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RESEARCH ARTICLE

# Assessment of the efficacy of six field cleaning protocols for hydrocarbon quantification

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**Abstract**
The defensibility of field sampling data collected in support of natural resource damage assessments and other environmental investigations depends on rigorous quality assurance and control both in the field and laboratory. One important step in field procedures is the cleaning of sampling equipment between samples to minimize the carryover of contaminants. Large-scale sampling efforts during the Deepwater Horizon oil spill event have highlighted the importance of understanding how multiple equipment cleaning protocols affect interstation cross-contamination and the resulting chemical data quality. In this study, six field cleaning techniques were tested on metal sampling equipment using two different sediment types spiked with crude oil in order to understand their relative and absolute effectiveness in reducing chemical carryover. The complexity of the cleaning protocols ranged from a simple water and scrub brush application to protocols that included soap and/or solvent. In this study, percent residual hydrocarbon transfer, relative to total loading in sediments, never exceeded 0.032%. The least labor-intensive protocol, water and scrub brush application, had the highest potential for hydrocarbon transfer (0.011–0.032%). Statistical differences were observed among treatments, and it was found that protocols containing a solvent step were more effective than protocols without solvents. Depending on the data quality objectives, the differences may not be meaningful, and choosing a cleaning technique should be governed by health, safety, and environmental factors. The residual hydrocarbons measured after equipment cleanings for all techniques in this study were negligible when compared with other variables that occur during routine sampling and laboratory activities.

**Keywords** Decontamination · Field sampling · Sediment · Polycyclic aromatic hydrocarbons (PAHs) · Oil spill

## Introduction

Environmental oil and chemical spills will continue to be recurring events. It has been reported that, in the United States (US) alone, the National Oceanic and Atmospheric Administration (NOAA) responds to at least 150 spills per year; however, it is estimated that there are thousands of spills occurring in US waters each year (NOAA OR&R 2017). Oil spills have been occurring since the mid 1800s when exploration and drilling first began but did not gain national attention until England's Torrey Canyon oil spill in 1967 (ICCOPR 2015). After the Santa Barbara, California spill in 1969, national awareness increased to the point that federal agencies began to develop programs related to oil spill research (ICCOPR 2015). Broadly, the research is divided into four areas: prevention, preparedness, response, and injury assessment and restoration (ICCOPR 2015).

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One of the worst oil spills in US waters was the Deepwater Horizon (DWH) spill in 2010 that released approximately 3.1 million barrels of Louisiana Sweet Crude oil into the Gulf of Mexico (DWH Trustees 2016). During the course of the response and damage assessment for the DWH spill, field personnel from numerous agencies and organizations collected more than 100,000 environmental samples (DWH Trustees 2016). The Interagency Coordinating Committee on Oil Pollution Research (ICCOPR), established under the Oil Pollution Act of 1990, has developed recommendations for research and improvements in spill response activities (ICCOPR 2015). One of the identified recommendations for improvement pertains to differences in sample collection methods, which may affect contaminant quantitation, data quality/data management, and the ability to make comparisons across laboratory data sets (ICCOPR 2015).

Consistent sampling protocols in the field are important for research that involves analyzing environmental samples. Ensuring the integrity and comparability of those samples begins with how they are collected. In many cases, field sampling logistics can make sample integrity difficult to maintain since sampling scenarios often differ from study to study. These factors include, but are not limited to, site location/condition (e.g., tidal salt marsh versus open ocean) and the type and amount of equipment and materials (e.g., sampling gear, soap, solvents) that can be brought into the field and disposed of properly. Due to the physical and logistical constraints of taking large amounts of sampling gear into the field, sampling gear is decontaminated and reused between sampling stations.

Generally, most decontamination protocols for sediment sampling gear follow a similar progression of steps, which include a gross, physical removal of sample material (e.g., water rinse with scrub brush), detergent wash and rinse, rinse with solvent(s), and/or acid depending on the sample analyses to be performed, followed by a deionized (DI) water rinse. However, there is no single protocol that has been universally implemented. Various factors determine which techniques will be used to clean field gear between sampling stations. These factors include limitations on the types of materials that can be used (e.g., use of flammable solvents, such as acetone, may not be allowed for safety or environmental compliance reasons), and the type of analytes being quantified in the samples. For example, in instances where samples are being analyzed for volatile organic compounds (VOCs), samples must be collected, stored, and shipped in conditions that are free of volatile organic solvents to avoid contaminating the samples, thereby limiting the types of solvents used for field gear cleaning (USEPA 2014a). Consequently, understanding the advantages and disadvantages of different protocols is important when developing a sampling plan for collecting environmental samples. The goal of this study was to understand the efficacy of different decontamination protocols related to sediment sampling as it specifically pertains to hydrocarbon analysis.

## Materials and methods

### Selected equipment decontamination (cleaning) protocols

Six different decontamination protocols were identified to assess the carryover potential of hydrocarbons, specifically polycyclic aromatic hydrocarbons (PAHs) and total extractable hydrocarbons (TEH). These are compounds usually targeted for sampling and analysis to characterize impacts at oil spill contamination sites. The protocols chosen (Table 1) to examine the potential for cross-contamination ranged in complexity from very basic (site water and scrub brush, for times when there are limited resources, supplies, time, etc.) to more involved (e.g., the addition of soap and/or solvents). The decontamination protocols were chosen based on a combination of professional experience of the investigators and a review of existing decontamination protocols from several sources. The goal in protocol selection was to select diverse protocols, which could provide a basis for future field samplers faced with decisions about the tradeoffs between health, safety, and disposal concerns of bringing solvents into the field versus the objective of preventing contaminant carryover.

