Sediment Grain Size: Results of an Interlaboratory Intercalibration Experiment

Most coastal benthic monitoring programs include biological measurements (e.g., community composition), chemical measurements (e.g., sediment chemistry), and physical measurements (e.g., sediment grain size). Physical measurements are used to distinguish changes in community structure caused by anthropogenic impacts from changes caused by natural factors, such as wave energy and substrate type. Sediment grain size is a measure of substrate type and an important determinant of benthic community structure. Since trace metal and organic contaminants are generally associated with the fine fraction of sediment, grain size is also used to normalize sediment chemistry data.

Southern California Coastal Water Research Project (SCCWRP) hosted a workshop on sediment grain size analysis in September 1993. The workshop brought together participants from the various wastewater outfall monitoring programs in Southern California to discuss the analytical techniques used for measuring sediment grain size. The objective was to find a consistent method that could be used by everyone.

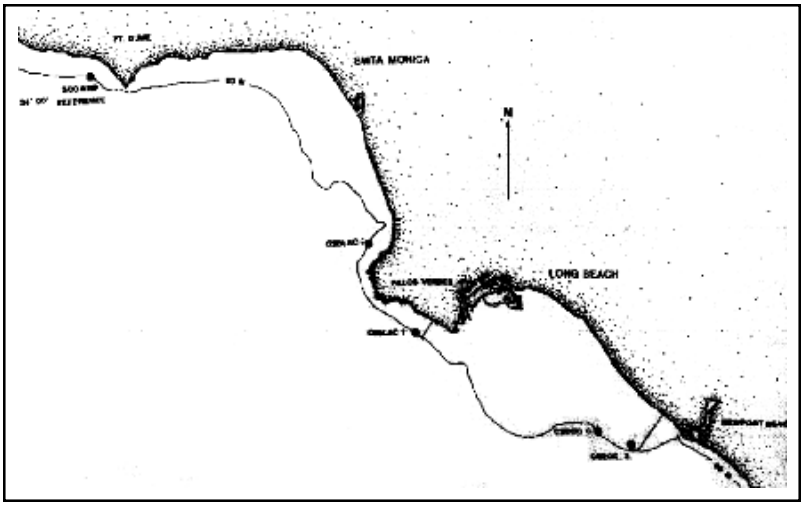
It became apparent during the workshop that there were significant differences in instrumentation and sample preparation among the participants. Most participating agencies measured sand and gravel with sieves, and measured silts and clays with pipettes (Plumb 1981). However, the City of San Diego used a laser particle analyzer to measure particles <1.0 mm in diameter and MBC Applied Environmental Sciences, Inc. used hydrometers to measure silt and clay. The City of Los Angeles and SCCWRP removed organic material from the sample prior to analysis while other participants did not.

Since there was no *a priori* procedure to determine which method was preferable, nor to determine how analytical differences affected the results, the group decided to conduct an interlaboratory intercalibration experiment. The results of this intercalibration experiment are reported here.

MATERIALS AND METHODS

Sediments were collected with a 0.1 m^2 modified Van Veen grab from County Sanitation Districts of Orange County (CSDOC) stations ZB2 (CSDOC2) and C (CSDOCC), and County Sanitation Districts of Los Angeles County (CSDLAC) stations 7C (CSDLAC7) and 0C (CSDLACC) on December 6, 1993 (Figure 1). Approximately 3 kg of sediment were collected from the top two centimeters of several grabs at each station. The sediment was thoroughly homogenized, placed into containers, and stored on ice for transport back to CSDOC. A reference sediment was also distributed to the laboratories for analysis. It was collected on October 1992 at SCCWRP Reference Station R15 (Word and Mearns 1979, Thompson *et al.* 1987) and maintained dry at SCCWRP.

FIGURE 1. Location of stations sampled in the experiment.



Seven laboratories participated in the intercalibration experiment: the City of San Diego, Wastewater Chemistry Lab (San Diego); the City of Los Angeles, Hyperion Treatment Plant (Hyperion); Horiba, Inc.; Kinnetics Laboratories, Inc. (KLI); MBC Applied Environmental Sciences, Inc. (MBC); MEC Analytical Systems, Inc. (MEC); and the Southern California Coastal Water Research Project (SCCWRP).

KLI, MEC, and SCCWRP used sieves to separate sediment fractions >63µm and pipette analysis to measure smaller fractions. Hyperion sieved the sediment through 2.0 mm, 63µm, and 38µm screens, and performed pipette analysis on the residual material. MBC used sieves for

sediment fractions >63µm and hydrometer analysis (ASTM D 422-63) to measure smaller fractions. San Diego and Horiba used a Horiba Model LA-900 laser analyzer to measure sediment particles <1.0 mm. They measured 74 size classes of particles; however, San Diego summed the data into one-phi intervals (phi = - [ln(particle diameter)/ln(2)]).

In laser analysis light scattering is used to count particles of a given size. In hydrometer and pipette analysis, the weight of material remaining in suspension is measured. The size of material in suspension is calculated from the theoretical full velocity of the particle.

