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Analysis of Organic Contaminants in Dredged Material using a Field-Portable GC-MS

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PURPOSE: This technical note describes the use of a field-portable gas chromatograph mass spectrometer for the in-field determination of organic contaminants in dredged material. During active dredging operations, sediment and water samples are collected as for traditional laboratory analysis of contaminants, however, in this case, field-portable instrumentation is used for quantitative analysis of certain organic contaminants, including Polycyclic Aromatic Hydrocarbons (PAHs).

INTRODUCTION: On July 23, 2008, a barge transporting fuel oil was involved in an incident that resulted in the barge sinking near Mile 96 above Head of Passes on the lower Mississippi River. The contents of the barge were discharged, and created a potential environmental hazard of unknown extent. Maintenance dredging activities being conducted by the U.S. Army Engineer District, New Orleans (MVN) downriver of the fuel oil spill were negatively impacted, necessitating that U.S. Coast Guard inspectors be present on dredges to detect 'sheen' on the water surface as the result of dredging operations.

In order to provide scientific data on which to base decisions about continuing or terminating dredging operations, MVN contacted the U.S. Army Engineer Research and Development Center (ERDC) for technical assistance. ERDC and MVN personnel developed a sampling and analysis plan to obtain definitive chemical concentration data on the extent of sediment contamination and the amount of contamination being disturbed by the dredging operations. The plan included collecting samples of sediment and water from active dredges for traditional laboratory analysis for a list of common, petroleum-related contaminants, including PAHs, diesel range organics (DRO), oil range organics (ORO), vanadium, and lead.

Additionally, the ERDC Environmental Chemistry Branch (ECB) deployed its Griffin 400 field-portable gas chromatography ion trap mass spectrometer (GC-MS). This instrument was developed as part of the Environmental Quality and Installations Long Term Monitoring Program for field analysis of explosives in groundwater (Kirgan et al. 2008). However, PAHs are commonly determined in laboratory methods using GC-MS following U.S. Environmental Protection Agency (USEPA) method SW-846 8270 (USEPA 2007), therefore, only minor modifications to the explosives detection method (temperature program, gas flows, ions monitored, etc.) were required to detect PAH compounds of interest in dredged material as a marker for petroleum contamination.

The investigation team, consisting of ERDC and MVN personnel, deployed to Venice, LA, for 4 days during August 2008 to collect samples and perform in-field analysis. The team collected

sediment and water samples from the dredge B.E. Lindholm during active dredging at various locations above Head of Passes on the lower Mississippi River. Samples were analyzed on the dredge during active operations, and sample splits were stored in coolers at 4°C and transported back to the Environmental Chemistry Laboratory in Vicksburg for further analyses.

MATERIALS AND METHODS:

Dredged Material Collection. Sediment and water samples were collected from the dredge's hopper while dredging was occurring using a 3-gallon galvanized bucket attached to a rope on the hopper catwalk. The bucket was allowed to sink as far as possible beneath the surface of the dredged material slurry while the water/sediment slurry was pumped in by the dredge pumps. The bucket was then retrieved and the slurry poured into precleaned 1-gallon glass jars; each sampling event yielded at least 2 gallons of material. A second bucket of material was then collected and allowed to settle for 10 to 15 minutes before decanting the water to collect the sediment in precleaned 8-ounce glass jars. A minimum of 16 ounces of sediment were collected for each sampling event. All sediment and water samples were then stored on ice in coolers until analyzed, either on the dredge with the field-portable GC-MS, or after transport to the ECB laboratory.

Field Extraction Techniques. Dredged material slurries were allowed to settle for about 15 minutes before the water was decanted for PAH extraction and analysis. The decanted water samples were extracted for PAHs using a modification of EPA method 3510C using Teflon separatory funnels (USEPA 2007). Briefly, 100 mL of dredged water was added to the 125-mL Teflon separatory funnel to which 20 mL of dichloromethane was added. The funnel was then hand shaken for 5 minutes with periodic degassing to prevent overpressurization. The dichloromethane layer separates and sinks to the bottom of the container because it is immiscible with the aqueous phase. The dichloromethane layer, now containing extracted PAHs from the sample, was then drained using the separatory funnel stopcock and collected in a 20-mL borosilicate glass vial containing 10 g of sodium sulfate to remove any residual water from the dichloromethane sample. This solvent sample was then spiked with internal standards and analyzed for PAHs using the field-portable GC-MS following modifications of EPA method 8270 as described below (USEPA 2007).

