

NOAA National Status and Trends Program
Sixth Round Intercomparison Exercise Results for Trace
Metals in Marine Sediments and Biological Tissues

S. Willie and S. Berman
Institute for Environmental Research and Technology
National Research Council
Canada

Abstract

This report, prepared by the National Research Council of Canada, summarizes results of the NOAA National Status and Trends Program sixth round intercomparison exercise for trace metals in marine sediments and biological tissues. This exercise is one in a series of annual intercomparisons sponsored by NOAA and EPA doing agency-funded chemical analyses. In addition, the exercises have been opened to other laboratories resulting in forty-two potential participants for the 1992 exercise. The exercise materials were a spray dried sample of filleted flounder collected off the coast of the east coast of Nova Scotia and a freeze dried marine sediment collected in the Chesapeake Bay. Reference materials NRC CRM DORM-1 and BCSS-1 were also analyzed as part of the exercise. The elements determined were Al, Cr, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb for both matrices, plus Si, Mn, Sb and Tl for sediments. Thirty-five sets of results were received.

[Abstract by A. Cantillo, Quality Assurance Project Manager, NOAA National Status and Trends Program.]



Silver Spring, Maryland
April 1995

United States
Department of Commerce

Ronald H. Brown
Secretary

National Oceanic and
Atmospheric Administration

D. James Baker
Under Secretary

National Ocean Service

W. Stanley Wilson
Assistant Administrator

INTRODUCTORY REMARKS

The National Oceanic and Atmospheric Administration's National Status and Trends (NS&T) Program measures levels of chemical contaminants in organisms and sediments from around the coasts of the United States. A number of different laboratories have participated in making these measurements. In order to help assure and document the intercomparability of the data from various participating laboratories, the NS&T Program has supported a series of intercomparison exercises. This has included providing support to the Institute of Environmental Chemistry, National Research Council (NRC) of Canada to conduct and evaluate the results from intercomparisons of analyses for trace metals in marine sediments and biological tissues. The following is a reproduction of a previously unpublished report provided to the NS&T Program by NRC Canada regarding one of these intercomparison. It is being reproduced here to provide a permanently available record of the exercise results.



**National Research
Council Canada**

**Conseil national
de recherches Canada**

Institute for
Environmental Chemistry

Institut de
chimie de l'environnement

NRC · CNRC

NOAA/6

***Sixth Round Intercomparison
for Trace Metals
in Marine Sediments
and Biological Tissues***

Scott Willie and Shier Berman

Prepared for the
Ocean Assessments Division
National Oceanic and Atmospheric Administration

November 1992

Canada

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1. INTRODUCTION

This is the sixth intercomparison exercise organized by the National Research Council of Canada (NRC) on behalf of the Ocean Assessments Division of the National Oceanic and Atmospheric Administration (NOAA). The purpose of this exercise is to assess the capabilities of a number of NOAA and other laboratories involved in the Ocean Assessments Division's National Status and Trends program to analyze marine sediment and biological tissue for trace metals. In 1990 a small number of USEPA and state laboratories was allowed to join the fourth exercise. External participation was further expanded in 1991 with 29 laboratories, including four from Australia, submitting results. The opportunity for external participation was again offered in this study.

Participating laboratories, meeting at the annual NOAA quality assurance workshop after the fifth intercomparison exercise in Beaufort, NC, had agreed to analyze one sediment and one biological tissue as well as the certified reference materials (CRMs) NRC sediment BCSS-1 and muscle tissue DORM-1 for the sixth study. Because the mussel sample for the fifth exercise contained relatively high concentrations of contaminants there was a request for a biological sample closer to environmental backgrounds for NOAA/6. It was also decided that the biological sample should be a fish muscle tissue. The materials prepared for distribution by NRC were:

Sediment R, a freeze dried sediment from Chesapeake Bay donated by the Standard Reference Materials Project of the National Institute for Science and Technology, and

Fish Q, a spray dried sample of filleted flounder collected off the east coast of Nova Scotia and prepared for NRC by the Technical University of Nova Scotia..

The participating laboratories were each sent a ten gram sample of each of the two unknowns with the understanding that each participating laboratory would be responsible for procuring its own samples of the recommended CRMs. The participants were also sent data sheets on which to record their results and analytical procedures.

Each laboratory was requested to perform five replicate analyses of each of the sediment and biological samples and CRMs for the thirteen metals Al, Cr, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Hg and Pb. For the sediments, the determination of Si, Mn, Sb and Tl was also required.

In order to help provide benchmarks of accuracy for Sediment R and Fish Q, NRC also analyzed each of the samples by two different analytical methods. Where possible, one set of results was produced using isotope dilution inductively coupled plasma mass spectrometry (IDICPMS). This technique, when used correctly, is capable of producing very reliable analytical values. This is not to infer that the NRC laboratory is infallible, however, it does have a long and successful record regarding analysis of marine samples and the production of certified reference materials for trace metal analysis.

2. RESULTS

The prepared samples were mailed to the forty-two laboratories listed in Appendix A on March 19, 1992 with the deadline for receipt of results set at September 14. This date was moved a full month earlier than previous years' exercises to give the participants six months to perform the analyses. However, in true adherence to Parkinson's Law, almost all the data from thirty-five laboratories was

received on the final day by our overheated fax machine. This is an increase of six participants from the twenty-nine in 1991. Sequential numbers were assigned to each responding laboratory upon receipt of its data. Laboratory numbers 36 and 37 were assigned to NRC.

There were eight laboratories submitting results for the first time and two laboratories and two dropouts.

Of the thirty-five sets of results, seven laboratories did not submit data for the biological tissues and five did not submit data for the sediments. Laboratory 30 did not submit sufficient data to warrant evaluation.

A copy of the tabulated raw data was sent to each participant that had submitted data before the deadline in order to verify that no errors had been made by us in the transposition of numbers. This was not possible for data accepted from a few laboratories in the few days after the original deadline (we are a compassionate bunch). A small number of mistakes was caught and changes were made only if NRC was at fault. The data used for subsequent evaluation are listed in Appendix B. With the exception of Al and Fe for the sediment samples, the data are listed as received with respect to significant figures.

Each set of replicate analyses was examined using the Q test (Dixon's test)¹ for outliers and, when warranted, the laboratory mean and standard deviation were recalculated excluding the outlier. These sets are indicated by an apostrophe adjoining the laboratory number on the graphs and in Appendix B (e.g., 7'). If two or more "less than (<)" values were submitted in a set of replicate results the mean was not calculated and only the "less than" value was used for further data evaluation. The number of results used for the evaluation is noted next to the laboratory number in Appendix B. To ensure that all laboratories are compared on a rather even basis, sets containing less than four results were not evaluated.

One purpose of the exercise was to arrive at an accepted value for each analyte concentration in for each unknown in order to evaluate laboratory biases. The overall mean concentration for each metal was calculated from the mean of laboratory replicates and the NRC data. These means were assumed to be normally distributed, which may not be a valid assumption at very low concentrations, but for the purpose of this exercise it is felt to be adequate. A successively applied Student *t* test² at the 95 percent confidence level was used to identify outliers. Some very obvious outliers were initially rejected before statistical evaluations. The rationale of this approach is discussed in Appendix F which is a document prepared by one of the authors for the Marine Chemistry Working Group of the International Council for the Exploration of the Sea earlier this year.

All of the evaluated replicate data, including outliers, are plotted on the graphs where possible. Means that were outliers from the accepted or certified concentration are indicated by an asterisk following the laboratory number (e.g., 5*). "Less thans" are indicated by a downward arrow head and the reported value. Some high results that if plotted would distort the clarity of the graphs are indicated by an upward arrow head with the mean of the replicates reported. A solid horizontal line represents the accepted for an unknown or the certified value of a CRM. The shaded area represents the 95% confidence limits for these values. A short summary of results for each set of results is listed to the left of the appropriate graph. All concentrations are expressed in mg/kg on a dry weight basis except for aluminum, iron and silicon in the sediments where the concentrations are in percent.

ALUMINUM

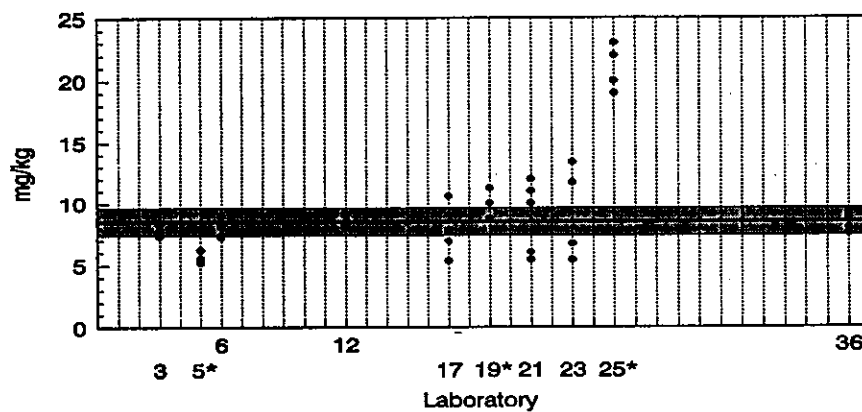
FISH Q

Accepted Value:
 $8.48 \pm 1.08 \text{ mg/kg}$

Results: 10

Quantitative
 Values: 10

Rejections: 3



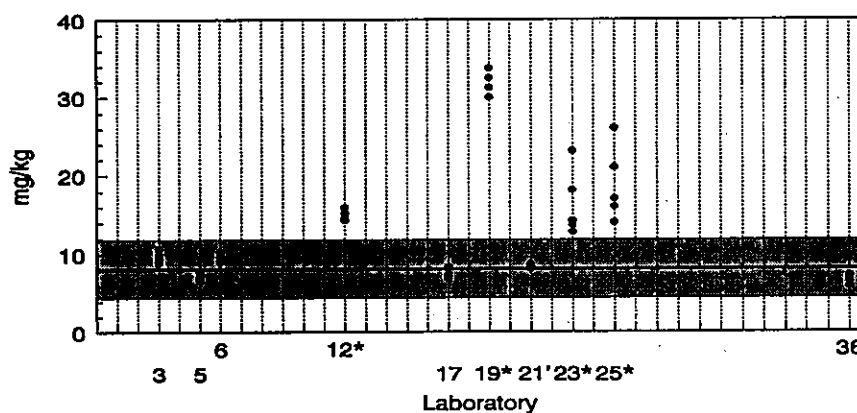
DORM-1

Accepted Value:
 $8.17 \pm 3.69 \text{ mg/kg}$

Results: 10

Quantitative
 Values: 10

Rejections: 4



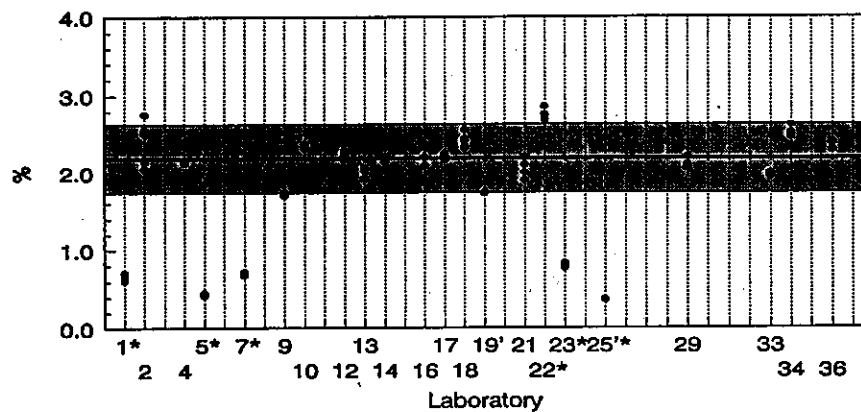
SEDIMENT R

Accepted Value:
 $2.19 \pm 0.44 \%$

Results: 22

Quantitative
 Values: 22

Rejections: 6



ALUMINUM

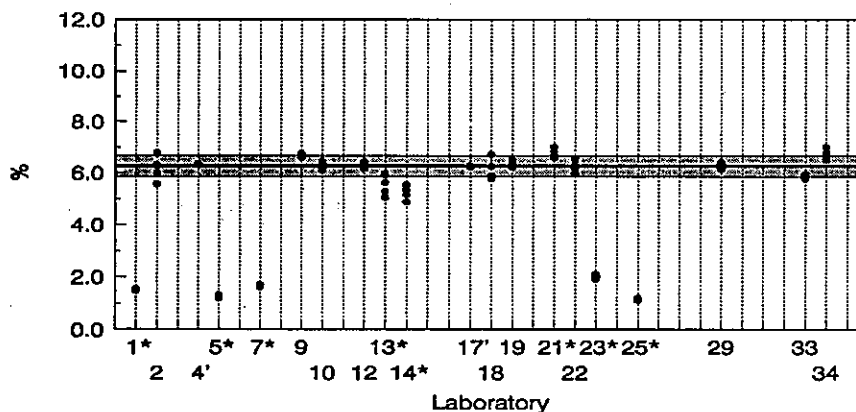
BCSS-1

Certified Value:
6.26 ± 0.41 %

Results: 20

Quantitative
Values: 20

Rejections: 8



Tissues

The determination of aluminum in biological tissues is difficult as shown by performances in past exercises and the relative lack of biological tissue CRMs for this analyte. Only nine laboratories, down from eighteen in 1991, submitted results for Fish Q and DORM-1 (the NRC results are evaluated but not counted in these summaries). For Fish Q three laboratories (5,19,25) had means outside the accepted range. Laboratories 21 and 23 had acceptable means but not one of their individual values was within the accepted confidence interval. This leaves four laboratories (3,6,12,17) with acceptable results. A RSD greater than 10 percent was reported by four laboratories.

Five laboratories (3,5,6,17,21) submitted sets of results for DORM-1 all within the acceptable range and with RSD's less than 10 percent. Results from the other four laboratories (12,19,23,25) were all high. Laboratories 19 and 25 had high results for both biological samples.

In spite of the lower participation rate, the overall performance is an improvement over that of NOAA/5.

Sediments

Twenty-one and twenty laboratories submitted results for aluminum in Sediment R and BCSS-1 respectively. As in NOAA/5, two data sets can be distinguished. Laboratories 1,5,7,23 and 25 did not use hydrofluoric acid in their digestion procedures and all reported low results for both samples. Of the remaining sixteen sets for Sediment R, fifteen laboratories (2,4,9,10,12,13,14,16,17,18,19,21,29,33,34) had acceptable means. Laboratory 22 was slightly high. Only three laboratories (1,2,21) submitted results with a RSD greater than 5 percent. Most laboratories had RSDs in the 2-3 percent RSD range.

Of the remaining fifteen sets for BCSS-1, twelve laboratories had acceptable means (2,4,9,10,12,17,18,19,22,29,33,34). Laboratories 13 and 14 submitted low results and Laboratory 21 was slightly high. The performance of all fifteen laboratories is quite good considering the relatively small confidence interval for the CRM. Three laboratories (2,13,18) reported results with a precision greater than 5 percent.

SILICON

The determination of silicon was not required
in the biological samples

SILICON

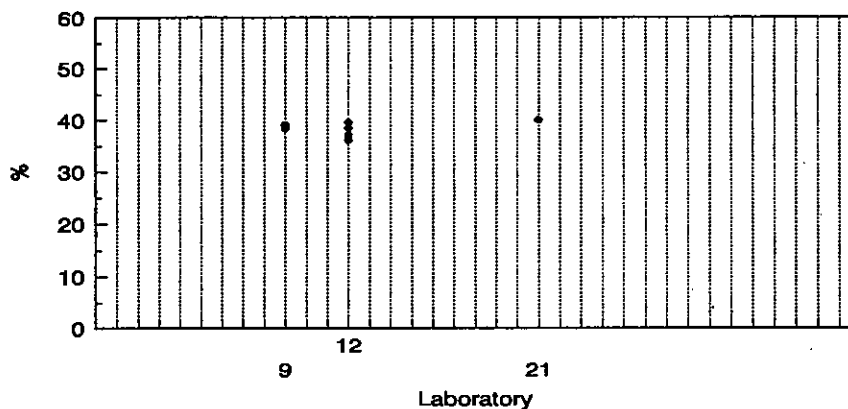
SEDIMENT R

Accepted Value:
not determined

Results: 3

Quantitative
Values: 3

Rejections:



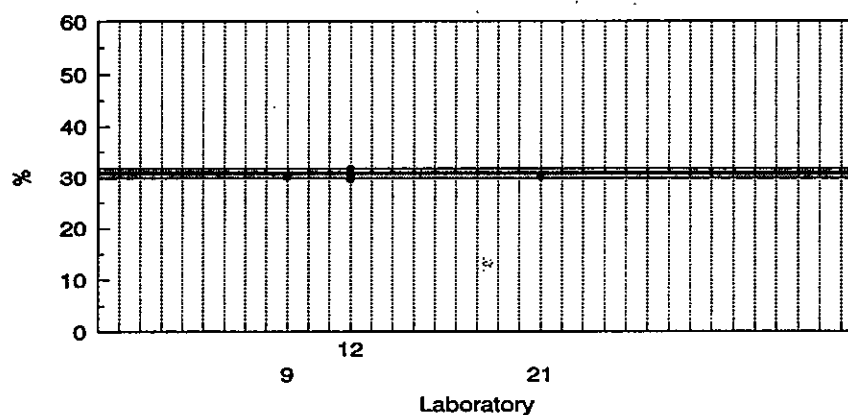
BCSS-1

Certified Value:
 $30.8 \pm 1.0 \%$

Results: 3

Quantitative Values: 3

Rejections:



Sediments

Only three laboratories (9,12,21) reported quantitative values for silicon in Sediment R and in BCSS-1. Although an acceptable value was not determined for Sediment R due to lack of data, the laboratories that did submit values were in good agreement with one another. And since all the values submitted by the three were within the certified range for BCSS-1 we may infer that these laboratories were able to determine Si in these sediment samples with good accuracy and precision.

CHROMIUM

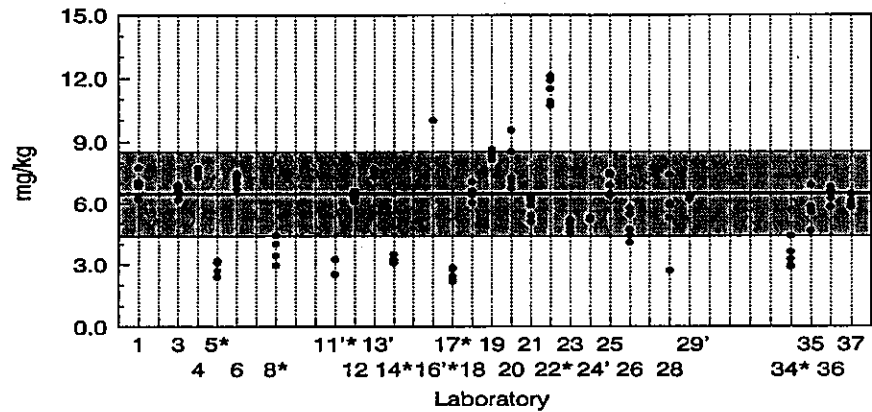
FISH Q

Accepted Value:
 6.45 ± 2.07 mg/kg

Results: 27

Quantitative
 Values: 27

Rejections: 8



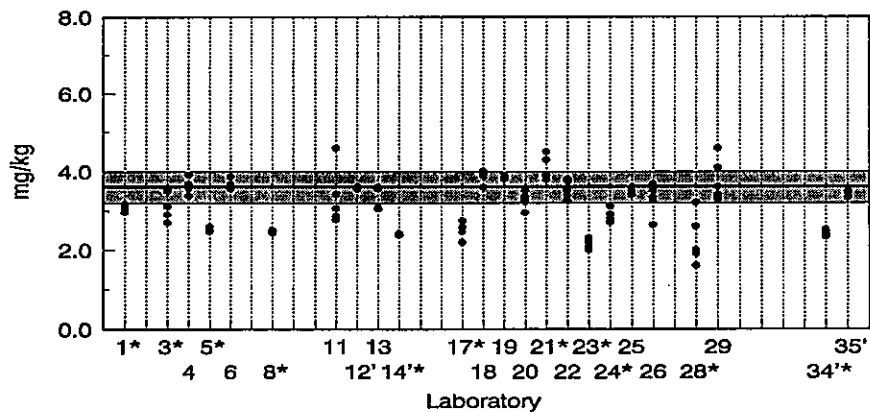
DORM-1

Certified Value:
 3.60 ± 0.40 mg/kg

Results: 24

Quantitative
 Values: 24

Rejections: 11



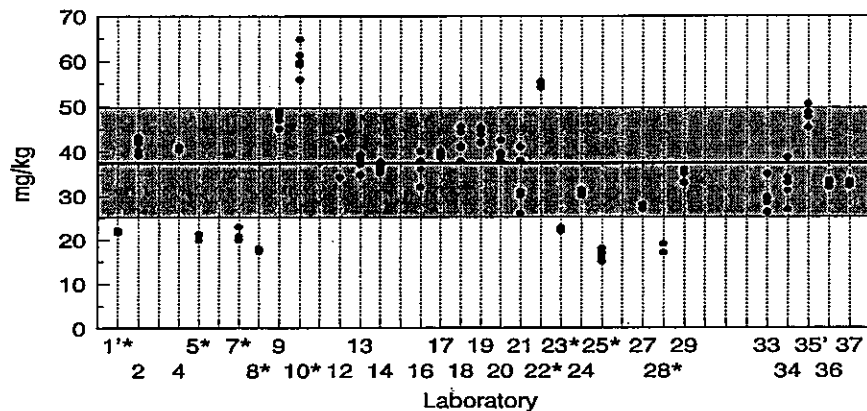
SEDIMENT R

Accepted Value:
 37.5 ± 12.3 mg/kg

Results: 29

Quantitative
 Values: 29

Rejections: 9



CHROMIUM

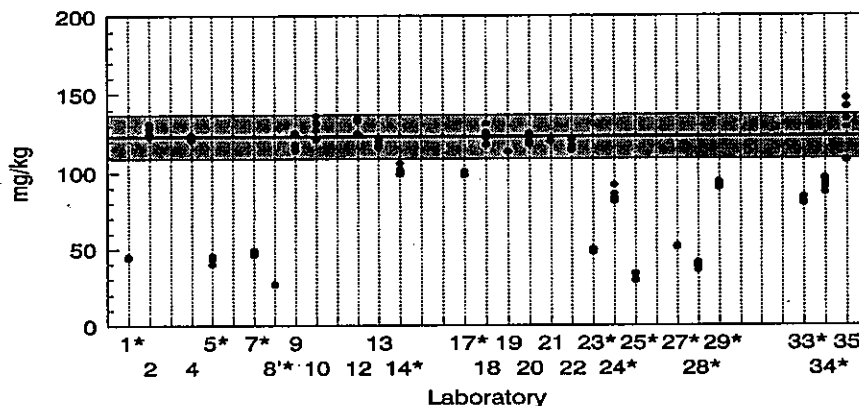
BCSS-1

Certified Value:
123 \pm 14 mg/kg

Results: 26

Quantitative
Values: 26

Rejections: 14



Tissues

Twenty-five laboratories submitted results for chromium in Fish Q. Eight of the means were outside the calculated \pm 32 percent confidence interval. In view of the higher Cr concentration, this is somewhat poorer performance than last year. Again, most outliers were low (5,8,11,14,17,34). Only two (16,22) reported high means. Four laboratories reported results with an RSD greater than 15 percent.

The certified range for chromium in DORM-1 is a tight \pm 11 percent. Means of thirteen of twenty-four laboratories (4,6,11,12,13,18,19,20,22,25,26,29,35) that submitted results were within this range. Ten reported low means (1,3,5,8,14,17,23,24,28,34) and Laboratory 21 had the only high value. Only two laboratories (11,28) reported results with a precision greater than 15 percent RSD, an improvement over last year. Laboratories 4,6,12,13,18,19,20,25,26,29 and 35 reported acceptable results for both biological tissue samples.

Sediments

Twenty-seven laboratories reported results for chromium in Sediment R. Nine means were rejected from the accepted range of \pm 33 percent. Laboratories 10 and 22 reported high results and Laboratories 1,5,7,8,23,25 and 28 reported low values. The same laboratories that reported low results for aluminum in the sediments also submitted low results for chromium, most likely due to incomplete dissolution procedures. Five laboratories reported results with a RSD greater than 10 percent.

Twelve (2,4,9,10,12,13,18,19,20,21,22,35) of twenty-six laboratories reported means within the \pm 11 percent confidence range for chromium in BCSS-1, an improvement over NOAA/5. As with NOAA/5, all of the outliers (1,5,7,8,23,24,25,27,28,29,33,34) were low. Only one laboratory reported results with a precision greater than 10 percent RSD. You can obviously have good precision with poor accuracy. Acceptable results for both sediment samples were reported by Laboratories 2,4,9,12,13,18,19,20,21 and 35.

MANGANESE

The determination of manganese was not required
in the biological samples

MANGANESE

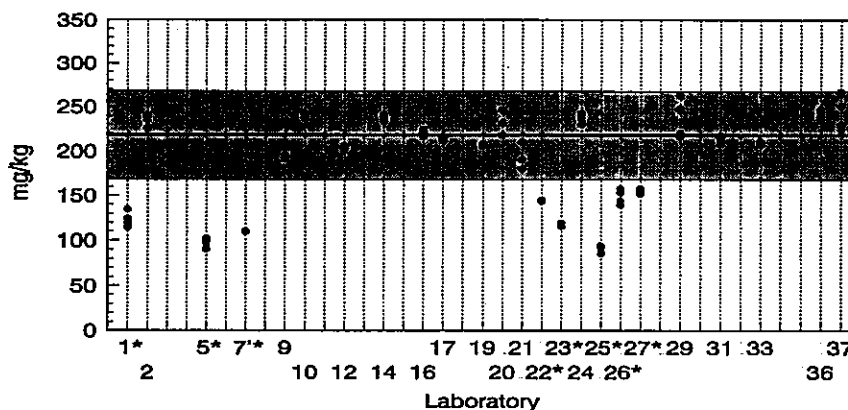
SEDIMENT R

Accepted Value:
 217 ± 50 mg/kg

Results: 24

Quantitative
 Values: 24

Rejections: 8



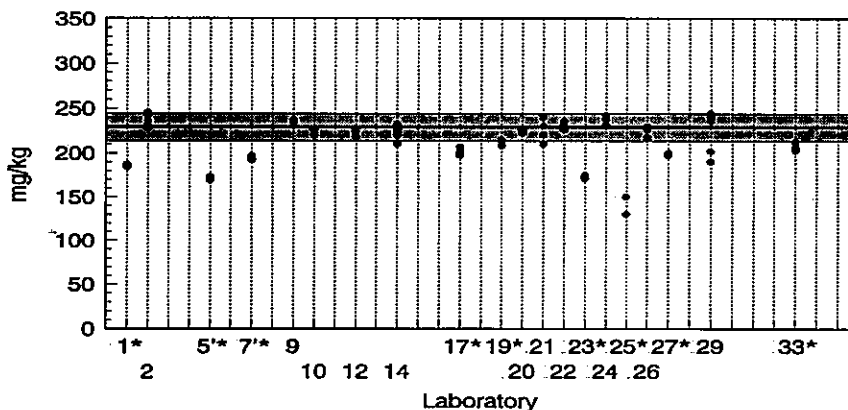
BCSS-1

Certified Value:
 229 ± 15 mg/kg

Results: 20

Quantitative
 Values: 20

Rejections: 9



Sediments

The manganese concentrations in these two sediments are approximately equal, however, the spread of results is rather larger for Sediment R than for BCSS-1. The calculated confidence interval for manganese in Sediment R was ± 23 percent. Eight (1,5,7,22,23,25,26,27) of the twenty-two laboratories submitting results produced outliers, all low.

