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Groundwater quality assessment of the Piney Point aquifer in the Virginia Coastal Plain

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
at Virginia Commonwealth University.

by

Elizabeth J. Keily

Bachelor of Science in Environmental Studies, Virginia Commonwealth University, 2012

Directors:

Arif M. Sikder

Assistant Professor, Center for Environmental Studies

and

S. Leigh McCallister

Associate Professor, Department of Biology

Virginia Commonwealth University
Richmond, Virginia
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Abstract

Groundwater quality assessment of the Piney Point aquifer in the Virginia Coastal Plain

By: Elizabeth J. Keily, M.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Biology at Virginia Commonwealth University.

Virginia Commonwealth University, 2019.

Directors: Arif M. Sikder, Assistant Professor, Center for Environmental Studies and S. Leigh McCallister, Associate Professor, Department of Biology

The solid phase of an aquifer has an effect on the aqueous phase; if groundwater quality is degraded by the solid phase of an aquifer this is referred to as geogenic pollution. In this study, the Piney Point aquifer in the Virginia Coastal Plain was assessed for mechanisms that may release anions from the solid to aqueous phases and effect water quality. This was done by conducting leaching experiments modified from Balintova et al. (2013). Piney Point aquifer sediments and groundwaters were also analyzed to give a baseline for these experiments. Sedimentary analysis was found to be consistent with McFarland (2017) and groundwater anion concentrations were found to be less than the U.S. Environmental Protection Agency's (EPA) established Maximum Contaminant Levels (MCL). Leaching experiments found that low pH environments may lead to the release of fluoride in association with phosphorus in sediments and general release of chloride. Nitrate release mechanisms in confined aquifers require further study, but it appeared as total inorganic carbon was dissolved, sedimentary total nitrogen concentrations increased. Sulfate concentrations in leaching experiments were found to be associated with sulfur concentrations in the solid phases. Furthermore, leaching experiments

showed that when sediments are exposed to oxic environments then re-exposed to groundwater, higher concentrations of anions were released to the aqueous phases. This could be a particular issue with sulfate concentrations, which were above the EPA MCL in the majority of sediment samples in all leachate treatments.

Introduction

Groundwater quality is related to weathering, recharge rate, and the quality of the recharge water, as well as solid-aqueous interactions in the aquifer. Thus, groundwater chemistry typically reflects the composition of the solid phases of the aquifer, i.e. the stratigraphic formations from which it is derived, since the water is in contact with aquifer sediments for prolonged periods of time (Mora et al. 2017). Anthropogenic activities, such as mining, deforestation, and agriculture, as well as other aspects of industrialization and modernization, increase sedimentation and erosion which frequently leads to increased concentrations of pollutants in aquatic environments (Ayotte et al. 2011, Du Laing et al. 2009).

While groundwaters are often polluted by anthropogenic processes, some groundwater systems can naturally contain pollutants as a result of the regional geologic setting; this is called geogenic pollution. One example is arsenic in Ganges Delta in Bangladesh. Wells were drilled in the 1970s to provide people of Ganges Delta with an alternative to contaminated surface water. The wells appeared to have potable water, however, at the time groundwater was not routinely analyzed for toxic metals and arsenic, and as a result, people ingesting water from these wells developed signs of chronic arsenic poisoning many years later (Younger 2007, Hasan et al. 2009). A similar situation to that in Bangladesh is currently occurring in California's Central Valley. California's San Joaquin Valley supports a large agriculture industry and population that puts high water demand on the aquifers in the area; this has led to approximately 60 m of groundwater level declines in the past century and arsenic was present in ten percent of wells at concentrations higher than 10 ppb (World Health Organization maximum acceptable level) (Smith et al. 2018). Smith et al. (2018) found that arsenic concentrations in groundwater decreased as overpumping of aquifers was avoided. Therefore, geogenic pollution is often

exacerbated by groundwater withdrawal, particularly from overpumping. Overpumping causes a drawdown of the water table which alters the redox state of the sediments, and is a mechanism that leads to acid mine drainage (Younger 2007).

Globally, arsenic and fluoride are the most common sources of geogenic pollution to groundwater; the former is an example of a toxic metal and while the latter is a naturally occurring anion (Younger 2007, Margat and van der Gun 2013). For this study, I will be assessing groundwater quality in terms of anion concentrations.

Anions

Groundwater quality is affected by the presence and concentration of different anions. Anions are negatively charged ions and are primarily nonmetals and nonmetal compounds (Younger 2007). Anion concentrations in groundwater often reflect the aquifer sediments from which they originated. Anions occur naturally in the earth's crust and are readily dissolved into water. Examples of anions include: fluoride, chloride, bromide, nitrite, nitrate, sulfate, and phosphate (AWWA 2014). Typically, ions affect the salinity of groundwater and high salinity can increase risk of high blood pressure or hypertension (Mora et al. 2017). Elevated concentrations of nitrate in groundwater can cause methemoglobinemia or "blue baby syndrome," and high concentrations of sulfate can have laxative effects (Mora et al 2017). Concentrations of fluoride less than 1 mg/L are beneficial to healthy teeth but higher concentrations may hinder bone development and cause fluorosis (Younger 2007, Brindha and Elango 2011).

Mechanisms for release into groundwater

Sediments are the main source of geogenic pollutants in aquifer systems and, depending on sediment surface area, can retain a million times more pollutants than an equivalent volume of

water (Fairbrother et al. 2007). Anions cannot be destroyed by biological or chemical processes, rather, they are transformed from one chemical state to another and their availability is highly dependent on sediment-water interactions (Ayotte et al. 2011). Groundwater frequently reflects the depositional conditions at the time of its formation. For example, ancient groundwaters trapped deep in sedimentary aquifers with high concentrations of chloride can denote ancient seawater trapped within the sediments (Younger 2007). Such is the case for the Chesapeake Bay impact crater where isolated groundwater is highly saline (McFarland 2010).

Prolonged exposure of groundwater with adjacent aquifer soils promotes active surface mineral processing. These processes include ions adhering to (sorption) or releasing from (desorption) the mineral phases of the aquifer sediments. The sorption/desorption potential of aquifer sediments is referred to as cation-exchange capacity (CEC). Aquifer materials associated with the highest CEC are sedimentary organic matter, oxides and hydroxides of iron and manganese, and clay minerals (Younger 2007).

When changes to aquifer chemistry occur, anions may dissociate from the solid phases of sediments and solubilize into groundwater. Factors that affect the CEC, and hence availability of anions, include pH, redox potential, and the presence of organic matter, as well as anthropogenic activities (Ayotte et al. 2011). Generally, in sediments, cationic elements will bind with solid mineral phases of sediment, while anionic elements tend to be located in the aqueous phase (i.e., pore water) (Fairbrother et al. 2007). Even minor alterations in the environmental parameters can mobilize these elements from solid phases to the aqueous phase. For example, at low pH the negative surface charge of organic matter, clay minerals, and Fe/Mn hydroxides is reduced, which prevents most anions from absorbing to the solid phase and promotes their release from the aquifer sediments' surfaces. Cations will compete for bonds to the solid phases, which

stimulates the release of anions to the aqueous phase (Du Laing et al. 2009). Once dissolved in water, anions are more bioavailable and readily consumed by organisms relying on the groundwater (Centioli et al. 2008, Fairbrother et al. 2007).

Groundwater quality may also be affected by the well infrastructure that is responsible for its transportation to the surface (Pieper et al. 2016). For the purpose of this study, I will focus solely on natural contamination of groundwater from sediments and will not be considering well infrastructure as a source of groundwater contamination.

Objective

As half the world's population is dependent on groundwater for their primary drinking water source, it is important to have a fundamental understanding of the factors regulating the transfer of elements and compounds from the solid to the dissolved (or aqueous) phase in global aquifers (Margat and van der Gun 2013). This study will focus on the Piney Point aquifer in the Virginia Coastal Plain, which, as of 2002, accounted for five percent of groundwater used in the region (McFarland and Bruce 2006). The primary objective of this study is to assess the potential groundwater quality in terms of anion concentrations of the Piney Point aquifer and to gain a mechanistic understanding of the release mechanisms of anions from the solid phases of the aquifer under varying pH conditions.

A more comprehensive understanding of dissolved anion concentrations, as well as, their controlling environmental factors is essential for continued use of groundwater for human consumption and agriculture. A study of this kind has not been performed on the Piney Point aquifer sediments, so this study will be of importance to understand the concentrations of the anions present and their potential for mobility, which has implications for the health and safety of the citizens dependent on the Piney Point aquifer as a primary source of water supply.

Furthermore, if there are instances of anion concentrations not in compliance with the EPA drinking water standards, these might pose a risk to public health (Table 1). The EPA drinking water standards used in this study are Maximum Contaminant Level (MCL), the highest level of a contaminant that is allowed in drinking water before human health is potentially affected, and Secondary Drinking Water Regulations (SDWR) or Secondary Maximum Contaminant Level (SMCL), the highest level of a contaminant allowed in drinking water before aesthetic conditions (such as taste, color, and odor) are affected that may cause people to stop using public water (U.S. EPA 2018, U.S. EPA 2017). It is hypothesized that all anion concentrations in the Piney Point aquifer will be less than the EPA standards for drinking water since all wells tested in this study are routinely monitored by their respective water authorities.

In the Piney Point aquifer, elevated concentrations of anions (if any) will most likely be caused by overpumping and associated alterations to the aquifer chemistry rather than runoff from agriculture and industry, since the wells sampled for this study draw from an area of the aquifer that is relatively deep and confined throughout its reach. The present study was carried out by conducting leaching experiments on the bulk sediments from the Piney Point aquifer and subsequently measuring the anion concentrations in leachate after pH had been manipulated. This was done to see how anion concentrations are affected by changes in pH. Groundwater and sediment samples from the Piney Point aquifer were collected and analyzed in order to understand the geochemistry and mineralogy of the solid and aqueous phases of the aquifer. Leaching experiments were meant to simulate redox changes due to water table drawn down via well water extraction and the resulting pH changes from aquifer sediments exposed to oxic conditions. The Piney Point aquifer was selected for this study since most of the groundwater is drawn from a productive limestone formation while the rest of the aquifer is typically not utilized

for drinking water. In the event of water table drawn down, water may be drawn from unwanted areas of the aquifer, and have an affect on drinking water quality.

Furthermore, this study will be critical in assessing future impacts of climate change on groundwater quality. As surface water sources become depleted or salinized (via saltwater intrusion) and populations become more dependent on groundwater, it will become increasingly important to have a fundamental understanding of regional groundwater supplies and how they may change due to increased water exploitation (Margat and van der Gun 2013).

Methods

1. Study area

The Virginia Coastal Plain has a temperate, humid climate and is generally heavily vegetated. The land surface is underlain by layers of unconsolidated to semi-consolidated sediments that increase in thickness eastward toward the Atlantic Ocean to depths of as much as 6,000 feet before reaching bedrock (Figure 1; McFarland and Bruce 2006, McFarland 2017).

The aquifer system of Virginia Coastal Plain consists of various geological formations formed by the layers of sediments that were deposited on the continental shelf between the Cretaceous to Quaternary age (McFarland 2010, McFarland 2017). In general, groundwater is primarily recharged by infiltration of precipitation. Groundwater in unconfined aquifers flows a relatively short distance before it is discharged into adjacent streams, however, small amounts of this groundwater may flow further downward and recharge the deeper confined aquifers. In the Virginia Coastal Plain, this typically occurs along the Fall Zone and at divides between major river valleys (McFarland 2010). Due to the stratification of the Coastal Plain sediments, groundwater flow in its confined aquifers is generally lateral along the eastward dip toward the ocean and also around major withdrawal centers (Figure 1; McFarland 2010). Over the past

century, groundwater withdrawal in this area has continuously increased, with most large withdrawals controlled by the Virginia Department of Environmental Quality (VA DEQ). There are also estimated to be 200,000 small, unregulated withdrawals generally for “individual domestic use” (McFarland 2017). Cones of depression can be as deep as 150 feet below sea level and are centered around large industrial facilities in the cities of Franklin and West Point (McFarland 2017). Due to this increased groundwater withdrawal rates, the hydraulic gradient of the region has been redirected landward and is approximately double what it was pre-pumping (McFarland 2017). Additionally, rates of water table decline are currently estimated to be between 1-2 feet per year (McFarland 2017).

