December 7, 2011
EMAIL: saif@crosslink.net

Reverend Gayl Fowler
SAIF Water Wells, Inc.
P.O. Box 839
Burgess, VA 22432

Re: Analysis of Groundwater Samples from the Piney Point Aquifer in Four Counties of the Northern Neck of Virginia

Dear Reverend Fowler:

aquaFUSION, Inc. (AFI) is pleased to provide this letter report to SAIF Water Wells, Inc. (SAIF) regarding our technical analysis of the groundwater chemistry from wells completed in the Piney Point Aquifer of the Northern Neck, which were sampled by SAIF and the USGS. This letter report documents the data review and the analysis completed by AFI as specified in our letter proposal dated January 14, 2011.

Scope of Work Summary

AFI combined chemical information provided by SAIF to produce a single spreadsheet database and constructed a digital base map which covers the extent of the sampled wells. These wells were located using the reported latitude and longitude coordinates. SAIF well samples were identified using a coding method utilized by SAIF for a previous database. AFI reviewed, in detail, the pertinent portions of two recently published United States Geological Survey (USGS) publications relating to the Virginia Coastal Plain: McFarland and Bruce (2006) and McFarland (2010). These publications discuss and summarize previous historical workers, provide a comprehensive hydrogeologic framework including both geologic and groundwater quality characterization and identify important processes that influence groundwater flow directions and the chemical character of groundwater in the Virginia Coastal Plain.

AFI reviewed the inorganic constituents contained in the combined database and identified parameters with a sufficient number of samples that exhibited concentrations above the constituent water quality standard or guidance level. AFI selected six constituents to map the distribution of the concentration values within this four county area for the Piney Point Aquifer. AFI utilized these maps to evaluate and discuss the observed trends in parameter concentration. Initially, SAIF indicated that arsenic concentrations were a constituent of concern. However, the database suggests that sodium, iron, manganese, fluoride, and total dissolved solids exhibit elevated concentrations above either their water quality standards or their constituent guidance level.

Significant Findings

Significant findings of this preliminary mapping of chemical constituents in the Piney Point Aquifer of the Northern Neck include:

1. The database utilized for this analysis shows maximum concentrations that exceed their water quality standard or guidance level for the constituents of pH, total ion concentration (filtered residue), sodium, nitrite, iron, manganese, and fluoride.

2. The chemical distribution of these parameters is consistent with the trends identified by McFarland (2010), which shows a progressive down-dip evolution from west to east of the groundwater character from “hard to soft to salty” type.

3. Sodium concentration in the Piney Point Aquifer is the lone constituent that pervasively represents an environmental health concern to the domestic well users. Sodium concentrations are elevated above the 20 mg/l "non-enforceable guidance level" throughout the four counties and exhibit an increasing spatial trend from west to east. This sodium increase maybe the result of desorption from marine sediments, the influence of mixing with seawater along discharge areas at the tidal streams and rivers at the eastern most end of the Neck, or the influence of the regional saltwater-transition zone near the margin of the Chesapeake Impact Crater.

4. The chemical distribution also suggests a progressive increase in total ion concentration along flowpaths from the drainage divide “interfluve” area to the regional discharge boundaries along the north and south of the Northern Neck at the Potomac and Rappahannock Rivers.

5. The three groundwater facies or water types of the Northern Neck present different types of water treatment problems for the domestic user. The soft water zone in the central portion of the Neck is generally suitable for a wide variety of uses and typically requires no treatment except for sodium. The “hard” water zone, most commonly in the western portion of the Neck, is typically treated by ion exchange systems. The treatment of “salty” water, predominately in the eastern portion of the Neck, is more complicated requiring the removal of sodium, fluoride, and possibly chloride.

6. To best serve the domestic supply users of the Northern Neck area, AFI recommends that SAIF perform a detailed review of potential treatment technologies to remediate the three common water types mapped in the four counties of the Neck. These ballpark costs should be provided to the groundwater users so that a cost-benefit analysis can be done to select the aquifer and its required drilling depth/cost, the potential chemical facies at that well location, which might be encountered, and the treatment cost of the groundwater to be tapped as the domestic source. Then, the individual user can

select the most cost effective and technically efficient methodology to treat their individual water supply on a long-term basis.

7. AFI recommends that future sampling include analysis for total alkalinity, carbonate, and bicarbonate parameters. Laboratory analysis results should undergo a quality assurance test by using an electric charge balance calculation utilizing the criteria discussed by McFarland (2010) to qualify each laboratory analysis so that meaningful comparison can be made between the individual samples in the database.

