NCDEQ PFAS Sediment Study – Performed January 2021 to August 2021

Summary

The N.C. Department of Environmental Quality performed a limited sediment characterization study in 2021 due to experimental design concerns with a 2020 Geosyntec Sediment Characterization Study funded by Chemours that included sampling in areas where per- and polyfluorinated substances (PFAS) were not likely to be found and using an analytical method that was not sensitive enough to detect several PFAS unique to the Chemours Fayetteville Works Site (Table 3+ compounds). These experimental design issues were thought to result in non-detect Table 3+ PFAS concentrations for several sediment samples in the Geosyntec study. Once the experimental design concerns were addressed in the NCDEQ study, a much higher percentage of samples had detectable Table 3+ PFAS compounds. The NCDEQ sediment characterization study detected Table 3+ compounds in more than 90 percent of samples as compared to the Geosyntec study, which detected Table 3+ compounds in 33 percent of samples. Legacy and other PFAS (some of which are present at, but not unique to, the Fayetteville works site) were measured with a sufficiently sensitive analytical method. As a result, legacy and other PFAS were detected in 100% of samples in both the 2020 Geosyntec study and the current DEQ sediment characterization study.

Introduction

NCDEQ performed a limited sediment characterization study from January through August 2021 to investigate concerns about the design of the 2020 Chemours Sediment Characterization Study that was performed as required under Paragraph 11.2 of the Consent Order. NCDEQ identified two main shortcomings of the Chemours study: 1) sampling in areas less likely to have PFAS present, and 2) the use of analytical method with a high limits of quantitation (LOQs) for Table 3+ compounds (Table 1).

The DEQ study addressed these issues by sampling in areas suspected to have higher PFAS concentrations and working with GEL Laboratories to lower the reporting limits for the Table 3+ PFAS compounds.

Location

Locations selected by Chemours potentially had low total organic carbon (TOC) values; however, NCDEQ scientists hypothesized that PFAS would adsorb to organic carbon in sediment such that sediments with higher TOC values would have higher PFAS concentrations. Many PFAS compounds adsorb to granular activated carbon (GAC), which enables their removal from drinking water using GAC home filtration systems.

Sampling locations in the Chemours Sediment Characterization Study were collected from the mid-channel and banks of the Cape Fear River. Samples collected from the mid-channel of the Cape Fear River are expected to have low TOC values due to the high-water velocity. Bank samples were collected near the edge of the River but were still along the main channel of the River. Only one of the bank samples in the Chemours study was collected from an area expected to have higher TOC values. This sample was collected from a secondary stream located off the River near an area where the main

channel forms a bend. The lower flow rates in the secondary stream allow sediments to settle out of the water column.

The NCDEQ sampling locations were selected in known floodplains along the Cape Fear River which are commonly inundated during seasonal flooding, allowing fine-grained sediments to settle out of suspension from floodwaters. PFAS are thought to accumulate in these finer-grained, higher organic sediments. The floodplain deposits commonly contain considerable plant debris and the soils in these areas may be disturbed or redistributed by land-dwelling organisms or plant roots. PFAS concentrations were determined in the samples using an analytical method with improved reporting limits. TOC and grain size data were also collected for a subset of samples.

Raven Rock State Park was chosen as the location to collect background (ambient) PFAS data upstream because this area was approximately 43 miles north of the Fayetteville Works Site, and was thought to be outside of the known Table 3+ PFAS aerial deposition area. Downstream locations ranged from Tar Heel Ferry Boat Ramp to International Paper as shown in Figure 1.

Analytical Methods

The analytical methods used in the Chemours Sediment Characterization Study had high reporting limits for Table 3+ compounds, likely resulting in non-detectable levels of PFAS in areas where the compounds are in fact present. DEQ worked with GEL Laboratories to lower its reporting limits, particularly on the Table 3+ compounds (see Table 1 below). Discussions with the Environmental Protection Agency Region 5 scientists also indicated that lower reporting limits for PFAS in soil are achievable. Reporting limits for various PFAS Soil Methods, including those used by the contract lab Chemours used (Eurofins), are given in Table 1.