The confidence interval for manganese in BCSS-1 is ± 7 percent. Nine of the twenty laboratories that analyzed the CRM for manganese produced outliers (1,5,7,17,19,23,25,27,33), again all low. Laboratories 1,5,7,23,25 and 27, all of which did not use a hydrofluoric dissolution procedure, reported low means for both samples. Precision was good for all laboratories for both samples.

There is some improvement over last year.

IRON

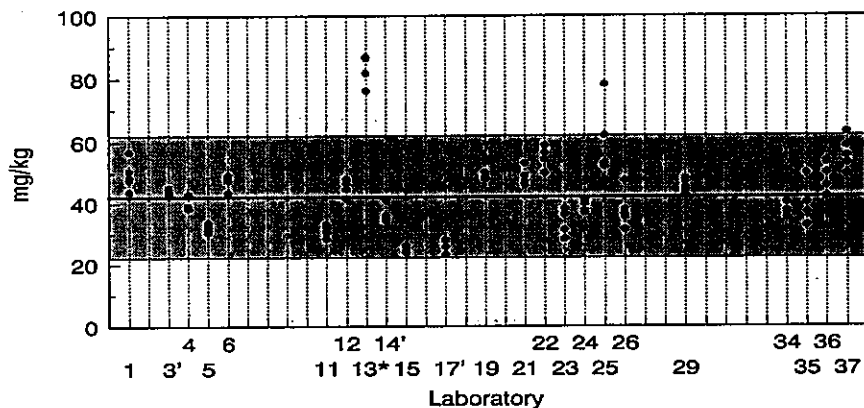
FISH Q

Accepted Value:
 42.0 ± 19.9 mg/kg

Results: 23

Quantitative
 Values: 23

Rejections: 1



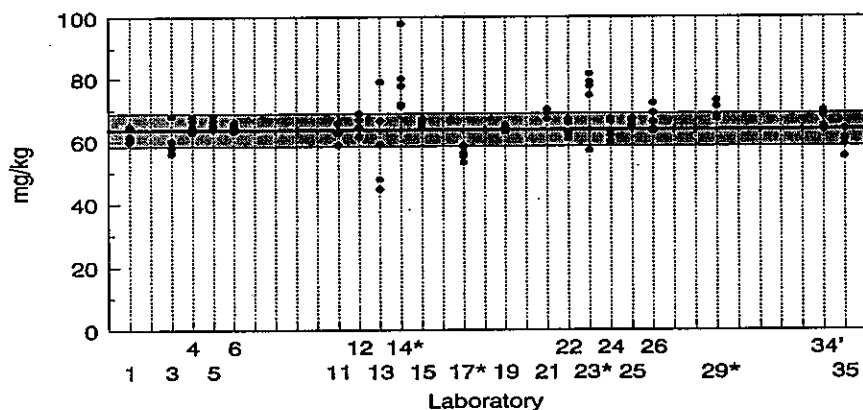
DORM-1

Certified Value:
 63.6 ± 5.3 mg/kg

Results: 21

Quantitative
 Values: 21

Rejections: 4



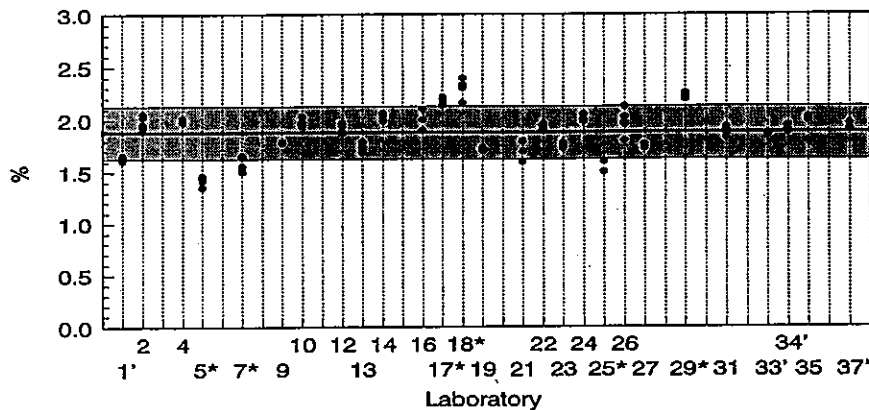
SEDIMENT R

Accepted Value:
 1.88 ± 0.25 %

Results: 27

Quantitative
 Values: 27

Rejections: 6



IRON

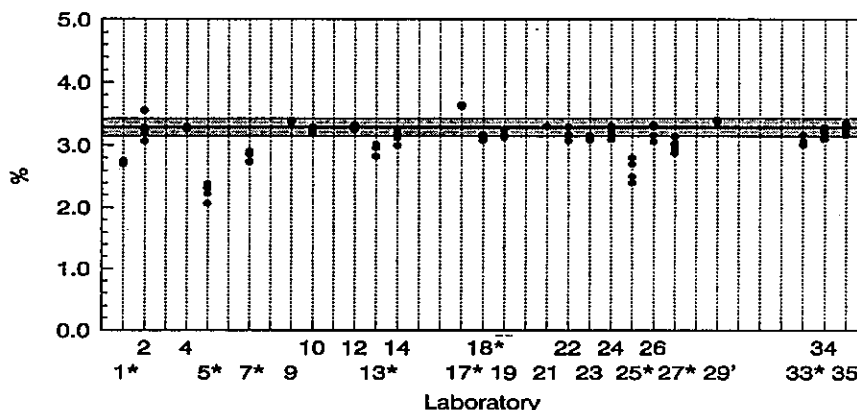
BCSS-1

Certified Value:
 $3.28 \pm 0.14 \%$

Results: 24

Quantitative
 Values: 24

Rejections: 9



Tissues

Twenty-one laboratories reported results for iron in Fish Q. The spread of accepted means, ± 47 percent, is rather large and only one laboratory (13) reported a mean outside this range, and even this may have been the result of an arithmetic error. The iron content of Fish Q is relatively low compared to the mussel tissue of last year and the material does not seem to be as homogeneous as the CRM. Four laboratories reported results with a precision greater than 10 percent.

The confidence interval for iron in DORM-1 is a low ± 8 percent, but only four laboratories (14,17,23,29) out of the twenty-one reporting results were outside this interval. All were high except for Laboratory 17. Three laboratories reported results with a precision greater than 10 percent RSD, only one (23) reported high RSDs for both biological tissue samples.

Sixteen laboratories (1,3,4,5,6,11,12,15,19,21,22,24,25,26,34,35) reported acceptable means for both samples.

Sediments

Twenty-six laboratories reported results for iron in Sediment R. The calculated accepted range was ± 13 percent which included the means from all but six laboratories (5,7,17,18,25,29). There were three high and three low rejected means. One laboratory reported results with a RSD greater than 5 percent.

The confidence interval for iron in BCSS-1 is ± 4 percent. Eight laboratories (1,5,7,13,18,25,27,33) had means below this narrow interval with only one (17) reporting a high value. Three laboratories reported results with a precision slightly greater than 5 percent. Thirteen laboratories (2,4,9,10,12,14,19,21,22,23,24,26,34,35) reported good results for both sediment samples.

The effect of the use of hydrofluoric acid in the digestion process for sediments does not seem to be as marked as for aluminum, chromium and manganese but its use is still to be recommended.

NICKEL

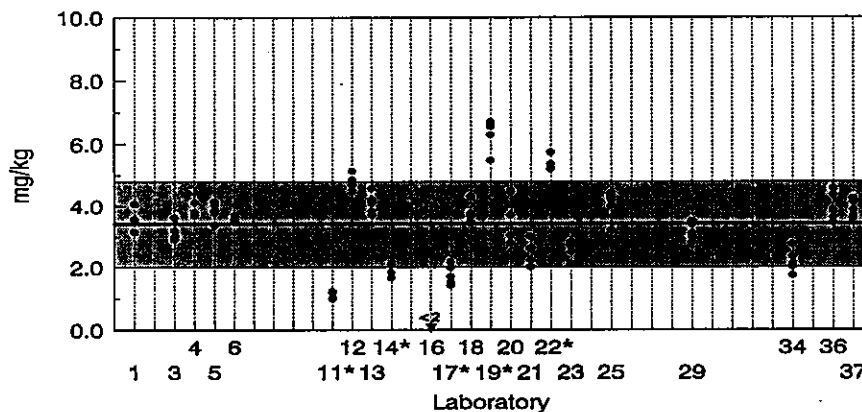
FISH Q

Accepted Value:
 3.40 ± 1.39 mg/kg

Results: 22

Quantitative
 Values: 21

Rejections: 5



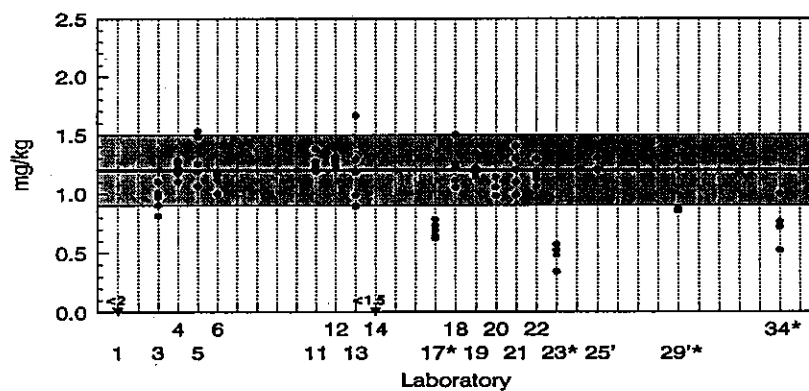
DORM-1

Certified Value:
 1.2 ± 0.3 mg/kg

Results: 19

Quantitative
 Values: 17

Rejections: 4



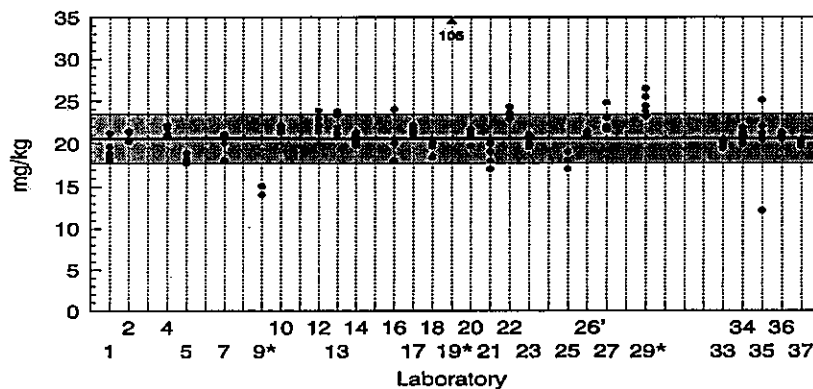
SEDIMENT R

Accepted Value:
 20.6 ± 2.9 mg/kg

Results: 27

Quantitative
 Values: 27

Rejections: 3



NICKEL

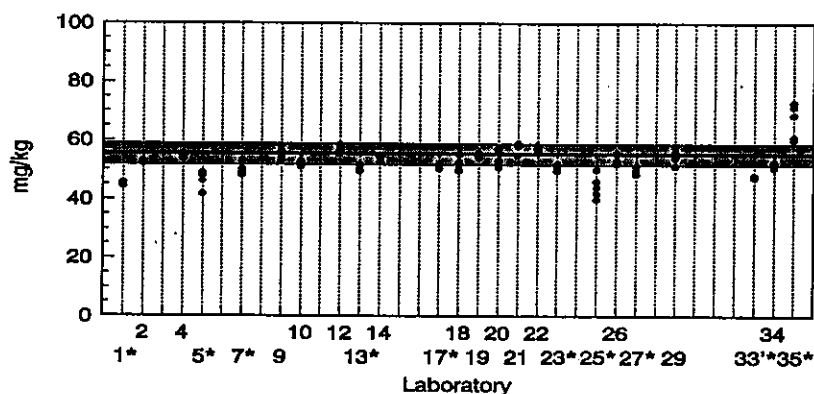
BCSS-1

Certified Value:
55.3 \pm 3.6 mg/kg

Results: 24

Quantitative
Values: 24

Rejections: 10



Tissues

Five laboratories (11,14,17,19,22) of twenty submitting results produced means outside the calculated \pm 41 percent acceptable range for nickel in Fish Q. Laboratories 11,14 and 17 reported low values while 19 and 22 reported high values. Four means were reported with a precision greater than 15 percent.

Four (17,23,29,34) of nineteen laboratories reported means outside the \pm 25 percent confidence interval for nickel in DORM-1, all low. Two laboratories reported results with a precision greater than 20 percent. Eleven laboratories (1,3,4,5,6,12,13,18,20,21,25) reported acceptable results for both biological tissue samples.

Nickel has not been a target analyte in the last few exercises but its determination in the biological tissues appears to be generally adequate, especially considering the relatively low concentrations of nickel in both.

Sediments

Twenty-five laboratories reported results for nickel in Sediment R. Three laboratories (9,19,29) reported means beyond the calculated \pm 14 percent acceptable range but 19's problem may be due to arithmetic error. Laboratories 16 and 35 reported results with a precision greater than 10 percent RSD.

Of twenty-four sets submitted ten sets of results (1,5,7,13,17,23,25,27,33,35) were outside the \pm 6.5 percent confidence range for BCSS-1 in spite of its relatively high nickel content. All but one of these laboratories (35) reported low means. Is hydrofluoric acid a factor here also? All laboratories reported good precision for BCSS-1.

Eleven laboratories (2,4,10,12,14,18,20,21,22,26,34) reported acceptable results for both sediment samples.

COPPER

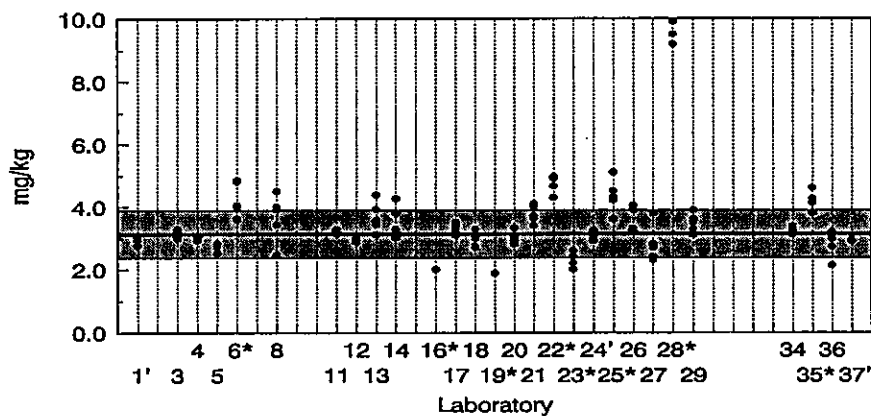
FISH Q

Accepted Value:
 3.15 ± 0.77 mg/kg

Results: 28

Quantitative
 Values: 28

Rejections: 8



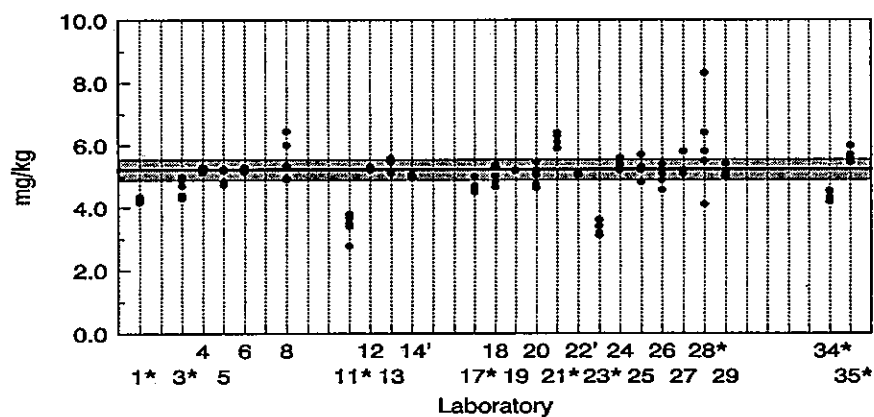
DORM-1

Certified Value:
 5.22 ± 0.33 mg.kg

Results: 25

Quantitative
 Values: 25

Rejections: 9



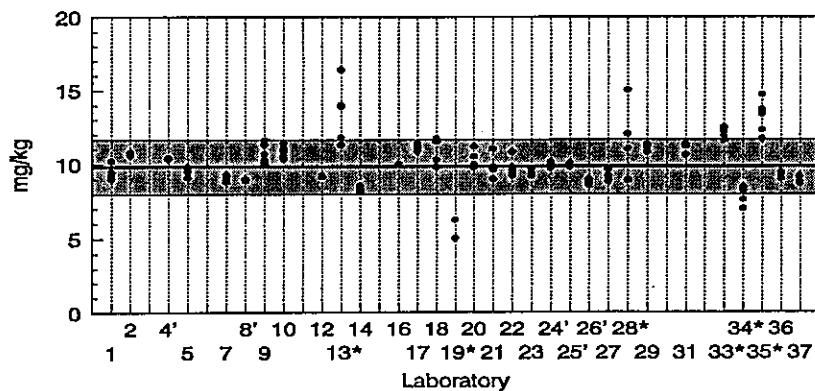
SEDIMENT R

Accepted Value:
 9.81 ± 1.84 mg/kg

Results: 31

Quantitative
 Values: 31

Rejections: 6



COPPER

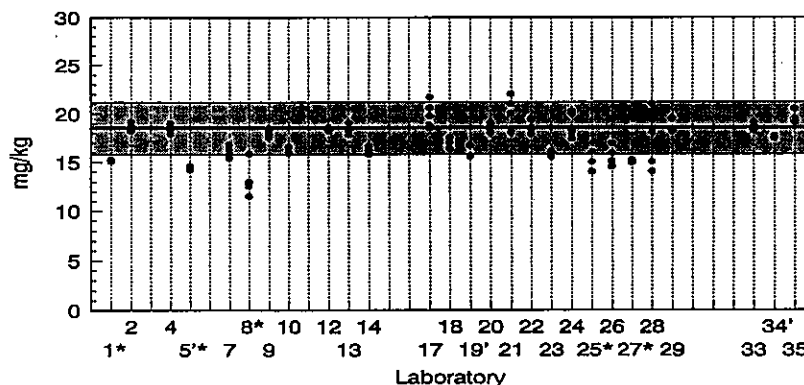
BCSS-1

Accepted Value:
 18.5 ± 2.7 mg/kg

Results: 27

Quantitative
 Values: 27

Rejections: 5



Tissues

Twenty-six laboratories reported results for copper in Fish Q ranging between 1.87 and 15 mg/kg. Eight laboratories (6,16,19,22,23,25,28,35) reported means outside the calculated accepted range of ± 24 percent. Laboratories 16,19 and 23 reported low results and Laboratories 6,22,25,28 and 35 reported high results. Four laboratories reported results with a RSD greater than 20 percent.

Of the twenty-five laboratories reporting results for copper in DORM-1, nine (1,3,11,17,21,23,28,34,35) were outside the confidence interval of ± 6 percent. Laboratories 1,3,11,17,23 and 34 reported low results while laboratories 21,28 and 35 reported high results. This is largely a different set of laboratories from those that produced outliers for copper in Fish Q. Only three laboratories (23,28,35) are common to both. The concentration of copper in Fish Q is similar to that in DORM-1 and there is no apparent reason for the disparity.

Twelve laboratories (4,5,8,12,13,14,18,20,24,26,27,29) reported acceptable results for both biological tissue samples. There is some general improvement compared to NOAA/5.

Sediments

Twenty-nine laboratories reported results for copper in Sediment R ranging between 5 and 16 mg/kg. Six laboratories (13,19,28,33,34,35) had means outside the calculated acceptable range of ± 19 percent. Four laboratories (13,28,33,35) submitted high results and two (19,34) reported low results. The overall precision of the results was acceptable with the exception of laboratory 28.

Of the twenty-seven laboratories reporting results for copper in BCSS-1, five different laboratories (1,5,8,25,27) had outliers beyond the ± 15 percent confidence interval. All of these means were low. Results with an RSD greater than 10 percent were reported by laboratories 2 and 28.

Sixteen laboratories (2,4,7,9,10,12,14,17,18,20,21,22,23,24,26,29) reported acceptable results for both sediment samples. There is some improvement for copper in sediments over NOAA/5.

ZINC

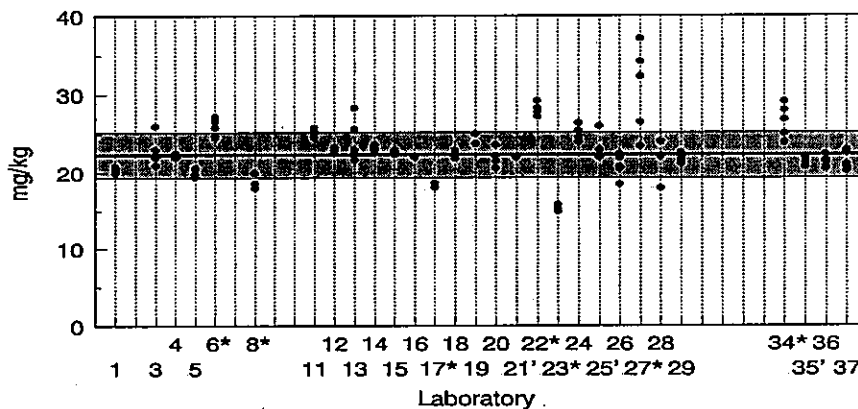
FISH Q

Accepted Value:
 22.3 ± 2.9 mg/kg

Results: 29

Quantitative
 Values: 29

Rejections: 7



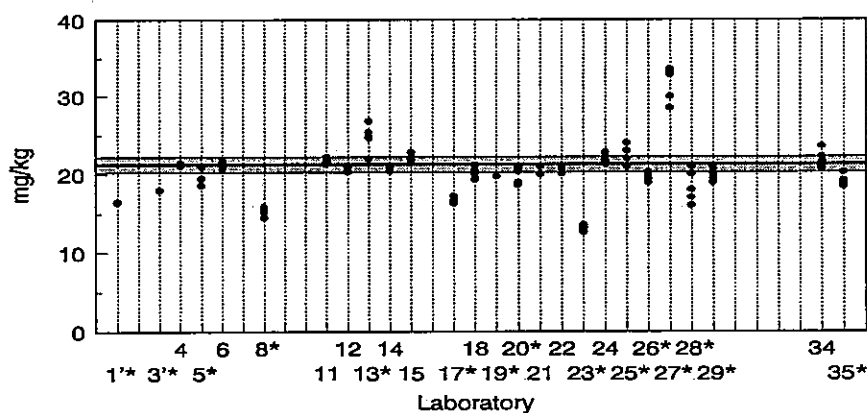
DORM-1

Certified Value:
 21.3 ± 1.0 mg/kg

Results: 26

Quantitative
 Values: 26

Rejections: 15



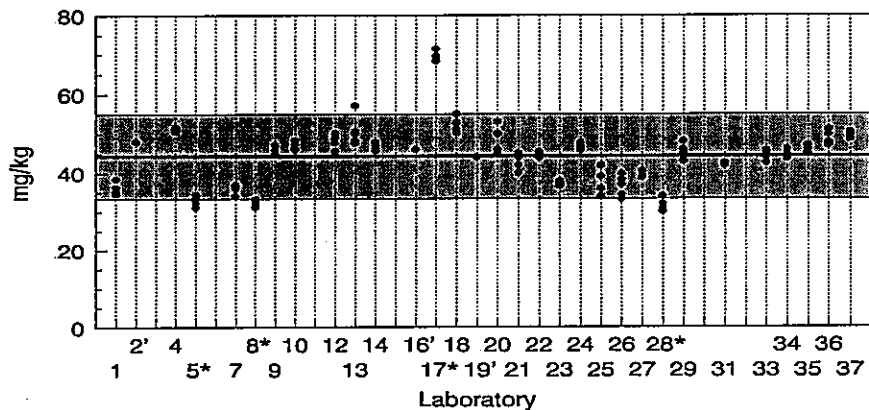
SEDIMENT R

Accepted Value:
 44.2 ± 10.8 mg/kg

Results: 31

Quantitative
 Values: 31

Rejections: 4



ZINC

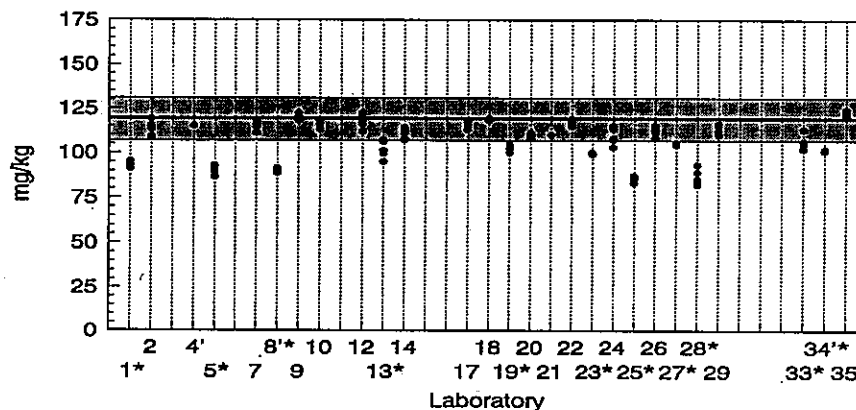
BCSS-1

Certified Value:
119 ± 12 mg/kg

Results: 27

Quantitative
Values: 27

Rejections: 11



Tissues

Twenty-seven laboratories reported results for zinc in Fish Q ranging between 15 and 37 mg/kg. Seven laboratories (6,8,17,22,23,27,34) reported means outside the calculated accepted range of ± 13 percent. Four of these were high results and three were low. Results with a RSD greater than 10 percent were reported by laboratories 13 and 27.

Of the twenty-six laboratories which submitted results for DORM-1, it is not surprising that fifteen (1,3,5,8,13,17,19,20,23,25,26,27,28,29,35) had means outside the very narrow confidence interval of ± 5 percent for DORM-1. However, it is unusual that twelve of these means were low. DORM-1 has about the same zinc content as Fish Q and a more symmetrical distribution would be expected. Only one laboratory reported results with a RSD greater than 10 percent.

Only eight laboratories (4,11,12,14,15,18,21,24) reported acceptable results for both biological tissue samples. We can not compare with earlier exercises because the concentrations of zinc in the fish tissues are more than an order of magnitude less than those in the mussel tissues previously used.

Sediments

Twenty-nine laboratories submitted results for zinc in Sediment R. The means of four laboratories (5,8,17,28) were outside the calculated accepted range of ± 24 percent. Three were low and one was high. Precision was good for all laboratories.

The confidence interval for zinc in BCSS-1 is ± 10 percent. Of the twenty-seven laboratories that reported results for zinc in BCSS-1 eleven (1,5,8,13,19,23,25,27,28,33,34) were outside of the range, all of which were low. Incomplete dissolution is probably playing a role here and we can see it as we did last year because of the relatively large participation. Precision was again good for all laboratories.

