An Interlaboratory Comparison Exercise for Organohalogens in Marine Mammal Blubber

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Introduction

Interlaboratory comparison exercises are an extremely useful way to improve the quality and comparability of data among laboratories. In such exercises, laboratories are generally requested to perform analyses on an unknown sample and a control or reference material that has either been certified for concentrations of target analytes or has been extensively used in prior exercises and has a consensus value. The National Institute of Standards and Technology (NIST) coordinates a number of these exercises such as the NIST Intercomparison Program for Organic Contaminants in the Marine Environment[1], which has been held annually since 1987. In that exercise, a marine sediment and a marine tissue, such as mussel or fish tissue, are distributed to the participants and they are requested to analyze the samples along with a Certified Reference Material (CRM) of a similar matrix. Participants are requested to provide data on selected polychlorinated biphenyl congeners (PCBs), chlorinated pesticides, and polycyclic aromatic hydrocarbons (PAHs). Results are then summarized in a form useful to the participants for evaluating their performance such as through visual scatter plots and the calculation of z and p scores [2].

For analytical data generated on marine mammal tissues, such as blubber, harmonizing measurements of organohalogen compounds is very important. Often organohalogen data on marine mammal samples from different laboratories are combined to provide an indication of geographical trends (e.g., [3,4]) or to help ascertain toxicological significance (e.g., [5,6]). In at least one study that combined data on organohalogen concentrations from marine mammal blubber to examine geographical trends, it was found that among laboratory variability contributed significantly to the observed data variability (Schwacke, personal communication). To help resolve such problems, NIST and the National Oceanic and Atmospheric Administration (NOAA) initiated an interlaboratory comparison exercise program patterned after the exercise described above but using marine mammal blubber as the exercise materials. The objective of this paper is to describe the exercises, summarize selected results, and discuss the value of these interterlaboratory comparison exercises. The exercises have been held on a small scale (<10 laboratories) starting in 1991[7] and on a larger scale (10 or more laboratories) starting in 1999. Twenty-four laboratories participated in the 2003 exercise.

Materials and Methods

Two tissue materials were sent to laboratories participating the exercises, SRM 1945 Organics in Whale Blubber and an homogenate of marine mammal blubber whose identity was unknown to the participants. Both materials were cryohomogenized using a procedure maximizing sample homogeneity and minimizing inadvertent contamination[8-10]. SRM 1945 is frozen, cryohomogenized blubber collected from a long-finned pilot whale (*Globicephala melas*) that stranded on Cape Cod, Massachusetts in 1991. This material has certified for concentrations for 27 PCB congeners and 15 chlorinated pesticides. Data for polybrominated diphenyl ether congeners, toxaphene, and chiral organohalogens have also been determined by NIST and other laboratories [11-13] making SRM 1945 a valuable analytical control material. The unknown blubber samples distributed to date include long finned pilot whale blubber (prior to 2000), California sea lion (2001), and polar bear fat (2003). Remaining aliquots from the materials are stored in the National Marine Mammal Tissue Bank [14] for use in other exercises or as control materials for future studies.

Laboratories participating in the exercise are requested to provide data from three measurements of SRM 1945 and the unknown for a target list of 18 chlorinated pesticides, 29 PCB congeners, and lipid content (Table 1). Participants are also requested to provide data on other compounds that their laboratories are currently measuring. Laboratories have provided data for additional PCB congeners, toxaphene and toxaphene congeners, coplanar PCB congeners, dioxins and furans, tris (4-chlorophenyl) methane and methanol, cyclodienes, polychlorinated naphthalene congeners, polybrominated diphenyl ether congeners, brominated biphenyls, octachlorostyrene, and fatty acids.

Once data are collected, they are compiled into a format useful to the participants for assessing their performance relative to other laboratories. For the unknown material, a consensus value is determined by taking the average of the reported results after screening for outliers. Generally, the consensus value is the geometric mean of these results. From this, a z-score is calculated where

$$z = \text{bias estimate/performance criterion} \quad (1)$$

and

$$z = (\text{reported value} - \text{consensus value})/\text{target error} \quad (2)$$

Z is reported two ways: based on the consensus value standard deviation and assuming 25% error. The interpretation of z is that a z = 1 is one standard deviation or 25% away from the consensus value depending on the definition of the target error[2]. To express precision, p-scores[2] are determined such that

$$p = \text{coefficient of variation (\%)}_{\text{lab}} / \text{coefficient of variation (\%)}_{\text{target}} \quad (3)$$

A target coefficient of variation has been set at 15% based on input from participants. The p-score represents within batch variation.

