PCBs could be greater than that due to polychlorinated dioxins (PCDDs) and PCDFs, two extremely toxic groups of chemicals (Tanabe, 1988; Safe 1990).

The objective of this study was to develop an automated method that would separate the non-ortho and ortho substituted PCBs, enabling detection and quantification of the non-ortho substituted PCBs, and to use this method to determine levels of the non-ortho substituted PCBs in marine mammal and fish samples from the Canadian Arctic, and the east and west coasts of Canada. A method to quantify and separate these congeners from the ortho substituted PCBs was needed, as the non-ortho PCBs were detected at much lower concentrations than the other congeners. A manual method which used activated carbon was available, but was time-consuming and required an operator to be present.

Non-ortho substituted PCBs had previously been determined in marine mammal samples from the North Pacific, and fish and bird samples from the Baltic Sea, but no data existed on their presence in the Canadian Arctic food chain (Tanabe *et al.*, 1987a; Asplund *et al.*, 1990a, 1990b; Haglund *et al.*, 1990). Fish and marine mammals are important foods in the diet of Canadian Inuit, and a study was already underway to determine levels of organochlorine and ortho substituted PCBs ingested by the Inuit via these foods (Kinloch *et al.*, 1992). Determination of non-ortho substituted PCB levels would complement this database, as well as provide information on concentrations of these chemicals in the Arctic.

1. Polychlorinated Biphenyls - Historical

PCBs were first synthesized by Schmidt and Schulz in 1881 (Safe, 1984). These chemicals were produced commercially from 1929 until 1975, when continuing evidence of their persistence in the environment resulted in a ban on further production and use in the United States, Western Europe, and Japan (Safe, 1984; Tanabe, 1988). PCBs have many physical properties which made them useful industrially, for example, as dielectric fluids in capacitors and transformers, heat transfer fluids, plasticizers, hydraulic fluids, and flame retardants. These properties included chemical stability in the presence of hydrolysis, acids, bases, and heat, and solubility with organic compounds (e.g., oils) (Safe, 1984, 1990; Tanabe, 1988). This wide range of uses led to PCBs being produced and used worldwide (Safe, 1984; Tanabe, 1988; Patterson *et al.*, 1990). The level of PCBs in the environment has decreased since 1975 (Safe, 1984; Addison *et al.*, 1984, 1986; Norstrom *et al.*, 1985),

but >60% of the world's total production is still either in storage or in use in older capacitors or transformers (Safe, 1984; Tanabe, 1988).

Since the first report on the presence of PCBs in the environment in 1966, they have been detected throughout the global environment (Jensen, 1966; Kannan *et al.*, 1988a; Tanabe, 1988; Safe, 1984, 1990, 1991). The persistence of PCBs in the environment is due to their low metabolism and biodegradability, properties which are enhanced with greater chlorine ring substitution (Tanabe, 1988; Skaare *et al.*, 1990; Safe, 1984, 1990, 1991). This worldwide distribution, resulting in the occurrence of PCB residues in the non-industrialized as well as the industrialized parts of the world, has been facilitated by atmospheric transport processes (Tanabe, 1988; Hawker, 1989; Kannan *et al.*, 1989a; Safe, 1984, 1991). PCBs have air/water partition coefficients that favour these processes (Norstrom and Muir, 1988). The presence of these chemicals in the Canadian Arctic has occurred through dry and wet deposition, from the atmosphere, onto land and ocean (Hargrave *et al.*, 1988, 1989). Aquatic ecosystems have been recognized as major sinks for these chemicals, especially the open ocean (Tanabe, 1988; Kannan *et al.*, 1989a). In the Arctic Ocean contaminant input remains concentrated in the surface water (Hargrave *et al.*, 1988). In both terrestrial and aquatic ecosystems, biomagnification occurs through the food chain, placing creatures in the higher trophic levels at greater exposure levels (Tanabe, 1988; Skaare *et al.*, 1990; Smith *et al.*, 1990; Safe, 1984, 1990, 1991).

2. Toxicity and Metabolism

A total of 209 isomers and congeners (isomer refers to PCBs with the same number of chlorines (Cl) but in different positions; congener refers to any one of the 209 PCBs) are theoretically possible; 132 congeners existed in the commercial PCB mixtures (Schultz *et al.*, 1989). Acute toxicity of PCB congeners (measured using lethal dose concentrations [LD_{50}] to terrestrial mammals) increases with the higher chlorinated congeners (Table 1) (Tanabe, 1988; Safe, 1984, 1990). In Table 1, toxic equivalency factors (TEF) were calculated based on the response of the target species (column 1, Table 1) towards non-ortho substituted PCBs relative to 2,3,7,8-tetrachloro-*p*-dioxin (2,3,7,8-TCDD); the relative potency range indicates the degree to which these responses varied among the target species. ED_{50} is the concentration level of the chemical at which 50% of the target species demonstrate the response; EC_{50} is the concentration level at which 50% of the target species have induction of the Ah receptor (Safe, 1990). Early studies of cases of PCB exposures from oil poisonings had assumed co-contaminants (traces of PCDFs) in the commercial mixtures were the main poisoning agents (Kannan *et al.*, 1987; Tanabe, 1988). In recent years toxic non-ortho substituted PCBs have been identified and research work is now being done to determine the extent of this toxicity (Tanabe, 1988; Safe, 1990). There are 20 PCBs in this group, and their para and meta Cl substitution and lack of ortho Cl substitution enable them to attain planarity of the biphenyl rings (Figure 1) (Safe *et al.*, 1985; Tanabe, 1988). Of these twenty, three congeners have the necessary structural conditions for aryl hydrocarbon hydroxylase (AHH) induction and biological effects - 3,3',4,4'-tetrachlorobiphenyl (IUPAC #77),

Table 1. Comparative Toxic and Biochemical Potencies of Non-ortho Substituted PCBs (Safe, 1990)

Response	Target species/cell	ED_{50} and EC_{50} Values[1] (3,3'4,4') 77	(3,3'4,4',5) 126	(3,3',4,4',5,5') 169	2,3,7,8-TCDD
body weight loss	rat (μmol/kg)	>500	3.3	15	0.05
thymic atrophy	rat (μmol/kg)	>500	0.95	8.9	0.09
bursal lymphoid growth	chick embryo (μg/kg)	50	4	300	--[2]
thymic lymphoid growth	mouse fetuses (M)[3]	3×10^{-7}	2×10^{-9}	2×10^{-7}	2×10^{-10}
immunotoxicity	mice (μmol/kg)	--	--	--	0.0024
teratogenicity	mice (μmol/kg)	--	--	0.055-0.110	0.011
AHH induction	rat (μmol/kg)	500	0.50	1.10	0.004
AHH induction	H-4-II E cells (M)	3.5×10^{-8}	2.4×10^{-10}	6.0×10^{-8}	7.2×10^{-11}
AHH induction	chick embryo heptocytes (M)	2.2×10^{-9}	2.0×10^{-9}	--	2.0×10^{-11}
receptor binding	rat cytosol (M)	4.3×10^{-7}	1.2×10^{-7}	Insoluble	1.0×10^{-8}
Proposed TEF values		0.01	0.1	0.05	1
relative potency range		0.009-0.00008	0.3-0.0006	0.1-0.0012	--

[1] - definition of ED_{50} and EC_{50} are given in the text

[2] - no data available; [3] - moles

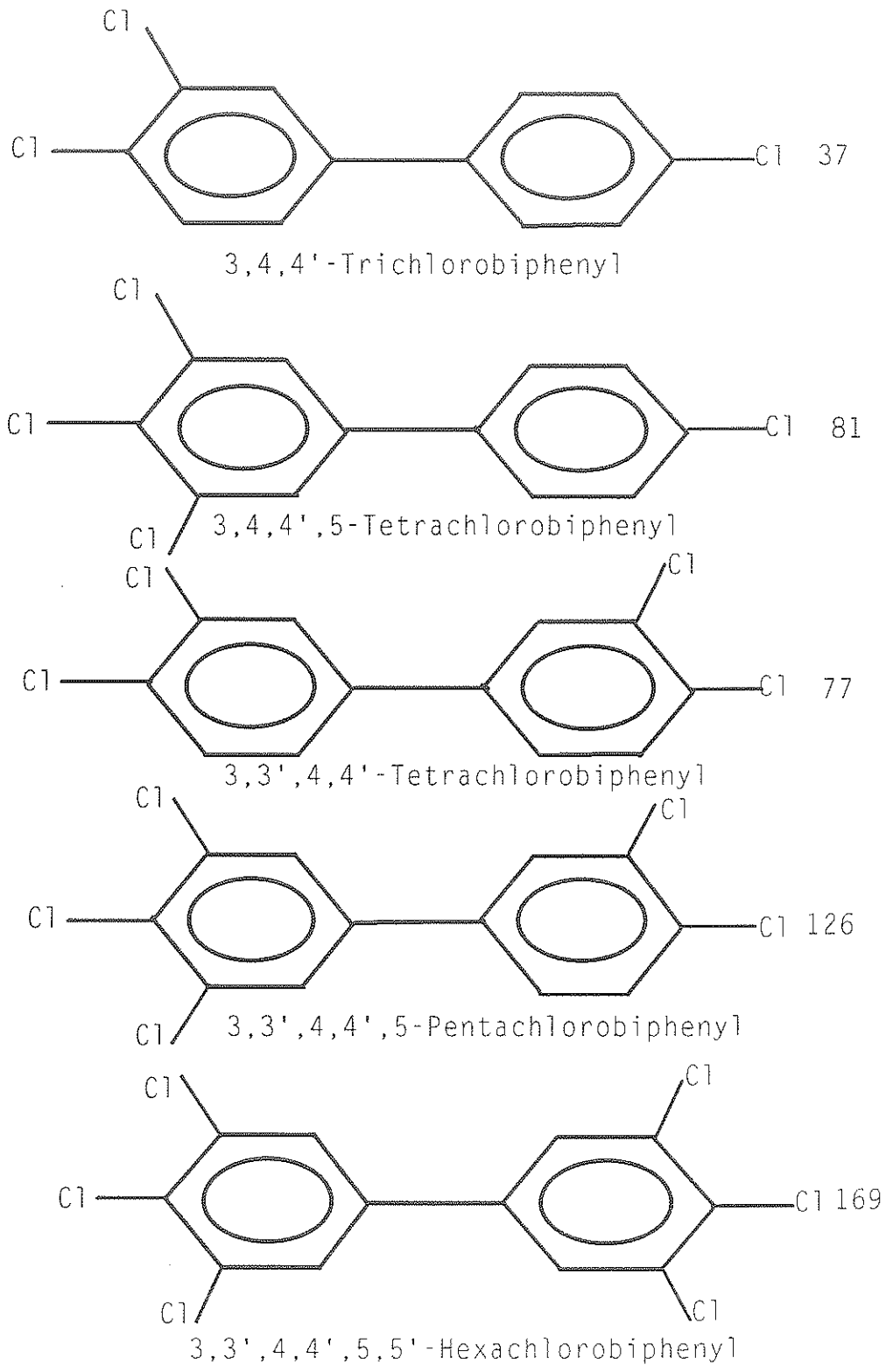

Figure 1. Structure and IUPAC Nomenclature of the Non-ortho Substituted PCBs

3,3',4,4',5-pentachlorobiphenyl (IUPAC #126), and 3,3'4,4'5,5'-hexachlorobiphenyl (IUPAC #169) (Kamops *et al.*, 1979; Ballschmiter *et al.*, 1980; Trotter *et al.*, 1982; Safe *et al.*, 1985; Olafsson *et al.*, 1987; Kannan *et al.*, 1988a; Tanabe, 1988; Safe, 1984, 1990, 1991). These three non-ortho PCBs are present in commercial Kanechlor and Aroclor mixtures in small quantities - 0.15% to 0.85% w/w in Kanechlors, 0.02% to 0.61% w/w in Aroclors (Table 2) (Kannan *et al.*, 1987; Patterson *et al.*, 1990). Their toxicity arises from their planar structure, which allows them to be approximate stereoisomers of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-T_4CDD) and 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-P_5CDF), as well as by the presence of two or more adjacent chlorines per ring (four Cl's, minimum) (Figure 1) (Huckins *et al.*, 1980; Tanabe, 1988; Tarhanen *et al.*, 1989; Safe, 1984, 1990, 1991). The biological effects of these three non-ortho PCBs include body weight loss, thymic degeneration, skin disorders, impaired functioning of the immune and endocrine system, teratogenicity, reproductive toxicity, hepatic damage, high binding affinity to the hepatic cytosolic receptor protein (Ah receptor), and induction of the cytochrome P450 (drug-metabolizing) enzyme system and its associated microsomal monooxygenases (including ethoxyresorufin *O*-deethylase (EROD) and aryl hydrocarbon hydroxylase (AHH)) (Table 1) (Kannan *et al.*, 1988a; Tanabe, 1988; Patterson *et al.*, 1990; Smith *et al.*, 1990; Safe, 1990, 1991). The effects vary with the animal species, age, sex and the body tissue examined (Table 1), and are sublethal and chronic rather than lethal and acute (Goldstein and Safe, 1989; Safe, 1984, 1990, 1991). An example of chronic effects is the observation of impaired reproductive ability in seals in the Dutch Wadden Sea and the

Table 2. Non-ortho Substituted PCB levels in Commercial Mixtures

Commercial Mixture	PCB Congener µg/g				Reference
	37 (3,4,4')	77 (3,3',4,4')	126 (3,3',4,4'5)	169 (3,3',4,4',5,5')	
Aroclor 1016	13200±1700	N.D.[1]	N.D.	N.D.	Huckins *et al.*, 1980
Aroclor 1242	16600±3100	2400±200	<250	N.D.	
Aroclor 1248	6100±1200	3400±330	<250	N.D.	
Aroclor 1254	300±40	210±12	<250	N.D.	
Aroclor 1260	67±7	N.D.	N.D.	N.D.	
Aroclor 1242	-	5080	19.0	N.D.[2]	Kannan *et al.*, 1987
Aroclor 1248	-	6230	52.1	N.D.	
Aroclor 1254	-	616	38.3	0.51	
Aroclor 1260	-	260	3.18	N.D.	
Kanechlor 300	-	4290	18.3	<0.08	
Kanechlor 400	-	8040	67.6	0.44	
Kanechlor 500	-	1690	28.0	0.64	
Kanechlor 600	-	969	5.3	<0.08	

[1] - detection limit of 0.4 µg/g reported by the author

[2] - detection limit not reported by the author

Baltic Sea, and premature births in California sea lions, with the presence of elevated levels of PCBs in these species (Safe, 1984; Tanabe *et al.*, 1988; Skaare *et al.*, 1990). However, other factors could be implicated in these health problems, including habitat disturbance, hunting pressures, and changes in food availability.

A strong correlation between *in vitro* dose-response biologic effects (microsomal enzyme induction), and *in vivo* toxic effects (body weight loss and thymic atrophy), has been shown in rats. The hepatic microsomal enzyme systems in mammals affects steroid hormone levels and in this way may be associated with reproductive effects (e.g., fertilized ova do not implant or develop) (Kannan *et al.*, 1988a; Tanabe, 1988). The cytochrome P450 enzyme system is involved in synthesis of steroid hormones (and the related physiological functions), and biodegradation and transformation of foreign compounds into water soluble (excretable) and methylsulfone metabolites (accumulative) (Jensen and Jansson, 1977; Clarke, 1986; Goldstein and Safe, 1989; McFarland and Clarke, 1989; Kuroki *et al.*, 1991). This system of monooxygenases occurs in many body tissues (mainly the liver, also the lungs, kidneys, spleen, reproductive organs), and the types of P450 enzymes and their substrate specificity differ among species (Goldstein and Safe, 1989). AHH induction is measured by determining the rate of the enzyme-catalyzed conversion of benzo[*a*]pyrene to 3-hydroxybenzo[*a*]pyrene (3-OH-BP) (Trotter *et al.*, 1982). Since the toxicity of halogenated aromatics in mammals seems to be directly related to its capability to induce AHH activity and bind to the Ah receptor, the stereoselectivity of the Ah receptor may affect the type of toxic response (Olafsson *et al.*, 1987; Päivi *et al.*, 1992). PCB

126 has the greatest toxicity of the non-ortho PCB congeners, followed by PCB 77 and 169, due to its high activity for AHH induction and binding for the rat 2,3,7,8-T_4CDD (Ah) cytosolic receptor protein (Table 1) (Huckins *et al.*, 1980; Tanabe, 1988; Safe, 1984, 1990). The degree of receptor response has been based on the induction of AHH and EROD enzymes in rat hepatoma cell lines (Kannan *et al.*, 1988a; Tanabe, 1988). Mono-ortho PCBs and di-ortho PCBs exhibit lower competitive binding affinities for the Ah receptor (di-orthos < mono-orthos) and a corresponding lower toxicity than TCDD and the non-orthos. One hypothesis to explain this is the amount of rotation about the phenyl-phenyl sigma bond (Kamops *et al.*, 1979; Goldstein and Safe, 1989). Non-ortho substituted PCBs have the greatest degree of rotation and can assume a planar configuration. Ortho substitution on the biphenyl rings increases the steric hindrance between the rings and favours the more energetically efficient non-planar configuration. This decreases the planar configuration of the molecule, decreasing its specificity for binding to the cytosolic receptor protein and lowering the toxicity (Kamops *et al.*, 1979; Safe, 1984, 1990; Safe *et al.*, 1985; Goldstein and Safe, 1989). PCBs without para substituents, and with a minimum of two substituents in the meta and ortho positions, do not induce AHH and show no toxic and biologic effects similar to non-ortho and mono-ortho PCBs (Niimi and Oliver, 1989; Smith *et al.*, 1990; Safe, 1984, 1990). The cytochrome P450 isozyme also changes as ortho-chlorines are added to biphenyl rings. Non-ortho PCBs are 3-methylcholanthrene (3-MC-type; isozymes P450 a, c, and d [P4501A1 and P4501A2]) inducers, mono-ortho PCBs are mixed-type inducers (induce 3-MC and phenobarbital (PB-type)), and the addition of more ortho-chlorines makes the PCB isomer or

congener a PB-type (isozyme P450 b and e [P450IIB1 and P450IIB2]) inducer. As cytochrome P4501A induction results in a greater toxic response than mixed or cytochrome P450IIB, this also accounts for the corresponding decrease in toxicity as the PCBs gain ortho-chlorines (Clarke, 1986; Goldstein and Safe, 1989; McFarland and Clarke, 1989; Päivi *et al.*, 1992). In fish, a corresponding decrease in toxicity was reported from non-ortho to mono-ortho, and di-ortho substituted PCBs, with PCB 126 having a larger toxic effect than PCB 77 (PCB 169 was not tested) (Janz and Metcalfe, 1991; Walker and Peterson, 1991). Based on AHH induction, rainbow trout (*Oncorhynchus mykiss*) had a similar level of induction as rats. However, in rainbow trout a correlation has not been determined between levels of AHH induction and toxic effects (e.g., weight loss) (Janz and Metcalfe, 1991; Walker and Peterson, 1991).

Although research is available on the toxic potential of the non-ortho PCBs, very little work has been done on the amounts present in the original commercial mixtures and their presence in the environment and subsequent consequences (Tanabe, 1988). Environmental monitoring of these chemicals has been limited by the lack of a suitable analytical method for detection and quantification (Kannan *et al.*, 1988a; Tanabe, 1988). This has been partially corrected by the development of isomer-specific PCB analysis, using high-resolution capillary gas chromatography (Safe, 1984). Jensen and Sundström (1974) found PCBs having only one or two ortho-chlorines made up the greatest body load in human tissues, especially PCBs with 3,4 substitution on one of the biphenyl rings. Studies have now shown the presence of PCBs, including the three toxic non-ortho PCBs, worldwide and frequently in higher

concentrations than 2,3,7,8-T_4CDD and 2,3,4,7,8-P_5CDF (Tanabe, 1988; Kannan *et al.*, 1989a, 1989b; Patterson *et al.*, 1990; Safe, 1990). These higher levels can be traced to the greater abundance of these compounds from industrial uses than PCDDs and PCDFs (Safe, 1991) and their wide global distribution by atmospheric transport through volatilization and deposition processes (Norstrom and Muir, 1988; Kannan *et al.*, 1989a, 1989b). In Kanechlor mixtures, PCB 77 is 2000 to 7400 times more abundant than TCDF, PCB 126 is present in 8.5 to 86 times the quantity of TCDF, and PCB 169 is 0.05 to 1.7 times more abundant (Kannan *et al.*, 1987). Human serum and adipose tissue samples, analysed in studies in Japan and the United States, have shown higher levels of non-ortho PCBs than of 2,3,7,8-T_4CDD and PCDFs. These levels vary from one to several orders of magnitude difference (Kannan *et al.*, 1988a; Patterson *et al.*, 1990). Using measurements of AHH and EROD induction, the higher concentration of PCB 126 resulted in higher toxic equivalent concentrations (TEC) than 2,3,7,8-T_4CDD (Patterson *et al.*, 1990). Studies by Tanabe *et al.* (1987a) showed that commercial PCB mixtures are the source for the non-ortho PCB congeners while combustion and incineration sources are the major sources of dioxins and furans.

The extent of biotransformation of PCBs 77, 126, and 169, in mammals, decreases with greater chlorine substitution, with PCB 169 the most metabolically stable (Tanabe *et al.*, 1987a; Tanabe, 1988; Wehler *et al.*, 1989). The greater metabolism of PCB 77 versus PCB 126 may account for its lower toxicity (Wehler *et al.*, 1989). PCB metabolism occurs in three instances: preferentially on congeners with adjacent meta-para unsubstituted positions on at least one ring, and any number of ortho-Cl's; secondly at vicinal unsubstituted ortho-meta positions on

at least one ring, with a maximum of one ortho-Cl; and lastly on a vicinal meta-para substituted biphenyl ring (Tanabe *et al.*, 1988; Boon *et al.*, 1989; Watanabe *et al.*, 1989; Norstrom *et al.*, 1992). The first type of metabolism is induced by the activity of cytochrome P450 b and e (P450IIB, PB), and the second and third types by cytochrome a, c, d (P450IA, 3-MC) (Boon *et al.*, 1989; Norstrom *et al.*, 1992). Early research indicated non-ortho PCBs required adjacent nonchlorinated ortho and meta carbons (as in PCB 77) on a minimum of one biphenyl ring in order to be metabolized (Tanabe *et al.*, 1987a). Norstrom *et al.* (1992) studied the ratios of PCB 52/PCB 153 (meta-para unsubstituted/no vicinal H atoms; 2,2',5,5'-, 2,2',4,4',5,5'-), and PCB 126/PCB 153 (meta-para substituted/no vicinal H atoms), in marine mammals, fish, and fish-eating birds from Eastern Canada and the Canadian Arctic. Cetaceans (beluga, *Delphinapterus leucas* and narwhal, *Monodon monoceros*) preferentially metabolized the meta-para substituted PCBs over meta-para unsubstituted congeners. Polar bears (*Ursus maritimus*), walrus (*Odobenus rosmarus*), ringed seal (*Phoca hispida*), arctic charr (*Salvelinus alpinus*), and two species of fish-eating birds (cormorant, *Phalocrocorax auritus*, and herring gull, *Larus argentatus*), demonstrated all three types of metabolism, to different degrees. Lower levels of cytochrome P450IA and cytochrome P450IIB activities were found in marine mammals versus terrestrial mammals, with cetaceans having no measureable P450IIB activity (Tanabe *et al.*, 1987a, 1988; Watanabe *et al.*, 1989). Some metabolism and biotransformation does occur, as different animal species exhibit simpler congener compositions and enrichment patterns than the congener patterns found in the commercial PCB mixtures (Tanabe, 1988; Safe,

1990). Higher animals are able to metabolize and eliminate many of the lower chlorine substituted PCBs (Safe, 1984; Tanabe *et al.*, 1988; Brown *et al.*, 1989). Identification and confirmation of individual PCB congeners is important under these conditions, in order to accurately determine the total toxic potential from the residue load (Smith *et al.*, 1990). Metabolic degradative pathways in mammals include the formation of arene oxide intermediates, formation of thiols and other water-soluble derivatives that are excreted, methylation of thiols and oxidation to methylsulfone metabolites in the liver, macromolecule binding, and microbial degradation of the aromatic ring (Safe, 1984; Larsen *et al.*, 1991). In humans, experimental animals and other higher animals, arene oxide intermediates are formed, from halogenated hydrocarbons, by oxidation activities of the cytochrome P450 and are very unstable. This process occurs preferentially at adjacent non-chlorinated carbons. These intermediates bind to an intracellular Ah receptor, this ligand complex interacts with cellular macromolecules (e.g., protein, DNA, RNA) and can affect gene transcription. This process can both metabolize and eliminate PCBs but can also further advance the toxicity caused by these compounds as further degradation and elimination is hindered by the stability of the ligand complex (Clarke, 1986; Olafsson *et al.*, 1987; Tanabe, 1988; McFarland and Clarke, 1989; Safe, 1984, 1991). Methylsulfone metabolities fall in the latter category, as they do not easily form ligand complexes and thus accumulate in body tissues instead of being excreted (Jensen and Jansson, 1977; Haraguchi *et al.*, 1986). In this manner carcinogenic, mutagenic or teratogenic substances can be formed from previously minimally toxic parent compounds (Clarke, 1986; McFarland and Clarke,

1989). Various PCB congeners may hinder the physiological functions of the cytochrome system (e.g., regulation of steroid hormones, oxidation of lipids) through causing induction of the isozymes while not being metabolized by them. This effectively "wastes" the function of the isozymes (Boon *et al.*, 1989).

3. Toxic Equivalency Factors

The toxicity due to the non-ortho PCBs can be greater than that of dioxins and furans due to their higher concentrations in the environment in both humans and animals (Kannan *et al.*, 1988b; Kannan *et al.*, 1989a, 1989b; Tanabe, 1988; Safe, 1991). Studies have shown that there is an good correlation between the structure, Ah binding capability, and biochemical and toxic activity of non-ortho PCBs and the 2,3,7,8-substituted dioxins and furans in terrestrial mammals. Long-term carcinogenicity data are available only for 2,3,7,8-TCDD and are extended to other halogenated aromatics based on the above relationship (Table 1). 2,3,7,8-TCDD is considered the most toxic member and is given a toxicity effect value of 1 (Safe, 1990, 1991). This value is referred to as a toxic equivalency factor (TEF). The toxicity effects of other compounds are compared relative to that of 2,3,7,8-TCDD and are dependent on exposure time, species, sex and age of the animal, route of intake into body tissues, commercial formulation used in the study, and the tissue or organ where the biochemical response was measured (Safe, 1984, 1990, 1991). The best estimate for a TEF would be calculated based on data from long term carcinogenicity studies, studies of reproductive effects, subchronic exposure data that measured Ah receptor-mediated responses (immune system malfunctioning, body weight

loss, thymic degeneration), acute toxicity studies, and lastly *in vivo* or *in vitro* biochemical responses. Even these latter responses can vary widely - *in vivo* measurements show the toxicity of PCB 169 to be 30 times greater than PCB 77, whereas *in vitro* tests give them similar potencies or a reverse order of potency (Safe, 1990). Safe (1990) used various responses to calculate a relative potency range, and from this range calculated a conservative value for TEF (Table 1).

An immediate (short-term) biological response used in calculating toxicity, is the induction of the hepatic microsomal enzyme cytochrome P450 system (Kannan *et al.*, 1988a; Tanabe, 1988). This response can be performed on individual samples in a laboratory assay. The PCB congeners causing this enzyme induction can be identified when individual PCB congener analysis is performed (Williams and LeBel, 1990; Safe 1991). Harris *et al.* (1985) calculated '2,3,7,8-T_4CDD toxic equivalents' based on the concentration of toxic halogenated aromatics present and the AHH induction potencies in relation to that of 2,3,7,8-T_4CDD (Kannan *et al.*, 1988a; Tanabe, 1988). This method provides the best estimation of toxicity until extensive short-term and long-term data are available for all classes of halogenated aromatics (Safe, 1990). However, this toxicity is based only on Ah receptor-mediated responses and not on responses based on other receptors (Safe, 1991). Toxic equivalent concentrations (TEC; ng/kg) are defined as the actual chemical concentrations (ng/kg) x its corresponding TEF (Safe, 1990). Calculations of TEC for various matrices, including fish extracts, fly ash extracts, PCB/PDCF contaminated rice oil and gelatin samples, indicate that usage of the AHH and EROD induction lab bioassay, will determine similar equivalents to those present in biological systems

(Kannan *et al.*, 1988a). Some researchers feel that TEC's can be underestimated unless the toxic load of each tissue is calculated separately (Olafsson *et al.*, 1987). Calculations of TECs in humans, marine mammals, fish, and birds have shown a greater contribution from non-ortho PCBs than either dioxins or furans (Kannan et al., 1988a, 1988b, 1989a; Tanabe, 1988; Safe, 1990, 1991; Smith et al., 1990). Mono-ortho substituted PCBs are also important contributors to this toxicity (Tanabe, 1988; Safe, 1990). Research is continuing on whether TEC's are affected by additive, antagonistic or synergistic interactions between PCDD's, PCDF's and PCBs. Since all of these interactions have been noted in laboratory experiments, the number of receptors involved is thought to be more than just the Ah system. This will affect the present calculation of TEC (Sawyer and Safe, 1982; Biegel *et al.*, 1989; Bol *et al.*, 1989; Goldstein and Safe, 1989; Gooch *et al.*, 1989; McFarland and Clarke, 1989; Safe *et al.*, 1989; Safe, 1990).