Table 1. Reporting limits for PFAS Soil Methods. GEL is the contract lab used by NCDEQ and Eurofins is the contract lab used by Chemours. Improved reporting limits are noted for Table 3+ compounds in GEL methods. The LOQ is the same as the reporting limits for all values in this table. **Note**: all units are in ng/g (parts per billion) dry weight of soil, which are 1000x higher than the ng/L (parts per trillion) units used to report PFAS concentrations in water and other liquid samples.

Lab	Method	Compound(s)	LOQ (ng/g)	Improved LOQ (ng/g)
GEL	EPA Method 537.1 Modified	GenX	0.5	0.15
	EPA Method 537.1 Modified	Table 3+	1.1	0.15
	EPA Method 537.1 Modified	Legacy/Other	0.7 to 1.5	NA
Eurofins	Method 537M/Table 3+*	GenX	0.25	NA
	Table 3+	Table 3+	1 to 2	NA
	Method 537M	Legacy/Other	0.2	NA
EPA Region 5	NA	GenX	NA	NA
	NA	Table 3+	NA	NA
	ATSM D7968.17a	Legacy/Other	0.025**	NA

* GenX is reported by Eurofins in some cases using Method 537M and in other cases using the Table 3+ Method.

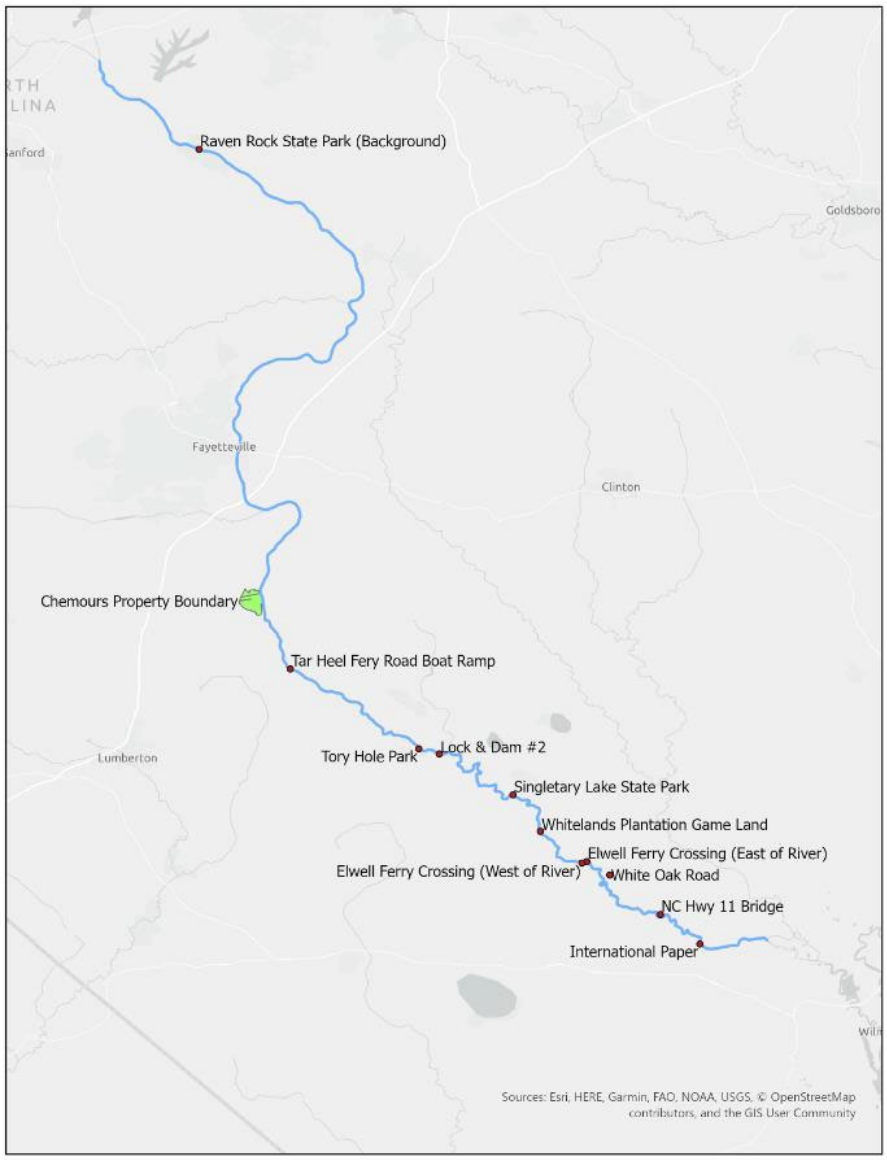
** A few legacy PFAS in ATSM D7968.17a have higher reporting limits. PFOS, PFPeA, and PFBA have reporting limits of 0.050, 0.125, and 0.125 ng/g, respectively.

