

UTAH DIVISION OF WATER QUALITY

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Willard Bay Project Proposal Form

NOTE: Proposal must be no longer than 6 pages. Supplemental documents such as letters of support, information to demonstrate previous project implementation and other relative supportive documents may be submitted in addition to this form.

Applicant Name: _____

Co-Applicant Name(s) (if applicable): _____

Project Title: _____

Agency or Business Name (if applicable): _____

Mailing Address: _____ City: _____ State: _____ Zip: _____

Phone: (____) ____-____ E-mail: _____

Individual Non-Profit Govt. Agency Academic Commercial Other

1. Estimated Project Costs:

Labor	\$_____
Materials	\$_____
Equipment	\$_____
Administration	\$_____
Miscellaneous	\$_____
TOTAL	\$_____

Other sources of project funding:

_____	\$_____	_____	\$_____
Source	Amount	Source	Amount
_____	\$_____	_____	\$_____
Source	Amount	Source	Amount
_____	\$_____	_____	\$_____
Source	Amount	Source	Amount
_____	\$_____	_____	\$_____
Source	Amount	Source	Amount

Total project cost including other sources of funding: \$_____ (please include bids for labor, equipment, rentals, etc.)

- 2. Describe the purpose and need of the project: _____
- 3. Estimated time frame of the project with significant milestones (Note: Project must be completed with final reports filed by January 1, 2018): _____

4. Describe the location of the project with attached location map, including details on the total area that will be directly enhanced by the project: _____
5. Describe how the project will specifically enhance and protect waterways affected by the Willard Bay diesel release and improve the conditions of one or more of the following: wildlife, habitat, natural vegetation, water quality or emergency response:
6. Describe project's connectivity to other natural areas or projects that further enhance wildlife, habitat, natural vegetation, water quality or emergency response:
7. Describe any additional social benefits of implementing this project:
8. Project plans and details, including rights to work on specified piece of land:
9. Describe your experience in implementing projects of similar scope and magnitude:
10. Describe how ongoing maintenance of the project will be funded and carried out:
11. List consultants or agency partners that have participated in project development (below):

Name/Company	Address	Phone
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Name/Company	Address	Phone
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Name/Company	Address	Phone
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Signature	<i>Otakeung Conway-Ben</i>	Date	5/2/2014
	Applicant		
Signature	<i>A. [Signature]</i>	Date	5/4/2014
	Co-Applicant (if applicable)		

2. Describe the purpose and need of the project

The overall objective of this project is to measure the endocrine disrupting potential of diesel contaminated water and sediments found at Willard Bay. Endocrine disruption describes the alteration of an organism's hormonal system due to exposure of environmental contaminants, called endocrine disrupting chemicals (EDCs). EDCs may interfere with sexual development and differentiation, metabolism, and/or thyroid function. These chemicals are classified as estrogens, androgens, obesogens, and thyroidigens, and include human hormones, surfactants, oil spill dispersants, solvents, antibiotics, and perfluorinated chemicals. In aquatic animals, endocrine disruption has resulted in male fish producing egg protein, reduced body weight, loss of fish populations, and physical mutations in frogs. In humans, environmental EDCs may be responsible for reduced sperm counts and increases in hormone dependent cancers.

To test for endocrine disruption in Willard Bay, water and sediment samples will be collected at designated sites, processed, and tested on various bioassays. These tests include the yeast estrogen screen and yeast androgen screen, EPA's Tier 1 in vitro battery (estrogen receptor binding, androgen receptor binding, estrogen receptor transcriptional activation, aromatase, and steroidogenesis), thyroid binding, and metabolic disruption. Results from these findings will show if the potential for endocrine disruption exists, and if there should be concern for animals living in the bay. Endocrine disruption quantification will add to water quality and sediment data collected by UDEQ in recreationally and environmentally significant surface water.

Endocrine disruption is an understudied area in the Wasatch Front, and little information exists regarding endocrine disruption potential of polluted surface water. This project will provide the opportunity for the research team to hold biannual seminars in this emerging field. To add benefit to education at Willard Bay, the research team will hold a Clean Water Day at the conclusion of the project (Year 3), where interested individuals can learn more about diesel spills, health effects, and clean-up of minor spills through hands-on activities.

3. Estimated time frame of the project with significant milestones

Year 1 (July 1, 2014 – June 30, 2015) – Implementation of EPA's Tier 1 in vitro bioassays; quarterly sampling of Willard Bay and sediments; recruitment and training of Ph.D. student in sampling and sample processing.

Year 2 (July 1, 2015 – June 30, 2016) – Quarterly sampling, testing of water and sediments for endocrine disruption, testing of diesel components for endocrine disruption, training of Ph.D. student in bioassays.

Year 3 (July 1, 2016 – June 30, 2017) – Quarterly sampling, testing of water and sediments for endocrine disruption, sampling wrap-up, Clean Water Day at Willard Bay

Year 4 (July 1, 2017 – January 1, 2018) – Review of endocrine disrupting data, completion of Final report, completion of scholarly manuscripts.

4. Describe the location of the project with attached location map, including details on the total area that will be directly enhanced by the project:

Water samples will be collected at the sites specified by UDEQ to be consistent with water quality data: #392-background monitoring site, drainage east of I-15; #394- between weirs; #395- east of boom #3; #396-west of boom #1; #397-north boom; #398- French drain south; #399- French drain north; #401- below weirs above reservoir; #402- east of boom #3; #495-background monitoring site, south marina off of dock; #496- west of main hard boom #2; #497-west of boom #3; #498- west of main hard boom #4; #499- open water monitoring site, west of

main hard boom #5; #502- 50 ft. from #497; #505- 50 ft. from #396; #508- 50 ft. from #397 (<http://www.deq.utah.gov/locations/G/greatsaltlake/willardbay/basemap.html>). See attached map in supplemental data.

5. Describe how the project will specifically enhance and protect waterways affected by the Willard Bay diesel release and improve the conditions of one or more of the following: wildlife, habitat, natural vegetation, water quality or emergency response.

This project will provide UDEQ with important information regarding endocrine disruption potential, a biological measurement of water quality, of the polluted waterway. The results will be of value to both UDEQ and Chevron, as it has been reported that diesel components are endocrine disruptors, and will be useful should a diesel pipeline breach occur again.

