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**A Report to BSEE: The Effect of Ohmsett Water Composition on the
Outcome of Dispersant Effectiveness Testing**

Michel Boufadel and Zhong Pan
Center for Natural Resources Development and Protection
New Jersey Institute of Technology
boufadel@gmail.com; <http://nrdp.njit.edu>

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Executive Summary

The study had two main goals: Goal 1- Evaluate the removal efficiency of the cellulose/diatomaceous earth (CDiA) filter and the powder activated carbon (PAC) chambers placed occasionally into the tank, and Goal 2- Evaluate the impact of the Ohmsett water on the dispersion effectiveness, and compare the DE in the Ohmsett tank to that of the baffled flask test (BFT) using the same Ohmsett water, oil, and dispersant at the same temperature. The oil used in the Ohmsett tank was HOOPS, and BSEE requested similar BFT using Alaskan North Slope (ANS) oil, which is widely used for testing. Additional BFTs were conducted using synthetic water and both HOOPS and ANS.

For Goal 1: It was found that the CDiE filter was effective in removing benzene, but not the remaining BTEX compounds. The results suggest that the PAC actually leached ethylbenzene and xylene back into the water on the third and fourth day of sampling. It was also found that the CDiE filter removes the total organic carbon. In addition, the increase in the surface tension of water-air as the water passes through the CDiE filter, suggests that the CDiE filter removes surfactants from the Ohmsett water. The PAC was not shown effective in removing the TOC nor surfactants.

The results from the BFT indicated that, in Ohmsett water, Corexit 9500 provided the highest dispersion effectiveness (DE) for Hoover Offshore Oil Pipeline System (HOOPS) crude oil at around 89%, followed by Accell Clean DWD at about 78%. The remaining three dispersants (Finasol OSR 52, Marine D-Blue, and ZI-400) provided a DE between 45% and 53%.

The DE of Alaska North Slope (ANS) oil in Ohmsett water was largest for Accell Clean at 91%, followed by Corexit 9500 at around 70%. Finasol and Marine D-Blue provided a DE around 50%, while ZI-400 had a DE around 40%.

The DE of HOOPS was lower when using synthetic seawater in comparison to Ohmsett water; the decrease in DE was 6% (i.e., 6 points on the 100 point scale) for Finasol, 12% for Corexit, and around 20% for Accell, Marine D-Blue, and ZI-400. However, the DE with ANS of most dispersants in synthetic seawater was similar the DE in Ohmsett water, with the exception of Marine D-Blue with ANS whose DE dropped from 50% in Ohmsett water to 30% in synthetic seawater.

This drop in DE going from Ohmsett water to synthetic seawater (for HOOPS mostly and for ANS with Marine D-Blue) is attributed herein to the small hardness of Ohmsett water whose hardness, expressed as mg/L of CaCO_3 was around 4,700 while that of seawater is 6,500 mg/L. Thus, calcium and magnesium salts might need to be added to the Ohmsett tank. It is possible, though, not probable, that the presence of trace surfactants in the Ohmsett water increased the DE. However, the increase of surface tension due to the CDiE filter was only by a few percents, which is not large enough to affect the DE.

The DE of HOOPS in the BFT was smaller than that of ANS. There was no direct correlation between the DE and measurements of either of the density or the viscosity of the oils. In fact, the viscosity of HOOPS is 12 cp in comparison to 18 cp for ANS (at 15°C), and thus one expects the DE of HOOPS to be larger. In terms of the SARA (saturates, aromatics, resins, and

asphaltenes) compositions of the oils, revealed that the main difference between the two oils is the asphaltene content; HOOPS contains 2% while ANS contains 7%. Noting that asphaltenes behave as slow surfactants, it is possible that their presence increased the DE of ANS in comparison to that of HOOPS.

A linear correlation between the DE (in percentage) of the oil HOOPS in the BFT and the DE of HOOPS in the Ohmsett tank revealed the relation:

$$\text{DE (BFT, Ohmsett water)} = 0.54 * \text{DE(Ohmsett tank)} + 16$$

As the slope is approximately 0.5 (i.e., less than 1.0), the DE in the BFT is smaller than that in the Ohmsett tank, which is probably due to dilution in the Ohmsett tank. However, the coefficient of determination, R^2 , was small, suggesting that more data are needed.

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1.0 PROBLEM STATEMENT

The Ohmsett tank is 203 m long, 2.4 m deep, and 20 m wide, giving a water volume of approximately 10,000 m³. The tank is equipped with a flap-type wave generator hinged at the bottom of the tank, which can be programmed to produce various types of waves (regular and irregular sea states). At the opposite end, a wave-damping artificial beach is placed to reduce reflection from the incoming waves. The tank is also equipped with two movable bridges (i.e., main towing bridge and auxiliary bridge) that span the width of the tank for mounting instruments (e.g., altimeter and high resolution camera). To inhibit biological growth, an electro-catalytic process is used to oxidize chloride ion to hypochlorite. In the standard operation, at 30 ‰ salinity, with a through reactor flow rate of approximately 80 liter per minute at 20°C, the optimal production of equivalent chlorine is approximately 0.75 kg per minute. More chlorine (and thus salt) can be added to the water if algal blooms are visually observed in the tank, which occurs usually in the summer.

A major operation in the Ohmsett tank is testing the dispersion effectiveness (DE) of dispersants on oils under select wave conditions. In each of these tests, around 80 liters of oil is applied onto the water surface along with approximately 8 liters of dispersants. There were concerns that the chemical composition of the Ohmsett water would alter the DE greatly from the DE that would be observed at sea. Studies (Krumrine et al., 1982 (Fainerman et al. 2012), (Park et al. 2016)) have noted that the anionic surfactants present in dispersants could be precipitated out of solution by hard water ions (e.g. calcium and magnesium). In essence, water hardness salts (CaCl₂ and MgCl₂ in the concentration ratio of 2:1) interact with the anionic surfactant (e.g. sodium dodecyl sulfate, SDS), to form Ca(DS)₂ and Mg(DS)₂, reducing therefore, the interaction of the DSD with oil, and subsequently the DE. Sulfate is a constituent of surfactant (specifically sulfate-based surfactant, e.g. Sodium lauryl sulfate and sodium dodecyl sulfate), acting as the hydrophilic head group to interact with water-soluble molecules.

The DE test is a major source of addition of oil and surfactant to the Ohmsett tank, and it was thought that subsequent DE test could be affected. This is in spite of the filters used by the Ohmsett personnel (discussed below). Free phase oil present in the tank would scavenge the surfactants and subsequently reduce the DE of a subsequent test. Also, dissolved organic matter (DOM) in the water column is expected to interact with added oil and dispersants. However, how it affects the DE is not been well quantified. On the one hand, the DOM tends to reduce the oil-water interfacial tension (IFT) due to the affinity of the oil to organic matter. On the other hand, surfactant molecules are hydrophilic on one side and hydrophobic on another, and they could be disoriented by high DOM in the water, therefore reducing their effectiveness in occupying the oil-water interface. For these reasons, we elected to measure the total organic carbon (TOC) in the water, and the main dissolved components of oil, which are the BTEX (benzene, toluene, ethylbenzenes, and xylenes), whose solubility in water exceed 500 mg/L (Fetter 1999).

It is evident that the presence of surfactant in the Ohmsett water would increase the DE of a test. The goal was to evaluate by how much. It was planned initially to measure select surfactants in the Ohmsett water such as the DOSS (dioctyl sodium sulfosuccinate) using liquid chromatography coupled to mass spectrometry (LC-MS). However, it was noted numerous other

surfactants are present in the Ohmsett water, and their compositions are not known as they are proprietary. For this reason, it was decided that the best approach would be to use a surrogate measure of the surfactant concentration, which is the oil-water interfacial tension or the water-air surface tension.

BSEE requested a comparison between the DE from the Ohmsett tank to that in the EPA's baffled flask test (BFT) using the same Ohmsett water, oil, and dispersant at the same temperature. The comparison would allow scale-up of the BFT DE results (or scale down of the Ohmsett tank DE results) to that using synthetic seawater. Additional BFT were also requested using Alaskan North Slope (ANS) oil, which is widely used for testing, and using synthetic water to "bracket" the possible variability.

To remove oil from the Ohmsett tank after a DE test, the Ohmsett personnel use water jets to flush (herd) the oil on the surface to concentrate it where it gets skimmed. But oil and suspended matter remain in the water, and water quality in the Ohmsett tank is mainly controlled by the aid of cellulose/diatomaceous earth (CDiE) filter placed outside of the tank. The influent to the CDiE filter comes through a 12 inch pipe located at the north east corner of the Ohmsett tank at a depth of four feet. The filtered water is then returned to the tank at the southwest corner through a 12-inch outlet also at a fixed depth of four feet. The filter is designed to remove suspended matters and organic matter from the water including total petroleum hydrocarbons (TPH) and surfactants. The cellulose and diatomaceous earth (CDiE) are not placed into the filtration system at the same time or in the same manner. Typically the cellulose is added as body feed at about 70 kg of cellulose (3 bags) diluted in approximately 1900 liter (1.9 m^3) of water. The CDiE material is typically added at 140 kg (6 bags) mixed in 1700 liter (1.7 m^3) of water, and is accomplished in an external filter vessel piped into the tank. When the pressure builds up, the flow rate of the water passing through the CDiE filter drops. For the body feed refill (i.e., cellulose), when the flow rate drops to below $0.2 \text{ m}^3/\text{hour}$ (60 gal/hour), which is about 50% of the initial flow rate, the spent cellulose is removed and the refill of cellulose is initiated. For the diatomaceous earth (DiE), when the flow rate drops to ($0.11 \text{ m}^3/\text{hour}$), which is about 40% of the initial flow rate, the caked DiE is removed and fresh DiE is refilled into the system.

After 10 to 15 DE tests, the Ohmsett water becomes very turbid with oil and particulates, and the Ohmsett personnel conducts a major operation of placing porous chambers filled with powder activated carbon (PAC) into the tank (Figure 1), and circulates water through them. Powder activated carbon (PAC) chambers are typically arranged end to end to span the 20 m tank width (Figure 1 and Figure 2). They are over 2.4 m in height in order to span the water depth. The chambers are fitted with filter cloth, bubblers, valves, and a steel walkway on the top supported by chains on two sides. Booms (Figure 2) are used to keep the oil away from the PAC chambers in the Ohmsett tank to prevent the oil from clogging PAC. The PAC adsorption operation involves placing two barrels ($\sim 180 \text{ kg}$ each) of PAC into each chamber (Figure 1), maintaining a water/PAC suspension through the lifting and agitation of bubbling. The water flow through the chambers is provided by the south-to-north flux created by the pumping required for the CDiE filtration system.

The filters were not designed to remove the ions. But it was thought that some of the ions would bind to organic matter, and thus would be removed during filtration in the CDiE filters or the PAC chambers.

Therefore, the overall objective of this project was to provide insights into oil dispersion in the Ohmsett tank, with two main goals: 1) Evaluate the removal efficiency of the CDiE filters and PAC chambers, and 2) Evaluate the impact of the Ohmsett water on the dispersion effectiveness, and compare the DE in the Ohmsett tank to that of the baffled flask test.

2.0 APPROACH

Two major tank filtration operations occurred during the project period: In April 2015 and in October/November 2015. The powder activated carbon (PAC) (Figure 1) chambers were placed in the Ohmsett tank on April 3rd starting at noon, and removed from the Ohmsett tank on April 7th, 2015. They were then placed into the Ohmsett tank on November 2nd, 2015 and removed on November 5th, 2015. Water samples were taken from before and after the CDiE filters using a tap in the pipes on April 2nd through April 7th 2015 (April 4th and 5th were the weekend), and during October 22nd through November 5th 2015 (two weekends included). Samples from before and after the PAC were taken using a LIMNOS water sampler (Hydro-Bios, Germany) (Figure 3).

Dispersion effectiveness (DE) tests were conducted in the Ohmsett tank on October 14 through October 22, 2015 by the Bureau of Safety and Environmental Enforcement (BSEE) personnel (Mr. Timothy Steffek) using Hoover Offshore Oil Pipeline System (HOOPS) oil and five commercially available dispersants: Accel Clean DWD, Corexit 9500, Finasol OSR 52, Marine D-Blue Clean, and ZI-400. General information about these dispersants is reported in Table 1. Baffled flask tests (BFT) were conducted at NJIT using the same oil and dispersant in both Ohmsett water and synthetic seawater (Aquarium System of Mentor, Ohio, USA) kept at the temperature of the water samples for that prior to the corresponding Ohmsett DE test. Also, Alaskan North Slope (ANS) BFT experiments were conducted at NJIT under the same conditions of those with HOOPS.

The details of the measurement techniques are reported in Methods (Section 3.0).

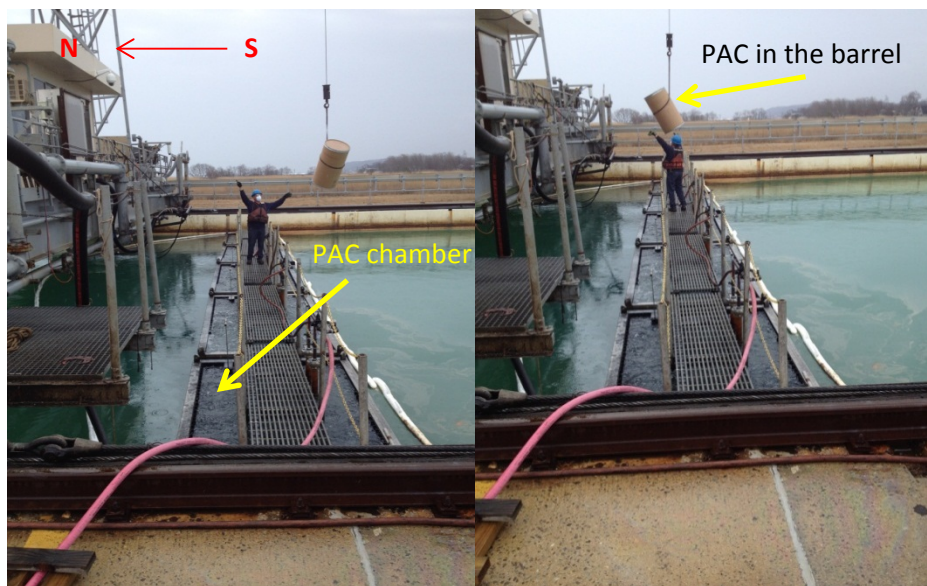


Figure 1. Placement of the PAC into the chambers. Two barrels each (180 kg) were placed in each chamber.

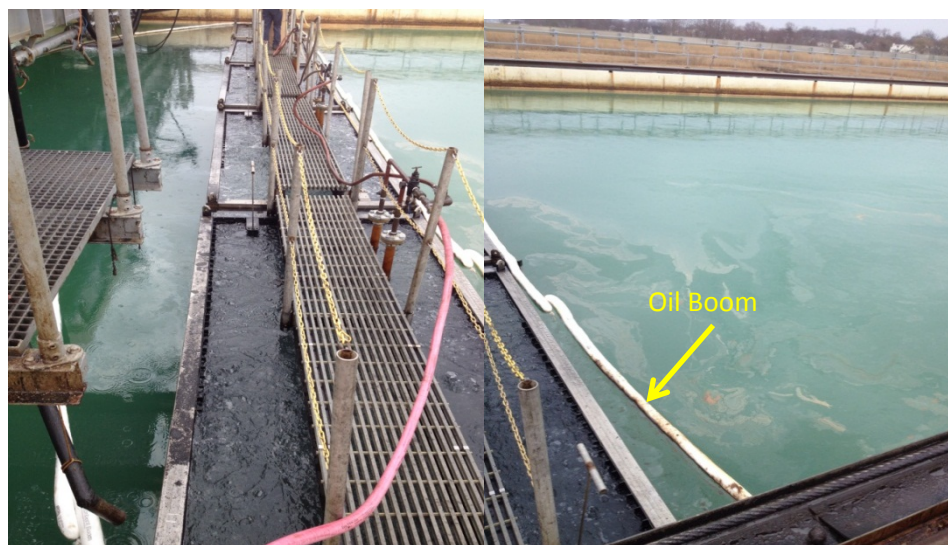


Figure 2. Oil booming to keep the surface oil away from the powder activated carbon (PAC) chambers.

Table 1: Information of dispersants tested in this work		
Dispersant	Manufacturer	Description
^a Accell Clean® DWD	Advanced BioCatalytics Corporation, CA, USA	1. Deep water dispersant. 2. Useful on oil spill in fresh or salt water. 3. Optimal DOR = 1:10.
^b Corexit® EC9500A	Nalco Env.Solution LLC, TX, USA	1. DOR of 1:50 to 1:10 is recommended. 2. For oil spills in saltwater
^c Finasol OSR 52	Total Fluides, France	1. DOR of 1:50 to 1:5 is recommended. 2. Diluted application in low salinity water is not recommended. 3. Designed to treat oil spills in saltwater.
^d Marine D-Blue Clean™	AGS Solutions, Inc., TX, USA	1. DOR of 1:20 is recommended. 2. At high concentration of crude oil spill or low temperature (<4.4 °C). Dispersant should be used without dilution. 3. Designed to treat oil spills in saltwater.
^e ZI-400	Z.I. Chemicals, CA, USA	1. For heavy oils, a dispersant to oil ratio (DOR) of 1:10 is recommended. 2. For lighter oils, DOR of 1:10 to 1:30 is recommended. 3. At warm water (>25.6 °C) and good agitation during application, less ZI-400 is suggested. 4. Application may be made at >1.7 °C, with optimum >8.9 °C.
Note: ^a From http://www.epa.gov/emergency-response/accell-cleanr-dwd and http://www.abiocat.com/petroleum-industry.php ; ^b From http://www.epa.gov/emergency-response/corexitr-ec9500a ; ^c From http://www.epa.gov/emergency-response/finasolr-osr-52 ; ^d From http://www.epa.gov/emergency-response/zi-400		



Figure 3. NJIT personnel performing water sampling from the Ohmsett tank using the LIMNOS.

Table 2: General information on the dispersion effectiveness tests conducted in October 2015 in the Ohmsett tank by BSEE (Mr. Timothy Steffek). The same water, oil, and dispersant were also used in the BF test at NJIT. Experiments were also conducted using synthetic seawater with the same oil and dispersants.			
Dispersant	Trial # 1	Trial # 2	Trial # 3
Accell Clean® DWD	10/14 at 14:17	10/22 at 10:40*	10/27 at 10:00**
Corexit® EC9500A	10/15 at 12:03	10/19 at 13:30	10/21 at 14:34
Finasol OSR 52	10/16 at 8:50	10/20 at 9:01	10/21 at 12:02
Marine D	10/15 at 9:15	10/16 at 11:51	10/20 at 13:32
ZI-400	10/15 at 14:20	10/20 at 11:13	10/22 at 13:13
*: BSEE ran out of dispersant in the Ohmsett tank experiment.			
**: Test conducted by BSEE after NJIT stopped taking samples.			

3.0 METHODS

For both Goal 1 (Filters) and Goal 2 (dispersion effectiveness, DE), a LIMNOS water sampler (Hydro-Bios, Germany) was used to collect water samples from the Ohmsett tank (Figure 3). Two certified-clean PYREX screw cap glass 250 ml jugs (Corning, NY) were attached to the sampler, and then the sampler was lowered in the water to a specific location using a rope attached to the device. When the sampler reached 1.2 m below the water surface, release a weighted messenger down the rope which triggers the bottles to open and start filling. In general,

it took around 30s to fill out the bottle. The jugs were preserved on ice in coolers and shipped to the laboratory at NJIT within 1 day of collection. At the laboratory, they were stored at 4 °C in the refrigerator prior to analysis and/or usage.

Water samples taken during April 2015 and October 22nd through November 5nd were analyzed for inorganic ions, BTEX (benzene, toluene, ethylbenzene, and xylene), and total organic carbon (TOC).

3.1 Measurement of Inorganic Ions (Goal 1)

Chloride and nitrate were analyzed using ion chromatography system (Dionex ICS-1500, Thermo Scientific, Somerset, NJ) consisting of a liquid eluent (10 mM KOH), a high-pressure pump, a sample injector, a guard and separator column, a chemical suppressor, a conductivity cell, and a data collection system. The ion chromatography system was coupled with a Dionex AS50 autosampler (Thermo Scientific, Somerset, NJ) for sample analysis. Before running samples, calibrations for chloride and nitrate were conducted using chloride and nitrate standard solution, respectively. The concentrations of chloride and nitrate were obtained from the calibration curves with the known standards.

Sulfate, SO_4^{2-} , was measured using the SulfaVer 4 method (EPA Method 8051). It relies on using a UV/Visible Spectrophotometer (Cole Parmer 4802 scanning double beam UV/Visible spectrophotometer, IL, USA) and test kits (HACH 2106769). All the water samples were diluted 1:10 with deionized water (DI) water, prior to analysis, as the instrument's range is from 2.0 mg/L to 70 mg/L.

Cations (sodium, calcium, magnesium, potassium, and zinc) were quantified using a flame atomic absorption spectrometer (Perkin Elmer Analyst 400, Waltham, MA). Appropriate hollow-cathode lamps for targeted metal elements were installed before analysis. Standard calibration curves for determining the targeted elements were conducted immediately before running samples.

3.2 Measurement of BTEX (Goal 1)

BTEX (benzene, toluene, ethylbenzene, o-, m-, and p- xylenes) was measured using the Purge and Trap (P&T) Gas Chromatography with Photon Ionization Detector (PID). BTEX standard stock solution were prepared based on Restek 502.2 Calibration Mix #4 (Cat #: 30045) and Mix #5 (Cat #: 30046). A series of BTEX standard working solutions (10, 25, 50, 100, and 200 ppb) were prepared by diluting the stock standards with DI water.

The chromatographic system consisted of a gas chromatograph (GC) (Varian 3400 GC, Varian, Walnut Creek, CA, USA) equipped with a PID (Model 4420, O-I Corporation). A Restek GC column (Crossbond 6% Cyanopropylphenyl-94% dimethylpolysiloxane) 105 m × 0.53 mm I.D. × 3.0 µm was used with helium as carrier gas. Injector and detection port temperatures were 150 °C and 200 °C, respectively, with splitless mode. The column oven temperature program involved an initial temperature of 35 °C for 10 min. The oven is heated at a rate of 7 °C/min to a final

temperature of 240 °C, which was held for 1.5 min. The helium flow was 1.5 mL/min. The column pressure is 20 psi at 22 °C. Under these conditions, the compounds eluted in less than 12 min and the total chromatographic run time was 35 min.