Sample Collection and Analysis

Four sampling trips were taken to collect sediment samples from 10 locations (Figure 1) within known floodplains along the Cape Fear River downstream of the Chemours Fayetteville Works Facility. PFAS contamination of soils from aerial deposition has been detected as far as 20 miles from the Chemours Fayetteville Works facility, with studies still ongoing to find the edge of contamination. All sites chosen were either able to be freely accessed or were sampled with permission in the case of International Paper. An initial reconnaissance trip was made in November 2020 to locate and determine accessibility at several of the proposed sampling sites. Some sample locations needed to be modified slightly due to vegetative growth present or signs or locks indicating that access was restricted in areas previously accessible during the reconnaissance trip.

Composite samples are collected from the surface, while grab samples are collected deeper from the subsurface. At least one grab sample and one composite sample were collected at each sampling location except at White Oak Road, where only one composite sample was collected under standing water; therefore, a grab sample at depth was not feasible. Composite samples were collected by removing five samples of soil from the top zero to six inches of sediment; four from each corner of a square about a meter apart; and one from the center of the square. These five samples were then mixed to form one composite sample. Grab samples were collected at a depth of approximately 12 inches in the center of the square. One duplicate sample (either a grab or composite duplicate) was collected on each sampling trip. Samples were analyzed by GEL laboratories for 55 PFAS using a modified version of EPA Method 537.1.

Figure 1. DEQ Sediment Study Sampling Locations along the Cape Fear River



Results

<u>TOC Results</u> - Data from the NCDEQ study indicated that samples were successfully chosen from areas with higher TOC values than are generally found in the mid-channel and edges of the Cape Fear River. Seven out of 11 samples had TOC values higher than the maximum TOC value of 33 g/kg in the Chemours study (Table 2). During the last sediment sampling event, lower TOC values were noted in samples collected. The DEQ Sampling Team indicated that lower TOC values may be associated with the sediment samples from the last sampling trip because there was no longer access to the specific locations that were chosen during the reconnaissance trip. Vegetative overgrowth, no trespassing signs,

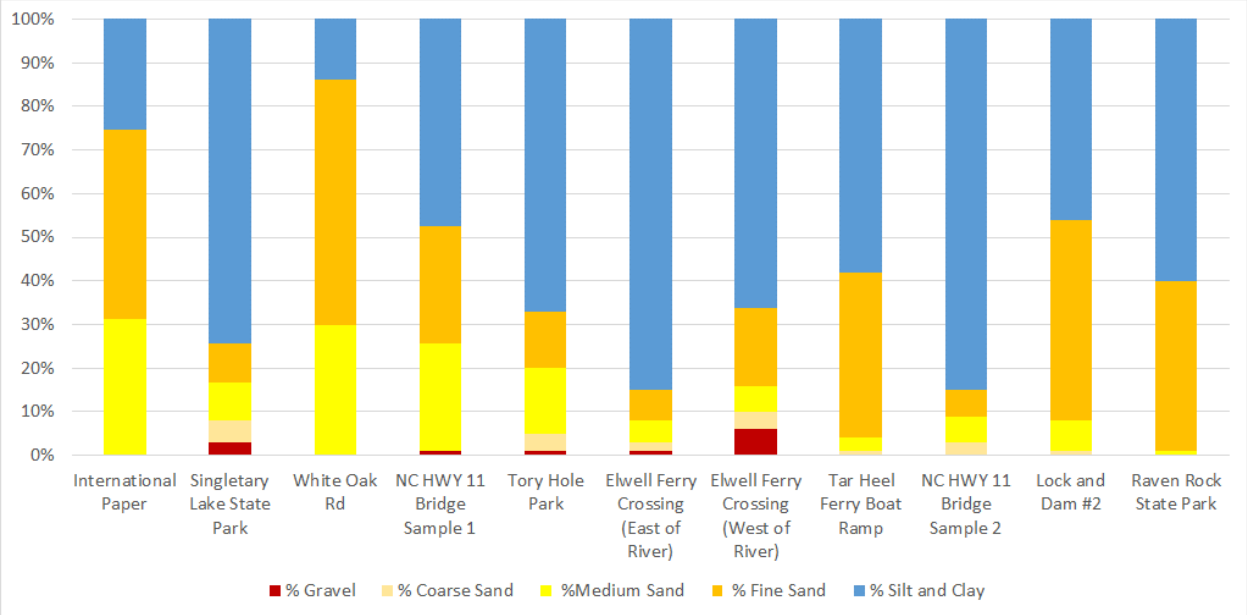
and locks that were not previously present prevented access to the originally designated sampling areas. In addition, these last samples collected, while downstream of the facility, were upstream of previous samples collected and were more likely to have steeper banks and stronger flow, making floodplain deposition less likely.

