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THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM
SELENIUM ROUND-ROBIN

A FINAL REPORT
TO THE

SAN JOAQUIN VALLEY DRAINAGE PROGRAM

BY

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INTRODUCTION

As part of a cooperative effort among the U.S. Bureau of Reclamation (USBR), the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service, the California Department of Fish and Game, and the California Department of Water Resources, the San Joaquin Valley Drainage Program (SJVDP) was established in 1984 to investigate problems associated with the drainage of irrigated agricultural lands, and to formulate, evaluate, and recommend alternatives for decreasing or mitigating elevated levels of selenium (Se) and other trace elements present in subsurface waters. Recognizing the difficulty of determining trace elements in different environmental matrices and of the need for accuracy and comparability of data generated in different laboratories, the SJVDP established a Quality Assurance/Quality Control program with the Department of Land, Air and Water Resources (LAWR), University of California, Davis. The purposes of the project were, in designated program laboratories, to (1) implement a round-robin test of their capability to determine selenium in reference samples of water, soil, sediment and biological tissue; (2) compare the resultant data to determine which methods and analytical tools provided the most consistent and reliable results; (3) determine reasons for the variations in results; (4) document existing QA/QC protocols ; and (5) recommend protocol improvements.

Twenty-nine laboratories were designated as participants in the project. All reference samples were prepared for distribution

by the Department of Land, Air and Water Resources, University of California, Davis which also received the results from each laboratory so that statistical analysis could be applied to determine the reliability of determination.

REFERENCE SAMPLES AND SAMPLE PREPARATION

Nine samples were prepared for distribution to participating laboratories. The test materials included four waters, a soil, a sediment, one tissue and two vegetation samples. The soil (USGS San Joaquin Soil Std) and sediment (USBR KS-1-5) samples were obtained from the U. S. Geological Survey (USGS) and the U.S. Bureau of Reclamation, respectively. The reference waters were obtained both from the USGS (USGS QAWS-7) and the National Bureau of Standards, (NBS-1643b). The USGS QAWS-7 sample was spiked with 0, 30, and 60 $\mu\text{g L}^{-1}$ (ppb) Se by the method outlined in the next section. The tissue sample (NBS RM-50 Albacore Tuna), or lyophilized marine biological tissue, is designated as a research material and was obtained from the National Bureau of Standards (NBS).

Two vegetation samples (typha and algae) were obtained from Anresco Analysis Research Inc. (San Francisco, CA). These samples were analyzed by Anresco Inc. under a contract to the USBR in order to develop these materials for use as internal reference samples.

With the exception of the NBS water, none of the materials could be considered a certified standard reference material. However, multiple analyses enabled us to assign a most-probable value for selenium concentration in all samples. This most-

probable concentration was then used as the accepted value against which we measured the reliability of selenium determinations in the round-robin study.

All the samples were considered homogenized at the time of receipt at U.C. Davis. Twenty five g subsamples of sediment, 50 g of soil, 10 g of typha, 10 g of algae, and 17.5 g of tuna were weighed into acid-washed jars and sent to each laboratory. Ninety five g of each water was sent to each laboratory in acid-washed plastic containers with doubly sealed lids to prevent water vapor loss. Samples were identified by a code number only.

PREPARATION OF SELENIUM STANDARD AND SPIKED SAMPLES

1. Fifty mL of nitric acid (Ultrex) was added to a 500 mL volumetric flask containing about 400 mL of distilled and deionized water (DDW). The contents were swirled gently.
2. Five +/- 0.01 mL of NBS Se Standard (SRM-3149) containing 10.0 +/- 0.01 mg Se/mL in 10% (v/v) nitric acid was added to the 500 +/- 0.2 mL volumetric flask. The contents were mixed by swirling and diluted to the mark with DDW.
3. The final solution contained 100 +/- 0.2 ug Se/mL in 10% nitric acid. This solution was used to spike the USGS QAWS-7 water sample in the following manner:
 - (a) The 30 ppb Se addition was made by adding 300 uL of the Se standard (100 ppm) and 700 uL of a 10% nitric acid (Ultrex) blank to a 1L volumetric flask. The flask was first filled to the mark with QAWS-7 and then 1mL was removed to allow addition of the spike and blank.

- (b) The 60 ppb Se addition was similarly made using 600 uL Se standard and 400 uL blank per 1 L.
- (c) The zero ppb addition (QAWS-7) was prepared by filling a one L volumetric flask with QAWS-7 and then removing exactly 1.0mL. Then 1.0mL of the nitric acid blank was added back. This procedure insured that all the QAWS-7 samples had exactly the same acid matrix composition.

SELENIUM IN REFERENCE SAMPLES

Table 1 lists the round-robin samples, code numbers, and associated selenium values. Some discussion of these values and how they were obtained is necessary.

The NBS water (1643b) has a certified Se value. The certified value is based on methods of known accuracy or by two or more independent, reliable, analytical methods. The USGS QAWS-7 water sample was provided to the project with a selenium concentration range of 50-55 ppb. Therefore, this range was used both in computing the spike sample concentration and in comparing round-robin results from the participating laboratories.

Independent analysis of the USGS water sample by LAWR - U.C. Davis reported the selenium concentration as 53 +/- 2 ppb. This laboratory reported Se in the spiked samples to be 82.7 +/- 0.6 ppb and 113.7 +/- 6.5 ppb for the 30 ppb and 60 ppb addition samples, respectively.

The USGS Soil Standard has a Se concentration of 0.94 +/- 0.05 ug/g. This was obtained from thirty separate determinations by the USGS laboratory in Denver, Colorado. The USBR sediment Se

concentration was determined from 10 splits of the sample analyzed twice in two different jobs. As noted previously, these materials are internal reference samples that do not have certified values.

Selenium in the NBS tuna research material (RM50) was determined by four different laboratories using neutron activation and atomic absorption. The range was from 3.27 to 4.01 ug/g with a most probable value of 3.6 ± 0.4 ug/g.

Anresco Inc. prepared and analyzed the algae and typha samples through a separate contract with the USBR and reported Se values of 33.3 ± 0.3 and 95.1 ± 1.1 ug/g for the algae and typha samples, respectively.

NEUTRON ACTIVATION ANALYSIS

In addition to the laboratories participating in the round-robin, four additional laboratories were contracted to analyze the reference samples by neutron activation. The purpose of this was (1) to compare neutron activation analysis with the methods employed by the other laboratories, and (2) to help validate the Se concentrations reported for the non-certified reference materials because neutron activation is a method of reputed accuracy and reliability for selenium.

RESULTS OF THE SELENIUM ROUND-ROBIN

Table 2 presents the results of the selenium round-robin for all samples by each laboratory. Twenty nine laboratories were included in the initial study. Two laboratories officially withdrew (12 and 14) and two laboratories did not submit results

(3 and 27). Twenty four laboratories analyzed all four water samples, 16 analyzed the soil sample, 18 analyzed the sediment sample, 15 analyzed the tissue sample and vegetation samples. Ten laboratories analyzed all nine reference samples.

Table 2 shows that the range of reported results, the number of replications for each sample, and the methods used for selenium determination varied widely. This, coupled with the additional complication of having few samples with certified Se values, posed certain problems for statistical comparisons. In evaluating the data, we have used several statistical approaches which we believe accurately compare the data without sacrificing statistical rigor.

The first comparison consisted of determining the number of laboratories whose results fell within some reasonable interval about the accepted mean value. For the purposes of this study, we chose to use a value of +/- 12.5% of the accepted mean value. Thus the greatest acceptable difference in this data on any one sample from any two laboratories would be 25%. The results of this test are presented in Figures 1-9. It should be noted that this comparison included all laboratories except those that used neutron activation.

For water 6871, 16 of the 21 laboratories reported data within these limits with no obvious bias (Fig 1). Twelve of the 21 laboratories reported data within these limits for water sample 6872 with a very definite positive bias. Results for water samples 6873 and 6874 were similar with six outlying observations in each case and no apparent bias. Results for soil sample 6875 were all positively biased and out of range with one lone

exception, probably due to the fact that the level of selenium in this sample approaches the limit of detectability for the procedures used in these laboratories. Only two outlying values were observed for sediment sample 6876. Finally, results for tissue sample 6877 appeared positively biased with four outlying observations among the pool of eleven submitted results (Fig 7).

Selenium values reported for samples 6878 and 6879 were compared in a similar manner, except that the observations for each laboratory were compared against the means of the pooled laboratory data with outliers removed, since no accepted value existed for these samples. The results show that eight laboratories determined selenium in sample 6878 within 12.5% of the pooled mean with only three outlying observations. For sample 6879, three of twelve laboratory values fell within the 12.5% range.