Several hydrogeological units are present in the Virginia Coastal Plain forming a series of aquifers and confining units (Figure 1; McFarland 2017). As of 2003, the Potomac aquifer is the most heavily used accounting for seventy-four percent of groundwater withdrawals in the region, while the Piney Point accounted for five percent of groundwater withdrawals (McFarland and Bruce 2006). This is a significant amount considering yields are typically 10-50 gal/min from wells in the middle reaches of Northern Neck, Middle Peninsula, and York-James Peninsula, but can be as high as 400 gal/min in heavily used municipal wells, such as those in James City County (McFarland and Bruce 2006). These numbers are likely to increase with increasing populations in these areas.

The Piney Point aquifer is considered confined throughout most of its reach. Outcrops of the Piney Point aquifer occur at steep slopes along the major river valleys on the western margin of the Coastal Plain, with the most significant in Virginia located along the Pamunkey River (McFarland 2017, Ward 1985). The Piney Point aquifer is present throughout the Virginia Coastal Plain and adjacent parts of Maryland and North Carolina. In Virginia, it is primarily

utilized as a groundwater source on the Northern Neck, Middle Peninsula, and York-James Peninsula, but is typically not utilized for groundwater south of James River, over the Chesapeake Meteor Impact, and on the Eastern Shore due to the presence of brackish water within the aquifer (McFarland and Bruce 2006, McFarland 2017).

The Piney Point aquifer is comprised of several geological formations deposited under relatively uniform conditions on the marine Continental Shelf; these are closely connected hydraulically and assumed to function as a continuous uninterrupted medium for water to move through (McFarland and Bruce 2006, McFarland 2017). It is generally made up of medium to coarse-grained glauconitic, phosphatic, variably calcified, fossiliferous sands, that were deposited between 11-49 million years ago, during early Eocene to early Miocene (McFarland and Bruce 2006, Ward 1985). Additionally, McFarland (2010) cites the median pH of the Piney Point aquifer to be 8. Below is a description of each geologic formation within the Piney Point aquifer and those formations immediately above and below it (Figure 2).

Only the uppermost formations in the Piney Point aquifer are continuous throughout its reach, most of the lower formations are not present across the Chesapeake Bay Meteor Impact (McFarland 2017). For the purpose of this study, only formations present where groundwater samples and sediment samples were collected were described in detail. This study focused specifically on the Piney Point formation, as most of the groundwater used for public supply is drawn from this formation, from the productive 'limestone' (McFarland 2017).

The Nanjemoy-Marlboro confining unit lies below the Piney Point aquifer for most of its extent and was deposited in the early Eocene. It consists of marine sediments that are silty and clayey, fine- to medium-grained glauconite with quartz sand and clay (McFarland 2017). The lower sediments of the Nanjemoy Formation Potapaco Member and the Marlboro Clay

underlying it make up the Nanjemoy-Marlboro confining unit, which are hydraulically similar and together impede horizontal flow. Within the Chesapeake Bay impact crater, the Chickahominy confining unit is below the Piney Point aquifer and is primarily composed of clay (McFarland 2017).

The Nanjemoy Formation Woodstock Member is the deepest formation within the Piney Point aquifer and was deposited in the early Eocene. It is composed of marine sediments that are variably shelly and pebbly, medium- to coarse-grained quartz, and glauconite sand (McFarland 2017).

The Piney Point Formation is next lowest and most groundwater is withdrawn from this formation (McFarland 2017). It was deposited in the middle Eocene and is composed of marine sediments, which are variably shelly, pebbly, and calcite-cemented with medium- to coarse-grained quartz and glauconite sand (McFarland 2017). The Piney Point Formation is composed of a productive 'limestone' and interbedded sands. Calcite cementation is developed well enough that it forms intervals of hardened limestone. Piney Point Formation limestone is composed of a low porosity massive structure that is solution-channeled and interbedded with uncemented sand (McFarland 2017).

Above the Piney Point Formation, lies the Old Church Formation, which was deposited in the late Oligocene. It is composed of marine sediments that are silty, variably shelly and pebbly with fine-to-medium grained quartz, glauconite, and phosphate sand (McFarland 2017).

The Calvert Formation Newport News unit and basal part of the Plum Point Member comprise the top formation of the Piney Point aquifer. Though these two units are geologically distinct, they are hydraulically similar and are considered one geological unit composing the uppermost part of the Piney Point aquifer. These formations were deposited from early and

middle Miocene and are composed of marine sediments that are silty, variably shelly and pebbly with medium- to coarse-grained quartz and phosphate sand (McFarland 2017).

The Calvert confining unit is above the Piney Point aquifer for most of its extent and is a silty, fine-grained quartz sand. The confining unit is made up of the fine-grained portion of the Plum Point Member that lies above the coarse-grains of the lower part of the formation member and the Calvert Beach Member, both of the Calvert Formation. These are hydrologically similar and together impede horizontal flow. The Calvert Formation fine-grained Plum Point Member was deposited in the middle Miocene and is composed of marine sediments that are silty and clayey, microfossiliferous, fine-grained quartz sand (McFarland 2017). In the southwestern part of its extent, the Piney Point aquifer is below the Saint Marys confining unit, which is a clay to clayey fine-grained quartz sand (McFarland 2017).

2. Sampling

a. Sediments

Twenty-five sediment samples were selected from the USGS Banbury Cross borehole (Latitude: 37.365, Longitude: -76.721) at regular intervals and allowed to dry at room temperature. These core samples represent different depths within the Piney Point aquifer (from 256-299 feet below land surface) and are from the Old Church, Piney Point, and Nanjemoy (Woodstock Member) formations (Table 2). Sediment samples were selected to be in as close to regular intervals as was possible with available samples, with representation from the Old Church (3 samples), Piney Point (18 samples), and Nanjemoy (Woodstock Member, 4 samples) formations.

b. Groundwater

Piney Point aquifer groundwater samples were collected from 26 public wells that access the Piney Point aquifer (Figure 3). Groundwater samples were collected with the help of the Newport News Waterworks, Virginia Department of Environmental Quality, and James City County Service Authority. Wells were flushed for approximately 15 minutes prior to sampling and water samples were collected directly from spigots as close to the well as possible. Water samples were filtered in the field through a pre-rinsed Pall Acropak™ 1500 Supor® Membrane 0.8/0.2 µm capsule filter. Sample containers, 40mL amber vials, were triple rinsed with filtered well water before collecting. Groundwater pH, temperature, and Eh were also collected in the field at each well site. Additionally, at one well site (Retreat; Latitude: 37.415, Longitude: -76.858) two 1L Nalgene bottles of raw well water were collected to be used as the Aquifer treatment for the leaching experiments. After collection, all groundwater samples were immediately placed on ice and stored in refrigeration (4°C) in the lab until analyzed or utilized in leaching experiments.

3. Laboratory Analysis

a. Sediment Analysis

Approximately 4g from each sediment sample was crushed with mortar and pestle into a fine powder. Bulk sediment chemistry was determined from crushed sediments by x-ray fluorescence (XRF) with a PanAnalytical Epsilon 3 XL at the VCU Nanomaterials Core Characterization Facility.

Crushed sediment samples were also analyzed for total inorganic carbon (TIC), total organic carbon (TOC), and total nitrogen (TN) in the Environmental Analysis Lab at VCU. Total carbon (TC) and total nitrogen values were obtained by adding approximately 6mg of each

crushed sediment to tin capsules that were combusted with a Perkin-Elmer CHN analyzer. In order to obtain TOC and total nitrogen after HCl wash (TN_{HCl}) values, approximately 1g of each crushed sediment sample was treated with HCl in order to remove all calcium carbonate and other inorganic carbon. Approximately 10mL of HCl was added to each sediment sample, stirred, and allowed to sit overnight. DI water (Milli-Q) was added to each sample, to dilute HCl, and the water-acid mixture was pored off. Remaining sediments were allowed to air dry at room temperature for one week and then placed in a drying oven ($45^{\circ}C$) for 24 hours prior to being analyzed again with Perkin-Elmer CHN analyzer. TIC values were obtained by subtracting TC values from TOC values.

b. Groundwater Analysis

All 26 groundwater samples were analyzed for anion concentration with a Thermo Integriion ion chromatograph (IC) at the Research Instrumentation Facility of the Department of Chemistry, VCU.

c. Leaching Experiments and Leachate Analysis

Leaching experiments were carried out on the dried bulk sediments from nine core samples from the USGS Banbury Cross borehole, in stratigraphical order: two from below the Piney Point Formation, five from the Piney Point Formation, and two from above the Piney Point Formation (Table 3). Leaching experiments followed methods modified primarily from Balintova et al. (2013). Hasan et al. (2009), von Bromssen et al. (2008), and Yu et al. (2015) were also used as reference when constructing experiment design.

Sediments were fully dried before initiation of leaching experiments to ensure they were fully exposed to an oxidized environment. Approximately 1g of each of the nine bulk sediment samples received one of the four treatments: acidic (pH 2.00), basic (pH 10.88), natural aquifer

water, and DI water (Milli-Q) (Table 4). The solutions for the basic and acidic treatments were mixed prior to the leaching experiments by adding 50% sodium hydroxide (NaOH) and ultrapure 68% nitric acid (HNO₃) to DI water, respectively. DI water was used as a control since it is free of anions and cations that may interfere with anion concentrations in the leachate. Natural aquifer water was collected at the same time as groundwater samples were collected at the Retreat well (Latitude: 37.475, Longitude: -76.858) and was filtered in the lab through a pre-rinsed Pall Acropak™ 1500 Supor® Membrane 0.8/0.2 µm capsule filter immediately prior to usage in leaching experiments.

Approximately 40mL of treatment solution was added to each 1g sediment sample to create a sediment-water slurry ratio of 1:40. Sediment samples were thoroughly mixed with added solutions and allowed to sit for 96 hours, 72 hours greater than Balintova et al. (2013), to allow the sediments to fully saturate.

The leachate was collected via vacuum filtration using glass microfibre filter (Whatman GF/A pore size 1.6µm) and placed in a 40mL plastic vial, for anion analysis, and stored at 4°C. There was a total of 36 sediment leachate samples for anion analysis. Additionally, a 40mL vial of each treatment solution were set aside to be analyzed for anion concentrations. Therefore, there were a total of 4 treatment solutions for anion analysis.

All leachate samples were analyzed for anion concentrations by a Thermo Integrion ion chromatograph (IC) at the Research Instrumentation Facility of the Department of Chemistry, VCU.

4. Statistical Analysis

Regression analysis was performed in Microsoft Excel for leaching experiments to determine possible relationships between sediment compound concentrations and anion concentrations in each leachate.

Results and Discussion

Sediments

Elemental concentrations in sediments were collected as a baseline for solids of the aquifer to be used in leaching experiments. Sediment samples from the Banbury Cross borehole were analyzed for elemental concentrations with XRF at the Nanomaterials Core Characterization Facility and CHN analyzer at the Environmental Analysis Lab (Table 5). The solid phases were analyzed because they will likely have a significant effect on the concentration of anions in the aqueous phases of the aquifer. There were several general trends in elemental sediment concentrations tested in this study (Figure 4). In general, silicon (Si) and calcium (Ca) were the most abundant elements in sediment samples with ranges of 5.89-34.26% and 0.57-49.65%, respectively. Samples from the younger Piney Point sediments tended to contain greater percentages of Ca than Si, which is consistent with location of the productive limestone (McFarland 2017). There did not appear to be any trends in total nitrogen (TN) before or after HCl wash (TN_{HCl} ; Table 5). TOC values ranged from 0.08-1.30% and had the highest concentrations in Old Church sediments. TIC values ranged from 0.05-10.24% and had the highest concentrations in Piney Point sediments, this is related to the limestone-like properties of the Piney Point formation (McFarland 2017). Sulfur ranged from 0.75-17.52% and was highest in younger sediments, those from Old Church sediments and younger Piney Point sediments.

These results could have significance as higher TOC and higher sulfur concentrations can lower the pH of water, while higher TIC concentrations can make water more basic.

Based on sediment TIC and sulfur concentrations, there appears to be a distinct difference between upper and lower Piney Point sediments (Figure 4). This is consistent with McFarland (2017). As described previously, the Piney Point Formation is made up of intervals of limestone and uncemented sands. It is likely that in sediments from the Banbury Cross borehole, the sediments that make up the upper part of the Piney Point formation consist primarily of limestone and the sediments of the lower part of the Piney Point formation consist primarily of uncemented sands as described in McFarland (2017). This is also consistent with the description of sediments used in this study from Table 3, which shows that in the Piney Point sediments there appears to be a change in color and a change from limestone to sand between samples 22 and 26 (272 feet and 276 feet below land's surface).