Fifteen laboratories (2,4,7,9,10,12,14,18,20,21,22,24,26,29,35) reported acceptable results for both sediment samples. This is almost the same list as those successful for copper. There is good improvement over NOAA/5.

ARSENIC

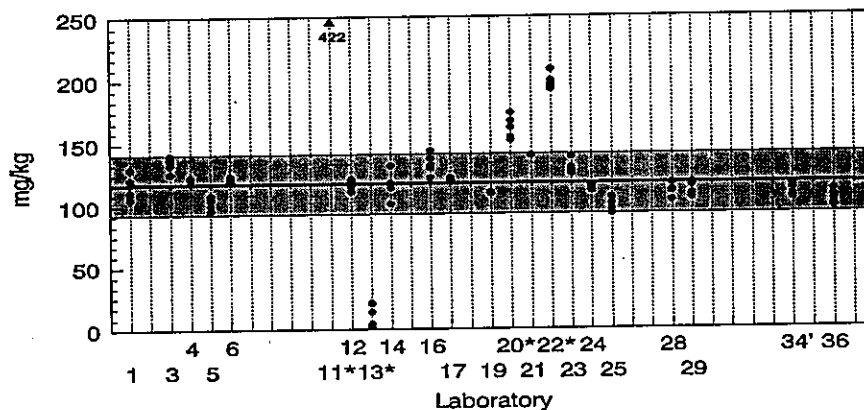
FISH Q

Accepted Value:
 117 ± 24 mg/kg

Results: 22

Quantitative
 Values: 22

Rejections: 4



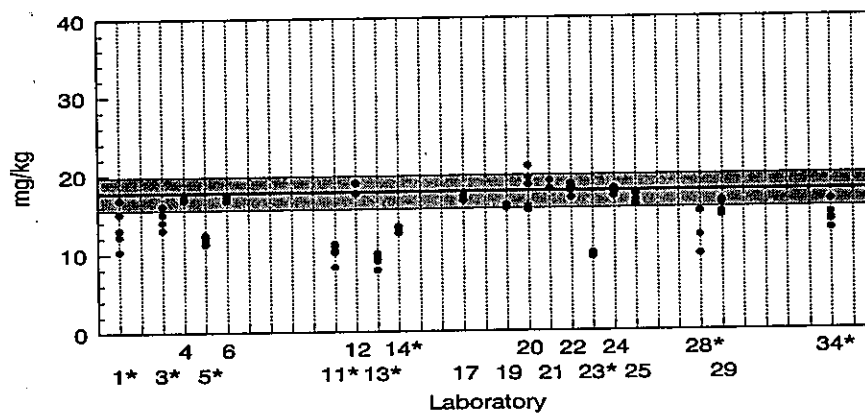
DORM-1

Certified Value:
 17.7 ± 2.1 mg/kg

Results: 20

Quantitative
 Values: 20

Rejections: 9



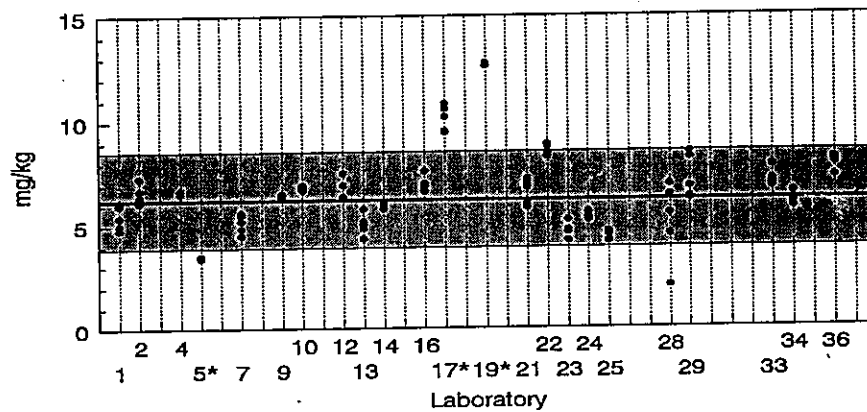
SEDIMENT R

Accepted Value:
 6.22 ± 2.33 mg/kg

Results: 23

Quantitative
 Values: 23

Rejections: 3



ARSENIC

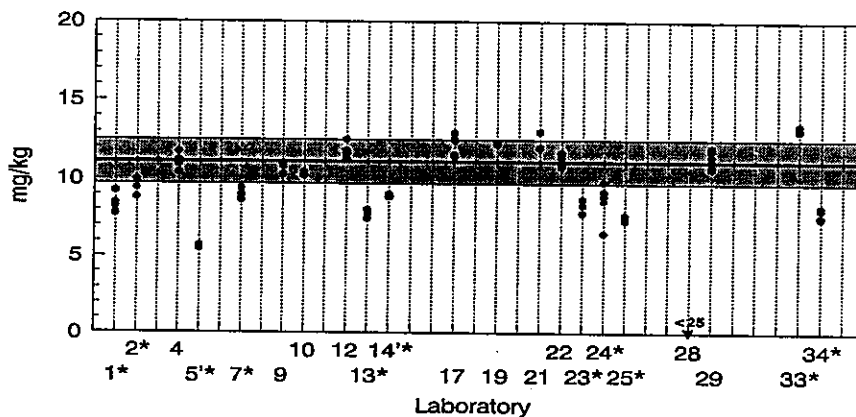
BCSS-1

Certified Value:
 11.1 ± 1.4 mg/kg

Results: 21

Quantitative
 Values: 20

Rejections: 11



Tissues

Twenty-one laboratories reported results for arsenic in Fish Q. Only four laboratories (11,13,20,22) reported means outside the calculated accepted range of ± 21 percent. Three were high and one was low. With the exception of laboratory 13, precision was good for all participants. The concentration of arsenic in Fish Q is relatively high and good results should be expected.

The concentration of arsenic in DORM-1 is almost an order of magnitude less than in Fish Q. Of the twenty laboratories that submitted results for DORM-1 nine (1,3,5,11,13,14,23,28,34) had means beyond the certified confidence interval of ± 12 percent, all low like the oyster tissue CRM in NOAA/5. Laboratories 1 and 28 reported values with a precision greater than 15 percent.

Only nine laboratories (4,6,12,17,19,21,24,25,29) reported acceptable results for both biological tissue samples. There is some improvement over last year. The low results may be due to incomplete digestion of the organoarsenics in the fish tissue. Unless completely destroyed they do not produce arsine when treated by the reductant in the normal cold vapour AAS determination.

Sediments

Twenty-two laboratories reported results for arsenic in Sediment R. With the calculated acceptable range of ± 38 percent only three laboratories (5,17,19) had means which were outliers. Laboratories 17 and 19 submitted high values and laboratory 5 submitted a low mean. Laboratories 28 and 29 submitted values with a precision greater than 15 percent.

Twenty-one laboratories submitted results for arsenic in BCSS-1. However, eleven of these (1,2,5,7,13,14,23,24,25,33,34) had means outside the certified confidence interval of ± 12 percent, only one of which was high. It would again appear that the narrow confidence interval of the CRM allows us to discern a problem which is otherwise hidden, probably related to incomplete decomposition of the sediments. Precision was good for all laboratories.

Eight laboratories (4,9,10,12,21,22,28,29) reported acceptable results for both sediment samples.

SELENIUM

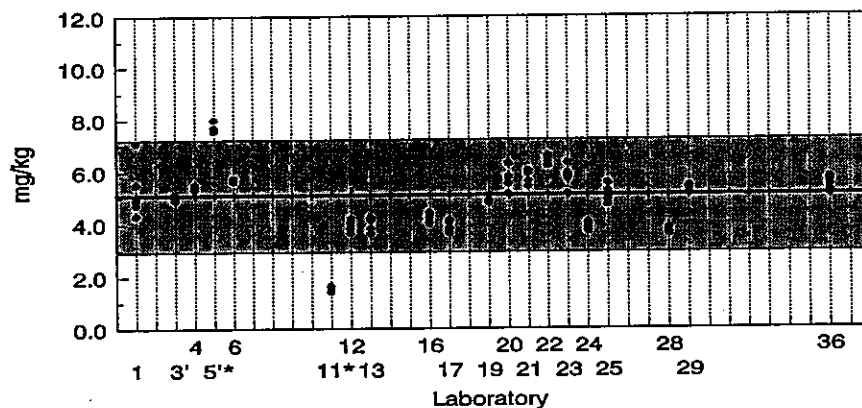
FISH Q

Accepted Value:
 5.08 ± 2.14 mg/kg

Results: 20

Quantitative
 Values: 20

Rejections: 2



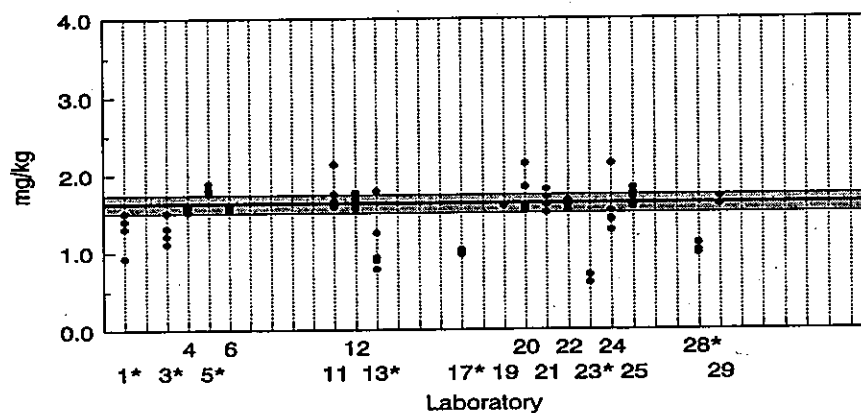
DORM-1

Certified Value:
 1.62 ± 0.12 mg/kg

Results: 18

Quantitative
 Values: 18

Rejections: 7



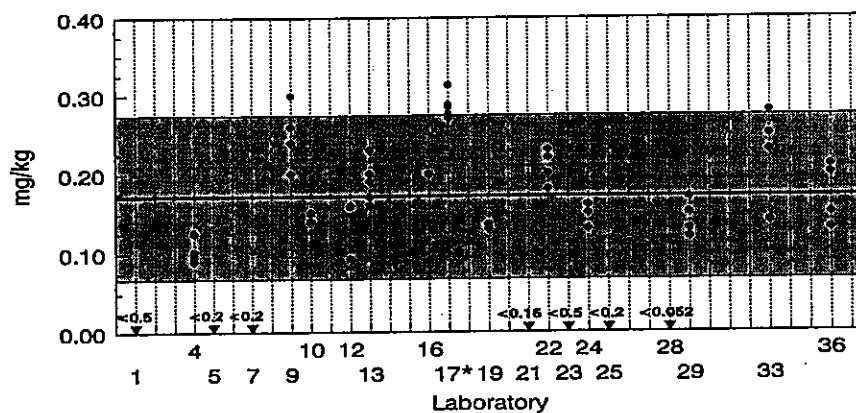
SEDIMENT R

Accepted Value:
 0.171 ± 0.104 mg/kg

Results: 20

Quantitative
 Values: 13

Rejections: 1



SELENIUM

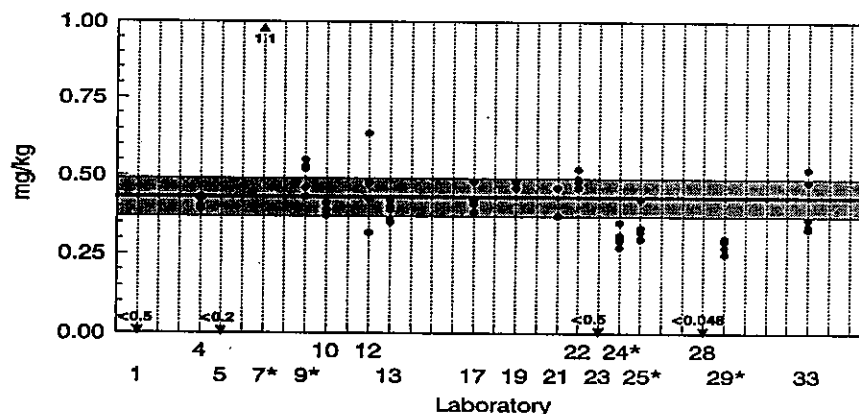
BCSS-1

Certified Value:
 0.43 ± 0.06 mg/kg

Results: 18

Quantitative
 Values: 14

Rejections: 5



Tissues

Nineteen laboratories reported quantitative results for selenium in Fish Q. Two laboratories (5,11) were outside the calculated acceptable range of ± 42 percent. Only one laboratory reported results with a RSD greater than 8 percent.

Eighteen laboratories analyzed DORM-1 for selenium. DORM-1 has a selenium content about one third that of Fish Q. Seven laboratories produced means outside the narrow certified confidence interval of ± 7 percent. Six laboratories (1,3,13,17,23,28) reported low results and only one (5) submitted high values. Six laboratories (1,3,11,13,20 and 24) reported results with greater than 10 percent RSD.

Nine laboratories (4,6,12,19,20,21,22,24,25,29) reported acceptable results for both biological tissue samples. The number of laboratories analyzing the biological tissues for selenium has risen and the quality of analysis is improving.

Sediments

The selenium concentration in Sediment R is quite low at 0.17 mg/kg with a calculated acceptable range of ± 61 percent. The spread is such that only one (17) of the twelve submitted means is outside this range. Seven acceptable "less than" values were also reported. Two laboratories reported RSDs larger than 20 percent.

Of fourteen laboratories reporting quantitative results for selenium in BCSS-1, five (7,9,24,25,29) had means outside the ± 42 percent confidence interval. Two laboratories (5,28) reported "less than" values lower than the certified concentration. The tendency is again toward low results. Results with a RSD greater than 20 percent were reported by two laboratories.

Only seven laboratories (4,10,12,13,19,22,33) reported acceptable results for both sediment samples but this is quite an improvement over performance in NOAA/5.

SILVER

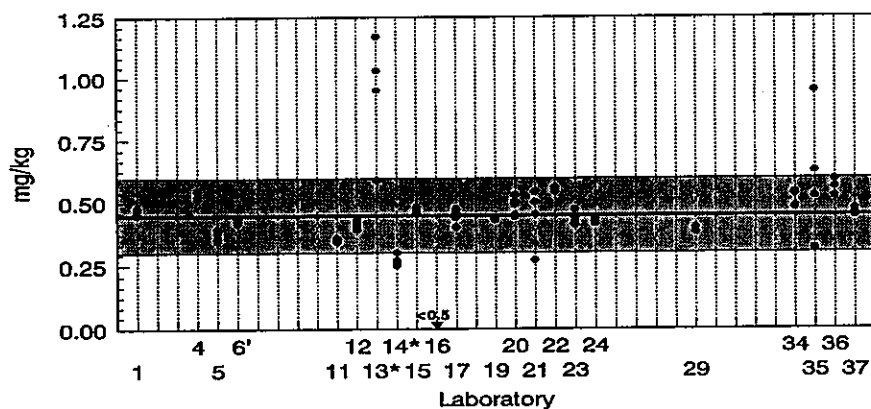
FISH Q

Accepted Value:
 0.449 ± 0.147
 mg/kg

Results: 22

Quantitative
 Values: 21

Rejections: 2



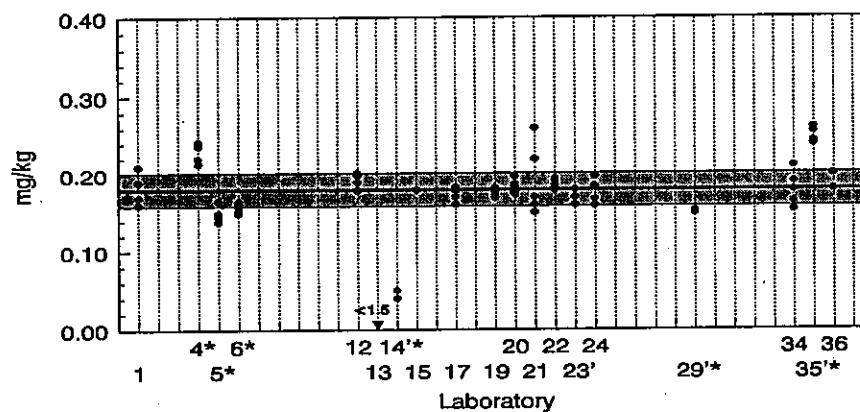
DORM-1

Accepted Value:
 0.180 ± 0.022 mg/kg

Results: 19

Quantitative
 Values: 18

Rejections: 6



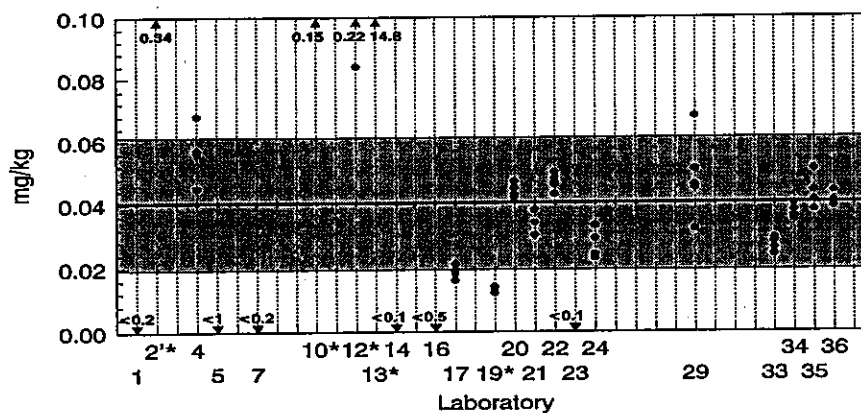
SEDIMENT R

Accepted Value:
 0.040 ± 0.022 mg/kg

Results: 22

Quantitative
 Values: 16

Rejections: 5



SILVER

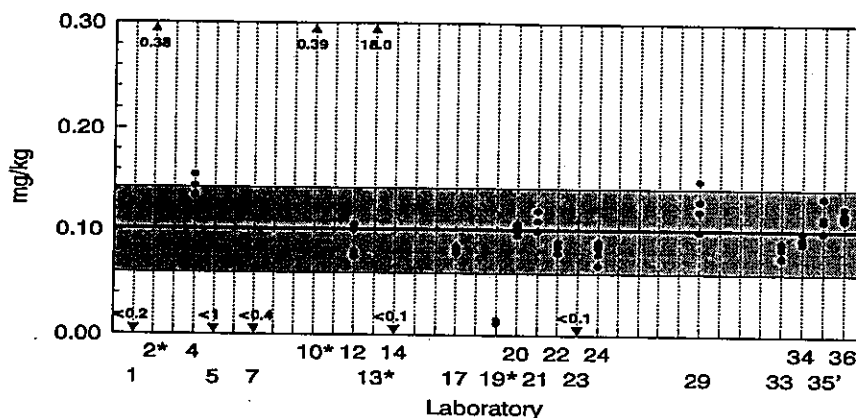
BCSS-1

Accepted Value:
 0.102 ± 0.042 mg/kg

Results: 21

Quantitative
 Values: 16

Rejections: 4



Tissues

Nineteen laboratories submitted quantitative results for silver in Fish Q. Two laboratories (13,14) were outside the ± 33 percent calculated acceptable range. Three laboratories reported results with a precision greater than 20 percent.

Nineteen laboratories submitted quantitative results for silver in DORM-1. DORM-1 is not certified for silver, but a good mean concentration with an acceptable range of ± 12 percent was calculated from the submitted data in spite of the low silver concentration. Laboratories 4 and 35 submitted high results and laboratories 5,6,14 and 29 submitted low results. Only one laboratory submitted results with a RSD greater than 20 percent.

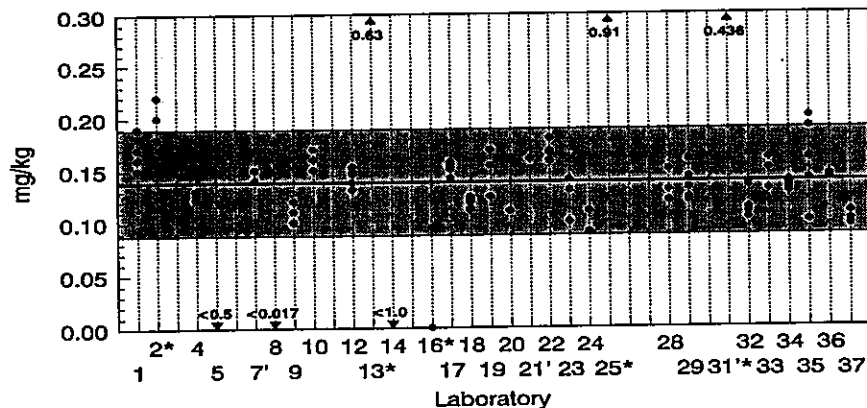
Twelve laboratories (1,12,15,17,19,20,21,22,23,24,34,36) submitted acceptable data for both biological samples. This is a good improvement over NOAA/5.

Sediments

The concentration of silver in Sediment R is quite low. Of the fifteen quantitative sets of values submitted, ten laboratories (4,17,20,21,22,24,29,33,34,35) had means within the acceptable range of ± 55 percent. Laboratories 7,14,16 and 20 submitted reasonable "less than" values in contrast to Laboratories 1 and 5. Laboratories 2,10,12, and 13 all reported very high results. The low result of Laboratory 19 may be due to an arithmetic error. Only two laboratories reported results with greater than 20 percent RSD.

BCSS-1 is not certified for silver, however our records show that the calculated mean concentration of 0.10 mg/kg is not far from the "truth". Of fifteen laboratories, eleven had means within the calculated acceptable range of ± 33 percent. Laboratories 2,10 and 13 submitted high results and Laboratory 19 reported a low mean (arithmetic?). Reasonable "less than" values were submitted by Laboratories 1,7,14 and 23. No results were submitted with a RSD greater than 20 percent.

Ten laboratories (4,17,20,21,22,24,29,33,34,35) submitted acceptable results for both sediment samples. This represents a great improvement over previous years.



CADMIUM

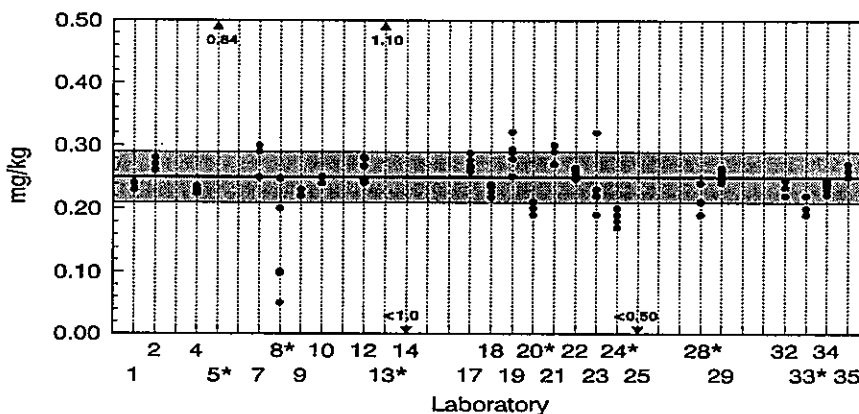
BCSS-1

Certified Value:
 0.25 ± 0.04 mg/kg

Results: 26

Quantitative
 Values: 24

Rejections: 7



Tissues

Twenty-three laboratories submitted results cadmium in Fish Q. Six of these (3,6,16,19,21,22) produced means beyond the calculated acceptable range of ± 24 percent, all high but one (16). This is not surprising considering the low concentration of cadmium. Laboratories 20 and 21 reported results with a precision greater than 20 percent.

Of the nineteen laboratories that reported quantitative cadmium results for DORM-1, only three laboratories (1,21,32) produced means that were outside the certified 95 percent confidence interval of ± 14 percent, one high and two low. Three laboratories reported results with a precision greater than 20 percent.

Eleven laboratories (4,5,11,12,15,18,20,24,28,29,34) reported acceptable results for both biological tissue samples. This is good performance, especially when the low concentrations of cadmium are considered and an improvement compared to NOAA/5.

Sediments

Twenty-five laboratories reported quantitative results for cadmium in Sediment R. Five laboratories (2,13,16,25,31) reported means outside the calculated acceptable range of ± 37 percent, all high but one (16). These are not the same laboratories that produce high cadmium values for the biological tissues but two of them (13,25) used ICPAES to determine the cadmium, a mistake for concentrations less than 2 mg/kg because of line interferences from iron and arsenic. Two laboratories reported results with a precision greater than 20 percent.

Seven of twenty-four laboratories were outside the certified confidence interval of ± 24 percent for cadmium in BCSS-1. Laboratories 5 and 13 submitted high results and Laboratories 8,20,24,28 and 33 reported low means. Laboratories 5,8 and 23 reported results with a precision greater than 20 percent.

Sixteen laboratories (1,4,7,9,10,12,17,18,19,21,22,23,29,32,34,35) reported acceptable results for both sediment samples. This is an improvement compared to NOAA/5.