6. Describe project's connectivity to other natural areas or projects that further enhance wildlife, habitat, natural vegetation, water quality or emergency response

This research will build upon existing health data collected by UDEQ regarding contaminated fish tissue and human cancer risk caused by the Chevron diesel spill by providing data on quarterly sampling of the affected area. Reports released by UDEQ showed no measurable diesel products found in fish tissue, while the calculated human cancer risk caused by diesel components was negligible. UDEQ concluded that fish exposed to diesel were not contaminated and posed no risk for human consumption, and direct human exposure to diesel would not result in increased cancer incidences. In order to provide a complete human risk assessment, additional information is needed on EDC risk, which this study will provide.

7. Describe any additional social benefits of implementing this project

The research team will host seminars on endocrine disruption of wildlife exposed to chemical contaminants, particularly diesel and oil spills. The seminars will give an overview of endocrine disruption, methods used, water quality data, and updates on this specific project. Seminars will be held at the University of Utah and a location near Willard Bay twice per year.

8. Project plans and details, including rights to work on specified piece of land

The overall objective of this project is to measure endocrine disruption potential of diesel-contaminated sediments and water following an oil spill. Diesel pollutants, even at the reported trace level, have the potential to interact with critical hormonal systems in aquatic animals that will likely impact sex ratio and future generations. To accomplish this research goal, the research team will: (Task 1) collect and process water and sediment samples, (Task 2) test samples on estrogen, androgen, thyroid, and metabolic bioassays, and (Task 3) test Chevron diesel and diesel components for endocrine disruption.

Task 1 – Sample collection and processing

Water processing. Water and sediment samples will be collected from the polluted site quarterly over three years (excluding winter). Samples will be collected in muffled glass bottles and filtered through a 0.45 µm glass fiber filter. Organics will be extracted from water by passing the filtrate through a C-18 resin. Organics will then be eluted from the disk with ethanol, the volume will be reduced, and the analytes will be resuspended in water. This sample will be subject to further testing on various endocrine disrupting bioassays. For quality assurance, ultrapure water will serve as the negative control.

Sediment extraction. Dr. Andy Hong, Professor of Civil and Environmental Engineering at the University of Utah, has developed a method to extract hydrophobic chemicals from a complex matrix called pressure cycle-assisted solvent extraction (PCAE). Collected sediments and diesel-spiked sediment will be extracted using PCAE and compared to soxhlet extraction. The benefits of this technique are: rapid extraction of organics from sediment samples in 10 minutes, use of a small 2-to-1 solvent/sample volume ratio, and use of 100 psi pressure and room temperature for extraction.

Task 2 – Test samples on estrogen, androgen, thyroid, and metabolic bioassays

Samples will be quantified for estrogenic, anti-estrogenic, androgenic, and anti-androgenic activity, in addition to thyroid and metabolic disruption. To test for estrogenic and androgenic activity, the yeast estrogen and androgen screens (YES and YAS) will be used, EPA standard *in vitro* methods, thyroid hormone binding assays, and metabolic binding assays.

Yeast estrogen and androgen screens. Samples will be analyzed for estrogen, androgen, antagonist activity using the yeast estrogen and androgen screens. This method is well-developed in the PI's lab. The yeast strain contains a plasmid with either estrogen or androgen response elements upstream of a reporter gene. If estrogens or androgens are present, they will bind to their respective receptors, then to the hormone response elements, and binding will induce expression of the reporter gene β -galactosidase. Estrogen/androgen activity is detected via UV-VIS absorption of chlorophenol-red β -D-galactopyranoside (CPRG).

EPA's Tier 1 *in vitro* assays. Samples concentrated and prepared will be tested on EPA's Tier 1 *in vitro* estrogenic and androgenic activity. All methods will be adapted in the Dr. Conroy-Ben's lab and validated using EPA's standard protocols prior to sample request and processing.

- **Estrogen receptor (ER) binding assay (EPA Method 890.1250)** – this method utilizes an estrogen receptor protein from rat uterine cytosol and a radio-labelled ligand. Displacement of the radio-labelled ligand by a chemical is indicative that it will bind to the receptor.
- **Androgen receptor binding assay (EPA Method 890.1150)** – similar to the ER binding assay, however the androgen receptor from the rat prostate is the protein of interest. Displacement of a radioligand indicates androgen active chemicals.
- **ER transcriptional activation (EPA Method 890.1300)** – an estrogen or anti-estrogen will bind to a human estrogen receptor, the complex will dimerize, and bind to estrogen response elements on a plasmid, upstream of the luciferase reporter gene. Estrogen active chemicals are measured by luciferase illumination.
- **Aromatase (EPA Method 890.1200)** – an *in vitro* test that measures the conversion of C19 steroids to estrogens using human recombinant enzyme CYP19. The test measures production of tritiated water using a scintillation counter.
- **Steroidogenesis H295R (EPA Method 890.1550)** – an *in vitro* test that also measures disruption to steroid synthesis, but evaluates the larger picture rather than a specific enzymatic activity.

Thyroid binding. Samples will be quantified for environmental thyroidogens using a competition-binding assay (Invitrogen Catalog No. PV4686). Dr. Conroy-Ben has experience with the company's estrogen receptor- α , estrogen receptor- β , and androgen receptor competition

binding assays. The thyroid receptor- β competition-binding assay utilizes a glutathione-S-transferase tagged receptor that exhibits a conformational change when bound to an agonist. Binding will be measured using a plate-reader with fluorescence detector.

Metabolic disruption. Metabolic disruption includes interactions with lipid and triglycerides synthesis, termed obesogens. At the cellular level, the peroxisome proliferator activated receptor, or PPAR, forms a dimer with the retinoid-X receptor (RXR). Two active sites on this complex allow for binding of two chemicals, which then becomes a transcription factor for various metabolic processes by binding to response elements (PPREs) on DNA. Here, the peroxisome proliferator activated receptor binding assay will be used to measure environmental obesogens. Competitive-binding assays supplied by Invitrogen will be used to measure metabolic agonists, and samples will be analyzed according to the manufacturer's specifications.

Task 3 – Test Chevron diesel and diesel components for endocrine disruption

The site described was contaminated in March of 2013. Contaminated sediment has since been dredged to eliminate further source release, and water has been naturally flushed with fresh water from upstream sources. Because of this, site samples may not reveal the endocrine disrupting potential that existed in March 2013. To address this issue, lab-fortified diesel contaminated samples, and will test individual diesel components on endocrine disrupting bioassays.

Lab fortified sample. The research team will obtain a sample of Chevron diesel, which will be serially diluted in ultrapure water and tested on individual bioassays described in Task 2.

