A hydrogeological assessment of arsenic in the Carolina terrane of Union County, North Carolina

Groundwater Circular #2009-01

Joju Abraham

Aquifer Protection Section

Resource Evaluation Program

subsequent work on development of best management practices to help reduce exposure to naturally-occurring arsenic in groundwater.

The study site is located in the Cid Formation, near the contact of Mudstone Member with the overlying Flat Swamp Member. At the site, a 150-foot soil-bedrock core was collected to characterize the geology and fracture patterns. Two (~ 250-foot deep) bedrock wells and a shallow (34-foot) water table well were constructed to determine the water quality and monitor As level changes with time. Bulk whole-rock chemistry was determined on representative samples. The onsite monitoring wells and 23 private water supply wells located near the site were sampled and analyzed for major and trace elements.

The saprolite generally consists of faintly laminated silty clay that is extensively oxidized along veins and fracture traces and is characterized by clay minerals and iron-oxides. Partially weathered rock is observed at a depth of about 28 feet, and is characterized by abundant sulfides along veins and fracture traces. At a depth of 35 feet, the bedrock is partially weathered and characterized by low to high-angle fractures. The bedrock is characterized as tuffaceous mudstones with layers of felsic and intermediate tuffs. The bedrock core shows multiple fractures that range from sub-horizontal ($<15^{\circ}$) to sub-vertical-dipping ($>75^{\circ}$). Sulfide minerals, mainly pyrite, often distinctly line the fractures and are also disseminated in the rock matrix. Iron and manganese oxide minerals are present along open fractures and vuggy zones, suggesting alteration of sulfides and precipitation of hydroxides.

Geologic and water quality data collected to date at the study site and its surrounding area suggest that groundwater As is naturally occurring, primarily derived from a bedrock source. While the primary source of As appears to be iron-sulfide minerals, redox processes appear to moderate the release of As to the groundwater. Oxidation of sulfides and desorption of As from Fe/Mn oxyhydroxides may be the main mechanisms for the release of As to the groundwater in the Mudstone Member of the Cid Formation of Carolina terrane. Additional work planned at the site include monitoring of As levels under varying redox or pumping conditions, that would help demonstrate the processes affecting the release of As to groundwater.

Acknowledgements

Abstract

Recent studies have identified hot spots for groundwater arsenic (As) in the Carolina (slate belt) terrane of North Carolina, notably in Union and Stanly counties (Pippin and others, 2003; 2005). These studies identified a relationship between As levels and a bedrock source and indicated that As is naturally occurring in the groundwater of the Carolina terrane. The present study investigates the geologic-source hypothesis at a study site in Union County and lays the foundation for

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INTRODUCTION

Introduction

Arsenic (As) is present in varying concentrations in groundwater across the United States (Welch and others, 2000). Arsenic levels in groundwater vary considerably due to the varied distribution of geologic sources of As, and the varied controls on As mobility in aquifers by biogeochemical processes, including oxidation of As-bearing sulfide minerals, desorption of As ions sorbed to aquifer solids, or by dissolution of As-bearing mineral oxides (Smedley and Kinniburgh, 2002).

In North Carolina, hot spots for groundwater arsenic (As) exist, notably in the (slate belt) Carolina terrane (Pippin and others, 2003; 2005). Within the Carolina terrane, there is a high probability for wells located in the Mudstone Member of the Cid Formation to show detectable levels of arsenic in private water supply wells (Pippin and others, 2005). Elevated levels of arsenic in the Carolina terrane are attributed to a geologic source, possibly associated with iron-sulfides in the bedrock (Pippin and others, 2003; 2005).

Groundwater is an essential resource for a significant suburban and rural population across the Piedmont-Blue Ridge region; roughly one-third of the total population relies on groundwater for potable supplies (Daniel and Dahlen, 2002). Exposure to elevated levels of As in drinking water can cause serious health effects that are shown to be dependent on the dose and duration of exposure (National Research Council, 2001). Understanding the sources of As and the processes and conditions affecting the release of As to groundwater is essential to address the As hot spots across the State. This study investigates the geologic-source hypothesis at a study site located in the mudstone geology in Union County – an area known to host wells with frequent As detects in the groundwater, but with variable levels of As. This study lays the foundation for subsequent work on development of best management practices to help reduce exposure to naturally-occurring As in groundwater.

To determine a geologic source for the elevated concentrations of arsenic reported in the Carolina terrane of Union County, a study site was chosen to represent the Cid Formation, which underlies a major portion of the Union County (Figure 1a, 1b). Regionally, the Cid Formation consists of a lower Mudstone Member, which is described as consisting of a lower cross-bedded, stratified siltstone and an upper laminated siltstone-mudstone containing minor tuff beds (Goldsmith and others, 1988). The overlying Flat Swamp Member consists of gray crystal and lithic tuffs, mainly rhyolitic or rhyodacitic in composition (Goldsmith and others, 1988). Rocks of the Cid Formation, like the majority of the rocks in the Carolina terrane, have been metamorphosed to at least the lower greenschist facies. The prefix meta- is often omitted by researchers due to the low

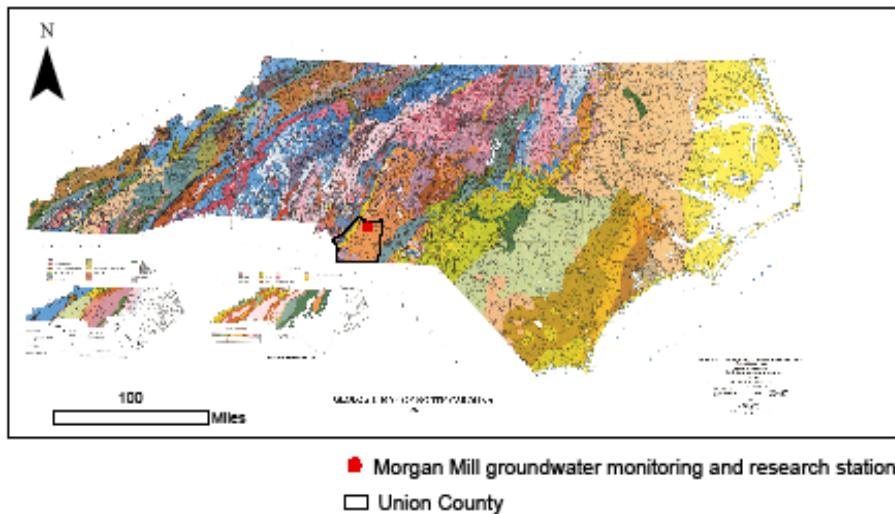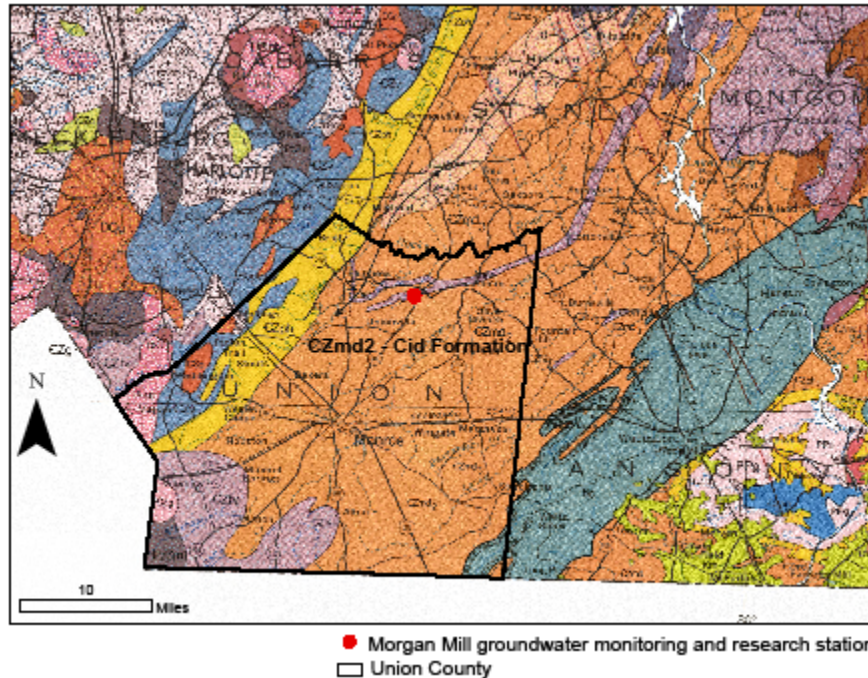● Morgan Mill groundwater monitoring and research station
☐ Union County

Figure 1a. Geologic map (1:500,000) of North Carolina (North Carolina Geological Survey, 1985). For explanation visit – http:gis.enr.state.nc.us/sid/bin/

Figure 1b. Location of the Morgan Mill groundwater monitoring and research station on a regional geologic map of North Carolina.

degree of metamorphism. The Cid Formation is generally considered to be of Neoproterozoic age (Hibbard and others, 2002). The study site is located close to the geologic contact between the Mudstone Member and Flat Swamp Member of the Cid Formation (Figures 1b, 2a).

The geologic contact between the Mudstone Member and Flat Swamp Member of the Cid Formation marks the transition between rock types dominated by volcaniclastic sedimentary rocks to primary pyroclastic rocks. Feiss and others (1993) indicate that this contact zone may be hydrothermally altered and may contain zones of sulfide mineralization. Thus, elevated levels of arsenic may be derived from (1) sulfide mineralization within the hydrothermally altered zone, or (2) the Mudstone Member may have originally been rich in arsenic derived from volcanic sources and that As is currently being released to groundwater by geochemical conditions favoring its release, or (3) a combination of the two. Sulfide mineralization is also known to occur in association with hydrothermal alteration from shallow intrusive bodies common in volcanic terranes. Shallow intrusive bodies have not been identified in the vicinity of the study area, but may play a role in As occurrence in other locations in the Carolina terrane.

Objectives

The overall objective of this study is to investigate the occurrence and distribution of arsenic in the Carolina terrane of Union County, North Carolina (Figure 1b). This study focuses at a research site (Figure 2a) that was selected because it represents the dominant geological formation that reportedly has elevated levels of As in groundwater. The investigation aims to (a) determine a geologic source to the occurrence and distribution of arsenic in the study area and (b) evaluate the geochemical processes affecting the arsenic concentrations in the groundwater through characterization of the hydrogeology and geochemistry of the regolith-bedrock aquifer system.

Background

Elevated levels of As in groundwater are noted across the United States. (e.g. Schreiber and others, 2000; Welch and others, 2000; Ayotte and others, 2003; Peters and Burket, 2008). Naturally-occurring As constitutes the main source of As in the groundwater of the U.S. (Welch and others, 2000).

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BACKGROUND

In North Carolina, elevated levels of As in groundwater are particularly noted in Union and Stanly counties in the Carolina terrane, and Lincoln and Gaston counties (Pippin and others, 2003, 2005) in the Inner Piedmont and Charlotte terranes. Groundwater As data compiled from North Carolina Department of Health and Human Services for Union County from 2000 to 2008 indicate that approximately 18 percent of samples (n = 3027) exceed the U.S. Environmental Protection Agency's Maximum Contaminant Level (MCL) of 10 µg/L for As in drinking water. Elevated levels of groundwater As appear to be derived from natural sources (Pippin and others, 2005).

In the U. S., As concentrations in groundwater are generally less than 1 µg/L (Welch and others, 2000). Twarakavi and Kaluarachchi (2006) determined median background concentrations ranging from <1 µg/L (detection limit) to 1.9 µg/L for different aquifer types across the U.S, based on groundwater As levels in public and private water supply wells located in forested areas. The background levels may be higher in regions associated with mining and smelting, or with geothermal sources (Smedley and Kinniburgh, 2002).

Average concentrations of As in the earth's crust are reported to range between 1 to 2 mg/Kg; shales have generally higher concentrations of As than other rocks (data compiled in Faure, 1991). Concentrations of naturally occurring As in groundwater vary regionally due to a combination of climate and geology and locally due to geochemical conditions in the subsurface (Welch and others, 2000). Elevated levels (>10 µg/L) of naturally occurring As in groundwater have been reported in the bedrock aquifers of the eastern U.S. (Peters and others, 1999; Ayotte and others, 2003; Robinson and Ayotte, 2006). Focazio and others (2006) examined approximately 7600 private water-supply wells in the U.S. and found that 11 percent of the samples exceeded the MCL of 10 µg/L.

Arsenic is found mainly in minerals where As occurs as the anion, dianion or the sulfarsenide anion, which are bonded to metals such as iron or cobalt and also occurs as a minor component in the relatively abundant pyrite (Vaughan, 2006). In aqueous solutions, arsenic forms oxy-anions – arsenite ($H_3As^{3+}O_3$) and arsenate ($H_3As^{5+}O_4$). Arsenite [As(III)] is generally the stable form under moderately reducing conditions, whereas arsenate [As(V)] is the stable form in oxidized aqueous solutions (Smedley and Kinniburgh, 2002).

Soluble arsenate can be generated by oxidation of As-bearing minerals such as pyrite and arsenopyrite and tends to adsorb on to the surfaces of Mn(IV) and Fe(III) oxyhydroxides (Smedley and Kinniburgh, 2002). Under Mn(IV) or Fe(III)–reducing conditions, adsorbed arsenate can be reduced to arsenite and mobilized (McMohan and Chapelle, 2008).

Reductive dissolution of As-bearing mineral oxides may occur at low dissolved oxygen, low Eh, and high Fe in the groundwater (Smedley and Kinniburgh, 2002). Elevated arsenic in deep groundwater may also result from surface and near-surface biogeochemical processes that mobilize arsenic from iron oxyhydroxides to deeper depths (Polizzotto and others, 2005). Thus, depending on the chemical composition of the aquifer matrix and ambient redox conditions, naturally-occurring As can be alternatively mobilized or immobilized (McMohan and Chapelle, 2008).

Other factors that are associated with elevated As levels but that may not be related to redox processes include high pH, elevated Cl, and mixing with geothermal water (Smedley and Kinniburgh, 2002). Both As(III) and As(V) have a strong pH-dependent sorption affinity for iron hydroxide and oxyhydroxide minerals such as ferrihydrite and goethite (O'Day, 2006). In low-iron settings, clays, aluminum oxyhydroxides, and Mn oxides may also take up arsenic (O'Day, 2006). Arsenate adsorbs strongly to iron-oxide surfaces in acidic and near neutral water but desorption from iron-oxides becomes favored as pH becomes alkaline (Fuller and Davis, 1989). Thus, changes in groundwater pH can promote adsorption or desorption of arsenic (Smedley and Kinniburgh, 2002). Arsenic adsorption can also be affected by the presence of competing ions, such as phosphate, which share similar geochemical behavior with arsenate; thus, both compete for sorption sites (Manning and Goldberg, 1997). Since As is present in natural waters in low concentrations, its adsorption and desorption on mineral surfaces play an important role in regulating its aqueous concentrations (Smedley and Kinniburgh, 2002; O'Day, 2006).

