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U.S. Department of Commerce
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DISCLAIMER

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ABSTRACT

The National Institute of Standards and Technology (NIST), in support of the National Oceanic and Atmospheric Administration's Marine Mammal Health and Stranding Response Program (NOAA/MMHSRP) conducts annual interlaboratory comparison exercises for the determination of chlorinated pesticides, polychlorinated biphenyl congeners, and trace elements in marine mammal tissues. These exercises provide one mechanism for laboratories to evaluate their measurement quality and comparability for these constituents in marine mammal tissues. Results of the 2000 NIST/NOAA/MMHSRP Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues are presented in two parts in this report, after a brief historical introduction of the program. Part 1 focuses on the development and analytical results of the organic contaminant component of this exercise, while Part 2 describes the features and analytical results for the trace elements component. For the organic contaminant exercise, 13 laboratories determined the concentrations of selected polychlorinated biphenyl congeners (PCBs) and organochlorine pesticides in a homogenized blubber control material "Marine Mammal Quality Assurance Exercise Control Material IV" (Control Material IV) and Standard Reference Material (SRM) 1945 Organics in Whale Blubber. Seven laboratories participated in the 2000 trace element exercise, where each laboratory performed measurements on a suite of elements (Cu, Cd, Pb, Fe, Se, As, Hg, Ni, Ag, and Zn) in three NIST quality assurance materials: Pilot Whale Liver Homogenate I (QC91LH1), Beluga Whale Liver Homogenate II (QC97LH2), and candidate SRM 1946 Lake Superior Fish Tissue. This report includes the results reported by the participating laboratories, combined consensus data results, and summary statistics for each analyte in the samples. The numerical indices used to assess laboratory performance are also discussed.

INTRODUCTION

Laboratories measuring contaminants in the marine environment must assess the accuracy and precision of their measurements. Quality control of measurements made on marine environmental samples is vital to the accurate assessment of marine pollution and its effects on wildlife and human health. Often, reference materials are limited or not available for many marine matrices of interest (*e.g.,* marine mammal tissues and marine fish). Consequently, marine resource management decisions may be based on subjective analytical results leading to potential environmental, health, or economic consequences. The National Institute of Standards and Technology's (NIST's) Analytical Chemistry Division has several programs to assess the data quality of laboratories and agencies performing chemical measurements on marine-related samples. NIST's reference material production, interlaboratory comparison exercises, and environmental specimen banking all contribute to the accuracy of chemical measurements in the marine environment.

NIST helps benchmark and improve the quality of analytical data gathered on the marine environment by administering annual interlaboratory comparison exercises. The largest exercise was initiated in 1987 and funded in part until 2000 by the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Marine Monitoring Program (NOAA/NS&T) (Cantillo and Parris, 1990, 1993; Cantillo 1995; Schantz *et al.,* 1999). NIST provides mechanisms for assessing the interlaboratory and temporal comparability of data and for improving measurements of polycyclic aromatic hydrocarbons, polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in bivalve mollusk, sediment, and fish samples. In addition, the National Research Council of Canada, with support from NOAA, administers a similar interlaboratory comparison exercise for trace elements in marine environmental materials. The NIST program for organic contaminants includes developing improved analytical methods, producing NIST Standard Reference Materials (SRMs) and other control materials, conducting annual interlaboratory comparison exercises, and coordinating workshops to discuss exercise results, thus providing a cooperative problem-solving forum for the participants. This program continues as the NIST Intercomparison Program for Organic Contaminants in the Marine Environment with partial support from fees paid by the participants.

Through the NIST National Marine Analytical Quality Assurance Program and with support from the NOAA Marine Mammal Health and Stranding Response Program (MMHSRP), the interlaboratory comparison activities have been expanded to include analyses of marine mammal tissues. The 2000 NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues was modeled after the exercises described above. Specifically, this exercise was designed to help laboratories assess data comparability and quality relative to other groups providing measurements of organochlorine contaminants and trace elements in marine mammal tissues and to link these important measurements to a national metrology laboratory. The results of the exercises presented in this report should be useful both for assessing current methodology and reducing the variability of contaminant data reported on marine mammals. Future exercises will allow for the assessment of analytical data quality over time. This report summarizes the results of the 2000 exercise including methods used for analysis, data reported by the laboratories on the intercomparison materials, and numerical indices used to assess laboratory performance.

Background on Interlaboratory Comparison Exercises and Associated Quality Assurance Activities Conducted by NIST for the MMHSRP

In 1987, the NOAA National Marine Fisheries Service (NMFS), Office of Protected Resources, established the National Marine Mammal Tissue Bank (NMMTB) as part of the National Biomonitoring Specimen Bank maintained by NIST. The NMMTB was designed for the long-term cryogenic archiving of marine mammal tissue specimens for future retrospective chemical analysis. In 1992, the Marine Mammal Health and Stranding Response Act (Public Law 102-587) formally established the NMMTB by legislation. NMFS implemented this Act by instituting the MMHSRP. Components of this program include marine mammal stranding networks, response to unusual mortality events, information management, real-time measurement of tissue contaminants, specimen banking, and analytical quality assurance.

Within the MMHSRP, real-time monitoring of contaminants in marine mammals is conducted by NMFS's Northwest Fisheries Science Center (NWFSC), Environmental Conservation Division. This monitoring includes analyses of samples collected specifically for real-time analysis and subsamples of banked specimens. NIST also analyzes aliquots of banked specimens to establish a baseline of concentration values for comparing with data generated by the NWFSC and other laboratories analyzing these specimens, and to monitor changes in analyte levels during specimen storage. Numerous other laboratories worldwide analyze marine mammal tissues for research and monitoring purposes. To assess the accuracy and comparability of results among NIST, NWFSC, and other laboratories, NIST in collaboration with NMFS developed a quality assurance (QA) program for analytical measurements of contaminants in marine mammal tissues. This QA program, described by Wise (1993), consists of (1) preparation, analysis, and distribution of marine mammal tissue control materials; (2) development of Standard Reference Materials (SRMs) for use in the analysis of marine mammal tissues; and (3) interlaboratory comparison exercises among laboratories analyzing marine mammal tissues.

Preparation, Analysis, and Distribution of Control Materials

Control materials, which are similar to the matrices being analyzed, are analyzed with regular samples with the results monitored to determine whether the analytical procedures are in control. The first control materials developed for the program were derived from liver and blubber tissues collected from pilot whales (*Globicephala melaena*) stranded in 1990 on Cape Cod, MA. Approximately 2 kg of each tissue were used to prepare tissue homogenates for use as analytical control materials and in interlaboratory comparison exercises. These homogenates are fresh frozen samples similar to marine mammal tissue samples routinely analyzed, rather than freeze-dried matrices frequently used as reference materials. The tissues were cryogenically pulverized and homogenized in Teflon mills to provide frozen powder-like materials (Zeisler *et al.,* 1983). These two control materials were analyzed at NIST to determine concentrations of trace elements (*Whale Liver Homogenate I*) and organic contaminants *(Whale Blubber Control Material*) and to assess sample homogeneity (Wise *et al.,* 1993).

The concentrations of 40 trace elements plus methylmercury were determined in the *Whale Liver Homogenate I* using INAA, differential pulse and square wave stripping voltammetry, cold vapor atomic absorption spectroscopy (CVAAS) for Hg, and ion-exchange chromatography plus

CVAAS (for methylmercury). Thirty PCB congeners and 16 chlorinated pesticides were determined in the *Whale Blubber Control Material* using gas chromatography-electron capture detection (GC-ECD) with both DB-5 and C-18 columns and gas chromatography-mass spectrometry (GC-MS) using a DB-5 column. The data resulting from analyses of both control materials, as well as a description of the analytical techniques and interpretation of the results, were published in Wise *et al.* (1993).

Both the pilot whale liver homogenate (*Whale Liver Homogenate I*) and the *Whale Blubber Control Material* have been available for use by laboratories as control materials during the routine analyses of marine mammal tissues. Based on experience gained in the preparation and analyses of *Whale Liver Homogenate I*, a second liver homogenate control material (*Whale Liver Homogenate II*) is being developed from livers collected in 1996 from beluga whales taken in Alaska native subsistence hunts. *Whale Liver Homogenate II* (fresh-frozen material) was distributed in 1997 to three laboratories participating in the interlaboratory comparison exercise on trace elements in marine mammal liver. This control material was also distributed to seven laboratories participating in the trace element part of the 2000 interlaboratory comparison exercise.

Whale Liver Homogenate II represents a 5 kg subsample of 30 kg of beluga whale liver that was originally collected for the development of a marine mammal liver SRM. The *Pilot Whale Liver Homogenate I* will be nearly exhausted by the end of calendar year 2001 (some portion is being retained for sample stability monitoring); therefore, *Whale Liver Homogenate II* will be the primary control material used in future analyses for trace elements in marine mammal tissues.