Individual diesel components. UDEQ has provided chemical and health data on the following chemicals found in diesel: benzene, naphthalene, xylenes, toluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-methylnaphthalene, ethylbenzene, isopropylbenzene. The solvents will be diluted to below toxic levels and tested on the bioassays.

9. Describe your experience in implementing projects of similar scope and magnitude

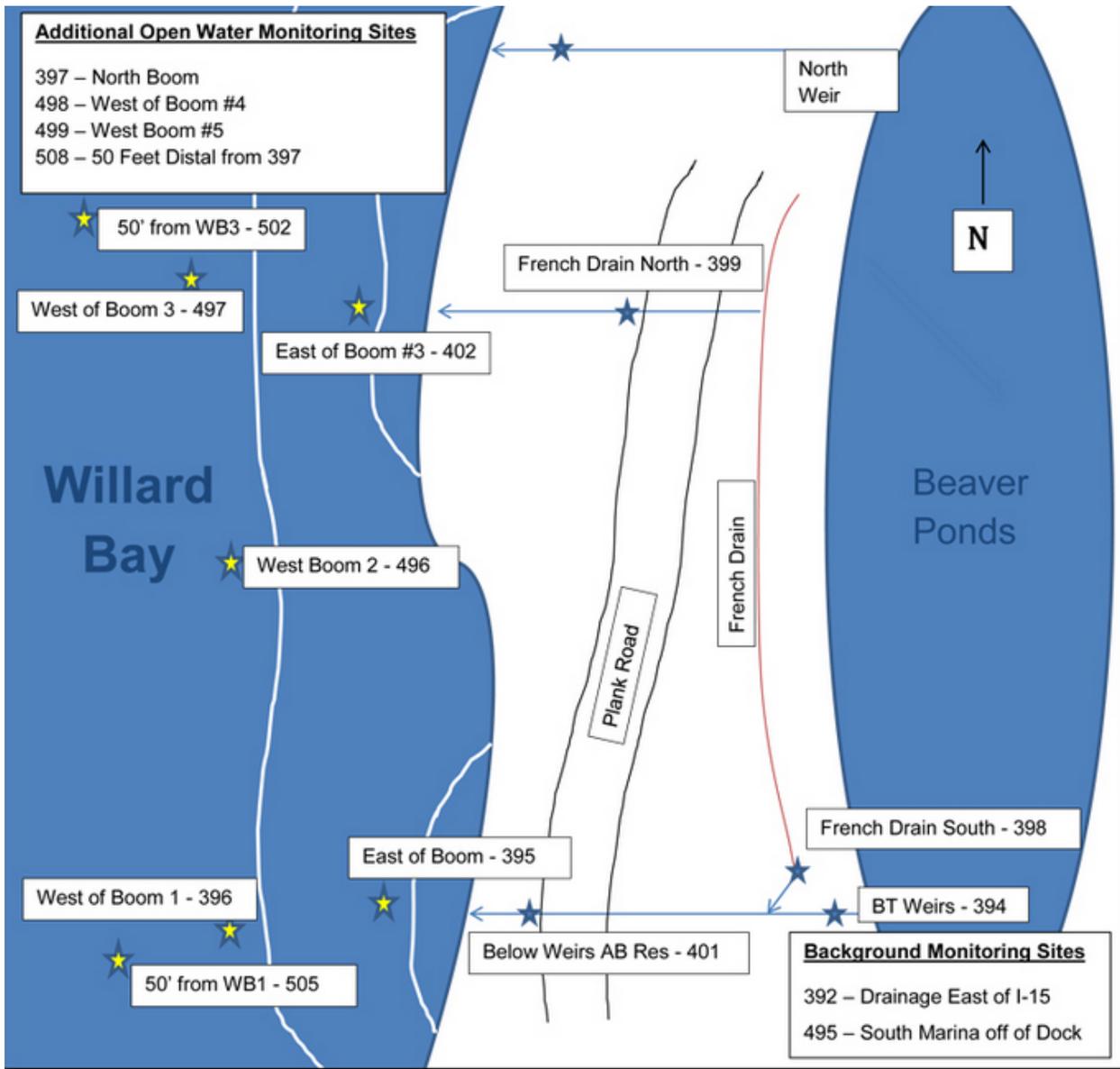
Dr. Conroy-Ben is well qualified to carry out the research outlined in this proposal. As a graduate student at the University of Arizona, she quantified estrogenic activity during wastewater treatment at local wastewater treatment facilities, in wastewater impacted surface water, and wells lying along surface water using the ER- β competition binding assay, the yeast estrogen screen, and the yeast androgen screen. She has continued this research as a faculty member in Civil and Environmental Engineering at the University of Utah. In education, Dr. Conroy-Ben has organized environmental hands-on seminars/activities regarding petroleum spills, and teaches a course in remediation of polluted water and sediments.

Dr. Andy Hong is a registered Professional Engineer and Professor of Civil Engineering at the University of Utah. He developed the method and holds the patent for organic extraction from sediments using pressure cycles.

10. Describe how ongoing maintenance of the project will be funded and carried out

This is a 3-year water quality monitoring project, so future research beyond the funding period will be reduced. At the request of UDEQ, the research team will work with the agency to facilitate additional testing.

Supplemental Information: Willard Bay Sampling Map



Courtesy: UDEQ



Rapid extraction of sediment contaminants by pressure cycles

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ABSTRACT

Sediment contamination is a significant issue. Assessment, management, and monitoring of contaminated sediment require routine analyses of a large volume of sediment samples, which require significant preparation time including extraction of contaminants from samples prior to analysis. This work tested a new method of extracting contaminants from sediment based on the use of rapid, successive pressurization cycles, which involve compression of a gas into the extractive solvent in contact with the sediment immediately followed by decompression via venting. The technique improved extraction amounts and shortened preparation time. Tested were PCB and PAH contaminated sediment samples from various locations of the US, including the Passaic River, St. Louis River, Waukegan Harbor, and Wells National Estuarine Research Reserve. The results were compared to those of Soxhlet extraction. Specifically, the extraction of 15 g of sediment with 50 mL of hexane–acetone (1:1) mixture at room temperature using 10 rapid, successive pressure cycles with N₂ attaining 1.0 MPa during compression was complete within 15 min. Using the new technique, consistently more PAHs and PCBs were extracted from the sediments in comparison to Soxhlet extraction. Extraction was evaluated according to key factors including the number of compression–decompression cycles, compression pressure, sample amount, moisture, and pressurizing gas type. The heightened extraction performance was explained by cyclic changes in gas solubility during repetitive compression and decompression steps, which introduce mechanisms to fragment sediment aggregates resulting in increased contaminant exposure and extraction.

