THE NATIONAL STATUS & TRENDS QUALITY ASSURANCE PROGRAM FOR MARINE ENVIRONMENTAL QUALITY

PROGRAM DESCRIPTION AND EXAMPLES OF RESULTS OF THE 1986 INTERLABORATORY COMPARISON

MAY 1987

OCEAN ASSESSMENTS DIVISION
OFFICE OF OCEANOGRAPHY AND MARINE ASSESSMENT
NATIONAL OCEAN SERVICE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

THE NS&T QUALITY ASSURANCE PROGRAM FOR MARINE ENVIRONMENTAL QUALITY

John M. Tokar, John A. Calder, Stewart E. Holm

Introduction

The NS&T Program provides comprehensive, high quality and continuing information about the status and trends of environmental quality in selected coastal areas of the United States. This geographically large study area warrants the use of a number of laboratories to collect samples and perform the analyses required for adequate temporal and spacial coverage. To ensure that data generated by these laboratories are of comparable quality, a program of Quality Assurance (QA) has been developed.

Quality Assurance is defined as a system of activities whose purpose is to assure the producer or user of analytical data that these data meet defined standards of quality. QA activities are of great importance to the NS&T Program and provide objective information for determining the degree of confidence in chemical measurement data. NS&T Quality Assurance efforts are designed to produce nationally uniform data of known and accepted quality and thereby enhance the comparability among data sets. The Quality Assurance Coordinator is responsible for the development and implementation of the QA Program and for recommending and taking action that will ensure that data meet required quality standards.

The QA Program Objective

The objective of the NS&T QA Program is to reduce measurement errors to acceptable limits (i.e., 10% intralaboratory and 20% interlaboratory precision), thereby ensuring a higher probability of accuracy. These measurements include concentrations of selected organics and metals in marine sediments, shellfish, and finfish.

The QA Program Approach

Quality Assurance and Quality Control (QC) techniques are employed during the collection of samples and in the laboratory. The objective of the NS&T QA Program is met by conducting five major activities:

1. the development and use of standardized field sampling procedures and analytical protocols;

2. the conduct of interlaboratory comparisons of analytical methods;

3. the conduct of periodic Quality Assurance Workshops;

4. the development of Standard Reference Materials (SRMs) and of Reference Materials (RMs) for marine sediments and tissues;

5. the development and a use of a standardized data base for QA data and information.

The activities mentioned above are discussed in greater detail in the sections to follow.

1. Standard Field Sampling and Analytical Methods

The development and use of standardized and accepted field sampling and analytical methods serve as the basis for ensuring quality data for the NS&T Program. Standardized sample handling procedures will minimize uncertainties in sample collection, processing, storage, and pretreatment prior to chemical analysis. A uniform set of laboratory analytical methodologies are used by the measurement laboratories as further assurance of data quality.

Good laboratory practices and accepted standardization procedures are followed routinely by NS&T Program laboratories. SRMs and/or other prepared reference materials with certified or consensus concentrations are used to verify accuracy. Blanks, spiked samples, and sample replicates are used to ensure laboratory precision and to validate analytical procedures and instrument calibrations.

Field sampling and analytical procedures are clearly defined and followed throughout the NS&T Program. These procedures are documented in the two publications listed below:

A. "Benthic Surveillance Project: Cycle III Field Manual" (Lauenstein et al., 1986). This manual was prepared using field sampling protocol information compiled from researchers in the NOAA Ocean Assessments Division (OAD), the NOAA National Marine Fisheries Service (NMFS), and the National Bureau of Standards (NBS). The manual contains a step-by-step description for necropsy of fish specimens for both visceral and muscle tissue, including flow diagrams and schematics of the prescribed NS&T dissection process. Emphasis has been placed on procedures required to minimize organic and metal contamination of fish tissues and marine sediments;

B. "Standard Analytical Procedures of the NOAA National Analytical Facility 1985-1986" (MacLeod et al., 1985). This publication is a detailed laboratory manual for analytical chemists working on samples for the National Benthic Surveillance Project and the National Mussel Watch Project. This document contains the prescribed analytical procedure used to measure extractable organics in bottom sediments, in bottom-dwelling fish, and in mussels and other bivalves.