Following are some further related findings:

- Overall, laboratories 6 and 11 were consistently high in their determination while 22 and 25 were consistently low.

- Laboratories 7, 13 and 18 were able to determine selenium in all the water samples with the most accuracy and precision.

- One laboratory (17) determined selenium in soil 6875 within the 12.5% range, while all but two determined selenium in sediment sample 6876. A single laboratory extracted samples 6875 and 6876, rather than exhaustively digesting them, and thus were not included in the analysis.

- Laboratories 10, 18, 20, and 21 reported the best estimates

of sediment selenium. For tissue sample 6877, seven laboratories reported values within 12.5% of the mean value (5a, 8, 13, 16, 20, 22, and 23). Overall, laboratories 13, 22, and 23 provided the best estimates of selenium in these samples.

The data were also analyzed by pooling the results of all laboratories to obtain a grand average. This pooled mean was then compared to the accepted values and tested for statistical significance. The first step in such a test was to determine the outliers from the pool of submitting laboratories. This was done using Grubb's test for outliers (Taylor, 1987). In this test, if a value in question (X_q) differs from the mean by more than some appropriate tabular value, T , of the known or assumed standard deviation, s , it may be rejected as an outlier. The appropriate equation is:

$$T = (X_q - \bar{X})/s$$

and X_q = value in question
 \bar{X} = mean of all values
 s = standard deviation
 T = tabular value

In this study, we chose to take no more than a 1% risk of rejecting a value. The tabular values for this level of risk ranged from 2.41 to 2.88 depending on the number of observations. In general, a single outlier was rejected from the data set by this test.

Next, the mean for each sample was calculated assuming that each value reported by each laboratory was similar with respect to precision or within appropriate control limits. The pooled laboratory results are presented in Table 4 for all laboratories except the neutron activation laboratories which are presented in

Table 5.

A comparison of the pooled means for all the data to the accepted values indicates that only water sample 6872 and soil sample 6875 were significantly different from the accepted values. The results for water sample 6872 were significantly different from the accepted value at the 95% confidence level, but not different at the (90%)^{? should this be 95%} level. The soil sample, on the other hand, had a selenium content approaching the limit of detectability for many of the procedures. Vegetation samples 6878 and 6879 were not compared in this fashion as noted previously, although it is of interest to know that sample 6879 (algae) had the greatest range of reported values as well as the widest distribution of reported values across the range of all the other samples (2.0-116 ug/g, Table 2).

Neutron activation results (Table 5) are somewhat more difficult to interpret. For the water samples, the pooled means were significantly higher than the accepted values. However, because of the large standard deviation, the pooled means were not significantly different than the accepted values. The neutron activation analysis appeared to provide better results for the solid samples, most likely because of the higher selenium concentrations in these samples. Although vegetation samples 6878 and 6879 had the widest range in reported values for the other methods of determination (Table 4), the neutron activation results for these samples gave a much tighter distribution (31-38 mgKg⁻¹ and 81-95 mgKg⁻¹ for typha and algae, respectively) indicating that this non-destructive method may be giving better estimates of tissue selenium than other methods that rely on

Careful and appropriate sample matrix destruction prior to analysis.

Another way of determining bias is to compare the results from laboratories that determined selenium by different methods. For example, one laboratory (20) determined selenium in water by first chelating then extracting the sample prior to analysis by atomic absorption spectrophotometry. If we compare these results to those obtained from continuous flow hydride generation (the most widely used method), we find that the extraction chelation method tends to give much higher selenium levels for water samples (Tables 6 and 8). No statistical test was used in comparing the two methods because only one laboratory used chelation extraction and other sources of error cannot be ruled out.

A similar comparison was made between batch hydride generation and continuous flow for the solid samples (Tables 7 and 8). Results were comparable between the two methods with the exception of sample 6879 (vegetation). Again no statistical significance can be attached since only one laboratory used batch hydride generation. The values reported for 6879 by continuous flow (76.7 ug/g) and batch hydride generation (95.1) may be different due to tissue digestion procedures rather than method of quantitation.

Other methods included x-ray fluorescence (laboratory 16), flameless atomic absorption (laboratories 5, 22, and 25), ICP (laboratory 19), plasma ICP hydride (laboratories 8 and 11), and fluorimetry (Lab 18). Table 9 illustrates the differences among

these methods. For example, x-ray fluorescence analysis of the solid samples appeared to give results comparable to the accepted values and agreed well with continuous flow hydride generation, ICP and manual fluorimetry. Water samples analyzed by continuous flow hydride generation or fluorimetry appeared to agree with the accepted values, and with each other, while ICP and flameless atomic absorption yielded high and low estimates, respectively when compared to the accepted values. The reasons for the high ICP values compared to the other methods and to the accepted values may be due to the low levels of selenium in the water samples, the wide range of the calibration curve, sample pretreatment methods or to the use of faulty standards. The low estimates observed for flameless atomic absorption methods in water are most likely due to loss of selenium during drying and ashing. Better recoveries are reported for this method in the solid samples because selenium is in the part per million range. However, there still appears to be significant loss of selenium in samples 6876, 6878, and 6879.

Another objective of the study was to determine some of the reasons for the variation in laboratory results. For the water samples, 6871-6874, most of the laboratories pretreated the samples in the same manner; that is, by acid digestion and selenium reduction with 6N HCl. Laboratories 19, 22, and 25, for example, reported low selenium values in at least 2 of the water samples. Laboratory 19 used a digestion procedure similar to those of the more successful laboratories and thus its results cannot be explained on the basis of sample pretreatment. Laboratories 22 and 25, on the other hand, determined selenium

after digestion in nitric acid with no HCl reduction step. This may explain the poor recovery of aqueous selenium by these laboratories. Another cause of poor selenium recovery by these laboratories may be related to the method of selenium detection. Most successful laboratories used hydride generation (ICP or AA) or fluorimetry.

For the solid samples, the wide variation in reported results is no doubt linked to both the difficulty of extracting selenium from the inorganic and organic matrices and the method of determination. Again laboratories using flameless atomic absorption techniques had the most difficulty probably due to interference from residual sample matrix components. Diminished performance of graphite furnace technique in the presence of high salt has been previously documented (Burau 1986). Since most laboratories attempting selenium in these materials used similar sample digestion procedures, the exact nature of the variation is difficult to ascertain.

EVALUATION OF LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

Another objective of this study was to document where appropriate the QA/QC programs of the participating laboratories and to suggest improvements to any or all of the existing laboratory protocols. In reviewing the QA/QC documents, it was evident that different laboratories had different ideas as to what constituted a quality assurance program.

In general, a quality assurance program will consist of methods of quality control and quality assessment. These methods

will attain and maintain acceptable laboratory performance, will allow evaluation of laboratory output, and will make laboratory data legally defensible. We have reviewed many QA/QC protocols from many diverse sources and have found no better guidelines than those suggested by Taylor (1987), thus most of the following suggestions have been taken from this excellent source. According to Taylor (1987) a detailed outline of a QA/QC program will have the following elements.

QUALITY ASSURANCE PROGRAM

Quality control through:

- suitable equipment and facilities
- competent staff-training programs
- good laboratory and measurement practice
- standard operating procedures
- protocols for specific purposes
- proper inspection/supervision
- good calibration and standardization techniques

Quality assessment through:

- statistical analysis
- documentation and control charts
- reference materials
- replication, spikes, surrogates
- audits and introspection

These elements are the criteria against which we compared the QA/QC programs submitted from each laboratory. It was assumed that suitable equipment and facilities existed at each laboratory and that competent personnel carried out the determinations. All the other criteria were evaluated based on what was received from each laboratory.

Eighteen of the 22 laboratories that submitted data, submitted some form of a QA/QC program. Of these only 10 laboratories met all of the criteria previously outlined. Overall, these laboratories were able to submit a quality assurance plan

in a self-contained document that was part of the laboratory's normal operating procedure.

Laboratories 1, 2, 4, 6, 11, 15, 16, and 18 considered QA/QC to consist of the use of replication, spikes, reference materials and statistical analysis in a non-formalized fashion. While these practices are essential for producing high quality data, the absence of a formalized method of control and /or the setting of appropriate and continuously updated control limits makes the detection and resolution of error a more difficult task.

Laboratory 4, indicated that it takes a research type attitude, rather than a routine one, towards its analysis requirements. This approach is quite acceptable especially for complex, non-routine type investigations. However, once confidence in a method has been established, it can only be properly validated through a formal QA program. In fact, this approach might be useful to the small research type laboratories which either do not process large numbers of samples routinely, or approach analysis in conjunction with a given research objective. Under these conditions, the following suggestions might be helpful in the development of an appropriate quality assurance plan.