### Sampling and decontamination materials

Stainless steel bowls (3.785 L) and spoons (28 cm) (SEVA Technical Services, Inc.) and natural bristle brushes (30.5 cm, Coronado Distribution Company, Inc.) were used in all decontamination protocols and reused throughout the study. All solvents used in this study have purities of ≥ 99.9% and were purchased from VWR (dichloromethane and acetone) or Fisher Scientific (n-hexane and methanol). Isopropyl alcohol (IPA) wipes (99.8% pure IPA, Techspray) and Liquinox® soap (Alconox, Inc.) were used in protocols that required those materials. Protocols requiring “site water” used seawater obtained from the Charleston Harbor, Charleston, SC, USA. Prior to use in this experiment, the seawater was settled for 72 h, mechanically filtered through a mixed media bed filter to ~30 μm, and then filtered through a 10-μm cartridge. Filtered seawater was then exposed to a 150 W UV sterilizer (Emperor Aquatics) to reduce bacterial growth.

For materials that were reused between cleaning protocols, brushes, and spoons were sonicated in Liquinox® soap and DI water for 30 min, rinsed with hot tap water and DI water, then air-dried and rinsed with methanol (brushes) or sequentially rinsed with acetone, dichloromethane, and hexane (spoons). Bowls were first scrubbed and washed by hand with Liquinox® soap then rinsed with hot tap water and DI water.

**Table 1** Cleaning protocols investigated in this study

| | Cleaning protocol (CP) | | | | | |
|---|---|---|---|---|---|---|
| | CP1 | CP2 | CP3 | CP4 | CP5 | CP6 |
| Step 1 | Rinse and brush with "site water" | Rinse and brush with "site water" | Rinse and brush with "site water" | Rinse and brush with "site water" | Rinse and brush with "site water" | Rinse and brush with "site water" |
| Step 2 | | Scrub with soap and brush | Rinse with acetone | Scrub with soap and brush | Wipe with IPA wipe | Scrub with soap and brush |
| Step 3 | | Rinse with "site water" | Rinse with DI water | Rinse with "site water" | Rinse with DI water | Rinse with "site water" |
| Step 4 | | Rinse with DI water | | Rinse with acetone | | Wipe with IPA wipe |
| Step 5 | | | | Rinse with hexane | | Rinse with DI water |
| Step 6 | | | | air dry | | |
| Citation | | DWH NRDA protocol (Fish 2011)[a] | NOAA/NCCOS/NS&T protocol (Apeti et al. 2012) | NOAA/OR&R protocol (Bejarano et al. 2014) | EPA protocol (Fisher et al. 2004)[b] | EPA protocol (Fisher et al. 2004)[b] |

*DI* deionized water, *IPA* isopropyl alcohol, *DWH NRDA* Deepwater Horizon National Resource Damage Assessment, *NOAA* National Oceanic and Atmospheric Administration, *NCCOS* National Centers for Coastal Ocean Science, *NS&T* National Status and Trends, *OR&R* Office of Response and Restoration, *EPA* Environmental Protection Agency

[a] This protocol follows closely with what was used during DWH NRDA, and the only difference between this study and the DWH NRDA protocol is in the order of rinses (steps 3 and 4); during DWH, after step 2, materials were rinsed with DI water followed by "site water"

[b] This protocol allows for the optional use of a soap and water rinse; thus, the protocol was performed both with and without soap and water (CP5 and CP6)

Afterwards, the bowls were rinsed sequentially with acetone, dichloromethane, and hexane.

## Sediment collection and spiking

Two different sediment types were used to assess the efficacy of each cleaning protocol: (a) predominately sand and (b) silt/sand mixture. Sediment was collected from two locations in Charleston, SC, USA. The sand sediment was collected from the Folly River (32.63898, −79.98767), and the silt/sand mixture was collected from Leadenwah Creek (32.64750, −80.22168). Both sediments have been extensively used as a reference sediment in toxicological research performed at the NOAA National Centers for Coastal Ocean Science (NCCOS) lab in Charleston, SC, USA, and determined to contain low to non-detectable levels of hydrocarbons (Chung 1999; Scott et al. 1999; Key et al. 2007).

Sediments (~3700 g wet) were spiked with a weathered form of Louisiana Sweet Crude (LSC) oil collected from surface slicks on July 10, 2010, during the DWH oil spill event ("slick B"), mixed on a mechanical jar roller for 8 h, and then stored in the dark at 4 °C. The targeted nominal oil concentration was 10,000-μg slick B/g wet sediment. This concentration was chosen based on data reported by Rouhani et al. (2017), which summarized PAH concentrations in soil/sediment samples collected during DWH and represents a reasonable worst-case scenario for PAH and TEH contamination related to a crude oil spill.

## Grain size analysis and total organic carbon determination

The sand and silt-clay content for sediments was determined by methods from Plumb (1981). Total organic carbon (TOC) was determined by using the loss on ignition method described by Heiri et al. (2001), and grain size distribution was determined by methods from Folk (1980), Lewis (1984), and Lewis and McConchie (1994).

## Cleaning protocol implementation and assessment of carryover

Oiled sediment was retrieved from storage, acclimated to room temperature, and homogenized by a mechanical roller for 1 h prior to cleaning protocol assessment. Three replicates were run for each sediment type (sediment type = sand or silt) using each cleaning protocol. A replicate consisted of approximately 500 g of sediment that was scooped into a stainless steel bowl, stirred for 30 s, and then removed. In this design, the sediment from the jar represented the sediment that would be obtained from the field from a sampler (e.g., grab sampler). Each bowl/spoon pair represented the step at which multiple sediment sample grabs from a location are composited and homogenized prior to placing aliquots into sample jars in the field. Following sediment removal, the bowl and spoon were cleaned according to each cleaning protocol (Table 1). In order to limit the variability that might be associated with different individuals collecting and processing samples, all sampling protocols were carried out by the same experienced field scientist. All personnel used nitrile gloves, which were changed at least once between each replicate. The steps for all individual protocols are detailed in the following sections.