Since McFarland (2017) describes the upper Piney Point sediments as limestone, these sediments are less porous. The presence of pyrite in the upper Piney Point sediments also indicates a reducing environment which was probably preserved due to calcification. McFarland (2017) also states that lower Piney Point sediments are sandy and, therefore, more porous. Therefore, sediments from the upper and lower Piney Point formation are different in terms of chemical and sedimentological characteristics. This data will serve as a baseline for leaching experiments since the solid phases of the aquifer will affect the aqueous phases. Since sediments were fully dried before XRF and CHN analysis these results represent a scenario in which the solid phases are exposed to oxic conditions.

Groundwater

Groundwater samples were collected to give a current assessment of the aqueous phases of the aquifer. Twenty-six groundwater samples were analyzed for anion concentrations with ion chromatograph (IC; Table 6). All anion concentrations were less than the EPA MCL values, so it is likely that currently there are no negative effects associated with these wells from excess fluoride, chloride, nitrate, and sulfate. One well (Surprise Hill) did exceed the EPA SMCL of 2 ppm for fluoride. However, this is a VA DEQ monitoring well located on the Northern Neck where the Piney Point aquifer is typically not utilized as a drinking water source, so there is likely no associated health or aesthetic concerns with this well. Future possible changes to anion concentrations in the aqueous phases of the aquifer from overpumping and its associated geochemical changes are discussed below.

Anions in Leaching Experiments

Fluoride

Fluoride in groundwater is typically associated with compounds in solid phases of the aquifer that are naturally high in fluoride. Fluoride in groundwater is associated with the following compounds: fluorite, fluorapatite, apatite, fluormica, biotite, epidote, micas, clays, and phosphorite (Brindha and Elango 2011). Fluorite can occur in igneous and sedimentary rocks, particularly those of marine origin (like those of the Piney Point formation) (Brindha and Elango 2011). In Virginia, fluoride in groundwater is associated with desorption from phosphatic sedimentary material (McFarland 2010).

Fluoride concentrations higher than the recommended levels can cause dental and skeletal fluorosis (Brindha and Elango 2011, Younger 2007). In Virginia, there is a broad belt of high fluoride concentrations in the groundwater underlying Suffolk. While our study area was

not within this belt, sediments used in this study were deposited in a similar environment, particularly the presence of phosphatic sedimentary material in the Old Church Formation, from which fluoride can desorb (McFarland 2010, McFarland 2017).

In general, fluoride concentrations did not appear to be affected by the different leachate treatments or sediment TOC, TIC, and sulfur concentrations. However, fluoride concentrations in acidic leachate samples from Old Church sediments were higher than in any of the other leachate (Figure 5). This could be related to the higher concentrations of TOC in Old Church sediments; there is also a strong relationship between fluoride concentrations in acidic leachate and TOC in sediments to support this (Figure 6; $r^2=0.7847$).

As described above, fluoride did not vary much in the different leachate treatments, except acidic. The lower pH environment likely caused dissolution of phosphate which released fluoride into leachate, as is described in Brindha and Elango (2011). Regression analysis could not be calculated on sediment phosphorous concentrations and fluoride concentrations in leachate as phosphorus was not present in enough sediment samples. Figure 5 shows that phosphate in sediments was detectable in Old Church sediments and the youngest sediment sample from the Piney Point formation, which is consistent with the higher concentrations of fluoride in acidic leachate samples from these sediments. Sediment phosphorus can be seen as a possible controlling environmental factor of aqueous fluoride. Therefore, the higher concentrations of fluoride in acidic leachate samples are likely due to the presence of phosphorus in sediments and possibly the presence of TOC. In terms of future possible effects to the Piney Point aquifer, if pH is lowered from the effects of overpumping, more fluoride may be released to the aqueous phase if phosphorus and TOC are present in the solid phases. As groundwater is drawn from formations other than the Piney Point within the aquifer, due to overpumping, more

fluoride may be released from sediments high in phosphorus and TOC. Therefore, there is a chance that fluoride concentrations may increase in the future.

Chloride

Natural sources of chloride in aquifers include solid-aqueous interactions and salt water intrusion in coastal areas (Panno et al. 2006, WHO 2013a). Increased chloride concentrations can increase the corrosivity of water: the chloride will react with metal ions and form soluble salts. This leads to increased metal concentrations in drinking water (WHO 2013a).

As climate change worsens, the saltwater transition zone could move further inland; however, McFarland (2017) indicated that the area of the Piney Point aquifer surrounding the productive limestone appears to be far enough inland that as of 2015 there has not been an increase in chloride concentrations. Salt water intrusion does not currently appear to be contributing to chloride concentrations in the Piney Point aquifer, but there is a potential risk for this in the future.

The chloride present in Piney Point wells is, therefore, likely from solid-aqueous interactions within the aquifer. The chloride present in the wells sampled, as well as the sediments, could be from marine inclusion, which makes sense since the Old Church, Piney Point, and Nanjemoy formations are made up of marine sediments (McFarland 2017). The sediments could possibly be preserving chloride, as well as other ions, from the time when the sediments formed the floor of an ancient sea. However, chloride concentrations do not appear to be affected by any sediment compounds concentrations or geological formations (Figure 7). The solid phases do not appear to be the mechanism for releasing chloride.

Chloride concentrations were affected by the different leachate treatments (Figure 7). Acidic leachate had the highest chloride concentrations, while DI leachate had the lowest

chloride concentrations. Basic and aquifer leachate chloride concentrations were comparable, with chloride concentrations in basic leachate slightly higher than aquifer leachate chloride concentrations. Additionally, the two-fold higher release of chloride in acidic leachate is likely due to the dissolution of calcite (TIC), which is also a source of the preservation of ancient sea water.

Future effects to the aquifer could be from either saltwater intrusion or overpumping. If aquifer pH is lowered as a result of overpumping, more chloride could be released to the aqueous phase of the aquifer from dissolution of TIC. Low pH likely releases more chloride to aqueous phases of the aquifer. As overpumping happens and pH changes occur in the aquifer more chloride could be released, possibly raising chloride concentrations in groundwater. This could become a problem especially if salt water intrusion begins occurring within the Piney Point aquifer.

Nitrate

Nitrate occurs naturally as part of the nitrogen cycle and is a stable ion. In the USA, natural concentrations of nitrate in groundwater do not exceed 4-9 ppm and depends on soil type and geological situation (WHO 2011). The major sources of nitrate in groundwaters are inorganic fertilizers from agricultural activity and waste bi-products from human and animal excrement, so nitrate contamination is typically only an issue in shallow aquifers (WHO 2011, Majumdar and Gupta 2000). Possible human health effects from high concentrations of nitrate include methemoglobinemia or “blue baby syndrome,” gastric cancer, birth malformations, and hypertension (WHO 2011, Majumdar and Gupta 2000). However, since the Piney Point aquifer is deep and confined, nitrate from these sources should not be an issue.

Nitrate is not supposed to have high concentrations in deep aquifers. The concentrations of nitrate in DI, basic, and aquifer leachates are within the range (4-9 ppm) the WHO (2011) establishes for natural nitrate concentrations in groundwaters. Nitrate concentrations in all leachate treatments do appear to be influenced by geological formation (Figure 8). Nitrate concentrations are highest in all leachate treatments from Nanjemoy sediments. Nitrate concentrations are also similar in all leachate treatments from Old Church sediments. And nitrate concentrations are the lowest in all leachate treatments from Piney Point sediments. Additionally, this pattern appears to be an inverse relationship with TIC concentration in sediments for nitrate concentrations all leachates (except acidic) (Figure 9; DI: $r^2=0.6081$; basic: $r^2=0.5877$; aquifer: $r^2=0.7133$). The poor relationship in acidic leachate could be due to the very high concentrations of nitrate due to the use of nitric acid. It is likely that the variation in nitrate is due to the nitric acid used to acidify leachate samples and create the acidic leachate treatment. This is likely the cause for the acidic leachate having several orders of magnitude higher nitrate concentrations than the other leachate treatments. The nitrate data from this study is therefore unreliable. In future leaching studies, if nitrate is going to be studied it would be best to use an acid other than nitric.

Sediments were treated with HCl in order to remove TIC and, as a result, total nitrogen after HCl wash was calculated (TN_{HCl}). It is possible that the increase in some sediment samples of TN_{HCl} is due to TOC having a greater effect on sediments (Figure 8). Since the TIC was dissolved with HCl it is likely that the higher TN_{HCl} concentrations are associated with TOC. There is a possible moderate relationship between nitrate in leachates (except acidic) and total nitrogen after HCl wash in sediments (Figure 10; DI: $r^2=0.3399$; basic: $r^2=0.3442$; aquifer: $r^2=0.3616$). Overpumping may lead to release of nitrogen compounds from TOC in deep

sediments but more research is required. However, since sediments used in leaching experiments were not treated with HCl, it is not possible to know how nitrate concentrations will be affected by possible lowered pH due to overpumping within the Piney Point aquifer. Additionally, in order to better understand the mechanisms controlling nitrate in confined aquifers, further analysis of solid phases of the aquifer and possibly characterization of TOC and TN in aquifer sediments will need to be carried out, as well as a possible repeat of leaching experiments with sediments treated with HCl.

The data suggests that if pH and redox changes occur in the Piney Point aquifer more nitrate may be released from dissolution of the limestone and sediment TOC may have a greater effect on the aqueous phases of the aquifer, but further analysis needs to be done.

Sulfate

Sulfate is the most stable form of sulfur in aqueous aerobic conditions and it is typically the most abundant anion in natural waters (Miao et al. 2012). Geogenic sources of sulfate in groundwater include: weathering of sulfide minerals, rainwater, and atmospheric deposition (Miao et al. 2012, Tostevin et al. 2016). In southern New Zealand, local basement rocks are rich in metamorphic sulfide minerals which contributes to sulfate in groundwater (Tostevin et al 2016). There are many anthropogenic sources of sulfates to water systems, such as fertilizers, dyes, soaps, paper, textiles, and sewage (Tostevin et al. 2016, WHO 2013b); these are likely not affecting the Piney Point aquifer due to its depth and that it is confined throughout its reach in this study.

High concentrations of sulfate are of concern in drinking water systems because they can have laxative effects, especially for infants (WHO 2013b, Miao et al. 2012). Sulfate was chosen for this study because of this health effect and since sulfur concentrations have important

implications for pH balance and redox potential of groundwaters, often associated with acid mine drainage (Tostevin et al. 2016, Miao et al. 2012).

Sulfate concentrations in all leachate samples appear to follow a similar pattern to sediment concentrations of sulfur (Figure 11). Regression analysis shows a strong relationship between sulfate concentration in leachates and sediment sulfur concentrations (Figure 12; DI: $r^2=0.7466$; acidic: $r^2=0.7657$; basic: $r^2=0.7025$; aquifer: $r^2=0.7270$). This indicates that the sulfate is leached from the sediments. Sulfate concentrations in acidic and basic leachates from sediment sample 19 also appear to anomalously high. This could be due to high sediment TIC concentrations and the correlations suggest a moderate relationship between sulfate concentrations in acidic and basic leachate and TIC concentrations in sediments (Figure 13; acidic: $r^2=0.3407$; basic: $r^2=0.2318$).

If overpumping of the Piney Point aquifer occurs as more sediments are exposed to oxic conditions, more sulfate may be released from them into the aqueous phase of the aquifer. This is suggested by the large difference between sulfate in groundwater samples and leachate samples (Table 6, Table 7).

Conclusion

This study was meant to help understand the mechanisms that release anions in the Piney Point aquifer from the solid phases of the aquifer, as leaching experiments have not been carried out on Piney Point aquifer sediments previously. It was found that in lower pH conditions, fluoride concentrations are affected by sediment concentrations of phosphorous, which is consistent with Brindha and Elango (2011). Chloride concentrations were affected the most by pH, with lower pH's releasing the most chloride to the aqueous phase. Nitrate concentrations require further research, but it appears as TIC is dissolved from pH changes, TOC may have a

greater effect on nitrogen chemistry in the aquifer. Sulfate concentrations in leachate were found to be directly associated with sediment concentrations.

