
QUALITY ASSURANCE PROJECT PLAN ADDENDUM 3

Enhanced Natural Recovery/Activated Carbon Pilot Study
Lower Duwamish Waterway
Analytical Methods for Carbon Analysis
and Sieving of Gravelly Sand ENR Substrate

Lower Duwamish Waterway Group

Port of Seattle / City of Seattle / King County / The Boeing Company

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FINAL

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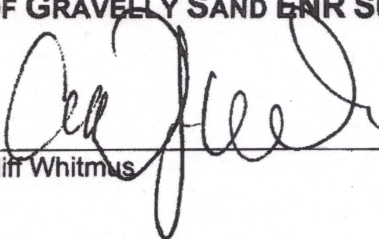
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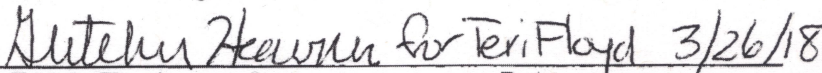
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QUALITY ASSURANCE PROJECT PLAN ADDENDUM 3
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AND SIEVING OF GRAVELLY SAND ENR SUBSTRATE

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Date

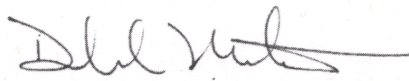
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ABBREVIATIONS AND ACRONYMS

AC	activated carbon
Alpha	Alpha Analytical, Inc.
ALS	ALS Environmental
ARI	Analytical Resources, Inc.
ASTM	American Society for Testing and Materials
BC	black carbon
CO ₂	carbon dioxide
°C	degrees Celsius
Ecology	Washington State Department of Ecology
ENR	enhanced natural recovery
ENR+AC	enhanced natural recovery amended with activated carbon
EPA	U.S. Environmental Protection Agency
g	gram
GAC	granulated activated carbon
LDWG	Lower Duwamish Waterway Group
mg	milligram
NIST	National Institute of Standards and Technology
PCB	polychlorinated biphenyl
PSEP	Puget Sound Estuary Program
QAPP	quality assurance project plan
RSD	relative standard deviation
TOC	total organic carbon
TVS	total volatile solids
UMBC	University of Maryland Baltimore Campus

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1.0 PROJECT DESCRIPTION AND OBJECTIVES

This Quality Assurance Project Plan (QAPP) Addendum serves as an addendum to the *Quality Assurance Project Plan, Enhanced Natural Recovery/Activated Carbon Pilot Study, Lower Duwamish Waterway* (Pilot Study QAPP, Amec et al., 2016) and details modifications to the analytical methods for carbon analysis and adds a sieving step to the preparation of samples comprised of the gravelly sand enhanced natural recovery (ENR) substrate. This addendum formally documents a series of discussions and decisions that have occurred between the Lower Duwamish Waterway Group (LDWG) and the Agencies (U.S. Environmental Protection Agency [EPA] and Washington State Department of Ecology). In addition, the East Coast laboratory that has been conducting the grain-size analysis will be replaced with a local laboratory.

The Pilot Study QAPP (Amec et al., 2016) identified a number of questions for which carbon analysis results would be used to assist in the overall performance evaluation for the ENR/ENR-AC Pilot Study. They are summarized briefly in Table 1.1 with references to the Pilot Study QAPP sections. During construction, it became evident that the originally-proposed carbon analysis methods were returning results that were biased low; too low to be useable for the intended use of the data. This led to a number of discussions and to the decision to modify the procedures in the Pilot Study QAPP in order to improve data quality. This addendum presents those changes and their rationale.

The remainder of this QAPP Addendum is organized as follows:

- Section 2 discusses the context for the proposed changes.
- Section 3 presents the analytical results using multiple methods to measure activated carbon (AC), black carbon (BC), natural organic carbon, total organic carbon (TOC), total volatile solids (TVS), and inorganic carbon. These results form the basis for selecting the methods that will be used to measure carbon during Years 1, 2, and 3.
- Section 4 outlines the changes to the Pilot Study QAPP and the methods that will be used for carbon measurements.
- References are included in Section 5.

2.0 FORMS OF CARBON AND CONTEXT

The intent of the pilot study is to assess the addition of activated carbon (AC) to an ENR substrate to determine whether it reduces the bioavailability of polychlorinated biphenyls (PCBs); this is evaluated through a measurable decrease in sediment PCB porewater concentrations in the Lower Duwamish Waterway. A form of carbon known as black carbon (BC) has been found in numerous studies to be one of the more absorbent forms of carbon found in urban sediments. AC is a manmade form of carbon that is very similar to BC in its characteristics and the manner in which it is formed; however, since it is intentionally manufactured, the purity of the original carbon source and the quality of the resulting AC can be controlled.

BC is a form of soot formed during the incomplete, high temperature combustion of fossil fuels, biofuels, wood and cellulose, and biomass. By incomplete, chemists mean that the combustion occurred with little or no oxygen present and rather than converting all of the carbon to carbon dioxide (the normal end-product of combustion of carbonaceous materials), the end-product is a fine-grained black solid consisting primarily of carbon with high surface area. BC is produced both naturally and by human activities with primary sources being diesel engines, cook stoves, wood burning, and forest fires.

AC is carbon produced from carbonaceous source materials such as nutshells, coconut husk, peat, wood, lignite, coal, and petroleum pitch. It can be produced by one of the two following processes:

1. Physical activation: The source material is developed into AC using hot gases. Air is then introduced to burn out the gasses, creating a graded, screened and de-dusted form of AC. This is generally done by using one or a combination of the following processes:
 - a. Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600 to 900 degrees Celsius (°C), usually in inert atmosphere with gases like argon or nitrogen (in the absence of oxygen).
 - b. Activation/Oxidation: Raw material or carbonized material is exposed to oxidizing atmospheres (oxygen or steam) at temperatures above 250°C, usually in the temperature range of 600 to 1200°C.
2. Chemical activation: Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (Kasaoka et al. 1989) (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride 25%). Then, the raw material is carbonized at lower temperatures (450 to 900°C). Activation occurs during the carbonization step.

Today, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material, and coconuts husks are a preferred material for environmental use because it is relatively easy to get clean, virgin materials (materials harvested

directly from coconut trees that have not been previously used for other industrial uses) (Phan et al., 2006).

In the Narrative Design Report for the pilot study (Amec et al., 2015), the AC specified for use was virgin granular activated carbon (i.e., not regenerated carbon) made from coconut husks using the low temperature chemical activation method. The material was documented to be free of measurable PCBs. The AC material was well graded across the grain-size range of 200 to 1,000 microns.

This QAPP Addendum presents testing of a method by Grossman and Ghosh (2009) that would be used to measure the amount of AC in samples collected from the pilot study. The QAPP Addendum also summarizes the analytical findings and exploration undertaken to reach resolution of using the Grossman and Ghosh method in place of the Pilot Study QAPP (Amec et al., 2016) method developed by Gustafsson et al. (1997)¹. The Gustafsson method was designed to measure the highly absorbent BC that is present in sediments, and often associated with sources of soot. However, findings during the construction material testing, reported below in Section 3, showed that the Gustafsson method combusted the type of AC used in the pilot study prematurely, making it impossible to measure AC. The Grossman and Ghosh method measures the BC or AC in a different way and overcomes this obstacle.

Using results presented in this QAPP Addendum, and based on discussions with EPA, this QAPP Addendum replaces the Gustafsson et al. (1997) method with a method developed and reported by Grossman and Ghosh (2009).