The purge and trap unit (Tekmar LSC 2000 and Tekmar ALS2016 Automatic Sample Heater) was used to extract BTEX from liquid matrix for introduction into a GC for separation and quantification. The purge and trap procedure was as follows. A 5-mL aliquot of each sample (BTEX standard solution or Ohmsett water samples) was poured into the purge vessel. BTEX was then extracted by purging helium through the aqueous solution and trapped. The BTEX is concentrated onto an adsorbent trap, and excess water is removed from trap. The adsorbent material was subsequently heated so that the desorbed analyst was directly transferred into the GC column and analyzed.

3.3 Measurement of Total Organic Carbon (Goal 1)

Total organic carbon content of the samples was measured using Shimadzu Total Organic Carbon Analyzer (TOC-L, Shimadzu, USA). The instrument utilizes a catalytic oxidation combustion technique at high temperature (680 °C), to convert organic carbon in the aqueous samples into CO₂. The CO₂ generated by oxidation is measured with a Non-dispersive Infra-Red (NDIR) sensor. Prior to TOC analysis, a volume of 30-40 mL water sample was filtered through a 0.45 µm syringe filter (Millipore) to remove suspended materials that might clog the sample flow line.

3.4 Baffled Flask Test (BFT), Goal 2.

The EPA official standard protocol baffled flask test (BFT), a modification of the swirling flask test (Venosa et al. 2002, Kaku et al. 2006, Venosa and Holder 2013, Zhao et al. 2015), was adopted to evaluate the oil dispersion effectiveness in the presence of different dispersants. The BFT relies on using a 200-mL screw-cap trypsinizing flask with four baffles equally distributed on the side to allow for better mixing. The baffled flask is equipped with a glass stopcock (Figure 4) near its bottom so that a subsurface water sample could be collected without disturbing the surface oil layer. The BFT protocol is as follows: A volume of 120 mL Ohmsett water (or synthetic seawater) are added to the baffled flask, followed by the addition of 100 µL of oil using a 250-µL SGE™ gastight glass syringe with a steel luer lock tip. The oil should be dispensed onto the center of the water surface gently. The exact mass of oil added is derived from the weight difference between the glass syringe with oil and that after dispensing the oil. Subsequently, 5 µL of the dispersant is added to the center of the oil slick in the baffled flask using a 1-10 µL Brinkmann Eppendorf repeater plus micropipette (Fisher Scientific, Pittsburgh, PA), giving the dispersant-to-oil volumetric ratio (DOR) of 1:20. The dispersant should be released as close as possible to the surface of the oil slick without actually touching it.

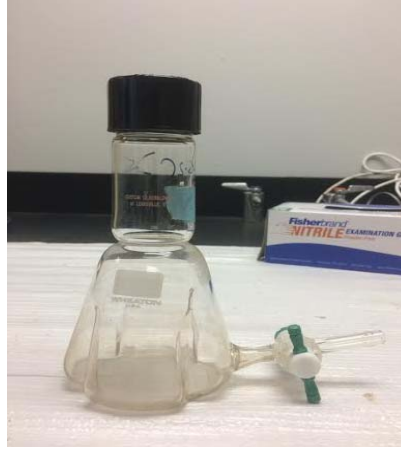


Figure 4: The EPA baffled flask. Bottom diameter is around 2.0 inches (5.0 cm).

Following the addition of oil and dispersants, the flask is placed on the orbital shaker (Lab-Line Instruments Inc., Melrose Park, IL), whose diameter is 2.0 cm. The rotation speed would be 200 rpm, to provide the mixing energy to the solutions in the test flasks, estimated to be approximately 1.0 watt/kg by the Boufadel group (Kaku et al. 2006, Zhao et al. 2015). At NJIT, the experiments were performed in the Thermo Scientific Precision™ refrigerated incubator at the desired temperature. After 10 min of mixing time, the flask is removed from the shaker and kept stationary on the bench top for 10 min. Subsequently, the first 5 mL of sample is drained from the stopcock and discarded (Sorial et al. 2004, Sorial et al. 2004). Then, 40 mL of sample is collected into a 50 mL graduated cylinder. A subsample of 30 mL is used for liquid-liquid extraction (EPA 1996) prior to oil concentration measurement. For each dispersion effectiveness test, triplicate experiments (three BFTs) were performed simultaneously.

The dispersion effectiveness (DE) is defined as the mass of dispersed oil in the water column, m_{disp} (g), divided by the total mass of oil added, m_{oil} . The DE in percentage is given as:

$$DE = \frac{m_{disp}}{m_{oil}} \times 100 \quad (1)$$

where, m_{oil} (g) is the mass of the specific test oil added to test flask.

3.5 Synthetic Seawater (Goal 2)

Synthetic seawater at the salinity of 34 ppt was also used in the BFT, and it was prepared by dissolving 34 g of the commercially available Instant Ocean sea salt (Aquarium System of Mentor, Ohio, USA) in 1 L of ultrapure deionized water (Millipore, 18.2 MΩ*cm). The mixture was vigorously agitated using a magnetic stirrer. The seawater was filtered through 0.2 μm membrane filters (Millipore) to remove any suspended materials that might interfere with oil droplet size measurements, and the solution was kept in the refrigerator at 15 ± 1 °C.

3.6 Measurement of Oil Chemical Properties (Goal 2)

At NJIT, the mass of dispersed oil in the BFT was obtained using gas chromatography with a flame ionization detector (GC-FID) as discussed next. The initial composition of the oil in terms of the major groups: saturates, aromatics, resins, and asphaltenes (SARA), was measured using thin layer chromatography (TLC), as discussed below.

3.6.1 Oil measurement using GC-FID

The extraction procedure included (1) decanting the 30 mL of water sample after BFTs to a 125-mL separatory funnel, (2) adding DCM and shaking vigorously for ~2 minutes, (3) allowing the DCM-oil and water phases to separate for ~5 minutes (the DCM is heavier than water and thus occupies the bottom of the separatory funnel), and (4) opening the stopcock and allowing the lower layer (DCM-oil phase) to drain into a clean glass beaker. Drain just to the point that the upper layer barely reaches the stopcock. The procedure should be repeated until complete separation (DCM layer turned colorless). Subsequently, the extract is then passed through medium of glass wool and anhydrous sodium sulfate to remove residual moisture, followed by adjusting the final extract to 16 mL using DCM. For this project, the samples were stored in 16-mL crimp style glass vials with aluminum/Teflon seals and mixed by inverting many times and then stored in a refrigerator at 4 °C until the time of analysis. The holding time was less than 2 weeks.

The solvent extract following the liquid-liquid extraction is then transferred into an auto-sampler vial and stored at -20°C for GC-FID analysis. Sample extracts (1 µL) are injected using an Agilent CTC Analytics and PAL Automatic Liquid Sampler into the Agilent GC (HP 6890 GC System) with dual FIDs. Sample introduction used splitless injection which is set to oven track mode (2°C higher than the oven temperature program). The column used for separations was a Supelco MDN-5s (Restek, Cat. No. 12723) 30 m × 250 µm × 0.25 µm (length × i.d. × film thickness). The column is Rtx-5Sil MS (Crossbond 5%, diphenyl 95%, dimethyl polysiloxane) and its maximum temperature limits was 350 °C. Hydrogen was used as a carrier gas with a flow rate of 3.0 mL/min. The GC oven is programmed to an initial oven temperature of 35°C, held for 2 min, followed by an increase to 320°C at 20°C/min, and held at 320°C for 10 min, with a total run time of 26.25 min. The GC-FID is operated at 320°C with the hydrogen flow set at 30 mL/min and the air flow set at 400 mL/min. The EzChrom Elite Chromatography Data System for data acquisition and processing.

For the calibration of the GC-FID on the oils at NJIT, a 10,000 ppm of crude oil stock solution in DCM was prepared by adding 500 mg of HOOPS or ANS (measured using a 1-mL gas-tight syringe) to 50 mL of volumetric flask, immediately followed by filling DCM up to the mark. Subsequently, the stopper was inserted the flask was shaken thoroughly to ensure the uniform mixing of the solution. An eight point calibration was generated using standards (25, 50, 100, 250, 500, and 1000 ppm) prepared from the serial dilution of 10,000 ppm of crude oil stock that was used to generate the oil samples (e.g. HOOPS and ANS). Then, the oil standards were transferred into an auto-sampler vial and stored at -20°C for GC-FID analysis. The mass of dispersed oil in the water column was computed as:

$$\text{Total oil dispersed (g)} = \text{Oil}_{\text{GC-FID}} \times V_{\text{DCM}} \times \frac{V_{\text{tw}}}{V_{\text{ew}}} \quad (2)$$

where, $\text{Oil}_{\text{GC-FID}}$ is the oil mass measured by GC-FID; V_{DCM} is the volume of DCM extract; V_{tw} is the total volume of seawater in the baffled flask and V_{ew} is the total volume of seawater extracted.

3.6.2 Saturates, aromatics, resins, and asphaltene (SARA)

The measurement of the SARA was conducted using thin layer chromatography with flame ionization detection (TLC-FID) using an Iatroscan MK-6 following the thin layer chromatography procedure of (Napolitano et al. 1998). The procedure includes four steps: (1) sample and standard preparation; (2) spotting; (3) solvent development; (4) scanning. A 5 mL subsample, initially extracted using dichloromethane (DCM, pesticide quality) and stored at 4 °C, was concentrated to 1 mL under nitrogen. A volume of 3 μL of samples was loaded into an auto-spotter, which served to deliver a consistent small amount of sample (2 μL) along a chromarod. Upon completion of spotting, the chromarods were developed to separate the four SARA oil fractions by placing successively the chromarods in a chamber of humidity (70 mL of pure water and 30 mL of concentrated sulfuric acid) for 10 min., hexane (100 mL) for 18 min., toluene (100 mL) for 8 min. and methanol-DCM (5–95 mL) for 2 min., respectively. The samples were then air-dried for 2 min., emplaced in the Iatroscan (Shell, USA) for blank scans (about 20 min) followed by a final scan. Sample peaks were integrated to determine the relative proportion of the alkane, aromatic, resin and asphaltene compounds of the samples.

3.7 Oil Physical Properties (Goal 2)

Measurements of the initial oil density and viscosity were obtained using an Anton Paar SVM 3000 Stabinger Viscometer equipped with a hot filling attachment (Anton Parr, Quebec, Canada). Approximately 10 mL of ANS and HOOP was aspirated into a syringe with a luer slip tip (Becton, Dickinson and Company, New Jersey, USA), taking care not to draw up any air bubbles into the sample. The syringe was then connected to the sample inlet port on the instrument and pressure was slowly applied to the plunger until oil was seen exiting the waste line. The sample measurement occurred at 15, 25, 40 and 50°C. The instrument would automatically take three readings of density and viscosity and report an average, and this process was repeated five times at each selected temperature. In between samples, the sample path was cleaned with toluene and acetone followed by air drying with a built-in blower.

The interfacial tension of oil and water was measured using a Kruss Wilhelmy Plate tensiometer, which was also used to measure the surface tension between water and air.

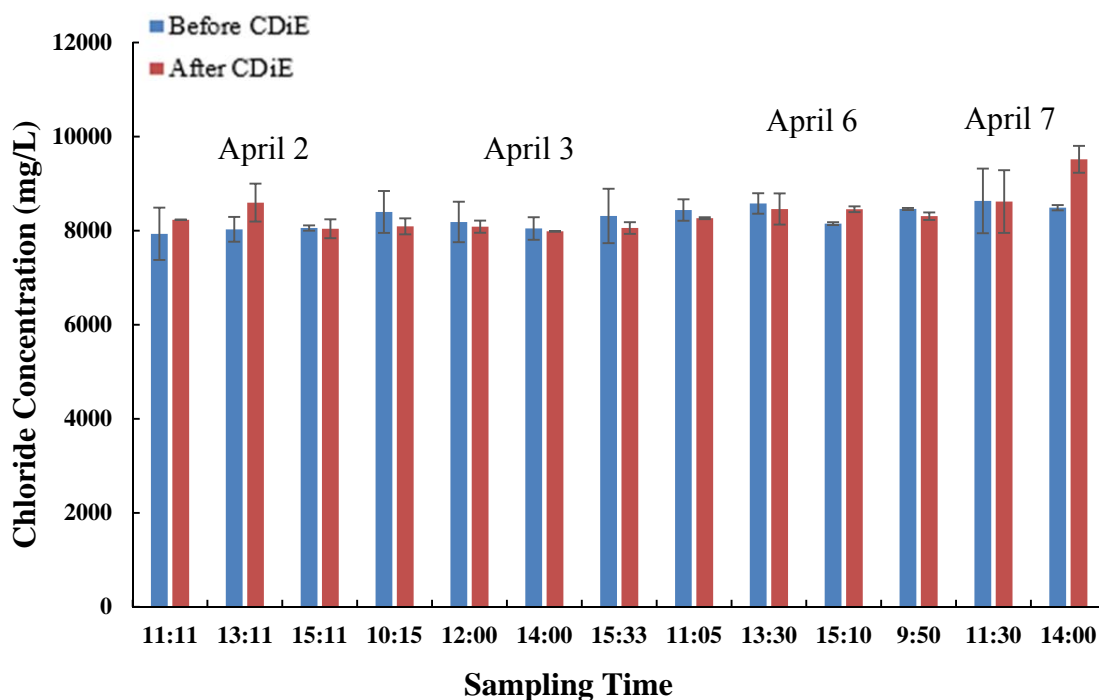
4.0 RESULTS

4.1 Results of Goal 1: Effectiveness of Filters

4.1.1 Results of April 2015

Figure 5 reports the chloride concentration before and after the diatomaceous earth (CDiE) filters (Figure 5a) and before and after the powder activated carbon (PAC) placed into the tank at 2:00 pm on April 3rd, 2015 (Figure 5b). One notes that a relatively higher chloride concentration was

detected in the last sample in Figure 5, which is the only exception. The Grubbs' test indicated that this value is a significant outlier ($P < 0.05$), but that the highest value before and after the PAC (Figure 5b) is not ($P > 0.05$). It is not obvious why such a spike occurs; it could be due to operation within the tank that might have pushed surface water into the filter inlet, and surface water would have a slightly higher concentration of solutes due to evaporation.



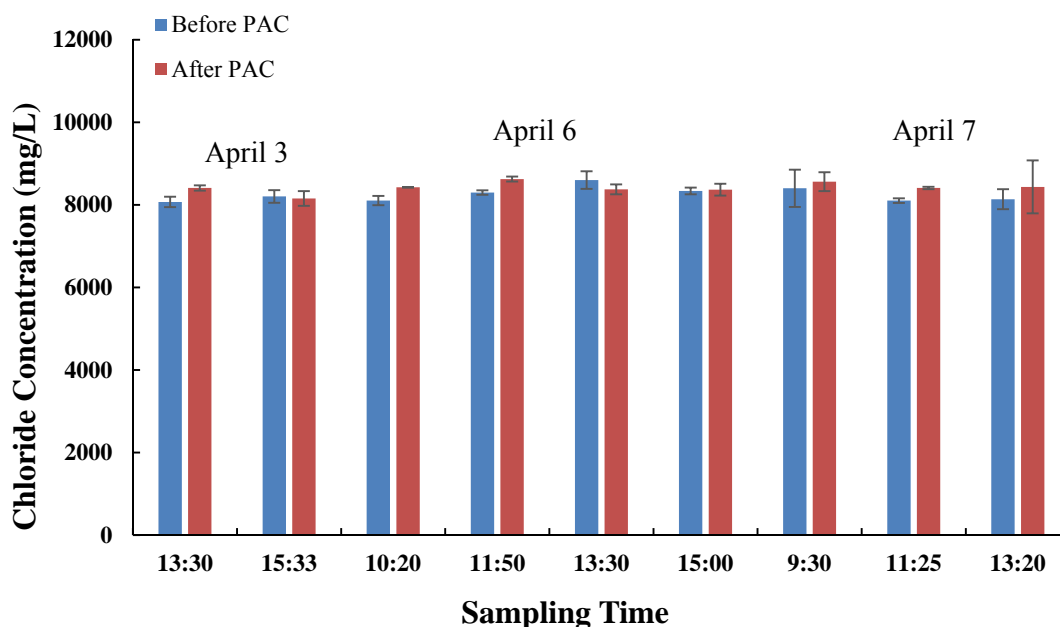


Figure 5: Chloride concentrations (a) before and after the CDiE filters and (b) before and after the PAC. A cellulose slurry and diatomaceous earth material was added to the CDiE filter on April 2nd 2015 and April 3rd 2015. The (PAC) was placed into the Ohmsett tank on April 3rd 2015.

Table 3 shows that the concentration of chloride was not different across either medium, which is not surprising as neither the CDiE nor the PAC were intended to remove ions.

Table 3: p-values for each compound in April 2015 before and after CDiE and before and after the PAC. p-values less than 0.05 indicate that the concentration across the CDiE or the PAC are statistically different. The percent difference is shown within parathenses.		
Compound	CDiE	PAC
Chloride	0.48	0.39
Nitrate	0.65	0.21
Sulfate	0.35	0.47
Sodium	0.63	0.064
Magnesium	0.34	0.09
Calcium	0.55	0.12
Potassium	0.15	0.34
Zinc	0.09	0.40
Benzene	0.042 (-29%)	0.59
Toluene	0.16	0.11
Ethylbenzene	0.32	0.035*
Xylene	0.27	0.0026*

*: The “before” concentration was smaller than the “after” concentration.

Figure 6 shows the changes of nitrate concentration before and after the CDiE filter and PAC chambers at different times. Some high values were observed in the samples collected on April 2nd and 3rd. However, the results of Grubbs’ test for significant outliers show that there is no significant outlier ($P > 0.05$) detected in the samples before and after CDiE, except the samples of Before CDiE at 14:00 of April 3rd and the last sample of April 7th (significant outliers ($P < 0.05$)) (Figure 6a). Grubbs’ tests for samples before and after PAC (Figure 6b) indicate the first sample of April 6th is the only significant outlier ($P < 0.05$). A notable increase in the nitrate concentration is noted for April 6th and April 7th. Mr. Alan Guarino of Ohmsett reported that cleaning agents used on the North side of the tank could be the reason for the high nitrate values. However, the values are only slightly larger than those found in seawater (see (Boufadel et al. 2010) and publications therein), and are thus too small to affect dispersion effectiveness. Table 3 shows that the concentration of nitrate was statistically the same across the CDiE filter and PAC.

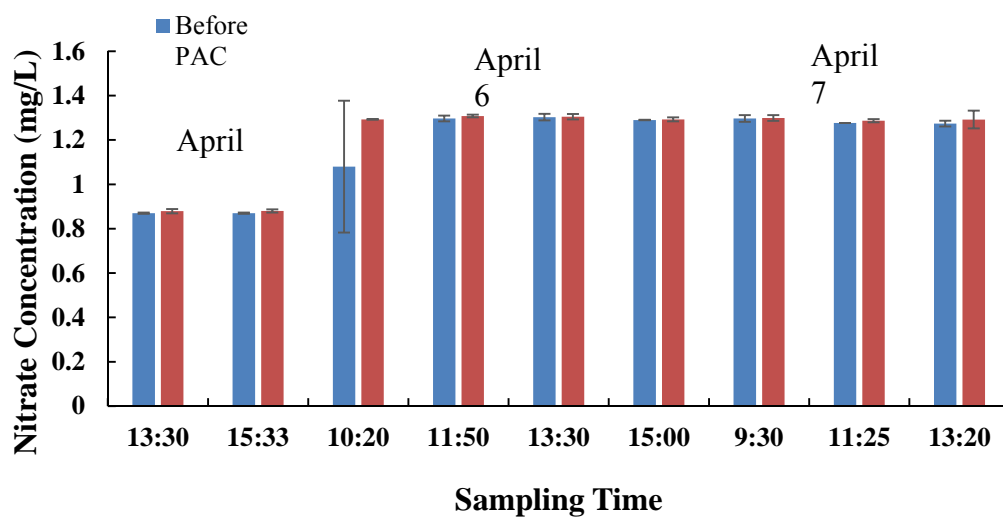
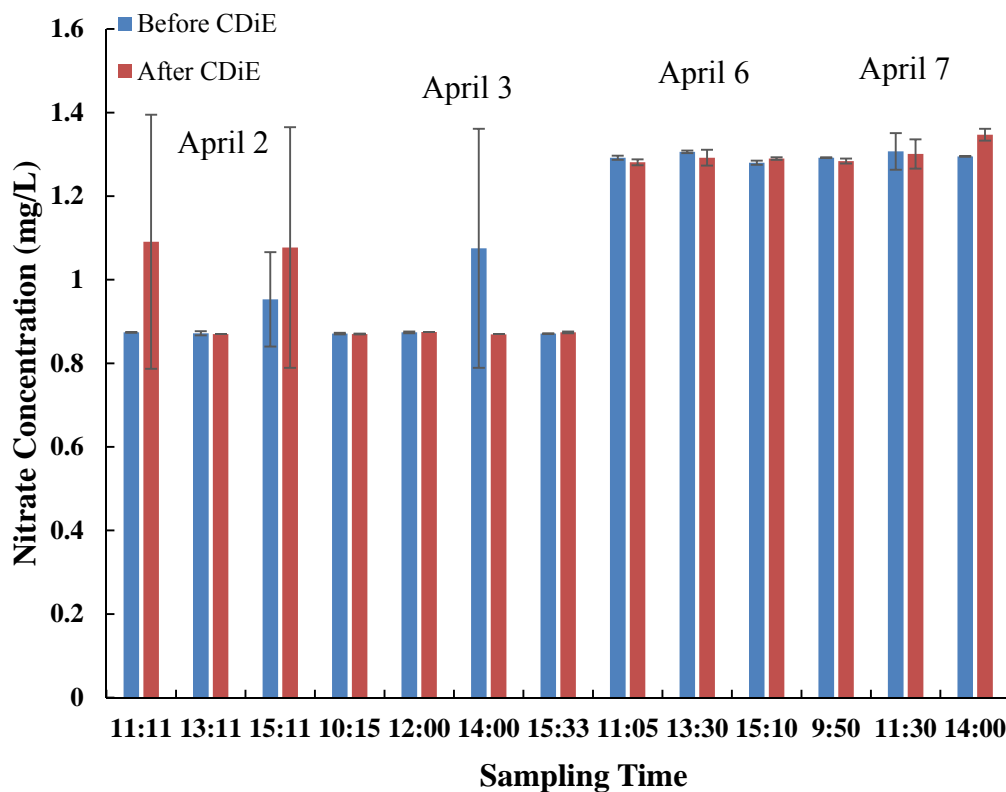
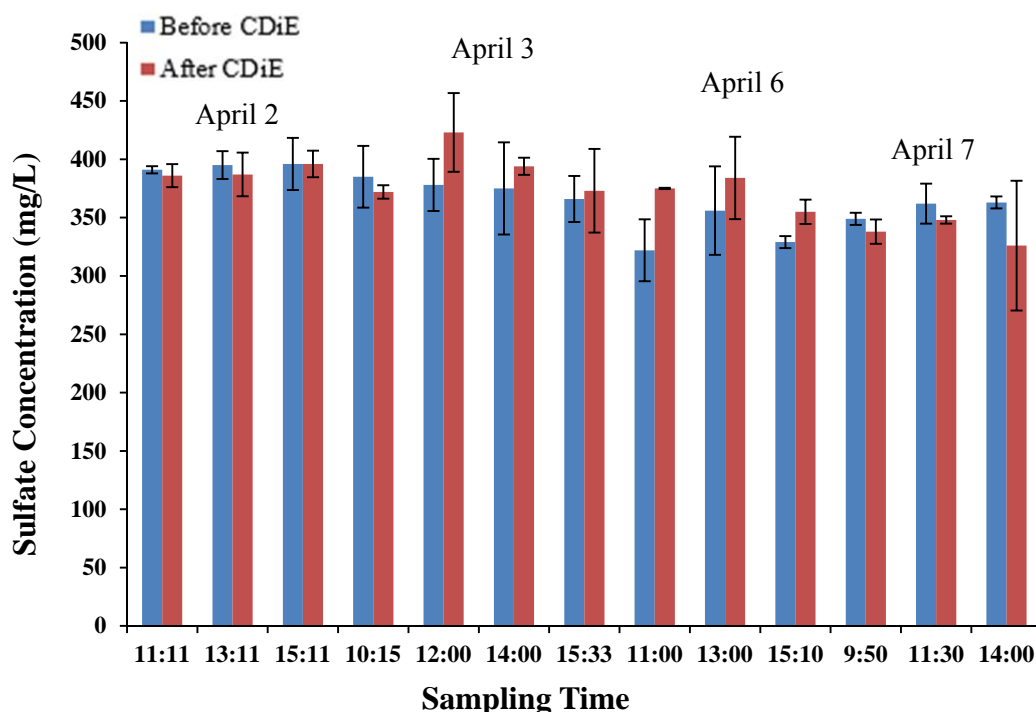


Figure 6: Nitrate concentrations (a) before and after the CDiE filters and (b) before and after the PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

Figures 7a and 7b show the concentration of sulfate before and after the CDiE and the PAC, respectively. the sulfate concentration on April 6th and 7th was slightly lower than that on April 2nd and 3rd. However, no pattern of decrease due to the filters is apparent (i.e., when comparing before and after). The Grubbs' test results for significant outliers show that there is no significant outlier ($P>0.05$) detected in these samples before and after CDiE and PAC, except the sample after CDiE at 12:00 April 3rd (Figures 7a and 7b). Table 3 shows that the concentration of sulfate was statistically the same across the CDiE filter and PAC.