TIN

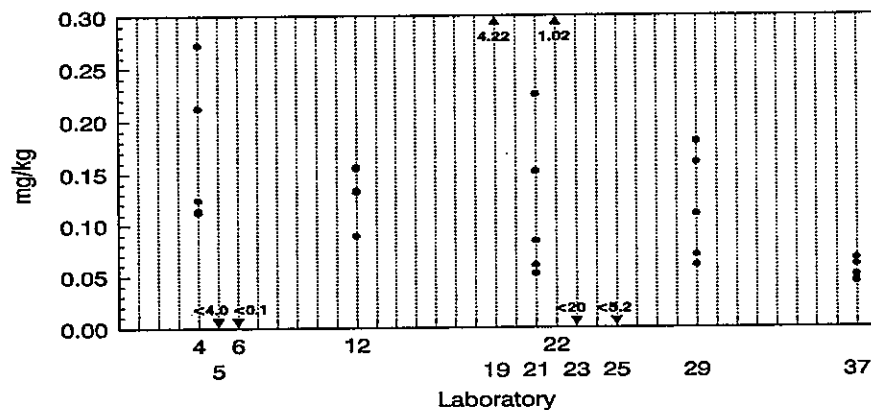
FISH Q

Accepted Value:
not determined

Results: 11

Quantitative
Values: 7

Rejections: -



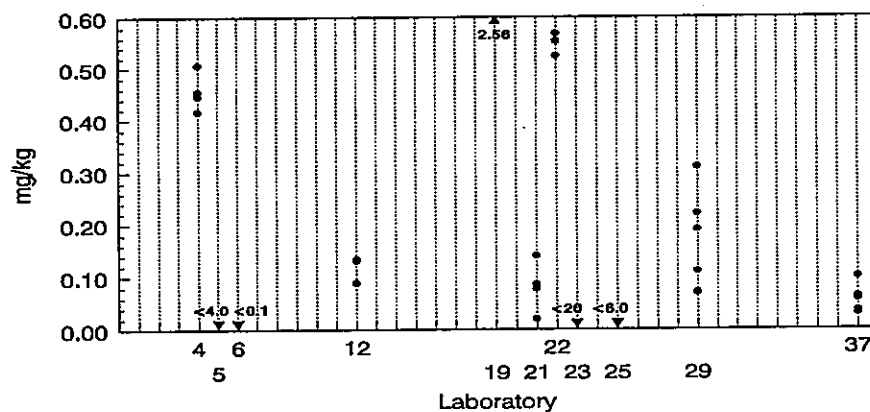
DORM-1

Accepted Value:
not determined

Results: 10

Quantitative
Values: 6

Rejections: -



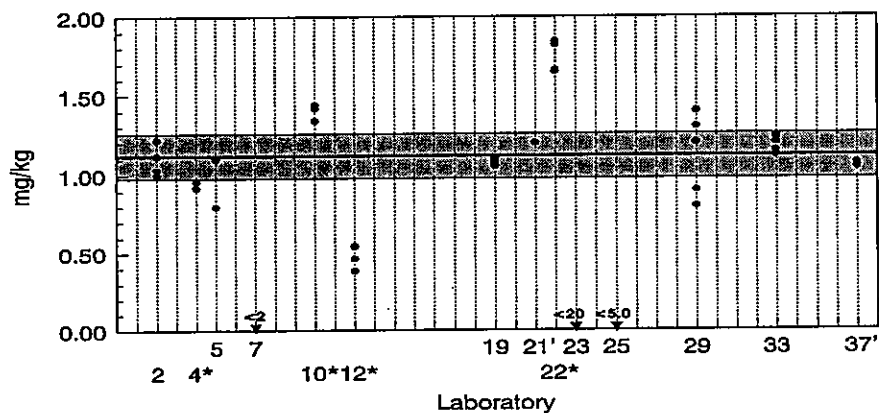
SEDIMENT R

Accepted Value:
 1.11 ± 0.14 mg/kg

Results: 14

Quantitative
Values: 11

Rejections: 4



TIN

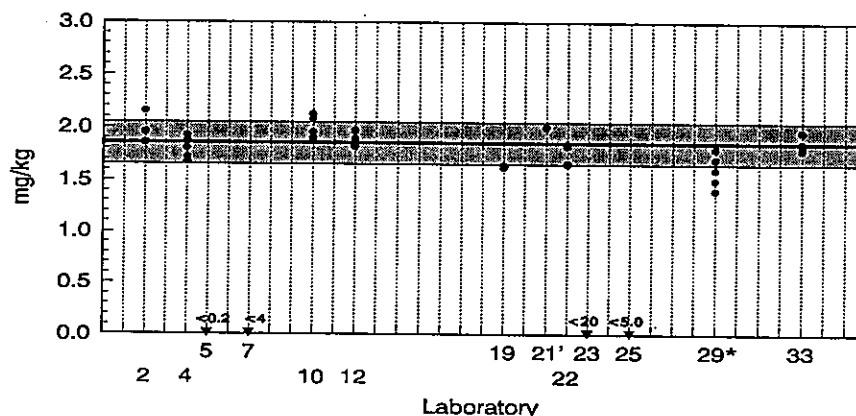
BCSS-1

Certified Value:
 1.85 ± 0.20 mg/kg

Results: 12

Quantitative
 Values: 9

Rejections: 1



Tissues

The concentration of tin in both biological samples is very low. Only six laboratories submitted quantitative results for tin in Fish Q. An accepted value for tin in Fish Q was not calculated because of the disparity of the results. We assume the concentration of tin to be between 0.05 and 0.1 mg/kg. The means of Laboratories 12, 21 and 29 are only a bit high but their precision is poor.

DORM-1 is not certified for tin, however, its tin content is also between 0.05 and 0.1 mg/kg. The same six laboratories also submitted quantitative results for tin in DORM-1 but only Laboratories 12 and 21 appear to be in the right ballpark.

The determination of tin in biological tissues at these low levels remains a problem for the participants. There is no apparent improvement compared to NOAA/5.

Sediments

Ten laboratories reported quantitative values for tin in Sediment R. Six laboratories (2, 5, 19, 21, 29, 33) reported means within the calculated acceptable range of ± 13 percent. Two laboratories (4, 12) reported low results and two (10, 22) high results. Only one laboratory reported a mean with a RSD greater than 15 percent.

Nine laboratories submitted quantitative results for tin in BCSS-1. Eight of these (2, 4, 10, 12, 19, 21, 22, 33) reported means within the certified confidence interval of ± 11 percent, the other (29) was slightly low. The concentration of tin in BCSS-1 is double that in Sediment R. Precision was good for all laboratories. Laboratories 7 and 25 reported reasonable "less than" values for both sediments.

Only four laboratories (2, 19, 21, 33) reported acceptable results for both sediment samples. There is some apparent improvement compared to NOAA/5 but tin in sediments remains a problem analyte.

ANTIMONY

The determination of antimony was not required
in the biological samples

ANTIMONY

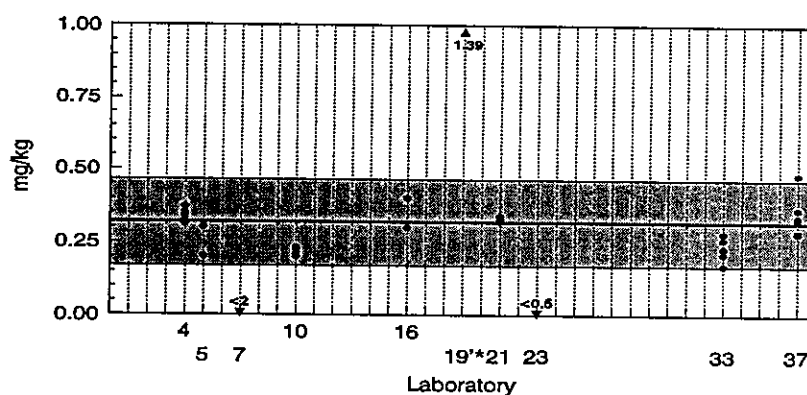
SEDIMENT R

Accepted Value:
 $0.32 \pm 0.15 \text{ mg/kg}$

Results: 10

Quantitative
 Values: 8

Rejections: 1



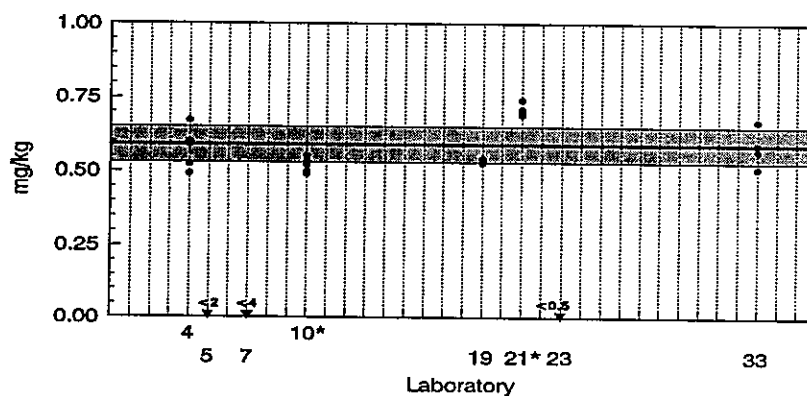
BCSS-1

Certified Value:
 $0.59 \pm 0.06 \text{ mg/kg}$

Results: 8

Quantitative
 Values: 5

Rejections: 2



Sediments

Seven laboratories submitted quantitative results for antimony in Sediment R. Six of these laboratories (4,5,10,16,21,33) reported means within the ± 47 percent calculated acceptable range. The seventh (19) was very high and may be a victim of poor arithmetic. The precision of the all the submitted sets was less than 20 percent RSD.

Only five laboratories submitted quantitative results for antimony in BCSS-1. The means of three of these (4,19,33) were within the ± 10 percent certified confidence interval. Laboratory 10 submitted slightly low results and Laboratory 21 results were high. The precision was good.

Only two laboratories (4,33) submitted acceptable results for antimony in both sediment samples. There is no apparent improvement for the determination of antimony in sediments compared to NOAA/5. This analysis remains a problem for the great majority of the laboratories.

MERCURY

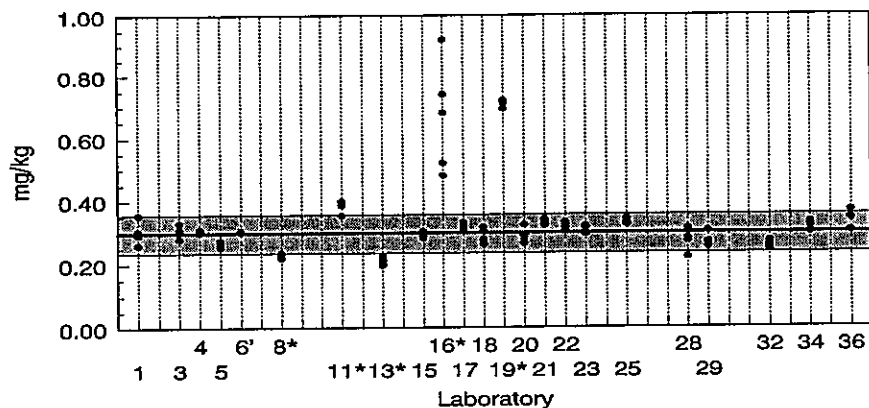
FISH Q

Accepted Value:
 $0.296 \pm 0.061 \text{ mg/kg}$

Results: 23

Quantitative
 Values: 23

Rejections: 5



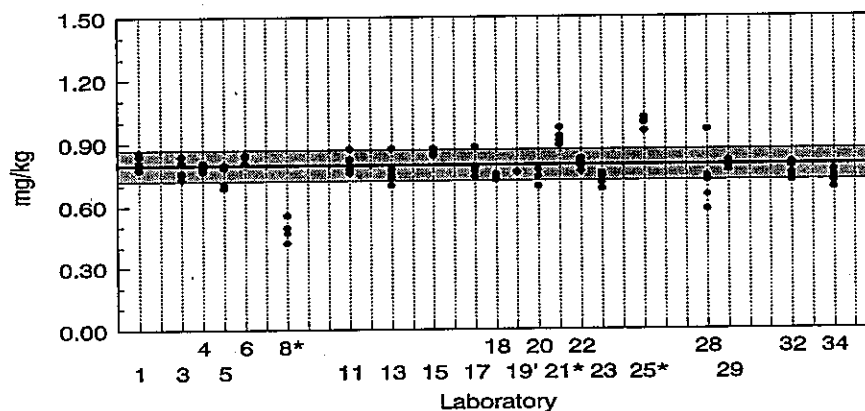
DORM-1

Certified Value:
 $0.798 \pm 0.074 \text{ mg/kg}$

Results: 21

Quantitative
 Values: 21

Rejections: 3



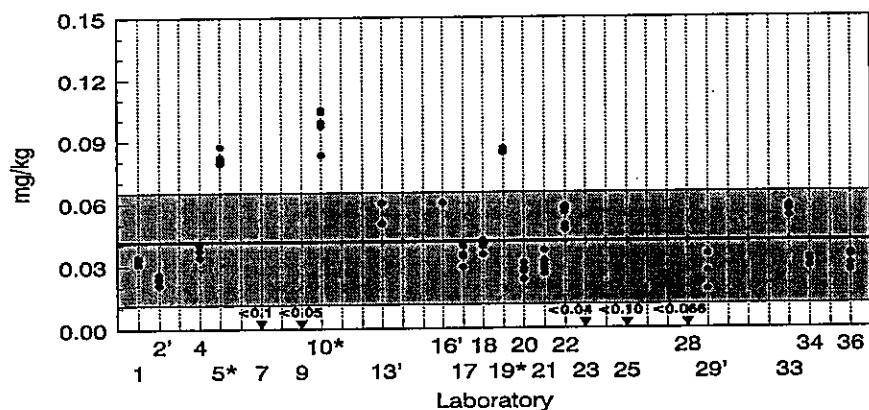
SEDIMENT R

Accepted Value:
 $0.038 \pm 0.027 \text{ mg/kg}$

Results: 22

Quantitative
 Values: 17

Rejections: 3



MERCURY

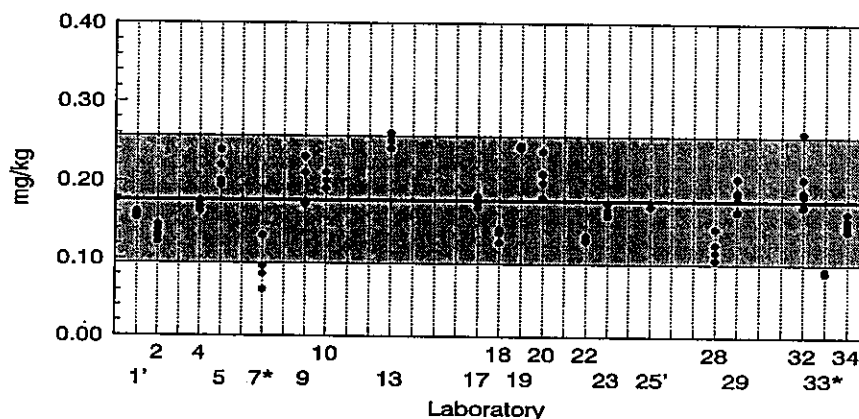
BCSS-1

Accepted Value:
 0.175 ± 0.081 mg/kg

Results: 20

Quantitative
 Values: 20

Rejections: 2



Tissues

Twenty-two laboratories reported values for mercury in Fish Q. Five laboratories (8,11,13,16,19) had means outside the ± 20 percent calculated acceptable range. Only Laboratory 16 had unacceptable precision.

Eighteen of the twenty-one laboratories which reported results for mercury in DORM-1 had means within the ± 9 percent certified confidence interval. Laboratories 21 and 25 reported high results and Laboratory 8 reported a low mean. Laboratory 8 was the only laboratory which produced an outlier for mercury in both biological tissue samples.

Fifteen laboratories (1,3,4,5,6,15,17,18,20,22,23,28,29,32,34) reported acceptable results for mercury in both biological tissue samples. This is good performance, especially when the low concentrations of mercury are considered and an improvement compared to NOAA/5.

Sediments

Sixteen laboratories reported quantitative results for mercury in Sediment R. Only three of these (5,10,19) were outside the calculated acceptable range of a very large ± 71 percent, all high. However, the concentration is quite low at $38 \mu\text{g/kg}$. The precision was good for all laboratories.

Twenty laboratories reported results for mercury in BCSS-1. Only two laboratories (4,33) reported means outside the calculated acceptable range of ± 46 percent. One laboratory (7) reported results with a RSD greater than 20 percent.

Eleven laboratories (1,2,4,9,13,17,18,20,22,29,34) submitted acceptable results for mercury in both sediment samples. This performance represents a great improvement over the early years, but not markedly better than last year.

THALLIUM

The determination of thallium was not required
in the biological samples

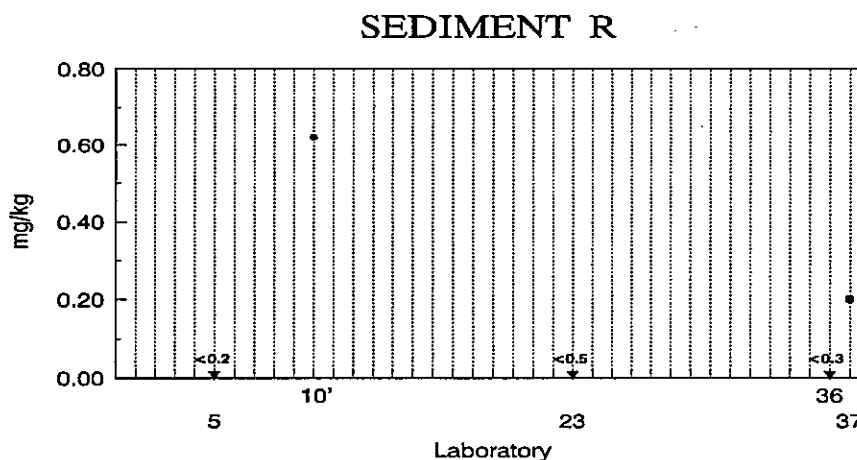
THALLIUM

Accepted Value:
not determined

Results: 4

Quantitative
Values: 2

Rejections:

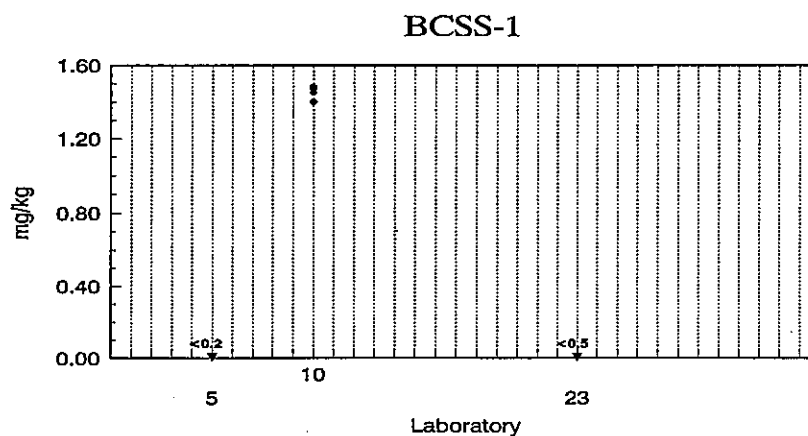


Accepted Value:
not determined

Results: 3

Quantitative
Values: 1

Rejections:



Sediments

The above diagrams speak for themselves. Laboratory 10 was the only participant to report quantitative values for thallium in Sediment R. If the isotope dilution results of NRC are to be believed, that laboratories results are high by a factor of three.

BCSS-1 is not certified for thallium and, again, only laboratory 10 reported quantitative values for this sample. The NRC result for thallium in BCSS-1 (not shown in the diagram) is approximately 0.5 mg/kg.

Why didn't more laboratories attempt to determine thallium in the sediments? We don't know. Maybe we'll find out at the NOAA QA workshop.

LEAD

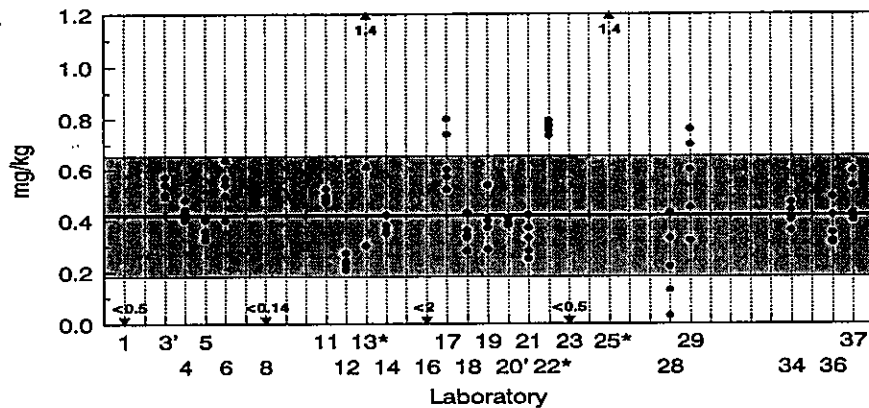
FISH Q

Accepted Value:
 $0.42 \pm 0.24 \text{ mg/kg}$

Results: 24

Quantitative
 Values: 20

Rejections: 3



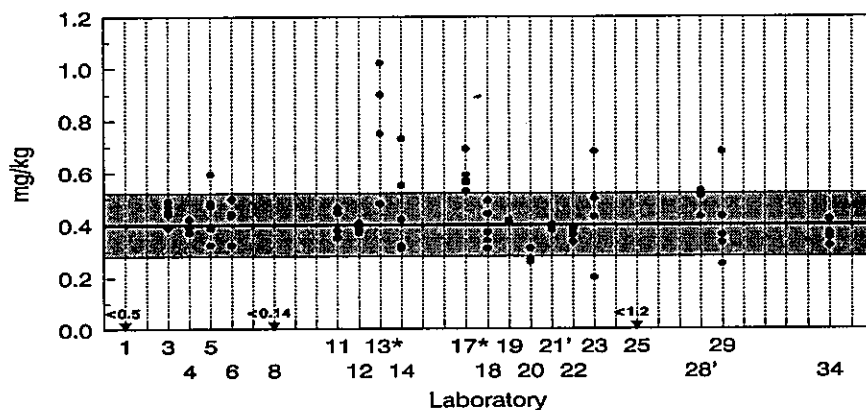
DORM-1

Certified Value:
 $0.40 \pm 0.12 \text{ mg/kg}$

Results: 21

Quantitative
 Values: 18

Rejections: 2



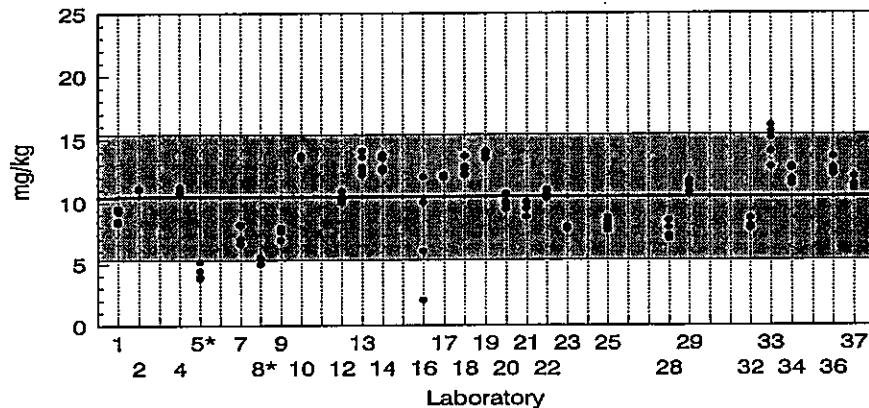
SEDIMENT R

Accepted Value:
 $10.4 \pm 5.1 \text{ mg/kg}$

Results: 27

Quantitative
 Values: 27

Rejections: 2



LEAD

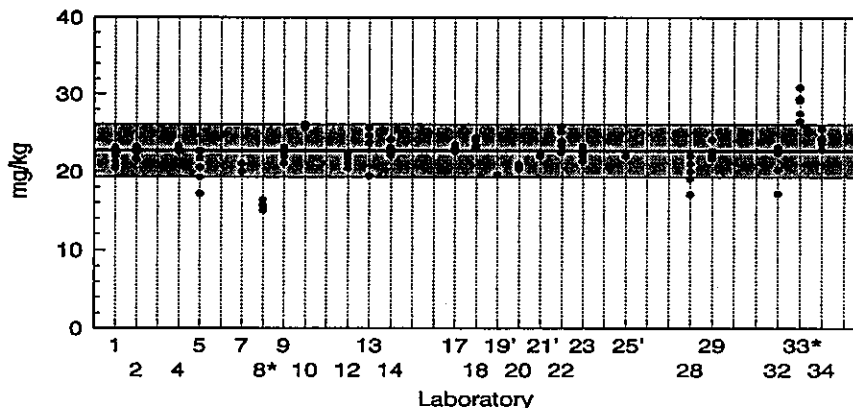
BCSS-1

Accepted Value:
 22.7 ± 3.4 mg/kg

Results: 24

Quantitative
 Values: 24

Rejections: 2



Tissues

Eighteen laboratories submitted quantitative results for lead in Fish Q ranging between 0.13 and 1.7 mg/kg. The means of only three laboratories (13,22,25) are excluded by the large calculated acceptable range of ± 57 percent, all high. The concentration of lead in the tissue is relatively low. Five laboratories submitted results with a precision greater than 20 percent RSD. Out of twenty laboratories, six reported a precision of less than 10 percent RSD.

Two laboratories (13,17) of eighteen reporting quantitative results were outside the certified confidence interval of ± 30 percent for lead in DORM-1, both high. DORM-1 and Fish Q have comparable lead contents. Historically, high lead values result from laboratory contamination problems. A precision greater than 20 percent RSD was reported by six laboratories.

Fifteen laboratories (3,4,5,6,11,12,14,18,19,20,21,23,28,29,34) reported acceptable results for lead in both biological tissue samples. This is very good performance, especially when the low concentrations of lead are considered and the fact that the analysis of fish tissue for lead was not long ago considered one of the most difficult trace metal analyses in marine chemistry. There is marked improvement compared to NOAA/5.

Sediments

Twenty-seven laboratories submitted quantitative results for lead in Sediment R. Twenty-five of these produced means within the calculated accepted range of ± 49 percent. The two outliers (5,8) were slightly low. Two laboratories reported results with a precision greater than 10 percent RSD.

Twenty-four laboratories reported results for lead in BCSS-1. Laboratory 33 was higher and 8 lower than the certified confidence limits of ± 15 percent. Precision was quite good with only three laboratories reporting a RSD slightly greater than 10 percent.

A record twenty-one laboratories (1,2,4,7,9,10,12,13,14,17,18,19,20,21,22,23,25,28,29,32,34) reported acceptable results for lead in both sediment samples. This is, surprisingly, the best performance in this exercise and a significant improvement compared to NOAA/5.

3. DISCUSSION

The intent of this exercise was to assess the capability of participating laboratories to determine selected trace metals in marine biological tissue and sediment samples. This is best measured through an evaluation of their accuracy and, through some extent, intralaboratory precision. Of the four samples, one sample of each type was a certified reference material (CRM). For these CRMs (except for aluminum, tin and silver in DORM-1 and mercury, silver and thallium in BCSS-1) accurate means and confidence intervals are known. This knowledge, however, presents an inherent difficulty when using CRMs in intercomparison studies. The answers are known to the participants and there is often an inclination to tend towards "the right answer". Our experience of the last several years with the NOAA exercises has shown that if this is happening, it is not a significant factor.

The combination of CRMs and unknowns and the substantially increased participation of the last two years have proven to be a powerful tool in discerning competence. The key factor, which characterizes and is almost unique to the NOAA exercises is the provision of a built in mechanism for obtaining reliable values for the concentrations of the analytes in the unknowns.

For each of the two unknown samples an excluded mean and confidence interval for each analyte were calculated from the submitted data, using the method outlined in Section 2. An implication of this approach is that the accuracy evaluation of a laboratory's performance for a particular analyte in a particular matrix is relative to the performances of all accepted laboratories. Thus we get an indication of the type of comparability we may expect if the accepted group were to analyze similar materials. In all cases in this study the calculated mean was not much different and certainly not significantly different from the NRC means for all analytes in both matrices..

If, for whatever reasons, we assume that NRC is competent, there also appears to always be a group of participating laboratories that are equally competent for various analytes in the particular matrices and, if there are sufficient data, an accurate mean can be established along with an appropriate 95 percent confidence interval that group of laboratories.

The use of the CRMs is a great aid in this type of exercise because their 95 percent confidence intervals are generally much narrower than those defined in the exercise for the unknowns. Laboratories which produce results within the confidence intervals of both the CRM and the unknown are obvious demonstrators of reliability and compatibility for that analyte in the particular matrix at the concentration range in question. Of equal importance is the ability to use the CRMs to discern general trends which might otherwise be lost in the wide confidence intervals calculated for the unknowns. For example, without the CRMs it would not be as obvious that there is a great tendency for many laboratories to produce low results for arsenic in both tissues and sediments (pp 20-21) or for zinc in sediments (pp 18-19) or demonstrate the great improvement in the analysis of marine samples for lead (pp 36-37).

A system to evaluate laboratory performance for the individual elements in the sediments and biological tissues was established using the following criteria:

- E - Excellent accuracy:** all replicate values are within the established confidence interval.
- G - Good accuracy:** the mean of the replicates is within the established confidence interval but one or more replicates is outside.
- L - Low results:** the mean of the replicates is less than the lower confidence limit.
- H - High results:** the mean of the replicates is greater than the upper confidence limit.
- ? - Accuracy can not be established.**
- G - Good precision:** the intralaboratory precision is within the criteria for precision listed below in Table I.
- X - Poor precision:** the intralaboratory precision is not within the criteria for precision listed below in Table I.
- - No results or a "less than" value submitted.

