# Day 1: Stormwater Particulate Sampling and Processing and Related Analyses

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Stirred and Settled Sample, Showing Settleable Solids (Madison high-efficiency street cleaning tests)



Observed/Perceived Problems with Stormwater Particulate Sampling and Analyses

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Bedload in corrugated stormdrain and mound of settleable material at discharge into wet detention pond after many years of operation at ski resort at Snowmass, CO (drain from several acre resort parking area having sand applications for traction control).



Results of Verification Monitoring of a Popular Hydrodynamic Device by WI DNR and USGS (Madison, WI)				
Sampled solids load in	1623 kg			
Sampled solids load out	1218 kg			
Trapped by difference	405 kg (25% removal)			
Actual trapped total sediment	536 kg (33% actual removal)			
Fraction total solids not captured by automatic samplers	8% (131 kg missed by sampler, out of 1623 kg in sampler)			

Standard automatic water samplers with single intakes at bottom of pipes. Influent samplers are affected by large particles while effluent samplers should not be, assuming most any stormwater control is capable of removing the larger particles that stress the samplers.  $$_{\rm 5}$$ 

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TSS (Total Suspended Solids) vs. SSC (Suspended Sediment Concentration) and PSD (Particle Size Distribution) Relationships

Two separate issues:

- sampling to obtain representative water samples with all particulates of interest, and
- laboratory processing to represent all particulates.

Most problems result in loss of large particles. The combination of methods used affects modeling approach, especially particle size distributions and confusion between TSS and SSC.



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# Sampling Effects on Particulate Solids Characteristics

- Sampling issues associated with stratified flows and bedload.
  - Sampler intakes on bottom of pipe may collect more bedload than represented in well-mixed sample, and
  - sampler tube velocity may not be able to transport large particles to sample bottles

These are two opposite problems that seldom cancel each other out nicely.

# Questions for Collection and Analysis of Solids

Sample Collection  $\rightarrow$  Preparation  $\rightarrow$  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?

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Loss	of Large Particulates in Sampling Lines
	(100 cm/sec sample line velocity)

Percentage loss of particulates	Critical settling rate (cm/sec)	Size range, μm (1.5 to 2.5 sp. gr.)
100	100	8,000 – 25,000
50	50	3,000 - 10,000
25	25	1,500 – 3,000
10	10	350 – 900
1	1	100 – 200

Problem isn't sample line velocity (few particles >100 um, resulting in expected errors of <10%), but location of intake is; therefore need bedload sampler

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Simple methods to obtain representative sample: create cascading and wellmixed flow at sampling location (well-mixed flow with bedload and no stratification). Examples shown for gutter and pipe flow installations.



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# Sample Splitting Methods

- Always needed to obtain subsamples for different laboratory analyses
- As an example, most particulate analyses require 100mL of sample, while the total sample volume is likely 1+L
- Typical subsampling methods to split the sample volume include:
  - Shake and pour into graduated cylinder
  - Pipette while on a stir plate
  - Funnel (cone) splitter

Comparison of sampling splitting for three T	rss/ssc
analytical methods	

	EPA TSS (160.2)/ ISO 11923	Standard Methods TSS (2540D)	USGS SSC (D3977-97(B)
Filter Nominal Pore Size	Not specified	< 2.0 µm	1.5 µm
Sample Mixing	Shake vigorously	Stir plate	Decant super- natant & flush bottle with DI
Aliquot Size	Not specified	Not specified	Entire sample
Method of Aliquot Collection	Pour aliquot into graduated cylinder	Pipet: mid-depth in bottle & mid- way between wall and vortex	Pour from original bottle

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# Sample Splitting for Volume and Sediment Accuracy

- USGS studies found that "shaking and pouring" (or worse, pipetting) 100 mL subsamples from sample bottles for TSS analyses frequently leads to unacceptable errors.
- The USGS found that if the sand fraction (>63 micrometers) comprised less than 25% of the total sample mass, then preferred cone or churn splitting methods were in reasonable agreement with pouring or pipetting methods.
- Since we are concerned with the complete range of particle sizes, and that some source area samples, or some seasonal outfall runoff samples, may exceed this amount of sandsized particles, stormwater sample splitting needs to be done with churn, or preferably, cone splitters.
- As part of a sediment transport in swales project and a large residential/commercial monitoring project, we evaluated three different cone splitters for a wide range of stormwater sediment conditions.



