

USE OF WET SIEVING TO IMPROVE THE ACCURACY OF SEDIMENT AND SEDIMENT-ASSOCIATED CONSTITUENT CONCENTRATIONS IN WHOLE-WATER SAMPLES

William Selbig, Hydrologist, U.S. Geological Survey, Madison, WI, wrselbig@usgs.gov; Roger Bannerman, Environmental Specialist, Wisconsin Department of Natural Resources, Madison, WI, banner@dnr.state.wi.us; George Bowman, Supervisory Chemist, Wisconsin State Laboratory of Hygiene, Madison, WI, gth@mail.slh.wisc.edu

Abstract: Sand-size particles (greater than 63 microns) in urban runoff have the potential to produce substantial bias and/or poor precision both during sample splitting and laboratory analysis. New techniques were evaluated in an effort to overcome some of the limitations associated with sample splitting and analyzing whole-water samples containing sand-size particles. Wet sieving physically separates sand-size particles from a whole-water sample. Once separated, both the sieved solids and the remaining aqueous samples were analyzed for total recoverable metals using a modified version of EPA method 200.7 which digests the entire sample, rather than an aliquot, of the sample container. Using a total recoverable acid digestion on the entire contents of the sieved solid and aqueous samples improved the accuracy of sediment-associated constituent concentration. However, heterogeneities associated with coarser particle sizes may contribute to increased variability in concentration results.

INTRODUCTION

There is a growing body of evidence that demonstrates that using both churn splitting and aliquoting can introduce significant bias and/or poor precision into the sediment and sediment-associated constituent concentration results (Horowitz and others, 1997; Capel and Larson, 1996; Gray and others, 2000). Much of the variability can be attributed to the presence of sand-size particles found in many stormwater runoff samples. Whole-water samples collected from storm sewers frequently contain suspended sediment concentrations (SSC) exceeding 1,000 mg/L with a large percentage of sediment particles larger than 250 microns (Waschbusch, 2003; Sansalone and Buchberger, 1997; Furumai and others, 2002). Modifications to these sample splitting and laboratory analysis methods must be evaluated to ensure the future quality of stormwater contaminant concentration data.

Wet sieving the whole-water sample is one modification that could remove the bias and poor precision from both the sample splitting and laboratory analysis methods. To ensure the success of this modification, the proper sieve size must be selected. Two previous studies have observed two different particle sizes critical to reducing the errors associated with processing the whole-water sample with a churn splitter. Horowitz and others (1997) found unacceptable bias and precision when using churn splitters to process whole-water samples with suspended-sediment concentrations greater than 1,000 mg/L or particles greater than 250 microns. Other studies concluded that churn splitters are unable to adequately split particles greater than 63 microns since the stirring action is unable to overcome the tendency of sand grains to settle (Meade, 1985, cited in Capel and Larson, 1996). Other sample-splitting methods such as cone-splitters may produce less bias but demonstrate poor precision when dealing with sand-size particles (Horowitz and others, 1997). Based on these studies, selection of a 63-micron sieve should improve the quality of the splitting process, but wet sieving with a 63 micron sieve would add considerable time to the processing of most whole-water samples. The first objective of this study was to further evaluate the sieve size needed to reduce the bias and improve precision when splitting whole-water samples for SSC and total recoverable metal analysis.

Sub-sampling at the analytical laboratory is another potential source of error when determining sediment and sediment-associated constituent concentrations in samples with sand-size particles. Gray and others (2000) recognized that one of the more commonly used methods to quantify concentrations of solid-phase material in natural waters, total suspended solids (TSS), was “fundamentally unreliable”, especially when the majority of the material is in the sand-size fraction. This method measures the dry weight of sediment from a known volume of a subsample of the original. A better representation of solid-phase material in natural waters, regardless of the amount or percent of sand-sized material in the sample, measures the dry weight of all the sediment without subsampling (Gray and others, 2000).