Additionally, in general, all anions studied have higher concentrations in leachate than in groundwater samples (Table 6, Table 7). This implies that when sediments are exposed to oxic conditions they will release more anions to the aqueous phase of the aquifer. Additionally, sulfate concentrations in leaching experiments exceeded their EPA SMCL for nearly every sediment sample and nitrate concentrations were close to their EPA MCL in Nanjemoy sediments. Water quality may be affected if overpumping occurs and the solid phases of the Piney Point aquifer are exposed to oxic conditions. It is likely that sulfate will become an issue for water quality. If groundwater is drawn from the Nanjemoy formation as a result of overpumping nitrate levels will need to be carefully monitored, as they will be close to the EPA MCL.

These findings establish an initial idea of how increased water exploitation may affect the groundwater quality of the Piney Point aquifer. Climate change may also worsen the effects of overpumping and further study is needed to more fully grasp the mechanisms releasing anions to aqueous phases of the aquifer.

Tables

Table 1. US EPA Drinking Water Standards: Maximum Contaminant Level (MCL) and Secondary Drinking Water Regulations (SMCL) (U.S. EPA 2017, U.S. EPA 2018).

Compound	MCL (ppm)	SMCL (ppm)
Aluminum	-	0.05-0.2
Antimony	0.006	-
Arsenic	0.01	-
Barium	2	-
Beryllium	0.004	-
Cadmium	0.005	-
Chloride	-	250
Chromium	0.1	-
Copper	1.3	1
Fluoride	4	2
Iron	-	0.3
Lead	0.015	-
Manganese	-	0.05
Mercury	0.002	-
Nitrate	10	-
Nitrite	1	-
Selenium	0.05	-
Sulfate	-	250
Thallium	0.002	-
Uranium	30 (ppb)	-
Zinc	-	5

Table 2. Depth below land surface and formation of sediment samples collected from the USGS Banbury Cross borehole. Samples in bold were used in leaching experiments.

Sample Code	Depth below land surface (ft)	Formation
5	255.9	Old Church
8	258.9	Old Church
10	260.9	Old Church
13	263.0	Piney Point
14	264.1	Piney Point
15	265.1	Piney Point
16	266.1	Piney Point
17	267.1	Piney Point
19	269.1	Piney Point
20	270.1	Piney Point
21	271.1	Piney Point
22	272.1	Piney Point
23	273.1	Piney Point
24	274.1	Piney Point
25	275.1	Piney Point
26	276.1	Piney Point
28	278.1	Piney Point
29	279.1	Piney Point
31	281.1	Piney Point
32	281.8	Piney Point
34	283.8	Piney Point
38	287.0	Nanjemoy
39	288.0	Nanjemoy
40	294.1	Nanjemoy
42	299.1	Nanjemoy

Table 3. Descriptions of sediment samples used in leaching experiments. All lithological descriptions are from Powars 2014.







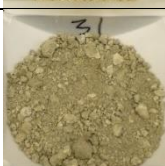
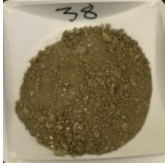

Sample Number	Depth (ft)	Picture	Lithological Description	Stratigraphy
5	255.9		Very silty with clear sand burrows. 5Y 3/1	Old Church Formation
8	258.9		Very silty quartz sand with clear sand burrows. 5Y 3/2	Old Church Formation
13	263.0		Soft limestone. Pyritic. 10YR 5/3	Piney Point Formation
19	269.1		Soft limestone. Pyritic. 10YR 7/3	Piney Point Formation
22	272.1		Soft limestone. 10YR 7/8	Piney Point Formation
26	276.1		Muddy sand, highly burrowed. 10 YR 5/5	Piney Point Formation
31	281.1		Glauconitic, quartz sand, very silty to slightly silty. Pyritic. 5G 4/1	Piney Point Formation
38	287.0		Glauconitic, quartz clay silt. Bioturbated and clay filled burrows. 5 Y 3/2	Nanjemoy Formation Woodstock Member
40	294.1		Glauconitic, quartz clay silty. Burrowed and bioturbated. 5 Y 3/2	Nanjemoy Formation Woodstock Member

Table 4. Weight (in grams) of sediment samples used for leaching experiments that were added to 40mL of each leaching solution.

Core Location	Sample Code	Depth below land surface (ft)	Munsell Color	Formation	Grams of sediment used in treatment solutions			
					DI water pH 6.24	Acidic pH 2.00	Basic pH 10.88	Aquifer pH 7.48
Banbury Cross	5	255.9	5Y 3/1	Old Church	1.0000	1.0064	0.9980	1.0233
	8	258.9	5Y 3/2		1.0038	1.0185	1.0043	1.0078
	13	263	10YR 5/3	Piney Point	1.0009	1.0029	0.9971	1.0207
	19	269.1	10YR 7/3		1.0127	1.0063	1.0100	1.0229
	22	272.1	10YR 7/8		1.0055	1.0046	0.9971	1.0075
	26	276.1	10 YR 5/5		1.0188	1.0055	1.0133	1.0260
	31	281.1	5G 4/1		1.0139	0.9978	1.0174	0.9980
	38	287	5Y 3/2	Nanjemoy	1.0077	1.0199	1.0214	1.0023
	40	294.1	5Y 3/2		1.0100	1.0664	1.0222	1.0158

Table 5. Total inorganic carbon (TIC), total organic carbon (TOC), total nitrogen (TN), and total nitrogen after HCl wash (TN_{HCl}) results for sediment samples from the USGS Banbury Cross borehole, as well as XRF results for elements with the highest concentrations in sediments. Sample code and intervals in bold indicate those used in leaching experiments. Blank spaces indicate when the sediment compound was below detection limit.

Sample Code	Depth below land surface (ft)	Geologic Formation	TIC (%)	TOC (%)	TN (%)	TN _{HCl} (%)	XRF Data								
							Si (%)	Ca (%)	S (%)	Fe (%)	Al (%)	Mg (%)	P (%)	K (%)	Cl (ppm)
5	255.9	Old Church	0.48	1.30	0.09	0.20	33.73	4.53	3.80	1.24	3.15	0.10	1.32	0.55	828.8
8	258.9	Old Church	0.05	1.23	0.24	0.20	34.26	2.87	4.28	2.25	2.58	0.12	1.10	0.70	932.6
10	260.9	Old Church	1.22	0.23	0.20	0.07	29.51	6.62	4.77	2.63	2.73	0.12	2.21	0.86	814.6
13	263.0	Piney Point	9.39	0.23	0.16	0.06	11.63	34.87	4.91	3.45	2.01	0.25	1.75	0.43	780.9
14	264.1	Piney Point	9.12	0.65	0.10	0.05	8.91	39.32	5.99	4.67	1.63	0.27		0.30	1020.0
15	265.1	Piney Point	10.24	0.22	0.16	0.08	11.38	32.30	8.29	4.90	0.94	0.20		0.22	1080.0
16	266.1	Piney Point	4.23	0.34	0.03	0.20	5.89	49.47	4.87	2.39	0.79	0.30		0.16	1060.0
17	267.1	Piney Point	10.13	0.32	0.11	0.05	6.31	49.65	4.60	1.96	0.84	0.31		0.17	1160.0
19	269.1	Piney Point	10.18	0.11	0.27	0.13	6.88	47.06	5.18	2.51	0.94	0.28		0.21	912.3
20	270.1	Piney Point	9.71	0.13	0.09	0.05	8.84	39.31	7.51	3.06	0.99	0.25		0.28	904.1
21	271.1	Piney Point	5.81	0.11	0.09	0.07	7.47	19.43	17.52	6.73	1.27	0.14		0.38	364.4
22	272.1	Piney Point	7.00	0.09	0.10	0.06	14.20	33.30	2.04	8.90	1.80	0.26		0.58	1340.0
23	273.1	Piney Point	7.45	0.31	0.21	0.06	17.86	22.56	1.69	13.59	2.35	0.28		0.82	935.9
24	274.1	Piney Point	6.73	0.08	0.13	0.12	20.19	23.73	0.75	11.37	1.81	0.26		0.82	1100.0
25	275.1	Piney Point	4.16	0.18	0.15	0.12	29.76	9.89	2.67	5.83	2.79	0.20		1.23	1030.0
26	276.1	Piney Point	5.05	0.18	0.12	0.16	22.01	22.09	1.43	7.90	2.66	0.24		0.99	865.3
28	278.1	Piney Point	3.62	0.45	0.11	0.09	27.71	10.86	3.36	5.84	2.50	0.21	0.76	1.31	884.8
29	279.1	Piney Point	3.90	0.24	0.19	0.19	25.78	14.55	3.25	5.83	2.78	0.24		1.60	1200.0
31	281.1	Piney Point	2.10	0.15	0.11	0.05	30.01	6.11	3.31	6.84	3.21	0.27		1.92	998.6
32	281.8	Piney Point	4.48	0.27	0.07	0.08	26.22	16.02	1.91	6.18	2.65	0.26		1.61	1080.0
34	283.8	Piney Point	0.13	0.28	0.08	0.14	27.86	0.57	1.01	17.14	4.74	0.36	0.44	1.17	993.6
38	287.0	Nanjemoy	0.54	0.33	0.30	0.13	30.00	1.55	2.33	11.16	4.30	0.35	0.36	1.57	1080.0
39	288.0	Nanjemoy	0.16	0.42	0.10	0.14	26.53	0.96	3.53	13.84	5.12	0.40	0.36	1.29	792.8
40	294.1	Nanjemoy	0.31	0.50	0.10	0.25	26.37	1.18	2.94	13.62	6.08	0.38	0.33	1.37	728.8
42	299.1	Nanjemoy	0.28	0.23	0.08	0.16	29.04	0.80	1.33	14.21	4.59	0.32	0.43	1.96	906.7

Table 6. Anions present in groundwater samples from wells drawing water from the Piney Point aquifer. EPA Maximum Contaminant Level and Secondary Maximum Contaminant Level are listed at bottom.

Well name	Well depth below land surface (ft)	pH	Anions (ppm)			
			F ⁻	Cl ⁻	NO ₃	SO ₄
Chickahominy Haven	126	7.33	0.8930	2.7947	2.2832	10.3051
Racefield	228	7.62	0.6322	2.8385	2.2782	10.4886
New Kent Courthouse	228	7.71	0.3430	2.1768	n.a.	15.3313
Retreat	230	7.51	0.5560	1.8977	n.a.	7.1740
Stonehouse - Fieldstone Parkway	241	7.61	0.6179	1.4975	n.a.	7.3276
Kings Village	250	7.67	0.5999	2.4469	n.a.	9.1086
Stonehouse - Mill Pond Run	256	7.64	0.5969	2.7488	2.2025	10.2626
Upper County Park	262	7.52	0.5743	2.3666	2.2971	10.1147
Lightfoot Well #3 (Banbury Cross)	265	7.96	1.0546	3.0041	2.2517	12.1848
Liberty Ridge	266	8.34	0.9611	5.6992	2.2031	9.7988
Lightfoot Well #1	271	8.28	1.0431	2.5216	2.1848	9.0085
Glenwood	272	7.76	0.7209	2.5281	n.a.	8.8019
Westport	273	8.4	1.2594	7.9500	2.3277	10.5308
Ware Creek	275	7.91	0.9115	2.1216	2.2501	8.2893
1B - Owens-Illinois	275	7.59	0.6094	2.5537	n.a.	9.3274
Owens-Illinois	277	7.61	0.6341	2.3903	2.1961	9.2641
Lightfoot Well #5	280	7.27	0.8384	2.4463	n.a.	9.1362
Kristiansand	282	7.92	1.6816	63.2899	2.2011	30.9164
Ford's Colony	290	8.24	0.9279	4.4457	n.a.	8.4683
Olde Towne Road	295	8.26	0.9303	2.9637	2.1899	9.2482
Pottery	296	7.86	0.8891	9.5414	2.2955	13.7851
Norge	297	7.55	0.7383	8.2363	2.2853	11.3128
Canterbury Hills	298	8.28	1.3324	40.0518	2.2654	11.8596
Ewell Hall	305	8.34	0.9903	2.6121	2.2192	9.0825
Wexford	306	7.81	0.8020	2.2341	2.5835	6.9372
Surprise Hill Well F	551	8.49	3.2356	3.2886	2.3346	12.1055
EPA Maximum Contaminant Level	-	-	4	-	10	-
EPA SMCL	-	6.5-8.5	2	250	-	250

Table 7. Concentrations of fluoride, chloride, nitrate, and sulfate in leaching experiments for each sediment sample and leachate treatment.