- 1) Determine the size and diversity of the organization. Large operations concerned with narrowly defined programs are easily adapted to formal QA programs.

- 2) For small laboratories, or those with a varied workload, a critical study will often identify commonalities of a group of measurement operations for which generic QA practices may be applicable.

3) Research organizations can formalize recurring parts of their programs and substantially reduce the overall quality assurance effort in many cases.

To a certain degree this has been done by many of the research laboratories in this study. The large commercial laboratories, for example tended to have the best, and most formalized of the quality assurance plans, while the small research-oriented laboratories have little formalized plans outside of statistical control and quality assessment through the use of replication, spikes, surrogates and standard reference materials.

The foregoing should suggest that the type of quality assurance program used by any one organization should be tailored to the objectives of that organization. Each organization, however must have some type of implementable and defensible quality assurance plan. To correct deficiencies in this area, we recommend that a self appraisal be implemented which would allow us to assist each laboratory in improving its quality assurance plan and the quality of its data. Taylor (1987) has suggested the use of an extensive laboratory self-appraisal checklist presented here in an abbreviated form.

LABORATORY QUALITY ASSURANCE PROFILE

- [] 1. Laboratory QA Program
 - Written plan adopted/in use []
 - Definite but informal plan []
 - Informal-variable program []

- [] 2. Written Analytical Methodology
 - Exclusively []
 - Usually/for critical data []
 - Few or none used []

- [] 3. Control Chart Use

- | | | |
|-----|--|-----|
| | Maintained for all critical operations | [] |
| | Variable but significant use | [] |
| | Little or no use | [] |
| [] | 4. Uncertainty Limits for Data | |
| | Limits for all data output | [] |
| | For critical only | [] |
| | Minority of cases | [] |
| [] | 5. Reports/Proposals | |
| | Screened for QA aspects | [] |
| | Critical areas screened only | [] |
| | Variable/seldom done | [] |
| [] | 6. Facilities & Equipment Maintenance | |
| | Excellent | [] |
| | Good | [] |
| | Poor | [] |
| [] | 7. Records | |
| | Judged excellent by any standards | [] |
| | Some difficulties | [] |
| | Variable-need improvement | [] |
| [] | 8. Audits | |
| | Regular | [] |
| | Occasional | [] |
| | Few/never | [] |
| [] | 9. Laboratory Function | |
| | Strictly research | [] |
| | Research and processing | [] |
| | Strictly processing | [] |

Laboratories could use the checklist and compare their responses to a statement of purpose and goals for the laboratory (i.e. research vs. production type laboratories) in order to maintain internal consistency. Another approach might involve the assigning of numerical values to the checklist response boxes which would be used to rank laboratory QA/QC in the context of type of laboratory. Assistance could then be provided to help each laboratory develop appropriate QA/QC protocol.

SUMMARY

The selenium round robin data showed that 17 of the

21 laboratories attempting to determine selenium in water reported values near the accepted values. Pooled laboratory results indicated that most samples were within the range of the accepted values. Water samples analyzed by hydride generation or manual fluorimetry, appeared to give better results than other methods. Different sample pretreatment procedures accounted for some of the variation among laboratories using similar selenium detection methods as well as for a given laboratory reporting high or low results.

The pooled results for soil sample 6875 were higher than the accepted value, while that for the sediment was in the range of the accepted value. Little variation among laboratories was evident for these two samples. Flameless atomic absorption methods yielded the lowest values for selenium in the sediment sample.

Pooled laboratory results of tissue sample 6878 (typha) compared well against neutron activation results, while 6879 (algae) appeared to be one of the more difficult samples to analyze. Pooled laboratory results for this sample were lower than that reported by neutron activation and appears to be linked to sample matrix destruction methodology. Results from this sample had the widest range in reported values (2.0 -111 ug/g). Again the flameless atomic absorption technique yielded the lowest estimates of total selenium.

Neutron activation results were inconclusive due the wide range and high variance associated with the reported values. It appears that longer counting times need to be implemented for

successful selenium determination, especially in the part per billion range.

The following recommendations are offered:

1) Laboratories attempting selenium determination in environmental samples, should use either continuous flow hydride generation (with atomic absorption or ICP spectrometry) or fluorimetry. If graphite furnace techniques are used, special consideration should be given to sample matrix interferences especially in high salt and high sulfate samples.

2) Laboratories engaged in analytical work need to improve or establish stricter controls on data analysis and output. It is particularly important that each laboratory run enough replicates in order to establish the reliability of results.

3) Laboratories routinely engaged in selenium determination should, as a matter of control, use a combination of standard reference materials, spiked samples, surrogates, and blind samples from outside sources.

REFERENCES

1. Taylor, John K. (1987) Quality Assurance of Chemical Measurements. Lewis Publishers, Michigan. 328p.
2. Burau, R.G. (1986) Laboratory performance for selenium analysis of reference water samples. Report to the Central Region Water Quality Control Board.

Table 1. Selenium concentrations in the reference sample materials.

Sample Type	Code	Origin	Accepted (Se)*
Water			
QAWS-7 + 60ppb	6871	USGS-UCD	112.5 (2.5) ppb
NBS -1643b	6872	NBS	9.87 (0.51)
QAWS-7 + 30ppb	6873	USGS-UCD	82.5 (2.5)
QAWS-7 + 0ppb	6874	USGS-UCD	52.5 (2.5)
Soil			
San Joaquin Std	6875	USGS	0.94 (0.05)ug/g
Sediment			
KS-1-5	6876	USBR	63.0 (5.9)
Tissue			
Albacore Tuna	6877	NBS	3.6 (0.4)
Vegetation			
Typha	6878	USBR	** 35.9 (3.56)
Algae	6879	USBR	** 86.7 (30.9)

 Values in parantheses are standard deviations.

*Only the NBS water sample has a certified Se value. The USGS samples are considered to be internal reference values only.

**Means determined from pooled laboratory data.

Table 2. Analytical data from the SJVDP selenium round-robin.

Laboratory Code	112		113		Sample		82.5		52.5	
	6871	6872	6873	6874	n	\bar{X}	s.d.	n	\bar{X}	s.d.
$\Delta 7.0$	1	1	116	1	11	1	83	1	54	
$\Delta 11.7$	2	6	108 (2.0)	6	9.2 (0.8)	6	79 (4.0)	6	49 (2.0)	
$\Delta 24.1$	4	6	103.5 (1.3)	5	11.5 (1.9)	5	78.0 (1.7)	5	54 (3.2)	
$\Delta 55$	6	11	134.9 (6.9)	8	13.0 (2.1)	11	98.0 (6.1)	11	66 (2.9)	
$\Delta 3.9$	* (7) *	2	111 (6.0)	2	10.0 (0.4)	2	85 (0.4)	2	52.8 (0.4)	
$\Delta 16.1$	8	4	118 (5.0)	4	11 (3.0)	4	87 (5.0)	4	57 (4.0)	
$\Delta 8.2$	(9)	3	112 (3.0)	3	9.7 (1.5)	3	86 (3.0)	3	57 (9.0)	
$\Delta 6.5$	(10)	2	114 (0.7)	3	10.8 (.23)	3	83.5 (.43)	3	55.1 (.32)	
$\Delta 69.6$	11	3	138 (6.0)	3	16.5 (0.5)	3	102 (5.0)	3	70 (2.1)	
$\Delta 2.1$	* (13) *	3	112 (1.2)	3	10 (1.2)	3	81 (1.2)	3	52 (0.6)	
$\Delta 22.1$	15	3	118 (2.0)	3	11 (0.2)	3	92 (4.0)	3	58 (1.0)	
$\Delta 13.45$	16	5	116.5 (6.6)	5	11.34 (.33)	5	85.2 (4.84)	5	57.4 (.92)	
$\Delta 8.1$	(17)	6	111 (2.0)	6	13 (1.0)	6	81 (2.0)	6	55 (1.0)	
$\Delta 5.5$	(18)	4	114.6 (2.3)	4	10 (0.2)	4	84.2 (1.2)	4	53.6 (1.1)	
$\Delta 56.4$	19	3	89.7 (1.4)	3	8.3 (0.2)	3	62.7 (1.2)	3	53.8 (2.4)	
$\Delta 34.1$	20	3	118 (1.0)	3	18 (1.0)	3	93 (4.0)	3	62 (5.0)	
$\Delta 48$	21	1	80	2	9.9	1	67	1	53	
$\Delta 172.9$	22	3	42 (17)	3	9 (1.0)	3	23 (4.0)	3	10 (0.7)	
$\Delta 29.1$	23	3	100 (0.0)	3	12 (0.0)	3	71 (5.2)	3	49 (1.0)	
$\Delta 13.1$	24	3	120 (10)	3	10 (0.0)	3	85 (5.0)	3	55 (0.0)	
$\Delta 36.1$	25	3	97 (10)	3	17 (6.0)	3	77 (6.0)	3	44 (7.0)	
$\Delta 30.6$	26*	3	100 (5.0)	3	8.1 (2.1)	3	71 (3.0)	3	47 (1.0)	
$\Delta 233.1$	28*	3	170 (20)	3	60 (10)	3	150 (10)	3	110 (10)	
$\Delta 34.8$	29*	3	118 (20)	3	<118	3	98.7 (13)	3	65.1 (14)	

* Neutron activation

175.6
57.5
233.1

Table 2. (cont.) Analytical data from the SJVDP selenium round-robin.

