Errors associated with sampling and measurement of solids: Application to the evaluation of stormwater treatment devices

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ABSTRACT

Solids removal often is the first parameter evaluated when testing the effectiveness of stormwater treatment devices. Therefore, it is imperative that the sources and magnitude of potential errors associated with each stage of sampling and measurement be understood and quantified. The following research examined the errors associated with the analysis of solids from collection via an automatic sampler through sample splitting with churn and cone splitters to, finally, solids concentration analysis by three common US analytical methodologies (Suspended Solids Concentration [SSC, ASTM D3977-97B] and Total Suspended Solids [TSS, by both US EPA Method 160.2, identical to ISO 11923, and *Standard Methods* 2540D]). Material gradient impacted the reliability of the autosampler. Sample splitting distributed representative and consistent subaliquots. SSC methodology best represented the known solids concentration in water for a representatively wide range of typical particle sizes. This research documented the magnitude of potential errors associated with each stage in solids measurement in stormwater. The question remains as to what effect these errors will have when combined into a single sampling and analysis activity. Large and variable errors may mask bias differences in the methods; also, error analysis and comprehension is a vital part of the stormwater control evaluation process.

KEYWORDS

Automatic sampler; churn splitter; cone splitter; solids analysis and errors; SSC; Stormwater; TSS

INTRODUCTION

Historical and present day solids' concentrations data for stormwater often do not contain detailed information on the methodology used during analysis (e.g., filter paper pore size, which methodology by organization used, aliquot size used, particle size distribution). There is also the misconception that Total Suspended Solids (TSS) and Suspended Solids Concentration (SSC) recoveries are interchangeable. Because the research by Gray et al. (US Geological Survey [USGS], 2000) showed that TSS has an inherent bias of excluding the larger sized particles in a

sample prior to subaliquot capture due to settling velocity, the US Geological Survey developed a method, SSC, that analyzed the entire sample bottle for solids. Solids concentration analysis in historical data, however, typically employed one of the TSS methodologies. All of the above have led to a debate among both stormwater managers and the stormwater industry on how to use both historical and present day data for data comparisons, particularly in stormwater treatment device evaluations. These evaluations, at present, analyze for both TSS and SSC, though some stormwater managers are not convinced this is the best course of action and do not want the added cost.

But to understand and elucidate the differences between these two methods and the entire solids analysis as a whole requires understanding what potential errors could be associated with the activities leading to solids analysis. Therefore, the research teams from both Penn State Harrisburg (PSH) and The University of Alabama (UA) examined each step throughout the analysis procedure. These steps included sample collection through the use of automatic samplers, sample division into subaliquots through churn and cone splitters, and the solids concentration analysis by three analytical methodologies. The results show the accumulation of these errors can affect the final recovery of solids. The research also shows this compounding of errors can mask the true bias, so much so that the source of bias cannot be differentiated. Interpreting and understanding these errors will lead to better stormwater control practices and evaluations.

METHODOLOGY
Stormwater sampling via automatic samplers
Similar autosamplers were used by both research teams for examining errors associated with stormwater sample collection (American Sigma 900 Max and ISCO 6712 Portable Autosampler) for tubing lengths of 1.8, 7.6, and 8.0 m. The longer tubing lengths represent typical lengths used in the field. Stormwater runoff was simulated by mixing sand(s) and silica sand(s) in tap water to achieve a particle size distribution (PSD) with a specific gravity of 2.65 similarly suggested by the New Jersey Department of Environmental Protection (NJ DEP) (NJ DEP, 2003).

PSH. Three different mixtures consisting of (a) ground silica only (d_{50}=90 μm), (b) sand and ground silica (d_{50}=260 μm), and (c) sand only (d_{50}≈257 μm) were created and used in this phase of testing. All mixtures had a concentration of 0.5 kg/m³. Samples were constantly and manually mixed in a 0.21 m³ container. Three replicates per mixture (silica sand only, sand+silica) were taken for the following conditions:

- Three probe locations within the water column (immediately below the water surface, mid-depth, and within 0.05 m of the container bottom) when the sampler arm of the autosampler was equal to the height of the surface water level,
- Three probe locations within the water column (immediately below the water surface, mid-depth, and within 0.05 m of the container bottom) when the sampler arm of the autosampler was 1.1 m above the water surface, and
- Three probe locations within the water column (immediately below the water surface, mid-depth, and within 0.05 m of the container bottom) when the sampler arm of the autosampler was 6.3 m above the water surface.

