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Martin O'Malley, *Governor*
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STATE HIGHWAY ADMINISTRATION

RESEARCH REPORT

EVALUATION OF WASTE CONCRETE ROAD MATERIALS FOR USE IN OYSTER AQUACULTURE

Kelton L. Clark, PH.D.
James G. Hunter, PH.D.
Mark M. Bundy, PH.D.
Dong Hee Kang, PH.D.

MORGAN STATE UNIVERSITY

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16. Abstract

The primary objective of this study was to determine the suitability of recycled concrete aggregate (RCA) from road projects as bottom conditioning material for on-bottom oyster aquaculture in the Chesapeake Bay. The testing was designed to (1) evaluate the impact on water chemistry from the introduction of RCA and (2) evaluate the effect of RCA on the survivorship and growth of oyster spat. The results of this project showed that using RCA as a base material for oyster reefs did not adversely affect oysters spat growth and survival, or the surrounding environment.

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EXECUTIVE SUMMARY

The Maryland State Highway Administration (SHA) has a commitment to maintaining at least 84 percent of the SHA pavement network in acceptable overall condition. The SHA also intends to increase the use of recycled materials and to use products in an environmentally responsible manner. One way of meeting these objectives is by incorporating recycled materials in an environmentally responsible project. As roads and bridges are resurfaced, old concrete is removed and is usually discarded. It would be in the best interest of SHA and the environment if these materials were recycled into an alternative use, such as to condition portions of the Chesapeake Bay bottom to support spat-on-shell aquaculture projects.

Recycled concrete aggregate (RCA) is created by crushing and milling old concrete pavement or road infrastructure. The material is processed and sorted for reuse as base, sub-base, fill material for embankments, and new concrete mix. For RCA to be used within the aquatic setting of the Chesapeake Bay, its chemical behavior under saturated conditions must be understood to avoid potential adverse impacts to the bay's aquatic ecosystem.

The primary objective of this study was to determine the suitability of recycled concrete from road projects as conditioning material for on-bottom oyster aquaculture in the Chesapeake Bay. The testing was designed to

- evaluate the impact on water chemistry from the introduction of RCA
- evaluate the effect of RCA on the survivorship and growth of oyster spat

The results of this project showed that using RCA as a base material for oyster reefs did not adversely affect oyster spat growth and survival, or the surrounding environment. None of the metals leached at a rate that exceeded the Environmental Protection Agency (EPA) drinking water standards. This standard is more stringent than the current EPA total maximum daily loads (TMDLs) for Chesapeake Bay waters. There was no statistical difference between shell and RCA on the growth, survivorship, average length, or recruitment of young oysters. Initial pH was slightly higher for the RCA (8.20 to 8.36) than the oyster shell control (8.0 to 8.2), but pH stabilized to around 7.6 to 7.8 for all treatments after seven days.

Based on the findings of this study, the recommendation is to initiate a second phase that places RCA on test plots in the Chesapeake Bay to validate the laboratory tests in situ.

INTRODUCTION

Objective 5.6 (Recycled Materials Usage) of the SHA 2012-2015 Business Plan, includes strategies to

- "increase contractor recycling of highway construction by-products and waste.
- evaluate opportunities to salvage and recycle concrete, aggregate and rebar from bridge demolition."

One way of meeting these objectives is to recycle materials in an environmentally responsible project. As roads and bridges are resurfaced, old concrete is removed and is usually discarded, which places a burden on society to absorb the waste concrete in landfills or other disposal sites. Instead of discarding this waste concrete, it would be in the best interest of SHA and the environment to recycle it to support spat-on-shell aquaculture projects.

Native oyster populations in the Chesapeake Bay are at less than 1 percent of historic levels due to two protozoan diseases (MSX disease caused by *Haplosporidium nelsoni* and Dermo disease caused by *Perkinsus marinus*), overharvesting, and pollution (CRC, 1999). This tremendous decline in the oyster population has dramatically changed the bay's ecosystem and the oyster industry. Individual oysters filter 4-34 liters of water per hour, removing phytoplankton, sediments, pollutants, and microorganisms from the water column (CERP, 2007). Historic oyster populations of Chesapeake Bay could filter excess nutrients from the estuary's entire water volume every three to four days. Today that would take nearly a year.

The State of Maryland has embraced aquaculture as a mechanism to offset the significant decline in the natural oyster population. Aquaculture places a large number of individual oysters in the bay. After profits are taken, part of the sales of these oysters is used to purchase new baby oysters. The baby oysters are returned to leased beds where they continue to support the industry. During the time spent on the bottom between planting and harvest, the oysters perform the aforementioned critical cleansing function that benefits the bay's ecology.

Spat-on-shell is the most ecologically friendly and the most traditional method of aquaculture. It is also the most common method of oyster restoration. In this method, oyster larvae are placed in a tank with cleaned oyster shells. The larvae set on the shells and metamorphose into juvenile oysters called spat. The shells with spat are then placed on bay bottom, where the oysters grow to adulthood. Spat-on-shell aquaculture requires the creation of oyster reefs. The bottom needs to be built-up with a hard material that will support the shell and prevent it from sinking into soft muddy bottoms (a process known as bottom conditioning). Taller reefs have been shown to provide better growth rates and survivorship than shorter reefs (Kevan et al., 2008).

Historically, old oyster shell was used for conditioning the bay's bottom. However, the decline of the Chesapeake Bay region's oyster resources has led to the scarcity of shells; thus, using them for bottom conditioning is no longer practical. The lack of available oyster shells has required the investigation of alternative materials.

The construction of bridges and highways has been steadily increasing. These facilities need to be repaired or replaced when their service life ends or the original design no longer satisfies the needs due to population or traffic growth. This regular turnover has led to an increase in construction waste. Two billion tons of aggregate are produced each year in the United States. Historically, the most common method of managing this material has been through disposal in landfills. As cost, environmental regulations, and land-use policies for landfills become more restrictive, the need to seek alternative uses of the waste material increases.

The Federal Highway Administration (FHWA) and the U.S. Environmental Protection Agency (EPA) encourage beneficial use of recycled materials, including pavement materials. However, some of these recycled materials may contain toxic substances, such as heavy metals, that could leach when inundated with water, impact neighboring aquifers or streams, and impair ecological health and function. Therefore, the recycled materials' leaching characteristics must be assessed before they are used (Kang et al., 2011). The fate and transport of contaminants depend on the following processes: solubility, desorption/adsorption, diffusion, and advection (Kang et al., 2011).

Recycled concrete aggregate (RCA) is created by crushing and milling old concrete pavement or road infrastructure. The material is processed and sorted for reuse as base, sub-base, fill material for embankments, and new concrete mix. For RCA to be used within the aquatic setting of the Chesapeake Bay, its chemical behavior under saturated conditions must be understood to avoid potential adverse impacts to the bay's aquatic ecosystem. Understanding this behavior will ultimately help determine the suitability of RCA for supporting oyster aquaculture.

Study Objectives

The primary objective of this study is to determine the suitability of recycled concrete from road projects as conditioning material for on-bottom oyster aquaculture in the Chesapeake Bay. Initial testing will evaluate how the introduction of RCA affects water chemistry and evaluate the effect of RCA on the survivorship and growth of oyster spat. The objectives will be met through the completion of the following five tasks.

Task 1: Sequential Extractions Leaching Test: Sequential extraction will provide some initial information on the availability of potentially toxic metals to oysters and the estuarine ecosystem.

Task 2: TCLP (Modified) Leaching Test: EPA test method 1311—toxicity characteristic leaching procedure (TCLP) (USEPA, 2000)—will be used to determine the mobility of organic and inorganic analytes present in the recycled concrete.

Task 3: Tank Leaching Test: EPA preliminary version of method 1315—semi-dynamic tank leaching procedure (USEPA, 2009)—will be used to evaluate mass transfer rates (release rates) and estimate the diffusivity of the RCA.

Task 4: Flow-through-Leaching Test: To simulate the bottom condition in the Patuxent River, average river bottom velocity will be applied as flow rate to the column experiments.

Task 5: Growth and Survivorship: The Chesapeake Bay's bottom habitat will be simulated in flow-through mesocosms.

LITERATURE REVIEW

Oyster populations have experienced an historic decline. To reverse this trend managers have constructed oyster reefs. Restored reefs can enhance habitat function and oyster populations (Coen et al., 1999; Rodney and Paynter, 2006; Luckenbach et al., 2005; Weimin et al., 2012). Reefs are constructed by placing oyster shell on the bottom. One common obstacle to these programs is a lack of oyster shell (MacKenzie, 1989; Breitburg et al., 2000). Various materials have been used as alternative substrate (Brodtmann, 1991). These include clam shell (Nestlerode, 2007), gypsum (Haywood and Soniat, 1992), coal ash (O'Beirn et al., 2000), slate (Haven et al., 1987), shale and tires (Mannet et al., 1990), and most commonly limestone (Chatry et al., 1986; Lenihan and Grobowski, 1998; Soniat et al., 1991; Lavergne and Diagne, 2004; Ippolito, 2010).

While there are often cost differences between oyster shells and alternative materials, the relative performance may mediate the difference. An economic analysis based on preliminary performance and the relative cost of alternative substrates indicated that, though crushed concrete was the most expensive choice, the number of oysters produced per unit substrate made it the most economical choice (LWF, 2004). The price difference between shell and alternative substrate becomes increasingly moot as the shell becomes increasingly scarce.

The expected life-span of oyster shell reef material has been criticized on the basis of natural shell decomposition (Mann and Powell, 2007). Many alternative materials such as granite and concrete have persisted in marine and estuarine environments for decades (Schultze et al., 2008).

Alternative substrates can provide advantages to benthic organisms by providing refuge from predation and increased settlement surface. Interstitial spaces within a habitat are important features that provide refuge from predation and settlement sites for recruits. A number of studies attributed the differences in recruitment and settlement success between substrates to the number and size of interstitial spaces. In one of the earliest studies, Lunz (1958) found that oyster shell that contained large amounts of small fragmented shells had lower recruitment than those less fragmented pieces. O'Beirn et al. (2000) compared coal ash and surf clam shell to oyster shell. They found equal recruitment but lower survivorship on the alternative substrates. The authors noted that the alternatives substrates had much fewer and smaller interstitial then oysters. These smaller spaces would provide equal recruitment sites, but their refuge value would decrease as the oyster grew.

Interstitial spaces can be very large as in the case of riprap. Riprap is unconsolidated stone used to armor shorelines. The size of stones can vary but are usually orders of magnitude larger than oyster shells. In oysters shell reefs, oysters settle and grow up to 3.94 inches (10 cm) within the intestinal spaces (Bartol and Mann, 1999). In samples of concrete and granite riprap, Burke (2010) found oysters and mussels growing to more than 50 cm within the mounds.

Concrete has been used as an alternative substrate as both fabricated structures and unconsolidated recycled material. Fabricated concrete structures are typically commercially available and often trademarked. Fabricated concrete forms provide a three-dimensional structure and are used in small-scale, less than one acre, restoration and in shoreline protection.

In all reported cases, forms have attracted oyster spat and produced viable oyster communities. One form in particular, Reef Balls, has become popular with non-profit restoration activities (Walker, 1988).

Recycled concrete is a "material of opportunity." It results from deconstruction projects such as bridge demolition. Examples of large components include the Alabama roads to reefs program. The program is a partnership between state and local agencies, conservationists groups, and private industry. They have built a number of reefs in Mobile Bay to enhance habitats, with a portion of the reefs set aside for oyster nurseries. They use a variety of concrete material including pipe and block. Virginia constructed a reef system from a mixture of oyster shell reefs, recycled concrete from a deconstructed bridge, and fabricated concrete forms (Burke, 2007).

On their website the Maryland Artificial Reef Program (Maryland DNR Fisheries Service) lists 21 reefs in the Chesapeake Bay. Of these, nine are built wholly or partially with concrete, bridge sections or bridge slabs. The reefs were designed as habitats to enhance local fish populations, with an understanding that there would be benefits to the benthic community. The reefs have been sampled by a number of agencies. Numerous populations of finfish have been identified and they are popular sites for anglers. At many of the sites robust populations of oysters have also been reported. However these reports are from websites or news articles. We could find no published results as relatively few restoration efforts in Maryland were monitored (Kennedy et al. 2011). In perhaps the largest single project, 60,000 tons of material from the replacement of the Woodrow Wilson Bridge was used to build four to five reefs. Over 1300 acres were planted from 2006 to 2008. In another notable project, Maryland built a reef from the deconstruction of Memorial Stadium, the former home of the Baltimore Orioles professional baseball team.

There is some research that shows crushed concrete is a superior cultch compared to crushed limestone and crushed oyster shell (Cirino, 2002). Cirino's work is supported by a study by the Louisiana Department of Wildlife and Fisheries that compared crushed limestone, crushed concrete, and crushed oyster shells as oyster reef materials (Issacs et al., 2004). All materials were crushed to #57 crushed stone, which ranges from about from one half to one inch. Each plot used 66.6 cubic yards of material to produce one-acre plots. Nine plots were planted in the fall of 2000 and sampled in summer of 2002. They found no difference between the sizes of oyster on crushed concrete (34.3 mm) and crushed oyster shell (34.6 mm). Oysters on the limestone were smaller than either of the other substrates (30.5 mm). They found no statistical difference in the number of live oysters on concrete (143.2) and limestone (103.6). However, on average there were fewer live oysters on oyster shells (28.8) than either of the other substrates. Issacs et al. (2004) reported another study in Louisiana that compared crushed concrete to oyster shell. In this study, crushed concrete had higher oyster abundance in the first year, oyster shell had higher oyster abundance in the second year, and concrete had a higher combined abundance. They were not able to report the size of the crushed concrete. An economic analysis based on the preliminary performance and the relative cost of the substrate indicated that, though crushed concrete was the most expensive choice, the number of oysters produced per unit on substrate made it the most economical choice.

RCA is not mentioned in the literature at any other sizes than riprap and #57, but one comment in a USDOT (2004) report stated that Virginia has approved the use of RCA in oyster beds.

METHODOLOGY

This study evaluated the potential leachability of chemicals from RCA. The saturated RCA's water chemistry was evaluated through a sequential extraction, toxicity characteristic leaching procedure (TCLP), tank test (EPA method 1315), and flow-through leaching test. De-ionized water with different salinities was used for the tank test. RCA leaching was also observed using a flow-through column setup to simulate a range of naturally occurring flow conditions with brackish water.

Approximately 5 cubic yards of 2-inch and 4-inch crushed, recycled concrete were collected and used for this project from the P. Flanigan and Sons Inc. facility in Baltimore, Maryland (fig. 1). Additional laboratory recycled concrete material samples were collected from a building demolition site near Morgan State University in Baltimore, Maryland (fig. 2), representing a known, homogenous sample.

The oyster shells used as a control were collected from a stockpile at the Morgan State University Estuarine Research Center (fig. 3). Prior to testing, the shells were washed to remove surface debris.

The study was conducted at the Morgan State University Estuarine Research Center. The center is located in St. Leonard, Maryland, on the Patuxent River, a sub-estuary of the Chesapeake Bay. The seawater used in the experiments was drawn 200 meters off shore. The center's facilities include an oyster hatchery, setting tanks, and 10-acre oyster lease. The waters surrounding the center contain state managed and private oysters bars.

Figure 1. Recycled concrete material samples collected from the P. Flanigan and Sons Inc., facility in Baltimore, MD

Figure 2. Recycled concrete material samples collected from a building demolition site near Morgan State University in Baltimore, MD

Figure 3. Oyster shell washing

The resulting water chemistry from the following leaching tests (tasks 1 to 5) was used to evaluate acute and chronic water quality necessary for protecting marine and estuarine life. Water samples collected for tasks 1 to 4 were measured for inorganic constituents, pH, alkalinity, conductivity, chloride, oxidation-reduction potential (ORP), nitrate, salinity, and total dissolved solids (TDS). For analysis of metals, collected water samples were filtered using 0.45 µm borosilicate glass fiber filters, acidified (pH<2) with 0.2 mL of nitric acid, and then stored at 4°C. Inorganic chemicals in the acidified samples were analyzed using a PerkinElmer ELAN 6100 inductively coupled plasma mass spectrometry (ICP-MS). The pH and total alkalinity were measured with an Orion9107BN pH meter. Forston Labs, based in California, provided the standard solutions used in this project. Conductivity, chloride, ORP, nitrate, salinity, and TDS were measured with a Forston Labs LabNavigator, a multiparameter instrument. The inorganic chemicals analyzed were aluminum, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, and zinc.

Figure 4. PerkinElmer ELAN 6100 inductively coupled plasma mass spectrometry (ICP-MS)

Task 1: Sequential Extractions Leaching Test

Sequential extraction is useful to indirectly assess the potential mobility and bioavailability of heavy metals (Ma and Lao, 1997). Sequential extraction provides some initial information on the availability of potentially toxic metals to oysters and the estuarine ecosystem. The sequential extraction method (Silveira et al., 2006) utilizes a series of agitated extractions, in which increasingly aggressive leaching fluids are used to investigate the leaching behavior of metals from the RCA. The chemical fraction of heavy metals leaching from recycled concrete can possibly pollute water where RCA is applied as a bottom material. Heavy metals—such as arsenic, beryllium, cadmium, chromium, copper, lead, mercury, selenium, and thallium—can be potential pollutants of concern at elevated concentrations. Heavy metal distribution among specific forms varies widely based on the metal's chemical properties. Evaluating the leachability of heavy metals from recycled concrete is important to understanding behavior and fate of those heavy metal contaminants. The five chemical fractions are defined by an extraction sequence that follows the order of decreasing solubility (Tessier et al., 1979): exchangeable elements > element bounded to carbonates > element bounded to iron > elements bounded to organic matter > residual.

Each extraction procedure was performed using four replicates of 1 g ground, air-dried RCA samples and extracting solutions. For each test, the solution and solid phases were separated by centrifugation at 10,000 rpm for 10 minutes. The solution was filtered through a 0.45µm filter and the solid residues were preserved for the subsequent extractions. ICP-MS determined the concentrations of the following metals: aluminum, arsenic, barium, beryllium, cadmium, chromium, copper, lead, manganese, mercury, selenium, thallium, and zinc. Exchangeable elements were extracted at room temperature with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation for 1 hour. The elements bounded to carbonates were extracted using the residue from fraction 1. The residue was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained. Lead carbonate prior to the experimental trials determined that 3 hours were necessary for complete extraction. The elements bounded to iron were extracted using the residue from fraction 2. The residue from fraction 2 was extracted with 20 mL of 0.04 M $NH_2OH \cdot HCl$ in 25 percent (v/v) HOAc. This fraction experiment was performed at 96 ± 3 °C with occasional agitation for 6 hours. The next extraction consisted of the elements bounded to organic matter. Twenty milliliters of 7 M NaOCl (adjusted to pH 8.5 with HCl) were added to the residue from fraction 3, and the mixture was heated to 90 ± 2 °C for 2 hours with occasional agitation. After centrifugation, a second 20 mL aliquot of NaOCl (adjusted to pH 8.5 with HCl) was added and the sample was heated again to 90 ± 2 °C for 2 hours with intermittent agitation. The final step was extraction of residual elements. The residue from fraction 4 was digested through the aqua regia method with a mixture of concentrated HNO_3 and HCl in a 1 to 3 ratio.