Laboratory Code Number	n	0.94		63			3.6		
		6875 soil \bar{X}	s.d.	6876 sediment \bar{X}	s.d.	6877 Tuna \bar{X}	s.d.		
Δ 53.1 2	1	0.018		10.8					
Δ 4.0 5a	3	1.5 (1.5)		66 (1.0)		4.0 (1.4)			
Δ 4.8 5b	3	1.7 (.06)		60 (2.0)		4.6 (0.2)			
6						20 4.3 (0.2)			
8						4 4.05 (.08)			
10				3 65 (1.7)		6 4.1 (.09)			
Δ 3.5 11	4	1.628 (.115)		4 66.28 (6.89)					
13	3	1.07 (.02)		3 59.7 (2.4)		3 3.63 (.22)			
16				3 59 (5.0)		3 4.0 (.04)			
17	8	1.0 (.10)		6 55 (1.0)					
Δ 1.8 18	4	1.36 (.04)		4 62.3 (0.8)		4 4.24 (.11)			
19	3	<0.6		3 67 (10)					
Δ 2.1 20	4	1.19 (.07)		2 64.4 (3.8)		3 3.23 (.06)			
21	2	1.1		2 64		2 <0.3			
Δ 3.3 22	3	1.2 (0.4)		4 32 (2.5)		3 3.6 (2.6)			
Δ 7.3 23	3	1.2 (0.1)		3 56 (2.1)		3 3.6 (0.2)			
Δ 45.6 24	3	1.25 (.18)		3 56 (1.0)					
25	1	0.32		1 19		1 2.6			
Δ 4.4 26	3	0.95 (.57)		3 59 (13)		3 3.2 (0.8)			
28	3	2.4 (0.1)		3 57 (3.0)		3 4.7 (0.5)			
Δ 8.6 29	3	<17.0		3 58 (4.0)		3 4.3 (2.4)			
Δ 6.6									

Table 2. (cont.) Analytical data from the SJVDP selenium round-robin.

Laboratory Code Number	Sample					
	n	6878 \bar{X}	35.9 <i>cattal</i> s.d.	n	6879 \bar{X}	86.7 <i>algae</i> s.d.
5a	3	41.0	(3.0)	3	91.0	(5.0)
5b	3	39	(4.0)	3	110	(19)
10	6	36	(1.7)	6	87	(2.1)
11	4	38.53	(1.97)	4	106.0	(4.24)
13	3	36.6	(0.15)	3	97.9	(2.7)
16	3	37	(3.0)	3	116	(8.0)
18	4	38.0	(0.9)	4	110.6	(3.1)
20	3	33.3	(0.3)	3	95.1	(1.1)
21	2	36		2	52	
22	3	29	(1.5)	3	11	(1.4)
23	3	31	(0.0)	3	77	(6.1)
25	1	6.2		1	2.0	
26	3	31	(7)	3	81	(23)
28	3	38	(2)	3	95	(2)
29	3	37.7		3	92.5	(0.7)

Table 3a. Selenium round-robin results for water sample reference material.

Lab Code	Sample								$\sum dev $
	6871		6872		6873		6874		
	(ppb)	%dev.	(ppb)	%dev.	(ppb)	%dev	(ppb)	%dev.	
1	116	3.1	11.0	11.4	83.0	0.6	54.0	2.9	18.0
2	108	-4.0	9.2	-7.0	79.0	-4.0	49.0	-7.0	22.0
4	104	-7.6	11.5	16.5	78.0	-5.0	54.0	2.9	32.0
6	135	20.0	13.0	31.7	98.0	18.0	66.0	25.7	18.4
7	111	-1.4	10.0	1.3	85.0	3.0	52.8	-0.6	6.3
8	118	4.9	11.0	11.4	87.0	5.4	57.0	8.6	10.3
9	112	-0.1	9.7	-2.0	86.0	4.2	57.0	8.6	14.9
10	114	4.9	10.8	9.4	83.5	1.2	55.1	5.0	10.5
11	138	4.0	16.5	67.0	102.0	23.6	70.0	33.3	11.1
13	112	-0.1	10.0	1.3	81.0	-2.0	52.0	-1.0	4.4
15	118	4.9	11.0	11.4	92.0	11.5	58.0	10.5	38.2
16	117	4.0	11.3	14.5	85.2	3.3	57.4	9.3	31.1
17	111	-1.4	13.0	31.7	81.0	-2.0	55.0	4.8	34.9
18	114	1.3	10.0	1.3	84.2	2.1	53.6	2.1	6.3
19	90	-20	8.3	-16.0	62.7	-24	53.8	2.3	12.1
20	118	4.9	18.0	82.0	93.0	12.7	62.0	18.1	10.7
21	80	-29	9.9	0.0	67.0	-19	53.0	1.0	11.1
22	42	-13	9.0	-9.0	23.0	-72	10.0	-80.0	7.1
23	100	-11	12.0	21.6	71.0	-14	49.0	-7.0	53.2
24	120	6.7	10.0	1.3	85.0	3.0	55.0	4.8	15.3
25	97	-14	17.0	72.0	77.0	-7.0	44.0	-16.0	11.1

Table 3b. Selenium round-robin results for soil, sediment, and tissue reference sample material.

Lab Code	6875		6876		6877	
	(ug/g)	%dev.	(ug/g)	%dev.	(ug/g)	%dev.
5a	1.50	59.6	66.0	5.0	4.00	11.1
5b	1.70	81.0	60.0	-5.0	4.60	27.8
6	-		-		4.30	19.4
8	-		-		4.05	12.5
10	-		65.0	3.1	4.10	13.8
11	1.63	73.4	66.3	5.2	-	
13	1.07	13.8	59.7	-5.3	3.63	1.0
16	-		59.0	-6.4	4.00	11.1
17	1.00	6.4	55.0	-13.0	-	
18	1.36	44.7	62.3	-2.0	4.24	17.8
19	-		67.0	6.3	-	
20	1.19	26.5	64.4	2.2	3.23	-10.0
21	1.10	17.0	64.0	1.6	-	
22	1.20	27.7	32.0	-49.0	3.60	0.0
23	1.20	27.7	56.0	-12.0	3.60	0.0
24	1.25	33.0	56.0	-12.0	-	

Lab Code	6878		6879	
	(ug/g)	%dev.	(ug/g)	%dev.
5a	41.0	14.2	91.0	4.9
5b	39.0	8.6	110.0	26.9
10	36.0	0.3	87.0	0.3
11	38.5	7.2	106.0	22.3
13	36.6	1.9	97.9	12.9
16	37.0	3.1	116.0	33.8
18	38.0	5.8	110.6	27.6
20	33.3	-7.2	95.1	9.7
21	36.0	0.3	52.0	-40.0
22	29.0	-19.2	11.0	-87.0
23	31.0	-13.6	77.0	-12.2
25	6.2	-82.7	2.0	-97.8

Table 4. Pooled laboratory results** - selenium round-robin.

Sample	Range	n	Mean (outliers rejected)	Accepted
Water				
6871	80-138	20	*111.6 (13.4)	110- 115
6872	8.3-18	21	11.5 (2.65)	9.87 (0.51)
6873	62.7-102	20	*83.0 (9.47)	80 - 85
6874	44-70	20	*55.4 (5.75)	50 - 55
Soil				
6875	1-1.7	11	1.29 (0.23)	0.94 (0.05)
Sediment				
6876	10.8-67	16	*53.9 (17.4)	63.0 (5.90)
Tissue				
6877	2.6-4.6	12	*3.83 (0.54)	3.60 (0.40)
Vegetation				
6878		?	35.9 (3.56)	?
6879		?	86.7 (30.9)	?

** Excluding neutron activation results.

* Not significantly different from accepted values at the 95% level of probability.

Table 5. Results of neutron activation analysis.

