INTERCALIBRATION AND INTERCOMPARISON STUDY OF RADIONUCLIDE CONCENTRATIONS
IN LAKE MICHIGAN SAMPLES

Draft Report

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ABSTRACT

An intercalibration (measurements on aliquots of the same sample)/intercomparison (measurements on aliquots of the same source) program has been conducted under the auspices of the Division of Biomedical and Environmental Research (formerly the Division of Biology and Medicine), U. S. Atomic Energy Commission by national laboratories and laboratories under contract to the Atomic Energy Commission. The initial plans were to compare many samples from Lake Michigan for radionuclide and stable element concentrations in order to assess the status, in fresh water samples as opposed to sea water samples, of laboratories especially capable of low-level environmental measurements. A limited response has been obtained from eight laboratories for radionuclides on samples of lake water, lake water spiked with known mixtures of radionuclides (^{54}Mn , ^{60}Co , ^{65}Zn , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{90}Sr and ^{239}Pu) prepared by the National Bureau of Standards, and lake sediment from the effluent channel of a nuclear power plant, and from two laboratories for stable elements on samples of lake bottom sediment.

The evaluation indicates that the precision and accuracy of these select laboratories is much better than found in an open program. Even so, some discrepancies occur which suggest both systematic and variable errors. The variability of $\sim \pm 15\text{--}30\%$ in the measurement of the γ -emitting elements is unexplainedly constant over a concentration range covering 4-5 orders of magnitude. There is a possible suggestion that Sr and Pu, involving chemical procedures, can be measured as well as or better than the γ emitters. The response on trace elements was very low, but, while the results are encouraging, no deductions can be made. The use of

National Bureau of Standards spiked water samples for radionuclide mixtures is very useful and should be considered in all such programs both for radionuclides and trace elements. The evaluation indicated that environmental samples can be measured reasonably well by competent laboratories but that the capability for routine environmental monitoring will not easily approach that of these laboratories.

A. Introduction

The concentrations of radionuclides in most environmental samples are generally so low that serious problems can be encountered in their measurement. These problems are associated not only with the difficulties in the measurement of such low values but include the constant awareness needed to minimize contamination or losses. The problems in the measurement are further compounded in fresh waters as opposed to sea waters since the concentrations of bulk elements in sea water help to minimize losses.

The great potential for error in such measurements where so many pitfalls are possible makes it necessary to compare the capabilities of different laboratories and their methods in order to determine whether or not satisfactory results can be obtained by all. Many laboratories are now engaged in such low-level measurements, and, in order for data gathered by them to be useful in the interpretation of the present state of the environment and its changes, it is prudent to show that all are on a common basis in their ability to measure the presumed "true" concentrations.

A number of organizations, both in the National Laboratories and under contract, are making measurements of environmental samples to fulfill the responsibility of the U. S. Atomic Energy Commission, Division of Biomedical and Environmental Research (DBER, formerly the Division of Biology and Medicine) in its understanding of certain aspects of the environment, involving radionuclides and elements in very low concentrations. The Division of Biomedical and Environmental Research has observed significant differences in some of the fresh water results from these laboratories and has noted similar differences in international intercomparison studies

on sea waters. For these reasons, DBER deemed it important to conduct a preliminary intercalibration and intercomparison program in order to assess the situation with the laboratories presently reporting to it, that is, to show comparability or the lack of it, and to assist the laboratories in determining their status, relatively and absolutely. The results from these studies, obtained from laboratories engaged in research programs would also provide information on what less demanding levels of accuracy and precision would be realistic for similar samples measured by organizations involved in environmental monitoring programs.

B. Plan

Accordingly, DBER established a preliminary program, the aims of which would be to make some initial findings and to prepare for a more definitive program at a future date. The program was planned as both an intercalibration (the measurement of aliquots of the same material) and an intercomparison (the measurement of aliquots of the same source of the material, that is, each laboratory would use its own sampling methods). The program would include measurements of radionuclides and trace elements. For perhaps the first time there would be an opportunity to compare on an absolute basis measurements by the laboratories on known radioactive water samples (known concentrations of radionuclides introduced into lake water) prepared by the National Bureau of Standards (NBS) and known trace element solid samples (certified Standard Reference Materials from the NBS of botanical origin [orchard leaves] and of zoological origin [bovine liver]).