Task 2: Toxicity Characteristic Leaching Procedure (TCLP)

TCLP is designed to determine the mobility of analytes present in liquid, solid, and multiphasic wastes. The use of recycled concrete requires this type of evaluation to determine the potential leachability of RCA. EPA's TCLP (USEPA, 2000) was used to determine the mobility of inorganic analytes present in the RCA. The RCA was crushed to smaller than 9.5 mm and added to an acid extractant (acetate buffer) at a solid to liquid ratio of 1:20 by mass in 250 mL Polytetrafluoroethylene (PTFE) bottles. Extractions were carried out in triplicate. An agitation apparatus rotated the extraction vessels continuously (at 30 rpm) for 18 hours. Analysis of the samples was performed in triplicate. After mixing, the suspension was filtered with a borosilicate glass fiber filter (0.45 µm) and the filtrate was collected in 50 mL centrifuge tubes and stored at $4^{o}C$ until chemical analysis. The laboratory followed a strict quality assurance and quality control protocol. Heavy metal concentrations in the leachate were measured using ICP-MS.

Task 3: Tank Leaching Test

EPA preliminary version of method 1315— semi-dynamic tank leaching procedure (USEPA, 2009)—was used to evaluate mass transfer rates (release rates) and estimate the diffusivity of the RCA. The method consists of tank leaching of recycled concrete with periodic renewal of the three different salinity solutions. Varying salinities of de-ionized water were used as eluent in the RCA-filled tanks. The water's salinity was achieved with Instant Ocean sea salt. Leachate was withdrawn and analyzed. RCA was subjected to leaching in a closed tank using an eluent to RCA volume ratio (L/V) of 5. Approximately 500 g of recycled concrete, 400 g of recycle concrete with 100 g of oyster shell, and 500 g of oyster shell were placed into 1 L PVC cylinders. One liter of eluent was added to PVC cylinders and changed at six intervals. RCA and oyster shell were used together to simulate the field conditions. Pure oyster shells were used as a control. The eluent was renewed after 2, 27, 42, 121, 360, and 504 hours. The tank leaching test assessed the potential and speed of leaching of the recycled concrete over the long term. Triplicates of each treatment were run. Half of the collected water samples were measured for pH, alkalinity, conductivity, chloride, ORP, nitrate, salinity, and TDS. The other half of the collected water samples were filtered using borosilicate glass fiber filters, acidified (pH<2) with 0.2 mL of nitric acid, and then stored at 4^0C until analysis with ICP-MS.

Figure 5. Tank leaching test

Task 4: Flow-through-leaching Test

Two flow regimes, which were based on the river velocity's seasonal minimum (13 cm^3/sec in August) and maximum (30 cm^3/s in March), were applied. This report refers to the seasonal minimum as the slow flow, and the seasonal maximum as the fast flow. To simulate the bottom condition in the Patuxent River, two river bottom velocities (maximum and minimum) were applied as the flow rate to the column experiments. The column experiments were used to evaluate material size's and water flow rate's effects on chemical concentrations leaching from RCA. The column effluent was measured for pH, alkalinity, conductivity, chloride, salinity, TDS, and organic and inorganic constituents. Ambient Patuxent River water was used for the column experiment to infer recycled concrete performance under specific environmental conditions. Approximately 47 kg of RCA with 3 kg of oyster shell, and pure oyster shell were placed in each column. The columns were made of 15.2 cm diameter and 86.4 cm long white PVC tubes. The column design consisted of two sections. The upper section was filled with the materials. The top of each column had an outlet (5 cm in diameter). The lower section had a screen that prevented sidewall flow when river water was added. The columns were vertically placed on a stand. At each column's base was an inlet (2.5 cm in diameter) connected to a brackish water supply system that was directly connected to the Patuxent River.

Figure 6. Column experiment

In total, twelve columns used in this study: two RCA with fast flow, two RCA with slow flow, two RCA and oyster shell with fast flow, two RCA and oyster shell with slow flow, one oyster shell with fast flow, one oyster shell with slow flow, and two controls. The brackish water was kept flowing by flow controller with water pump, and water samples were collected at 0, 1, 6, 21, 28, 139, 288, 508, and 1016 hours. Half of the collected water samples were measured for pH, alkalinity, conductivity, chloride, ORP, nitrate, salinity, and TDS. The other half of the samples was filtered with borosilicate glass fiber filters, acidified (pH<2) with 0.2 mL of nitric acid, and stored at 4^0C until analysis with ICP-MS.

Task 5: Oyster Growth and Survivorship

The growth and survival experiments were conducted in four flow-through fiberglass tanks that measured 178 x 91 x 25 cm. Stand pipes, cut to 19 cm, were placed in each tank to keep the water level consistent at 19 cm throughout the experiment. Patuxent River ambient seawater was used. Flow was maintained at minimum flow rates for the Patuxent River. Two of the tanks contained shell and two contained shell and rubble. The material was stacked in 60 x 60 x 16 cm piles in the center of each tank. Each tank contained 75,708 cubic cm (20 gallons). In the shell and rubble tanks, the rubble was covered with a layer of shell at a ratio of 3:1. Ambient Patuxent River water was allowed to flow over the materials for two days prior to the spat planting.

Oyster spat were acquired from the State of Maryland Hatchery at Piney Point. The spat are part of the aquaculture oysters annually supplied to the Calvert County Watermen's Association. Larvae were spawned from locally collected oysters and set on oyster shell. To simulate the 1 million spat per acre required by Maryland Department of Natural Resources for oyster aquaculture, 140 spat were placed in each tank. Each shell was numbered, and the number and length of each spat was measured and recorded. Shells were arranged into two lines on top of the materials already in the tank. One line had shells face up and the other had shells face down. Length and survivorship were recorded. The pH, salinity, dissolved oxygen, and temperature were checked regularly using a Yellow Springs Instrument Professional Plus multiparameter meter. The experiment was run twice in 2011, once in the beginning of the spawning season (July-August) and again later in the season (September-October). Growth was analyzed as average length with a two-way ANOVA: treatment (rubble, shell) and season (summer, fall). Survivorship was analyzed with a three-way ANOVA on arcsin transformed percent survivorship.

RESULTS AND DISCUSSION

Task 1: Sequential Extractions Leaching Test

The high concentration elements (13 to 47 mg/Kg) found in the RCA were chromium, copper, arsenic, selenium, and lead. The low concentration elements (0.06 to 0.6 mg/kg) found in the RCA were beryllium, cadmium, mercury, and thallium (fig. 7 and 8). The highest total concentration in recycled concrete was chromium (47.1 mg/kg). In addition, chromium was highly concentrated in the residual fraction (13 mg/kg) and present in other fractions (fig. 7). The percentage of residual chromium in the total chromium was 28.3 percent. The residual fraction of copper (29.7 percent) was similar to that of chromium. The greatest percentage in the residual fraction was arsenic (69.8 percent). This reflects that arsenic will have a greater tendency to become unavailable. However, the exchangeable percentages of arsenic and cadmium were higher (6 to 8. 2 percent) than the other elements (0 to 0.8). The order of total concentration in recycled concrete was as follows: chromium (Cr) > lead (Pb) > copper (Cu) > selenium (Se) > arsenic (Ar) > beryllium (Be) > mercury (Hg) > cadmium (Cd) > thallium (Tl). The highest percentage element bounded to carbonates was cadmium (21.4 percent). The highest percentage element bounded to iron was beryllium (66.4 percent). The highest percentage element bounded to organic matter was mercury (99.6 percent) (fig. 9).

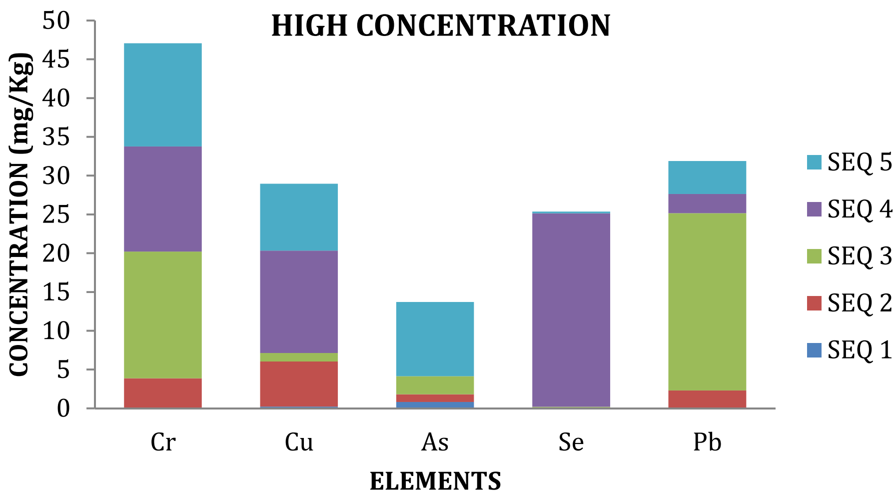


Figure 7. High concentration elements in recycled concrete

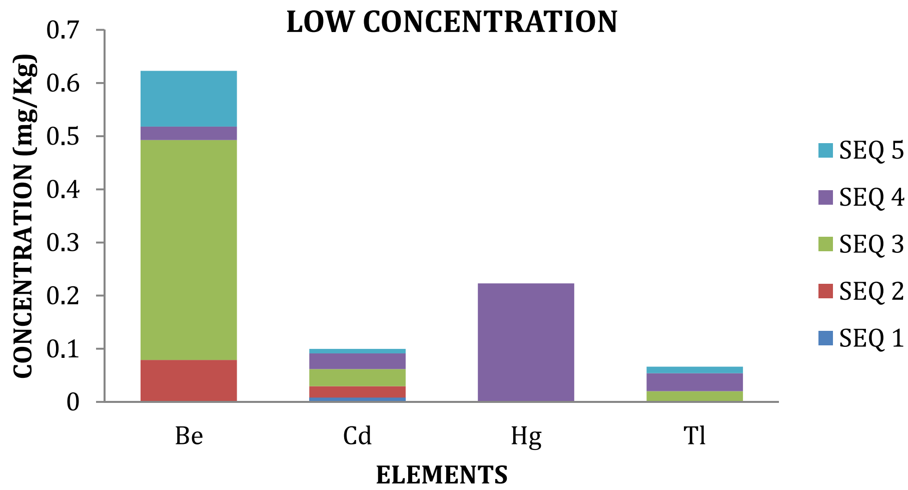


Figure 8. High concentration elements in recycled concrete

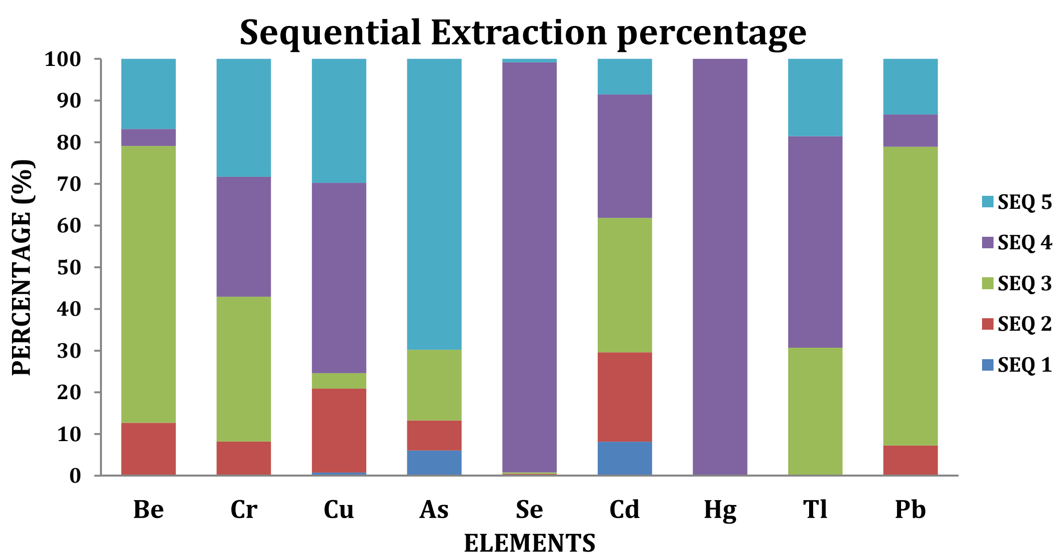


Figure 9. Sequential extraction percentage of elements in recycled concrete

Task 2: Toxicity Characteristic Leaching Procedure (TCLP)

Manganese and barium leached at higher concentrations (1.35 mg/L and 0.71 mg/L, respectively) than the other observed elements. Beryllium, mercury, and thallium were not released. The EPA regulates and has set maximum concentration arsenic (5 mg/L), barium (100 mg/L), cadmium (1 mg/L) chromium (5 mg/L), lead (5 mg/L), mercury (0.2 mg/L), and selenium (1 mg/L). Based on the TCLP results, none of the leached elements were higher than the maximum concentration of contaminants for toxicity characteristics (table 1).

Table 1. Toxicity characteristic leaching procedure (TCLP) results

	Average	Stdev
μg/L		
Al	24.02	3.59
As	3.68	0.79
Ba	710.04	37.69
Be	0	0
Cd	0.21	0.15
Cr	40.98	8.37
Cu	23.76	5.07
Hg	0	0
Mn	1353.24	67.37
Pb	2.5	1.89
Se	33.95	2.11
Tl	0	0
Zn	173.4	57.43

Task 3: Tank Leaching Test

The cumulative leached element concentrations were plotted as a function of cumulative time. The cumulative aluminum concentration (0.79 mg/kg) of RCA in low salinity was higher than RCA in high salinity (0.49 mg/kg) and RCA in de-ionized water (0.57 mg/kg). The cumulative concentration from the RCA-oyster shell treatment was 0.07 mg/Kg in high salinity, 0.14 mg/kg in low salinity, and 0.51 mg/kg in de-ionized water. The average cumulative concentration of the RCA-oyster shell treatment was higher than the oyster shell treatment and lower than the RCA treatment. The cumulative concentration of leached aluminum in the oyster shell treatment decreased with increasing salinity. It was highest in de-ionized water (0.05 mg/kg), lower in low salinity (0.21 mg/kg) and lowest in high salinity (0.16 mg/kg). In general, the RCA and RCA-oyster shell treatments released a higher aluminum concentration than the oyster shell treatment (fig. 10). RCA in low salinity had the highest cumulative concentration of chromium (0.017 mg/kg). As shown in figure 11, the low and high salinities had a higher cumulative chromium concentration (0.009 to 0.017 mg/kg) than the de-ionized water application (0.001 to 0.006 mg/kg). Beryllium and thallium were not released from any treatments based on the salinities' difference. For manganese, copper, arsenic, and selenium the cumulative concentrations also decreased with increasing salinity (fig. 12-fig. 16.) The cumulative concentrations of manganese, copper, arsenic, and selenium did not exceed 1 mg/kg in any treatment, with the exception of selenium. Selenium concentration was 1.1 mg/kg in high salinity on oyster shells (fig. 12 - fig. 16). The highest concentrations of arsenic occurred in RCA-oyster shell (0.16 mg/kg) and oyster shell (0.15 mg/kg) in high salinity (fig. 14). The cumulative concentrations of barium did not follow the same inverse relationship with salinity. While the de-ionized treatment had the highest cumulative concentration, the lowest concentrations were in the low salinity treatments (fig. 16).

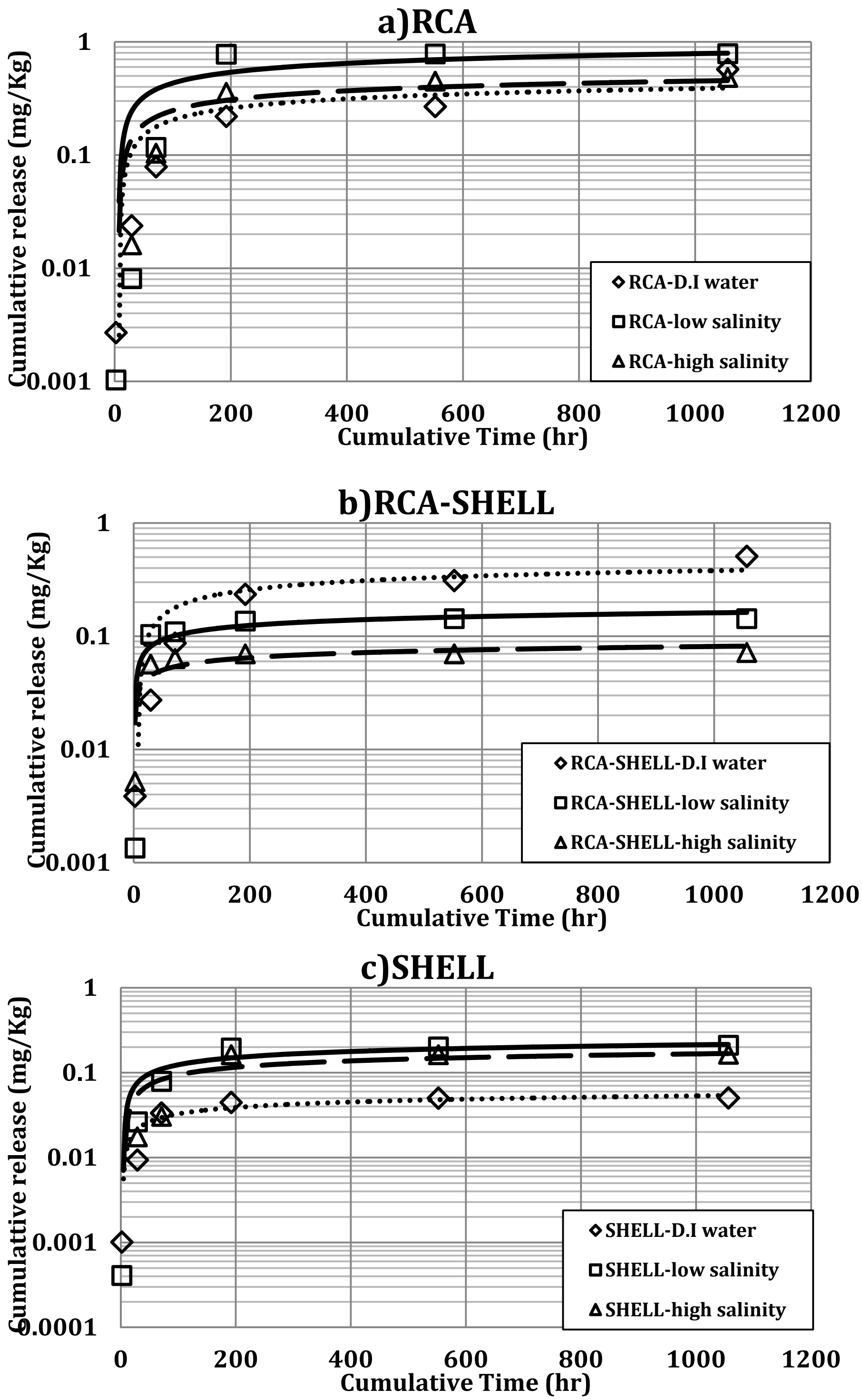


Figure 10. Cumulative aluminum release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