### Cleaning protocol 1

Bowls and spoons were first rinsed with "site water," which was applied using a 2-gal pressurized garden sprayer (D. B. Smith). The garden sprayer was pressurized by a hand pump and was repressurized in the same manner prior to each cleaning protocol implementation. The reservoir was refilled as needed so that levels remained relatively consistent throughout the study. After the initial rinse, bowls and spoons were scrubbed thoroughly using a clean brush to remove any visible sediment residue that still remained on the bowl or spoon. Each replicate had its own brush. After scrubbing, the bowl and spoon were rinsed again with "site water" in the same manner as described above.

### Cleaning protocol 2

CP2 follows closely with decontamination steps outlined in Fish (2011). Briefly, bowls and spoons were first rinsed with "site water" and scrubbed as detailed in CP1 (step 1). Next, the bowl and spoon were cleaned with soap and a scrub brush. The same brush that was used in the first step was used in the second step. A mixture of Liquinox® soap and DI water was made and applied by submerging the scrub brush into the soap and water mixture and then cleaning the bowl or spoon. The soap and water mixture was made prior to the start of the protocol and used for the duration of all replicates within the protocol. Afterwards, the bowl and spoon were rinsed with site water until no visible soap residue remained (step 3) and then rinsed with DI water for the final step.

### Cleaning protocol 3

The protocol for CP3 is detailed in Apeti et al. (2012). Bowls and spoons were first rinsed and scrubbed with a brush as described in CP1, after which they were rinsed with acetone. Acetone was applied using a 500-mL fluorinated ethylene propylene (FEP) squirt bottle. Solvent was applied so that all areas of the bowl/spoon were thoroughly rinsed. Approximately 25 mL of solvent was used to rinse both the bowl and the spoon. The final step was a rinse with DI water.

### Cleaning protocol 4

The protocol for CP4 is detailed in Bejarano et al. (2014). Bowls and spoons were first rinsed and scrubbed with "site water" and a brush and then cleaned with soap and a brush as detailed in CP1 (step 1) and CP2 (steps 2 and 3). Next, the bowl and spoon were rinsed with acetone (step 4; ~25 mL of acetone), followed by a rinse with hexane (step 5; ~25 mL of hexane), and then allowed to air dry for 2 min (step 6).

### Cleaning protocol 5

The protocol for CP5 is detailed in Fisher et al. (2004). Bowls and spoons were first rinsed with "site water" and then scrubbed with brushes as detailed in CP1. Next, bowls and spoons were wiped with IPA wipes. One to two wipes were used to wipe the inside of the bowl. Additional one to two wipes were used to wipe the spoon. A new set of wipes were used for each replicate. Afterwards, the bowl and spoon were rinsed with DI water.

### Cleaning protocol 6

The protocol for CP6 is detailed in Fisher et al. (2004). Bowls and spoons were rinsed with "site water" and scrubbed with a brush, and then scrubbed with soap and rinsed with "site water" again as detailed in earlier protocols (CP1/step 1; CP2/steps 2 and 3). Next, bowls and spoons were wiped with IPA wipes and rinsed with DI water as detailed in CP5.

After cleaning protocol completion, sequential rinses of dichloromethane and hexane were used to rinse the bowl and spoon to remove any residual hydrocarbons. Fifty milliliters of each solvent (applied using a 500-mL FEP squirt bottle) was used to rinse the bowl, and 25 mL of each solvent was used to rinse the spoon. Solvent rinses were collected and composited into precleaned 500-mL wide-mouth amber bottles.

Upon completion of all sediment replicates for each cleaning protocol, process blanks were also analyzed in order to test if the materials (e.g., brushes, stainless steel bowls and spoons, soap and water bath, "site water") used in the cleaning protocol contributed to measured hydrocarbon residues. Process blanks consisted of executing the cleaning protocol on a clean bowl and spoon (i.e., no sediment involved), then rinsing the bowl and spoon with dichloromethane and hexane, as detailed earlier, to remove and measure any hydrocarbons present. A flowchart for the steps involved during the implementation of each cleaning protocol is found in Fig. 1.

Once the solvent rinses were collected from each replicate and process blank, isotopically labeled PAH and alkane internal standards were added to each sample (Cambridge Isotope Laboratories, Inc./Online Resource Table S1). Each sample was passed through anhydrous sodium sulfate to remove