Since DBER already had a large environmental research program on the Great Lakes through the Argonne National Laboratory and the University

of Michigan and since results on fresh water samples had not been inter-compared adequately, it was decided to obtain subsurface water, bottom sediments and benthic biota (pontoporeia and mysis) from Lake Michigan. For higher level radionuclide concentrations, samples of water and sediment would be taken from the effluent channel of a nuclear power plant on the lake.

Even as a preliminary program this was an ambitious undertaking. As it turns out, it was much more than the laboratories could do, and this report analyzes only a small fraction of the results that were expected.

C. Collection and Preparation of Samples

The samples described in this section are only those for which sufficient results have been reported by the laboratories for analysis. Thus only three sample types are involved, lake water, spiked lake water and lake sediment near a nuclear power plant.

1. Lake Water

Open, subsurface lake water was obtained on 13 September 1971 from the University of Michigan Research Vessel Inland Seas at an offshore station 10 miles west of Grand Haven, Michigan. Water was taken with a noncontaminating (polyethylene) submersible pump (designed by the University of Michigan) at a point 45 m below the surface (thermocline at 18 m, lake depth 83.8 m). Thirteen-gallon polyethylene carboys, previously cleaned, were rinsed with the lake water and then filled on a rotating basis approximately one quarter to one fifth of the volume at a time. After the first partial filling, 100 ml 12 N HCl were added to reduce possible

effects of adsorption on the polyethylene walls. The screw caps were rinsed with lake water, placed on the carboys, and, on land, were taped to the carboy neck to reduce dust contamination.

2. Spiked Lake Water

Lake water containing known concentrations of specific radionuclides was prepared by taking lake water from the Chicago intake, a point approximately six miles offshore, into 5-gal polyethylene carboys in a manner similar to that for the water in the 13-gal carboys, including the use of HCl to lower the pH. To each of these carboys each of the following radionuclides were added, ^{54}Mn , ^{60}Co , ^{65}Zn , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{90}Sr and ^{239}Pu , in amounts to make a mixture with nominal final concentrations of 2-5 pCi/kg each (~ 1 pCi/kg for ^{90}Sr and ^{239}Pu). This spiking was done by NBS at Argonne National Laboratory by pouring into the carboys the contents of vials each containing a known amount of one nuclide and rinsing the vial several times with the water in the carboy. Each vial contained a dilution (using weight by the usual NBS methods) from a master solution of each radionuclide which was standardized by the methods shown in Table 1.

Table 1
Methods of Standardization for Radionuclides
Used to Spike Lake Water

<u>Nuclide</u>	<u>Method</u>
^{54}Mn	x- γ coincidence
^{64}Co	β - γ , γ - γ and sum coincidence
^{65}Zn	γ intercomparison with ^{46}Sc which in turn standard- ized by γ - γ coincidence
^{134}Cs	total efficiency γ measurement using 8" NaI(Tl) detector
^{137}Cs	calibrated reentrant $4\pi\gamma$ ion chamber
^{144}Ce	$4\pi\beta$ - γ coincidence
^{90}Sr	$4\pi\beta$ -absolute
^{239}Pu	$1\pi\alpha$ counting, $2\pi\alpha$ counting

The amount of carrier for each radionuclide, except for Pu, ranged from 0.1-0.6 ng/kg final solution. The degree of purity and the error in the standardizations of each radionuclide are shown in Tables 2 and 3, respectively.

Table 2

Purity of Radionuclides Used to Spike Lake Water

<u>Nuclide</u>	<u>Purity Information</u>
^{54}Mn , ^{60}Co , ^{65}Zn , ^{134}Cs , ^{137}Cs , ^{144}Ce	contamination with other γ -emitters $\leq 0.1\%$ by Ge(Li) measurement
^{90}Sr	chemical isolation and purification, constancy of $T_{1/2}$ over 10-y period
^{239}Pu	99.99% pure by mass spectroscopy, 7.9 ppm ^{240}Pu , no ^{238} , ^{241}Pu

Table 3

Overall Error in the Absolute Standardization of the Radionuclides
Used to Spike Lake Water

<u>Nuclide</u>	<u>$\pm$ % Error</u>	<u>Nuclide</u>	<u>$\pm$ % Error</u>
^{54}Mn	2.6	^{137}Cs	1.5
^{60}Co	1.8	^{144}Ce	2.0
^{65}Zn	2.1	^{90}Sr	2.1
^{134}Cs	2.0	^{239}Pu	1.2

