

# LEVELS IN BIOTIC COMPARTMENTS

## ORGANOHALOGEN POPS IN FISH OF THE NORTHERN PACIFIC

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### Introduction

The enrichment of halogenated Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls (PCB), dichlorodiphenyltrichlorethane and its metabolites (DDTs), chlordane compounds (CD), isomers of hexachlorocyclohexane (HCHs), toxaphenes (Tox), and brominated flame retardants (e.g. PBDE) in biota from pristine areas such as the North Pacific Ocean are a matter of concern. Local input and long-range transport of these compounds by air and ocean currents are likely to occur<sup>1-3</sup>. Especially the Aleutian Islands are known for a specific organochlorine exposure because of their military history<sup>4,5</sup>. They act as rather defined local sources in an otherwise unpopulated and unindustrialized area. Recent studies have shown appreciable concentrations of organochlorines in marine biota from coastal regions of the North Pacific<sup>6-10</sup>.

The Bering Sea and the Gulf of Alaska are one of the major commercial fishing areas of the USA and Canada specifically for Pacific cod and Pacific halibut. The present study reveals the biomagnification of POPs in fish from the Aleutian Archipelago, and it compares the pattern of organic pollutants in biota from the North Pacific with those from the West Coast of North America. It reveals geographical trends of organohalogen contamination in the North Pacific.

### Sampling and Method

Sampling sites and data (1997-2001) of Pacific cod (*Gadus macrocephalus*), Pacific halibut (*Hippoglossus stenolepis*), Pacific Sand Dab (*Citharichthys sordidus*) and Blue Mussels (*Mytilus*

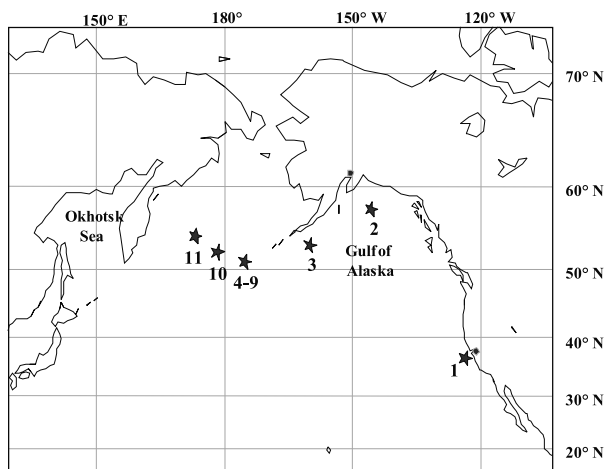


Figure 1. North Pacific sampling sites of cod, halibut, sand dab and blue mussels

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*Edulis*) are shown in Figure 1. Fishes were caught at Attu (#11), Amchitka (#10), Adak (#4-9), in the Western (#3)- and Central (#2)- Gulf of Alaska and in San Francisco coastal regions (#1).

Organohalogenes in liver and muscle samples of Pacific cod, halibut, sand dab, and blue mussels were extracted according to the method recently described by Arend<sup>11</sup>. Identification and quantitative analysis were performed by gas chromatography (HP 5890 II) with electron capture detection (ECD) on a CP SIL19 (60m, 0,25 mm i.d., 0,25 µm film thickness) and mass selective detection (MSD, HP 5973) with electron impact (EI) and negative chemical ionization (NCI, reactand gas: CH<sub>4</sub>, source temperature: 150 °C) on a CP SIL8 (60 m, 0,32 mm i.d., 0,25 µm film thickness).

## Results

### Organochlorines (OCs)

Polychlorinated biphenyls are the most abundant OCs in all analyzed samples except those from the California coast (#1). For an estimation of the total PCB concentration a factor of four is selected for multiplication with the sum of the seven indicator congeners (PCB 28, 52, 101, 118, 138, 153, 180). As shown in Table 1, highest levels of PCB (up to 1490 µg/kg) were found in cod- and halibut from Adak Island. Fish from the Gulf of Alaska and the Californian Coast indicate a regional input in these areas, whereas halibut from the Western Gulf of Alaska, Attu and Amchitka is significantly lower contaminated (66 – 255 µg/kg).

**Table 1.** Concentrations (µg/kg lipid weight) of halogenated POPs in muscle and liver of halibut, cod and sand dab and in blue mussels of the North Pacific (n.d.: not detected)