Regional Geology

A major part of Union County lies in the Carolina terrane, which consists of low-grade metaigneous and associated metasedimentary rocks. The Carolina terrane extends for more than 500 km from central Virginia to eastern Georgia, with a maximum outcrop width of about 140 km in central North Carolina (Hibbard and others, 2002). The Carolina terrane is comprised of four metavolcanic-dominated sequences: Virgilinia sequence in Virginia and North Carolina; the Albermarle sequence in North
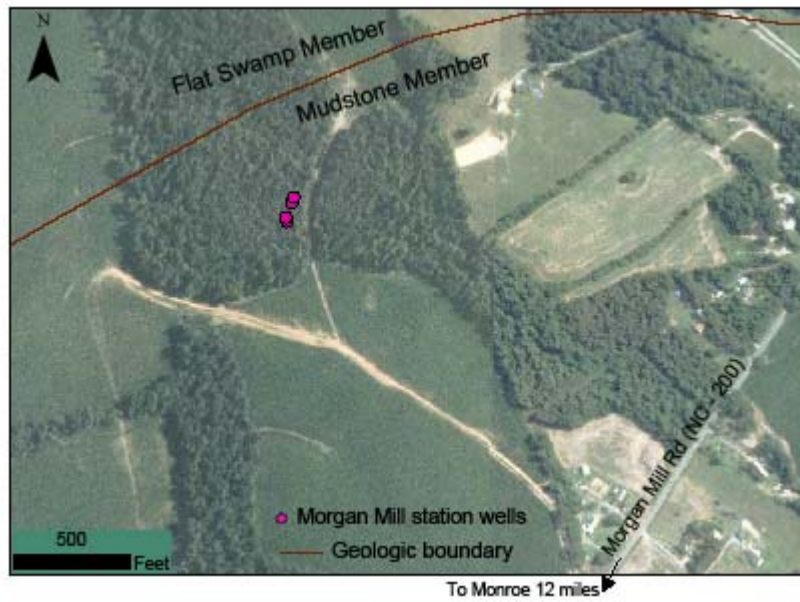
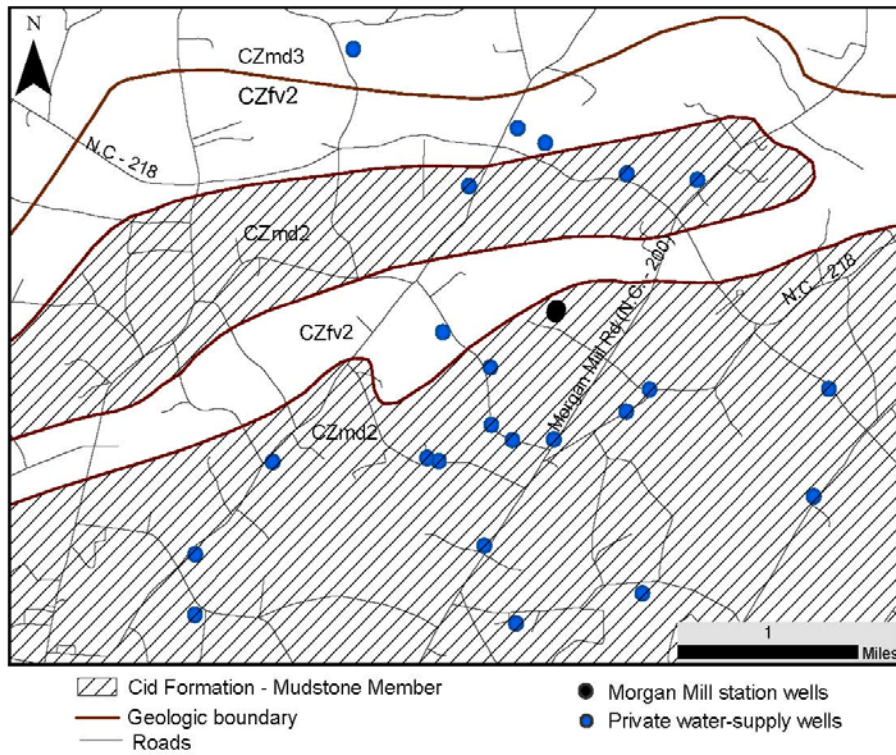Figure 2a. Site map of the Morgan Mill station, Union County, North Carolina.

Figure 2b. Locations of private water-supply wells sampled near the Morgan Mill station.

STUDY AREA

Carolina; the South Carolina sequence in South Carolina and northeast Georgia; and the Cary sequence in eastern North Carolina (Hibbard and others, 2002). These sequences collectively represent a long-lived, suprasubduction zone magmatic arc system (Hibbard and others, 2002 and references therein).

The study site is located in the Albemarle sequence of the Carolina terrane. The Albemarle sequence is interpreted to have formed above the continental crust during the Neoproterozoic through the Cambrian (Hibbard and others, 2002). The Uwharrie Formation forms the base of the sequence (Figure 3); it is dominated by felsic volcanic rocks with lesser amounts of mafic and sedimentary members. Overlying the Uwharrie Formation is the Albemarle Group, which is dominated by submarine epiclastic sedimentary rocks with lesser amounts of felsic and mafic volcanic rocks.

The sedimentary rocks of the Albemarle Group are interbedded siltstone, claystone, shale, and mudstone (Stromquist and Sundelius, 1969; and Milton, 1984). Five distinct sedimentary lithologies are present in the Albemarle Group: (1) thinly laminated siltstone and claystone of the (lowermost) Tillery Formation; (2) partly blocky and tuffaceous thick-bedded mudstone with numerous interbeds and lenses of felsic tuff in the Mudstone Member of Cid Formation; (3) shale at the top of the Mudstone Member; (4) siltstone and mudstone of the Floyd Church Formation; and (5) a thick sequence of alternating layers of volcanic sandstone and volcanic siltstone of the (topmost) Yadkin Formation (Stromquist and Sundelius, 1969; and Milton, 1984).

The Cid Formation is characterized by thicker-bedded, fine-grained clastic sedimentary rocks, containing more felsic and mafic volcanic members than the underlying Tillery Formation (Stromquist and Sundelius, 1969). The Tillery Formation mainly consists of thin-bedded to laminated fine-grained clastic sedimentary rocks with subordinate felsic and mafic volcanic rocks. A distinct felsic pyroclastic unit, the Flat Swamp Member, defines the top of the Cid Formation (Stromquist and Sundelius, 1969). The Flat Swamp Member contains distinct felsic lavas that are interpreted to have not extended far from their sources. Additionally, the Flat Swamp Member contains lesser amounts of andesitic basalt rocks (Stromquist and Sundelius, 1969).

Structurally, the Carolina terrane rocks have been folded in a series of northeast trending synclines and anticlines and show several minor faults and displacements (Goldsmith and others, 1988). The Troy anticlinorium, extending from central Randolph County through Union County into South Carolina, is a major structural feature defining the regional geology in the vicinity of the study area.

Description of Study Area

Location

The study site is located on a 200-acre private property along Morgan Mill Rd (N.C. Highway 200) about 1 mile southwest of its intersection with N.C. Highway 218 in northern Union County, North Carolina (Figure 2b), A large portion of the property is used for agriculture (e.g. corn, hay), but a small wooded area is located in the middle of the property. The locations for rock coring and wells at the Morgan Mill station were strategically chosen in the wooded area, which minimizes potential contamination from surface runoff. From the well locations, land elevation drops about 30 feet toward an intermittent stream that drains into Grassy Creek, a tributary of Rocky River. The Rocky River receives about three-fourths of the drainage from Union County (Floyd, 1965) and is part of the Yadkin-Pee Dee River basin. Regionally, the streams are generally characterized by a trellis drainage pattern, reflecting a structural control on the streams.

Geology

Existing geologic data for the study area is at the reconnaissance scale of 1:250,000 (Goldsmith and others, 1988). Site-specific geologic data did not exist prior to this study. Based on the mapping of Goldsmith and others (1988), the study site is located close to the geologic contact between the Mudstone Member and Flat Swamp Member (Figure 2a). The well cluster was installed within the Mudstone Member with the geologic contact with the Flat Swamp Member located approximately 500 feet to the north. Based on Goldsmith and others (1988), the site is located on the northwestern limb of the Troy Anticlinorium with original sedimentary bedding striking to the northeast and dipping toward the northwest from 10 to 40 degrees. Locally, bedding dips toward the southeast when small-scale folds are present.

Goldsmith and others (1988) describe the Mudstone Member and Flat Swamp Member of the Cid Formation as gray, typically tan-weathering, commonly in graded beds 10-40 cm thick, consisting of a lower, ripple-marked, cross-bedded, stratified siltstone, and an upper laminated siltstone-mudstone unit that contains minor tuff beds. Goldsmith and others (1988) describe the Flat Swamp Member as gray, crystal and lithic tuff, predominantly rhyolitic and rhyodacitic in composition. Its coarser phase west of Denton, NC, may include ash flow tuff and tuff breccia, but bulk of the unit consists of water-lain

deposits (Goldsmith and others, 1988).

The Mudstone Member is interpreted to have been deposited in a sub-aqueous environment (Stromquist and Sundelius, 1969). The upper part of the Mudstone Member consists of shale and contains less volcanics, indicating a quiet period of deposition without the input of volcanic debris. The dormant interval is succeeded by an explosive phase represented by the tuffs and lavas of the Flat Swamp Member (Stromquist and Sundelius, 1969).

The transitional rocks defining the contact between the Flat Swamp Member and Floyd Church Formation are tuffaceous siltstone and claystone and are typically speckled with sulfides (Stormquist and Sundelius, 1969). Based on thin sections, Stormquist and Sundelius (1969) describe that pyrite or pyrrhotite of diagenetic or metamorphic origin straddle bedding planes as irregular laths or granules. In some samples the sulfide grains are elongate in form or are in stringers parallel to bedding planes, while in other samples the sulfides are parallel to metamorphic cleavage (Stormquist and Sundelius, 1969).

Figure 3 General stratigraphy of the Albemarle Group: modified from Hibbard and others (2002, 2006); Milton (1984); and Stromquist and Sundelius (1969)

● Radiometric age date

Hydrogeology

Groundwater in the Piedmont and Blue Ridge Physiographic Provinces occurs in complex hydrogeologic settings composed of assemblages of metamorphic, igneous, and sedimentary rocks and secondary fracture networks. Weathered regolith, composed of soil, saprolite, alluvium, and colluvium, overlies the fractured bedrock and provides storage to the underlying fractures in the bedrock (Heath, 1980). Groundwater flows through intragranular pore spaces or through relict fractures in soil and saprolite. In contrast, groundwater in the underlying bedrock flows through secondary fractures and discontinuities because the unweathered bedrock has low porosity and permeability.

Piedmont aquifers, although described as a two-component (regolith and bedrock) groundwater system, commonly have a third component - the transition zone, which, through its numerous open fractures, provides the hydraulic connection between the regolith and bedrock. Conceptual models for groundwater flow in the Piedmont and Mountains groundwater systems have been described by Daniel and Dahlen (2002) and LeGrand (2004). Typically, natural groundwater recharge occurs in uplands and along slopes, while groundwater discharge occurs in valleys and bottom slopes, particularly near streams.

In the vicinity of the study site, the geology is characterized by sedimentary rocks interbedded with volcanic rocks and is represented mainly by tuffaceous mudstone. Underlying about two-thirds of Union County, the mudstones form the main water-bearing unit, having a relatively high permeability and yield (Floyd, 1965). Data reported by Floyd (1965) for 87 wells located in the mudstones of Union County indicate an average well yield of 11 gpm. In this dataset, the average well depth was 138 feet and the wells located in draws had the highest yield per foot of well.

Groundwater movement in the mudstones appears to be mainly along bedding planes, joints, and fractures. The shallow bedrock and extensive fractures in the bedrock provide a strong hydraulic connection between the regolith and bedrock. A short-term (4-hour) aquifer test conducted at the Morgan Mill station indicates a strong hydraulic connection between the regolith and bedrock groundwater systems. Thus, there is a strong potential for contaminant transport from shallow-subsurface sources to the groundwater system.

METHODS

Therefore, wells drilled in the Carolina terrane of Union County are subject to a minimum casing depth of 35 feet according to the North Carolina well construction standards (15A NCAC 02C.0117).

Methods

Geologic Mapping

Limited geologic mapping was conducted at the site to locally identify rock types and confirm the existing geologic mapping by Goldsmith and others (1988). The mapping consisted of an on-foot stream traverse from Grassy Creek toward the southeast along the tributary draining the study site. Coordinates of rock outcrops were determined using a recreational-grade GPS unit, and basic field characteristics (weathering, color, presence / absence of bedding, orientation of bedding or joints, etc) were recorded and measured if present.

Geologic Coring

A 150-foot continuous soil to bedrock core was collected near the contact of mudstone member with the Flat Swamp Member of the Cid Formation.

The core hole was designated as CH-1. Methods for conducting the geologic coring are described in Chapman and others (2005). The core hole was drilled by using a wire-line coring rig owned by the North Carolina Division of Water Quality. A 5-feet long, 2.5-inch inside diameter core barrel sampler was used with a wire-line retrieval system. A carbide-tipped soil sampling core barrel bit was used to penetrate the unconsolidated material and a diamond-tipped bit was used to penetrate the competent bedrock.

Well Construction

Monitoring well locations at the Morgan Mill station were selected to represent the Cid Formation of the Carolina terrane. Topographically, the wells are located on the mid-slope section of a hill. Well-construction methods used in the Resource Evaluation Program are described in Chapman and others (2005). Well-construction data are summarized in Table 1.

The monitoring well cluster consists of a shallow well and two deep wells that are designed to monitor the groundwater quality in the regolith and the deeper bedrock zones of the aquifer. The regolith zone of the aquifer includes soil residuum, alluvium, colluvium, and saprolite. The core hole was left open and converted into an observation well.

Table 1. Well construction record for the arsenic research station, Union County, North Carolina.

Well No	Date Drilled (finish)	Total Depth (ft)*	Well Diam (inch)	Casing Depth (ft)*	Casing Material	Screen/ Open hole (ft)*	Water Level (ft)*	Sand (ft)*	Grout (ft)*	Yield gpm~	Lat dd^	Long dd^	Distance from MW-1D (ft)
							10/14/2008						
CH-1	9/9/2008	154	4	34	Steel	34 - 154	22.41	na	0 to 34	20	35.12115	-80.44378	28
MW-1S	9/10/2008	35	4	25	PVC	25 - 35	18.94	22 to 35	0 to 22	1	35.12092	-80.44385	56
MW-1D	9/23/2008	252	6	64	PVC	64 - 252	21.89	na	0 to 64	30	35.12097	-80.44386	0
MW-2D	10/7/2008	252	6	63	Steel	63 - 252	21.97	na	0 to 63	20	35.12121	-80.44375	54

* feet below land surface; ~ gallons per minute; ^ decimal degrees

Regolith Well

The shallow regolith well was drilled using the air rotary method. After the boring reached the prescribed depth, a 4-inch PVC well casing was placed in the boring. The screen was 10 feet long with a diameter of 0.01 inch. Clean sand filter material filled the annular space between the PVC casing and the borehole to 2 feet above the top of the well screen. Bentonite was placed above sand filter to 3 feet below land surface. The top 3 feet of the annular space was grouted with cement.

The regolith well is screened between 25 and 35 feet and may partially include the top of the transition zone as described in the slope-aquifer system of LeGrand (2004). The transition zone, consisting of partially weathered rock near the top of bedrock, is generally considered to be the most transmissive part of the groundwater flow system in the North Carolina Piedmont.

Bedrock Wells

Two bedrock wells (identified as MW-1D and MW-2D) were constructed in accordance with North Carolina Rules governing the construction of water supply wells. A 12-inch air hammer was used to set the surface casings for the bedrock monitoring wells. Bedrock casing borings were terminated after about 5 feet of competent bedrock was penetrated. A 6.25-inch diameter PVC casing was used in MW-1D and a 6.25-inch diameter steel casing was used in MW-2D to hold the regolith material. The annular space between the casing and the borehole was filled with bentonite with a tremie pipe to 3 feet below land surface. The top 3 feet of the annular space was grouted with cement. A smaller diameter drill bit was used to drill the open borehole section of the bedrock to depths up to 252 feet.

The bedrock wells are located about 30 feet away from the core hole and are constructed similarly, except for the casing material (PVC and steel). The bedrock monitoring well with PVC casing is considered to represent the typical construction of private wells of the region. The bedrock well with a steel casing is constructed to evaluate the water quality against the well with PVC casing. The second deep well will be also used to characterize the groundwater flow characteristics at the site.