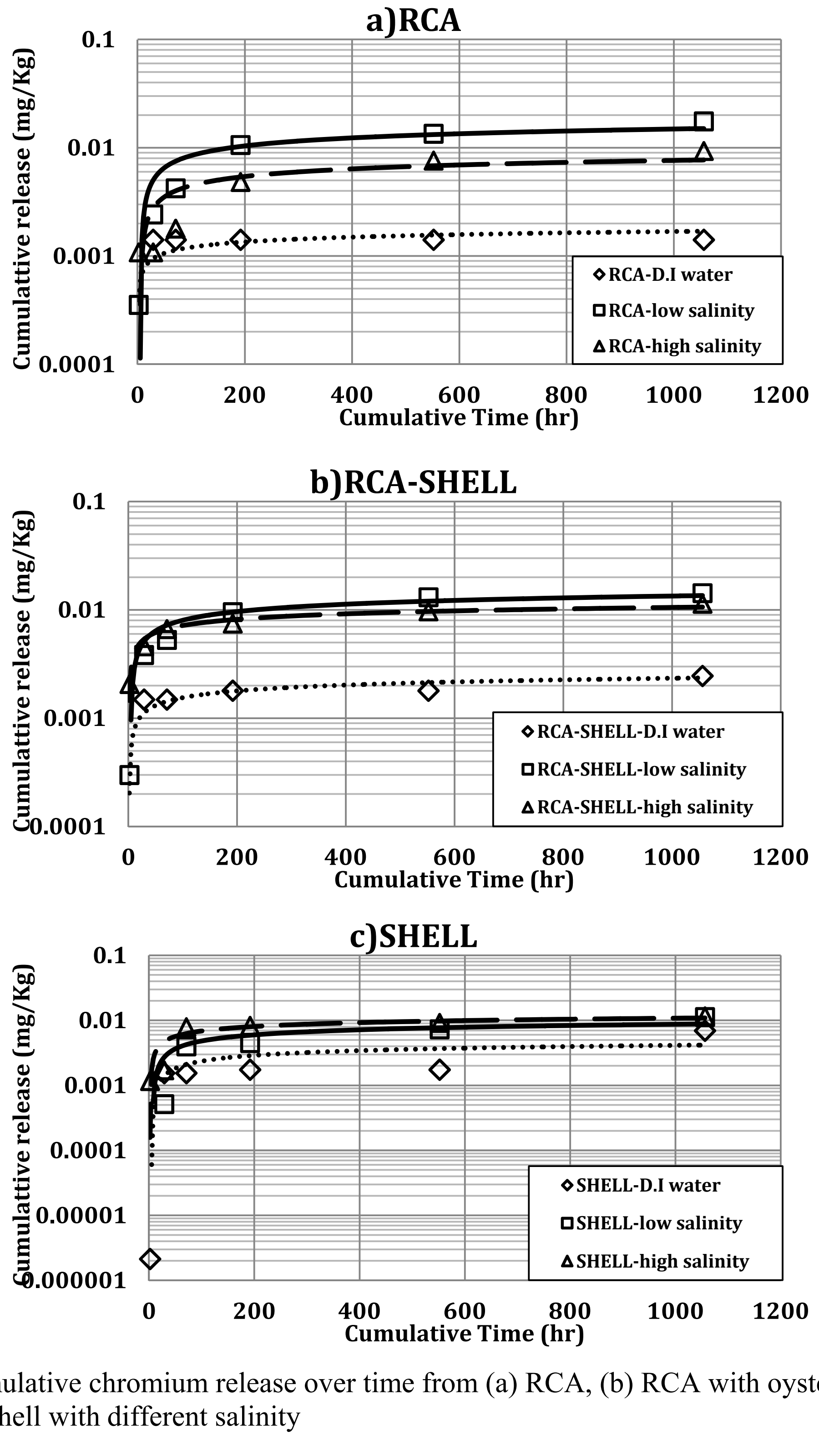


Figure 11. Cumulative chromium release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

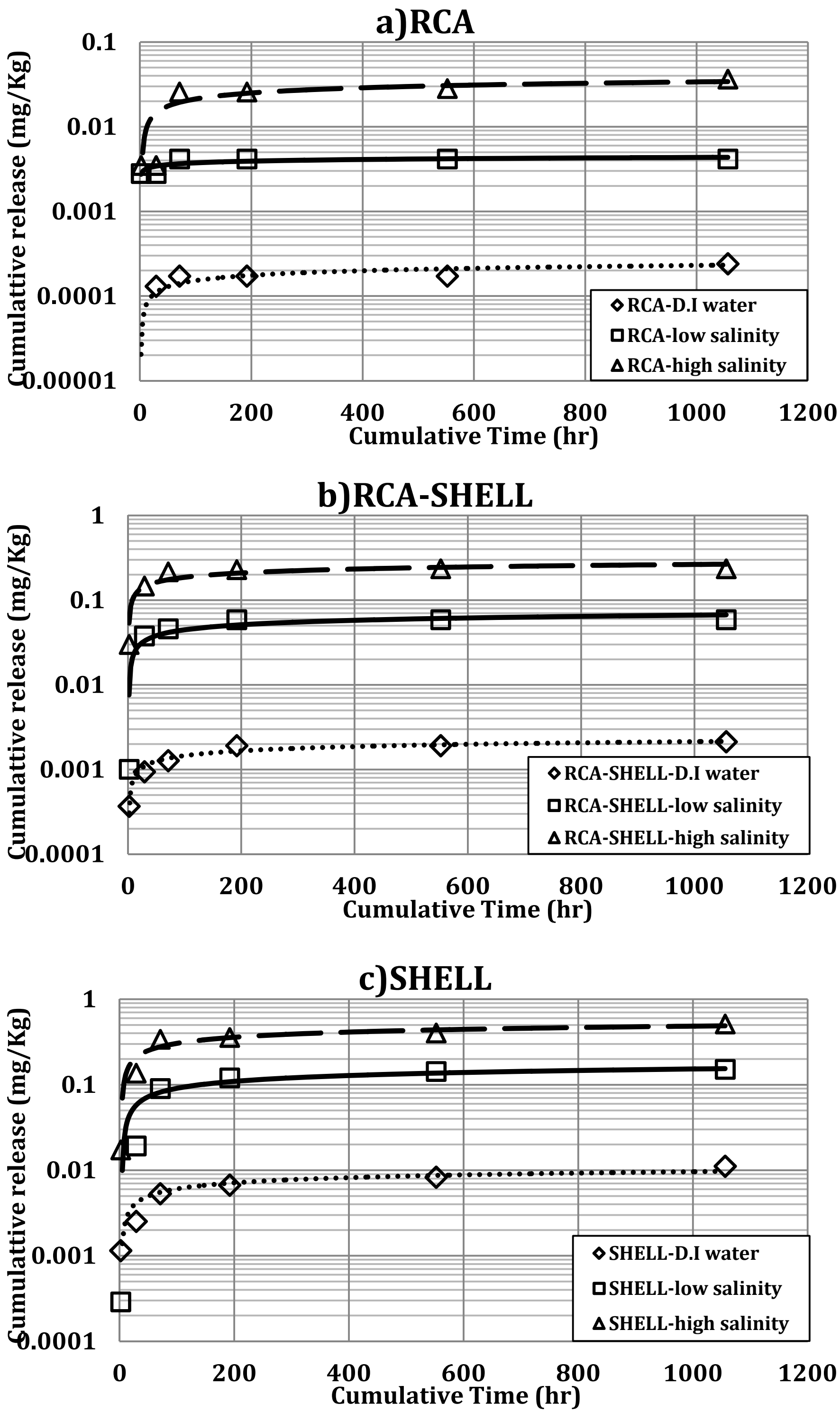


Figure 12. Cumulative manganese release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

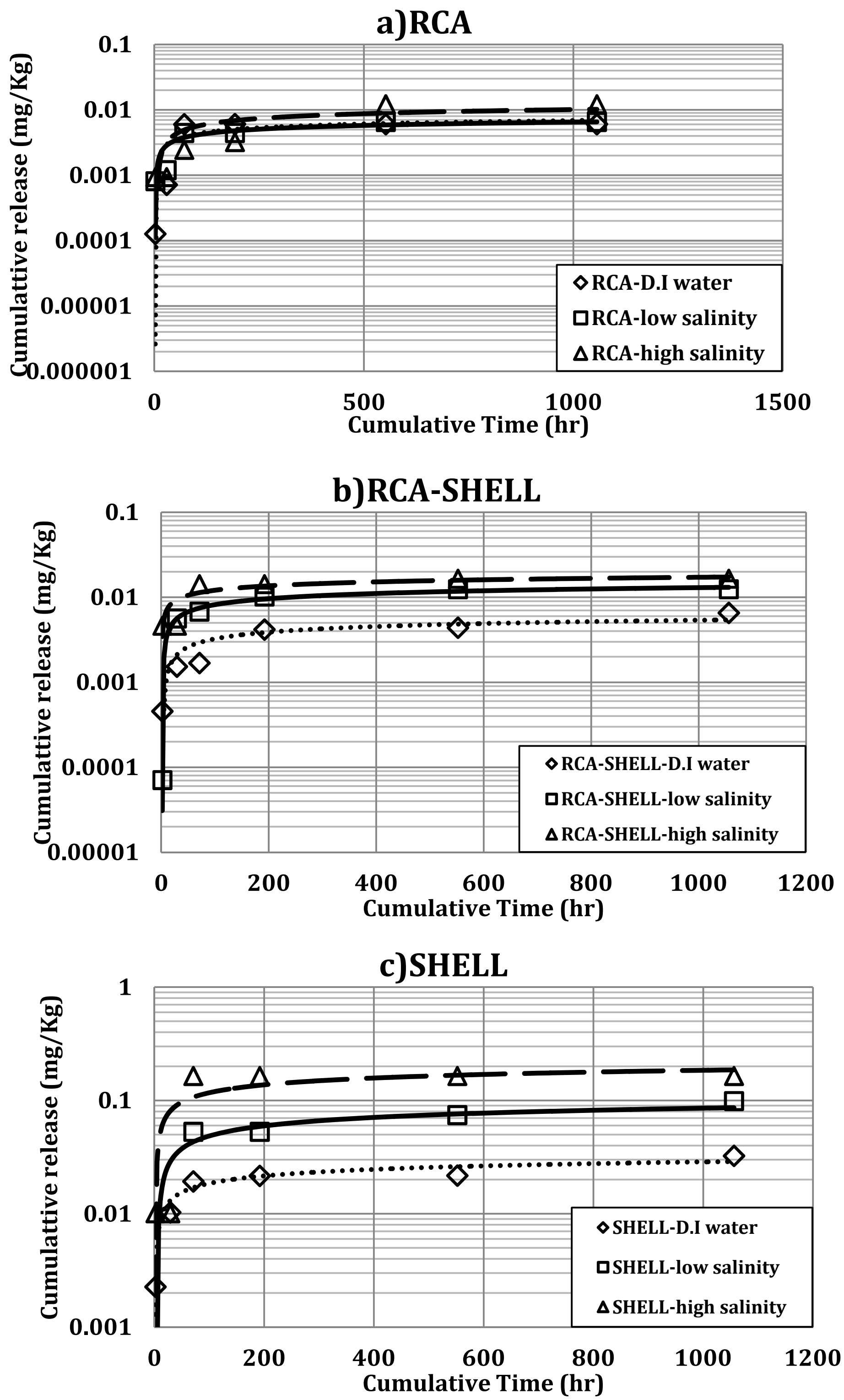


Figure 13. Cumulative copper release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

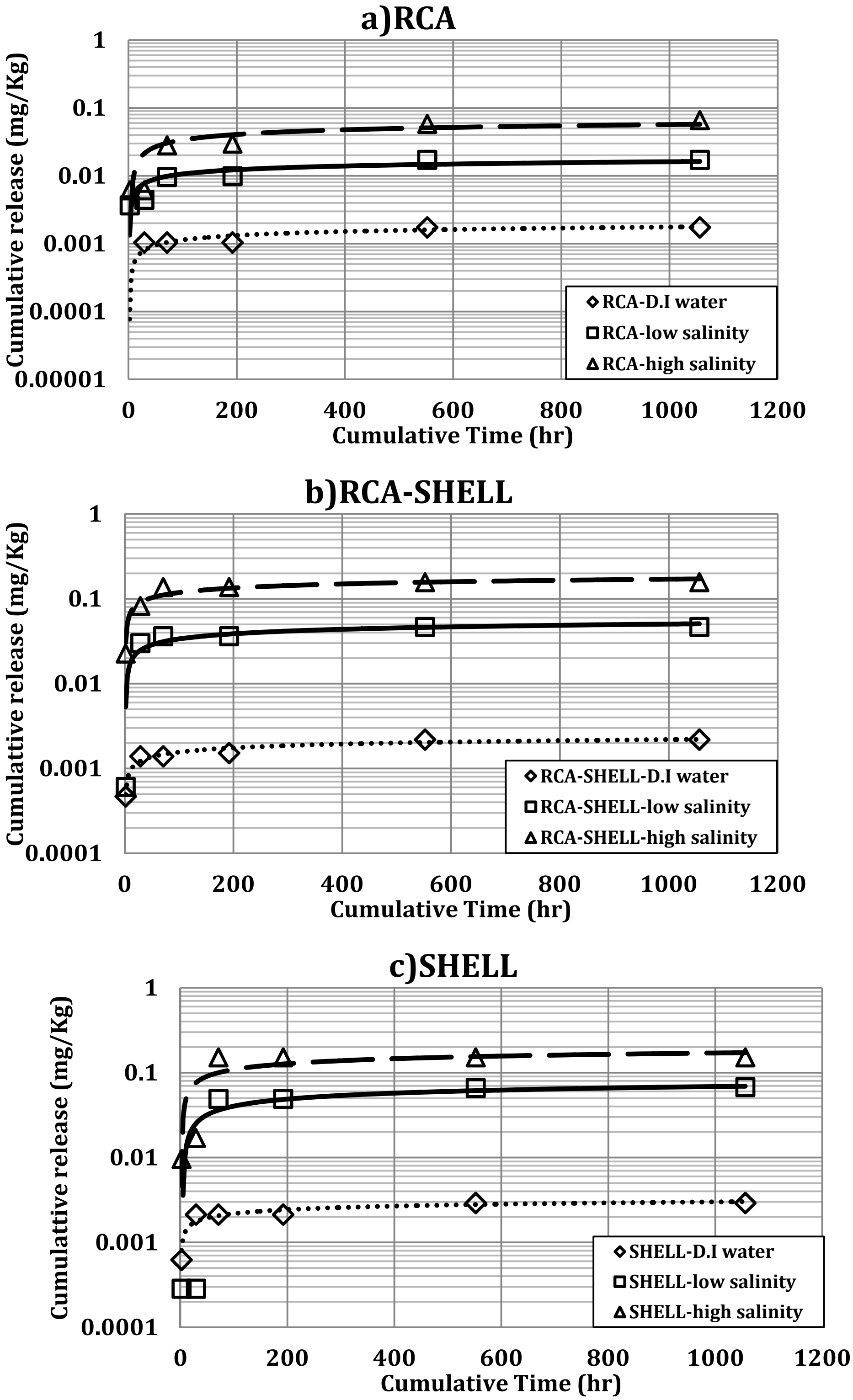


Figure 14. Cumulative arsenic release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

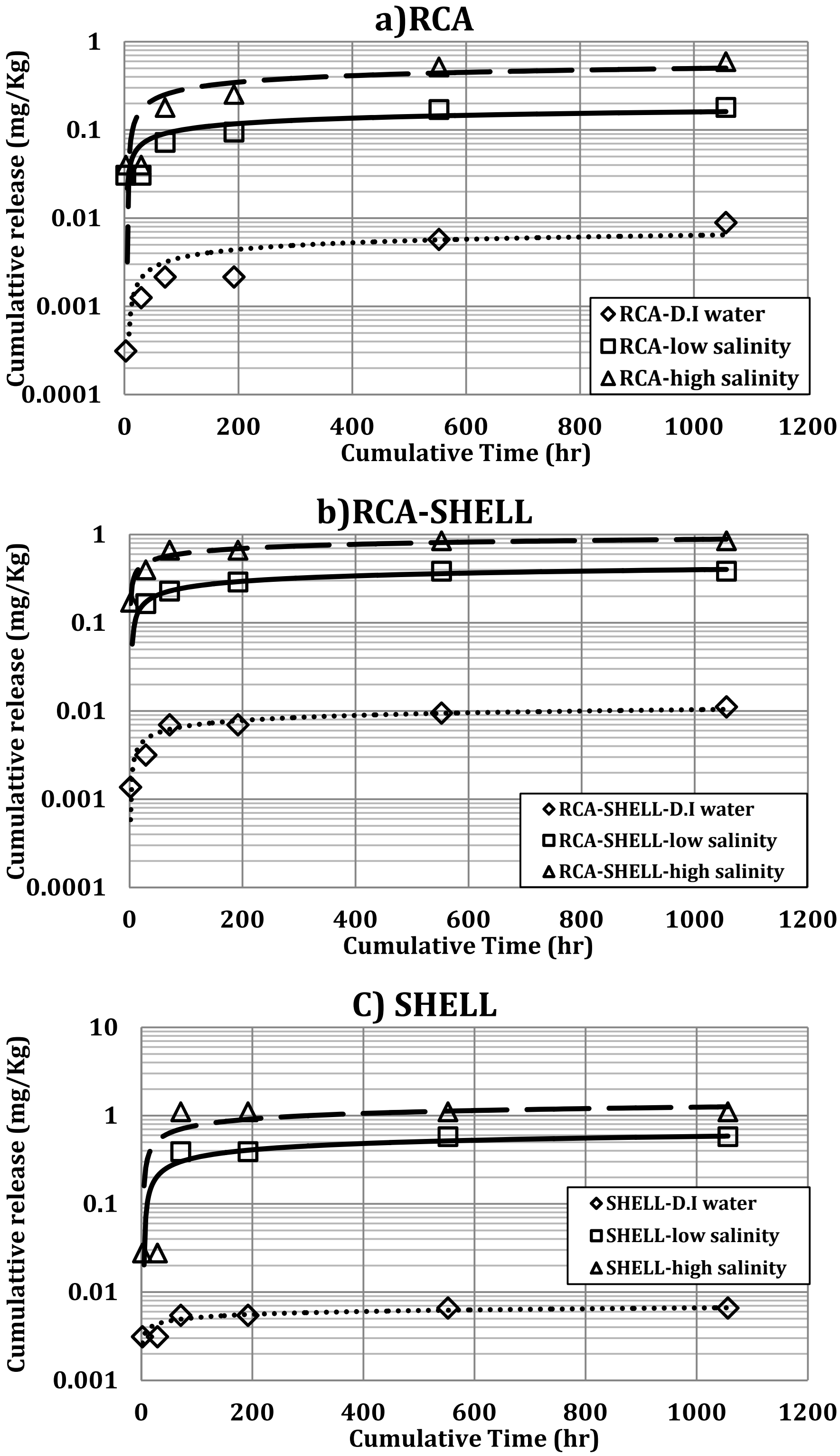


Figure 15. Cumulative selenium release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