Sample Code	Depth below land surface (ft)	Formation	F in leachates (ppm)				Cl in leachates (ppm)				NO3 in leachates (ppm)				SO4 in leachates (ppm)			
			DI Leachate	Acidic Leachate	Basic Leachate	Aquifer Leachate	DI Leachate	Acidic Leachate	Basic Leachate	Aquifer Leachate	DI Leachate	Acidic Leachate	Basic Leachate	Aquifer Leachate	DI Leachate	Acidic Leachate	Basic Leachate	Aquifer Leachate
			pH 6.24	pH 2.00	pH 10.88	pH 7.48	pH 6.24	pH 2.00	pH 10.88	pH 7.48	pH 6.24	pH 2.00	pH 10.88	pH 7.48	pH 6.24	pH 2.00	pH 10.88	pH 7.48
5	255.9	Old Church	1.21	3.50	1.12	1.35	4.92	14.78	10.64	12.03	6.29	1894.69	5.51	6.33	600.16	532.12	494.64	650.31
8	258.9	Old Church	1.08	2.74	1.12	1.25	4.18	13.35	11.05	9.69	6.64	1736.85	6.51	6.34	706.79	595.65	982.60	747.14
13	263.0	Piney Point	1.17	2.07	1.11	1.24	4.74	14.25	11.08	9.90	4.45	1837.20	4.07	3.73	1105.18	897.24	840.96	1028.80
19	269.1	Piney Point	1.11	1.36	1.07	1.19	5.19	13.60	10.61	9.35	4.40	1803.76	3.95	3.73	613.85	1545.49	1922.87	543.76
22	272.1	Piney Point	1.15	1.18	1.14	1.23	3.99	14.13	10.14	8.94	4.43	1836.67	4.18	3.94	144.29	99.79	91.25	102.20
26	276.1	Piney Point	1.18	1.19	1.19	1.26	4.23	14.01	10.33	8.82	4.61	1847.20	4.53	3.94	184.36	160.37	250.59	165.48
31	281.1	Piney Point	1.23	1.33	1.26	1.36	4.27	14.54	10.30	8.95	6.08	1892.20	5.45	5.50	293.77	261.63	423.81	309.63
38	287.0	Nanjemoy	1.34	1.29	1.33	1.42	4.10	14.70	10.34	9.37	9.11	1891.03	8.90	8.47	194.54	177.20	219.28	225.99
40	294.1	Nanjemoy	1.37	1.17	1.39	1.41	4.02	14.46	10.61	9.46	9.93	1871.00	9.55	8.75	341.59	279.26	373.39	301.27

Figures

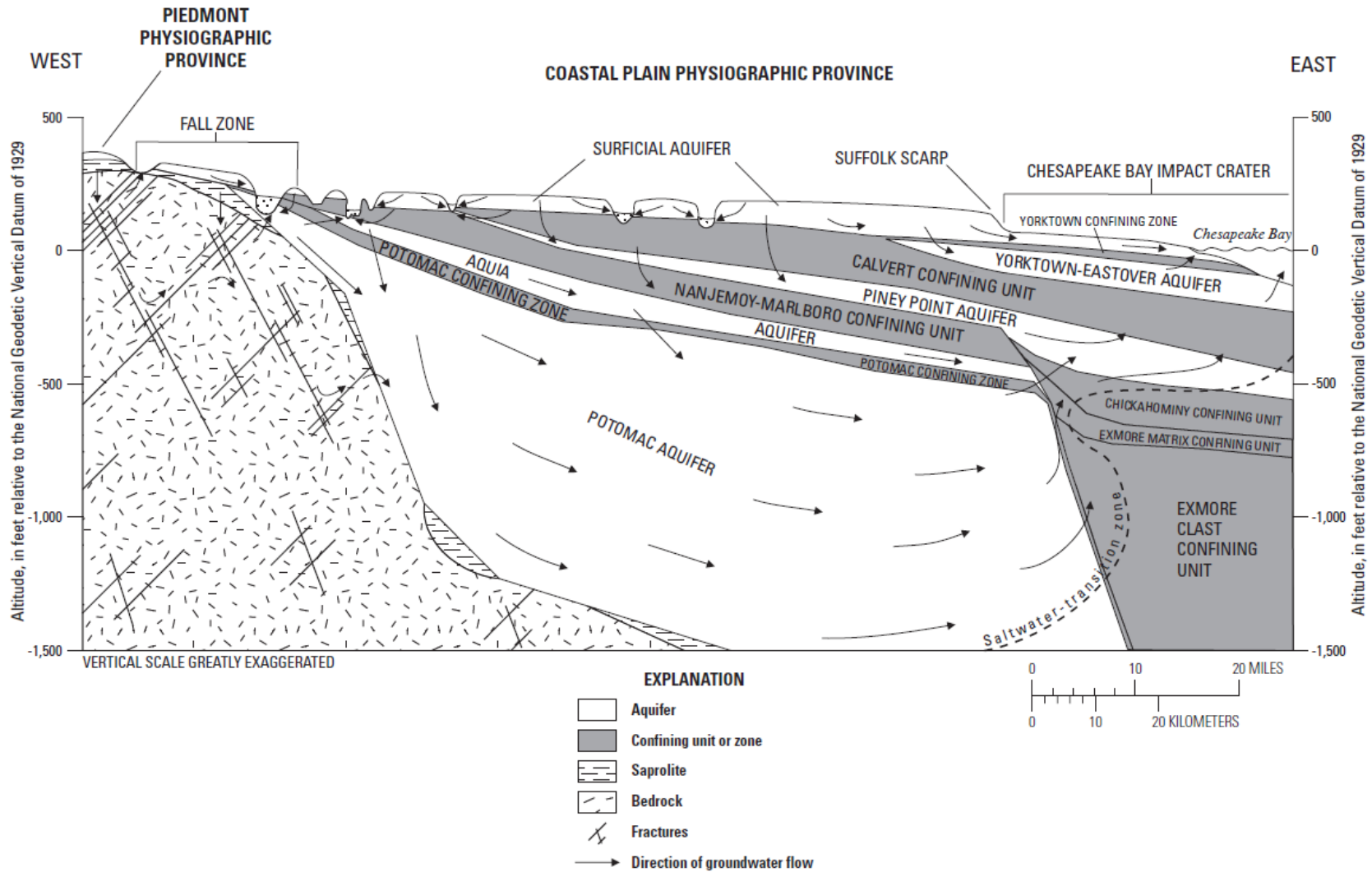


Figure 1. Generalized hydrogeology of the Virginia Coastal Plain (McFarland 2017).

Hydrogeologic units (From McFarland and Bruce, 2006)		Geologic units in this report	
	Surficial aquifer		
	Yorktown confining zone		
	Yorktown-Eastover aquifer		
	Saint Marys confining unit		
	Saint Marys aquifer		
	Calvert confining unit	Calvert Formation, Calvert Beach Member	
		Calvert Formation, fine-grained Plum Point Member	
	Piney Point aquifer	Calvert Formation, basal Plum Point Member	
		Calvert Formation, Newport News unit	
		Old Church Formation	Present only in eastern Northern Neck and Middlesex County
		Oligocene-age sediments	
Present only within Chesapeake Bay impact crater	Chickahominy confining unit	Gosport Formation equivalent sediments	Laterally continuous limestone present only north of James River
	Exmore Matrix confining unit	Piney Point Formation	
	Exmore Clast confining unit	Nanjemoy Formation, Woodstock Member	Not present within Chesapeake Bay impact crater
	Nanjemoy Formation, Potapaco Member		
	Nanjemoy-Marlboro confining unit	Marlboro clay	
	Aquia aquifer		
Present only in southeastern Virginia	Peedee confining zone		
	Peedee aquifer		
	Virginia Beach confining zone		
	Virginia Beach aquifer		
	Upper Cenomanian confining unit		
	Potomac confining zone		
	Potomac aquifer		
	Basement bedrock		

Figure 2. Hydrologic units of the Virginia Coastal Plain and geologic units that make up the Piney Point aquifer (McFarland 2017).

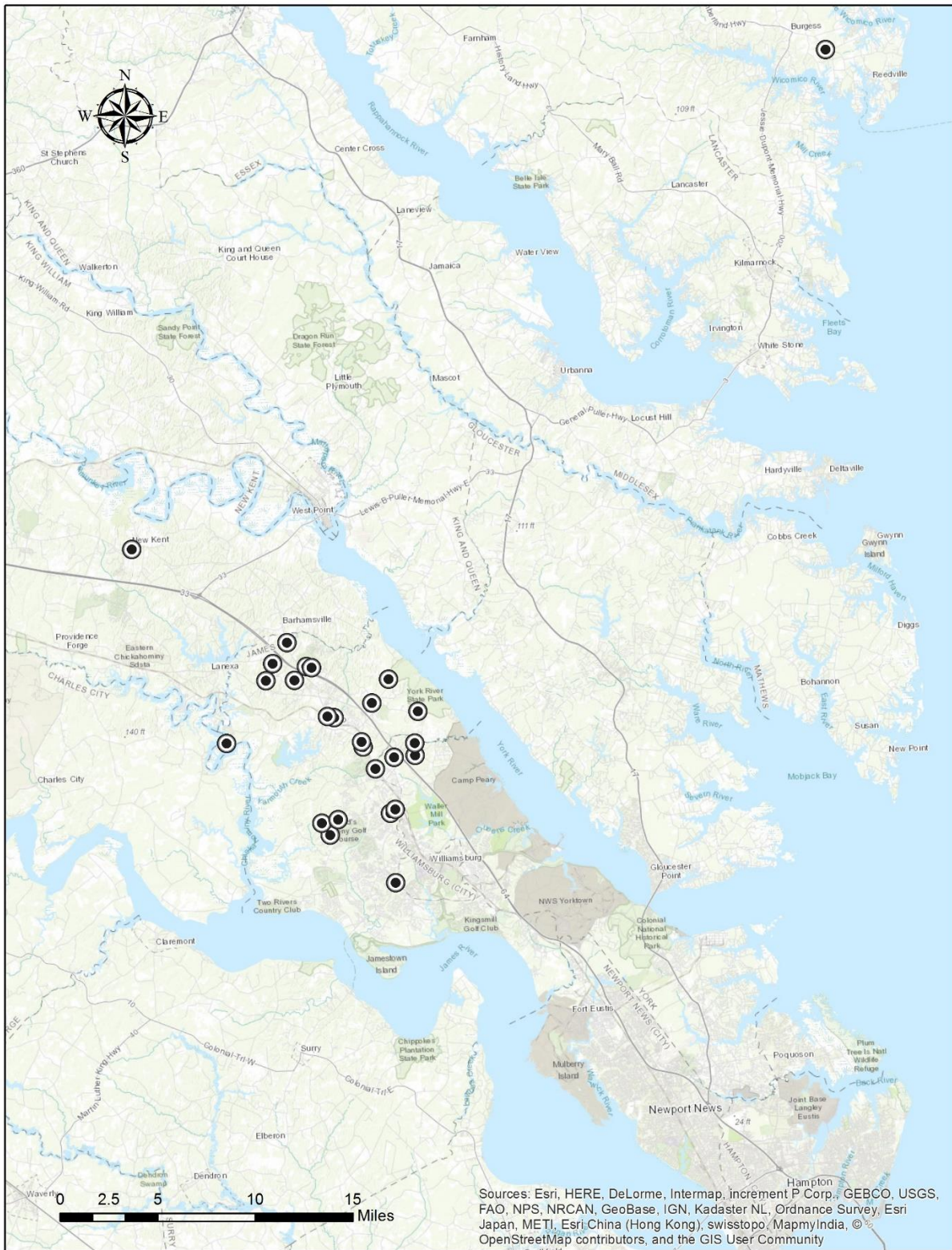


Figure 3. Location of wells from which groundwater samples were withdrawn.