Well Development

Following well construction, the wells were developed by air-lift method, according to standard well construction procedures used in this area.

METHODS

Bulk Chemistry

Selected core samples were analyzed by Acme Laboratory (Vancouver, B.C., Canada) for bulk chemistry from selected depths, including fracture zones and unfractured mudstone and tuff. Total abundances of major oxides and minor elements were determined by ICP-emission spectrometry following a lithium metaborate-tetraborate fusion and nitric acid digestion. Portions of the sample digestates were also used to determine the concentrations of rare earth and refractory elements using ICP-mass spectrometry. Precious and base metals were determined by ICP-MS following an aqua-regia digestion. Total carbon and sulfur were determined by combustion in a C-S analyzer.

Groundwater Sampling

Sampling of 23 residential water-supply wells (Figure 2b) was performed over 15 days in August 2008. The wells for sampling were chosen randomly within a two square mile area of the Morgan Mill station, but ultimately the homeowner's interest determined whether or not their well water was tested for arsenic. All of the wells are located in the Cid Formation, except for one well located in the Floyd Church Formation is considered with the Flat Swamp Member because of its close proximity to it. At each location, the wells were purged for at least 20 minutes or until the field parameters stabilized. Measured field parameters included temperature, pH, specific conductance (SC), dissolved oxygen (DO) and oxidation-reduction potential (ORP). Samples were collected for the analysis of major ions, nutrients, and selected trace elements. At each location, an unfiltered and a (0.45 micron) filtered sample were collected for the determination of total and dissolved metal concentrations, respectively. The samples were preserved immediately upon collection according the sample preservation guidance of the Division of Water Quality laboratory. At selected locations, a field speciation cartridge developed by Meng and others (2000) was used to separate As(III) from As(V) through anion exchange process. The adsorbent in the cartridge adsorbs As(V). The filtered water is analyzed in the lab for As and the results are assumed to equal As(III).

The first set of groundwater samples from the monitoring wells at the Morgan Mill station was collected during September-October 2008, immediately following the development of each well. Two sampling events were later conducted in

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November 2008 and January 2009 following recommended well purging procedures (Standard Operating Procedures, 2008). Field parameters, namely, pH, SC, DO and ORP were measured to obtain representative groundwater samples. The samples were analyzed for selected major ions, nutrients, and metals by following standard EPA methods adapted by the Division of Water Quality laboratory.

Data Analyses

Scatter plots and Piper diagrams were used to analyze the statistical and geochemical variability in the periodic water-quality data. Water quality data are presented by groundwater-system zone (regolith and bedrock). Whole-rock data were analyzed using Geochemical Data Toolkit (GCDkit, free version) for geochemical classification and developing graphics.

Limited geologic mapping at the study site indicates that the rocks exposed near the surface are consistent with the Mudstone Member and the Flat Swamp Member (Table 2), corresponding to the geologic map of Goldsmith and others (1988). At the study site, the bedrock outcrops along the banks of stream channels, on the streambed, and at land surface along roadside ditches. Rocks assigned to the Mudstone Member are typically green to dark green but weathered to light gray, thinly bedded siltstone to mudstone (Figure 4a). The rocks assigned to Flat Swamp Member are light brown weathered, gray, vitric tuff or bedded tuff with an aphanitic groundmass. Outcrops of the tuffs are locally brecciated (Figure 4b). Strike orientation of bedding in the Cid Formation displays a maxima approximately in the E-W direction (Figure 5a) and has an average dip of 24 degrees toward the northwest. Multiple sets of joints (Figure 5b) with an average dip of 79 degrees characterize the bedrock.

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Figure 4. Outcrop photographs of (a) Mudstone Member and (b) Flat Swamp Member at the Morgan Mill station.

The continuous soil-regolith-bedrock core (Appendix I) indicates that the saprolite consists of bluish gray finely laminated clay to silty-clay with reddish-brown mottles and patches; the veins and fracture traces show evidences of oxidation and reduction. Along the veins and fracture traces in the partially weathered bedrock, which is observed beginning at about 28 feet, (fresh and partially weathered) sulfides and Fe and Mn oxides are commonly present. At a depth of about 35 feet, the bedrock appears relatively less weathered, but it is extensively fractured.

The relatively less weathered bedrock is represented by finely laminated shale at 35 feet. The underlying tuffaceous mudstones are distinguished from the laminated shale by their lack of bedding plane cleavage. The tuffaceous mudstones are light to

dark gray, bedded, and interlayered with intermediate and felsic volcanic rocks. The layering is characterized by mudstone and lighter colored felsic to intermediate tuff. Diagenetic or metamorphic pyrites are present along the bedding planes and fractures as laths, granules, crusts, or disseminated in the rock.

The rock core is fractured throughout its length; however, the fracture density decreases in the lower parts of the core (Appendix I). Both shallow (horizontal to sub-horizontal) and sub-vertical dipping fractures characterize the core to a depth of about 55 feet. There is generally a predominance of shallow-dipping (< 30º) factures

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Table 2. Lithological and structural characteristics of rocks at the Morgan Mill station, Union County, North Carolina. (source: Phil Bradley, North Carolina Geological Survey)

Quadrangle	site_ID	station	station2	Description	Azimuth (rhr)	Dip	Meas_type	Cid Member	lat	long
Watson	Ua1-1	1	1.01	abundant quartz debris and boulders of white weathering, hard, probable tuff	0	0	none	flat swamp	35.12385	80.44677
Stanfield	Ua1-2	2	2.01	small outcrop of greenish gray, bedded fine tuff or tuffeaceous siltstone - assigned to Cid mudstone	341	26	bedding	mudstone	35.12685	80.44785
Stanfield	Ua1-3	3	3.01	outcrop of light gray weathering rind, green to dark green on fresh surfaces, bedded siltstone	268	40	bedding	mudstone	35.12702	80.44794
Stanfield	Ua1-3	3	3.02	outcrop of light gray weathering rind, green to dark green on fresh surfaces, bedded siltstone	346	84	joint	mudstone	35.12702	80.44794
Stanfield	Ua1-3	3	3.03	outcrop of light gray weathering rind, green to dark green on fresh surfaces, bedded siltstone	61	71	joint	mudstone	35.12702	80.44794
Stanfield	Ua1-4	4	4.01	outcrop area of brownish weathering rind, green, bedded siltstone and/or fine tuff - assinged to Cid mudstone	0	0	none	mudstone	35.12687	80.44706
Stanfield	Ua1-5	5	5.01	outcrop of light brownish to white weathering, hard gray coarse tuff. Outcrop looks brecciated with no uniform orientation of planar features	0	0	none	flat swamp	35.12679	80.44667
Stanfield	Ua1-6	6	6.01	outcrop of light brown weathering, hard, aphanitic groundmass (almost flinty), dark gray, bedded tuff	296	24	bedding	flat swamp	35.12639	80.44689
Stanfield	Ua1-6	6	6.02	outcrop of light brown weathering, hard, aphanitic groundmass (almost flinty), dark gray, bedded tuff	104	69	joint	flat swamp	35.12639	80.44689
Stanfield	Ua1-6	6	6.03	outcrop of light brown weathering, hard, aphanitic groundmass (almost flinty), dark gray, bedded tuff	216	78	joint	flat swamp	35.12639	80.44689
Stanfield	Ua1-7	7	7.01	outcrop of resistant, white weathering, hard, greenish gray, probable devitrified vitric tuff	168	85	joint	flat swamp	35.12578	80.44645
Stanfield	Ua1-7	7	7.02	outcrop of resistant, white weathering, hard, greenish gray, probable devitrified vitric tuff	310	81	joint	flat swamp	35.12578	80.44645
Stanfield	Ua1-7	7	7.03	outcrop of resistant, white weathering, hard, greenish gray, probable devitrified vitric tuff	324	16	joint	flat swamp	35.12578	80.44645
Watson	Ua1-8	8	8.01	Tree rootball of white weathering, gray with orange mottling, plagioclase porphyritic lava or plag crystal tuff. Abundant quartz debris present.	0	0	none	flat swamp	35.12419	80.44552
Watson	Ua1-9	9	9.01	outcrop of light brown weathering, brownish gray siltstone or fine tuff	256	28	bedding	flat swamp	35.12292	80.44598
Watson	Ua1-9	9	9.02	outcrop of light brown weathering, brownish gray siltstone or fine tuff	69	72	joint	flat swamp	35.12292	80.44598
Watson	Ua1-9	9	9.03	outcrop of light brown weathering, brownish gray siltstone or fine tuff	342	82	joint	flat swamp	35.12292	80.44598
Watson	Ua1-10	10	10.01	Large boulders greater than 2 feet diameter of white weathering, felsic tuff with amorphous white zones that may be relict pumice - probable devitrified vitric tuff	0	0	none	flat swamp	35.12249	80.44569
Watson	Ua1-11	11	11.01	Location of groundwater spring/seep and outcrop of white with red mottling, gray plagioclase crystal shard rich tuff	0	0	none	flat swamp	35.12193	80.44567
Watson	Ua1-12	12	12.01	outcrop of dark gray to greenish gray bedded siltstone or fine tuff	225	20	bedding	flat swamp	35.12121	80.44562
Watson	Ua1-12	12	12.02	outcrop of dark gray to greenish gray bedded siltstone or fine tuff	322	79	joint	flat swamp	35.12121	80.44562
Watson	Ua1-12	12	12.03	outcrop of dark gray to greenish gray bedded siltstone or fine tuff	246	88	joint	flat swamp	35.12121	80.44562
Watson	Ua1-13	13	13.01	outcrop of brown weathering rind, dark gray thinly laminated siltstone or fine tuff - outcrop looks brecciated - interpreted as outcrop of Flat Swamp	0	0	none	flat swamp	35.12066	80.44554
Watson	Ua1-14	14	14.01	outcrop of light brown weathering, very thinly bedded siltstone with sparse sulfides concentrated in bedding planes	264	21	bedding	mudstone	35.12034	80.44494
Watson	Ua1-15	15	15.01	outcrop in erosional gully of weathered, thinly bedded siltstone/mudstone with psuedo-mud cracks	276	10	bedding	mudstone	35.11970	80.44428
Watson	Ua1-15	15	15.02	outcrop in erosional gully of weathered, thinly bedded siltstone/mudstone with psuedo-mud cracks	166	78	joint	mudstone	35.11970	80.44428
Watson	Ua1-16	16	16.01	rock debris of felsic tuff and quartz debris in dirt road - probably in Flat Swamp member	0	0	none	flat swamp	35.12192	80.44315

GEOLOGY

(a)

Statistical Summary
Calculation Method: Length
Class Interval: 10 Degrees
Min.Length Filtering: Deactivated
Max.Length Filtering: Deactivated
Azimuth Filtering: Deactivated
Data Type: Unidirectional
Population: 7
Maximum Percentage: 28.6 Percent
Mean Percentage: 16.7 Percent
Standard Deviation: 5.83 Percent
Vector Mean: 86.12 Degrees
Confidence Interval: 32.57 Degrees
R-mag: 0.84

(b)

Statistical Summary
Calculation Method: Length
Class Interval: 10 Degrees
Min.Length Filtering: Deactivated
Max.Length Filtering: Deactivated
Azimuth Filtering: Deactivated
Data Type: Unidirectional
Population: 12
Maximum Percentage: 16.7 Percent
Mean Percentage: 12.5 Percent
Standard Deviation: 4.45 Percent
Vector Mean: 26.4 Degrees
Confidence Interval: 200.58 Degrees
R-mag: 0.15

Figure 5. Strike orientations of (a) bedding and (b) joints in the Cid Formation at the Morgan Mill station.

compared to sub-vertical (>60⁰) to vertical (>75⁰) fractures. However, the high-angle fractures appear to be more extensive, well-connected, and weathered to a greater degree than the low-angle fractures. The sulfides, interpreted as mainly pyrite, are present as: (a) cubic crystals, mostly as small aggregates; (b) pyritic crusts of < 2 cm diameter (Figure 6a, 6b); (c) infilling of vesicles, and (d) disseminated in the rock matrix. Oxidation products of sulfides are pronounced in open fractures and vuggy zones in the bedrock up to a depth of 55 feet.

The presence of iron-oxide minerals (goethite, limonite, and siderite along the fractures suggests alteration (oxidation) of sulfides followed by precipitation of iron-oxides. Mineral oxidation may have occurred some time in the geologic past, or the current levels of dissolved oxygen (~ 0.5 mg/L) may be sufficient to permit oxidation to occur slowly, given that there are numerous well-connected open fractures, which may provide an efficient pathway for groundwater flow in the regolith and bedrock zones of the aquifer.

Figure 6. Core photographs showing (a) disc-shaped pyrites on a horizontal fracture, (b) pyritic crusts on subvertical and horizontal fractures, and (c) a fractured section (113' – 120') showing evidence of water-rock interactions.

GEOLOGY

Table 3. Concentrations of major oxides and trace elements in the bedrock core samples.
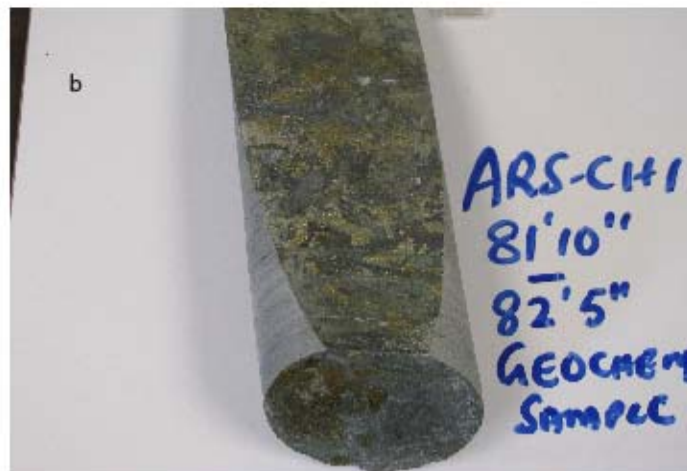
Sample #	SiO$_2$ (wt%)	TiO$_2$ (wt%)	Al$_2$O$_3$ (wt%)	Fe$_2$O$_3$ (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na$_2$O (wt%)	K$_2$O (wt%)	Cr$_2$O$_3$ (wt%)	P$_2$O$_5$ (wt%)	LOI (wt%)	Tot-C (wt%)
ARS-1-35	63.88	0.83	16.46	6.39	0.12	2.27	1.06	2.24	3.09	0.010	0.33	3.20	0.05
ARS-1-46	62.07	0.84	17.38	7.26	0.13	2.49	0.81	2.11	3.33	0.009	0.13	3.30	0.05
ARS-1-54	61.95	0.79	17.40	7.27	0.15	2.34	0.71	1.90	3.52	0.008	0.13	3.70	0.10
ARS-1-59	63.36	0.79	16.74	6.72	0.14	2.21	0.70	1.94	3.37	0.008	0.11	3.70	0.09
ARS-1-76	61.73	0.82	16.92	7.91	0.15	2.43	0.66	1.99	3.30	0.008	0.13	3.80	0.11
ARS-1-82	61.47	0.84	17.36	7.58	0.15	2.44	0.83	1.99	3.49	0.008	0.14	3.50	0.08
ARS-1-91	62.16	0.82	17.25	7.52	0.14	2.40	0.81	2.27	3.32	0.010	0.14	3.00	0.07
mean	62.37	0.82	17.07	7.24	0.14	2.37	0.80	2.06	3.35	0.01	0.16	3.46	0.08