In the 1999 interlaboratory comparison exercise *Whale Blubber Control Material* was re-labeled *Marine Mammal Blubber Control Material III*, and distributed as an "unknown" to participants. Because the amount of this control material is now very limited, *Whale Blubber Control Material IV* is presently being developed as a replacement. *Whale Blubber Control Material IV* was derived from blubber that was collected by the NMFS Beaufort Laboratory, from a single pilot whale that stranded in 1999 on Pea Island, North Carolina. This material was cryogenically homogenized and labeled, *QC00-WB4 Whale Blubber Control Material IV*, and was distributed as an "unknown" to participants in the 2000 interlaboratory comparison exercise for the organic analysis.

Development of Standard Reference Materials (SRMs)

One of the goals of the marine mammal QA program is to develop certified reference materials (CRMs) for validating analytical measurements of trace elements and organic contaminants in marine mammal tissues. At the beginning of the program, there were several CRMs available from NIST, the National Research Council of Canada (Ottawa, Canada), and the Community Bureau of Reference (Brussels, Belgium) for inorganic contaminants in marine tissues including oyster tissue, mussel tissue, fish muscle and liver tissue, and lobster tomalley. However, for organic contaminants such as PCB congeners and chlorinated pesticides, there were only mussel tissue, SRM 1974 Organics in Mussel Tissue (*Mytilus edulis*) and cod fish liver oil, SRM 1588 Organics in Cod Liver Oil. SRM 1588, which serves as a suitable surrogate for a tissue extract with a high lipid content, had certified concentrations for 5 PCB congeners and 10 chlorinated

pesticides and noncertified values for 20 additional PCB congeners and 4 additional chlorinated pesticides (Schantz *et al.*, 1992). This material was reissued in 1998 as SRM 1588a and now has certified or reference values for over 80 organic contaminants. The mussel tissue SRM 1974 was reissued as SRM 1974a and has certified or reference values for over 100 organic and inorganic constituents (Schantz *et al.,* 1997).

Because of the lack of organic reference materials, blubber was selected as the first priority tissue for development of SRMs as part of the marine mammal QA Program. The experience gained from the preparation and analysis of the pilot whale blubber control material (Wise *et al.,* 1993) was used to develop SRM 1945 Organics in Whale Blubber, a certified material that can be used for validating measurements of organic contaminants in marine mammal blubber.

SRM 1945 was prepared from approximately 15 kg of blubber that was collected in September 1991 from a stranding of pilot whales on Cape Cod, MA. The material was cryogenically pulverized and homogenized in the same manner as described for the control materials. The resulting frozen blubber homogenate was analyzed using three different analytical techniques based on GC-ECD on two stationary phases with different selectivities for the separation of PCB congeners and on GC-MS. The results of these three techniques provided certified concentrations for 27 PCB congeners (PCBs 18, 44, 49, 52, 66, 87, 95, 99, 101/90, 105, 110, 118, 128, 138/163/164, 149, 151, 153, 156, 170/190, 180, 183, 187, 194, 195, 201, 206, and 209) and 15 chlorinated pesticides (HCB, α-HCH, γ-HCH, heptachlor epoxide, oxychlordane, mirex, *cis*-chlordane, *cis*-nonachlor, *trans*-nonachlor, 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, and 4,4'-DDT). Noncertified values for two additional PCB congeners (PCB 28 and 31) and chlorinated pesticides (dieldrin and β-HCH) are available.

Analytical data for the certification of PCBs and chlorinated pesticides in SRM 1945 were published by Schantz *et al.* (1995). SRM 1945, which represents the most highly characterized natural-matrix SRM with respect to these organic compounds, complements the other frozen tissue SRM (*e.g.,* SRM 1974a) by providing concentrations that are generally a factor of 10 to 100 times higher for the PCB congeners and chlorinated pesticides. Solvent extraction of the whale blubber produces an oil matrix similar to that of the cod liver oil SRM; however, the concentrations of PCB congeners and pesticides in SRM 1945 are generally 2 to 3 times lower than the NIST cod liver oil SRM except for the PCB congeners with higher degrees of chlorination, which have concentrations similar to the cod liver oil.

Additional concentration values for constituents not originally measured in SRM 1945 (*i.e.,* dioxins, furans, non-ortho PCBs, and polyhalogenated diphenyl ethers) have been provided for this material by the National Wildlife Research Center, Canadian Wildlife Service (CWS). These data are found in CWS *Lab Services Section Reports CHEM-OC-97-40*, *CHEM-PCDD-98-1*, and *CHEM-PCDD-98-4*). SRM 1945 was found to have relatively high amounts of twelve polybrominated diphenyl ethers (tetra through hepta congeners). More recently, measurements have been made by NIST on additional analytes in SRM 1945, including congeners of polychlorinated naphthalenes (PCNs) and co-planar PCBs (77, 126, 169).

The low relative uncertainties associated with the majority of analyte concentrations (5 % to 10 %) and the extensive list of certified analytes makes SRM 1945 a valuable resource for

validating analytical methods for the determination of halogenated compounds in marine mammal blubber and other high lipid-containing materials.

Interlaboratory Comparison Exercises

An interlaboratory comparison made on common, well-homogenized reference samples is one method to assess and improve data comparability. Such exercises currently involve the analysis of an unknown sample, a control material, and a NIST-traceable SRM by the participants. A list of analytes to be compared among the laboratories is provided to the participants. Participants submit their results to the NIST coordinator who evaluates data comparability using the performance measures recommended by the International Union of Pure and Applied Chemistry (IUPAC, 1993). Reports on the comparability evaluation are provided to the participants. NIST then conducts a workshop with the participants to discuss the results and ways to improve comparability.

Table 1 summarizes several important aspects of the interlaboratory comparison exercises conducted from 1991 to date, including target analytes, matrix samples, and the number of participating laboratories. The first exercise was conducted in 1991-92 and consisted of the distribution of the liver and blubber control materials to NWFSC and several other laboratories for analysis, *i.e.,* Department of Fisheries and Oceans (DFO) Canada in Winnipeg, the Geochemical and Environmental Research Group (GERG) at Texas A&M University, and the Department of Analytical and Environmental Chemistry at the University of Ulm in Germany.

In 1992, three laboratories (NIST, DFO Canada in Winnipeg, and the Department of Analytical and Environmental Chemistry at the University of Ulm in Germany) analyzed blubber subsamples from four to six beluga whales, the pilot whale blubber control material, and SRM 1588 in an interlaboratory exercise to compare results of analyses for PCB congeners and chlorinated pesticides. The analytical methods used by these three laboratories are described in Schantz *et al.* (1996). To minimize variability resulting from the source of calibration solutions, all three laboratories used common solutions to prepare calibration standards. Different internal standards and volume correction standards were used by each laboratory. Each laboratory used its preferred methods of extraction (Soxhlet extraction at NIST, ball-milling extraction at DFO, and column extraction at Ulm). All three laboratories used a size-exclusion chromatography cleanup, but with different columns, to remove the lipid material from the extracts and separated the PCB congeners from the majority of the pesticides as part of the cleanup procedures. GC-ECD was used by all three laboratories for the final analysis employing different columns. The results of this exercise were published in Schantz *et al.* (1996).

Table 1: Interlaboratory comparison exercises conducted for the MMHSRP from 1991-2001.

Dates	Analytes	Matrices	Objective	Participants
1991-92	PCBs/Cl pesticides[1]	Whale blubber	Laboratory comparability	NIST;NWFSC;DFO[3] Canada; Texas A&M Univ.; Univ. Ulm
	Trace Elements	Whale liver CM[2]	Analytical control	NIST;NWFSC
1992-93	PCBs/Cl pesticides	Whale blubber; whale blubber CM	Laboratory comparability	NIST; DFO Canada; Univ. Ulm
1993-1994	PCBs	Whale blubber; whale blubber CM	SRM development	NIST;NWFSC; DFO Canada; Texas A&M Univ.; Arthur D. Little; NW Aquatic Sciences; Univ. Ulm
1993-1997	PCBs/Cl pesticides and Trace Elements	Whale / seal liver	Sample comparability	NIST; NWFSC
1997-1998	Trace Elements	Whale liver	Laboratory comparability and CM development	NIST;NWFSC; Texas A&M Univ., Veterinary College
1999	PCBs/Cl Pesticides	SRM 1945 Organics in Whale Blubber Whale blubber CM	Laboratory comparability	10 laboratories
2000	PCBs/Cl Pesticides	SRM 1945 Organics in Whale Blubber	Laboratory comparability and program expansion	13 laboratories (organics)
	Trace Elements	Whale Livers (QC91LH1) (QC97LH2) SRM 1946 Lake Superior Fish Tissue		7 laboratories (trace elements)
2001 (projected)	PCBs/Cl Pesticides	SRM 1945 and Whale blubber CM	Laboratory comparability and program expansion	21 laboratories (organics)[4]
	Trace Elements	Whale Livers (QC91LH1) (QC97LH2) Candidate SRM 1947 Lake Michigan Fish Tissue		31 laboratories (trace elements)[4]