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1. Introduction

Sediment contamination by persistent, bioaccumulative toxins including PCBs, PAHs, and other recalcitrant organics is a significant concern worldwide including the US (US EPA, 2004). At numerous locations of the US, coastal or inland sediment contamination has impacted marine life, disrupted ecological food chain, and resulted in fish advisories issued for human health protection. Chemical analysis of sediment is central in determining contamination level, the progress and outcome of remediation, as well as for post-remediation monitoring. These analyses require routine preparation of a large volume of sediment samples. Sample preparations are time-consuming, generally involving extraction of contaminants from the sediment matrix into an organic solvent phase, removal of interfering substances, and concentration of the extract before analysis by GCMS.

Soxhlet extraction (SE) (US EPA 3540C, 2008) has long been a standard method for extraction of contaminants from environmental matrices. While Soxhlet extraction requires a relatively large solvent volume and as long as 24 h to complete, it is widely used and remains a benchmark that other new extraction methods are

compared to. Viable alternatives include microwave-assisted extraction (MAE) (US EPA 3546, 2008), supercritical fluid extraction (SFE) (US EPA 3562, 2008), and pressurized liquid extraction (PLE) (US EPA 3545, 2008) have been developed that save time and reduce solvent use, which have since resulted in commercially available devices. However, these devices often operate at elevated temperature or pressure or both to extreme degrees. Extraction of PCBs and PAHs from sediment and soil by SFE using CO₂ (*T* of 40–200 °C; *P* of 15–66 MPa) has shown good recovery (Langenfeld et al., 1993; Librando et al., 2004). Examples of contaminant extraction by PLE with good recoveries abound, e.g., sterol with water/isopropanol (Burkhardt et al., 2005), PAHs with hexane at 150 °C and 10–15 MPa (Li et al., 2003), PAHs with hot water at >300 °C and 20 MPa (Kuosmanen et al., 2003; Kronholm et al., 2004), and PAHs with dichloromethane (ultrasound-assisted PLE) at 300 °C and 12 MPa (Richter et al., 2006). Extraction of PAHs from soil and sediment with excellent recovery was shown feasible with MAE using widely varied solvent types and compositions including 30% of water (Pastor et al., 1997; Budzinski et al., 1999; Shu et al., 2003).

This work presents a new pressure cycles-assisted extraction method (PCAE) utilizing successive compression–decompression cycles with gas for extraction of contaminants from sediment, as a means to economize sample preparations while improving

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effectiveness under mild conditions. The role of rapid, successive pressure cycles in altering soil aggregates and its application in conjunction with ozonation for effective remediation of contaminated sediment have been reported (Hong, 2007; Hong et al., 2008a,b). In the present application, PCAE has at least one or more advantages over existing methods in key factors such as reduced processing time and solvent, higher recovery, and mild pressure conditions at room temperature. Extraction results of PCBs and PAHs obtained by PCAE are compared to those by SE for sediment samples from contaminated sites including the Waukegan Harbor, Passaic River, St. Louis River, and Wells National Estuarine Research Reserves. These process parameters are studied for their influence on extraction performance. The optimized results may form the basis of a new method and equipment design that exploits the unique technique of pressure cycles for extraction.

2. Experimental

Naphthalene, anthracene, pyrene, benzo[a]pyrene (all PAHs from Sigma–Aldrich), and Aroclor 1242 (neat, Supelco) were dissolved in hexane (HPLC grade) for GC/MS calibrations. Sediment samples from the Passaic River, Waukegan Harbor, St. Louis River, and Wells NERR were obtained. Organic contents of 11%, 19%, and 29% were found in the Passaic River, Waukegan Harbor, and St. Louis River sediments, respectively (per ASTM, 1988). Sieve and hydrometer analyses (per ASTM, 1990) were used to determine particle size distributions. Coarse-medium, fine, and silt/clay portions were 47%, 31%, and 22%, respectively, for the Passaic River sediment; 9%, 51%, and 40%, respectively, for the Waukegan Harbor sediment; and 65%, 24%, and 11%, respectively, for the St. Louis River sediment.

The extraction vessel was built of stainless steel tubing (316 SS grade; length of 26 cm; OD of 2.5 cm; wall thickness of 0.25 cm) to withstand the pressure used in this study, which ranged from 340 kPa (50 psi) to 1.4 MPa (200 psi). As shown in Fig. 1, the reactor was connected at the top and bottom to smaller tubing of 0.64 cm OD via a 2.5–0.64 cm NPT reducer. The T-joint at the bottom of the extraction vessel was connected to two 0.64 cm stainless steel ball valves (316 SS grade). One of the ball valves was connected to the compressed gas tank and acted as an inlet for nitrogen or air. The other ball valve could be connected to a second extraction vessel or more for concurrent extraction if desired (only single vessel was used for this study). The vessel top was connected to a pressure gauge and further connected to a 0.64 cm ball

valve, which allows venting and decompression of the vessel. An aluminum mesh with 1.7 mm openings between two metal washers was placed at the bottom of the reactor to support the sediment solids. The pressure gauge mounted at the top of the vessel confirmed the pressure of extraction that was regulated by the pressure regulator of the compressed gas tank. The vessel had a volume of 80 mL when empty. Nitrogen or air from compressed gas cylinders was used to pressurize the extraction vessel.

Extraction of the sediment was performed by contacting the sediment with the extraction solvent consisting of 1:1 (v/v) hexane and acetone mixture (HPLC grades). For a typical extraction run, a wet sediment sample was weighted, drained of free liquid to obtain a moisture content of 35–40%; the sediment (e.g., 15 g, dry basis) was added into the extraction vessel, and then 50 mL of the extraction solvent was added. Another small sample of the wet but free of excess water was taken and dried to ascertain the moisture content so that contaminant concentrations could be calculated on a dry basis. When dry sediment was called for, the sediment was dried by laying evenly on a Petri dish and placed in the hood to air-dry for 24 h. To start an extraction run, N₂ gas was introduced into the bottom of the vessel at 1.8 L min⁻¹ driven by the compressed gas cylinders at the pressure regulated at the desired pressure. The time to reach the target pressure varied depending on the target pressure and the remaining headspace in the vessel, which took 3, 8, 14, and 20 s to reach 0.34, 0.69, 1.0, and 1.4 MPa, respectively (i.e., 50, 100, 150, and 200 psi, respectively). Once the pressure was reached, the inlet valve was closed and the vessel was shaken manually for about 1 min. Afterward, the valve at the top of the reactor was open to release the pressure, completing one cycle of extraction. Thus, an extractive pressure cycle consists of the compression of N₂ gas (or air where specified) into the extraction vessel to a target pressure, agitation of the extraction vessel by shaking at the attained pressure, and then followed by rapid decompression via venting (seconds) of the overhead gas. The number of extraction cycles employed in this study was 1–10, typically completed within 15 min for 10 cycles or shorter time for fewer cycles.