4. Methodology for the Determination of Non-Ortho PCBs

Initial work in the determination of non-ortho substituted PCBs was hindered by the lack of a method to separate them from the ortho substituted PCBs, which are present in much greater quantities in commercial PCBs and environmental samples (Kannan *et al.*, 1988a; Smith *et al.*, 1990). TEC calculations indicated a large contribution of these PCBs in the "dioxin-like" activity of both commercial PCB mixtures and environmental samples, necessitating specific isomer identification and quantification (Stalling *et al.*, 1980; Tanabe *et al.*, 1987a; Safe, 1990; Smith *et al.*, 1990). Method development was based on the separation of non-ortho substituted PCBs from other organochlorines on

the basis of their planar configuration (Huckins *et al.*, 1980; Stalling *et al.*, 1980; Rubick *et al.*, 1981; Tanabe *et al.*, 1987a; Patterson *et al.*, 1989; Hong and Bush, 1990). This was done on an activated carbon column, because carbon has been shown to separate on the basis of molecular planarity (Huckins *et al.*, 1980; Stalling *et al.*, 1980; Tanabe *et al.*, 1987b). Carbon exhibits strong adsorptive properties towards planar aromatic compounds, especially those with adjacent aromatic rings and electronegative substitutents on the rings, but exhibits poor adsorption for biogenic substances (Stalling *et al.*, 1979; Smith *et al.*, 1984; Tanabe *et al.*, 1987b).

Stalling *et al.* (1980) used two columns of activated carbon, one of particle size >325 mesh by itself, and one of particle size <325 mesh mixed with foam adsorbent, to separate non-ortho PCBs. Toluene was used to elute the planar compounds off carbon. Gas chromatography-mass spectrometry (GC-MS) was used to confirm gas chromatography-electron capture detector (GC-ECD) results due to the interference of polychlorinated naphthalene compounds in the non-ortho PCB quantification. Many laboratories have since used carbon columns to successfully separate non-ortho PCBs (Smith *et al.*, 1984; Tanabe *et al.*, 1987a, 1987b; Kannan *et al.*, 1988a, 1989a, 1989b, 1989c; Kubiak *et al.*, 1989; Mes and Weber 1989; Patterson *et al.*, 1989; Tarhanen *et al.*, 1989; Hong and Bush 1990; Smith *et al.*, 1990).

Tanabe *et al.* (1987a, 1987b) have done analyses of non-ortho PCBs in marine mammal blubber, fish tissue, and adipose tissue of humans, dogs, and cats. Their technique separated chlorinated pesticides and ortho substituted PCBs from non-ortho PCBs, on a 125 mg column containing activated carbon with mesh sizes ranging from <63 μm to 297

μm. The different particle sizes of the carbon eliminated any back-pressure problems without requiring a carrier such as glass fibre filters to pack the column (Smith *et al.*, 1984). The carbon column was washed with hexane and samples were loaded onto the column in hexane. The first elution fraction of 100 mL of 20% DCM in hexane contained the chlorinated pesticides, ortho substituted PCBs, and biogenic materials remaining after the initial extraction with alkali ethanol; the second fraction containing the non-ortho PCBs was eluted with 100 mL of 50% benzene in ethyl acetate. PCDDs and PCDFs were eluted with toluene, in a third fraction. All three fractions were eluted in the same direction through the carbon column. Lipids were removed from the second fraction before analysis by GC-ECD and GC-MSD (mass selective detector). Tanabe *et al.* (1987b) used GC-ECD, after carbon separation, to quantitate the levels of non-ortho PCBs but high levels of co-contaminants present after clean-up necessitated confirmation using GC-MSD. GC-MSD analysis was done in the selected ion monitoring (SIM) mode using the M^+ molecular ion and $(M+2)^+$ base peak ions to identify and quantify: m/z 290 and 292 for PCB 77, m/z 324 and 326 for PCB 126, and m/z 358 and 360 for PCB 169. The base peak ion was used for quantification as it was present in greater abundances than the molecular ion. Comparison of the ratios of identification ion intensity $(M)^+$ to quantifying ion intensity $(M+2)^+$ were further compared with the ratios in the standard to confirm the peaks. Recoveries through the procedure ranged from 68% to 99% for standards, and 55% to 95% for blubber samples (Tanabe *et al.*, 1987b).

The method of Tarhanen *et al.* (1989) used only 50 mg of activated carbon (80 to 100 μm) and a total volume of 25 mL solvent to separate nonplanar and planar organochlorine compounds. The technique was used

in the determination of organochlorine compounds in Baltic salmon (*Salmo salar*) and white-tailed eagles (*Haliaetus albicilla*). Internal standards of ^{13}C-TCDD or TCDD were added before the initial sample extraction, and lipids removed with a concentrated sulphuric acid cleanup. Sample extracts, in hexane, were loaded onto a dry column. Nonplanar organochlorine compounds were first eluted with 10-15 mL of 1:1 DCM:hexane, then the column was turned upside down and the planar compounds (polychlorinated naphthalenes, non-ortho PCBs, PCDDs and PCDFs) eluted with 10 mL of toluene. Quantification and confirmation were performed by GC-ECD for the nonplanar compounds, and GC-MS (SIM) for the planar compounds. Peak identification was accomplished by comparing retention times to a standard chromatogram, and quantification was based on internal standards. Further confirmation was obtained by comparing the intensity ratio of the two ions of that isomer group to standard ratios.

Smith *et al.* (1990) used a carbon/glass fibre column to separate out AHH-active PCBs in sediments, fish, and bird egg samples. ^{13}C-77 was added as an internal standard after the initial extraction and sample clean-up was done using sulphuric acid-impregnated silica gel. The sample was applied to a carbon column and three elutions were collected. The first and second, 100 mL of 10% DCM in hexane (v/v) and 100 mL of 30% DCM in hexane, contained most of the PCB congeners. The third elution, 50 mL of toluene in reverse flow through the column, contained the mono-ortho and non-ortho congeners. Final quantification of the non-ortho PCBs was done by GC-MS.

Mes and Weber (1989) used the carbon column techniques of Tanabe (1987b) to determine non-ortho PCB levels in fatty foodstuffs and human

milk. Quantification and conformation were performed on GC-ECD and GC-MS. SIM was performed using the ions (m/z) 290, 292, 294 for PCB 77; 324, 326, and 328 for PCB 126; and 358, 360, 362 for PCB 169. Peaks with sample isotope ratios within ±20% of the theoretical ratios and the correct retention times were accepted.

Kannan *et al.* (1988a, 1989a, 1989b, 1989c) used the carbon technique of Tanabe (1987b) to determine levels of non-ortho PCBs in sediments, mussels, marine mammals, and human adipose tissue. Patterson *et al.* (1989) and Isaacs *et al.* (1990) adapted the carbon/glass fibre column of Smith *et al.* (1984) to an automated system for PCDD/F separation. In this system the column was washed with solvent and regenerated between samples, and many samples could be processed through the same carbon column (Smith *et al.*, 1984; Patterson *et al.*, 1989; Isaacs *et al.*, 1990). Hong and Bush (1990) used a column of carbon mixed with silica gel in the ratio of 1:12 to determine non-ortho PCB levels in fish.

Haglund *et al.* (1990) had many problems with their activated charcoal columns. These included poor efficiency, elution profiles with severe tailing, unacceptable batch-to-batch variations, and irreversible adsorption. They successfully used gel permeation and PYE (2-(1-pyrenyl)ethyldimethylsilylated silica gel) columns on a high pressure liquid chromatograph (HPLC) with an ultraviolet (UV) detector for clean-up, separation, and quantification of ortho and non-ortho PCBs. PYE columns are electron-donor acceptor high performance liquid chromatography columns that separate according to the number of ortho chlorines. The gel permeation clean-up column (GPC) for non-hydrolyzable lipids consisted of a 10 x 250 mm S-X3 (styrene-

divinylbenzene copolymer with 3% cross-linkage) 200-400 mesh (Bio-Bead) column. PCB separation was performed on two 150 x 4.6 mm Cosmosil 5-PYE columns (5 µm particles) in series. Three fractions were collected off the PYE columns - the first contained di-ortho PCBs, the second the mono-ortho PCBs, and the third, obtained by backflushing the column, contained the non-ortho PCBs. The first two fractions were quantified by GC-ECD and the latter fraction by GC-MS, due to interferences by chlorinated naphthalenes in the quantification of the internal standards ^{13}C-77 and ^{13}C-126. Biological samples, including reindeer suet (*Rangifer tarandus*), grey seal blubber (*Halichoerus grypus*), and herring (*Clupea harengus*), were analyzed with this procedure. Internal recovery standards ^{13}C-77 and ^{13}C-126 were added before any clean-up procedures. All samples were treated with 98% sulphuric acid to eliminate hydrolyzable lipids, and a further cleanup on GPC to eliminate non-hydrolyzable lipids. Accurate quantification of the mono-ortho and di-ortho PCBs was obtained by GC-ECD analysis. In the non-ortho PCB analysis, the $(M+2)^+$ ion for the respective chlorinated naphthalene peak had to be monitored in order to correctly calculate the peak areas for ^{13}C-77 and ^{13}C-126. This interference could be resolved by using high resolution mass spectrometry (HRMS), increasing the peak resolution on the gas chromatograph, or by increasing the spiking concentration of the ^{13}C-PCBs.

This technique was also successfully used by Asplund *et al.* (1990a) to quantify non-ortho PCBs in sediments, pike muscle, Baltic herring muscle, and Baltic cod muscle and liver samples. Asplund *et al.* (1990a) had earlier used a charcoal column to separate non-ortho and ortho substituted PCBs, after initial sample clean-up with sulphuric

acid, compound separation on GPC, and further clean-up on silica gel. Asplund *et al.* (1990a) switched to the HPLC PYE column when the problems with carbon column separation were encountered (Haglund *et al.*, 1990). The PYE column gave good selectivity for planar aromatic compounds, compound elution was accomplished without using an aromatic solvent, and the chromatographic peak shape was symmetrical (Asplund *et al.*, 1990b). Hong *et al.* (1992) switched to a HPLC porous graphitic carbon column (PGC) (100 x 4.7 mm, 7 μm particle size) from carbon for similar reasons as Haglund *et al.* (1990) and Asplund *et al.* (1990b). Using this column hexane is the only eluting solvent, enabling the use of a UV detector to detect the solute and direct injection onto GC-ECD. Non-ortho PCBs elute in approximately ten minutes with 20 mL of hexane whereas carbon elution takes almost ninety minutes and larger amounts of aromatic solvents resulting in more background interferences. Samples of human milk were analyzed using this technique.

5. Environmental Levels

Non-ortho substituted PCBs have been detected in environmental samples since 1980, when Huckins *et al.* (1980) determined mean PCB 77 concentrations of 0.11±0.03 μg/g in carp contaminated with Aroclor 1248 and 1254 (PCBs 126 and 169 were not detected) (Table 3). A Finnish study examined non-ortho PCB and PCDD/F levels in salmon and eagles from southern Finland (Table 3) (Tarhanen *et al.*, 1989). In salmon only 2,3,7,8-T_4CDF and PCB 77 contributed to TEC, and at levels too low to justify banning their use as food. Higher levels of non-ortho PCBs than of PCDD/F's were found in adult eagle samples, the liver of a juvenile eagle, and in an eagle egg. The non-ortho PCB TEC in these birds was

Table 3. Environmental Levels of Non-ortho PCBs and TECs

Location	Species	Tissue	PCB Congener ng/g 77	126	169	TEC[1] pg/g	Reference
Ohio River	Carp	Whole fish	110	N.D.	N.D.	---	Huckins *et al.*, 1980
Gulf of Bothnia	Salmon (*Salmo salar*)	muscle	0.638	<0.2	<0.2	0.80	Tarhanen *et al.*, 1989
Baltic Sea	Salmon	muscle	1.12	<0.2	<0.2	1.40	
E. Finland	White-tailed eagle (*Haliaetus albicilla*), juvenile	muscle	9.76	6.33	2.37	1829	
Baltic sea	eagle, F	muscle	71.2	51.0	19.9	14735	
	eagle, F	muscle	12.6	4.02	1.07	1169	
W. Finland	eagle, M	muscle	34.4	18.8	4.78	5434	
W. Finland	eagle, j	muscle	10.3	0.970	<0.2	290	
S. Finland	eagle	egg	21.0	20.6	6.02	5936	
N. Finland	eagle	egg	9.79	0.954	<0.2	285	
Green Bay	Forster's tern (*Sterna forsteri*)	egg	0.563	3.84	1.06	2175	Kubiak *et al.*, 1989
Lake Poygan	Forster's tern	egg	<0.05	0.295	0.295	210	
Hong Kong	Junk Bay	sediment	0.08-7.6	0.01-3.0	<0.005-0.02	--	Kannan *et al.*, 1989b
	Tolo Harbour	sediment	0.06-0.09	<0.002-0.005	<0.005	---	

Location	Species	Tissue	PCB Congener ng/g 77	126	169	TEC pg/g	Reference
Junk Bay	Green-lipped mussel (*Perna viridis* L.)	soft tissue	0.7	0.05	0.007	---	Kannan *et al.*, 1989c
Tolo Harbour	mussel	soft tissue	0.09	<0.005	<0.001	---	
Percentage of ΣPCBs, mussel:sediment			3.53:1	7.20:1	12.0:1	---	Kannan *et al.*, 1989b
Green Bay	Forster's tern	egg	18	2.7	<1	2269	Smith *et al.*, 1990
	Common tern	egg	30	7.0	<1	2881	
Green Bay	sediment		<0.5	<0.5	<0.5	<200	
Fox River	sediment		8.5	<0.01	<1	23	
Saginaw Bay	Carp	whole fish	<5	<5	<5	<2000	
Lake Michigan	Lake trout	egg	1.68	0.260	0.018	110	
Lake Ontario	Brown trout	whole fish	5	<2	<2	---	Niimi and Oliver,
	(*Salmo trutta*)	muscle	2	<2	<2	---	1989
	Rainbow trout	whole fish	6-11	<2-10	<2	---	
	(*Salmo gairdneri*)	muscle	<2-4	<2	<2	---	
	Coho salmon	whole fish	8-10	<2	<2	---	
	(*Oncorhynchus kisutch*)	muscle	3-5	<2	<2	---	
	Lake trout	whole fish	18	<2-19	<2	---	
	(*Salvelinus namaycush*)	muscle	8	<2	<2	---	

Location	Species	Tissue	PCB Congener ng/g 77	126	169	TEC pg/g	Reference
Matsuyama	Dog	adipose, M	0.044	0.009	0.042	---	Tanabe *et al.*, 1987a
		adipose, F	0.011	0.005	0.012	---	
	Cat	adipose, M	0.370	0.087	0.070	---	
	Human	adipose, M	0.400	0.400	0.120	---	
		adipose, F	0.270	0.240	0.053	---	
Seto-Inland Sea, Japan	Striped mullet (*Mugil cephalus*)	muscle	2.100	0.100	0.002	---	
N. Pacific (*Phocoenoides dalli,d.*)	Dall's Porpoise	blubber, M	3.100	0.200	0.150	---	
		blubber, F	0.930	0.092	0.053	---	
Japan	Baird's beaked whale (*Berardius bairdii*)	blubber, M	1.600	0.480	0.310	---	
		blubber, F	0.700	0.100	0.093	---	
Japan	Pacific white-sided dolphin (*Lagenorhyncus obliquidens*)	blubber, M	27.0	3.8	1.2	---	
Seto-Inland Sea, Japan	Finless porpoise (*Neophocoena phocoenoides*)	blubber, M	14.0	0.89	0.64	---	
Japan	Killer whale (*Orcinus orca*)	blubber, F	42.0	4.0	3.6	---	

[1] - as calculated by the author; dash indicates was not calculated by the author

ten times greater than in killer whale muscle and 100 times greater than in human adipose tissue (latter two samples from Japan). A greater toxicity load was attributed to the non-ortho PCBs, especially PCB 126. For these eagles, a greater biomagnification through the food chain was observed for non-ortho PCBs than for PCDD/Fs. It was observed that the age and sex of the eagles was significant when correlated with their pesticide levels and the amounts present in muscle and liver. Southern Finland samples contained higher levels than Northern Finland (Lappland) samples. Paasivirta *et al.* (1989) calculated ratios (eagle/salmon) for ΣPCBs and PCB 77, 126, and 169 in salmon and eagles (both from the Archipelago Sea, 1985-1987) and found enrichment: 38.1, 93.5, 106.8, >160, respectively.

A comprehensive study of Forster's tern (*Sterna forsteri*) eggs from a clean (Lake Poygan) and contaminated (Green Bay) location in Wisconsin, implicated elevated non-ortho PCB concentrations in the decreased fledgling success at the contaminated location (Table 3) (Harris *et al.*, 1985; Kubiak *et al.*, 1989). Green Bay tern eggs contained significantly higher concentrations of 2,3,7,8-TCDD, other PCDDs, non- and mono-ortho PCBs, and ΣPCBs than eggs from Lake Poygan. Of eggs laid, 45% produced fledgling chicks at Lake Poygan and 21% at Green Bay. Unhatched eggs from Green Bay had ten times greater TECs than that found in eggs from Lake Poygan; the data supported an additive effect in the calculation of total TECs. The unborn chicks had congenital abnormalities, which were not present in Lake Poygan eggs, and successful hatchlings from Green Bay had enlarged livers, lower body weights, and elevated liver microsomal AHH levels. Parental effects on hatchling success included longer egg incubation time at Green Bay, and

nest abandonment or disapearance (not observed at Lake Poygan). This abnormal behaviour was attributable to inattentiveness by the parents. Of the contaminants measured in this study, AHH-active PCB congeners (the non-ortho and mono-ortho congeners) and ΣPCB levels were the only contaminants present at levels sufficient to produce these effects. ΣPCB levels could account for the extrinsic effects (abnormal parental behaviour), while the non and mono-ortho PCBs could account for the intrinsic effects on reproductive success (unhatched eggs, deformed chicks). Other factors, including the effects due to viruses and other organochlorine contaminants, were considered as possible causal factors in the poor hatchling success but were regarded as being of less significance.

Kannan *et al.* (1989b) reported that sediments from Hong Kong harbours showed levels of PCBs 77>126>169, similiar to the levels present in commercial PCB formulations (Table 2, 3). This reflected contributions of PCBs from runoff and atmospheric transport. In contrast, green-lipped mussels (*Perna viridis* L.) contained a preferential enrichment of the non-ortho PCBs. Mussels also demonstrated a slower uptake rate, and clearance (K_2) of the non-orthos than other PCB isomers (half-life of PCB 126 was 13 days compared to 6 days for other pentachlorobiphenyl isomers), with uptake and clearance times increasing with the higher chlorinated congeners. PCBs with low K_2 values usually have high log Kow values; PCB 77 has a lower K_2 value but a lower log Kow relative to other tetra PCBs (Hawker and Connell, 1988; Kannan *et al.*, 1989c). Kow is defined as the partitioning of a chemical's concentration between an aqueous phase and an octanol phase, in a two-part octanol/water system.

$$K_{OW} = \frac{\text{Concentration in octanol phase}}{\text{Concentration in aqueous phase}}$$ (Lyman *et al.*, 1982)

It is inversely related to a compound's water solubility and is used in calculating the degree of bioaccumulation of the compound (Hawker and Connell, 1988; Kannan *et al.*, 1989c; Warne *et al.*, 1990). This difference in K_2 could be explained by the binding of PCB 77 to cellular proteins (Kannan *et al.*, 1989c).

Smith *et al.* (1990) found low ng/g levels of PCB 81, 77, 126, and 169 in sediment, whole carp, lake trout eggs, common tern, and Forster's tern collected from locations around Lake Michigan (Table 3). In all of the samples, PCBs 77, 126, and 105 (2,3,3',4,4'-) comprised >95% of total TECs, with PCB 126 being the most significant toxicologically. Salmonids sampled from Lake Ontario contained PCBs 81, 77, and 126; the proportion of TEC accountable to these congeners was greater than that of PCDDs and PCDFs in these fish (Table 3) (Niimi and Oliver, 1989).

In marine mammals, organochlorine pesticide accumulation is a severe problem as these animals have a thick blubber (subcutaneous fat) layer, occupy a high trophic level, and live for many years (Tanabe *et al.*, 1988; Skaare *et al.*, 1990). Organochlorine concentrations increase with age, and maternal transfer via lactation is a major source to the next generation (Norstrom and Muir, 1988; Tanabe, 1988; Tanabe *et al.*, 1988; Skaare *et al.*, 1990). This group of mammals also have a lower capacity to metabolize the non-ortho and mono-ortho PCBs than do terrestrial mammals (Tanabe *et al.*, 1987a, 1988). These factors have contributed to organochlorine pesticide levels in marine mammals which are several orders of magnitude greater than in land-based birds and mammals, including humans (Tanabe *et al.*, 1987a, 1987b; Skaare *et al.*,

1990; Smith *et al.*, 1990). Tanabe *et al.* (1987a) analysed for non-ortho PCBs in marine and terrestrial mammals. Terrestrial mammals had lower levels of non-ortho and ΣPCBs (all ortho substituted PCBs) than any of the marine mammals. In both types of mammals, there existed a significant correlation between the concentration of ΣPCBs and the concentration of the non-orthos, and females contained lower levels than males. The fish samples had proportions of non-orthos similar to commercial PCB mixtures, 77:126:169 as 95:5:<1, suggesting a poor capacity to metabolize these compounds. McFarland and Clarke (1989) proposed that fish have a detoxifying capability one-tenth that of mammals. Boon *et al.* (1989) and Norstrom *et al.* (1992) found similar results. In mammals, bioaccumulation of PCB 126 and PCB 169 relative to Aroclor 1254 and Kanechlor 500 mixtures occurred, with these two congeners making up a larger proportion of total non-ortho concentrations in terrestrial than in marine mammals. The ability of terrestrial mammals to metabolize PCB 77, and to some extent PCB 126, may explain the high proportions of PCB 169 relative to total non-ortho concentrations. Marine mammals contained higher levels of the non-ortho PCBs, suggesting a greater accumulation potential and a lower capacity to metabolize these compounds. In humans, concentrations of non-ortho PCBs were 1 to 43 times greater than levels of PCDDs and PCDFs, with PCB 126 making the largest contribution to TEC's. Females contained lower levels of non-ortho PCBs than males. Marine mammals had a far higher proportion of TEC due to mono- and non-ortho PCBs than to PCDDs and PCDFs (Kannan *et al.*, 1989a). Higher levels of non-ortho PCBs in marine than terrestrial mammals may be due to a lower activity of cytochrome P4501A and no activity of P450IIB enzymes in cetaceans,

resulting in less metabolism and excretion (Tanabe *et al.*, 1988; Kannan *et al.*, 1989a). Norstrom *et al.* (1992) concluded that the degree of cytochrome activity varied among marine mammal species, but did not compare it to any terrestrial mammals. Thus, other marine mammals (other than cetaceans) may have a similar cytochrome activity to terrestrial mammals.

Asplund *et al.* (1990b) found non-ortho PCBs made a greater contribution to TEC's than PCDDs and PCDFS, but no biomagnification of these PCBs similar to the ortho substituted congeners. Samples of Baltic herring (*Clupea harengus*) contained levels of ΣPCBs 80 times lower than Baltic grey seal (*Halichoerus grypus*), while concentrations of non-ortho PCBs were similar in both species. Baltic grey seal and ringed seal (*Pusa hispida*) from Spitzbergen (northern Norway) displayed a geographical difference in ΣPCB levels but had similar levels of the non-ortho PCBs and dioxins. Higher ΣPCB levels (on a lipid weight basis) were observed in grey seal than in osprey, *Pandion haliaetus*, but the reverse was true for the non-ortho PCBs: 550,000 ng/g ΣPCB in grey seal and 220,000 ng/g ΣPCB in osprey ; 8 ng/g non-ortho PCBs in grey seal and 54 ng/g non-ortho PCBs osprey.

1. Materials

Sodium sulfate (anhydrous, granular grade, obtained from Baxter-Canlab, Winnipeg, MB, or Fisher Scientific, Edmonton, AB) and Florisil (60-100 mesh, Fisher Scientific) were heated at 600°C for 6 h and 100°C overnight before use. Florisil, 1.2% deactivated, was prepared by adding 1.2 mL HPLC-grade water (Caledon Labs, Edmonton, AB) to 100 g of the activated (heated) Florisil. The mixture was allowed to equilibrate for 12 h before use. Silica gel (various mesh sizes, for chromatographic analysis, BDH Inc., Toronto, ON) was activated before use by heating to 150°C for 12 h. Silica gel, 5% deactivated, was made by adding 2 mL of HPLC-grade water to 40 g of activated silica gel and equilibrating similar to the Florisil procedure. Samples requiring lipid and pesticide separation by gel permeation chromatography (GPC) were first filtered through 0.2 μm Fluoropore filters (Whatman/Millipore Canada Ltd., Mississauga, ON). The ultra-high pure (UHP) gases used on the GC-ECD and GC-MSD were obtained from Welders Supplies Ltd., Winnipeg, MB. The capillary columns used were obtained from Chromatographic Specialties, Brockville, ON. Hamilton syringes (Chromatographic Specialties) were used for manual injections on both MSDs.

2. GC-ECD and GC-MSD Conditions

High resolution capillary gas chromatography (GC) was used to analyze all samples. Organochlorine pesticides and all PCB congeners (except non-orthos) were quantified using a Varian 6000 GC-ECD.

Determinations of non-ortho PCB levels were performed on a Hewlett Packard (HP) GC-MSD. Instrument parameters are listed in Tables A1 and A2; Tables A3 to A5 outline data analysis parameters used on the MSDs.

The early work (recovery studies and carbon column fractionation) was analysed on a Varian 6000 GC-ECD, model 8080 autosampler, and a DS651 data system. After the first six months, a Hewlett-Packard 5890 GC-ECD with a 7673A autosampler and a Pascal 3.2 work station was used for non-ortho PCB work. Mass spectrometer work was completed first on a Hewlett-Packard 5970 MSD with a HP5890 GC and UNIX data system, and later on a HP5971A MSD with a HP5890 GC and a Pascal 3.2 work station. Both MSDs used a manual tune that optimized the ions 219, 414 and 502 to give greater high end sensitivity (Table A5). Detection limits for non-ortho PCBs were <3 pg on 5970B MSD, and <1 pg on 5971A MSD, at a signal to noise of 3:1 (Table 4).

3. Methods

A. Carbon Column Preparation

Early work to determine the amount of carbon needed in the column and the solvent elution volumes was done by Simon and Mulvihill, of the Canadian Wildlife Service, Hull, PQ (personal communication, 1988). These quantities were modified in the work described below.

The carbon columns used in these procedures consisted of 0.6 g Whatman GF/D glass fibre filters (Whatman/Millipore Canada Ltd.), and 0.06 g Super A activated carbon (Lot #610202-30, Anderson Development Co., Adrian, MI, U.S.A.). The carbon was activated before use by heating to 200^{o}C for 4 h, cooled, and transferred to a glass jar

Table 4. Detection Limits, at a Signal to Noise Ratio of 3:1, for Non-ortho PCBs on MSD

MSD	Injection No.	PCB Congener (pg) 37	81	77	126	169
5970B	1	1.9	---[1]	---	3.0	3.7
	2	1.1	---	3.1	2.3	3.3
	3	1.3	---	2.6	2.5	2.4
	average	1.5	---	2.9	2.6	3.1
5971A	1	0.7	0.3	0.6	0.8	0.7
	2	0.6	0.3	0.5	0.6	0.6
	3	0.6	0.3	0.5	0.6	0.5
	4	0.6	0.3	0.6	0.7	0.5
	average	0.6	0.3	0.5	0.7	0.6

[1] - dash indicates not determined

(Norstrom, CWS, Hull, P.Q., personal communication 1988). The filters were cut up into small pieces (approximately 1 cm x 1 cm, of any shape) and added to a 150 mL glass Corex tube with 80 mL of dichloromethane (DCM) (pesticide grade, Burdick and Jackson Ltd., obtained from Baxter-Canlab). This mixture was homogenized using a Kinematica Polytron (Brinkman Instruments, Rexdale, ON) for 1-2 min, then the carbon was added to produce a black-coloured slurry. The carbon column was prepared in an Omni, flanged, low-pressure analytical Pyrex column, 6.5 mm i.d. x 100 mm, with one fixed and one adjustable end fitting (Anspec Co. Inc., Ann Arbor, MI, U.S.A.). A 2 µm fritted-glass disc was placed on top of the fixed fitting and the slurry was transferred using a Pasteur pipette. As the slurry was added and the solvent drained away the carbon-filter mixture was compressed, to give a final length of 7 cm. A second fritted-glass disc was placed on top of the mixture and the adjustable fitting was put into place (Norstrom and Simon, 1991).

B. Automated Carbon Column System

Using a manual pumping setup (Appendix B), elution volumes were determined to be 80 mL 5% DCM/hexane, 200 mL DCM, and 110 mL toluene, with a column regeneration procedure after each sample of 40 mL toluene, 40 mL methanol (MeOH), 40 mL toluene, and 40 mL hexane (hexane, methanol, and toluene obtained from Caledon Labs). The method was now applied to a low pressure automatic pumping system with a Quick-Load peristaltic pumphead and size 13 Viton tubing, from Fluid Management Systems (FMS) (Watertown, MA, U.S.A.; marketed by Nortech Control Equipment Inc., Etobicoke, ON). This system was selected because FMS had worked with the Centre for Disease Control in Atlanta, GA, U.S.A.,

to develop an automated carbon column process for dioxin analysis (Issacs *et al.*, 1990; Lapeza *et al.*, 1986; Tiernan *et al.*, 1990). The controller with the pump automatically reversed column flow, regenerated the carbon column, loaded the sample, and then through three different valves, collected the three elutions - 5% DCM/hex, DCM, and toluene (Figure 2). Two problems occurred with this system. The system pressure, while pumping, was so high that tubing connections leaked - this was corrected by having the carbon-filter mixture less compressed in the glass column (length of 7 cm). The second problem was that the Viton tubing (Cole-Parmer Canada Ltd., Toronto, ON) gradually became more elastic as DCM was pumped through it. This affected recoveries of the non-ortho PCBs (Table 5). Constant elution volumes were obtained when the peristaltic pumphead was replaced with a stainless steel piston pumphead (adapted by FMS from a model available from Cole-Parmer). With the new pumping system, samples were prepared in 15 mL hexane in a graduated test-tube. The pump loaded this and then switched to pumping the 5% DCM/hex elution solvent. A plug of air would be present between the sample in hexane and the 5% DCM/hex solvent. 1/8" OD x 1/16" ID (3 mm x 1.5 mm) teflon tubing was used on all valves except the sample load valve; 1/16" OD x 1/32" ID (1.5 mm x 0.8 mm) teflon tubing was used for sample take-up, to minimize dead volume and thus sample loss. Elution volumes were adjusted to 80 mL of 5% DCM/hex, 190 mL of DCM (>95% PCB 105 and 156 [2,3,3',4,4',5-] in here), and 130 mL of toluene.