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The sand only mixture was tested only at the 6.3 m height in triplicate. For all tests, triplicate grab samples were collected. All samples, excluding the sand only samples, were analyzed by SSC without sieving and sieving at 500 µm and 250 µm. The sand only samples were analyzed by SSC but sieved at 106, 250, 500, and 1,000 µm due to the larger particle sizes in this mixture.

UA. The mixture was a ratio blend of 25 % each of two different silica sands (Sil-Co-Sil 106® and Sil-Co-Sil 250®, US Silica Company) and two sand types (PSDs=90 – 250 µm and 300 – 450 µm). Mixture concentration was 5 kg/m^3. A 0.014 m^3 churn splitter was used to mix the samples. Samples were taken at four elevations for this mixture: 2.4, 4.0, 6.7, and 7.9 m. Grab samples were collected as well. All samples were analyzed for SSC.

The statistical analysis for this phase included one-way analysis of variance (ANOVA) with *a posteriori* Bonferroni pairwise comparisons (as appropriate). An in-depth discussion for this phase of solids analysis can be found in Clark et al., 2008.

Sample processing
This second phase of the research was performed by UA only. The composition of the challenge waters used in the various tests were as follows for:
  (a) Nara (2005) and University Transportation Center for Alabama (2005):
      (i) challenge solution consisting of:

           • 15 % Sil-Co-Sil 106®
           • 50 % Sil-Co-Sil 250®
           • 25 % Sand (sieved, 90 – 250 µm)
           • 10 % Sand (sieved, 300 – 425 µm)

      (ii) Sil-Co-Sil 250® only
      (iii) Sand only (sieved, 90 – 250 µm)
  (b) US Environmental Protection Agency (US EPA) (2006) and Khambhammettu (2006); challenge water contained specific particle size distributions with concentrations of 0.05 – 0.5 kg/m^3.

Sample preparation. A protocol was created by this research team to ensure a repeatable procedure for sample processing, especially when the resultant subaliquots are designated for particulate and particle size analyses. This procedure can be used during traditional field sampling and laboratory device verifications. The steps are as follows:
  (1) Determine the number of analyses needed for the sample. Adjust the splitter tube on the cone splitter accordingly to produce the number of subaliquots needed
  (2) With a coarse nylon screen with 1200 µm openings laying on top of the cone splitter, pour the sample through. Rinse any screened out material with distilled water and place in an oven to dry. This material is weighed prior to chemical analyses.
  (3) Sieve subaliquots through an appropriate 0.0762 m (diameter) mesh sieve.
  (4) Filter the sieved subaliquots through a 0.45 µm membrane filter.

Subaliquots by cone splitter. Morquecho (2005) used 0.005 m^3 of water per run to test the evenness of the splitting action of this splitter type. She allocated two splitter tubes per subaliquot. This analysis was performed in triplicate.

Subaliquots by churn splitter. Evaluation of the performance of the churn splitter was made through the use of data collected during treatment device evaluations by Pitt and Khambhammettu (US EPA, 2006) and Khambhammettu (2006). Three 0.001 m^3 effluent samples were collected from a continually mixed churn splitter and, in turn, split by a cone splitter, producing 126 subaliquots for a variety of tests.