[1]Chlorinated pesticides
[2]Control material
[3]Department of Fisheries and Oceans
[4]Projected number of laboratories based on jars of material shipped to participants

In 1993, two intercomparison exercises were initiated. The first exercise focused on determining PCB congeners and chlorinated pesticides in blubber tissue using the blubber homogenate prepared as a proposed SRM (see discussion above). This material was distributed to NWFSC and several other laboratories for analysis (*i.e.,* DFO Canada, GERG, Northwestern Aquatic Sciences in Newport, OR, Arthur D. Little in Cambridge, MA, and University of Ulm). The second QA activity involved a "sample split" between NIST and NWFSC of blubber and liver samples from three marine mammals for both inorganic and organic analyses. These tissue samples were from specimens collected as part of the tissue banking and monitoring components of the program. In the past, for many of the liver and blubber specimens in the NMMTB, similar tissue samples were collected using NWFSC protocols and shipped to NWFSC for analysis as part of the monitoring effort. For this intercomparison exercise, NIST homogenized the selected liver and blubber samples from the tissue bank and provided a subsample of each homogenate to NWFSC. NIST and NWFSC analyzed tissue homogenate subsamples from the bank (liver for trace elements and blubber for PCBs and pesticides). The NWFSC analyzed the "monitoring" liver and blubber samples from the same animals. This provided an assessment of interlaboratory comparability on the same tissue homogenates and the comparability of the analyses of banked and the monitoring specimens collected from the same animals. This QA activity was an informal exercise only; the results have not been published.

In 1995 NIST, in collaboration with NOAA, formally instituted the National Marine Analytical Quality Assurance Program (NMAQAP). The mission of this program is to expand QA and specimen banking activities in marine environmental research and monitoring. To help accomplish the NMAQAP mission, a NIST satellite laboratory was established in Charleston, SC, in association with the NOAA Center for Coastal Environmental Health and Biomolecular Research (CCEHBR). The NMMTB is housed both at the NIST-Gaithersburg and at the NIST-Charleston facilities. NIST-Charleston provides the primary infrastructure for the marine mammal QA program and the NMMTB.

In 1997, an interlaboratory comparison exercise on trace elements in beluga whale liver sample splits was initiated among NIST-Gaithersburg, NWFSC, and the Texas A&M University Veterinary Medical Center. All three laboratories were involved in analyzing marine mammal tissues collected in Arctic Alaska. For this exercise, sample splits of beluga whale liver tissues collected during the 1996 subsistence hunts in Alaska were provided to the participants, as well as the pilot whale liver control material (*Whale Liver Homogenate I*) and the new beluga whale liver control material (*Whale Liver Homogenate II*).

The 1999 exercise included only laboratories conducting organic analyses. The 10 participating laboratories (NIST-Gaithersburg, NIST-Charleston, CCEHBR, NWFSC, GERG, Mississippi State Chemistry Laboratory, University of Connecticut, National Lab for Environmental Testing [Canada], Ehime University [Japan], and University of Utah) measured PCB congeners and organochlorine pesticides in SRM 1945 and in the "unknown," *Marine Mammal Blubber Control Material III* (this material is described above in the control material section). Also in 1999, the program began holding meetings of participants in conjunction with the annual meeting of the Society of Environmental Toxicology and Chemistry (SETAC).

Participation in the 2000 exercise included laboratories conducting both organic analyses (13 laboratories) and inorganic analyses (7 laboratories). The description and results of this exercise are presented in Parts 1 and 2 of this report. In 2001, there were approximately 21 laboratories participating in the organic exercise and 31 laboratories participating in the inorganic exercise. Expanding the number of laboratories provides an essential benefit for the participants in yielding higher quality consensus data. NIST also benefits from the preliminary concentration data and information gained on the candidate SRM materials that are routinely inserted into the exercises.

The QA program performs a major function in maintaining the quality of data resulting from the analysis of NMMTB specimens. Scientists requesting specimens from the bank for retrospective studies must demonstrate their analytical capabilities through appropriate QA activities, including participation in the NIST-administered QA program. In addition, NMFS requires that all researchers analyzing marine mammal tissues for contaminants under NMFS funding be participants in this program. This requirement ensures that the analytical results from marine mammal monitoring and research programs are of high quality and comparable.

PART 1: DESCRIPTION AND RESULTS OF THE 2000 NIST/NOAA INTERLABORATORY COMPARISON EXERCISE PROGRAM FOR ORGANIC CONTAMINANTS IN MARINE MAMMAL TISSUES

Materials Used in the Exercise

The exercise used two materials that were provided to 16 laboratories, of which 13 submitted data (Table 1.1). Participants were asked to make three measurements each on two materials: SRM 1945 Organics in Whale Blubber and "Marine Mammal Quality Assurance Exercise Control Material IV" (Control Material IV). Details on the preparation and certification of SRM 1945 are given in Schantz *et al.* (1995). The control material was prepared from blubber taken from a 350 cm female pilot whale. The animal stranded alive on the beach at Pea Island, NC (35° 69.228' N 75° 48.359' W) and was euthanized on November 18, 1999. Approximately 50 kg of blubber was excised, wrapped in aluminum foil, and shipped to the NIST Charleston Laboratory on February 18, 2000 inside a biological dry shipper. At NIST Charleston, the blubber tissue was stored in a liquid nitrogen (LN_2) vapor phase freezer at –150 °C until prepared for this exercise. The material was trimmed on Teflon sheeting using a titanium knife. A total of 7 kg of trimmed blubber was placed in Teflon bags, which were heat sealed and shipped to NIST Gaithersburg for cryohomogenization according to established procedure (Zeisler *et al.*, 1983). After homogenization, the material was placed inside a Teflon bag and blended manually by repeated inversion. The blended material was bottled as 12 g subsamples in glass jars and stored at -80 °C. One bottle of this material along with one bottle of SRM 1945 were sent either on dry ice or using a biological dry shipper via overnight express to each participating laboratory.

Table 1.1: Laboratories participating in the NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

National Laboratory for Environmental Testing National Water Research Institute Environment Canada Canada Centre for Inland Waters 867 Lakeshore Road Burlington, Ontario Canada	Energy and Geoscience Institute Department of Civil and Environmental Engineering University of Utah 423 Wakara Way, Suite 300 Salt Lake City Utah 84108
MS State Chemical Lab P.O. Box CR MS State, MS 39762	Geochemical and Environmental Research Group Texas A&M University 833 Graham Road TAMU Mail Stop 3149 College Station, Texas 77845
Center for Marine Environmental Studies (CMES), Ehime University Tarumi 3-5-7, Matsuyama, Ehime 790-8566 Japan	National Institute of Standards and Technology Analytical Chemistry Division 100 Bureau Drive Gaithersburg, MD 20899-8392
National Marine Fisheries Service Northwest Fisheries Science Center 2725 Montlake Blvd East Seattle, WA 98112-2097	NOAA/CCEHBR at Charleston 219 Fort Johnson Road Charleston, SC 29412
Department of Environmental Sciences Kumamoto University 2-39-1 Kurokami, Kumamoto, 860-8555 Japan	Fisheries and Oceans Canada Institute of Ocean Sciences 9860 West Saanich Road Sidney, B.C. V8L-4B2 Canada
Environmental Research Institute University of Connecticut Storrs, CT 06269	National Institute of Standards and Technology Analytical Chemistry Division Charleston Laboratory 219 Fort Johnson Road Charleston, SC 29412
University of Barcelona Av. Diagonal 645 08071 Barcelona Spain	

Exercise Requirements and Target Analytes

A suite of analytes was chosen for the exercise based on those used in the NIST/NOAA/NS&T exercise and several additional analytes were included to broaden this list (Table 2.1). Laboratories were requested to make triplicate measurements of these compounds in each of the materials and report their data using a data template provided by NIST. Laboratories were also asked to provide results from additional analytes, such as coplanar PCBs or chlorobenzenes that

were determined in the two materials. Results from the exercise were discussed during a workshop held in conjunction with the 2000 Society of Environmental Toxicology and Chemistry annual meeting held in Nashville, TN.

Table 2.1: Target analytes for the second annual NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

Pesticides	PCB Congeners	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-trichlorobiphenyl
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'-hexachlorobiphenyl
cis -nonachlor	132	2,2',3,3',4,6'-hexachlorobiphenyl
trans -nonachlor	138	2,2',3,4,4',5'-hexachlorobiphenyl
dieldrin	149	2,2',3,4',5',6-hexachlorobiphenyl
mirex	151	2,2',3,5,5',6-hexachlorobiphenyl
	153	2,2',4,4',5,5'-hexachlorobiphenyl
	156	2,3,3',4,4',5-hexachlorobiphenyl
	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

Evaluation of the Exercise Results

Determination of Laboratory Analyte Means

Each laboratory reported the results of their analyses (Sample 1, Sample 2, and Sample 3) and the mean for each laboratory was calculated. Non-numerical results were reported as "NA" (not analyzed). None of the target analytes were below the limit of detection for the participating laboratories (Tables 3.1-6.1 and Appendix A).