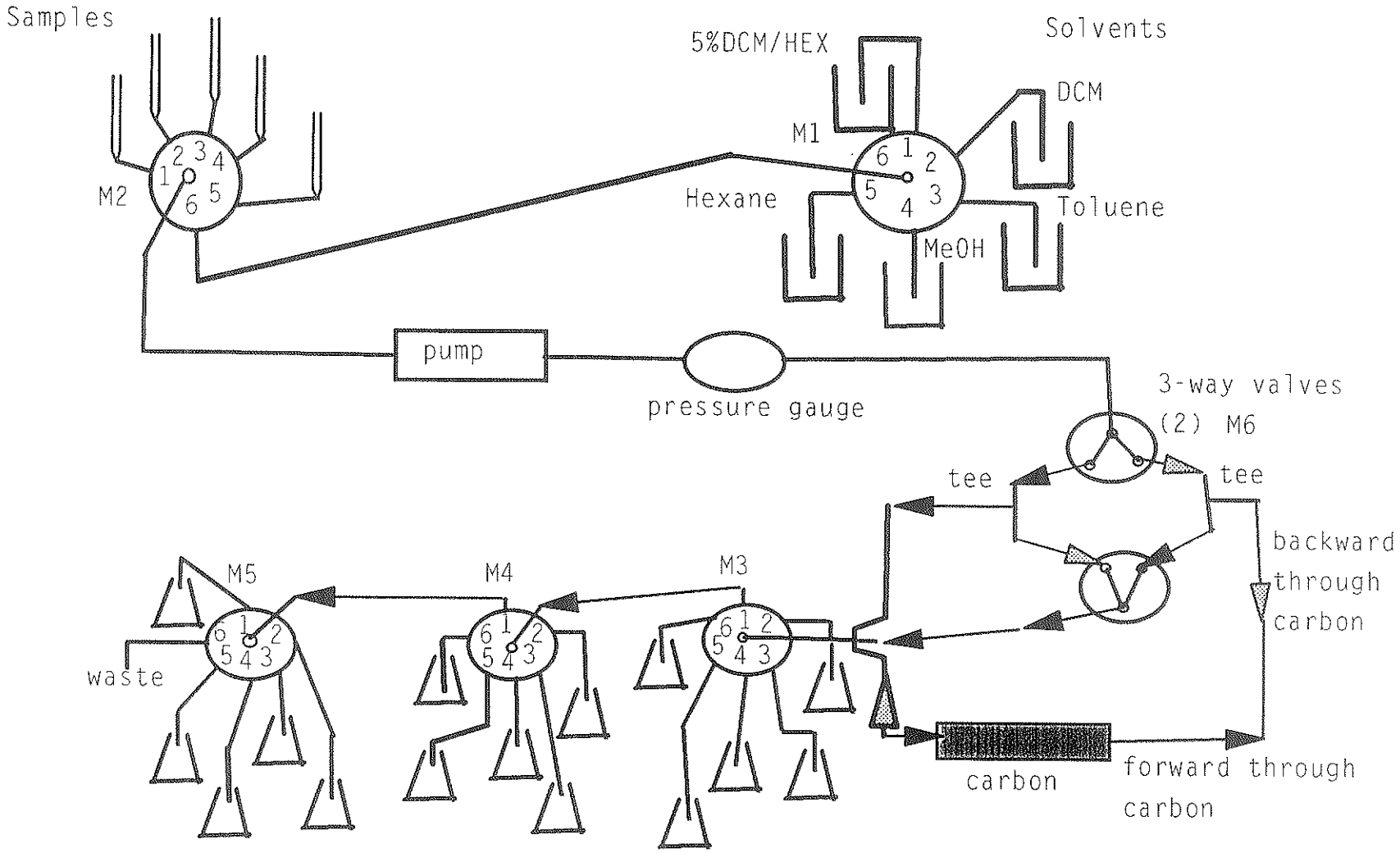

Figure 2. FMS Automatic Pumping System for Carbon Column Separations

Table 5. Effect of DCM volumes on the Carbon Column Fractionation of the Non-ortho PCBs

Volume of Solvent	Percent Recovery								
	37	77	126	169	105	156	^{13}C-77	^{13}C-126	^{13}C-169
170 mL DCM	0	0	0	0	29	29	0	0	0
130 mL tol	34	35	35	30	1	1	44	43	37
190 mL DCM	0	0	0	0	41	42	0	0	0
130 mL tol	72	73	74	63	1	2	84	83	69
210 mL DCM	1	1	1	1	57	56	1	1	1
130 mL tol	69	73	74	67	1	1	85	84	74

4. Sample Analysis

A. Marine Mammal Blubber

High lipid content samples (see section 4C) were extracted using hexane and ball mill (maximum 2.5 g of blubber/ball mill) (Figure 3; Muir *et al.*, 1990a). 10 µL of ^{13}C-PCBs (4000 pg) (^{13}C-77, 126, and 169 mixture; Cambridge Isotope Labs, Woburn, MA, U.S.A.), were added at the initial extraction stage and used as a recovery standard. After the initial extraction, gravimetric determination of the lipid content, GPC and 5% deactivated silica gel column chromatography for lipid and pigment removal were performed. Samples were made to 15.0±0.1 mL in hexane for the carbon column. The column regeneration procedure was done immediately before sample loading. For most samples, the 5% DCM/hex and DCM fractions were collected together in round bottom flasks (RBF), evaporated down, and stored in 7 mL scintillation vials. This eluate could be analysed for OC's and ortho substituted PCBs on GC-ECD, but usually an aliquot of the sample was removed after the GPC step for this procedure. The toluene fraction was evaporated and transferred to a graduated test-tube, using hexane to rinse the round bottom flask. It was evaporated to a small volume on the N'EVAP (Organomation Associates Inc., South Berlin, MA, U.S.A.), and transferred to a 200 µL autosampler vial insert with rinses of toluene and hexane. 20 µL of t-NON (40 ng) (lot no. H01Y, 98.1% purity; EPA Research, Triangle Park, SC) was added for the final sample volume (Figure 3).

The working standard for MSD quantification consisted of non-ortho PCBs 37, 81, 77, 126, 169, mono-ortho PCBs 105 and 156, internal standards ^{13}C-PCBs 77, 126, 169, and t-NON (Table A3). One

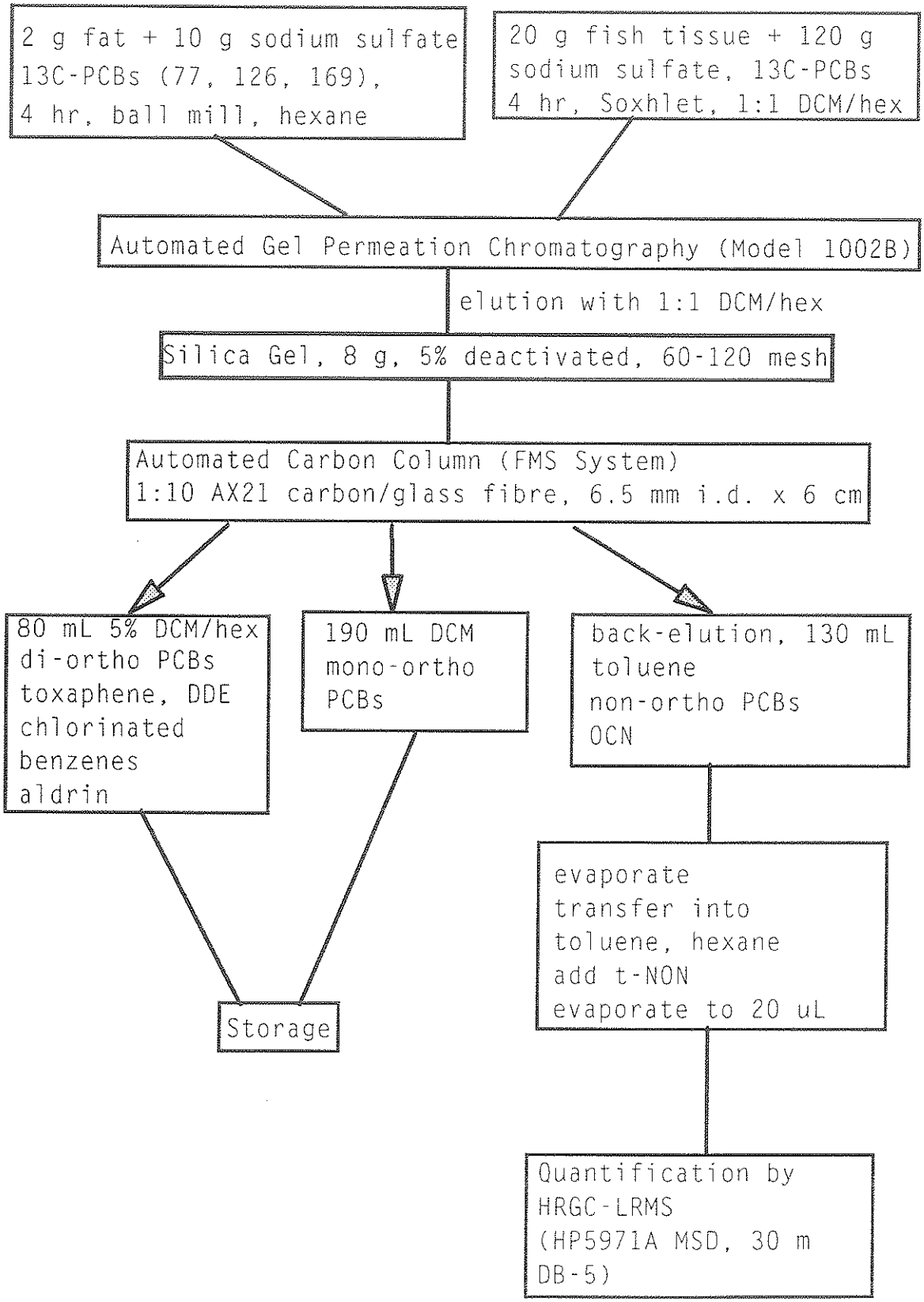

Figure 3. Schematic of Extraction Procedure for Non-Ortho Substituted PCBs

concentration of standard was used for the sample analysis, and the concentration of non-orthos was calculated using the internal standard procedure. This calculation procedure was accurate for concentrations within the linear range of the ^{13}C-PCB and ^{12}C-PCB standards (100-300 pg) (Figure 4). Response factors for the ratios ^{13}C-PCB/^{12}C-PCB were calculated for each standard injection and used for those samples injected with that standard (Norstrom and Simon, 1991).

$$\text{Response factor (rf)} = \frac{\text{area } ^{13}C\text{-PCB in the std} \times \text{conc. } ^{12}C\text{-PCB in std}}{\text{area } ^{12}C\text{-PCB in std} \times \text{conc. } ^{13}C\text{-PCB in std}}$$

To calculate the concentration of an unknown peak, the following equation was used.

$$\text{concentration unknown (pg/g)} = \frac{\text{area unknown} \times 4000 \text{ pg } ^{13}C\text{-PCB} \times \text{rf } ^{13}C/^{12}C}{\text{area } ^{13}C\text{-PCB in unknown} \times \text{sample weight (g)}}$$

(^{13}C-PCB amount: 4000 pg = 400 pg/μL x 10 μL)

For each group of samples run through MSD, a few samples were quantified and the non-orthos confirmed using both primary and secondary ions. No carryover was observed between samples.

B. Fish Tissues

Fish tissues were homogenized with dry ice in a blender and then Soxhlet extracted with 50% DCM/hex (Figure 3). Extracts were prepared for injection on GC-MSD using the GPC, silica gel and carbon column procedures above. An aliquot of the extract, if required for OC and ortho substituted PCB quantitation, was removed after cleanup by GPC. All other procedures were identical to those described for marine mammal blubber.

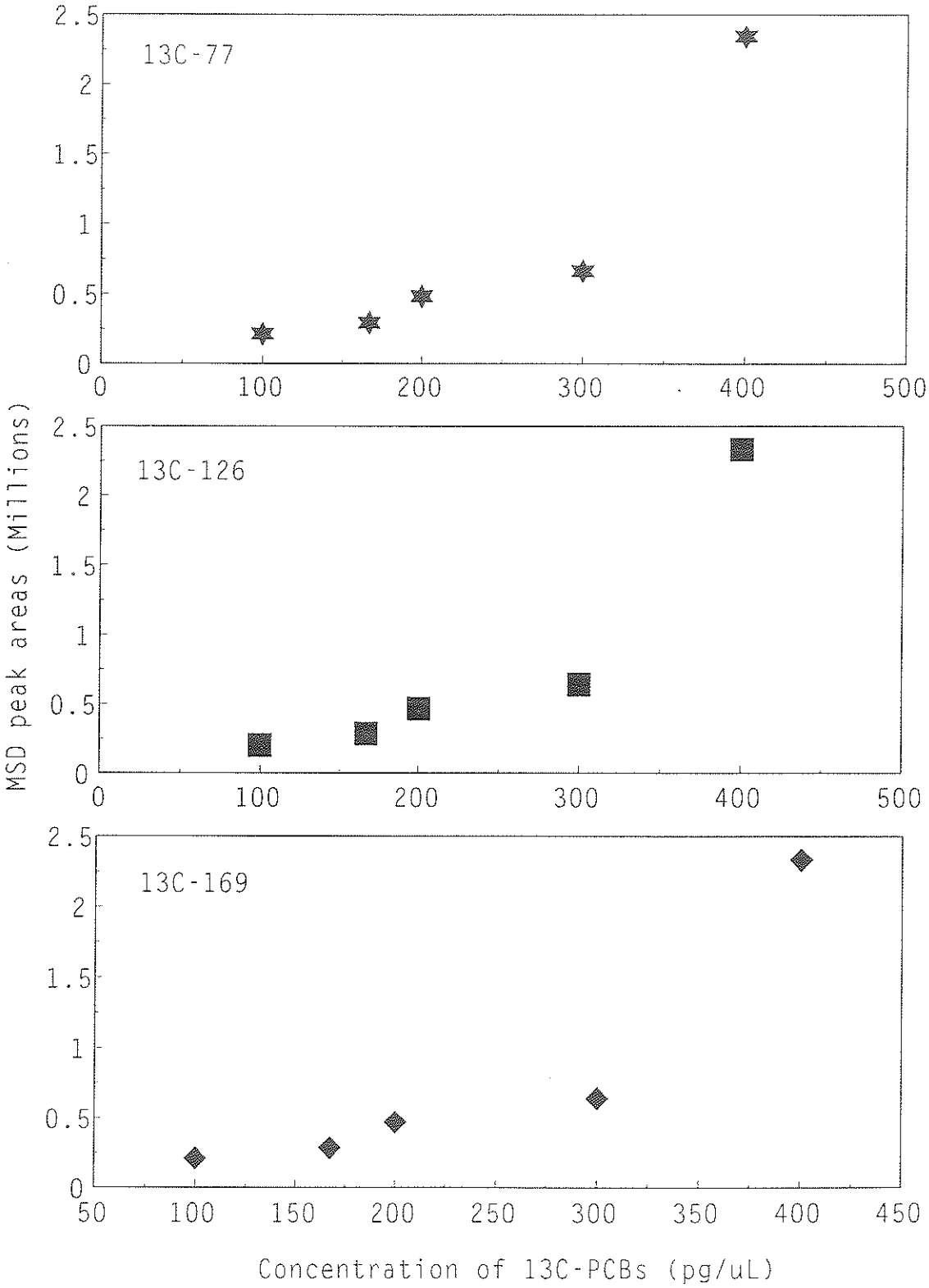

Figure 4. Linearity Check of 13C-PCB Standard, 5971A MSD

C. Samples Analysed

The method of isolating and quantifying non-ortho PCBs, developed in this study, has been used for analysis of marine mammal blubber and whole fish (Table 6; Figure 5). Narwhal (*Monodon monoceros*), beluga (*Delphinapterus leucas*), polar bear (*Ursus maritimus*), walrus (*Odobenus rosmarus*), ringed seal (*Phoca hispida*), and Arctic charr (*Salvelinus alpinus*) from the Canadian Arctic were analyzed, as well as beluga and Atlantic cod (*Gadus morhua*) from the east coast of Canada, and killer whales (*Orcinus orca*), false killer whale (*Pseudorca crassidens*), Dall's porpoise (*Phocoenoides dalli*), harbour porpoise (*Phocoena phocoena*), and a dolphin (*Lagenorhynchus obliquidens*) from waters around Vancouver Island. Species analysed from Broughton Island, West Davis Strait, were part of a native food diet study and sex, age, length and weight data were not available. This study was conducted to determine the contaminant levels in native foodstuffs; samples were collected in the state in which they would be consumed and then frozen until analysis (Kinloch *et al.*, 1992). All samples were stored at -40^{o}C until analysis.

D. Statistical Analysis

Various statistical techniques were used to determine precision and accuracy. Percent bias calculations were performed on ^{13}C-PCB recoveries to determine accuracy, following a procedure used by the U.S. Environmental Protection Agency.

$$\% \text{ Bias} = 100 * (C_a - C_b)/T$$

where C_a is the concentration of ^{13}C-PCB in the final sample extract, C_b is the original concentration of ^{13}C-PCB in sample, and T is the amount

Table 6. Year Sampled and Location of Arctic and Mid-latitude Samples[1]

Species	Year	Code	Location	N	Mean Age or Size
Polar Bear	1987		Broughton Island, West Davis Strait, Eastern Canadian Arctic	1	Diet[2]
Arctic Charr	1985	a	Broughton Island	8	Diet[2]
	1989	b	George River, Ungava Bay, N. Québec	4	4150 g
	1987	c	Creswell Bay, Prince Regent Inlet, Central Canadian Arctic	8	987 g
	1987	d	Spence Bay, St. Roch Basin, C. Cdn. Arctic	10	2526 g
	1987	e	Pond Inlet, Baffin Bay, E. Cdn. Arctic	10	979 g
Cod Liver Oil	1990		Newfoundland	4	UNK
Ringed Seal	1985		Broughton Island	8	Diet[2]
Walrus	1987		Broughton Island	5	Diet[2]
Beluga	1989	a	Husky Lake, MacKenzie Delta, Western Cdn. Arctic	13	453 cm
	1983, 84	b	Panguirtung, Cumberland Sound, E. Cdn. Arctic	6	22 GLGs
	1988	c	Broughton Island	1	Diet[2]
	1987, 88	d	St. Lawrence River, Québec	10	25 GLGs
Narwhal	1982, 83	a	Pond Inlet, Baffin Bay, E. Cdn. Arctic	17	419 cm
	1987	b	Broughton Island	5	Diet[2]
Killer Whale	1989, 90		Georgia Strait, British Columbia	6	Adult

False K. Whale	1989, 90	Georgia Strait, British Columbia	2	Adult
Harbour Porpoise	1989, 90	Georgia Strait, British Columbia	7	Adult
Dall's Porpoise	1989, 90	Georgia Strait, British Columbia	3	Adult
Dolphin	1989, 90	Georgia Strait, British Columbia	1	UNK

1 - Marine mammal samples were blubber, Arctic charr were whole fish composites.

2 - Diet samples were part of a Inuit dietary study, and no age or length data were collected due to the nature of this study (Kinloch *et al.*, 1992).

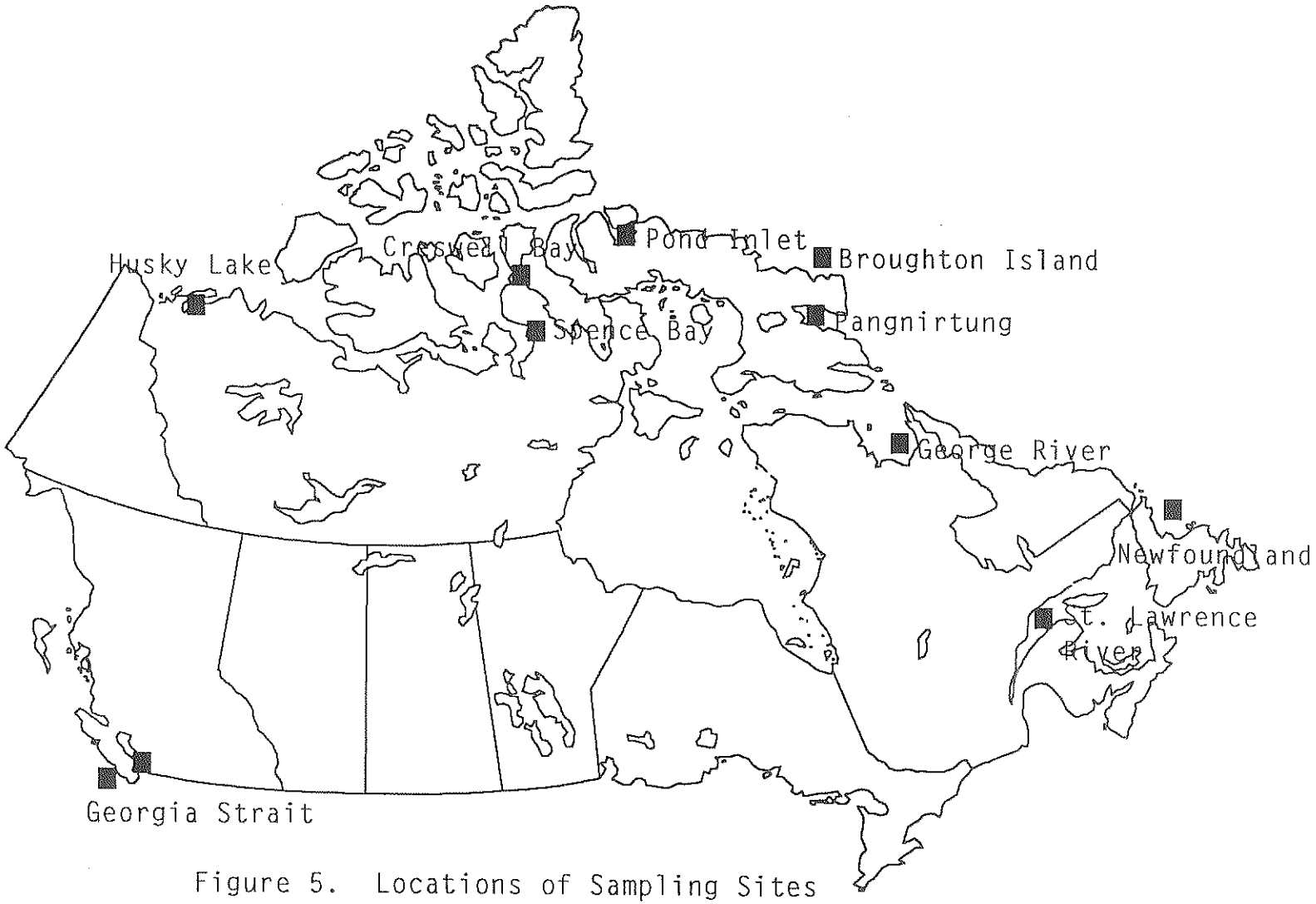

Figure 5. Locations of Sampling Sites

of ^{13}C-PCB added to the sample (4000 pg) (EPA Contract No. 68-C9-0013, 1991). Z Test, confidence interval (CI), and precision calculations were done on duplicate samples and injections, using the following equations and conditions to determine acceptable Z and precision values (Moore *et al.*, 1989; EPA Contract No. 68-C9-0013, 1991).

$$Z = \frac{\text{original pg/g - repeat pg/g}}{(\text{original } s^2 + \text{repeat } s^2)^{1/2}}$$

where CI = 122.8 * EF, EF = range/mean, and

s = lipid wt. (pg/g) * CI/173.7.

If the absolute value of Z is within a confidence interval of ≤68% and is <1, the EPA will accept two results as statistically the same. If the absolute value of Z has a confidence interval of >95% and is >2, the EPA will consider the two results as statistically different. Z values within 1 and 2 are considered unacceptable when the majority of sample results fall within this range.

Precision = range/mean * 100

where values closer to 0% indicates better precision. Errors were also calculated for each step in the method, and total error determined by calculating the square root of the total addition of each percent error squared (Skoog and West, 1982).

E. Swedish Interlab Study

In March and April of 1991, an international interlab calibration study for the quantitation of the non-ortho PCBs 77, 126, 169, and the mono-ortho PCBs 118 (2,3',4,4',5-) and 105, was organized by Dr. L. Reutergårdh of the Swedish Environmental Protection Agency, Special Analytical Laboratory, Solna, Sweden. The organizing lab sent three

small bottles of herring oil - one unspiked (presumably natural levels), one spiked at a low level, and one spiked at a high level. Five replicates were run out of each bottle, along with a blank and a spiked standard (10 µL of the Swedish standard, which contained PCBs 77, 126, 169, 105, and 118), according to the procedures followed in the marine mammal blubber analysis. The 5% DCM/hex and DCM elutions, as well as the spillover into the toluene elution, were used to quantitate PCB 105 and 118, and the toluene elution was used to quantitate the non-ortho PCBs and ^{13}C-PCBs. These quantifications were done on GC-MSD.

Two repeats of the Swedish samples were done in June and July of 1992. In June 0.5 g of oil was analysed for non-ortho PCB levels; in July 1.0 g. Oil samples were analysed in triplicate, except for the July repeat of the unspiked oil, which was done in duplicate. Two blanks and triplicates of spiked samples were also analysed.

Results and Discussion

This section is presented in two parts - a discussion of analytical methodology, including accuracy and precision, and a discussion of environmental samples analysed. The latter section will include concentration levels, proportions of non-ortho PCBs to ΣPCBs, and TECs - similarities and differences between fish and marine mammals, food chain relationships, and species differences. Detailed data tables are located in Appendix C.

1. Method Development

The carbon column used in this method consisted of activated carbon and glass fibre filters. Other media have been used to suspend the carbon, but glass fibre filters gave the least matrix interferences (Smith, 1981). The carbon column used for non-ortho PCB determinations was larger than the carbon column used for dioxin analysis (Norstrom and Simon, 1991); it was found a shorter column provided too few adsorption sites for all of the non-orthos in a sample (Simon, CWS, Hull, P.Q., personal communication 1988). The carbon column could be allowed to dry out and be rewetted with solvent with no harmful effect on its fractionation and recovery ability (Smith, 1981). Solvent elution volumes for the carbon column were adjusted such that the di-ortho, mono-ortho and non-ortho PCBs were separated into three distinct fractions. Recovery work showed that the volume of DCM pumped through the carbon had an effect on the fractionation of the non-ortho congeners - too much DCM (>210 mL) would elute non-ortho PCBs from the carbon before the reverse toluene elution began (Table 5).

After determining that the carbon column was separating the di-ortho, mono-ortho and non-ortho PCBs and giving good recoveries, using standards (Table 7 and Table A6), various clean-up techniques were tried on the toluene fraction. GC-ECD analysis of this fraction showed many unidentified interfering peaks around the retention time of PCB 169, making it hard to quantify the area of this peak (Table A7). At this point in the method development, it was assumed that the GPC (Model 1002B, ABC Laboratories, Columbia, MO, U.S.A.) step before carbon was adequate clean-up. The presence of the interfering peaks seemed to indicate that furthur clean-up was necessary after carbon. Columns of Florisil and silica gel were tried (Table A8). The toluene fraction of the sample was evaporated to dryness and the flask rinsed with a volume of hexane to elute the clean-up column. The first technique tried was Florisil, a common clean-up and separation step for ortho PCBs and organochlorines (CWS Analytical Methods Manual, 1982). After various attempts using different elution solvents and different amounts of solvents, as well as varying the concentration of non-orthos, it was determined that over 60% of PCB 169 would not elute from the Florisil column. Other researchers also had poor success with Florisil (Kamops *et al.*, 1979). Activated silica gel also gave very poor recoveries of non-orthos. A silica Sep-pak (Waters Associates, Milford, MA, U.S.A.) gave good recoveries but also many noise peaks on the chromatogram. A column of 5% deactivated silica gel, 60-120 mesh, eluted with 15 mL (1.2 g column) of hexane, gave 100% recovery for all of the non-ortho PCBs of interest (Table A8). A change in the method was later made such that the silica gel column clean-up step was put before the carbon column, after lipid contamination of the carbon occurred (see section 3). This

Table 7. Non-ortho and Mono-ortho PCB Standard Recoveries and Fractionation through Carbon[1]

Date	PCB	5% DCM/hex 80 mL	DCM 190 mL	Toluene 130 mL	Total Recovery
		Recoveries (%)			
Oct. 24/91	37	0	0	77	77
	81	0	0	99	99
	77	0	0	103	103
	105	0	127	2	129
	126	0	0	106	106
	156	0	123	1	124
	169	0	0	108	108
	^{13}C-77	0	0	88	88
	^{13}C-126	0	0	95	95
	^{13}C-169	0	0	89	89
Oct. 2/90	37	0	0	107±4	107
	81	0	0	118±2	118
	77	0	0	113±3	113
	105	0	62±5	0	62
	126	0	0	133±3	133
	156	0	91±11	0	91
	169	0	0	114±6	114
Oct. 11/89	37	0	0	71	71
	77	0	0	137	137
	126	0	0	78	78
	169	0	0	127	127

[1] - full data set in Appendix Table A7

column consisted of 8 g of 5% deactivated, 60-120 mesh silica gel, with an 100 mL hexane elution. This has extended the usable life of the carbon column. Deactivated silica gel and Florisil had a maximum shelf life of 30 days - recoveries and separation were unreliable after this period of time (Table 8).