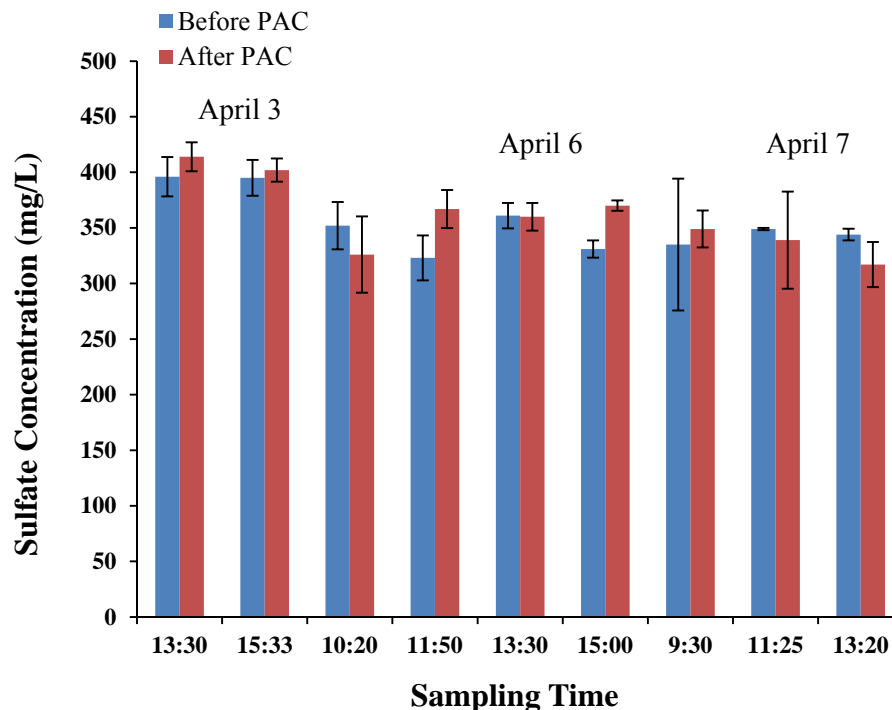


Figure 7: Sulfate concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015. The (PAC) was placed into the Ohmsett tank on April 3rd 2015.

Figure 8 through Figure 12 report the concentration of cations, including metals. Figure 8 shows the sodium concentration before and after the CDiE and before and after the PAC chambers at different times. The relatively larger value in the last sample after the CDiE is consistent with the increase of chloride at that time (Figure 5a). The filter and PAC do not seem to have any effect on the sodium concentration. The Grubbs' test results for significant outliers show that there is no significant outlier ($P > 0.05$) detected in these samples before and after CDiE and PAC, except the last sample after CDiE at 14:00 of April 7th (Figures 8a and 8b). Table 3 shows that the concentration of sodium was statistically the same across the CDiE filter and PAC.

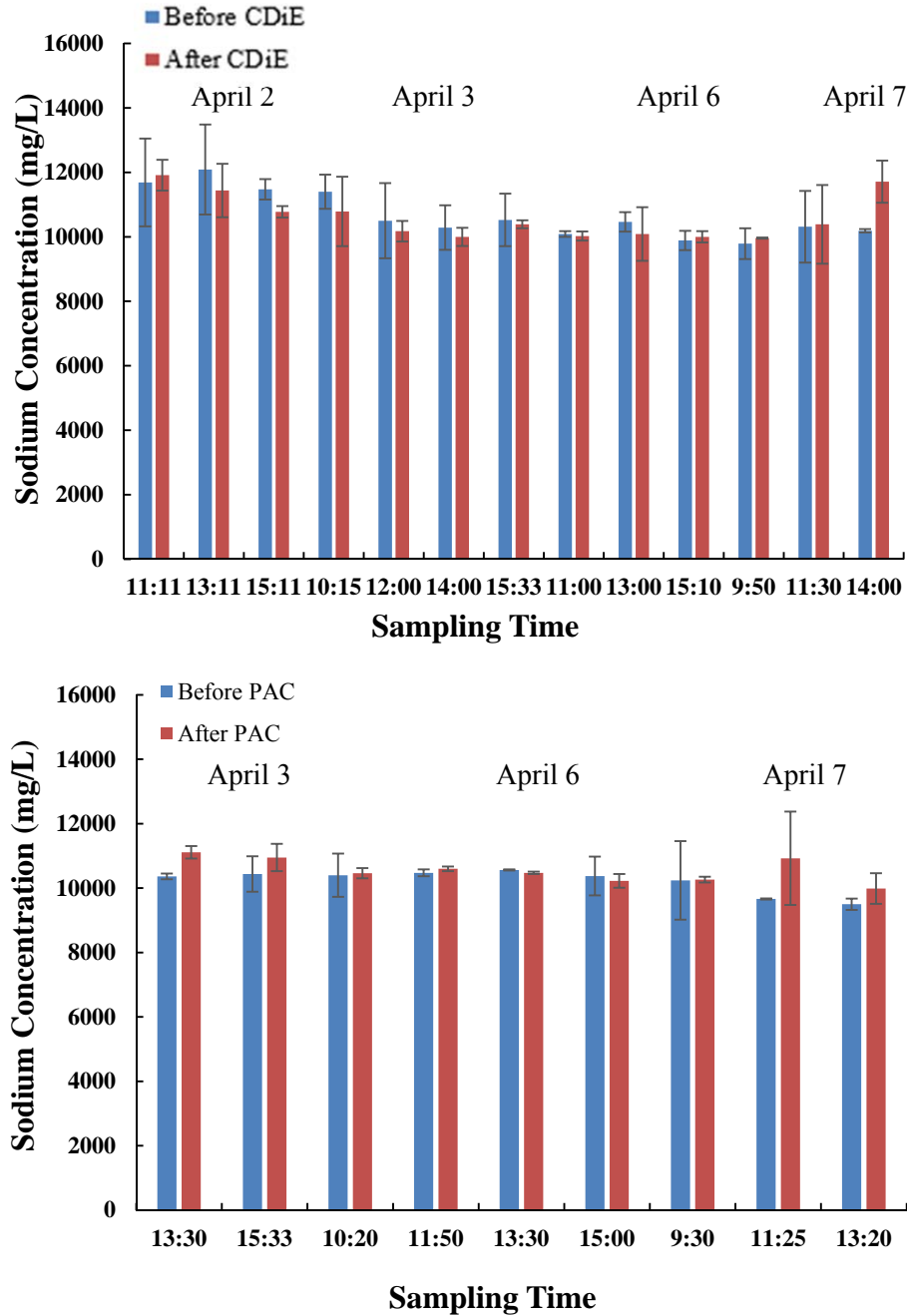
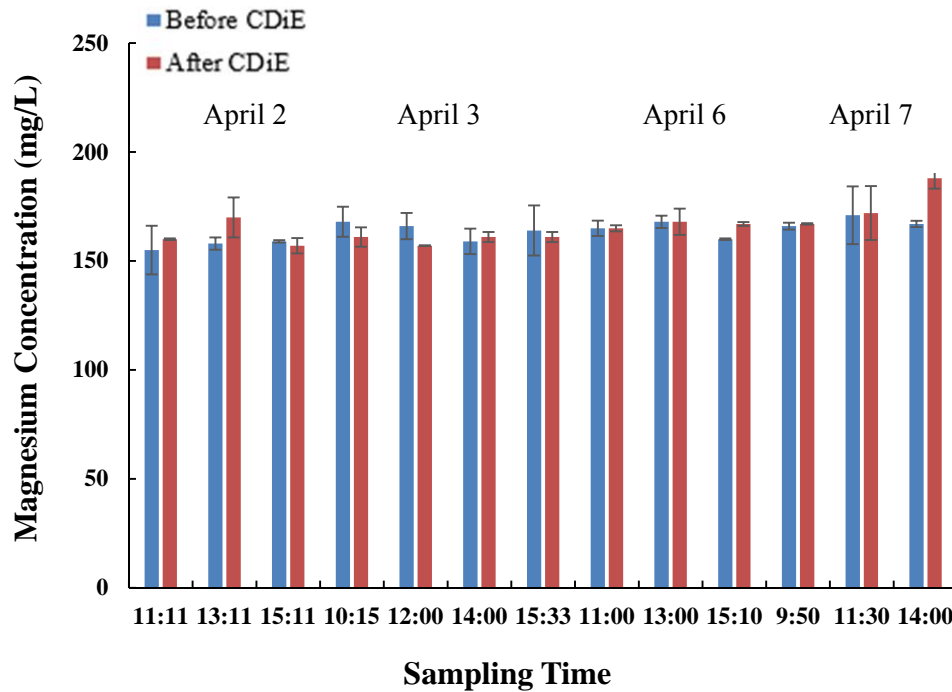


Figure 8: Sodium concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015. The (PAC) was placed into the Ohmsett tank on April 3rd 2015.

The behavior of the concentration of magnesium (Figure 9) and calcium (Figure 10) was similar to that of sodium, including the slightly larger value in the last sample, especially after the CDiE. Thus, the filtration system did not remove calcium cations, consistent with the literature (Dvorak and Skipton 2013). In Figures 9a and 10a, the high values observed in the last sample were

determined as significant outliers ($P < 0.05$) based on the Grubbs' test. In contrast, the Grubbs' test results for significant outliers show that there are no significant outliers ($P > 0.05$) detected in the samples before and after PAC (Figures 9b and 10b). Table 3 shows that the concentration of magnesium was statistically the same across the CDiE filter and PAC, and the same can be said about the concentration of calcium.



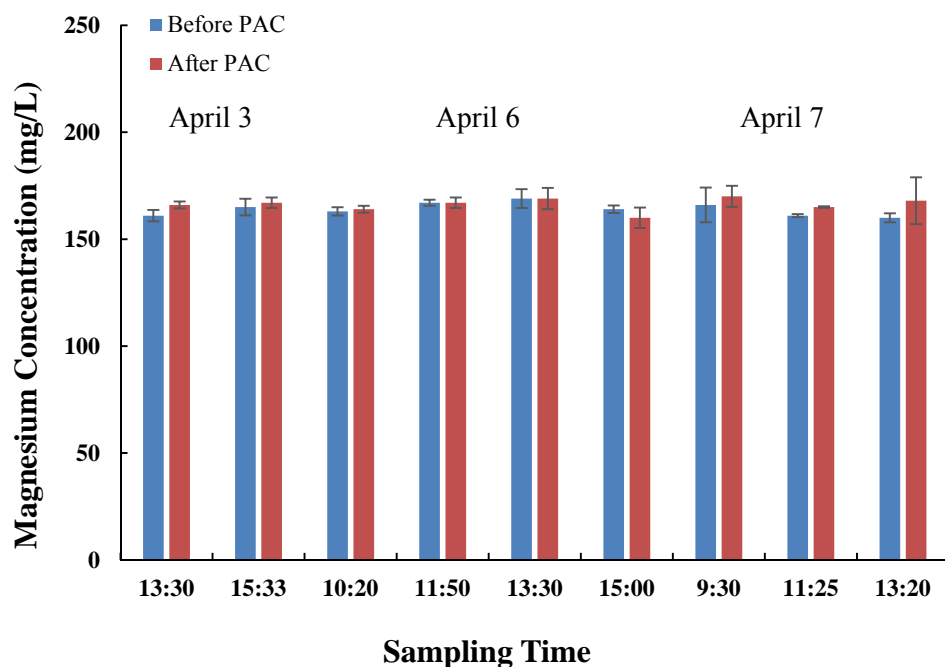
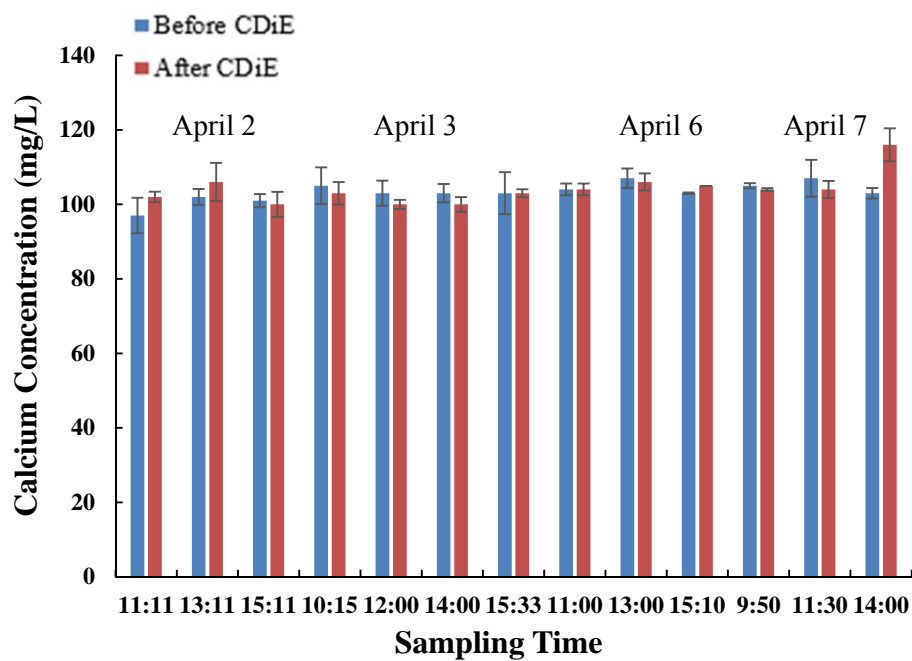


Figure 9: Magnesium concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.



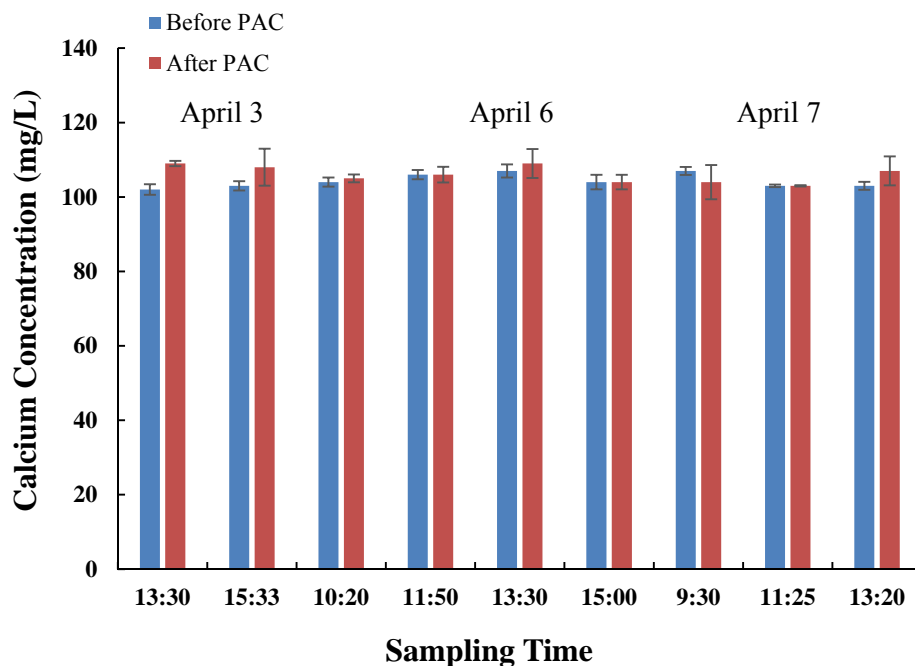


Figure 10: Calcium concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

Figure 11 shows that the potassium concentration on April 6th and April 7th was lower than that on April 2nd and April 3rd. This could be due to the role of PAC played in removing potassium ion. Some samples with a large degree of variability can be also noted (e.g. the samples after CDiE at 11:11, April 2nd and 15:33, April 3rd; the last samples). The Grubbs' test results for significant outliers show that there are no significant outliers ($P > 0.05$) detected in these samples before and after CDiE and PAC (Figures 11a and 11b). Table 3 shows that the concentration of potassium was statistically the same across the CDiE filter and PAC.

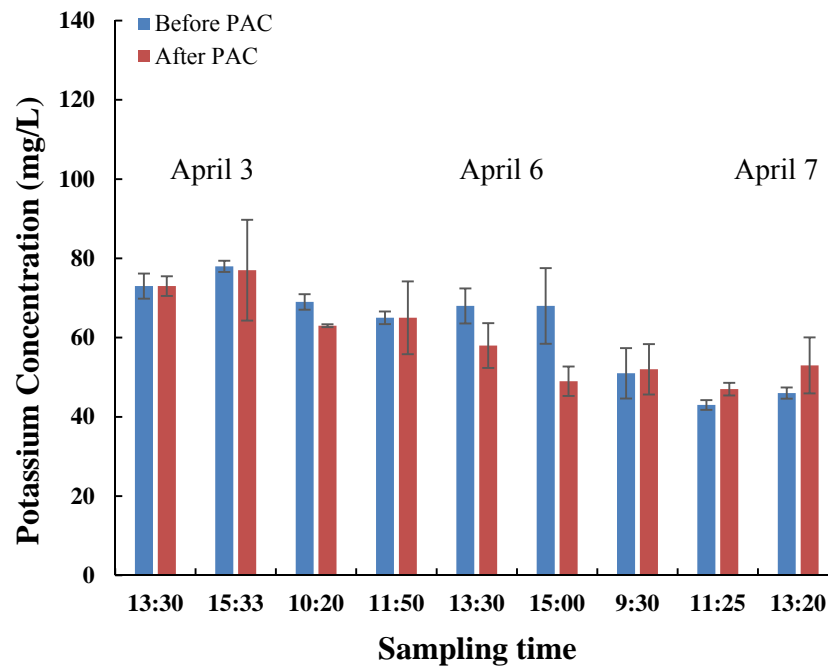
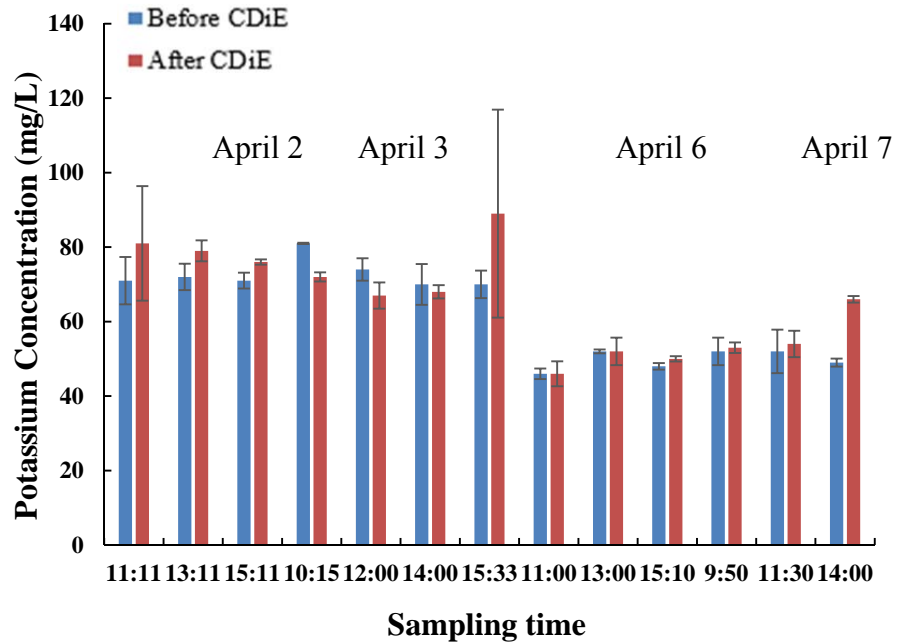
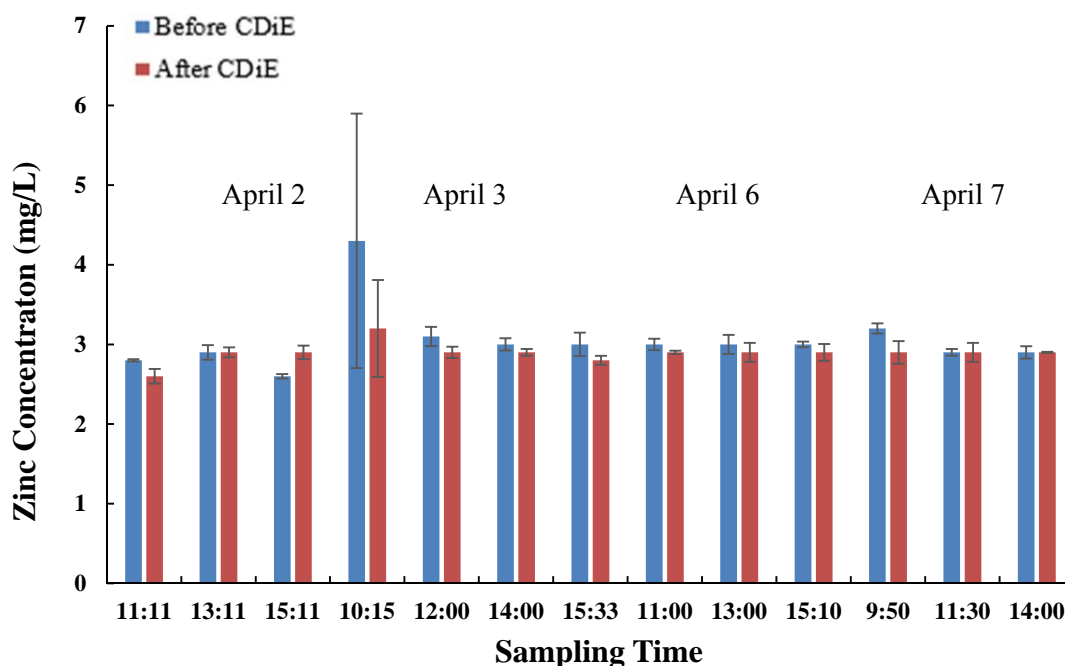


Figure 11: Potassium concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015. The (PAC) was placed into the Ohmsett tank on April 3rd 2015.