Following extraction, the solution was collected from the bottom of the vessel and vacuum-filtered to remove any remaining sediment solids. The extract was then passed through the florilid cleanup column (Alltech, Part #204650) to remove nitrogen compounds, oils, fats and waxes (US EPA 3620C, 2008) that could hinder analysis. The lower water layer was discarded and the organic extract was concentrated and further removed of sulfur compounds (US EPA 3660B, 2008). In this procedure, 1 mL of extract was transferred to a 50 mL clear glass bottle and 1 mL of tetrabutylammonium sulfite reagent (Sigma Chemical Co.) along with 2 mL of 2-propanol were added to the extract. The bottle was capped and shaken for at least 1 min, and then added with 5 mL of deionized water. The mixture was again agitated for 1 min and then allowed to stand for 5–10 min. The top organic layer was transferred to a concentrator tube and the extract was concentrated to 1 mL by a gentle nitrogen stream before quantification. The new extraction method being reported was compared with the Soxhlet extraction method (US EPA 3540C, 2008). SE was conducted in parallel and extract (200 mL on 20 g sediment) was concentrated by a rotary evaporator (Büchi Rotavapor R-124 and Büchi Waterbath B-481, Büchi). The concentrated extract was then subject to the same cleanup, sulfur removal, and concentration procedures as described above prior to analysis. The purified extracts were analyzed using a gas chromatograph (GC 6890N, Agilent Technologies) with a mass selective detector (MSD 5973N, Agilent Technologies) controlled by the MSD Productivity ChemStation software (Agilent Technologies). A capillary column (HP-5ms, non-polar column, 30 m × 0.25 mm × 0.25 μm, Agilent Technologies) was used. One μL of sample was injected in a splitless mode

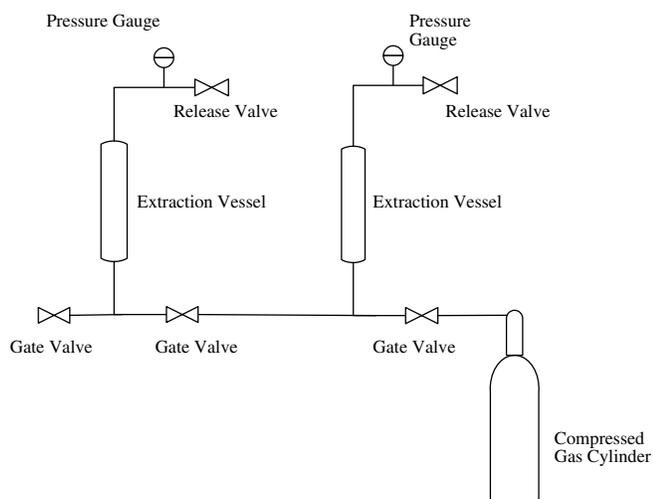


Fig. 1. Extraction vessels and setup.

at 250 °C and a full scan range from 50 to 550 m/z was used. The oven temperature was raised from 50 °C (initially held for 1 min) to 100 °C at 25 °C min⁻¹, and from 100 °C to 300 °C at 5 °C min⁻¹. The oven temperature was then held for 5 min at 300 °C. Helium was used as the carrier gas at 35 cm s⁻¹. The calibration, identification, and quantification of PAHs and PCBs were as previously described (Hong et al., 2008b).

Experiments were conducted in duplicates with ranges shown; results without errors shown were not replicated. Due to the heterogeneity of the sediment, contaminant concentrations varied significantly in grabbed batches and, therefore, they were determined individually with each series of extraction experiments.

3. Results and discussion

The extraction of organic contaminants such as PAHs and PCBs from sediment was examined under different conditions. Parameters thought to be potentially relevant in affecting the extraction

amounts are the number of extraction cycles, pressure, solid contents, moisture content, and the type of gas used for pressurization. These extraction parameters were varied for Passaic River sediment, and workable conditions were identified and further tested for extraction of other sediments including the Waukegan Harbour, Wells NERR, and St. Louis River. The results are compared to those of SE and presented below.

3.1. Effect of number of pressure cycles on extraction

Fig. 2a shows the extracted total PAHs from Passaic River sediment according to the number of pressure cycles throughout extraction. Fig. 2a shows gradual increases in extracted total PAHs with increasing pressure cycles. With 10 pressure cycles, the extraction is complete and the extracted amount is at its maximum, which is consistently about 30 mg kg⁻¹ (with up to 20 cycles) in comparison to about 25 mg kg⁻¹ found by SE (with 24 h) for the same sediment sample.