The number of sample aliquots analyzed varied among the laboratories (Table 1). Only three replicates were used in the data analysis. The data from Hyperion for digested samples differed; the aliquots were run in two batches separated by three months. For Hyperion, two data points were used from the first run and one data point was used from the second run.

Laboratories that digested samples used hydrogen peroxide to remove organic material from the sediment. In addition, MEC digested samples CSDOC2 and CSDOCC with acetone. Detailed descriptions of the analytical techniques used by each laboratory are found in Sediment Grain Size Intercalibration Committee (1994).

The percent weight of sample in each size class was graphed on the midpoint of the size range except for the largest and smallest sizes measured. The smallest measurement was the material less than the size indicated on the x-axis; the largest measurement was the material greater than the size indicated on the x-axis. Since the laser analyzer only measured particles <1 mm diameter, the percent weight for each size class from the pipette analysis was recomputed for the comparison between the laser and pipette analyses.

RESULTS

Interlaboratory Comparison of Pipette/Sieve Analysis (Undigested Samples)

Measurement variability within laboratories variation was generally less than 1.5% (Figure 2); the maximum sample standard deviation was 2.9%. However, there was considerable variation among laboratories in the shape of the size distribution. The shape of the curve was better defined when more size intervals were measured.

The apparent differences among laboratories are reduced when the data were presented as a cumulative distribution (Figure 3). The curves for MEC and KLI were nearly identical. The curve for SCCWRP was similar for grain sizes <0.063 mm, except that there was considerably less material in the smallest size interval for three of the samples. MEC measured 10-15% of the sample in the 0.002 mm size class, a size not measured by SCCWRP. SCCWRP measured more material than MEC in the 0.004 and 0.0078 mm size classes (Figure 2). The portion of the SCCWRP curve for grain size >0.063 mm was poorly defined because only two sieve sizes were used. The curve

	LABORATORY						
SAMPLE	HYP[a]	HOR[b]	KLI[c]	MBC[d]	MEC[e]	SD[f]	SCC[g]
Digested							
SCCWRP	4	0	0	3	3	0	5
CSDOC2	4	0	0	3	3	0	5
CSDOCC	4	0	0	3	3	0	5
CSDLAC7	4	0	0	3	3	0	5
CSDLACC	4	0	0	3	3	0	5
Undigested							
SCCWRP	2	5	3	3	3	3	5
CSDOC2	2	5	3	0	3	3	5
CSDOCC	2	5	3	0	3	3	5
CSDLAC7	2	5	3	0	3	3	5
CSDLACC	2	5	3	0	3	3	5

[a]Hyperion Treatment Plant
[b]Horiba
[c]Kinnetics Laboratories, Inc.
[d]MBC Applied Environmental Sciences, Inc.
[e]MEC Analytical Systems, Inc.
[f]City of San Diego, Wastewater Chemistry Lab
[g]Southern California Coastal Water Research Project

TABLE 1. The number of aliquots of each sample analyzed by each laboratory. All aliquots were run at the same time except for the digested samples analyzed by Hyperion; Hyperion ran two aliquots in each of two runs.

FIGURE 2. Normal size distribution curves for undigested samples measured with pipette/sieve analysis.

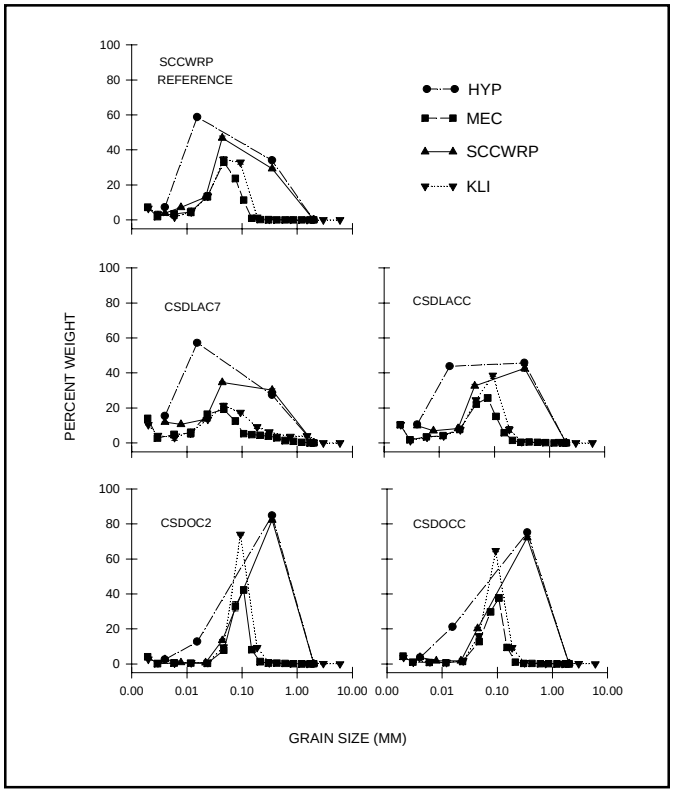
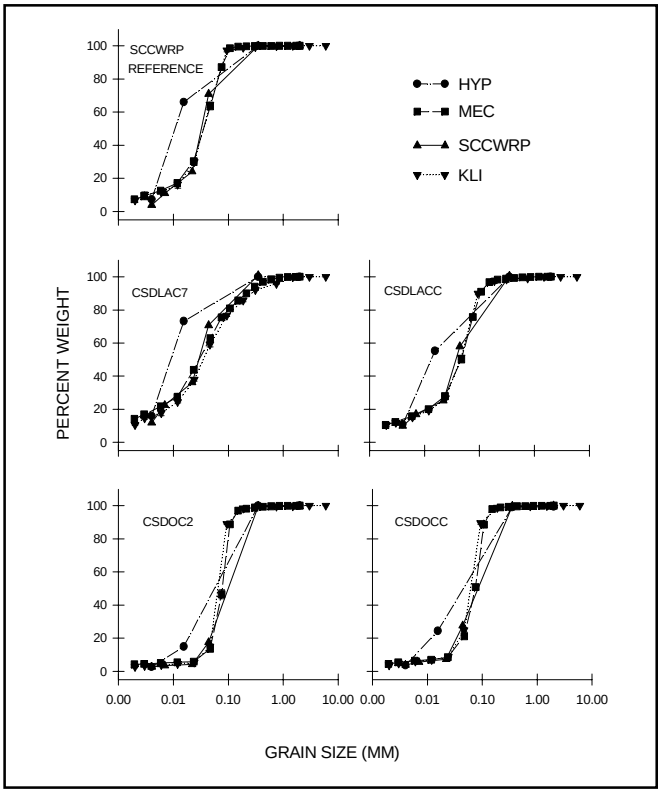