Results from laboratories which did not submit full sets of values for an analyte have not been evaluated here.

Detailed charts of this assessment are tabulated in Appendix C.

Table I

Criteria for Intralaboratory Precision Evaluation

Analyte Concentration	Expected RSD
≥ 10 mg/kg	± 10 percent*
≥ 1 and < 10 mg/kg	± 15 percent
< 1 mg/kg	± 20 percent

* ± 5 percent for aluminum and iron in sediments

These criteria for intralaboratory precision were established several years ago. Judging from the results of this and the last exercise (see the data sheets in Appendix B) they are very conservative and are in need of adjustment downwards. This will be done for NOAA/7.

The overall assessment based on the above criteria and the number of sets of results submitted allowed four distinct categories of accuracy performance to be discernible. These are shown in Table II for the biological tissues and in Table IV for the sediments. In general, **Superior** laboratories submitted results for most analytes within the 95 percent confidence intervals; **Good** laboratories submitted many results within the accepted range with a minimum number of outliers; **Fair** laboratories had some problems with certain elements or did not report results for a number of elements. Laboratories with a high proportion of outliers or "less thans" or which did not submit results for a large number of analytes were categorized as having **Many Problems**. It should be noted that the dividing lines between the categories, especially between good and fair, are somewhat diffuse. The last two columns in Tables II and IV compare the number of laboratories in each category for the last two exercises.

A similar evaluation for intralaboratory precision based largely on the criteria of Table I produced three distinct categories: **Good**, **Fair** and **Poor** (Tables III and V).

Biological Tissues

Table II
Accuracy Evaluation for the Biological Tissues*

	Laboratory Number	NOAA/6	NOAA/5
Superior	4,6,12,21,29	5	3
Good	1,3,5,15,18,19,20,22,24,25,34	11	7
Fair	11,14,17,26,35	5	7
Many Problems	8,13,16,23,27,28,32	7	6

Table III
Intralaboratory Precision Evaluation for the Biological Tissues*

	Laboratory Number
Good	3,6,12,15,18,22,32
Fair	1,4,5,8,11,14,16,17,19,24,25, 26,27,29,34,35
Poor	13,20,21,23,28

* - Laboratories 2,7,9,10,31 and 33 did not submit results for the tissues.

Of the twenty-eight laboratories which submitted data for the tissues there are sixteen laboratories in the superior and good categories, an increase of six over NOAA/5. It is encouraging to note that four (4,12,21,29) of the five laboratories rated superior in accuracy for biological tissues (Table II) are veterans which have analyzed biological tissues and sediments in all five previous NOAA exercises in this series. The fifth (6) is a laboratory which joined the studies last year. The two other long term veterans were rated good and fair. The latter laboratory, down from a good rating last year, only analyzed the tissues this year and we note that the name of the responsible person has changed.

Two laboratories in the good category had many problems last year. Six of the new laboratories submitted results for the tissues. Five of these are in the good or fair categories. Four of the seven laboratories with many problems were in the same category last year. Of the twenty laboratories that submitted tissue data for NOAA/5 eight improved their ratings and five have worse ratings.

In general, the group situation for tissues is improved over NOAA/5. The most significant improvements were made by Laboratories 1 and 19, both of which rose from many problems to good.

There are still a good number of problems concerning the analysis of marine biological tissues for trace metals. The following analytes present difficulties to at least twenty-five percent of the participants: aluminum, chromium, copper, arsenic, selenium, cadmium, tin and lead. These problems are generally related to the inherently low levels of these metals in the tissues. The situation was somewhat magnified this year because the chosen materials were fish tissues rather than shellfish tissues. The tendency towards low results for arsenic probably stems from the incomplete decomposition of organoarsenic compounds in the tissues prior to the determination.

Sediments

Table IV
Accuracy Evaluation for the Sediments*

	Laboratory Number	NOAA/6	NOAA/5
Superior	4,9,10,12,21,22,29	7	4
Good	2,14,16,17,18,19,20,24,34	9	8
Fair	1,7,13,23,26,31,32,33,35	9	9
Many Problems	5,8,25,27,28	5	5

* - Laboratories 3,6 11 and 15 did not submit results for the sediments.

Table V
Intralaboratory Precision Evaluation for the Sediments*

	Laboratory Number
Good	4,9,10,14,17,20,22,27,31
Fair	1,2,7,8,12,16,18,19,21,23,24, 25,26,28,32,33,34,35
Poor	5,13,29

* - Laboratories 3,6 11 and 15 did not submit results for the sediments.

Of the thirty laboratories which submitted data for the sediments there are sixteen laboratories in the superior and good categories, an increase of four over NOAA/5. The same four veteran laboratories (4,12,21,29) that performed well for the tissues were included in the seven rated superior in accuracy for sediments (Table IV). Two of the other three were rated good last year and one is a new participant. The other long term veteran which sent sediment data was rated good, the same as last year.

Two laboratories in the good category had many problems with sediments last year. Seven of the new laboratories submitted results for the sediments. Four of these are in the good or fair categories. Only one of the five laboratories with many problems was in the same category last year. Of the twenty-six laboratories that submitted sediment data for NOAA/5 eight improved their ratings and four have worse ratings.

In general, the group situation for sediments is, like the for tissues, improved over NOAA/5. The most significant improvements were made by Laboratories 17 and 19, both of which rose from many problems to good.

There are still a good number of problems concerning the analysis of marine sediments for trace metals. The following analytes present difficulties to at least twenty-five percent of the participants: aluminum, chromium, manganese, zinc, arsenic, selenium, silver, cadmium, tin, antimony and thallium. Many of the problems are generally related to the incomplete dissolution of the sediment prior to analysis as well as the low concentrations of some of these metals in the sediments.

Fourteen of the sixteen laboratories whose accuracies were rated superior or good for the sediments (Table II) also analyzed the tissues. Eleven of the fourteen were also rated superior or good for the tissues (Table IV). In general, a laboratory with capabilities for one matrix appears to also do well for another.

It can be seen from both Tables III and V that it is obviously easier to get superior or good precision than superior or good accuracy. In general, most laboratories meet the precision criteria of Table I. While it is apparent that it is necessary to have acceptable precision in order to have good accuracy, even outstanding precision is not a guarantee of good accuracy. We probably pay too much attention to intralaboratory precision in these studies.

Fourteen of the sixteen laboratories which were rated as superior or good accuracy for tissues were rated either good or fair for precision (Table III). Laboratories 20 and 21, rated good and superior respectively for accuracy, had, on average, poor precision.

Also, fourteen of the sixteen laboratories which were rated as superior or good accuracy for sediments were rated either good or fair for precision (Table V). Laboratory 29, rated superior for accuracy, generally had poor precision. An accurate laboratory is usually a precise laboratory but this is not a given and the compromise eventually reached should usually favour accuracy. Obviously, we have not yet found the correct balance of accuracy and intralaboratory precision criteria.

Participation in intercomparison exercises should assist laboratories to assess the quality of their work and whether there is improvement from year to year. In Appendix D we compare the number of submitted and rejected sets of results for the twenty-two laboratories (identified by their NOAA/6 codes) that were evaluated in both the NOAA/5 and NOAA/6 studies.

For the tissues (Table D-1) there were 368 sets of results evaluated for NOAA/6 and 317 sets for NOAA/5. The rejection rates were respectively 99 (27%) and 93 (29%) sets. This does not appear to be a significant difference but it does mean that, on the average, each laboratory that participated in both exercises determined one to two more analytes in each of the tissues, yet averaged no more rejections.

An examination of Table D-1 shows that some laboratories (1,3,6,14,19,25) performed much better for the analysis of the tissues this year in spite of the lower concentration of trace elements. In particular, Laboratories 1 and 19 improved from many problems to good. Others (8,11,16,32,34) worsened somewhat in performance.

For the sediments (Table D-2) there were 511 sets of results evaluated for NOAA/6 and 407 sets from the same laboratories for NOAA/5. The rejection rates were respectively 125 (24%) and 128 (31%) sets. This does appear to be a significant difference and it also shows, on the average, each laboratory that participated in both exercises determined two to three more analytes in each sediment, yet averaged no more rejections.

An examination of Table D-2 shows that a good proportion of the participants (1,2,9,10,14,17,19,21,34) performed much better for the analysis of the sediments this year. In particular, Laboratory 10 improved from fair to superior and Laboratories 17 and 19 from many problems to good. Only two participants (5,8) were worse.

Top honours go to the four veteran Laboratories 4,6,21 and 29 for achieving a superior rating for both matrices. Next in line are Laboratories 18,19,20,22,24 and 34, all in the superior or good category for tissues and sediments.

If we were to give a prize for the overall improvement of the year for the analysis of the four samples it would have to go to Laboratory 19 in rising from the many problems category to a good rating for both matrices.

Appendix E summarizes the digestion methods and instrumental techniques used for determination of the metals. Graphite furnace atomic absorption spectrometry (GFAAS) is the most frequently used with flame atomic absorption (FAAS) and inductively coupled plasma (ICPAES) reported an equal number of times. Almost every laboratory used more than one instrumental method for this exercise. The importance of using the right tool for the job is being more and more recognized by the participants.

The majority of the laboratories also report using closed vessel digestion procedures with microwave heating. The popularity of this decomposition technique has risen steadily over the last few exercises and probably is a partial cause for the continued improvements.

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5. ACKNOWLEDGMENTS

The authors would like to thank V. Boyko, V. Clancy, J. Lam and B. Methvan of the Environmental Measurement Science Program of NRC's Institute for Environmental Chemistry for supplying analytical results for the intercomparison samples.

APPENDIX A

Participants in NOAA/6

Academy of Natural Sciences
Benedict Estuarine Research Lab
Benedict, MD, 20612
Dr. Jim Sanders

Alabama Department of Environmental
Management
2204 Parimeter Road
Mobile, AL, 36615
Dr. D.I. Wigger

Australian Nuclear Science and Technology
Organization
Environmental Chemistry
Private Mail Bag 1
Menai, N.S.W. 2234, Australia
Dr. David Waite

Australian Government Analytical Laboratories
PO Box 385
Pymble, N.S.W. 2073, Australia
Mr. John Dalins

Battelle Ocean Science
397 Washington St.
Duxbury, MA, 02332
Dr. Dion Lewis

Battelle Pacific Northwest
439 W. Sequim Bay Road
Sequim, WA, 98382
Dr. E. Crecelius

California Department of Fish and Game
2201 Garden Road
Monteray, CA, 93940
Dr. M. Stephenson

Cat Cove Lab. - Marine Fisheries
Commonwealth of Massachusetts
92 Fort Ave.
Salem, MA, 01970
Dr. Jack Schwartz

Chesapeake Biological Lab
1 William Street
Solomons, MD, 20688
Dr. Tim Shaw

Deer Island Treatment Plant
MWRA
Winthrop, MA, 02152
Mr. David Duest

EPA
College Station Rd.
Athens, GA, 30613
Mr. William McDaniel

Florida Dept. Environmental Regulation
Chemistry Section
2600 Blair Stone Rd.
Tallahassee, FL, 32399-2400
Dr. Bill Coppenger

Goverment Chemical Laboratories
PO Box 594
Archerfield, Queensland 4108, Australia
Dr. Des Connell

Laboratory for Inorganic and Nuclear
Chemistry
Empire State Plaza
Albany, NY, 12201
Dr. Edmond Canelli

MD Health & Mental Hygiene
201 West Preston St.
Baltimore, MD, 21201
Mr. Al Bober

New York State Dept. of Environment
Conservation
Hale Creek Field Station
7235 Steele Ave. Extension
Gloversville, NY, 12078
Mr. Samuel Jackling

NOAA/NMFS
212 Rogers Ave.
Milford, CT, 06460
Mr. George Sennefelder

Northeast Fisheries Center
Sandy Hook Laboratory
Highlands, NJ, 07732
Dr. V.S. Zdanowicz

Northwest Fisheries Science Center
2725 Montlake Blvd. East
Seattle, WA, 98112-2097
Dr. Jim Meador

Old Dominion University
Applied Marine Research Laboratory
1034 West 45th St.
Norfolk, VA, 23529
Mr. Adam Abbg

PA Dept. of Environmental Resources
Division of Water Quality
Harrisburg, PA, 17120
Mr. Ted Lyter

Patuxent Wildlife Research Ctr.
Stickel Laboratory
Laurel, MD, 20708
Dr. John Moore

Queensland Department of Primary Industries
Animal Research Institute
665 Fairfield Road
Yeerongpilly Old, Queensland 4105, Australia
Dr. Hugh Mawhinney

Queensland Department of Primary Industries
Agricultural Chemistry Branch
Meiers Road
Indooroopilly, Queensland 4068, Australia
Mr. George Rayment

Southeast Fisheries Center
Beaufort Laboratory
Beaufort, NC, 28516
Dr. P. Hanson

State of Florida, Department of HRS
1217 Pearl St.
Jacksonville, FL, 32202
Ms. Tammie Stouter

SUNY Marine Sciences Research Center
Stony Brook, NY, 11794-5000
Mr. David Hirschberg

Texas A. & M
Department of Oceanography
College Station, TX, 77843
Dr. B. Presley

U. Massachusetts at Boston
Environmental Science Program
Boston, MA, 02125
Dr. Gordon Wallace

University of Mississippi
School of Pharmacy
University, MS, 38677
Dr. James O'Neal

US Dept. of Agriculture
Beltsville, MD, 20705
Dr. Nancy Miller-Ihli

USEPA
Environmental Monitoring Systems Laboratory
26 W. Martin Luther King Dr.
Cincinnati, OH, 45268
Mr. Nate Malof

USEPA
Environmental Research Laboratory
South Ferry Road
Narragansett, RI, 02882
Dr. W.S. Boothman

USGS
6481-B Peachtree Blvd.
Doraville, GA, 30360
Dr. Arthur Horowitz

Water Pollution Control
515 West 6th St.
Jacksonville, FL, 32206
Mr. Roger Baskin

Data was not received from the following laboratories:

The College of William & Mary
Department of Chemistry
Rogers Hall
Williamsburg, VA, 23185
Dr. Gary Rice

Environmental Resources Management
METRO-Dade County
211 West Flagler St.
Miami, FL, 33130
Mrs. Jana Bares

Hatfield Marine Science Center
EPA
2111 SE Marine Science Dr.
Newport, OR, 97365-5260
Mr. Scott Echols

Office of Maryland State Chemist
50 Harry S. Truman Parkway
Annapolis, MD, 21401
Mr. Warren Bontoyan

Oregon State University
College of Oceanography
Covallis, Oregon, 97331-5503
Mr. Chih-Ann Huh

Rensselaer Polytechnical Inst.
Dept. of Earth and Environ. Sci.
West Hall
Troy, NY, 12180-3590
Mr. Richard Bopp

State of Louisiana
Technical Service Division
8618 GSRI Road
Baton Rouge, LA, 70810
Ms. Elaine Sorbet

VA Bureau of Chemistry
1 North 14th St.
Richmond, VA, 23219
Mr. Dick Pitts

APPENDIX B

DATA

Aluminum	B-2
Silicon	B-4
Chromium	B-6
Manganese	B-8
Iron	B-10
Nickel	B-12
Copper	B-14
Zinc	B-16
Arsenic	B-18
Selenium	B-20
Silver	B-22
Cadmium	B-24
Tin	B-26
Antimony	B-28
Mercury	B-30
Thallium	B-32
Lead	B-34

ALUMINUM
BCSS-I
6.26 ± 0.41 %

B-3

The determination of silicon was not required in the biologicals.

SILICON
Sediment R
%

Lab 1 0
2 0
3 0
4 0
5 0
6 0
7 0
8 0
9 5
10 0
11 0
12 5
13 0
14 0
15 0
16 0
17 0
18 0
19 0
20 0
21 5
22 0
23 0
24 0
25 0
26 0
27 0
28 0
29 0
30 0
31 0
32 0
33 0
34 0
35 0

Mean SD RSD
39.64 39.59
38.3 38.5 38.7 38.8 39.1 38.7 0.3 0.8
37.2 39.5 38.4 37.2 36.1 37.7 1.3 3.5
40 40 40 40 40 40 0 0

SILICON
BCSS-1
30.8 ± 1.0 %

Lab 1 0
2 0
3 0
4 0
5 0
6 0
7 0
8 0
9 5
10 0
11 0
12 5
13 0
14 0
15 0
16 0
17 0
18 0
19 0
20 0
21 5
22 0
23 0
24 0
25 0
26 0
27 0
28 0
29 0
30 0
31 0
32 0
33 0
34 0
35 0

Mean SD RSD
30.1 30.1 30.2 30.1 30 30.1 0.1 0.2
31.7 30.6 29.5 31.7 29.5 30.6 1.1 3.6
30 30 30 30 30 30 0 0

CHROMIUM
Fish Q
6.45 ± 2.07 mg/kg

Lab	5	6.20	7.06	7.76	6.82
1	5	6.20	7.06	7.76	6.82
2	0				
3	5	6.2	6.8	6.9	6.6
3	5	6.2	6.8	6.9	6.6
4	5	7.26	7.28	7.69	7.73
5	5	2.69	3.18	3.06	3.16
5*	5	6.97	7.12	7.48	7.31
6	5	6.97	7.12	7.48	7.31
7	0				
8*	5	4.00	4.00	4.41	3.43
9	0				
10	0				
11*	4	5.40	3.24	2.51	3.26
12	5	6.37	6.09	6.23	6.62
13'	4	7.30	7.58	7.66	8.66
14*	5	3.21	3.05	3.25	3.48
15	0				
16*	4	10	10	10	12
17*	5	2.26	2.42	2.77	2.17
18	5	6.02	6.40	7.06	6.60
19	5	8.120	8.520	8.300	8.630
20	5	7.24	9.55	6.75	8.53
21	5	6.1	5.9	6.3	5.4
22*	5	11.5	10.7	12.1	10.9
23	5	4.6	5.2	4.8	5.0
24'	4	5.2	5.3	5.2	4.8
25	5	7.4	7.5	6.4	6.9
26	5	4.40	4.07	5.76	4.71
27	0				
28	5	17.4	6.0	5.3	5.9
29'	4	6.3	6.4	6.2	6.4
30	0				
31	0				
32	0				
33	0				
34*	5	3.25	3.61	2.87	2.95
35	5	6.89	5.76	5.84	5.55
36	5	5.8	6.2	6.6	6.5
37	5	6.46	6.44	6.10	5.80

CHROMIUM
DORM-1
3.60 ± 0.40 mg/kg

Lab	5	2.96	3.05	2.97	3.02	3.15	Mean	SD	RSD
1*	5	2.96	3.05	2.97	3.02	3.15	3.03	0.08	2.5
2	0								
3*	5	3.1	2.9	2.7	3.1	3.5	3.1	0.3	9.7
4	5	3.67	3.91	3.59	3.38	3.57	3.62	0.19	5.3
5*	5	2.59	2.47	2.52	2.53	2.53	2.53	0.04	1.7
6	5	3.67	3.64	3.64	3.56	3.86	3.67	0.11	3.0
7	0								
8*	5	2.43	2.48	2.50	2.48	2.45	2.47	0.03	1.1
9	0								
10	0								
11	5	4.60	2.77	3.05	2.86	3.42	3.34	0.75	22.4
12'	4	3.56	3.59	3.56	3.36	3.54	3.56	0.02	0.6
13	5	3.56	3.60	3.08	3.04	3.08	3.27	0.28	8.6
14*	4	2.38	2.38	2.38	2.41	2.59	2.39	0.02	0.6
15	0								
16	0	3	5	4					
17*	5	2.58	2.58	2.46	2.19	2.74	2.51	0.20	8.2
18	5	3.88	4.01	3.93	3.59	3.91	3.86	0.16	4.2
19	5	3.920	3.810	3.860	3.870	3.900	3.872	0.042	1.1
20	5	2.94	3.21	3.28	3.50	3.36	3.26	0.21	6.4
21*	5	3.8	4.3	3.9	4.5	4.5	4.2	0.3	7.9
22	5	3.79	3.39	3.24	3.74	3.51	3.53	0.23	6.6
23*	5	2.2	2.0	2.1	2.1	2.3	2.1	0.1	5.3
24*	5	3.1	2.8	2.9	2.7	2.9	2.9	0.1	5.2
25	5	3.50	3.50	3.60	3.40	3.60	3.52	0.08	2.4
26	5	3.51	3.24	3.34	3.66	2.63	3.28	0.40	12.1
27	0								
28*	5	3.3	2.6	1.9	1.6	2.0	2.3	0.06	28.3
29	5	3.3	4.6	3.4	3.6	4.1	3.8	0.5	14.3
30	0								
31	0								
32	0								
33	0								
34*	4	2.33	2.51	1.71	2.46	2.39	2.42	0.08	3.3
35'	4	3.98	3.33	3.48	3.44	3.48	3.54	0.25	7.1

The determination of manganese was not required in the biologicals.

MANGANESE
Sediment R
217 ± 50 mg/kg

Lab	134	119	118	114	124	Mean	SD	RSD	Lab	185	186	184	184	187	Mean	SD	RSD
1*	5	134	119	118	114	124	8	6.3	1*	5	185	186	184	187	185	1	0.7
2	5	240	235	238	225	227	7	2.9	2	5	245	234	236	242	237	7	2.8
3	2	210	190						3	0							
4	0								4	0							
5*	5	100.0	97.3	102.0	90.0	96.0	5	4.7	5*	5	169	147	173	171	171	2	1.2
6	0								6	0							
7*	4	106	109	109	109	110	1	0.5	7*	4	194	195	212	192	195	2	1.0
8	0								8	0							
9	5	193	194	192	195	195	1	0.7	9	5	235	236	236	234	235	1	0.4
10	5	238	237	242	241	238	2	0.9	10	5	220	221	222	226	223	2	1.1
11	0								11	0							
12	5	202	205	202	203	206	2	0.9	12	5	219	225	218	219	221	3	1.5
13	0								13	0							
14	5	240	237	236	237	234	2	0.9	14	5	222	210	232	219	221	8	3.6
15	0								15	0							
16	5	222	218	220	224	216	3	1.4	16	0							
17	5	215.4	213.7	211.2	214.1	213.8	2	0.7	17*	5	197.6	201.6	201.4	206.3	203	4	1.9
18	0								18	0							
19	5	207.50	206.25	206.25	207.25	206.25	0.62	0.3	19*	5	214.66	213.33	209.33	208.00	211	3	1.4
20	5	232	231	246	231	218	10	4.3	20	5	222	225	224	227	225	2	0.8
21	5	210	190	180	190	180	12	6.4	21	5	210	230	210	220	222	13	5.9
22*	5	143	143	145	143	144	1	0.6	22	5	226	231	235	227	229	4	1.7
23*	5	117	115	118	119	116	2	1.4	23*	5	171	172	175	173	173	1	0.9
24	5	237	242	230	236	238	4	1.8	24	5	230	238	242	239	232	5	2.1
25*	5	92	89	94	85	93	4	4.0	25*	5	130	150	130	150	142	11	7.7
26*	5	158	154	144	153	139	8	5.2	26	5	229	226	217	216	221	6	2.8
27*	5	158.0	156.8	153.6	157.1	151.2	3	1.8	27*	5	199.8	198.6	198.4	198.0	197.2	1	0.5
28	0								28	0							
29	5	216	262	246	221	248	19	8.1	29	5	190	241	244	202	223	25	11.1
30	0								30	0							
31	4	217	217	213	208	214	4	2.0	31	0							
32	0								32	0							
33	5	211	207	208	207	209	2	0.8	33*	5	206	204	203	203	206	4	1.8
34	0								34	0							
35	0								35	0							
36	5	240	236	247	245	238	5	1.9									
37	5	224	230	267	251	228	18	7.7									

IRON
Sediment R
1.88 ± 0.25 %

Lab	1.79	1.63	1.61	1.62	1.66	1.63	Mean	SD	RSD	Lab	5	2.72	2.74	2.70	2.70	3.28 ± 0.14 %	Mean	SD	RSD
1*	4	1.79	1.63	1.61	1.62	1.66	1.63	0.02	1.3	1*	5	2.72	2.74	2.70	2.70	3.28 ± 0.14 %	2.72	0.02	0.8
2	5	2.052	2.027	1.914	1.958	1.920	1.974	0.063	3.2	2	5	3.245	3.278	3.548	3.174	3.064	3.262	0.180	5.5
3	2	2.01	1.99							3	0								
4	5	2.01	2.01	1.98	1.98	2.01	2.00	0.02	0.8	4	5	3.28	3.26	3.27	3.27	3.29	3.27	0.01	0.3
5*	5	1.44	1.44	1.46	1.41	1.35	1.42	0.04	3.0	5*	5	2.22	2.06	2.38	2.33	2.31	2.26	0.13	5.6
6	0									6	0								
7*	5	1.50	1.53	1.66	1.56	1.64	1.58	0.07	4.4	7*	5	2.85	2.85	2.90	2.73	2.74	2.81	0.08	2.7
8	0									8	0								
9	5	1.79	1.78	1.78	1.79	1.79	1.79	0.01	0.3	9	5	3.37	3.36	3.39	3.38	3.37	3.37	0.01	0.3
10	5	1.98	1.94	1.97	1.96	2.03	1.98	0.03	1.7	10	5	3.23	3.19	3.20	3.21	3.28	3.22	0.04	1.1
11	0									11	0								
12	5	1.94	1.88	1.969	1.88	1.95	1.92	0.04	2.1	12	5	3.32	3.25	3.24	3.32	3.26	3.28	0.04	1.2
13	5	1.69	1.72	1.74	1.79	1.78	1.74	0.04	2.4	13*	5	2.83	2.82	3.00	2.96	3.01	2.92	0.09	3.2
14	5	2.00	2.00	2.04	2.06	1.99	2.02	0.03	1.5	14	5	3.16	2.99	3.23	3.11	3.21	3.14	0.10	3.1
15	0									15	0								
16	5	1.9	2.0	2.0	2.1	2.1	2.0	0.1	4.1	16	0								
17*	5	2.17	2.14	2.20	2.16	2.21	2.18	0.03	1.3	17*	5	3.61	3.62	3.62	3.64	3.62	3.62	0.01	0.3
18*	5	2.330	2.158	2.297	2.316	2.392	2.299	0.086	3.8	18*	5	3.075	3.166	3.160	3.098	3.114	3.123	0.039	1.3
19	5	1.73	1.73	1.71	1.71	1.73	1.72	0.01	0.6	19	5	3.22	3.25	3.12	3.17	3.23	3.20	0.05	1.6
20	0									20	0								
21	5	1.8	1.7	1.6	1.7	1.8	1.7	0.1	4.9	21	5	3.3	3.3	3.3	3.3	3.3	3.3	0	0.0
22	5	1.91	1.96	1.90	1.95	1.94	1.93	0.03	1.3	22	5	3.15	3.17	3.17	3.29	3.07	3.17	0.08	2.5
23	5	1.76	1.75	1.76	1.78	1.73	1.76	0.02	1.0	23	5	3.08	3.08	3.15	3.12	3.12	3.11	0.03	1.0
24	5	2.01	2.01	1.99	2.01	2.05	2.01	0.02	1.1	24	5	3.30	3.09	3.19	3.21	3.15	3.19	0.08	2.4
25*	5	1.50	1.60	1.60	1.50	1.50	1.54	0.05	3.6	25*	5	2.40	2.70	2.50	2.70	2.80	2.62	0.16	6.3
26	5	1.954	2.023	1.799	2.123	1.967	1.973	0.118	6.0	26	5	3.322	3.057	3.147	3.289	3.299	3.223	0.115	3.6
27	5	1.7496	1.7623	1.7353	1.7322	1.7313	1.742	0.013	0.8	27*	5	2.9395	2.8742	3.0332	2.9998	3.1320	2.996	0.097	3.3
28	0									28	0								
29*	5	2.25	2.2	2.25	2.19	2.23	2.22	0.03	1.3	29*	4	3.40	3.37	3.38	3.10	3.36	3.37	0.02	0.5
30	0	0.0151								30	0	2.782							
31	4	1.93	1.83	1.87	1.91		1.89	0.04	2.4	31	0								
32	0									32	0								
33*	4	1.97	1.85	1.86	1.85	1.87	1.85	0.01	0.5	33*	5	3.06	3.03	3.00	3.02	3.16	3.05	0.06	2.1
34*	4	1.88	1.91	1.94	1.63	1.94	1.92	0.03	1.5	34*	5	3.19	3.12	3.28	3.09	3.24	3.18	0.08	2.5
35	5	2.02	2.02	2.01	1.99	2.02	2.01	0.01	0.6	35	5	3.35	3.24	3.32	3.22	3.15	3.26	0.08	2.5
36	0																		
37*	4	1.90	1.90	2.20	1.96	1.91	1.92	0.03	1.5										