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Recommended Laboratory Methods for Stormwater Particle Analyses

Example Sediment Splitting Accuracy lests using						
Dekaport/USGS Cone Splitter						
tube ID	First test (mg/L)	Second test (mg/L)	Average (mg/L)	Standard deviation	Coefficient of Variation (COV)	
1	547.4	561.9	554.6	10.2	0.018	
2	549.5	572.6	561.1	16.4	0.029	
3	560.6	556.0	558.3	3.2	0.006	
4	550.0	561.5	555.8	8.2	0.015	
5	565.0	552.0	558.5	9.2	0.017	
6	576.2	563.4	569.8	9.1	0.016	
7	573.8	572.9	573.4	0.7	0.001	
8	556.8	587.5	572.2	21.7	0.038	
9	560.0	561.0	560.5	0.7	0.001	
10	563.3	572.4	567.9	6.5	0.011	
Average (mg/L)	560.26	566.12				
Standard deviation	9.83	10.33				
COV	0.018	0.018			22	

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#### Comparison of Three TSS (total suspended solids) and SSC (suspended sediment concentration) Analytical Methods

EPA TSS 160.2 Shake sample bottle vigorously then pour aliquot into graduated cylinder

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Standard MethodsASTM SSC D3977-TSS 2540D97BUse stir plate andUse entire samplepipet at mid-and pour fromdepth in bottleoriginal bottleand midwaybetween wall andvortex





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Stormwater Particle Size Distributions (PSD) from Different Source Areas Compared by TSS or SSC Sample Splitting Methods

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Paved parking, storage, loading dock, vehicle service area, and street runoff particle size distributions (for shake and pour TSS on left and for stir and pipette TSS and SSC on right)





#### Particulate Sampling and Analyses Conclusions

- The largest particles found in sheetflows from source areas are preferentially deposited along the flow paths and drainage system.
- Shake and pour TSS methods do not measure these large particles, while stir and pipette TSS and SSC methods do include these particles.
- Most outfall particle size distributions lack these large particles, and different TSS or SSC methods do not result in significant PSD differences at the outfalls. Better sampling methods reduce the variability of the results.
- "Short" drainage systems that do not retain the large particulates do result in different particle size distributions if different methods are used.
- Appropriate PSDs must be matched with the correct TSS or SSC values with modeling stormwater particulates.

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Large sample volume (about 5 L) separated into subsamples using cone splitter. The sample is first poured through a 1,200 µm fiberglass window screen to remove leaves and grass clippings, and coarse sediment that would clog the splitter. This captured material is also analyzed. Each subsample is about 1 L in volume. One of these can then be split again using the cone splitter for ten 100 mL samples. Each of these 100 mL samples can be filtered to obtain filtrate only having particles smaller then the sieve or filter.









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# Wet Sieving Procedure Outline

- About 12 sieves and membrane filters are used for the wet sieving for particle size analyses (and for particulate strength analyses for pollutants).
- Determine the volume needed for the chemical analyses for each size fraction. Particulates (for PSD analyses) require about 100 mL, but will likely be greater due to low concentrations.
- Use cone splitter to separate the original sample into needed subsample volumes for the number of sieves and filters to be used (plus additional subsamples for replicate analyses for QA/QC).
- Pour one subsample through one of the sieves or filters (not in a stack, as there will be very little sediment captured on each sieve).
- Place the filtrate in a pre-weighed evaporating dish and evaporate to dryness, and re-weigh.

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## **Particle Size Pollutant Associations**

- Concentrations of particles associated with different particle sizes are used to better design stormwater controls and to identify pollutant sources.
- Samples are first split using the cone splitter, and the individual subsamples are further individually separated using a variety filters and sieves.
- The filtered samples are then individually analyzed and the concentrations are determined by difference. Sediment samples can also be examined by saving the filters, or by removing some of the captured debris from the sieves.