Establishment of Consensus Values

The following guidelines were used by NIST for establishing the "assigned values" or "consensus values" for the exercise. The consensus values for Control Material IV were the mean of all the reported laboratory means for a compound after the data were first screened by a Grubb's Single Iteration Outlier Test (Motulsky, 1997). Generally, most or all the values were included in the determination of the consensus value. The target values for the SRM were the certified values, reference values, or the consensus values from the 1999 exercise where SRM 1945 was also analyzed (Tables 5.1 and 6.1). In the NIST/NOAA/NS&T exercise, the assigned values for the unknown material were calculated based on the performance of each laboratory on the SRM. If the laboratory was within ± 30% of the SRM value, their values for the corresponding unknown were used to determine the consensus value. This approach was not used in the present exercise for two reasons. First, if the SRM comparison method using ± 30% is used, nearly one-third of the data are excluded from the calculation of the control material consensus value. Relaxing the ± 30% criterion to ± 50% still results in the rejection of approximately 20% of the data that could be used to calculate the consensus value. Second, the concentration of Control Material IV was significantly greater than SRM 1945. For instance, the concentration of PCB 153 was 35 times greater in Control Material IV than in SRM 1945. Hence there was concern regarding the performance on the SRM being reflective of the performance on the control material.

Reported Results

Laboratories were assigned a numerical identification code based on the order in which data were received with the exception of NIST-Charleston, which is Laboratory 1. The same code was used for both materials. The results from the analysis of Control Material IV and SRM 1945 are summarized in Tables 3.1-6.1. Appendix A shows the tabulated results from the individual laboratories for both materials and the results are shown graphically in Appendix B. Appendix C gives the methods used for analysis by each laboratory and Appendix D shows data for additional analytes.

Table 3.1. PCB congeners in Control Material IV (ng/g wet mass) reported by the participants the NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

Control Material IV	Laboratory													Reported Values			Consensus Values			
Congener	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**Mean**	**1 SD**	**n**	**Mean**	**n**	**1 SD**	**95%CI**
18	9.74	9.09	16.3	**42.7**	14.9	14.4	NA	NA	5.14	22.4	NA	13.3	12.9	16.1	10	10	13.1	9	4.9	3.2
28	36.0	22.1	37.0	21.0	24.7	20.7	**67.2**	NA	35.9	NA	34.0	30.4	32.3	32.9	13	11	29.4	10	6.6	4.1
31	6.99	2.35	NA	11.7	2.6	NA	NA	NA	1.54	NA	NA	NA	3.05	4.71	3.9	6	4.71	6	3.9	3.1
44	31.8	29.2	36.3	53.3	32.7	28.2	40.9	22.3	41.7	48.0	NA	40.1	30.5	36.3	8.9	12	36.3	12	8.9	5.0
49	77.3	86.5	89.4	150	89.6	NA	134	77.2	113	80.6	NA	121	97.7	102	25	11	102	11	25	15
52	267	282	294	403	284	228	417	204	362	245	283	222	274	290	67	13	290	13	67	36
66/95*	578	365	615	**1260**	552	267	851	394	600	498	483	647	603	593	248	13	538	12	152	86
87	207	204	246	NA	180	NA	291	124	249	NA	NA	240	189	214	49	9	214	9	49	32
99	644	438	770	260	666	NA	1059	571	863	575	NA	1017	619	680	237	11	680	11	237	140
101 (+90)	1036	1110	595	1967	909	1102	1684	655	1386	897	676	1067	1066	1088	397	13	1088	13	397	216
105	324	302	301	497	387	349	**657**	303	444	302	358	249.9	328	369	109	13	345	12	69	39
118	1097	1133	57.6	1487	1167	1296	**2585**	1050	1374	1053	949	1032	1106	1184	540	13	1067	12	353	200
128	411	437	392	917	457	494	489	294	556	435	764	576	405	510	166	13	510	13	166	90
132	NA	NA	NA	183	457	NA	1336	691	**12560**	265	NA	NA	NA	2582	4905	6	587	5	462	405
138 (+163+164)	4475	4750	1253	6577	4643	3595	6793	4150	7689	3107	2867	5349	3905	4550	1755	13	4550	13	1755	954
149	2261	1033	2303	3763	3130	NA	2930	1557	3216	1803	1535	2476	2259	2355	801	12	2355	12	801	453
151	701	534	720	980	822	NA	844	404	938	573	518	931	613	715	189	12	715	12	189	107
153	7424	6723	6781	7353	7860	6304	10288	6137	12465	4890	5420	8932	7525	7546	2044	13	7546	13	2044	1111
156	243	189	218	**627**	214	NA	364	159	244	189	342	400	228	285	131	12	254	11	79	47
170 (+190)	1274	1303	663	2063	1137	1335	1444	884	1221	1177	1786	1499	1162	1304	357	13	1304	13	357	194
180	3664	3740	3851	**6337**	3770	2773	4885	3313	4013	2810	2793	4049	3355	3796	967	13	3585	12	621	351
183	777	NA	758	1390	774	NA	72.2	783	867	637	NA	624	775	746	319	10	746	10	319	198
187	2408	2560	53.5	3657	2917	2273	1108	1957	2858	1727	1748	2690	2393	2181	904	13	2181	13	904	491
194	259	301	383	323	387	NA	350	210	365	300	265	356	250	312	58	12	312	12	58	33
195	88.9	96.0	137	123	142	101	96.1	48.0	93.2	NA	**345**	125	90.5	124	74	12	104	11	27	16
201	46.7	NA	64	NA	NA	NA	398	NA	510	337	512	73.3	46.3	249	212	8	249	8	212	147
206	24.7	27.0	38.5	52.3	45.3	18.2	NA	NA	35.2	28.6	31	53.1	29.1	34.8	11	11	34.8	11	11	6.7
209	12.3	9.02	14.6	18.3	NA	20.7	NA	NA	14.8	12.8	NA	22.9	11.6	15.2	4.5	9	15.2	9	4.5	3.0
66	105	105	NA	**463**	113	NA	224	109	86.2	92.3	NA	73.4	136	151	117	10	116	9	44	29
95	473	259	NA	797	439	NA	627	285	513	405	NA	573	467	484	158	10	484	10	158	98

***summed by coordinator if reported separately**

Outliers are in bold; not used to calculate the consensus value

Table 4.1: Organochlorine pesticides in Control Material IV (ng/g wet mass) reported by the participants in the NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

Control Material IV	Laboratory													Reported Values			Consensus Values			
Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**Mean**	**1 SD**	**n**	**Mean**	**n**	**1 SD**	**95%CI**
2,4'-DDT	1031	971	1026	1263	**2043**	1570	NA	NA	NA	NA	1310	1159	1035	1268	347	9	1171	8	202	140
4,4'-DDT	2581	1750	2310	2493	5027	2518	4157	1940	NA	2433	1697	2231	2887	2669	981	12	2669	12	981	555
2,4'-DDE	349	350	384	417	644	544	NA	NA	NA	NA	440	332	344	423	106	9	423	9	106	70
4,4'-DDE	24361	20600	19967	24533	20533	22360	**52569**	29000	NA	12400	16514	22670	28819	24527	9984	12	21978	11	4884	2886
2,4'-DDD	266	260	363	338	303	**1130**	NA	NA	NA	273	NA	447	284	407	278	9	317	8	64	44
4,4'-DDD	2033	1367	1764	1647	1493	2003	2477	1353	NA	2060	1156	1788	2029	1764	379	12	1764	12	379	214
HCB	246	264	199	223	249	219	330	298	NA	218	271	235	243	250	37	12	250	12	37	21
alpha-HCH	9.54	5.89	NA	5.93	5.81	10.1	8.47	6.44	NA	5.59	NA	2.28	10.4	7.05	2.5	10	7.05	10	2.5	1.6
beta-HCH	25.8	37.6	NA	42.0	62.5	38.5	50.9	40.7	NA	45.7	NA	30.4	25.2	39.9	11	10	39.9	10	11	7.1
gamma-HCH	4.34	5.43	NA	4.73	6.13	5.50	6.69	4.78	NA	5.36	NA	3.72	3.52	5.02	1.0	10	5.02	10	1.0	0.62
Heptachlor Epoxide	54.5	71.1	71.7	103	74.8	63.2	NA	66.7	NA	55.5	NA	95.0	53.0	70.9	17	10	70.9	10	17	10
Cis-Chlordane	88.0	101	88.4	119	104	87.5	129	103	NA	77.6	NA	56.1	86.9	94.5	20	11	94	11	20	12
Trans-Chlordane	7.04	7.13	8.00	NA	18.5	25.4	24.3	37.0	NA	NA	NA	9.39	13.4	16.7	10	9	16.7	9	10	6.8
Oxychlordane	113	74.9	NA	60.7	74.8	64.8	103	104	NA	35.8	NA	48.7	91.0	77.1	25	10	77.1	10	25	16
Cis-Nonachlor	137	159	143	198	240	194	272	196	NA	142	NA	172	128	180	46	11	180	11	46	27
Trans-Nonachlor	387	455	431	582	576	798	801	530	NA	294	NA	392	377	511	167	11	511	11	167	99
Dieldrin	347	395	394	412	391	544	NA	466	NA	362	NA	439	NA	417	60	9	417	9	60	39
Mirex	36.2	43.9	48.8	45.3	**87.9**	57.3	NA	NA	NA	43.4	NA	61.3	44.4	52.1	15	9	47.6	8	8.1	5.6
Lipid	67.0	64.7	66.2	68.7	76.1	70.2	71.0	66.6	71.4	65.7	65.9	80.8	68.9	69.5	4.6	13	69.5	13	4.6	2.5