Study Location

The Virginia Coastal Plain occupies an area of approximately 13,000 square miles (mi2) between approximately latitude 36°30' and 39°00' N. and longitude 75°15' and 77º30' W. The Province is characterized by rolling terrain and deeply incised stream valleys in the northwestern part, and gently rolling-to-level terrain, broad stream valleys and extensive wetlands in the eastern and southern parts. Topography is dominated by the valleys of major rivers, including the Potomac and Rappahannock, Pamunkey, York, Chickahominy, and James. Lowlands consisting of terraces, flood plains, and wetlands occupy valley floors, which can be flanked by broad dissected uplands along drainage basin divides such as the central portion of the Northern Neck. Land-surface altitude ranges from higher than 200 ft-MSL across some of the western uplands to 0 ft-MSL along the Atlantic Coast. These rivers collectively drain to the east and southeast into Chesapeake Bay; which creates southeast trending necks or peninsulas bounded by the rivers. Figure 1 shows the location of the Northern Neck of Virginia in the northern portion of the Virginia Coastal Plain. The Northern Neck is bounded by the Potomac River on the north and the Rappahannock River on the south.

Chemical Database Summary

AFI developed a single database combining data SAIF with those identified by SAIF in the USGS Professional Paper 1772 by E.R. McFarland (2010) for wells that were completed in the Piney Point Aquifer. The database is populated with only inorganic constituents; although, an isolated number of organic compounds were detected in a few of the water samples in the Piney Point. McFarland (2010) cautioned the potential users of this data stating that: “The data originate from diverse sources having long and potentially complex but not fully documented histories. Potential data errors range from well construction and sample collection, preservation, and analysis, to typographic mistakes and other reporting problems. Moreover, reported chemical-constituent values vary widely among the original sources, and do not necessarily reflect analytical precision limits. In practical terms, most values should be considered no more accurate than three significant figures. Some erroneous values also likely remain in the compiled dataset….Techniques used to validate the accuracy of the laboratory analysis included calculations of major ion charge balance and correlation between chloride-concentration and specific conductance values. However, judgment should be utilized in the application of individual groundwater-sample data, based on the limitations described previously. Sampled well and borehole locations should be verified in the field whenever possible.

Moreover, the likely representativeness of chemical constituent values at any given location should be evaluated, using sound hydrogeologic experience and common sense." AFI attempted to do this by comparing the concentrations in the upper portion of the Piney Point aquifer sampled at Surprise Hill by Scott Bruce (personal communication, 2011) and analyzed by the USGS laboratory.

The wells in the combined database are located in Lancaster, Northumberland, Richmond, and Westmoreland Counties of the Northern Neck peninsula. Table 1 provides a summary of the pertinent inorganic chemical parameters which help to conceptualize the groundwater conditions in the four counties of the Northern Neck. Note that the recent groundwater sample from the VADEQ Surprise Hill Research Station is provided to compare to the statistical parameters reported on Table 1 for all the samples. An inspection of the Table indicates that the Surprise Hill sample is typical of soft type water (sodium-bicarbonate facies) water which has low iron and manganese and slightly elevated fluoride.

Regional Geologic Setting

The Virginia Coastal Plain consists of a seaward-thickening wedge of eastward-dipping strata which were classified into a series of 19 hydrogeologic units. These units are based on interpretations of geophysical logs and descriptions and analyses from 403 boreholes by McFarland and Bruce (2006). These sedimentary strata form an extensive framework of aquifers and confining units from which substantial amounts of water can be withdrawn. None of the aquifers or confining units extends across the entire Virginia Coastal Plain. This framework of strata has a complex history of sediment deposition due to fluctuation of sea level, which has produced numerous lateral variations in lithology. Consequently, the aquifer and confining-unit form a complex distribution, which is described as by McFarland and Bruce (2006) as "patchwork" configuration. As exhibited on Figure 2, some aquifers and confining units pinch out westward toward the Fall Zone.

Piney Point Aquifer System

The following section is a summary of the description of the Piney Point aquifer system extracted from McFarland and Bruce (2006). The Piney Point extends across most of the Virginia Coastal Plain except for the southern half of the Fall Zone. The thickness of this aquifer varies from near zero on the west to several hundred feet or more on its eastern extent as shown on Figure 2. The Aquifer is stratigraphically above the Nanjemoy-Marlboro confining unit across most of its extent except within the Chesapeake Bay impact crater, where it is above the Chickahominy confining unit. The Piney Point provides public water supplies for some small towns and private supplies in the rural areas of the Northern Neck.