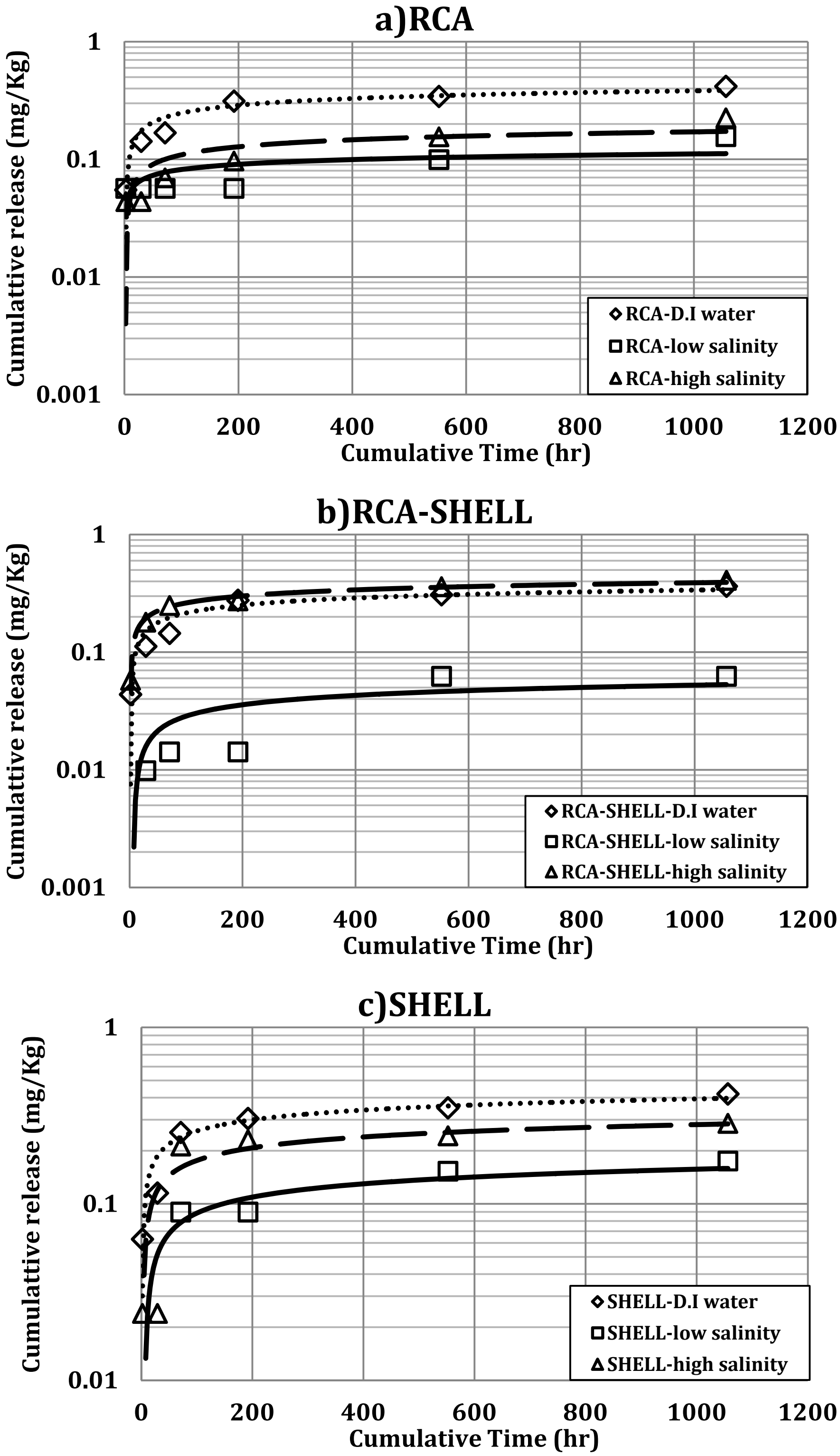


Figure 16. Cumulative barium release over time from (a) RCA, (b) RCA with oyster shell, and (c) oyster shell with different salinity

The eluents from each leaching interval were analyzed for pH, alkalinity, conductivity, chloride, ORP, nitrate, salinity, and TDS (fig. 17 - fig. 21). The pH of the eluents from the tank tests of the RCA, RCA-oyster shell, and oyster shell was evaluated at different salinities and elapsed time (fig. 17 - fig. 21). In general, recycled concrete had higher pH values than the oyster shell or de-ionized water applications. RCA in de-ionized water achieved the highest pH value, 11.01, at hour 1056. Of the control treatments, de-ionized water had a pH range of 4.95 to 5.59, low salinity had a pH range of 7.91 to 8.37, and high salinity had a pH range of 7.49 to 7.89. Eluent pH trended as follows: RCA > RCA-oyster shell > oyster shell > control. The eluent pH of RCA and RCA-oyster shell treatments were higher than the eluent pH of the oyster shell control. In the low salinity applications, the RCA and RCA-oyster shell treatments had a pH of 8.00 that increased to 9.57 and 9.28, respectively. At the high salinities treatments the pH not exceed 8.30 even with longer contact times. The eluents collected from the tank test of RCA may contain dissolved solids that cause high pH, including calcium oxide (free lime content), aluminum and iron as oxides, oxyhydroxides, and hydroxides from cement.

ORP indicates a chemical substance's ability to oxidize or reduce another chemical substance and gives a qualitative sense of the redox condition (James, 2006). The measurements indicated that RCA, RCA-oyster shell, and oyster shell's ORP reduced over time more than the controls did. The reductions were related to the release of reductants such as iron and manganese (fig. 18). The low and high salinity treatments exhibited high ORP due to the oxidants contained in sea salts.

Conductivity tests use water's ability to conduct an electrical current to evaluate the amount of inorganic dissolved solids (James, 2006). Conductivity is measured in units of μS/m. It is the concentration of dissolved ions in the water: the more ions, the more conductive the water. The general conductivity trend was as follows: RCA > RCA-oyster shell > oyster shell > control at de-ionized application. Salinity is directly proportional to the amount of chloride ions; therefore increasing salinity correlated to increased conductivity. The range of conductivity was 54,750 to 66,496 μS/m for high salinity; 23,105 to 25,876 μS/m for low salinity; and 79 to 755 μS/m for de-ionized water, respectively (fig. 19).

TDS is similar to conductivity measurements. TDS measures the concentrations of common ions in water (James, 2006). TDS generally followed the trend: RCA-oyster shell > RCA > oyster shell > control. TDS increased with increasing salinity. TDS was 582 mg/L at high salinity, 224 mg/L at low salinity, and 9.9 mg/L in de-ionized water (fig. 20).

Alkalinity indicates the buffering capacity of a solution by measuring its ability to maintain a stable pH. Alkalinity generally trended as follows: RCA-oyster shell > RCA > oyster shell > control at de-ionized application. Due to the chloride in sea salt, alkalinity increased as the salinity increased.

RCA-oyster shell had a higher alkalinity than the other treatments. Alkalinity ranged from 1322 to 1480 mg/L at high salinity, 504 to 673 mg/L at low salinity, and 8.1 to 213 mg/L in de-ionized water (fig. 22). Nitrate concentrations in the eluents are shown in the appendix.

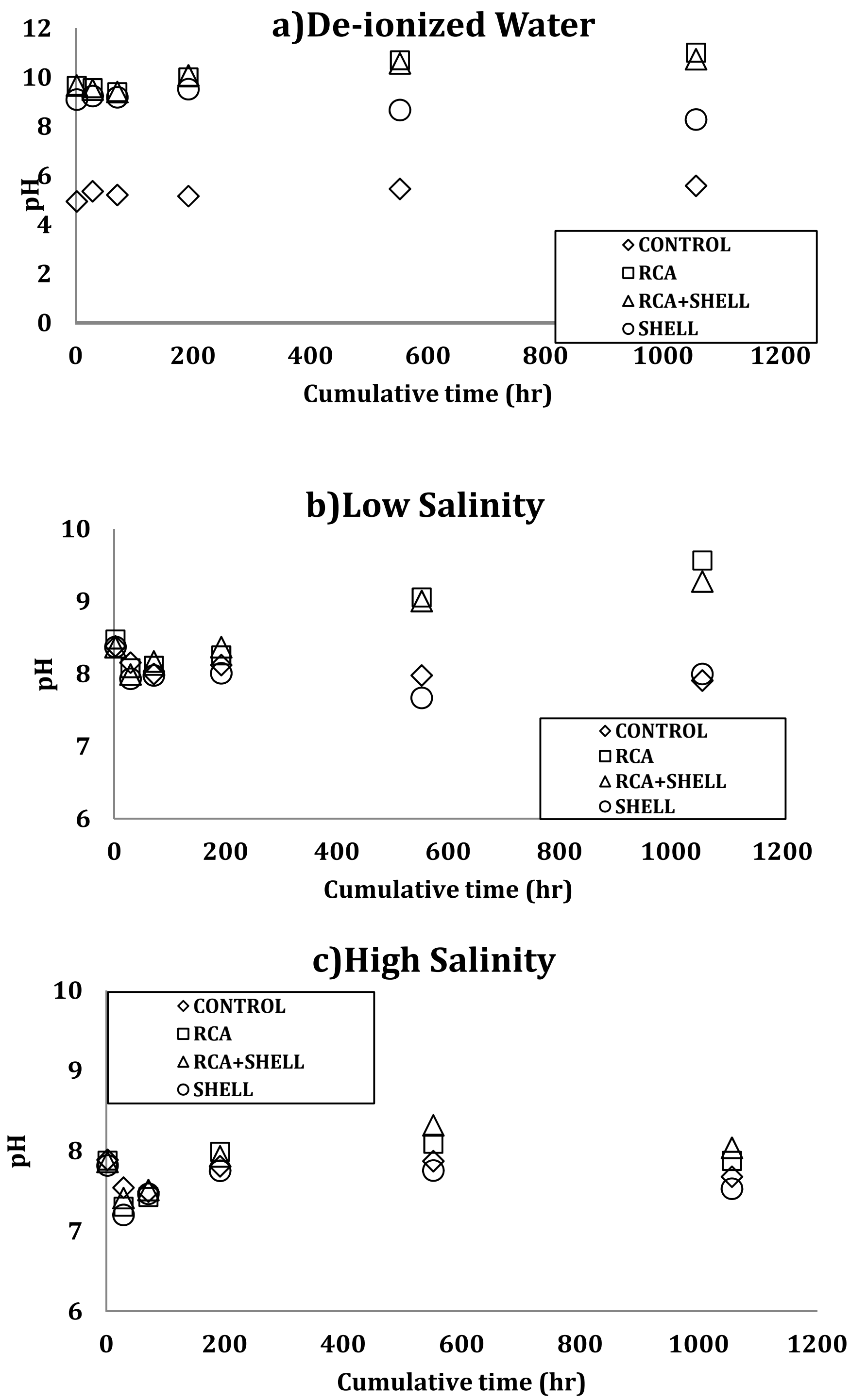


Figure 17. pH by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

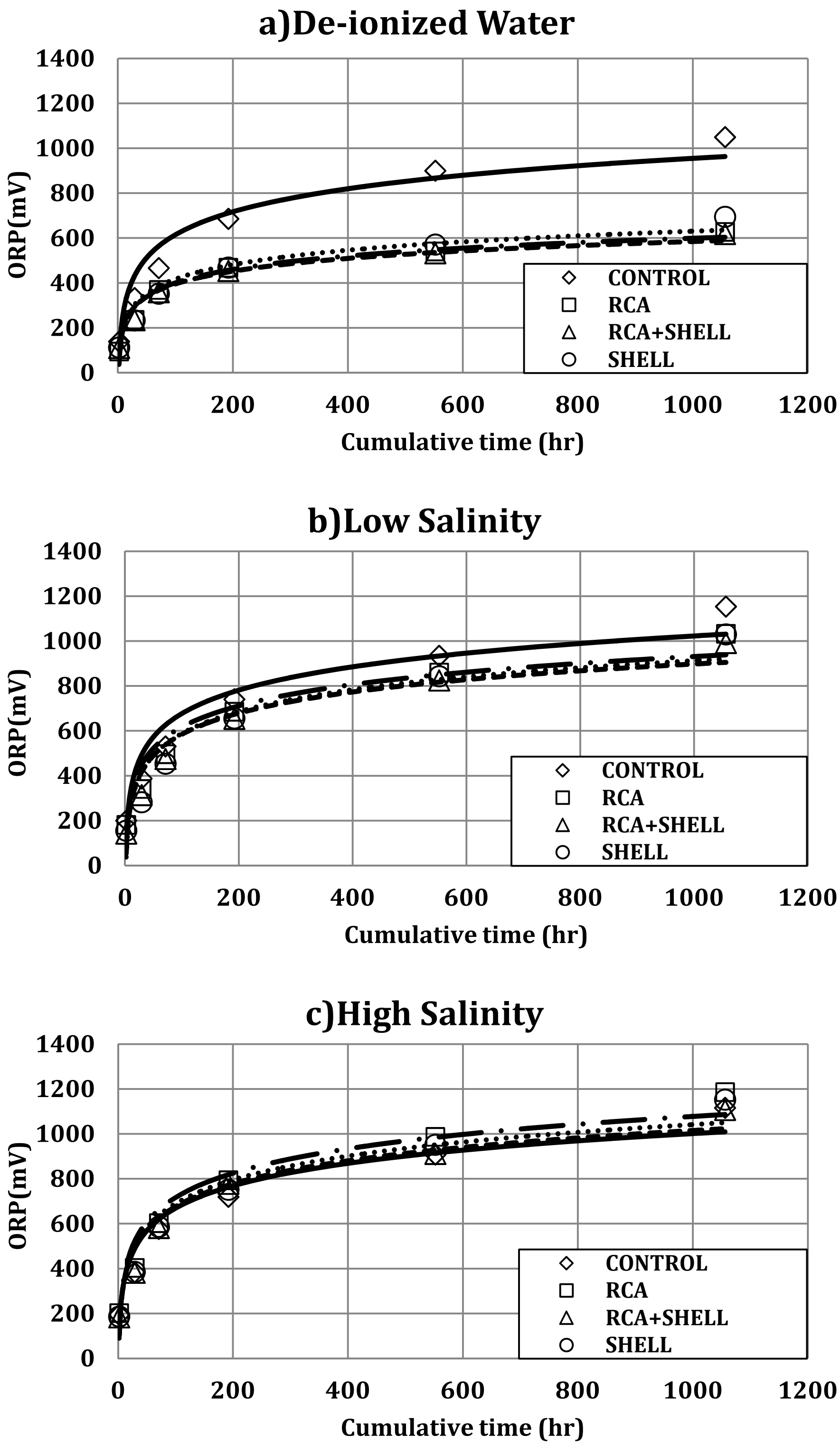


Figure 18. Oxidation Reduction Potential (ORP) by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