Analysis for solids concentration
Clark and Siu (2008) used two different challenge solutions for each analysis method for a variety of conditions. The solutions consisted of (a) Sil-Co-Sil 250® in tap water and (b) sand plus Sil-Co-Sil 250® in tap water. All samples were made individually. Median particle size diameters of the solutions were 100 μm for the former and 500 μm for the latter. Concentrations of all solutions were 0.5 kg/m^3. Glass fiber filters with a pore size of 47 μm were used for all tests. Table 1 lists the conditions and protocols used for analysis

Table 1. Summary of solids concentration analytical methodologies and conditions used. (ISO=International Organization for Standardization)

Test	Method #	Filter nominal pore size	Aliquot size	Sampling location	Reference
TSS	US EPA Method 160.2, ISO 11923	47 μm	1.0 e^{-4} m^3	N/A	US EPA, 1999; ISO, 1997
TSS	US EPA Method 160.2, ISO 11923	47 μm	2.5 e^{-4} m^3	N/A	US EPA, 1999; ISO, 1997
TSS	*Standard Methods* 2540D	47 μm	1.0 e^{-4} m^3	Mid-depth between wall and vortex	APHA, 1999
TSS	*Standard Methods* 2540D	47 μm	1.0 e^{-4} m^3	Within 0.01 m from bottom and between wall and vortex	APHA, 1999
SSC	ASTM D 3988-97	47 μm	All	N/A	ASTM, 1997

Linear regressions were used for statistical analysis of this phase of research to determine the relationships between the measured concentration by each method and the known concentration. Both regression coefficients and confidence intervals were calculated. The regressions were examined for validity through the use of the Durbin-Watson statistic and the examination of errors for normal distribution. The slopes were compared as described by Clark and Siu (2008).

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RESULTS AND DISCUSSION
Automatic samplers
Statistically significant differences were found in recoveries when examining the effect of particle size distribution on the performance of autosamplers used in this study. The challenge solution (at PSH) with the lower median particle size diameter (d_{50}=100 μm) recovered approximately twice as much solids as the challenge solution with the greater median particle size diameter (d_{50}≈257 μm): 80 % versus 40 – 50 %. Sampling at different depths within the container did not show any statistical significance. Due to the heavier mass of the greater fraction of the larger particles in the sand+silica sand solution, the autosamplers were inconsistent in obtaining a representative sample. A more representative and repeatable sample, however, was obtained using the silica sand only challenge water. Although 40 % of the mass was greater than 250 μm, sieved and unsieved samples could not be distinguished statistically from one another.

At UA, solids recoveries were less than half the measured concentration of the challenge solution for all elevations, with the exception of one sample at the 2.4 m height. This sample was taken near the container bottom, therefore, more solids may have been recovered due to this location. These low recoveries were attributed to the poor mixing technique used. Elevation was found to be a factor in these tests at UA. A wider particle size range was recovered at the lowest elevation while the distribution range decreased in the remaining three elevations.