COPPER Fish Q 3.15 ± 0.77 mg/kg										COPPER DORM-1 5.22 ± 0.33 mg/kg									
Lab	Mean	SD	RSD	Lab	Mean	SD	RSD	Lab	Mean	SD	RSD	Lab	Mean	SD	RSD				
1*	2.95	4.34	3.04	2.76	2.97	0.11	3.8	1*	4.22	4.3	4.17	4.34	4.24	0.07	1.6				
2								2											
3	3.1	3.3	3.2	3.2	3	0.11	3.6	3*	4.3	4.7	4.4	5.0	4.9	0.30	6.5				
4	3.07	3.05	2.97	2.99	2.93	0.06	1.9	4	5.16	5.22	5.25	5.3	5.14	0.07	1.3				
5	2.73	2.77	2.84	2.84	2.54	0.12	4.5	5	5.24	5.19	5.19	4.73	4.85	0.23	4.6				
6*	4.85	4.00	4.81	4.04	3.61	0.55	12.8	6	5.28	5.29	5.20	5.20	5.14	0.06	1.2				
7								7											
8	4.50	4.00	3.92	3.43	2.45	0.78	21.2	8	5.34	4.95	6.00	6.44	4.90	0.67	12.2				
9								9											
10								10											
11	3.15	3.28	3.17	3.28	3.15	0.07	2.1	11*	3.68	3.39	3.49	3.79	2.77	0.40	11.6				
12	2.94	2.96	2.93	2.89	2.97	0.03	1.1	12	5.28	5.21	5.29	5.31	5.25	0.04	0.7				
13	3.11	3.43	3.55	3.92	4.37	0.48	13.2	13	5.11	5.59	5.56	5.19	5.45	0.22	4.1				
14	3.02	3.16	3.78	3.29	4.26	0.51	14.6	14*	5.45	5.03	4.94	5.06	4.94	0.06	1.2				
15								15											
16*	2	2	2	2	2	0	0	16	4	4									
17	3.2	3.1	3.5	3.3	3.4	0.2	4.8	17*	4.5	4.6	4.7	5.0	4.6	0.2	4.1				
18	3.29	3.12	3.01	2.76	2.71	0.24	8.2	18	5.28	4.81	4.65	5.36	5.02	0.30	6.0				
19*	1.875	1.875	1.875	1.875	1.875	0	0.0	19	5.19	5.19	5.19	5.19	5.19	0	0				
20	3.04	2.93	3.32	2.81	2.85	0.20	6.8	20	5.20	4.62	5.46	5.05	4.75	0.34	6.8				
21	4.0	3.7	3.6	3.4	4.1	0.3	7.7	21*	5.9	6.4	6.3	6.1	6.1	0.2	3.2				
22*	4.29	4.29	4.96	4.66	4.91	0.32	7.0	22*	5.07	5.24	5.07	5.05	5.05	0.01	0.2				
23*	2.4	2.6	2.0	2.2	2.4	0.2	9.8	23*	3.4	3.4	3.6	3.2	3.1	0.2	5.8				
24*	3.09	2.99	2.91	5.01	3.24	0.14	4.6	24	5.34	5.43	5.20	5.27	5.60	0.16	2.9				
25*	3.6	5.1	4.5	4.2	4.3	0.5	12.5	25	5.3	5.3	4.8	5.7	5.2	0.3	6.1				
26	3.22	3.31	4.04	3.90		0.41	11.4	26	4.86	5.21	5.06	5.38	4.55	0.32	6.4				
27	3.8	2.3	2.8	2.4	2.7	0.6	21.3	27	5.8	5.2	5.1	5.8	5.2	0.3	6.4				
28*	15.0	9.2	9.5	11.0	9.9	2.4	21.8	28*	4.1	8.3	6.4	5.8	5.5	1.5	25.4				
29	3.3	3.9	3.6	3.5	3.1	0.3	8.7	29	5.1	5.0	5.1	5.4	5.4	0.2	3.6				
30	3.35							30	5.21										
31								31											
32								32											
33								33											
34	3.22	3.25	3.13	3.37	3.18	0.09	2.8	34*	4.20	4.32	4.53	4.49	4.18	0.16	3.7				
35*	4.12	4.26	3.80	4.6	3.81	0.33	8.1	35*	5.70	5.44	5.98	5.52	5.59	0.21	3.7				
36	3.21	2.72	2.13	2.97	3.05	0.42	15.0												
37*	3.28	2.93	2.91	2.94	2.93	0.16	5.3												

COPPER
Sediment R

9.81 ± 1.84 mg/kg

Lab	Mean	SD	RSD	Lab	Mean	SD	RSD
1	10.2	9.28	9.02	9.46	9.47	9.49	4.6
2	10.8	10.6	10.8	10.6	10.6	10.7	1.0
3	10	10	10.4	10.4	10.4	10.4	0.4
4	10.4	10.3	9.8	9.1	9.5	9.4	3.2
5	9.1	9.5	9.3	8.8	9.2	9.1	0.2
6	9.0	9.2	8.50	8.91	8.91	8.96	0.05
7	9.0	9.00	10.3	10.1	11.3	10.8	0.6
8	11.6	10.7	11.4	10.3	10.9	10.8	0.4
9	11.1	10.5	9.18	9.17	9.21	9.19	0.02
10	9.19	11.3	11.8	14.0	16.4	13.5	2.0
11	8.27	8.2	8.54	8.40	8.20	8.32	0.15
12	10	10	10	10	10	10	0
13	10.9	11.34	11.19	11.04	10.86	11.10	0.18
14	11.09	9.82	11.54	11.72	10.26	10.98	0.88
15	6.25	5.00	5.00	5.00	6.25	5.50	0.68
16	9.8	10.5	11.2	10.5	10.0	10.4	0.5
17	9.8	11	9.0	9.6	11	10.1	0.9
18	10.8	9.39	9.80	9.23	9.58	9.76	0.62
19	9.2	9.7	9.4	9.7	9.4	9.5	0.2
20	9.7	11.3	9.7	10.0	10.1	9.9	0.2
21	9.8	9.9	10	10	11	9.9	0.1
22	8.78	8.96	8.71	10.9	8.55	8.75	0.17
23	9.6	9.0	9.2	9.6	8.8	9.2	0.4
24	29.0	12.0	11.0	15.0	8.9	15.2	8.0
25	11.2	11.2	11.3	10.8	11.1	11.1	0.2
26	8.6	10.6	10.6	11.2	10.9	10.9	0.4
27	12.2	12.5	11.9	11.6	12.4	12.1	0.4
28	8.45	8.30	8.21	7.00	7.61	7.91	0.60
29	13.7	12.3	14.7	11.7	13.4	13.2	1.2
30	9.25	9.45	9.01	9.36	9.26	9.27	0.16
31	8.69	9.10	9.20	8.85	9.14	9.00	0.22
32							
33							
34							
35							
36							
37							

COPPER
BCSS-1

18.5 ± 2.7 mg/kg

Lab	Mean	SD	RSD	Lab	Mean	SD	RSD
1*	15.1	15.3	15.2	15.1	15.2	15.2	0.1
2	18.2	18.4	18.5	19.1	18.7	18.6	0.3
3	0	0	0	0	0	0	1.8
4	17.9	19	18.6	18.3	18.4	18.4	0.4
5*	16.2	14.2	14.6	14.5	14.4	14.4	0.2
6	0	0	0	0	0	0	1.4
7	15.8	16.3	16.8	15.4	15.9	16.0	0.5
8*	11.50	12.50	15.84	13.00	12.75	13.12	1.62
9	18.1	17.5	17.9	18.5	18.4	18.1	0.4
10	16	16	16.5	15.9	16.6	16.2	0.3
11	0	0	0	0	0	0	2.0
12	18.3	18.2	18.4	18.3	18.6	18.4	0.2
13	18.1	19.1	19.1	18.2	17.8	18.5	0.6
14	16.6	15.9	16.2	15.8	16.2	16.1	0.3
15	0	0	0	0	0	0	1.9
16	0	0	0	0	0	0	0
17	21.67	19.73	18.83	18.52	20.58	19.87	1.29
18	16.93	17.47	16.93	16.38	17.47	17.04	0.46
19*	16.66	15.55	16.66	16.66	16.66	16.66	0.01
20	19.0	18.6	18.5	18.0	18.5	18.5	0.4
21	20	22	21	21	18	20	2
22	18.5	17.9	19.3	19.5	18.4	18.7	0.7
23	16.0	15.5	16.1	16.0	15.9	15.9	0.2
24	20.0	17.4	17.9	20.2	18.1	18.7	1.3
25*	16	15	14	16	15	15	1
26	15.0	14.5	15.1	15.9	16.9	15.5	0.9
27*	15.2	15.2	14.9	15.2	15.0	15.1	0.1
28	15.0	15.0	18.0	14.0	21.0	16.6	2.9
29	19.5	18.1	18.3	19.4	19.5	19.0	0.7
30	15.3	0	0	0	0	0	3.7
31	0	0	0	0	0	0	0
32	0	0	0	0	0	0	0
33	18.3	18.4	18.2	18.6	19.1	18.5	0.4
34*	19.2	17.7	17.7	17.7	17.4	17.6	0.2
35	19.1	19.2	20.4	19.5	20.5	19.7	0.7
36							3.4
37							

[illegible]

[illegible]

ARSENIC
Sediment R
6.22 ± 2.33 mg/kg

Lab	5	5.4	5.0	6.0	4.8	5.4	Mean	SD	RSD	Lab	5	8.4	7.8	7.7	9.2	8.2	Mean	SD	RSD
1	5	5.4	6.0	4.8	5.4	5.3	5.3	0.5	8.7	1*	5	8.4	7.8	7.7	9.2	8.2	8.3	0.6	7.2
2	5	6.7	6.1	7.3	6.3	6.6	6.6	0.5	7.1	2*	5	9.9	9.4	8.8	9.4	9.4	9.4	0.4	4.2
3	2	6	6							3	0								
4	5	6.72	6.65	6.54	6.65	6.71	6.65	0.07	1.1	4	5	11	10.9	11.7	11.2	10.4	11.0	0.5	4.3
5*	5	3.4	3.4	3.4	3.5	3.5	3.44	0.05	1.6	5*	4	5.6	5.5	5.5	5.7	6.3	5.6	0.1	1.7
6	0									6	0								
7	5	4.5	4.8	5.5	5.2	5.6	5.1	0.5	9.1	7*	5	8.8	8.9	9.4	8.6	9.0	8.9	0.3	3.3
8	0									8	0								
9	5	6.3	6.4	6.3	6.3	6.5	6.4	0.1	1.4	9	5	10.8	10.8	10.3	10.3	10.9	10.6	0.3	2.8
10	5	6.71	6.85	6.87	6.80	6.94	6.83	0.09	1.3	10	5	10.4	10.3	10.4	10.3	10.2	10.3	0.1	0.8
11	0									11	0								
12	5	7.51	6.94	6.36	7.51	6.37	6.94	0.57	8.3	12	5	11.3	11.6	11.5	11.8	12.5	11.7	0.5	3.9
13	5	5.16	4.33	4.83	5.01	5.76	5.02	0.52	10.4	13*	5	7.44	7.80	7.94	8.02	7.73	7.79	0.22	2.9
14	5	6.06	5.8	6.04	5.83	5.76	5.90	0.14	2.4	14*	4	9.01	8.99	8.85	9.04	8.19	8.97	0.08	0.9
15	0									15	0								
16	5	7.6	6.9	7.0	6.7	6.6	7.0	0.4	5.6	16	0								
17*	5	10.58	10.83	10.21	9.48	9.53	10.13	0.61	6.0	17	5	12.54	12.91	11.58	11.46	12.47	12.19	0.64	5.2
18	0									18	0								
19*	5	12.62	12.75	12.71	12.73	12.75	12.71	0.05	0.4	19	5	12.23	12.2	12.26	12.23	12.21	12.23	0.02	0.2
20	0									20	0								
21	5	7.2	7.0	5.8	6.0	6.8	6.6	0.6	9.5	21	5	12	12	13	13	12	12	1	4.4
22	5	8.32	8.27	8.49	8.76	8.88	8.54	0.27	3.1	22	5	10.8	11.1	11.7	11.4	11.5	11.3	0.4	3.1
23	5	4.2	4.2	5.2	4.6	4.7	4.6	0.4	9.1	23*	5	7.8	8.7	8.3	8.3	8.7	8.4	0.4	4.4
24	5	5.3	5.2	5.2	5.4	5.6	5.3	0.2	3.1	24*	5	9.8	8.9	8.6	9.2	6.5	8.6	1.3	14.6
25	5	4.549	4.158	4.470	4.627	4.198	4.400	0.211	4.8	25*	5	7.32	7.68	7.597	7.48	7.68	7.55	0.15	2.0
26	0									26	0								
27	0									27	0								
28	5	6.4	5.5	6.9	2.0	4.5	5.1	1.9	38.3	28	5	<25	<21	<24	<25	<25			
29	5	8.2	8.5	6.2	6.3	6.8	7.2	1.1	15.0	29	5	12.0	10.7	11.4	10.8	11.8	11.3	0.6	5.1
30	0	4.58								30	0	8.24							
31	0									31	0								
32	0									32	0								
33	5	7.12	7.82	6.77	7.01	6.88	7.12	0.41	5.8	33*	5	13.4	13.4	13.1	13.2	13.3	13.3	0.1	1.0
34	5	5.77	6.53	5.98	6.48	5.83	6.12	0.36	5.9	34*	5	8.18	8.06	7.59	8.14	7.50	7.89	0.32	4.1
35	0									35	0								
36	5	7.89	7.27	8.02	8.02	8.16	7.87	0.35	4.4										
37	0																		

$5.08 \pm 2.14 \text{ mg/kg}$

Lab	5.00 ± 2.14 mg/kg					1.62 ± 0.12 mg/kg										
	Mean	SD	RSD	Lab	Mean	SD	RSD	Lab	Mean	SD	RSD					
1	5.5	4.3	4.7	4.9	7.1	5.3	1.1	20.7	1.3	1.4	0.92	1.5	1.3	1.3	0.22	17.1
2	0								5							
3*	4	5.0	5.1	5.0	4.9	5.0	0.08	1.6	3*	1.3	1.2	1.1	1.3	1.5	1.3	0.15
4	5	5.47	5.35	5.43	5.33	5.38	0.07	1.3	4	5	1.51	1.52	1.56	1.58	1.60	0.04
5*	4	5.58	7.98	7.68	7.55	7.70	0.20	2.6	5*	5	1.88	1.78	1.81	1.75	1.77	0.05
6	5	5.62	5.72	5.67	5.71	5.67	0.05	0.8	6	5	1.53	1.57	1.57	1.56	1.60	0.03
7	0								7	0						1.6
8	0								8	0						
9	0								9	0						
10	0								10	0						
11*	5	1.64	1.65	1.43	1.48	1.56	0.10	6.4	11	5	1.63	1.58	1.65	1.74	2.13	12.7
12	5	3.66	3.99	3.84	4.17	3.87	0.22	5.6	12	5	1.76	1.68	1.57	1.76	1.56	5.9
13	5	4.24	3.82	4.19	4.14	4.00	0.27	6.6	13*	5	1.78	1.24	0.93	0.88	0.78	36.2
14	0								14	0						
15	0								15	0						
16	5	4.3	4.4	4.0	4.0	4.2	0.2	4.3	16	2	1.1	1.1				
17	5	3.74	4.07	3.83	3.66	3.88	0.20	5.2	17*	5	1.024	0.992	0.996	0.967	0.965	2.4
18	0								18	0						
19	5	4.82	4.86	4.82	4.85	4.83	0.02	0.5	19	5	1.584	1.581	1.587	1.586	1.587	0.03
20	5	5.52	5.11	5.48	6.27	5.63	0.43	7.6	20	5	1.83	2.14	1.53	1.57	1.52	15.6
21	5	6.0	5.4	5.6	5.6	5.7	0.2	4.3	21	5	1.7	1.8	1.6	1.5	1.6	8.0
22	5	6.20	6.32	6.58	6.37	6.39	0.14	2.3	22	5	1.53	1.58	1.65	1.60	1.62	2.8
23	5	5.8	5.9	5.7	6.3	5.1	0.4	7.5	23*	5	0.6	0.6	0.7	0.7	0.6	8.6
24	5	3.95	3.70	3.82	3.91	3.88	0.13	3.3	24	5	1.27	2.14	1.40	1.52	1.42	22.0
25	5	4.865	5.525	5.225	4.899	5.043	0.330	6.5	25	5	1.753	1.576	1.69	1.679	1.821	5.4
26	0								26	0						
27	0								27	0						
28	5	3.7	3.8	3.7	3.6	3.7	0.1	2.2	28*	5	1.1	1.0	0.99	0.97	1.01	5.0
29	5	5.1	5.3	5.3	5.4	5.2	0.1	2.6	29	5	1.7	1.6	1.7	1.6	1.7	3.3
30	0								30	0						
31	0								31	0						
32	0								32	0						
33	0								33	0						
34	0								34	0						
35	0								35	0						
36	5	5.22	5.41	5.09	5.72	5.59	0.26	4.8								
37	0															

SELENIUM
Sediment R
0.171 ± 0.104 mg/kg

Lab	5	<0.50	<0.50	<0.50	<0.50	<0.50	Mean	SD	RSD	Lab	5	<0.50	<0.50	<0.50	<0.50	<0.50	Mean	SD	RSD
1	5	<0.50	<0.50	<0.50	<0.50	<0.50				1	5	<0.50	<0.50	<0.50	<0.50	<0.50			
2	0									2	0								
3	2	0.14	0.14							3	0								
4	5	0.125	0.095	0.090	0.102	0.096	0.102	0.014	13.5	4	5	0.43	0.39	0.39	0.42	0.41	0.02	4.5	
5	5	0.9	0.2	<0.2	<0.2	<0.2				5	5	1.0	0.2	<0.2	<0.2				
6	0									6	0								
7	5	<0.2	<0.2	<0.2	<0.2	<0.2				7*	5	1.2	1.1	1.1	1.0	1.1	0.1	6.4	
8	0									8	0								
9	5	0.30	0.26	0.24	0.30	0.20	0.26	0.04	16.3	9*	5	0.52	0.43	0.55	0.53	0.50	0.05	10.2	
10	5	0.14	0.14	0.15	0.15	0.14	0.14	0.01	3.8	10	5	0.39	0.37	0.39	0.41	0.39	0.01	3.8	
11	0									11	0								
12	5	0.158	0.093	0.159	0.158	0.093	0.132	0.036	27.1	12	5	0.422	0.317	0.475	0.423	0.634	0.454	0.116	25.5
13	5	0.20	0.19	0.17	0.16	0.23	0.19	0.03	14.4	13	5	0.35	0.36	0.42	0.40	0.39	0.03	7.5	
14	0									14	0								
15	0									15	0								
16	5	0.2	0.2	0.2	0.2	0.2	0.2	0	0.0	16	0								
17*	5	0.271	0.277	0.313	0.288	0.285	0.287	0.016	5.6	17	5	0.481	0.421	0.416	0.407	0.383	0.422	0.036	8.6
18	0									18	0								
19	5	0.131	0.130	0.136	0.134	0.131	0.132	0.003	1.9	19	5	0.48	0.46	0.48	0.46	0.47	0.01	2.3	
20	0									20	0								
21	5	<0.16	<0.16	<0.16	<0.16	<0.16				21	5	0.37	0.37	0.37	0.46	0.46	0.41	0.05	12.1
22	5	0.22	0.23	0.22	0.20	0.18	0.21	0.02	9.5	22	5	0.52	0.49	0.48	0.46	0.46	0.48	0.02	5.2
23	5	<0.5	<0.5	<0.5	<0.5	<0.5				23	5	<0.5	<0.5	<0.5	<0.5	<0.5			
24	5	0.13	0.15	0.16	0.15	0.15	0.15	0.01	7.4	24*	5	0.30	0.31	0.29	0.35	0.27	0.30	0.03	9.8
25	5	<0.2	<0.2	<0.2	<0.2	<0.2				25*	5	0.2962	0.3017	0.3342	0.4230	0.3200	0.335	0.051	15.4
26	0									26	0								
27	0									27	0								
28	5	<0.053	<0.052	<0.052	<0.093	<0.096				28	5	<0.043	<0.048	<0.049	<0.047				
29	5	0.13	0.17	0.12	0.15	0.12	0.14	0.02	15.7	29*	5	0.3	0.29	0.27	0.25	0.27	0.28	0.02	7.1
30	0									30	0								
31	0									31	0								
32	0									32	0								
33	5	0.25	0.23	0.14	0.28	0.23	0.23	0.05	23.1	33	5	0.34	0.48	0.36	0.33	0.52	0.41	0.09	21.6
34	0									34	0								
35	0									35	0								
36	5	0.20	0.21	0.20	0.15	0.13	0.18	0.04	20.0										
37	0																		

Lab	5	0.36	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	Mean	SD	RSD
1	5										
2	0										
3*	5	0.04	0.05	0.05	0.05	0.04	0.05	0.05	0.01	11.9	11.9
4	5	0.032	0.031	0.032	0.034	0.033	0.032	0.032	0.001	3.5	3.5
5	5	0.028	0.035	0.036	0.028	0.037	0.033	0.033	0.004	13.5	13.5
6*	5	0.040	0.050	0.042	0.055	0.043	0.046	0.046	0.006	13.7	13.7
7	0										
8	5	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017			
9	0										
10	0										
11	5	0.037	0.031	0.033	0.043	0.043	0.037	0.037	0.006	14.8	14.8
12	5	0.0295	0.0305	0.0282	0.0293	0.0306	0.030	0.030	0.001	3.3	3.3
13	5	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0			
14	5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1			
15	5	0.029	0.029	0.029	0.028	0.030	0.029	0.029	0.001	2.4	2.4
16*	4	1	0	0	0	0	0	0			
17	0										
18	5	0.031	0.029	0.029	0.031	0.028	0.030	0.030	0.001	4.5	4.5
19*	4	0.197	0.121	0.117	0.118	0.126	0.121	0.121	0.004	3.4	3.4
20	5	0.033	0.029	0.03	0.038	0.050	0.036	0.036	0.009	23.8	23.8
21*	5	0.098	0.082	0.042	0.14	0.066	0.086	0.086	0.037	43.0	43.0
22*	5	0.110	0.104	0.114	0.108	0.116	0.110	0.110	0.005	4.3	4.3
23	5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1			
24'	4	0.034	0.034	0.033	0.079	0.034	0.003	0.003	0.001	14.8	14.8
25	5	<0.52	<0.52	<0.52	<0.54	<0.52	<0.52	<0.52			
26	0										
27	0										
28	5	0.039	0.049	0.038	0.038	0.047	0.042	0.042	0.005	12.7	12.7
29	5	0.030	0.032	0.040	0.034	0.030	0.033	0.033	0.004	12.5	12.5
30	0	0.073									
31	0										
32	0										
33	0										
34	5	0.037	0.032	0.031	0.039	0.033	0.034	0.034	0.003	10.0	10.0
35	0										
36	5	0.033	0.035	0.038	0.038	0.036	0.036	0.036	0.002	5.9	5.9
37	5	0.029	0.033	0.031	0.032	0.028	0.031	0.031	0.002	6.8	6.8

[illegible]

CADMIUM
Sediment R

0.138 ± 0.051 mg/kg

Lab	Mean	SD	RSD
1	0.17	0.19	0.15
2*	0.2	0.22	0.18
3	<1	<1	0.18
4	0.122	0.13	0.126
5	<0.5	<0.5	0.7
6	0.10	0.15	0.14
7	<0.017	0.05	0.099
8	0.11	0.11	0.10
9	0.17	0.17	0.15
10	0.148	0.146	0.138
11	0.57	0.62	0.69
12	<1.0	<1.0	<1.0
13*	0	0	0
14	0.153	0.157	0.151
15	0.113	0.121	0.119
16*	0.154	0.154	0.154
17	0.11	0.11	0.11
18	0.16	0.16	0.16
19	0.166	0.18	0.167
20	0.10	0.10	0.14
21*	0.09	0.11	0.09
22	0.78	0.79	0.98
23	0.120	0.130	0.150
24	0.142	0.159	0.120
25*	0.14	0.164	0.441
26	0.359	0.164	0.509
27	0.108	0.103	0.112
28	0.15	0.16	0.16
29	0.135	0.138	0.133
30	0.16	0.20	0.14
31*	0.143	0.140	0.140
32	0.096	0.100	0.099
33	0.136	0.136	0.136
34	0.135	0.135	0.135
35	0.436	0.436	0.436
36	0.112	0.112	0.112
37	0.13	0.13	0.13
	0.131	0.131	0.131
	0.10	0.10	0.10
	0.142	0.142	0.142
	0.099	0.099	0.099
	0.100	0.100	0.100
	0.005	0.005	0.005
	4.5	4.5	4.5

CADMIUM
BCSS-1

0.24 ± 0.04 mg/kg

Lab	Mean	SD	RSD
1	0.24	0.24	0.23
2	0.28	0.28	0.27
3	0.236	0.236	0.229
4	0.23	0.23	0.226
5	1.1	0.8	0.7
6	0.25	0.30	0.30
7	0.050	0.200	0.248
8*	0.22	0.22	0.23
9	0.25	0.25	0.24
10	0.281	0.281	0.267
11	1.06	1.12	1.09
12	<1.0	<1.0	<1.0
13*	0.279	0.279	0.245
14	0.88	1.37	1.37
15	<1.0	<1.0	<1.0
16	0.276	0.276	0.266
17	0.235	0.235	0.235
18	0.321	0.278	0.294
19	0.20	0.19	0.20
20*	0.27	0.29	0.30
21	0.264	0.254	0.247
22	0.23	0.19	0.32
23	0.20	0.18	0.17
24*	<0.50	<0.50	<0.50
25	0.21	0.19	0.19
26	0.264	0.259	0.246
27	0.24	0.24	0.24
28*	0.21	0.19	0.24
29	0.264	0.259	0.246
30	0.24	0.24	0.24
31	0.234	0.245	0.22
32	0.19	0.19	0.22
33*	0.230	0.222	0.237
34	0.25	0.26	0.25
35	0.26	0.26	0.26
36	0.27	0.27	0.27
37	0.26	0.26	0.26

[illegible]

TIN
Sediment R
1.11 ± 0.14 mg/kg

Lab	Mean	SD	RSD	Lab	Mean	SD	RSD
1	1.22	1.12	1.00	1	1.95	1.85	1.85
2	<5	<5	0.92	2	1.80	1.87	1.92
3	0.96	1.1	0.8	3	<0.2	<0.2	<0.2
4*	2.5	<2	<2	4	<4	<4	<4
5	<2	<2	<2	5	2.12	2.08	1.95
6	1.34	1.34	1.44	6	1.81	1.83	1.89
7	0.382	0.462	0.540	7	1.96	1.96	1.97
8				8			
9				9			
10*	1.052	1.102	1.068	10	1.626	1.620	1.638
11	1.2	1.2	1.2	11	1.641	1.629	1.641
12*	1.61	1.66	1.58	12	2.0	2.0	2.1
13	<20	<20	<20	13	1.84	1.65	1.82
14	<4.9	<5.0	<4.9	14	<20	<20	<20
15				15	<5.00	<5.00	<5.00
16				16	<5.00	<5.00	<5.00
17				17			
18				18			
19				19			
20				20			
21'	1.3	1.4	0.9	21'	1.6	1.5	1.4
22*	1.61	1.66	1.45	22	1.96	1.85	1.84
23	<20	<20	<20	23	1.96	1.85	1.84
24	<4.9	<5.0	<4.9	24	1.96	1.85	1.84
25				25	1.96	1.85	1.84
26				26	1.96	1.85	1.84
27				27	1.96	1.85	1.84
28				28	1.96	1.85	1.84
29	1.3	1.4	0.9	29*	1.96	1.85	1.84
30				30	1.96	1.85	1.84
31				31	1.96	1.85	1.84
32				32	1.96	1.85	1.84
33	1.24	1.20	1.15	33	1.96	1.85	1.84
34				34	1.96	1.85	1.84
35				35	1.96	1.85	1.84
36				36	1.96	1.85	1.84
37'	1.16	1.07	1.05	37'	1.96	1.85	1.84

The determination of antimony was not required in the biologicals.