Hydraulically, the Piney Point aquifer is composed of a closely associated group of several geologic formations consisting generally of marine, medium- to coarse-grained, glauconitic, phosphatic, variably calcified, and fossiliferous quartz sands. The base of the Piney Point aquifer in some places outside of the Chesapeake Bay impact crater includes the well-sorted, fine-grained sands of the Woodstock Member that forms the upper part of the Nanjemoy Formation. Most of the Piney Point aquifer extending across the area outside of the crater north of the James River is composed of variably calcite-cemented sands and moldic limestones. Both the Nanjemoy Formation and the Piney Point Formation predate the impact crater and their sediments are truncated along the crater margin. The upper part of the Piney Point aquifer consists of additional formations that postdate the crater and these upper units extend across the crater. In addition, much of the upper part of the Piney Point aquifer consists of a basal lag deposit of coarse-grained, very phosphatic sands within the Plum Point Member, which forms the middle part of the overlying Calvert Formation. Other parts of the Calvert Formation consist primarily of fine-grained sands and silts and are not considered part of the Piney Point aquifer, but are designated as the Calvert confining unit. North of the James River and in the Northern Neck, portions of the Piney Point aquifer are split into two portions, an upper and lower separated by a clay layer of variable thickness.

Figure 3 exhibits the elevation of the top of the Piney Point aquifer. Near its western margin across Westmoreland County and the northern half of the Fall Zone, the aquifer is on the order of 0 to 55 ft-MSL in elevation. The Piney Point aquifer dips generally eastward across its entire extent and is as thick as nearly 150 ft across the lower reaches of the Northern Neck at elevations from approximately –200 to –350 ft-MSL. This Aquifer continues beneath the upper Chesapeake Bay and the northern part of the Virginia Eastern Shore to elevations between approximately –850 to –1,000 ft-MSL.

In addition, McFarland and Bruce (2006) also point out that the Piney Point Aquifer outcrops along the valleys and tributaries of the Potomac and Rappahannock, across the western part of the Northern Neck. These locally incised areas along the Potomac, Rappahannock and other Rivers and some of their tributaries provide direct contact between the Piney Point aquifer and surficial aquifer, which creates some important hydraulic connections between the confined and unconfined ground-water systems of the Neck. This connection is particularly prominent along the main stem of the Potomac River where a relatively broad area is incised along the northern boundary of the Northern Neck by almost the entire river channel (see Figure 1).

The top of the Piney Point aquifer has closely spaced displacements of a few tens of feet or less that are attributed to faults as interpreted from geophysical logs. The faults intersect the Piney Point aquifer by extension upward from the Potomac aquifer and through intervening hydrogeologic units, which generally exhibit larger displacements. Although discrete fractures that are either open or lined with fault gouge probably are not pervasive, in these incompetent sediments. However, the disruption of their depositional structure by fault movement possibly has produced locally poor sorting, compaction, and or some decrease in hydraulic conductivity. In addition, the faults create local-scale irregularities in the altitude of the Piney Point aquifer and laterally abut varying volumes of the aquifer against adjacent hydrogeologic units. These displacements generally are of similar magnitude relative to the thickness of the Piney Point aquifer, which in most cases results in a lateral-flow constriction where the aquifer is partly truncated by the adjacent confining units. These displacements can also present water quality anomalies in the vertical sequence of the confining beds and aquifers.

Regional Groundwater Flow System

Ground water in the Coastal Plain is recharged principally by precipitation infiltration and percolation to the water-table. Most of the unconfined ground water flows relatively short distances and discharges to nearby streams but some water flows downward as vertical leakage to the deeper confined aquifers such as the Piney Point. This vertical movement is primarily along the Fall Zone and beneath surface-drainage divides between major river valleys such as the upland area that forms the Northern Neck between the Potomac and the Rappahannock. Because of stratification of the Coastal Plain sediments, horizontal movement (hydraulic conductivity) generally is much greater than the vertical movement (vertical hydraulic conductivity). Hence, flow through these confined aquifers is predominately horizontal in three general directions: 1) down the eastward dip of the sediments as illustrated in Figure 2, 2) toward large withdrawal or pumping centers, or 3) toward major discharge areas represented by the large rivers and their incised tributaries, and the Chesapeake Bay. Note that the chemical distributions of some of constituents mapped in this analysis appear to fit an intermediate flow path from the middle of the Neck with groundwater discharge to both the Potomac and Rappahannock Rivers from the Piney Point Aquifer. The general direction of flow is from the Fall Line toward coastal areas and from the interfluves along the surface drainage divides toward major river valleys and tributaries. Flow through the intervening confining units is predominantly downward between major river valleys and along the Fall Line and upward toward the major river valleys and coastal waterways. Most downward movement of water into the confined aquifers, such as the Piney Point, occurs along a narrow band parallel close to the Fall Line and under the interfluves (surface drainage divides) of the peninsulas such as the Northern Neck.