	Tot-S (wt%)	Ba (ppm)	Be (ppm)	Co (ppm)	Cs (ppm)	Ga (ppm)	Hf (ppm)	Nb (ppm)	Rb (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Sn (ppm)
ARS-1-35	0.19	402	1	16.4	6.6	19.3	5.1	13.1	111	2	135	1.1	2
ARS-1-46	0.36	422	2	20.4	7.5	21.9	5.1	11.7	126	2	115	0.9	2
ARS-1-54	0.63	485	2	19.4	8.2	21.5	5.3	11.5	140	2	108	1.0	2
ARS-1-59	0.48	460	3	18.1	7.4	19.4	5.1	11.7	133	2	114	0.9	2
ARS-1-76	0.64	464	2	19.5	7.8	21.1	6.0	10.9	127	2	113	0.9	2
ARS-1-82	0.48	498	2	21.4	8.3	21.5	5.9	12.8	138	2	108	0.9	2
ARS-1-91	0.49	473	2	20.6	7.0	20.8	5.6	13.2	122	2	131	0.9	2
mean	0.47	458	2	19.4	7.5	20.8	5.4	12.1	128	2	118	0.9	2

	Sr (ppm)	Ta (ppm)	Th (ppm)	U (ppm)	V (ppm)	W (ppm)	Zr (ppm)	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)
ARS-1-35	135	1.1	9.8	2.3	153	1.6	190	35.7	24.8	52.0	7.00	28.6	6.23
ARS-1-46	115	0.9	9.9	2.0	121	2.0	185	34.4	28.7	62.8	7.77	30.6	6.17
ARS-1-54	108	1.0	9.6	2.2	126	1.5	175	33.7	27.1	59.1	7.42	60.6	5.75
ARS-1-59	114	0.9	9.8	2.0	120	1.6	175	32.8	28.6	61.1	7.60	29.9	6.05
ARS-1-76	113	0.9	8.3	2.4	128	1.7	183	35.2	28.3	63.9	7.92	32.8	6.5
ARS-1-82	108	0.9	9.7	2.3	128	1.3	191	35.9	31.9	68.2	8.34	33.6	6.68
ARS-1-91	131	0.9	9.9	2.3	149	1.5	182	34.7	30.5	65.2	8.13	30.8	6.31
mean	118	0.9	9.6	2.2	132	1.6	183	34.6	28.6	61.8	7.74	35.3	6.24

	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)
ARS-1-35	7.00	28.6	6.23	1.39	6.41	1.10	5.79	1.26	3.66	0.59	3.84	0.60
ARS-1-46	7.77	30.6	6.17	1.47	6.03	1.02	5.83	1.25	3.61	0.57	3.65	0.56
ARS-1-54	7.42	60.6	5.75	1.37	5.77	0.99	5.47	1.24	3.62	0.55	3.62	0.52
ARS-1-59	7.60	29.9	6.05	1.45	5.70	0.97	5.69	1.18	3.45	0.54	3.38	0.53
ARS-1-76	7.92	32.8	6.5	1.46	6.25	1.04	5.82	1.29	3.66	0.60	3.78	0.55
ARS-1-82	8.34	33.6	6.68	1.53	6.39	1.06	5.84	1.30	3.72	0.58	3.75	0.57
ARS-1-91	8.13	30.8	6.31	1.47	5.89	1.04	5.37	1.13	3.34	0.58	3.55	0.56
mean	7.74	35.3	6.24	1.45	6.06	1.03	5.69	1.24	3.58	0.57	3.65	0.56

|	Ag (ppm)	As (ppm)	Au (ppb)	Bi (ppm)	Cd (ppm)	Cu (ppm)	Hg (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Se (ppm)	Sb (ppm)	Tl (ppm)	Zn (ppm)
ARS-1-35	<0.1	18.1	0.7	0.2	<0.1	35.8	<0.01	0.7	31.8	14.3	<0.5	<0.1	<0.1	79
ARS-1-46	<0.1	22.1	2.3	0.3	<0.1	47.5	<0.01	0.4	38.5	13.2	0.6	0.4	<0.1	97
ARS-1-54	<0.1	19.6	3.5	0.5	<0.1	58.9	<0.01	0.5	35.8	20.9	<0.5	0.8	<0.1	83
ARS-1-59	<0.1	14.3	0.9	0.2	<0.1	49.9	<0.01	0.5	32.1	7.9	<0.5	0.3	<0.1	82
ARS-1-76	<0.1	12.5	1.8	0.2	<0.1	74.1	<0.01	0.6	43.2	9.7	<0.5	0.4	<0.1	105
ARS-1-82	<0.1	23.0	1.7	0.1	<0.1	43.0	<0.01	1.7	35.9	6.7	<0.5	0.3	<0.1	84
ARS-1-91	<0.1	19.2	1.7	0.2	<0.1	50.5	<0.01	1.1	37.0	9.2	<0.5	0.2	<0.1	89
mean	<0.1	18.4	1.80	0.2	<0.1	51.39	<0.01	0.79	36.33	11.70	0.60	0.40	<0.1	88.43
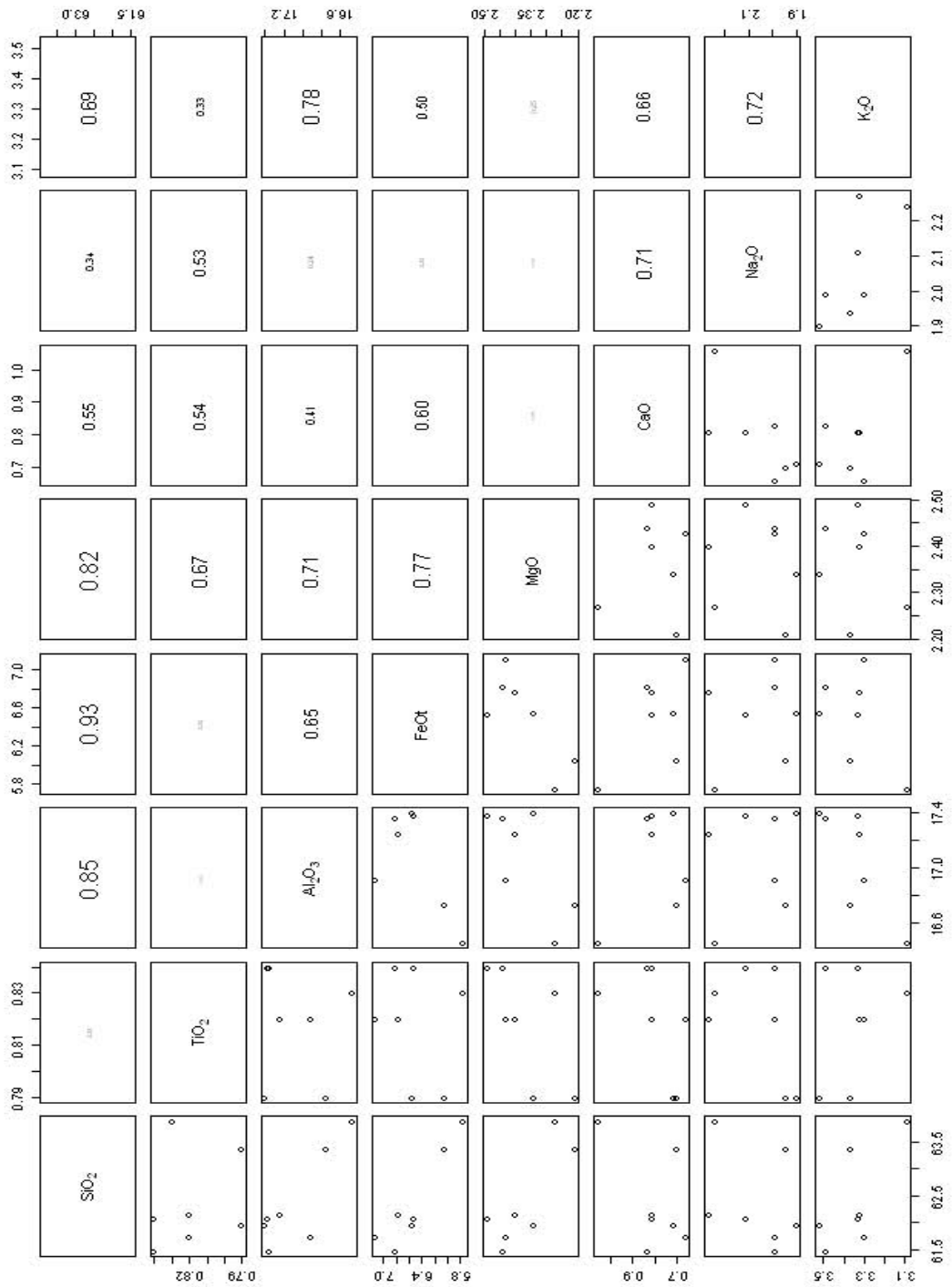
Figure 7. Correlation matrix for oxides in the bedrock core at the Morgan Mill station, Union County, N.C.
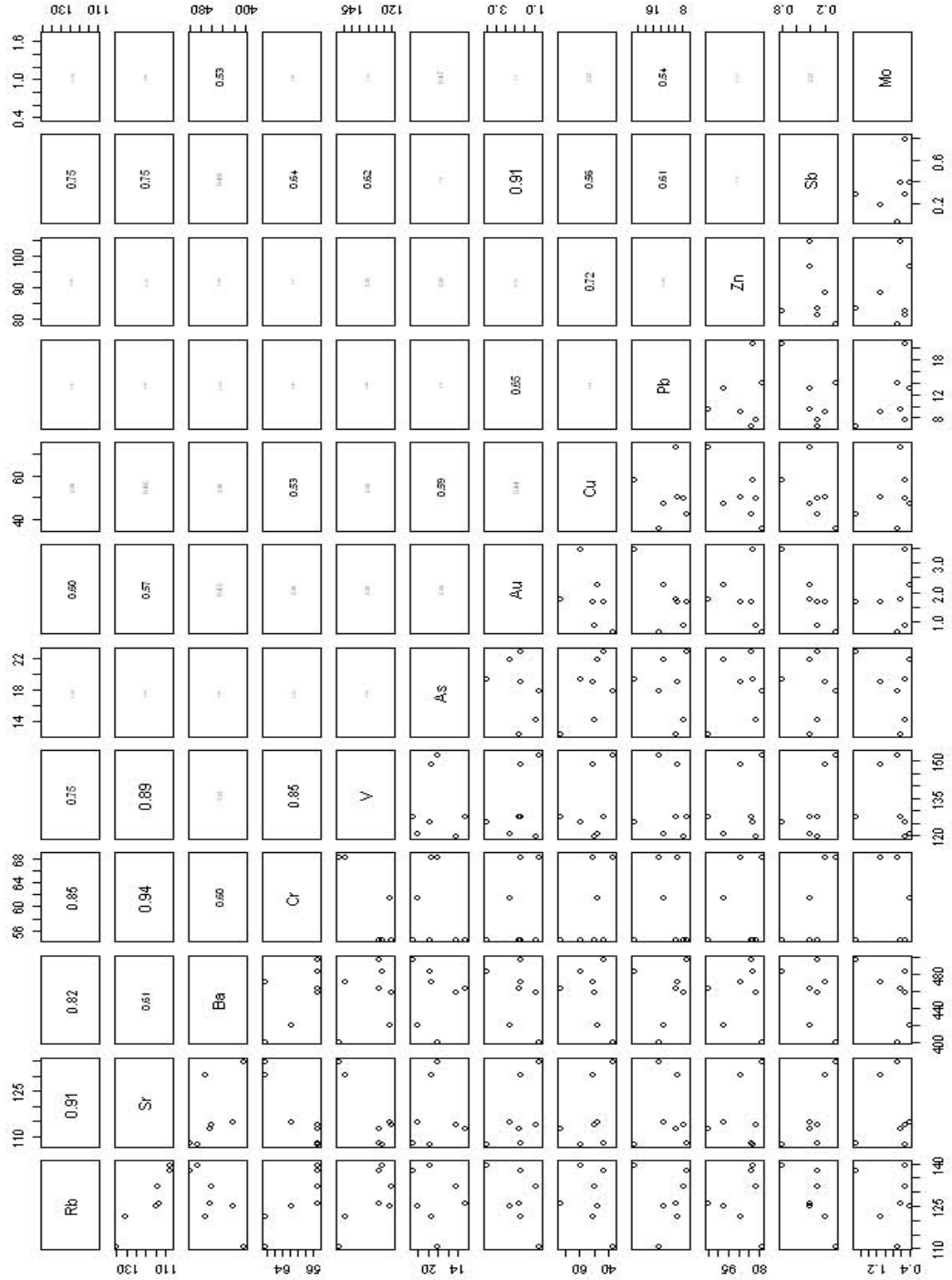
Figure 8. Correlation matrix for trace elements in the bedrock core at the Morgan Mill station, Union County, N.C.

At depths greater than 55 feet, the water-bearing fractures include sub-horizontal to vertical-dipping fractures. High-angle fractures become distinctive (Figure 6b), although fewer in number compared to low-angle fractures. Notable features include rock displacement along a fairly continuous vertical fracture that contains sulfides and the presence of two structureless fracture-fill zones of clay at depths of 63 and 80 feet. Sulfides, interpreted as pyrite, are present as: (a) well-developed euhedral crystals as clusters or aggregates and as isolated crystals in fractures; (b) large (>2 cm diameter) disc-shaped (dollar) and crustiform pyrite along fractures; (c) infilling of vesicles; and (d) disseminated in the rock matrix.

Clusters of euhedral pyrite and crustiform pyrite are particularly present along the sub-vertical partings and its intersection with shallow-dipping fractures. Well-developed cubic crystals of pyrite are generally observed only along high angle (sub-vertical) fractures. The presence of pyrite crusts and crystals along water-bearing fractures may indicate post-depositional water-rock interactions without any implications for its origin. Disseminated pyrite crystals, however, are present in the rock matrix at all depths, which may suggest a syn-depositional origin. Iron oxides, pyrite, chlorite and other clay minerals dominate the mineralogy at depths less than 55 feet, whereas, at greater depths, sulfides are more abundant with lesser amounts of iron oxides.

Results of whole-rock analyses indicate an average SiO_2 content of 62 wt.% with relatively high Al_2O_3 (17 wt.%) and Fe_2O_3 (7 wt.%), and low CaO (0.8 wt.%) contents (Table 3). Average concentrations of Na_2O and K_2O are 2.1 and 3.4 wt.%, respectively, while the total sulfide abundance is less than 1 percent in all the samples. The bulk chemical composition of rocks reflects an intermediate to felsic composition.

The Al_2O_3, Fe_2O_3, MgO, and K_2O are negatively correlated with SiO_2, whereas, Fe_2O_3, MgO, and K_2O contents are positively correlated with Al_2O_3 (Figure 7, negative or positive signs are not indicated on this figure). The strong positive correlation (r = 0.78) between Al_2O_3 and K_2O indicates a strong influence of clay minerals on the chemical composition. CaO contents generally show a scattered behavior (weak to moderate correlations) with other elements (Figure 7), suggesting that CaO content reflects silicate (plagioclase) and non-silicate (carbonate) sources.

Overall, the trace element concentrations are comparable to the average reported concentrations from 13 to 23 mg/kg (Table 3) with an average concentration of 18 mg/kg. The As levels are comparable to the levels of 0.5 to 43 mg/kg

reported in the felsic to mafic metavolcanic tuffs of the Uwaharrie Formation in the Carolina terrane of central North Carolina (S. Wang, 2009, unpublished data, report in preparation).