Figure 12 shows negligible changes in the zinc concentration before and after the CDiE filter and the PAC, respectively, with the exception of two samples where relatively large values are observed, but they were also associated with large standard deviations. The Grubbs' test was performed to determine whether the most extreme values that in the sample of Before CDiE at 10:15 of April 3rd (Figure 12a) and in the sample of Before PAC at 15:00 of April 6th (Figure 12b) are significant outliers from the rest. The Grubbs' test result show that the two most extreme values are significant outliers ($P < 0.05$). The typical zinc level contained in seawater is about 0.005 mg/L (Turekian 1968), and the measured values were around 3 mg/L. The high concentration of zinc in the Ohmsett water is probably because it was used as a sacrificial anode in the Ohmsett tank to reduce corrosion. Table 3 shows that the concentration of zinc was statistically the same across the CDiE filter and PAC.



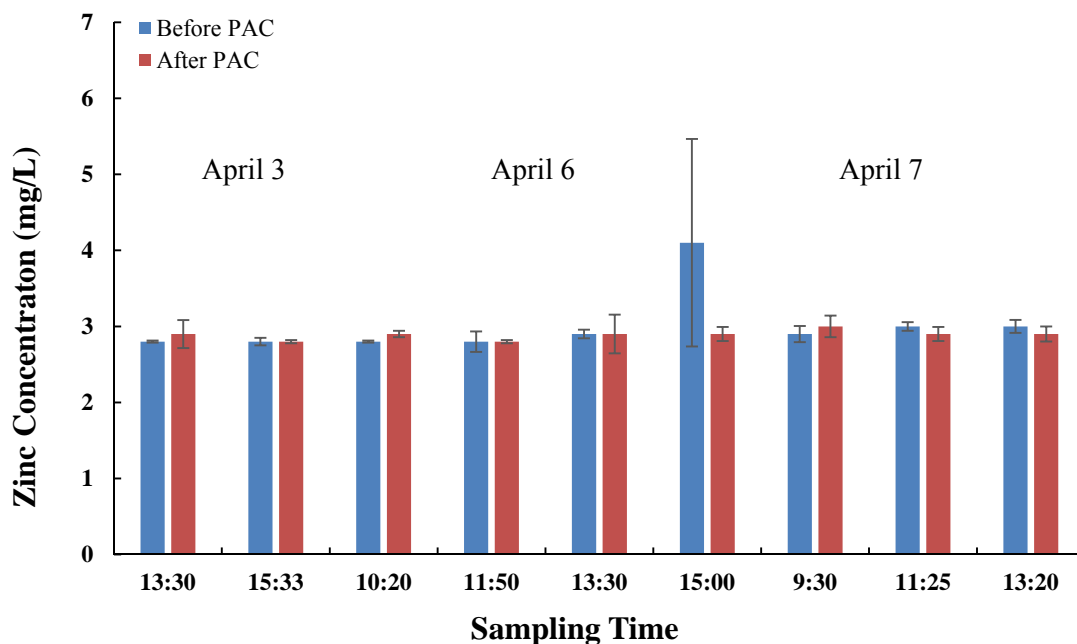


Figure 12: Zinc concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

Figure 13a and Figure 13 b show the concentrations of benzene before and after CDiE and PAC, respectively. Benzene concentration was found to be $\sim 650 \mu\text{g L}^{-1}$ initially. Figure 13a shows a continuous and consistent decrease of benzene with time until April 3rd, excluding a relatively large value in the sample before CDiE at 13:11, April 2nd. However, the measurement is accompanied with a large degree of variability as noted from the large error bars. It is possible that the benzene evaporated from the Ohmsett tank over the weekend between April 3rd and April 6th. The Grubbs' test showed that the large values in the samples of Before CDiE at 13:11 of April 2nd and 15:10 of April 6th (Figure 13a) are significant outliers ($P < 0.05$) from the rest. There were no significant outliers detected in these samples before and after PAC (Figure 13b). No measurement of the benzene before and after the PAC was made on April 2nd and 3rd. Note that the solubility limit of benzene in water is around 1700 mg/L (Fetter 1999) and the measured values are less than 1.0 mg/L. Table 3 shows that the concentration of benzene after the CDiE was statistically smaller than that before ($p < 0.05$) indicating that the CDiE filter removed benzene from the water. However, the benzene concentration before and after the PAC was statistically the same.

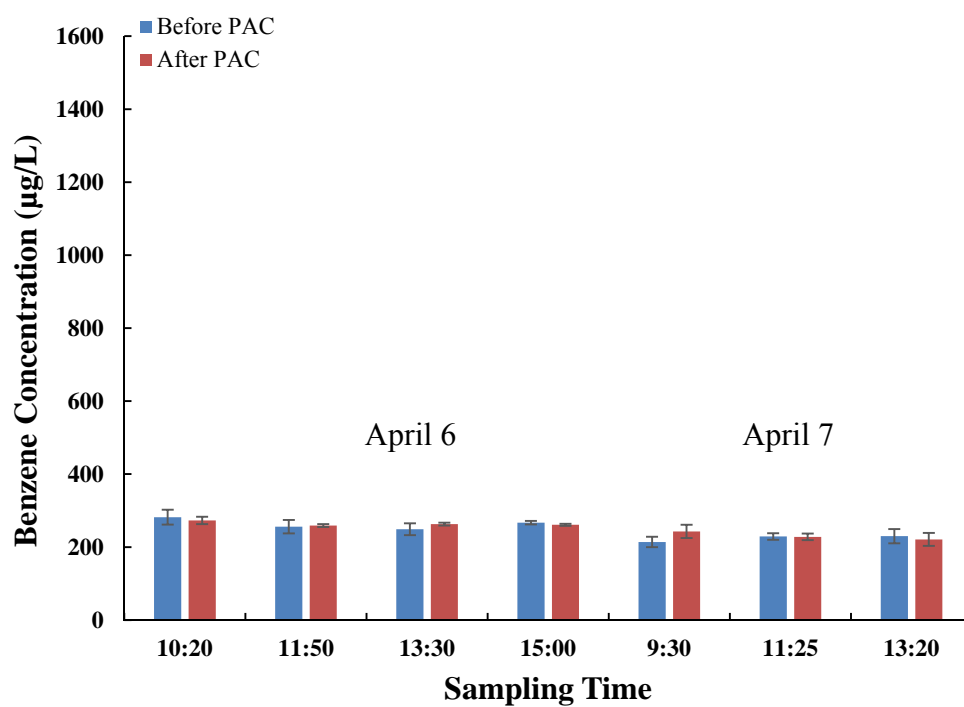
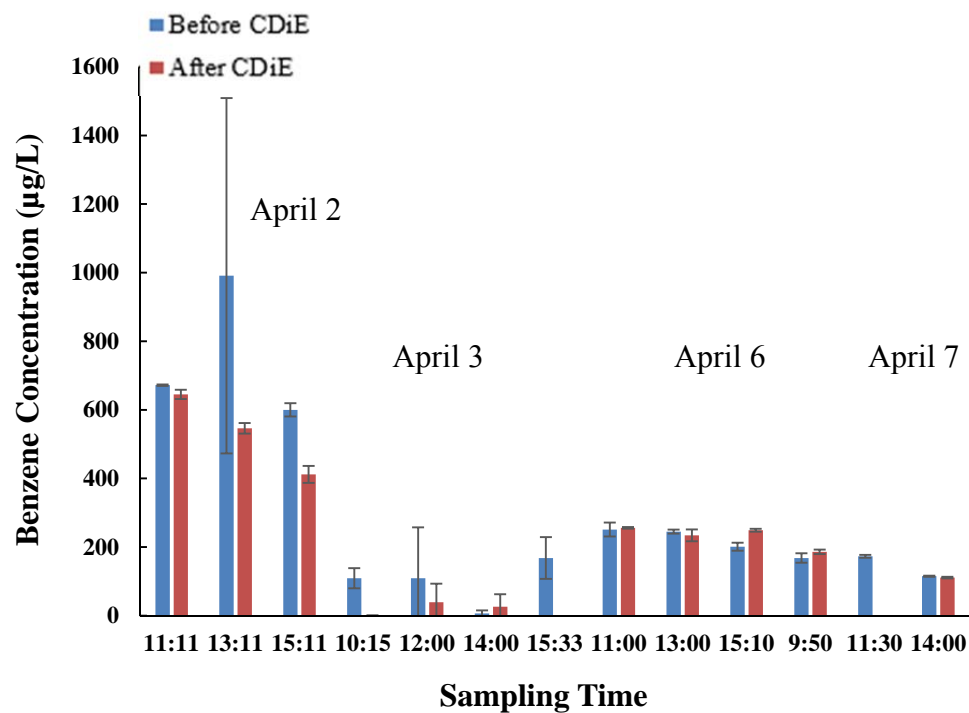
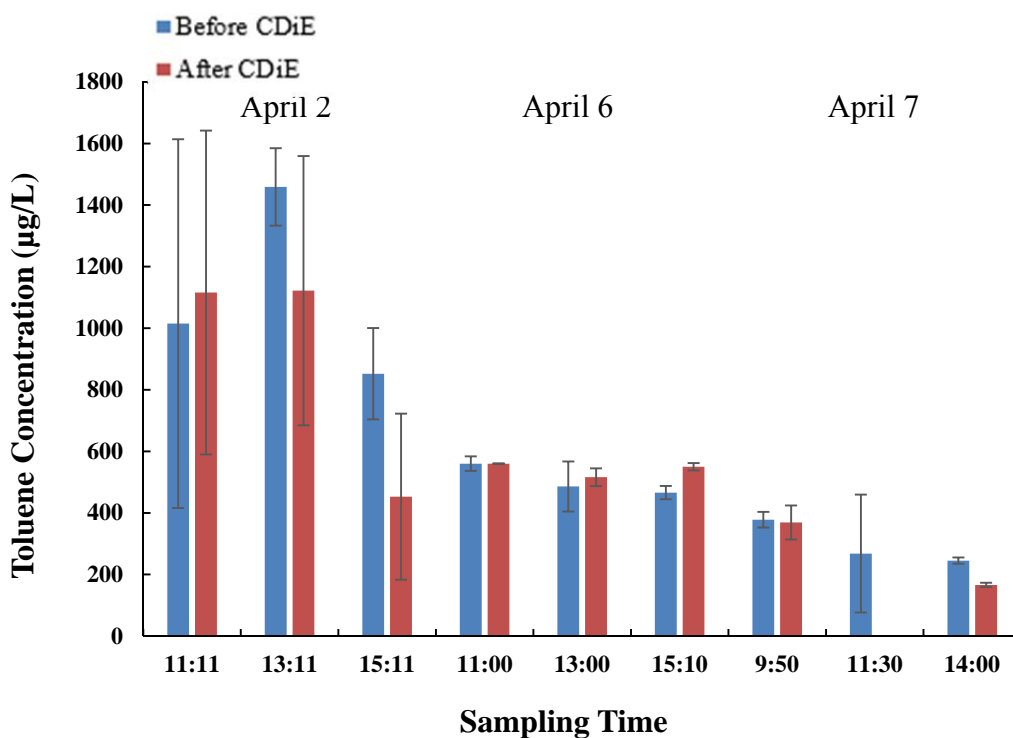


Figure 13: Benzene concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

The concentration of toluene is reported in Figure 14, and similar to benzene, it shows a large decrease from April 2nd to April 6th. Small increases across the CDiE filters and PACs were noted on April 6th and 7th, which could be due to leaching of toluene from these media. However, the increases were small, and they could be interpreted as due to measurement errors. Note that the solubility limit of toluene in water is around 500 mg/L (Fetter 1999) and the measured values are less than 1.0 mg/L, and thus very small. The Grubbs' test results for significant outliers indicated that no outliers are present in these samples before and after CDiE and PAC, except the most extreme values for the samples Before CDiE at 13:11 of April 2nd Before PAC at 13:30 of April 6th, and the sample Before CDiE at 15:10 of April 6th (Figures 14a and 14b). Table 3 shows that the concentration of toluene was statistically the same across the CDiE filter and PAC.



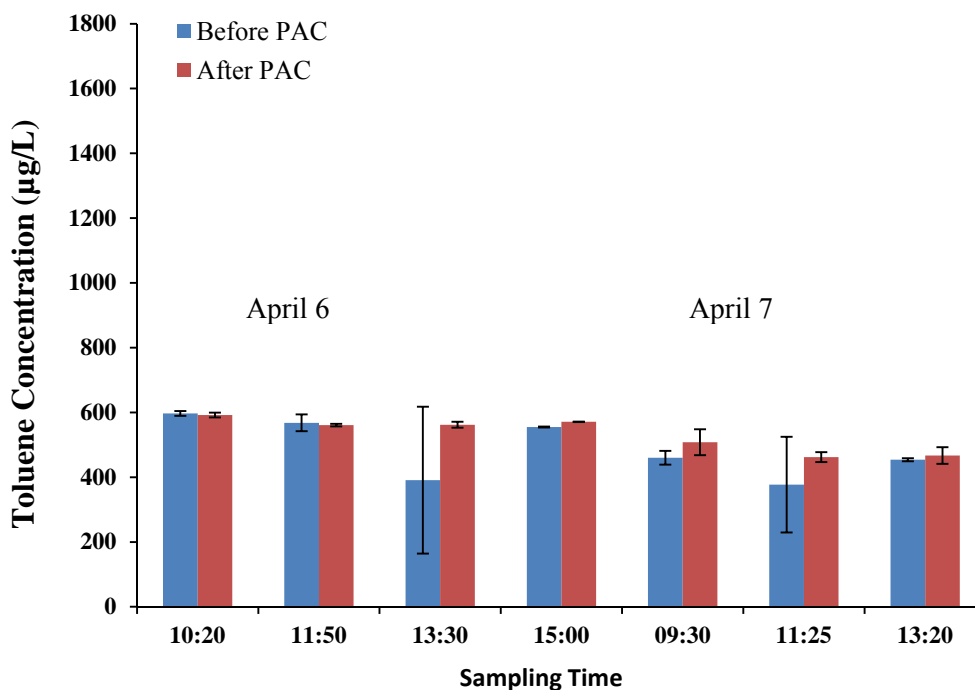


Figure 14: Toluene concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

Figure 15 shows the concentration for ethylbenzene, which shows a similar trend to toluene; some variability during April 2nd and 3rd, but then a major drop in the concentration is noted on April 6th and 7th, which is probably due to evaporation over the weekend (April 4th and 5th). The concentration of ethylbenzene was less than 0.20 mg/L, while its solubility limit in water is around 150 mg/L (Fetter 1999), and thus the measured values were very small. The Grubbs' test indicated that there are no significant outliers detected in these samples before and after CDiE and PAC, except the samples Before CDiE at 13:00 of April 6th and Before PAC at 13:30 of April 6th (Figures 15a and 15b). Table 3 shows that the concentration of ethylbenzene across the CDiE filter was statistically the same. However, it shows that the concentration of the ethylbenzene after the PAC is larger than that before it, which suggests leaching of the ethylbenzene from the PAC.

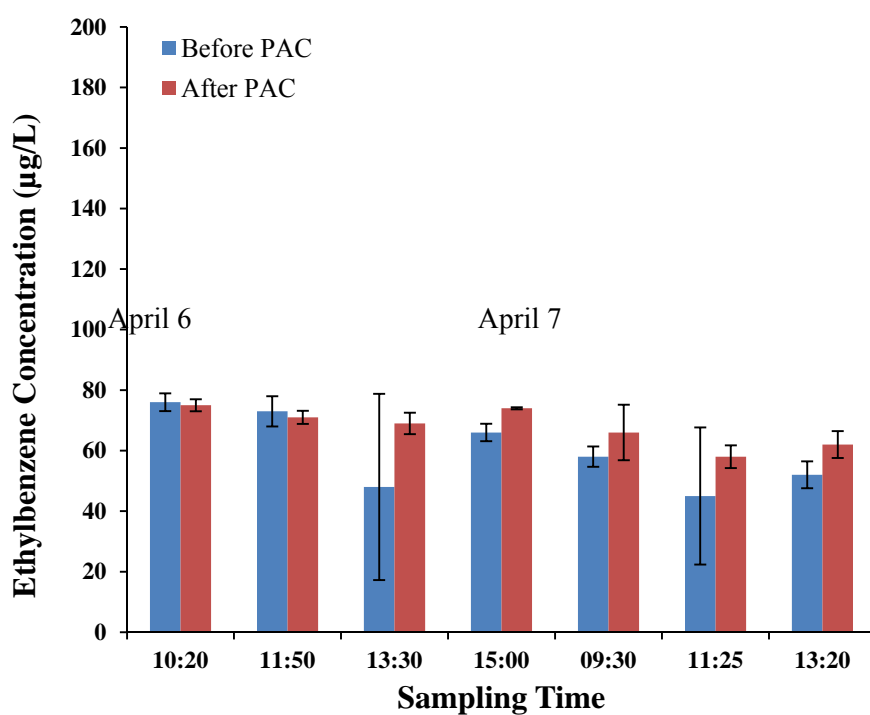
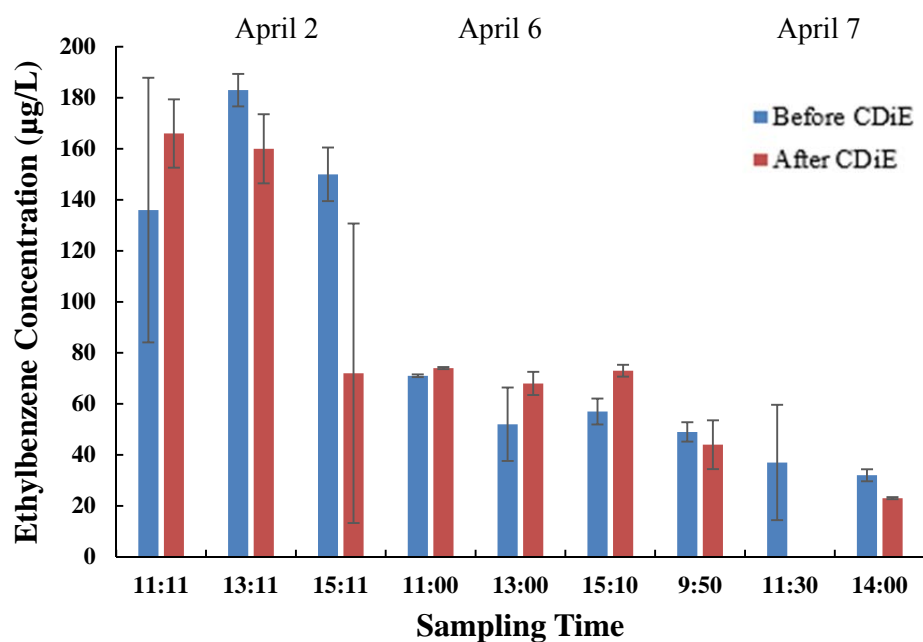
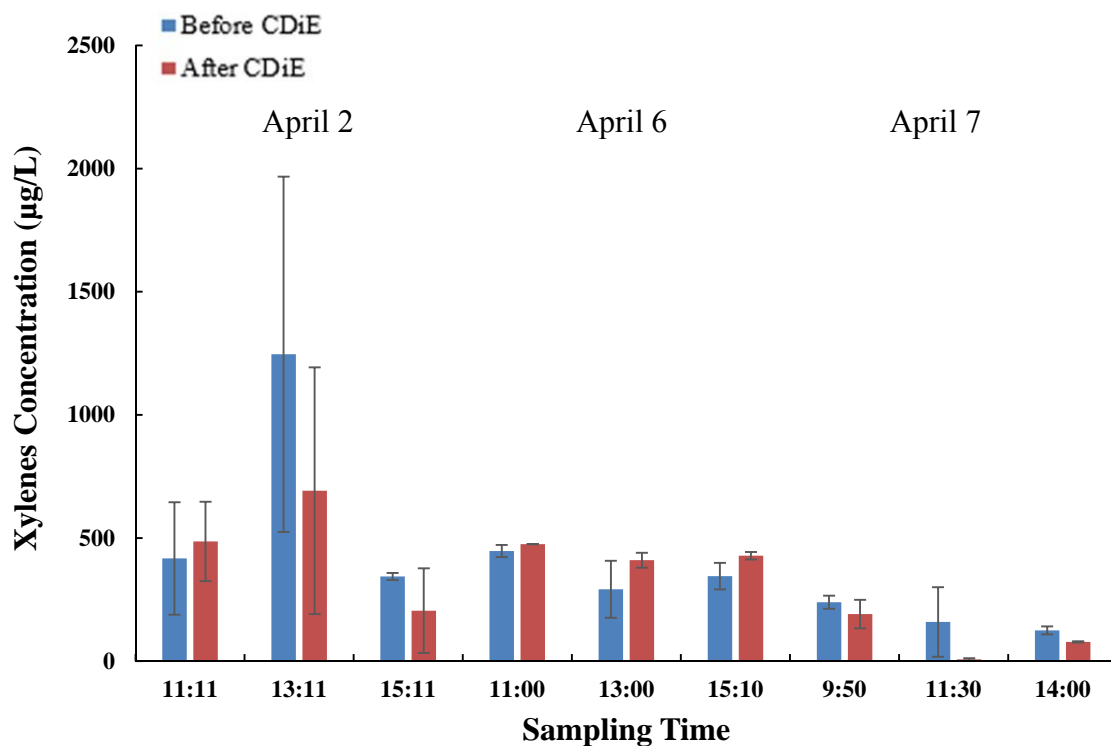


Figure 15: Ethylbenzene concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

Figure 16 for xylene display a similar trend to ethylbenzene (Figure 15) and toluene (Figure 14), where the concentrations on April 6th and 7th were smaller than those on April 2nd. However, the concentrations of xylene were around 0.50 mg/L while the solubility limit of xylene in water is around 170 mg/L (Fetter 1999). The Grubbs' test results for significant outliers show that the most extreme values that in the sample of Before CDiE at 13:11 of April 2nd (Figure 16a) is a significant outlier ($P < 0.05$) from the rest. While there are no significant outliers ($P > 0.05$) detected in these samples before and after PAC (Figure 16b). Table 3 shows that the concentration of xylene across the CDiE filter was statistically the same. However, it shows that the concentration after the PAC is larger than that before it, which suggests leaching of xylene from the PAC.