FIGURE 3. Cumulative size distribution curves for undigested samples measured with pipette/sieve analysis.



for Hyperion was poorly defined because only gravel, sand, silt and clay were measured.

To compare the results among laboratories, the distributions were computed as percent gravel, sand, silt and clay (Figure 4). There was relatively good agreement among the laboratories for samples CSDOCC and CSDOC2, which were 70-80% sand; the maximum difference was 6-10%. However, for the other samples, there was as much as 16-18% difference in the results. In each case, SCCWRP measured the most silt and MEC the least; KLI and Hyperion were intermediate. The difference in the percent silt was reflected in the other size classes; that is, MEC had proportionately more sand and clay than SCCWRP.

Laser vs. Pipette/Sieve Analysis

To reduce the effect of size intervals on the comparison between laser (San Diego) and pipette/sieve (KLI and MEC) analyses, the data were plotted at one-phi intervals (Figure 5). For grain size <0.063 mm, laser analysis measured more material than pipette analysis, except in the smallest size class. For larger grain sizes, the shapes of the distributions were generally similar between laser and pipette. However, in sample CSDLAC7, pipette analysis measured more material in size classes >0.1 mm. In samples CSDOC2 and CSDOCC, pipette analysis measured most of the material in one size class while the laser analysis distributed the peak across two size classes.

The cumulative distributions were compared between laser analysis (San Diego and Horiba) and pipette/sieve analysis (MEC and SCCWRP). For grain size <0.01 mm, SCCWRP was nearly identical to Horiba and San Diego (Figure 6). MEC measured more material <0.01 mm than the other three laboratories. For grain sizes between 0.016 and 0.032 mm, SCCWRP and MEC measured less material than Horiba or San Diego in three samples. In the other two samples, the results from the four laboratories were similar.

For grain sizes >0.63 mm, the distributions for San Diego and SCCWRP were poorly defined because relatively few size intervals were measured. The results for sample CSDLACC were similar between MEC and Horiba. In samples SCCWRP-REF, CSDOC2, and CSDOCC, the size distribution for MEC was offset to the left; more material was measured in the low end of the distribution. In sample CSDLAC7 the curve for Horiba was offset to the left; more material was measured in smaller size classes.

The difference between San Diego and Horiba was the same order of magnitude as the difference between Horiba

FIGURE 4. Percent gravel, sand silt and clay measured in undigested samples by pipette/sieve analysis.