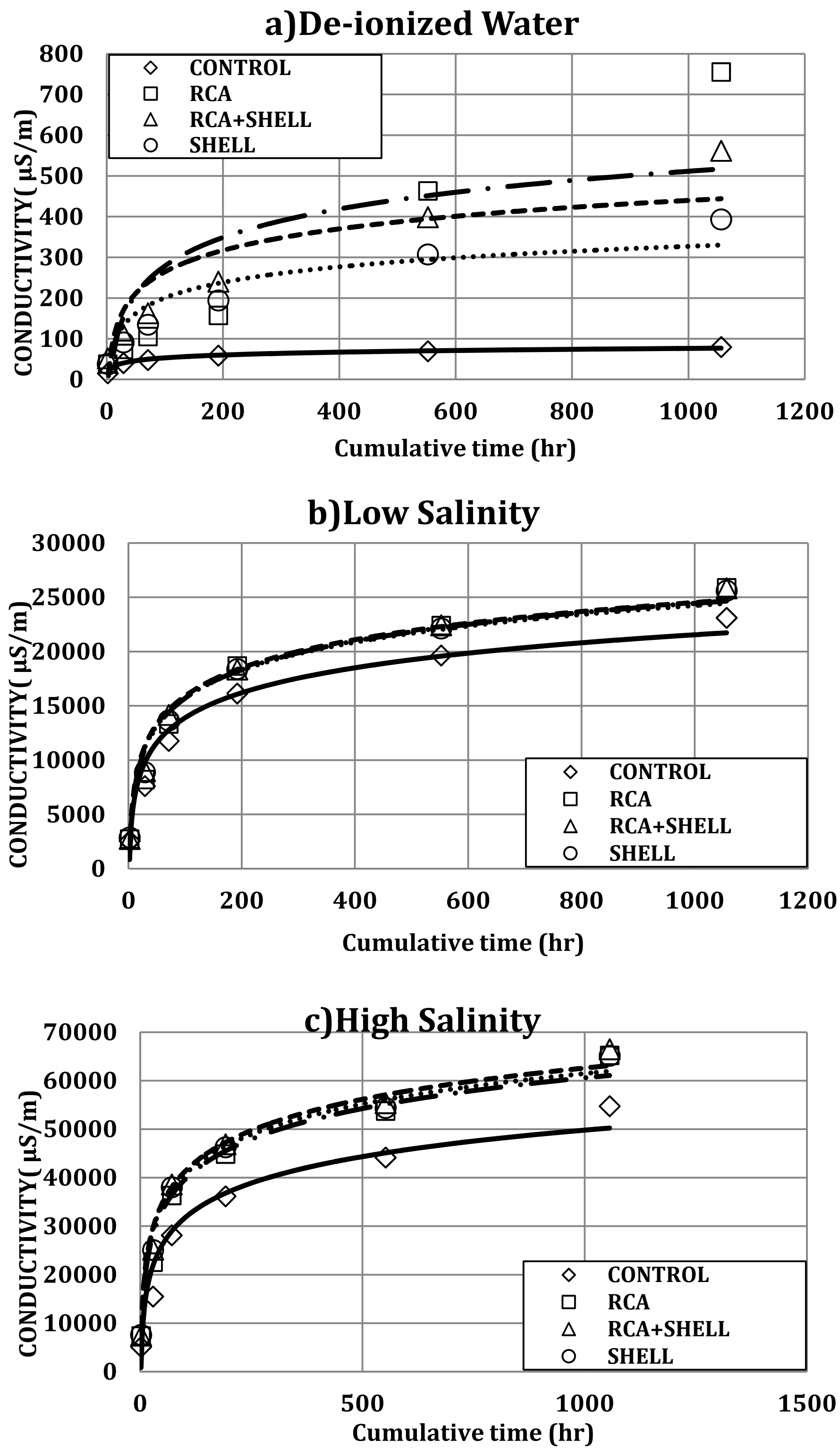


Figure 19. Conductivity by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

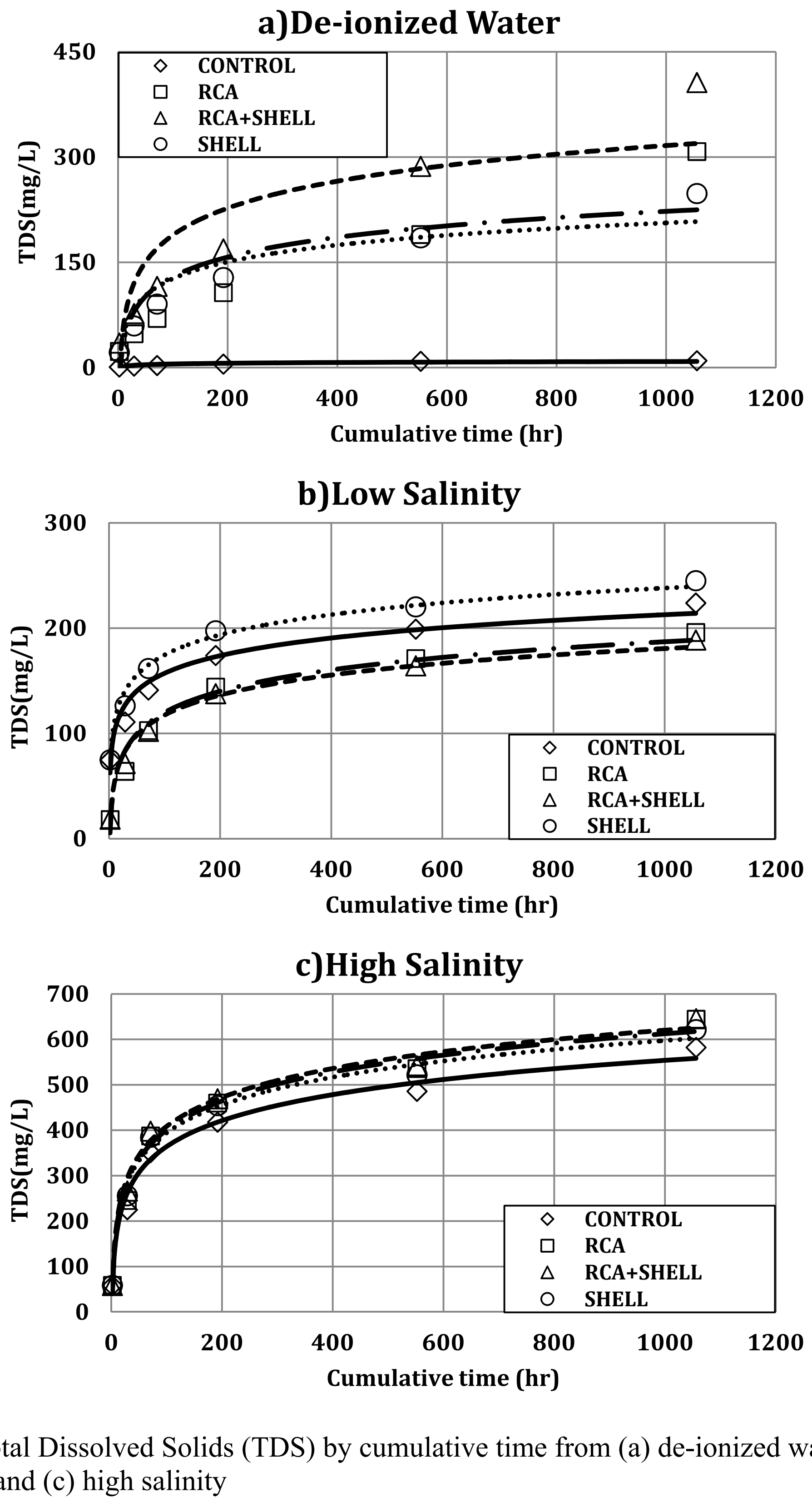


Figure 20. Total Dissolved Solids (TDS) by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

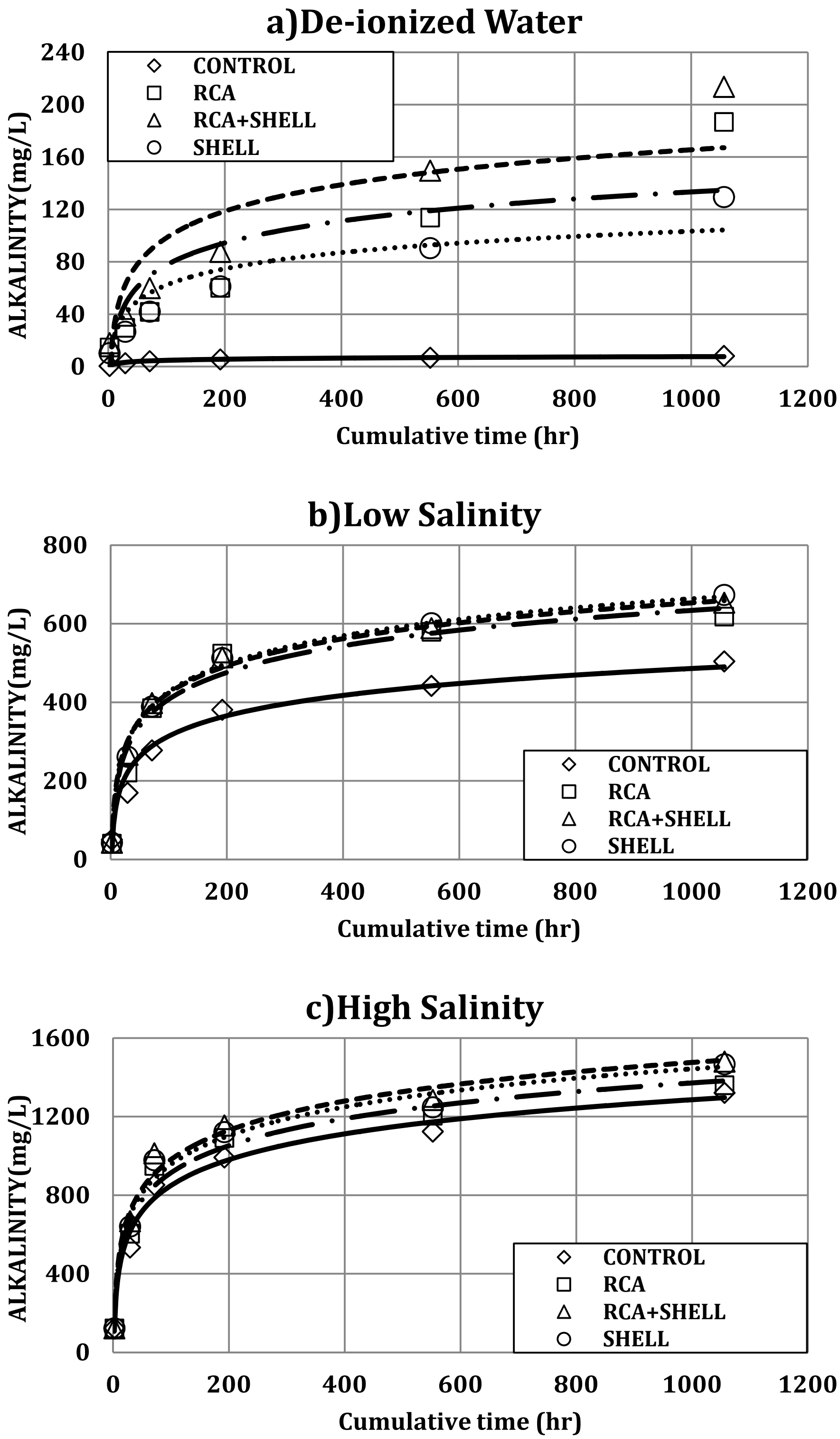


Figure 21. Alkalinity by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

Task 4: Flow-Through-Leaching Test

This study evaluates the potential leachability of chemicals from recycled concrete with brackish water supplied from the Patuxent River, near St. Leonard, Maryland. The leachability tests were run in fast (30 cm^3/s) and slow (13 cm^3/s) flow conditions.

Based on the detected concentrations, the analyzed chemicals from the recycled concrete were divided in three groups: high, medium, and low. The high group consisted of selenium, barium, and zinc, which are shown in figures 21-23. However, high concentrations of these chemicals are also detected in brackish water. Therefore, these chemicals naturally exist in the Patuxent River (21 to 58 µg/L for selenium, 8 to 83 µg/L for barium, and 5 to 28 µg/L for zinc).

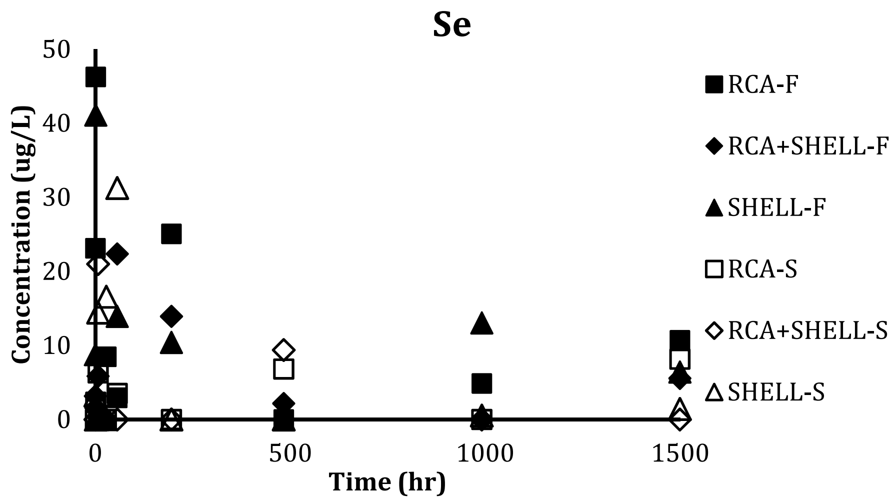


Figure 22. Selenium concentration in brackish water over cumulative time, F: fast flow rate, S: slow flow rate

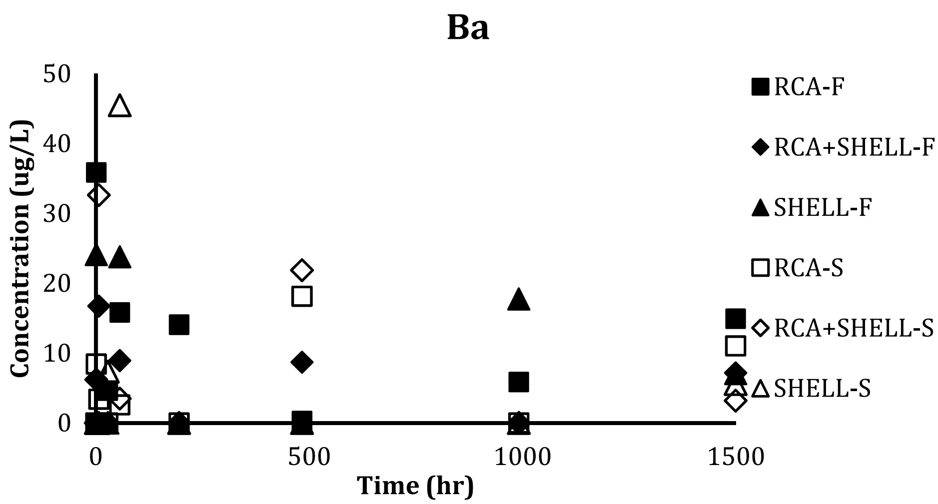


Figure 23. Barium concentration in brackish water over cumulative time, F: fast flow rate, S: slow flow rate

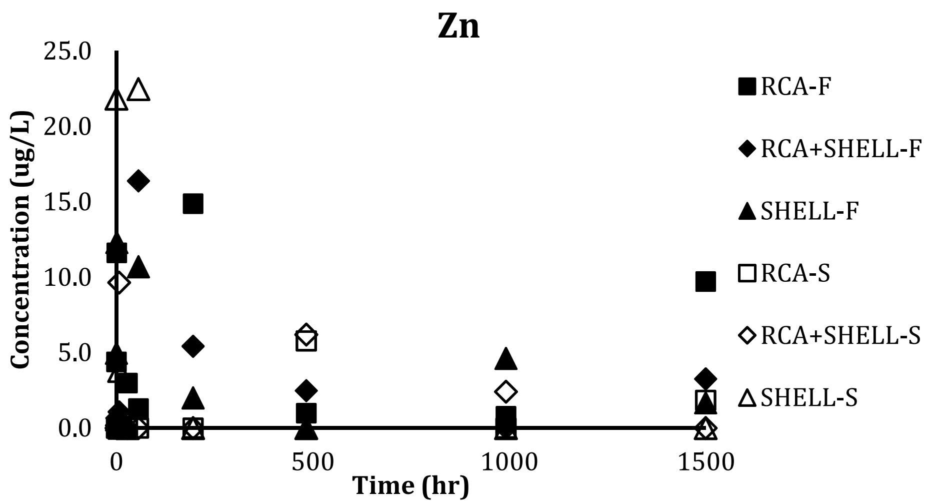


Figure 24. Zinc concentration in brackish water over cumulative time, F: fast flow rate, S: slow flow rate

As shown in figure 23, the highest barium concentrations were seen in RCA in fast-flow conditions (36 µg/L) and oyster shell in low-flow conditions (45 µg/L). The highest zinc concentrations were 16 µg/L (RCA-oyster shell in fast flow) and 22 µg/L (oyster shell in low flow) (fig. 24). However, selenium, barium, and zinc concentrations gradually decreased with time.

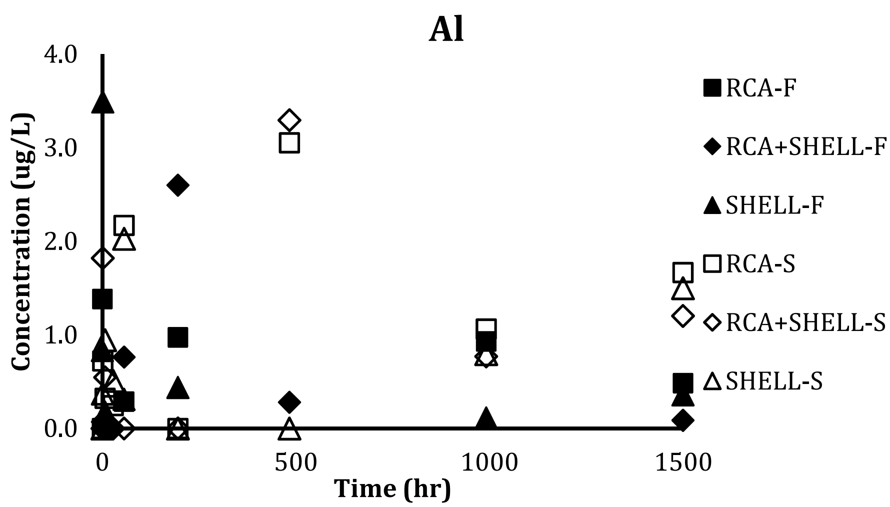


Figure 25. Aluminum concentration in brackish water over time, F: fast flow rate, S: slow flow rate

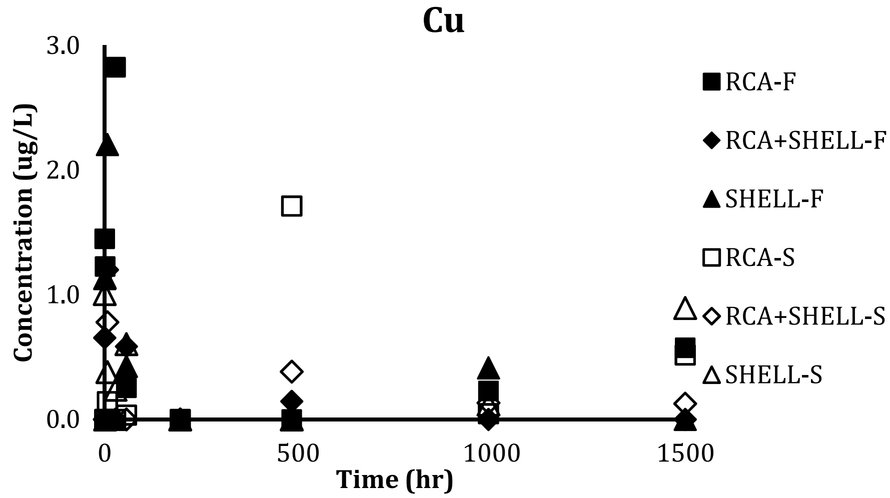


Figure 26. Copper concentration in brackish water over time, F: fast flow rate, S: slow flow rate

The medium concentration group includes aluminum, copper, and arsenic (fig. 25-27). The highest aluminum concentrations were seen in oyster shell under fast flow (3.5 µg/L) and RCA-oyster shell under low flow (3.3 µg/L). The highest copper concentrations were in RCA under fast flow (2.8 µg/L) and RCA under low flow (1.7 µg/L). The highest arsenic concentrations were RCA under fast flow (6.2 µg/L) and oyster shell under low flow (4.0 µg/L).