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The majority of the copper concentrations (and mass) are associated with the 10 to 100  $\mu$ m particle size range in these industrial area samples. Necessary to remove particulates down to about 10 micrometers to remove most of the particulate-bound copper.





#### **Pollutant Strengths of Stormwater Particulates**

- Pollutant strengths are the contaminant concentrations associated with the particulate matter in the stormwater.
- Particulate strengths are determined by calculating the pollutant concentration only associated with the particulates (measured as TSS or SSC, depending on how the sample was collected and analyzed) in the runoff water.
- They are calculated by the following equation, and are usually expressed as mg pollutant/kg solids:

(total conc. -filterable conc.) particulate solids conc.

in pollutant discharges after controlling down to indicated particle size:					
	250 µm	45 µm	10 µm	2 µm	0.45 µm
Suspended Solids	22	71	95	94	100
Turbidity	23	41	72	77	86
COD	0	23	36	37	40
Total Phosphorus	12	32	48	51	52
Zinc	2	15	23	30	31
Copper	4	14	34	30	36
Cadmium	0	8	0.1	0.1	7
Lead	3	21	23	23	24

Residential and commercial area example: Average percent reductions

For these samples, the control of filterable pollutants (using chemical precipitation, ion exchange or sorption, for example) is also necessary for high levels of control. Control down to about 35  $\mu$ m (removal of all particulates larger than this size) can result in about 80% TSS reductions (a common goal), but that would only result in about <25 to 50% control of total forms of other stormwater pollutants (probably lower than desired).

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# **Particulate Strength Conclusions**

- Knowing the distribution of pollutants associated with different sized stormwater particles allows more accurate determinations of their sources, transport, and control.
- Urban stormwater quality models can use this information when routing stormwater particulatebound pollutants from their source areas and then through the drainage system and stormwater controls.
- The discharged particle size distributions and associated pollutants can then be used in receiving water models to calculate their fates and effects.

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Filterable forms of the metals determine their ability to be removed using ion exchange or sorption methods (higher valence ionic forms easiest to remove, large organic-metal complexes are difficult to remove)

	Filterable metal percentage in ionic forms	Filterable metal percentage bound in organic complexes
Zinc	15	85
Copper	70	30
Cadmium	10	90
Lead	12	88
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# Fugacity Modeling Fugacity equilibrium models (several levels available)

- Fugacity equilibrium models (several levels available) (Mackay, et al. 1992) were used by Bathi (2008) for predicting the phase partitioning of selected PAHs for comparison with observed partitioning.
- Equations used in the fugacity Level 1 modeling included:

Fugacity, 
$$f = \frac{M}{\sum (V_i * Z_i)}$$
 Where,  $Z_i$  = fugacity capacities of air, water, sediment, SS, and fish for i =1, 2, 3, 4, and 5 respectively

$$Z_1 = \frac{1}{RT} \qquad Z_2 = \frac{1}{H} \qquad Z_3 = Z_2 * P_3 * \phi_3 * \frac{K_{OC}}{1000} \qquad Z_4 = Z_2 * P_4 * \phi_4 * \frac{K_{OC}}{1000} \qquad Z_5 = Z_2 * P_5 * L * \frac{K_{OW}}{1000} = \frac{1}{2} + \frac{1}{2}$$

Where, R = gas constant (8.314 J/mol K), T = absolute temperature (K), H= Henry's law constant (Pa.m3/mol),  $K_{OC}$  = Organic-water partition coefficient,  $K_{OW}$  = Octonal-water partition coefficient, P = density of phase (kg/m3), Ø= organic fraction of in the phase, L= Lipid content of fish.