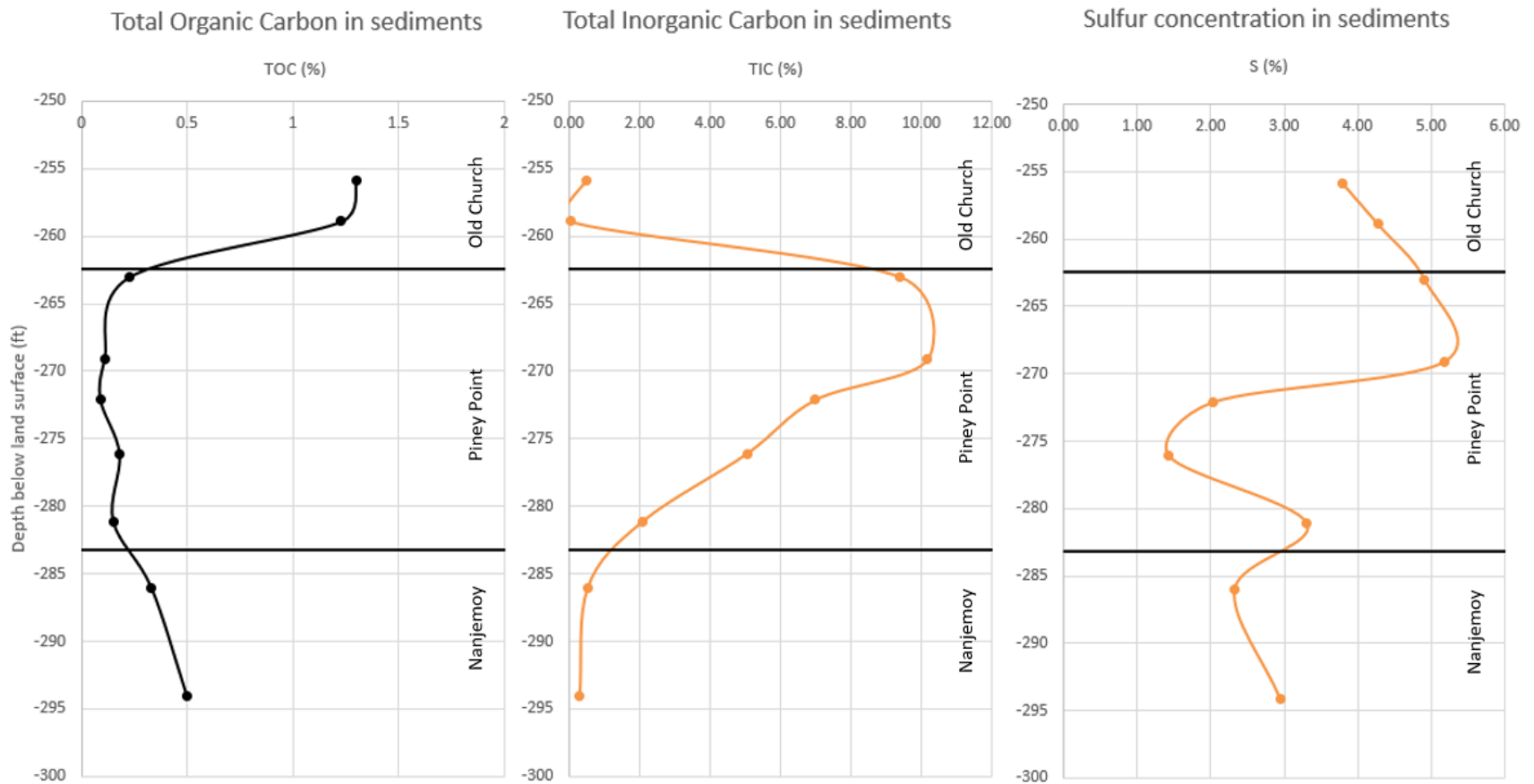


Figure 4. Total organic carbon (TOC), total inorganic carbon (TIC), and sulfur concentrations in sediment samples used for leaching experiments.

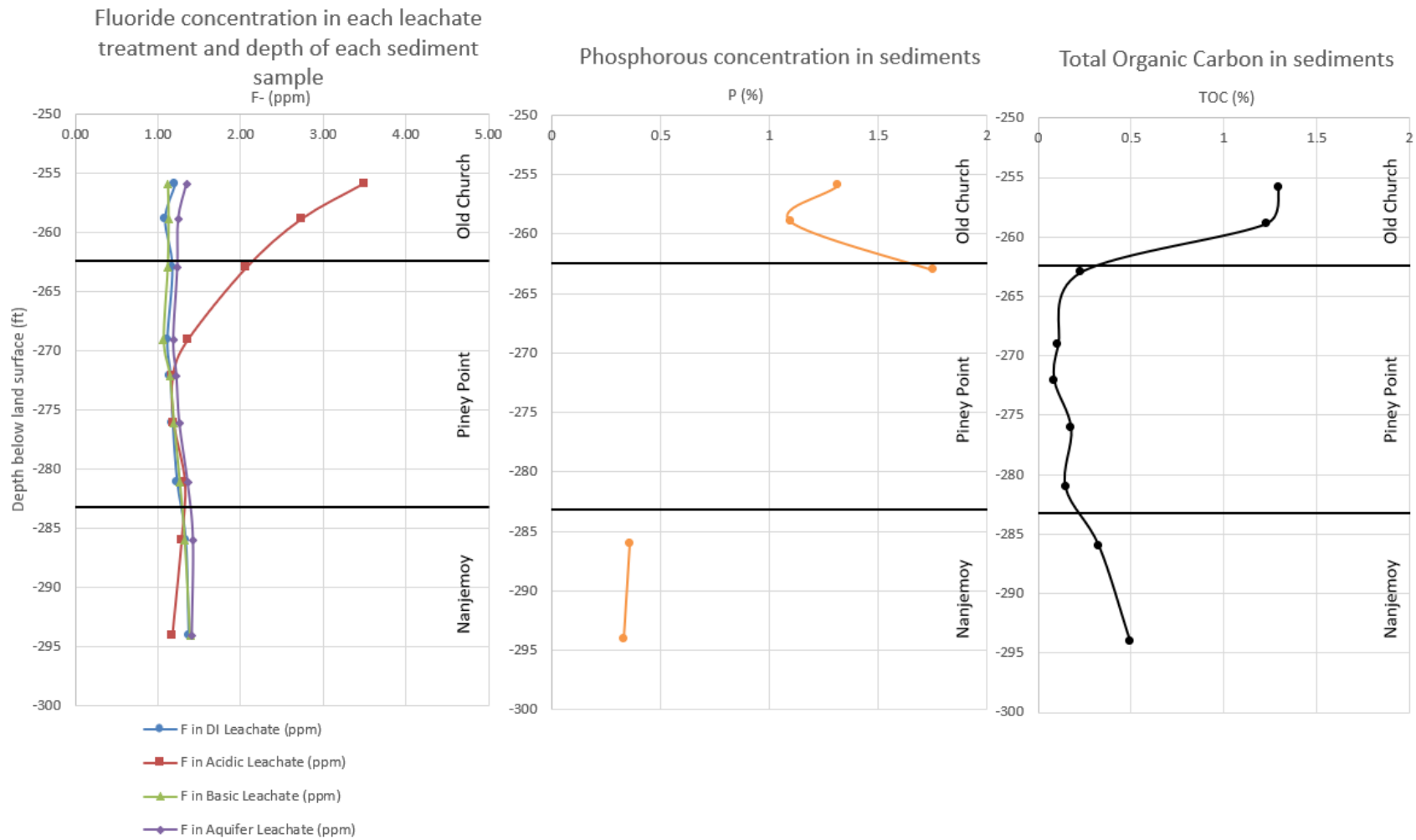


Figure 5. Fluoride concentrations in each leachate treatment and phosphorous and total organic carbon (TOC) concentrations in sediment samples.

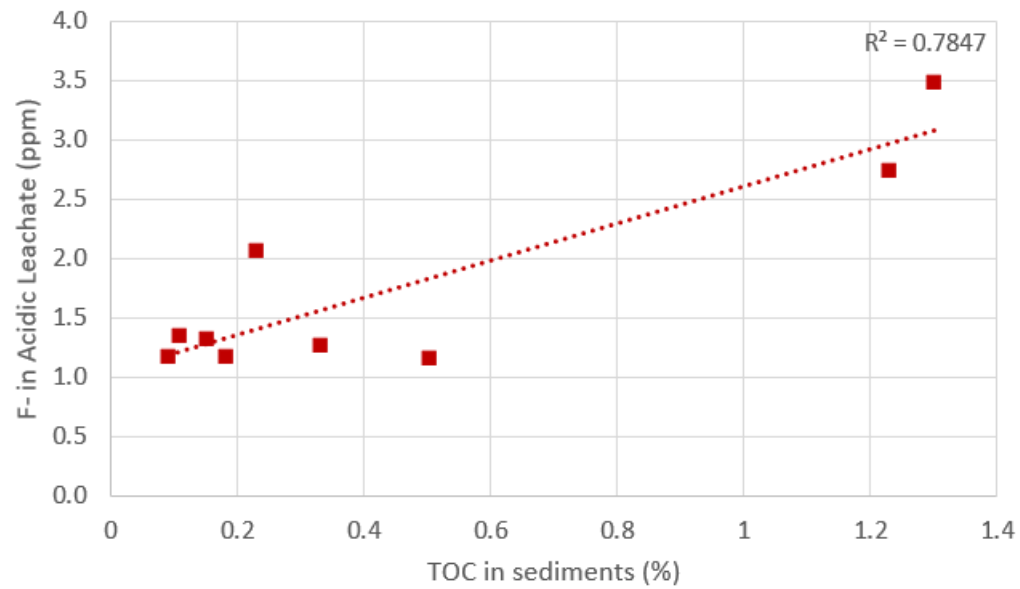


Figure 6. Regression analysis of fluoride concentrations in acidic leachate and total organic carbon concentrations in sediments.

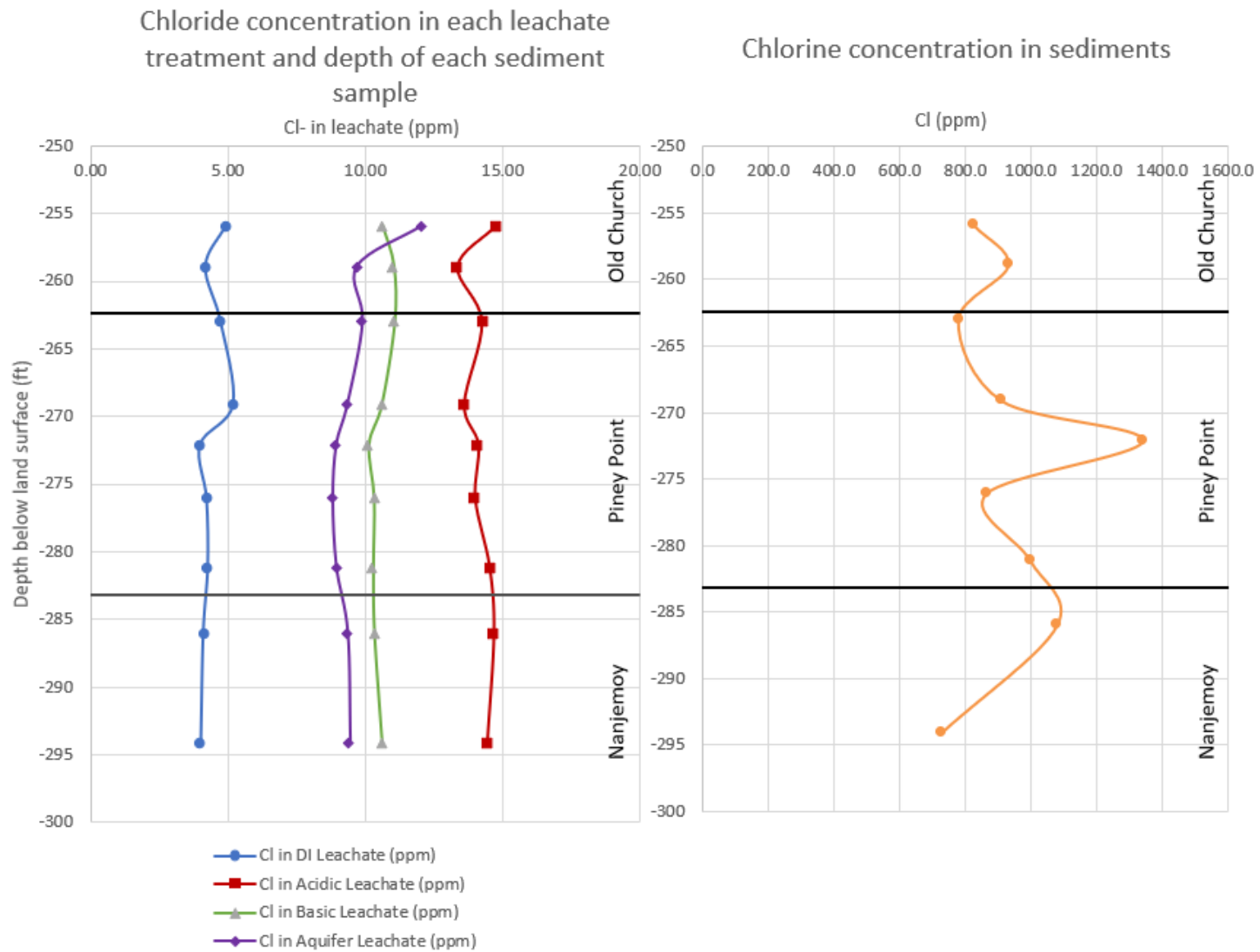


Figure 7. Chloride concentrations in leachate treatments and chlorine concentrations in sediments.