Sample	Range	n	Mean	Accepted
Water				
6871	100-170	9	129.3 (36.4)	112.5 (2.5)
6872	8.1-60	9	34.1 (36.7)	9.87 (.51)
6873	71-150	9	106.6 (40.1)	82.5 (2.5)
6874	47-110	9	74.0 (32.4)	52.5 (2.5)
Soil				
6875	0.95-2.4	9	1.68 (1.03)	0.94 (.05)
Sediment				
6876	57-59	9	58 (1.0)	63 (5.9)
Tissue				
6877	3.2-4.7	9	4.07 (.78)	3.6 (0.4)
Vegetation				
6878	31-38	9	35.6 (3.96)	
6879	81-95	9	89.5 (7.47)	

Table 6. Selenium round-robin results. Selenium determined by atomic absorption spectrometry - chelation/extraction method.

Sample	# of labs	n	Mean -----ug/mL-----	Accepted
Water				
6871	1	3	118 (1)	112.2 (2.5)
6872	1	3	18 (1)	9.87 (.51)
6873	1	4	93 (4)	82.5 (2.5)
6874	1	6	62 (5)	52.5 (2.5)

Table 7. Selenium round-robin results. Selenium determined by atomic absorption spectrometry - batch hydride generation method.

Sample	# of labs	n	Mean ---(ug/g)---	Accepted
Soil				
6875	1	4	1.19 (.07)	0.94 (.05)
Sediment				
6876	1	2	64.4 (3.8)	63.0 (5.9)
Tissue				
6877	1	3	3.23 (.06)	3.6 (0.4)
Vegetation				
6878	1	3	33.3 (0.3)	
6879	1	3	95.1 (1.1)	

Table 8. Selenium round-robin results. Selenium determined by atomic absorption spectrometry - continuous flow hydride generation.

Sample	# of Labs	Mean	Accepted
----- (ug/mL) -----			
Water			
6871	16	110.7 (12.0)	112 (2.5)
6872	16	11.3 (1.89)	9.87 (0.51)
6873	16	82.4 (7.41)	82.5 (2.5)
6874	16	54.3 (4.82)	52.5 (2.5)
----- (ug/g) -----			
Soil			
6875	5	1.16 (0.17)	0.94 (0.05)
Sediment			
6876	6	59.5 (4.23)	63.0 (5.90)
Tissue			
6877	4	3.85 (0.27)	3.60 (0.40)
Vegetation			
6878	4	34.9 (2.62)	
6879	4	78.5 (19.6)	

Table 9. Comparison of different methods used to determine selenium in different samples.

Sample	Hydride c.f.	X-ray fluor.	ICP hyd.	Fluor.	Flameless AA
6871	110.7	-	138	115	42.0
6872	11.3	-	16.5	10.0	9.0
6873	82.4	-	102	84.2	23.0
6874	54.3	-	70.0	53.6	10.0
6875	1.16	-	1.63	1.36	1.18
6876	59.5	59.0	66.3	62.3	47.7
6877	3.85	4.00	-	4.24	3.92
6878	34.9	37.0	38.5	38.0	33.3
6879	78.5	116	106	111	63.8