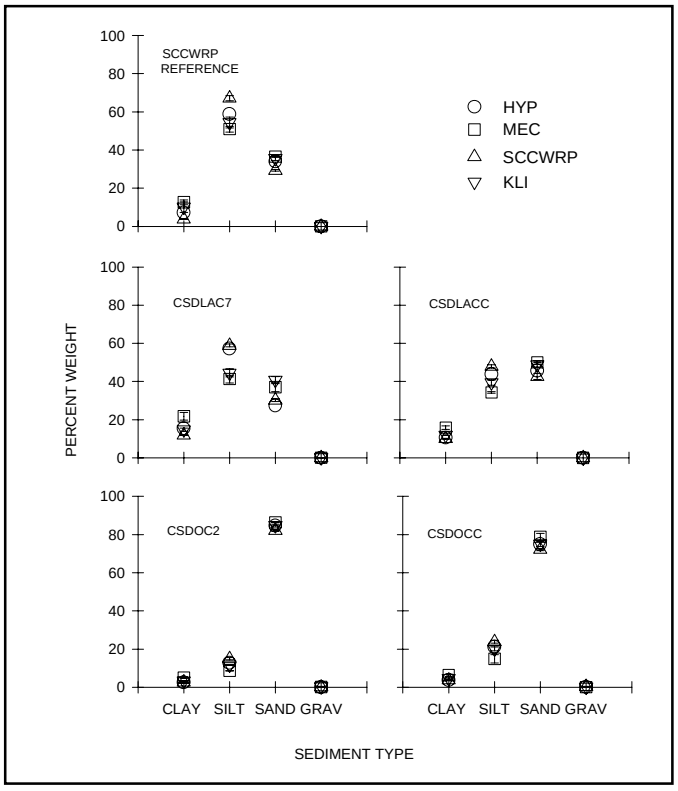


FIGURE 5. Normal size distribution curves of undigested samples measured by San Diego using laser analysis and by KLI and MEC using pipette/sieve analysis.

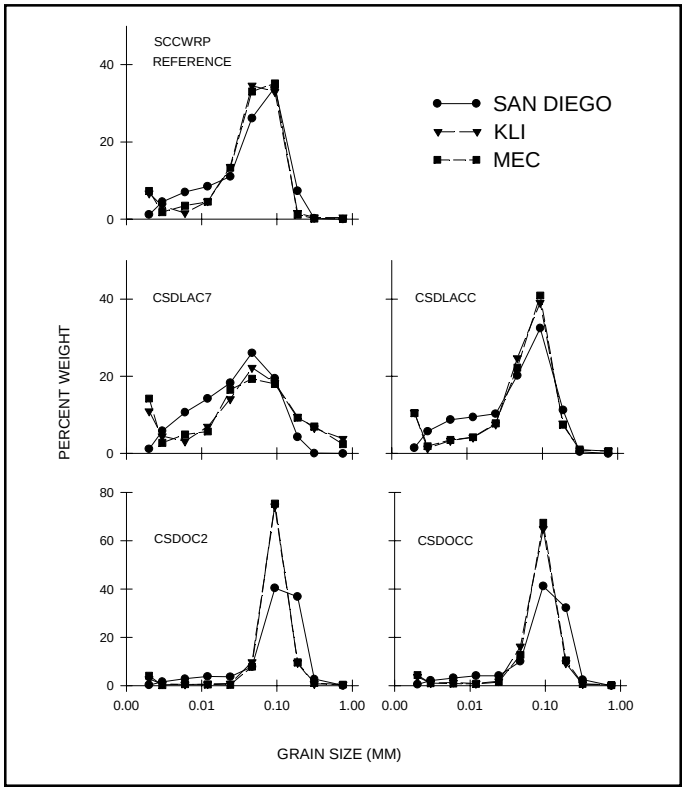


FIGURE 6. Cumulative size distribution curves of undigested samples measured by San Diego and Horiba using laser analysis and by MEC and SCCWRP using pipette/sieve analysis.

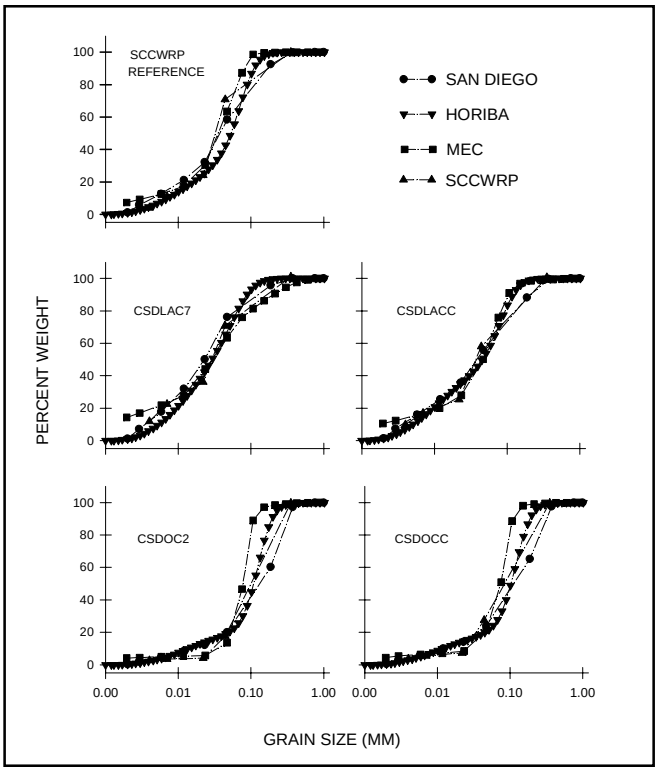


FIGURE 7. Comparison of cumulative size distribution curves of undigested samples measured by San Diego with data summed to one-phi intervals and by Horiba summed and not summed to one-phi intervals.