Outliers are in bold; not used to calculate the consensus value

Table 5.1: PCB congeners in SRM 1945 (ng/g wet mass) reported by the participants in the NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

SRM 1945	Laboratory																	Target			
Congener	1	2	3	4	5	6	7	8	9	10	11	12	13	Mean	1 SD	95% CI	n	Value			Comment
18	4.90	3.30	4.90	5.27	3.29	4.27	NA	NA	1.65	4.47	NA	**9.07**	4.67	4.08	1.3	0.83	9	4.48	±	0.88	certified value
28	14.2	8.87	13.5	14.1	11.3	10.6	23.1	NA	17.8	NA	15.0	18.5	14.0	14.6	4.0	2.4	11	14.1	±	1.4	reference value
31	5.35	3.95	NA	5.57	2.17	NA	NA	NA	4.24	NA	NA	4.06	3.28	4.09	1.2	0.86	7	3.12	±	0.69	reference value
44	14.5	9.87	22.0	15.4	11.2	11.2	12.6	10.2	15.4	17.2	NA	16.9	12.5	14.1	3.5	2.0	12	12.2	±	1.4	certified value
49	16.7	15.5	16.1	22.4	22.3	NA	21.3	17.4	20.2	17.4	NA	26.8	18.4	19.5	3.5	2.0	11	20.8	±	2.8	certified value
52	39.4	37.4	52.6	45.2	39.0	38.6	45.3	33.0	45.3	36.5	38.9	25.4	41.8	39.9	6.6	3.6	13	43.6	±	2.5	certified value
66/95*	NA	NA	80.5	NA	NA	23.1	NA	NA	NA	NA	50.9	NA	NA	51.5	29	33	3	57.4			sum of the cert. values
87	23.4	22.8	29.1	NA	20.3	NA	22.9	15.3	26.4	NA	NA	32.9	15.9	23.2	5.7	3.7	9	16.7	±	1.4	certified value
99	56.8	56.1	68.2	53.5	56.9	NA	69.2	51.1	66.9	50.8	NA	**105**	44.8	57.4	8.2	4.8	11	45.4	±	5.4	certified value
101 (+90)	77.6	84.3	47.9	104	76.0	66.8	97.7	53.3	95.5	79.6	68.0	114	67.3	79.4	19	11	13	65.2	±	5.6	certified value
105	31.0	24.3	24.0	36.3	30.9	25.0	36.7	24.3	34.6	33.8	29.8	20.9	31.4	29.5	5.2	2.9	13	30.1	±	2.3	certified value
118	74.3	70.8	95.8	69.6	74.7	75.3	**133**	72.6	96.3	72.5	84.2	85.9	76.7	79.1	9.3	5.1	13	74.6	±	5.1	certified value
128	23.4	18.7	15.4	40.3	24.0	24.2	17.1	13.7	23.8	24.4	38.6	49.2	23.7	25.9	10	5.7	13	23.7	±	1.7	certified value
132	NA	NA	NA	7.23	21.1	NA	41.4	27.7	347	NA	NA	NA	NA	88.9	145	127	5	29.1	±	6.0	consensus of 99 QA
138 (+163+164)	141	165	55.2	90	129	123	192	156	234	121	144	247	129	148	53	29	13	132	±	7.4	certified value
149	77.4	78.3	90.2	82.6	85.8	NA	81.5	58.2	108	69.9	72.9	91.2	101	83.1	14	7.7	12	107	±	8.4	certified value
151	24.7	23.2	26.6	34.8	31.1	NA	24.4	15.3	32.3	22.6	30.8	40.4	28.0	27.8	6.6	3.7	12	28.7	±	5.2	certified value
153	230	207	255	290	192	206	253	202	347	180	249	397	215	248	64	35	13	213	±	19	certified value
156	12.9	8.82	9.43	**26.9**	11.7	NA	15.7	8.99	11.6	10.5	15.1	14.0	10.5	11.7	2.4	1.4	11	10.3	±	1.1	certified value
170 (+190)	40.4	35.8	23.8	44.1	40.3	38.6	36.5	28.9	39.8	42.1	50.3	**77.4**	41.1	38.5	6.9	3.9	12	40.6	±	2.6	certified value
180	134	116	174	175	136	116	160	143	170	134	138	**244**	112	142	23	13	12	107	±	5.3	certified value
183	35.2	31.1	34.0	42.5	36.4	NA	NA	36.9	44.9	29.9	NA	31.4	35.8	35.8	4.8	3.0	10	36.6	±	4.1	certified value
187	110	111	123	110	117	103	41	100	159	97.7	101	157	103	110	29	16	13	105	±	9.1	certified value
194	50.1	42.2	72.4	48.1	58.3	NA	64.9	43.0	61.7	55.8	36.9	78.5	41.1	54.4	13	7.4	12	39.6	±	2.5	certified value
195	14.4	6.60	11.5	9.90	13.3	12.3	8.29	5.22	9.40	NA	25.1	**38.0**	16.8	12.1	5.5	3.3	11	17.7	±	4.3	certified value
201	13.0	NA	14.0	NA	NA	NA	68.9	NA	96.9	65.2	82.0	20.6	16.3	47.1	35	24	8	17.0	±	0.89	certified value
206	42.8	31.7	58.8	52.8	54.3	34.1	54.2	NA	56.7	43.3	36.0	65.5	32.5	46.9	12	6.6	12	31.1	±	2.7	certified value
209	18.4	8.4	21.6	12.3	NA	15.4	26.2	NA	21.7	18.4	NA	27.6	12.4	18.3	6.2	3.9	10	10.6	±	1.1	certified value
66	37.0	20.3	NA	37.0	21.1	NA	37.3	22.8	25.2	19.3	NA	20.7	21.8	26.2	7.7	4.7	10	23.6	±	1.6	certified value
95	36.3	35.3	NA	49.0	33.4	NA	36.7	25.1	39.0	33.8	NA	49.9	31.2	37.0	7.6	4.7	10	33.8	±	1.7	certified value

***summed by coordinator if reported separately**

Outliers are in bold; not used to calculate the consensus value

Table 6.1: Organochlorine pesticides in SRM 1945 (ng/g wet mass) reported by the participants in the NIST/NOAA Interlaboratory Comparison Exercise Program for Organic Contaminants and Trace Elements in Marine Mammal Tissues.