One of the more commonly used methods to determine total recoverable metals concentrations in aqueous samples also recommends using a subsample of the water in the sample bottle submitted to the laboratory. Since most of the total recoverable metals in a stormwater sample are associated with the particulate matter (Bannerman and others, 1996), the sub-sampling procedure might under- or over-estimate the total recoverable metals concentration in the sample. As with the sediment analysis, the potential errors in the total recoverable metals analysis might be reduced by processing all the water in the sample bottle. A second objective of this study was to compare the results of a total recoverable analysis on a subsample from the sample bottle with a similar analysis on all the water in the bottle. The magnitude of the sub-sampling error is probed using two metals, zinc and copper, since they are two metals of concern in urban runoff (Bannerman and others, 1983; Bannerman and others, 1996)

MATERIALS AND METHODS

Experimental Design: The approach to both selecting the best sieve size for splitting whole-water samples and the best laboratory method for total recoverable metals analysis is based on comparing test results from water samples with known SSC and total recoverable metals concentrations when various modifications to these procedures are used. Results of the tests that best match the known values would provide guidance on the optimum sample splitting and laboratory analysis procedures.

Preparation of the Water Samples for Evaluation of Sieve Sizes: Reference samples with known sediment concentrations and particle sizes were created in the laboratory using sediment captured *in situ* by a storm sewer bedload sampler during a rainfall event. After the sediment was collected, it was dried and sieved into the following particle-size fractions: >2,000; 500–1,000; 250–500; 125–250; 63–125; and <63 microns.

Size-separated dry bedload material was added to deionized water in a tared, 14-liter, Teflon-lined churn splitter to create simulated urban runoff samples with known suspended sediment concentrations (figure 1). Two suspended sediment concentrations were made for each of three ranges of particle sizes (table 1). These samples were then well mixed for a period of approximately 1 minute using protocols developed by the USGS when processing whole-water samples in a churn splitter (USGS, 1999). Five aliquots of approximately 250 mL were transferred to laboratory bottles, placed on ice, and delivered to the State Laboratory of Hygiene (WSLH) for SSC analysis. Analysis results from these samples were compared to the known initial concentrations. The particle sizes that show the least amount of error after being processed in the churn splitter should indicate the sieve size to use on whole-water samples with sand-size particles.

Table 1 Prepared Suspended Sediment Concentrations for Selected Particle Size Ranges.

Particle Size Range, microns	Prepared Suspended Sediment Concentrations, mg/L		
63 to 125	1,000	--	5,000
250 to 500	--	2,000	5,000
500 to 1,000	--	2,000	2,000

Evaluation of Total Recoverable Metal Analysis Methods: Two analytical methods are used to determine total recoverable metals concentrations in aqueous samples. The whole-bottle analysis method uses an acid digestion on the entire contents of a 250-mL sample bottle submitted to the laboratory. The standard EPA method, on the other hand, performs the acid digestion only on a 25-mL aliquot taken from the sample bottle. When taking an aliquot from a sample containing sand-size particles, the particles that fall out of suspension quickly may be omitted from the sample analyzed. Tests comparing the results of these two methods were performed on a wide range of particle sizes and suspended sediment concentrations (table 2). Prepared sediment suspensions were split with a churn splitter and aliquots submitted to the laboratory.

The bedload material used to prepare the reference samples for these tests was processed in two different ways. Concentrations of zinc and copper were determined for both the dry bedload material and the sediments sieved from the sediment-water mixture in the churn splitter. The dry bedload material was used as a target because it precludes any bias or precision problems associated with the churn splitter. However, the concentration units from analysis on the dry material (mg/kg) are not directly comparable to the concentration units used for the water samples (mg/L).

Since the sieved sediment should have dry concentrations (mg/kg) of zinc and copper similar to the ones observed for the dry bedload material, the volume of the prepared sediment suspension was used to convert the dry weight concentrations to the concentrations in water.

Table 2 SSC Concentrations Prepared for Total Recoverable Metals Tests.

Particle Size Range, microns	Prepared Suspended Sediment Concentrations, mg/L		
63 to 125	2,000	5,000	--
250 to 500	--	5,000	10,000
500 to 1,000	--	5,000	10,000

A total of four aliquots were removed from the churn splitter for each particle-size range and corresponding suspended sediment concentration (figure 1): three aliquots of approximately 250 mL for the whole-bottle analysis and one 250-mL aliquot for the standard EPA analysis. The aliquots were then preserved with nitric acid, placed on ice, and delivered to the WSLH within 24 hours for analysis. The whole-bottle and standard EPA method samples were then analyzed for total recoverable zinc and copper (figure 2).