A manual for trace element analysis is in preparation and the NS&T Mussel Watch contractors have prepared a detailed field manual for the collection and handling of bivalve molluscs and sediments.

2. Interlaboratory Comparison Exercise

A series of interlaboratory comparisons are periodically conducted in order to assess the comparability of data generated by the NS&T contractor laboratories. These exercises are conducted using specially prepared intercalibration materials containing the target analytes whose component concentrations are known to the preparer, but not to the participating laboratories. Each laboratory is given a set of prepared materials, and reports results on a defined set of analytes. The results are

then reviewed and evaluated statistically by a QA reference laboratory. The individual laboratory results are often compared with consensus concentrations derived from reputable international organizations (such as the International Council for the Exploration of the Sea (ICES)) to increase the level of confidence for the values. Interlaboratory comparisons were conducted in 1985 and in 1986 with ten laboratories, including five NOAA laboratories and five contractor laboratories.

A Quality Assurance Reference Laboratory serves as the central focus for controlling and conducting QA activities. These activities encompass a wide range of functions from laboratory analyses and data evaluation to program design and coordination. The head of the Reference Laboratory works closely with the NS&T Quality Assurance Coordinator (QAC) to direct and coordinate the activities of the NS&T QA Program.

The NOAA National Analytical Facility (NAF) in Seattle, Washington, served as the reference laboratory for organics, and the National Research Council of Canada (NRCC) (Analytical Chemistry Section) was the reference laboratory for metals for the 1985/1986 exercise. An interlaboratory comparison for 1987 will be conducted in similar fashion to last year's exercise. The National Bureau of Standards, Center for Analytical Chemistry, will serve as the Reference Laboratory for trace organic analysis for this incomparison, while NRCC will continue as the trace metals Reference Laboratory.

The sequence of events of the 1986 interlaboratory comparison was as follows:

1. preparation of uncompromised reference materials (i.e. natural and spiked mollusc homogenates and marine sediments);

2. distribution of reference materials to the participating laboratories;

3, laboratory replicate (N = 3 or 4) analysis of reference materials;

4. discussion of results with the Quality Assurance Coordinator and participants;

5. evaluation of results followed by interpretive report.

This intercomparison was quite successful and has provided evidence of individual laboratory performance. These exercises serve as a self-help mechanism to improve the overall quality of the data reported from the participating laboratories. If a laboratory's performance is found to be less than optimal, a cause is sought, and corrective measures are then proposed and implemented to remedy the problem. The results of the most recent intercalibration exercises are discussed in the latter part of this document.

3. Quality Assurance Workshops

Quality Assurance Workshops are held annually following each laboratory intercomparison. They serve as the focus for an exchange of ideas and philosophies on various aspects of QA/QC methodology, as it relates to the improvement of the quality of NS&T marine-monitoring data. The workshops

are attended by senior principal investigators from the NS&T Program laboratories and by scientists from the Ocean Assessments Division of NOAA.

Several purposes of these workshops are:

- to promote improved inter-comparability of data from the NS&T contractor laboratories and NOAA laboratories;

- to identify and seek solutions to problems encountered with analytical methodology;

- to discuss Quality Assurance practices, their implementation, and their value;

- to discuss and review results from previous laboratory inter-comparisons and plan future ones;

- to improve the application of uniform statistical methods to marine environmental quality measurements.

The 1986 QA Workshop was organized by the National Bureau of Standards (NBS) and held at the NMFS Northwest and Alaska Fisheries Center in Seattle, Washington. The workshop consisted of a series of contributed papers and group discussions of the results of collaborative measurements on a set of test samples. Reports (Taylor, 1986, 1987) summarizing the proceedings of the last two workshops are available through the NBS.