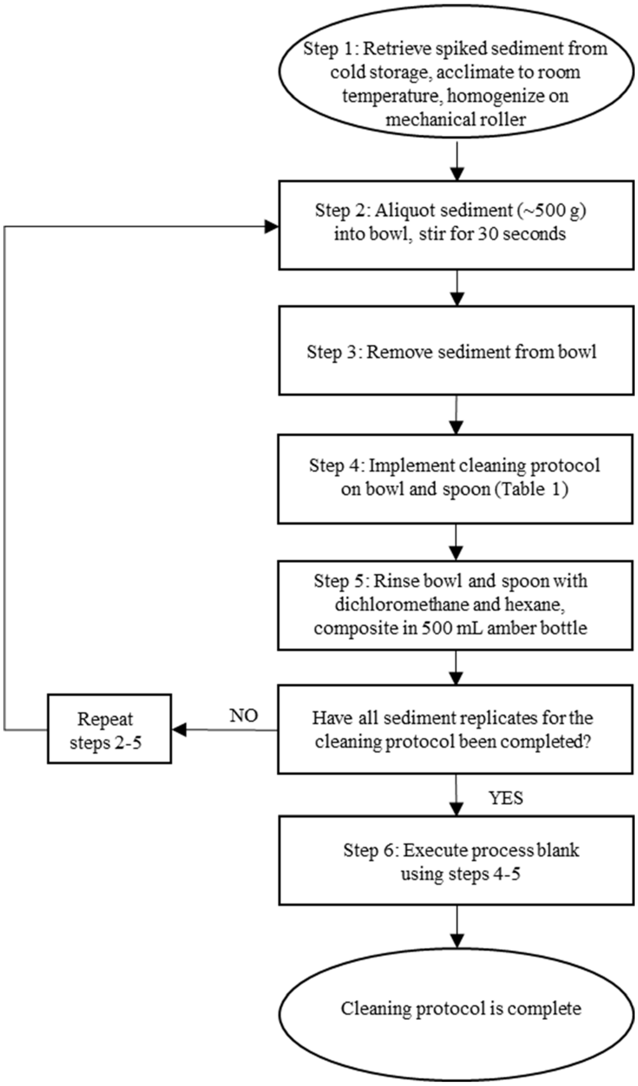

**Fig. 1** Flowcharts of the steps that were used during the implementation of each cleaning protocol

residual water, concentrated in a 40 °C water bath under a stream of nitrogen (Biotage TurboVap II) and then passed through 0.5 g silica solid phase extraction (SPE; Phenomenex, Strata SI-1) cartridges to remove the polar constituents of oil (e.g., asphaltenes and resins).

## Sediment analysis

PAH and TEH concentrations were measured in both (sand and silt) oiled sediments using methods adapted from Kucklick et al. (1997), Long et al. (1998), and Balthis et al. (2012). Thawed samples were homogenized, and 10 g of sediment aliquots were ground with sodium sulfate (~27 g). Samples were transferred to 33-mL accelerated solvent extraction (ASE) cells followed by the addition of labeled PAH and alkane internal standards to each cell. Samples were extracted by ASE using acetone:dichloromethane (1:1 v/v) (Thermo Fisher Dionex ASE 200). Solvent extracts were treated with activated copper, filtered through anhydrous sodium sulfate, and cleaned up using gel permeation chromatography and silica SPE (J2 Scientific Biobead column; Phenomenex, Strata SI-1).

## Instrumental analysis

All sample extracts were analyzed with a gas chromatograph coupled to a mass spectrometer (Agilent GC/MS 6890/5973) using electron impact ionization. The GC/MS was operated in selected ion monitoring mode and contained a split/splitless injector and DB17ms analytical column (Agilent J&W 60 m × 0.25 mm × 0.25 μm). Calibration standards for PAH (0.1–10,000 ng) and TEH (0.25–20 mg) were used to develop calibration curves ($r^2 \geq 0.995$) for the analytes of interest. The calibration curve for TEH was developed by diluting "slick B" oil and extracting the calibration points through silica SPE. After the initial calibration of the instrument, continuing calibration verification (CCV) standards were run every 10–15 samples. Data analysis was performed using MSD ChemStation software (Agilent Technologies, Inc. version E.02.02.1431). Total PAH (PAH50) is reported for 50 parent and alkylated PAHs (Table 2), and TEH is reported based on the signal generated from the mass to charge ratio (m/z) 57.

## Limit of detection and blank correction

The limit of detection (LOD) for TEH data was calculated by dividing the mass (or volume) of the sample by the lowest calibration point (0.25 mg). PAH detection limits were calculated according to Ragland et al. (2014) by the following equation:

$$\mathrm{LOD}_{\mathrm{MDPA}_{ji}} = \frac{\mathrm{ISm}_{ji} \times \left(\frac{\mathrm{SAC}_i}{\mathrm{ISa}_{ji}} - b\right)}{m}$$

where $j$ is the sample, $i$ is the analyte, Isa is the internal standard area, Ism is the internal standard mass, $\mathrm{SAC}_i$ is the average minimum detectable peak area (MDPA) of the analyte plus three standard deviations of the MDPA (average $\mathrm{MDPA}_i + 3\sigma_{\mathrm{MDPA}i}$), $m$ is the calibration slope, and $b$ is the calibration intercept. The MDPA was estimated for each analyte using procedural blanks. The procedural blanks used for estimating the MDPA were obtained by concentrating 150 mL of 1:1 (v/v) dichloromethane/hexane in a 40 °C water bath under a stream of nitrogen (Biotage TurboVap II), then passing the extract through silica SPE. The LODs reported for this study are found in Online Resource Table S2.