The Piney Point Aquifer is moderately used as a public groundwater supply resource, which is limited geographically to the middle reaches of Northern Neck, Middle Peninsula, and York-James Peninsula. The wells yields of supply wells in this area are commonly 10 to 50 gallons per minute (gpm). During 2002, the Piney Point aquifer produced an estimated 5 percent of the ground water used in the Virginia Coastal Plain at a rate of 6.8 million gallons per day (MGD) McFarland and Bruce (2006). A rate of 4.9 MGD was reported to the DEQ by regulated industrial, municipal, and commercial users; unregulated domestic use was estimated at a rate of 1.9 MGD.

Public water-supply wells generally are completed in the lower part of the Piney Point aquifer. The upper part of the Piney Point aquifer is typically not utilized as a production well interval because it is dominated the basal phosphatic sands of the Calvert Formation Plum Point Member, which exhibits low yield and a prevalence of hydrogen sulfide. Observation wells completed across this interval have yielded only 5 to10 gpm. Unregulated withdrawals from the Piney Point aquifer generally are dispersed across rural areas. A random sample of domestic-well records from county health departments indicates that the Piney Point aquifer supplies roughly a quarter of the unregulated wells constructed since approximately 1985 across the middle reaches of the Northern Neck, Middle Peninsula, and York-James Peninsula (McFarland and Bruce, 2006). In the

Northern Neck, the Piney Point aquifer is an important water supply for the rural water user.

Regional Groundwater Quality

McFarland (2010) provides a comprehensive discussion on the controls of chemical character in the Virginia Coastal Plain. Analysis of these combined data for the Piney Point aquifer indicates that the chemical character and trends are consistent with some or all of the controlling processes identified by McFarland. The following is a summary of the processes described by McFarland that control the chemical character of groundwater in the Virginia Coastal Plain and that apply to the groundwater conditions in the Piney Point aquifer.

Diverse processes can potentially affect the chemical composition of groundwater in coastal aquifers, including mixing, ion exchange, diagenesis, and oxidation-reduction reactions (Jones and others, 1998). All groundwater in the system likely originated as precipitation that has infiltrated the land surface. During movement through the flow system from recharge to discharge, the groundwater undergoes processes that change its chemical composition as it moves from west to the east and vertically downward from the Fall Zone and or the interfluve recharge areas to the ultimate discharge in the Bay or boundary Rivers.

Regional trends in groundwater quality are typically determined by looking at the variation in the concentration of major ions that comprise the groundwater. The major ions that typically are used for mapping to evaluate region trends include the cations: calcium ($Ca2+$), magnesium ($Mg2+$), sodium ($Na+$), and potassium ($K+$), and the anions: bicarbonate ($HCO3^{-}$), carbonate ($CO3^{-}$–), sulfate ($SO4^{--}$), and chloride (Cl^{-}).

Major ion type classification, together with the total ion concentration in well water samples, provides an efficient method to document spatial variations in groundwater quality in aquifers. Most of groundwater samples can be categorized as one of four major water types or facies:

1. Calcium-Magnesium-bicarbonate **("hard") type water**, dominated by calcium and magnesium cations, bicarbonate and carbonate anions,
2. Sodium-Potassium-bicarbonate **("soft") type water**, dominated by sodium and potassium cations, bicarbonate and carbonate anions,
3. Sodium-Potassium-chloride **("salty") type water**, dominated by sodium and potassium cations, chloride anions,
4. Sodium-Potassium-bicarbonate **("mixed") type water**, which results from the sampling a saltwater mixing or transitional zone in this Coastal Plain Setting.

Using these water types, sometimes called hydrochemical facies; McFarland (2010) was able to map regional trends of groundwater quality and to identify processes that control the groundwater chemistry in the confined aquifers of the Virginia Coastal Plain including the Piney Point aquifer. His analysis shows that total ion concentration in the Coastal Plain aquifers, increases generally eastward and down the dip of the aquifers. Although areas to the west exhibit some local-scale variability, a consistent and abrupt eastward increase in total ion concentration conforms to the outer margin of the Chesapeake Bay impact crater. In addition, the samples show a spatial sequence or evolution of the hydrochemical facies west to east. Hard type waters are present generally toward the western portion of the Coastal Plain, near the recharge area of the Fall Zone. Soft type waters primarily occupy a broad north-south trending belt spanning much of the central part of the Virginia Coastal Plain and the central portion of the Northern Neck. Towards the east, the distribution of “salty” water and “mixed” type waters conforms closely to the abruptly increase in total ion concentration along the outer margins of the impact crater.