4. Development of SRMs for Marine Sediments and Tissues

One of the major needs of the NS&T QA Program is a set of suitable SRMs for marine sediments and tissues. In response to this need, NOAA's Ocean Assessments Division and the NOAA National Marine Pollution Program Office have jointly undertaken an effort with the NBS to develop a set of SRMs for marine sediments and tissues. This effort has sparked great interest among researchers in the marine science community and has received support from other U.S. Government agencies, including the Environmental Protection Agency, Department of the Interior, Coast Guard, and the Navy. The first phase of this work has centered on development of sediment SRMs, in which the analytes will include selected aromatic hydrocarbons, PCBs, and chlorinated pesticides. The NBS SRMs will be issued in an air-dried state.

Recently, there has been public concern over organotin compounds used as active ingredients in vessel anti-foulant paints due to their toxicity to non-target organisms. This concern has prompted the inclusion of organotin compounds as an additional measure in the NS&T Program. As part of the SRM work, NBS is also investigating several approaches to determine tributyltin and dibutyltin compounds in marine sediments and identify at least two independent methods for certification of all selected organotin species in marine sediment and tissue SRMs.

5. Standardized Data Base for QA Data and Information

All Quality Assurance data generated by the program is archived and

stored in a unified data base. These data include results of the interlaboratory comparisons as well as the other QA/QC information (i.e. precision, accuracy, SRM results) in hard copy form and in a suitable computerized medium. A standardized data reporting format is being developed for use throughout the program. Data interpretation and evaluation is accomplished through the use of accepted statistical methods.

Results of the 1985/1986 Laboratory Intercomparison Exercise

This section will provide a preliminary interpretation of results from the most recent laboratory intercomparison. This evaluation is based on information obtained from a partial data set of organics in marine sediments and metals in marine tissue materials. These data were generated by the following participating laboratories: NMFS Laboratories in Sandy Hook, NJ, Seattle, WA, Beaufort, NC, Charleston, SC, and Gloucester, MA, and by Science Applications International Corp., Battelle Northwest, Battelle New England, Texas A&M Research Foundation, National Research Council of Canada, and the NBS, Gaithersburg, MD. The labatories are referred to by number only, so that their identities may remain anonymous. The standard deviations shown are based on either three or four (N = 3 or 4) sample replicates.

Organics in Marine Sediments

The sediment used in this intercomparison was collected from an industrial area of the Duwamish River, Seattle, Washington. A large suite of chlorinated hydrocarbons (CHC) and aromatic hydrocarbons (AH) were analyzed. For the purpose of this discussion, four AH have been selected, and the results from up to seven laboratories have been compared. The compounds were separated into two categories: lower molecular weight, higher volatility AH; and higher molecular weight, lower volatility AH. Naphthalene and 2,6-dimethylnaphthalene (Figures 1 and 2) represent compounds in the first category while benzo[a]pyrene and fluoranthene (Figures 3 and 4) represent compounds in the second category.

The naphthalene data (Figure 1) show good overall agreement except for laboratory number 6. Data for 2,6-dimethylnaphthalene (Figure 2) show results similar to naphthalene. The low results obtained for naphthalene by laboratory 6 may suggest losses of these more volatile compounds during sample extraction and concentration steps prior to quantification.