2. Sample Recoveries and Method Errors, Precision and Accuracy

A listing of method errors is contained in Table 9. The largest error present was in the final sample volume. This was corrected by the addition of 20 µL t-NON to each vial, before the evaporation to final sample volume (Figure 3). The error in this addition procedure was the same for all samples, and was corrected through the comparison of the t-NON peak area between samples. All other errors were inherent to the glassware and syringes used during sample extraction and clean-up; total method error, after the volume correction by the addition of t-NON, was 7%. Total method error for the ortho substituted PCB and organochlorine method was 5%. These errors were corrected by using the ^{13}C-PCB internal standards. The internal standard calculation calculated sample amounts (pg/g) based on the ^{13}C-PCB amount added initially (4000 pg) and the amount in the final sample volume. Standards were run every 3-6 samples. Sample recoveries, based on ^{13}C-PCB recoveries, are listed in Table 10. Method ^{13}C-PCB recoveries generally varied from 40 to 100%, with recoveries as low as 17% for the St. Lawrence beluga and West Coast whales (Table 10 and Table A9). Low recoveries, for the mid-latitude whale blubber samples, were due to interferences on carbon because of their high levels of ΣPCBs and DDT. Low recoveries in Arctic samples were traced to the GPC step of the procedure. Sample recoveries were

Table 8. Silica Gel Column clean-ups - recoveries and elutions

Date	Solvent Elution (mL, hex)	PCB Congener - Percent Recovery									
		37	81	77	105	126	156	169	^{13}C-77	^{13}C-126	^{13}C-169
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, fresh											
Oct. 19/91	0-90	98	110	105	106	111	120	109	92	99	97
	90-100	3	1	3	3	2	2	1	4	3	1
	100-110	0	0	0	0	0	0	0	0	0	0
	110-120	0	0	0	0	0	0	0	0	0	0
	15, 15% DCM/hex	0	0	0	0	0	0	0	0	0	0
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, <30 days old (average of 2 runs)											
Jan. 31/91	0-100	93	89	91	94	89	94	93	80	84	84
	101-150	0	0	0	0	0	0	0	0	0	0
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, >30 days old (2 elutions done)											
Jan. 30/91	0-100	228	199	222	134	40	103	0	N.A.[1]	N.A.	N.A.
	101-150	9	29	19	67	62	74	0	N.A.	N.A.	N.A.
	151-200	0	0	0	27	0	0	0	N.A.	N.A.	N.A.

1 - ^{13}C-PCBs were not used in this recovery study

Table 9. Propagation of Errors in the Analytical Procedure

Procedure	Weight or Volume	Error (g or mL)	% Error
Weighing samples	25.00 g fish tissue	±0.01 g	0.04
	2.50 g blubber	±0.01 g	0.4
Addition of ^{13}C-PCBs	10.0 µL	±0.2 µL	2
Spiked standard	100.0 µL	±0.3 µL	0.3
% lipid - pipette	1.00 mL	±0.01 mL	1
- test tube	11.0 mL	±0.1 mL	0.9
GPC - test tube	7.0 mL	±0.1 mL	1.4
Addition of t-NON	20.0 µL	±0.5 µL	2.5
Final sample volume	20 µL	±2-5 µL	10-25
Sample volume with t-NON	20 µL	---	5
GC injection - manual	5.0 µL	±0.1 µL	2
- automatic	10.0 µL	±0.2 µL	2

Total error was 7%, after correction of the final sample volume by t-NON.

Table 10. Sample Recoveries of ^{13}C-PCBs

Species	N	Tissue	^{13}C-PCBs		
			^{13}C-77	^{13}C-126	^{13}C-169
Polar Bear	1	Raw Blubber	77[1]	99	95
	1	Cooked Blubber	77	99	95
Narwhal a	11	Blubber	73-85[2]	79-98	78-93
Beluga a	8	Blubber	53±8[3]	54±9	53±8
Beluga b	6	Blubber	73-85	79-98	78-93
Beluga c	1	Blubber	77	99	95
Charr a	8	Whole Fish	77	99	95
Charr c	4	Whole Fish	52±10	56±10	57±10
Charr d	4	Whole Fish	63±16	64±15	63±13
Charr e	5	Whole Fish	65±15	71±15	76±14
Ringed Seal	4	Blubber	77	99	95
Walrus	5	Blubber	77	99	95

1 - single recovery

2 - range of 2 recoveries

3 - mean, standard deviation of N recoveries

locations - see Table 6 for identification

comparable to de Boer *et al.* (1991), Smith *et al.* (1990), and Mes and Weber (1989). de Boer *et al.* (1991) reported ^{13}C-PCB recoveries of 90-92% of PCB 77, 97-104% of PCB 126, and 81-93% of PCB 169; method blanks had highest values for PCB 77 (^{12}C-PCB), decreasing for PCB 126, and lowest for PCB 169. Smith *et al.* (1990) reported percent recoveries of 97±23 for PCB 81, 106±10 for PCB 77, 90±3 for PCB 126, and 77±14 for PCB 169, at the 1 ng/g (1 ppb) level. Detection limits reported by Smith *et al.* (1990) increased to a lower level as the sample size decreased.

Mes and Weber (1989) determined recoveries of PCBs 77, 126, and 169 at three concentrations - 3600, 360, and 36 ng/kg. Recoveries of method blanks were comparable at all three levels; recoveries decreased, from the highest to lowest concentrations, in the carbon column checks and samples (butter). Lowest recoveries, for all three congeners, were reported in the samples.

The present study also found an increase in detection limits with smaller sample size, and lower recoveries in samples as opposed to samples spiked with an analytical standard, and method blank samples. The lower sample recoveries might be due to a matrix effect. The method detection limit increased from 10 to 100 pg/g (based on signal to noise ratios of 3:1 in the samples), with an increase in sample size. Percent bias calculations based on the ^{13}C-PCB internal standard recoveries, at the 200 and 400 pg/µL concentrations, showed a small deviation from 0 (except for the St. Lawrence beluga and West Coast whales), indicating good method accuracy (Table A10). The St. Lawrence and West Coast samples had poor recoveries and percent bias results due to their high levels of ΣPCBs and DDT compounds. The good percent bias calculations confirms the reproducibility of the method for different sample types

containing various concentrations of non-ortho PCBs. Acceptable precision (between 0 and 50%), and a Z value within the confidence interval of 68%, was found for repeated GC injections of samples (Table A11). However, unacceptable precision was found among repeated samples of Arctic charr, indicating a large variability at low pg/g (<100) concentrations. These samples had an absolute Z value <0.97, and precision ranged from 57 to 200%. PCB 169 had the worst precision of the three non-ortho PCB congeners, and PCB 77 the best precision. This may be due to the integration, on GC-MSD, of chromatographic peaks very close to a signal to noise ratio of 3:1.

A. Ion Ratios

Ion ratios (secondary to primary ion) were used to confirm the identity of each peak in question (Table A3). Mes and Weber (1989) used a guideline of ±20% of the ratio in the standard, as well as the correct retention times, to assign a non-ortho PCB congener to the chromatographic peak. Agreement with this deviation was found in whale and fish samples from Japan, samples containing high levels (>200 ng/kg) of the non-ortho PCBs (Tanabe *et al.*, 1987a, 1987b). On few occasions were results obtained within this deviation (±20%) in this study, especially for PCB 77 (Table A12). PCB 169 could usually be determined within the ±20% guideline, PCB 126 varied from ±11 to ±153%, and PCB 77 ±0.5 to ±345%. Better agreement occurred, generally, with samples containing higher concentrations of ΣPCBs and non-ortho PCBs. However, the best agreement (±11%), for all three congeners (PCBs 77, 126, and 169), was found in Pond Inlet Arctic charr (whole fish) samples. The Husky Lake beluga samples had a lower deviation (±1 to ±49%) than the

St. Lawrence beluga and West Coast whales. The St. Lawrence beluga samples had a higher deviation (±1 to ±100%) than the West Coast whales (±31 to ±55%). In the largest deviations, a wide, broad peak in the secondary ion chromatogram was observed at the correct retention time for that ion. Using GC-MSD, it was not possible to distinguish how much of the peak was secondary ion, and how much was an interfering peak. This deviation from the standard ion ratios may have been a consequence of the low ng/kg levels being integrated (signal to noise [S/N] 3:1 or less, which could involve subjective interpretation of the MSD peaks) (Storr-Hansen and Cederberg, 1992), or interfering peaks such as chloronaphthalenes. For PCB 77, an interference in the 290 ion peak integration could be due to the presence of a tetrachlorobiphenyl breakdown fragment from the pentachlorinated di-ortho PCB 110, which coelutes with PCB 77 on a DB-5 GC column (Smith *et al.*, 1990). Ion 404.0 (for OCN) was sometimes identified in samples, although none had been added. Other researchers have detected chloronaphthalene ions as interferences in the analysis for non-ortho PCBs (B. Jansson, Swedish Environmental Protection Agency, Solna, Sweden, personal communication, 1989; Asplund *et al.*, 1990a). Analysis of the samples by high resolution mass spectrometry (HRMS), or the use of larger sample sizes might provide the answer.

3. Problems Encountered during Method Development

During the processing of samples, various analytical problems were discovered which directly affected the fractionation and recovery of the non-ortho PCBs from the carbon column. During the processing of some Arctic charr, the GPC column did not have the correct dump and collect

times and some lipid and pigments were present in the final sample. When loaded onto the carbon column, the lipids and pigments degraded its performance, decreasing sample recoveries over time. No increase in column back-pressure was observed over this period of time. Solvent clean-up could not remove these contaminants and a new carbon column had to be built. This problem was eliminated with the addition of the silica gel clean-up step (Figure 3). Haglund *et al.* (1990) reported a similar problem when analyzing biological samples using GPC and PYE columns on HPLC. Samples treated to a clean-up procedure using only 98% sulphuric acid, gave low recoveries of mono-ortho PCB 118 (2,3',4,4',5) and non-ortho PCB 77; the first congeners to elute in their respective fractions. Recoveries improved after the addition of a second clean-up by GPC. The lipids remaining after sulphuric acid treatment decreased the ability of the PYE column to adsorb PCBs. Degradation of the carbon column was also observed during the analysis of samples containing high concentrations of ortho substituted PCBs and the DDT family of compounds (Table A7 and A9). Sample recoveries decreased as increased numbers of these samples were processed on carbon (Table A9). This effect has been attributed to an overwhelming of the adsorption sites on carbon by these compounds, leaving too few sites for adsorption of the non-orthos (D. Tilluit, U.S. Fish and Wildlife, Columbia, MO, personal communication 1989; Smith *et al.*, 1984).

4. Swedish Interlab Study

This study was done in April 1991, and repeated in June and July, 1992. In April 1991, results for the unspiked and low level oil results were higher than the Swedish results; in June 1992 this study and the

Swedish results agreed for all oil samples, except for PCB 169. In July 1992 only the concentrations of PCB 77, 126, and 169 at the unspiked level, and PCB 169 concentrations in the low and high level oil, agreed for both labs. Standard deviations decreased between the initial analysis in 1991 and the repeat analysis in 1992. In the 1992 repeats the ion ratio agreement between standard and samples improved with increasing concentration. In June 1992, 0.5 g of oil was processed. Interpretation of the MSD chromatography showed that the small sample size gave poor peak shape, subsequent poor integration, and undetectable concentrations of PCB 169 (signal to noise ratio of 3:1). Sample size in July was doubled to 1.0 g. Peak shape improved and PCB 169 was detectable, although its ion ratios varied from 60 to 140% (Table 11). In both repeats, ^{13}C-PCB recoveries varied widely among the samples, due to loading problems on the GPC. ^{13}C-PCB recoveries were higher for the procedural blanks and samples spiked with an analytical standard.

In the April 1991 study, a loading problem was observed with the automated carbon column system such that only 50% of the sample was being loaded. As no immediate cause could be found to explain this, and $^{13}1C$-PCB internal standard recoveries on GPC and silica gel were >80%, the samples were processed. Sample recoveries ranged between 30-40% (of a possible 50%). At the completion of the study, a detailed look at the workings of the valves revealed that one position on valve M6 was leaking. This faulty seal allowed the sample to leak past the first T-junction on the second 3-way valve, instead of loading onto the carbon (Figure 3). The leaked sample then was loaded onto the carbon during the first few mL of the 5% DCM/hex solvent elution, resulting in immediate elution of the non-ortho congeners. This fault confirmed a

Table 11. Swedish Interlab Study Results - April 1991, June 1992, and July 1992

Sample	N	PCB Congener ng/kg			Ion Ratio		
		77	126	169	77 Std:sample	126 Std:sample	169 Std:sample
Swedish Results[1]							
Unspiked oil: mean	10-11	710±180	460±100	87±21	---[2]	---	---
Low level: mean	8-14	1080±220	950±330	158±77	---	---	---
High level: mean	9-14	2520±880	1930±450	266±108	---	---	---
July 1992							
Unspiked oil: mean	2	576±155	381±118	93±10	79:88	60:74	80:140
Low level: mean	3	674±22	481±14	110±50	79:80	60:72	80:60
High level: mean	3	1425±34	990±26	236±49	79:78	60:67	80:87
June 1992							
Unspiked oil: mean	2	653±1	411±88	<10	81:71	61:70	81:N.D.[3]
Low level: mean	3	942±52	771±110	<10	81:87	61:72	81:N.D.
High level: mean	3	2083±197	1503±100	186±165	81:96	61:60	81:45
April 1991							
Unspiked oil: mean	5	1490±110	1310±180	230±80	---	---	---
Low level: mean	5	480±230	400±200	48±10	---	---	---

High level:	mean	5	2430±270	2080±350	320±290	---	---	---

[1] - mean calculated from data from all participating labs, with outliers removed, P. de Voogt, University of Amsterdam, Amsterdam, The Netherlands, personal communication 1992

[2] - Ion ratio values not calculated

[3] - not detected

previous observation that samples must be loaded onto carbon in hexane (Simon and Mulvihill, CWS, Hull, P.Q., personal communication 1988).

5. Non-ortho PCB levels in Arctic Environmental Samples

Non-ortho substituted PCBs were detected in tissues of Arctic marine species at parts per trillion levels (ng/kg, lipid weight basis). Detailed tables outlining non-ortho PCB concentrations (wet weight, lipid weight), proportions of non-ortho PCBs to ΣPCBs, TEC calculations, are found in Tables C1 to C3, and C5 to C8. PCBs 37 and 81 were reported but not discussed, as they have very low cytochrome P4501A1 enzyme induction potential (comparable to di-ortho substituted PCBs) and as such there is little discussion in the literature about their effects. The levels of mono-ortho PCBs are included here for the interpretation of TECs, but will not be discussed further.

A. Narwhal and Beluga

Narwhal blubber from Broughton Island contained higher total non-ortho PCB levels (983±605 ng/kg) than were found in the narwhal blubber from Pond Inlet (634±457 ng/kg) (Table C2). This trend was also observed in Arctic charr from these two locations. In the Broughton Island narwhal blubber, PCB 169 was present at levels comparable to PCB 126. The pattern of non-ortho PCB concentrations was 77 > 126 ≈ 169. Narwhal blubber from Pond Inlet contained levels of PCBs 77 and 126 at similar concentrations (77 ≈ 126 > 169), with males containing higher levels than females. Beluga blubber from Broughton Island had higher concentrations of PCB 77 than of PCB 126 or PCB 169 (Table C2). PCB 126 was present in the highest concentrations in beluga blubber samples from

Pangnirtung, with levels of PCB 169 similar to levels of PCB 77. Elevated levels of PCB 169 were observed in the Husky Lake beluga. These animals had become entrapped by ice in a series of small lakes in the MacKenzie Delta in the western Canadian Arctic, and were shot as they were starving. In both sexes, levels of PCB 169 exceeded PCB 126 and PCB 77. As lipid stores were utilized for food and energy, PCBs 77 and 126 would be metabolized before PCB 169. A study of ringed seals in poor condition (low lipid levels) from the Baltic Sea, had elevated TCDD levels; other researchers had noted elevated PCB and DDT levels in marine mammals under starvation conditions (Bignert *et al.*, 1989). In the whale analyses, higher levels of non-ortho PCBs were detected in the males than in the females, reflecting a trend observed in the mono-ortho and ΣPCB concentrations (Table C2 and C3). Females of reproductive age have a decrease in their PCB body burdens as they transfer them to suckling young through lactation (Sargeant, 1986; Sargeant and Hoek, 1988; Muir *et al.*, 1988, 1990a, 1990b). Both narwhal and beluga contained similar amounts of the non-ortho PCBs (with the exception of the Broughton Island beluga), as expected from their similar lifestyles. Both mammals are exposed to PCBs through atmospheric deposition into the Arctic Ocean (local sources are considered negligible), both migrate along the pack ice in summer, and both eat at the same trophic level, with a similar diet of various species of fish and bottom-dwelling invertebrates including crustaceans, squid, and octopus (Hoyt, 1984a; Strong, 1988; Stewart and Stewart, 1989; Muir *et al.*, 1990a, 1992).

B. Arctic Charr

Differences in non-ortho substituted PCB levels were observed in Arctic charr samples from various locations (Table C2). Highest levels were observed in the samples from George River and Broughton Island (1154±780 and 1154±1029 ng/kg, respectively) and lower levels in the more northerly and westerly locations of Creswell Bay, Spence Bay, and Pond Inlet (438±462, 162±185, and 131±108 ng/kg). Paasivirta and Rantio (1991), in a study of salmon muscle from various sampling sites throughout Finland, also noted geographic differences in non-ortho PCB levels. The differences were related to whether the salmon lived in the Baltic Sea or in a lake, and the depth of the water column, demonstrating that contamination of food sources affected PCB levels. Salmon living in the Baltic Sea had ΣPCB levels 8.4 times higher than those from the Arctic region of Finland, while PCBs 77, 126 and 169 were 4.6, 7.0, and 1.3 times higher. PCB 77 was the dominant non-ortho PCB present in both the salmon and Arctic charr. Muir *et al.* (1990b) reported a similar geographic variation for the PCBs in ringed seals and polar bears from Hudson Bay and the central and western Canadian Arctic. These samples contained higher levels of total non-ortho and ΣPCBs than similar species analysed from other Canadian Arctic locations. Norstrom *et al.* (1990) found higher ΣPCB levels in polar bear and seal blubber samples from the southerly and easterly latitudes of Baffin Island and Hudson Bay, a trend noticed here with total non-ortho PCBs. This was thought to be related to the proximity of these locations to air masses carrying contaminants from southern latitudes in North America (Patton *et al.*, 1989; Muir *et al.*, 1990b; Norstrom *et al.*, 1990). Organochlorines are carried north on aerosols and in the gaseous phase,

where they are deposited on snow and pack ice. In summer runoff and melting ice transfer these contaminants to the ocean and the marine ecosystem (Bidleman *et al.*, 1989; Cotham and Bidleman, 1991).

The higher levels in George River charr than Creswell Bay and Spence Bay charr could be related to weight and age differences - George River charr were heavier than charr from the other locations (Table 6). Differences in levels were also observed among charr from Creswell Bay, Spence Bay, and Pond Inlet (Table C2). The smallest and youngest charr were from Pond Inlet, which had the lowest levels of all locations. The highest levels were in charr from Creswell Bay, which were slightly larger than the charr from Pond Inlet but less than half the size of Spence Bay charr (Table 6). The food source is likely to be the main factor determining non-ortho and ΣPCB levels in these fish (Patton *et al.*, 1989; Muir *et al.*, 1988, 1990b; Hargrave *et al.*, 1992). In Arctic charr there was not a large difference in non-ortho PCB levels between sexes, unlike the results found for whales (Table C2 and C3).

C. Ringed Seal

Ringed seal blubber from Broughton Island contained similar levels of total non-ortho PCBs as did the Creswell Bay charr (on a lipid weight basis), with males (349±102 ng/kg) having lower levels than females (628±392 ng/kg) (Table C2). When compared to charr from Broughton Island, the ringed seal blubber contained lower levels of PCB 77, but higher levels of PCB 126 and 169. ΣPCB concentrations had a similar pattern - 602±36 μg/kg (males) and 820±105 μg/kg (females) (Table C3). This is unusual but may be explained if all were young seals - the females before reproductive maturity and the males having only maternal

PCB inputs and very minimal exposure from food sources. This hypothesis can not be tested as no age data was available for the Broughton Island samples.

D. Walrus

Walrus blubber from Broughton Island had non-ortho PCB levels comparable to the concentrations found in the Broughton Island narwhal blubber (1138±1044 and 983±605 ng/kg; Table C2). The walrus samples had a wide range of non-ortho PCB and ΣPCB (4314±3555 μg/kg) levels; high levels of non-ortho PCBs corresponded to high levels of ΣPCBs (Table C2 and C3). The three samples with high ΣPCB levels were a raw, boiled, and aged bubber, whereas the samples with lower ΣPCB levels were a raw and aged blubber. This range in concentrations can be related to the diet of the walrus, which ranges from benthic invertebrates (e.g., bottom-dwelling bivalve molluscs) and Arctic charr to ringed seals (Born *et al.*, 1981; Taylor *et al.*, 1989; Muir, 1992). Born *et al.* (1981) found ΣPCB levels of 180±123 (female) to 358±309 μg/kg (male) in walruses from northwest Greenland.

E. Polar Bear

The polar bear is at the top of the Arctic marine food chain, feeding on young ringed seals (<5 years old), which in turn have fed on Arctic cod (*Boreogadus saida*) (Stirling and Archibald, 1977; Muir *et al.*, 1988, 1990b). Two samples were analysed, both from Broughton Island - a raw fat sample, and a cooked fat sample. Only the raw fat sample was used in comparing concentrations, proportions of non-ortho PCBs to ΣPCBs, and TECs. Total non-ortho PCB levels were 1272 ng/kg and

ΣPCB levels 1382 ng/kg (Table C2 and C3). PCB 126 was present in the highest concentrations, and PCB 77 and PCB 169 at similar concentrations: 126 > 169 ≈ 77.

6. Proportions of Non-ortho PCBs to ΣPCBs

Metabolism of PCB congeners is used below as the major pathway resulting in the proportion patterns seen in fish and marine mammals. However, other mechanisms to explain these proportions could be selective adsorption (uptake), differential elimination rates, and equilibrium partitioning to organs which a higher lipid content (Boon 87). These mechanisms, including metabolism, are affected by the degree of chlorination on the PCB congener (Boon *et al.*, 1984). Equilibrium partitioning is a major pathway for excretion of these chemicals by fish (Boon *et al.*, 1984, 1987). In marine mammals, excretion of a metabolite is the major pathway, and hydroxylated and methylsulfone metabolites of PCBs have been found in seal faeces (Boon *et al.*, 1987, 1989).

In all of the Arctic species analysed, males and females had similar proportions of non-ortho PCBs to ΣPCBs, even for animals with different PCB (non-ortho and ortho substituted) levels between sexes (Table C3). The proportion of non-ortho PCBs to ΣPCBs varied among species, with Arctic charr having the highest proportion, even though their non-ortho PCB and ΣPCB levels were the lowest (Table C2 and C3; Figure 6a, 6b, and 6c). In all of the Arctic charr samples, except for George River charr, PCB 77 was present in much greater proportions than PCB 126 and PCB 169, a pattern similar to Aroclor 1254 (Table C3 and C4; Figure 6b and 6c). In George River charr, PCB 77 and PCB 126 were

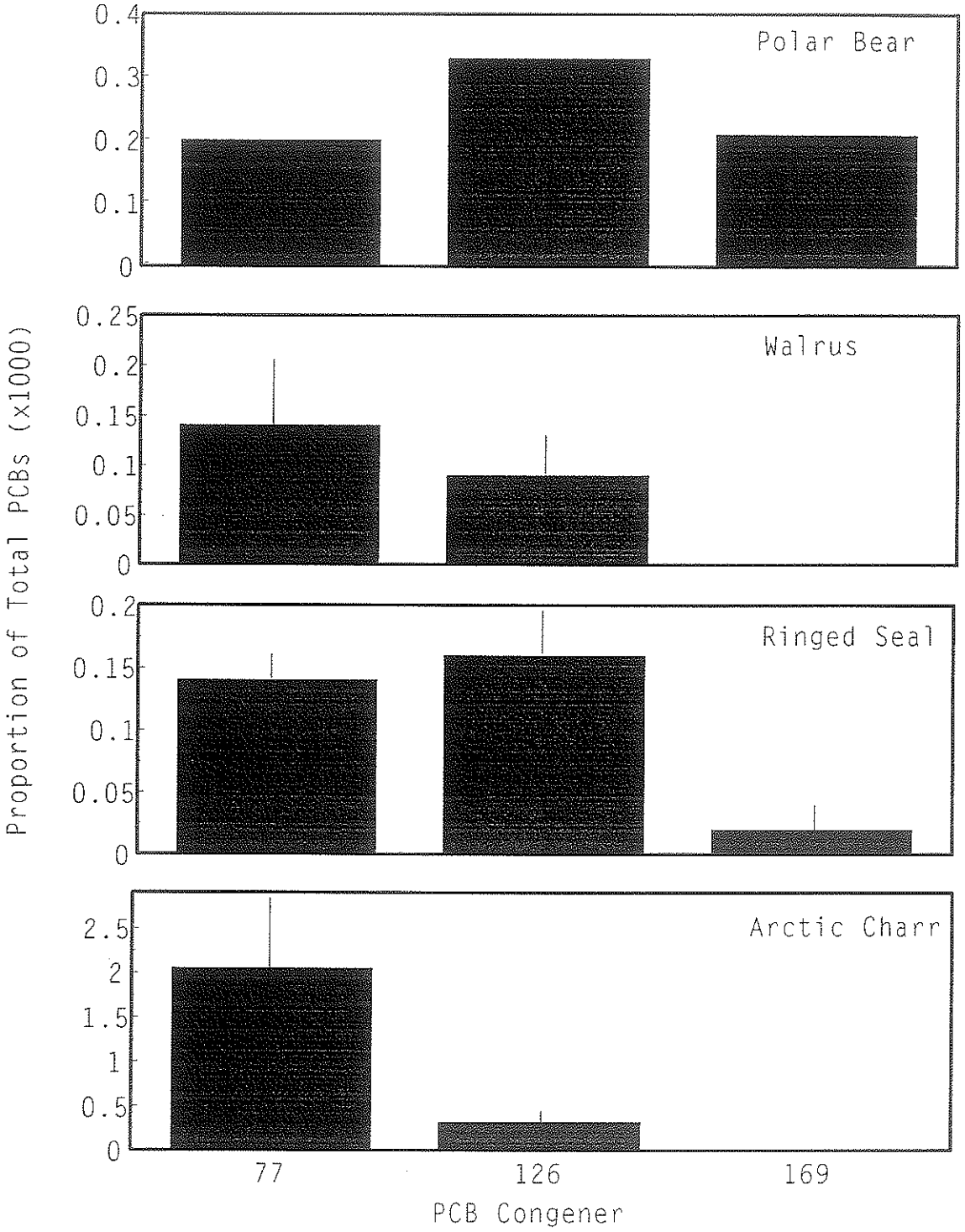

Figure 6a. Proportion of Non-ortho PCBs to Total PCB, in Broughton Island samples. Vertical line represents one standard deviation

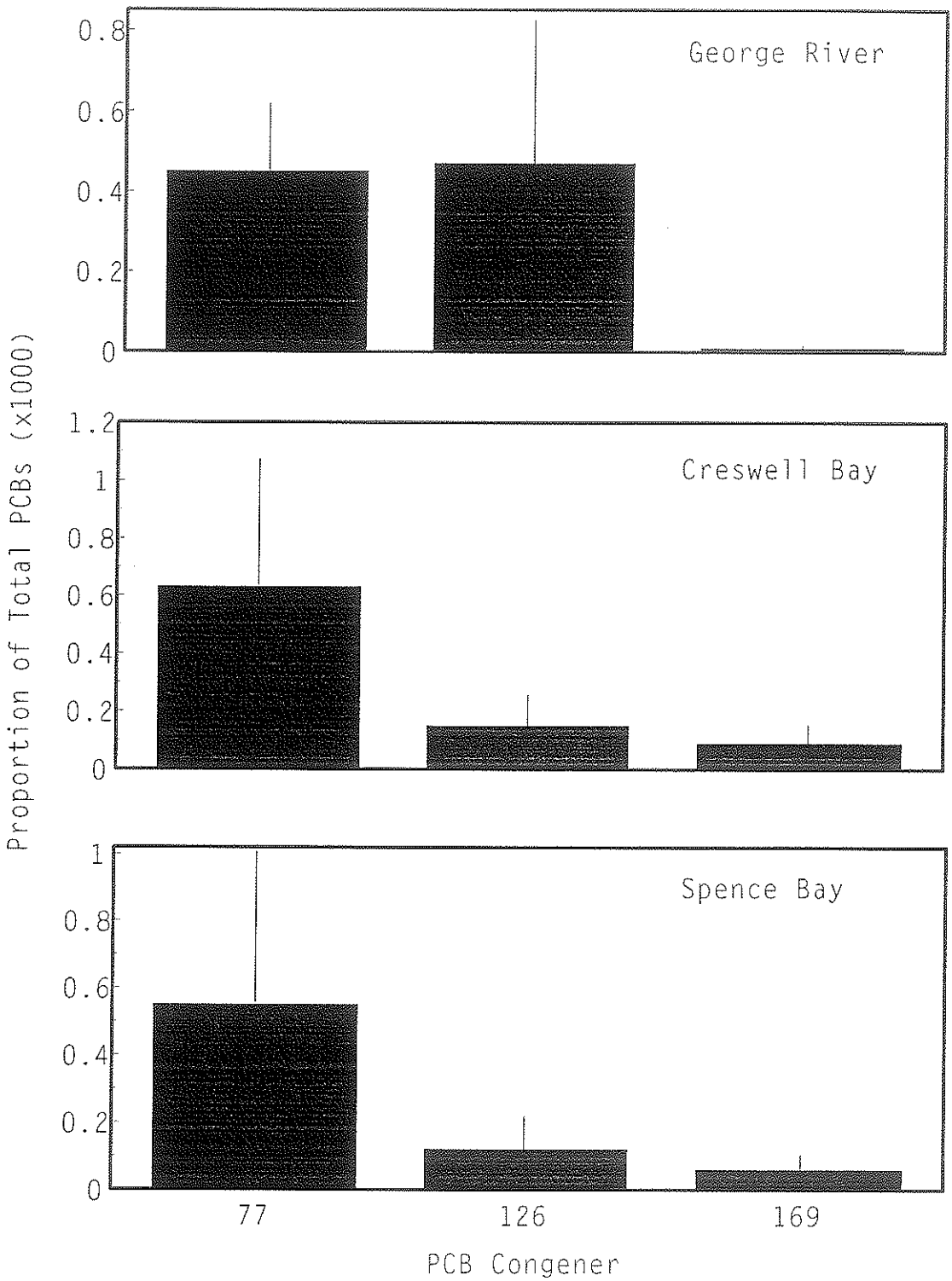

Figure 6b. Proportion of Non-ortho PCBs to Total PCB, in Arctic Charr from George River, Creswell Bay, and Spence Bay