Figure 1. Laboratory results for water sample 6871

112 $\mu\text{g/L}$

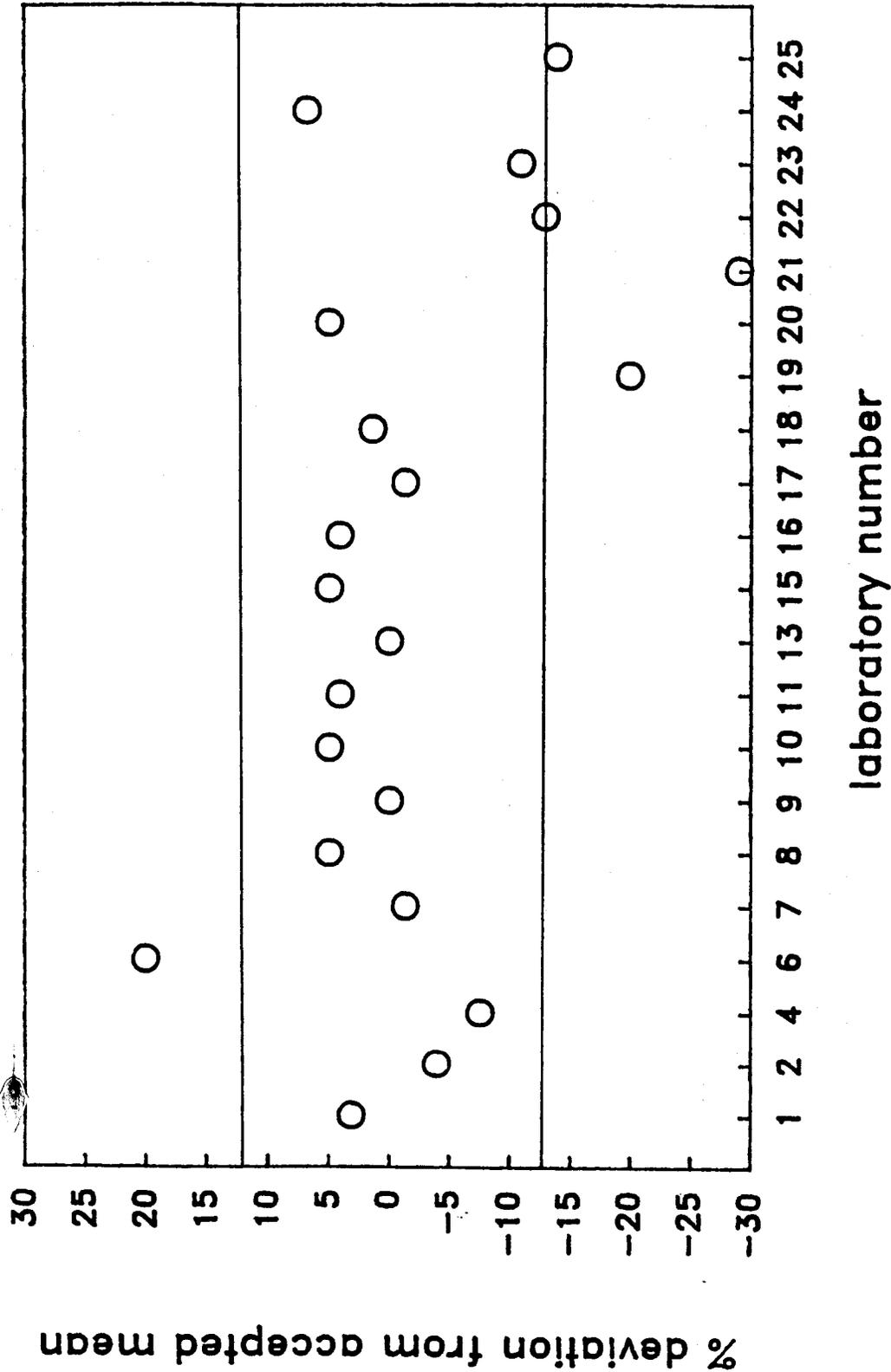


Figure 2. Laboratory results for water sample 6872

9.87 $\mu\text{g/L}$

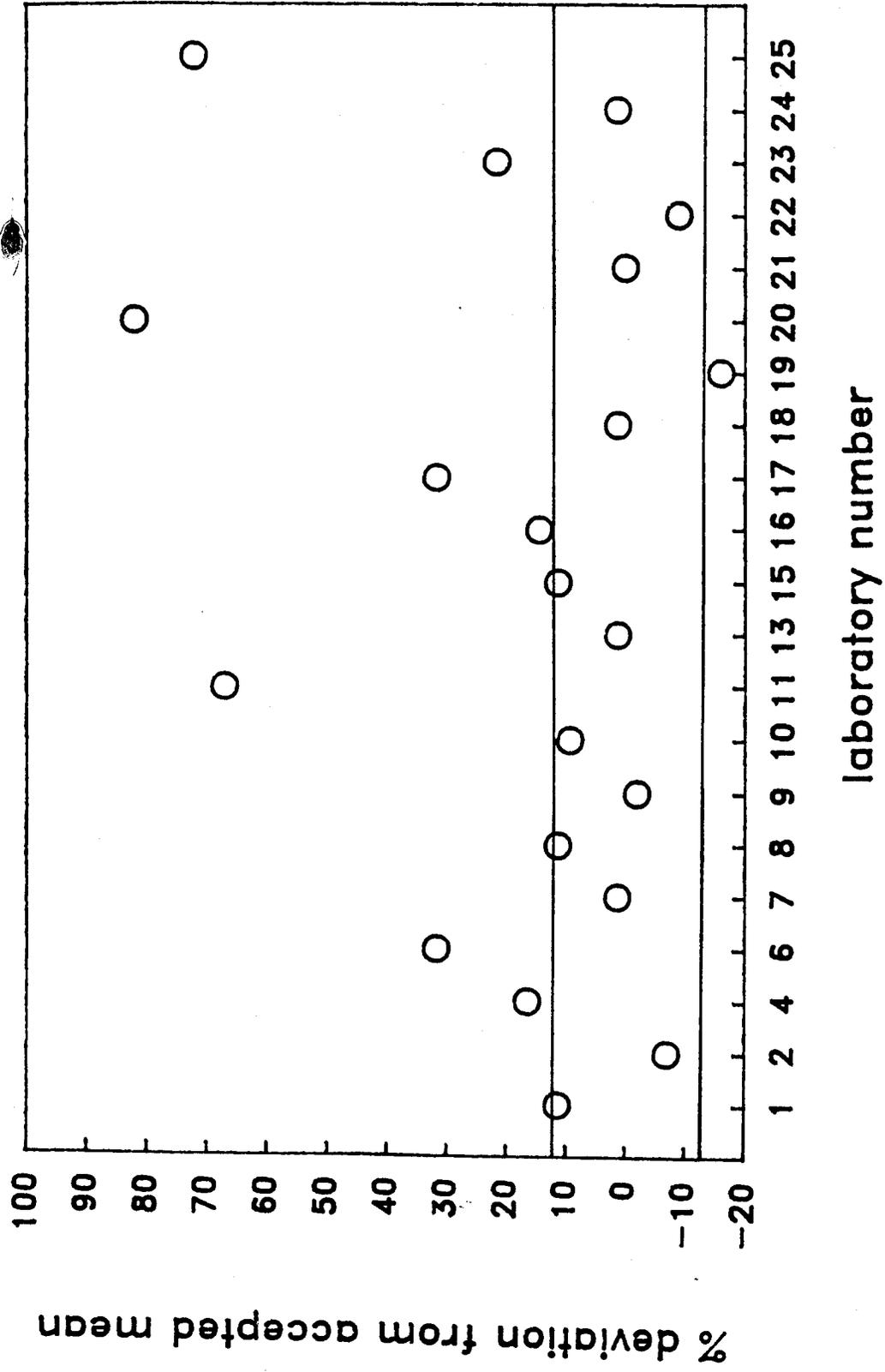


Figure 3. Laboratory results for water sample 6873

82.5 $\mu\text{g/L}$