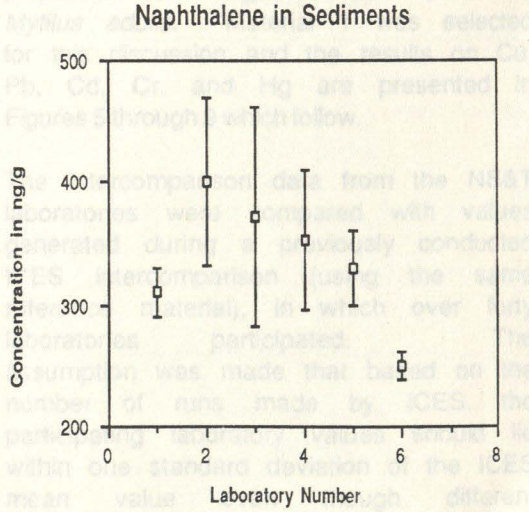

Figure 1

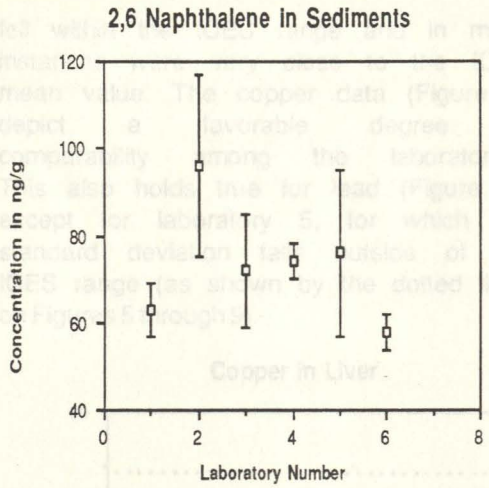

Figure 2

Although supposedly homogeneous sediment samples were supplied to the participating laboratories, the results from the higher molecular weight compounds (Figures 3 and 4) show what could possibly be two different concentrations. Figure 4 displays this most effectively with laboratory numbers 1 through 4 and 7 reporting a concentration of approximately 4,000 ng/g and laboratory numbers 5 and 6 reporting values of approximately 2,000 ng/g. This difference could be a function of the analytical scheme. However, other reasons for these concentration discrepancies can not be ruled out.

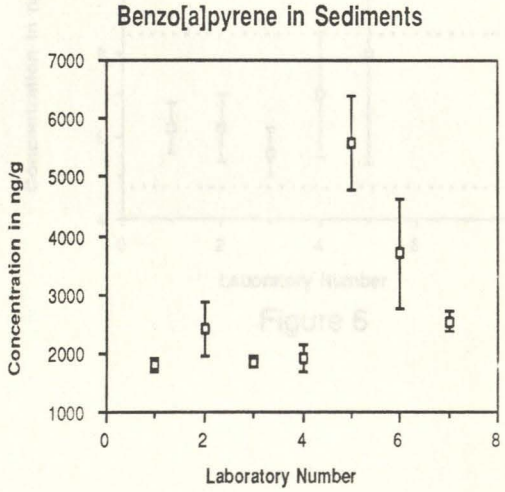

Figure 3

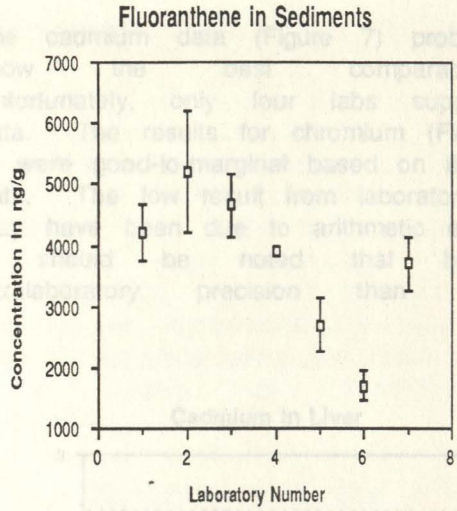

Figure 4

Metals in Marine Tissue Materials

The participating laboratories were provided with three reference materials containing the elements of interest (Cu, Zn, As, Cd, Hg, Pb, Cr, Mn, Fe, Ni, and Se). The materials were: (1) freeze-dried dogfish liver, (2) freeze-dried soft parts of *Mytilus edulis*, (3) a solution prepared from digested soft parts of *Mytilus edulis*. Material 1 was selected for this discussion and the results on Cu, Pb, Cd, Cr, and Hg are presented in Figures 5 through 9 which follow.

The intercomparison data from the NS&T laboratories were compared with values generated during a previously conducted ICES intercomparison (using the same reference material), in which over forty laboratories participated. The assumption was made that based on the number of runs made by ICES, the participating laboratory values should lie within one standard deviation of the ICES mean value even though different digestion methods and analytical instruments were used. The values of the NS&T intercomparison almost always

fell within the ICES range and in many instances were very close to the ICES mean value. The copper data (Figure 5) depict a favorable degree of comparability among the laboratories. This also holds true for lead (Figure 6), except for laboratory 5, for which the standard deviation falls outside of the ICES range (as shown by the dotted lines on Figures 5 through 9).