As noted earlier, process blanks were run at the end of each cleaning protocol to determine if the materials used during the cleaning protocol (e.g., "site water", soap, and water bath)

**Table 2** Parent and alkylated PAHs measured in the study. Abbreviations are given for all analytes measured and used in lieu of their full name in certain figures throughout the paper. Alkylated PAH nomenclature of C1, C2, C3, and C4 refer to the number of additional carbons that are substituted onto the parent structure. For example, a C1-naphthalene is the PAH naphthalene with one additional carbon substituted onto the ring structure. A "C2," "C3," and "C4" compounds mean that there are two, three, and four additional carbons substituted onto the ring structure

| Parent PAHs in PAH50 | Abbreviation | Alkylated PAHs in PAH50 | Abbreviation |
|---|---|---|---|
| Naphthalene | N0 | C1-naphthalenes | N1 |
| Biphenyl | BPHN | C2-naphthalenes | N2 |
| Acenaphthene | ACE | C3-naphthalenes | N3 |
| Acenaphthylene | ACY | C4-naphthalenes | N4 |
| Fluorene | F | C1-fluorenes | F1 |
| Dibenzofuran | DBF | C2-fluorenes | F2 |
| Dibenzothiophene | DBT0 | C3-fluorenes | F3 |
| Phenanthrene | PH | C1-dibenzothiophenes | DBT1 |
| Anthracene | AN | C2-dibenzothiophenes | DBT2 |
| Fluoranthene | FL | C3-dibenzothiophenes | DBT3 |
| Pyrene | PY | C4-dibenzothiophenes | DBT4 |
| Benz[a]anthracene | BaA | C1-phenanthrenes/anthracenes | PH1 |
| Benzo[b]naphtha[2,1-d]thiophene | NBT0 | C2-phenanthrenes/anthracenes | PH2 |
| Chrysene+triphenylene | CHRY+TRIP | C3-phenanthrenes/anthracenes | PH3 |
| Benzo[a]fluoranthene | BaF | C4-phenanthrenes/anthracenes | PH4 |
| Benzo[b]fluoranthene | BbF | C1-fluoranthenes/pyrenes | FP1 |
| Benzo[j]fluoranthene | BjF | C2-fluoranthenes/pyrenes | FP2 |
| Benzo[k]fluoranthene | BkF | C3-fluoranthenes/pyrenes | FP3 |
| Benzo[a]pyrene | BaP | C4-fluoranthenes/pyrenes | FP4 |
| Benzo[e]pyrene | BeP | C1-chrysenes/benzanthracenes | CHRY1 |
| Dibenzo[a,h]anthracene | DA | C2-chrysenes/benzanthracenes | CHRY2 |
| Indeno[1,2,3-c,d]pyrene | IND | C3-chrysenes/benzanthracenes | CHRY3 |
| Benzo[g,h,i]perylene | BghiP | C4-chrysenes/benzanthracenes | CHRY4 |
| | | C1-naphthobenzothiophenes | NBT1 |
| | | C2-naphthobenzothiophenes | NBT2 |
| | | C3-naphthobenzothiophenes | NBT3 |
| | | C4-naphthobenzothiophenes | NBT4 |

contributed to measured PAH or TEH residues. To account for any hydrocarbon residue related to the cleaning protocol, measured PAHs (or TEH) in the process blanks (Online Resource Table S3) were subtracted from PAHs (or TEH) in samples from the same cleaning protocol. The blank corrected data is how the data will be reported in this paper.

## Statistical analysis

All statistical analyses were performed using SAS version 9.4 (SAS Institute Inc., Cary, NC). The data were transformed using the arcsine square root transformation for percent (%) residual PAHs to meet the assumptions of normality and homogeneity of variances for parametric statistics. One of the percent residual PAH values was identified and removed as an outlier (or influential observation) since the absolute value of studentized residual (the residual divided by its standard error) of the observation was found to be greater than three (3) and the Cook's D statistic (Cook 1977) was greater than $4/n$ (where $n$ equals the sample size). A two-factor analysis of variance (ANOVA) of the remaining dataset was performed with a posteriori contrasts in order to determine potential differences between cleaning protocols. The factors of the model were sediment type (sand and silt) and cleaning protocol (CP1–CP6). With the six different cleaning protocols (CP1–CP6), three groupings were constructed to perform the contrasts in an all-pairwise fashion. The groupings for the contrasts were water methods (CP1 and CP2), solvent methods (CP3 and CP4), and wipe methods (CP5 and CP6). Sediment data were then pooled, and a one-factor ANOVA was performed using cleaning methods as the factor (water methods vs. solvent methods vs. wipe methods). The alpha for all statistical tests was set to 0.05 a priori. Attempts were made to run statistical analyses on the TEH dataset; however, the small sample size, coupled with roughly half of the dataset being below the detection limit, was not amenable to statistics.

## Results and discussion

### Sediment grain size and total organic carbon content

Grain size analysis confirmed that the sediment from the Folly River ("sand") was predominantly sand (93.8% sand, 5.2% silt/clay), while the sediment from Leadenwah Creek ("silt") was a mixture of sand and silt (48.8% sand, 51.2% silt/clay) (Online Resource Table S4). Grain size classification for silt/clay was less than 63 μm, while a particle size greater than 63 μm was broadly classified as sand. Measured percentages of TOC for sand and silt sediments were 1.27 ± 0.04% and 7.92 ± 0.05%, respectively (Online Resource Table S5). Testing the efficacy of cleaning protocols on different sediment types was important as properties including grain size and TOC have been reported to be factors in how contaminants bind to sediment, thus affecting their bioavailability (Piwoni and Keeley 1990). Previous studies have noted that contaminants with a higher log $K_{ow}$ (i.e., less polar and less soluble in water) are correlated with TOC (Karickhoff et al. 1979; Means et al. 1980; Piwoni and Keeley 1990; Maruya et al. 1996). Sediments with higher TOCs tend to be composed of silt or clay rather than sand (Piwoni and Keeley 1990).

### Hydrocarbons in spiked sediments

Targeted nominal "slick B" oil concentration was 10,000-μg/g wet weight. Measured sediment concentrations for PAH50 and TEH for both the sand and silt sediments are found in Table 3. Average TEH concentrations (used as a surrogate for total oil concentration) were 8930 ± 780 and 9350 ± 1470 μg/g wet weight for the sand and silt sediments, respectively. Average PAH50 concentrations were 27.6 ± 1.2 and 28.6 ± 5.4 μg/g wet weight for sand and silt sediments, respectively.

