Organohalogen Compounds, Volume 60, Pages 126-129 (2003)

Concentrations of Polybrominated Diphenyl Ether Congeners and Toxaphene in Selected Marine Standard Reference Materials

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Introduction

Polybrominated diphenyl ether (PBDE) congeners and the complex mixture, toxaphene, are stable in the environment and readily bioaccumulated into wildlife and human tissues. PBDEs are presently used in large quantities worldwide as flame retardants in textiles, furniture, computer equipment and cables [1]. Measurements in human and wildlife samples have demonstrated that the PBDEs are increasing with time which is in line with the continued use of these compounds [2-4]. This observation along with studies showing the toxic effects from PBDE exposure, have fueled extensive new research on the occurrence, fate, and toxicology of PBDEs[5]. Toxaphene is a complex mixture of chlorinated bornanes and bornenes that was at one time the most heavily-used pesticide in the United States until it was banned in 1982; however, some countries still manufacture and use toxaphene [6]. Toxaphene is persistent in the environment and responsible for fish consumption advisories in some locations [7]. This presentation discusses the current activities of NIST aimed at providing reference values for these classes of compounds in Standard Reference Materials (SRMs). The materials chosen were SRM 1945 Organics in Whale Blubber consisting of cryohomogenized pilot whale (*Globicephala melas*) blubber [8]; SRM 1588a Organics in Cod Liver Oil which was prepared from a commercial cod liver oil [9]; and SRM 1946 consisting of cryohomogenized lake trout (*Salvelinus namayacush*) fillets collected from southern Lake Superior [10].

Materials and Methods

The materials used in this study were prepared for analysis using methods similar to those given in detail elsewhere [10,11] but are summarized here. One gram of SRM 1588a or SRM 1945 or 3 to 4 grams of SRM 1946 were mixed with anhydrous sodium sulfate, then added to a pressurized fluid extraction cell (ASE, Dionex, Salt Lake City, Utah) along with a mixed internal standard containing PCBs not occurring in Aroclors, deuterated and ^{13}C-labeled analogs of selected target analytes. Samples were extracted with dichloromethane using the ASE. Interfering high-molecular weight compounds were removed by size exclusion liquid chromatography. This extract was initially separated using an aminopropyl silane liquid chromatographic method into two fractions for the measurement of PCBs and pesticides by GC-MS. The fractions were then recombined for PBDE and toxaphene determination. Some elements of toxaphene were found to split between the two fractions, hence the need to recombine the fractions. PBDEs eluted in fraction 1, but were quantified from the recombined fractions.

Toxaphene was quantified in the sample extracts using gas chromatography mass spectrometry with negative ion chemical ionization (GC-MS-NCI) equipped with a 60 m x 0.25 mm x 0.25 μm DB-5ms capillary column (J&W Scientific, Folsom, CA) using a method similar to that described elsewhere [12]. Total toxaphene was determined from a calibration curve made from SRM 3067 Toxaphene in Methanol and either ^{13}C *cis*-chlordane or endosulfan-d_4 as the internal standard. A calibration curve was also prepared from toxaphene congeners 32, 50, and 62 (Parlar) that were obtained from Promochem (Wesel, Germany) and these congeners were quantified using the same internal standards as mentioned above.

PBDE congeners (Table 1; congeners were obtained from Cambridge Isotope Laboratories, Andover, MA) were quantified by GC-MS in the electron impact mode (GC-MS-EI) using selected ion monitoring utilizing a method similar to that described elsewhere [13]. A calibration curve was prepared using three to five congener concentrations. Either PCB 198, PCB 204, or ^{13}C-PBDE 99 was used as the internal standard.