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Example Stormwater Particulate Strengths from Different
<b>Residential and Commercial Source Areas (unfiltered samples</b>

Mean values from several studies	Copper (mg Cu/kg SS)	Lead (mg Pb/kg SS)	Zinc (mg Zn/kg SS)	Chromium (mg Cr/kg SS)	
Resid./Commer. road shoulder	35	230	120	25	
Residential streets	39	87	350	11	
Resid./Commer. pvd sidewalk	44	1200	430	32	
Resid./Commer. unpvd parking	45	160	170	20	
Paved driveways	89	240	650	11	
Resid./Commer. roofs	130	980	1,900	77	
Resid./Commer. pvd parking	145	630	420	47	
Residential roofs	160	870	2,900	n/a	
Resid./Comer. pvd driveways	170	900	800	70	
Street Dirt Residential	230	1,615	431	81	
Residential NSQD outfalls	431	358	1,262	n/a	
The coefficients of variation (COV, standard deviation/mean concentrations) ranged from about 0.75 to 1.5 for these data.					

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# **Fugacity Modeling**

- Model predications indicated that high molecular weight PAHs are predominately partitioned with sediments, while low molecular weight PAHs are predominant in the air and water phases. Most of the 13 PAHs investigated during this study were HMW PAHs and therefore more associated with particulates.
- HMW PAHs indicate pyrogenic (combustion) sources.
- · LMW PAHs indicate petrogenic (oil) sources.



#### PAH Associations with Stormwater Particulates (MCTT Treatability Tasks)

DALL	% Association			
РАН	Water	Particulate Matter		
Naphthalene	22	78		
Fluorene	3	97		
Phenanthrene	2	99		
Anthracene	8	92		
Fluoranthene	29	71		
Pyrene	19	81		
Benzo(a)anthracene	3	99		
Chrysene	1	99		
Benzo(b)fluoranthene	1	99		
Benzo(k)fluoranthene	2	98		
Benzo(ghi)perylene	1	99		
Benzo(a) pyrene	1	99		

The fugacity modeling generally under-predicted the particulate bound fractions, but was very useful in identifying significant factors affecting the partitioning. 57

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### **Coulter Counter Particle Size Analyses**

- The Coulter Counter Multi-Sizer 3 is an example of high-resolution particle size analyser. It is most suitable for particles in the range of about 1 to 200  $\mu m.$
- Larger particles (especially those of about 500 µm and larger) settle to the bottom of the measurement vessel and are not kept suspended and drawn through the analytical aperture.
- Coulter recommends increasing the viscosity of the analytical solution (such as by using Karo syrup) to keep particles as large as 1,200 μm suspended. We were never pleased with this messy option, so we use wet sieving for the larger particles.

- Normally, we have found only a few "sand" grains in the bottom of sample bottles, or in the Coulter vessel, when the instrument was not recording their presence. We were not concerned due to their few number and minimal affect on sample mass.
- During the past several years, we have started to separate the samples into at least three size fractions and measuring directly using sieves and filters: <0.45, 0.45 to 106, and >106  $\mu$ m (usually 256 and 1200 also). Generally, we describe the "suspended solids" fraction as 0.45 to 106  $\mu$ m.
- The intermediate fraction (0.45 to 106 μm) is also used in the Coulter Counter, with no possible interference with large particles. The relatively small fraction of particles >106 μm are therefore quantified and added to the size distribution (as is the <0.45 μm "dissolved" fraction when determining "total solids").</li>



Pre-sieving a sample with 20 micrometer sieve (before use of 32 micrometer aperture tube)



Sieving with a 106 µm sieve to remove large debris before Coulter counting. Similar sample analyzed for total solids.

Screened material showing grass debris (from 5L of sample)







Settling and Scour of Stormwater Particulates: Example of need to know Particle Size Distribution (PSD)



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Specific Gravity a	nd Volatile Solids	of Sediment	
Collected from Stormwater Treatment Device			
	Augrage Specific	Average Velati	

Sieve size range (um)	Average Specific Gravity (g/cc)	Average Volatile Solids (%)
Large organic material (leaves, etc.)	0.84	81.2
>2800	0.66	70.9
1400 - 2800	1.15	57.8
710-1400	1.43	42.7
355-710	2.56	26.1
180-355	2.76	19.4
75-180	2.97	20.6
45-75	3.30	25.7
<45 (Pan)	3.46	26.0

Specific gravity decreases as the volatile solids content increases; larger particle sizes have lower specific gravity and greater volatile solids as they contain larger amounts of light-weight organic debris for these industrial area stormwater sediment samples. Their settling rates are still large due to their large sizes. 67



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#### Hydrodynamic Test Results: Air entrainment effect

Observations during the tests showed that air entrainment reduces the impacting effect of the plunging water jet.