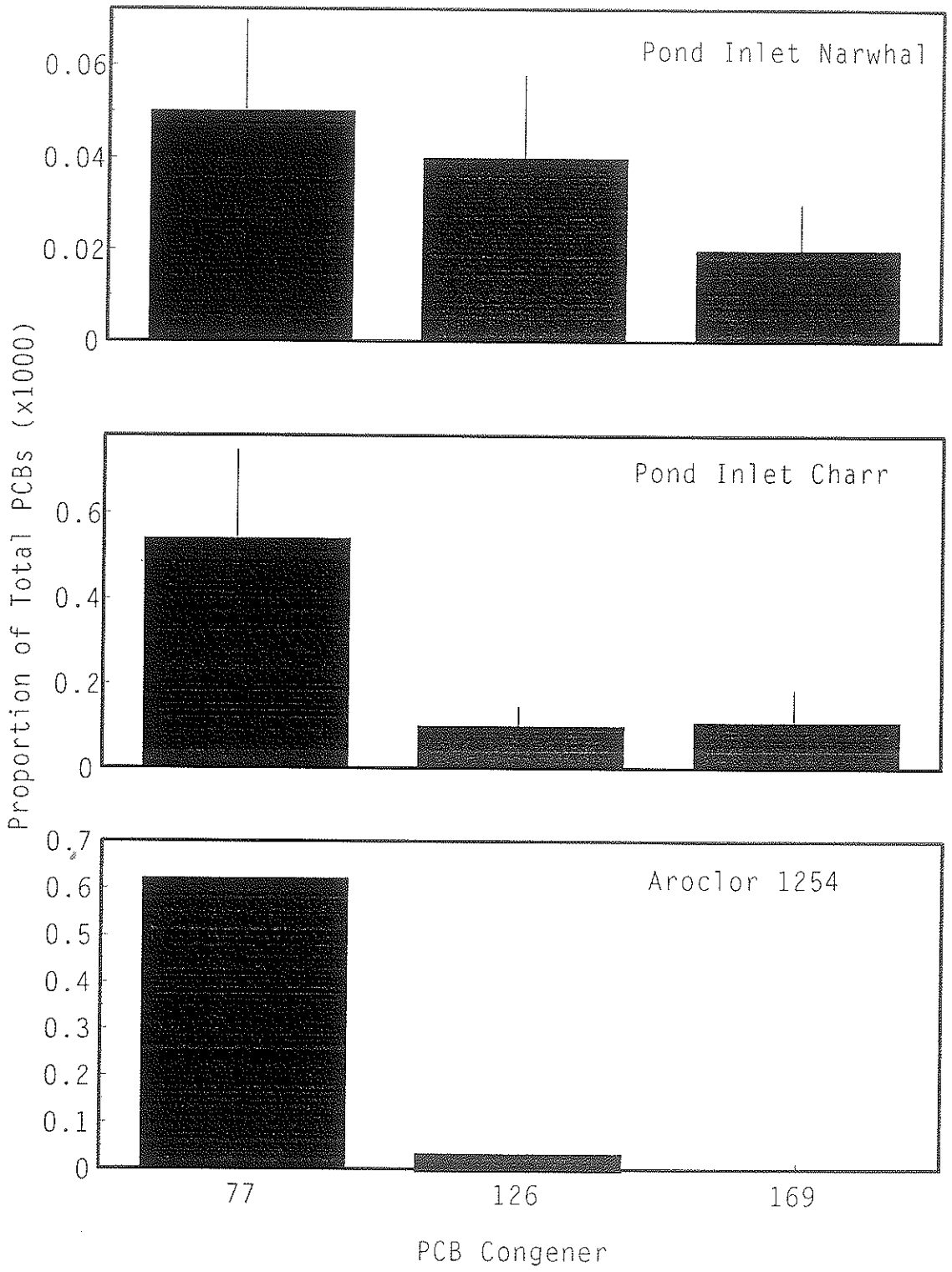

Figure 6c. Proportion of Non-ortho PCBs to Total PCB, in Aroclor 1254, and Pond Inlet Charr and Narwhal. Aroclor results from Kannan et al., 1987

present in similar proportions, and PCB 169 was at the lowest proportion for any of the charr samples. In female charr from Spence Bay, PCB 126 was found in the same proportion as PCB 169, while in female charr from Pond Inlet the proportion of PCB 169 exceeded PCB 126. ΣPCB levels in Arctic charr reflected a similar pattern of congener abundance as a 0.6:3:1 mixture of Aroclors 1242:1254:1260 (Muir *et al.*, 1988, 1990b).

Fish have a lower detoxifying capability than that of the marine mammals, and minimal metabolism and breakdown occurs as they accumulate PCBs through their food (Tanabe *et al.*, 1987b; Muir *et al.*, 1988; McFarland and Clarke, 1989). Norstrom *et al.* (1992) found Arctic charr had the lowest ability to metabolise meta-para substituted congeners, and an intermediate ability, between narwhal and beluga, and ringed seal, to metabolise meta-para unsubstituted congeners. For these reasons, fish have the greatest proportions of non-ortho PCBs to ΣPCBs. Paasivirta and Rantio (1991) observed higher proportions of non-ortho PCBs to ΣPCBs in salmon than in ringed seals from the Baltic. Baltic and Finnish Arctic salmon muscle samples had a similar pattern, even though Baltic levels were 5 to 7 times greater than the Arctic concentrations.

In ringed seal blubber, males have an enrichment of PCB 126 relative to Aroclor 1254 and Arctic charr: 126 > 77 > 169, whereas females have the same pattern as Arctic charr and Aroclor 1254 (Table C3 and C4; Figure 6a). Ringed seal blubber from the Baltic had this latter pattern (Paasivirta and Rantio, 1991). It has been suggested that a certain level of PCBs may be necessary to induce the enzymatic system and cause metabolism and breakdown (Watanabe *et al.*, 1989; Muir *et al.*, 1992; Norstrom *et al.*, 1992). PCB 77 would be metabolized first,

before PCB 126 and 169, as it is the least stable of the three congeners (Tanabe *et al.*, 1987a; Tanabe, 1988; Wehler *et al.*, 1989). The enrichment of PCB 126 in the male ringed seals could be due to the metabolism of PCB 77.

The walrus samples with low ΣPCB levels had non-ortho PCB proportions similar to the Pond Inlet narwhal and Broughton Island female ringed seal and Arctic charr, and to Aroclor 1254: 77 > 126 > 169 (Table C3, Figure 6a). The walrus samples with higher ΣPCB levels showed similar proportions and enrichment of PCB 126 as did the Broughton Island male ringed seals: 126 > 77 > 169. This change in proportions could be explained if the walrus with the high concentrations ate prey from a higher trophic level (seals versus fish) than the walrus with the low concentrations, as well as by a higher level of metabolism of PCB 77 (as for the male and female ringed seals). Walrus, as do polar bears, appear to have the enzymatic capability to metabolise adjacent meta-para substituted and unsubstituted positions on the biphenyl rings (based on the PCB congener pattern). In this process, accumulation of the higher chlorinated PCB congeners (both non-ortho and ortho substituted) occurs (Norstrom *et al.*, 1992).

Narwhal and beluga blubber, except for the Broughton Island samples, had the lowest proportions of non-ortho PCBs to ΣPCBs, $1x10^{-5}$ to $9x10^{-5}$, of all Arctic biota analysed (Table C3; Figure 6c). The proportion of PCB 77 to ΣPCB in both species was lower than in the commercial mixture ($2x10^{-5}$ to $6x10^{-5}$ versus $6x10^{-4}$) (Table C3 and C4; Figure 6c). In both species, PCB 126 and PCB 169 were present at greater proportions than was found in Aroclor 1254 (Table C4; Figure 6c). The low enrichment in narwhal and belugas is explained by their

selective metabolism of meta-para substituted congeners, resulting in a lower bioaccumulation of non-ortho PCBs relative to ΣPCBs (Norstrom *et al.*, 1992). Polar bear had proportions similar to the walruses and ringed seals, and lower than the Arctic charr. These four species have a lower metabolism of non-ortho PCBs than the beluga and narwhal (Table C3; Figure 6a) (Norstrom *et al.*, 1992). Proportions of PCB 77, 126, and 169 were higher in the polar bear than in Aroclor 1254, with PCB 126 > PCB 169 > PCB 77, due to biomagnification of these congeners (Table C3; Figure 6a and 6c).

Of the individual congeners, PCB 169 showed the greatest enrichment in its proportionality of ΣPCBs relative to Aroclor 1254, an increase from Arctic charr (196 times) to polar bear of 4118 times (Table C3 and C4; Figure 6a and 6c). PCB 126 increased 118 times (from Aroclor 1254 to George River Arctic charr), and PCB 77 was only enhanced by 34 times (Aroclor 1254 to Broughton Island Arctic charr). For PCB 77, a greater enrichment relative to Aroclor 1254 was found in Arctic charr, with a decrease in the marine mammals from polar bear to walrus to ringed seal, and then beluga and narwhal. Beluga and narwhal had the least enrichment of all the species, for all three non-ortho PCB congeners. These increases in proportionality correlate with the clearance rates, uptake equilibrium times, and biological half-lives for the three congeners in mammals (Kannan *et al.*, 1989b). The longest half-life and uptake equilibrium time, as well as the shortest clearance rate, is found for PCB 169, while the reverse is true for PCB 77. PCB 126 had intermediate values.

A. Biomagnification

Polar bears were the only Arctic species with PCB 126 levels greater than the other non-ortho PCBs; all three congeners were present at higher concentrations than were found in ringed seals (Table C2). This enrichment would occur through biomagnification, i.e. an increase in concentration relative to that in prey, of the non-ortho PCB congeners. A similar biomagnification exists for the higher chlorinated PCBs (Muir *et al.*, 1988). Polar bears can metabolize and eliminate lower chlorinated PCB congeners with adjacent unsubstituted para-meta and ortho-meta positions, including 3,4-substituted congeners (Muir *et al.*, 1988; Norstrom *et al.*, 1988). Therefore, PCB 77 comprises a smaller proportion of the ΣPCB profile in polar bears than it does in ringed seals. Comparing ΣPCB and non-ortho PCB levels for all of the Arctic species, a higher biomagnification through the polar bear food chain was obtained for the non-ortho PCBs than for the ΣPCBs (individual congeners) (Table 12). Arctic charr have been found to contain similar levels of ΣPCBs as Arctic cod, and as such will be substituted in the food chain biomagnification calculations (Muir *et al.*, 1990b). These calculations were based on knowledge that polar bears eat ringed seals, seals eat Arctic cod, and walrus eat both ringed seals and Arctic charr. In the ringed seal to polar bear link, the biomagnification factor for total non-ortho PCBs was greater than for ΣPCBs. In the charr to ringed seal to walrus food chain, the mono-ortho PCB isomers had a greater degree of biomagnification than the corresponding non-ortho PCB isomers. Greatest biomagnification was seen for PCB 170, from charr to walrus and charr to polar bear; it is not compared to a non-ortho PCB as it is a heptachlorobiphenyl. In the polar bear food chain, a larger

Table 12. Biomagnification of Non-ortho and Mono-ortho PCB Congeners, in the Arctic Marine Food Chain

PCB Congener	Biomagnification Factor for each Food Chain Link				
	Charr to Seal	Charr to P. Bear	Seal to P. bear	Charr to walrus	Seal to walrus
77	0.1	0.5	4.8	0.4	4.2
126	1.2	4.9	13.5	3.0	2.7
169	2.3	71.0	31.6	--[3]	--[3]
105	---[1]	--[1]	1.2	--[1]	6.9
118	1.7	2.7	1.6	11.8	6.9
114	---[2]	--[2]	0.4	--[2]	0.7
156	1.4	17.4	12.1	6.9	4.8
170	11.6	103	8.9	165	14.2
ΣPCB	1.8	4.2	2.3	13.1	7.2
ΣNon-ortho PCB	0.2	1.4	5.8	0.7	3.0

[1] - PCB 105 (2,3,3',4,4') not determined during the analysis of ΣPCBs

[2] - PCB 114 (2,3,4,4',5) not detected in these Arctic charr samples

[3] - PCB 169 not detected in these walrus samples

PCB 118 is 2,3',4,4',5-pentachlorobiphenyl, PCB 156 is 2,3,3',4,4',5-hexachlorobiphenyl, and PCB 170 is 2,2',3,3',4,4',5-heptachlorobiphenyl.

biomagnification = PCB concentration at the higher trophic level (e.g., ringed seal) - PCB concentration at the lower trophic level (e.g., charr)

All samples used in this calculation were from Broughton Island. Seal numbers were based on male results.

biomagnification was seen with the higher chlorinated congeners. This also occurred in the charr to walrus food chain, but no pattern comparable to this was seen in the ringed seal to walrus food chain. Paasivirta *et al.* (1989) found biomagnification factors of 38 times for ΣPCBs, 94 times for PCB 77, 107 times for PCB 126, and 160 times for PCB 169, in the salmon to eagle food chain in Finland's Archipelago Sea. Asplund *et al.* (1990b) got opposite results in comparing non-ortho and ΣPCB levels in Baltic grey seal and herring from the same locations. Non-ortho PCB concentrations were similar in both species, whereas ΣPCB levels were 80 times greater in the seal than in the herring.

7. Environmental Levels in Samples from Canada's West and East Coasts

Samples of whale blubber, obtained from locations close to the 49th parallel, off both Canada's east and west coast, and Atlantic cod from Newfoundland, contained much higher levels than samples from the Canadian Arctic (Table C10). This can be related to the proximity of these mammals and fish to local sources of PCBs (Massé *et al.*, 1986; Muir *et al.*, 1991a). St. Lawrence beluga live within a 100 km stretch in the St. Lawrence River estuary, whereas the West Coast whales move along the coast (Sargeant and Hoek, 1988; Hoyt, 1984b). The killer whales and porpoises obtained for this study were permanent residents of the Strait of Georgia. The limited range of the St. Lawrence beluga increases their exposure to contaminants moving downstream from industrial sources upstream and from the Great Lakes. Higher ΣPCB levels (on a lipid weight basis) were observed in the St. Lawrence beluga than the West Coast whales, although non-ortho PCB levels were higher in the latter (Table C10 and C11). As in the Arctic samples,

higher levels of non-ortho PCBs and ΣPCBs were observed in males than females (Table C10 and C11). The exception to this were the male and female killer whales. Full data tables for these samples are located in Tables C9 to C15.

A. Newfoundland Cod

Similar total non-ortho PCB (527±122 ng/kg) and ΣPCB (669±57 µg/kg) levels were present in the cod liver samples from Newfoundland (Atlantic cod), and the Arctic charr from George River in northern Québec, when compared on a lipid weight basis (Table C2 and C10). By comparison, Atlantic cod from the Arctic coast of Finland contained 3170 ng/kg total non-ortho PCBs and 572 µg/kg ΣPCBs, and from the Baltic Sea 4980 ng/kg non-ortho PCBs and 4794 µg/kg ΣPCBs (Paasivirta and Rantio, 1991). The cod inhabit waters around Newfoundland and Labrador, as well as areas of shipping lanes and discharge from the heavily polluted St. Lawrence River (Massé *et al.*, 1986; Martineau *et al.*, 1988; Scott and Scott, 1988). Cod eat a diet of crustaceans when young; after attaining a length of 50 cm, they eat fish (Scott and Scott, 1988). These factors would contribute to cod acquiring high PCB levels from its food sources. This fish may be a minor part of the food web for the St. Lawrence beluga; however, the ortho substituted PCB pattern is similar in both species (Massé *et al.*, 1986).

B. St. Lawrence Beluga

The St. Lawrence beluga samples were from stranded or beached animals, and may not be representative of that population (Sargeant, 1986; Martineau *et al.*, 1987, 1988). Non-ortho PCB levels in blubber

from these mammals ranged from 5093±7123 ng/kg for males, and 4339±4372 ng/kg for females, an increase of 6 to 8 times over Arctic whales (Table C10). ΣPCB levels ranged from 179400±131500 µg/kg in males, to 33120±20470 µg/kg in females (Table C11). Massé *et al.* (1986) found a ΣPCB pattern similar to a mixture of Aroclor 1254 and 1260; this pattern was also found in Atlantic cod from the North Atlantic. The advanced age (>20 GLGs) of these beluga may account for their high ΣPCB levels, along with their exposure, through the food chain, to the industrial pollution of the St. Lawrence River (Massé *et al.*, 1986; Martineau *et al.*, 1987, 1988; Muir *et al.*, 1990a).

C. West Coast Whales

The West Coast samples were strandings and dead marine mammals from locations along south Vancouver Island, both the west and east sides, and from sites on the mainland close to the U.S. border. No information was sent with these samples detailing age, length or weight. Highest total non-ortho PCB (11760±5460, 32460±5460 ng/kg)and ΣPCB (34150±17760, 43760±10790 µg/kg) levels were seen in the killer whale and false killer whale (Table C10 and C11). The female killer whale (n=1) contained higher levels of non-ortho PCBs than the males (Table C10). Coastal killer whales are year-round residents and are piscivorous (Hoyt, 1984a, 1984b). False killer whales are also piscivorous and coastal inhabitants (Hoyt, 1984b; Slijper, 1984). Harbour porpoises live in the same coastal area year-round and are piscivorous (Hoyt, 1984a, 1984b). Dall's porpoises live in immediate offshore waters and eat a similar diet to the harbor porpoises (Hoyt, 1984a, 1984b). This similarity in food source is reflected in the

comparable levels of total non-ortho PCBs (8200±5840, 8470±8530 ng/kg), and ΣPCBs (11280±9050, 10580±8960 µg/kg) in the two porpoise species (Table C10 and C11). No large difference existed between the non-ortho PCB levels in the male and female harbour porpoises. The higher non-ortho PCB levels in the false killer whales and killer whales in relation to the porpoises could be due to age differences, as well as consumption of fish that feed at a higher trophic level, by the whales. Lowest levels of both non-ortho PCBs (12400 ng/kg) and ΣPCBs (5650 µg/kg) were observed in the dolphin (n=1), a piscivore that lives offshore (Hoyt, 1984a, 1984b) (Table C10 and C11). Only one species of dolphin lives off Canada's West Coast - the Pacific white-sided dolphin; no other species identification was sent with that sample (Hoyt, 1984a, 1984b).

8. Proportions of Non-ortho PCBs to ΣPCBs

Proportions of non-ortho PCBs to ΣPCBs in the Atlantic cod reflected a pattern like that seen in the Arctic charr: 77 > 126 > 169. For the individual congeners, PCBs 126 and 169 were present in similar proportions in both species, with the cod containing lower proportions of PCB 77 than the charr. As was observed in Arctic charr and Arctic whales, the cod contained a greater proportion of non-ortho PCBs to ΣPCBs than the St. Lawrence beluga (5 to 37 times greater) (Table C3 and C11; Figure 6c and 7a). The proportion of non-ortho PCBs to ΣPCB had a similar profile in the Arctic and St. Lawrence beluga (77 ≈ 126 > 169). This suggests that both populations have a similar capacity to metabolise these congeners and that similar proportions of non-ortho PCBs to ΣPCBs exists in their food sources. The beluga's food sources

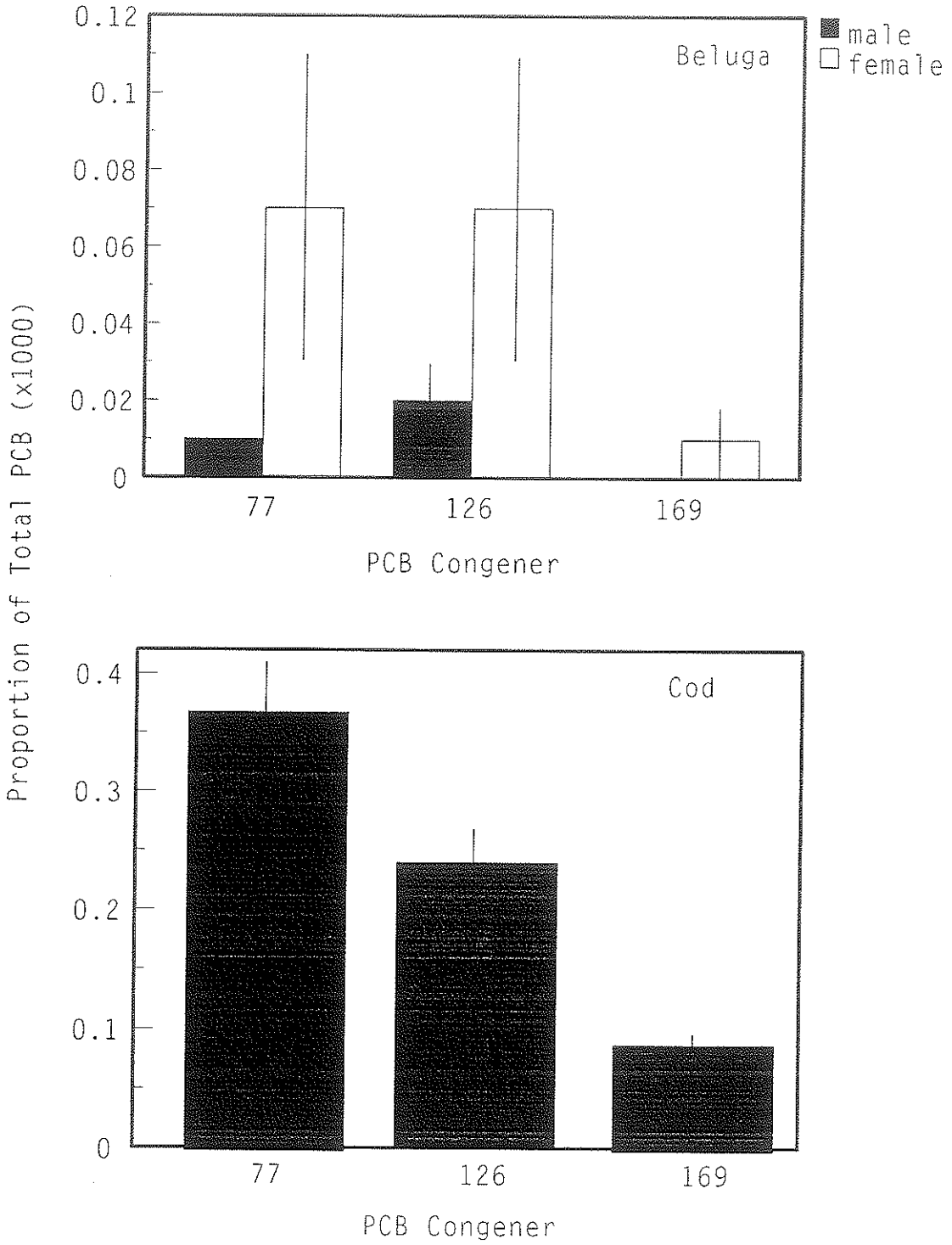

Figure 7a. Proportion of Non-ortho Substituted PCBs to Total PCB, in St. Lawrence Beluga Blubber and Newfoundland Cod Liver Oil

are exposed to PCBs only through atmospheric deposition processes in the Arctic, whereas in the St. Lawrence River their food sources have a direct exposure of PCBs through industrial pollution sources upstream. The St. Lawrence beluga, however, have lower proportions of non-orthos to ΣPCBs, in comparison to the Arctic whales. This could be explained by a higher activity of the P450 enzyme system, induced by the higher non-ortho and ΣPCB levels in the St. Lawrence beluga (Watanabe *et al.*, 1989).

The proportion of non-ortho PCBs to ΣPCBs was higher in the West Coast whales relative to the Arctic narwhal and beluga, and St. Lawrence beluga, ranging from $8x10^{-5}$ to $8x10^{-3}$ (Table C3 and C11; Figure 7b). One difference among these marine mammals is the family to which they belong - the West Coast Whales belong to the Delphinidae and Phocoenidae families, and the beluga and narwhal to the Monodontidae family. Kannan *et al.* (1989a) found a decrease in non-ortho and ΣPCB levels in killer whale relative to Dall's Porpoise. The killer whale samples were from the open ocean off Japan, and had levels of 43700-71400 ng/kg for total non-ortho PCBs, and 350000-410000 µg/kg ΣPCBs. The porpoises lived in the Seto-Naikai Sea, a coastal zone between Japan and the mainland, and had levels of 484-3950 ng/kg for total non-ortho PCBs, and 1000-18000 µg/kg for ΣPCBs. These two cetaceans had similar proportions of non-ortho PCBs to ΣPCBs as the Canadian samples. Dall's porpoise had proportions of $3x10^{-4}$ for PCB 77, $2x10^{-5}$ for PCB 126, and $1x10^{-5}$ for PCB 169 (Table C4). The killer whale had proportions of $1x10^{-4}$ for PCB 77, $1x10^{-5}$ for PCB 126, and $2x10^{-5}$ for PCB 169. Pacific white-sided dolphins analysed by Tanabe contained 18080-43800 ng/kg total non-ortho PCBs, and 40000-71000 µg/kg ΣPCBs, with proportions of non-ortho to

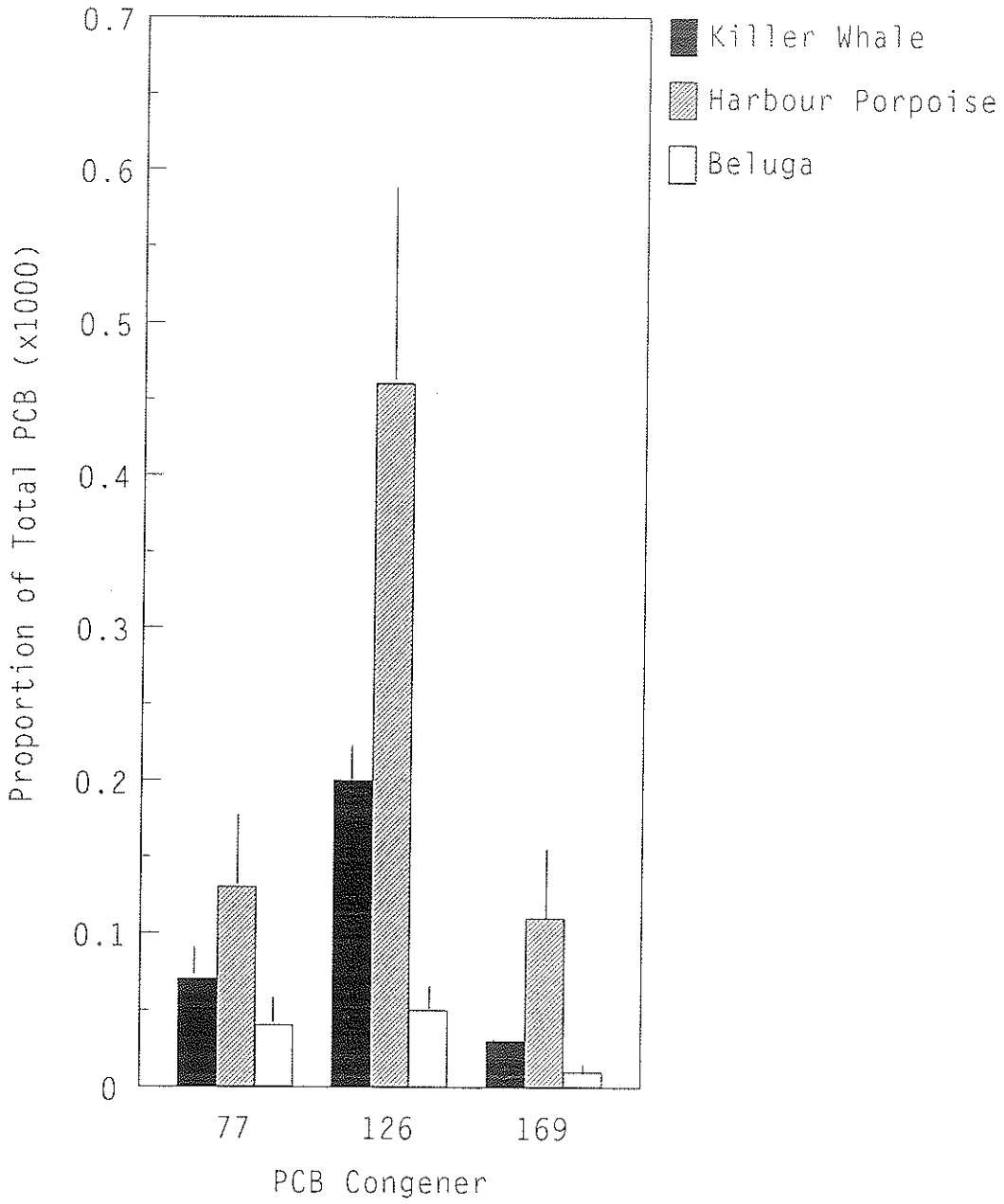

Figure 7b. Proportion of Non-ortho Substituted PCBs to Total PCB, in West Coast Killer Whales and Harbour Porpoises, and St. Lawrence Beluga

ΣPCBs similar to Kannan's samples (Tanabe *et al.*, 1987a). Kannan's and Tanabe's results support Norstrom's hypothesis that cetaceans are able to metabolise meta-para substituted PCB congeners using cytochrome P450 a, c, and d isozymes (3-MC-type activity) (Tanabe *et al.*, 1987a; Kannan *et al.*, 1989a; Norstrom *et al.*, 1992). The Japanese cetaceans may have higher activity of the cytochrome P450 isozymes due to the greater amounts of non-ortho and ΣPCBs present (Watanabe *et al.*, 1989). Higher proportions of non-ortho PCBs relative to ΣPCBs were found in the harbour porpoise and dolphin blubber relative to the killer whale and false killer whale (0.03-0.60 to 0.03-0.34). The male Dall's porpoise (n=2) contained the highest proportions of non-ortho PCBs to ΣPCBs for PCB 77 ($2x10^{-3}$) and PCB 126 ($8x10^{-3}$) of both Arctic and mid-latitude samples analysed, as its ΣPCB levels were lower than the total non-ortho PCB levels.