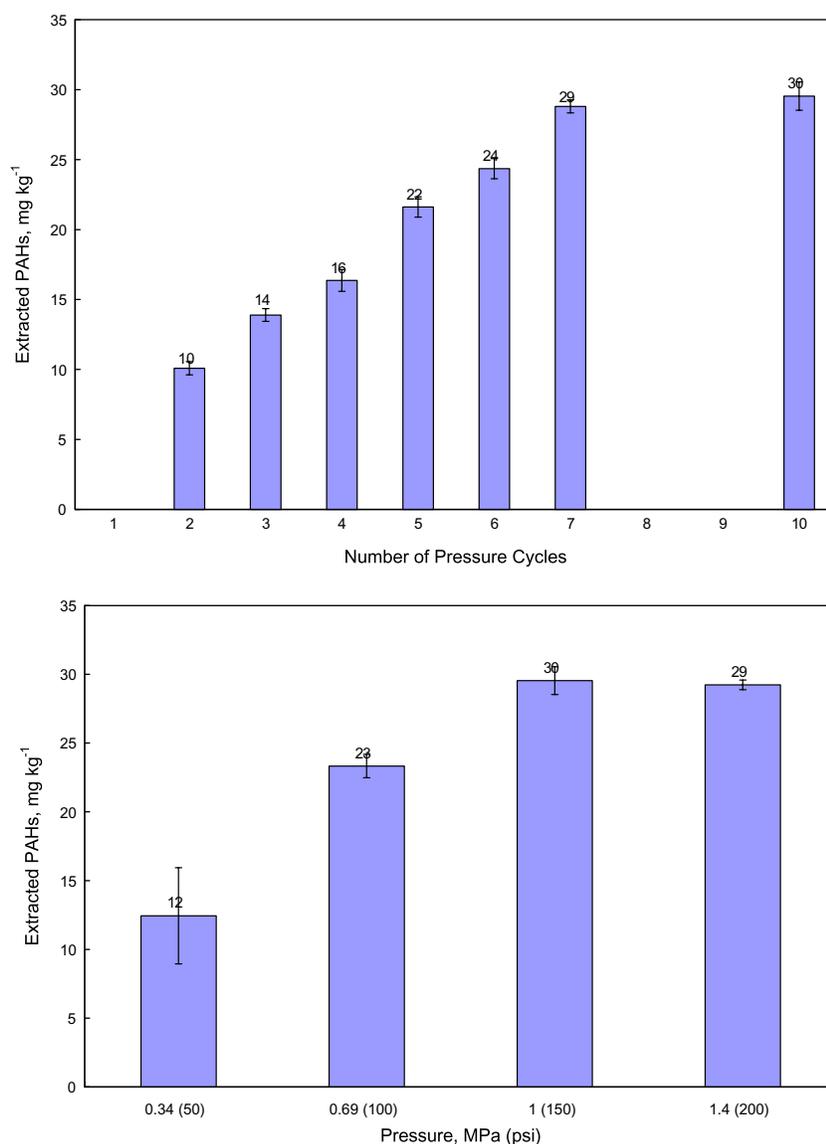


Fig. 2. (a) Upper: extraction of PAHs from the Passaic River sediment according to varying number of compression–decompression cycles used. Conditions: sediment, 15 g (dry basis); sediment moisture, 35%; compression pressure, 1.0 MPa; gas, N₂; flowrate, 1.8 L min⁻¹ (bars indicate measured duplicate results). (b) Lower: extraction of PAHs from the Passaic River sediment according to pressure used during the compression stage. Conditions: sediment, 15 g (dry basis); sediment moisture, 35%; no. of cycles, 10; gas, N₂; flowrate, 1.8 L min⁻¹.

3.2. Effect of compression pressure on extraction

Fig. 2b shows the extracted total PAHs according to the maximum pressure attained at the compression stage, which was varied from 0.34 to 1.4 MPa (50–200 psi). As shown, the extraction level increases with increasing compression pressure 0.34–1.0 MPa, and the extracted amount appears to have peaked out and the extraction is complete at 1.0 MPa (i.e., higher pressure at 1.4 MPa did not increase the yield).

3.3. Effect of sample size on extraction

The effect of varied sediment loadings in the extraction vessel was tested while holding the extraction solvent volume constant at 50 mL. The results indicate very close contaminant contents in the sediment, i.e., 26.0 ± 1.9 , 26.2 ± 1.2 , and 26.0 ± 0.6 mg kg⁻¹ for 5, 10, and 15 g of loaded sediment, respectively, indicating little dependence of extracted amount on the sample sizes tested. In this series, dry sediment batches were used that were obtained by air-drying in the hood for 24 h prior to extraction. The dried sediment appears to have resulted in reduced extraction when compared to those without prior drying, which will be examined below.

3.4. Effect of sediment moisture content on extraction

Extraction by PCAE was carried out for sediment samples containing different moisture contents at 0%, 26%, 35%, and 45%. The sediment was obtained and stored at about 35% moisture level and was used throughout the study. To examine the effect of moisture content, the sediment was first added with water and then drained to remove the excess free water to result in 45% moisture; the sediment was then air-dried to various moisture degrees (35% and 26%) and then to complete dryness (0%). The results indicate similar extracted PAH amounts of 28.7 ± 0.4 , 29.0 ± 0.6 , and 29.5 ± 1.0 mg kg⁻¹ for moisture levels at 26%, 35% and 45%, respectively, but a slightly lower value of 26.0 ± 1.6 mg kg⁻¹ at complete dryness (0%). The extracted amount, however, is yet slightly higher

than obtainable by SE (24.5 ± 2.0 mg kg⁻¹). This is a significant point of convenience when a sediment sample to be analyzed can be extracted without the drying step.

The presence of water in extractive solvent (e.g., 30%) can influence extraction, and it exerts a positive effect on recovery as studies of MAE have shown (Budzinski et al., 1999; Letellier and Budzinski, 1999; Shu and Lai, 2001). In the present case, it is likely that changes in accessibility to contaminants occur during drying, which may have resulted from dried pockets being formed within the sediment aggregates during drying; this limits solvent contact and reach into the sediment's interior space. It is also conceivable that during drying, inorganic minerals may have been formed and deposited on the organic matter that contained the contaminants, shielding the contaminants from access by the extractive solvent.

3.5. Effect of compression gas type on extraction

In all experiments, the pressurization of the extraction vessel during compression stage was driven by N₂ gas from the compressed gas cylinder. To delineate influence by gas type (e.g., the presence and effect of O₂) and feasibility of using ordinary air, a compressed air cylinder was used to achieve pressurization (conditions: 15 g, dry basis, sediment with 35% moisture; 10 cycles at 0.69 MPa driven by 1.8 L min⁻¹ of air and N₂, respectively). The results show 23.3 ± 0.8 and 23.1 ± 0.6 mg kg⁻¹ of extracted PAHs using N₂ and air, respectively, indicating no significant effects due to the substitution of N₂ by air for compression. It should be noted that these extractions were performed at 0.69 MPa, which resulted in less than complete extraction (23 mg kg⁻¹ at 0.69 MPa as compared to 30 mg kg⁻¹ at 1.0 MPa or higher; see Fig. 2b).