PAH50 patterns for both sediments, which were plotted on an average proportion basis (Fig. 2), were very consistent with one another. Fresh Louisiana Sweet Crude (LSC) oil has been previously characterized as having higher proportions of low molecular weight PAHs including naphthalene and its alkylated constituents (Boehm et al. 2016). Since slick B, a ~90-day weathered form of LSC oil, was used, the vast majority of the lower weight PAHs no longer remained; consequently, this oil profile is dominated by alkylated PAHs including C1–C4 phenanthrenes (PH1–PH4), C1–C4 dibenzothiophenes (DBT1–DBT4), and C1–C3 fluorenes (F1–F3) (Fig. 2).

### Residual hydrocarbons from cleaning protocols

The percent residual (% residual) TEH and PAH50 remaining on the bowl and spoon for all cleaning protocols are found in Table 4. Percent residual TEH (or PAH50) was calculated by using the average TEH (or PAH50) sediment concentration (Table 3) and multiplying that value by the mass of sediment placed in the bowl. This value is the total mass (i.e., initial mass) of TEH (or PAH50) for each cleaning protocol replicate. Measured TEH (or PAH50) residue from the bowl and spoon was then divided by the total mass of TEH (or PAH50) and multiplied by 100 to calculate the % residual TEH (or PAH50).

The highest % residual TEH and PAH50 values were measured in CP1. This cleaning protocol, which used only site

**Table 3** Measured sediment concentrations for spiked sediments

| Sediment | Replicate | TEH μg/g wet (ppm) | PAH50 μg/g wet (ppm) |
|---|---|---|---|
| Sand | 1 | 9670 | 28.8 |
| percent dry composition = 71.1% | 2 | 8120 | 26.5 |
| | 3 | 8990 | 27.5 |
| | Average | 8930 | 27.6 |
| | SD | 780 | 1.2 |
| | %RSD | 8.7% | 4.2% |
| Silt | 1 | 10500 | 33.5 |
| percent dry composition = 38.2% | 2 | 9820 | 29.6 |
| | 3 | 7700 | 22.8 |
| | Average | 9350 | 28.6 |
| | SD | 1470 | 5.4 |
| | %RSD | 15.7% | 18.9% |

*SD* standard deviation, *%RSD* percent relative standard deviation

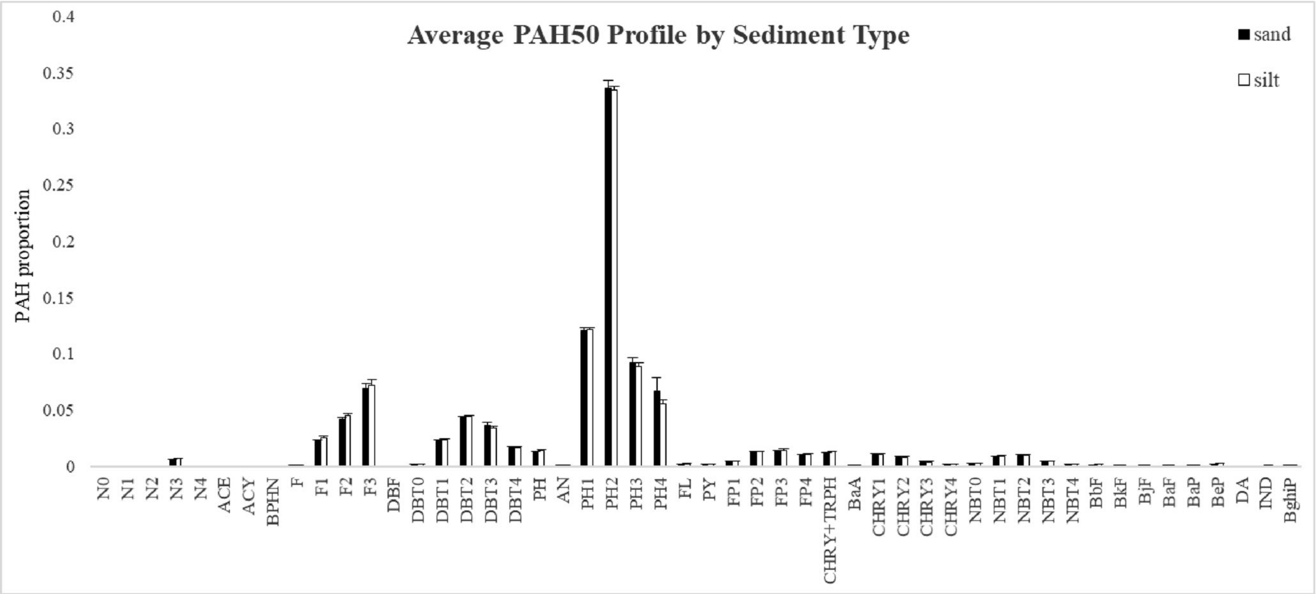

**Fig. 2** The average proportional PAH50 profile for both sediments, error bars are one standard deviation

water and a brush, was the least rigorous of all cleaning protocols. The highest measured % residual TEH and PAH50 found in the study were recorded in a silt replicate for CP1 and were 0.032 and 0.029%, respectively (Table 4). In many instances, residual TEH was found to be less than the LOD (0.25 μg/g), especially in protocols where more rigorous cleaning steps (e.g., involved solvents) were completed. The lowest % residual PAH50 was recorded for CP4 (0.0001%). This cleaning protocol (CP4) is a published technique used by the NOAA's Office of Response and Restoration and is perhaps the most labor and material-intensive of all protocols tested in this study. Steps involved in this protocol include scrubbing with soap and water, as well as solvent rinses with acetone followed by hexane.