Sediments were extracted using a modification of EPA method 3550C (USEPA 2007). For this work, 2 g of settled sediment material was mixed with 2 g of sodium sulfate to help dry the sample and minimize formation of an emulsion with the 12 mL of dichloromethane extraction solvent. The sediment/sodium sulfate/solvent mixture was sonicated for 30 minutes using an ultrasonic bath. After sonication, the dichloromethane layer was decanted into a 20-mL borosilicate vial containing an additional 1 g of sodium sulfate to remove any residual water. This solvent sample was then spiked with internal standards and analyzed for PAHs using the field-portable GC-MS following modifications of EPA method 8270 as described below.

Field GC-MS Analysis. The instrument used for all field analyses was an ICx Griffin 400 gas chromatograph with a cylindrical ion-trap Mass Spectrometer (Kirgan et al. 2008). The instrument is shown in Figure 1. The GC column was a 5-m Restek-TNT II column with helium as a carrier gas. One microliter was injected for all calibration and check standards and sediment and water extract samples.

Figure 1. Field-portable Griffin 400 GC-MS instrument as deployed on the dredge B.E. Lindholm.

Briefly, the operation conditions of the GC-MS are as follows. The injection inlet was maintained at 200°C with a constant helium carrier gas flow of 1 mL/min. The column temperature ramp started at 40°C and was 1 min, before ramping at 10°C/min to 100°C, second ramp at 25°C/min to 280°C, with a final 5°C/min ramp to the final temperature of 300°C with a holding time of 3 min. The entire temperature program and sample analysis is approximately 21 min. A standard list of PAH compounds was determined, with the ions used for quantitation and confirmation taken from the published method (USEPA 2007). Mixed analyte calibration standards were purchased from Restek and used to calibrate the instrument from 100 to 50,000 μg/L using a minimum of four analyte concentrations with typical linear response correlation factors greater than 0.98. Figure 2 is an example chromatogram of a 5000-μg/L mixed analyte standard (Supelco, Bellefonte, PA) analyzed in the field by this technique.

The detection limits were determined based on the lowest calibration standard. The low standard was 100 μg/L, therefore concentrations greater than 20 μg/L (in water) are quantifiable, due to the concentration factor of five in the extraction process. The sediment detection limits were calculated based on sample mass (approximately 2 g each) and the solvent extraction volume (12 mL), yielding a detection limit of 600 μg/kg.

Field Analysis Results. Due to the low levels of contaminants present in the samples, no PAHs were detected in any of the sediment or water samples above instrumental detection limits. However, some low level concentrations were determined to be estimated values, either because the concentrations were below the low calibration standard, or the qualifier ion used to confirm the presence of an analyte was not detected. Table 1 lists the concentrations determined for several sediment and water samples determined in the field using the portable GC-MS. At the end of the table the average values for the detection limit divided by the values observed is given. This is a measure of the degree to which these compounds are below the calculated detection limits. All of the values given for the in-field results would be reported as not detected, but are given as estimated values to compare to the laboratory methods, which have somewhat lower detection limits due to the ability in the laboratory to concentrate the solvent extracts prior to analysis.