3.0 PROBLEM UNDERSTANDING

The Pilot Study QAPP (Amec et al., 2016) included a conventional, thermal method (Gustafsson et al., 1997) to measure the percent BC (%BC). The accuracy of the thermal %BC method was tested at the laboratory using a standard reference material that is common for use on sediment projects: NIST 1650. This standard reference material is composed of diesel soot (a form of BC generated at high temperatures) and was used to validate the thermal %BC method.

Results of ENR+AC substrate materials² testing during the placement of the ENR layers, using various carbon testing methods, showed unexpected results. In general, initial carbon analysis results were biased low. It was discovered that the natural coconut-based fiber AC added to the ENR material was combusting at lower than expected temperatures, making it impossible to

¹ The BC measurement using the Gustafsson et al. method was expected to include both the AC added to the ENR material and any naturally occurring BC present (such as soot) in the existing sediments.

² The ENR+AC substrate is ENR materials (quarry sand or gravelly sand) amended with AC.

accurately quantify the AC content, or %AC using the method identified in the Pilot Study QAPP. The discussion below describes the problems and their source. This discussion is written to capture the issues, not to chronicle all testing performed.

3.1 THE CARBON TEST METHODS

3.1.1 Summary of Test Methods

Understanding the various carbon test methods is important to understand and resolve the problem encountered during ENR+AC substrate materials testing. The flowchart in Figure 3.1 outlines the three thermal methods that can be employed to measure different forms of carbon in environmental samples (TVS, TOC, and BC). The method temperatures provided in Figure 3.1 are for comparative purposes. Sample sizes and combustion temperatures may vary by lab. This section summarizes the various methods outlined in Figure 3.1 as well as analyses performed using these methods.

Prior to carbon analysis, ENR+AC substrate materials testing samples composed of the gravelly sand substrate were air dried and sieved to remove the gravel before it was handled by the chemical lab. This was done with a #4 sieve at a materials testing lab. This step was already part of the method for analysis of PCB congeners, and was added for all analyses on the gravelly sand matrix.

Upon receipt at the chemical lab, all samples were dried at 80°C to determine percent moisture. Then aliquots were removed for the total volatile solids (TVS), total organic carbon (TOC), and BC analyses.

The three thermal methods differ as shown in Figure 3.1 and as described below.

- TVS measures the weight of the sample loss on ignition at 550°C. Any volatile material will contribute to the loss: wood, organic contaminants, biogenics, the TOC fraction that combusts below 550°C, and inorganic carbonates. TVS is measured based on differences in sample weight before and after ignition. TVS uses a large sample size of approximately 25- to 50-grams (g) sample dried and homogenized and 10-g aliquot combusted.
- TOC is intended to capture only the organic carbon content. To do this, the sample is acidified to dissolve inorganic carbonates; carbon is measured using a carbon dioxide (CO₂) detector after complete ignition at high temperature (instrument dependent), instead of differences in weight before and after ignition. Because the CO₂ detector is sensitive, it works well on very small sample sizes (10 to 20 milligrams [mg]) as long as the sample is representative of the material. When the TOC is used to measure the AC in a sample, the carbon content of the AC is used to convert to a weight percent, or the result is presented as percent carbon.

- BC is intended to capture only the high temperature component of TOC, which is generally expected to be soot. This is accomplished by preparing the sample for a TOC analysis, and then performing a pre-combustion step at 375°C, which is intended to burn off the biogenics, wood, petroleum fuel and volatile organics, leaving only the soot to be ignited in the second step at 925°C. Carbon is measured using a CO₂ detector.

3.1.2 Pilot Study QAPP Method Performance for Assessing Carbon

The Pilot Study QAPP (Amec et al., 2016) included the following methods for tests of ENR materials (quarry sand and gravelly sand, which contain little to no native carbon) mixed with AC during construction of the subplots.

1. TOC would be run on duplicate 2- to 10-mg aliquots of a thoroughly homogenized and ground (5- to 10-g) sample with the average result reported. The combustion temperature at 925°C was expected to combust all of the AC in the substrate sample. The TOC value as a measure of %AC would be biased slightly low, because AC is not 100% carbon (AC is greater than 90% carbon, with oxygen, hydrogen, and nitrogen making up the rest). Note, the AC used in the pilot study was assayed afterwards to determine its carbon content so that %TOC could be converted to %AC in the sediment sample (see Section 3.5).
2. BC would be run on the samples prepared in the same manner as for TOC; however, there would be a pre-combustion burn at 375°C designed to remove volatile organics from sources such as biological materials and fuels. The method was not expected to combust the AC at the 375°C temperature, so that AC could be measured as the carbon that survives the 375°C temperature and is combusted at 925°C. Because the latter materials would not be present in the ENR substrate, the %BC was expected to return the same values as the %TOC in the ENR+AC substrate material samples.

3.2 FINDINGS ON ENR+AC SUBSTRATE MATERIALS

The initial TOC/BC results of the pre-placement material (ENR+AC) were lower than expected; the pilot study targeted a 4% AC addition to the ENR material (by weight), and results suggested substantially less than 4% was measured using the BC method.

Following receipt of the initial TOC and BC results, TVS analysis was run on the pre-placement ENR+AC substrate. TVS was added because this method uses a larger sample size (25- to 50-g sample dried and homogenized and 10-g aliquot combusted), helping to improve the representativeness of the samples. It was discovered that the ENR+AC substrate appeared to be too coarse for reliable analytical results using the smaller instrument sample sizes (2 to 10 mg) used in TOC/BC methods by Alpha Analytical, Inc. (Alpha) (see Section 3.3). In addition, because the source material was a mixture of AC and sand or gravelly sand only, the contribution from inorganic carbonates or other organics was expected to be relatively insignificant. Thus, TVS would produce representative results of organic carbon in the materials testing samples.

Initial findings were that the TVS method was more accurate for capturing the AC in the pre-placement ENR+AC substrate, compared to the BC method, which was the least accurate with a strong bias low when the results were compared to expected results based on weigh tickets (4% AC by weight).

Figure 3.2 compares the results of the pre-placement ENR +AC substrate measurements using the thermal BC, TOC, and TVS methods. The figure shows two mixtures, one with AC added to sand and the other with AC added to a gravelly sand mixture, reflecting the two types of ENR materials used in this pilot study. Only the TVS method approached 4% AC, the amount of AC added to the sand and gravelly sand mixtures. Thus, only TVS appeared to provide the level of accuracy needed for the study.

A sample of pure AC (the same material used in the pilot study) was analyzed using the BC method and found to be completely combusted at 375°C (during the “pre-combustion” burn). These results showed that the AC material was combustible at temperatures below 375°C, and thus the AC used in the pilot study was not measured in the BC method at all.

Standards were made in the lab consisting of the sand matrix, with AC added at 0.5, 2.0, 4.0, 6.0, and 8.0% by weight. These standards were analyzed using all three carbon methods at Alpha, using triplicate burns instead of the duplicate burns. Results are presented in Figure 3.3. The TVS method reproduced the standards with reasonable accuracy (the %AC by weight is a 1:1 line comparing measured and expected results); the TOC method was biased low and showed insufficient linearity, believed to be linked to the smaller sample size used, and the BC method was unable to quantify the AC at all, presumably because it was lost in the pre-combustion step at 375°C.