Table 2. TOC Data for NCDEQ Sediment Study Samples. Note: units for TOC are in grams (g) of TOC per kilogram (kg) of soil (dry weight). Seven out of 11 samples (sample above thick black line in table below) had TOC values higher than the maximum TOC value of 33 g/kg in the Chemours study.

Location	TOC Value (g/kg)
International Paper	119
Singletary Lake State Park	103
White Oak Rd	86.7
NC HWY 11 Bridge Sample 1	64.4
Tory Hole Park	60.3
Elwell Ferry Crossing (East of River)	57.3
Elwell Ferry Crossing (West of River)	41
Tar Heel Fery Road Boat Ramp	31.2
NC HWY 11 Bridge Sample 2	19.6
Lock & Dam #2	12.6
Raven Rock State Park (Background)	7.33

Grain Size - Grain size data was collected for a subset of samples. Figure 2 shows the percentage of gravel, sand, silt, and clay.

Figure 2. Grain Size Data for NCDEQ Samples. Samples are arranged from highest TOC (left) to lowest TOC (right), corresponding to the order in Table 2.

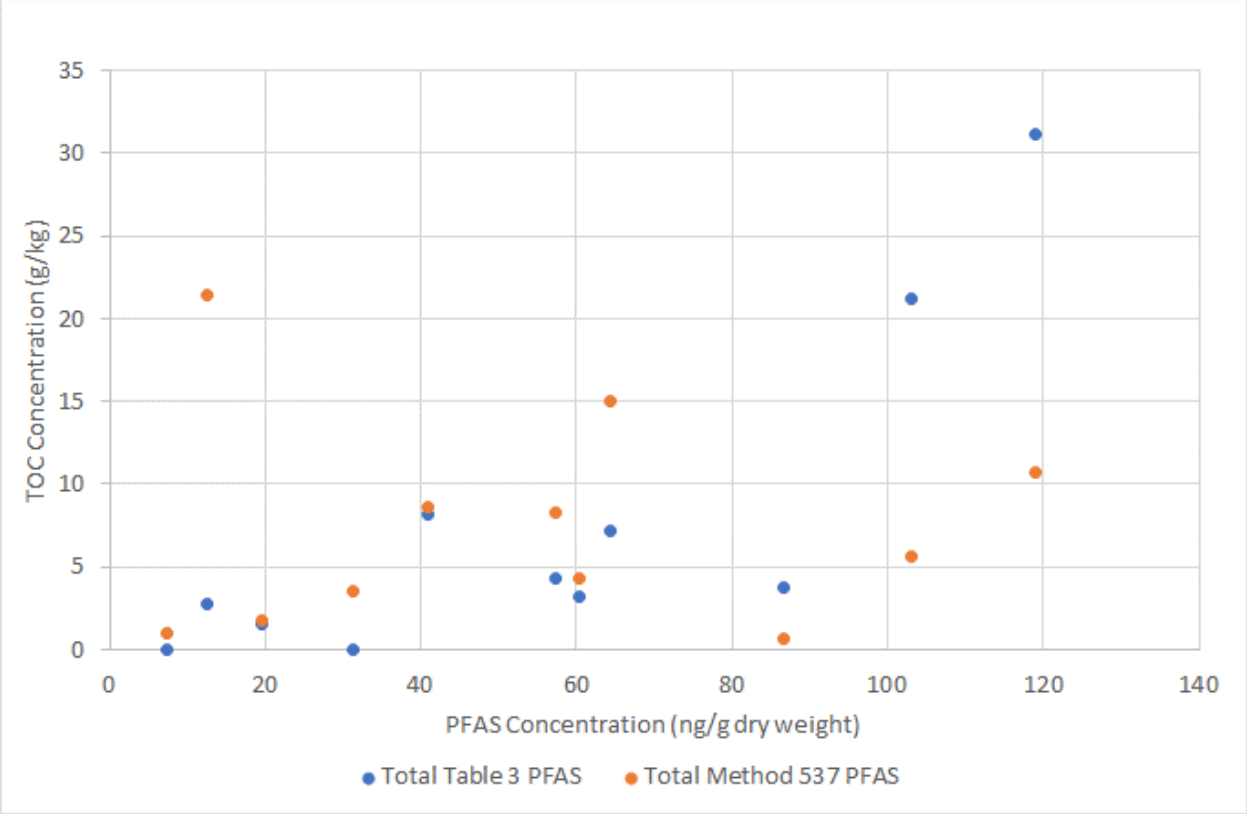


PFAS Concentrations - The concentrations for all PFAS are shown in Table 3, which is posted to the website as a separate file for easier viewing of the large table. Concentrations of a few PFAS (PPF Acid, PFMOPrA and PFMOBA) labeled as Chemours compounds in Table 3 are not reported in the 2020 Geosyntec Sediment Characterization Report due to issues with the analytical method.

All other PFAS not specifically labeled as Chemours compounds are designated as legacy PFAS or other PFAS in this report. Some of these legacy/other PFAS compounds are related to the Chemours Fayetteville facility, and many enter the Cape Fear River from sources other than Chemours.

The upstream background location in the DEQ study (Raven Rock State Park) had no detectable Table 3+ PFAS due to its distance from the Chemours facility and/or low TOC values. Total Table 3+ PFAS ranged from non-detect at Raven Rock State Park and Tarheel Ferry Boat Ramp to 31.3 ng/g at International Paper. Total Legacy and other PFAS ranged from 0.70 ng/g at White Oak Road to 39.0 ng/g at Elwell Ferry Road (East of the River). As shown in Figure 3, PFAS concentrations generally increased in areas with higher TOC values.

Figure 3. Relationship between TOC and PFAS concentrations in sediment samples.