Results and Discussion

Concentrations of PBDE congeners determined in SRMs 1945 and 1588a are given in Table 1. The major PBDE congeners detected in these two materials were PBDE congeners 47, 99, 100, 153, and 154. The PBDE congener concentrations were within a factor of four or less of three of the major PCB congeners present in these two materials (Table 1) indicating that PBDEs are important components in the SRMs. The PBDE congener concentration in SRM 1945 were considerably lower than those observed in long-finned pilot whales [14]. In that study, the average concentration for PBDE 47 in five pooled samples of pilot whale blubber was 1060 ng/g lipid mass (660 ng/g lipid mass). The concentration of organohalogens in SRM 1945 tend to be lower than most often observed in pilot whales stranding on the US East Coast [15]. PBDE concentrations determined in SRM 1945 were comparable to those determined previously by the Canadian Wildlife Service (Table 1). In general, PBDE concentrations in SRM 1588a were higher (greater than 10-fold) than observed in herring oil and were in the range found in North Atlantic salmon [16].

Toxaphene concentrations determined in SRMs 1945, 1588a, and 1946 are given in Table 2. Total toxaphene and toxaphene congener concentrations in SRM 1945 and SRM 1588a were comparable. For instance, total toxaphene in SRM 1945 was 1210 ng/g wet mass (127 ng/g wet mass) versus 1960 ng/g wet mass (133 ng/g wet mass) in SRM 1946. Total toxaphene in SRM 1946 is in the range observed previously in Lake Superior lake trout [7,17]. Total toxaphene and toxaphene congeners in SRM 1588a were higher relative to the other SRMs (Table 2). Total toxaphene in SRM 1588a was 3890 ng/g (248 ng/g) which was in good agreement with the average total toxaphene value determined by a toxaphene interlaboratory study using this material (Table 2 and [18]).

Acknowledgements

The authors thank J. Baker and H. Stapleton (University of Maryland, Chesapeake Biological Laboratory) for their assistance with the PBDE analyses.

Table 1: PBDE concentration values (ng/g wet mass) in SRM 1945 Organics in Whale Blubber and SRM 1588a Organics in Cod Liver Oil. The Canadian Wildlife Service (CWS) values were provided by B. Wakeford (personal communication). Certified values of selected PCB congener values (ng/g wet mass) are shown for comparison.

Compound	SRM 1945			SRM 1945	SRM 1588a		
	Mean	1 SD	*n*	(CWS)*	Mean	1 SD	*n*
PBDE 47	52.9	3.8	5	54.9	82.7	2.8	3
PBDE 99	32.0	2.3	5	23.3	10.9	2.1	3
PBDE 100	14.0	0.6	5	14.9	16.9	3.0	3
PBDE 153	22.4	1.5	5	18.3	< 1	--	3
PBDE 154	28.2	2.0	5	30.0	24.7	5.5	3
PBDE 183	< 1	--	5	--	< 1	--	3
ΣPBDE	150	7.0	5	141	135	12	3
PCB 118**	74.6	5.1	--	--	176	3.8	--
PCB 153**	213	19	--	--	274	7.7	--
PCB 180**	107	5.3	--	--	105	5.2	--

*No error estimates were provided.

**Certified values along with expanded uncertainty.

Table 2: Toxaphene congeners and total toxaphene concentration values (ng/g wet mass) determined in SRM 1945 Organics in Whale Blubber, SRM 1588a Organics in Cod Liver Oil, and SRM 1946 Lake Superior Fish Tissue.

Compound		Cong 26	Cong 52	Cong 60	Total Toxaphene
SRM 1945	**Mean**	42.0	68.8	36.9	1210
	1 SD	4.9	7.5	3.8	127
	n	6	6	6	6
SRM 1588a	**Mean**	154	199	106	3980
	1 SD	18	23	16	248
	n	6	6	6	6
SRM 1588a	**Mean**	--	--	--	4080
(Andrews et al., 1995)[17]	**1 SD**	--	--	--	1860
	n	--	--	--	17
SRM 1946	**Mean**	31.0	86.6	54.6	1960
	1 SD	3.7	5.6	4.1	133
	n	6	6	6	6

Literature Cited

1. Rahman F, Langford KH, Scrimshaw MD, Lester JN. Polybrominated diphenyl ether (PBDE) flame retardants. Sci Total Environ 2001;275:1-17.
2. Ikonomou MG, Rayne S, Addison RF. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. Environ Sci Technol 2002;36:1886-1892.