Wet Sieving Sediment in a Churn Splitter: The remaining sediment-water mixture was weighed using a large-capacity balance, then passed through a single 63-, 250-, or 500-micron nylon sieve to capture the remaining solid material for a specific particle-size fraction (figure 1). All material captured on the sieve was transferred into a 250-mL polypropylene container using deionized water. The container was then placed on ice and delivered to the WSLH within 24 hours. A total recoverable zinc and copper analysis was performed on the dried sieved sediment. To determine if any contaminants leached from the sediment particles in the churn splitter into the deionized water during the mixing process, a sample of the water passing through each sieve was submitted to the WSLH for total recoverable copper and zinc.

Dry Bedload Material Analysis: In addition to the aliquots from the splitter and sieved solid samples, a small amount of dry bedload material was sent to the WSLH for zinc and copper total recoverable metals analysis (figure 1). Deionized water was not added to the dry bedload sample.

Analytical Methods for Total Recoverable Metals: Figure 2 diagrams the procedures and methods used by the Wisconsin State Laboratory of Hygiene when analyzing the dry bedload material, sieved sediment, and aqueous samples from the splitter.

Split Water Samples: Historically, the USEPA has recommended the “total recoverable method” of sample preparation as an indication of the bioavailable pool of trace elements in sediments (U.S. Environmental Protection Agency, 1986a). We followed this approach as specified in EPA method 200.7 for liquids (U.S. Environmental Protection Agency, 2001) in the first of two approaches evaluated. The second method also used EPA method 200.7, but instead of sub-sampling the original sample, the entire contents of the 250-mL sample bottle (whole sample bottle method) were digested using a total recoverable acid digestion. Analyses for each method were performed in triplicate (figure 2).

The digestion protocol performed on all sediment suspensions was as follows: First, the samples were weighed to determine the volume. Nitric and hydrochloric acid were added to the entire contents of each vial to bring the concentration to 2.5 and 5 percent, respectively. Each vial was then heated in an Environmental Express Hotblock[®] at 95°C using EPA method SW846 3005A (U.S. Environmental Protection Agency, 1993), and subsequently analyzed for zinc and copper by inductively coupled plasma emission spectroscopy (ICP) according to EPA method 200.7 (U.S. Environmental Protection Agency, 2001). Resulting concentrations were reported in mg/L.

Dry Bedload Material and Sieved Sediment: The sieved solid fraction was quantitatively transferred to an acid-washed, tarred porcelain evaporating dish with the aid of deionized water. The dish was dried at 103–105°C overnight, desiccated and brought to a constant weight. The dried bedload material did not go through this process since it was delivered to the laboratory as a dried solid. The dried solids were then transferred to a clean, dry 250 mL polypropylene bottle. A 0.25- to 2.0-gram portion of the dried solid was weighed directly into a 125-mL digestion vial and 10 mL of deionized water was added to re-hydrate the sample. Although a 0.5-gram sample is typically

used for this type of solids analysis, we used a 2.0-gram subsample where sample mass permitted. Using a 2-gram sample should improve reproducibility, as errors associated with heterogeneities are reduced when sub-sampling sediments with sand-size particles. The digestate protocols used for the aqueous samples were duplicated for the sieved solid samples. Resulting concentrations were reported in mg/kg.

Figure 1 Diagram of processes to prepare dry bedload, sieved sediment, and water samples for laboratory analyses.