The combined results from all participants are compiled in a report. Also included in the report are compilations of additional analytes reported, methods used, and scatter plots of the data by core analyte. The exercise coordinator does not release the identity of participating laboratory to other laboratories taking part in the exercise. After the exercise is completed, participants are encouraged to attend a workshop that is generally held in conjunction with a major scientific meeting.

Table 1: Core Analytes for the Interlaboratory Comparison Exercise for Organohalogens in Marine Mammal Tissues.

Pesticides	**PCB Congener (Substitution)**
2,4'-DDT	18 (2,2',5-trichlorobiphenyl)
4,4'-DDT	28 (2,4,4'-trichlorobiphenyl)
2,4'-DDE	31 (2,4',5-trichlorbiphenyl)
4,4'-DDE	44 (2,2',3,5'-tetrachlorobiphenyl)
2,4'-DDD	49 (2,2',4,5'-tetrachlorobiphenyl)
4,4'-DDD	52 (2,2',5,5'-tetrachlorobiphenyl)
HCB	66 (2,3',4,4'-tetrachlorobiphenyl)
α-HCH	87 (2,2',3,4,5'-tetrachlorobiphenyl)
γ-HCH	95 (2,2',3,5',6-tetrachlorobiphenyl)
β-HCH	99 (2,2',4,4',5-tetrachlorobiphenyl)
heptachlor epoxide	101 (2,2',4,5,5'-tetrachlorobiphenyl)
cis-chlordane	105 (2,3,3',4,4'-tetrachlorobiphenyl)
trans-chlordane	118 (2,3',4,4',5-tetrachlorobiphenyl)
oxychlordane	128 (2,2',3,3',4,4'-hexachlorbiphenyl)
cis-nonachlor	132 (2,2',3,3',4,6'-hexachlorbiphenyl)
trans-nonachlor	138 (2,2',3,4,4',5'-hexachlorbiphenyl)
dieldrin	149 (2,2',3,4',5',6-hexachlorobiphenyl)
mirex	151 (2,2',3,5,5',6-hexachlorbiphenyl)
	153 (2,2',4,4',5,5'-hexachlorbiphenyl)
	156 (2,3,3',4,4',5-hexachlorbiphenyl)
	170 (2,2',3,3',4,4',5-heptachlorobiphenyl)
	180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)
	183 (2,2',3,4,4',5',6-heptachlorobiphenyl)
	187 (2,2',3,4',5,5',6-heptachlorobiphenyl)
	194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl)
	195 (2,2',3,3',4,4',5,6-octachlorobiphenyl)
	201 (2,2',3,3',4,5,5',6'-octachlorobiphenyl)
	206 (2,2',3,3',4,4',5,5',6-nonachlorobiphenyl)
	209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl)

Results and Discussion

Sample results from the 2003 exercise which used polar bear fat as the unknown are shown in Figure 1. Twenty-four laboratories participated in this exercise, two of which only submitted data on individual fatty acids in the two materials. One laboratory submitted two data sets on the organohalogen compounds that were generated using different methods. The 2003 exercise had the most participants to date and participation has been increasing at a rate of five additional laboratories per year since 1999. Eight laboratories have been participating in the exercises for four or more years.