There is generally a lack of correlation between As and other trace elements in the rock samples (Figure 8), except for weak positive correlations with Au and Mo, indicating a slight relationship with the siderophile elements. Arsenic shows a strong positive correlation with Fe, while Fe and total S are strongly correlated (Figure 9). This suggests that As is likely associated with Fe-bearing minerals, such as, pyrite, arsenopyrite, and pyrrhotite. However, the negative y-intercept for total S against Fe_2O_3 in Figure 9 suggests that Fe is also present in other phases, most likely oxyhydroxides that are evident along the fractures. These trends suggest that Fe is present in both primary and secondary phases with As being associated with Fe in both the phases.
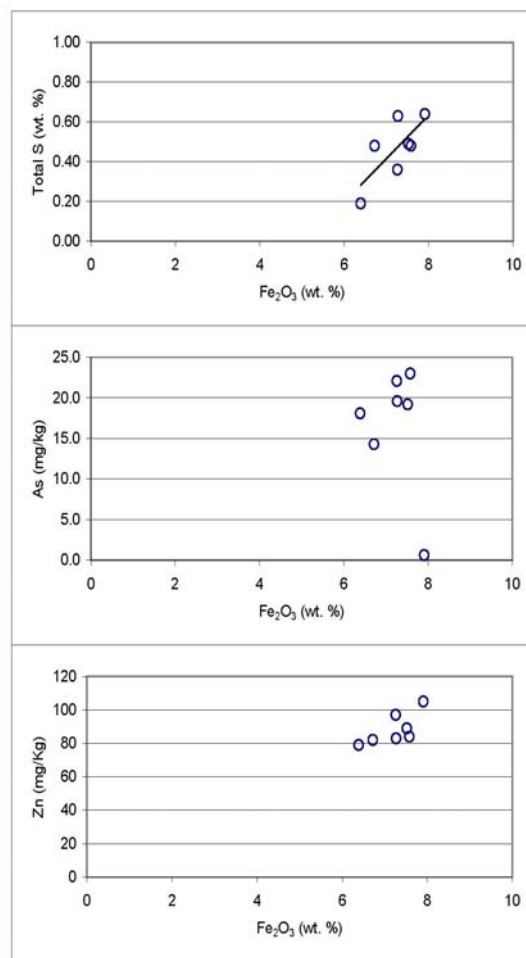

Figure 9. Scatter plots of iron oxide (Fe_2O_3) with total sulfur (S), arsenic (As), and zinc (Zn) concentrations.

WATER QUALITY

Water Quality

Measured field parameters at the Morgan Mill station indicate that the pH of groundwater increases from slightly acidic in the shallow regolith to alkaline in the bedrock wells (Table 4). Reducing conditions exist in the regolith and bedrock wells as indicated by low DO and ORP. Specific conductance values in the shallow well reflect the relatively high total dissolved solids. Alkalinity and Cl levels increase from the regolith to bedrock wells. Sulfate concentrations are lower in the bedrock wells compared to the shallow regolith. Concentrations of metals are low in the groundwater except for Fe and Mn. Levels of Cd, Cr, Cu, Ni, Pb, and Se were all below the reporting limits.

Groundwater in the bedrock wells represents a Ca-HCO_3 type water, whereas the shallow groundwater is a mixed Ca-Na-SO_4 type water (Figure 10). Groundwater in the regolith is enriched in Al, Fe, and SO_4 (Table 4). Higher levels of Al, Fe, K, Mg, and SO_4 in the shallow groundwater, compared to groundwater in the bedrock, are likely due to weathering of clay and sulfide minerals in the regolith. Redox reactions appear to affect the levels of Fe and Mn in the regolith groundwater. Elevated levels of Fe detected in the bedrock wells during the first sampling event may be due to mineral oxidation and the use of steel rods during well development. Iron concentrations decreased an order of magnitude during the second round of sampling, possibly due to a decrease in turbidity as a result of increased well development by purging the well for sampling. Nonetheless, groundwater is enriched in Fe, particularly in the shallow well (Table 4). A stream sample collected under baseflow condition was determined to have a Fe concentration of 340 µg/L. Iron is present mainly in the dissolved state (Table 4). Higher levels of Cl in the bedrock wells, compared to the regolith well, may simply reflect higher levels of Cl in the mudstones.

Comparison of water chemistry between the bedrock wells constructed of PVC (MW-1D) and galvanized steel (MW-2D) show a few differences in this limited data set. Concentrations of Fe, Mn, and Zn are slightly higher in the well with steel casing compared to the well with PVC casing. An evaluation of the effect of casing material on As concentrations was not possible due to the low levels of As at the site. Additional data being collected would be evaluated for water quality differences between the two casings and may be presented in a future report.

Groundwater chemistry from the bedrock wells is generally comparable to the water chemistry of

samples from the private water supply wells (Figure 11). However, the chemical compositions of private wells cover a broad range, primarily due to variations in the anionic composition. In the private wells, Cl concentrations range from 12 to 270 mg/L, SO_4 from 10 to 150 mg/L, and HCO_3 from 53 to 210 mg/L (Table 5). Higher levels of Ca (up to 180 mg/L) and Mg (up to 35 mg/L) are also noted in the private water supply wells compared to the bedrock monitoring wells (Table 4). Nonetheless, the chemical composition of groundwater at the study site and the area near the study site largely reflects a natural bedrock source that is associated with mudstones and volcanic rocks of felsic to intermediate composition.

Arsenic concentrations in the private water supply wells range from < 5 µg/L (below detection limit) to 77 µg/L (Table 5, Appendix II). Of the 23 wells sampled, 14 wells exceeded the U.S. EPA's Maximum Contaminant Level (MCL) of 10 µg/L for As. All of the wells that exceeded the MCL are located in the Mudstone Member (Figure 12). Wells located in the primary pyroclastics of Flat Swamp Member generally have As levels below 5 µg/L. Below detection levels are also noted in wells located in the areas represented by mudstone but sandwiched in between the Flat Swamp volcanics and in areas close to the contact between the two members (Figure 12). One private well located in the Mudstone Member closest to (southwest of) the Morgan Mill station (Figure 12) was excluded in the calculations for Table 5 since the water quality characteristics resembled the Flat Swamp Member.

Arsenic concentrations in the monitoring wells at the Morgan Mill station range from less than 2 µg/L to about 7 µg/L (Table 4). The low concentrations of As may be due to: (a) oxidation of As-bearing minerals near the borehole and its subsequent precipitation with oxyhydroxides during pumping or well development; (b) variability of As-bearing minerals in the bedrock at the site; or (c) dilution by a gradational mixing with the pyroclastic rocks of the Flat Swamp Member.

Arsenic concentrations do not show any definite trend in relation to total well depth (Figure 13). However, higher As levels are generally observed in wells with depth greater than 100 feet, which reflect wells drilled into the bedrock, particularly in the mudstones. Plots of As concentrations with concentrations of selected ions, pH, alkalinity, and DO are shown in Figure 14. Elevated (>10 µg/L) levels of As are generally present at low (< 100 µg/L) Fe and (< 25 mg/L) SO_4. Elevated concentrations of As are also noted at DO levels ranging from 0.2 to 1.5 mg/L. In addition, higher As levels are associated with a pH greater than 6.8 (Figure 14).

Redox conditions in the groundwater were calculated (Table 6) using the workbook developed by Jurgens and others (2009). The framework initially developed by McMohan and Chapelle (2008) for the identification of redox processes is used with some improvements in Jurgens and others (2009). Table 6 indicates that O_2 to Mn-reducing conditions are active at concentrations greater than 10 µg/L.

Arsenic concentrations are lower than 10 µg/L under Fe/SO_4-reducing conditions. Due to a lack of hydrogen sulfide data in the present study, it was not possible to distinguish Fe-reducing from SO_4-reducing conditions (Chapelle and others, 2009).

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Table 4. Chemical characteristics of groundwater in the monitoring wells at Morgan Mill station, Union County, N.C.

Well ID	Collect date	Lab Sample ID	Sample type*	Water level bmp	Sampling depth	DO	pH	pH	ORP	Water Temp.	Specific Cond.	Specific Cond.	Bicarbonate	Carbonate	Turbidity	Residue, Suspend	Total Dissolved solids
				field	field	field	field	lab	field	field	field	AHPA2510B	AHPA2320B	AHPA2320B	AHPA2130B	AHPA2540D	AHPA2540C
				(ft)	(ft)	(mg/L)	(std)	(std)	(mV)	(oC)	(uS/cm)	(uS/cm)	(mg/L)	(mg/L)	(NTU)	(mg/L)	(mg/L)
MW-1S	10/2/2008	AB36179	Total	na	34	na	na	6.8	na	na	na	180	38	<1	na	na	141
MW-1D	9/24/2008	AB35935	Total	na	230	na	8.0	8.1	na	16.3	249	240	95	<1	na	na	168
MW-2D	10/8/2008	AB36387	Total	na	230	na	7.9	8.0	na	16.6	270	260	100	<1	na	na	175
CH-1	10/14/2008	AB36638	Total	na	40	na	na	7.6	na	na	na	280	110	<1	na	na	170
MW-1S	11/3/2008	AB37243	Total	21.35	34	0.38	6.1	6.6	-173	16.3	205	190	33	<1	1.5	<6.2	152
MW-1S	11/3/2008	AB37244	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-1S	11/3/2008	AB37245	Spec	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-1D	11/3/2008	AB37246	Total	24.38	118	0.63	7.5	7.6	-158	16.7	291	270	110	<1	<1	<6.2	178
MW-1D	11/3/2008	AB37247	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-1D	11/3/2008	AB37248	Spec	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-2D	11/12/2008	AB37616	Total	24.66	118	0.44	7.5	7.8	-36	17.0	310	300	120	<1	2.6	<6.2	193
MW-2D	11/12/2008	AB37617	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-2D	11/12/2008	AB37618	Spec	na	na	na	na	na	na	na	na	na	na	na	na	na	na
CH-1	11/3/2008	AB37240	Total	25.08	40	0.15	7.4	7.6	-199	16.1	202	270	110	<1	2.4	<6.2	182
CH-1	11/3/2008	AB37241	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
CH-1	11/3/2008	AB37242	Spec	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-1S	1/26/2009	AB39781	Total	19.97	34	1.3	6.2	6.3	67	16.0	194	na	39	<1	na	na	144
MW-1S	1/26/2009	AB39783	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-1D	1/26/2009	AB39782	Total	22.97	118	0.38	7.5	7.7	2	16.8	292	na	120	<1	na	na	178
MW-1D	1/26/2009	AB39784	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
MW-2D	1/26/2009	AB39786	Total	23.11	118	0.15	7.7	7.7	-104	16.8	308	na	120	<1	na	na	186
MW-2D	1/26/2009	AB39788	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na
CH-1	1/26/2009	AB39785	Total	23.67	40	0.37	7.4	7.6	-45	15.8	301	na	120	<1	na	na	179
CH-1	1/26/2009	AB39787	Diss	na	na	na	na	na	na	na	na	na	na	na	na	na	na

* Total samples represent raw unfiltered water; * Dissolved samples represent water filtered through a 0.45 micron filter.

* Speciated samples represent water filtered through a 0.45 micron filter and an As speciation filter to determine As(III) concentration.

^ J8 - Data Qualifier Code: Temperature limits exceeded (samples frozen or >6°C) during storage, the data may not be accurate.

WATER QUALITY

Table 4 Continued

Well ID	Collect date	Sample type	TOC	Chloride^	Flouride^	Silica	Sulfate^	Nitrite plus Nitrate as N	Phosphorus	Silver	Aluminum	Arsenic	Barium	Calcium	Cadmium
			APHA5310B	EPA 300.0	EPA 300.0	AC10-114-27-1-	EPA 300.0	LAC10-107-04-1-C	LAC10-115-01-1EF	EPA 200.8	EPA 200.7	EPA 200.8	EPA 200.7	EPA 200.7	EPA 200.8
			(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)	(ug/L)
MW-1S	10/2/2008	Total	<2	4.7	<0.4	na	35	0.32	0.03	<5.0	490	<5.0	<10	15	<1
MW-1D	9/24/2008	Total	<2	9.8	<0.4	na	12	0.22	0.13	<5.0	970	<5.0	13	36	<1
MW-2D	10/8/2008	Total	<2	12	<0.4	na	13	<0.02	0.04	<5.0	210	<5.0	18	38	<1
CH-1	10/14/2008	Total	<2	14	<0.4	na	12	0.02	0.02	<5.0	<50	<5.0	12	40	<1
MW-1S	11/3/2008	Total	<2	3.7	<0.4	35	55	<0.02	<0.02	<5.0	<50	<5.0	<10	16	<1.0
MW-1S	11/3/2008	Diss	na	na	na	na	na	na	na	<5.0	<50	<5.0	<10	17	<1.0
MW-1S	11/3/2008	Spec	na	na	na	na	na	na	na	<5.0	790	<5.0	<10	17	<1.0
MW-1D	11/3/2008	Total	<2	15	<0.4	25	11	0.06	0.04	<5.0	<50	5.0	<10	43	<1.0
MW-1D	11/3/2008	Diss	na	na	na	na	na	na	na	<5.0	<50	5.7	<10	40	<1.0
MW-1D	11/3/2008	Spec	na	na	na	na	na	na	na	<5.0	960	<5.0	<10	41	<1.0
MW-2D	11/12/2008	Total	<2	17	<0.4	26	13	<0.02	<0.02	<5.0	<50	<2.0	32	35	<1.0
MW-2D	11/12/2008	Diss	na	na	na	na	na	na	na	<5.0	<50	2.2	34	40	<1.0
MW-2D	11/12/2008	Spec	na	na	na	na	na	na	na	<5.0	580	<2.0	34	39	<1.0
CH-1	11/3/2008	Total	<2	15	<0.4	23	15	<0.02	<0.02	<5.0	<50	<5.0	10	39	<1.0
CH-1	11/3/2008	Diss	na	na	na	na	na	na	na	<5.0	<50	<5.0	<10	40	<1.0
CH-1	11/3/2008	Spec	na	na	na	na	na	na	na	<5.0	900	<5.0	11	39	<1.0
MW-1S	1/26/2009	Total	<2	7.9 J8	<0.4 J8	na	40 J8	<0.02	0.03	<5.0	340	<2.0	<10	15	<1.0
MW-1S	1/26/2009	Diss	na	na	na	na	na	na	na	<5.0	<50	2.4	<10	14	<1.0
MW-1D	1/26/2009	Total	<2	16 J8	<0.4 J8	na	12 J8	0.03	0.05	<5.0	<50	5.3	<10	43	<1.0
MW-1D	1/26/2009	Diss	na	na	na	na	na	na	na	<5.0	<50	6.9	<10	43	<1.0
MW-2D	1/26/2009	Total	<2	17 J8	<0.4 J8	na	13 J8	<0.02	0.02	<5.0	<50	2.2	33	40	<1.0
MW-2D	1/26/2009	Diss	na	na	na	na	na	na	na	<5.0	<50	3.6	34	40	<1.0
CH-1	1/26/2009	Total	<2	16 J8	<0.4 J8	na	14 J8	<0.02	0.02	<5.0	56	2.5	12	39	<1.0
CH-1	1/26/2009	Diss	na	na	na	na	na	na	na	<5.0	<50	3.6	12	40	<1.0