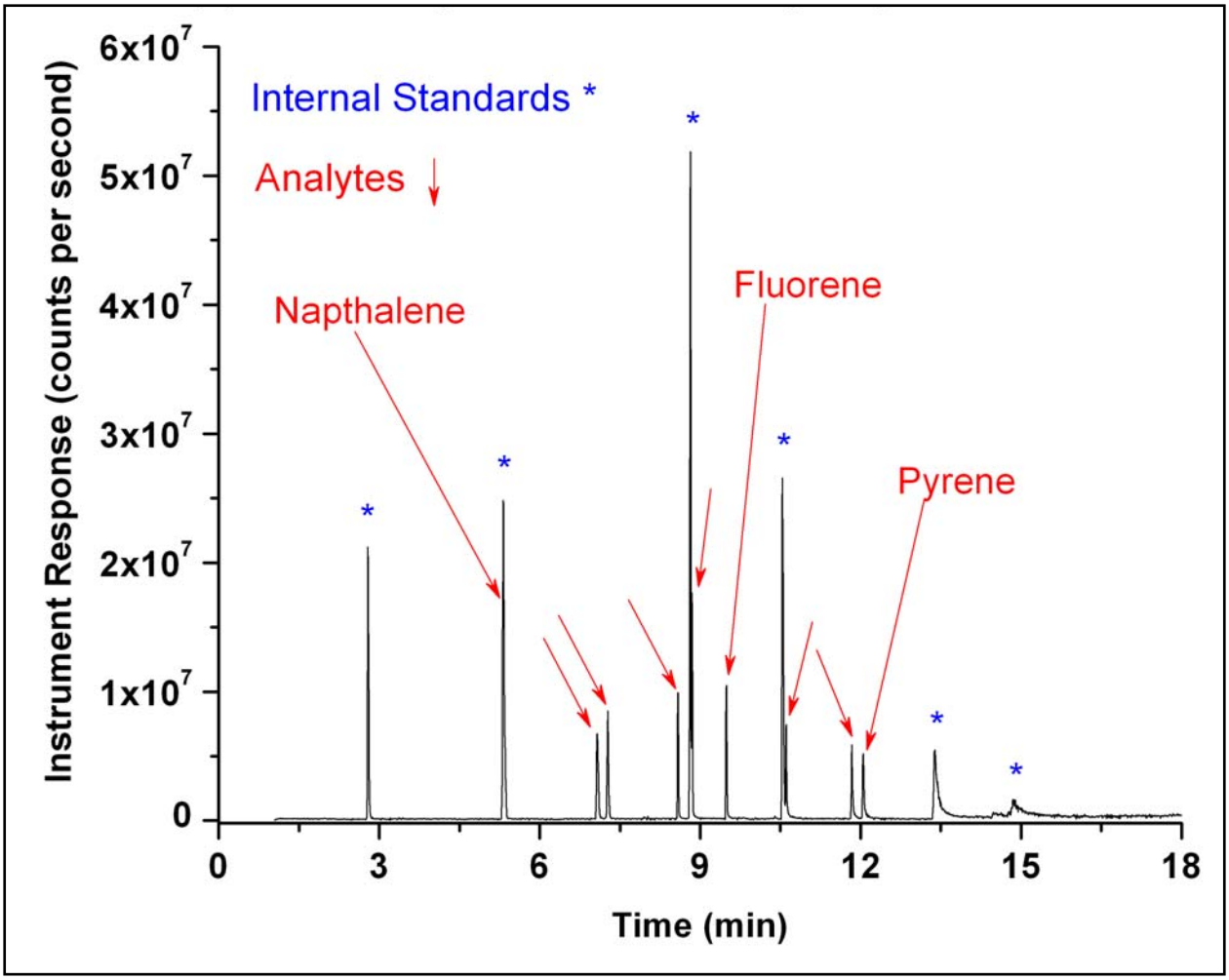

Figure 2. Example chromatogram of a 5000-μg/L PAH standard using the Griffin 400 GC-MS. Internal standard compounds are labeled with an "*", select PAH compounds are also indicated.

Comparison to Laboratory Results. Table 1 also lists concentrations of several PAH analytes in sediment and water samples analyzed by the Environmental Chemistry Branch laboratory in Vicksburg, MS. The analyte extraction efficiency of the fixed laboratory methods and the ability to concentrate the final solvent extracts allows the laboratory method to provide lower detection limits than the field techniques. However, the analyte concentrations measured by the laboratory and field methods do qualitatively agree, with no concentration measured in the laboratory analyses above that of the field method's reporting limit, indicating the field method does not produce false positives or negatives. The laboratory and field results for the water and sediment samples are plotted in Figures 3 and 4, respectively, showing generally consistent results between the two techniques considering the field values being compared are estimated concentrations well below the instrumental reporting limit (Table 1).

Table 1. Concentrations of PAH compounds in water and sediment samples determined by the field-portable and laboratory-based methods.
All concentrations reported are below the field instrument reporting limit.