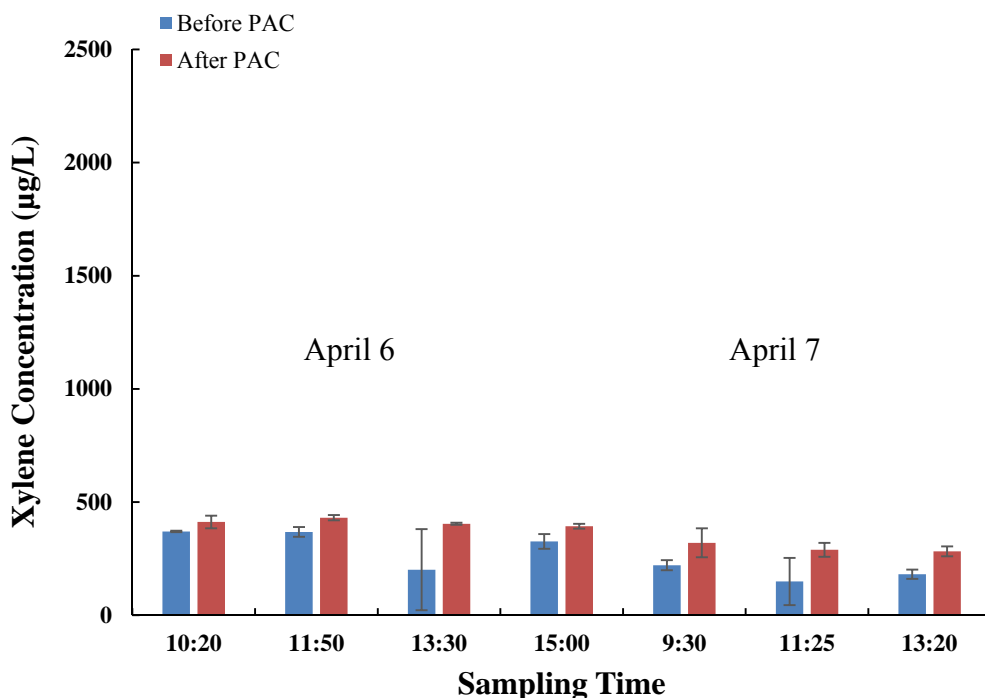


Figure 16: Xylene concentration (a) before and after the CDiE filters and (b) before and after PAC. A cellulose slurry and diatomaceous earth material were added to the CDiE filter on April 2nd 2015 and April 3rd 2015.

From Figures 13 through 16, one concludes that the concentrations of BTEX in water were small, and thus, the CDiE and the PAC chambers might not have removed much mass of these compounds.

4.1.2 Results of October 2015

Figure 17 shows the chloride concentration in the Ohmsett water samples before and after CDiE and PAC filters. The chloride concentration in each sample was approximately 25,000 mg/L. Negligible differences in chloride ion concentration before and after CDiE and PAC filters were noted. relatively higher chloride concentration was detected in the Before PAC sample at 14:00, Nov. 4 in Figure 17, which is the only exception and is an outlier by the Grubb test at $P < 0.05$. No other outliers were detected in the samples before and after PAC (Figure 17). Table 4 shows that the concentration of chloride was statistically the same before and after either of the CDiE or the PAC.

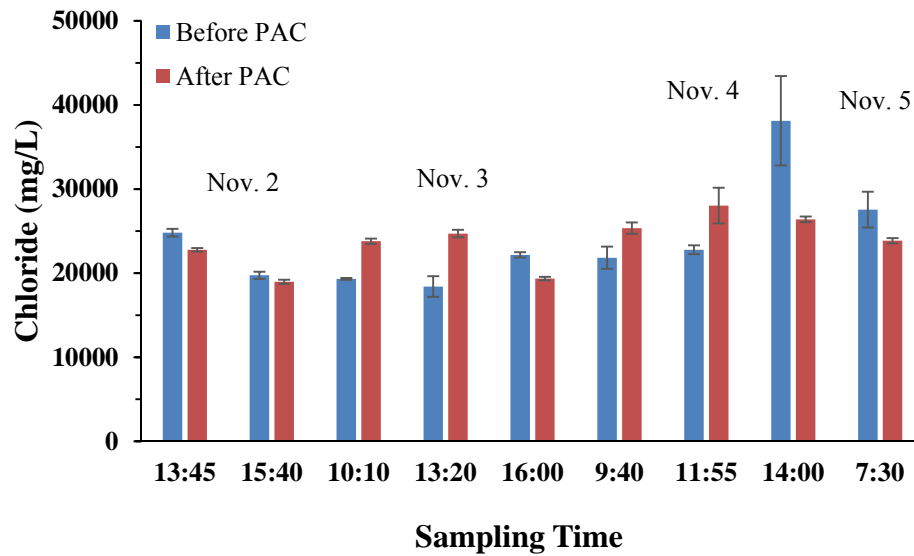
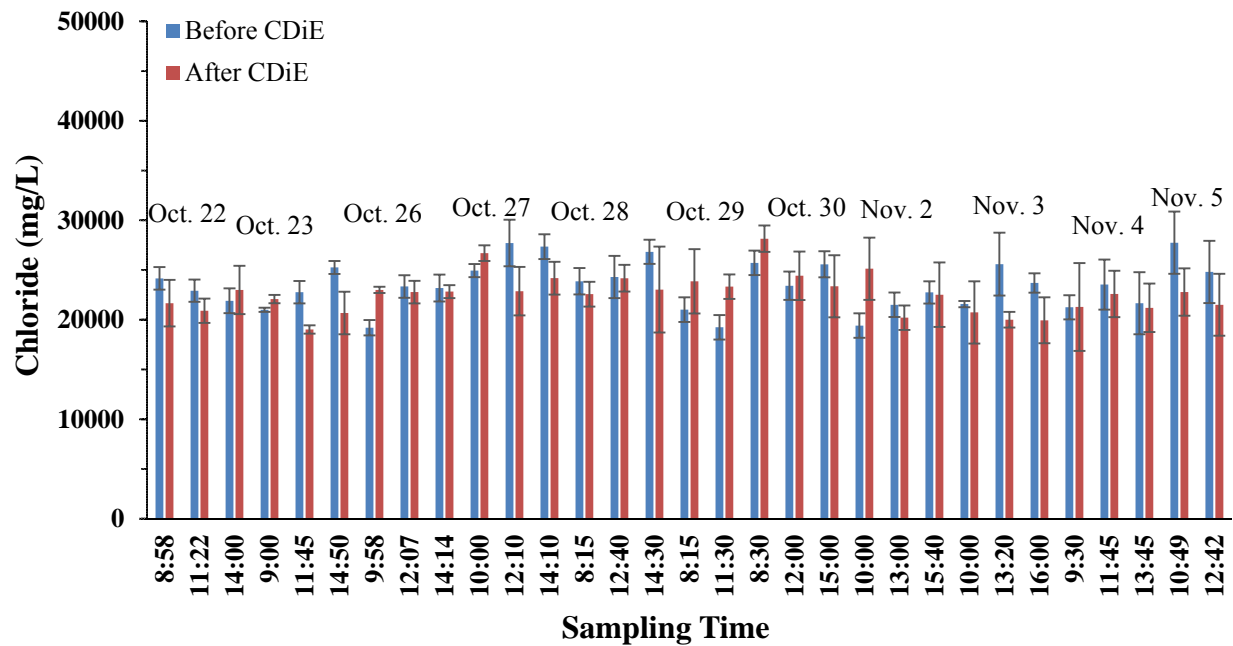


Figure 17: Chloride concentrations (a) before and after CDiE, and (b) before and after PAC.

Table 4: p-values for October 2015 measurements before and after CDiE and before and after the PAC. p-values less than 0.05 indicate that the concentration across the CDiE or the PAC are statistically different. Percent difference is reported within parentheses.

Compound/Parameter	CDiE	PAC
Chloride	0.10	0.93
Nitrate	0.38	0.95
Sulfate	0.30	0.10
Sodium	0.32	0.63
Magnesium	0.26	0.40
Calcium	0.26	0.83
Potassium	0.005 (-12.0%)	0.56
Zinc	<0.001 (-14.4%)	0.002 (-14.2%)
TOC	0.002 (-4.1%)	0.90
Surface Tension	0.038 (+2.2%)	0.68

Figures 18a and 18b show nitrate concentration in the Ohmsett water samples before and after CDiE and PAC filters, respectively. The nitrate level was similar to that observed in April 2015 (Figure 6). The October measurements of Before and After were similar to each other excluding some outliers observed in the samples collected on Oct. 22 and 27. The Grubbs' test results for significant outliers show that the most extreme value that in the sample of Before CDiE at 14:00 of October 22nd (Figure 18) is a significant outlier ($P < 0.05$) from the rest. There were no significant outliers detected in these samples before and after PAC (Figure 18b). Table 4 shows that the concentration of nitrate was statistically the same before and after either of the CDiE or the PAC.

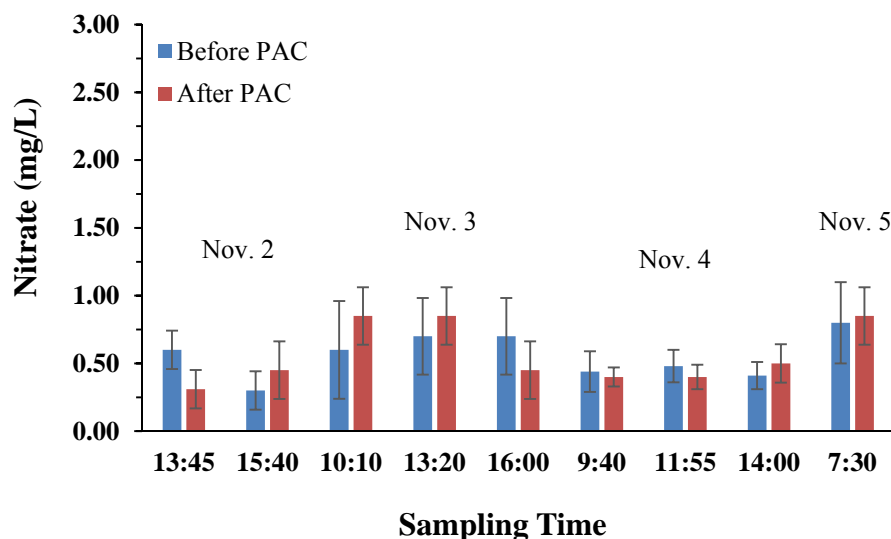
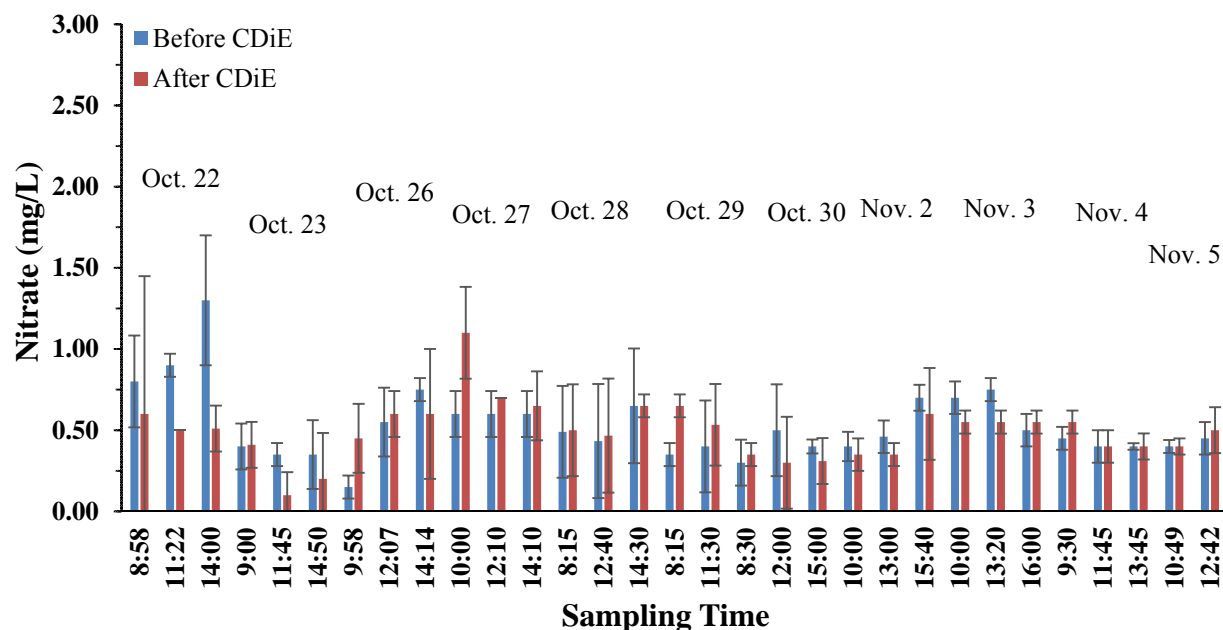


Figure 18: Nitrate concentrations (a) before and after CDiE, and (b) before and after PAC.

Figures 19a and 19b show sulfate concentration before and after CDiE filter and PAC filters, respectively. The sulfate concentrations in all samples were essentially in the same level, about 1,750 m/L. No obvious temporal variability in the sulfate concentration was noted in the samples, indicating that the filters cannot effectively remove the sulfate ion in the water for a given sampling period. The Grubbs' test results for significant outliers show that there are no significant outliers ($P > 0.05$) detected in these samples before and after CDiE and PAC (Figures 19a and 19b). Table 4 shows that the concentration of sulfate was statistically the same before and after either of the CDiE or the PAC.

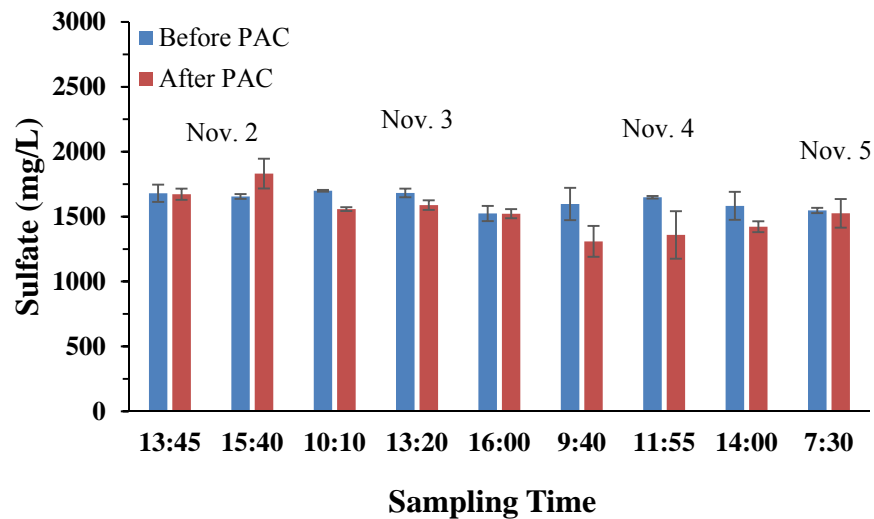
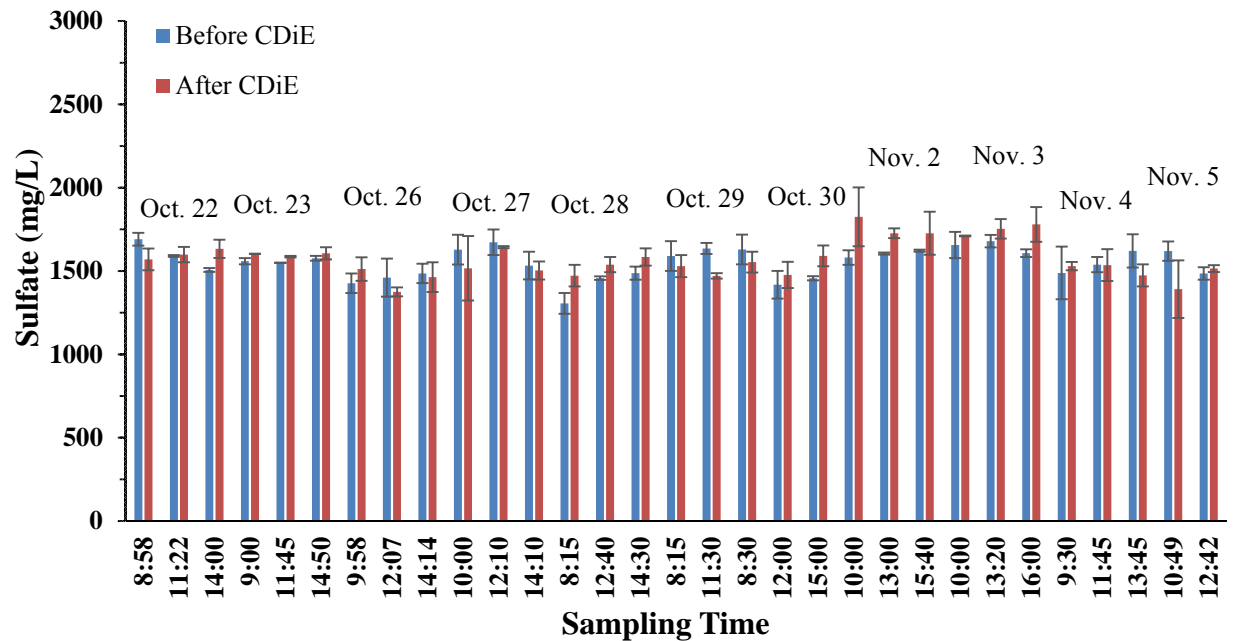


Figure 19: Sulfate concentration (a) before and after CDiE and before and after PAC.

Figures 20a and 20b show sodium concentration in the samples before and after CDiE and PAC filters. They were around 15,000 mg/L. Negligible differences in sodium concentration of samples before and after CDiE and PAC filters were observed, reflecting the ineffectiveness of the filters in eliminating sodium ions in the water. The Grubbs' test results for significant outliers show that the most extreme value that in the first sample of Figure 20a is a significant outlier ($P < 0.05$) from the rest. While there are no significant outliers ($P > 0.05$) detected in these samples

before and after PAC (Figure 20b). Table 4 shows that the concentration of sodium was statistically the same before and after either of the CDiE or the PAC.