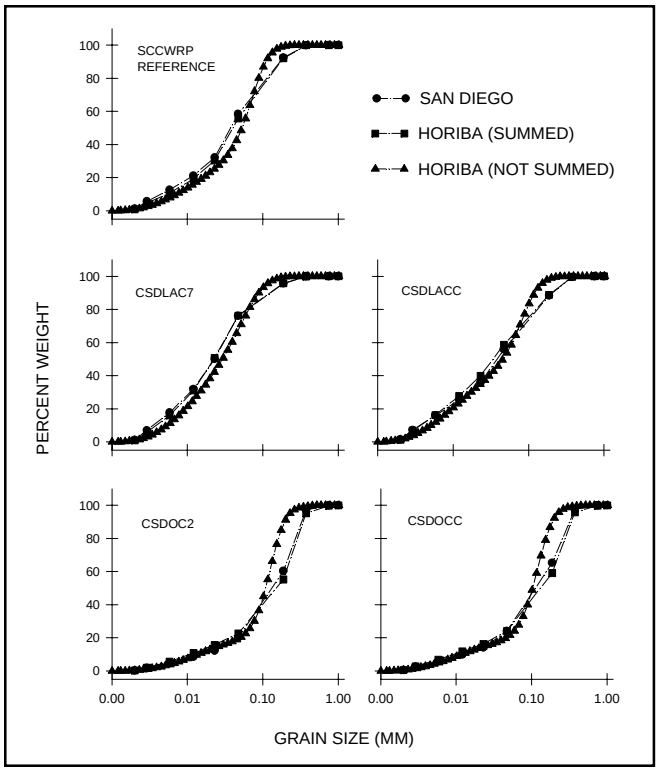


FIGURE 8. Normal size distribution curves of samples measured by San Diego and Horiba using laser analysis with data summed to one-phi intervals.

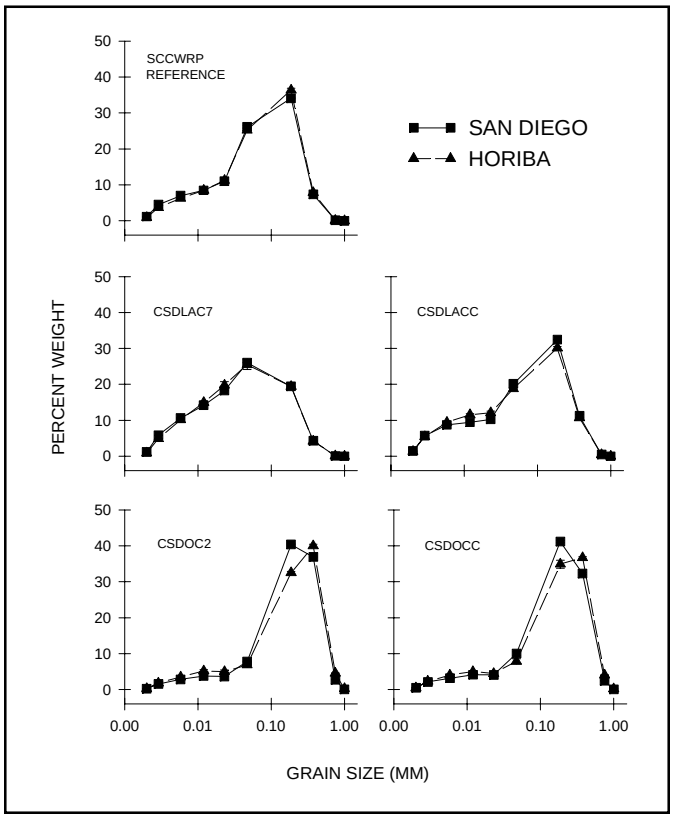
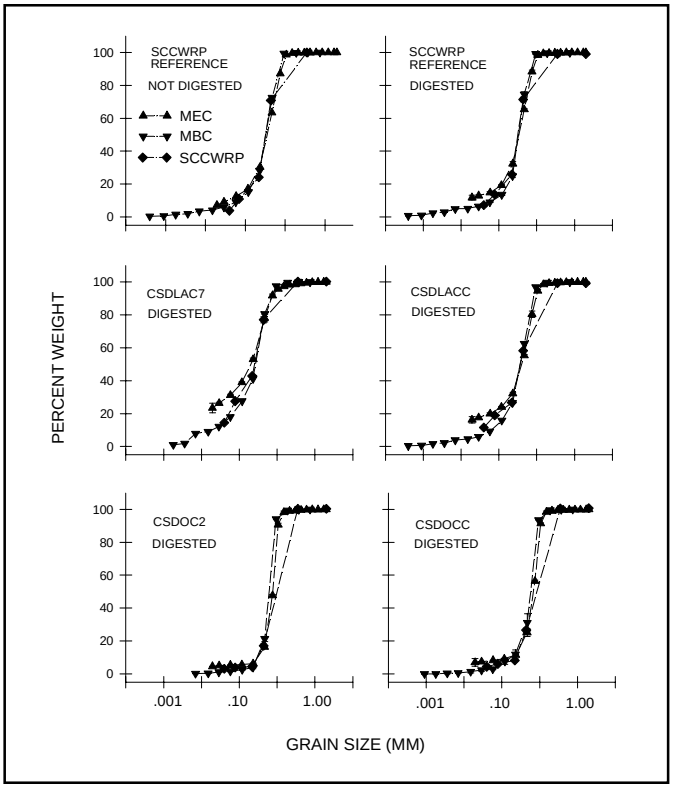