Using the concepts described by McFarland (2010), the evolution of the groundwater chemistry in the Piney Point aquifer is described from recharge to discharge beneath the Chesapeake Bay. Following recharge at the water table, groundwater in the Piney Point continues to flow generally eastward and downward through the saturated zone as far as several tens of miles, to depths as great as several hundred feet or more. The contact time (flow time with the marine sediments of the Piney Point) is estimated to be as long as several tens of thousands of years. Total ion concentrations increase along these regional flow paths, as more dissolved load in groundwater is produced by continued chemical weathering. Other processes, however, act to alter the relative dominance among the major ions and change the water types or facies. In water flowing sufficient distances and depths, calcium and magnesium cations are adsorbed by the marine sediments onto grains of clay and glauconite, displacing previously adsorbed sodium and potassium cations into the groundwater. This transforms the hard type water to soft type waters. The bicarbonate anions remain unaffected. It remains to be seen whether the sufficient time and distance results in transition from soft to salty facies in the Northern Neck.

Toward the coast, groundwater mixes along a broad transition zone with seawater which is contained in the sediments beneath the Atlantic Ocean and the impact crater. Cations remain dominated by sodium and potassium, but the concentration of chloride originating from seawater increases markedly and supersedes bicarbonate as the dominant anion. Thus, “soft” water evolves to “salty” type water. The total ion concentration of groundwater does increase abruptly into the brackish range, as a result of mixing with seawater. McFarland (2010) states that the saltwater-transition zone has a complex configuration resulting from long term changes in groundwater flow over time and its interaction with sources of salt and brackish water.

The widespread presence of “soft” water in much of the aquifer east of the Fall Zone infers that any additional recharge to that part of the aquifer has first leaked downward through a substantial thickness of clay and marine sediments of overlying hydrogeologic units and thereby exchanged much of the calcium and magnesium cations for sodium and potassium cations. The complete absence of any groundwater samples of mixed composition between hard and soft types indicates the efficiency with which cation exchange by the marine sediments alters the dominance of cation types. Still farther east, the presence of mixed composition type waters indicates a gradual mixing front or a transition zone of the “soft” water with sea water.

The surficial or shallow water-table aquifer in the Northern Neck area is not a good target for domestic water supplies. The shallow aquifer exhibits mostly hard type water, which requires treatment of a domestic supply. The hard water is produced by dissolution of large amounts of calcium-magnesium carbonates that compose the marine sediments and the presence of pyrite and organic materials that dissolve iron, manganese, and create hydrogen sulfide. The groundwater-flow paths of the surficial aquifer are too short for cation exchange processes to effectively "soften" the water. In addition, the shallow groundwater waters are in hydraulic communication with "salty" type either laterally along discharge areas at the Atlantic Coast, Chesapeake Bay, and tidal streams and rivers, or vertically with the regional saltwater-transition zone. Lastly, shallow groundwaters are subject to contamination locally from surface processes.

Distribution of Selected Groundwater Quality Constituents in the Northern Neck

AFI selected concentration distribution maps for six parameters from the combined database for mapping in the Northern Neck, Piney Point aquifer. A common color scheme is utilized on Figures 4 – 9 such that the size of the circle and the infilling color relate the individual sample concentration value and their proximity to the given water quality standard or guidance level. The larger the circle the greater the concentration value is for that given sample. Yellow and red infilling suggest concentrations that are close to or exceed the given water quality standard or guidance level. The colors of white, blue, and green indicate acceptable water quality concentration. The following sections describe the spatial distribution of selected chemical constituents in the Piney Point aquifer in the Northern Neck of the Virginia Coastal Plain. These distributions support the concepts regarding groundwater flow and the evolution of chemical quality put forth by the McFarland (2010) and McFarland and Bruce (2006) for the Virginia Coastal Plain.