ANTIMONY
Sediment R
0.32 ± 0.15 mg/kg

Lab	Mean	SD	RSD
1			
2			
3			
4	0.34	0.33	0.31
5	0.3	0.3	0.2
6			
7	<2	<2	<2
8			
9			
10	0.23	0.21	0.2
11			
12			
13			
14			
15			
16	0.4	0.4	0.3
17			
18			
19*	1.391	1.420	1.386
20			
21	0.33	0.34	0.34
22			
23	<0.5	<0.5	<0.5
24			
25			
26			
27			
28			
29			
30			
31			
32			
33	0.17	0.26	0.21
34			
35			
36	0.364	0.334	0.481
37			

ANTIMONY
BCSS-1
0.59 ± 0.06 mg/kg

Lab	Mean	SD	RSD
1			
2			
3			
4	0.49	0.52	0.59
5	0.2	0.2	<0.2
6			
7	<4	<4	<4
8			
9			
10*	0.55	0.50	0.53
11			
12			
13			
14			
15			
16			
17			
18			
19	0.534	0.526	0.531
20			
21*	0.70	0.69	0.71
22			
23	<0.5	<0.5	<0.5
24			
25			
26			
27			
28			
29			
30			
31			
32			
33	0.59	0.57	0.67
34			
35			

The determination of thallium was not required in the biologicals.

THALLIUM
Sediment R
mg/kg

Lab	Mean	SD	RSD
1	0		
2	0		
3	0		
4	0		
5	<0.2	<0.2	<0.2
6	<0.2	<0.2	<0.2
7	0		
8	0		
9	0		
10	0.62	0.62	0.62
11	0.62	0.61	0.62
12	0.62	0.62	0.62
13	0.62	0.62	0.62
14	0.62	0.62	0.62
15	0.62	0.62	0.62
16	0.62	0.62	0.62
17	0.62	0.62	0.62
18	0.62	0.62	0.62
19	0.62	0.62	0.62
20	0.62	0.62	0.62
21	0.62	0.62	0.62
22	0.62	0.62	0.62
23	<0.5	<0.5	<0.5
24	<0.5	<0.5	<0.5
25	<0.5	<0.5	<0.5
26	<0.5	<0.5	<0.5
27	<0.5	<0.5	<0.5
28	<0.5	<0.5	<0.5
29	<0.5	<0.5	<0.5
30	<0.5	<0.5	<0.5
31	<0.5	<0.5	<0.5
32	<0.5	<0.5	<0.5
33	<0.5	<0.5	<0.5
34	<0.5	<0.5	<0.5
35	<0.5	<0.5	<0.5
36	<0.3	<0.3	<0.3
37	0.202	0.197	0.199
	0.201	0.201	0.201
	0.200	0.002	1.0

THALLIUM
BCSS-1
mg/kg

Lab	Mean	SD	RSD
1	0		
2	0		
3	0		
4	0		
5	<0.2	0.2	<0.2
6	<0.2	0.2	<0.2
7	0		
8	0		
9	0		
10	1.48	1.47	1.47
11	1.40	1.45	1.45
12	1.40	1.47	1.47
13	1.40	1.47	1.47
14	1.40	1.47	1.47
15	1.40	1.47	1.47
16	1.40	1.47	1.47
17	1.40	1.47	1.47
18	1.40	1.47	1.47
19	1.40	1.47	1.47
20	1.40	1.47	1.47
21	1.40	1.47	1.47
22	1.40	1.47	1.47
23	<0.5	<0.5	<0.5
24	<0.5	<0.5	<0.5
25	<0.5	<0.5	<0.5
26	<0.5	<0.5	<0.5
27	<0.5	<0.5	<0.5
28	<0.5	<0.5	<0.5
29	<0.5	<0.5	<0.5
30	<0.5	<0.5	<0.5
31	<0.5	<0.5	<0.5
32	<0.5	<0.5	<0.5
33	<0.5	<0.5	<0.5
34	<0.5	<0.5	<0.5
35	<0.5	<0.5	<0.5

[illegible]

LEAD Sediment R 10.4 ± 5.1 mg/kg				LEAD BCSS-1 22.7 ± 3.4 mg/kg			
Lab	Mean	SD	RSD	Lab	Mean	SD	RSD
1	9.2	8.3	5	1	23.0	22.0	5
2	11.1	11.1	5	2	22.4	21.6	5
3	9	9	5	3	0	0	0
4	10.8	11.1	5	4	22.6	22.9	5
5*	5.1	3.8	5	5	19.2	17.1	5
6	0	0	0	6	0	0	0
7	6.9	7.0	5	7	20	20	5
8*	5.50	5.00	5	8*	15.50	15.50	5
9	7.9	7.9	5	9	21.1	23.1	5
10	13.5	13.6	5	10	25.7	25.9	5
11	0	0	0	11	0	0	0
12	10.2	9.99	5	12	21.1	21.8	5
13	12.2	12.8	5	13	25.6	19.4	5
14	13.5	12.7	5	14	22.1	22.4	5
15	0	0	0	15	0	0	0
16	6	6	5	16	0	0	5
17	12.13	12.09	5	17	22.90	23.39	5
18	12.70	12.21	5	18	23.97	23.37	5
19	14.01	13.93	5	19	19.177	19.528	4
20	9.4	9.8	5	20	20.9	20.3	5
21	8.8	9.4	5	21	23	22	4
22	10.8	10.6	5	22	22.5	23.3	5
23	7.8	7.9	5	23	23.2	22.4	5
24	0	0	0	24	0	0	0
25	7.7	8.1	5	25	22.0	23.0	4
26	0	0	0	26	0	0	0
27	0	0	0	27	0	0	0
28	7.3	7.1	5	28	17	20	5
29	11.3	11.6	5	29	21.7	21.9	5
30	12.8	12.8	0	30	29.8	22.1	0
31	0	0	0	31	0	0	0
32	7.87	8.7	5	32	23.0	23.1	5
33	14.0	15.1	5	33	29.2	26.5	5
34	12.8	11.6	5	34	23.6	24.3	5
35	0	0	0	35	0	0	0
36	12.7	12.3	5				
37	11.0	11.4	5				

APPENDIX C **Laboratory Evaluation for Biological Tissues**

		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
Al	FSH Q	--	--	GG	--	LG	GG	--	--	--	--
	DORM	--	--	EG	--	EG	EG	--	--	--	--
Cr	FSH Q	EG	--	EG	EG	LG	EG	--	LG	--	--
	DORM	LG	--	LG	EG	LG	EG	--	LX	--	--
Fe	FSH Q	EG	--	EG	EG	EG	EG	--	--	--	--
	DORM	EG	--	GG	EG	EG	EG	--	--	--	--
Ni	FSH Q	EG	--	EG	EG	EG	EG	--	--	--	--
	DORM	--	--	GG	EG	GX	EG	--	--	--	--
Cu	FSH Q	EG	--	EG	EG	EG	HG	--	GX	--	--
	DORM	LG	--	LG	EG	GG	EG	--	GG	--	--
Zn	FSH Q	EG	--	GG	EG	EG	HG	--	LG	--	--
	DORM	LG	--	LG	EG	LG	EG	--	LG	--	--
As	FSH Q	EG	--	EG	EG	EG	EG	--	--	--	--
	DORM	LX	--	LG	EG	LG	EG	--	--	--	--
Se	FSH Q	EX	--	EG	EG	HG	EG	--	--	--	--
	DORM	LX	--	LG	EG	HG	EG	--	--	--	--
Ag	FSH Q	EG	--	--	EG	EG	EG	--	--	--	--
	DORM	GG	--	--	HG	LG	LG	--	--	--	--
Cd	FSH Q	--	--	HG	EG	EG	HG	--	--	--	--
	DORM	HG	--	EG	EG	EG	EG	--	--	--	--
Sn	FSH Q	--	--	--	?X	--	--	--	--	--	--
	DORM	--	--	--	?G	--	--	--	--	--	--
Hg	FSH Q	EG	--	EG	EG	EG	EG	--	LG	--	--
	DORM	EG	--	EG	EG	GG	EG	--	LG	--	--
Pb	FSH Q	--	--	EG	EG	EG	EG	--	--	--	--
	DORM	--	--	EG	EG	GX	EG	--	--	--	--

Laboratory Evaluation for Biological Tissues

		Lab 11	Lab 12	Lab 13	Lab 14	Lab 15	Lab 16	Lab 17	Lab 18	Lab 19	Lab 20
Al	FSH Q	--	EG	--	--	--	--	GX	--	HG	--
	DORM	--	HG	--	--	--	--	EG	--	HG	--
Cr	FSH Q	LG	EG	EG	LG	--	HG	LG	EG	GG	GG
	DORM	GX	EG	GG	LG	--	--	LG	EG	EG	GG
Fe	FSH Q	EG	EG	HG	EG	EG	--	EG	--	EG	--
	DORM	EG	EG	GX	HX	EG	--	LG	--	EG	--
Ni	FSH Q	LG	GG	EG	LG	--	--	LX	EG	HG	EX
	DORM	EG	EG	GX	--	--	--	LG	EG	EG	EG
Cu	FSH Q	EG	EG	GG	GG	--	LG	EG	EG	LG	EG
	DORM	LG	EG	EG	EG	--	--	LG	GG	EG	GG
Zn	FSH Q	GG	EG	GX	EG	EG	EG	LG	EG	EG	EG
	DORM	EG	EG	HG	EG	GG	--	LG	GG	LG	LG
As	FSH Q	HG	EG	LX	EG	--	GG	EG	--	EG	HG
	DORM	LX	EG	LG	LG	--	--	EG	--	EG	GX
Se	FSH Q	GG	EG	EG	--	--	EG	EG	--	EG	EG
	DORM	HG	EG	LX	--	--	--	LG	--	EG	GX
Ag	FSH Q	EG	EG	HX	LG	EG	--	EG	--	EG	EG
	DORM	--	EG	--	LG	--	--	EG	--	EG	EG
Cd	FSH Q	GG	EG	--	--	EG	LG	--	EG	HG	GG
	DORM	GX	EG	--	--	EG	--	GG	EG	GG	EG
Sn	FSH Q	--	?G	--	--	--	--	--	--	?X	--
	DORM	--	?G	--	--	--	--	--	--	?X	--
Hg	FSH Q	HG	--	LG	--	EG	HX	EG	EG	HG	EG
	DORM	GG	--	GG	--	GG	--	GG	EG	EG	GG
Pb	FSH Q	EG	EG	HX	HG	--	--	GG	EG	EX	GX
	DORM	EG	EG	HX	GX	--	--	HG	EG	EG	GG

Laboratory Evaluation for Biological Tissues

		Lab 21	Lab 22	Lab 23	Lab 24	Lab 25	Lab 26	Lab 27	Lab 28	Lab 29	Lab 30
Al	FSH Q	GX	--	GX	--	HG	--	--	--	--	--
	DORM	EG	--	HX	--	HX	--	--	--	--	--
Cr	FSH Q	EG	HG	EG	EG	EG	GG	--	GX	EG	--
	DORM	HG	EG	LG	LG	EG	GG	--	LX	GG	--
Fe	FSH Q	EG	EG	EX	EG	GX	EX	--	--	EG	--
	DORM	GG	EG	HX	EG	EG	GG	--	--	HG	--
Ni	FSH Q	EX	HG	EG	--	EG	--	--	--	EG	--
	DORM	EG	EG	LX	--	EG	--	--	--	LG	--
Cu	FSH Q	GG	HG	LG	EG	HG	GG	GX	HX	EG	--
	DORM	HG	EG	LG	GG	GG	GG	GG	HX	EG	--
Zn	FSH Q	EG	HG	LG	GG	GG	GG	HX	GX	EG	--
	DORM	GG	GG	LG	GG	HG	LG	HG	LX	LG	--
As	FSH Q	EG	HG	--	EG	EG	EG	--	EG	EG	--
	DORM	EG	EG	LG	EG	EG	--	--	LX	GG	--
Se	FSH Q	EG	EG	EG	EG	EG	--	--	EG	EG	--
	DORM	GG	EG	LG	GX	GG	--	--	LG	GG	--
Ag	FSH Q	EX	EG	EG	EG	--	--	--	--	EG	--
	DORM	EX	EG	EG	EG	--	--	--	--	LG	--
Cd	FSH Q	HX	HG	--	EG	--	--	--	GG	EG	--
	DORM	LX	EG	--	GG	--	--	--	GX	EG	--
Sn	FSH Q	?X	?G	--	--	--	--	--	--	?X	--
	DORM	?X	?G	--	--	--	--	--	--	?X	--
Hg	FSH Q	EG	EG	EG	--	EG	--	--	GG	EG	--
	DORM	HG	EG	GG	--	HG	--	--	GG	EG	--
Pb	FSH Q	EG	HG	--	--	HG	--	--	GX	GG	--
	DORM	EG	EG	EX	--	--	--	--	EG	EX	--

Laboratory Evaluation for Biological Tissues

		Lab 31	Lab 32	Lab 33	Lab 34	Lab 35
Al	FSH Q	--	--	--	--	--
	DORM	--	--	--	--	--
Cr	FSH Q	--	--	--	LX	EG
	DORM	--	--	--	LG	EG
Fe	FSH Q	--	--	--	EG	EX
	DORM	--	--	--	GG	GG
Ni	FSH Q	--	--	--	GX	--
	DORM	--	--	--	LX	--
Cu	FSH Q	--	--	--	EG	--
	DORM	--	--	--	LG	--
Zn	FSH Q	--	--	--	HG	EG
	DORM	--	--	--	GG	LG
As	FSH Q	--	--	--	EG	--
	DORM	--	--	--	LG	--
Se	FSH Q	--	--	--	--	--
	DORM	--	--	--	--	--
Ag	FSH Q	--	--	--	EG	GX
	DORM	--	--	--	GG	HG
Cd	FSH Q	--	--	--	EG	--
	DORM	--	LX	--	EG	--
Sn	FSH Q	--	--	--	--	--
	DORM	--	--	--	--	--
Hg	FSH Q	--	EG	--	EG	--
	DORM	--	GG	--	GG	--
Pb	FSH Q	--	--	--	EG	--
	DORM	--	--	--	EG	--

Laboratory Evaluation for Sediments (Al-Sn)

		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
Al	SED R	LX	GX	--	EG	LG	--	LG	--	GG	EG
	BCSS	LG	GG	--	EG	LG	--	LG	--	GG	EG
Si	SED R	--	--	--	--	--	--	--	--	?G	--
	BCSS	--	--	--	--	--	--	--	--	EG	--
Cr	SED R	LG	EG	--	EG	LG	--	LG	LG	EG	HG
	BCSS	LG	EG	--	EG	LG	--	LG	LG	EG	EG
Mn	SED R	LG	EG	--	--	LG	--	LG	--	EG	EG
	BCSS	LG	EG	--	--	LG	--	LG	--	EG	EG
Fe	SED R	GG	EG	--	EG	LG	--	LG	--	EG	EG
	BCSS	LG	GG	--	EG	LG	--	LG	--	EG	EG
Ni	SED R	EG	EG	--	EG	EG	--	EG	--	LG	EG
	BCSS	LG	EG	--	EG	LG	--	LG	--	EG	EG
Cu	SED R	EG	EG	--	EG	EG	--	EG	EG	EG	EG
	BCSS	LG	EG	--	EG	LG	--	GG	LX	EG	EG
Zn	SED R	EG	EG	--	EG	LG	--	EG	LG	EG	EG
	BCSS	LG	EG	--	EG	LG	--	EG	LG	EG	EG
As	SED R	EG	EG	--	EG	LG	--	EG	--	EG	EG
	BCSS	LG	LG	--	EG	LG	--	LG	--	EG	EG
Se	SED R	--	--	--	EG	--	--	--	--	GX	EG
	BCSS	--	--	--	EG	--	--	--	--	HG	EG
Ag	SED R	--	HG	--	GG	--	--	--	--	--	HG
	BCSS	--	HG	--	GG	--	--	--	--	--	HG
Cd	SED R	GG	HG	--	HG	--	--	HG	--	EG	EG
	BCSS	EG	EG	--	EG	HX	--	GG	LX	EG	EG
Sn	SED R	--	EG	--	LG	GG	--	--	--	--	HG
	BCSS	--	GG	--	EG	--	--	--	--	--	GG

Laboratory Evaluation for Sediments (Al-Sn)

		Lab 11	Lab 12	Lab 13	Lab 14	Lab 15	Lab 16	Lab 17	Lab 18	Lab 19	Lab 20
Al	SED R	--	EG	EG	EG	--	EG	EG	EG	GG	--
	BCSS	--	EG	LG	LG	--	--	EG	GG	EG	--
Si	SED R	--	?G	--	--	--	--	--	--	--	--
	BCSS	--	EG	--	--	--	--	--	--	--	--
Cr	SED R	--	EG	EG	EG	--	EG	EG	EG	EG	EG
	BCSS	--	EG	EG	LG	--	--	LG	EG	EG	EG
Mn	SED R	--	EG	--	EG	--	--	EG	EG	EG	EG
	BCSS	--	EG	--	GG	--	--	LG	LG	LG	EG
Fe	SED R	--	EG	EG	EG	--	EG	HG	HG	EG	--
	BCSS	--	EG	LG	GG	--	--	HG	LG	GG	--
Ni	SED R	--	EG	GG	EG	--	GX	EG	GEG	HG	EG
	BCSS	--	EG	LG	EG	--	--	LG	GG	EG	GG
Cu	SED R	--	EG	HX	EG	--	EG	EG	EG	LX	EG
	BCSS	--	EG	EG	EG	--	--	GG	EG	GG	EG
Zn	SED R	--	EG	GG	EG	--	EG	HG	EG	EG	EG
	BCSS	--	EG	LG	EG	--	--	EG	EG	LG	EG
As	SED R	--	EG	EG	EG	--	EG	HG	--	HG	--
	BCSS	--	EG	LG	LG	--	--	GG	--	EG	--
Se	SED R	--	EX	EG	--	--	EG	HG	--	EG	--
	BCSS	--	GX	GG	--	--	--	EG	--	EG	--
Ag	SED R	--	HG	HX	--	--	--	GG	--	LG	EG
	BCSS	--	EG	HG	--	--	--	EG	--	LG	EG
Cd	SED R	--	EG	HG	--	--	--	EG	EG	EG	EG
	BCSS	--	EG	HG	--	--	--	EG	EG	GG	LG
Sn	SED R	--	LG	--	--	--	--	--	--	EG	--
	BCSS	--	EG	--	--	--	--	--	--	GG	--

Laboratory Evaluation for Sediments (Al-Sn)

		Lab 21	Lab 22	Lab 23	Lab 24	Lab 25	Lab 26	Lab 27	Lab 28	Lab 29	Lab 30
Al	SED R	EX	--	LG	--	LG	--	--	--	EG	
	BCSS	HG	EG	LG	--	LG	--	--	--	EG	
Si	SED R	?G	--	--	--	--	--	--	--	--	--
	BCSS	EG	--	--	--	--	--	--	--	--	--
Cr	SED R	EG	HG	LG	EG	LG	--	EG	LG	EG	--
	BCSS	EG	EG	LG	LG	LG	--	LG	LG	LG	--
Mn	SED R	EX	LG	LG	EG	LG	LG	LG	--	EG	--
	BCSS	GG	EG	LG	EG	LG	EG	LG	--	GX	--
Fe	SED R	GG	EG	EG	EG	LG	EG	EG	--	HG	--
	BCSS	EG	GG	GG	GG	LG	GG	LG	--	EG	--
Ni	SED R	GG	GG	EG	--	GG	EG	GG	--	HG	--
	BCSS	EG	EG	LG	--	LG	EG	LG	--	EG	--
Cu	SED R	EG	EG	EG	EG	EG	EG	RG	HX	EG	--
	BCSS	GG	EG	GG	EG	LG	GG	LG	GX	EG	--
Zn	SED R	EG	EG	EG	EG	EG	EG	EG	LG	EG	--
	BCSS	EG	EG	LG	GG	LG	EG	LG	LG	EG	--
As	SED R	EG	GG	EG	EG	EG	--	--	GX	EG	--
	BCSS	GG	EG	LG	LG	LG	--	--	--	EG	--
Se	SED R	--	EG	--	EG	--	--	--	--	EX	--
	BCSS	EG	GG	--	LG	LN	--	--	--	LG	--
Ag	SED R	EG	EG	--	EG	--	--	--	--	GX	--
	BCSS	EG	EG	--	EG	--	--	--	--	GG	--
Cd	SED R	EG	EG	EG	EG	HN	--	--	EG	EG	--
	BCSS	GG	EG	GX	LG	--	--	--	LG	EG	--
Sn	SED R	EG	HG	--	--	--	--	--	--	GG	--
	BCSS	EG	EG	--	--	--	--	--	--	LG	--

Laboratory Evaluation for Sediments (Al-Sn)

		Lab 31	Lab 32	Lab 33	Lab 34	Lab 35
Al	SED R	--	--	EG	EG	--
	BCSS	--	--	GG	GG	--
Si	SED R	--	--	--	--	--
	BCSS	--	--	--	--	--
Cr	SED R	--	--	EG	EG	GG
	BCSS	--	--	LG	LG	GG
Mn	SED R	--	--	EG	--	--
	BCSS	--	--	EG	--	--
Fe	SED R	EG	--	EG	EG	EG
	BCSS	--	--	LG	GG	EG
Ni	SED R	--	--	EG	EG	GX
	BCSS	--	--	LG	GG	HG
Cu	SED R	EG	--	HG	LG	HG
	BCSS	--	--	EG	EG	EG
Zn	SED R	EG	--	EG	EG	EG
	BCSS	--	--	LG	LG	EG
As	SED R	--	--	EG	EG	--
	BCSS	--	--	HG	LG	--
Se	SED R	--	--	GX	--	--
	BCSS	--	--	GG	--	--
Ag	SED R	--	--	EG	EG	EG
	BCSS	--	--	EG	EG	EG
Cd	SED R	HG	EG	EG	EG	GX
	BCSS	--	EG	LG	EG	EG
Sn	SED R	--	--	EG	--	--
	BCSS	--	--	EG	--	--

Laboratory Evaluation for Sediments (Sb-Pb)

		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
Sb	SED R	--	--	--	EG	EX	--	--	--	--	EG
	BCSS	--	--	--	GG	--	--	--	--	--	LG
Hg	SED R	EG	EG	--	EG	HG	--	--	--	--	HG
	BCSS	EG	EG	--	EG	--	--	LG	--	EG	EG
Tl	SED R	--	--	--	--	--	--	--	--	--	?G
	BCSS	--	--	--	--	--	--	--	--	--	?G
Pb	SED R	EG	EG	--	EG	LX	--	EG	LG	EG	EG
	BCSS	EG	EG	--	EG	GX	--	EX	LG	EG	EG

		Lab 11	Lab 12	Lab 13	Lab 14	Lab 15	Lab 16	Lab 17	Lab 18	Lab 19	Lab 20
Sb	SED R	--	--	--	--	--	EG	--	--	HG	--
	BCSS	--	--	--	--	--	--	--	--	GG	--
Hg	SED R	--	--	EG	--	--	EG	EG	EG	HG	EG
	BCSS	--	--	GG	--	--	--	EG	EG	EG	EG
Tl	SED R	--	--	--	--	--	--	--	--	--	--
	BCSS	--	--	--	--	--	--	--	--	--	--
Pb	SED R	--	EG	EG	EG	--	GX	EG	EG	EG	EG
	BCSS	--	EG	EG	EG	--	--	EG	EG	EG	EG

Laboratory Evaluation for Sediments (Sb-Pb)

		Lab 21	Lab 22	Lab 23	Lab 24	Lab 25	Lab 26	Lab 27	Lab 28	Lab 29	Lab 30
Sb	SED R	EG	--	--	--	--	--	-	--	--	--
	BCSS	HG	--	--	--	--	--	--	--	--	--
Hg	SED R	EG	EG	--	--	--	--	--	--	EG	--
	BCSS	--	EG	EG	--	EG	--	--	EG	EG	--
Tl	SED R	--	--	--	--	--	--	--	--	--	--
	BCSS	--	--	--	--	--	--	--	--	--	--
Pb	SED R	EG	EG	EG	--	EG	--	--	EG	EX	--
	BCSS	EG	EG	EG	--	EG	--	--	GG	EG	--

		Lab 31	Lab 32	Lab 33	Lab 34	Lab 35
Sb	SED R	--	--	EX	--	--
	BCSS	--	--	GG	--	--
Hg	SED R	--	--	EG	EG	--
	BCSS	--	GG	LG	EG	--
Tl	SED R	--	--	--	--	--
	BCSS	--	--	--	--	--
Pb	SED R	--	EG	GG	EG	--
	BCSS	--	GX	HG	EG	--

APPENDIX D

Table D-1

Comparison of NOAA/5 and NOAA/6
Laboratory Performance for Tissues

Lab	NOAA/6		NOAA/5	
	Sets	Rej	Sets	Rej.
1	22	6	23	14
3	22	6	9	0
4	24	1	23	0
5	26	7	NR*	
6	26	4	10	0
8	11	8	10	4
11	21	6	23	3
12	24	0	NR	
13	22	11	21	12
14	18	6	19	13
15	10	0	14	4
16	10	5	9	1
17	23	9	10	0
18	14	0	NR	
19	26	9	23	15
20	20	2	17	1
21	26	5	23	2