A. Biomagnification

Atlantic cod were used in the food chain biomagnification calculations because they may be part of the St. Lawrence beluga food web. Major prey species of these beluga include eels, crustaceans and fish, including Atlantic cod (Hoyt, 1984a; Béland and Martineau, 1988). The cod in this study were from the North Atlantic and not the St. Lawrence River estuary. Cod have a varied diet (Scott and Scott, 1988), and those from the North Atlantic may have lower PCB levels due to a less contaminated food web. As such, the biomagnification factors for cod to beluga may be underestimated, but no non-ortho PCB data exist for fish from the St. Lawrence.

In the St. Lawrence beluga, greatest biomagnification of the non-ortho PCBs, relative to Atlantic cod, was observed for PCB 126 (Table 13). A higher biomagnification was observed for the mono-ortho PCBs and ΣPCBs than the non-ortho PCB isomers and total non-ortho PCBs. As in the Arctic food chain, PCB 170 showed the greatest biomagnification. These results agree with the proportion data, where non-ortho PCBs have a lower proportion relative to ΣPCBs than the mono-ortho PCBs, which reflects the beluga's metabolism of non-ortho PCBs. As such, the ortho-substituted PCB congeners biomagnify to a much greater extent than do the non-ortho substituted congeners (Norstrom *et al.*, 1992). de Boer *et al.* (1991) examined the biomagnification from North Sea cod to a dolphin from the west side of Ireland. Comparable levels of non-ortho PCBs were found between this dolphin (12200 ng/kg) and the Canadian sample. In comparing the difference in congener levels among species, the Irish dolphin had PCB 77 levels comparable to the cod, PCB 126 was two times higher, and PCB 169 increased by 24 times. The Canadian West Coast dolphin had similar PCB 77 levels, levels of PCB 126 were 26 times higher, and PCB 169 was 6 times lower than in the East Coast Atlantic cod.

9. Toxic Equivalent Concentrations

TEC values calculated in this study are based on the TEF values calculated with values reported by Safe 1990 and Smith *et al.*, 1990. Future research will provide a larger toxic potential data base, applicable to both terrestrial and marine species, and as such these values will change with time. The TEC values were calculated from non-ortho and mono-ortho PCB data only. For many of the samples, PCDD/F

Table 13. Biomagnification of Non-ortho and Mono-ortho PCB Congeners, from Atlantic Cod to St. Lawrence Beluga

PCB Congener	Biomagnification Factor for the Food Chain Link[1] Atlantic cod to St. Lawrence Beluga
77	4.1
126	21.7
169	0.8
105	12700
118	253
114	2040
156	---[2]
170	2680
ΣPCB	268
ΣNon-ortho PCB	9.7

1 - calculations were performed using the male St. Lawrence beluga

2 - PCB 156 not detected in the St. Lawrence beluga samples

data were not available or had been calculated on pooled as opposed to individual samples. In Arctic charr levels were close to detection limits (M. Whittle, DFO, Burlington, ON, personal communication, 1991). In Arctic samples PCDD/F levels were significant in ringed seal, where they contributed 25% of total TEC (Norstrom *et al.*, 1990). In West Coast whales, St. Lawrence beluga, and the other Arctic marine mammals they contributed <5% to total TEC (Norstrom *et al.*, 1990; Muir *et al.*, 1991a; Norstrom *et al.*, 1992).

A. Arctic Marine Mammals and Fish

Toxic equivalent concentrations (TECs), in all Arctic samples with the exception of polar bear, Husky Lake beluga, and Broughton Island narwhal and Arctic charr, were directly related to the concentrations of PCB 126 and PCB 105 in the sample (Table C7 and C8; Figure 8a and 8b). In the polar bear, PCBs 126 and 169 were the main contributors, in the Husky Lake beluga, PCBs 105 and 169, and in the narwhal, the mono-ortho PCBs 105 and 114. PCB 105 was not determined during ortho substituted PCB analysis of the Arctic charr from Broughton Island; its TEC contribution from PCB 105 was calculated as an average of the other Arctic charr. In Broughton Island Arctic charr PCBs 77 and 126, followed by PCB 105, were the major contributors to TEC; Arctic charr from all other locations had TECs determined by their levels of PCBs 105 and 126. TEC levels in Arctic charr followed the same trend as non-ortho PCB and ΣPCB levels, increasing from Pond Inlet to Spence Bay to Creswell Bay to Broughton Island, and to George River. Arctic charr had the lowest TECs, followed by Broughton Island narwhal, ringed seal, female beluga and narwhal from all locations, walrus, polar bear, and

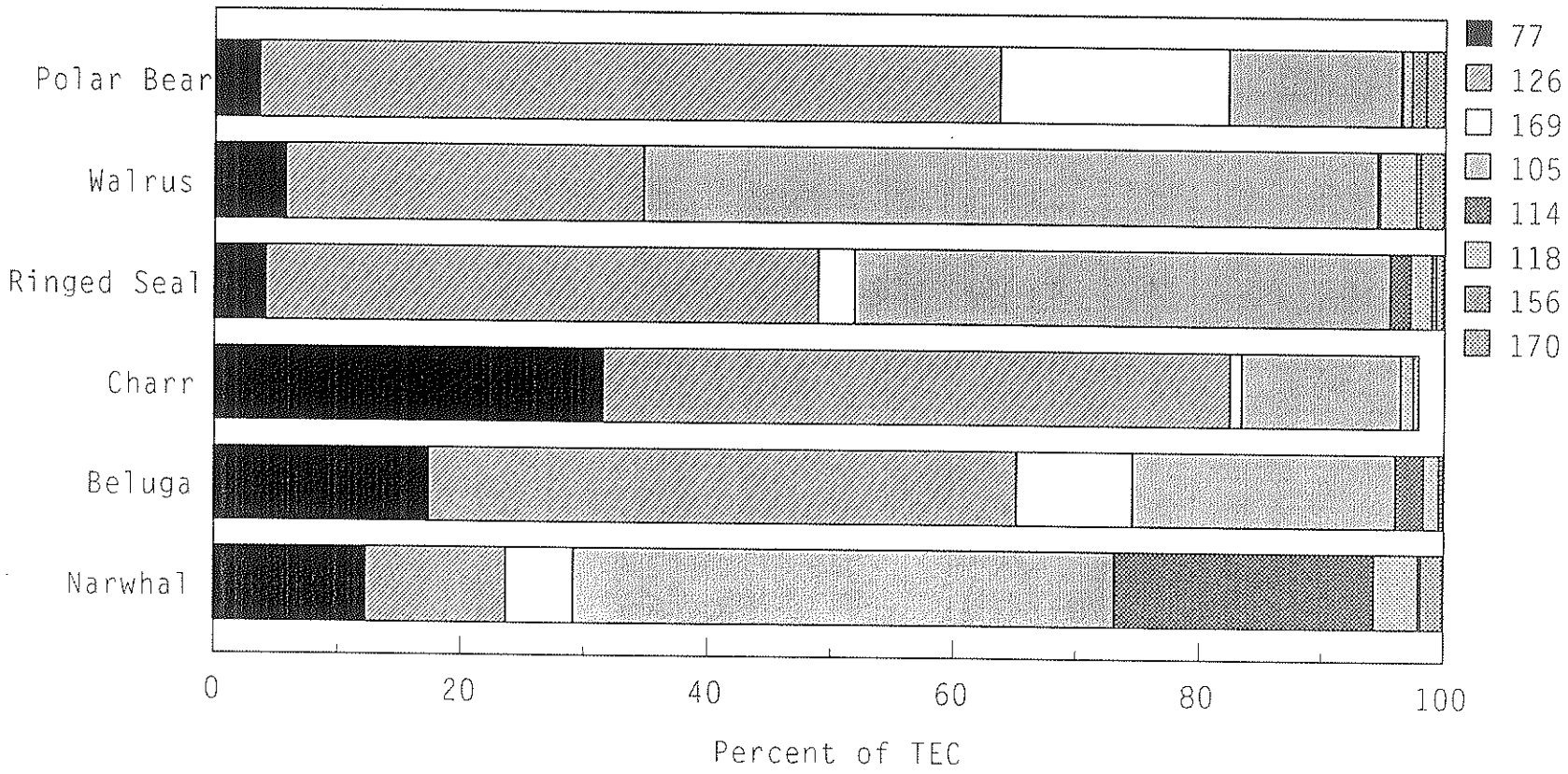

Figure 8a. Percentage of TEC, from Non-ortho and Mono-ortho Substituted PCBs, in Species from Broughton Island

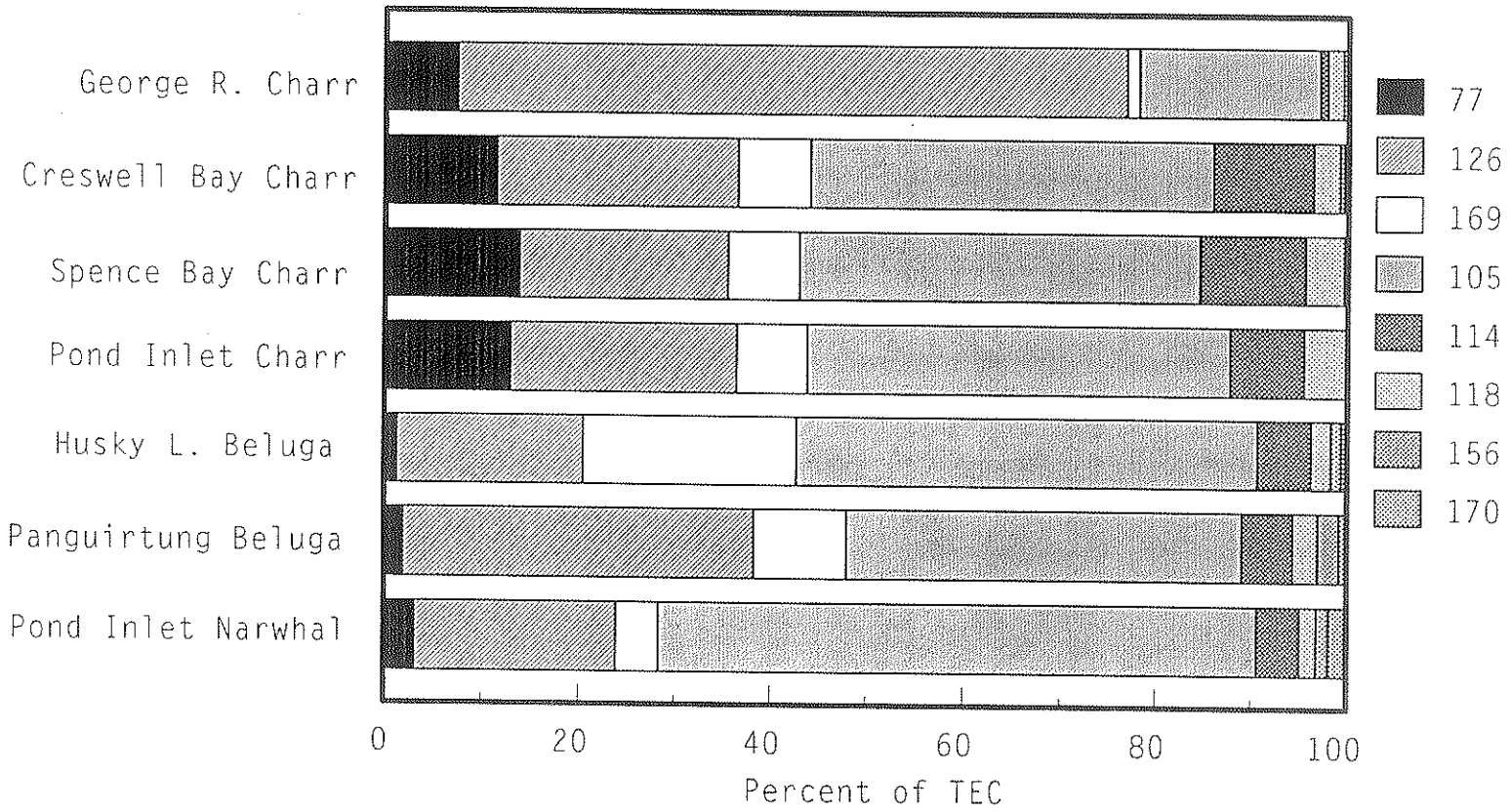

Figure 8b. Percentage of TEC, from Non-ortho and Mono-ortho Substituted PCBs, in Arctic Fish and Marine Mammal Species

the male beluga and narwhal with the highest concentrations. TECs followed the sex differences observed in the non-ortho and ΣPCB levels, with higher levels in the male of the marine mammal species. Similarly, little difference was observed between male and female Arctic charr (Table C7 and C8). The TEC levels for Arctic charr, as calculated in this study, may be overestimated. Work done by Walker and Peterson (1991) on rainbow trout eggs (*Oncorhynchus mykiss*) suggested that non-ortho PCBs had a lesser effect on early life mortality in these fish than was expected based on their toxicities in mammals. In the Husky Lake and Pangnirtung beluga, PCB 77 contributed less to TEC than the mono-ortho PCBs 105, 114 (2,3,4,4',5-), and 118 (Table C7 and C8). This can be explained by the high levels of PCB 126 and 169, relative to PCB 77, observed in these samples (Table C2; Figure 8b). A food chain effect can be seen by the increase in TECs from Arctic charr to ringed seal to polar bear, and Arctic charr to ringed seal to walrus (Table C6 and C7). A greater increase was seen in the walrus food chain. As with the non-ortho and ΣPCB levels, female ringed seals contained higher TECs than the male ringed seals (Table C2, C3, C6, and C7).

B. East and West Coast Marine Mammals and Fish

Highest TEC levels were found in the St. Lawrence beluga, followed by the West Coast false killer whale, Dall's porpoise, killer whale, harbour porpoise, and dolphin, and lastly the cod. A similar decrease, from marine mammal to fish, was observed in the Arctic species. The cod had five times higher TEC than the George River charr, and a greater proportion of its TEC came from the non-ortho rather than the mono-

ortho substituted PCBs (Table C7, C8, C14, and C5, Figure 8b and 9). The cod had the lowest PCB 105 contribution to TEC of all the species analysed (Table C15). In the whales (both east and west coast), TEC contributions were primarily from PCBs 105, 126 and 169, a comparable pattern to the Arctic narwhal and beluga (Table C7, C8, C14, and C15; Figure 8a, 8b, and 9). In the St. Lawrence beluga, unlike the Arctic beluga with lower non-ortho and ΣPCB levels, PCBs 105 and 126 make a larger contribution to ΣTEC than PCB 169, even though PCB 126 is present in similar proportions in both locations. These beluga had TEC levels ten times greater than the levels found in the cod. TEC levels and ΣPCB levels were 18 times greater in St. Lawrence female beluga than the female Arctic beluga, and up to 32 times greater for the males (Table C3, C7, C8, C11, C14, and C15). Similar increases in ΣPCB concentrations were observed by Muir *et al.* (1990a). The West Coast whales, with the exception of the false killer whale, showed a similar increase in TEC over Arctic narwhal and belugas as seen in the St. Lawrence beluga - 16 times greater for females, 28 times greater for males. In the false killer whale, TEC levels increased 50 times for females, and 42 times for males over the levels in Arctic whales. The false killer whale and killer whale blubber samples had the highest TEC levels, then the harbour porpoise and Dall's porpoise, and the lowest TEC levels were found in the dolphin, the offshore species. This mammal was the only West Coast whale to have no PCB 169 contribution to TEC, an observation also reported in walrus (Table C7 and C14). This pattern reflects the concentrations of non-ortho PCBs and ΣPCBs in these species.

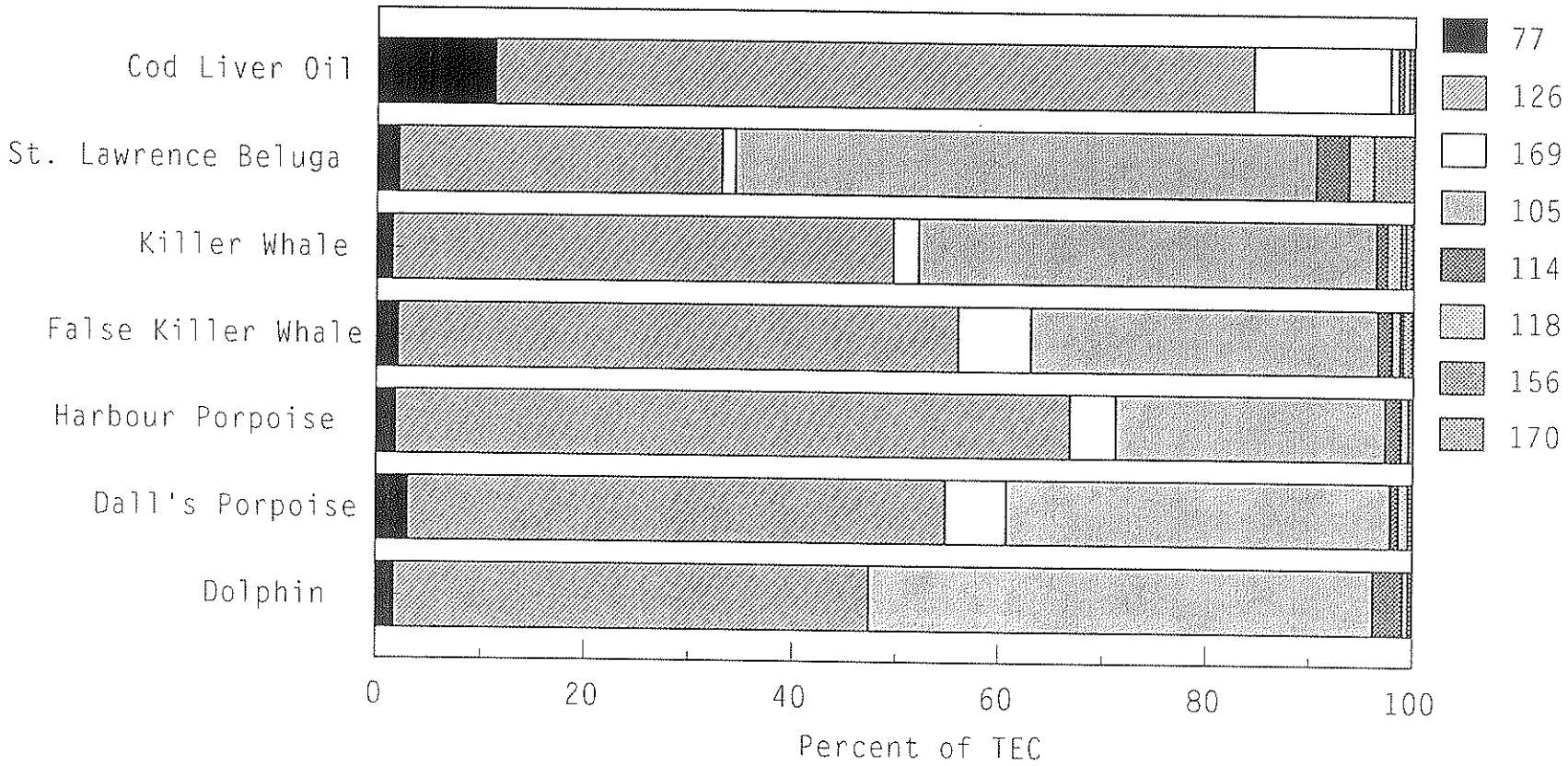

Figure 9. Percentage of TEC, from Non-ortho and Mono-ortho Substituted PCBs, in Cod Liver and Marine Mammals, South of 60 N

Summary and Conclusions

The methodology developed in this study was used in the analysis of trace ng/kg levels, as well as µg/kg levels of non-ortho substituted PCBs. Percent bias and precision measurements indicate the method is reproducibile for a range of sample types (whole fish, blubber, fat). Good accuracy was obtained for the ^{13}C-PCB internal standard results. Recoveries within each batch of samples analysed were consistent; decreasing recoveries in the St. Lawrence beluga and West Coast whale samples were explained by their high (parts-per-million) levels of ortho substituted PCBs and DDT compounds. Acceptable agreement existed between the results from this study, and the mean results from all of the labs in the Swedish Interlab Study. In the three analyses of the interlab samples, recovery problems were traced back to sample loading on the FMS pumping system or on the automated GPC. Poor precision in the analysis of trace parts-per-trillion levels (<100 pg/g) was related to peak integration, at a signal to noise ratio close to 3:1, on the GC-MSD. Sample ion ratios were usually greater than ±20% of the standard ratios, with a larger deviation found in whole fish rather than marine mammal blubber. The addition of the silica gel clean-up before the carbon procedure has lengthened the life of the carbon column, as well as eliminating some interfering noise peaks at the low levels.

Non-ortho PCB congeners 77 (3,3'4,4'), 126 (3,3'4,4'5), and 169 (3,3'4,4'5,5'), were detected in the Arctic marine food chain at parts-per-trillion (ng/kg) levels, with concentrations and TECs increasing through the food chain. Levels in cod liver oil and whale blubber

samples from the mid-latitudes of Canada ranged from parts-per-trillion in the cod, to parts-per-billion (μg/kg) in whale blubber. Non-ortho PCBs were found to bioaccumulate and biomagnify, to various degrees, through the Arctic food chain. In the Arctic charr to ringed seal to polar bear food chain, the biomagnification of non-ortho PCB isomers was greater than for the ortho substituted PCB congeners. In the Arctic charr to walrus, ringed seal to walrus, and ringed seal to polar bear food chain, only the latter showed a greater biomagnification for total non-ortho PCBs than ΣPCBs; otherwise, biomagnification of ΣPCBs was greater than for total non-ortho PCBs (Table 12). In the Atlantic cod to St. Lawrence beluga food chain, ΣPCB levels and mono-ortho PCB isomers biomagnified to a greater extent than for total non-ortho PCB levels and the non-ortho PCB isomers (Table 13). Total non-ortho PCB and ΣPCB biomagnification in the beluga agrees with their selective metabolism of the meta-para substituted PCB congeners, as reported by Norstrom *et al.* (1992). This increases the proportion of ortho substituted PCBs in relation to the non-ortho congeners; thus, greater biomagnification should exist for the ortho substituted congeners. Arctic charr, from five locations, had differing concentrations of non-ortho PCBs and ΣPCBs, but in all cases the proportion of non-ortho PCBs to ΣPCBs was higher than in Arctic marine mammal species. This is thought to be due to the Arctic charr having a lower ability to metabolise these congeners. Highest non-ortho PCB concentrations were observed in the George River and Broughton Island charr, the most southerly and westerly samples. This parallels observations in ΣPCB concentrations reported by Muir *et al.* (1990b) and Norstrom *et al.* (1990). The lowest proportion of non-ortho PCBs to ΣPCBs were found in

the Arctic beluga and narwhal, and St. Lawrence beluga. These cetaceans demonstrated a greater ability to metabolise the non-ortho PCB congeners than do walruses, polar bears, ringed seals, and Arctic charr (in that order). Higher proportions were found in the Arctic beluga, with low levels of ΣPCBs, than in the St. Lawrence beluga, which have levels of ΣPCBs 18 to 32 times the Arctic beluga. The proportion of non-ortho PCBs to ΣPCBs, in West Coast whales from the families Delphinidae and Phocoenidae, seems to indicate that these mammals have a metabolic capacity for PCBs similar to that of the Arctic charr. This differs from the metabolic capacity seen in the whale family Monodontidae. Varying levels of non-ortho PCBs and ΣPCBs, among samples from the same species that live in different areas (e.g., the high Arctic and Northern Québec), demonstrates the important effect of contamination of the food web, on concentrations in the entire food chain.

TEC calculations showed that non-ortho and mono-ortho PCBs were the major contributors to total TEC, with PCBs 126 and 105 having the largest contribution in all species, except for Atlantic cod, polar bear, and the Husky Lake beluga blubber samples. In these latter samples PCB 126 and 169 were the two largest contributors to TEC. Fish acceptable for human consumption in Canada must have levels of ≤20 ng/kg of 2,3,7,8-TCDD. Under these guidelines, walrus, narwhal, beluga, and polar bear exceed this value, assuming 20 ng/kg of 2,3,7,8-TCDD is equivalent to 20 ng/kg TEC of non- and mono-ortho PCBs. Consumption on a regular basis of the fat of these marine mammals by the Inuit could lead to chronic health problems. Exposure to PCBs due to consumption of Arctic biota by the Inuit is evident from the higher levels found in northern Québec women. Women from this part of Québec have ΣPCB levels

six times greater, and non-ortho PCB levels three to seven times greater than women from southern Québec (Dewailly *et al.*, 1991). However, a switch to a diet similar to southern Canadians could cause its own set of health problems (Kinloch *et al.*, 1992). Health problems to newborns, exposed to elevated ΣPCB and non-ortho PCB levels in mother's breast milk, are being studied by Dewailly *et al.* (1991) in Inuit in northern Québec.

TEC levels in the Arctic biota were lower than in any of the biota from mid-latitude locations in Canada, and the Baltic region, Japan, and the Great Lakes. High levels of organochlorines and PCBs, including the non-ortho congeners, could be a factor in the population decline of the St. Lawrence beluga and Baltic seals (Sargeant and Hoek, 1988; ICES, 1990; Skaare *et al.*, 1990). Non-ortho PCB and ΣPCB concentrations in Canadian Arctic biota may not yet be at a level to cause health problems.