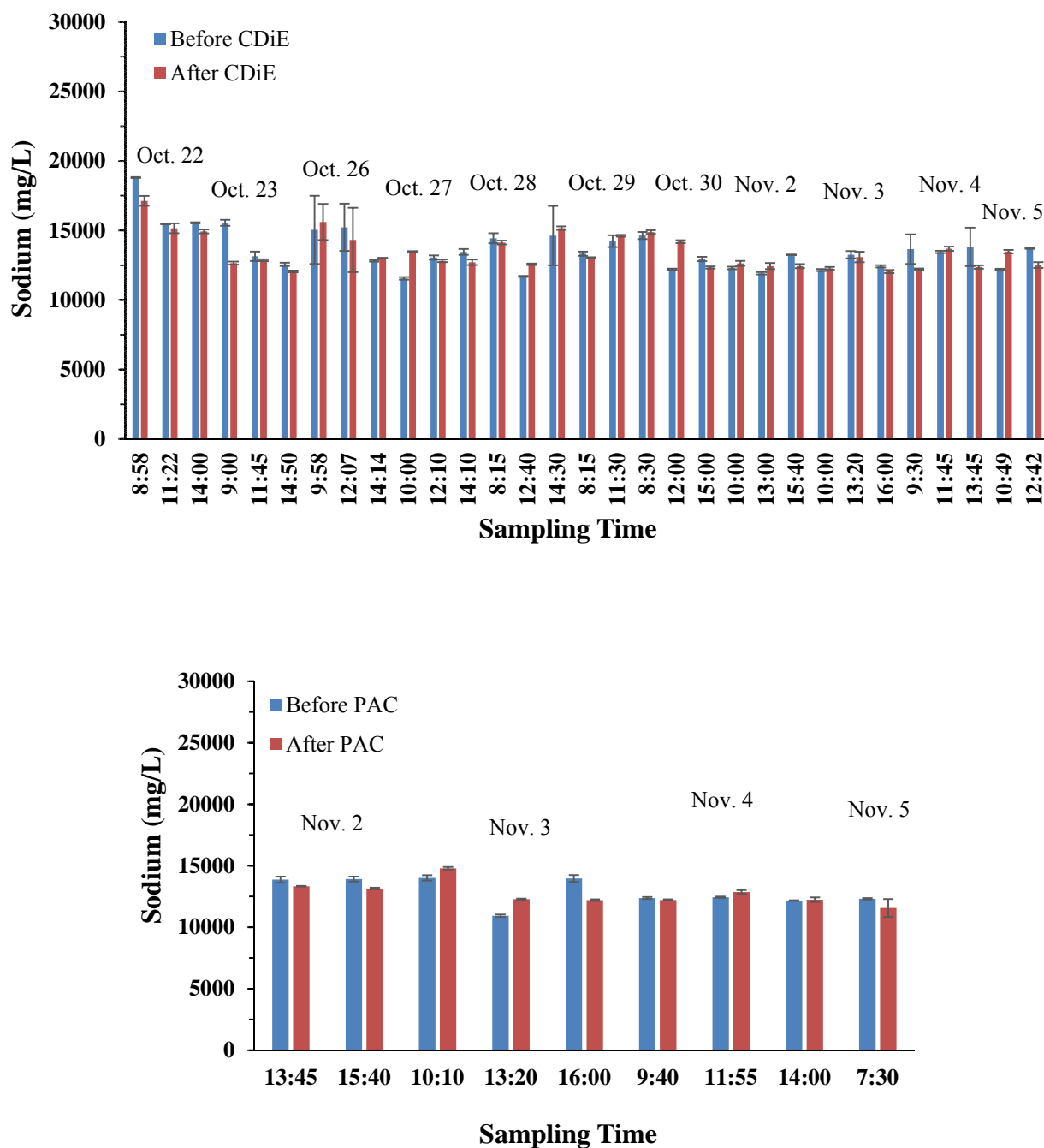


Figure 20: Sodium concentration (a) before and after CDiE , and (b) before and after PAC.

Similar to the sodium ion, Figures 21a and 21b show the measured magnesium concentration was around 1000 mg/L, a relatively stable level of magnesium cation in the collected samples. This indicates that CDiE and PAC filters are incapable of removing magnesium ions in the water samples, which is consistent with the published report demonstrating that activated carbon

filtration will not remove hard water minerals (magnesium and calcium) (Dvorak and Skipton 2013). The Grubbs' test results show that there are no significant outliers ($P>0.05$) of magnesium detected in these samples before and after CDiE and before and after the PAC. Table 4 shows that the concentration of magnesium was statistically the same before and after either of the CDiE or the PAC.

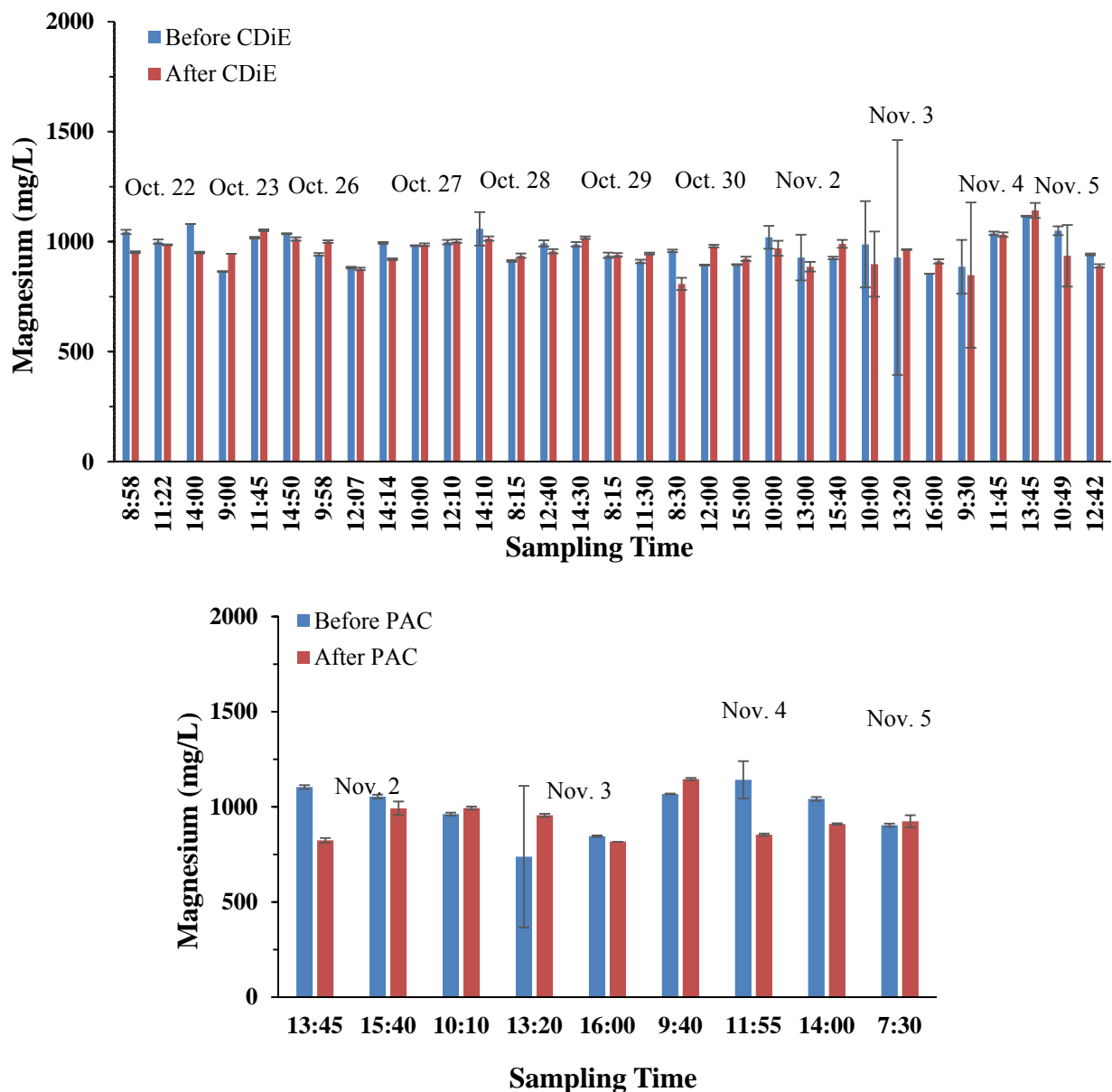


Figure 21: Magnesium concentration (a) before and after CDiE and (b) before and after PAC.

Figures 22a and 22b show calcium concentration in the water samples before and after CDiE and PAC filters, respectively. The measured calcium concentrations were around 400 mg/L. Similar to magnesium concentration, calcium content remained more or less constant due to the

incapability of filtration system in removing calcium cation (Dvorak and Skipton 2013). The Grubbs' test results gave no significant calcium outliers ($P>0.05$) in these samples before and after CDiE and PAC. Table 4 shows that the concentration of calcium was statistically the same before and after either of the CDiE or the PAC.

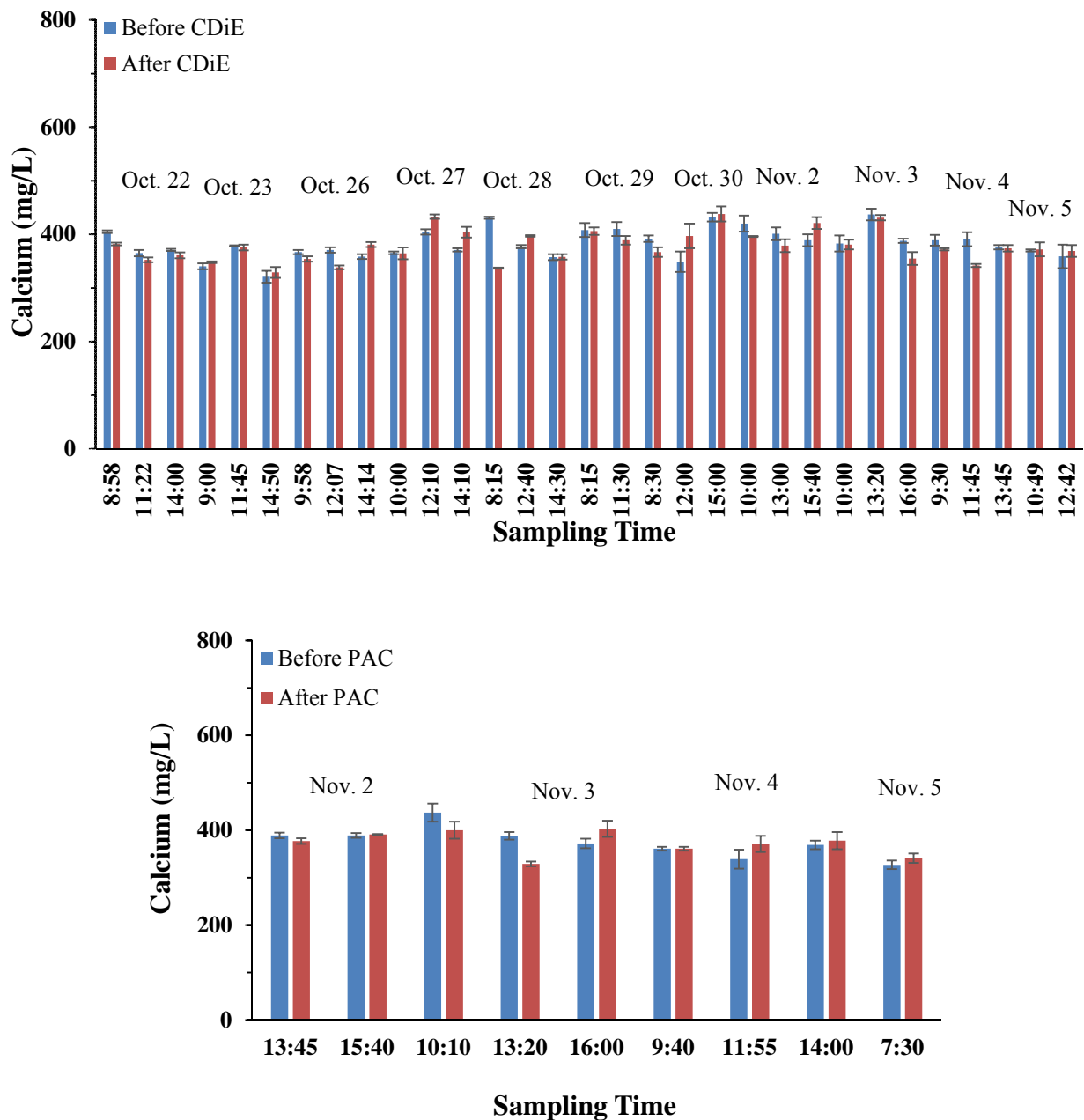


Figure 22: Calcium concentration (a) before and after CDiE and (b) before and after PAC.

Figure 23 show a few percent of decrease in potassium content after a few days of filtration by CDiE filter. However, there is no decreasing trend in potassium concentration in the water samples before and after PAC filters. No outliers were detected by the Grubbs test. Table 4 shows that the concentration of potassium before the CDiE filter was lower than that after it at

the significant level of 0.005. But the concentration of potassium before and after the PAC was statistically the same.

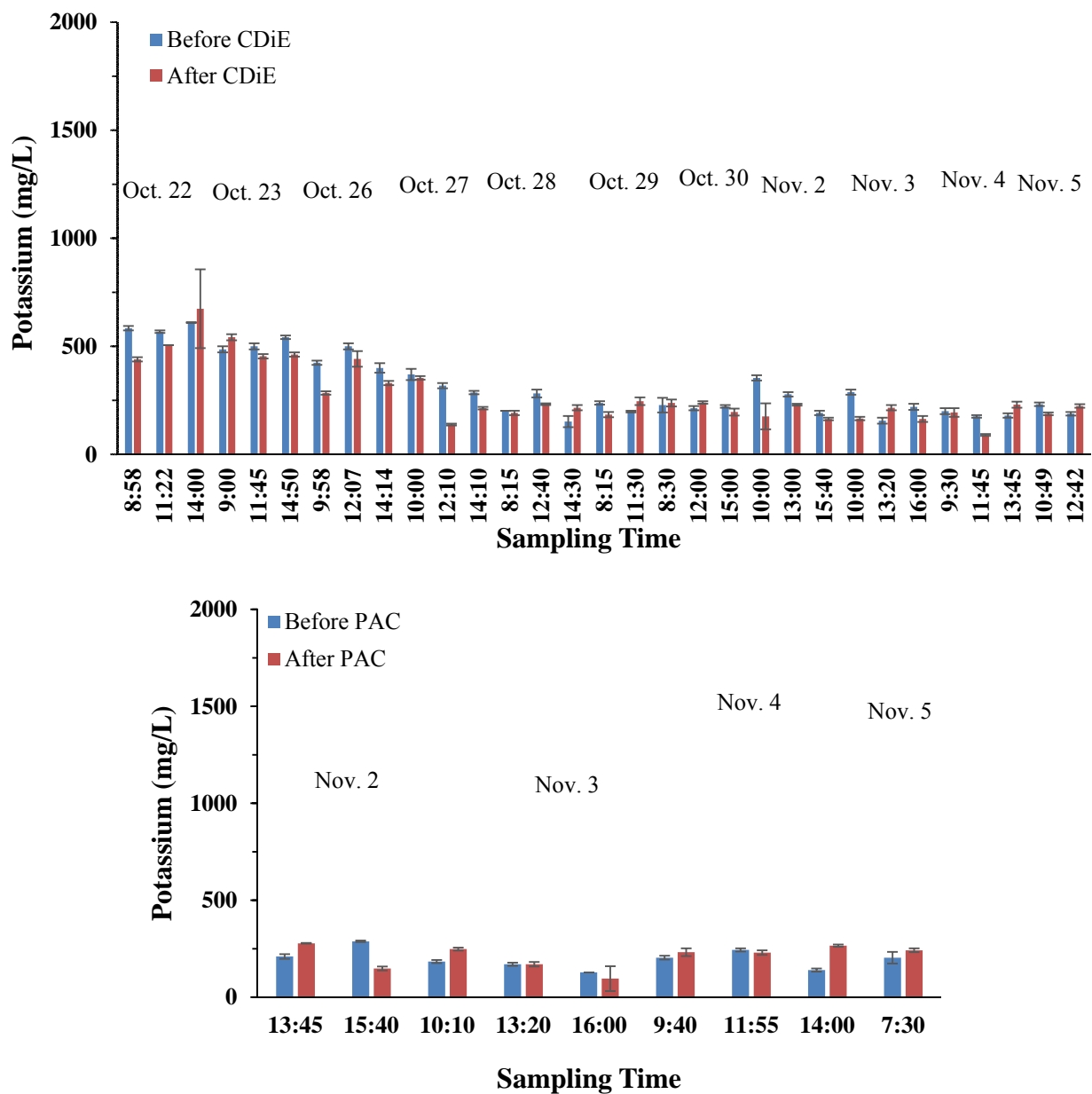


Figure 23: Potassium concentration (a) before and after CDiE and (b) before and after PAC.

Figures 24a and 24b show general declining trends in zinc concentration. In particular, a steady decrease in zinc concentration in the water samples before and after PAC filters was observed, which indicated that the PAC filter played an effective role in removing zinc ion in the water. The typical zinc level contained in sewerage is about 0.005 mg/L (Turekian 1968). Our measured zinc content is more than 5-fold larger than the typical value which is probably because zinc is

used as sacrificial anode in the Ohmsett tank where we collected the samples. The Grubbs' test results for significant outliers show that there are no significant outliers ($P > 0.05$) detected in these samples before and after CDiE and PAC (Figures 24a and 24b). Table 4 shows that the concentration of zinc before the CDiE filter and before the PAC was lower than that after the CDiE filter and the PAC, respectively. The significance level was very high, where p was less than 0.2%. We have considered and ruled out various possibilities for the reduction of zinc and at this level, the source of difference is assumed unknown.

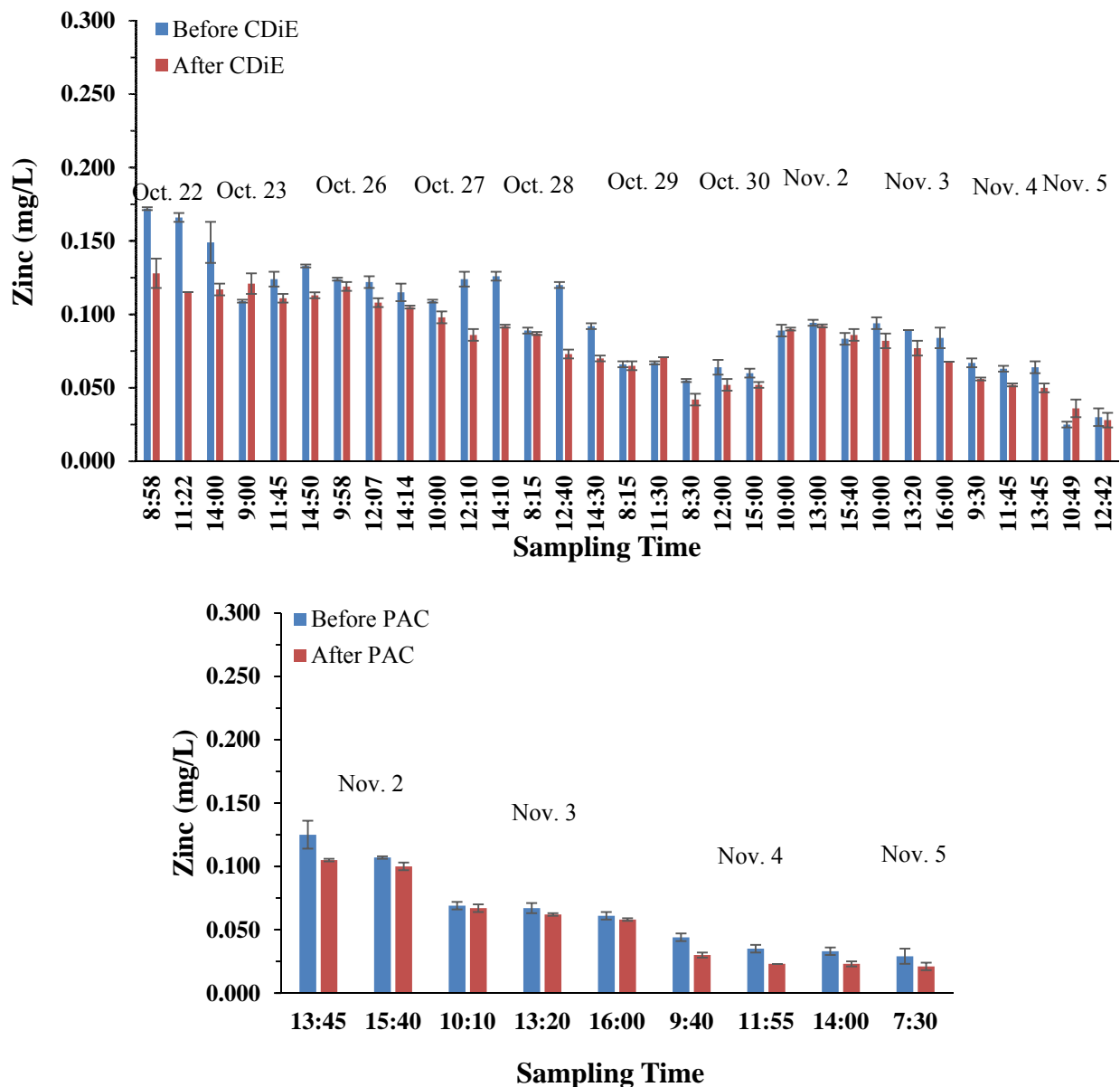
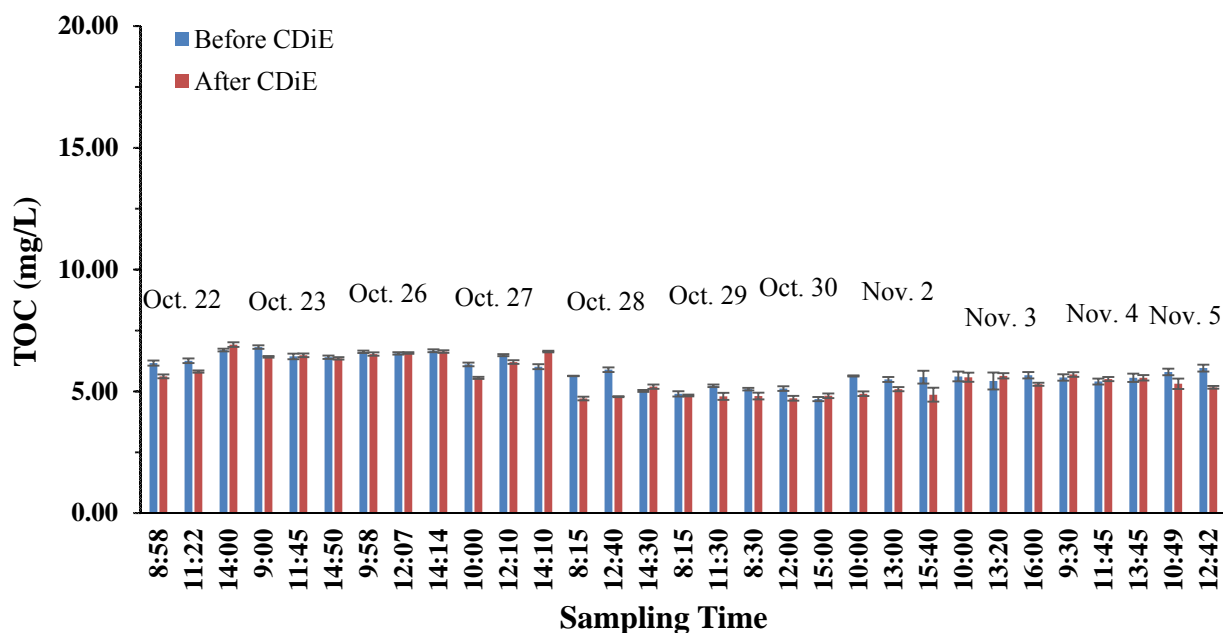


Figure 24: Zinc concentration (a) before and after CDiE and (b) before and after PAC.