Because the combustion of the AC at 375°C was unexpected, the literature was reviewed again to determine if other studies reported similar results. The majority of the study designs were such that the effect would not have been noticed. However, the following studies were helpful in confirming the behavior of the AC.

- Several studies were conducted in industrial engineering in the 1980s and 1990s when AC was beginning to be used for fluidized bed applications. The first AC materials were derived from coke (a high temperature material). When the industry was switching to cellulose derived AC, unexpected fires were triggered during pilot and bench scale studies. Researchers reported that AC made from cellulose materials (wood and coconut husks) was quite combustible at low temperatures. Fine-grained granular AC that was very dry could combust as low as 125°C. A good discussion can be found in Thermal Stability of Activated Carbon in an Adsorber Bed (Hoye et al., 1997).

- Grossman and Ghosh (2009) mentioned the problem with coconut husk-based AC being biased low using the Gustafsson method, but it was a comment in passing in the paper, and they reported a low bias and not a complete loss.
- Phan et al. (2006) used coconut husk fibers to make AC using chemical activation (similar to that used to create the commercial AC used in the pilot study). The AC made by coconut husk fibers had a composition of 70% carbon, which mean carbonization of the organic material was incomplete.

It should be noted that while coconut husk AC combusts at a temperature that is too low to make the %BC method of Gustafsson appropriate for use, coconut husk AC is still a clean, highly absorbent form of carbon.

3.3 THE INFLUENCE OF SAMPLE SIZE

Measurement of TOC by EPA Method 9060 is an established method that measures carbon in a solid substrate. This method was developed for use in sediment, and thus can use a small sample size to analyze the fine-grained substrate. Many commercial labs process (dry and grind) approximately 10 to 20 g and then actually analyze only 10- to 20-mg of sample. For the baseline sediment samples, which are composed of well-dispersed, fine-grained sediments, the small sample size works fine. However, the ENR substrate is different from the native sediments and the results described in this QAPP Addendum indicate that a larger instrument sample size of ENR substrate improves the carbon analysis accuracy compared to smaller sample sizes. Reasons for this include:

- A much coarser material (sand or gravelly sand) makes up the bulk of the ENR material. The coarse material makes it difficult to select representative 20-mg samples for testing.
- During construction, the AC is mixed with sand using a physical mixing system. While this mixing process is adequate for field purposes, at the 20-mg scale, it can be relatively heterogeneous, and the utensil used to collect the 20-mg sample (a small scoopula) tends to preferentially collect sand.

TOC was run, using the same analytical method, at three different labs with different equipment and sample sizes, to evaluate the impact of sample size. Figure 3.4 shows the results of the standards analyzed for TOC by King County Environmental Laboratory (20 to 25 g ground, 200 mg analyzed), ALS Environmental (ALS) (10 g ground, 250 mg analyzed), and Alpha (25 g ground, 20 mg analyzed). The TOC results showed better performance with the larger instrument sample size. The best TOC results were obtained when 10 or 25 g were ground to establish a 200-mg aliquot sample for the instrument used by the method.

3.4 TOC AND TVS FINDINGS IN BASELINE SEDIMENTS

Baseline sediment samples were originally analyzed for TOC, BC, and grain size. Results showed that baseline sediments were composed of primarily fine sand and silts, with 1.29 to 2.8% TOC, consistent with previous studies. BC was detected and replicates showed high reproducibility. Results showed that BC was approximately 9% (average) of the TOC. These findings indicate that the baseline sediment results for BC are valid to use in the pilot study.

To evaluate the ability of TVS to serve as a surrogate for TOC, two baseline sediment samples of different %fines and %TOC were analyzed for TVS by King County Environmental Laboratory. Using homogenized samples that were split to measure TVS and TOC, the TVS result (4.5% and 7.2%) was significantly higher than the TOC result (1.5% and 2.4%, respectively) in the same samples, and likely reflects the presence of carbonates from microscopic shell material in the sediments. These results indicated that TVS would not be a good surrogate for organic carbon measurements once ENR+AC materials are mixed with native sediments in the years following placement.

The same two baseline sediment samples were tested by King County Environmental Laboratory for TOC using the same method as Alpha but a different instrument that uses a larger sample size (approximately 200 mg). The two laboratories had comparable results. These findings show that the baseline sediment results for TOC are valid to use in the pilot study.

3.5 ELEMENTAL ANALYSIS OF PURE AC

The Phan et al. 2006 information on percent carbon in AC led to having the pure AC used in the pilot study analyzed for its carbon composition. The percent carbon in the pure AC used in the pilot study was determined using method ASTM D5373-08. The pure AC material is composed of 93.93% carbon, <0.05% hydrogen, 0.61% nitrogen, and 1.09% oxygen. The percent carbon in the pure AC can be used to convert the expected percent by weight of the AC in the ENR substrate materials to the expected percent carbon by weight due to added AC. This expected percent carbon by weight can then be compared to the TOC measured in samples.

3.6 BLACK CARBON ANALYSIS OF ENR+AC SUBSTRATE MATERIALS

University of Maryland Baltimore Campus (UMBC), under the direction of Professor Upal Ghosh, was contracted to analyze activated carbon in samples from the Lower Duwamish Waterway ENR/AC Pilot Study, using the Grossman and Ghosh method (2009). Five types of samples were analyzed by the method to test its efficacy: pure AC; sand and AC; native sediment; native sediment and AC; and sand, native sediment, and AC (Table 3.1). The Grossman and Ghosh method performed extremely well in measuring the AC used in the ENR/ENR-AC Pilot Study (Table 3.2, Figure 3.5).

The Grossman and Ghosh method achieved high recovery and low %RSD (relative standard deviation) values (except for the 2% sample in the calibration curve analysis) and established a high degree of confidence with a high r^2 value for the standard curve regression. The %RSDs for the 0.5, 2, 4, and 6% AC by weight calibration curve samples were 19, 52, 12, and 4%, respectively. The method was used to differentiate AC from other types of organic carbon.

The method also performed extremely well when tested against known carbon concentrations in native sediment; native sediment and activated carbon; and sand, native sediment, and activated carbon (Table 3.2). Additionally, the method confirmed that the pure AC was composed of 93% carbon, as calculated by elemental analysis.

3.7 FINDINGS

The following findings were established at the end of the ENR and ENR+AC substrate and standards testing:

- For the ENR+AC substrate, the TVS method was able to confirm that the %AC levels measured in samples of the material coming down the conveyer for placement in the plots was consistent with the %AC indicated by weigh slips for the ENR and AC materials.
- The AC used in the pilot study had a composition of 93.93% carbon. This composition can be used to convert between percent by weight and percent carbon by weight.
- The Pilot Study QAPP specified TOC method is valid to assess TOC of sediment samples but a larger instrument sample aliquot is recommended for testing ENR substrate.
- The original black carbon analysis method yielded results that were biased low and the TVS method will not be suitable to measure AC for sediments containing both AC and natural organic carbon-containing material and natural inorganic carbonates. Therefore, the TVS method, while suitable for construction monitoring at time zero, is not suitable for monitoring during Years 1, 2, and 3 once native material is mixed in.
- The Grossman and Ghosh BC method performed very well at differentiating between natural organic material found in native sediment and AC and this method will be used to monitor the AC in the ENR and ENR+AC subplots during Year 1, 2, and 3 sampling.