Table 4 Continued

Well ID	Collect date	Sample type	Chromium EPA 200.8 (ug/L)	Copper EPA 200.8 (ug/L)	Iron EPA 200.7 (ug/L)	Potassium EPA 200.7 (mg/L)	Magnesium EPA 200.7 (mg/L)	Manganese EPA 200.8 (ug/L)	Sodium EPA 200.7 (mg/L)	Nickel EPA 200.8 (ug/L)	Lead EPA 200.8 (ug/L)	Selenium EPA 200.8 (ug/L)	Zinc EPA 200.7 (ug/L)
MW-1S	10/2/2008	Total	<10	7.7	1200	1.1	7.8	330	14	<10	<10	<5.0	<10
MW-1D	9/24/2008	Total	<10	2.4	1500	0.71	4.7	95	16	<10	<10	<5.0	<10
MW-2D	10/8/2008	Total	<10	<2	1300	0.70	4.7	300	16	<10	<10	<5.0	<10
CH-1	10/14/2008	Total	<10	<2	93	0.96	4.9	190	19	<10	<10	<5.0	<10
MW-1S	11/3/2008	Total	<10	<2.0	870	1.1	8.5	330	14	15	<10	<5.0	11
MW-1S	11/3/2008	Diss	<10	<2.0	910	1.0	8.7	350	14	15	<10	<5.0	10
MW-1S	11/3/2008	Spec	<10	<2.0	940	1.0	8.8	350	14	14	<10	<5.0	<10
MW-1D	11/3/2008	Total	<10	<2.0	74	0.38	4.5	32	19	<10	<10	<5.0	<10
MW-1D	11/3/2008	Diss	<10	<2.0	<50	0.35	4.6	33	20	<10	<10	<5.0	<10
MW-1D	11/3/2008	Spec	<10	<2.0	<50	0.38	4.6	33	20	<10	<10	<5.0	<10
MW-2D	11/12/2008	Total	<10	<2.0	240	0.50	6.1	130	22	<10	<10	<5.0	140
MW-2D	11/12/2008	Diss	<10	<2.0	120	0.41	6.1	88	23	<10	<10	<5.0	82
MW-2D	11/12/2008	Spec	<10	<2.0	100	0.39	6.0	85	23	<10	<10	<5.0	140
CH-1	11/3/2008	Total	<10	<2.0	190	0.90	5.0	180	20	<10	<10	<5.0	<10
CH-1	11/3/2008	Diss	<10	<2.0	150	0.85	5.1	180	20	<10	<10	<5.0	<10
CH-1	11/3/2008	Spec	<10	<2.0	330	0.99	5.3	220	19	<10	<10	<5.0	<10
MW-1S	1/26/2009	Total	<10	<2.0	2000	0.85	7.1	280	14	<10	<10	<5.0	<10
MW-1S	1/26/2009	Diss	<10	<2.0	1400	0.78	7.0	280	14	<10	<10	<5.0	10
MW-1D	1/26/2009	Total	<10	<2.0	<50	0.37	4.5	31	21	<10	<10	<5.0	<10
MW-1D	1/26/2009	Diss	<10	<2.0	<50	0.39	4.5	30	21	<10	<10	<5.0	<10
MW-2D	1/26/2009	Total	<10	<2.0	180	0.39	5.9	98	22	<10	<10	<5.0	140
MW-2D	1/26/2009	Diss	<10	<2.0	170	0.34	5.9	98	22	<10	<10	<5.0	170
CH-1	1/26/2009	Total	<10	<2.0	680	0.58	5.0	160	20	<10	<10	<5.0	<10
CH-1	1/26/2009	Diss	<10	<2.0	280	0.57	5.1	150	21	<10	<10	<5.0	<10

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Table 5. Summary statistics of water quality parameters of private water-supply wells sampled near the Morgan Mill station, Union County, North Carolina.

Analyte	Units	Mudstone Member* n	Mean	Median	Min	Max	Flat Swamp Member** n	Mean	Median	Min	Max
Arsenic	µg/L	15	28	20	<5	77	7	<5	<5	<5	6.7
Calcium	mg/L	15	75	69	23	160	7	68	59	0.1	180
Iron	µg/L	15	<50	<50	<50	<50	7	1119	470	<50	4500
Potasium	mg/L	15	0.49	0.48	0.29	0.83	7	0.57	0.60	0.1	0.90
Magnesium	mg/L	15	12	9.4	5.5	28	7	12	7.6	0.1	35
Manganese	µg/L	15	130	135	11	240	7	588	655	230	840
Sodium	mg/L	15	29	21	11	63	7	44	39	13	91
Chloride	mg/L	15	62	41	12	270	4	100	94	32	180
Sulfate	mg/L	15	16	15	10	26	4	90	83	46	150
Alkalinity	mg/L	15	131	140	53	210	4	121	108	79	190
pH	pH	15	7.1	7.2	6.6	7.6	4	7.0	7.0	6.7	7.3
^ORP	mV	15	-214	-225	-278	-146	4	-278	-278	-291	-146
DO	mg/L	15	0.8	0.5	0.16	2.55	4	0.2	0.3	0.18	0.27
SC	uS/cm	15	540	538	214	1161	4	625	460	375	1206

* One sample was excluded in the calculation since the sample (located near the contact, closest to the Morgan Mill station) characteristics resemble the Flat Swamp Member.

** Includes mudstone areas that lie in between the Flat Swamp volcanics (see Figure 12).

^ORP = oxidation reduction potential; DO = dissolved oxygen; SC = specific conducatance

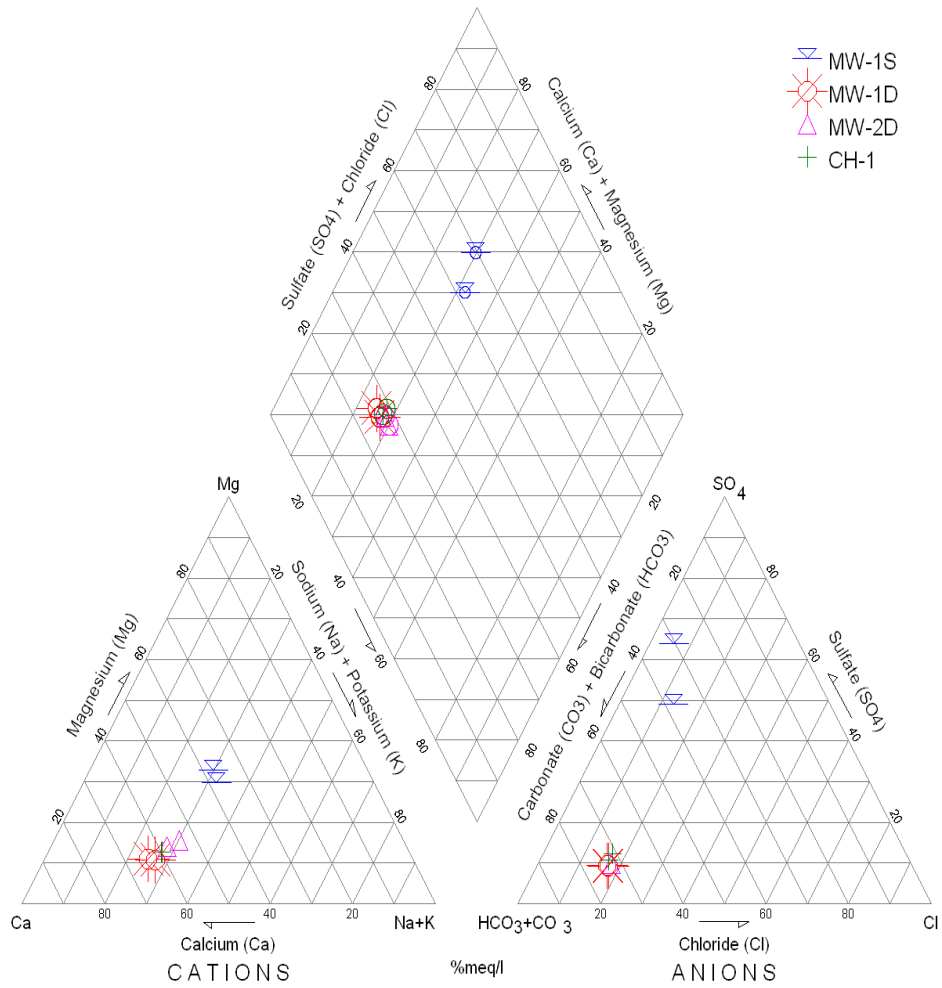October

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Figure 10. Average chemical composition of groundwater at the Morgan Mill station as represented on a Piper diagram from sampling events conducted on 11/2008 and 01/2009.
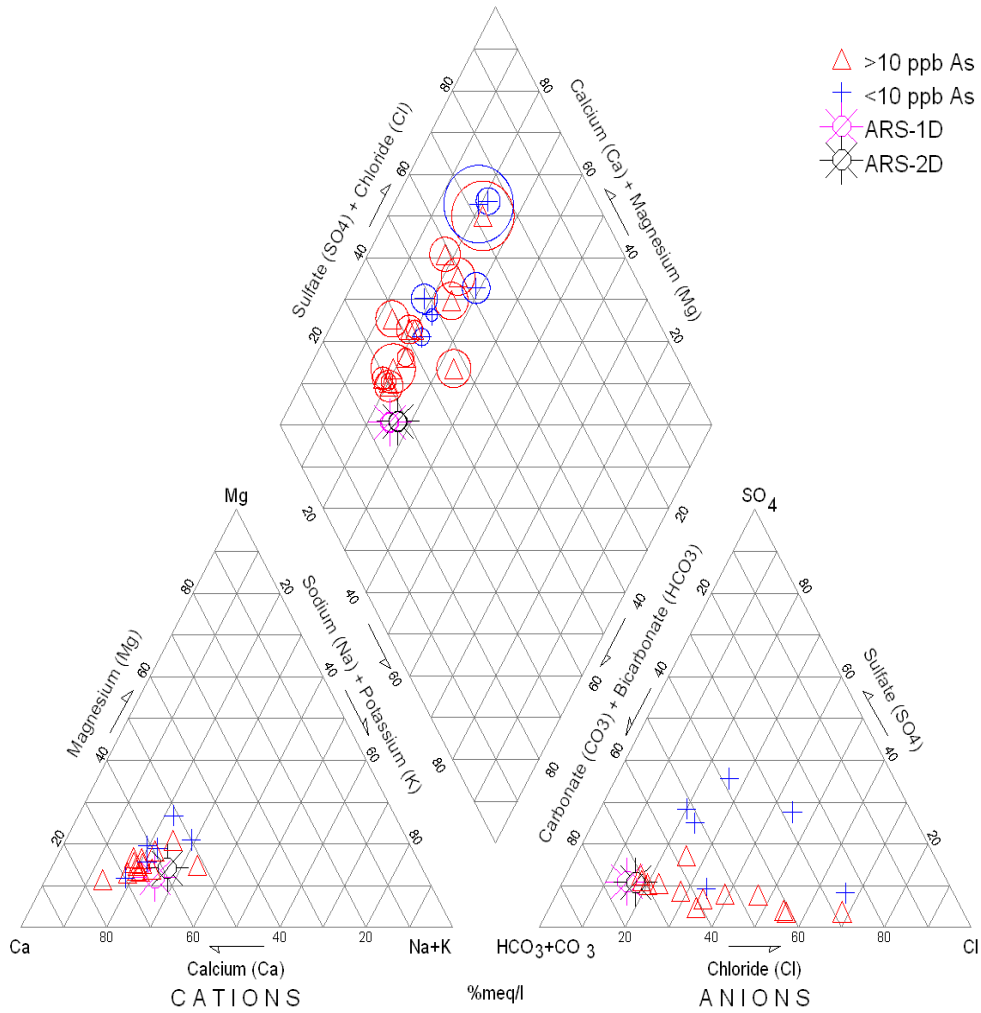
Figure 11. Chemical composition of groundwater sampled from the private water-supply wells and the bedrock wells at the Morgan Mill station. Private supply wells are represented as either > or < 10 μg/L of As.

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Figure 12. Arsenic concentrations (μg/L) in private water-supply wells sampled near the Morgan Mill groundwater monitoring and research station. Area underlain by geologic unit, Mudstone Member (CZmd2) is shaded, while areas underlain by Flat Swamp Member (CZfv2) and Floyd Church Formation (CZmd3) are not shaded. A location shown in lighter shade (60 ug/L) was sampled six times over 6 years.

Figure 13. Arsenic concentrations with well depth (data available for 14 private and 4 monitoring wells).

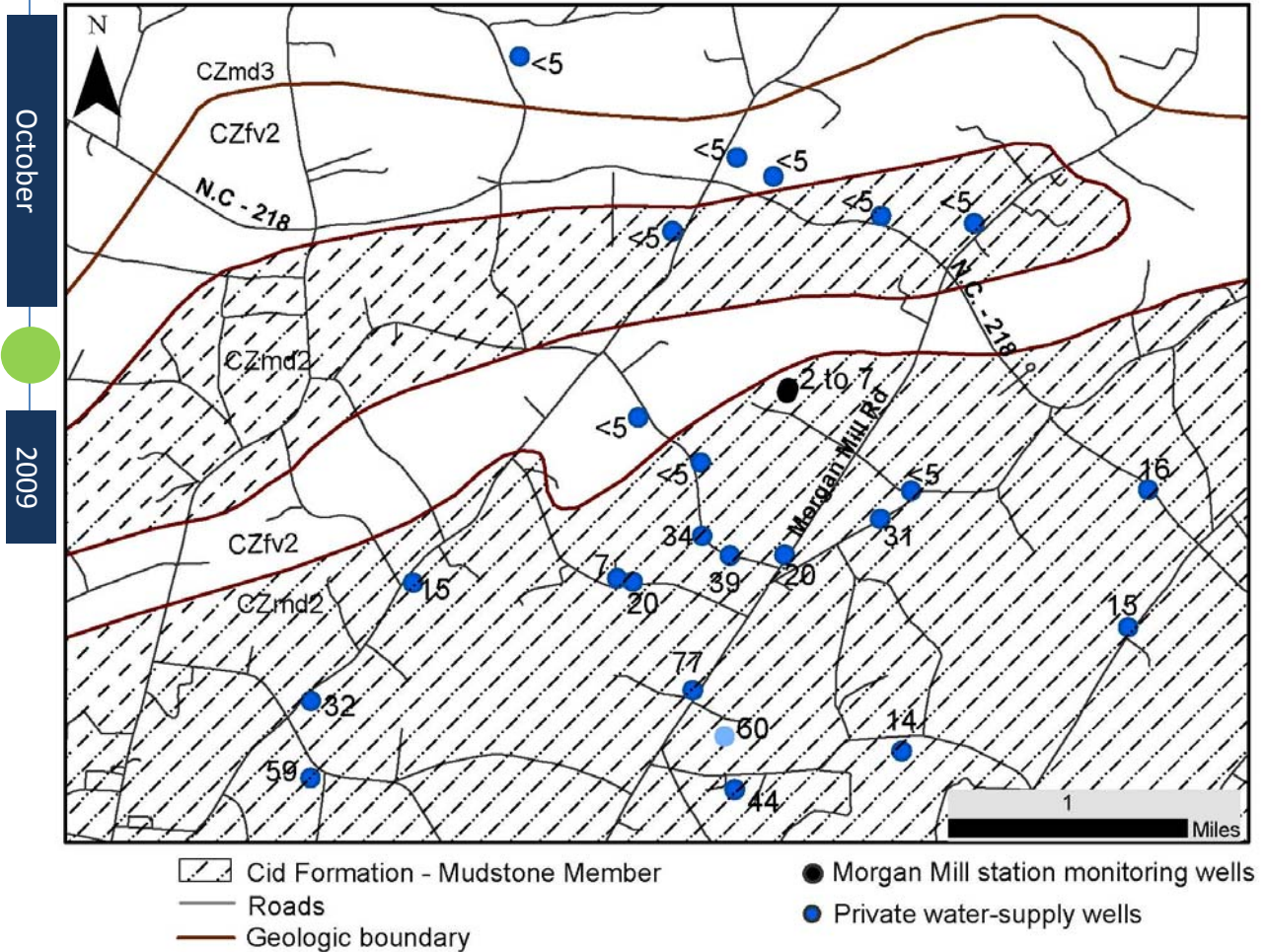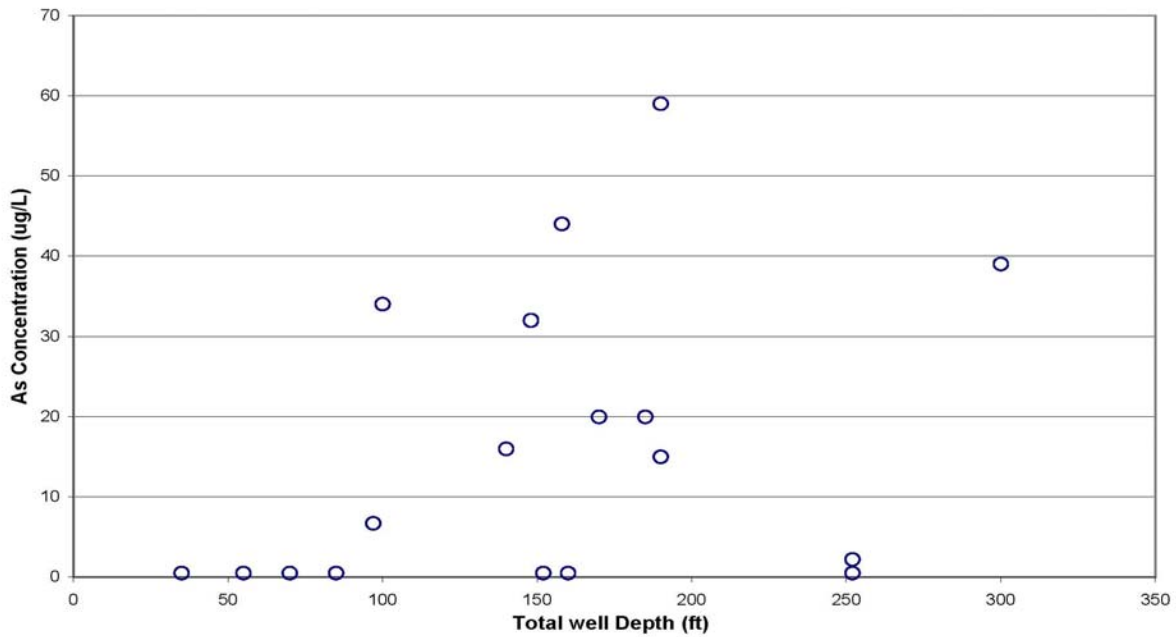Table 6. Arsenic concentrations in the private water-supply wells and redox conditions determined by the workbook of Jurgens and others (2009).