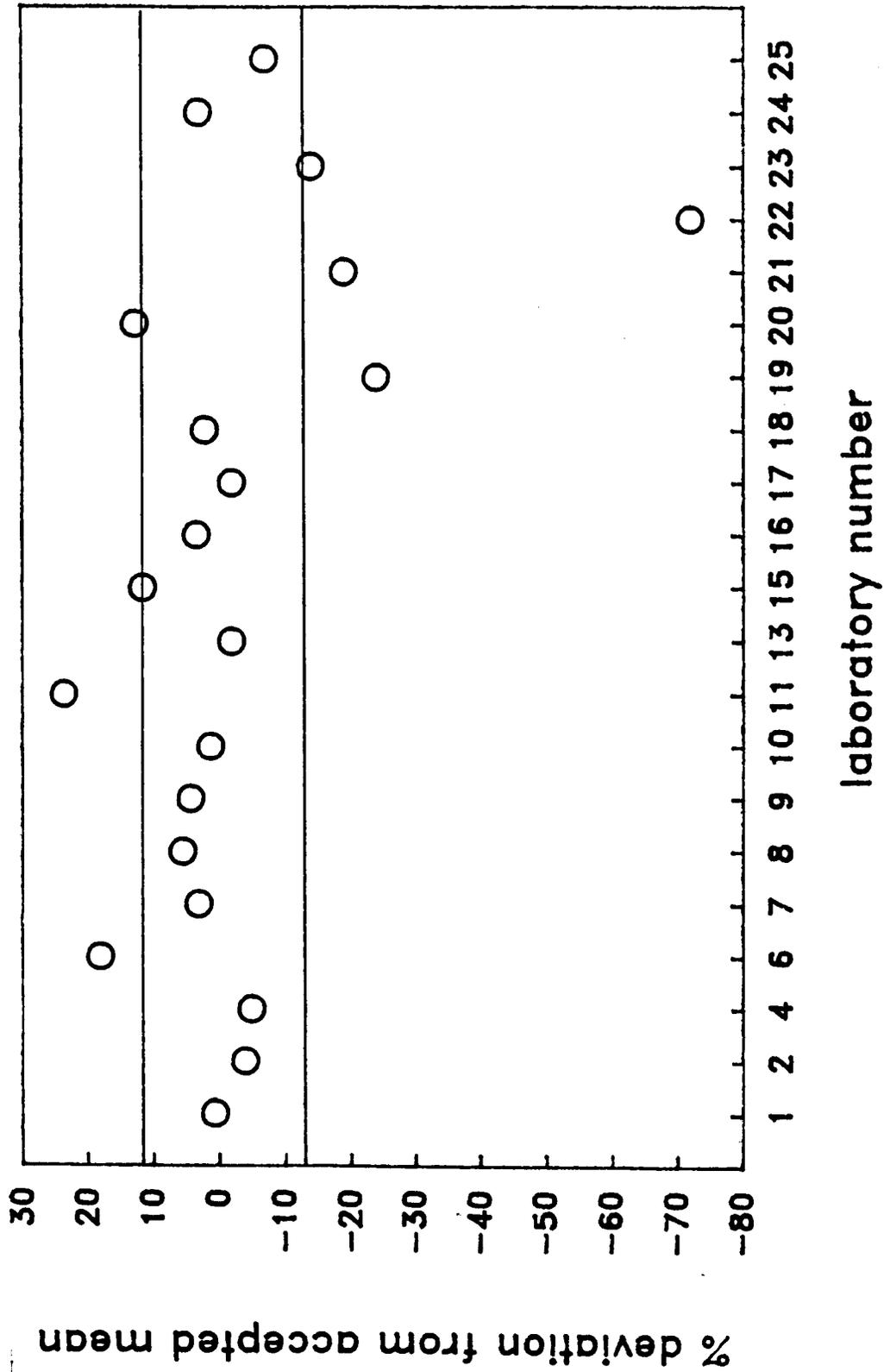


Figure 4. Laboratory results for water sample 6874

52.5 mg/L

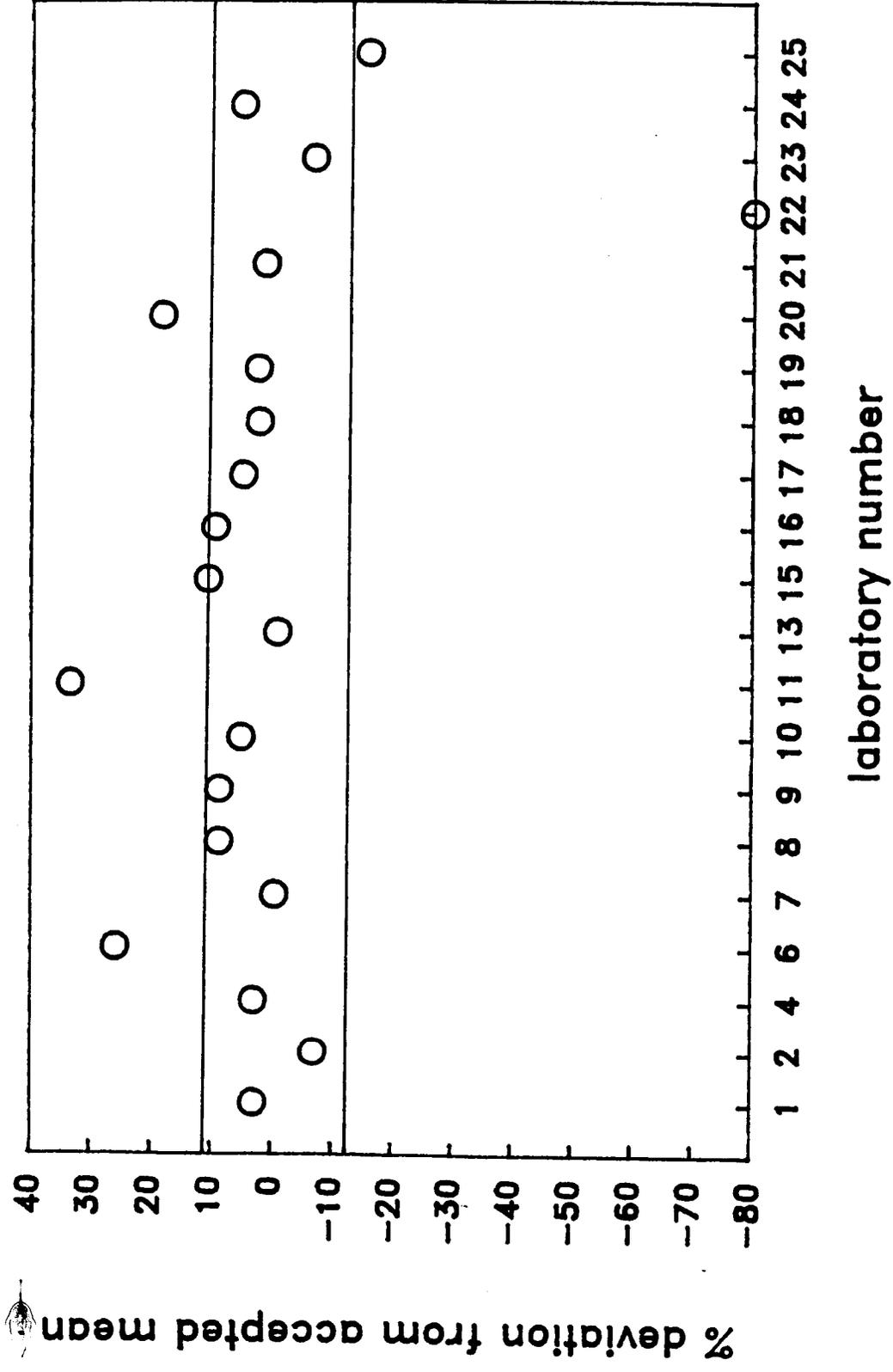


Figure 5. Laboratory results for soil sample 6875

0.9 mg/g

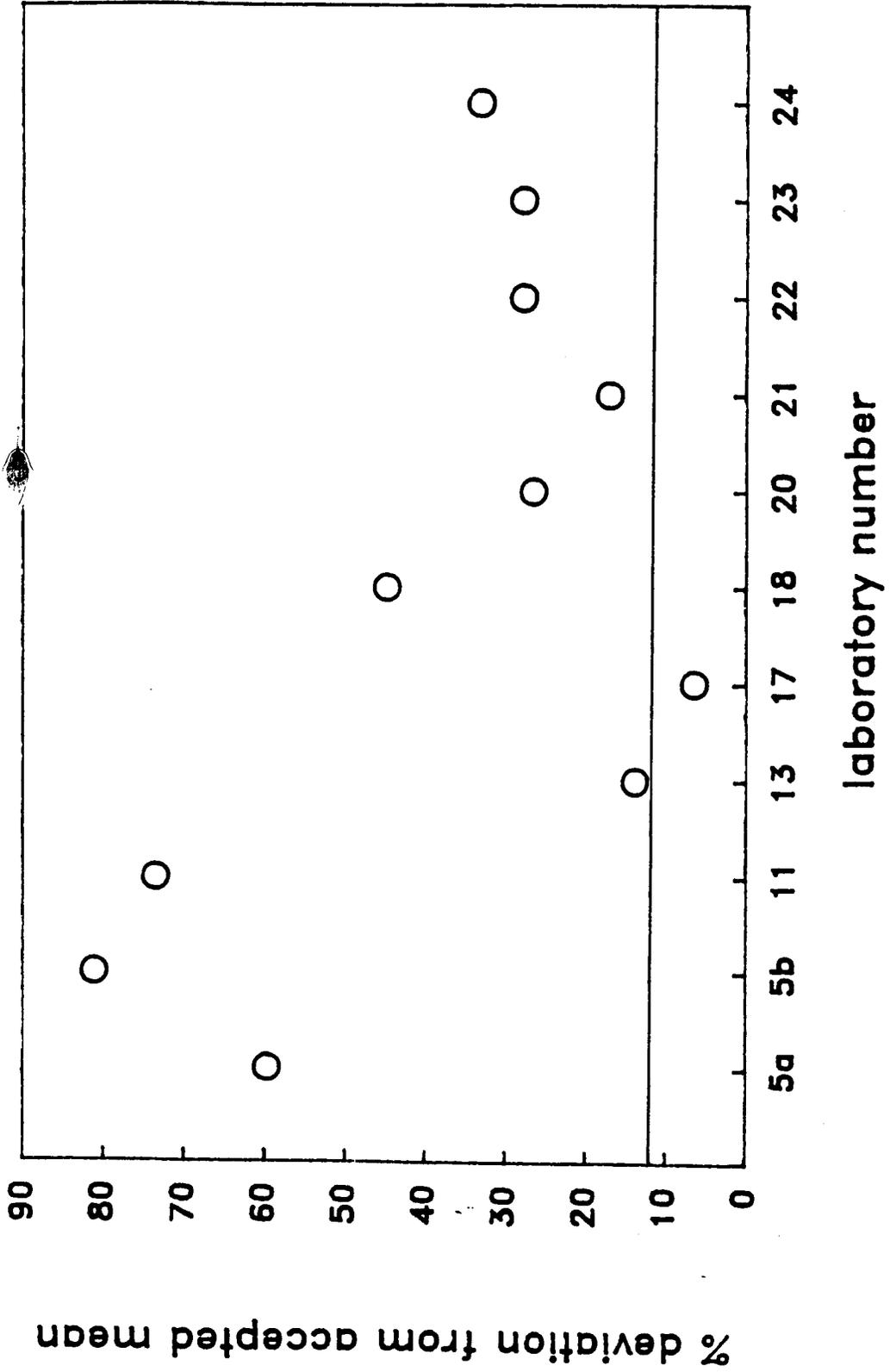


Figure 6. Laboratory results for sediment sample 6876

63 mg/g