4.0 METHOD MODIFICATIONS FOR ENR AND ENR+AC TESTING

The sample processing procedures and analytical methods for measurement of TOC and the method for calculating %AC for future years are to:

1. Sieve the gravelly sand as a processing step prior to shipment to the chemical laboratory for further analyses. The sieved fractions are weighed and percent gravel retained is recorded and available as part of the data set.
2. Use a lab (ALS in Kelso, Washington) that analyzes for TOC by EPA Method 9060 using equipment that allows for the larger samples sizes; approximately 10-g sample for initial homogenization and grinding and an approximately 250-mg aliquot for analysis of TOC.
3. Eliminate the Gustafsson BC method and replace it with the Grossman and Ghosh method for measuring BC/AC; the method will be performed by UMBC lab.
4. Discontinue use of TVS analysis because inorganic carbonates have the potential to be present in future years and would result in interferences when using the method as a surrogate for TOC.

The laboratory that was conducting the BC analysis (Alpha) also conducted the grain-size analysis. Alpha was selected since they were one of the few commercial labs that could conduct the BC analysis. Since Alpha was receiving the samples for BC analysis, it was decided to also send them the samples for TOC and grain-size analysis. This was done to reduce the number of labs that were analyzing samples. During development of the Pilot Study QAPP, the original intent was to have the grain-size samples analyzed using Puget Sound Estuary Program (PSEP) methods; however, Alpha could not perform the PSEP analysis. To meet the requirements of the study, a modification of ASTM D422 was made to provide data equivalent to PSEP methods. Alpha will no longer be performing the BC or TOC analysis; therefore, only the samples for grain-size analysis would be sent to them. To reduce the chance of samples being lost or compromised during shipment to the East Coast, a local laboratory, Analytical Resources, Inc. (ARI) in Tukwila, Washington, will conduct the grain-size analysis. This will have the additional benefit of ARI being able to perform the analyses using PSEP methods that were originally planned. A flow chart delineating sample processing and analysis is included as Figure 4.1.

In Section 2.5.3 of the Pilot Study QAPP (Amec et al., 2016), the reference to Alpha is no longer relevant and is replaced by ALS-Kelso for TOC analysis and ARI for grain size.

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In Table 3.3 of the Pilot Study QAPP (Amec et al., 2016), Alpha was the designated laboratory to analyze samples for BC, TOC, and grain size. Going forward, BC will be analyzed at UMBC, TOC will be analyzed at ALS, and grain size will be analyzed at ARI.

5.0 REFERENCES

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TABLES

**Table 1.1
Questions by Event that Utilize Carbon Analysis Results**

Event	Sample Type	Question	Carbon Methods¹	Pilot Study QAPP Section²
Construction	ENR+AC substrate	Confirm AC content of the substrate prior to placement, but after mixing with ENR materials	TOC and black carbon ³	Construction QAPP and 3.2.1
Baseline	Sediment samples	Establish a baseline for existing sediments prior to placement of ENR materials	TOC and black carbon	3.1.1.1
Year 0	ENR+AC substrate after placement	How uniform was the ENR+AC placement; how much of the carbon was loss during its transit to the sediment bed?	TOC and black carbon	3.1.1.2
Years 1, 2, and 3	Sediments in the ENR plots (assumed to contain ENR substrate plus some amount of newly deposited sediment)	How much AC remains in the ENR+AC subplots compared to the ENR only subplots?	TOC and black carbon	3.1.1.3 and 3.1.1.4

Notes:

1. Per Section 3.4.2.1 of the Pilot Study QAPP (Amec et al., 2016), samples will be analyzed for TOC by SW-846 9060, for black carbon by Gustafsson et al. (1997).
2. Pilot Study QAPP: Amec et al. (Amec Foster Wheeler; Dalton, Olmsted & Fuglevand, Inc.; Ramboll Environ; Floyd|Snider; and Geosyntec Consultants). 2016. Quality Assurance Project Plan, Enhanced Natural Recovery/Activated Carbon Pilot Study, Lower Duwamish Waterway. Lower Duwamish Waterway Group, Seattle, WA. February 22.
3. As stated in Section 3.4.2.1 of the QAPP, the intent of the black carbon method was intended to “measure the more sorptive forms of carbon in the sediments. The black carbon measurement include both the GAC added to the ENR material and any naturally occurring active carbon present such as soot in the existing sediments).”

Abbreviations:

AC = activated carbon
ENR = enhanced natural recovery

ENR+AC = enhanced natural recovery amended with activated carbon
GAC = granular activated carbon

QAPP = quality assurance project plan
TOC = total organic carbon

**Table 3.1
Proposed UMBC Sampling Matrix**

Sample Set #	Sample Matrix	UMBC Labels ¹	Setup	No. of Samples ²	Test Condition
1	Pure AC	LDW-BA-PC-ERNMAT-GAC-#	Pilot Study sample of AC	3	Go/no-go to determine whether method works with natural sourced AC used in Pilot Study. Uses potassium dichromate oxidant to remove non-AC natural organic carbon.
1a	Pure AC	LDW-BA-PC-ERNMAT-GAC-#-HCl	AC using HCl ³	3	HCl removes inorganic carbon, and also non-AC natural organic carbon. Used to compare to potassium dichromate.
1b	Pure AC	LDW-BA-PC-ERNMAT-GAC-#-UT	Conventional TOC method ⁴	3	Thermal method to look at total carbon, without acid digestion.
2	Sand + AC	LDW-BA-PC-ERNMAT-SAND1-# LDW-BA-PC-ERNMAT-SAND2-# LDW-BA-PC-ERNMAT-SAND3-# LDW-BA-PC-ERNMAT-SAND4-#	Calibration Curve: Sand + 0.5%, 2%, 4%, 6% AC by weight	12	AC calibration and test recovery of AC fines (observe whether fines are lost).
3	NS	LDW-Y0-ERNMAT-NS-#	NS only	3	Sets baseline for NS+AC samples. For NS (and thus NS+) samples, the Grossman and Ghosh method measures BC, and not TOC.
4	NS + AC	LDW-Y0-ERNMAT-NSAC1-#	NS + 2% AC, NS + 4% AC	6	Test the recovery of AC in the presence of NS; also test the recovery of AC under site-specific saline conditions
5	Sand + NS + AC	LDW-Y0-ERNMAT-NSACSAND-#	Sand + 25% NS + 4% AC	3	Test how all three materials (sand, NS, AC) interact and the recovery of AC under this condition.
Total				33	

Notes:

- # = Sample Replicate Number (1, 2, or 3 for triplicates).
- All samples analyzed in triplicate.
- HCl samples are the samples that are not run through the full Grossman and Ghosh method (chemical=oxidation treatment), but only acidified with HCl.
- Samples designated "UT" are untreated samples that do not receive the chemical-oxidation treatment or acidification with HCl.