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Appendix A. Gas Chromatographic Parameters and Detailed Results from Method Development

Table A1. GC-ECD Conditions for Analysis of OC's and PCBs (except non-ortho substituted)

	Varian 6000	Hewlett-Packard 5890
column	DB-5, J&W, 60 m	DB-5, J&W, 60 m
column type	fused silica	fused silica
film thickness, i.d.	0.25 μm, 0.25 mm	0.25 μm, 0.25 mm
carrier gas	UHP hydrogen	UHP hydrogen
makeup gas	UHP nitrogen	UHP nitrogen
makeup gas flow rate	30 mL/min	30 mL/min
column head pressure	22 psi	22 psi
column linear velocity	33 cm/sec	37 cm/sec
detector type	^{63}Ni	^{63}Ni
detector temperature	300°C	300°C
injection mode	splitless	splitless
injector port purge	0.75 min	0.75 min
injector temperature	220°C	220°C
initial oven temperature	100°C	100°C
hold time	0.00 min	0.00 min
first temperature ramp	15°C/min to 150°C	15°C/min to 150°C
hold time	0.00 min	0.00 min
second temperature ramp	3°C/min to 265°C	3°C/min to 265°C
hold time	15.34 min	15.34 min
total run time	57.0 min	57.0 min

Table A2. GC-MSD Conditions for Analysis of Non-Ortho PCBs

	Hewlett-Packard 5970B	Hewlett-Packard 5971A
column	DB-5, J&W, 30 m	DB-5, J&W, 30 m
column type	fused silica	fused silica
film thickness, i.d.	0.25 μm, 0.25 mm	0.25 μm, 0.25 mm
carrier gas	UHP helium	UHP helium
column head pressure	15 psi	15 psi
column linear velocity	not measured	36 cm/sec
split vent flow rate	52 mL/min	29 mL/min
purge vent flow rate	9 mL/min	1 mL/min
detector temperature	280°C, 70EV	280°C, 70EV
injection mode	splitless	splitless
injector port purge	0.75 min	0.75 min
injector temperature	250°C	280°C
initial oven temperature	100°C	100°C
hold time	0.00 min	0.00 min
first temperature ramp	15°C/min to 150°C	20°C/min to 180°C
hold time	0.00 min	0.00 min
second temperature ramp	3°C/min to 265°C	3°C/min to 265°C
hold time	5.34 min	5.67 min
total run time	47.0 min	38.0 min

Table A3. Ions and Ion Ratios used on the MSD for PCB Congener Analysis

PCB Congener/ IUPAC No.	Primary (m/z)	Secondary (m/z)	Standard Ion Ratio	Concentration in MSD Standard (pg/μL)
Non-Ortho PCB				
3,4,4'-; 37	256	258	95.50	80
3,4,4',5-; 81	292	290	80.00	35
3,3'4,4'-; 77	292	290	80.54	60
3,3'4,4'5-; 126	326	324	65.74	40
3,3'4,4'5,5'-; 169	360	362	80.54	24
Mono-ortho PCB				
2,3,3'4,4'-; 105	326	324	60.00	54
2,3,3',4,4',5-; 156	360	362	82.00	22
Internal Standards				
^{13}C-77	304	-[1]	-[1]	400
^{13}C-126	338	-	-	400
^{13}C-169	372	-	-	400
t-Nonachlor	409	-	-	20000
octachloronaphthalene	404	-	-	8900

[1] - no secondary ions used or ion ratios calculated for the internal standards

Table A4. Integration Events for the MSD Analysis of PCB Congeners

	Ion (amu)	Time Window (min)	Threshold[1]	Dwell Time (msec)
HP5970B:	222	11.0-16.5	8	20
	222, 256, 258	16.5-20.5	6	20
	290, 292, 304, 409	20.5-26.0	6	20
	324, 326, 338	26.0-30.2	6	20
	360, 362	30.2-35.0	6	100
	372	30.2-35.0	6	20
	394, 430	35.0-38.9	8	20
	404	38.9-41.1	8	20
HP5971A:	222, 256, 258	12.0-16.0	6	20
	290, 292, 304, 409	16.0-20.0	6	20
	324, 326, 338	20.0-25.0	6	20
	360, 362	25.0-29.5	6	100
	372	25.0-29.5	6	20
	394, 430	29.5-33.8	8	20
	404	33.8-35.3	8	20

[1] - threshold is a variable that determines how sensitive data analysis is to distinguishing compound peaks from background noise (HP Unix manual, 1989)

Table A5. "Hightune" Parameters used in Sample Analysis on the MSDs

Parameters	HP-MSD5970B	HP-MSD5971A
Mass Spectrometer Parameters		
multiplier	1800, 2000	1800
dc polarity	N.A.	neg
filament	1	1
emission	on	on
amu gain	100	340
amu offset	50	82
219 width	N.A.	0.01
repeller	10.2	18.0
ion focus	0.0	56.0
entrance lens	48	21
entrance lens offset	N.A.	0.0
X-ray	44.0	60.0
mass gain	-207	290
mass offset	18	6
Acquisition and Display		
tuning masses	219, 414, 502	219, 414, 502
calibration tuning standard	PFTBA	PFTBA
mass window	5.0	5.0
averages	1	1
stepsize	0.10	0.10
scale mode	autoset	autoset
scan range: low mass	10.0 amu	10.0 amu
high mass	800.0 amu	650.0 amu
threshold	500	500
samples	2	4
Normalization Factors		
mass/charge, target %	50, 1.5	50, 1.5
	69, 100.0	69, 100.0
	131, 55.0	131, 55.0

	219, 55.0	219, 55.0
	414, 4.0	414, 4.0
	502, 4.0	502, 4.0

Mass Spectrometer Parameter Ramp Limits

parameter: minimum, maximum, stepsize		
repeller:	4.0, 10.20, 0.20	4.0, 19.80, 0.40
ion focus:	0.0, 204.0, 4.0	0.0, 127.5, 2.0
entrance lens:	0, 255, 5	0, 128, 1
X-ray:	0.0, 204.0, 4.0	0.0, 218.0, 4.0
amu gain:	0, 255, 1	0, 255, 1
amu offset:	0, 255, 1	0, 255, 1
multiplier:	0, 3000, 200	0, 3000, 50
entrance lens offset:	N.A.	0, 64, 1
219 width:	N.A.	-0.15, 0.15, 0.01

Table A6. Qualitative Fractionation of Organochlorines and Ortho-Substituted PCBs through Carbon

Class	Elution Fraction	Compound
Organochlorines	5% DCM/hex	1234TCB, 1245TCB, PCBz, HCH's, ppDDE, ppDDD, opDDT, ppDDT, mirex, photomirex, PCA, heptachlor epoxide, dieldrin, endrin, endosulfan, MeOCl, aldrin
	DCM	HCB, aldrin, OCN
	Toluene	N.D., OCN
Chlordanes	5% DCM/hex	"C", C1A, C2/U-5, C1B/U-6, C3, C4, t-chlordane, c-chlordane, t-nonachlor, c-nonachlor, heptachlor, oxychlordane, octachlorstyrene
	DCM	<10% of above chlordanes
	Toluene	N.D.
Toxaphene	5% DCM/hex	all toxaphene peaks T1-T19
	DCM	<10% T2, T12, T13, T18
	Toluene	N.D
PCBs	5% DCM/hex	di-ortho substituted PCBs in Aroclor Standards 1232, 1242, 1254, 1260
	DCM	22, 31, 33, 74, 70/76, 95/66, 56/60, 114, 118, 105, 156
	Toluene	37, 77

Table A7. Non-ortho and Mono-ortho PCB Standard Recoveries and Fractionation through Carbon

Date	PCB	5% DCM/hex 80 mL	DCM 190 mL	Toluene 130 mL	Total Recovery	Note
		Recoveries (%)				
Oct. 24/91	37	0	0	77	77	
	81	0	0	99	99	
	77	0	0	103	103	
	105	0	127	2	129	
	126	0	0	106	106	
	156	0	123	1	124	
	169	0	0	108	108	
	^{13}C-77	0	0	88	88	
	^{13}C-126	0	0	95	95	
	^{13}C-169	0	0	89	89	
Jan. 31/91	37	3	4	89	96	0.44 g carbon
	81	6	0	98	103	column,
	77	9	0	102	108	adjusted to
	105	8	79	0	86	0.66 g to
	126	5	0	103	108	eliminate non-
	156	0	83	0	83	orthos from 5%
	169	0	0	113	113	DCM/hex elution
	^{13}C-77	0	0	84	84	
	^{13}C-126	0	0	76	76	
	^{13}C-169	0	0	91	91	
Nov. 21/90	37	18	0	59	77	Carbon column
	81	19	2	67	88	fractionation
	77	15	3	65	83	done after
	105	15	64	4	83	all of the
	126	15	3	61	79	St. Lawrence
	156	15	64	5	84	belugas
	169	18	2	89	108	

Oct. 28/90	37	52	-[1]	99	151	Carbon column
	81	45	-	100	145	fractionation
	77	45	-	101	146	done after
	105	95	-	6	101	4 St. Lawrence
	126	40	-	101	141	belugas
	156	95	-	6	101	
	169	32	-	101	133	
	^{13}C-77	46	-	100	146	
	^{13}C-126	40	-	101	141	
	^{13}C-169	36	-	101	137	
Oct. 2/90	37	0	0	107±4	107	Further clean-
	81	0	0	118±2	118	up of the
	77	0	0	113±3	113	carbon column
	105	0	62±5	0	62	made Sept.
	126	0	0	133±3	133	26/90; average
	156	0	91±11	0	91	of two runs
	169	0	0	114±6	114	
Sept. 26/90	37	6	0	64	70	Average of two
	81	10	0	68	78	runs; one run
	77	12	0	69	81	only for
	105	15	17	9	41	PCB169 due to
	126	11	0	71	82	baseline noise
	156	0	25	6	31	
	169	0	0	66	66	
Sept. 18/90	37	10±4	0	99±31	109	Effect of fish
	81	11±2	0	103±32	114	lipid and
	77	13±2	2±1	113±29	128	pigments
	105	16±2	35±14	15±11	66	inadvertently
	126	16	1±1	123±22	140	loaded onto
	156	46±19	51±22	6±6	103	carbon
	169	12±11	0	noise[2]		

Oct. 11/89	37	0	0	71	71
	77	0	0	137	137
	126	0	0	78	78
	169	0	0	127	127

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1 - columns with no numbers in the DCM fraction indicate the 5% DCM/hex and DCM fractions were collected together

2 - noise peak interfered with integration of PCB169

Table A8. Silica Gel and Florisil Column clean-ups - recoveries and elutions

Date	Solvent Elution (mL, hex)	PCB Congener - Percent Recovery									
		37	81	77	105	126	156	169	^{13}C-77	^{13}C-126	^{13}C-169
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, fresh											
Oct. 19/91	0-90	98	110	105	106	111	120	109	92	99	97
	90-100	3	1	3	3	2	2	1	4	3	1
	100-110	0	0	0	0	0	0	0	0	0	0
	110-120	0	0	0	0	0	0	0	0	0	0
	15, 15% DCM/hex	0	0	0	0	0	0	0	0	0	0
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, <30 days old (average of 2 runs)											
Jan. 31/91	0-100	93	89	91	94	89	94	93	80	84	84
	101-150	0	0	0	0	0	0	0	0	0	0
Silica gel, 60-120 mesh, 8 g/column, 5% deactivated, >30 days old (2 elutions done)											
Jan. 30/91	0-100	228	199	222	134	40	103	0	N.A.[1]	N.A.	N.A.
	101-150	9	29	19	67	62	74	0	N.A.	N.A.	N.A.
	151-200	0	0	0	27	0	0	0	N.A.	N.A.	N.A.
Silica gel, 60-120 mesh, 8 g/column, activated											
Dec. 21/90	0-100	0	26	6	32	31	68	55	1	2	4

Silica gel, 60-120 mesh, 1.2 g/column, 5% deactivated, fresh											
Oct. 2/89	10	51	--[2]	49	56	54	61	57	N.A.	N.A.	N.A.
	12	65	--	63	69	66	72	66	N.A.	N.A.	N.A.
	14	145	--	139	151	138	151	137	N.A.	N.A.	N.A.
Silica gel, 60-200 mesh, 1.2 g/column, 5% deactivated, fresh											
Jun. 7/89	10	46	--[2]	65	N.A.	72	N.A.	72	N.A.	N.A.	N.A.
	13	72	--	76	N.A.	77	N.A.	64	N.A.	N.A.	N.A.
Silica sep-pak[3]											
Jun. 6/89	10	64	--[2]	84	N.A.	88	N.A.	88	N.A.	N.A.	N.A.
Silica gel, 100-200 mesh, 1.2 g/column, 5% deactivated, fresh											
Jun. 1/89	10	64	--[2]	65	N.A.	66	N.A.	56	N.A.	N.A.	N.A.
	13	41	--	62	N.A.	62	N.A.	33[3]	N.A.	N.A.	N.A.
Silica gel, 100-200 mesh, 1.2 g/column, activated											
May 31/89	15	25	--[2]	27	N.A.	44	N.A.	56	N.A.	N.A.	N.A.
	20	23	--	28	N.A.	34	N.A.	46	N.A.	N.A.	N.A.
	25	32	--	37	N.A.	43	N.A.	51	N.A.	N.A.	N.A.
Florisil, 60-100 mesh, 1.15 g/column, 1.2% deactivated											
May 23/89	16	99	--[2]	85	N.A.	57	N.A.	23	N.A.	N.A.	N.A.
	20	70	--	68	N.A.	51	N.A.	29	N.A.	N.A.	N.A.

Florisil, 60-100 mesh, 1.15 g/column, 1.2% deactivated											
May 20/89	10 + 3, 5% DCM/hex	103	--[2]	104	N.A.	68	N.A.	[3]	N.A.	N.A.	N.A.
Florisil, 60-100 mesh, 1.2 g/column, 1.2% deactivated; determining if a concentration effect exists											
May 18/89	low conc., 10	144	--[2]	160	N.A.	91	N.A.	28	N.A.	N.A.	N.A.
	high conc., 10	171	--	154	N.A.	93	N.A.	32	N.A.	N.A.	N.A.

1 - ^{13}C-PCBs were not used in these recovery studies

2 - PCB 81 was not used for these recovery studies

3 - noise peaks on the chromatograms interfered with peak area calculations

Table A9. ^{13}C-PCB Recoveries from Carbon, Showing the Effects of High Levels of Ortho Substituted PCBs and the DDT family of Compounds on Recoveries and Fractionation through Carbon

Sample	Date	Percent Recovery		
		^{13}C-77	^{13}C-126	^{13}C-169
St. Lawrence Belugas:				
Method Blank, before any samples; tol elution	Oct. 20/90	61	70	73
Carbon Check, after all samples; tol elution	Oct. 23/90	17	18	20
West Coast Whales: tol elution				
1st sample	Feb. 7/91	87	84	90
5th sample	Feb. 11/91	75	77	82
9th sample	Feb. 12/91	33	33	34
Non-ortho Std. Check #1	Feb. 13/91	25	28	27
13th sample	Feb. 14/91	44	45	46
Non-ortho Std. Check #2	Feb. 19/91	38	42	43
17th sample	Feb. 20/91	25	38	39
21st sample	Feb. 21/91	29	29	30

Table A10. Percent Bias for the ^{13}C-PCB Recoveries in Samples

Sample	^{13}C-77 Std.	^{13}C-77 Sample	% Bias ^{13}C-77	^{13}C-126 Std.	^{13}C-126 Sample	% Bias ^{13}C-126	^{13}C-169 Std.	^{13}C-169 Sample	% Bias ^{13}C-169
Charr c, d, e	200.0	97.0	-2.6	200.0	102.6	-2.4	200.0	107.6	- 2.3
Husky L. Beluga	200.0	141.9	-1.5	200.0	156.5	-1.1	200.0	161.7	- 1.0
St. Lawrence Beluga	400.0	91.0	-7.7	400.0	95.4	-7.6	400.0	100.6	- 7.5
W. Coast Whales	400.0	149.8	-6.3	400.0	145.8	-6.4	400.0	143.9	- 6.4
Pond Inlet Narwhal	400.0	317.5	-2.1	400.0	357.4	-1.1	400.0	341.9	- 1.5
Broughton Island Ringed Seal, arctic charr, beluga, polar bear	400.0	307.2	-2.3	400.0	394.5	-0.1	400.0	381.1	- 0.5

% Bias = 100 * $(C_a - C_b)/T$[1]

C_a - concentration of ^{13}C-PCB in final sample extract

C_b - original concentration of ^{13}C-PCB in sample

T - amount of ^{13}C-PCB added to sample = 4000 pg

[1] - EPA Contract No. 68-C9-0013, 1991

Table A11. Confidence Interval, Z Test, and Precision Measurements for Arctic Samples

Species, Tissue Location	Injection (I) or Sample (s)	Non-ortho PCB 77	126	169	Non-ortho PCB Congener	Mean	Range	CI	Z	Precision (%)
		lipid wt. basis pg/g								
Beluga Blubber Husky Lake	I-original	201	345	898	77	207	12	7	1.00	6
	I-repeat	213	354	554	126	350	9	3	1.00	3
					169	726	344	58	0.97	47
Beluga Blubber Husky Lake	I-original	46	62	150	77	47	1	3	1.00	2
	I-repeat	47	66	147	126	64	4	8	1.00	6
					169	149	3	3	1.00	2
Beluga Blubber Husky Lake	I-original	25	239	1386	77	47	43	113*	0.91*	93*
	I-repeat	68	244	1306	126	242	5	3	1.00	2
					169	1346	80	7	1.00	6
Whole Charr Northern Québec	I-original	300	165	<10	77	282	37	16	1.00	13
	I-repeat	263	132	<10	126	149	33	27	1.00	22
					169	---[4]				
Whole Charr	I-original	294	52	<10	77	321	54	21	1.00	17

Northern Québec	I-repeat	348	46	<10	126	49	6	15	1.00	12
					169	---				
Whole Charr	S-original	225	54	51	77	162	127	96*	0.93*	79*
Creswell Bay	S-repeat	98	21	6	126	38	33	108*	0.92*	88*
					169	29	45	194*	0.79*	158*
Whole Charr	S-original	98	21	7	77	75	46	75*	0.96*	61*
Pond Inlet	S-repeat	52	5	<10	126	13	16	151*	0.85*	123*
					169	4	7	245*	0.71*	200*
Whole Charr	S-original	145	44	15	77	113	64	69*	0.96*	57*
Pond Inlet	S-repeat	81	12	85	126	28	32	140*	0.87*	114*
					169	50	70	172*	0.82*	140*

[1] - CI = 122.8 * EF; EF = range/mean

[2] - s = lipid wt. (pg/g) * CI/173.7; $Z = \frac{\text{original pg/g - repeat pg/g}}{(\text{original } s^2 + \text{repeat } s^2)^{1/2}}$

$|Z|$ = 1 CI ≤ 68% to accept two results as statistically the same

$|Z|$ = 0.5 CI ≤ 38% to accept two results as statistically the same

* values are outside the confidence interval and have unacceptable precision

[3] - Precision = range/mean * 100; closer to 0% means better precision

[1] - Moore *et al.*, 1989, Attachment 2

[2] - Moore *et al.*, 1989, Attachment 5

[3] - EPA Contract No. 69-C9-0013, 1991

[4] - no calculated values for PCB 169 as peak was below detection limits

Table A12. Comparison of Ion Ratios, Secondary to Primary Ion (Table A3), between Standards and Samples

Sample	Location	Non-ortho PCB			Concentration ng/kg	Reference
		77	126	169	77, 126, 169	
		Standard:Sample				
Finless Porpoise	Japan	79:79	59:61	51:50	16200, 1200, 710	Tanabe *et al.*, 1987a
Dall's Porpoise	Japan	72:75	64:65	54:53	3600, 270, 230	Tanabe *et al.*, 1987b
Killer Whale	Japan	64:67	63:65	53:49	39000, 3300, 3500	Tanabe *et al.*, 1987b
Striped Mullet	Japan	72:79	64:65	---	4800, 260, <25	Tanabe *et al.*, 1987b
Beluga (n=3)	St. Lawrence	74:174	59:149	80:79	667, 2501, 33	This study
Killer Whale (n=3)	West Coast	80:135	63:123	78:109	1859, 5916, 483	This study
Beluga (n=2)	Husky Lake	74:125	60:97	80:79	120, 212, 588	This study
Whole Charr (n=3)	George River	76:338	63:83	54:47(n=1)	24, 10, <1	This study
Whole Charr (n=3)	Pond Inlet	81:89	64:75	83:71(n=1)	11, 2, 3	This study
Lake Trout (n=3)	Sydney Lake	76:406	61:90	87:N.D.	16, 12, 3	Unpublished data, Muir and Ford, 1992
Whole Charr (n=4)	Buchanan Lake	80:80	60:76	78:111(n=1)	11, 1, 1	Unpublished data, Muir and Ford, 1992

Appendix B. Manual Carbon Column System

This system consisted of the carbon column connected to a Waters 6000 HPLC (Whatman/Millipore Canada Ltd.). Using this set-up, a Valco 6-port injection valve with a 2 mL sample loop was used to load samples, and three Rheodyne valves were used to control solvent flow through the carbon column (all valves from Anspec Co. Inc). A 4-way Rheodyne valve determined the direction of flow through the carbon column, and two 3-way valves were used to direct elution of the 3 solvent fractions. Solvent flow rate was 5 mL/min. This system was manual - the Rheodyne valves were switched after each step and the amount of solvent pumped was determined using the flow rate and a stopwatch. One solvent line and frit had to be transferred between two solvent bottles.

The procedure for separating non-orthos from ortho substituted PCBs and other organochlorines consisted of the following: valve in "load" position, load sample in 1 mL of hexane (pesticide grade, Caledon Labs), rinse test-tube with 1 mL of hexane and add to the sample, switch valve to inject and start pumping the first eluting solvent of 5% DCM/hex. Early work had shown that the non-ortho PCBs would only adsorb to the carbon when loaded in hexane (Simon and Mulvihill, CWS Hull, personal communication, 1988). After 2 min. of pumping the valve was switched back to the load position. 80 mL of 5% DCM/hex, pumped forward through the column, eluted all ortho substituted PCBs, except the mono-ortho substituted which were eluted with 200 mL of 100% DCM. The last solvent, which eluted the non-ortho substituted PCBs, was 110 mL of toluene (pesticide grade, Caledon Labs), pumped in reverse direction through the column. This back-elution caused an increase in the system operating pressure. A column regeneration step was performed between each sample. It consisted of a volume of 40 mL toluene, 40 mL methanol

(MeOH), 40 mL toluene, and 40 mL hexane, in this order and backwards through the carbon column.

Initial runs through the manual carbon system were done using solvent blanks. These blanks showed that the carbon column needed to be washed before use for samples (Smith *et al.*, 1984). Initial runs of PCB standards (Ultra Scientific, North Kingston, RI, U.S.A.) had elution volume problems due to air in the lines. This was solved by a routine of sonicating, for approximately 10-15 min. every day before use, the 5% DCM/hex and DCM solvents. Very little adsorption of the non-orthos to the carbon was observed in these runs. There were three reasons for this: 1. air in the lines and in the pumphead was effecting the elution volumes (eliminated by sonicating the solvent bottles before use and placing them above the height of the pump head); 2. the carbon contained co-extractive material which limited the number of adsorption sites available to the non-orthos (corrected by solvent washing of new columns); and 3. the regeneration step needed to be performed immediately before loading a sample (Tiernan *et al.*, 1990).

Appendix C. Results for non-ortho PCBs (and related congeners), in Arctic and Mid-latitude Fish and Marine Mammal Species

Table C1. Concentrations of Non-ortho and Mono-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	% Lipid	Sex		ng/kg wet weight									
						Non-ortho PCBs					Mono-ortho PCBs				
						37	81	77	126	169	105	118	156	170	114
Polar Bear	1	Raw Blub	76.3	UNK		91	105	211	348	217	8200	51900	15300	54700	900
	1	Cooked Blubber	71.2	UNK		27	49	69	88	41	6900	57400	16750	62900	1200
Narwhal a	11	Blubber	85.3	M	mean[1]	91	76	203	187	50	57000	183000	6000	113000	2000
					s.d.	62	21	204	100	24	25000	63000	4000	182000	3300
	6		86.1	F	mean	83	121	128	93	42	31000	96000	30000	38000	2800
					s.d.	55	130	70	68	30	24000	93000	62000	24300	2000
Narwhal b	5	Blubber	83.90	UNK	mean	559	---[2]	218	21	21	8300	68000	790	19300	46000
					s.d.	352	---	110	11	24	3900	31700	560	4200	30000
Beluga a	8	Blubber	85.2	M	mean	57	42	88	194	583	53000	270000	25000	39000	33000
					s.d.	15	14	57	85	385	20500	94000	9000	14000	13000
	5		80.3	F	mean	54	25	50	63	126	15000	75000	6300	10500	24000
					s.d.	36	27	45	37	52	7000	33500	2400	3300	9700
Beluga b	6	Blubber	83.8	M	mean	66	73	105	201	97	25000	150000	22000	23000	25300

					s.d.	54	81	106	127	29	22000	32000	11000	10500	10100
Beluga c	1	Blubber	82.0	UNK		780	111	1767	486	192	22000	155000	100	22000	25000
Charr a	8	Whole	11.0	UNK	mean	36	7	63	10	1	<10	2900	130	800	---
		Fish			s.d.	36	5	36	5	1	<10	1550	150	1400	---
Charr b	4	Whole	7.8	M	mean	26	4	24	25	1	410	4200	110	110	220
		Fish			s.d.	22	3	16	39	1	230	2000	150	70	150
Charr c	4	Whole	6.5	M	mean	12	2	13	3	2	330	2000	40	160	960
		Fish			s.d.	10	1	6	1	1	180	1200	30	100	1100
	4			F	mean	28	1	6	1	1	260	2400	70	160	700
					s.d.	49	1	5	1	1	100	1300	40	70	300
Charr d	4	Whole	13.0	M	mean	5	3	10	3	2	210	2200	20	70	540
		Fish			s.d.	5	4	7	3	2	100	650	40	60	190
	6			F	mean	3	1	11	1	1	250	3000	30	80	70
					s.d.	4	1	17	1	1	100	1800	30	80	45
Charr e	5	Whole	11.5	M	mean	6	1	6	1	1	170	1850	10	30	300
		Fish			s.d.	7	1	6	1	1	40	700	20	50	90
	5			F	mean	8	1	6	2	2	160	1600	<10	10	30
					s.d.	4	1	4	1	5	30	650	<10	20	10

Ringed Seal	4	Blubber	87.0	M	mean	106	46	49	94	8	7900	37700	1450	7100	2900
					s.d.	26	22	27	3	11	170	230	160	950	350
	4		82.8	F	mean	186	90	123	95	21	9600	46100	1800	10100	4400
					s.d.	134	75	3	63	30	1800	13000	60	3950	1600
Walrus	5	Blubber	73.9	UNK	mean	427	---	166	194	<4	43000	207600	5400	81350	1600
					s.d.	301	---	140	241	<4	36000	160800	4500	75000	1300

1 - arithmetic mean

2 - not determined at this point in time

Blub - blubber

locations - see Table 6 for identification

Table C2. Lipid Based Concentrations of Non-ortho and Mono-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	% Lipid	Sex		ng/kg lipid weight									
						Non-ortho PCBs					Mono-ortho PCBs				
						37	81	77	126	169	105	118	156	170	114
Polar Bear	1	Raw Blub	76.3	UNK		119	137	276	456	284	10700	68000	20000	72000	1200
	1	Cooked Blubber	71.2	UNK		38	68	97	124	57	9750	80700	23500	88400	1700
Narwhal a	11	Blubber	85.3	M	mean[1]	107	96	237	221	60	67000	216000	6650	133500	23600
					s.d.	72	39	240	120	26	28800	74800	4700	215300	38200
	6		86.1	F	mean	96	143	150	108	49	35300	111200	35100	44000	32500
					s.d.	65	153	83	80	35	26700	108100	73000	28000	23000
Narwhal b	5	Blubber	83.90	UNK	mean	671	---[2]	261	26	25	9900	80800	950	23000	53600
					s.d.	428	---	135	13	29	4800	37800	700	5300	36500
Beluga a	8	Blubber	85.2	M	mean	67	49	103	231	688	63600	324000	30000	47200	40200
					s.d.	18	16	67	102	444	26200	121000	11400	17500	16500
	5		80.3	F	mean	67	31	62	77	156	18000	92800	7700	12900	29400
					s.d.	43	32	54	42	60	8200	39400	2700	3600	12000
Beluga b	6	Blubber	83.8	M	mean	77	84	122	233	115	29100	179800	26400	27500	30300

					s.d.	61	91	119	141	29	24900	39200	13100	13500	12000
Beluga c	1	Blubber	82.0	UNK		950	136	2154	592	235	26600	188600	120	26800	30000
Charr a	8	Whole Fish	11.0	UNK	mean	370	69	617	94	4	<10	25500	1150	700	---
					s.d.	465	57	450	45	12	<10	11200	1280	1200	---
Charr b	4	Whole Fish	7.8	M	mean	427	83	341	296	7	6800	73300	3680	2150	3150
					s.d.	219	97	119	336	9	5600	67400	6800	2150	2200
Charr c	4	Whole Fish	6.5	M	mean	134	23	177	48	30	5700	35000	750	2700	17600
					s.d.	101	16	35	15	13	4500	29000	600	2300	22300
	4			F	mean	358	2	75	16	13	6100	53800	1900	4150	16850
					s.d.	640	4	58	20	22	4000	31200	2250	3500	11000
Charr d	4	Whole Fish	13.0	M	mean	45	28	94	24	14	1850	18400	200	650	4550
					s.d.	42	38	65	26	15	1000	5000	350	600	1350
	6			F	mean	19	5	83	5	6	2000	23100	200	650	5350
					s.d.	25	6	141	7	4	800	14200	200	600	3700
Charr e	5	Whole Fish	11.5	M	mean	52	6	55	9	2	1600	18250	100	300	2900
					s.d.	59	8	48	11	2	300	8250	200	450	1200
	5			F	mean	60	5	46	9	18	1350	14100	<10	60	2300
					s.d.	18	3	25	3	38	450	10100	<10	150	1250

Ringed Seal	4	Blubber	87.0	M	mean	122	53	57	108	9	9100	43500	1650	8100	3300
					s.d.	31	26	31	2	12	300	700	170	1000	400
	4		82.8	F	mean	227	110	149	116	26	11600	55450	2200	12300	5350
					s.d.	170	95	9	81	37	1800	13400	150	5200	2100
Walrus	5	Blubber	73.9	UNK	mean	614	---	238	286	<4	63000	299600	7900	115250	2300
					s.d.	481	---	212	351	<4	54850	237900	7000	102800	2000

1 - arithmetic mean

2 - not determined at this point in time

Blub - blubber

locations - see Table 6 for identification

Table C3. Proportion Non-ortho Substituted PCBs to ΣPCB in Arctic Samples

Species/ Location	N	Tissue	Sex		ΣPCB µg/kg (lipid wt.)	Non-ortho PCBs ($X10^3$) 37	81	77	126	169
Polar Bear	1	Raw Blubber	UNK		1382	0.09	0.10	0.20	0.33	0.21
	1	Cooked Blub	UNK		1687	0.02	0.04	0.06	0.07	0.03
Narwhal a	11	Blubber	M	mean[1]	6343	0.02	0.01	0.04	0.03	0.01
				s.d.	1972	0.01	0.01	0.03	0.02	0.01
	6		F	mean	3184	0.04	0.02	0.06	0.04	0.02
				s.d.	2145	0.03	0.04	0.04	0.02	0.01
Narwhal b	5	Blubber	UNK	mean	2283	0.32	0.00	0.13	0.01	0.01
				s.d.	908	0.22	0.00	0.07	0.01	0.02
Beluga a	8	Blubber	M	mean	5868	0.01	0.01	0.02	0.04	0.11
				s.d.	2041	0.01	0.00	0.01	0.02	0.06
	5		F	mean	1866	0.04	0.02	0.04	0.04	0.09
				s.d.	753	0.02	0.02	0.03	0.02	0.02
Beluga b	6	Blubber	M	mean	5605	0.02	0.02	0.03	0.05	0.02
				s.d.	1325	0.01	0.02	0.03	0.04	0.01