Five-gallon carboys were prepared with individual nuclides in the same manner in order to study adsorption losses as a function of time. These measurements were made at and by NBS on aliquots removed from each carboy at ~ 2-week intervals over a period of four months. Results on ^{137}Cs (and by implication on ^{134}Cs), ^{60}Co and ^{65}Zn indicate a difference

of $\leq$ over the 4-month period. Manganese-54 showed a difference of $\leq 10\%$, but the counting statistics were not as good as the first three, and if any change did take place the change appears to have occurred at the beginning. It has not been possible to make accurate measurements to date for ^{144}Ce since its low energy γ -ray is located in a region of high background. The ^{90}Sr and ^{239}Pu measurements are in process, the present indications being that no important change has been observed for ^{90}Sr so far.

3. Lake Sediment

Lake sediment was collected from the effluent channel of the Big Rock Point Nuclear Power Station at Charlevoix, Michigan. The lake bottom is almost entirely sand with a proportion of rocks. A composite sample was made from four grab samples, side by side, air dried, sifted, homogenized and divided into 500-g aliquots. The particle size is ~ 0.25 - 0.5 mm in diameter, and there should be very few fines.

D. Participating Laboratories

Originally eleven laboratories planned to participate in this program. One laboratory did not submit results on the radionuclide concentrations, and two laboratories had to withdraw because of commitments beyond their control. The remaining eight laboratories are listed in alphabetical order and the responsible individual is also designated:

<u>Laboratory</u>	<u>Responsible Individual</u>
Radiological Sciences Department	
Battelle Northwest Laboratory	Dr. Wyatt B. Silker
Richland, Washington 99352	

<u>Laboratory</u>	<u>Responsible Individual</u>
Radiochemistry Laboratory Canada Center for Inland Waters Burlington, Ontario, Canada	Dr. Ray W. Durham
Health and Safety Laboratory U. S. Atomic Energy Commission New York, New York 10014	Dr. Herbert L. Volchok
Radiochemistry Division Lawrence Livermore Laboratory Livermore, California 94550	Dr. Chris Gatrousis
Biomedical Division Lawrence Livermore Laboratory Livermore, California 94550	Dr. Robert Heft
H8 Los Alamos Scientific Laboratory Los Alamos, New Mexico 87544	Dr. Harry Jordan
Scripps Institute for Oceanography University of California La Jolla, California 92308	Dr. T. R. Folsom
Department of Chemistry Woods Hole Oceanographic Institute Woods Hole, Massachusetts 02543	Dr. Victor Noshkin*

A request was made for anonymity, and, therefore, the laboratory designations by number in the tables which follow have no relation to the alphabetical listing of the laboratories above.

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E. Results

Since in practice the response to the program has been so limited as compared to the original plans, it is difficult to make very firm conclusions from the results except in a general way. In particular, it should be clear that the laboratories cannot be compared very critically and that statements about the general conditions in Lake Michigan cannot be made especially since enough replicate samples were not available. Conversely, one would wish to attach some credibility or incredibility to the results when the laboratories state, for example, that they believe that the errors in the absolute values of their own standards to be $\sim \pm 2-5\%$. Finally, these laboratories represent the major portion of the laboratories most competent to perform such analyses in the United States, and the results ought to have some meaning in light of the abilities of these laboratories.

1. Spiked Lake Water

The results on the spiked lake water samples are presented in Table 4 as ratios between the laboratory values and the NBS values. This table also summarizes the results in terms of a laboratory average only for the γ -emitting elements reported and in terms of an element average for all the reporting laboratories. The ratios in this table are given in the form of $\bar{x} \pm \sigma_x$ where $\bar{x}$ is the average value and σ_x is the standard deviation of a single observation, to give a measure of the variability, and is not $\sigma_{\bar{x}}$ which is the standard deviation of the average value and represents the variability of the laboratories as a group or how well the laboratories can do as a group. Since there appear to be no significant differences based on method of analysis, these methods are not noted except for special points. The main method was γ -ray spectroscopy on a