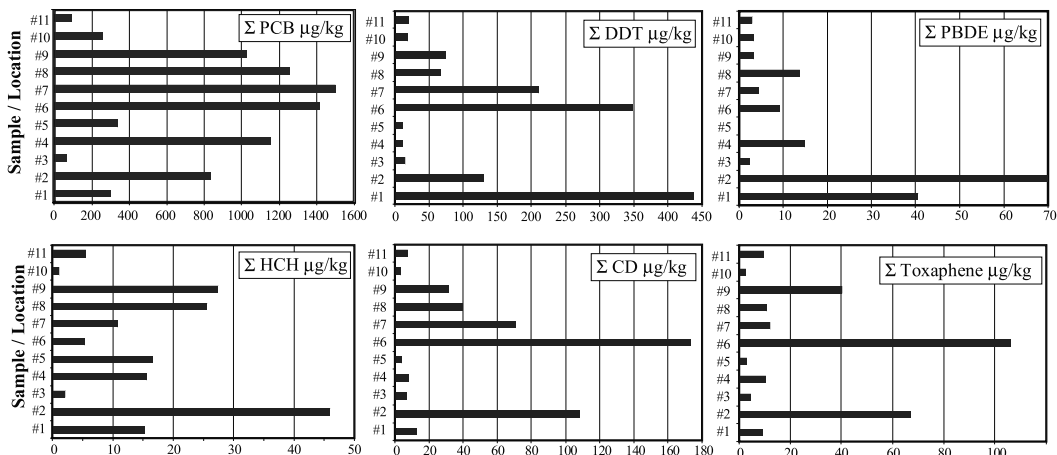
Species	Location	No.	Concentrations in µg/kg lipid weight							
			PCB	DDT	CD	HCH	HCB	A33	Tox.	PBDE
Halibut	Attu	<b>11</b>	93	21	7	5	7	2	10	3
Halibut	<i>Amchitka</i>	<b>10</b>	255	18	3	1	3	1	3	3
Hal. Liver	<i>Adak</i>	<b>9</b>	1030	74	32	27	16	4	40	3
Cod Liver 1	<i>Adak</i>	<b>8</b>	1250	210	71	11	14	2	12	4
Cod Liver 2	<i>Adak</i>	<b>7</b>	1490	350	170	5	13	1	105	9
Cod Liver 3	<i>Adak</i>	<b>6</b>	1410	12	8	16	3	15	11	15
Halibut	<i>Adak</i>	<b>5</b>	330	11	4	17	4	1	3	2
Blue Mussels	<i>Adak</i>	<b>4</b>	1150	12	8	16	3	15	11	15
Halibut	<i>West. Gulf of Alaska</i>	<b>3</b>	66	15	7	2	3	n.d.	4	2
Halibut <sup>12</sup>	<i>Gulf of Alaska</i>	<b>2</b>	830	130	107	46	75	n.d.	75	70
Sand Dab Liver	<i>San Francisco</i>	<b>1</b>	300	440	13	15	7	1	9	41

All of the samples had 4,4'-DDE as the major residue metabolite from 4,4'-DDT. Total DDT (sum of the 4,4'- and 2,4'- isomers of DDT, DDD, DDE) levels was highest in the sand dab livers from the Californian coast near San Francisco (440 µg/kg); relatively low levels were found in the Aleutian samples with the exception of Adak cod liver samples (#7,8) with a generally high OC contamination caused by military activity on that island. The low-level samples may be indicative for a long-range transport and global distribution of DDT still used by subtropical countries<sup>13</sup>. Consistently low levels (3-7) µg/kg) of chlordanes were determined (cis/trans-chlordane, oxy-CD, cis-heptachloroepoxide, cis/trans-nonachlor) in the pristine area samples (#3,10,11) compared to some

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industrial/military sites (#2,7,8) with obviously high levels (71-173  $\mu\text{g}/\text{kg}$ ). The relatively low concentrations (13  $\mu\text{g}/\text{kg}$ ) of CD in the sand dab livers indicate that there is no actual local input at the Californian coast near San Francisco.

Similarly low levels (3-12  $\mu\text{g}/\text{kg}$ ) as for the chlordanes were found for the sum of the major toxaphene-congeners (T 26, T 50 and T 62, representing up to 50 % of the toxaphene contamination in fish) in most samples. Except halibut liver (#9), cod Liver (#6) (both from Adak) and halibut muscle from the Gulf of Alaska (#2) indicate the regional occurrence of toxaphenes caused by old neglected deposits.



**Figure 2.** Pattern and levels ( $\mu\text{g}/\text{kg}$  lipid weight) of halogenated POPs in muscle and liver of halibut, cod and sand dab and in blue mussels of the North Pacific.

Hexachlorobenzene (HCB) occurs in high levels at Adak and the Gulf of Alaska (13-75  $\mu\text{g}/\text{kg}$ ). Total HCH (a, b, g-isomers) levels show uniformly distribution of these compounds, except for the ratio of the isomers. a/g -HCH ratios up to 25 were found in the colder regions of the Aleutians.

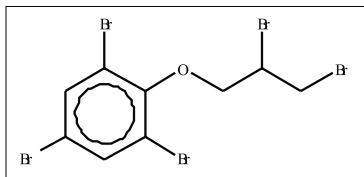
### *Brominated Organic Pollutants*

2,4,6-Tribromoanisole (A 33) could be found in noticeable concentrations in blue mussels (#4) (15  $\mu\text{g}/\text{kg}$ ) and cod liver 3 (#6) from the same location indicating its regional biogenic origin<sup>14</sup>. Polybrominated diphenyl ethers (PBDE) with the dominant congeners BDE-47, 99 and 100 (Bromkal 70-5DE) have been detected in all samples. Their global background distribution is revealed by low levels in remote areas (2-3  $\mu\text{g}/\text{kg}$ ); the input near urban and industrialized areas is indicated by samples with higher concentrations (9-70  $\mu\text{g}/\text{kg}$ )<sup>15</sup>.

In addition to the PBDEs a new brominated flame retardant, Bromkal 73-5PE, containing 2,3-dibromopropyl - 2,4,6 - tribromophenyl ether (DPTE) is reported here for the first time as an environmental pollutant (see Figure 3)<sup>16</sup>. DPTE has been detected in all samples analyzed in the range of 0,3-5,6  $\mu\text{g}/\text{kg}$  extracted lipid.

The Identification of this substance was performed by HRGC/MSD with negative chemical ionisation (NCI) in the Full Scan modus (30-800 amu).

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**Figure 3.** Structure of the major compound of the brominated flame retardant Bromkal 73-5 PE (2,3-dibromopropyl - 2,4,6 - tribromophenyl ether) found in Pacific Fish.

## Acknowledgments

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