The % residual hydrocarbon data in Table 4 estimates the maximal proportion of what could be transferred from a given collection after gear is cleaned. Sampling designs in this study were defined a priori in order to address the worst-case scenario where all sediments were transferred from the collection device. Thus, in this study, potential for transfer is likely overestimated since most sampling protocols direct samples will be collected from the center of a grab or collection device, thereby limiting the amount of material that would be in contact with the sampling device. Collecting sediment from the interior and avoiding material along the sidewalls of the sampler, by design, minimizes the potential for carryover. As noted, the highest percentage of residual hydrocarbon measured in this study was 0.032% (TEH). Based on the information generated from this study, the authors feel that the level of hydrocarbons available for cross-contamination after any of the cleaning protocols would be indistinguishable from any sort of sampling, laboratory, or instrumental variability. While there are many factors that influence variability in any given study, the measure of relative standard deviation (% RSD) for hydrocarbon concentrations in this study is one that is readily quantifiable. The % RSD for sand sediment ($n = 3$) was calculated to be 8.7% and 4.2% for TEH and PAH, respectively. Data for the silt sediment resulted in % RSD of 15.7% and 18.9% for TEH and PAH, respectively. Following good laboratory practices associated with environmental chemical analysis, a continuing calibration verification (CCV) standard was run every 10–15 samples to ensure that the initial instrument calibration was still valid. Acceptable variation of CCV results is often defined as ±20% of the known concentration (USEPA 2014b). Thus, analytical measurements already allow for up to ±20% variability, demonstrating that the residues measured in this study would be negligible.

## Cleaning protocol comparison

While residual hydrocarbons were low in all protocols (≤0.032%), understanding the potential differences in the efficacies of each protocol was the goal of this study. A two-factor ANOVA, with factors of cleaning protocol (CP1–6) and sediment type (sand, silt), was run on the arcsine square root transformed residual PAH data. An initial assessment of the dataset indicated the occurrence of a potential outlier. Upon analyzing the studentized residuals (and Cook's distance measure) of the dataset, an outlier data point was observed and removed (CP1, silt sediment, rep 3). Using the amended dataset, the two-factor ANOVA was rerun on the arcsine square root residual PAH data (Shapiro-Wilk test for normality $p = 0.589$). The two-factor ANOVA revealed that there were significant differences among cleaning protocols ($p < 0.0001$), and the interactive term (cleaning protocol × sediment type, $p = 0.02$); however, there was no significant

**Table 4** The percent residual (% residual) TEH and PAH50 values for each cleaning protocol. Values that were less than the limit of detection are denoted with <LOD. Percent residual TEH and PAH50 values were calculated dividing the mass of residual TEH (or PAH50) by the initial mass of hydrocarbons placed in the bowl (sediment mass × average sediment concentration) and multiplying that number by 100. Additional data that was used to calculate the % residual TEH and PAH can be found in Online Resource Table S6

| Cleaning protocol (CP) | Sediment | % Residual TEH | % Residual PAH |
|---|---|---|---|
| CP1—site water and brush | Sand | 0.020 | 0.017 |
| | | 0.015 | 0.013 |
| | | 0.018 | 0.013 |
| | Silt | 0.011 | 0.009 |
| | | 0.017 | 0.008 |
| | | 0.032 | 0.029* |
| CP2—site water/soap and brush/site water/DI | Sand | 0.006 | 0.005 |
| | | 0.017 | 0.007 |
| | | 0.017 | 0.011 |
| | Silt | 0.006 | 0.005 |
| | | < LOD | 0.004 |
| | | < LOD | 0.002 |
| CP3—site water and brush/site water/acetone/DI | Sand | < LOD | 0.0005 |
| | | 0.015 | 0.002 |
| | | < LOD | 0.0009 |
| | Silt | 0.013 | 0.005 |
| | | 0.006 | 0.0007 |
| | | < LOD | 0.001 |
| CP4—site water/soap and brush/site water/acetone/-hexane/air dry | Sand | < LOD | 0.0001 |
| | | < LOD | 0.0002 |
| | | < LOD | 0.0005 |
| | Silt | < LOD | 0.0001 |
| | | 0.017 | 0.006 |
| | | 0.007 | 0.002 |
| CP5—site water and brush/IPA wipe/DI | Sand | < LOD | 0.002 |
| | | < LOD | 0.0008 |
| | | < LOD | 0.002 |
| | Silt | < LOD | 0.002 |
| | | 0.007 | 0.005 |
| | | 0.012 | 0.003 |
| CP6—site water/soap and brush/site water/IPA wipe/DI | Sand | < LOD | 0.0003 |
| | | < LOD | 0.0002 |
| | | < LOD | 0.0005 |
| | Silt | < LOD | 0.0005 |
| | | 0.006 | 0.002 |
| | | 0.007 | 0.002 |

* Indicates the value that was identified as a statistical outlier and was not included in any statistical analyses

difference between sediment types ($p = 0.418$). While a significant difference was observed in this two-factor ANOVA, the assumption of homogeneity using Levene's test was not met ($p = 0.028$). In an effort to meet the assumption of homogeneity, and to elucidate the significant differences among cleaning protocols, we repeated the two-factor ANOVA with the cleaning protocols reclassified (i.e., contrasts) according to the types of materials used during the protocol. The cleaning protocols were reclassified as either "water," "solvent," or "wipe." Protocols reclassified as "water" are cleaning protocols that did not contain any solvent as part of the process and include CP1 and CP2. Protocols reclassified as "solvent" were cleaning protocols that included solvent as a step, but the solvent was applied via a squirt bottle, CP3 and CP4, instead of applied using a wipe, which is CP5 and CP6 (“wipe”). A significant difference was found among the reclassified cleaning protocols ($p < 0.001$). This test passed both the Shapiro-Wilk test for normality ($p = 0.921$) and Levene’s test for homogeneity ($p = 0.099$).