The results also were compared to grab samples collected near the sampler inlet. Grab samples were better able to capture the particle sizes greater than 500 μm. Figure 1 shows solids' recovery was due to the particle size distribution of the challenge water and not to either the location of the sampler relative to the water or to the location in the bucket. No statistical differences were seen between the samples in this data analysis, even though a slight increasing trend in concentration is visible from the top of the barrel to the bottom. Ninety percent of the captured particles in the sand only samples were greater than 106 μm in diameter. Statistical differences were significant among particle diameters of 106, 250, and 500 μm but not between 500 μm and 1,000 μm. Significantly statistical differences were seen between grabs and automated for sieve sizes 250, 500, and 1,000 μm. The larger particle sizes, even in a well mixed sample, were not easily collected by the peristaltic pump used by the autosampler. . The SSC recoveries for the entire range of particle sizes are shown in Figure 2 for the sand+silica mixture when the sampler arm was located in two different elevations from the water surface. At the higher elevation and for the larger particles sizes, both grab and automated samples were close or above the known concentration. Though grab samples had slightly higher SSC concentrations at the lower elevation than the automated samples, the recoveries were similar. The figure demonstrates that differences occurred between the two sample types in the sand sized range (250 μm). The figure also shows that variability was higher for the grab samples in the larger particle size range. This was due to the greater probability of capturing the larger sand sized particles at the spigot near the bottom of the barrel. Greater repeatability and precision were demonstrated by the autosamplers, though accuracy was diminished. These tests were rerun with a sand only mixture (Clark et al., 2008, submitted). The recoveries were decreased compared to the Figure 2 results, demonstrating the concern about the ability of the autosamplers to reliably capture and retain the larger solids in stormwater runoff.
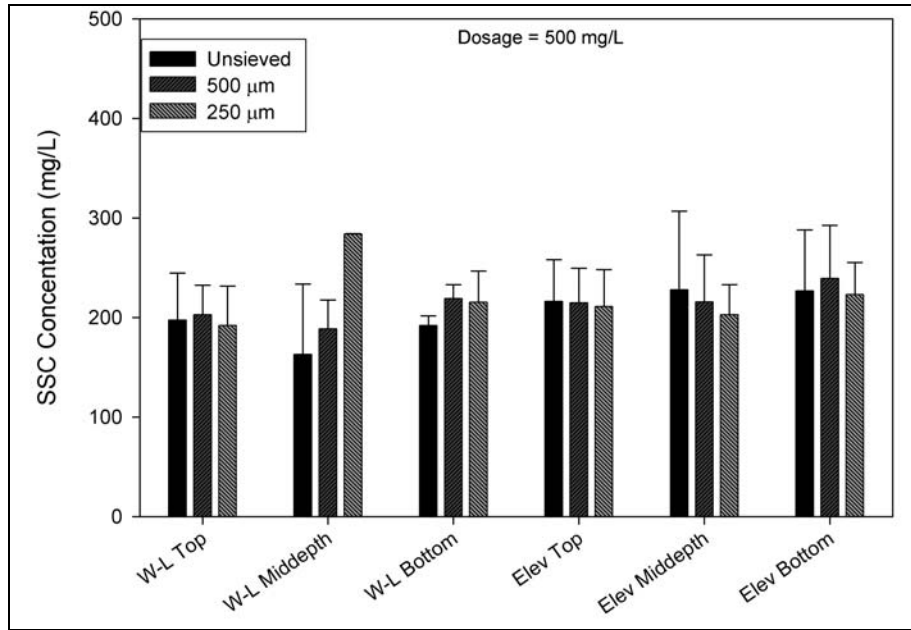
Figure 1. Effect of sampler elevation relative to the water level on recovery of sand+silica. (W-L = water-level, Elev = elevated; Error bars equal one standard deviation).
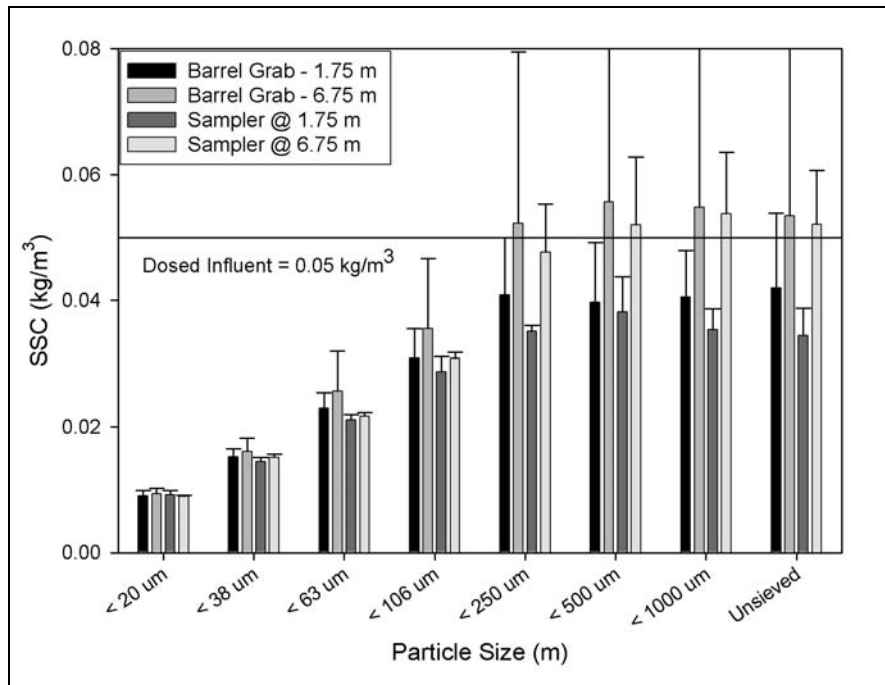

Figure 2. SSC recoveries for automated and grabbed samples at two different elevations for the entire particle size range.