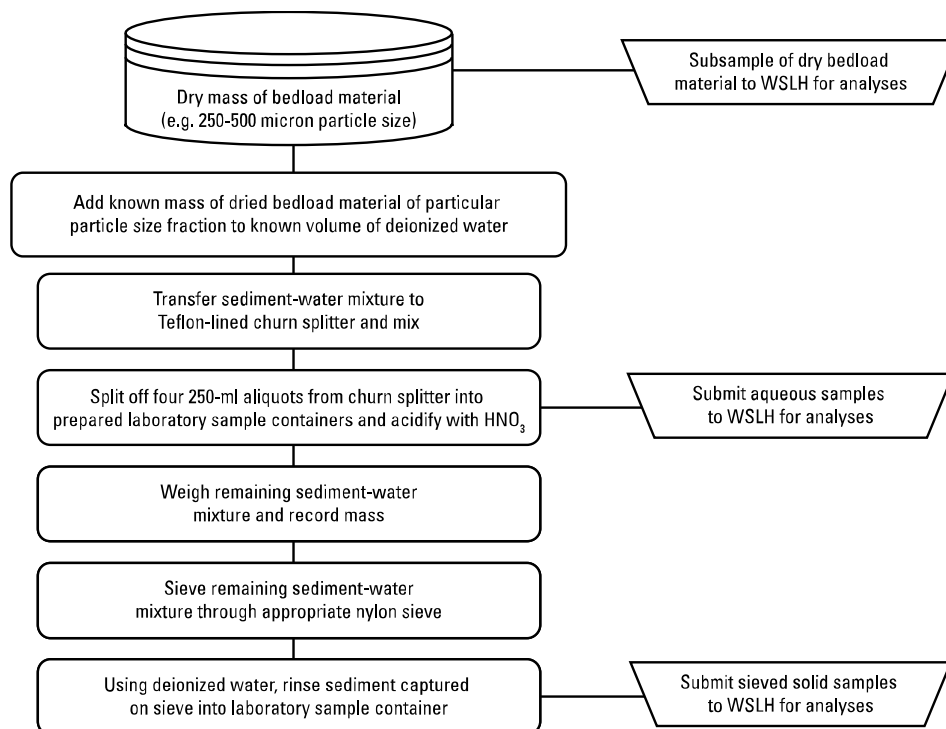
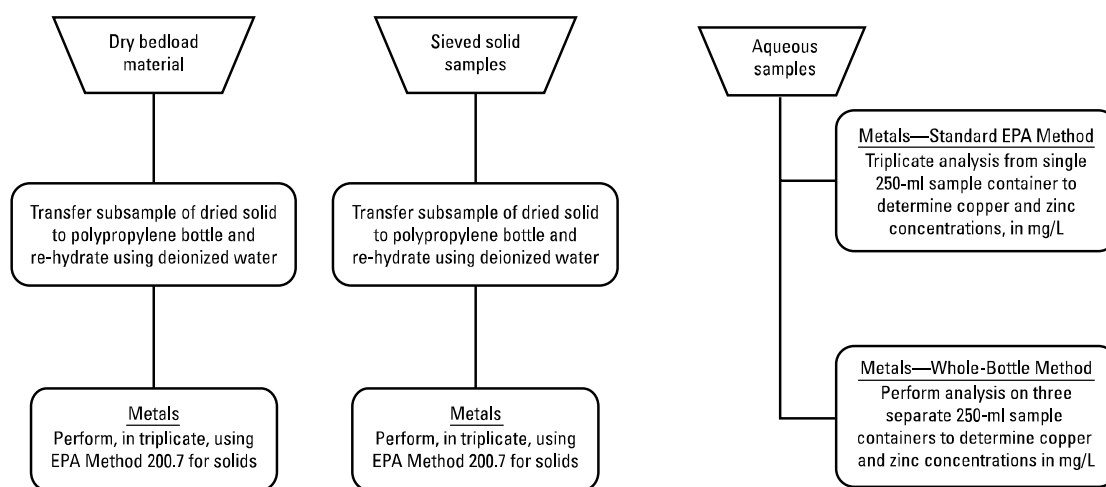


Figure 2 Diagram of analytical techniques used to determine total recoverable zinc and copper concentrations on dry bedload, sieved sediment, and water samples from the splitter.



RESULTS

Selection of Sieve Size for Processing Whole-Water Samples: Above a particle size of about 250 microns, a significant positive bias in the suspended sediment concentration (table 3) is observed in the churn split samples. For particles over 250 microns in size, the average percent difference between the target suspended sediment concentration and the split water samples ranges from 26 to 85 percent. In all the particle size ranges the bias is larger for the higher suspended sediment concentrations. A dramatic decrease in the degree of positive bias occurs for the samples in the particle size range of 63 to 125 microns. In this lower range, average percent differences ranged from only 1 to 6 percent. It is apparent that sieving a whole-water sample with a 125-micron sieve before using the churn splitter will greatly reduce the positive bias in suspended sediment concentrations for samples with sand size particles.

Sub-sampling precision was also degraded in water samples with larger particles. Coefficient of variation (COV) values increased from 0.01 for the 63 to 125 micron particles to 0.25 for the 500 to 1,000 micron particles. Removing particles greater than 125 microns from a whole-water sample before it is split will improve precision in the suspended sediment concentrations.

Table 3 Impact of Churn Splitter on SSC concentrations.