3.6. Comparison of Soxhlet extraction with PCAE on various sediments

Fig. 3 provides a visual comparison of chromatograms obtained for the same batch of the Waukegan Harbor sediment by PCAE and SE, respectively. As shown, PCAE extracted more organics from the

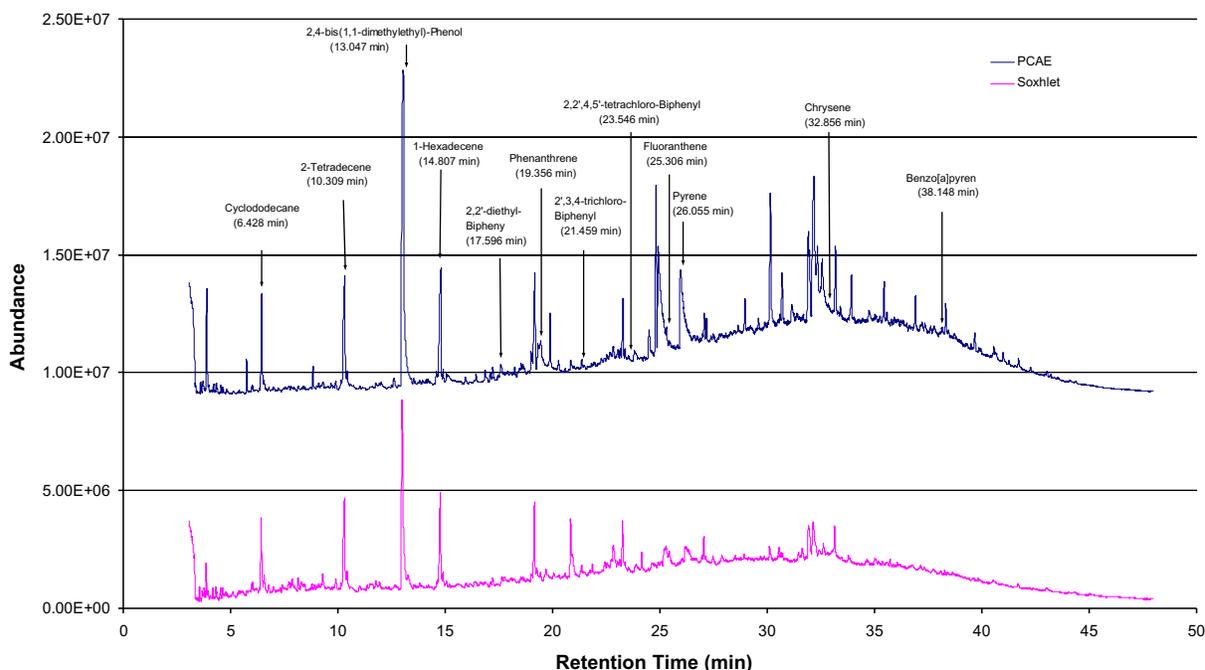


Fig. 3. Chromatograms of sample extracts of Waukegan Harbor sediment obtained by SE (lower line) and PCAE (upper line; baseline shifted for clarity). Conditions: 15 g with 140 mL solvent by SE over 24 h; 15 g with 50 mL by PCAE using 10 cycles at 1.0 MPa in 15 min.

Table 1

Comparison of Soxhlet extraction with PCAE for extracted contaminants from various sediments (duplicates and ranges shown) (PCAE conditions: 10 cycles at 1.0 MPa completed in 10 min).

Sediment contaminant	Soxhlet	PCAE
	(mg kg ⁻¹)	(mg kg ⁻¹)
<i>Passaic River</i>		
PAHs of 2 rings	5.7 ± 1.2	5.3 ± 0.8
PAHs of 3 rings	9.6 ± 1.0	9.7 ± 1.4
PAHs of 4 rings	9.4 ± 2.0	13 ± 1.6
PAHs of 5 rings	<0.5	2.6 ± 0.4
Total	25 ± 2.3	30 ± 1.0
<i>Waukegan Harbor</i>		
PAHs of 2 rings	5.8 ± 0.8	5.6 ± 1.0
PAHs of 3 rings	4.6 ± 0.5	6.0 ± 0.9
PAHs of 4 rings	3.2 ± 0.9	4.6 ± 1.2
Total	14 ± 2.3	16 ± 0.7
Trichlorobiphenyls	2.6 ± 0.7	3.2 ± 0.7
Tetrachlorobiphenyls	1.9 ± 0.3	1.6 ± 0.6
Total	4.5 ± 0.3	4.8 ± 1.3
<i>St. Louis River</i>		
PAH of 2 rings	150 ± 3.8	270 ± 5.2
PAH of 3 rings	170 ± 8.8	460 ± 4.1
PAH of 4 rings	54 ± 2.5	93 ± 6.8
PAH of 5 rings	5.2 ± 1.9	48 ± 3.5
PAH of 6 rings	< 0.5	14 ± 2.2
Total	380 ± 8.4	880 ± 16
<i>Wells NERR</i>		
Total	3.6 ± 0.8	3.9 ± 1.0
Natural matrix certified reference material ^a	46.7 ^b	49.0 ± 6.6

^a PAH Contaminated Soil/Sediment CRM104-100/Lot: 002500 (Sediment of Chesapeake Bay area, US); obtained from R.T. Corporation, Laramie, WY.

^b Total of Certified PAHs by SE method.

same amount of soil with a smaller solvent volume. Further, Table 1 compares extraction results for different sediment samples using SE and PCAE, respectively. PAHs of a specific ring number would include those without and with substituted groups such as methyl and dimethyl groups; PAHs were identified individually and summed to yield total PAHs, as previously described (Hong et al.,

2008b). In Waukegan Harbor sediment, trichlorobiphenyls and tetrachlorobiphenyls were found and likewise summed to yield total PCBs. As shown, PCAE consistently achieves higher extraction of PAH, specifically 22%, 19%, 130%, and 8% higher than SE for Passaic River, Waukegan Harbor, St. Louis River, and Wells NERR sediments, respectively. For Waukegan Harbor sediment, PCB extraction with PCAE was also 7% higher than with SE. The difference in extracted amounts, i.e., 380 mg kg⁻¹ by SE over 24 h vs. 880 mg kg⁻¹ by PCAE in 10 min, is salient in the case of the highly loaded St. Louis River sediment. At the end of 24 h of SE, pale yellow extract was observed to still ooze out of the thimble, indicating incomplete extraction even after 24 h. Extraction by PCAE of a certified reference material was performed that showed 49.0 ± 6.6 mg kg⁻¹ of total PAHs in comparison to the certified value of 46.7 mg kg⁻¹ (Table 1).