Water Samples			Sediment Samples		
Compounds	**In-Field Results (µg/L)**	**Laboratory Results (µg/L)**	**Compounds**	**In-Field Results (µg/kg)**	**Laboratory Results (µg/kg)**
Naphthalene	0.548	0.200	2-methylnapthalene	0.181	3.679
Fluoranthene	0.005	0.017	Phenanthrene	11.790	11.958
Pyrene	0.023	0.017	Anthracene	1.040	2.760
2-methylnapthalene	0.001	0.013	Fluoranthene	0.199	19.317
Acenaphthene	0.017	0.013	Pyrene	0.054	16.557
Acenaphthylene	0.036	0.010	Acenaphthylene	0.687	3.766
Acenaphthene	0.013	0.010	Fluorene	4.906	7.517
Fluoranthene	0.134	0.010	Anthracene	0.372	15.092
Pyrene	0.024	0.010	Fluoranthene	0.305	111.566
Acenapthene	0.674	0.100	Pyrene	5.259	104.090
Athracene	0.307	0.130	Acenaphthylene	0.689	4.284
Fluoranthene	0.083	0.040	Acenapthene	3.152	11.402
Pyrene	0.356	0.220	Phenanthrene	4.092	102.687
Acenaphthene	0.107	0.05	Anthracene	1.079	27.015
Phenanthrene	0.131	0.210	Fluoranthene	4.135	167.164
Fluoranthene	0.16	0.010	Pyrene	4.770	142.537
Phenanthrene	0.024	0.012	Acenapthene	4.278	2.963
			2-methylnapthalene	3.272	3.763
Average DL / Concentration Measured					
	1880	4		1440	0.5

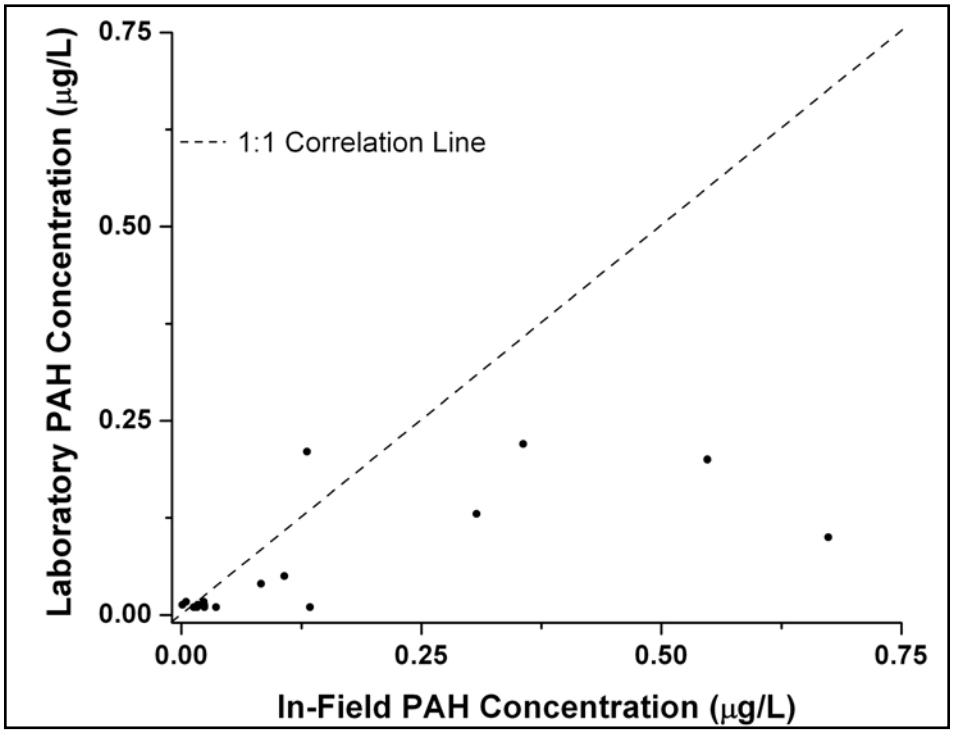

Figure 3. Comparison of field and laboratory PAH concentration data for water samples, all in-field concentration data is below the instrument detection limit, resulting in estimated values.