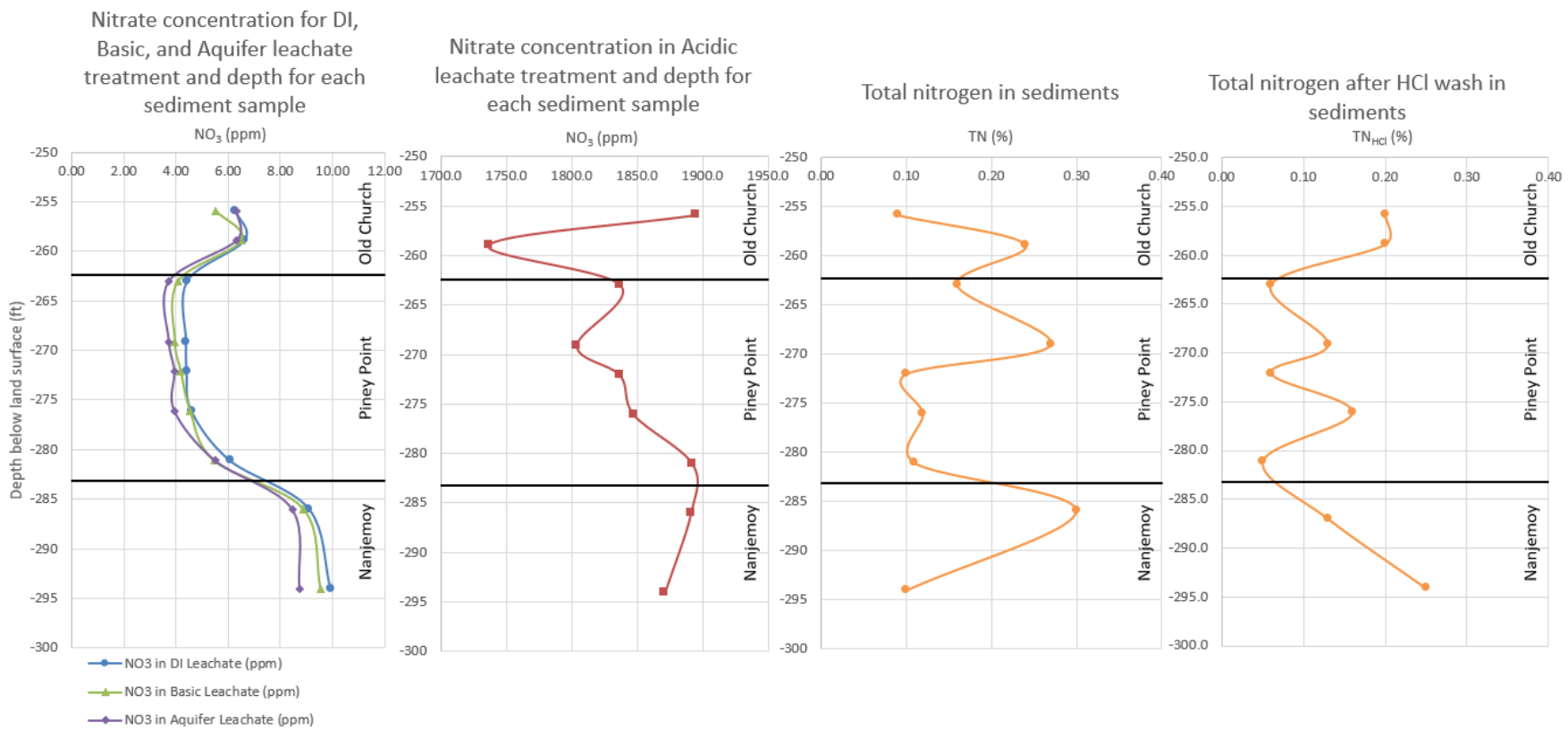


Figure 8. Nitrate concentrations in leachate samples and total nitrogen concentration with and without HCl wash in sediment samples.

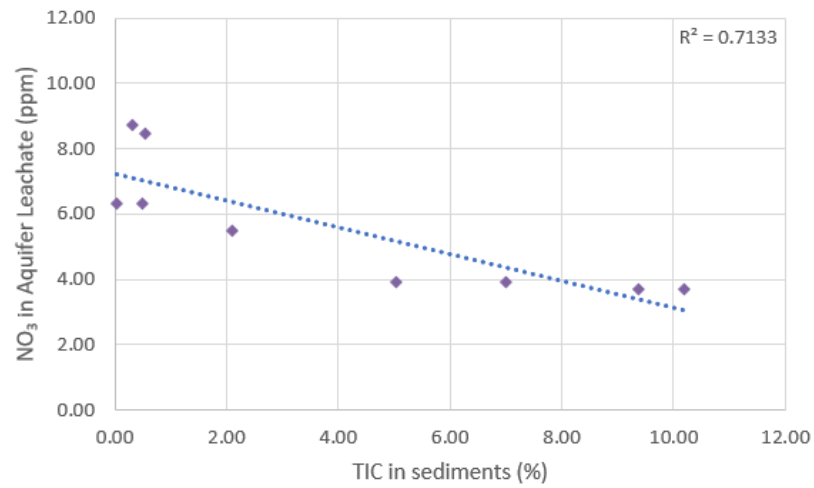
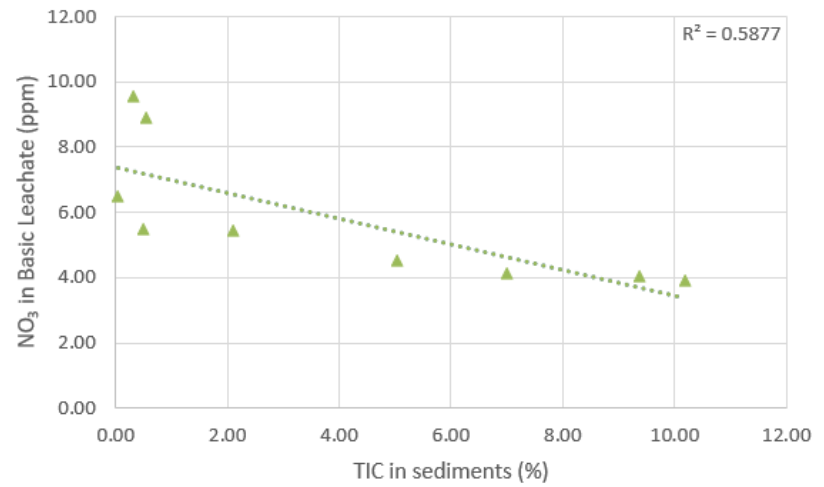
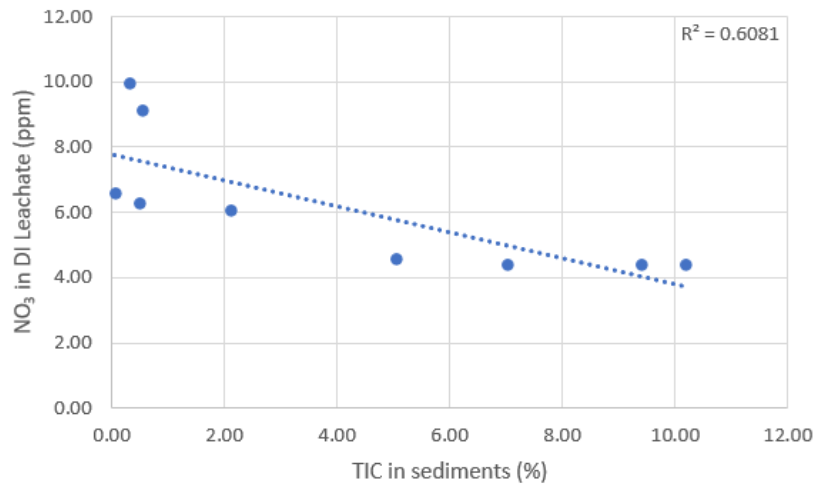


Figure 9. Regression analysis of nitrate concentrations in DI, basic, and aquifer leachates and total inorganic carbon concentrations in sediments.

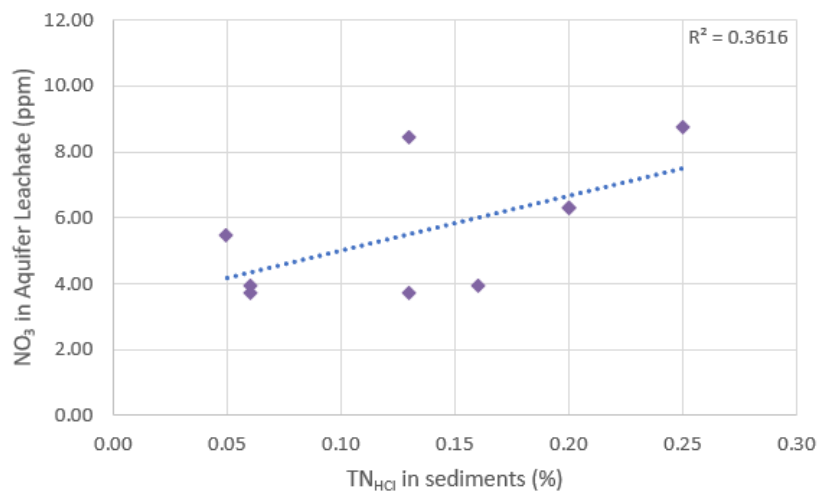
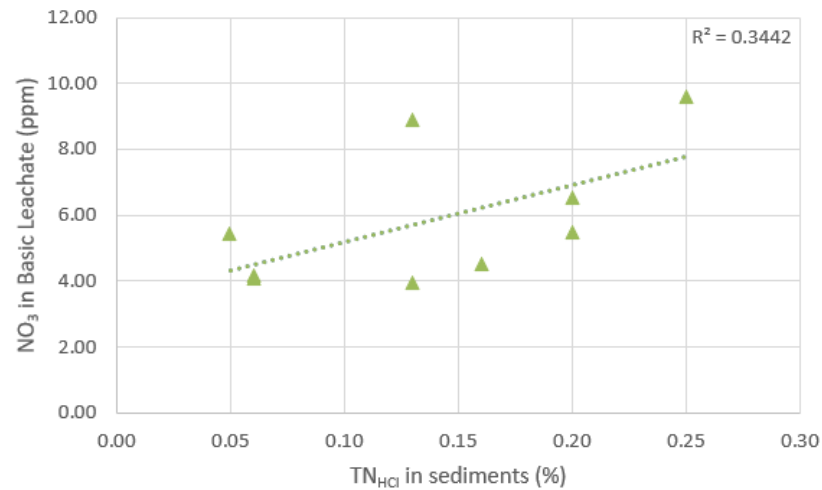
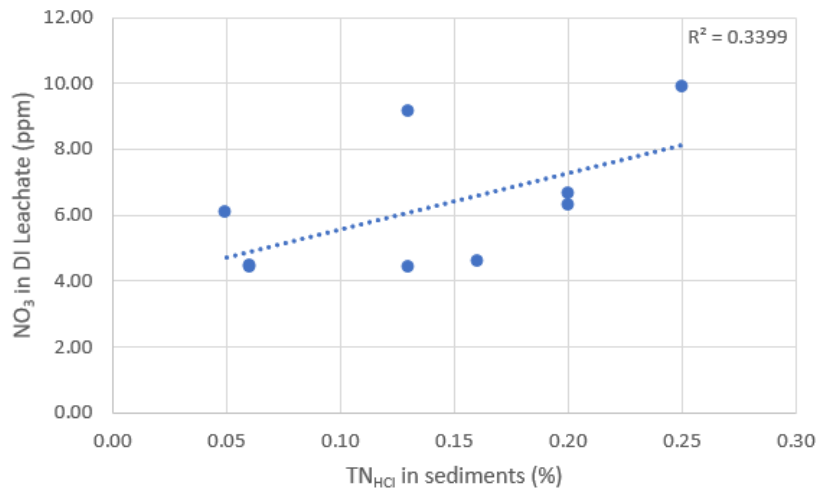


Figure 10. Regression analysis of nitrate concentrations in DI, basic, and aquifer leachates and total nitrogen concentrations after HCl wash in sediments.