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Sample processing
The research team at UA developed a methodology, described previously, that is consistent and repeatable for use in obtaining representative subaliquots for sample analysis, particularly in PSD analyses.

Cone splitting. Morquecho (2005), Nara (2005), and Pitt and Nara (University Transportation Center for Alabama, 2005) found this splitter type to produce representative (in concentration) and reproducible subaliquots of a given sample. The small COVs seen by all three researchers indicated that variability among the samples were small. This device also demonstrated that sample variability among the samples were small. Sample variability also was smaller than that seen with the churn splitter. Median COV values were 11 % and 27 % TSS, 5 % and 8 % Total Solids for the cone and churn splitter, respectively. COV values were highest when the initial sample concentration was low.

Churn splitting. Results in a treatment device evaluation performed by Pitt and Khambhammettu (US EPA, 2006) and Khambhammettu (2006) were used in the evaluation of the performance of the churn splitter. The COVs (25 % TSS and 8 % Total Solids) showed that samples possessing a smaller concentration of solids (<1.0 e^{-4} kg) had larger analytical variability than samples containing a larger concentration of solids.

Solids Analysis
Clark and Siu (2008) found that substantial method differences did exist between the two commonly used TSS methodologies. They also observed differences between both TSS methodologies and the SSC method. However, differences among researchers and their respective laboratory techniques will contribute to the compound of errors also. For example, the selection of the glass fiber filter pore size is arbitrary even though a recommended size is given for both *Standard Methods* TSS and SSC. In addition, there is no definitive aliquot size recommendation for either TSS methods; however, the typical aliquot size used in industry is 1.0 e^{-4} m^3 of sample. SSC, however, utilizes the entire sample bottle. Thus, without this information reported with the sample results, comparisons between both historical and contemporary data become more difficult. In this phase of research, the median particle size diameters were 100 μm for the challenge water containing ground silica only and 500 μm for the sand+silica mixture.

TSS (US EPA/International Organization for Standardization [ISO]). The larger aliquot size (2.5 e^{-4} m^3) showed a slightly higher recovery over the smaller aliquot size (1.0 e^{-4} m^3) for the silica sand only solution. The aliquot size for the sand+silica solution did not make a difference in recoveries; they were similar. However, the solids composition did demonstrate a significant statistical difference between the two challenge solutions used. The solution containing ground silica only recovered about twice as much solids (65 – 70 %) as the sand+silica solution (36 – 37 %). Nonetheless, all samples for this testing method did not recover the known concentration of solids (0.5 kg/m^3). Because the sample was shaken vigorously and then poured after removing the lid, there was sufficient time for the heavier particles to settle out of solution. It was difficult to pour and measure fast enough to capture these larger particles. Also, the amount and intensity of sample shaking was found to be subjective, thus, creating another opportunity for bias.

TSS (Standard Methods). This wide-bore pipet method demonstrated extremely well the effects of particle size distribution. Even for a well mixed sample, the heavier particles still settled out of

solution. The speed setting for the magnetic stir bar was subjective, though direction was given to shear the large particles. Nevertheless, the heavier particles were found to settle out of solution and travel along the bottom of the sample bottle. The heavier particles also tended to settle out of solution into the tip of the pipet tip as a subaliquot was taken for analysis. Though a wide bore pipet tip was used, this particle settling interfered with subaliquot collection. Because the tip was blocked, the full subaliquot size could not be obtained unless what was collected was released back into the sample bottle and another collection attempt was made.