Figures 25a and 25b show TOC level in the water samples before and after CDiE and PAC filters, respectively. The TOC level is around 6 mg/L for each sample for a given sampling period. This indicated that both filters are unable to reduce TOC concentration effectively. The Grubbs' test results for significant outliers show that there are no significant outliers ($P>0.05$) detected in these samples before and after CDiE and PAC. Table 4 shows that the concentration of TOC decreased across the CDiE at a significant statistical level indicating that the CDiE removed TOC from the water. However, the concentration of TOC across the PAC remained statistically the same.



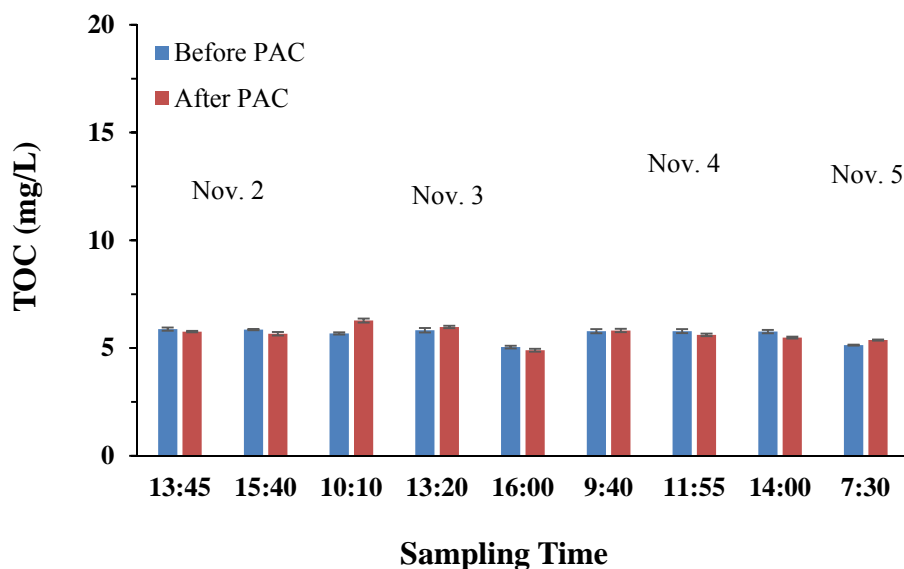


Figure 25: Total organic content (TOC) concentration (a) before and after CDiE, and before and after PAC.

Figure 26 reports surface tension measurements of the Ohmsett tank water as function of time starting October 22nd 2015 through 11/06/2015. The surface tension values varied from an outlier of 53 mN/m to around 75 mN/m. The expected value of no surfactant water is around 73 mN/m, and thus the slight increase is likely due to experimental errors. There were numerous values less than 70 mN/m and these occurred early on, and always before water entered the CDiE filter. The drop in the surface tension on 10/27/2015 could be due to an additional DE test conducted by BSEE in the Ohmsett tank on that day. Measurements of the surface tension (Figure 28) of water following the BSEE DE testing in the Ohmsett tank revealed that the diatomaceous earth (CDiE) filters and the PAC chambers remove surfactants, and cause the surface tension to increase from an average of 69 mN/m to an average of 73 mN/m. The usage of the PAC chambers, which started on 11/03/2015 seems to have “bumped” the surface tension by a point or two. But it seems that the CDiE has performed well on its own (prior to 11/03/2015).

Even with the low values on October 27th due to the DE test in the Ohmsett tank, one notes a trend of increasing surface tension with time as the filtration continues, which suggests that the filtration was removing surfactants from the water. Note that the trend should not be used for extrapolation as the surface tension cannot increase beyond its upper theoretical value of 75 mN/m, the situation with no surfactant in the water.

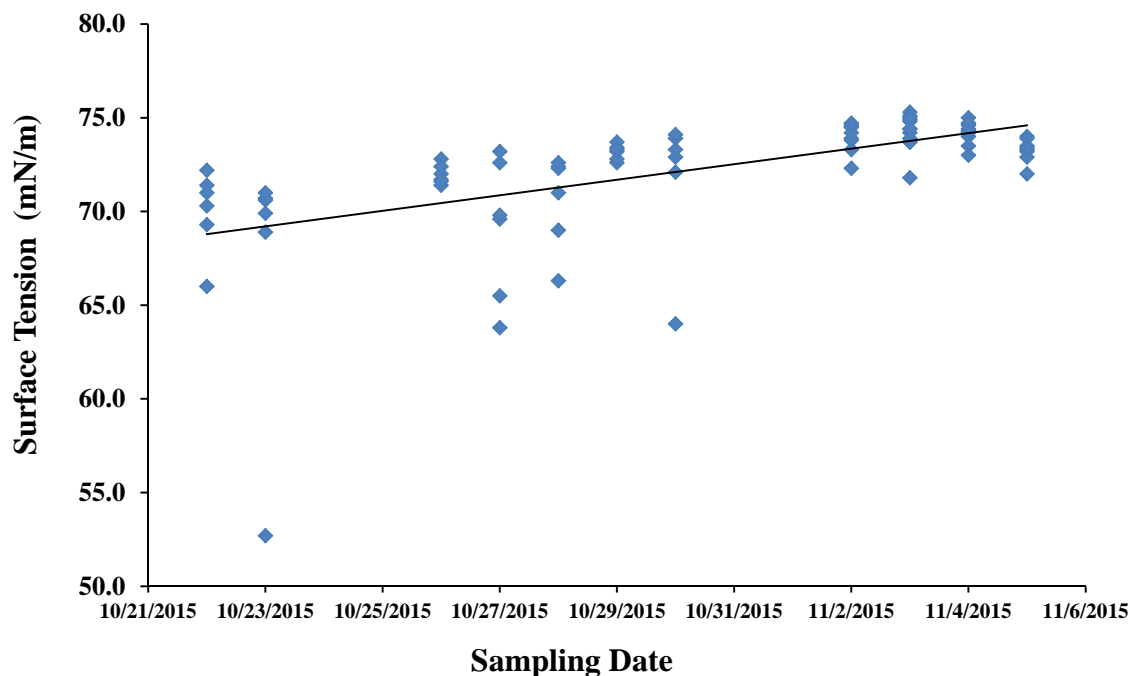


Figure 26: Surface tension (i.e. water-air) measured with time during tank filtration and after the Ohmsett tank dispersion effectiveness (DE) tests were conducted. The samples represent before and after the CDiE and the PAC. A DE test was conducted by the BSEE personnel on 10/27/2015, and was followed by a drop in the surface tension on 10/27/2015 and 10/29/2015.

4.2 Results of Goal 2 (Dispersion Effectiveness)

This goal was addressed during a DE test conducted October 14 through October 22nd (prior to filtration measurements, whose results are reported in Section 4.1.2).

Table 5 provides the physical properties of the oils used in the study at four different temperatures selected to provide a broad characterization of the oils. One notes that the density of HOOPS is slightly smaller than that of ANS; by approximately 5% at the corresponding temperature. However, the viscosity of HOOPS is around 2/3 of that of ANS at the corresponding temperature. Note that the Ohmsett water temperature was around 15°C.

Oil	Temperature (°C)	Density (g/mL)	Viscosity (Kinematic, mm ² /s)
HOOPS crude	15	0.862 ± 0.00014 ^a	12.60 ± 0.25
	25	0.854 ± 0.00011	9.10 ± 0.20
	40	0.844 ± 0.00018	5.98 ± 0.11
	50	0.837 ± 0.00022	4.78 ± 0.13
ANS crude	15	0.879 ± 0.00015	18.97 ± 0.29

	25	0.872 ± 0.00019	13.18 ± 0.22
	40	0.862 ± 0.00016	8.37 ± 0.12
	50	0.855 ± 0.00021	6.46 ± 0.06

Note: ^a Average \pm standard deviation based on replicate measurements for five times

Table 6 provides the oil chemical composition in terms of the four major groups known as SARA (Saturates, Aromatics, Resins, and Asphaltenes). The two oils have essentially the same fraction of aromatics (around 28%). The fractions of saturates and resins in the HOOPS are a few percent larger than those in the ANS. The asphaltenes fraction in the HOOPS is less than 2% while it is around 7% for the ANS. Thus, the major difference between the two oils seems to be the asphaltenes fraction.

Table 6: SARA (Saturates, Aromatics, Resins, and Asphaltenes) composition				
Oil	Saturates	Aromatics	Resins	Asphaltenes
HOOPS crude	34.72 ± 0.96^a	27.41 ± 1.29	36.47 ± 0.33	1.42 ± 0.15
ANS crude	31.77 ± 0.85	28.48 ± 0.95	32.01 ± 0.43	7.73 ± 0.32

Note: ^a Average \pm standard deviation based on replicate measurements for four times

Figure 27 reports HOOPS dispersion effectiveness in the baffled flask with different dispersants using Ohmsett wavetank water and synthetic seawater. Each “trial” in the figure represents a time/day where a DE experiment was conducted in the Ohmsett tank by the BSEE personnel, as reported in Table 2 (The selection of dispersant, time, and date was made random, as communicated to us by Mr. Tim Steffek of BSEE). The average DE values of all trials and the DE results of the BSEE investigation are reported in Table 7 along with their standard deviations. Note that the BSEE investigation in the Ohmsett tank was only with HOOPS.

One notes in Figure Table 7 that Corexit 9500 had the highest overall DE (around 85%). The DE of Accel Clean in Ohmsett water was close to that of Corexit 9500 in Ohmsett, but its DE in synthetic water seems to drop to below 60%. The remaining three dispersants behaved similar to each other in Ohmsett water with a DE of approximately 50%. The DE of Marine D Blue and ZI-400 was only around 30% in synthetic seawater. The DE of all dispersants in synthetic seawater was lower than the DE in Ohmsett water.

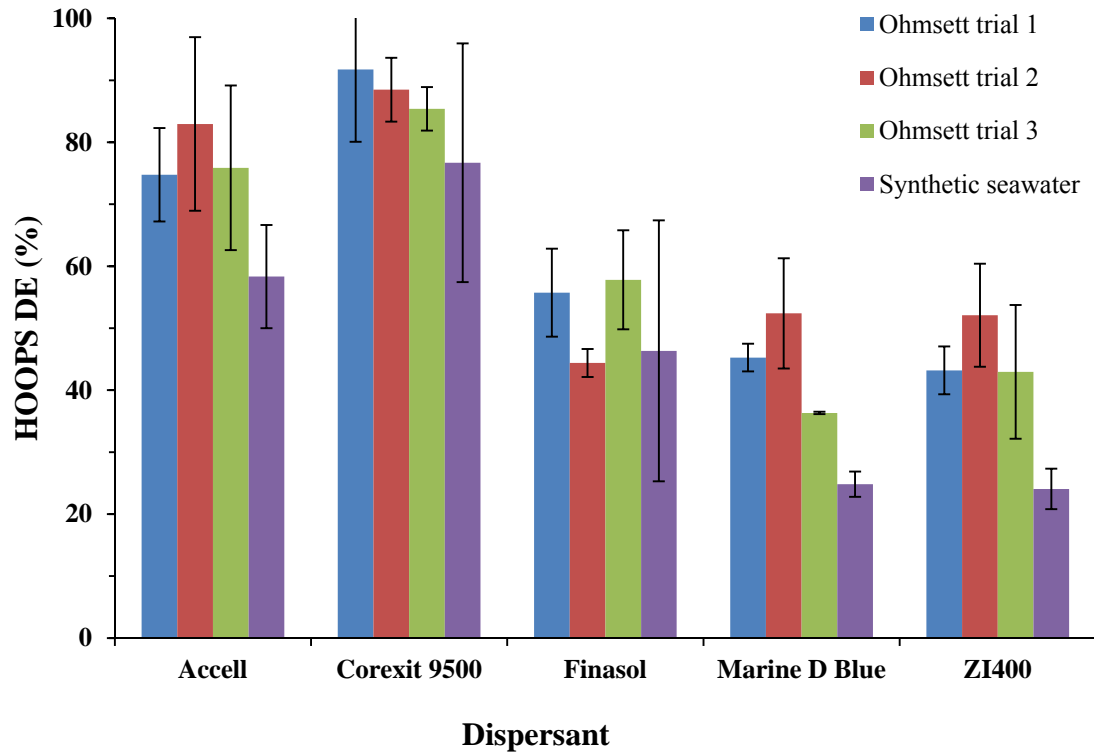


Figure 27: Dispersion effectiveness using the Baffled Flask Test and HOOPS oil for five dispersants. The error bars represent the standard deviation based on triplicate measurements.

Figure 28 reports the DE of the ANS in the baffled flask with different dispersants using Ohmsett wavetank water and synthetic seawater. The averages are reported in Table 7, where one notes that the dispersant Accel Clean performed the best in Ohmsett water with an average DE of 91%. Corexit 9500 was second at around 70%. The DE of the remaining dispersants in Ohmsett water was markedly lower (50% to 40%), and the DE of ANS in synthetic seawater was comparable to its DE in Ohmsett water for all dispersants, except for Marine D Blue, which was 20 points lower in synthetic seawater. Thus, in general the impact of water source (Ohmsett water or synthetic seawater) seems to be less important for the ANS than for the HOOPS. Also, when comparing the BFT results, one notes a larger variability for the DE of ANS in comparison with the DE of HOOPS for both Ohmsett water and synthetic seawater.

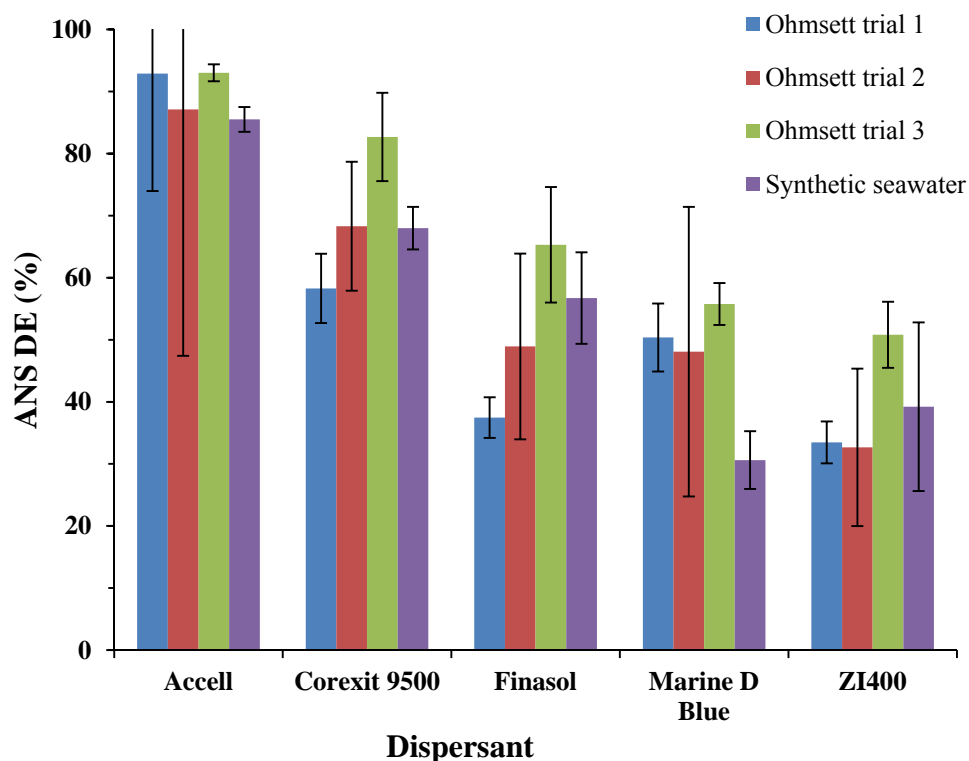


Figure 28: Dispersion effectiveness using the Baffled Flask Test and Alaskan North Slope (ANS) oil for five dispersants. The error bars represent the standard deviation based on triplicate measurements.

Dispersant	Ohmsett Tank DE (%)	Baffled Flask DE (%)			
	HOOPS	HOOPS in Ohmsett water	HOOPS in synthetic seawater	ANS in Ohmsett water	ANS in synthetic seawater
Accell Clean® DWD	87.2 ± 9.1	77.86 ± 4.4 ^a	58.33 ± 8.3	91.00 ± 3.4	85.50 ± 2.0
Corexit® EC9500A	91.7 ± 3.4	88.55 ± 3.2	76.70 ± 19.3	69.75 ± 12.3	67.99 ± 3.4
Finasol OSR 52	95.8 ± 7.3	52.64 ± 7.2	46.34 ± 21.1	50.56 ± 14.0	56.72 ± 7.4
Marine D-blue	73.4 ± 7.7	44.66 ± 8.0	24.83 ± 2.0	51.41 ± 4.0	30.61 ± 4.7
ZI-400	76.9 ± 27.9	46.08 ± 5.2	24.06 ± 3.3	38.98 ± 10.2	39.22 ± 13.6

Figure 29 shows the correlation between the dispersion effectiveness (DE) for HOOPS and all dispersants using the BFT with Ohmsett water and the DE in the Ohmsett tank with HOOPS (only HOOPS was used in the Ohmsett tank). A linear correlation was obtained between the DEs as:

$$\text{DE(BFT, Ohmsett water)} = 0.54 * \text{DE(Ohmsett tank)} + 16 \quad (3)$$

The positive intercept (16%) suggests that at low DE (e.g., due to an ineffective dispersant), the DE of the BFT would be larger than that in the Ohmsett tank, which could be viewed as reflecting the high mixing energy in the baffled flask test in comparison with the Ohmsett tank; the energy dissipation rate in the BFT is around 1.0 watt/kg (Zhao et al. 2015), while it can be estimated at less than at 0.1 watt/kg in the Ohmsett tank under the current breaking conditions.

The slope value of 0.54 (instead of 1.0) is most likely due to the large dilution in the Ohmsett tank which allows the dispersed oil to spread into the water column. Note that if a dispersant is not effective, the effect of dilution is minimal (as the oil remains at the surface), and such is borne out by Eq. 3.

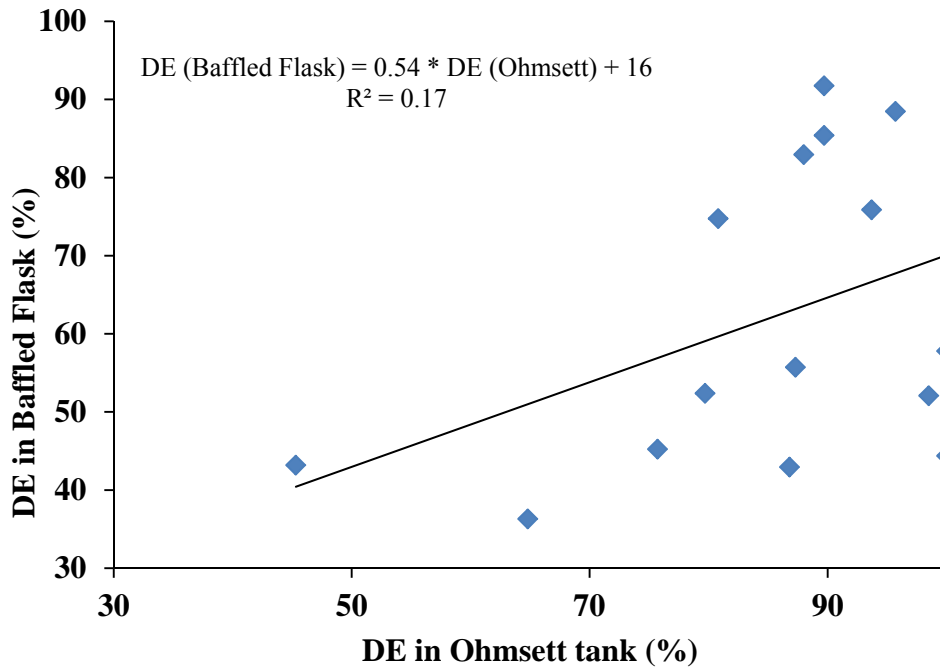


Figure 29: Correlation between the dispersion effectiveness (DE) of the oil HOOPS in the lab (Baffled Flask Test) using Ohmsett water versus the DE in the Ohmsett tank. The R² is small, suggesting that more data are needed.

Figure 30 shows the correlation between the DE in the BFT with synthetic seawater and HOOPS to that in the Ohmsett tank (where only HOOPS was used). A best fit straight line gave the equation:

$$\text{DE}(\text{BFT, synthetic seawater}) = 0.72 * \text{DE}(\text{Ohmsett tank}) - 13.7 \quad (4)$$

The negative intercept suggests that at low DE in the Ohmsett tank, the DE in synthetic seawater would be much smaller (essentially zero, as a negative value is not realistic).

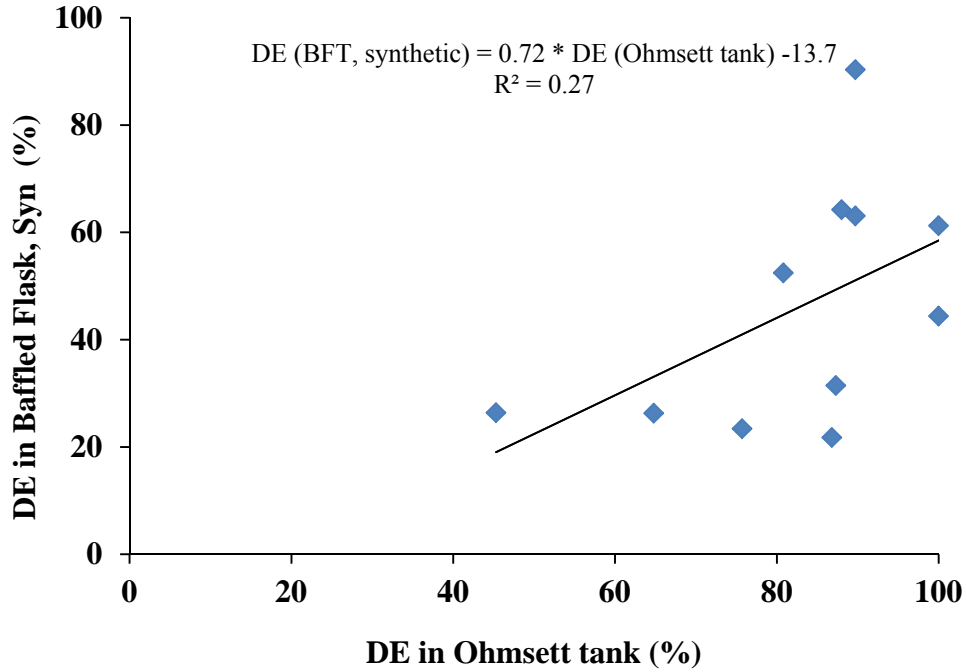


Figure 29: Correlation between the dispersion effectiveness (DE) of the oil HOOPS in the lab (Baffled Flask) using synthetic seawater versus the DE in Ohmsett tank. The R^2 is small, suggesting that more data are needed.