3. Solomon GM, Weiss PM. Chemical contaminants in breast milk: time trends and regional variability. Environ Health Perspect 2002;110:A339-47.
4. Hovander L, Malmberg T, Althanasiadou M, Athanassiadis I, Rahm S, Bergman A, Wehler EK. Identification of hydroxylated PCB metabolites and other phenolic halogenated pollutants in human blood and plasma. Arch Environ Contam Toxicol 2002;42:105-117.
5. Boon JP, Lewis WE, Tjoen-A-Choy MR, Allchin CR, Law RJ, de Boer J, Ten Hallers-Tjabbes CC, Zegers BN. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. Environ Sci Technol 2002;36:4025-4032.
6. Voldner EC, LI YF. Global usage of selected persistent organochlorines. Sci Total Environ 1995;160/161:201-210.
7. Glassmeyer ST, De Vault DS, Hites RA. Rates at which toxaphene concentrations decrease in lake trout from the Great Lakes. Environ Sci Technol 2000;34:1851-1855.
8. Schantz MM, Koster BJ, Oakley LM, Schiller SB, Wise SA. Certification of polychlorinated biphenyl congeners and chlorinated pesticides in a whale blubber standard reference material. Anal Chem 1995;34:901-910.
9. Schantz MM, Parris RM, Wise SA, Won HT, Turle R. Polychlorinated biphenyl (PCB) congeners and chlorinated pesticides in a cod liver reference material. Chemosphere 1992;24:1687-1698.
10. Poster DL, Kucklick JR, Schantz MM, Porter BJ, Leigh SD, Wise SA. Determination of polychlorinated biphenyl congeners and chlorinated pesticides in a fish tissue standard reference material. Anal Bioanal Chem 2003;375:223-41.
11. Kucklick JR, Struntz WDJ, Becker PR, York GW, O'Hara TM, Bohonowych JE. Persistent organochlorine pollutants in ringed seals and polar bears collected from northern Alaska. Science of the Total Environment 2002;287:45-59.
12. Kucklick JR, Harvey HR, Ostrom PH, Ostrom NE, Baker JE. Organochlorine dynamics in the pelagic food web of Lake Baikal. Environ Toxicol Chem 1996;15:1388-1400.
13. Stapleton HM, Letcher RJ, Baker JE. Metabolism of PCBs by the deepwater sculpin (*Myoxocephalus thompsoni*). Environ Sci Technol 2001;35:4747-4752.
14. Lindstrom G, Wingfors H, Dam M, von Bavel B. Identification of 19 polybrominated diphenyl ethers (PBDEs) in long-finned pilot whale (*Globicephala melas*) from the Atlantic. Arch Environ Contam Toxicol 1999;36:355-363.
15. Tilbury KL, Adams NG, Krone CA, Meador JP, Early G, Varanasi U. Organochlorines in stranded pilot whales (*Globicephala melas*) from the coast of Massachusetts. Arch Environ Contam Toxicol 1999;37:125-134.
16. Jacobs MN, Covaci A, Schepens P. Investigation of selected persistent organic pollutants in farmed Atlantic salmon (*Salmo salar*), salmon aquaculture feed, and fish oil components of the feed. Environ Sci Technol 2002;36:2797-805.
17. Kucklick JR, Baker JE. Organochlorines in Lake Superior's food web. Environ Sci Technol 1998;32:1192-1198.
18. Andrews P, Headrick K, Pilon J-C, Lau B, Weber D. An interlaboratory round robin study on the analysis of toxaphene in a cod liver oil standard reference material. Chemosphere 1995;31:4393-4402.