Table 4
Intercalibration of Spiked Lake Michigan Water

Laboratory number ^b	Radionuclide Concentration Ratios ^a								Laboratory average for γ elements only ($\bar{L} \pm \sigma_L$)
	⁵⁴ Mn	⁶⁰ Co	⁶⁵ Zn	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁴ Ce	⁹⁰ Sr	²³⁹ Pu	
1	0.89 $\pm$ 0.12	0.94 $\pm$ 0.08	0.77 $\pm$ 0.09	1.00 $\pm$ 0.08	1.10 $\pm$ 0.09	—	—	1.15 $\pm$ 0.07	0.94 $\pm$ 0.12
2	—	—	—	1.11 $\pm$ 0.03	0.99 $\pm$ 0.03	—	—	0.73 $\pm$ 0.03	1.05 $\pm$ 0.08
3	1.22 $\pm$ 0.07	(1.68 $\pm$ 0.95) ^c	1.28 $\pm$ 0.14	1.01 $\pm$ 0.05	(2.21 $\pm$ 0.07) ^c	1.18 $\pm$ 0.10	—	—	1.17 $\pm$ 0.12
4	—	—	—	—	—	—	2.63 $\pm$ 0.96 (1.41 $\pm$ 0.51) ^d	1.11 $\pm$ 0.89	—
5	0.95 $\pm$ 0.04	0.96 $\pm$ 0.02	0.98 $\pm$ 0.04 ^e	1.04 $\pm$ 0.11	0.99 $\pm$ 0.03	1.29 $\pm$ 0.14	—	—	1.04 $\pm$ 0.13
6	0.75 $\pm$ 0.08	0.94 $\pm$ 0.08	0.72 $\pm$ 0.14	0.93 $\pm$ 0.08	0.61 $\pm$ 0.05	1.45 $\pm$ 0.34	—	0.98 $\pm$ 0.06	0.90 $\pm$ 0.30
7	—	—	—	—	1.46 $\pm$ 0.02	—	1.43 $\pm$ 0.24 (0.76 $\pm$ 0.13) ^d	0.83 $\pm$ 0.05	—
8	0.74 $\pm$ 0.05	1.03 $\pm$ 0.02	1.05 $\pm$ 0.07	1.04 $\pm$ 0.02	1.14 $\pm$ 0.05	0.85 $\pm$ 0.26	—	—	0.98 $\pm$ 0.15
Element average for all laboratories ($\bar{E} \pm \sigma_E$)									
0.91 $\pm$ 0.20 0.97 $\pm$ 0.04 0.96 $\pm$ 0.23 1.02 $\pm$ 0.06 1.05 $\pm$ 0.27 1.19 $\pm$ 0.25 (1.09 $\pm$ 0.46) ^d 0.97 $\pm$ 0.16									

^aRatio = lab value (pCi/kg)/NBS value (pCi/kg) = $\bar{R} \pm \sigma_R$, where σ_R is the standard deviation reported by or calculated for the laboratory and excluding error of NBS standardization.

^bLaboratory order has no correlation with alphabetical listing in Section D.

^cLaboratory has evidence that sample was contaminated, excluded from analysis.

^dThe lake water contains fallout ⁹⁰Sr in a concentration of ~ 0.83 pCi/kg (see results on lake water, Table 5) comparable to what was added by NBS. (The initial plans, however, were to add ~ 10 times more to preclude this difficulty.) The values in the parentheses take this fallout ⁹⁰Sr into consideration and are the preferred ratios.

^eTwo separate analyses were made and reported. One is about half the NBS value and is obviously incorrect but no explanation has been found; it is not included in this evaluation.

sample or concentrated sample for the γ emitters, while ^{90}Sr and ^{239}Pu were analyzed by chemical separation.

As a point of reference, one can start with how well a laboratory may perform on the basis of the compounding of assumed known errors. If the following reasonable errors are assumed (error in laboratory standards, $\pm 5\%$; error in counting, $\pm 5\%$, and error in sample treatment, $\pm 10\%$) then the combined error in the laboratory value would be $\pm 12-13\%$. Using this value as a criterion, 30 of 37 entries, or better, 30 of 35 entries (if Laboratory #4 is omitted because of its marginal sensitivity) are within this combined error, a satisfactory result.