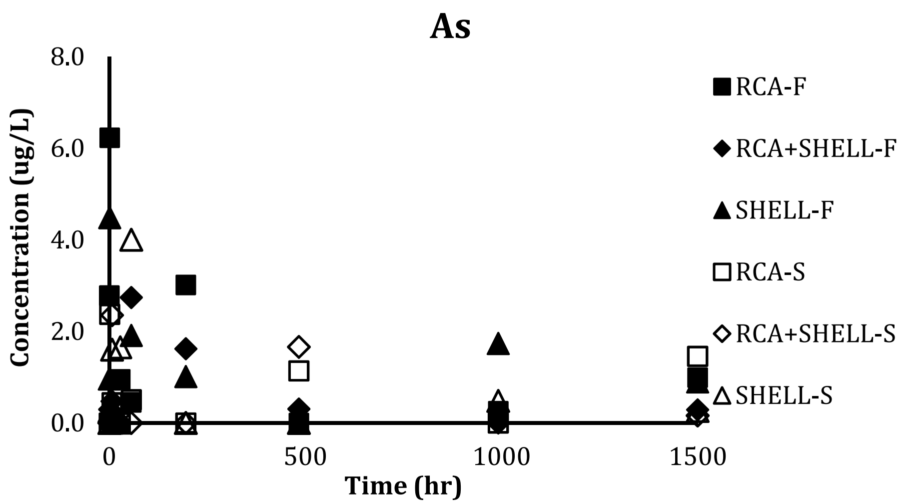


Figure 27. Arsenic concentration in brackish water over cumulative time, F: fast flow rate, S: slow flow rate

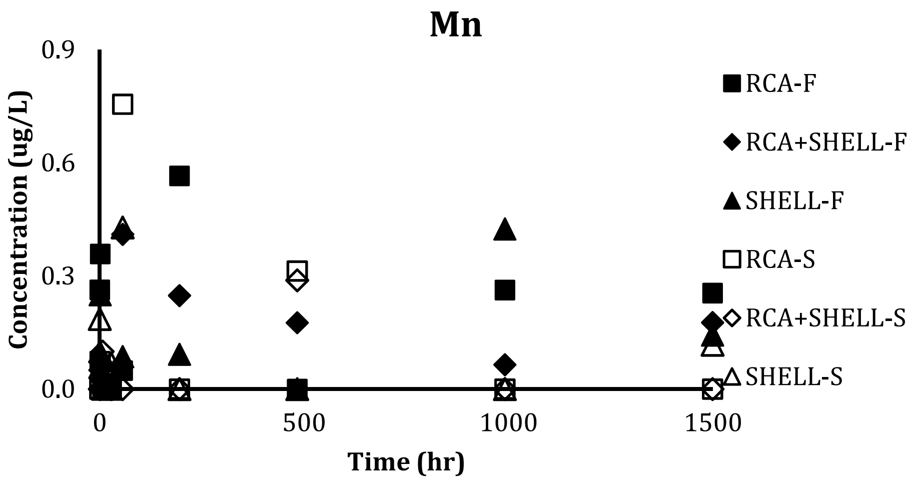


Figure 28. Manganese concentration in brackish water over time, F: fast flow rate, S: slow flow rate

The low leachability group includes manganese, chromium, lead, cadmium, and mercury. The highest concentration in the low leachability group did not exceed 1 µg/L. The highest concentrations of lead, cadmium, and mercury, around 0.1 µg/L, were detected at the beginning of the column experiment. The highest manganese concentrations—0.57 µg/L and 0.76 µg/L—occurred with RCA in fast-flow and low flow conditions (fig. 28). Manganese concentration also decreased with time. The highest chromium concentrations were 0.78 µg/L (RCA with fast flow) and 0.66 µg/L (RCA-oyster shell with low flow). Chromium's leaching concentration did not decrease with time. Beryllium and thallium were not detected from the collected samples.

The collected samples from the column experiment were analyzed for pH, conductivity, TDS, ORP, alkalinity, and salinity (fig. 30 to 35). The pH for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from the Patuxent River near St. Leonard, Maryland, was evaluated at the time of collection (fig. 30). At the beginning of column experiment, RCA and RCA-oyster shell had slightly higher pH values (8.20 to 8.36) than the oyster shell and control (8.00 to 8.20), but the pH for all treatments stabilized to 7.60 to 7.80 after seven days. The highest pH value of 8.36 (7 hr) corresponded to RCA-oyster with slow flow rate, even though recycled concrete contains aluminum and iron as oxides, oxyhydroxides, and hydroxides that can raise pH. Initial values of conductivity, TDS, ORP and alkalinity, TDS were higher than those detected over time except ORP (fig. 33). The values for the RCA, RCA-oyster shell, and oyster shell with brackish water were not significantly different and the values stabilized over time (fig. 31 to 35). The salinity of brackish water changed depending on the surrounding area's weather conditions. Salinity may decrease during a rainy period. The range of salinity was 5 to 14 parts per thousand (fig. 35).

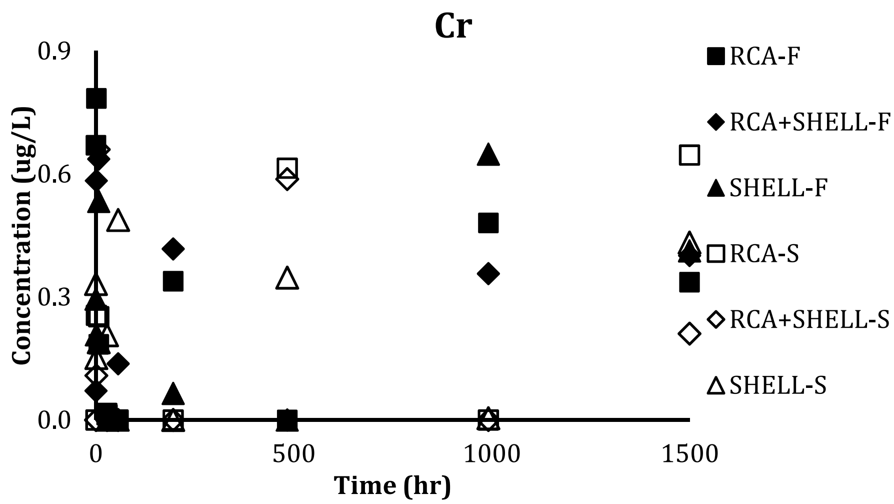


Figure 29. Chromium concentration in brackish water over time, F: fast flow rate, S: slow flow rate

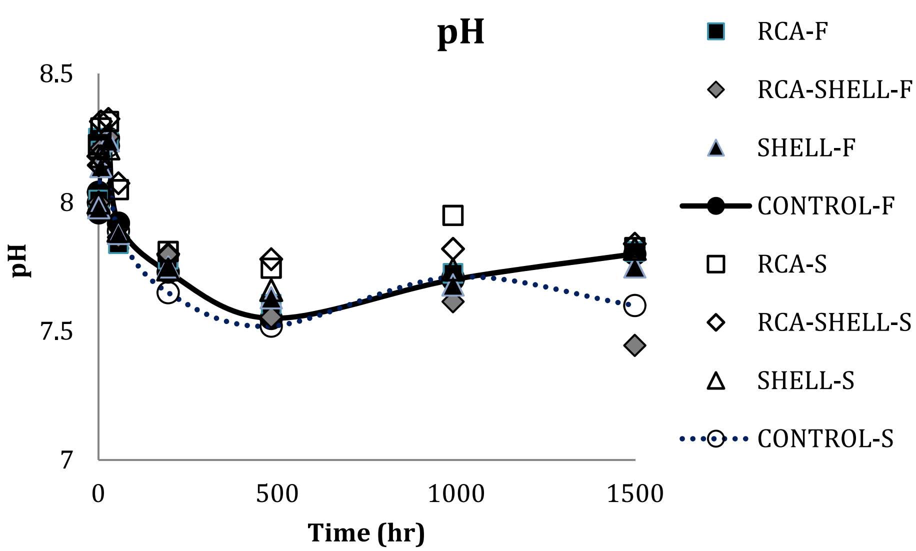


Figure 30. pH for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

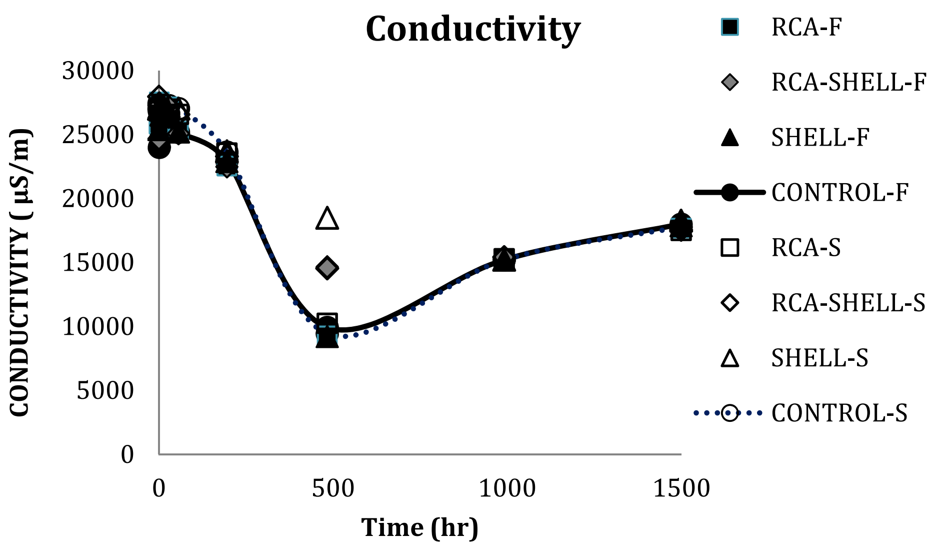


Figure 31. Conductivity for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

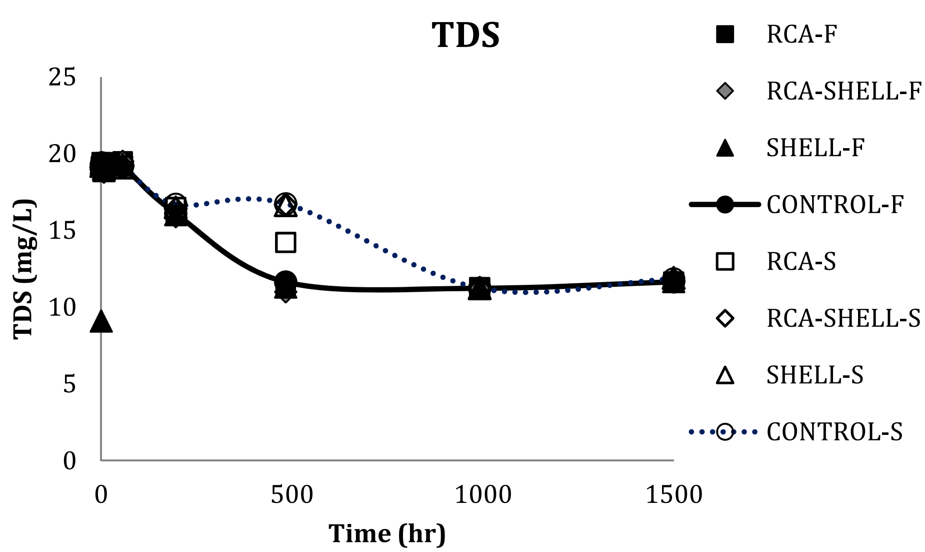


Figure 32. TDS for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

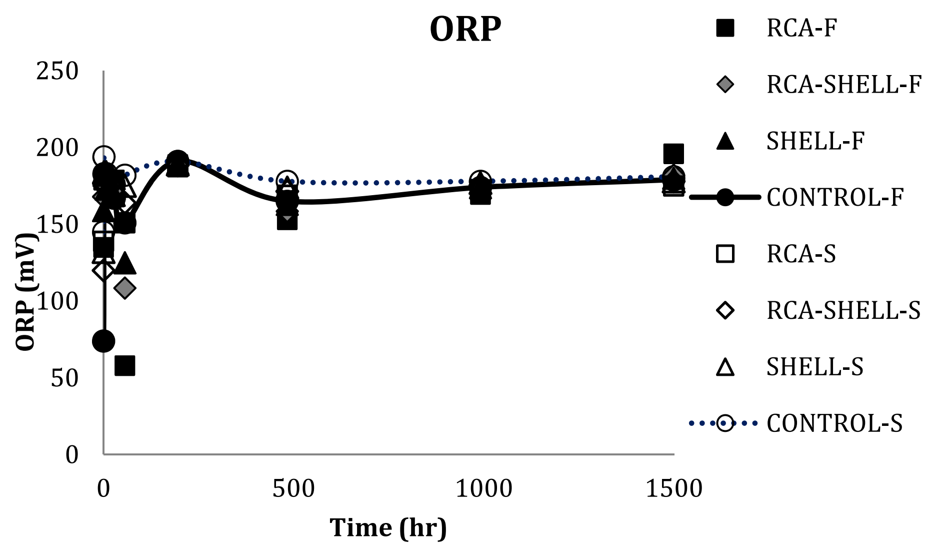


Figure 33. ORP for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

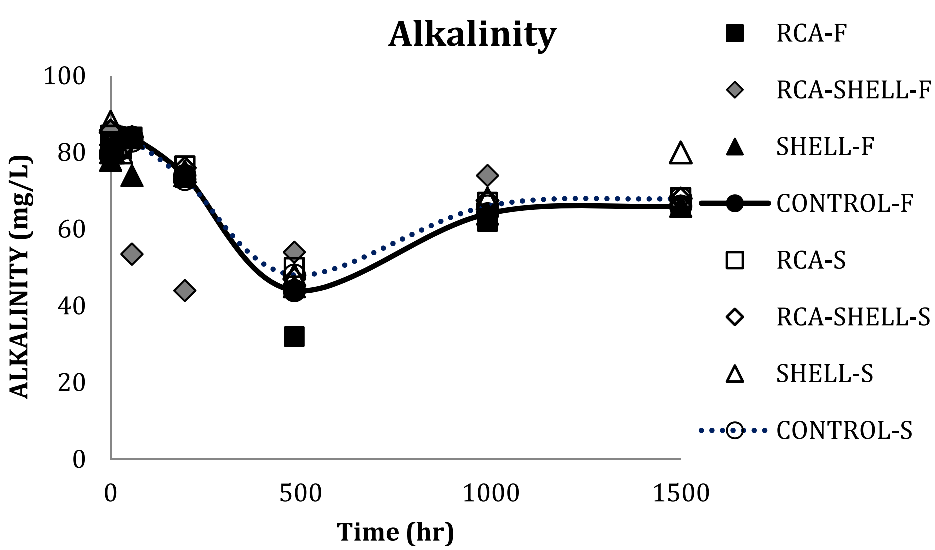


Figure 34. Alkalinity for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

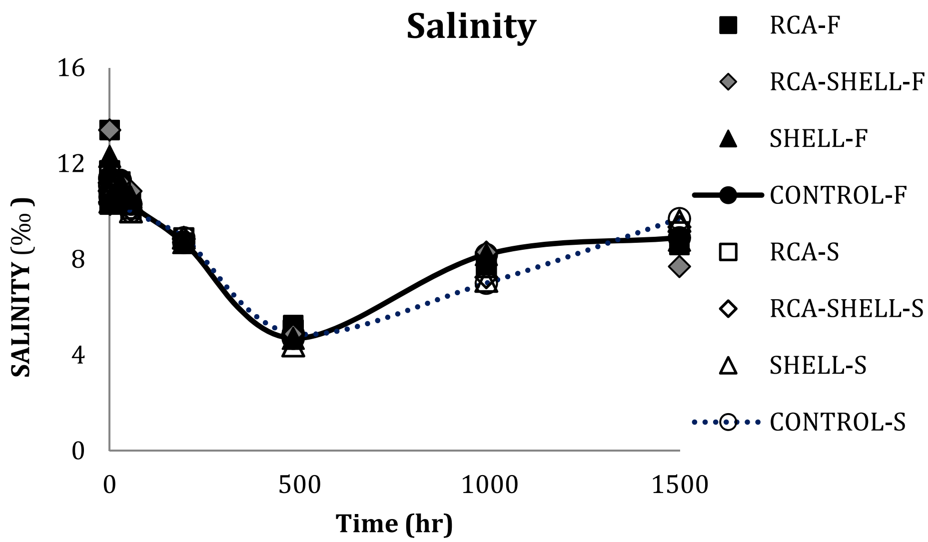


Figure 35. Salinity for the RCA, RCA-oyster shell, and oyster shell with brackish water supplied from Patuxent River near St. Leonard, MD, by collected time, F: fast flow rate, S: slow flow rate

Task 5: Oyster Growth and Survivorship

The oyster growth and survivorship experiments were run twice: once in July 2011 and again in October 2011. Spring 2011 experienced high rainfall, which kept salinities below the 9 parts per thousand (ppt) required for oyster spawning until midsummer. Fortunately, water temperatures remained within the optimum range for spat growth into October.

Temperature, salinity, pH, and dissolved oxygen (DO) were monitored during the experiments. The recorded values were within historical characteristics of the Patuxent River. As shown in figure 36, there was no statistical difference in any of the water quality parameters between treatments (t-test, $p < 0.05$).

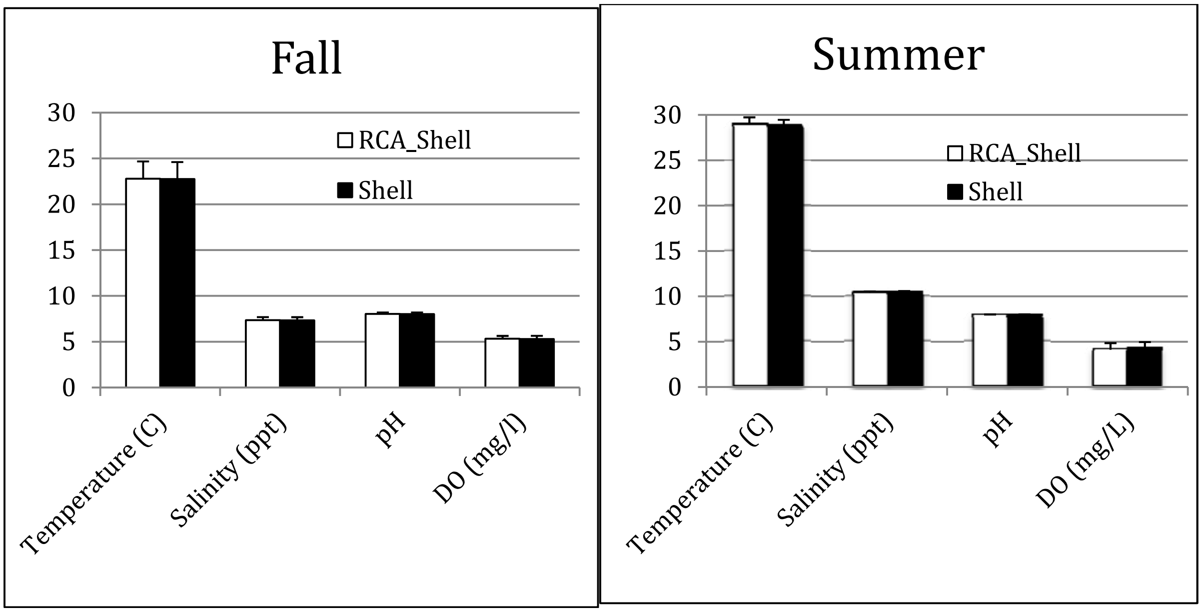


Figure 36. Average water quality conditions within experimental tanks

Temperature, salinity, and DO differed by seasons (t-test $p < 0.05$) (fig. 37). Summer's temperatures (average 29.1^{0}C) were higher than fall's (average 22.8^{0}C). Summer temperatures changed little over the experiment, ranging from 27.8 to 29.5^{0}C. Fall temperatures had a slightly larger range, 20.1 to 24.9 ^{0}C, and decreased over the experiment (fig. 38). Salinity was also lower during the fall, averaging 7.4 ppt relative to the summer average salinity of 10.4 ppt. The fall average values for DO, 5.3mg/l, were higher than the summer average of 4.2 mg/l. The fall variance in DO values for the, +/-.71 mg/l, was lower than the summer variance, +/-1.8 mg/l. pH was not different between seasons. For all treatments and time periods, pH ranged from 7.70 to 8.30.