FIGURE 9. Cumulative size distribution curves of samples measured by MBC using hydrometer/settling tube analysis and by MEC and SCCWRP using pipette/ sieve analysis.



and MEC (Figure 6). However, when the Horiba data were summed to match the San Diego data (Figure 7), the difference was primarily caused by collapsing the data into one-phi intervals. The maximum difference between the summed distribution data of Horiba and San Diego was generally 2% (Figure 8). However, for grain sizes 0.25 and 0.50 mm in samples CSDOC2 and CSDOCC, the difference was 3-8%.

Hydrometer/Sieve Analysis vs. Pipette/Sieve Analysis

Data produced using hydrometers and sieves (MBC) were compared to data produced using pipettes and sieves (MEC and SCCWRP). Only data for samples with comparable treatments are presented (Table 1). The sieve analysis results from MEC and MBC were similar for grain sizes >0.063 mm (Figure 9). The distribution produced by SCCWRP was poorly defined in this range because fewer intervals were measured. For grain sizes <0.063 mm, the distributions produced by SCCWRP and MBC were similar for the most part. However, MEC measured more material than MBC and SCCWRP for grain sizes <0.01 mm. The difference was primarily due to one size class, the smallest size measured by the pipette (Figure 10).

Effect of Digestion

Hyperion, MEC, and SCCWRP measured sediment grain size on all samples with and without hydrogen peroxide digestion; MEC also digested two samples (CSDOC2 and CSDOCC) with acetone. Digestion had little effect on the coarsest samples (CSDOC2 and CSDOCC; Figures 11 and 12). In the other samples, digestion generally increased the amount of material in the smallest size class. The smallest size class increased by 4-9% in the MEC samples and by less than 3% in the SCCWRP samples. Digestion had the largest effect on sample CSDLAC7. The digestion by MEC decreased the amount of sand-sized (0.063-2.0 mm) particles, narrowed the peak in the silt range (0.0078-0.63 mm), and increased the amount of material in the smallest size class (0.002 mm). The digestion by SCCWRP decreased the amount of sand-sized particles and increased slightly the amount of material in the two smallest size classes (0.004 and 0.0078 mm).

FIGURE 10. Normal size distribution curves for sample SCCWRP (digested) and sample CSDLAC7 (digested) measured by MBC using hydrometer/settling tube analysis and by MEC using pipette/sieve analysis.

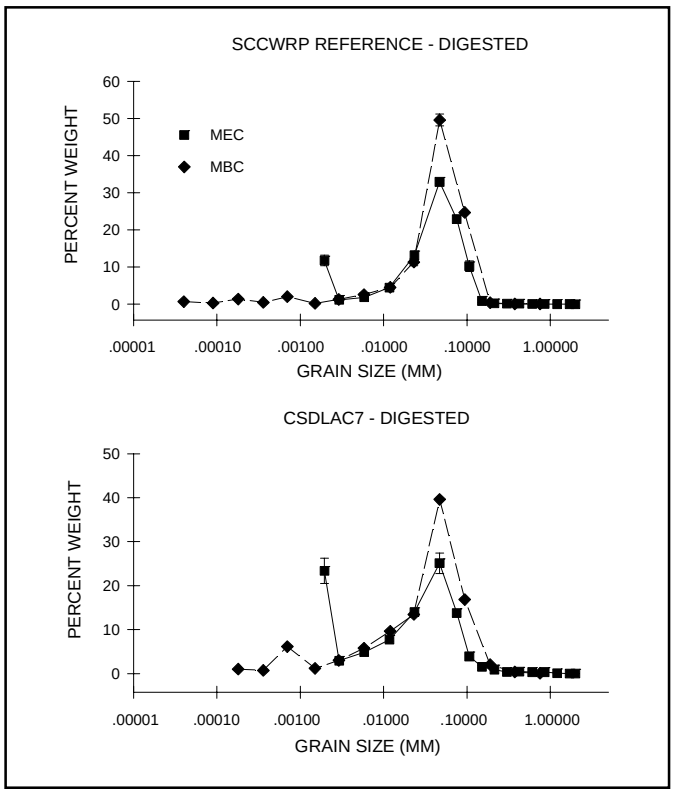


FIGURE 11. Normal size distribution curves measured by MEC for undigested samples and samples digested with hydrogen peroxide and acetone.