Lab	NOAA/6		NOAA/5	
	Sets	Rej.	Sets	Rej.
22	24	8	NA**	
23	26	11	NA	
24	16	1	NA	
25	24	5	21	9
26	8	1	NA	
27	4	2	NA	
28	16	6	16	7
29	24	4	20	4
32	3	1	6	2
34	20	5	20	2
35	10	4	NA	

*NR - no results for biologicals last year

**NA - did not participate in NOAA/5

APPENDIX D

Table D-2

Comparison of NOAA/5 and NOAA/6
Laboratory Performance for Sediments

Lab	NOAA/6		NOAA/5	
	Sets	Rej.	Sets	Rej.
1	26	10	24	14
2	26	4	19	9
4	28	1	24	2
5	32	19	24	2
7	30	10	NR*	
8	10	8	8	4
9	26	2	20	4
10	32	6	16	10
12	28	2	24	0
13	24	10	22	8
14	22	4	20	10
16	14	1	11	0
17	26	7	22	15
18	18	2	16	1
19	30	8	22	14
20	18	1	14	0
21	31	2	23	3

Lab	NOAA/6		NOAA/5	
	Sets	Rej.	Sets	Rej.
22	28	4	NA**	
23	32	10	NA	
24	18	4	NA	
25	26	13	25	14
26	10	1	NA	
27	12	7	NA	
28	16	7	16	7
29	28	5	22	0
31	4	0	NA	
32	5	0	NR	
33	28	9	24	7
34	22	4	11	4
35	14	2	NA	

*NR- no results for sediments last year

**NA - did not participate in NOAA/5

APPENDIX E

Table E-1
Biological Tissue Dissolution Procedures

Lab No.	Tissue Dissolution Procedure	Instrumentation
1	-1.0g -HNO ₃ , H ₂ O ₂ -reflux	
2	-NA	
3	-HNO ₃ (Cr,Fe,Ni,Cu,Zn,Cd,Pb) or ash at 500°C and HNO ₃ extract	
4	-0.2g -HNO ₃ -closed vessel	GFAAS - Ag,As,Cd,Cr,Cu,Ni,Pb,Se,Sn FAAS - Fe,Zn
5	-0.5g -HNO ₃ -closed vessel, microwave heating	
6	-0.2g -HNO ₃ -open beaker	ICPMS - Al,Cr,Fe,Ni,Cu,Zn,As,Se,Ag, Cd,Sn,Pb
7	-NA	
8	-1g HNO ₃ , H ₂ O ₂ -open beaker reflux	GFAAS - Cr,Cu,Zn,Cd,Pb
9	-NA	
10	-NA	
11	-0.25g -HNO ₃ -closed vessel, microwave heating	GFAAS - Cr,Ni,Cu,As,Se,Ag,Cd,Pb FAAS - Fe,Zn
12	-0.5g -HNO ₃ -closed vessel	FAAS - Zn,Fe GFAAS - Cu,Al,Ag,Cd,Cr,Ni,Pb,Sn,As,Se
13	-0.25g -HNO ₃ , HF -microwave heating -HNO ₃ , HCl, H ₂ O ₂	ICPAES - Cr,Fe,Ni,Cu,Zn,Ag,Cd,Pb HGAAS - As,Se

Lab No.	Tissue Dissolution Procedure	Instrumentation
14	-2.0g -HNO ₃ , H ₂ O ₂ -closed vessel, microwave heating	ICPAES - Fe,Mn,Cu,Zn,Cr,Pb GFAAS - Cd,Ni,As,Sn,Ag,Sb
15	-HNO ₃ -closed vessel, microwave heating	GFAAS FAAS
16	-NA	
17	-1.0g -HNO ₃ , H ₂ O ₂ -open beaker	ICPAES - Al,Fe,As,Zn, GFAAS - Ni,Cu,Cr,Ag,Pb,Cd HGAAS - Se
18	-0.25g -HNO ₃ ,HCl -closed vessel, microwave heating	GFAAS - Al,Cr,Ni,Cu,Cd,Pb FAAS -Fe,Zn
19	-1.0g -HNO ₃ , HCl -H ₂ SO ₄ -H ₂ O ₂ -open beaker	GFAAS FAAS
20	-0.5g -HNO ₃ , HClO ₄ -closed vessel	
21	-0.30g -HNO ₃ -microwave heating	XRF - As,Cu,Fe,Se,Si,Zn ICPMS - Al,Ag,Cd,Cr,Ni,Pb,Sb,Sn
22	-no information	
23	-1.0g -HNO ₃ , H ₂ O ₂	GFAAS - Al,Fe,Ni,Cu,As,Se,Ag,Cd,Pb ICPAES - Cr,Zn,Sn
24	-0.1-0.5g -HNO ₃ , HCl, HF, HClO ₄ -open beaker or Mg(NO ₃) ₂ dry ash (As,Se)	GFAAS - Ag,Cd,Cr,Cu FAAS - Mn,Zn,Fe HGAAS - As,Se
25	-0.5g -HNO ₃ , H ₂ O ₂	GFAAS - Al,Cr,Fe,Ni,Cu,Zn,As,Se,Cd,Sn,Pb
26	-0.5g -HNO ₃ , H ₂ O ₂ -wet ash	ICPAES - Cr,Fe,Cu,Zn
27	-HNO ₃ -hot plate digestion	FAAS - Cu,Zn

Lab No.	Tissue Dissolution Procedure	Instrumentation
28	-1g -HNO ₃ , H ₂ O ₂ -heat in digestion tube -HCl	ICPAES FAAS
29	-0.30g -HNO ₃ -closed vessel, microwave heating	FAAS - Cu,Mn,Fe,Zn GFAAS - Cr,Ni,As,Se,Ag,Cd,Sn,Pb
30	-1.0g (5.0 g Fe,Zn) -HNO ₃ , H ₂ O ₂	FAAS - Fe,Zn GFAAS - Ni,Cu,As,Ag,Cd,Pb
31	-NA	
32	-0.2g -HNO ₃ , CH ₃ OH, H ₂ O, glycerin -homogenized in blender	slurry GFAAS - Pb, Cd
33	-NA	
34	-0.25g -HNO ₃ -closed vessel, microwave heating	
35	-no information	
36	-0.25g -HNO ₃ -closed vessel, microwave heating	GFAAS -Al,Cr,Fe,Ni,Cu, As,Se,Ag,Cd,Pb ICP - Zn,
37	-0.25g -HNO ₃ -closed vessel, microwave heating	IDICPMS - Ag,,Cd,Cr,Cu,Ni,Pb,Zn,Sn ICPAES - Fe

Table E-2
Sediment Dissolution Procedures

Lab No.	Sediment Dissolution Procedure	Instrumentation
1	-1.0 g -HNO ₃ , H ₂ O ₂ HCl reflux	
2	-0.5 g -HNO ₃ , HF, HClO ₄ -closed vessel, microwave heating	FAAS - Al,Cr,Cu,Fe,Ni,Zn GFAAS - Ag,As,Cd,Pb,Sn
3	- XRF loose powder or fused beads	XRF - Si,Al,Fe,Mn,Ni,Zn,As,Pb,Sn FAAS - Ag,Cr HGAAS - Se
4	-0.2g -HNO ₃ , HF -closed vessel	FAAS - Al,Fe,Zn GFAAS - Ag,As,Cd,Cu,Ni,Pb,Se,Sn INAA - Cr,Sb
5	-1g -HNO ₃ ,H ₂ O ₂ reflux -HCl or HNO ₃ final reflux	
6	-NA	
7	-1g - reverse aqua regia	ICPAES - Al,Cr,Fe,Zn,Sn,Sb ICPMS - Mn,Ni,Cu,As,Se,Ag,Cd,Hg,Pb
8	-1g -HNO ₃ ,H ₂ O ₂ open beaker reflux -filter	GFAAS - Cr,Cu,Zn,Cd,Pb
9	-0.5g -pellet (XRF) -HNO ₃ ,HClO ₄ ,H ₂ SO ₄ (Cu,As,Se) -HNO ₃ ,HCl extraction (Cd,Pb)	XRF - Al,Si,Cr,Mn,Fe,Ni,Zn ICPAES - Cu HGICP - As,Se GFAAS - Cd,Pb
10	-0.2g -HCl,HNO ₃ ,HF -closed vessel, microwave heating	ICPAES - Fe,Al FAAS -Cr,Mn HGAAS- As,Se,Sb ICPMS - Ni,Cu,Cd,Tl,Pb
11	-NA	

Lab No.	Sediment Dissolution Procedure	Instrumentation
12	-0.45g -HNO ₃ , HCl, HF -closed vessel -filter	FAAS - Cu, Zn, Cr, Mn, Fe, Al, Si GFAAS - Cd, Pb, Ni, Se, As, Ag
13	-0.25g -HNO ₃ , HF -microwave heating -HNO ₃ , HCl -H ₂ O ₂	ICPAES - Al, Cr, Fe, Ni, Cu, Zn, Ag, Cd, Pb HGAAS - As, Se
14	-0.5g -HNO ₃ , HF -closed vessel, microwave heating	ICPAES - Al, Fe, Mn, Cu, Zn, Cr, Pb, Ni GFAAS - Cd, As, Sn, Ag, Sb
15	-NA	
16	-no information	
17	-0.5g -HNO ₃ , HCl, HF -closed vessel, microwave heating	GFAAS - Cu, As, Ag, Cd, Pb ICPAES - Cr, Fe, Ni, Al, Zn, Mn
18	-0.3g -HNO ₃ , HCl, HF -closed vessel, microwave heating	GFAAS - Al, Cu, Cd, Pb FAAS - Fe, Zn
19	-0.5g -HNO ₃ , HF closed vessel (Fe, Zn, Al, Cu) -1.0g -HNO ₃ , HF, H ₂ O ₂ open beaker	FAAS - Fe, Zn, Al, Cu GFAAS - Cr, Mn, Ni, As, Se, Ag, Cd, Sn, Sb, Pb
20	-0.5g -HNO ₃ , HClO ₄ , HF -closed vessel	
21	-0.2g -HNO ₃ , HClO ₄ , HF -closed vessel	XRF - Al, Cr, Fe, Ni, Cu, Zn, As, Si, Mn GFAAS - Ag, Cd, Se, ICPMS - Sb, Sn
22	-no information	
23	-1g -HNO ₃ , H ₂ O ₂	ICPAES - Al, Cr, Mn, Fe, Ni, Zn, Sn GFAAS - Cu, As, Se, Ag, Cd, Sb, Tl, Pb
24	-0.1-0.5g -HNO ₃ , HCl, HF, HClO ₄ -open beaker	GFAAS - Ag, Cd, Cr, Cu FAAS - Mn, Zn, Fe HGAAS - As, Se

Lab No.	Sediment Dissolution Procedure	Instrumentation
25	-0.5g -HNO ₃ , H ₂ O ₂ , HF(As, Se) -1g -HNO ₃ , HCl -open beaker (ICP)	GFAAS - As, Se ICP - Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Sn, Pb
26	-0.75-1.0g -HNO ₃ , H ₂ O ₂ , HCl -open beaker	ICPAES - Cu, Zn, Fe, Ni, Cr, Mn
27	-0.5g -HNO ₃ , HCl -open beaker	ICPAES - Cr, Mn, Fe, Ni, Cu, Zn,
28	-1g -HNO ₃ , H ₂ O ₂ -heat in digestion tube -HCl	ICPAES GFAAS
29	-0.12g -HF, HCl, HNO ₃ -closed vessel, microwave heating	FAAS - Al, Mn, Fe, Zn GFAAS - Cr, Ni, As, Ag, Cd, Sn, Pb HGAAS - Se
30	-1.0g (5.0g Cd) -HNO ₃ , H ₂ O ₂ , HCl -open beaker	GFAAS - As, Ag, FAAS - Cr, Fe, Ni, Cu, Zn, Pb
31	-1g -HNO ₃ , HCl, HF, HClO ₄	FAAS - Mn, Fe, Cu, Zn, Cd
32	-0.5 or 1g -HNO ₃ , H ₂ O ₂ -open beaker -filter	GFAAS - Pb, Cd,
33	-0.5g -HNO ₃ , HF, HClO ₄ -open beaker (ICP) -HNO ₃ , HF, HCl -closed vessel, microwave heating (GFAAS)	
34	-0.25g -HNO ₃ , HF -closed vessel, microwave heating	
35	-no information	

E-7

Lab No.	Sediment Dissolution Procedure	Instrumentation
36	-0.25g -HNO ₃ , HF, HClO ₄ -closed vessel, microwave heating	GFAAS - Cr, Mn, Ni, Cu, As, Ag, Cd, Pb, Tl ICP - Al, Zn HGGFAAS - Se
37	-0.25g -HNO ₃ , HF, HClO ₄ -closed vessel, microwave heating	IDICPMS - Cr, Ni, Cu, Zn, Cd, Sn, Sb, Pb, Tl ICPAES - Mn, Fe,

Table E-3
Dissolution Procedures for the Determination of Mercury

Lab No.	Tissue Dissolution	Sediment Dissolution	Instrumentation
1	-0.2g -HNO ₃ , H ₂ SO ₄ @ 60°C -KMNO ₄ and H ₂ O ₂	-0.2g -HNO ₃ , H ₂ SO ₄ , KMNO ₄ @ 121°C -H ₂ O ₂	-CVAAS
2	-0.5g -HCl, HNO ₃ -closed vessel, microwave heating		-CVAAS
3	-HNO ₃ , H ₂ SO ₄ , HCl 60°C	-1.0g -HNO ₃ , H ₂ SO ₄ , HCl -KMNO ₄	-CVAAS
4	-0.2g (0.5g sediment) -H ₂ SO ₄ , HNO ₃ @ 95°C -KMNO ₄ and K ₂ S ₂ O ₈ - NH ₂ OH.HCl		-CVAAS
5	-0.5g -HNO ₃ -closed vessel, microwave heating -KMnO ₄ water bath @95°C	-0.2g -H ₂ SO ₄ , HNO ₃ , KMnO ₄ -autoclave @121°C	-CVAAS
6	-0.2g -HNO ₃ -closed vessel, microwave heating	-NA	-vapour generation ICP-MS

Lab No.	Tissue Dissolution	Sediment Dissolution	Instrumentation
7	-NA	-1g -HNO ₃ , HCl	-ICPMS
8	-1g -HNO ₃ , H ₂ O ₂ -open beaker reflux	-NA	
9	-NA	-HNO ₃ , HCl extraction	-vapour generation ICPAES
10	-NA	-0.2g -HNO ₃ , HCl, HF -closed vessel microwave heating	-CVAAS
11	-0.25g -HNO ₃ -closed vessel, microwave heating	-not determinend	-CVAAS with gold trap
12	-0.5g -HNO ₃ -closed vessel	-0.45g -HNO ₃ , HCl, HF -closed vessel	-CVAAS with gold trap
13	-0.5g (0.25g sediment) - H ₂ SO ₄ , HNO ₃ -closed vessel, microwave -KMnO ₄ , heat @ 80°C -NH ₂ OH.HCl		-CVAAS
14	- NA		
15	-HNO ₃ -closed vessel, microwave heating	- NA	-CVAAS
16	-no information		
17	-0.2g -HNO ₃ , H ₂ SO ₄ -heat 58°C - KMnO ₄ , K ₂ S ₂ O ₈ -heat @ 95°C -NH ₂ OH.HCl	-0.5g -HNO ₃ , H ₂ O ₂ -cool and treat as biological tissue	
18	-microwave heating -HNO ₃ , HCl	-microwave heating -HNO ₃ , HCl, HF, H ₃ BO ₃	-CVAAS with two-phase gold trap

Lab No.	Tissue Dissolution	Sediment Dissolution	Instrumentation
19	-1g -H ₂ SO ₄ , HNO ₃ -heat - KMnO ₄ , K ₂ S ₂ O ₈ - NH ₂ OH.HCl		-CVAAS
20	-0.5g -HNO ₃ , HClO ₄ -closed vessel		
21	-0.3g -HNO ₃ -closed vessel, microwave heating	-0.2g -HNO ₃ , HClO ₄ , HF -closed vessel, microwave heating	-CVAAS
22			
23	-1g -HNO ₃		-CVAAS
24	-NA		
25	-1g -HNO ₃ , H ₂ SO ₄ -reflux		-CVAAS
26	-NA		*
27	- NA		
28	-0.3g - H ₂ SO ₄ , HNO ₃ -heat @ 60°C - KMnO ₄ -heat - NH ₂ OH.HCl		-CVAAS
29	-0.30g -HNO ₃ -closed vessel, microwave heating	-0.12 g -HNO ₃ , HF, HCl -closed vessel, microwave heating	-CV flow injection AAS
30	-0.2g -HNO ₃ , HCl -heat @ 95°C -KMnO ₄		
31	- NA		

Lab No.	Tissue Dissolution	Sediment Dissolution	Instrumentation
32	-0.25g -H ₂ SO ₄ -heat @ 70°C -H ₂ O ₂ , heat - KMnO ₄ , NH ₂ OH.HCl		-CVAAS
33	- NA	-0.5g -HNO ₃ , HF, HCl -closed vessel	
34	-0.25g -HNO ₃ -closed vesssel, microwave	-1g -HNO ₃ , HCl -closed vessel, mirowave	
35	- NA		
36	- 0.2g -HNO ₃ , H ₂ SO ₄ , HClO ₄ -open beaker	-0.1g -HNO ₃ , H ₂ SO ₄ -closed vessel, microwave	-CVAAS

APPENDIX F

COMMENTS ON THE EVALUATION OF INTERCOMPARISON STUDY RESULTS

The purpose of an intercomparison study is to provide the participating laboratories and the intercomparison study organizers with a means of objectively assessing the reliability of results produced by those laboratories. There are three parameters which are assessed most frequently:

1. Accuracy

The assessment of accuracy is usually the most important goal of an ICES intercomparison study. This is an estimate of the bias of the participating laboratory with respect to the assigned value for the concentration of the analyte. In the best of cases the assigned value will have been predetermined by the coordinator and will be a practical estimate of the true value of the concentration of the analyte in the matrix. In some instances this is not possible and the assigned value will be a consensus value established by the coordinator by a critical evaluation of the set of results returned by the participants.

The assigned value can not be merely the consensus value of the participants because there may not be a consensus, or the consensus may be biased due to widespread use of faulty methodology.

The bias is equal to $(x-X)$ where

x is the analyte concentration determined by the participant, and

X is the analyte concentration value assigned by the coordinator.

The relative bias is $(x-X)/X$. The relative bias is usually used as the measure of accuracy rather than the absolute bias.

If the user community is able to estimate the precision s needed in order to ensure proper data interpretation, the quotient $z = (x-X)/s$ is a very valuable indicator. If z exceeds 2 there is less than a five percent probability that the laboratory can produce reliable data.

2. Intralaboratory Precision

This is an estimate of the repeatability of a procedure within the individual participating laboratory. Repeatability for a particular analyte concentration can be assessed by the analysis of replicate samples and is usually described by the standard deviation (s) of a single determination. The computation is simple:

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

where x_i is the determined concentration of an individual replicate,

\bar{x} is the determined mean of the replicate analyses, and

N is the number of replicate analyses.

The relative standard deviation (RSD) is s/\bar{x} . This number is often multiplied by 100 to yield the percent standard deviation.

An estimate of the repeatability can also be calculated from a set of samples of different analyte concentrations. This is done by a linear regression procedure and yields an overall value of the standard deviation for the range of concentrations tested.

The calculation of the intralaboratory precision is always done in intercomparison exercises but, except for identifying a laboratory with serious precision problems, is of limited value. An intercomparison study is usually a snapshot in time and only provides an estimate of the true standard deviation. The number of replicate samples analyzed is usually rather small and the errors in this estimate can be very large as indicated in Figure 1 below.

The confidence limits for the estimation of a standard deviation are not symmetrical and are surprisingly large for small numbers of replicates¹. The standard deviation calculated from the results of five replicate analyses has a 95 percent confidence interval ranging from 0.6 to 2.4 times its calculated value. The probability of a "bad" result is quite high. Also, it is obvious that studies based on only one or two measurements may produce misleading results.

A far superior estimate of the standard deviation for a particular analytical procedure is acquired from long term control chart data maintained by any laboratory employing good laboratory practices.

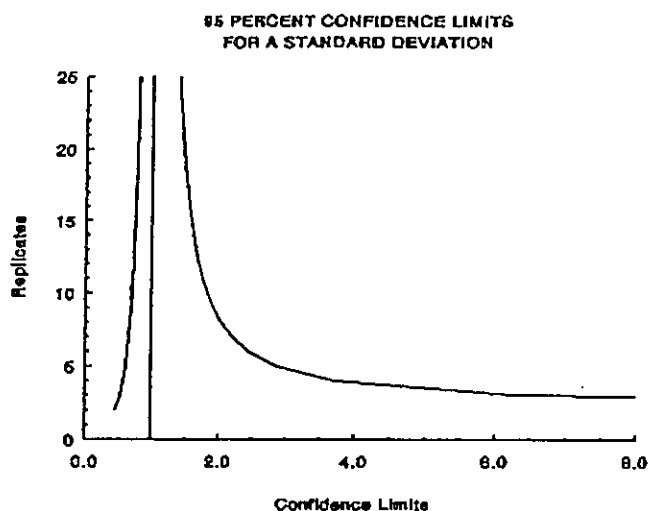


Figure 1

3. Interlaboratory Precision

This is an estimate of the reproducibility of submitted analyte concentrations between the participating laboratories. If there is acceptable accuracy and intralaboratory precision, then the interlaboratory precision can be used to determine whether a cooperative project is feasible between the set of laboratories. It is usually described by a standard deviation and the calculation is identical to that shown above but here

x_i is the determined concentration of an analyte from a single participating laboratory.

\bar{x} is the assigned value for the analyte concentration, and

N is the total number of laboratories whose results are being intercompared.

Other information may be acquired from an intercomparison study such as the efficacy of various analytical procedures. Also, the distribution of laboratory results about the assigned values could lead to a better understanding of the causes of laboratory bias.

There may be a tendency to try to describe the population of results by a rigorous multivariate model which assumes that the determined values of the analyte concentrations are interdependent. This is a difficult concept for an experienced analytical chemist to accept. The response is, that if this is indeed the case, the analytical procedures are inadequate. However, it is possible that a portion of the population is distorting the distribution. If the former is true then this area of analysis has severe problems. If the latter is true then it would be best to find a means of isolating the group whose results may be of an acceptable calibre from the group which is distorting the distribution.

Experiences over the last decade with respect to the analysis of trace metals in various matrices indicate that, as long as the analyte concentrations are above their quantitative limits of determination (at least twice the limit of detection), a group of competent laboratories will produce a set of results homogeneously distributed about a mean which is seldom significantly different from the assigned value. There is no basic reason to believe that organic analytes would produce a dissimilar distribution. The fundamental problem is that, at the current state of the practice of analytical chemistry, the quantitative analysis of materials for trace organic constituents is a much more difficult and challenging task.

Figure 2 is an example taken from a recent intercomparison study regarding the determination of 13 trace metals in sewage treatment plant (STP) effluents². Thirty-five sets of zinc concentrations were submitted by the participants for this sample. The distribution of their mean values is shown in the diagram. The consensus mean is 59.3 micrograms zinc per litre. Aside from what is probably a high biased mean the group can not distinguish concentration differences from between 29 to 115 micrograms zinc per litre. The standard deviation can not be used to calculate this range.

The distribution is obviously skewed towards the higher concentrations and does not appear to be normally distributed. However, what we have here are some quite good laboratories and some poor laboratories. The poor laboratories generally produce high results in trace analysis because they do not have their blanks and contamination under control. They also may produce both high and low results because of poor calibration techniques, improper instrument usage, poor choice of methods and poorly trained staff. The problem is to find a relatively simple method to separate the under-achievers from the good performers (i.e., get rid of the outliers).

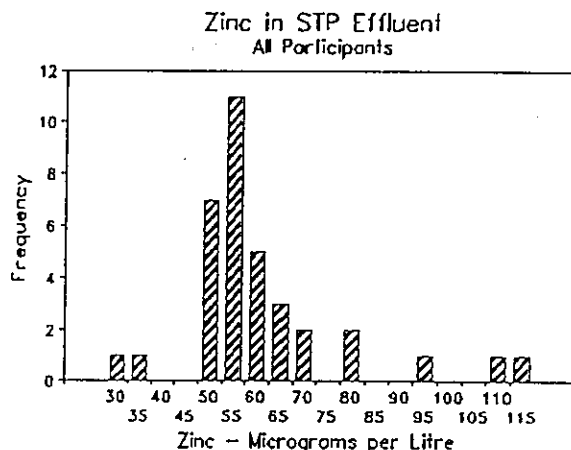


Figure 2

There are many suggestions on how to do this. ISO/REMCO, for example, supports a procedure based on the successive application of the Cochran test and the Grubbs tests³. At NRC we prefer a more statistically transparent method involving the successive application of a *t*-test at the 95 percent confidence level to isolate what we believe is a fair approximation of a normal distribution. The results of this procedure on the population of Figure 2 are shown in Figure 3 on the next page.

Eight laboratories were eliminated from the distribution in this example, a larger than usual number. The excluded mean is 55.7 ± 9.8 micrograms zinc per litre. The mean is no longer biased and the range of

indiscrimination is reduced to 36 to 75 micrograms zinc per litre with 95 percent confidence.

This method may not be statistically rigorous. One or two laboratories may have been rejected (or accepted) when they should not have been. However, we have found that this type of evaluation of the results is readily understandable to the participants and to the user community of the data, most of whom have a rather unsophisticated understanding of even elementary statistics.

The main purpose of the study has been achieved. A subset of the participants has been identified as a homogeneous group and its performance has been characterized. The organizers of the study and the user community are aware of the possible consequences of using any one of the participants in a future project. They are also aware of the limitations on the quality of the data which can be produced by the group as a whole or any subset of laboratories they may choose from this group. This knowledge should be incorporated in their planning. They should be wary of any laboratory, regardless of reputation, which has not participated in an intercomparison study or which has not been accredited through some harmonized proficiency testing program related to their project interests.

The participating laboratories have gained in that they are aware of their own capabilities, based on an objective assessment. The "rejected" laboratories must examine their procedures in order to improve their capabilities, seeking outside advice if necessary. The others must also continually seek to improve. The range of indiscrimination between laboratories is still too large to produce the necessary quality of data for many environmental projects.

References

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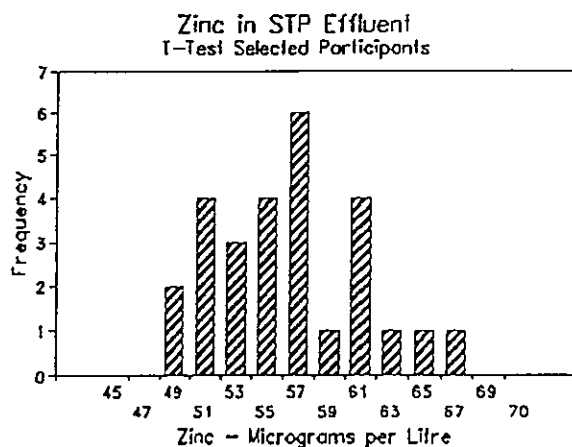


Figure 3