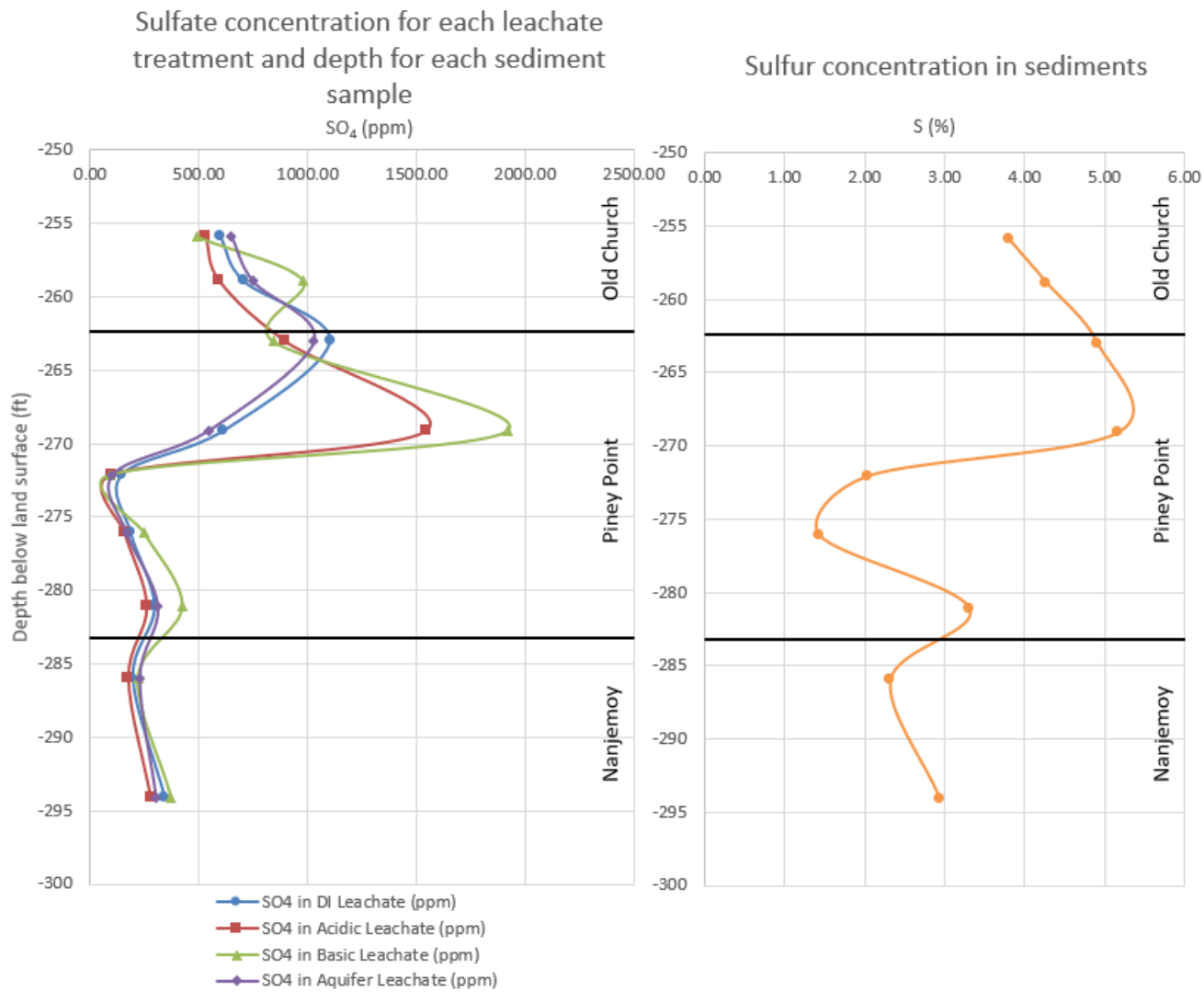


Figure 11. Sulfate concentration in leachate treatments samples and sulfur concentration in sediment samples.

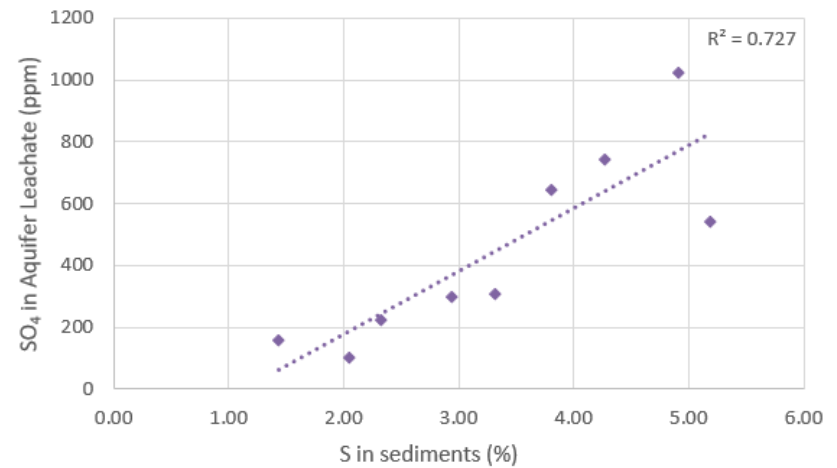
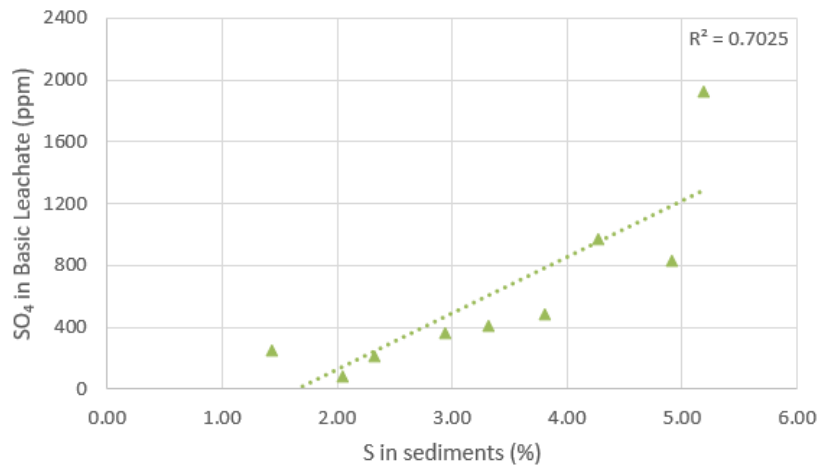
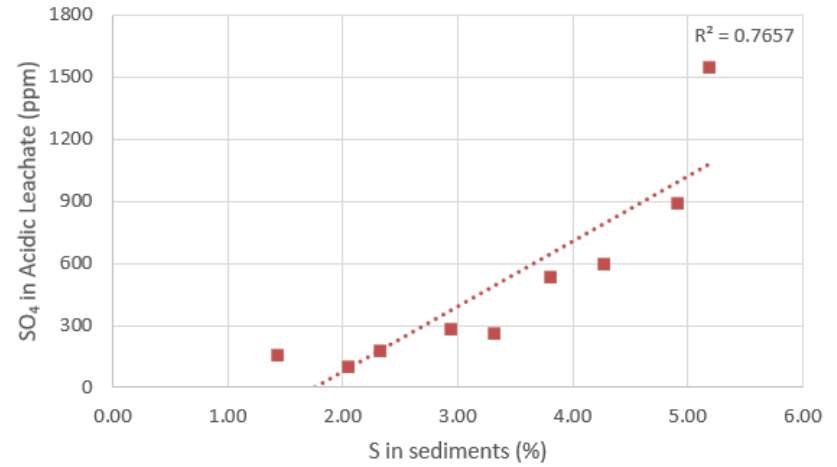
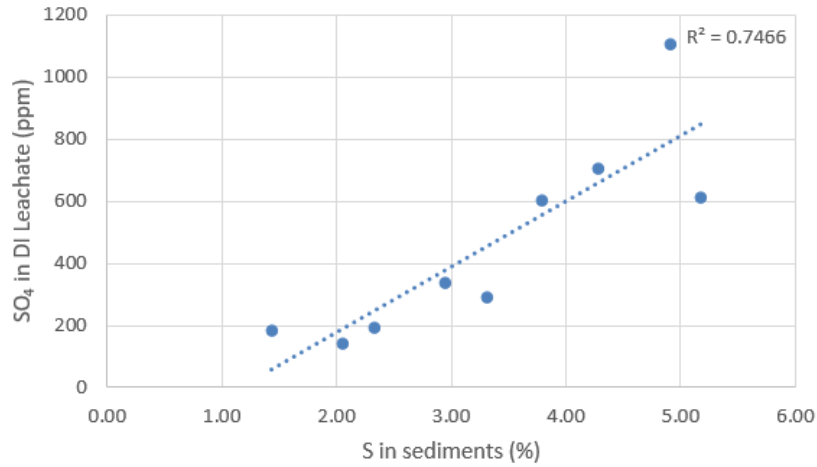


Figure 12. Regression analysis of sulfate concentrations in DI, acidic, basic, and aquifer leachates and sulfur concentrations in sediments.

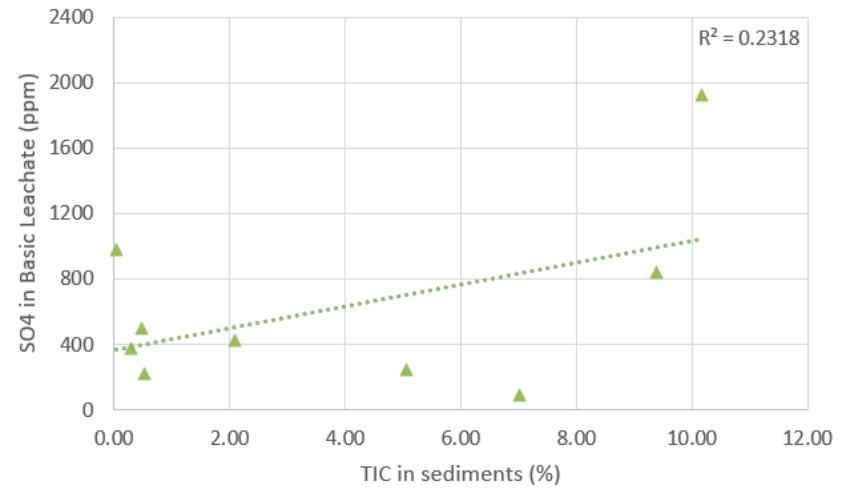
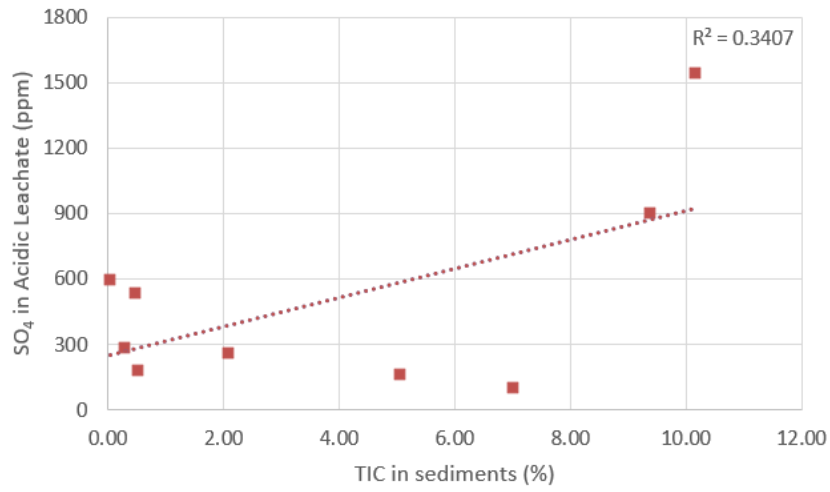


Figure 13. Regression analysis of sulfate concentrations in acidic and basic leachates and total inorganic carbon concentrations in sediments.

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