The Piney Point aquifer has acceptable groundwater quality for domestic supplies for most of the Northern Neck except for the concentration of sodium. The water quality begins to deteriorate in the eastern most portions of Northumberland and Lancaster Counties, where the influence of the Chesapeake impact crater and the long residence time of the groundwater results in high total ion concentration and in salty or mixed type waters. Domestic wells in this eastern part of the Piney Point most likely will need treatment systems to remediate and improve the water quality. In contrast, McFarland (2010) analyses indicate that the surficial aquifer in this area generally exhibits hard water and elevated concentrations of inorganic constituents. Thus, an economic cost benefit analysis must be completed to evaluate both the cost of drilling a well and the required treatment cost for both the shallow, surficial water-table and the Piney Point aquifer in order understand the long-term maintenance and operation costs to the domestic well user. Obviously, the cost to drill a well to the shallow aquifer is less than to the deeper Piney Point; however the total cost to the homeowner must include the required treatment technology and its long-term operational cost. In the eastern portion of the Neck, the chemical quality of the Potomac Aquifer may also be comprised; thus, drilling a more costly deeper well may also require expensive treatment and maintenance costs.

Filtered Residue Distribution

Figure 4 exhibits the distribution of filtered residue in the Northern Neck wells. Concentration values for filtered residue reflect a singular measurement of the total ion concentration of the sample, similar to the total dissolved solid concentration. Figure 4 demonstrates the influence of flowpath length, residence time in the aquifer, and proximity of the salty water near the margin of the Chesapeake impact crater. Note that the lower values, white and blue circles are generally observed in the central portion of the Northern Neck, near the principal recharge area associated with the interfluves. The moderate values are located along the discharge boundaries of the Potomac and Rappahannock Rivers. This distribution either reflects the hydraulic communication of the Piney Point with the river waters or the intermediate flowpaths and residence time associated with discharge to the river boundaries. The yellow and red circles are distributed in the eastern most portion of the Neck in Lancaster and Northumberland Counties, where the longer residence time and flowpath length provide the opportunity to dissolve greater chemical load. These eastern most wells are also influenced by the salty waters along the margin of the impact crater as discussed by McFarland (2010)

pH Distribution

This constituent (pH) exhibited the greatest number of measurements in the combined database. Figure 5 displays the distribution of pH in the Northern Neck. The pH measurements exhibit the greater percentage of values in the range of 7.5 to 8.2. This range is reflective of the Piney Point aquifer being comprised of marine sediments, which buffers the groundwater system in the bicarbonate range. Note on Table 1 that pH has an average value of 7.99 and a geometric mean of 7.98 and very small (0.37) standard deviation indicating a narrow range for most of the measurements. Thus, most pH values are relatively close to a pH value of 8 indicating bicarbonate equilibrium. The extreme values of pH are probably controlled by local pH-Eh conditions near the specific well.

Iron and Manganese

Iron and manganese are pervasive in groundwater throughout the Virginia Coastal Plain with highly variable concentrations at the local scale. Generally, furthest up dip to the west, the distribution of iron and manganese exhibit higher concentrations commonly exceeding drinking-water standards and where hard water is the dominant type. Concentrations of iron and manganese in groundwater decrease eastward and vertically downward from the west because the major ion composition of groundwater evolves from hard to soft water as a result of ion exchange. Similar to calcium and magnesium, iron and manganese cations are adsorbed by clay and glauconite within the marine sediments and release previously adsorbed sodium and potassium cations into the groundwater. Eastward from the Fall Zone; the groundwater in the Piney Point is typically at or below the drinking-water standards where soft water is more dominant and iron and manganese are low in concentration. Figures 6 and 7 for the constituents of iron and manganese, respectively, exhibit concentrations below the water quality standard. The Piney Point aquifer in the central portion of the Northern Neck exhibits soft type water. Note that only two samples in the central and eastern portions of the Neck exceed the water quality standard of 300 ug/l for iron and only one exceeds the manganese standard of 50 ug/l (See red and yellow circles on Figures 6 and 7).

Contrary to the Piney Point Aquifer, the surficial/shallow aquifer exhibits many concentrations that exceed the drinking-water standard far to the east in the Coastal Plain (McFarland, 2010). These large iron and manganese concentrations at shallow depths occupy a broad belt spanning the lower parts of the Middle Peninsula and York-James Peninsula northeastward across the Virginia Eastern Shore and southeastward across the cities of Chesapeake and Virginia Beach. Thus, the surficial (water-table) aquifer of the Northern Neck may have poorer water quality than the Piney Point aquifer for a domestic water supply well. For the individual homeowner, this distribution of iron and manganese as well as other surficial aquifer constituents leads to an economic decision regarding the increased cost to drill a well deeper into the Piney Point with the probability of obtaining better water quality or drilling a shallower well with poor quality that may require water treatment.