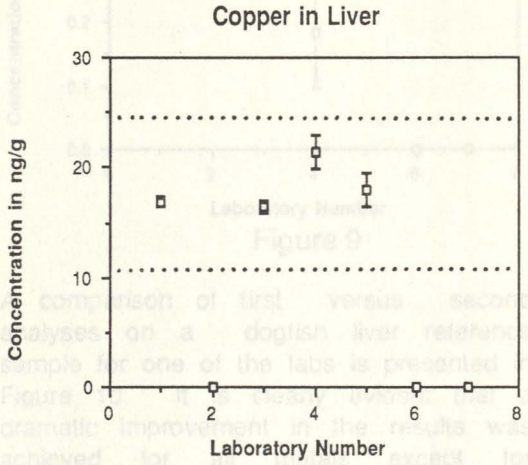

Figure 5

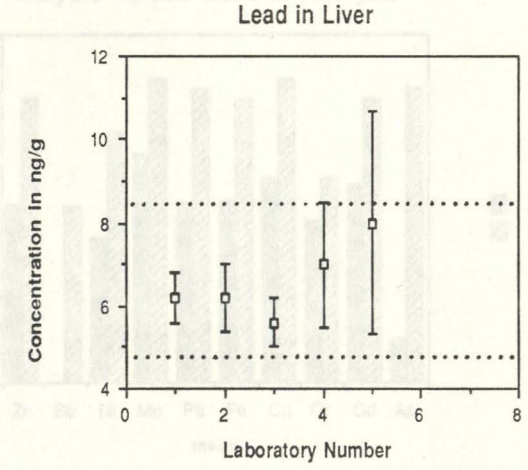

Figure 6

The cadmium data (Figure 7) probably show the best comparability. Unfortunately, only four labs supplied data. The results for chromium (Figure 8) were good-to-marginal based on these data. The low result from laboratory 2 may have been due to arithmetic error. It should be noted that better intralaboratory precision than was

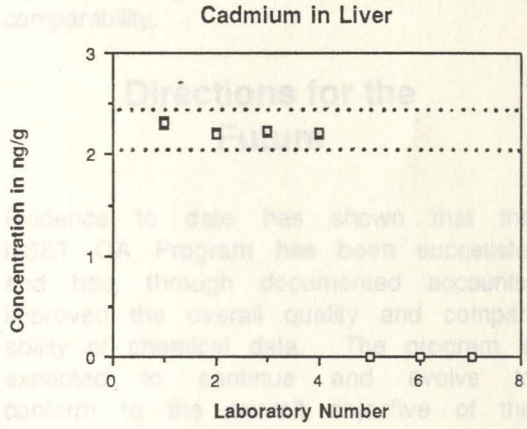

Figure 7

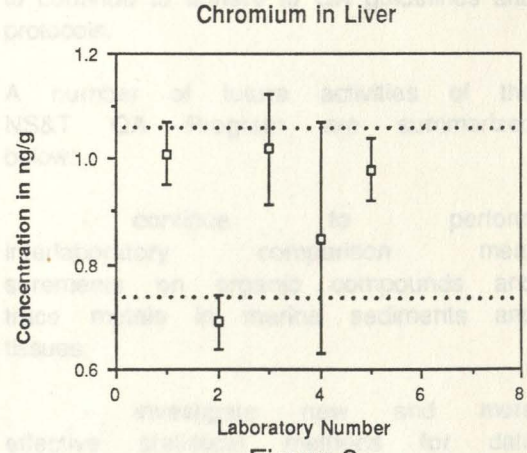

Figure 8

The analysis of mercury (Figure 9) was performed well, and the data were in good agreement, except for laboratory 4.