On the other hand, if the errors attributed to each of the ratios are compared and if the elemental and laboratory averages are observed closely, then some discrepancies or unusual relationships appear. Taking the laboratory averages for the γ -emitting elements first, the following results of especial interest are observed:

1. For Laboratory #1, the laboratory ratio is reasonable, but one finds that the ratio for ^{65}Zn is less than 1.00 by more than 2.5 times the error attributed to it. Is this a real deviation and due to what?

2. For Laboratory #3, the laboratory ratio is larger than 1.00 by more than its standard deviation. Inspection of the individual ratios indicates that they are all > 1.00 . Is this a systematic error due to sample handling or standards?

3. For Laboratory #5, the laboratory ratio is close to 1.00, but the standard deviation is large. The individual ratios indicate excellent results except for ^{144}Ce . Is this due to counting statistics or an incorrect standard?

4. For Laboratory #6, the laboratory ratio is low, and its standard deviation is large. The individual ratios are consistently low except for ^{144}Ce which is quite high but not inconsistent with the standard deviation attributable to it. Is there a systematic error in these results? The ^{137}Cs value for this laboratory is based on chemistry. A value by γ spectroscopy was also reported identical to this but with a larger error. Thus, there is consistency within the laboratory, but the systematic deviation is emphasized. Is the ^{137}Cs standard correct?

5. For Laboratory #8, the laboratory ratio is close to 1.00, but the standard deviation is large. The ratio for ^{54}Mn is < 1.00 by an amount five times the standard deviation while the ratio for ^{137}Cs is > 1.00 by three times the standard deviation. Are these differences in opposite directions real, and are they due to errors in the standards?

Proceeding in similar fashion with the element averages for each laboratory the following results of interest are observed:

1. Starting with the γ -emitting elements the ratios on the whole are good, with those for ^{60}Co , ^{65}Zn , ^{134}Cs and ^{137}Cs very good.

2. The variability is quite high for ^{54}Mn , ^{65}Zn , ^{137}Cs and ^{144}Ce and much higher than the standard deviations of the individual ratios. In particular, why is it possible to measure ^{134}Cs as well as ^{60}Co while the variability for ^{137}Cs is the largest of all? (It may be noted that the carrier Cs added with the spike ^{137}Cs is on the order of the natural Cs content of the lake water as found by one laboratory [$\sim 5 \text{ ng/kg}$]).

3. The greatest difference from 1.00 occurs for the ^{144}Ce ratio although the difference is not inconsistent with the standard deviation of this ratio or the individual ratios. On the other hand, three of the

four ratios are much greater than 1.00. Because of its low energy γ ray, it can be more difficult to make a good measurement for ^{144}Ce . Is the high ratio due to a systematic error attributable to the measurement or to the adequacy of a Ce standard or some other reason?

4. Turning to the non- γ -emitters, not very much can be said about ^{90}Sr since only two results were reported, one of which has a very high error because of low sensitivity. In addition, as indicated, a correction for fallout ^{90}Sr was necessary. Taking these factors into account the ratio for ^{90}Sr is not unreasonable.

5. The ratio for ^{239}Pu is very good although the variability is three times the average standard deviation of the individual ratios (excluding the standard deviation of Laboratory #4). On the other hand, the ^{239}Pu variability is not inconsistent with the variability for the γ emitters.

A comparison of this intercalibration on fresh water with these selected laboratories to that on sea water with 46 laboratories on an international basis as described by Fukai et al. (1) is of interest. Only the standard deviations can be compared for the corresponding radioelements which are duplicated. The fresh water standard deviations are 6% for ^{134}Cs , 26% for ^{137}Cs and 21% for ^{144}Ce (average 18%), and the respective sea water results are 74, 71 and 108% (average 76%). This represents a greater than fourfold improvement in the measurement of samples having comparable or somewhat lower radionuclide concentrations than the "spiked" sea water.

The conclusion is that this intercalibration, using known spiked samples as reference, is reasonably good. There are, however, certain

results which are sufficiently suspicious to warrant some attention by each laboratory. If these discrepancies are found to be real, then the implication is that a similar intercalibration can be even better in the future.