Removal of iron and (or) manganese is one of the most common necessary treatments of water for domestic supply wells. Unfortunately, the origin of iron and manganese in groundwater and a given domestic well is controlled by a variety of geologic conditions. The type of conditions that increase the concentration of iron and manganese may be well understood, but the control on the distribution of these conditions is not well understood and in fact is not predictable geographically. Both constituents can take part in a broad array of chemical reactions with various sediment components, which influence their concentration in groundwater. In the up dip areas to the west, iron and manganese probably originate from the dissolution of various minerals in the residual marine sediments exposed in the Fall Zone. Both finely disseminated pyrite and nodular forms of pyrite (FeS_2) are commonly associated with fossil plant debris and other organic material contained within these terrestrial and marine sediments of the Coastal Plain stratigraphic sequence. If the given domestic well is in hydraulic communication with a zone of concentrated pyrite; high hardness, iron and manganese results; where, an adjacent well penetrates “cleaner sediment” with more favorable pH-Eh conditions the groundwater is less hard. Dissolved iron originating from dissolution of pyrite is also often associated with large concentrations of hydrogen sulfide in groundwater. Hydrogen sulfide is not associated with negative health effects and is not regulated by USEPA drinking-water standards, but it can produce a strong objectionable odor and taste and induce corrosion in plumbing.

McFarland (2010) points out that the removal of iron, manganese, and hydrogen sulfide are common necessary treatments for supply wells. Systems are designed for individual domestic wells and small community or commercial water supplies. Appropriate system design depends on the water-production capacity and other considerations, including the required treatment level. For example, water softening used to treat hard water efficiently removes iron and manganese at concentrations up to 5 mg/L, but only by systems designed to do so. Hydrogen sulfide at concentrations less than 1 mg/L can be removed by activated carbon filters. Larger concentrations of iron, manganese, and hydrogen sulfide generally require some form of oxidation combined with filtering, either by chemical solutions, greensand, or aeration. These methods require varying degrees of pre- and post-treatment, and potentially costly maintenance for the homeowner. For the domestic homeowner, the operational costs of treatment can become prohibitive because of long-term maintenance. Thus, it should become more economical to drill a deeper well, which encounters “softer” water.

Although generally considered superior to hard water for most uses, soft water possesses some limitations. For privately owned softening systems, the concentration of sodium produced should be evaluated by users for whom sodium consumption is a health concern (<500 mg/day). Some systems can use potassium instead of sodium, whereas others include a bypass feature to supply untreated water for drinking and cooking. In addition, as an aesthetic consideration, bathing with soft water (either treated or naturally present) can produce a slippery feel on skin. Alternative explanations are that (1) the non-reactivity of soft water with soap possibly hinders its ability to remove soap from the surface of skin or (2) when hard water is used, small amounts of insoluble residue possibly absorb oil from the skin to produce a greater drying sensation.

Sodium

Figure 8 exhibits the distribution of the sodium in the Piney Point Aquifer. Note that most reported concentrations exceed the 20 mg/l non-enforceable guidance level throughout the Northern Neck. Sodium shows a general increase from west to east which is consistent with expected evolution of the groundwater from hard to soft type. In the central portion of the Neck, yellow and green values tend to be near the River boundaries suggesting a mixing front with the tidal influence of creeks and tributaries. Sodium concentrations in the eastern portion of the Neck are exhibiting concentrations at or above 108 mg/l, yellow or red circles.

McFarland (2010) reports that most groundwater-flow paths are too short for cation exchange mechanism to “soften” the water. If this is the case, other factors in the Northern Neck are responsible for the eastward increase in sodium. “Hard” water is produced by dissolution of large amounts of calcium-magnesium carbonates that compose the aquifer sediments, but then evolves directly to “salty” water by mixing with seawater, in the marginal Chesapeake Bay impact crater zone and tidal streams and rivers, which would increase the sodium concentration.

Fluoride

Groundwater fluoride concentrations in shallower sediments are generally less than 2 mg/l in the Coastal Plain. Figure 9 exhibits the fluoride concentrations in the Northern Neck. Most concentrations are below the 2 mg/l water quality standard with an average below 1 mg/l. However, a spatial trend does exist in the Northern Neck as fluoride concentrations are greater in the eastern most portions of Northumberland and Lancaster Counties (see yellow and red circles)

Widespread small concentrations of fluoride probably originate by desorption from phosphatic sedimentary material contain in the marine sediments of the Piney Point aquifer. McFarland suggests several mechanisms including the initial adsorption of fluoride onto sediment oxyhydroxides, followed by desorption along the leading edge of a saltwater-transition zone. The higher fluoride concentrations are located near the Chesapeake Bay impact crater zone.