SRM 1945	Laboratory																	Target			
Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**Mean**	**1 SD**	**95% CI**	**n**	**Value**			**Comment**
2,4'-DDT	69.0	67.4	78.5	78.7	137	122	NA	NA	NA	NA	88.2	98.4	96.3	92.8	24	15	9	106	±	14	certified value
4,4'-DDT	224	162	265	258	286	239	357	237	NA	313	163	248	232	249	55	31	12	245	±	15	certified value
2,4'-DDE	15.7	12.3	15.8	12.0	31.3	15.0	NA	NA	NA	NA	**46.7**	9.14	13.1	15.5	6.7	4.7	8	12.3	±	0.87	certified value
4,4'-DDE	502	476	526	519	487	533	599	720	NA	379	601	540	477	530	84	47	12	445	±	37	certified value
2,4'-DDD	24.4	24.9	24.7	21.8	13.7	24.5	NA	NA	NA	16.9	NA	24.8	19.0	21.6	4.2	2.7	9	18.1	±	2.8	certified value
4,4'-DDD	121	117	148	143	115	124	172	120	NA	124	99	122	115	127	19	11	12	133	±	10	certified value
HCB	31.0	27.6	26.2	22.7	26.6	26.7	24.3	27.6	NA	24.3	32.7	29.5	32.0	27.6	3.2	1.8	12	32.9		1.7	certified value
alpha-HCH	17.2	15.9	16.8	15.6	9.3	16.2	18.4	15.3	NA	12.6	NA	8.09	17.7	14.8	3.4	2.0	11	16.2	±	3.4	certified value
beta-HCH	3.34	6.34	NA	NA	3.07	5.67	2.88	2.05	NA	2.47	NA	7.77	5.85	4.38	2.0	1.3	9	8.00	±	1.4	reference value
gamma-HCH	4.74	NA	NA	3.10	3.81	3.43	4.24	3.24	NA	4.47	NA	4.36	3.17	3.84	0.6	0.41	9	3.3	±	0.81	certified value
Heptachlor Epoxide	12.8	10.1	13.3	15.4	10.7	10.8	NA	12.4	NA	7.85	NA	7.67	10.7	11.2	2.4	1.5	10	10.8	±	1.3	certified value
Cis-Chlordane	51.6	52.0	48.6	40.6	39.3	47.7	53.7	51.7	NA	34.6	NA	40.2	44.7	45.9	6.4	3.8	11	46.9	±	2.8	certified value
Trans-Chlordane	12.0	10.3	NA	8.7	9.9	13.0	NA	17.5	NA	13.1	NA	10.3	12.4	11.9	2.6	1.7	9	12.9	±	3.5	consensus of 99 QA
Oxychlordane	24.5	25.9	NA	18.9	18.7	21.9	25.0	31.0	NA	14.3	NA	17.5	21.5	21.9	4.8	3.0	10	19.8	±	1.9	certified value
Cis-Nonachlor	43.2	48.8	41.3	53.8	52.1	45.8	62.1	54.5	NA	46.8	NA	57.7	45.4	50.1	6.4	3.8	11	48.7	±	7.6	certified value
Trans-Nonachlor	174	160	172	203	174	231	195	213	NA	115	NA	161	228	184	34	20	11	231	±	11	certified value
Dieldrin	53.1	59.2	43.4	38.3	37.8	42.9	NA	58.1	NA	40.0	NA	55.9	NA	47.6	8.8	5.8	9	37.5	±	3.9	reference value
Mirex	27.3	30.1	32.3	22.7	11.8	28.7	NA	NA	NA	33.2	NA	52.5	20.3	28.8	11	7.3	9	18.9	±	2.8	certified value
Lipid (reported as %)	70.8	68.9	64.3	72.9	77.5	75.9	75.7	73.0	74	69.2	73.0	81.3	74.3	73.1	4.3	2.3	13	74.3	±	0.45	certified value

Outliers are in bold; not used to calculate the consensus value

Assignment of z-and p-scores

Performance Scores: Different programs have different data quality needs. The acceptability of the results submitted by a laboratory will be decided by the individual program(s) for which the laboratory provides data. Typically, the program will use these exercise results in conjunction with the laboratory's performance in the analysis of certified reference materials and/or control materials, and of other quality assurance samples. These exercise results are shown in a number of ways in this report to aid in the evaluation of data quality.

IUPAC guidelines (IUPAC 1997) describe the use of "z-scores" and "p-scores" for assessment of accuracy and precision in interlaboratory comparison exercises, such as described in this report. These indices assess the difference between the result of the laboratory and the exercise assigned value, and can be used, with caution, to compare performance on different analytes and on different materials.

Accuracy Assessment (z-score):

$$z = \text{bias estimate} / \text{performance criterion}$$

or

$$z = (x - X)/\sigma$$

where x is the individual laboratory result, X is the "Exercise Assigned Value," and σ is the target value for the standard deviation. As described in the IUPAC guidelines, the choice of σ is dependent upon the data quality objective of a particular program. It can be fixed or determined by reference to validated methodology (*e.g.,* the calculated σ from the exercise data, see Tables 3.1-6.1). The fixed performance criterion is more useful in the comparison of a laboratory's performance on different materials, while the use of the actual variation may be more useful within a given exercise, for example, if the determination of a particular analyte is more problematic than usual.

The z-scores calculated using both approaches and applied to each laboratory's data are given in Appendix A. The same criterion was adopted for use in this exercise as was used in the former NIST/NOAA/NS&T program, where the target standard deviation was set to 25% of the exercise assigned value. The z-scores for the Control Material IV represent 25% of the assigned value so that Z = +1 is the assigned value plus 25%, Z = -1 is the assigned value minus 25% and so forth. From a scientific point of view, IUPAC does not recommend the classification of z-scores, but does allow for such classification, *e.g.,*

$|z| \leq 2$ Satisfactory

$2 \leq |z| \leq 3$ Questionable

$|z| \geq 3$ Unsatisfactory

The tables in Appendix A summarize the results and performance indices including the number of analytes that fall within each category for each laboratory.

Precision Assessment (p-score):

$$p = \sigma_{lab} / \sigma_{target} \approx CV_{lab} / CV_{target}$$

where σ_{lab} and σ_{target} are variance estimates for the individual laboratory and the target variance, respectively. The CV_{lab} is the coefficient of variance (or ratio of standard deviation to the mean), while the CV_{target} is a reasonable value chosen by the participants. During the workshop that accompanied this exercise, a CV of 15% was agreed upon, which is the same value used by the former NIST/NOAA/NS&T program. Note that the precision that p describes is that which occurs within a batch of analyses. Between batch variance is likely larger and was not assessed in this exercise.

Results and Discussion

Summarized results are shown in Tables 3.1-6.1. The concentration of many organochlorines in Control Material IV was considerably higher than in SRM 1945. The consensus value for the sum of PCB congeners in Control Material IV (Table 3.1) was 30,050 ng/g wet mass versus 1,393 ng/g wet mass in SRM 1945 (Table 5.1). Likewise the sum of the organochlorine pesticides in Control Material IV was 29,270 ng/g wet mass versus 1,446 ng/g wet mass in SRM 1945. 4,4'-DDE was present in the highest concentration in both samples with a consensus value of 21,141 ng/g wet mass in Control Material IV and certified value of 445 ng/g wet mass in SRM 1945. The levels observed in Control Material IV, while higher than SRM 1945, are typical of other delphinids from the North Atlantic Ocean (Kuehl *et al.,* 1991). Lipid or "total extractable organics" 69.5 % ± 2.5 % in Control Material IV (mean ± 95 % confidence interval; Table 4.1) and the average value determined by the participants in SRM 1945 was 73.3 % ± 2.3 % relative to the certified value of 74.3 % ± 0.45 % (Table 6.1).

The relative scatter among the laboratories appeared similar for many of the compounds with some exceptions. All laboratories, with the exception of Lab 13 had difficulty obtaining the certified value for PCB 31 (Appendix B). This was evident by the large scatter in this plot. There was also considerable scatter among the laboratories for the values of PCB 31 in the Control Material IV. Laboratories also had difficulty agreeing on the value of PCB congener 201, both for the control material and the SRM. This may be a result of the two nomenclature systems used for this PCB congener (Guitart *et al*., 1993). High biases (most values exceeding the certified value) were observed among the values determined in the SRM relative to the certified value for the following compounds: PCB 87, PCB 99, PCB 180, PCB 194, PCB 206, PCB 209, 4,4'-DDE, and mirex. Low biases (most values below the certified or reference value) were observed for PCB 149, PCB 195, HCB, β-HCH, and *trans*-nonachlor.

A number of laboratories reported results for analytes in addition to the target compounds (Appendix D). Additional analytes that were reported included other PCB congeners (Labs 1, 2, 9, 10, and 12), coplanar PCBs (Labs 1 and 9), dioxins and furans (Lab 9), *tris*-(4-chlorophenyl)

methane and methanol (Lab 8), and endosulfan II and nonachlor III (Lab 2). Interestingly, PCB 169 was found in Control Material IV in relatively high concentrations for a marine mammal tissue (*e.g.,* Kuehl *et al.,* 1991 and Berggrena *et al.,* 1999). The concentration of PCB 169 in this material was determined to be 1.93 ng/g wet mass ± 0.040 ng/g wet mass by Lab 1 and 1.84 ng/g wet mass ± 0.048 ng/g wet mass by Lab 9. The concentration of PCB 169 (mean ± 95 % confidence interval) in SRM 1945 was 0.21 ng/g wet mass ± 0.02 ng/g wet mass measured by Lab 1 and 0.13 ng/g wet mass to 0.15 ng/g wet mass measured by Lab 9.

The participants used a variety of different methods to analyze the materials in this exercise (Appendix E). Six laboratories used Soxhlet extraction to extract the materials, two used pressurized fluid extraction, and the remaining laboratories used other techniques including sonication and column elution. Six laboratories performed a pre-separation on the sample extracts prior to GC analysis (*i.e.*, fractionation), while seven did not. Most laboratories (n = 8) used GC-ECD to quantify organochlorines, while five laboratories used GC-MS. Internal standards were used by eight laboratories, while four laboratories used external standards.