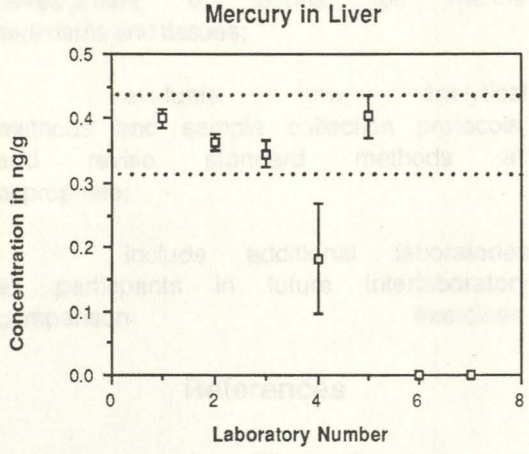

Figure 9

A comparison of first versus second analyses on a dogfish liver reference sample for one of the labs is presented in Figure 10. It is clearly evident that a dramatic improvement in the results was achieved for all metals except for chromium and for selenium.

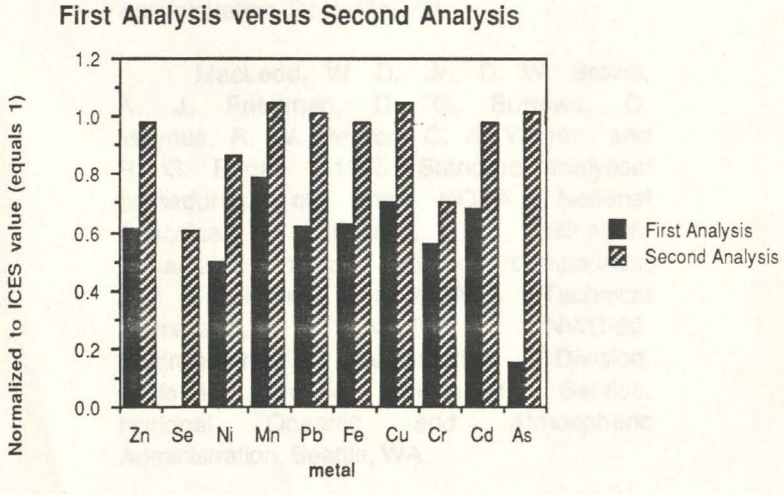

Figure 10

It should be emphasized that this set of interlaboratory comparisons was conducted prior to initiation of routine analysis of NS&T samples. Each laboratory took steps to improve its performance where necessary. It is anticipated that the next intercomparison exercise will demonstrate the effectiveness of the steps taken and result in a higher degree of interlaboratory comparability.

Directions for the Future

Evidence to date has shown that the NS&T QA Program has been successful and has, through documented accounts, improved the overall quality and comparability of chemical data. The program is expected to continue and evolve to conform to the overall objective of the NS&T Program: to provide reliable environmental quality data. The contractor laboratories will be expected to continue to adhere to QA guidelines and protocols.

A number of future activities of the NS&T QA Program are summarized below:

- continue to perform interlaboratory comparison measurements on organic compounds and trace metals in marine sediments and tissues;

- investigate new and more effective statistical methods for data quality evaluation;

- continue to publish a biannual NS&T QA newsletter to disseminate information on the program to interested

members of the marine scientific community;

- continue work on the development of SRMs for marine sediments and tissues;

- evaluate new analytical methods and sample collection protocols, and revise standard methods as appropriate;

- include additional laboratories as particpants in future interlaboratory comparison exercises.

References

Lauenstein, G. G., and D. R. Young. 1986. National Status and Trends Program for Marine Environmental Quality, Benthic Surveillance Project: Cycle III field manual. NOAA Technical Memorandum NOS OMA 28. Ocean Assessments Division, Office of Oceanography and Marine Assessment, National Oceanic and Atmospheric Administration, Rockville, MD.

MacLeod, W. D., Jr., D. W. Brown, A. J. Friedman, D. G. Burrows, O. Maynes, R. W. Pearce, C. A. Wigren, and R. G. Bogar. 1985. Standard analytical procedures of the NOAA National Analytical Facility, 1985-1986: Extractable toxic organic compounds, 2nd edition. NOAA Technical Memorandum NMFS F/NWC-92. Environmental Conservation Division, National Marine Fisheries Service, National Oceanic and Atmospheric Administration, Seattle, WA.

Taylor, J. K. 1986. A collection of abstracts of selected publications related to quality assurance of chemical measurements. Technical Report NBSIR 86-3352. Center for Analytical Chemistry, National Bureau of Standards, Gaithersburg, MD.