Particle Size (microns)	Replicate Number	SSC Target = 1,000 mg/L		SSC Target = 2,000 mg/L		SSC Target = 5,000 mg/L	
		Result (mg/L)	Percent Difference	Result (mg/L)	Percent Difference	Result (mg/L)	Percent Difference
63 - 125	1	1,000	0%	--		5,350	7%
	2	1,020	2%	--		5,240	5%
	3	1,020	2%	--		5,300	6%
	4	1,010	1%	--		5,330	7%
	5	1,010	1%	--		5,190	4%
Mean		1,012	1%			5,282	6%
Std. Dev.		8				66	
COV		0.01				0.01	
250 - 500	1	--		3,340	67%	6,470	29%
	2	--		3,020	51%	8,140	63%
	3	--		2,800	40%	8,600	72%
	4	--		2,540	27%	7,500	50%
	5	--		2,150	8%	7,760	55%
Mean				2,770	39%	7,694	54%
Std. Dev.				454		800	
COV				0.16		0.10	
500 - 1,000	1	--		3,250	63%	6,600	32%
	2	--		2,700	35%	12,300	146%
	3	--		1,850	-8%	11,000	120%
	4	--		2,450	23%	8,540	71%
	5	--		2,350	18%	7,740	55%
Mean				2,520	26%	9,236	85%
Std. Dev.				512		2,354	
COV				0.20		0.25	

Both the precision and bias errors observed for the larger particle sizes indicate the churn splitter is not able to keep all the large particles in suspension. Since the churn paddle is unable to distribute sand grains evenly, a gradient in concentration occurs inside the churn splitter where sand is more concentrated near the bottom (where the spigot is)

than the top (Mead, 1985, cited in Capel and Larson, 1996). This accumulation of larger particles near the bottom of the splitter would also be highly variable depending on the particle size, suspended sediment concentration, density of the particles, and the rate of mixing in the splitter. These errors caused by the churn splitter will obviously also impact measurements of particle-associated contaminant levels, both on a volumetric and mass basis.

Wet sieving a whole-water sample before splitting will require more effort to process a sample and more careful tracking of the volumes in the splitter. The mass of the sediment on the sieve will have to be added to the mass of sediment determined by the SSC analysis on the split samples. A final suspended sediment concentration will require knowledge of the volume of water in the splitter.

SELECTION OF METHOD FOR TOTAL RECOVERABLE METALS ANALYSIS

Concentrations of copper and zinc determined in the sieved sediment were reasonably close to those measured in the dry bedload material for each particle-size fraction (table 4). Therefore, we can assume the sieved solid concentrations, when converted to mg/L, are reasonable target concentrations for each method performed on the aqueous samples. Assuming 1 kilogram of water is equal to 1 liter of water, the following equation can be used to convert the concentration of copper and zinc as a solid, in mg/kg, to a concentration as a liquid, in mg/L:

$$C_l = \frac{(S_m / 1000) * C_s}{V} \quad (1)$$

where C_l = concentration of sieved solid represented in mg/L; S_m = mass of sieved solids after drying, in grams; C_s = concentration of sieved solid, in mg/kg; and V = volume of water sieved, in liters.

Concentrations of copper and zinc determined in the two methods evaluated are compared to the sieved sediment in table 5. In most cases, concentrations determined using the whole-bottle method came close to the target values established from the sieved sediment concentration. However, the standard EPA method 200.7 consistently produced lower copper and zinc concentrations than the sieved solid for each particle-size fraction. Though we cannot definitively determine the reason for the bias, it is likely that sedimentation or fractionation of particles within the bottle is the primary cause. Therefore, in aliquoting the bottle, the likelihood of unrepresentative sampling is great. Depending on where the aliquot is acquired from a sample container, the resulting concentrations could either be positively or negatively biased. For this reason, the whole-bottle version of EPA method 200.7 is recommended as the most appropriate technique for measuring metals concentration in an unfiltered water sample.

The observed bias for the zinc and copper concentrations was less than the large positive bias observed for the suspended sediment concentrations. This may partly be explained by the effect of increasing metal concentrations with decreasing particle sizes (table 5) (Bannerman and others, 1983). Smaller particles in each of the particle-size ranges might be transferred (aliquoted) with less error than the larger particles. Increasing the number of larger particles in the water sample has a significant impact on the suspended sediment concentrations, but a similar effect on metal levels is not observed because these large particles tend to have lower metals concentrations.