Conclusions

During the Nashville workshop there was some discussion regarding materials for future exercises. Blubber is typically the marine mammal tissue analyzed for organochlorine constituents; hence the program will continue to use this matrix. The exercise coordinators plan to vary the type of control material used to include other species of interest such as pinnepeds and delphinids. NIST is constrained somewhat on the choice of the material as a fairly large quantity (≈1 kg) is needed and this amount of material is not available on a routine basis. SRM 1945 will continue to be the SRM used in this exercise, since it is the only marine mammal tissue available with certified and reference values. This material also has had a number of other organochlorine compounds measured and reported, such as coplanar PCBs. The timing of the 2001 exercise will be similar to the 2000 exercise, with sample material distributed to the participants in April 2001 and the results due by October 26, 2001. A workshop to discuss the results will be held in conjunction with the 2001 SETAC meeting in Baltimore, Maryland, which is held from November 11-15, 2001.

PART 2: DESCRIPTION AND RESULTS OF THE 2000 NIST/NOAA INTERLABORATORY COMPARISON EXERCISE PROGRAM FOR TRACE ELEMENTS IN MARINE MAMMAL TISSUES

Materials Used in the Exercise

Two whale liver homogenate materials and candidate SRM 1946 Lake Superior Fish Tissue were issued to the participating laboratories. *Whale Liver Homogenate I* (QC91LH1) was derived from liver tissues collected from Pilot whales stranded in 1990 on Cape Cod, MA (Wise *et al.,* 1993). Similarly, *Whale Liver Homogenate II (*QC97LH2) was developed from liver tissue collected from Beluga whales taken in Alaska native subsistence hunts in 1996 at Point Lay, AK. This material served as the unknown for the exercise. Candidate SRM 1946 Lake Superior Fish Tissue was derived from the filleted tissue of Lake Trout (*Salvelinus namaycush*) collected from the Apostle Island region of Lake Superior through coordination with the Wisconsin Department of Natural Resources. All of the tissues were cryogenically pulverized and homogenized to provide powder-like materials as described above.

Exercise Requirements and Target Analytes

The seven participating laboratories (Appendix F, Table 1.2) were each sent ≈ 8 g of each of the above materials in frozen jars using liquid nitrogen vapor shippers. A letter of instructions for the exercise was included in the shipment along with a reprint of the manuscript containing NIST values for the exercise control material (QC91LH1) derived from instrumental neutron activation measurements (Wise *et al.,* 1993). Each laboratory submitted data by email using a standard data template.

The following requirements were stipulated to the participants:

1. Analyze samples for core (Cd, Cu, Hg, Fe, Pb) and optional (Ni, Se, As, Zn, Ag) elements using accepted analytical procedures. Provide brief descriptions of sample preparation and analysis schemes.

2. Digest, process, and analyze five subsamples of QC97LH2

3. Digest, process, and analyze five subsamples of Candidate SRM 1946

4. Digest, process, and analyze three subsamples of QC91LH1

Evaluation of the Exercise Results

Establishment of Consensus Values

A set of guidelines was used by the NIST exercise coordinator to assign concentration (wet mass) values for each element in the "unknown" samples. First, the results for each element reported from the individual laboratories were evaluated by comparing their results for the QC91LH1 control sample against NIST-published data that were collected in 1991 using

instrumental neutron activation analysis (INAA) and made available to each participating laboratory. Periodic reanalysis of this cryogenically stored material continues to show that the mass fractions of trace elements remain stable. These original measurements provided a good estimate of the concentration and range for each element in the QC91LH1 material, as jar-to-jar sample heterogeneity was incorporated into the uncertainty estimate and accuracy was verified with concurrent analyses of SRM 1577a Bovine Liver. A laboratory's result for a particular element was used if the difference between the reported mean for the participating laboratory and the mean of the INAA data differed by no more than 30 %. This criterion was not enforced for Pb as it was later determined that Pb was inhomogeneous in all three of the exercise materials. No data were rejected as outliers upon application of this criterion.

A consensus mean (derived from a "mean of laboratory means" determination) for each element in each sample was established once the laboratory means and 95 % confidence intervals were computed. The 95 % confidence limits (in subsequent tables) and corresponding error bars (in subsequent graphs) are expressed as $\pm$ ts/$\sqrt{n}$. The raw laboratory results and summary statistics are tabulated in Appendix G, Table 2.2. The corresponding consensus mean summary statistics are located in Table 3.2 in Appendix H. Consensus mean plots for each reported element in the unknown samples (QC97LH2 and SRM 1946) are given in Appendix I. The consensus mean data was used in conjunction with z-scores to evaluate laboratory performance.

Assignment of z-and p-scores

A discussion on the assignment of z- and p-scores and their classification categories can be found in Part 1 of this report. The performance criteria used for the trace element component of the exercise were different than the criteria used in the organic contaminants exercise and are discussed subsequently. For the trace elements exercise, z-scores were calculated using a target standard deviation (σ) of $\pm$ 10 % of the consensus mean. For example, for $z = \pm 1$ or $z = \pm 2$ the result would be 10 % or 20 % higher (or lower) than the consensus mean, respectively. Z-scores should be used to comment on relative and not absolute concentration accuracy, which is considered in the next section. With this caveat, z-scores can be classified into the three categories described in Part 1 to assess the performance of each laboratory. Using a "fixed" performance criterion offers a way for each laboratory to compare their performance on different samples. It should be recognized that any particular laboratory might have a detection limit or analytical method deficiency for a particular analyte. For marine mammal analyses, the acceptability of a particular laboratory's results should be judged in the context of the data quality needs of a particular program. The z-score results for the QC97LH2 and SRM 1946 samples are displayed in Appendix J, in both tabular (Table 4.2) and graphical format.

The external repeatability of each laboratory for individual elements was assessed using a p-score where laboratory repeatability (coefficient of variation) was normalized to an assigned target value for the coefficient of variation. The value for CV_{Target} was fixed at 10 % for the trace elements exercise. For example, for $p = \pm 0.5$ or $p = 1.2$ the laboratory repeatability would be 5 % or 12 %, respectively. The p-score results for the QC97LH2 and SRM 1946 samples are displayed in Appendix J, in Table 5.2.

Normalization Factors

Interlaboratory comparability helps each participating laboratory demonstrate method validity, but method accuracy cannot necessarily be inferred by comparability alone. Ideally, if the exercise includes a relatively large number of participants (*e.g.,* >20), the consensus mean should provide an unbiased estimate of the true mean. However, when the number of participating laboratories is low, the consensus mean value may be skewed by the results from one or two laboratories, making it a less useful benchmark for assessing laboratory performance. As the number of participating laboratories, and correspondingly, the number of analytical methods increase, biases from multiple independent methods will tend to cancel and the consensus mean should provide a more useful benchmark.

It was difficult to assess method accuracy in this round-robin exercise from the consensus data, because of the relatively small number of participating laboratories (n = 7), so normalization factors computed from the QC91LH1 control data were employed to test the robustness and accuracy of each laboratory's analytical method as applied to the unknown samples. The assumption of method robustness and accuracy was challenged because success or failure in determining a suite of elements in a particular sample matrix cannot be assumed if the sample matrix changes significantly**.**

The computation of normalization factors was based on the assumption that the mean of the NIST values generated in the Gaithersburg and Charleston laboratories using two independent techniques (INAA and standard additions ICPMS) provided a good estimate of the "true" concentration values of elements in the control sample. Subsequently, the control data generated by each laboratory was normalized to this "true" value as a quotient:

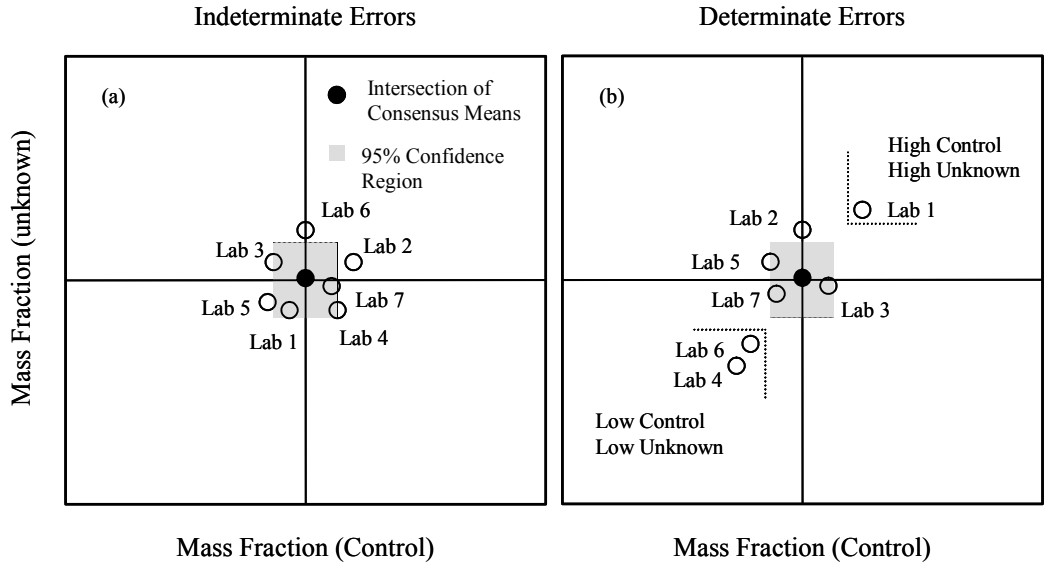
$$\text{Normalization Factor} = \frac{\text{Lab Mean}}{\text{True Value}}$$