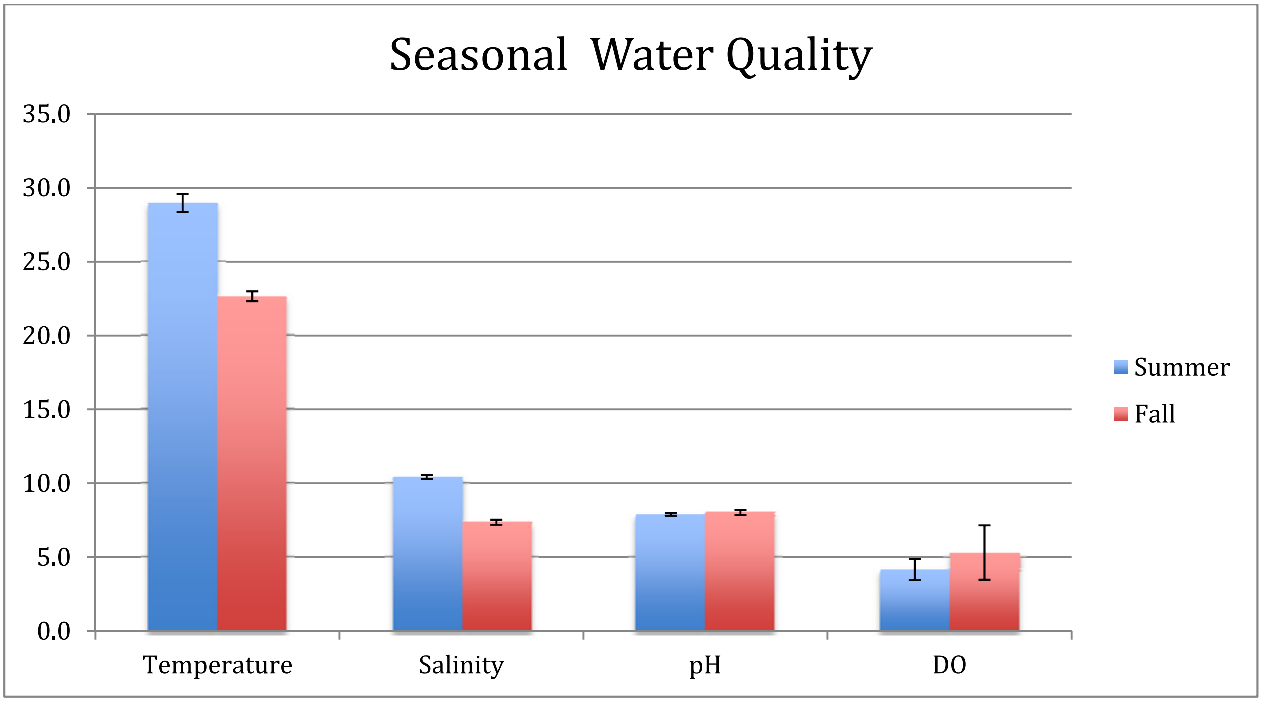
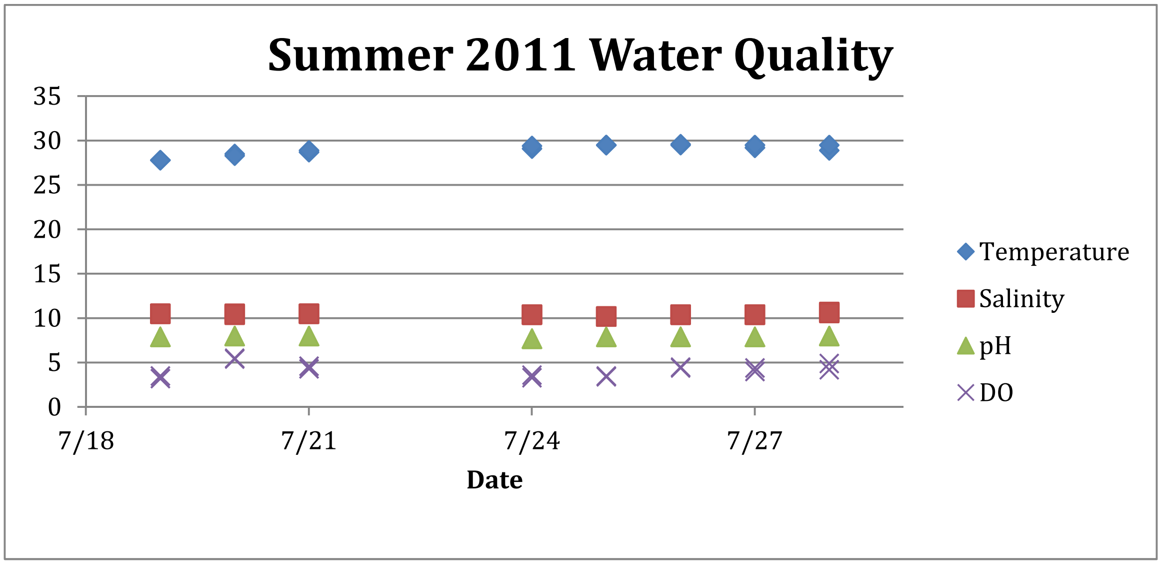


Figure 37. Average water quality in experimental tanks during summer and fall



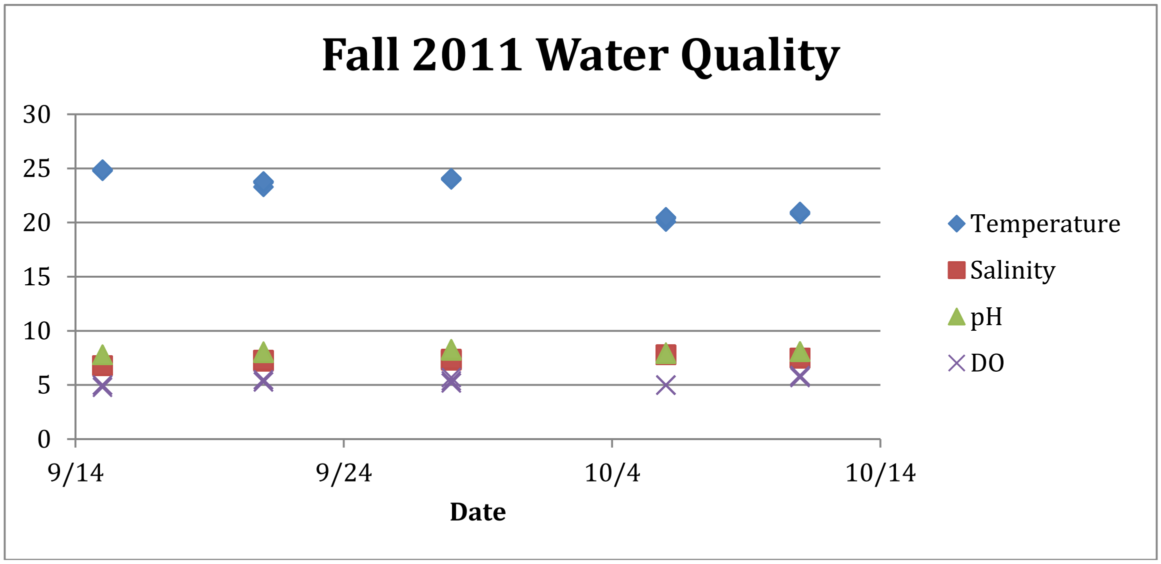


Figure 38. Fall and summer water quality

Growth

In the summer oyster spat were obtained from the State of Maryland Hatchery at Piney Point. Sixty-three shells, with a total of 617 spat, were distributed equally among the treatments. The initial mean length of oysters was 5.5 mm. There was no difference (Tukey HSD p=0.98, df=2) in initial length between shell (5.5 +/-2.9 mm) and RCA_shell (5.54 +/- 3.2 mm). After two weeks, there was no significant difference (ANOVA p=0.99, df=1) between the mean length of oysters in the RCA_shell (9.32 mm +/- 4.87 mm) and shell (9.36 mm +/-4.62 mm). In the fall, the experiment was run for six weeks and an interim measurement was taken at week two. Two hundred and thirty-two shells with a toal of 583 spat were planted. The mean length of oysters at the beginning was 8.73 mm. There was no difference (Tukey HSD p=0.98, df=2) in initial oyster length between shell (8.73 +/- 3.67 mm) and RCA_shell (8.73 +/-3.44 mm). Over the six-week period, the spat grew an average of 12.1 mm. Treatment had no effect on the initial, two-week, or six-week length.

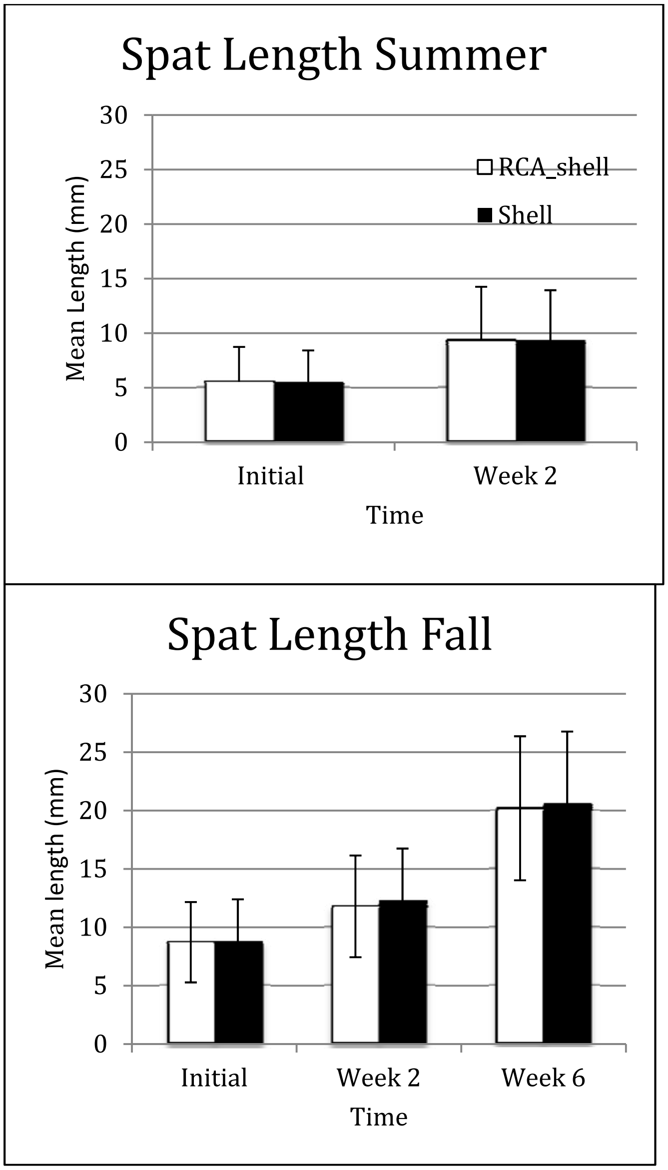


Figure 39. Mean length of oyster spat grown on RCA_shell and oyster shell

Survivorship was high and did not differ between treatments. In the summer, spat were mapped on the shell. When the shells were recovered, the map was used to identify spat that survived the experiment. Thirteen were missing from the 280 spat identified from each treatment, resulting in a survivorship of 95 percent for each treatment. The shells were not mapped in the fall treatment, so the number of dead oysters identified on each shell was used as a measure of survivorship. Of the 578 were counted, 15 were dead. The 99.99 percent survivorship was not significantly different in either treatment (ANOVA on arcsine square root transformed data (p=0.4, f=0.59, df =1).

CONCLUSIONS

The results of this project showed that using RCA as a base material for oyster reefs did not adversely affect oyster spat growth and survival, or the surrounding environment. None of the metals leached at a rate that exceeded the Environmental Protection Agency (EPA) drinking water standards. This standard is more stringent than the current EPA total maximum daily loads (TMDLs) for Chesapeake Bay waters. There was no statistical difference between shell and RCA on the growth, survivorship, average length, or recruitment of young oysters. Initial pH was slightly higher for the RCA (8.20 to 8.36) than the oyster shell and control (8.00 to 8.20), but pH stabilized to 7.60 to 7.80 for all treatments after seven days.

Recommendations

Based on the findings, this study recommends a second phase of this project. This second phase would place large quantities of RCA on test plots in the Chesapeake Bay. Phase 2 would be designed to

1. evaluate the potential introduction of organisms attracted to the RCA pile in situ that may be potential predators of oyster spat. Studies have shown that in aquatic systems, hard substrates will attract a variety of aquatic organisms. However, the type and number of attracted organisms vary according to substrate. RCA may cause an unexpected increase in flatworms or other organisms that feed on oyster spat. Higher concentrations of these predatory organisms may have significant impacts on the survivability of oyster spat placed on RCA.
2. determine potential impacts or disruptions in the use of traditional harvesting gear on aquaculture areas conditioned with RCA. This will help determine the “catchability” of oysters grown on RCA piles. Included will be an assessment of the optimum thickness of native shell required to mitigate any identified harvesting impacts.

APPENDIX

Cumulative Mass Leachate

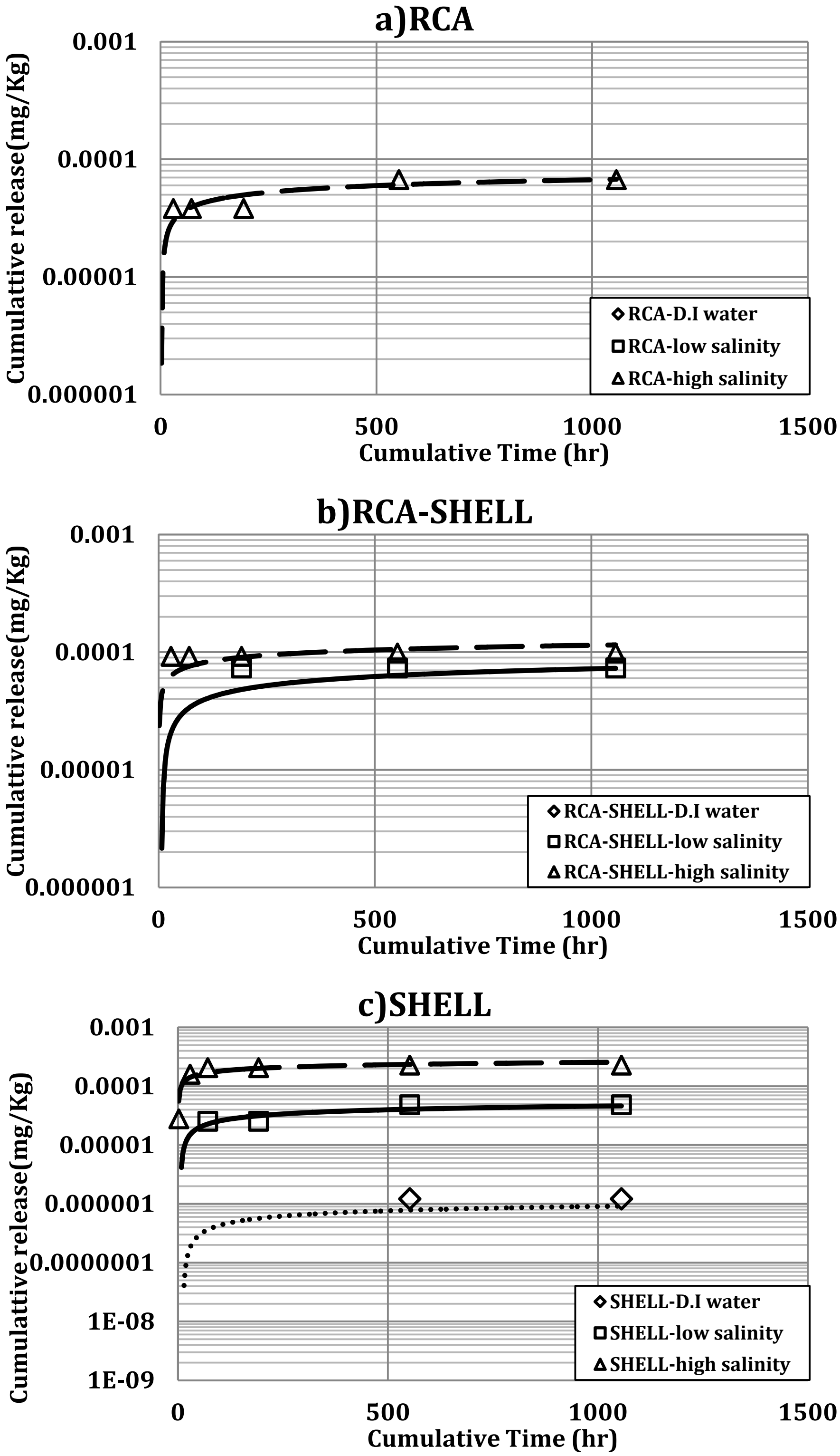


Figure A-1. Cumulative mass release for cadmium by cumulative time from (a) recycled concrete, (b) recycled concrete with oyster shell, and (c) oyster shell with different salinity

