Errors Associated with Solids Collection and Analysis

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Testing vs. Reality?

Particle Size Distributions for Stormwater and Suggested Test Simulants

Particulates Traditionally of Interest in Control Device Evaluation?

1. It is the primary parameter of interest for most regulatory agencies when evaluating treatment performance, and

2. Certain pollutants are strongly associated with the particulates in runoff.
   - Therefore, removal of solids will lead to removal of other pollutants.
   - However, associations are not evenly distributed across all particle sizes in runoff.
Associations of Pollutants with Specific Particle Sizes

From: Morquecho 2005

Total Phosphorus

Chemical Oxygen Demand

Questions for Collection and Analysis of Solids


Sample Collection → Preparation → Analysis

- Collection method?
- Location in the flow stream?
- Effectiveness of autosamplers? Where in the flow stream?
- Sample processing methods?
- Sample analytical methods?
- Particle size distribution effects?
- Impact of variability on final solids analysis?
Field Sampling

Autosamplers for Sample Collection: What Particle Sizes and Where in Flow Path?

Sampler efficiency drops with increasing particle size.

Effect of Intake Location and Solids PSD?

Recovery of Larger Particles – Sand Only Mix

Dosed Influent Concentration = 100 mg/L

Multiple Sampling Locations (by moving sample bottle in flow path) = 76 mg/L

- 59 mg/L
- 30 mg/L
- 187 mg/L

<table>
<thead>
<tr>
<th>SSC Concentration (mg/L)</th>
<th>Autosampler - 6.53 m</th>
<th>Barrel Grab</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>500</td>
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</tr>
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<tr>
<td>0</td>
<td>500</td>
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</table>

<table>
<thead>
<tr>
<th>SSC Concentration (mg/L)</th>
<th>&lt;106 μm</th>
<th>&lt;250 μm</th>
<th>&lt;500 μm</th>
<th>&lt;1060 μm</th>
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</thead>
<tbody>
<tr>
<td>Autosampler</td>
<td>500</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Barrel Grab</td>
<td>500</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Field Samples – Controlled Sediment Tests

Sample triplicates made using a churn splitter; analytical duplicates made using cone splitter.

Dekaport/USGS Cone Splitter (Teflon and stainless steel)

Churn Splitter Total Solids Replicates

Standard Deviations typically between 5 and 7 mg/L.

Variabilities (expressed as COVs) higher for low-concentration samples (<100 mg/L).

Median COV for TSS analysis = 27%.
Median COV for TS analysis = 8%.

Cone Splitter Replicate Analyses (Post-Split with Churn Splitter)

High variabilities (greater than churn splitter) seen with low solids concentration.

Median COV for TSS analyses = 11%.
Median COV for TS analyses = 5%.
Analytical Methodology for Solids

Analytical methods inconsistent across jurisdictions.
- NJDEP/TARP Tier II Protocol, including NJ amendments: both TSS and SSC
- EPA/NSF ETV: both TSS and SSC
- TAPE: TSS only.
- City of Portland Bureau of Environmental Services (BES) guidance (2004): SSC only.

Both methods intended to quantify the concentration of solids in a sample, but the two methods often give varying results (Gray et al. 2000, Guo 2005, Clark and Siu 2008).

However, distinct differences exist between methods in terms of solids recovery. In addition, sample temperature has a slight but significant effect.

Comparison of three TSS/SSC analytical methods

<table>
<thead>
<tr>
<th>Method</th>
<th>EPA TSS (160.2)</th>
<th>S.M. TSS (2540D)</th>
<th>USGS SSC (D3977-97(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter Nominal Pore Size</td>
<td>Not specified</td>
<td>&lt; 2.0 µm</td>
<td>1.5 µm</td>
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<tr>
<td>Sample Mixing</td>
<td>Shake vigorously</td>
<td>Stir plate</td>
<td>Decant supernatant &amp; flush bottle with DI</td>
</tr>
<tr>
<td>Aliquot Size</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Entire sample</td>
</tr>
<tr>
<td>Method of Aliquot Collection</td>
<td>Pour aliquot into graduated cylinder</td>
<td>Pipet: mid-depth in bottle &amp; midway between wall and vortex</td>
<td>Pour from original bottle</td>
</tr>
</tbody>
</table>

Effect of Storage and Mixing on Oily Flocs

Effect of Method tested using samples from 0 – 500 mg/L of two PSDs.

Suspended Sediment Concentration Compared to Known Laboratory Additions

- SSC methodology able represent entire sample – regardless of sample size distribution.
PSD and Sample Location Effects
(Standard Methods 2540D)

• Pipet location critical in TSS results.
• At midpoint sampling depth (method location), PSD of samples very important (statistically significant).

PSD and Aliquot Size Effects
(EPA Method 160.2)

• Aliquot size has no/minimal effect on TSS.
• PSD has large, statistically significant effect on TSS.

Effect of Sample Temperature
(Method 160.2)

Effect of Sample Salinity
(Method 160.2)
How Does Inherent Variability Affect Field Results?

- 215 paired influent effluent samples from two field verification tests analyzed for TSS and SSC.
- Samples (both the entire set and the influent-only) compared through a scatterplot analysis.
- Results compared to known solids addition from dry hopper of test apparatus.
- In some cases, errors overshadow effects of individual methods.

SSC vs. TSS vs. Mass Balance

SSC 1.4% less than TSS, but slope coefficient contained 1.0.

Gray et al. (2000): TSS typically 25% to 34% less than corresponding SSC.

SSC results best represented hopper additions, but TSS results statistically identical to known additions from hopper.

SSC vs. TSS for 215 full-scale laboratory verification tests

Effluent samples had almost all large solids (> 100 µm) removed.

When effluent samples not included in analysis, variability increases, indicating the effects of slight differences in techniques between analysts and analytical methods. Still statistically identical to each other and to known addition.

Conclusions

- Standardization and documentation to reduce variability in sampling and analytical techniques is recommended.
  - Methodologies should be better, in order to allow for appropriate comparisons.
  - Once the methods are standardized and the variability is reduced, then the “true” associations of pollutants such as heavy metals, organics and nutrients with particle size can be determined.
- The purpose of standards are to ensure that the comparison is “apples-to-apples” but the lack of attention to the details of testing and analysis has left the profession using a “red-apples-to-green-apples” approach.
- Then what happens if we go to discharge limits? What limits? TMDLs? Chronic aquatic toxicity limits?
- What about irreducible concentrations?
Questions?

REFERENCES