Another mechanism is desorption of fluoride from phosphatic material. Fluorine is present in solid form within some marine sediments as phosphatic material composed of fluorapatite ($Ca_5(PO_4)_3F$), which makes up fossil bones and teeth deposited as remains of marine animals (McFarland and Bruce, 2006). Fluorapatite releases dissolved fluoride to groundwater by ion exchange with hydroxyl (OH^-) ions to form hydroxylapatite ($Ca_5(PO_4)_3OH$). Adsorption of hydroxyl results from an increase in its concentration in groundwater, thereby displacing adsorbed fluoride into groundwater and increasing its concentration. Dissolved hydroxyl concentration also varies directly with pH and bicarbonate concentration. Thus, increases in pH and bicarbonate concentration also correspond to desorption of fluoride. Note that Figure 5 exhibits generally higher pH values in the same eastern most area of the Northern Neck which is coincident with higher fluoride concentrations.

Relative Concentrations of Sodium, Fluoride, and Filtered Residue

Figure 10 is a plot of the relative concentration of these three constituents for the Northern Neck database. This triangle map illustrates the distribution of the relative percentages of filtered residue, fluoride and sodium at each sampling point. Each triangle "axis" is scaled independently based on the minimum and maximum measured value of that constituent normalized to values ranging from 0 to 100. The larger size of a triangle indicates a greater relative concentration of each of the three constituents. A change in "shape" of the triangle reflects a change in the relative concentration for one of the given parameters between sampling points. Note that the triangles on Figure 10 only exhibit subtle changes in their shape suggesting that the proportion of the three constituents remains relatively constant between each sampling point throughout the Northern Neck.

The triangle map does show an increase in the three constituents from west to east along the Neck, as illustrated by larger triangles in Northumberland and Lancaster Counties. A more subtle trend in distribution can be seen when comparing the triangles located along the groundwater divide (which generally follows the northeastern border of Richmond County) to those closer to the two River boundaries. There appears to be a correlation between distance to a river and the amount of filtered residue, sodium and fluoride in well water. This could suggest an increase in dissolved load with flow/residence time or reflect a mixing zone from the tidal influence of the river water. The larger triangles in the Northumberland or Lancaster Counties may suggest influence of the salt water transition zone along the margin of the impact crater.

Summary

The chemical composition of groundwater in the Piney Point aquifer evolves eastward and with depth, from hard to soft to salty. Chemical weathering of subsurface sediments is followed by ion exchange by clay and glauconite, and subsequently by mixing with seawater along the saltwater-transition zone. Total ion concentration in the Piney Point shows an abrupt eastward increase, which conforms to the outer margin of the Chesapeake Bay impact crater and the tidally-influenced rivers, bays, and inlets of the eastern most extent of the Neck. A spatial distribution is suggested with “hard” water present generally toward the west end of the Neck, “soft” water primarily occupies a broad area of the central portion of the Neck in Richmond, eastern Westmoreland, and western portions of Northumberland and Lancaster Counties, and “salty” water occurs in the eastern portions of Lancaster and Northumberland Counties, which conforms closely to the outer impact crater margin.

Arsenic, chloride, and nitrate-nitrogen do not appear to be elevated or widely detected in the Northern Neck groundwaters. The buffered pH-Eh conditions are not conducive to the mobilization of arsenic. Although chloride is a widespread elevated constituent of most of the Virginia Coastal Plain, concentrations in the Northern Neck were below 20 mg/l. The depth of the Piney Point aquifer precludes the vertical migration of nitrogen constituents from their source release points at the surface or in the surficial water-table aquifer.

Sodium concentrations are elevated above the 20 mg/l water quality guidance level throughout the four counties and exhibit an increasing spatial trend from west to east. This sodium increase may be the result of desorption from marine sediments, the influence of mixing with seawater along discharge areas at the tidal streams and rivers, or the influence of the regional saltwater-transition zone near the margin of the Chesapeake Bay impact crater.

To best serve the domestic supply users of the Northern Neck area, AFI recommends that SAIF perform a detailed review of potential treatment technologies and select the most cost effective and technically efficient methodology to remediate the three common water types, which are mapped in the Northern Neck.

Please don’t hesitate to contact me regarding the analysis or recommendations provided. Thank you for using the professional services of aquaFUSION, Inc.

Sincerely,

aquaFUSION, Inc.

David R. Buss, Ph.D.
Principal Hydrogeologist

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