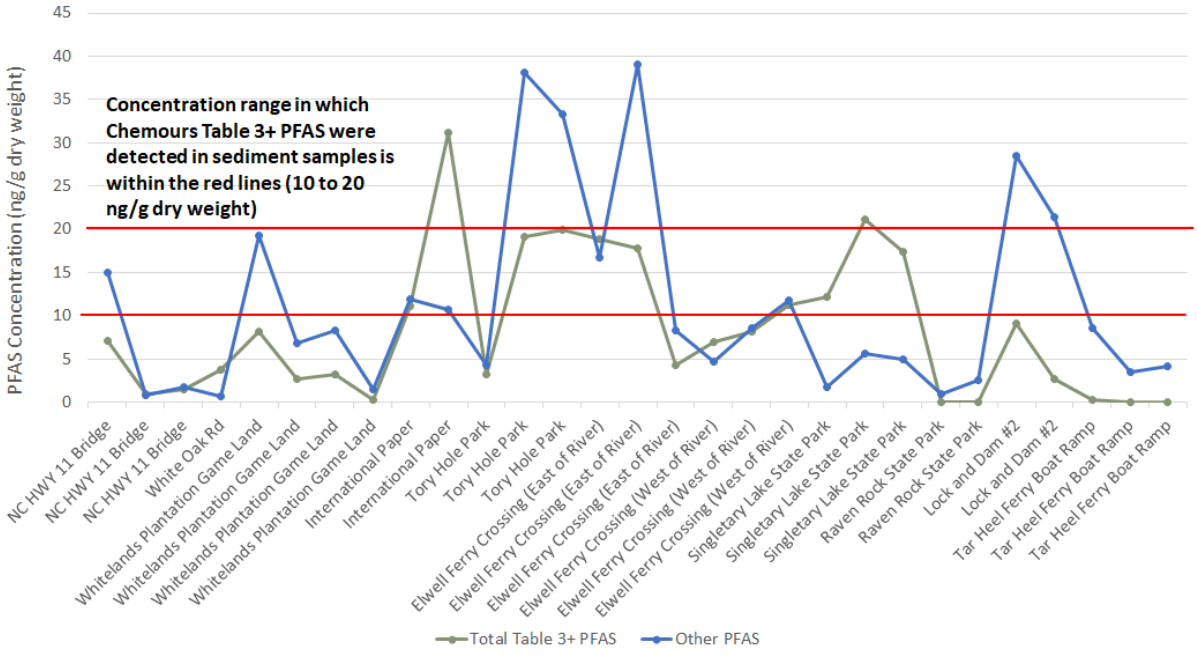


<u>Analytical Method Reporting Limits</u> - The use of an analytical method with lower reporting limits for the Table 3+ PFAS allowed for a much higher rate of detection of the compounds. Table 3+ PFAS were found in more than 90 percent of downstream sediment samples in the DEQ study as compared to a detection rate of 33 percent for riverbank sediment samples in the Chemours study. Two of the three samples with detectable Table 3+ PFAS in the Chemours study were collected beside the Fayetteville Works Site, and all three samples had PFAS concentrations between 10 and 20 ng/g (denoted by red lines in Figure 4). No total Table 3+ PFAS were detected between the LOQ of 1 to 2 ng/g and 10 ng/g in the Chemours study; whereas, two-thirds of the Total Table 3+ PFAS detected in the DEQ Sediment Study samples were detected between 0.15 ng/g and 10 ng/g (note: 0.15 ng/g is the reporting limit).

The Chemours study had a lower reporting limit of 0.2 ng/g for many legacy and other PFAS using Method 537M and detected these PFAS in 100 percent of samples – with about half of these detections at levels below 10 ng/g. Legacy and other PFAS were also detected in 100 percent of samples in the NCDEQ Sediment Study.

Taken together, these results suggest that while the Chemours analytical method 537M is able to measure many of the legacy/other PFAS at lower levels, the Chemours Table 3+ Method is not capable of measuring lower concentrations of Table 3+ PFAS in sediment samples. The improvements made to the NCDEQ analytical method allows for the detection of Table 3+ PFAS at lower levels.

Figure 4. Total Table 3+ and Total Other PFAS Detected at Each Location as Compared to Chemours Data. *There were a wider range of Table 3+ PFAS found in the NCDEQ study, with most detections below 10 ng/g. All detectable Total Table 3+ PFAS in the Chemours Sediment Characterization Study were either between 10 and 20 ng/g (between the red lines below) or were non-detect.*



<u>Sampling of Surface and Subsurface Sediment Layers</u> – Composite samples are collected from the surface, while grab samples are collected deeper from the subsurface. Grab samples and their duplicates collected for the DEQ study are shown in two shades of blue in Figure 5 below. Composite samples and their duplicates are shown in two shades of orange in the same figure. Duplicate samples agree with one another for both Table 3+ PFAS and legacy/other PFAS, indicating that both the sampling procedures and analytical method provide reproducible results for all compounds. However, when comparing grab and composite samples (blue compared to orange), sampling results can vary for both Table 3+ PFAS and legacy/other PFAS. There is no clear trend as to which type of sampling at which depth yields higher PFAS concentrations. Surface soils that have higher concentrations of PFAS may indicate more recent PFAS deposition. Subsurface sediment samples with higher PFAS concentrations may indicate areas where PFAS deposition occurred at an earlier time point, such as when PFAS discharge to the Cape Fear River was greater before the Consent Order was signed in 2019. These results indicate that it is important to collect both surface and subsurface sediment samples to better characterize PFAS in sediment.