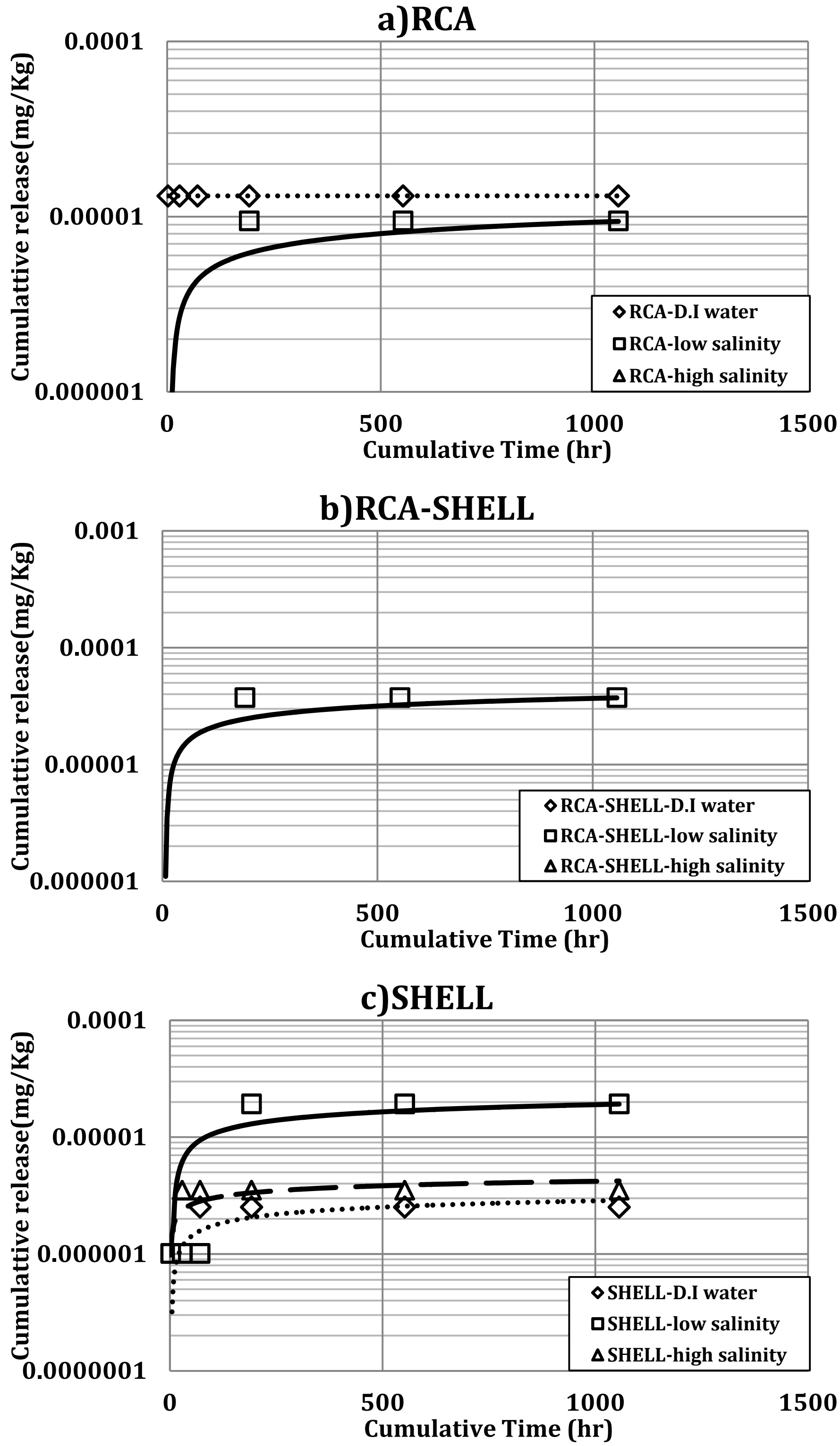


Figure A-2. Cumulative mass release for mercury by cumulative time from (a) recycled concrete, (b) recycled concrete with oyster shell, and (c) oyster shell with different salinity

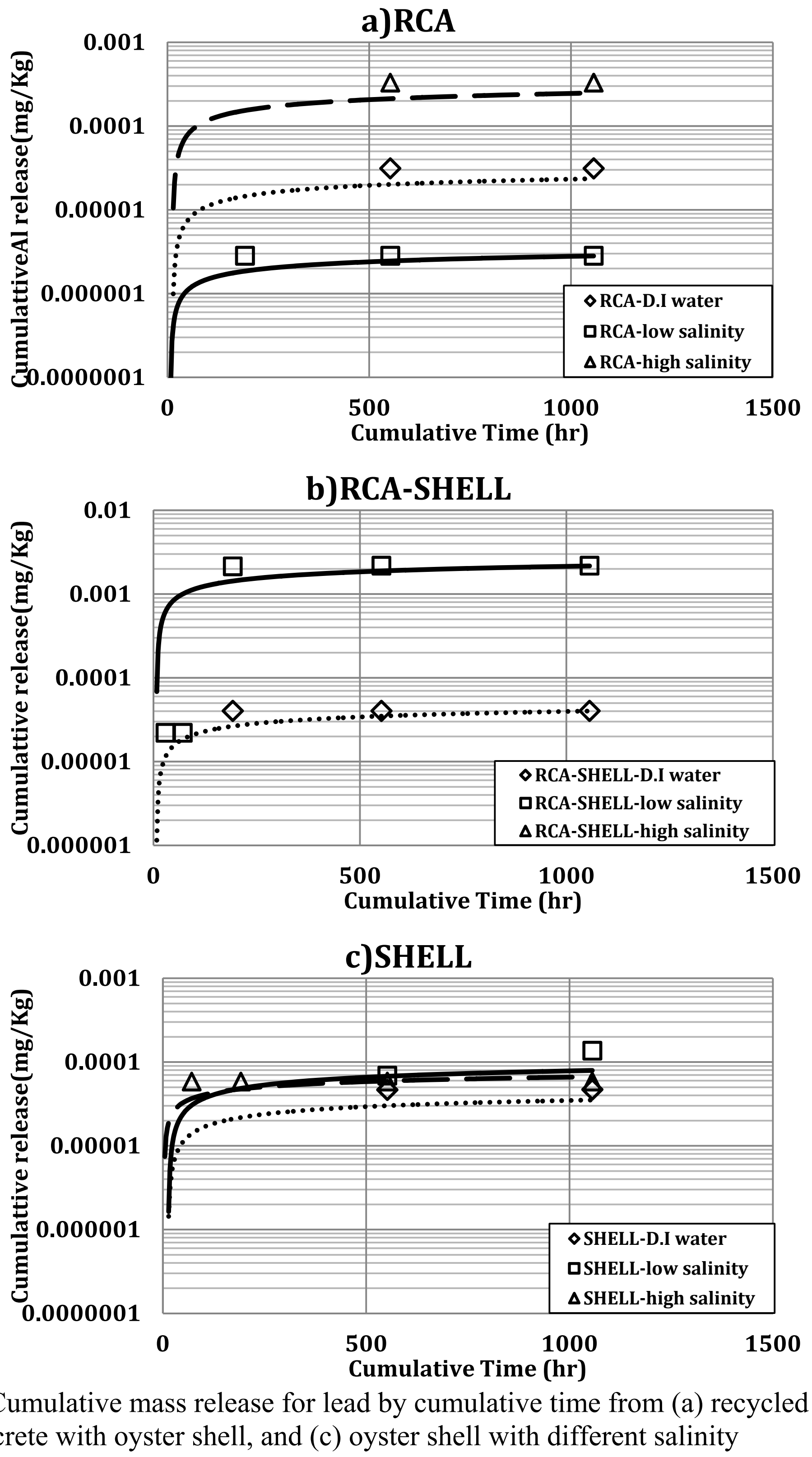


Figure A-3. Cumulative mass release for lead by cumulative time from (a) recycled concrete, (b) recycled concrete with oyster shell, and (c) oyster shell with different salinity

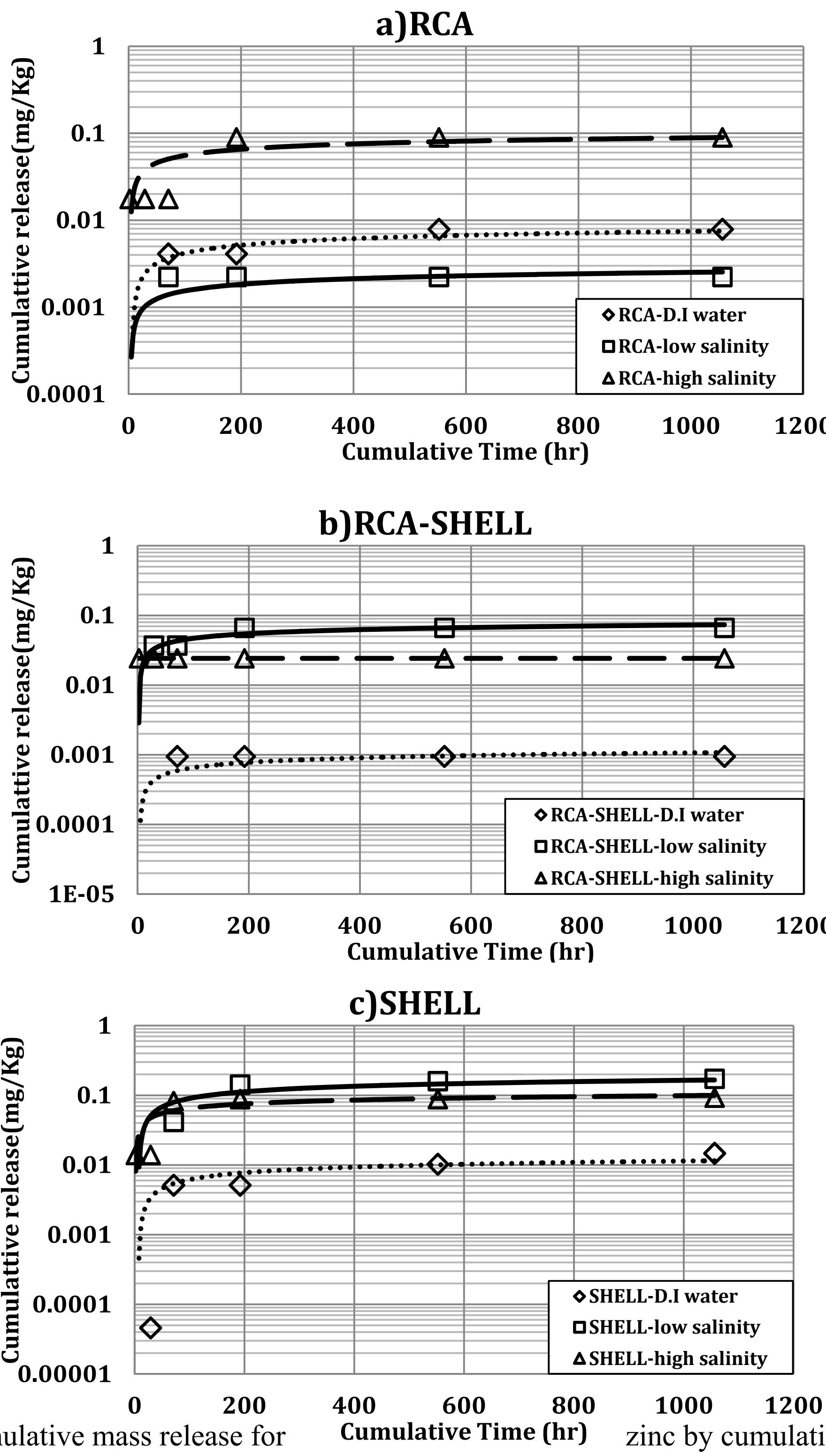


Figure A-4. Cumulative mass release for zinc by cumulative time from (a) recycled concrete, (b) recycled concrete with oyster shell, and (c) oyster shell with different salinity

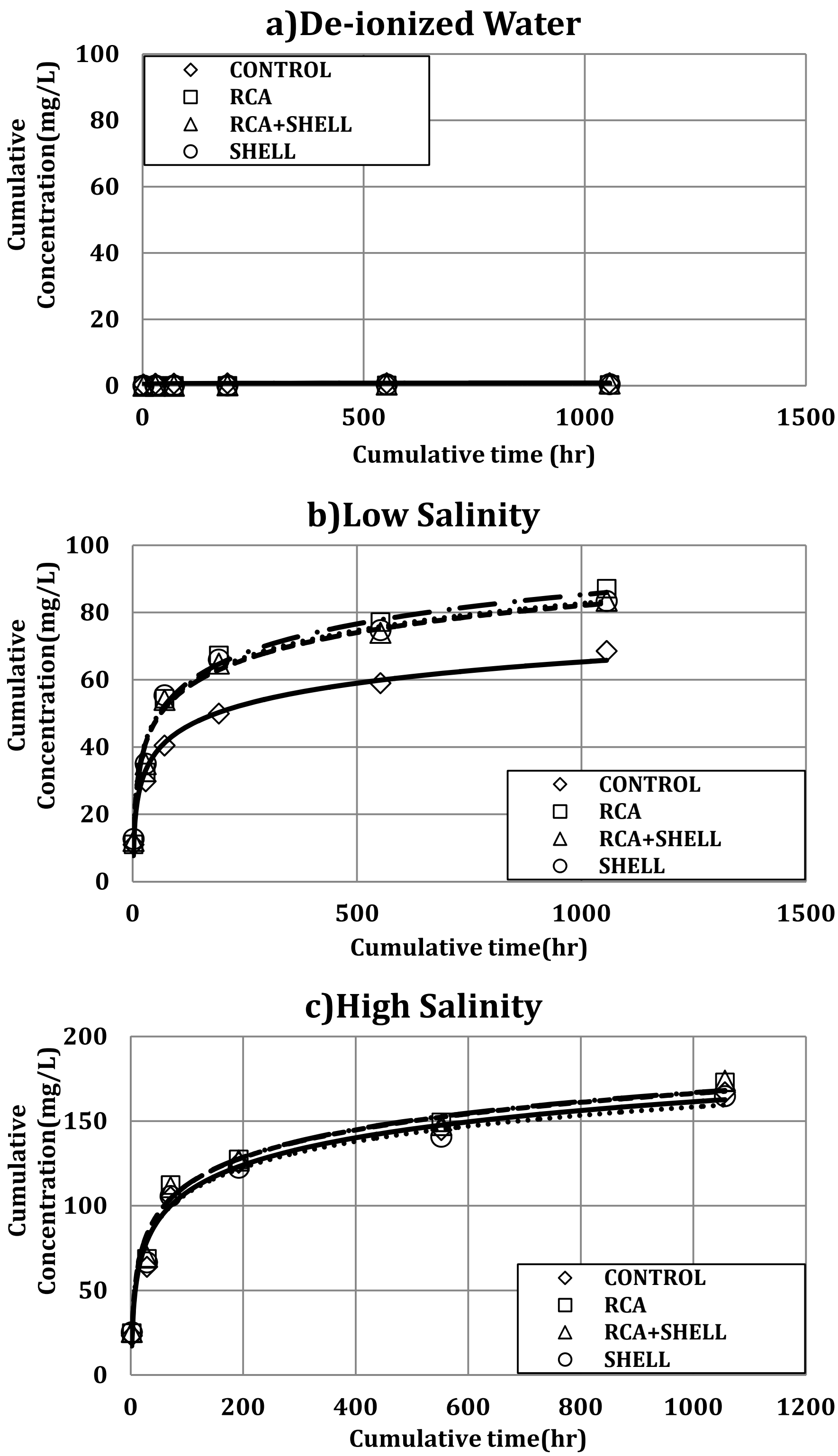


Figure A-5. Nitrate concentration by cumulative time from (a) de-ionized water (DI), (b) low salinity, and (c) high salinity

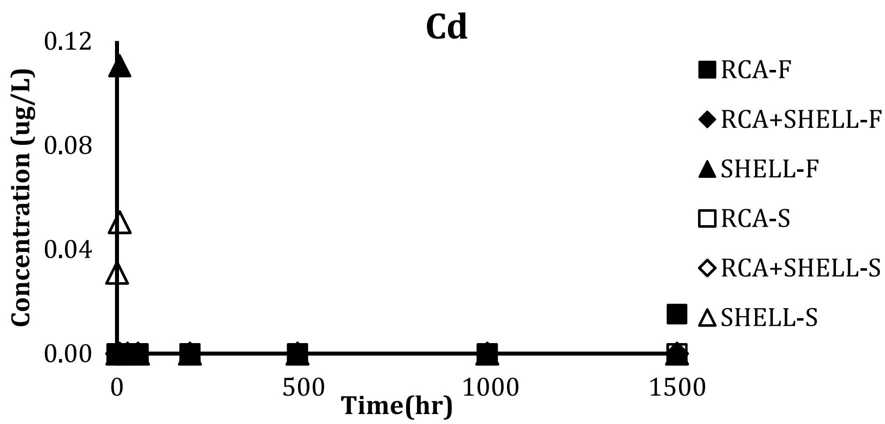


Figure A-6. Cadmium concentration with brackish water (Patuxent River near St. Leonard, MD) by cumulative time, F: fast flow rate, S: slow flow rate

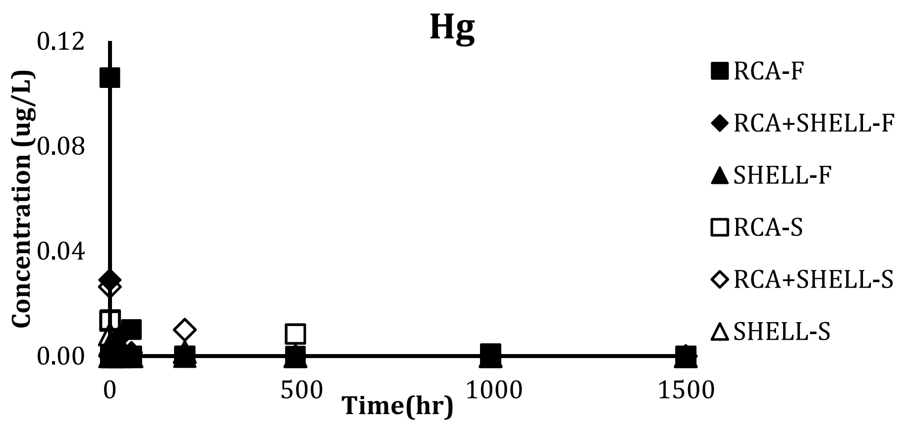


Figure A-7. Mercury concentration with brackish water (Patuxent River near St. Leonard, MD) by cumulative time, F: fast flow rate, S: slow flow rate

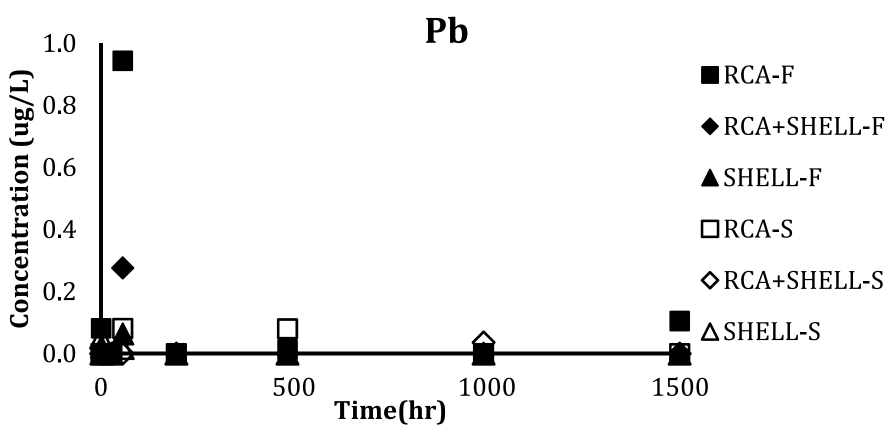


Figure A-8. Lead concentration with brackish water (Patuxent River near St. Leonard, MD) by cumulative time, F: fast flow rate, S: slow flow rate

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