Normalization factors were computed for each element analyzed in the control material and normalized laboratory means for the unknown samples were generated by dividing the original laboratory mean by the normalization factor. Thereafter, new consensus mean and standard deviation data were generated and compared to the original consensus data. This comparison was performed to determine if the standard deviation of the consensus mean would be reduced after normalization. If an improvement in the standard deviation occurred, the correction factor was warranted, implying that the normalized consensus mean provided a better method accuracy benchmark. If the standard deviation of the consensus mean increased after normalization, the correction factor was not warranted and normalized data would not provide a useful benchmark for method accuracy. Appendix K, Table 6.2 lists the normalization factors computed for the element suite analyzed by each participating laboratory and Table 7.2 lists the normalized consensus mean and summary statistics, along with the results of the correlation tests for the unknown QC97LH2 and SRM 1946 samples.

Error Assessment

Sources of error in interlaboratory comparison exercises can be assessed with a two-sample Youden Plot (Youden, 1959). Figure 2.1 illustrates how a Youden plot can be used to provide information on the occurrence of indeterminate (random) and determinate (systematic) errors, if the concentrations of the analytes are similar in both samples. Results will tend to group at random around the intersection of the consensus means if indeterminate errors are occurring (Fig. 2.1a). Determinate errors lead to bias in a measurement technique. Typical sources of determinate errors are calibration errors, blank correction errors and analytical method errors such as analyte volatility (loss) and contamination. Results will tend to group about a line running from the origin through the intersection of the consensus mean if determinate errors are occurring. This phenomenon is illustrated in Fig. 2.1b in the lower left and upper right quadrants of the Youden plot. Youden plots (Appendix L) were generated for elements analyzed in the QC91LH1 and QC97LH2 samples, if more than three laboratories reported results. Ninety-five percent confidence regions ($\pm$ ts/$\sqrt{n}$) were centered on the intersection of the laboratory means and superimposed on the intersection of the consensus means, so that the significance of the deviation from the consensus values could be judged.

Figure 2.1. Using Youden plots for error assessment.



Results and Discussion

The participants used several different methods to analyze the materials in this exercise, depending on the element: inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma optical emission spectroscopy (ICP-OES), flame, furnace and cold-vapor atomic absorption spectroscopy (AAS), and instrumental neutron activation analysis (INAA). The NIST

laboratory in Charleston, SC used ICPMS and the method of standard additions for all elements except Hg, which was determined using cold vapor isotope dilution ICPMS. The Nuclear Methods group at NIST performed the INAA analyses.

Data for the full element suite (Cd, Cu, Hg, Fe, Pb, Ni, Se, As, Zn, and Ag) are reported in tabular form in the Appendices, where possible. However, consensus data plots, z-plots, and Youden diagrams were only generated for Cd, Cu, Hg, Fe, Pb, Se and As due to an insufficient number of reporting laboratories for Ni, Zn, and Ag. Accordingly, the results for Ni, Zn, and Ag are of limited value and will not be discussed further.

z- and p-scores

The z-plots (Appendix J) for QC97LH2 or SRM 1946 show that subgroups of the exercise participants have demonstrated comparability within the $|0\text{-}2|$ z-range for most elements regardless of the sample, using 10% of the consensus mean as the performance criterion. This z-score range implies that a laboratory in this subgroup can distinguish between two samples when their respective analyte concentrations differ from 0% to 40%. It should be expected that the z-scores of greater than $z = \pm 1$ should occur with greater frequency for the SRM 1946 sample, as the analyte concentrations for certain elements are 1 to 2 orders of magnitude lower than their respective levels in the QC97LH2 sample. The frequency of higher p-scores for the SRM 1946 sample can be rationalized using the same argument. The fact that sample inhomogeneity may be a limiting factor when evaluating p-scores (*i.e.,* intralaboratory repeatability) should not be ignored. In fact, comparing the large variation in p-scores for Pb with those of other elements across the laboratories suggests Pb inhomogeneity in the samples.

Normalization Procedures

The z-score method fundamentally cannot address the absolute accuracy of consensus data unless a lack of bias in the analytical data that yields the consensus value is verified. Application of the normalization procedure to the consensus data provided a means to assess the accuracy of the consensus data by linking individual measurements (and methods) from a participating laboratory to a "true" value. Ideally, the "true" value would be derived from a NIST SRM, so that confidence would be implied and agreed upon by all laboratories. In the absence of this situation, the results determined by NIST for the pilot whale liver control sample (QC91LH1) using standard additions ICPMS and INAA analysis were combined. The comparison test results from the normalization procedure (Appendix K) indicated that the standard deviation of the consensus value could be improved for Cu, Hg, Fe, and As in QC97LH2 and Hg, Fe, and As in candidate SRM 1946. The normalization procedure did not lower the standard deviation of the consensus value for Se in either of the samples or Cu in SRM 1946. This implies that the laboratory performance on the control standard was not correlated with the performance on the unknown sample, suggesting that the robustness of a particular method used in one or more of the laboratories was questionable. For example, this may be related to a method detection limit phenomenon for Cu. Referring to Table 6.2 in Appendix K, the "true" concentration of Cu in the control material (QC91LH1) is 3.26 mg/kg. In QC97LH2 (Table 7.2), normalization improves the consensus standard deviation and yields a normalized consensus value of 12.8 ± 0.853 mg/kg, compared to an original consensus value of 13.1 ± 1.22 mg/kg in Table 3.2. However, in

SRM 1946, normalization worsens the consensus standard deviation and yields a consensus value of 0.450 ± 0.212 mg/kg, compared to an original consensus value of 0.473 ± 0.204 mg/kg in Table 3.2. The Cu concentration in SRM 1946 is an order of magnitude lower than the concentration of Cu in the control material, so good performance on the control material (a normalization factor approaching unity) does not infer similar success for SRM 1946. Similarly, the Se results suggest a matrix effect rather than a detection limit phenomenon for Se.

Youden Diagrams

Youden plots (Appendix L) for Cd, As and Se indicate the presence of indeterminate errors only. The results for As and Se were encouraging because two of the laboratories used ICPMS as the analytical procedure, where determinations involving these elements are often problematic. The INAA methods used by NIST for Cu (Laboratory 2) seemed to produce a low value for the QC91LH1 and QC97LH2 samples that was significantly different from the consensus data, while Laboratory 4 produced a high Fe value for the QC91LH1 and QC97LH2 samples. The most complete data set was reported for Hg, which indicated random errors for all laboratories with the possible exception of Laboratory 5, which produced a low value for the QC91LH1 and QC97LH2 samples. Youden plots were not generated for QC91LH1 and SRM 1946 because of the large differences in trace element concentration.

Methylmercury Data

One of the laboratories reported data for methylmercury in the three materials: QC91LH1 (1.422 mg/kg ± 0.074 mg/kg, n = 12), QC97LH2 (1.296 mg/kg ± 0.074 mg/kg, n = 22) and SRM 1946 (0.304 mg/kg ± 0.024 mg/kg, n = 17). The latter data may prove useful for comparison with methylmercury data produced by the methods that are used in the value assignment and certification process for methylmercury in SRM 1946.

Conclusions

Several rounds of the exercise will be required to fully assess the state of the practice of trace element measurements in marine mammals. Incorporation of more laboratories will also be important, as an increased sample size will serve to improve the analytical results and utility of any future exercises. Some of the participants have expressed the desire to incorporate analysis of an SRM into the exercise (at the expense of the participant) for the purposes of method validation. This and other comments are being considered to improve the QA model for 2001 and beyond. Increasing participation nationally and internationally, and possibly incorporating a NIST SRM into the exercise, will allow for a more robust outlier rejection scheme to be employed. This aspect is important to consider so that more informative data can be disseminated back to the exercise participants. Increasing laboratory participation will also help NIST gain access to more reliable consensus values for the candidate SRM materials that are distributed in the exercises, providing a secondary benefit from the QA program. It is projected that the 2001 trace elements exercise will have 30 participating laboratories, including 12 international laboratories.

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