2. Lake Water

The limited results on the lake water radionuclide concentrations are shown in Table 5. The title in this table uses the terms

Table 5

Intercalibration/Intercomparison of Offshore Lake Michigan Water

Laboratory number ^a	Radionuclide concentration (pCi/kg)		
	¹³⁷ Cs	⁹⁰ Sr	²³⁹ Pu
1	-----	-----	0.0012 ± 0.0002
2	0.058 ± 0.014	-----	0.0007 ± 0.0003
3	-----	-----	-----
4	-----	(1.4 ± 1.6) ^b	(0.03 ± 0.03) ^b
5	0.085 ± 0.015	-----	-----
6	0.077 ± 0.001	0.85 ± 0.01	0.0011 ± 0.0001
7	0.066 ± 0.005	0.80 ± 0.02	-----
8	0.114 ± 0.007	-----	-----

Element average for

all laboratories

($\bar{E} \pm \sigma_E$)   0.080 ± 0.022   0.83 ± 0.03   0.0010 ± 0.0003

^aLaboratory order has no correlation with alphabetical listing in Section D.

^bOmitted from averages because of large error.

"intercalibration/intercomparison" since two laboratories used their own methods (one sampled independently, one added its own carriers at collection) and since the other laboratories analyzed the lake water as submitted. However, the total information is so limited that separation of the variables is impossible. On the other hand, the results are close enough to state that there appears to be no obvious difference between the intercalibration and the intercomparison.

The concentrations of ^{137}Cs and ^{239}Pu in the lake water are ~ 45 times less than those of the spiked lake water samples. In view of this fact, the results on ^{137}Cs and ^{239}Pu are very good. Interestingly, the fractional standard deviation is the same for both the lake and spiked samples ($\sim 27\%$). Did something really occur to give the high standard deviation for the spike samples, or is the standard deviation for the lake samples too good? The standard deviation for the lake ^{239}Pu is twice that of the spike sample and essentially equal to that of the lake ^{137}Cs . Thus, lake ^{137}Cs and ^{239}Pu have been measured with the same variability representing good consistency from this standpoint. There appears to be no correlation between the results for the spike ^{137}Cs and ^{239}Pu and for lake ^{137}Cs and ^{239}Pu ; that is, a laboratory that is high (or low) for the spike sample is not necessarily high (or low) for the lake sample.

The two ^{90}Sr results for the lake sample are remarkably, perhaps unbelievably, good. Very little more can be said about ^{90}Sr except to note that the values are in line with previous measurements on Lake Michigan by Machta et al. (2).

3. Lake Sediment

The results on the lake sediment from the Big Rock Nuclear Station are shown in Table 6. The measurements on the γ emitters of this sample should produce the most consistent results for two reasons. All four laboratories measured just a weighed aliquot of the material sent to them, and the concentrations of the radionuclides are 2-3 orders of magnitude higher than the spiked lake water. The results show, however, that the variability or the precision of the average value is the same as for the results in Tables 4 and 5. Why should the variability for γ emitters, for three types of samples the radionuclide concentrations of which range over 4-5 orders of magnitude, be the same? Inspection of the table indicates that one laboratory deviates significantly from the other three but that it is a different laboratory for each element. While it happens that we do not have information on the homogeneity of these samples, by the measurement of aliquots at one laboratory (which should be obtained), it is difficult to make a good case that inhomogeneity will produce the results observed.

On the other hand, the two ^{239}Pu results are in very good agreement, especially since the analysis involved the dissolution of solid samples. While two results are not enough, there is the suggestion that homogeneity may be adequate.

In considering all the results of Tables 4, 5 and 6, there seems to be a pattern developing which can only be suggested in view of the limited total amount of information. It seems that Pu and Sr, the analysis of which involves careful chemistry, can be measured as well as or better than the γ -emitting radionuclides, most, but not all, of which were measured either

Table 6

Intercalibration of Big Rock Sediment

Laboratory number ^a	Radionuclide concentration (pCi/kg)				
	⁶⁰ Co	⁶⁵ Zn	¹³⁴ Cs	¹³⁷ Cs	²³⁹ Pu
1	707 ± 49	1912 ± 380	983 ± 44	2410 ± 145	1.6 ± 0.2
2	-----	-----	-----	-----	-----
3	410 ± 11	2671 ± 89	789 ± 18	2419 ± 33	-----
4	-----	-----	-----	-----	(2 ± 2) ^b
5	-----	-----	-----	-----	-----
6	430 ± 45	1937 ± 67	415 ± 18	1900 ± 180	1.66 ± 0.01
7	-----	-----	-----	-----	-----
8	480 ± 10	1800 ± 100	940 ± 10	2800 ± 100	-----

Element average for

all laboratories

 $(\bar{E} \pm \sigma_E)$

510 ± 140

2080 ± 400

780 ± 260

2380 ± 370

1.6 ± 0.05

^aLaboratory order has no correlation with alphabetical listing in Section D.^bOmitted from averages because of large error.

by no sample preparation or by a minimum preparation of concentration only. If this is eventually shown to be true, there is no obvious, a priori, reason why this should be related to the fresh water origin of these samples.