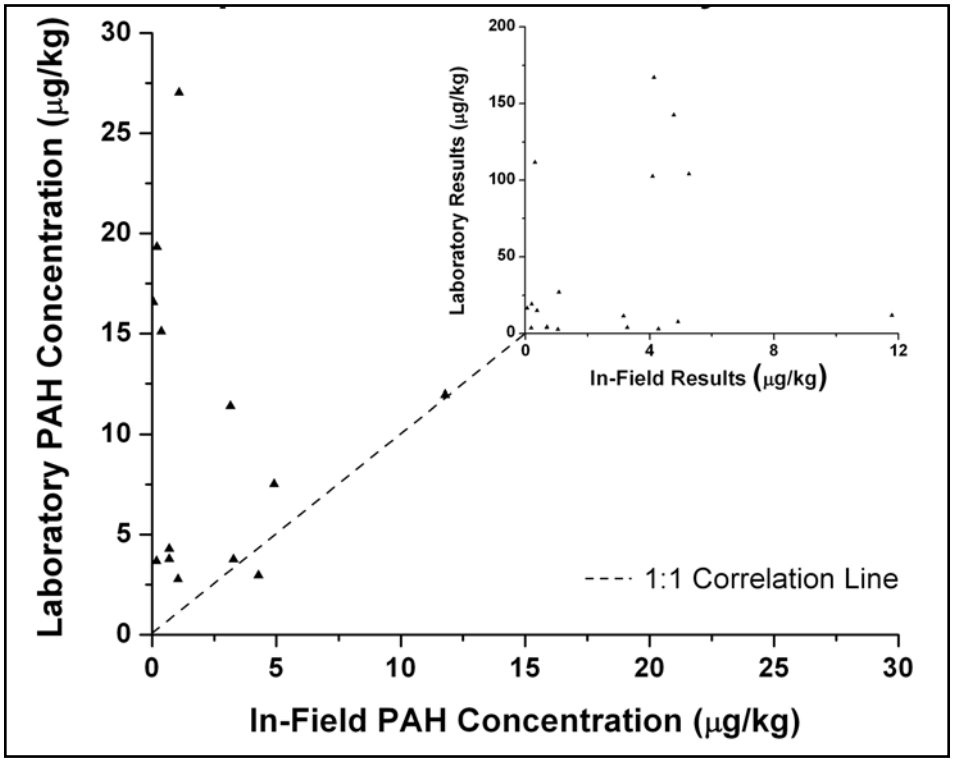

Figure 4. Comparison of field and laboratory PAH concentration data for sediment samples, all in-field concentration data is below the instrument detection limit, resulting in estimated values.

Qualitative Field Screening Kit. Due to the need to detect oil residue as dredging operations continue, a field screening test kit was also developed based on the slight color tint imparted to hexane extraction solvent when No. 6 fuel oil dissolves in it. This color change is proportional to the amount of fuel oil present, and therefore can be used as a qualitative indicator of the presence and relative amount of oil present. Figure 5 shows photographs of the field kit and example standards provided in each kit used to judge the amount of oil present in a sample. This field kit is being used by all active dredges on the lower Mississippi River during FY2009 dredging operations being conducted by MVN.