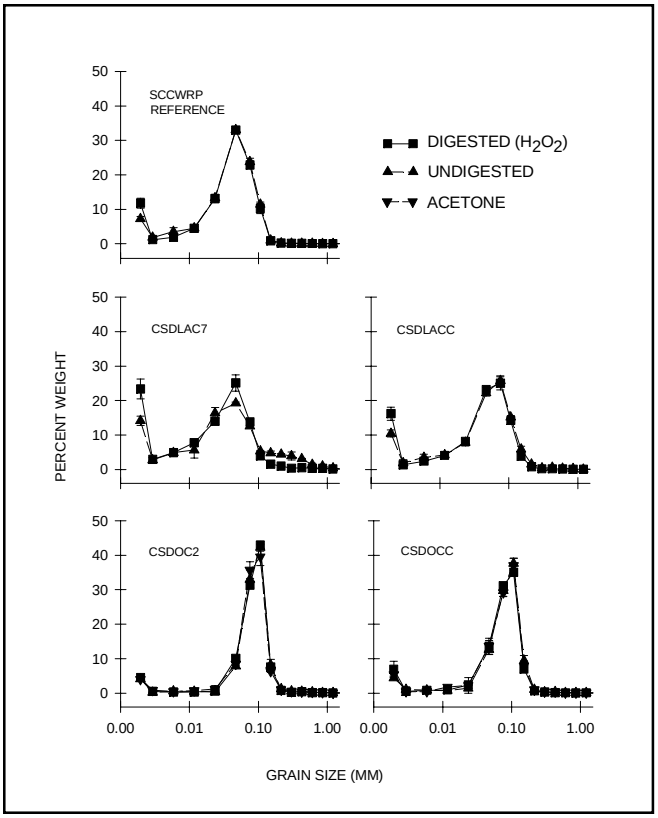
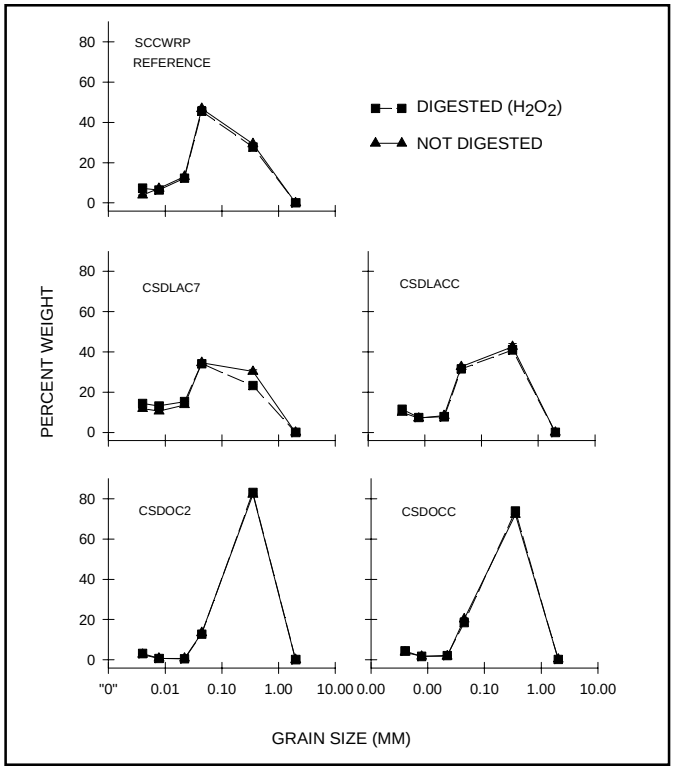


FIGURE 12. Normal size distribution curves measured by SCCWRP for undigested samples and samples digested with hydrogen peroxide.



DISCUSSION

The sediment intercalibration experiment was designed to: 1) determine variation in measurement precision: a) within a laboratory, b) between laboratories using the same method, and c) between laboratories using different methods; and 2) determine the effect of digestion on the size distributions. Within laboratory measurement errors were low. The maximum standard deviation for sample replicates was 2.9% for pipette/sieve, 5.4% for hydrometer/sieve, and 0.5% for laser analysis.

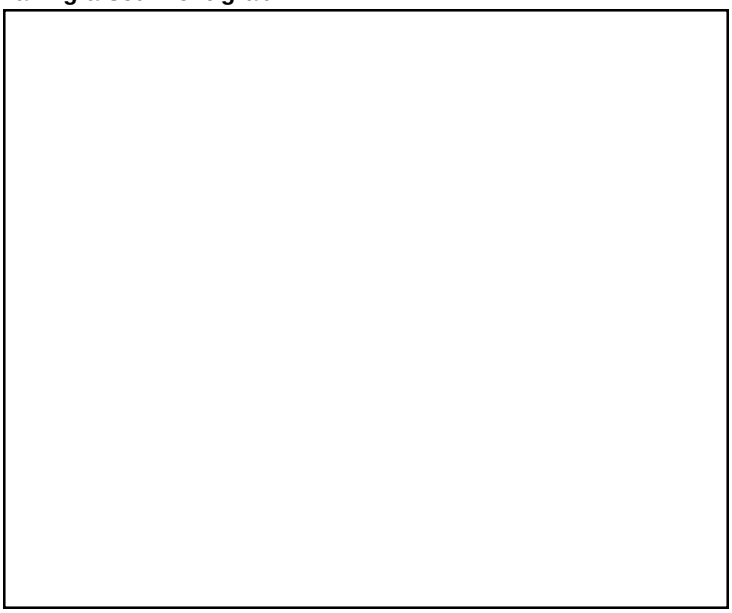
Interlaboratory comparisons were complicated by the varying number of size intervals measured among laboratories. The number of size intervals strongly affected the shape of the distributions because each point was interdependent. The position of the point on the x axis, and the percent of the sample represented by that point, was controlled by the number of intervals measured. For example, the shape of the size distribution for Horiba was changed significantly by summing the data into one-phi size intervals (Figure 7).