Well	As (ug/L)	General Redox Category	Redox Processes
Hs-1	77	Mixed(anoxic)	$NO_3.Mn(IV)$
Re-1	59	Anoxic	$Mn(IV)$
Mr-1	44	Oxic	O_2
Ss-1	39	Oxic	O_2
Ws-1	34	Anoxic	NO_3
Tn-1	32	Oxic	O_2
Lg-1	31	Oxic	O_2
Cn-1	20	Anoxic	NO_3
Mc-1	20	Anoxic	NO_3
Oa-1	16	Anoxic	NO_3
Dl-1	15	Mixed(anoxic)	$NO_3.Mn(IV)$
Pr-1	15	Oxic	O_2
Bg-1	14	Oxic	O_2
Wm-1	7.2	Oxic	O_2
Ge-1	6.7	Anoxic	$Fe(III)/SO_4$
ARS-MW-1D	5.0	Oxic	O_2
ARS-MW-2D	2.2	Anoxic	$Fe(III)/SO_4$
Kr-1	<5.0	Anoxic	$Fe(III)/SO_4$
Hr-1	<5.0	Anoxic	$Fe(III)/SO_4$
Hn-1	<5.0	Anoxic	$Fe(III)/SO_4$
ARS-MW-1S	<5.0	Anoxic	$Fe(III)/SO_4$
ARS-CH-1	<5.0	Anoxic	$Fe(III)/SO_4$
De-1	<5.0	Anoxic	$Mn(IV)$
Le-1	<5.0	Mixed(anoxic)	$NO_3.Mn(IV)$
Sh-1	<5.0	Oxic	O_2
Sn-1	<5.0	Mixed(oxic-anoxic)	$O2-Mn(IV)$
Jn-1	<5.0	Suboxic	Suboxic

* Concentrations above the reporting limits are sorted descendingly in values.
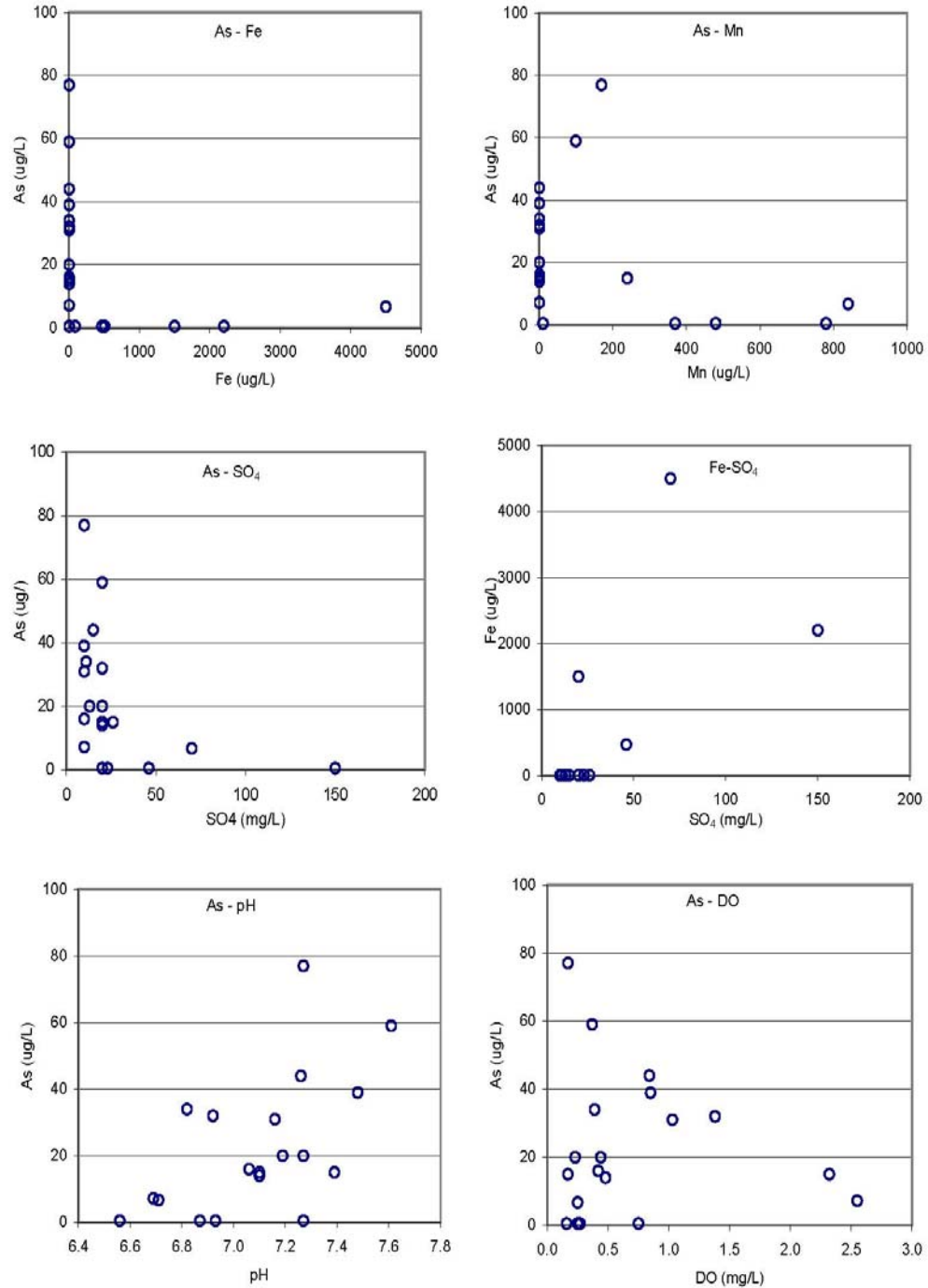
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Figure 14. Scatter plots of arsenic (As) with iron (Fe), manganese (Mn), sulfate (SO_4), pH, and dissolved oxygen concentrations in the private water-supply wells.

Discussion

The occurrence of As in the groundwater system near the study site is generally consistent with a natural source of As derived from the bedrock. Arsenic concentrations appear to be regulated by exchange reactions between the aqueous and solid phases in the aquifer. Higher As concentrations are observed in the Mudstone Member compared to the Flat Swamp Member (Table 5). The concentrations of As generally increase in the Mudstone Member away from the contact with the Flat Swamp Member (Figure 12), suggesting that the contact may not be a zone for migration of hydrothermal fluids enriched in As and other trace elements as initially hypothesized for this study. Rather, areas near the contact may serve to dilute the As levels by facilitating a mixing of high and low As groundwater. The primary pyroclastics may, thus, provide a dilution effect resulting in the lower As levels, as observed at the Morgan Mill station.

Summary statistics of water quality for private water supply wells (Table 5) indicate that concentrations of As, Fe, Mn, and SO_4 represent the main differences in water quality between the Mudstone Member and the Flat Swamp Member. High As levels are associated with low Fe, Mn and SO_4 concentrations (Figure 14). Samples containing less than 10 µg/L As show variable concentrations of Fe ranging up to 4800 µg/L and SO_4 ranging up to 150 mg/L. Arsenic concentrations show an exponential relation with Fe and SO_4 concentrations and there is a significant decline in As levels with increased Fe levels in the private supply wells, consistent with regional-scale data (Abraham and others, 2008).

The results suggest that oxidative dissolution of sulfide minerals in the tuffaceous mudstones provide the original source of As and subsequently, As is adsorbed or coprecipitated with Fe oxyhydroxides. The shallow bedrock and the well-connected fracture system in the regolith-bedrock groundwater system provide an effective framework for oxidation of sulfides to liberate As from the host minerals, at relatively great depths as observed in the core. Oxidation of sulfide minerals may also occur due to increased water withdrawal (Gotkowitz and others, 2004; Schreiber and others, 2000), or during normal pumping cycles. Arsenic may be released to groundwater following an exposure of pyrite in aquifer solids to atmospheric oxygen caused due to the lowering of water table in response to groundwater development (Gotkowitz and others, 2004). Lowering of water table due to extensive pumping, however, does not appear to affect private water-supply wells of the Piedmont, but may affect larger, public water-supply systems (Pitner and others, 2008). Increased water-rock interactions or other mechanisms (e.g. carbonate dissolution) increase the pH and alkalinity in the bedrock

groundwater, which in turn may play role in the release of As from the Fe oxyhydroxides. At the Morgan Mill station, it appears that Fe concentration has a strong control on the As levels in groundwater by promoting precipitation onto Fe/Mn hydroxides and by releasing As under mixed redox conditions as discussed below.

Trends of As with pH (Figure 14) indicate that higher As levels are generally associated with higher pH in the regional groundwater. High pH in groundwater may be caused by hydrolysis of common silicates (feldspars) and dissolution of carbonates (calcite). Since water-rock interaction increases with increased residence time of groundwater, the pH increases in older water and may result in increased As levels. High As levels have been noted in alkaline groundwater within felsic volcanic rocks by dissolution of iron oxyhydroxides in the presence of organic carbon (Welch and others, 2000). Alternatively, high As levels in the regional groundwater may occur by desorption from Fe oxyhydroxides under oxidizing conditions due to an increase in pH or competition from other anions (Welch and others, 2000; Smedley and Kinniburgh, 2002). However, low levels of As in the groundwater at Morgan Mill station may likely be due to dilution by mixing with the pryroclastic rocks or reactions with carbonate or silicate gangue minerals partially filling the fractures that may limit the movement of As from the bedrock to groundwater (e.g. Foley and others, 2006).

Based on the redox framework established by McMohan and Chapelle (2008), there is a wide range of redox processes operating near the study site. Table 6 indicates that elevated levels of As are generally associated with O_2-reducing to NO_3 and Mn-reducing conditions. Under Fe(III)/SO_4 reducing conditions, the concentrations of As are generally low, although elevated levels of As are present under mixed to anoxic conditions. The monitoring wells (MW-1S, MW-2D, and CH-1) are characterized by DO < 0.5 mg/L, NO_3 < 0.5 mg/L, Fe >100 µg/L, Mn > 100 µg/L, and 11 to 55 mg/L of SO_4. These concentrations correspond to the threshold concentrations for Fe(III)/SO_4-reducing conditions according to McMohan and Chapelle (2008). Where sulfate-reducing bacteria are active, the sulfide produced reacts to precipitate As or coprecipitate it with Fe, leaving little As in solution (Kirk and others, 2004). In some high-As wells located in the Mudstone Member, arsenate-reducing bacterial communities are present (Oates and Song, 2008) that may have a control on the distribution of As levels in the regional groundwater system.

SUMMARY

Summary

Geologic and geochemical data from the Morgan Mill station indicate that groundwater arsenic is naturally occurring, primarily derived from a bedrock source. The main source of arsenic in groundwater appears to be arsenic-bearing sulfide minerals that are present along the bedding planes, fractures and veins, and associated with the disseminated sulfide minerals in the rock matrix throughout the core length. Secondary minerals containing As are apparently limited to Fe-hydroxides. Results of this study support regional-scale studies of groundwater quality (Pippin and others, 2003; 2005) relating a geologic source to groundwater arsenic concentration, which is regulated by hydrogeologic and geochemical factors in the subsurface.

The regional relationship between elevated arsenic concentrations in groundwater and the mudstones (Pippin and others, 2005) is substantiated the elevated levels of As, above EPA's drinking water standard, noted in private water supply wells located in the mudstones compared to lower (below detection) levels noted in supply wells located in the Flat Swamp volcanics. Elevated concentrations of As are associated with lower Fe and SO_4 concentrations, suggesting that As is derived from Fe-sulfides through redox reactions. The shallow nature of the bedrock and the well-connected fracture system in the regolith-bedrock groundwater system provide an efficient framework for oxidation of sulfides to liberate As from the host minerals, at relatively great depths. Redox parameters indicate that oxidation of sulfides and desorption from Fe-Mn hydroxides appear to be the main mechanisms for the release of As to groundwater in the Cid Formation of Carolina terrane.

References

Abraham, J., A.H. Pitner, and C.G. Pippin, 2008. Geochemical processes affecting arsenic in private wells of the North Carolina Piedmont. Geological Society of America Abstracts with Program, 40, no. 4, p. 53.

Ayotte, J.D., D.L. Montgomery, S.M. Flanagan, and K.W. Robinson, 2003. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environmental Science and Technology, 37, p. 2075–2083.

Chapelle, F.H. P.M. Bradley, M.A. Thomas, and P.B. McMahon, 2009. Distinguishing iron-reducing from sulfate-reducing conditions. Groundwater, 47, 300–305.

Chapman, M.J., R.E. Bolich, and B.A.Huffman, 2005. Hydrogeologic setting, groundwater flow, and groundwater quality at the Lake Wheeler Road research station, 200–03.U.S. Geological Survey Scientific Investigations Report 2005–5166, 85 p.

Daniel, C.C., III, and P.R. Dahlen, 2002. Preliminary hydrogeologic assessment and study plan for a regional groundwater resource investigation of the Blue Ridge and Piedmont Provinces of North Carolina: U.S. Geological Survey Water-Resources Investigations Report 02–4105, 60 p.

Faure, G., 1991. Principles and applications of inorganic geochemistry. McMillan, NY, 500 p.

Feiss, G., Vance, K., Wesolowski, D., 1993. Volcanic rock-hosted gold and base-metal mineralization associated with Neoproterozoic–Early Paleozoic back-arc extension in the Carolina terrane, southern Appalachian Piedmont. Geology, 21, p. 439–442.

Floyd, E.O., 1965. Geology and ground—water resources of the Monroe area, North Carolina. Division of Water Quality, Groundwater Bulletin No. 5, 109 p.