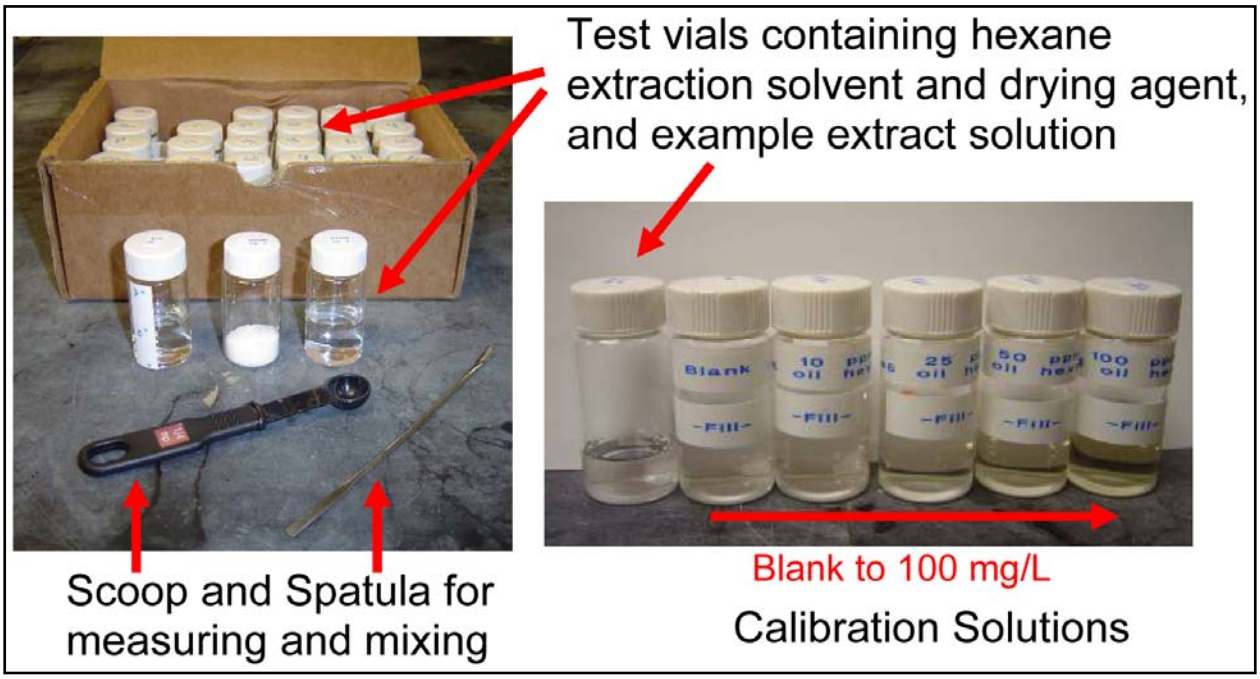

Figure 5. ERDC-developed field screening test kit for fuel oil #6 in dredged material (left). Dissolved fuel oil #6 in hexane standards used for calibration (right) in field screening test kit.

APPLICABILITY: The field-portable instrumentation described above has the capability to analyze for a wide variety of organic contaminants in complex environmental matrices. The Griffin 400 GC-MS weighs approximately 35 kg, has dimensions of approximately 40 × 40 × 40 cm, and can be operated on a 2-kW portable generator. Therefore the instrument can be deployed to any environment where this space and power is available. The only potential limitation is humidity. Previous work has shown that relative humidity levels above approximately 80 percent can cause electronic problems with the instrument, and therefore it is recommended that the instrument only be operated in conditions below approximately 75 percent relative humidity. However, the current work was successfully performed on an active dredge operating near the mouth of the Mississippi River during the summer, and humidity was not observed to cause any problems.

The work discussed above was specifically focused on PAHs; however, the technology was originally developed for explosives, and therefore can be modified to analyze for a wide variety of organic compounds. For example, during the instrumentation's original prove-out deployment for explosives in groundwater analysis, an unknown chromatographic peak in certain monitoring

wells was identified as a plasticizer compound because of the mass spectrometer's ability to detect and identify organic molecules based on their molecular weight and structure (Kirgan et al. 2008). Therefore, this technique can potentially be extended to other classes of organic compounds. Work is currently underway to expand capability to include polychlorinated biphenyls, and extension to pesticides is also possible.

SUMMARY: The use of a field-portable GC-MS is described for the near-real-time analysis of PAHs in dredged material. Although detection limits are not as low as traditional laboratory analyses, the data agree reasonably well between field and laboratory-based analyses considering the concentrations of analytes observed in the samples tested. The data provided by this research allowed real-time dredging decisions to be made based on sound scientific data, rather than subjective human observations. Future work is needed to improve detection limits through modified extraction techniques and real-time data processing through software modifications and upgrades; however, the current methods do allow for quantitative determination of PAHs in dredged material. Additionally, a qualitative field screening test kit was developed based on color changes in organic solvent used to extract fuel oil #6 from sediment and water samples. This test kit can be used as a rapid indicator for the need to collect samples for more quantitative and thorough laboratory analyses.

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> Bednar, A. J., R. A. Kirgan, J. M. Corbino, and A. L. Russell. 2009. *Analysis of dredged material for organic contaminants using a field-portable GC-MS.* DOER Technical Notes Collection. ERDC TN-DOER-E26. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

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U.S. Environmental Protection Agency (USEPA). 2007. *SW-846 methods for the analysis of hazardous waste.* Methods 3510, 3550, and 8270.

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