3.7. Mechanisms contributing to rapid extraction

We attribute the rapid extraction of contaminants from sediment to increased exposure of the contaminants, which is made possible by fracturing of the soil particles (or aggregates) during successive cycles of compression and decompression with a soluble gas. Fig. 4 illustrates the operation principle. As described, the pore space of the soil aggregates is initially filled or partially filled with natural water; increasing pore liquid replacement by air occurs during successive pressure cycles that results in an increasingly “hollow” soil aggregate. This hollow soil aggregate has to resist great pressure exerted on it as long as the water or extraction solvent cannot be transported through the pore space fast enough to equilibrate against the pressure differential during rapid compression or decompression. When the pressure tolerance of the wall is exceeded, breakage of the soil aggregate occurs by implosion or explosion, leading to increased exposure of the contaminants to extractive solvent in the bulk liquid phase. Thus, the mechanisms at work for increased exposure may be flushing, implosion, and explosion caused by repeated pressure cycles.

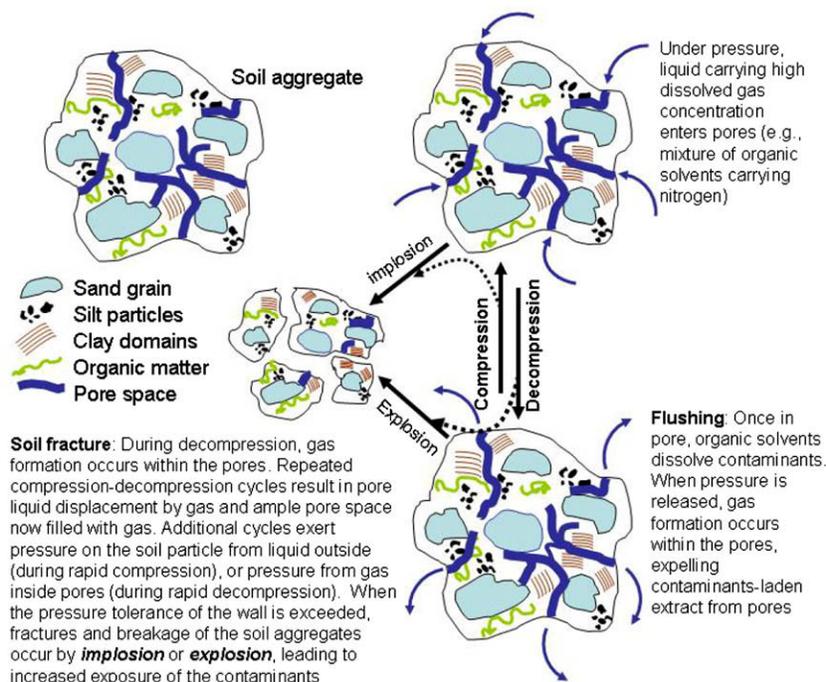


Fig. 4. Mechanisms contributing to increased exposure and extraction of contaminants.

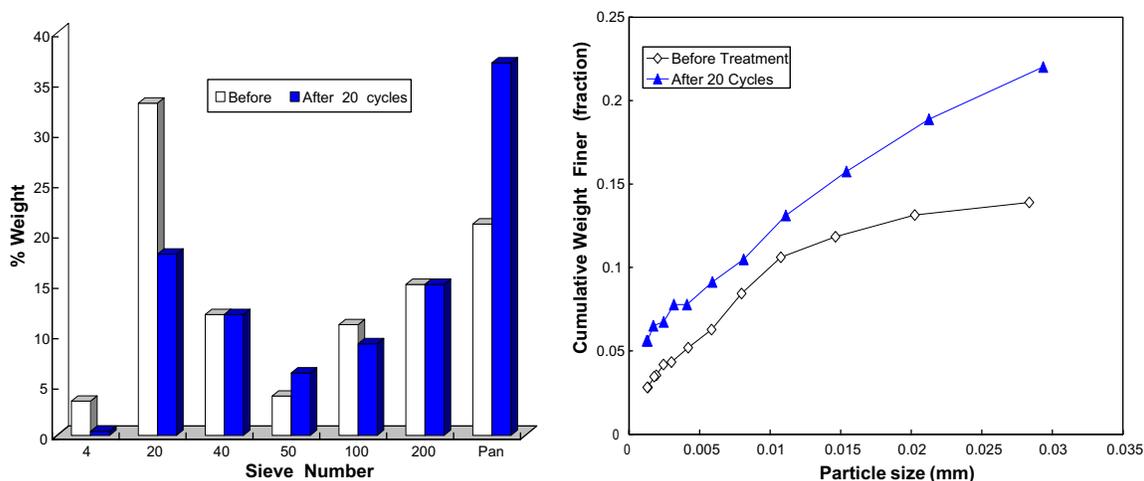


Fig. 5. Particle size distributions of Passaic River sediment before treatment and after pressure cycles ($P = 0.69$ MPa; 20 cycles). (Left: sieve results for particle sizes larger than sieve no. 200. Right: hydrometer results for particle sizes smaller than sieve no. 200.)

3.8. Particle size distribution changes after pressure cycles

Our thesis that soil aggregates are fragmented under rapid, successive compression and decompression cycles is further tested. Soil particle size distributions were measured prior to pressure cycles and after subjecting the soil slurry (soil in water at 100 g L^{-1} water) to 20 pressure cycles reaching 0.69 MPa. Fig. 5 (left) shows various size fractions of the Passaic River sediment particles as collected by sieves for soil batches before and after 20 pressure cycles, respectively. The soil batches after pressure cycles were dried at 105°C for 24 h prior to sieve analysis. As shown, the batch prior to treatment has the most soil particles in the larger sizes as collected by sieves numbers 4 and 20 accounting for nearly half of the soil mass, and it has much less soil particles collected in the bottom pan. The soil batch after pressure cycles has significantly more particles in the bottom pan (38%), much higher than without pressure cycles (22%). The decrease in particle sizes suggests significant breakage of the soil aggregates into the smaller ones (<0.07 mm) by the pressure cycles. It is likely that the coarse-medium fraction of the sediment was of aggregates of clay-sized particles rather than typical quartz sand particles; the aggregates were disrupted by pressure cycles into constituent fine-grained particles. It should be noted these results were obtained with pressure cycles for soil slurry in water; likewise, finer soil particles were observed with pressure cycles for slurry in organic solvent.

Fig. 5 (right) illustrates particle size changes of the soil batch (100 g total) in the finer range by hydrometer results obtained before and after 20 pressure cycles, respectively. The results show increases in the fine fraction of the soil particles (e.g., <0.03 mm) by over 50% after 20 cycles at 0.69 MPa. Thus, Fig. 5 suggests that the decrease in soil particle sizes results from fragmentation of soil aggregates when subject to rapid pressure cycles, which leads to increased contaminant exposure and extraction.

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