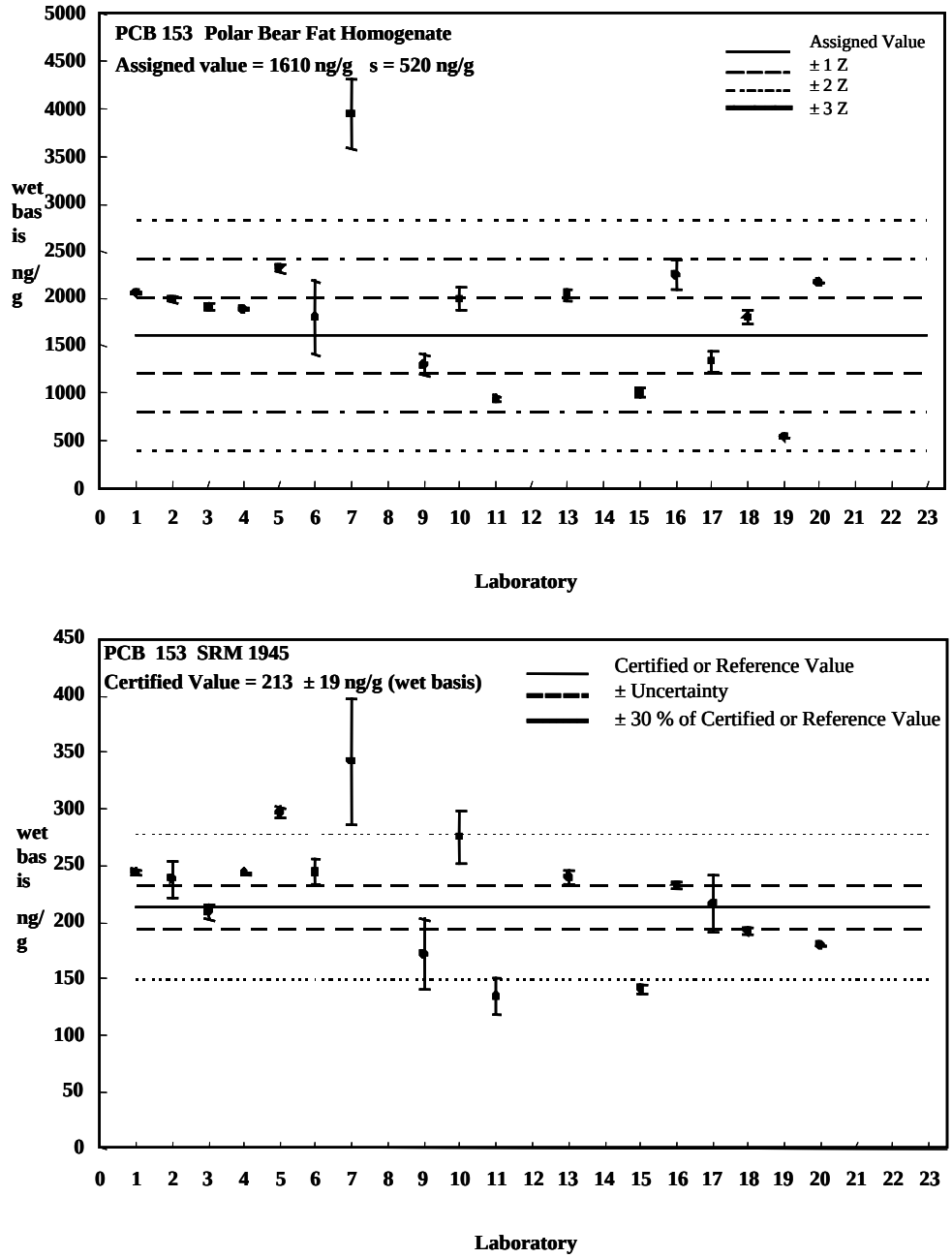

Figure 1: Mean (1 SD) values for PCB 153 determined in SRM 1945 and polar bear fat homogenate for the 2003 exercise.

The exercises have been valuable for a number of reasons. For instance, the average z-scores for laboratories that have participated in the exercise for at least four years are much lower than for laboratories that are participating for the first time. The average z-score for first year laboratories in the 2003 exercise was 7.0 versus 1.6 for laboratories that have participated in the exercise for four or more years. The exercise has also been an important source of new data on SRM 1945 and an important mechanism for comparing data on compounds of emerging interests. Table 2 shows data generated on SRM 1945 for selected polybrominated diphenyl ether congeners and coplanar PCBs. There were some discrepancies observed for the PBDE congeners especially for BDE 154 where the participants found lower values than those reported in the literature.

The exercise will continue and new laboratories will be solicited to participate. In the near future, data generated on SRM 1945 to date will be compiled and used to help update the Certificate of Analysis for this material.

Table 2: Data generated on SRM 1945 for selected polybrominated diphenyl ether congeners and coplanar PCBs. Values are in ng/g wet mass.

	Summary of Exercise Values			Literature Values			
Compound	**Mean**	**1 SD**	**n**	**Zhu and Hites (2003)[12]**		**Kucklick et al. (2004)[11]**	
BDE 47	36.9	4.7	5	46.6	2.0	52.9	3.8
BDE 99	17.0	0.9	5	23.0	1.9	32.0	2.3
BDE 100	9.2	2.4	5	11.8	0.9	14.0	0.6
BDE 153	7.5	0.8	5	10.1	1.0	22.4	1.5
BDE 154	12.9	5.4	5	20.8	3.0	28.2	2.0
PCB 77	0.368	0.068	5	--	--	--	--
PCB 126	0.167	0.034	6	--	--	--	--
PCB 169	0.133	0.044	5	--	--	--	--

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