Beluga c	1	Blubber	UNK		3178	0.30	0.04	0.68	0.19	0.07
Charr a	8	Whole Fish	UNK	mean	329	1.19	0.24	2.05	0.32	0.01
				s.d.	96	1.40	0.22	1.64	0.20	0.04
Charr b	4	Whole Fish	M	mean	1118	0.54	0.09	0.45	0.47	0.01
				s.d.	1086	0.47	0.10	0.34	0.73	0.01
Charr c	4	Whole Fish	M	mean	304	0.95	0.14	0.96	0.24	0.14
				s.d.	239	0.99	0.11	0.72	0.17	0.10
	4		F	mean	400	1.12	0.01	0.30	0.06	0.04
				s.d.	205	1.75	0.03	0.29	0.07	0.05
Charr d	4	Whole Fish	M	mean	143	0.30	0.23	0.62	0.18	0.08
				s.d.	54	0.28	0.31	0.29	0.22	0.08
	6		F	mean	149	0.19	0.04	0.47	0.05	0.04
				s.d.	52	0.25	0.05	0.61	0.06	0.03
Charr e	5	Whole Fish	M	mean	112	0.57	0.06	0.56	0.10	0.02
				s.d.	28	0.74	0.08	0.55	0.13	0.03
	5		F	mean	96	0.67	0.06	0.52	0.10	0.19
				s.d.	19	0.28	0.04	0.30	0.04	0.40
Ringed Seal	4	Blubber	M	mean	602	0.20	0.09	0.10	0.18	0.01

				s.d.	36	0.06	0.05	0.06	0.01	0.02
	4		F	mean	820	0.27	0.13	0.18	0.14	0.03
				s.d.	105	0.17	0.10	0.01	0.08	0.04
Walrus	5	Blubber	UNK	mean	4314	0.58	---	0.14	0.09	0.00
				s.d.	3555	0.91	---	0.16	0.08	0.00

1 - arithmetic mean

2 - not determined at this point in time

locations - see Table 6 for identification

Table C4. Proportion of Non-ortho PCBs in Aroclor and Kanechlor Commercial PCB Mixtures[1]

Commercial Mixture	Non-ortho PCB ($x10^3$)		
	77	126	169
Aroclor 1242	5.08	0.19	N.D.
Aroclor 1248	6.23	0.55	N.D.
Aroclor 1254	0.62	0.04	$5.1x10^{-4}$
Aroclor 1260	0.26	$3.2x10^{-3}$	N.D.
Kanechlor 300	4.29	0.02	$<8.0X10^{-5}$
Kanechlor 400	8.04	0.07	$4.4X10^{-4}$
Kanechlor 500	1.69	0.03	$6.4X10^{-4}$
Kanechlor 600	0.97	$5.3X10^{-3}$	$<8.0X10^{-5}$

[1] - Kannan *et al.*, 1987

Table C5. "TCDD Equivalent Concentrations" (TECs) of Non-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	Sex		Non-ortho PCBs 81	77	126	169	ΣTEC ng/kg
TEF Values					9.0E-06[2]	1.0E-02[3]	1.0E-01[3]	5.0E-02[3]	
Polar Bear	1	Raw Blubber	UNK		0.00	2.11	34.81	10.83	58.0
	1	Cooked Blubber	UNK		0.00	0.69	8.82	2.03	20.8
Narwhal a	11	Blubber	M	mean[1]	0.00	1.99	18.68	2.59	85.7
				s.d.	0.00	1.96	9.90	1.14	32.7
	6		F	mean	0.00	1.28	9.27	2.10	48.7
				s.d.	0.00	0.70	6.82	1.50	31.5
Narwhal b	5	Blubber	UNK	mean	0.00	2.18	2.14	1.03	18.8
				s.d.	0.00	1.10	1.06	1.20	7.7
Beluga a	8	Blubber	M	mean	0.00	0.88	19.42	29.15	107.5
				s.d.	0.00	0.57	8.49	19.23	39.6
	5		F	mean	0.00	0.50	6.25	6.32	30.9
				s.d.	0.00	0.45	3.67	2.61	12.6
Beluga b	6	Blubber	M	mean	0.00	1.05	20.11	4.84	55.6
				s.d.	0.00	1.06	12.71	1.43	24.3

Beluga c	1	Blubber	UNK		0.00	17.67	48.55	9.61	101.6
Charr a	8	Whole Fish	UNK	mean	0.00	0.63	1.02	0.02	2.0
				s.d.	0.00	0.36	0.51	0.07	0.7
Charr b	4	Whole Fish	M	mean	0.00	0.24	2.48	0.02	4.3
				s.d.	0.00	0.16	3.85	0.01	4.6
Charr c	4	Whole Fish	M	mean	0.00	0.13	0.34	0.10	1.0
				s.d.	0.00	0.06	0.14	0.04	0.3
	4		F	mean	0.00	0.06	0.08	0.03	0.5
				s.d.	0.00	0.05	0.10	0.04	0.1
Charr d	4	Whole Fish	M	mean	0.00	0.10	0.26	0.07	0.7
				s.d.	0.00	0.07	0.29	0.08	0.4
	6		F	mean	0.00	0.11	0.08	0.05	0.6
				s.d.	0.00	0.17	0.10	0.03	0.3
Charr e	5	Whole Fish	M	mean	0.00	0.06	0.11	0.01	0.4
				s.d.	0.00	0.06	0.13	0.01	0.2
	5		F	mean	0.00	0.06	0.12	0.11	0.5
				s.d.	0.00	0.04	0.04	0.24	0.3

Ringed Seal	4	Blubber	M	mean	0.00	0.49	9.43	0.38	19.0
				s.d.	0.00	0.27	0.27	0.54	0.4
	4		F	mean	0.00	1.23	9.45	1.06	22.4
				s.d.	0.00	0.03	6.33	1.49	6.1
Walrus	5	Blubber	UNK	mean	0.00	1.66	19.34	0.00	67.3
				s.d.	0.00	1.40	24.05	0.00	58.8

[1] - arithmetic mean

[2] - Smith *et al.*, 1990; [3] - Safe 1990

locations - see Table 6 for identification

Table C6. "TCDD Equivalent Concentrations" (TECs) of Mono-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	Sex		Mono-ortho PCBs 105	114	118	156	170	ΣTEC ng/kg
TEF Values					1.0E-03[3]	9.5E-05[2]	8.3E-06[2]	4.6E-05[2]	1.6E-05[2]	
Polar Bear	1	Raw Blubber	UNK		8.15	0.09	0.43	0.70	0.88	58.0
	1	Cooked Blubber	UNK		6.92	0.12	0.48	0.77	1.01	20.8
Narwhal a	11	Blubber	M	mean[1]	56.97	1.90	1.52	0.26	1.81	85.7
				s.d.	24.76	3.10	0.52	0.19	2.90	32.7
	6		F	mean	30.63	2.66	0.80	1.38	0.61	48.7
				s.d.	23.55	1.88	0.77	2.86	0.39	31.5
Narwhal b	5	Blubber	UNK	mean	8.25	4.24	0.56	0.04	0.31	18.8
				s.d.	3.85	2.83	0.26	0.03	0.07	7.7
Beluga a	8	Blubber	M	mean	52.87	3.17	2.24	1.15	0.63	107.5
				s.d.	20.46	1.24	0.78	0.42	0.22	39.6
	5		F	mean	14.55	2.23	0.62	0.29	0.17	30.9
				s.d.	6.92	0.92	0.28	0.11	0.05	12.6
Beluga b	6	Blubber	M	mean	24.53	2.40	1.25	1.01	0.36	55.6
				s.d.	21.68	0.96	0.27	0.49	0.17	24.3

Beluga c	1	Blubber	UNK		21.80	2.34	1.28	0.01	0.35	101.6
Charr a	8	Whole Fish	UNK	mean	0.26[4]	0.00	0.02	0.01	0.00	2.0
				s.d.	0.11	0.00	0.01	0.01	0.00	0.7
Charr b	4	Whole Fish	M	mean	0.41	0.02	0.04	0.01	0.00	4.3
				s.d.	0.23	0.01	0.02	0.01	0.00	4.6
Charr c	4	Whole Fish	M	mean	0.33	0.09	0.02	0.00	0.00	1.0
				s.d.	0.18	0.10	0.01	0.00	0.00	0.3
	4		F	mean	0.26	0.07	0.02	0.00	0.00	0.5
				s.d.	0.10	0.03	0.01	0.00	0.00	0.1
Charr d	4	Whole Fish	M	mean	0.21	0.05	0.02	0.00	0.00	0.7
				s.d.	0.10	0.02	0.01	0.00	0.00	0.4
	6		F	mean	0.25	0.07	0.03	0.00	0.00	0.6
				s.d.	0.10	0.04	0.01	0.00	0.00	0.3
Charr e	5	Whole Fish	M	mean	0.17	0.03	0.02	0.00	0.00	0.4
				s.d.	0.04	0.01	0.01	0.00	0.00	0.2
	5		F	mean	0.16	0.03	0.01	0.00	0.00	0.5
				s.d.	0.03	0.01	0.01	0.00	0.00	0.3

Ringed Seal	4	Blubber	M	mean	7.88	0.27	0.31	0.07	0.11	19.0
				s.d.	0.17	0.03	0.00	0.01	0.02	0.4
	4		F	mean	9.62	0.42	0.38	0.08	0.16	22.4
				s.d.	1.83	0.15	0.11	0.00	0.06	6.1
Walrus	5	Blubber	UNK	mean	42.93	0.15	1.72	0.25	1.30	67.3
				s.d.	35.75	0.12	1.33	0.21	1.20	58.8

[1] - arithmetic mean

[2] - Smith *et al.*, 1990; [3] - Safe 1990

[4] - No PCB 105 determined for Broughton Island Arctic charr; TEC is an average based on the other Arctic charr

locations - see Table 6 for identification

Table C7. Percentage of ΣTECs from Non-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	Sex		ΣTEC ng/kg	Non-ortho PCBs 81	77	126	169
Polar Bear	1	Raw Blubber	UNK		58.0	0.00	3.64	60.03	18.67
	1	Cooked Blubber	UNK		20.8	0.00	3.30	42.36	9.75
Narwhal a	11	Blubber	M	mean[1]	85.7	0.00	2.61	21.61	4.35
				s.d.	32.7	0.00	2.32	8.53	5.21
	6		F	mean	48.7	0.00	3.68	20.09	4.55
				s.d.	31.5	0.00	2.32	11.33	3.37
Narwhal b	5	Blubber	UNK	mean	18.8	0.00	12.32	11.40	5.44
				s.d.	7.7	0.00	6.34	4.76	7.59
Beluga a	8	Blubber	M	mean	107.5	0.00	0.95	18.62	23.92
				s.d.	39.6	0.00	0.79	6.47	9.58
	5		F	mean	30.9	0.00	1.67	19.82	20.55
				s.d.	12.6	0.00	1.30	6.49	1.68
Beluga b	6	Blubber	M	mean	55.6	0.00	1.94	36.37	9.69
				s.d.	24.3	0.00	1.62	20.69	3.36

Beluga c	1	Blubber	UNK	101.6	0.00	17.39	47.78	9.46
Charr a	8	Whole Fish	UNK mean	2.0	0.00	31.50	51.00	1.00
			s.d.	0.7	0.00	11.94	10.65	3.91
Charr b	4	Whole Fish	M mean	4.3	0.00	7.40	69.52	1.24
			s.d.	4.6	0.00	2.16	20.28	1.17
Charr c	4	Whole Fish	M mean	1.0	0.00	13.28	34.26	10.34
			s.d.	0.3	0.00	6.27	14.40	3.87
	4		F mean	0.5	0.00	9.73	15.87	4.78
			s.d.	0.1	0.00	9.17	19.11	6.46
Charr d	4	Whole Fish	M mean	0.7	0.01	14.30	29.69	7.60
			s.d.	0.4	0.00	5.29	26.12	7.60
	6		F mean	0.6	0.00	13.45	13.58	7.31
			s.d.	0.3	0.00	16.69	16.99	4.57
Charr e	5	Whole Fish	M mean	0.4	0.00	13.15	21.58	2.11
			s.d.	0.2	0.00	10.32	20.66	2.98
	5		F mean	0.5	0.00	12.77	25.52	12.51
			s.d.	0.3	0.00	6.48	8.60	24.89
Ringed Seal	4	Blubber	M mean	19.0	0.00	2.61	49.77	1.99

				s.d.	0.4	0.00	1.45	0.47	2.82
	4		F	mean	22.4	0.00	5.70	39.82	3.95
				s.d.	6.1	0.00	1.43	17.38	5.59
Walrus	5	Blubber	UNK	mean	67.3	0.00	5.73	29.04	0.00
				s.d.	58.8	0.00	5.41	22.33	0.00

1 - arithmetic mean

locations - see Table 6 for identification

Table C8. Percentage of εTECs from Mono-ortho Substituted PCBs in Arctic Samples

Species/ Location	N	Tissue	Sex		εTEC ng/kg	Mono-ortho PCBs 105	114	118	156	170
Polar Bear	1	Raw Blubber	UNK		58.0	14.06	0.15	0.74	1.21	1.51
	1	Cooked Blubber	UNK		20.8	33.23	0.56	2.29	3.70	4.83
Narwhal a	11	Blubber	M	mean[1]	85.7	64.14	2.47	1.98	0.73	2.11
				s.d.	32.7	12.93	3.67	0.79	1.63	2.85
	6		F	mean	48.7	60.46	6.29	1.57	1.90	1.46
				s.d.	31.5	12.67	3.69	0.62	2.90	0.76
Narwhal b	5	Blubber	UNK	mean	18.8	44.03	21.17	3.66	0.20	1.78
				s.d.	7.7	10.30	6.48	2.18	0.16	1.47
Beluga a	8	Blubber	M	mean	107.5	49.74	2.95	2.14	1.08	0.60
				s.d.	39.6	12.03	0.55	0.50	0.15	0.14
	5		F	mean	30.9	46.22	8.20	2.04	0.95	0.56
				s.d.	12.6	9.46	4.88	0.44	0.13	0.06
Beluga b	6	Blubber	M	mean	55.6	41.13	5.30	2.56	2.27	0.74
				s.d.	24.3	24.00	3.27	1.09	0.58	0.52

Beluga c	1	Blubber	UNK	101.6	21.46	2.30	1.26	0.01	0.35
Charr a	8	Whole Fish	UNK mean	2.0	13.00	0.00	1.00	0.50	0.00
			s.d.	0.7	15.71	0.00	1.68	0.75	0.00
Charr b	4	Whole Fish	M mean	4.3	18.95	0.74	1.64	0.41	0.00
			s.d.	4.6	15.39	0.58	1.47	0.78	0.00
Charr c	4	Whole Fish	M mean	1.0	32.16	7.92	1.62	0.19	0.00
			s.d.	0.3	16.39	6.97	0.71	0.13	0.00
	4		F mean	0.5	51.60	12.92	3.88	0.69	0.00
			s.d.	0.1	21.31	4.63	1.69	0.62	0.00
Charr d	4	Whole Fish	M mean	0.7	35.21	9.74	3.17	0.08	0.00
			s.d.	0.4	21.01	7.51	2.22	0.16	0.00
	6		F mean	0.6	47.95	12.48	4.79	0.19	0.00
			s.d.	0.3	17.97	6.63	2.45	0.24	0.00
Charr e	5	Whole Fish	M mean	0.4	48.62	9.02	5.30	0.09	0.00
			s.d.	0.2	15.58	5.80	3.92	0.21	0.00
	5		F mean	0.5	39.43	6.39	3.34	0.00	0.00
			s.d.	0.3	16.54	3.61	2.30	0.00	0.00
Ringed Seal	4	Blubber	M mean	19.0	41.61	1.43	1.65	0.35	0.60

				s.d.	0.4	1.70	0.19	0.04	0.03	0.07
	4		F	mean	22.4	45.77	1.83	1.84	0.38	0.71
				s.d.	6.1	20.71	0.15	0.98	0.09	0.09
Walrus	5	Blubber	UNK	mean	67.3	59.74	0.21	2.96	0.38	1.94
				s.d.	58.8	22.91	0.13	1.31	0.28	1.30

[1] - arithmetic mean

locations - see Table 6 for identification

Table C9. Concentrations of Non-ortho and Mono-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	% Lipid	Sex		ng/kg wet weight Non-ortho PCBs 37	81	77	126	169	Mono-ortho PCBs 105	118	156	170	114
Beluga d	5	Blubber	76.3	M	mean[1]	202	172	708	2475	36	2161300	2643700	<10	2094500	1286300
					s.d.	207	122	392	1458	18	2406900	1335700	<10	1085400	1688900
	5		81.8	F	mean	291	217	1347	1529	121	360700	940200	<10	402200	102000
					s.d.	307	188	1602	1565	116	530500	321600	<10	229900	111700
Cod Liver	4	Oil	94.0	UNK	mean	20	35	233	152	55	170	13900	1800	1000	1000
					s.d.	17	23	40	20	5	30	2800	1000	800	300
Killer Whale	5	Blubber	89.6	M	mean	1944	939	1468	3730	411	339400	1915200	181200	597600	143800
					s.d.	338	594	1413	2537	255	294300	1920200	306300	791100	139700
	1		96.0	F		2062	2601	1506	6829	509	781000	1960000	<10	317000	99000
False K. Whale	2	Blubber	91.0	M	mean	3731	4391	3937	14377	2800	700000	2310000	186000	1118000	351000
					s.d.	529	6209	756	12499	41	135800	1021800	263000	135800	232000
Harbour Porpoise	4	Blubber	94.3	M	mean	1816	989	675	3625	225	115800	335500	<10	184500	81000
					s.d.	1752	966	476	2392	369	75600	258000	<10	222500	24500

	3		89.3	F	mean	1454	747	1163	3258	886	104300	397700	7300	129000	53000
					s.d.	295	686	706	2013	1010	27800	307100	12700	105100	61500
Dall's Porpoise	2	Blubber	97.3	UNK	mean	1902	2412	1992	5821	640	173000	524300	<10	216300	41300
					s.d.	909	1986	705	4564	274	154600	529000	<10	280000	43000
	1		96.0	F		857	389	1181	769	536	180000	515000	<10	98000	38000
Dolphin	1	Blubber	30.0	UNK		1628	1038	295	759	<10	81000	101 00	<10	38000	51000

1 - arithmetic mean

locations - see Table 6 for identification

Table C10. Lipid Based Concentrations of Non-ortho and Mono-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	% Lipid	Sex		ng/kg wet weight									
						Non-ortho PCBs					Mono-ortho PCBs				
						37	81	77	126	169	105	118	156	170	114
Beluga d	5	Blubber	76.3	M	mean[1]	303	246	1008	3488	48	3388600	3765500	<10	2684000	2044400
					s.d.	316	203	732	2548	24	4082600	2636000	<10	1383000	2936800
	5		81.8	F	mean	434	309	1613	1804	179	412200	1216800	<10	494200	120900
					s.d.	576	337	1707	1645	214	554500	561000	<10	246000	115900
Cod Liver	4	Oil	94.0	UNK	mean	20	38	249	161	59	180	14900	1900	1000	1000
					s.d.	17	25	51	21	8	40	3400	1100	700	350
Killer Whale	5	Blubber	89.6	M	mean	2200	1049	1589	4119	483	390200	2230800	232300	645000	166100
					s.d.	473	644	1463	2557	318	336700	2265400	408300	813500	160100
	1		96.0	F		2147	2709	1569	7114	531	813500	2041700	<10	330200	103100
False K. Whale	2	Blubber	91.0	M	mean	4111	4933	4316	16021	3076	777400	2556600	209000	1226900	390000
					s.d.	709	6977	697	14233	51	173400	1202300	295600	111000	267000
Harbour Porpoise	4	Blubber	94.3	M	mean	1976	1059	722	3948	239	126000	366300	<10	204500	86800
					s.d.	1901	1029	508	2778	393	89600	290900	<10	255200	29900

	3		89.3	F	mean	1648	805	1368	3676	964	121500	491000	7800	158500	67900
					s.d.	371	650	943	2107	994	48600	453600	13500	152400	86300
Dall's Porpoise	2	Blubber	97.3	UNK	mean	1948	2457	2042	5937	659	178900	542400	<10	223300	42800
					s.d.	921	2001	709	4617	285	159600	545400	<10	288500	44400
	1		96.0	F		893	405	1231	802	558	187500	536500	<10	102100	39600
Dolphin	1	Blubber	30.0	UNK		5426	3459	982	2530	<10	270000	336700	<10	126700	170000

[1] - arithmetic mean

locations - see Table 6 for identification

Table C11. Proportion Non-ortho Substituted PCBs to ΣPCB in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	Sex		ΣPCB µg/kg (lipid wt.)	Non-ortho PCBs ($X10^3$) 37	81	77	126	169
Beluga d	5	Blubber	M	mean[1]	179443	0.00	0.00	0.01	0.02	0.00
				s.d.	131504	0.00	0.00	0.00	0.01	0.00
	5		F	mean	33124	0.01	0.01	0.07	0.07	0.01
				s.d.	20472	0.02	0.01	0.07	0.07	0.01
Cod Liver	4	Oil	UNK	mean	669	0.03	0.06	0.37	0.24	0.09
				s.d.	57	0.03	0.04	0.08	0.05	0.01
Killer Whale	5	Blubber	M	mean	35842	0.12	0.06	0.08	0.18	0.03
				s.d.	35525	0.08	0.06	0.07	0.09	0.03
	1		F		32458	0.07	0.08	0.05	0.22	0.02
False K. Whale	2	Blubber	M	mean	43756	0.10	0.10	0.10	0.34	0.07
				s.d.	10786	0.01	0.14	0.04	0.24	0.02
Harbour Porpoise	4	Blubber	M	mean	12743	0.18	0.12	0.08	0.31	0.03
				s.d.	8619	0.24	0.15	0.08	0.16	0.05
	3		F	mean	9811	0.27	0.16	0.18	0.60	0.18
				s.d.	9476	0.17	0.19	0.15	0.60	0.27

Dall's Porpoise	2	Blubber	UNK	mean	13961	2.04	3.73	2.06	8.27	0.40
				s.d.	17927	3.37	6.35	3.35	14.05	0.61
	1		F		7198	0.12	0.06	0.17	0.11	0.08
Dolphin	1	Blubber	UNK		5653	0.96	0.61	0.17	0.45	0.00

1 - arithmetic mean

locations - see Table 6 for identification

Table C12. "TCDD Equivalent Concentrations" (TECs) of Non-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	Sex		Non-ortho PCBs 81	77	126	169	ΣTEC ng/kg
TEF Values					9.0E-06[2]	1.0E-02[3]	1.0E-01[3]	5.0E-02[3]	
Beluga d	5	Blubber	M	mean[1]	0.00	7.08	247.51	1.80	2595
				s.d.	0.00	3.92	145.76	0.88	2661
	5		F	mean	0.00	13.47	152.88	6.06	557
				s.d.	0.00	16.02	156.53	5.82	546
Cod Liver	4	Oil	UNK	mean	0.00	2.33	15.16	2.74	20.5
				s.d.	0.00	0.40	2.02	0.27	2.1
Killer Whale	5	Blubber	M	mean	0.01	14.68	373.00	20.55	795
				s.d.	0.01	14.13	253.67	12.75	574
	1		F		0.02	15.06	682.92	25.46	1535
False K. Whale	2	Blubber	M	mean	0.04	39.37	1437.74	139.94	2401
				s.d.	0.06	7.56	1249.85	2.05	1417
Harbour Porpoise	4	Blubber	M	mean	0.01	6.75	362.47	11.25	510
				s.d.	0.01	4.76	239.20	18.46	318

	3		F	mean	0.01	11.63	325.77	44.28	497
				s.d.	0.01	7.06	201.31	50.50	237
Dall's Porpoise	2	Blubber	UNK	mean	0.02	19.92	582.08	32.01	1076
				s.d.	0.02	7.05	456.41	13.69	72
	1		F		0.00	11.81	76.94	26.79	305
Dolphin	1	Blubber	UNK		0.01	2.95	75.89	0.00	166

[1] - arithmetic mean

[2] - Smith *et al.*, 1990; [3] - Safe 1990

locations - see Table 6 for identification

Table C13. "TCDD Equivalent Concentrations" (TECs) of Mono-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	Sex		Mono-ortho PCBs					ΣTEC
					105	114	118	156	170	ng/kg
TEF Values					1.0E-03[3]	9.5E-05[2]	8.3E-06[2]	4.6EE-05[2]	1.6E-05[2]	
Beluga d	5	Blubber	M	mean[1]	2161.33	122.20	21.94	0.00	33.51	2595
				s.d.	2406.95	160.45	11.09	0.00	17.37	2661
	5		F	mean	360.70	9.69	7.80	0.00	6.44	557
				s.d.	530.48	10.61	2.67	0.00	3.68	546
Cod Liver	4	Oil	UNK	mean	0.17	0.09	0.12	0.08	0.02	20.5
				s.d.	0.03	0.03	0.02	0.05	0.01	2.1
Killer Whale	5	Blubber	M	mean	339.40	13.66	15.90	8.34	9.56	795
				s.d.	294.33	13.27	15.94	14.09	12.66	574
	1		F		781.00	9.41	16.27	0.00	5.07	1535
False K. Whale	2	Blubber	M	mean	705.00	33.35	19.17	8.56	17.89	2401
				s.d.	135.77	22.03	8.48	12.10	2.17	1417
Harbour Porpoise	4	Blubber	M	mean	115.75	7.70	2.79	0.00	2.95	510
				s.d.	75.57	2.32	2.14	0.00	3.56	318

	3		F	mean	104.33	5.04	3.30	0.34	2.06	497
				s.d.	27.79	5.84	2.55	0.58	1.68	237
Dall's Porpoise	2	Blubber	UNK	mean	169.50	4.09	4.39	0.00	4.41	1076
				s.d.	218.50	5.78	6.21	0.00	5.89	72
	1		F		180.00	3.61	4.28	0.00	1.57	305
Dolphin	1	Blubber	UNK		81.00	4.85	0.84	0.00	0.61	166

[1] - arithmetic mean

[2] - Smith *et al.*, 1990; [3] - Safe 1990

locations - see Table 6 for identification

Table C14. Percentage of ΣTECs from Non-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	Sex		ΣTEC ng/kg	Non-ortho PCBs 81	77	126	169
Beluga d	5	Blubber	M	mean[1]	2595	0.00	0.77	27.16	0.26
				s.d.	2661	0.00	0.80	31.97	0.32
	5		F	mean	557	0.00	3.49	34.84	2.33
				s.d.	546	0.00	2.38	21.64	2.32
Cod Liver	4	Oil	UNK	mean	20.7	0.00	11.31	73.10	13.26
				s.d.	2.1	0.00	2.06	3.34	1.03
Killer Whale	5	Blubber	M	mean	795	0.00	2.09	51.89	3.24
				s.d.	574	0.00	1.41	16.21	3.22
	1		F		1535	0.00	0.98	44.48	1.66
False K. Whale	2	Blubber	M	mean	2401	0.00	2.10	53.91	7.09
				s.d.	1417	0.00	1.55	20.25	4.27
Harbour Porpoise	4	Blubber	M	mean	510	0.00	1.51	68.26	2.19
				s.d.	318	0.00	0.82	9.00	3.43
	3		F	mean	497	0.00	2.22	61.78	6.73

				s.d.	237	0.00	0.85	11.96	7.00
Dall's Porpoise	2	Blubber	UNK	mean	1076	0.00	2.23	78.34	3.17
				s.d.	72	0.00	0.06	22.32	1.49
	1		F		305	0.00	3.87	25.23	8.78
Dolphin	1	Blubber	UNK		166	0.01	1.77	45.68	0.00

1 - arithmetic mean

locations - see Table 6 for identification

Table C15. Percentage of ΣTECs from Mono-ortho Substituted PCBs in Samples from Mid-latitude Locations in Canada

Species/ Location	N	Tissue	Sex		ΣTEC ng/kg	Mono-ortho PCBs 105	114	118	156	170
Beluga d	5	Blubber	M	mean[1]	2595	58.55	4.68	2.29	0.00	6.29
				s.d.	2661	41.12	2.13	2.18	0.00	8.10
	5		F	mean	557	53.74	1.68	2.41	0.00	1.52
				s.d.	546	23.80	1.26	1.60	0.00	0.53
Cod Liver	4	Oil	UNK	mean	20.7	0.82	0.45	0.57	0.42	0.08
				s.d.	2.1	0.17	0.17	0.17	0.29	0.05
Killer Whale	5	Blubber	M	mean	795	37.75	1.42	1.61	0.98	1.03
				s.d.	574	13.72	0.78	1.08	1.52	0.61
	1		F		1535	50.87	0.61	1.06	0.00	0.33
False K. Whale	2	Blubber	M	mean	2401	33.53	1.35	0.84	0.25	0.93
				s.d.	1417	14.13	0.12	0.14	0.36	0.64
Harbour Porpoise	4	Blubber	M	mean	510	25.11	2.01	0.45	0.00	0.46
				s.d.	318	10.13	1.29	0.31	0.00	0.32
	3		F	mean	497	26.91	1.05	0.76	0.14	0.41

				s.d.	237	18.55	1.03	0.50	0.24	0.28
Dall's Porpoise	2	Blubber	UNK	mean	1076	15.12	0.36	0.39	0.00	0.39
				s.d.	72	19.31	0.51	0.35	0.00	0.52
	1		F		305	59.02	1.18	1.40	0.00	0.51
Dolphin	1	Blubber	UNK		166	48.75	2.92	0.51	0.00	0.37

1 - arithmetic mean

locations - see Table 6 for identification