Because each laboratory measured different size intervals, the interlaboratory comparison for pipette/sieve analysis was based on the percent of gravel, sand, and silt and clay (Figure 4). Interlaboratory variation was 6-10% for sandy samples (CSDOC2 and CSDOCC) and 16-18%

for silty samples. Variation in the measurement of percent silt followed a consistent pattern: SCCWRP measured the most silt and MEC measured the least; Hyperion and KLI were intermediate. While the absolute difference among the laboratories varied from sample to sample, the rank order was consistent. The reason for the difference was not clear, but it did not appear to be related to analytical factors such as the number or range of intervals measured, drying temperature, or the point of dispersant addition.

The interlaboratory comparison of the results of laser analysis was based on the data summed at one-phi intervals (Figure 7). The results were generally within 2%. However, for sand-sized particles (CSDOC2 and CSDOCC), the results varied by 6-8%. Since there was good agreement in the measurement of sand-sized particles in the other samples, there may have been something specific to these two samples that increased measurement variability. It is possible that summing the data into one-phi intervals contributed to the difference. The peak in sediment distribution for Horiba occurred between 0.116 and 0.152 mm. Since the break in the size class occurred at 0.125 mm, the peak was distributed between two size classes. If San Diego measured slightly more material in the interval between 0.116 and 0.125 mm, the apparent difference would be magnified by summing the data.

Taking a sediment grab.



A comparison among the pipette/sieve, hydrometer/sieve, and laser techniques was complicated by the variability in the number of intervals measured. Since there was no standard reference material for measuring accuracy, it was not possible to determine which measurement was most accurate. And because of the effect of the number of intervals on the data (e.g., Figure 7), it was not possible to determine the magnitude of difference among techniques.

As the number of intervals increased, the size distribution became better defined and the proportionate error of each size class decreased. For pipette analysis, the number of intervals measured was limited by the time needed to withdraw the sample relative to the withdrawal time for the size interval. For pipette and sieve analysis, the number of intervals was limited by the amount of equipment (e.g., oven and desiccator space) and labor needed for drying and weighing the samples. The advantage of the laser analyzer was the ability to measure a large number of intervals (74 in this experiment) in a short time.

The within-laboratory measurement error was lower for laser analysis than for pipette/sieve or hydrometer/sieve analyses. Interlaboratory variation ranged from 2-8% for laser analysis and from 6-18% for pipette analysis. Since only one laboratory used hydrometers, interlaboratory variation could not be assessed. Thus precision was higher for laser analysis than for pipette analysis. Since the true size distribution of the samples was not known, it was not possible to assess the accuracy of the different types of analyses.

Surprisingly, sample digestion had relatively little effect on the size distributions. The size distributions for the digested and undigested coarser samples (CSDOC2 and CSDOCC) were virtually identical. Digestion had the greatest effect on the sample with the most organic material (CSDLAC7). For MEC, digestion decreased the amount of sand-sized particles, narrowed the peak in the silt range, and increased the amount of material in the smallest size class. For SCCWRP, digestion decreased the amount of sand-sized particles and increased the amount of material in the two smallest size classes.

The justification for digesting samples presented in the workshop preceding the intercalibration experiment was the reduction in the variability of replicates. This proved not to be the case. In fact, the standard deviations were generally higher for digested samples than for undigested samples. For example, the standard deviations in the 0.002 mm size class of CSDLAC7 were 1.38% for undigested samples and 2.88% for digested samples by MEC. The standard deviations in the 0.047 mm size class were 0.49% for undigested samples and 2.34% for digested samples.

CONCLUSIONS

The number of intervals measured significantly affected the shape of the size distributions. A relatively large number of intervals is needed to obtain a well-defined curve. The fact that the number of measured intervals differed among laboratories limited the comparability of data in this experiment.

Within laboratory measurement error was relatively small. The maximum standard deviation for sample replicates was 0.5% for laser analysis, 2.9% for pipette/sieve analysis, and 5.4% for hydrometer/sieve analysis. Between laboratory measurement error was 6-18% for pipette/sieve analysis and 2-6% for laser analysis.

Sample digestion had little effect on coarse samples. In silty samples digestion increased the amount of material in some size classes by 6-9% and increased the within laboratory variability. Because of the increased within laboratory variability, sample digestion is not recommended.

Overall, laser analysis is preferable to pipette analysis because: 1) within- and between-laboratory precision was higher for laser than for pipette analysis, 2) laser analysis was faster and less labor-intensive than pipette analysis, and 3) laser analysis produced a well-defined size distribution curve.

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