These tests showed that sampling location within the sample bottle did make a difference in solids recoveries. When sampling at mid-depth between the vortex and the bottle wall, as stated in the methodology, the silica only solution recovered solids concentrations similar to that by the other TSS methodology. The lower sampling depth was able to recover more solids than the mid-depth location (≤ 150 % vs <100 %). However, this lower depth also showed greater sample variability.

SSC. Recoveries (98 %) were near known concentrations since the entire bottle was used for analysis. This method was the most consistent, based on small standard deviations, and more accurately represents the "true" solids concentration in the sample.

Of the two TSS methods, TSS by the US EPA/ISO method showed better consistency in recoveries. Linear regression slopes were greater than those for the *Standard Methods* protocol. The variability was less in the former method, most likely because the heavier solids had settled by the time the full aliquot size was obtained. There was greater opportunity to capture the larger, heavier particles depending on sampling location; thus, greater sample variation occurred in the *Standard Methods* protocol. If one's concern is the particles in the smaller sized particle range, then TSS by US EPA/ISO method is acceptable. However, if the larger particle sizes are of concern, then this method will underestimate the solids in this particle size range. The SSC method was found to be the best method for analyzing solids for the entire particle size range since the whole sample bottle is used and there are no other potential biases similar to those observed in both TSS methods (e.g., particle settling in the bottle and in the pipet tip).

Effect of accumulated errors on sample results
The effect of accumulated errors on solids measurement was documented in Clark and Pitt (2008) during the field and full-scale laboratory testing of a manufactured stormwater treatment device. Relationships were developed between the TSS and SSC concentrations on the aliquots of the same sample (collected by autosampler [field samples] or grab [laboratory] and split by cone splitter). The regressions showed that, while the slope of the regression line appeared to indicate a difference of 25 % between the recoveries of the two methods, statistically the two methods were indistinguishable. In addition, comparisons were made between the two methods and the known solids addition during the full-scale laboratory testing. The results showed that, for verification activities involving laboratory testing, collecting influent samples that reflected the concentration and PSD of the known solids addition was difficult. This was not a concern in the effluent because the larger particles were removed in the device and the smaller solids that remained in solution were well mixed in the water column. Therefore, it was recommended to use the known data when possible, rather than relying on correctly sampling poorly mixed water columns, especially when the poor mixing is due to the number of heavier solids in the mixture.

CONCLUSION

Testing the various steps in solids analysis has shown that particle size distribution of solids in the water column and in the samples themselves can affect solids analysis from sample collection to solids concentration determination. When sampling with an automatic sampler, if the water column is poorly mixed and a greater distribution of solids falls into the sand size range or greater, then the intake valve will less likely obtain a sample representative of all particle size ranges. In a well mixed environment, the likelihood of the larger particles entering the intake valve is greater. Solids concentration recoveries also were affected by PSD and were dependent on the methodology used for solids determination. Greater recoveries were obtained for challenge solutions containing a smaller median particle size diameter. Also, with this challenge solution, the aliquot size affected recoveries, producing slightly larger recoveries with larger aliquots. Challenge solutions containing sand sized particles recovered less than half of the known concentration value. Aliquot size in this solution did not demonstrate a significant difference in recoveries.

Our research team created a reliable and reproducible protocol for processing samples for particle size analysis by sample splitting through a cone splitter. Both the cone splitter and churn splitter demonstrated the ability to produce representative and consistent samples in volume, concentration, and particle size distribution.

It must be understood that:

- Each step of the solids analysis process contains errors, whether inherent to the method itself or because of the laboratory techniques, equipment biases, or biases from the researchers themselves. The compounding of these errors will affect final solids concentrations.
- The best solids determination protocol will be dependent on what particle size distribution a researcher needs. The TSS US EPA/ISO method is adequate when data is not needed for the larger particle sizes. However, SSC will give a better indication of actual concentrations when all particle sizes are relevant.
- For future data comparisons, it is recommended that methodology details and particle size distribution analysis be included in reports, etc. This additional valuable information will allow the work to be comparable to other data, particularly when evaluating stormwater treatment devices.
- Mass balance of influent concentrations also will prove useful during treatment device evaluations.

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