Figure 31 illustrates the correlation between the dispersion effectiveness (DE) using the BFT with synthetic seawater with HOOPS and the DE in the BFT using Ohmsett water with HOOPS. A linear correlation was obtained between the DE and is given by:

$$\text{DE}(\text{BFT, synthetic seawater}) = 0.98 * \text{DE}(\text{BFT, Ohmsett water}) - 13.2 \quad (5)$$

The almost 1.0 slope and the negative intercept suggest a close one-to-one relation between the DEs where that of the synthetic seawater is lower by 13.2%.

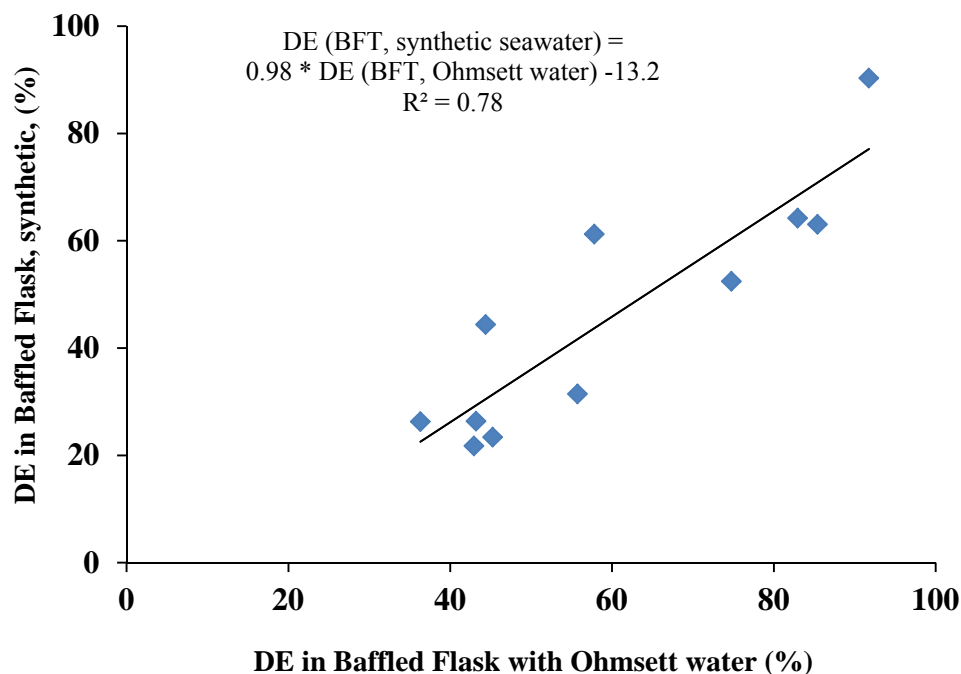


Figure 30: Correlation between the dispersion effectiveness (DE) of the BFT with synthetic seawater and HOOPS and the DE of the BFT using Ohmsett water with HOOPS. Note the relatively high R^2 value.

5.0 SUMMARY, DISCUSSION, AND RECOMMENDATIONS

The study had two main goals: Goal 1- Evaluate the removal efficiency of the CDiE filters and PAC chambers, and Goal 2- Evaluate the impact of the Ohmsett water on the dispersion effectiveness, and compare the DE in the Ohmsett tank to that of the baffled flask test (BFT) using the same Ohmsett water, oil, and dispersant at the same temperature. The oil used in the Ohmsett tank was HOOPS, and BSEE requested similar BFT using Alaskan North Slope (ANS) oil, which is widely used for testing. BSEE also requested additional BFTs using synthetic water and both HOOPS and ANS.

The NJIT team worked closely with the team of Ohmsett and took water samples before and after the diatomaceous earth (CDiE) filter and the powder activated carbon (PAC) filter from April 2nd to April 7th and on October 22nd through November 3rd 2015. The BFT tests were conducted during October 14th through November 15th 2015, practically in parallel to the DE conducted in the Ohmsett tank by the BSEE staff October 14th through October 22nd, 2015.

Goal 1- Evaluate the removal efficiency of the CDiE filters and PAC chambers

Water samples were analyzed for ions, for BTEX, for total organic carbon (TOC), and for surface tension. The removal effectiveness of the filter and PAC is reported in Tables 3 and 4 in

the form of the significance level for different Before and After parameters. (*Tables 3 and 4 are reported again herein due to their importance and for convenience*). The ions were measured before and after the CDiE and before and after the PAC, as it was thought that due to formation of large organic complexes with ions, some of the ions could be trapped on the CDiE filter and/or the PAC. However, such was not the case, and the concentration of ions was in general unaffected by the filtration process. (Note that the level of ions is needed to better interpret the dispersion effectiveness (Goal 2)).

Table 3: p-values for each compound in April 2015 before and after CDiE and before and after the PAC. p-values less than 0.05 indicate that the concentration across the CDiE or the PAC are statistically different. The percent difference is shown within parentheses.

Compound	CDiE	PAC
Chloride	0.48	0.39
Nitrate	0.65	0.21
Sulfate	0.35	0.47
Sodium	0.63	0.064
Magnesium	0.34	0.09
Calcium	0.55	0.12
Potassium	0.15	0.34
Zinc	0.09	0.40
Benzene	0.042 (-29%)	0.59
Toluene	0.16	0.11
Ethylbenzene	0.32	0.035*
Xylene	0.27	0.0026*

As Table 3 indicates, the CDiE filter was effective in removing benzene, and not the remaining BTEX compounds. The results indicate that the PAC actually released ethylbenzene and xylene back into the water on the third and fourth day of sampling. However, the concentration of the BTEX was generally small (less than or equal to 1.0 mg/L) and one cannot ascertain great effectiveness of the CDiE based on these values.

Table 4: p-values for October 2015 measurements before and after CDiE and before and after the PAC. p-values less than 0.05 indicate that the concentration across the CDiE or the PAC are statistically different. Percent difference is reported within parentheses.

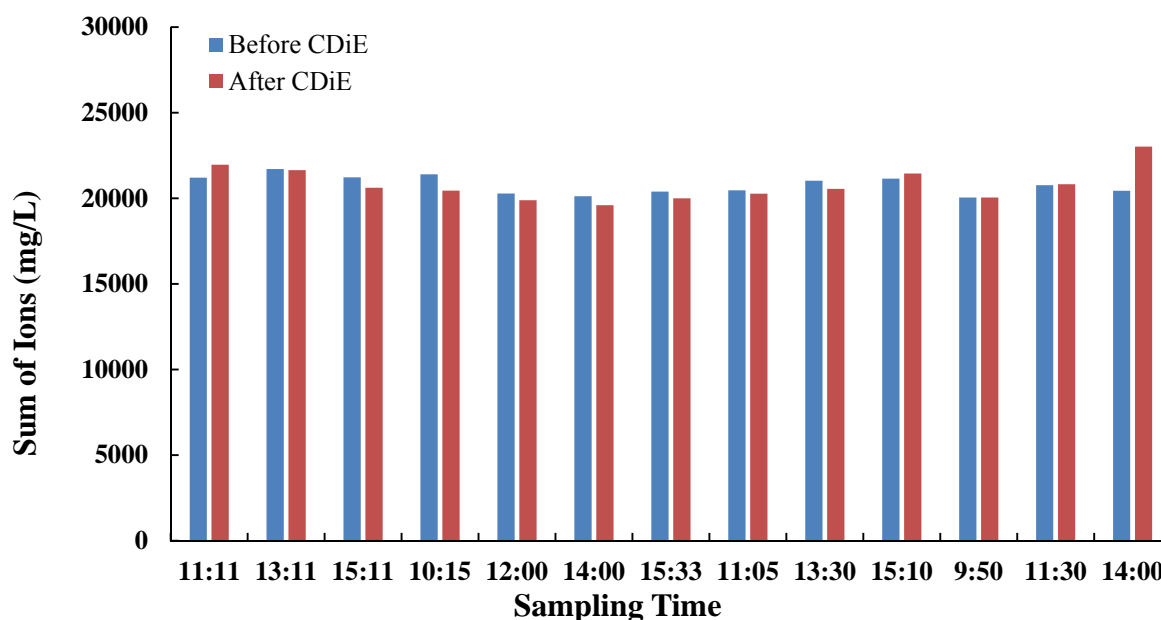
Compound/Parameter	CDiE	PAC
Chloride	0.10	0.93
Nitrate	0.38	0.95
Sulfate	0.30	0.10
Sodium	0.32	0.63
Magnesium	0.26	0.40
Calcium	0.26	0.83

Potassium	0.005 (-12.0%)	0.56
Zinc	<0.001 (-14.4%)	0.002 (-14.2%)
TOC	0.002 (-4.1%)	0.90
Surface Tension	0.038 (+2.2%)	0.68

Table 4 shows that the CDiE was capable of removing the total organic compounds (TOC) from the water at high level of significance. However, the effectiveness of the PAC was not demonstrated at the 5% significance level. The CDiE filter was also able to increase the surface tension of the water with air, and the average increase between before and after was around 2 % at a high significance level. The PAC did not seem to reduce the TOC concentration nor to increase the surface tension.

Goal 2- Evaluate the impact of the Ohmsett water on the dispersion effectiveness, and compare the DE in the Ohmsett tank to that of the baffled flask test (BFT)

The salinity of water was very different in April 2015 in comparison to October 2015; the sum of the ions gave an average of around 20,000 mg/L in April 2015 (Figure 32), and an average of 35,000 mg/L in October 2015 (Figure 33). The difference, however, is not expected to impact the dispersion effectiveness (DE) in the Ohmsett tank as the salinity remains larger than 18,000 mg/L, and thus the effectiveness of dispersants is already at its maximum (NRC 2005).



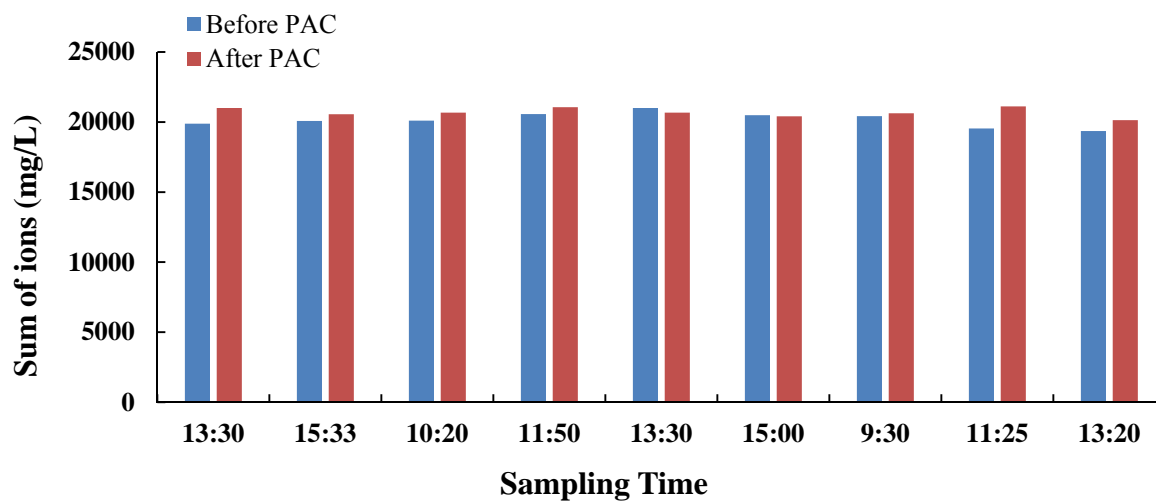
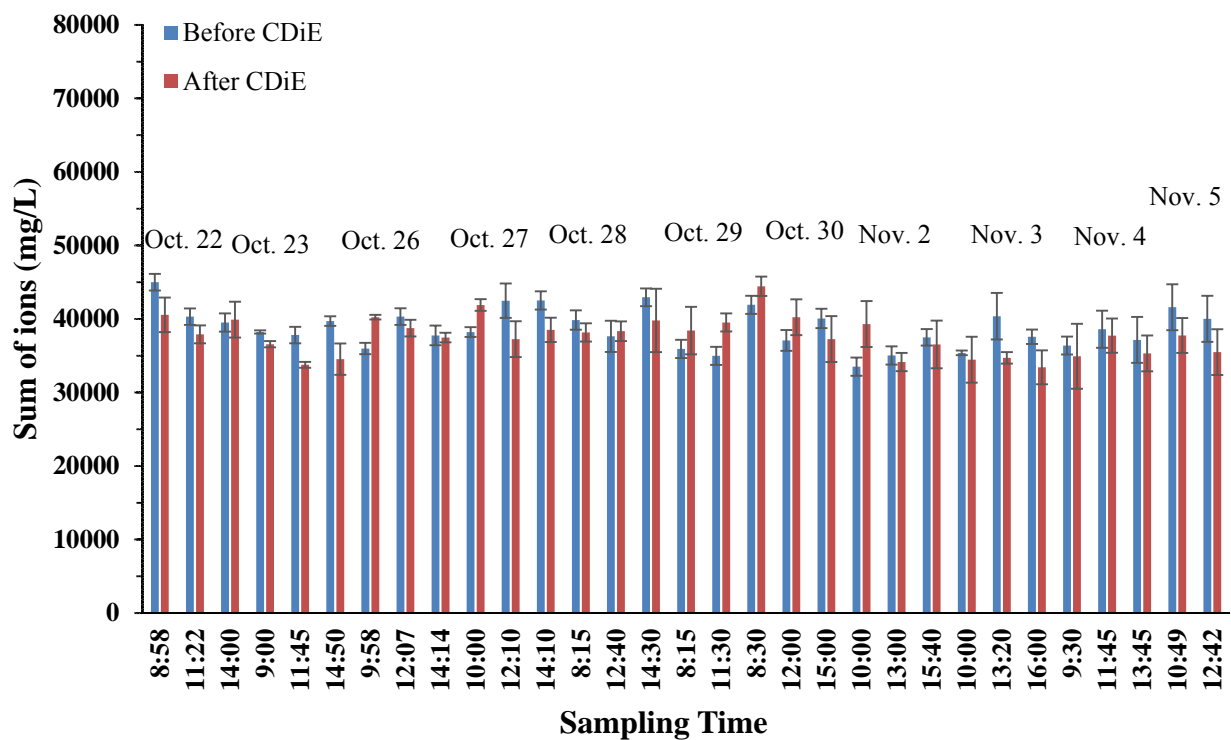


Figure 32: Sum of ion concentration for April samples (a) before and after CDiE, and before and after PAC.



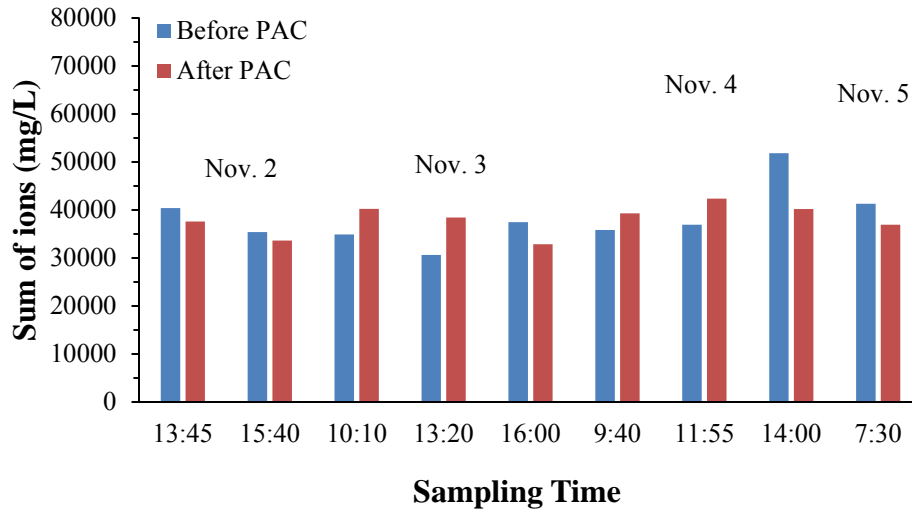


Figure 33: Sum of ion concentrations for October 2015 samples (a) before and after CDiE, and (b) before and after PAC.

However, the composition of the water could impact the DE, as discussed in the Introduction. Table 8 reports the proportion of major ions in the Ohmsett tank during April 2015 and during October 2015 events, along with that in the oceans and in synthetic water. The total salinity (in parts per thousand, ppt) is also reported as found from Figures 32 and 33, for April 2015 and October 2015, respectively. Note that the Ohmsett October 2015 salinity was close to that found in the oceans. Table 8 indicates that the proportion of major ions in synthetic water is very close to that in the oceans, and thus, the two waters (ocean and synthetic) would be considered identical in terms of major ions. The concentrations of chloride and sodium of the Ohmsett water in October 2015 are close to those of the synthetic water. However, those of April 2015 seem to be reversed (40% chloride in Ohmsett water to 55% chloride in synthetic water, and 52% sodium in Ohmsett water to 31% sodium in synthetic water). During both events, the sulfate concentration in the Ohmsett tank is much smaller (1.8 % and 4%) than that reported in synthetic water or the oceans (8%).

The hardness (Ca and Mg) is an important parameter as increases in hardness reduces the effectiveness of dispersants through precipitation. The hardness is defined as:

$$\text{Hardness} = \text{Hardness due to Ca} + \text{Hardness due to Mg} \quad (6)$$

To compute the hardness as mg/L of CaCO_3 , one notes that the equivalent weights of CaCO_3 , Ca, and Mg are 50, 20, and 12, respectively. Thus, the hardness as mg/L of CaCO_3 , is expressed as:

$$\text{Hardness (as mg/L of } \text{CaCO}_3) = C_{\text{Ca}} * \frac{50}{20} + C_{\text{Mg}} * \frac{50}{12} \quad (7)$$

Where C_{Ca} and C_{Mg} are the concentrations of the calcium and magnesium ions in mg/L, respectively.

Converting the percentages of Table 8 to mg/L by multiplying by the salinity (34,000 mg/L or 36,000 mg/L), one obtains the following values. For ocean water, $C_{Ca}=1\%*34,000=340$ mg/L and $C_{Mg}=4\%*34,000=1,360$ mg/L. For April 2015, $C_{Ca}=0.5\%*20,000=100$ mg/L and $C_{Mg}=0.8\%*20,000=160$ mg/L. For October 2015, $C_{Ca}=1\%*36,000=360$ mg/L and $C_{Mg}=2.5\%*36,000=900$ mg/L. Then inputting the values in Eq. 7, one obtains that the water hardness is equal to approximately 6500 mg/L for ocean water, 900 mg/L for Ohmsett water in April 2015, and 4,650 mg/L for Ohmsett water in October 2015. Thus, the hardness of the Ohmsett water in October 2015 is around 70% that of ocean water (or synthetic seawater).

Therefore, the larger DE of HOOPS in the BFT in Ohmsett water in comparison with BFT in synthetic water and for ANS with Marine D-Blue (Table 7) is likely due to the smaller hardness of the Ohmsett water. However, the small hardness does not explain that there was no difference in the DE of ANS between Ohmsett water and synthetic seawater with the remaining dispersants.

Table 8: Proportion of major ions in (%) in seawater and the Ohmsett tank during April and October 2015 events.				
Ion	Ocean Water (34 ppt)	Synthetic Water (35 ppt)	Ohmsett April 2015 (20 ppt)	Ohmsett October 2015 (36 ppt)
Chloride, Cl	55	55.1	41.5 ± 0.6^a	56.3 ± 1.0
Sodium, Na	31	30.8	52.3 ± 1.5	34.8 ± 1.0
Sulfate, SO ₄	8	7.6	1.8 ± 0.1	4.0 ± 0
Calcium, Ca	1	1.1	0.5 ± 0	1 ± 0
Magnesium, Mg	4	3.8	0.8 ± 0	2.5 ± 0.1
Potassium, K	1	1.2	0.3 ± 0	0.7 ± 0.1
Note : ^a Average \pm standard deviation				

The increase in the surface tension of water (with air) following the DE testing period (i.e., after October 22nd, 2015), as shown in Figure 26 suggests that surfactants were present in the water, and thus likely to increase the DE. However, the reduction in the surface tension was, in general, less than 5% of the theoretical value of 75 mN/m, and thus should not be viewed as a major factor affecting the DE in the Ohmsett tank. This is because natural systems (oceans) have natural surfactants in them, and thus, the actual surface tension is always smaller than the theoretical value by a few percents.

When using the Ohmsett water in the BFT, the performance of each dispersant with the two oils (HOOPS and ANS) was comparable; dispersants Accell and Corexit 9500 performed well (70% to 90%), while the remaining dispersant's DE was less than 50% with either oil. The DE was much smaller when using synthetic seawater, and the decrease was largest for HOOPS.

The DE of HOOPS was smaller than that of ANS in the BFT for both Ohmsett and synthetic water. To provide an interpretation of these results, we consider the physical and chemical properties of each oil reported in Tables 5 and 6, respectively. Table 5 shows that there was a decrease in the density of both oils with temperature, and HOOPS is slightly lighter than ANS at the same temperature. The difference in density between the two oils (Table 5) is small (less than

5%), and is not expected to affect dispersion effectiveness, surely not by providing a smaller DE for the lighter oil (i.e., HOOPS). The viscosity of ANS at 15°C was 18 cp which is approximately 1.5 times that of HOOPS (12 cp) at that temperature. But a higher viscosity suggests a lower DE, while the opposite was noted herein. Therefore, the difference in the DE of the two oils could not related directly to their physical properties. But looking at the SARA of both oils in Table 6, one notes that the asphaltenes content in the ANS is around 7% per mass, while it is less than 2% per mass for the HOOPS. As the asphaltenes molecules are large polar molecules and behave as slow surfactants, it is possible that they worked with the added surfactants to increase the dispersion effectiveness (DE).

Recommendations

It is recommended that the usage of the PAC be further evaluated with the intent of discontinuing the usage. This is because the PAC was not found efficient in removing the total organic carbon nor surfactants.

It is recommended to add calcium or magnesium salts to the Ohmsett tank to increase its hardness to a value comparable to that of ocean water of 6500 mg/L as CaCO_3 . This recommendation is based on the fact that the dispersion effectiveness in the baffled flask test using Ohmsett water was larger for HOOPS and for ANS with one dispersant than with synthetic water.

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