With sediment type not being a significant factor in the two-factor ANOVA, the decision was made to run a one-factor ANOVA using pooled sediment data. Cleaning protocols classified as “water,” “solvent,” or “wipe,” as detailed earlier, were the factor being tested. The one-way ANOVA revealed a significant difference among cleaning protocols ($p < 0.0001$; Shapiro-Wilk $p = 0.584$; Levene’s test $p = 0.335$) (Fig. 3). A Tukey-Kramer pair-wise comparison of the three cleaning protocol groupings revealed that there was a significant difference between “water” classified cleaning protocols (CP1 and CP2) and “solvent” protocols (CP3 and CP4) ($p < 0.0001$), and “water” and “wipe” (CP5 and CP6) protocols ($p < 0.0001$). There was no difference between “solvent” and “wipe” protocols ($p = 0.945$). Therefore, cleaning protocols that used solvent/IPA wipes (CP3–CP6) as a step were more effective at removing hydrocarbons than protocols that did not (CP1–CP2).

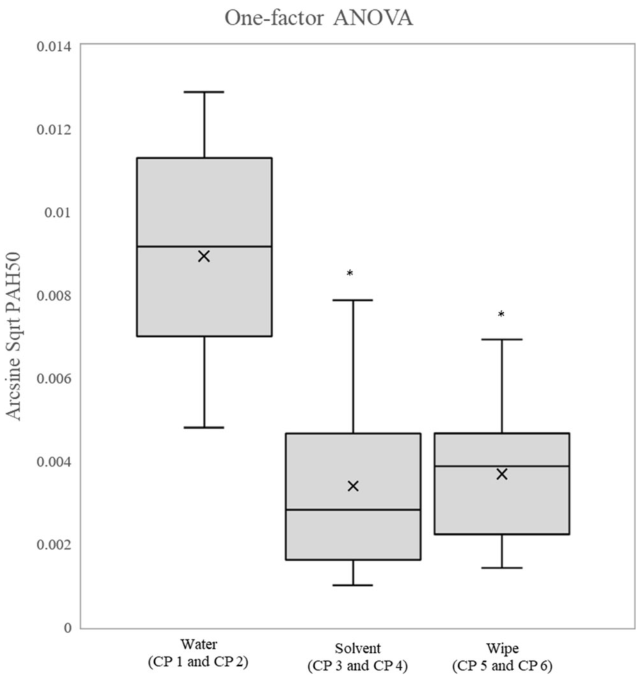

**Fig. 3** The distribution results from the one-factor ANOVA shown as a box and whisker plot, using pooled sediment data and cleaning protocol methods classified as either “water,” “solvent,” or “wipe.” The box itself represents the interquartile range, with the bottom on the box representing the 1st quartile and the top of the box representing the 3rd quartile. The *x* denotes the mean, and the horizontal line in the box is the median. The bottom whisker indicates the lowest observation, and the upper whisker indicates the highest observation. Solvent and wipe protocols were significantly different from water protocols and are denoted by an asterisk (*)

## Conclusions

The efficacy of six different decontamination protocols, ranging in complexity, was examined for two different sediment types after being spiked with a weathered Deepwater Horizon oil (“slick B”). Statistically significant differences between cleaning protocols were observed but not between sediment types. A key finding was that decontamination protocols that included a solvent step (e.g., acetone, hexane, IPA wipe) were more effective at removing hydrocarbons than decontamination protocols that lacked solvent; however, the method of application for the solvent (i.e., squirt bottle versus solvent soaked wipe) did not factor into the efficacy of the cleaning protocol. Despite both sediments having an oil concentration representing a worst-case scenario, percent residual hydrocarbons measured in this study never exceeded 0.032%. While the addition of solvent reduces the level of hydrocarbon carryover, cross-contamination values of this magnitude are negligible and indistinguishable from other sources of expected variability (e.g., field, laboratory, and/or analytical variability). Therefore, this study provides evidence that all six investigated cleaning protocols were sufficiently effective at removing hydrocarbons for purposes of field assessments involving collection and analysis of sediment samples for hydrocarbon and/or PAH contamination, and thus have a low potential for carryover. Ultimately, those preparing sampling plans should consider the tradeoffs between health, safety, and environmental concerns and an aim to eliminate as much hydrocarbon carryover as possible. Solvents may be warranted in circumstances where the risks are manageable, and investigators strive for the most rigorous method possible. In such cases, the use of IPA wipes presents a practical and effective alternative to more hazardous solvents in squirt bottles and other containers.

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**Availability of data and materials** All data generated or analyzed during this study are included in this published article and its supplementary information files.

**Author contribution** All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Emily C. Pisarski, Edward F. Wirth, Ian Hartwell, Brian S. Shaddrix, and Paul L. Pennington. The first draft of the manuscript was written by Emily C. Pisarski, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## Declarations

**Ethical approval** Not applicable

**Consent to participate** Not applicable

**Consent for publication** Not applicable

**Conflict of interest** The authors declare that they have no conflict of interest.

**Disclaimer** The scientific results and conclusions, as well as any opinions expressed herein, are those of the author(s) and do not necessarily reflect the views of NOAA of the Department of Commerce. The mention of any commercial product is not meant as an endorsement by the Agency or Department.

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