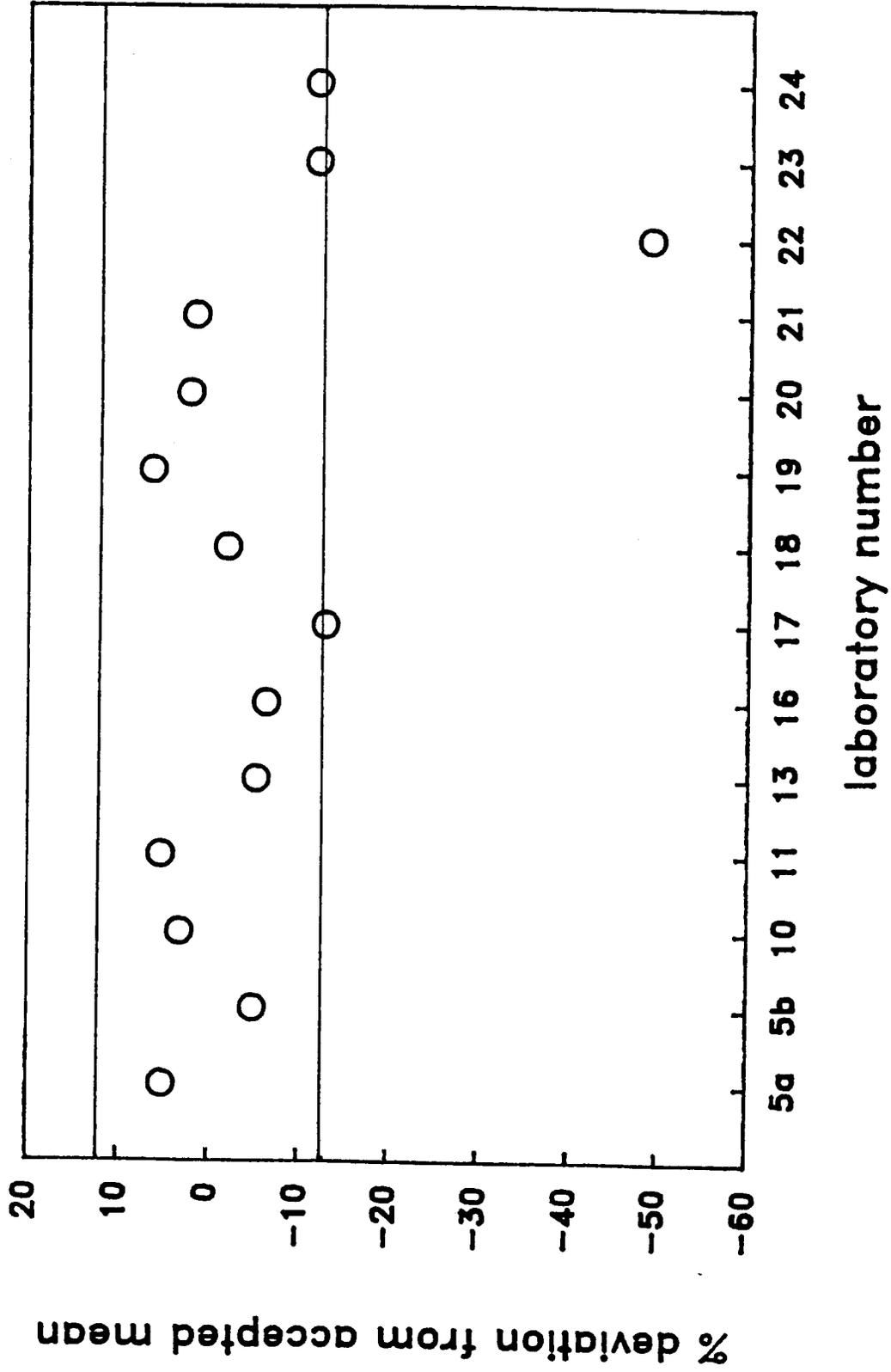


Figure 7. Laboratory results for tissue sample 6877

3.6 $\mu\text{g/g}$
Tma

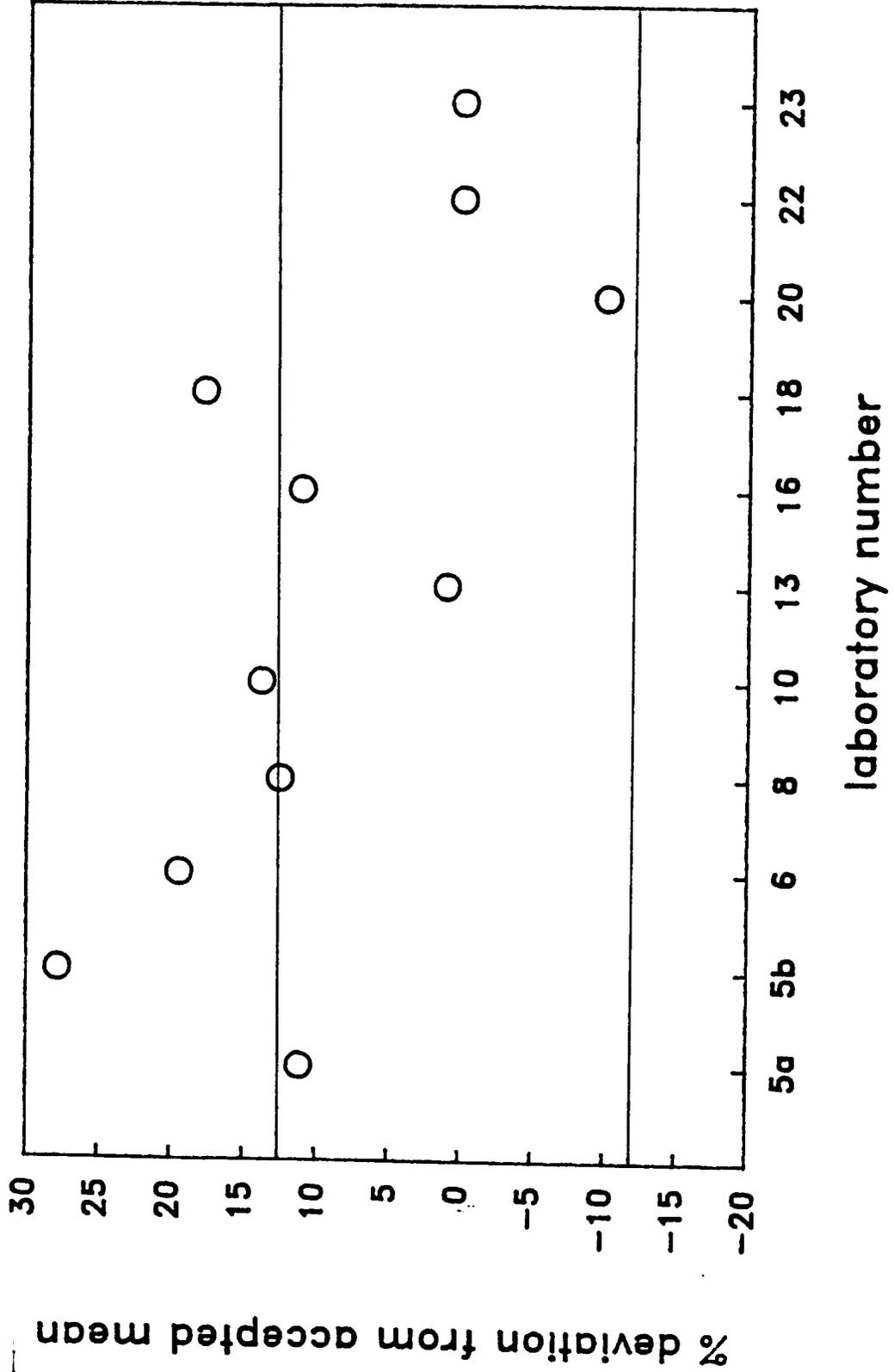


Figure 8. Laboratory results for vegetation sample 6878

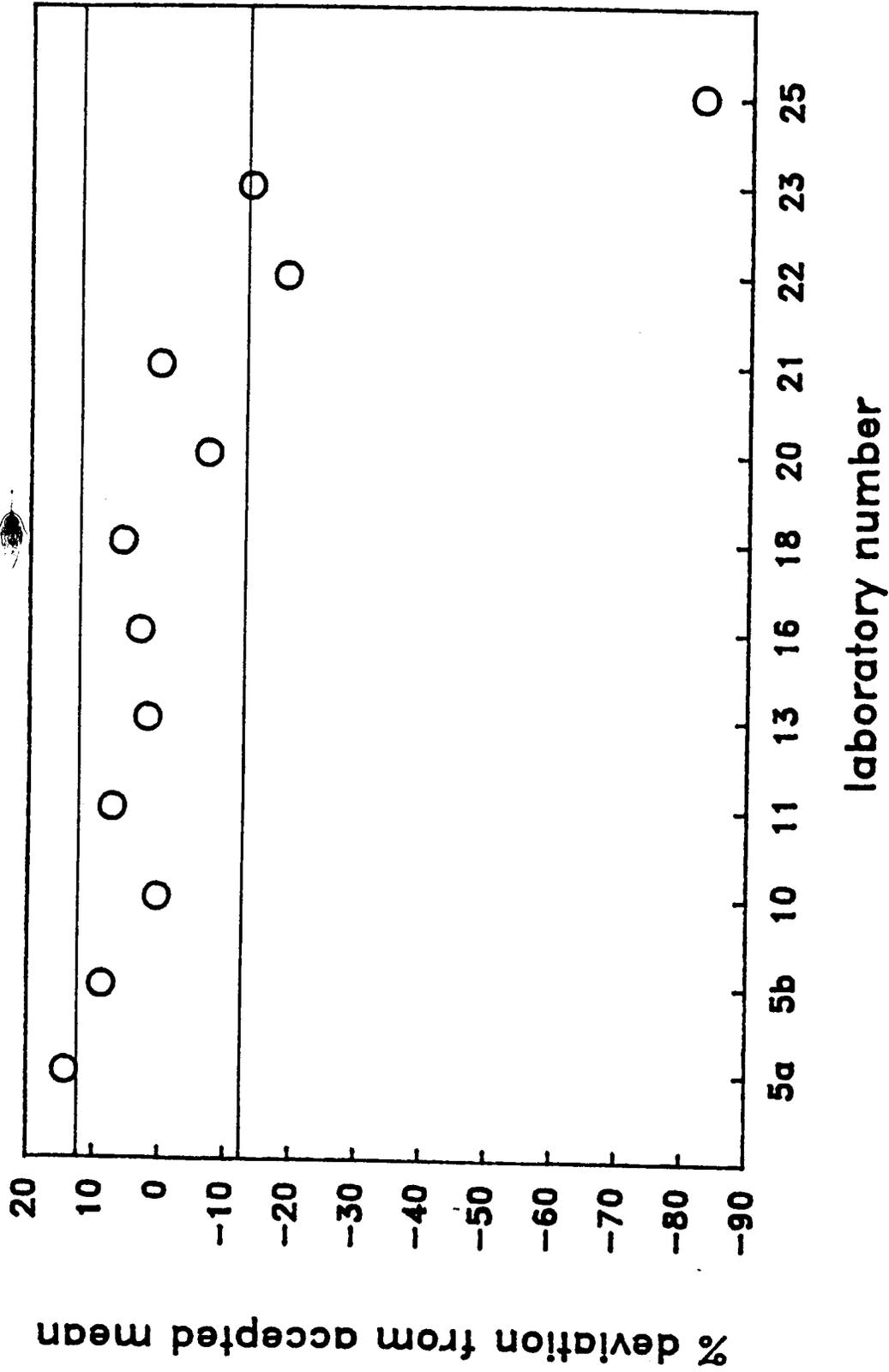


Figure 9. Laboratory results for vegetation sample 6879