F. Results on Trace Elements

As indicated in the plan of this program, stable element analysis was to be an important endpoint. Such information was supplied by only two laboratories, one of which is already included in the previous sections. The other laboratory was the

Great Lakes Research Division

University of Michigan

Dr. Edward Callender

Ann Arbor, Michigan 48104

Unfortunately, even these two laboratories did not work on the same samples, and their different analytical methods did not provide results for the same elements. For completeness of the report on this program and to acknowledge credit for work done, the very limited results on elemental concentrations are presented.

The measurements were made on lake sediment obtained on 14 September 1971 in approximately the same position off Grand Haven at which the lake water was obtained. Water depth was 56 m. The interior portion of sediment from 2-7 cm below the surface of eight successive Ponar grab samples was wet sieved through a nylon screen to remove shells and other large artifacts. The combined, sieved, grab samples were stored in a polyethylene bag under refrigeration until the bulk sample could be freeze dried to essentially constant weight. The dried sample was further mixed by rotating 10,000 times in a plastic blender.

The results are shown in Table 7. Both laboratories report a standard deviation for each measurement of $\sim \leq \pm 10\%$. However, one

Table 7

Stable Element Intercalibration of Lake Sediment

Laboratory	Elemental concentration (ppm)		
	Na	Fe	Cr
A	5200	28,000	68
B	4000	24,000	49

laboratory made replicate measurements of replicate aliquots which indicate a variation between aliquots of $\sim \pm 50\%$, while the variation between aliquots for the other laboratory was $\leq \pm 10\%$. In view of this information, the results on the three elements (Na, Fe and Cr) of Table 7 are acceptable, but not much more can be said at this time.

G. Conclusions

Although the intercalibration/intercomparison program as finally executed fell far short of the original plans, a number of conclusions can be made from the limited results which have been submitted for evaluation. These general, but tentative, conclusions are as follows:

1. The accuracy and precision of these selected laboratories is much greater than is found in intercalibrations or intercomparisons where many laboratories participate in an open program.

2. Even with these selected laboratories enough discrepancies have appeared to suggest that there may be systematic errors affecting the

accuracy of the measurements (including possible errors in the laboratory standards) and that the variation actually found between the laboratories is much greater than the quoted or calculated precision of each laboratory.

3. The variability in the measurement of γ -emitting radionuclides ranges from $\pm 15-30\%$ and is independent of the concentration even though the concentration range varies by 4-5 orders of magnitude. There is no explanation for this unusual result.

4. There is the glimmer of a suggestion that Sr and Pu, involving extensive chemical preparation can be measured as well as or better than the γ -emitting radionuclides.

5. The very meager results on stable element concentrations are encouraging, but no evaluation can be made at this time.

6. The use of the NBS spiked radionuclide mixture is very helpful in the evaluation, and the use of such known samples (also, as intended with the Standard Reference Materials of orchard leaves and bovine liver for the stable elements) is to be highly encouraged in future intercomparisons.

7. No serious problems have been encountered in the measurement of environmental fresh water samples, and, with good and careful techniques, there is no reason why other competent laboratories cannot attain such results.

8. It has been impossible to make any extensive statistical evaluation because of the limited results which have been submitted. However, with the limited data available, there do not seem to be major or significant differences between intercalibration and intercomparison measurements or between chemical and physical measurements.

9. On the basis of the present information, it should be possible to conduct another carefully planned intercalibration/intercomparison in such a way as to minimize the workload on each laboratory while maximizing the information.

10. Since, even with these select laboratories, some possible discrepancies have been noted, it is clear that methods for routine environmental monitoring are going to have problems of sensitivity, accuracy and precision. There is no clear-cut way, at this time, to make a judgment on the potential adequacy of environmental monitoring programs. One might intuitively guess that a factor of two would be surprisingly good and that an order of magnitude would, in turn, not be surprising.

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