Air bubbles create an ascending velocity component due to buoyancy.

Air entrainment must be considered during calibration and verification of sediment scour in CFD modeling.



#### Scour of Captured Sediment in Storm Drain Catchbasin Inlets (Avila 2008)

- Three flow rates: 10, 5, and 2.5 LPS (160, 80, and 40 GPM)
- Velocity measurements (Vx, Vy, and Vz)
- Five overlying water depths above the sediment: 16, 36, 56, 76, and 96 cm



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# CFD Modeling to Calculate Scour/Design Variations Used CFD (Fluent 6.2 and Flow 3D) to determine scour from stormwater controls; results being used to expand WinSLAMM analyses after verification with full-scale physical model This is an example of the effects of the way that water enters a sump on the depth of the water jet and resulting scour CFD Model gutter flow CFD Model pipe inflow





Scour Test Results: Turbidity Time Series -

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 A decreasing exponential pattern was found in the turbidity time series for each flow rate at

steady conditions.

- The initial impact of the plunging water jet disturbs the sediment bed exposing all the particle sizes.
- Small particles are suspended and washed out creating a hole and leaving the large particles on the sediment bed surface.
- The large particles create armoring on the sediment surface bed which protects the small particles below from being scoured, until larger flow occurs that disturbs the armoring layer.
- Deeper water layer over sediment protects sediment from scour





#### Main References and Sources of Information used in Presentation

- Avila, H. Scour of Captured Sediment from a Stormwater Hydrodynamic Device. Ph.D. dissertation. Department of Civil, Construction, and Environmental Engineering, the University of Alabama. 2008. http://unix.eng.ua.edu/~rpitt/Publications/11 Theses and Dissertations/Humberto Avila Diss ertation.pdf
- Bathi, Jejal. Ph.D. Associations of Polycyclic Aromatic Hydrocarbons (PAHs) with Urban Stream Sediments. Ph.D. dissertation. Department of Civil, Construction, and Environmental Engineering, the University of Alabama. 2008. http://unix.eng.ua.edu/~rpitt/Publications/11 Theses and Dissertations/Dissertation Jejal bat
- <u>hi.pdf</u>.
   Clark, S.E. and C.Y.S. Siu. "Measuring solids concentration in stormwater runoff: Comparison of analytical methods." *Environmental Science and Technology*, 42(2):511-516.
- Clark, S.E. and R. Pitt. "Comparison of stormwater solids analytical methods for performance evaluation of manufactured treatment devices." *Journal of Environmental Engineering*, 134(4):259-264.
- Clark, S.E., C.Y.S. Siu, R. Pitt, C.D. Roenning, D.P. Treese. Peristaltic pump autosamplers for solids measurement in stormwater runoff. *Water Environment Research*, Vol. 81, No. 2, pp. 192-200. Feb. 2009.
- Morquecho, R. Pollutant Associations with Particulates in Stormwater. Ph.D. dissertation. Department of Civil, Construction, and Environmental Engineering, the University of Alabama. 2005. http://unix.eng.ua.edu/~rpitt/Publications/11 Theses and Dissertations/Renee dissertation.pdf
- Pitt, R., Clark, S., Eppakayala, V., Sileshi, R. (2017). "Don't Throw the Baby Out with the Bathwater—Sample Collection and Processing Issues Associated with Particulate Solids in Stormwater." *Journal of Water Management Modeling*, CHI JWMM 2017; C416: <u>https://www.chijournal.org/C416</u>



The total mass scoured with a 10 cm overlying water depth was 15 Kg, equivalent to about 0.9 cm depth of material, while with a 46 cm overlying water depth, the scoured mass was 270 g, equivalent to about 0.02 cm depth of material in the catchbasin. 78

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