Abbreviations:

AC = activated carbon
BC = black carbon
GAC = granulated activated carbon

HCl = hydrochloric acid
NS = native sediment
TOC = total organic carbon

UMBC = University of Maryland Baltimore Campus
UT = untreated

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January 31, 2018

**Table 3.2
UMBC Analytical Results**

Sample ID	Baseline Results (not corrected for moisture)						Moisture	Moisture-Corrected Results			
	Sample Description	Mass Sample (mg)	Mass C (mg)	Carbon (%)	Average (%)	Stdev (%)	Avg. Moisture (%)	% Carbon	Average (%)	Stdev (%)	RSD (%)
LDW-BA-PC-ERNMAT-GAC-1	Activated Carbon (AC)	49.7	42.3	85.11	83.3	1.7	6.0%	90.54	88.6	1.8	2.1%
LDW-BA-PC-ERNMAT-GAC-2	Using Grossman &	50.2	41.77	83.21				88.52			
LDW-BA-PC-ERNMAT-GAC-3	Ghosh Method	50.1	40.91	81.66				86.87			
LDW-BA-PC-ERNMAT-GAC-1-HCl	AC Using HCl ¹	50.5	41.56	82.30	81.1	1.9	6.0%	87.55	86.3	2.0	2.3%
LDW-BA-PC-ERNMAT-GAC-2-HCl		48.5	39.83	82.12				87.37			
LDW-BA-PC-ERNMAT-GAC-3-HCl		49.7	39.25	78.97				84.01			
LDW-BA-PC-ERNMAT-GAC-1-UT	AC Without Acid Prep (TOC Method) ²	53.2	46.57	87.54	86.9	0.88	6.0%	93.13	92.5	0.94	1.0%
LDW-BA-PC-ERNMAT-GAC-2-UT		53.2	46.48	87.37				92.95			
LDW-BA-PC-ERNMAT-GAC-3-UT		56.3	48.38	85.93				91.42			
LDW-BA-PC-ERNMAT-SAND1-1	Calibration Curve 1: Sand + 0.5% AC	540.4	4.366	0.81	0.68	0.13	0.4%	0.81	0.68	0.13	19%
LDW-BA-PC-ERNMAT-SAND1-2		532.5	2.925	0.55				0.55			
LDW-BA-PC-ERNMAT-SAND1-3		547.1	3.698	0.68				0.68			
LDW-BA-PC-ERNMAT-SAND2-1	Calibration Curve 2: Sand + 2% AC	575.2	9.277	1.61	1.35	0.70	0.5%	1.62	1.35	0.70	52%
LDW-BA-PC-ERNMAT-SAND2-2		541.2	10.12	1.87				1.88			
LDW-BA-PC-ERNMAT-SAND2-3		525.4	2.931	0.56				0.56			
LDW-BA-PC-ERNMAT-SAND3-1	Calibration Curve 3: Sand + 4% AC	514.2	20.2	3.93	3.62	0.43	0.6%	3.95	3.65	0.44	12%
LDW-BA-PC-ERNMAT-SAND3-2		523.5	19.97	3.81				3.84			
LDW-BA-PC-ERNMAT-SAND3-3		529.5	16.56	3.13				3.15			
LDW-BA-PC-ERNMAT-SAND4-1	Calibration Curve 4: Sand + 6% AC	517.2	28.05	5.42	5.56	0.19	0.7%	5.46	5.60	0.19	3.5%
LDW-BA-PC-ERNMAT-SAND4-2		568.7	32.88	5.78				5.82			
LDW-BA-PC-ERNMAT-SAND4-3		581.4	31.86	5.48				5.52			
LDW-Y0-ERNMAT-NS-1	Native Sediment (NS)	247.5	0.4304	0.17	0.17	0.01	6.5%	0.19	0.18	0.01	5.8%
LDW-Y0-ERNMAT-NS-2		252.6	0.401	0.16				0.17			
LDW-Y0-ERNMAT-NS-3		254	0.4505	0.18				0.19			
LDW-Y0-ERNMAT-NSAC1-1	NS + 2% AC	250.2	4.587	1.83	1.79	0.12	5.8%	1.95	1.90	0.12	6.6%
LDW-Y0-ERNMAT-NSAC1-2		285.6	4.737	1.66				1.76			
LDW-Y0-ERNMAT-NSAC1-3		273.8	5.152	1.88				2.00			

**Table 3.2
UMBC Analytical Results**

Sample ID	Baseline Results (not corrected for moisture)						Moisture	Moisture-Corrected Results			
	Sample Description	Mass Sample (mg)	Mass C (mg)	Carbon (%)	Average (%)	Stdev (%)	Avg. Moisture (%)	% Carbon	Average (%)	Stdev (%)	RSD (%)
LDW-Y0-ERNMAT-NSAC2-1	NS + 4% AC	250.6	10.33	4.12	3.87	0.25	6.5%	4.41	4.14	0.26	6.3%
LDW-Y0-ERNMAT-NSAC2-2		268.7	10.36	3.86				4.13			
LDW-Y0-ERNMAT-NSAC2-3		252.9	9.187	3.63				3.89			
LDW-Y0-ERNMAT-NSACSAND-1	NS + 25% Sand + 4% AC	245.6	8.174	3.33	4.05	0.64	2.1%	3.40	4.14	0.66	16%
LDW-Y0-ERNMAT-NSACSAND-2		245.6	11.21	4.56				4.66			
LDW-Y0-ERNMAT-NSACSAND-3		240.3	10.23	4.26				4.35			

Notes:

- HCl samples are the samples that are not run through the full Grossman and Ghosh method (chemical-oxidation treatment), but only acidified with HCl.
- UT are untreated GAC samples; samples designated "UT" are untreated samples that do not receive the chemical-oxidation treatment or acidification with HCl.

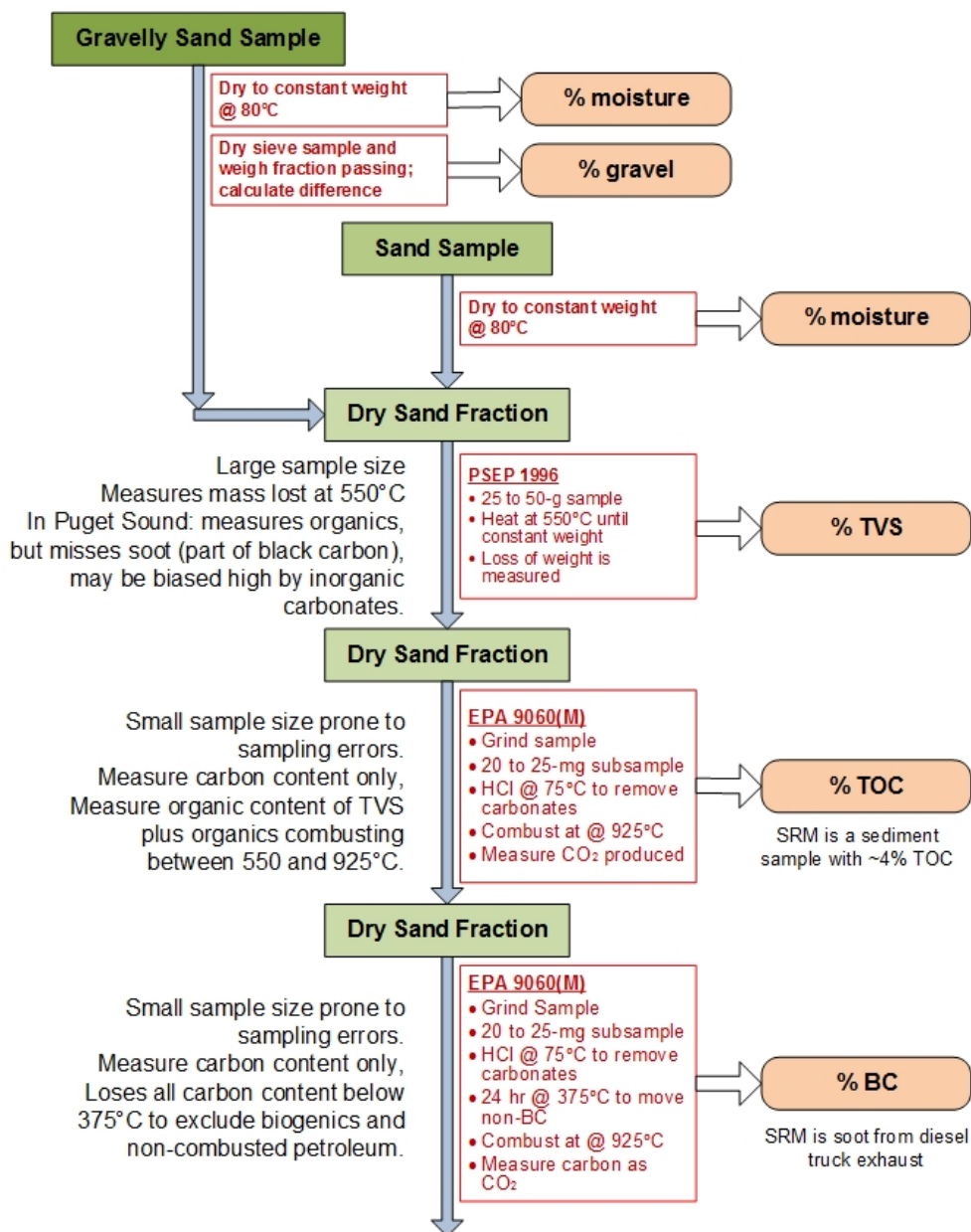
Abbreviations:

AC = activated carbon
GAC = granulated activated carbon
HCl = hydrochloric acid
mg = milligram

NS = native sediment
RSD = relative standard deviation
Stdev = standard deviation
TOC = total organic carbon

UMBC = University of Maryland Baltimore Campus
UT = untreated

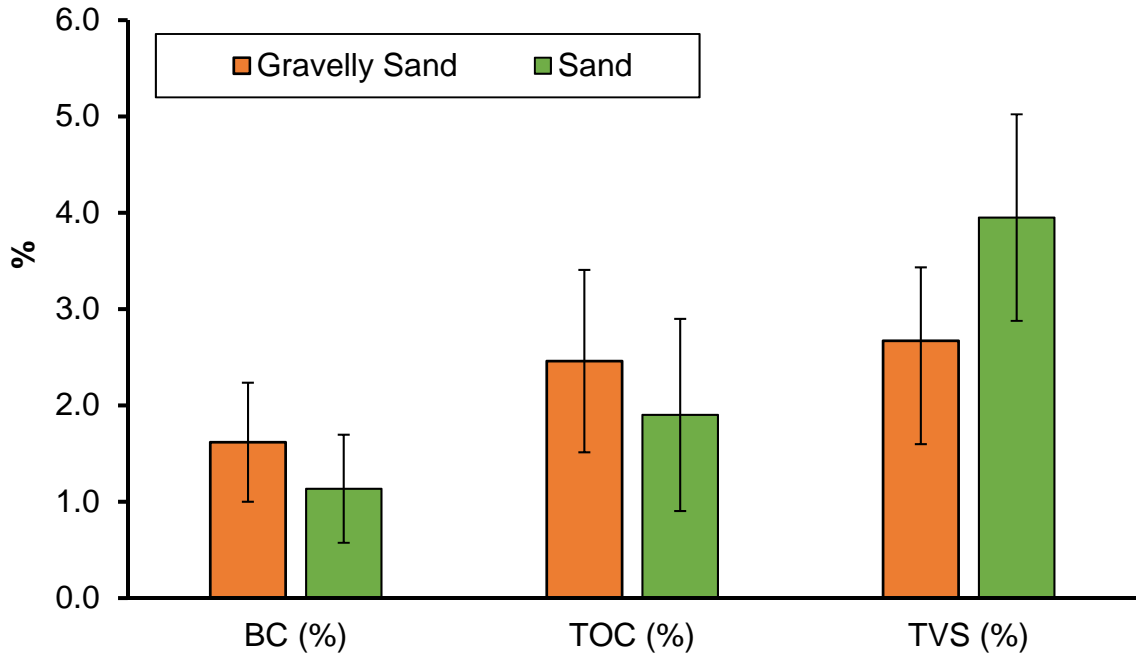
FIGURES



Carbon Test Methods. Samples consisted of the ENR substrate (before and after placement) and sediment samples collected from the Lower Duwamish Waterway. Sediments were fine-grained silts and sand. ENR substrates ranged from sand to a gravelly sand depending on plot. Samples consisting of gravelly sand required pre-sieving to remove the larger particles before they were handled by the analytical laboratory. Method specifics are for Alpha Analytical, Inc., only. Sample sizes and combustion temperatures vary by lab.

Abbreviations:

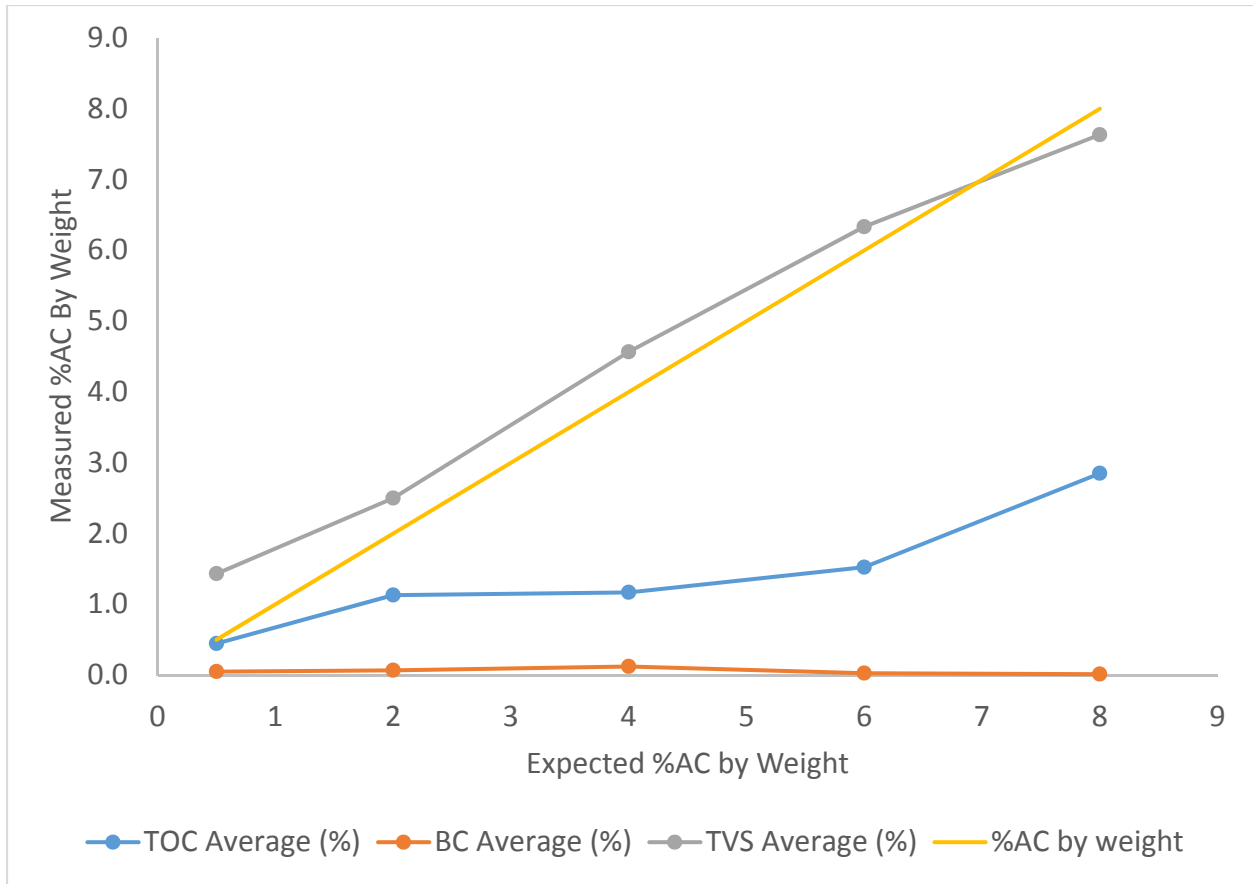
BC	black carbon	HCl	hydrochloric acid
CO ₂	carbon dioxide	mg	milligram
°C	degrees Celsius	PSEP	Puget Sound Estuary Program
ENR	enhanced natural recovery	SRM	standard reference material
EPA	U.S. Environmental Protection Agency	TOC	total organic carbon
g	gram	TVS	total volatile solids