Figure 5. DEQ-collected samples: Comparison of Table 3+ PFAS Concentrations Using Grab and Composite Sampling

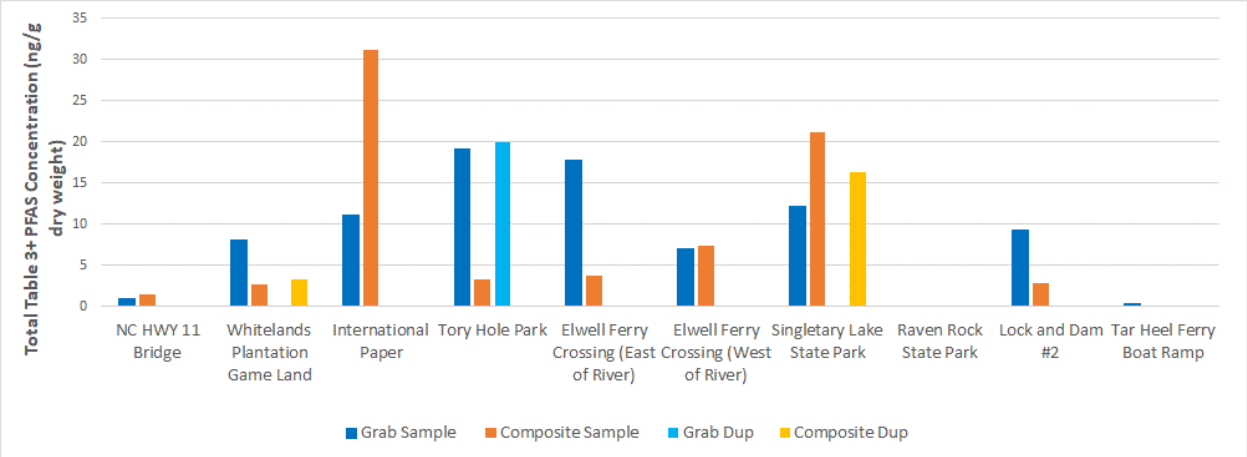
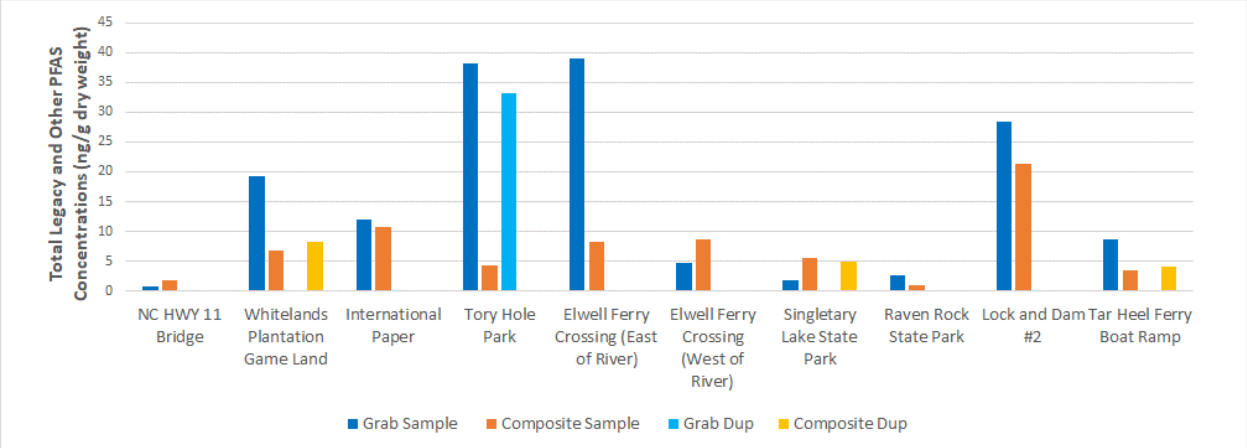


Figure 6. DEQ-collected samples: Comparison of Legacy and Other PFAS Concentrations Using Grab and Composite Sampling



Conclusions

The NCDEQ Sediment Study showed that once concerns about sampling location and analytical method reporting limits were addressed, a much higher percentage of Table 3+ PFAS compounds are detected in sediment samples. Sediment with higher TOC values generally had higher PFAS concentrations. The Chemours Table 3+ method is not sensitive enough to detect and quantitate Table 3+ PFAS at the concentrations at which most Table 3+ PFAS are found in the environment.

Results also showed that PFAS concentrations in samples collected from the same location were often quite different for surface soils and subsurface soils. These differences were not predictable because some locations had higher PFAS concentrations in surface sediments while other locations had higher

PFAS concentrations in subsurface sediments. A better characterization of PFAS in sediment can be achieved by 1) using an analytical method with a lower reporting limit, 2) sampling in areas where PFAS are likely to deposit, and 3) sampling in both surface and subsurface soils.