Table 5 also describes how a single value from the triplicate analysis can bias the average concentration away from the sieved solid target. The italicized value for zinc in the 500–1000 micron particle-size fraction can likely be attributed to heterogeneities in larger sand-sized particles. Due to laboratory error, only two concentrations were recorded for copper in the 63–125 micron particle-size fraction. Addition of a third value would have provided useful information to estimate the true value. While concentrations of copper and zinc appear somewhat more variable for the whole-bottle analysis compared to the standard EPA analysis, the improved accuracy of the whole-bottle analysis more than compensates for the difference in the precision.

Table 4 Comparison of dry bedload and sieved solid copper and zinc concentrations

Particle Size Range (microns)	SSC Concentration (mg/L)	Copper			Zinc		
		Raw Bedload (mg/kg)	Sieved Solid (mg/kg)	Absolute RPD (%)	Raw Bedload (mg/kg)	Sieved Solid (mg/kg)	Absolute RPD (%)
500-1,000	5,000	8.1	6.3	25%	20.2	30.2	40%
	10,000		6.0	30%		29.9	36%
250-500	5,000	4.3	3.7	14%	17.4	19.7	13%
	10,000		3.6	17%		17.9	3%
63-125	2,000	41.2	37.0	11%	151.0	138.3	9%
	5,000		41.7	1%		156.7	4%

Table 5 Triplicate concentration values for two sediment-associated metals using the whole-bottle and standard EPA methods for aqueous samples. All concentrations are expressed in mg/L.

Particle Size Fraction (microns)	SSC Concentration	Copper			Zinc		
		EPA 200.7 Method Aliquot	Whole Bottle	Sieved Solid	EPA 200.7 Method Aliquot	Whole Bottle	Sieved Solid
63 - 125	2,000	53	70	68	218	272	271
		49	69	74	204	291	252
		53	60	71	225	291	269
	Mean	52	67	71	216	285	264
	RPD	-37%	-6%		-22%	7%	
	5,000	111	360	190	606	698	764
		114	194	209	553	725	740
		72		202	508		754
	Mean	99	277	200	556	712	753
	RPD	-102%	28%		-35%	-6%	
250 - 500	5,000	12	23	19	45	123	111
		11	24	16	33	88	90
		11	26	18	35	133	78
	Mean	11	24	18	38	115	93
	RPD	-56%	27%		-147%	19%	
	10,000	11	38	35	52	201	159
		10	62	34	57	233	177
		11	40	32	52	191	166
	Mean	11	47	34	54	208	167
	RPD	-216%	28%		-212%	20%	
500 - 1,000	5,000	12	34	29	47	135	148
		11		29	47		175
		13	31	29	57	126	100
	Mean	12	33	29	50	131	141
	RPD	-142%	11%		-180%	-8%	
	10,000	16	56	59	55	141	271
		16	71	53	57	246	247
		15	77	50	58	299	280
	Mean	16	68	54	57	229	266
	RPD	-245%	21%		-369%	-16%	

CONCLUSION

Limitations associated with churn and cone splitters can be overcome by wet sieving sand-sized particles from the aqueous portion of a whole-water sample. This physical separation increases the efficiency of churn splitters and improves the overall accuracy of concentration data. Once sand-sized particles are removed from the sediment-water mixture, they can be analyzed independently using the same analytical methods as the parent aqueous sample. The process of transferring sieved solids from the nylon sieve to the sample container had negligible effects on metals concentrations. Analysis of the deionized water used after transferring solids indicated no leaching of metals from the solid particles into the residual water.

Digesting the entire contents of a sample container reduced bias normally associated with taking an aliquot from a sample containing sand-sized particles. Of the two analytical methods used to determine metals concentrations in an aqueous sample, those using an acid digestion on the entire contents of the sample container (the whole-bottle version of EPA method 200.7) produced concentrations that were closer to the sieved sediment concentration.

The presence of outliers in the concentration data using the whole-bottle version of EPA method 200.7 suggests difficulties in maintaining a high level of precision. The standard EPA method 200.7 produced results with high precision but lacked accuracy. The difference in precision is a function of subsampling an original sample. By taking an aliquot near the top of the sample container, particles that fall out of suspension quickly will be omitted from the sample analyzed. Similarly, an aliquot taken from the bottom of a sample container might acquire a sediment-enriched sub-sample. Therefore, in aliquoting a bottle, the likelihood of unrepresentative sampling is great. When compared to the corresponding sieved solid target concentrations, concentrations of copper and zinc using the whole-bottle version of EPA method 200.7 displayed greater accuracy over the standard EPA method 200.7.

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