Thermal Methods Comparing BC, TOC, and TVS. Results of %BC, %TOC, and %TVS of the ENR+AC substrate materials prior to placement that had material weigh tickets indicating that they were 4% AC (approximately 3.8% carbon) in a sand or gravelly sand matrix.

Abbreviations:

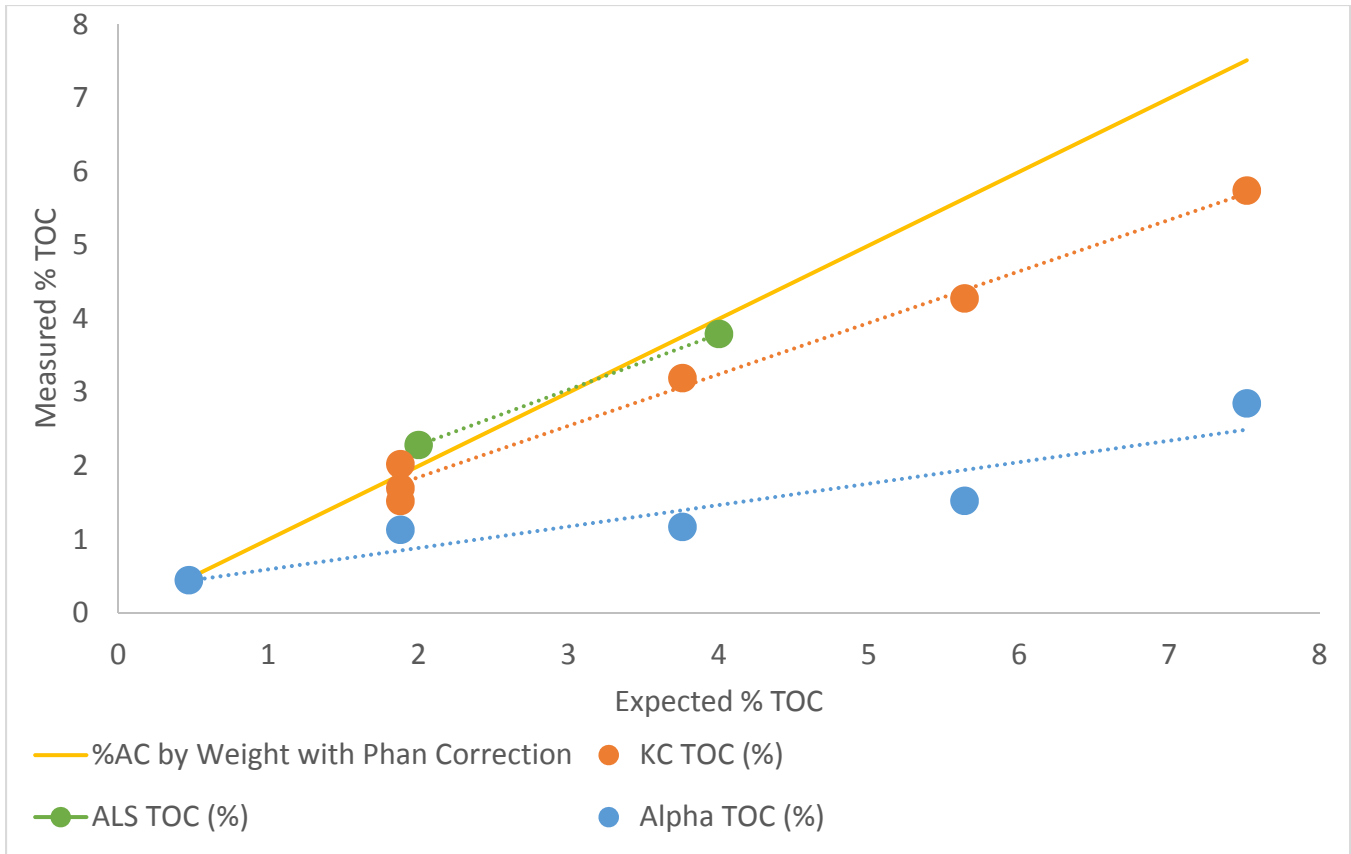
- AC activated carbon
- BC black carbon
- ENR+AC enhanced natural recovery amended with activated carbon
- TOC total organic carbon
- TVS total volatile solids



Standard Curve Comparison of Thermal Carbon Measurement Methods. Alpha Analytical, Inc., results using standards made in the lab consisting of the sand matrix, with 0.5, 2.0, 4.0, 6.0, and 8.0% by weight AC added.

Abbreviations:

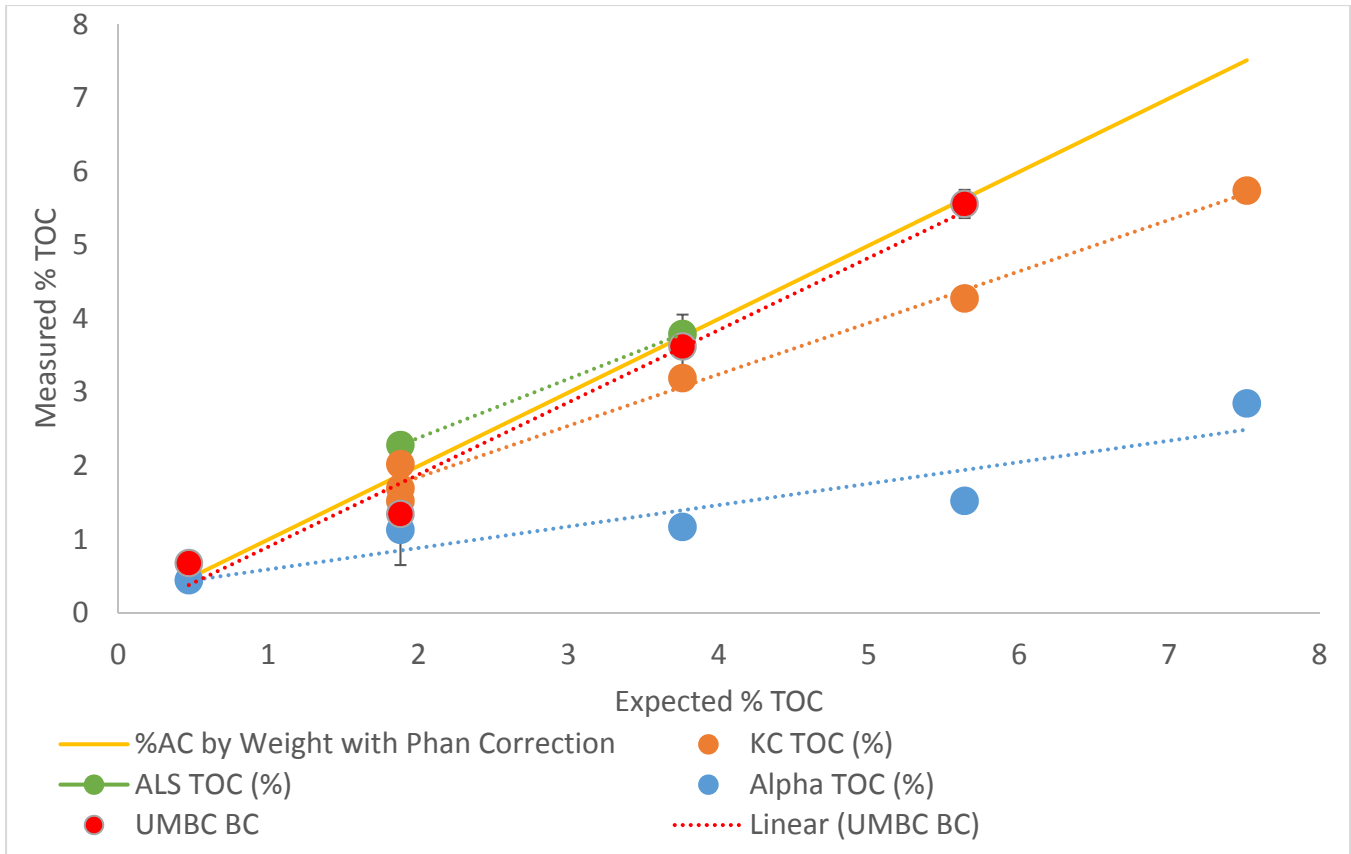
- AC activated carbon
- BC black carbon
- TOC total organic carbon
- TVS total volatile solids



Comparison of TOC Sample Sizes from Various Labs. Results from King County Environmental Laboratory (KC) and ALS Environmental Kelso, Washington Laboratory (ALS; TOC analyzed using large sample size) and Alpha Analytical Laboratory (Alpha; TOC analyzed using small sample size) to the expected %TOC of the calibration curve. The expected %TOC was corrected using the results of elemental analysis on the GAC (Phan et al., 2006; percent carbon of 93.93%).

Abbreviations:

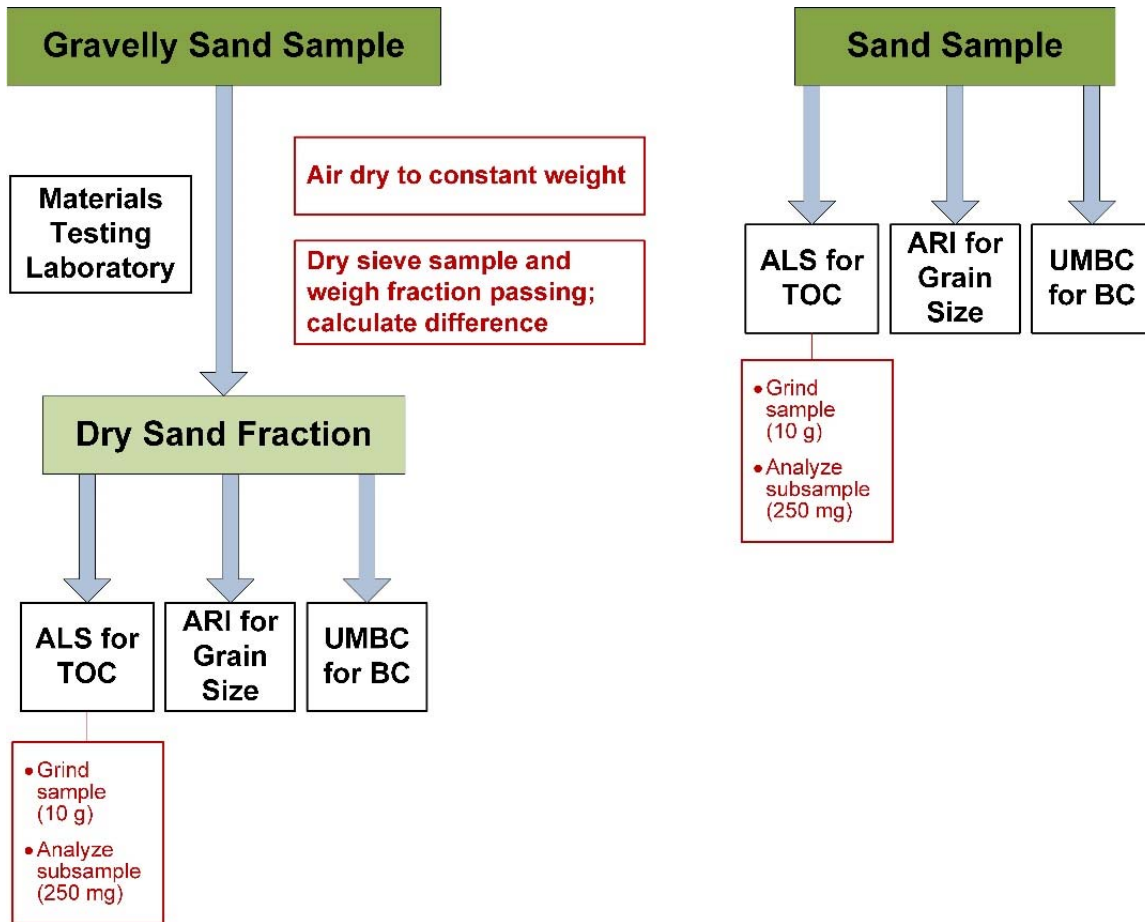
- AC activated carbon
- Alpha Alpha Analytical, Inc.
- ALS ALS Environmental
- GAC granulated activated carbon
- KC King County Environmental Laboratory
- TOC total organic carbon



Comparison of BC Results from the UMBC Laboratory to Thermal TOC Results. UMBC, KC, ALS, and Alpha TOC results are compared to the expected %TOC of the calibration curve. The expected %TOC was corrected using the results of elemental analysis on the GAC (Phan et al., 2006; percent carbon of 93.93%).

Abbreviations:

- AC activated carbon
- Alpha Alpha Analytical, Inc.
- ALS ALS Environmental
- BC black carbon
- GAC granulated activated carbon
- KC King County Environmental Laboratory
- TOC total organic carbon
- UMBC University of Maryland Baltimore Campus



Sample Processing and Analysis Flow Chart.

Abbreviations:

- ALS ALS Environmental
- ARI Analytical Resources, Inc.
- BC black carbon
- g gram
- mg milligram
- TOC total organic carbon
- UMBC University of Maryland Baltimore Campus