Focazio, M.J., D. Tipton, S.D. Shapiro, and L.H. Geiger, 2006. The chemical quality of self-supplied domestic well water in the United States. Ground Water Monitoring and Remediation, 26, p. 92–104.

Foley, N.K., R.A. Ayuso, J.D. Ayotte, D.L. Montgomery, and G.P. Robinson, 2006, Geological assessment of cores from the Great Bay National Wildlife Refuge, New Hampshire. U.S. Geological Survey Scientific Investigations Report 2006-5203, 74 p.

Fuller, C.C., and J.A. Davis, 1989, Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters: Nature, v. 340, p. 52–54.

Goldsmith, R., D.J. Milton, and J.W. Horton, Jr., 1988. Geologic map of the Charlotte 1º x 2º quandrangle, North Carolina and South Carolina. Map I-1251-E, U.S. Geological Survey Miscellaneous Investigations Series.

Gotkowitz, M.B., M.E. Schreiber, and J.A. Simo, 2004. Effects of water use on arsenic release to well water in a confined aquifer. Groundwater, 42, p. 568–575.

Heath, R.C., 1980. Basic elements of groundwater hydrology with reference to conditions in North Carolina: U.S. Geological Survey Open-File Report 80-44, 86 p.

Hibbard, J.P., E.F. Stoddard, D.T. Secor, and A.J. Dennis, 2002. The Carolina Zone: overview of Neoproterozoic to Early peri-Gondwanan terranes along the eastern flank of the s. Appalachians. Earth-Science Reviews, 57, p. 299–339.

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Hibbard, J.P. M.A.S. McMenamin, J. Pollock, P.G. Weaver, R.C. Tacker, B.V. Miller, S. Sampson, and D. Secor, 2006. Significance of a new Ediacaran fossil find and U-Pb zircon ages from the Albemarle Group, Carolina terrane of North Carolina. Carolina Geological Society Field Trip, November 4-5, 2006, p. 29–33.

Jurgens, B.C., J.B. McMahon, F.H. Chapelle, and S.M. Eberts, 2009. An Excel workbook for identifying redox processes in ground water. U.S. Geological Survey Open-File Report 2009-1004. 8 p and workbook.

Kirk, M.F., T.R. Holm, J. Park, Q. Jin, R.A. Sanford, B.W. Fouke, and C.M. Bethke, 2004. Bacterial sulfate reduction limits natural arsenic concentrations in groundwater. Geology, 32, p. 953–956.

LeGrand, H.E., 2004. A master conceptual model for hydrogeological site characterization in the Piedmont and Mountain region of North Carolina, A guidance manual: N.C. Division of Water Quality, Groundwater Section, 50 p.

Manning, B.A., and S. Goldberg, 1997. Adsorption and stability of arsenic (III) at the clay mineral-water interface: Environmental Science and Technology, v. 31, p. 2005–2011.

McMohan, P.B. and F.H. Chapelle, 2008. Redox processes and water quality of selected principal aquifer systems. Groundwater, 46, p. 259–271.

Meng, X, S. Bang, and G.P. Korfiatis, 2000. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. Water Research, 34, p. 1255–1261.

Milton, D., 1984. Revision of the Albemarle Group, North Carolina. U.S. Geological Survey Bulletin 1537-A, A69–A72.

Oates, H. and B. Song, 2008. Molecular detection of dissimilatory arsenate-respiring bacteria in North Carolina groundwater, In, S. Ahuja, ed., Arsenic contamination of groundwater, John Wiley & Sons, New Jersey, p. 83–94.

O'Day, P.O., 2006. Chemistry and mineralogy of arsenic. Elements, 2, p. 77–83.

Peters, S.C., J.D. Blum, B. Klaue, and M.R. Karagas, 1999. Arsenic occurrence in New Hampshire drinking water. Environmental Science and Technology, 33, p. 1328–1333.

Peters, S.C. and L. Burkert. 2008. The occurrence and geochemistry of arsenic in groundwater of the Newark basin of Pennsylvania. Applied Geochemistry, 23, p. 85–98.

Pippin, C.G., M. Butczynski, and J. Clayton, 2003. Distribution of total arsenic in groundwater in the North Carolina Piedmont. N.C. Division of Water Quality, 80 p.

Pippin C.G., C. Withers, L. Ennis, 2005. Arsenic occurrence in the unconfined fractured bedrock aquifer system of the North Carolina Piedmont. Geological Society of America Annual Meeting, Salt Lake City, 37, p. 171.

Pitner, A.H, C.G. Pippin, and J. Abraham, 2008. Assessment of arsenic attenuation in public and domestic supply wells. Geological Society of America Abstracts with Program, 40, no. 4, p.54.

Polizzotto, M.L., C.F. Harvey, S.R. Sutton, and S. Fendorf, 2005. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. Proceedings of the National Academy of Sciences, 102, p. 18819–18823.

Robinson G.R. and J.D. Ayotte, 2006. The influence of geology and land use on arsenic in stream sediments and ground waters in New England, USA. Applied Geochemistry, 21, p. 1482 –1497.

Schreiber, M.E., J.A. Simo, and P.G. Freiberg, 2000. Stratigraphic and geochemical controls on naturally-occurring arsenic in groundwater, eastern Wisconsin. Hydrogeology Journal, 8, p. 161–176.

Smedley, P.L. and D.G. Kinniburgh, 2002. A review of the source, behavior, and distribution of arsenic in natural waters. Applied Geochemistry, 17, p. 517–568.

Standard Operating Procedures, 2008, North Carolina Piedmont-Mountains Program. accessed 5/20/09, http://h2o.enr.state.nc.us/gwp/documents/GWREP_SOP-Draft_Apr_08.pdf

Stromquist, A.A. and H.W. Sundelius, 1969. Stratigraphy of the Albemarle Group of the Carolina Slate Belt in Central North Carolina. U.S. Geological Survey Bulletin 1274-B, 22 p.

Turekian, K.K., and K.H. Wedepohl, 1961. Distribution of the elements in some major units of the Earth's crust. Geological Society of America Bulletin, 72, p. 175–192.

Twarakavi, N.K.C. and J.J. Kaluarachchi, 2006. Arsenic in the shallow ground waters of conterminous United States: Assessment, health risks, and costs for MCL compliance. Journal of American Water Resources Assoc, 42, 275–294.

Vaughan, D.J., 2006. Arsenic. Elements, 2, p. 71–75.

Welch, A.H., D.B. Westjohn, D.R. Helsel, and R.B. Wanty, 2000. Arsenic in groundwater of the United States: occurrence and geochemistry. Groundwater, 38, p. 589–604.

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APPENDIX - I

Appendix I. Regolith Log Sheet

REGOLITH LOG SHEET									PAGE: 1 OF 2

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE
BORING ID: CH-1	CORE DIAMETER: 3.5"
LOGGED BY: ABRAHAM	LATITUDE:
BEGIN DATE: 07-09-2008	LONGITUDE:
END DATE: 07-10-2008	LAND SURFACE ELEVATION:

INTERVAL	RECOVERY	GRAIN SIZE	DRY / WET	COLOR	DRY STRENGTH	PLASTICITY	UNIFIED CLAS	GROUNDWATER ZONE	DESCRIPTION
									DRY/WET: D=DRY, M=MOIST, W=WET DRY STRENGTH: N=NONE, L=LOW, M=MODERATE, H=HIGH, VH=VERY HIGH TOUGHNESS: L=LOW, M=MEDIUM, H=HIGH PLASTICITY: N=NONPLASTIC, L=LOW, M=MEDIUM, H=HIGH
0' TO 1'	0'								No recovery
1' TO 6"	4'8"	F	W	5YR 5/6	M	H	CH	R (res)	Yellowish red CLAY; mottled red patches in yellow matrix; root fragments absent; high FeO content; color becomes brownish red between 5' and 6'.
6' TO 11"	3'4"	F TO M	W	10YR 5/2	M	H	CH	R (res)	No recovery 6' to 7'8"; grayish brown to red CLAY; highly oxidized layer; FeO concretions; at 9', color changes to l gray and clay content decreases;
11' TO 16'	4'	F	M	10YR 5/2	M	M	CL	R (res)	No recovery 11' to 12'; grayish brown clay with reddish patches; finely (2 mm) laminated CLAY; layers of FeO & MnO indicate periods of oxidation and reduction; highly oxidized along relict fractures and bedding, and parallel to laminations.
16' TO 21'	4'6"	F	M	2.5YR 5/6	H	L	CL	R (res)	Light olive brown SILTY CLAY. Difficult to extract from core barrel; few laminations; oxidation along fracture traces; reddish brown mottles & patches but fewer than above; beginning at 17.5', core broken into small fragments; reddish brown patches decrease 19' to 21'.

REGOLITH LOG SHEET   PAGE: 2 OF 2

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE
BORING ID: CH-1	CORE DIAMETER: 3.5"
LOGGED BY: ABRAHAM	LATITUDE:
BEGIN DATE: 07-09-2008	LONGITUDE:
END DATE:	LAND SURFACE ELEVATION:

INTERVAL	RECOVERY	GRAIN SIZE	DRY / WET	COLOR	DRY STRENGTH	PLASTICITY	UNIFIED CLAS	GROUNDWATER ZONE	DESCRIPTION
									DRY/WET: D=DRY, M=MOIST, W=WET; DRY STRENGTH: N=NONE, L=LOW, M=MODERATE, H=HIGH, VH=VERY HIGH; TOUGHNESS: L=LOW, M=MEDIUM, H=HIGH; PLASTICITY: N=NONPLASTIC, L=LOW, M=MEDIUM, H=HIGH
21' TO 26'	4'10"	F	M	GLEY2 5/10B	M	L	SC	R (res)	Interval recovered from two runs of length 36" and 22"; bluish gray finely laminated SILTY CLAY; reddish brown patches absent but brownish black (MnO?) patches present, which may indicate the presence of reducing conditions; FeO and MnO line the fracture traces and veins, suggesting alternate oxidation and reducing environments; highly weathered at 23'.
26' TO 31"	4'10"	F	M	GLEY2 5/10B	M	L	SC	R (res)	Similar to the interval above, two runs of 36" and 22" were recovered; bluisg gray finely laminated (1-3 mm) SILTY CLAY; mechanically broken; PARTIALLY WEATHERED ROCK at 29'; finely laminated weathered MUDSTONE with two subvertical fractures and one horizontal fracture; sulfides (pyrite) along veins and fractures; disseminated sulfides also present.
END									END OF REGOLITH LOG

Appendix I. Bedrock Log Sheet

BEDROCK LOG SHEET		PAGE 1 OF 6	
PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION		DRILLING METHOD: WIRELINE	
BORING ID: CH-1		CORE DIAMETER:	
LOGGED BY: ABRAHAM		LATITUDE:	
BEGIN DATE: 07-10-2008		LONGITUDE:	
END DATE:		LAND SURFACE ELEVATION:	

		LITHOLOGIC		FRATURE INFO					
INTERVAL	RECOVERY	DESCRIPTION	G/ WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS	
31' TO 34'	3'	Finely laminated (1-3 mm) bluish gray SHALE; sulfides (mainly pyrite) on bedding planes; several enechelon cracks in conjugate array; cavities lines with metallic minerals; disseminated sulfides produce greenish black streak.	TRANS	H SH M SV V		5 1	5 1	Py Cpy FeO	
34' TO 36'	2'	Finely laminated bluish gray MUDSTONE with TUFFACEOUS layers and primary PYROCLASTICS; highly fractured.	TRANS	H SH M SV V	1	7 3 1	7 3	Py Cpy FeO	
36' TO 41'	5'	Massive light to medium gray TUFFACEOUS SILTSTONE, interbedded with layers of TUFF; crustiform (dollar-shaped) pyrite present; fractures SH to SV up to 38'; 38' – 41' mostly H fractures; Black concoidal MnO on the SV fracture; At 39', an annealed SV fracture.	TRANS	H SH M SV V	5 3 1	7 7 1 1	7 7 1 1	Py FeO	
41' TO 46'	5'	Massive, l to m gray TUFFACEOUS SILSTONE; highly fractured; low angle factures dominant; few sulfides at 41'; sulfides generally abundant from 42' to 46'; at 42' to 42.5', a layer of TUFF with clasts of qtz and feld laths (1-3 mm) with large (1 mm) cubic pyrite; from 43' to 46', only low angle fractures.	TRANS	H SH M SV V		22 1 2	22 1 2	Py FeO	
46' TO 51'	5'	Massive l to m gray TUFFACEOUS SILSTSONE; highly fractured; low angle factures dominant; several annealed low angle veins with sulfide fillings; at 46'2" to 47'2", siltstone lacks sulfides; at 47'2" to 50', highly fractured; a sv facture shows yellowish brown oxidation surface; crustiform pyrite and chlorite on low angle fractures.	TRANS	H SH M SV V		15 4 2	15 4 2	Py FeO Chl Kao?	

BEDROCK LOG SHEET PAGE 2 OF 6

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE
BORING ID: CH-1	CORE DIAMETER:
LOGGED BY: ABRAHAM	LATITUDE:
BEGIN DATE: 07-10-2008	LONGITUDE:
END DATE:	LAND SURFACE ELEVATION:

		LITHOLOGIC		FRATURE INFO				
INTERVAL	RECOVERY	DESCRIPTION	G/WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS
51' TO 56'	5'	L to m gray, massive TUFFACEOUS MUDSTONE; fractures are mainly low angle; 0.5' thick layers of TUFF at 52' and 53' contain crustiform and disseminated pyrites; few, large dollar-shaped pyrite at 55'.	TRANS	H SH M SV V		5 14 1	5 14 1	Py FeO
56' TO 59.5'	3'6"	L to m gray, massive TUFFACEOUS MUDSTONE; rock is harder than above interval; at 56'3", a 2" layer of dark gray, mafic volcanic TUFF with crustiform pyrite; at 56'5", massive MUDSTONE that lack sulfides with fractures are mainly low angle; alteration of qtz and feld at 57'5"; at 58" abundant cubic (unaltered) pyrite crystals over a matrix of sulfide minerals; low angle fractures are dominant, but one high angle annealed fracture is present at 58'5".	TRANS	H SH M SV V — 1		2 8	2 8	Qtz Feld Py FeO
59.5' TO 61.5'	0'	No recovery; lost water circulation; cemented bore hole from 54'1" to 59'6"; resumed coring without recovery.	TRANS	H SH M SV V				
61.5' TO 66'	4'4"	At 61.5', coarse TUFF with mm-scale qtz and feld laths; at 61' 8", medium gray with greenish tinge , TUFFACEOUS MUDSTONE with crustiform pyrite; at 62'10" and 63'3" are two 0.5" thick layers of CLAY without any structure; mechanically broken near the clay layers; at 64'2" and 64'10", crustiform pyrite and disseminated sulfides.	BEDROCK	H SH M SV V — 1 4		4 2	4 2	Qtz Feld Py Cpy? FeO
66' TO 68'	2'	At 66', d gray TUFFACEOUS MUDSTONE with two large crusts of pyrites; a layer of d gray, mafic TUFF that lacks sulfides at 66'5"; at 68", disseminated pyrite fills vesicular TUFF; two high angle annealed fractures.	BEDROCK	H SH M SV V — 2		1	1	Py

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BEDROCK LOG SHEET		PAGE 3 OF 6

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE	
BORING ID: CH-1	CORE DIAMETER:	
LOGGED BY: ABRAHAM	LATITUDE:	
BEGIN DATE: 07-10-2008	LONGITUDE:	
END DATE:	LAND SURFACE ELEVATION:	

INTERVAL	RECOVERY	LITHOLOGIC DESCRIPTION	G/WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS
68' TO 73'	5'	Laminated TUFFACEOUS MUDSTONE with several layers of TUFF; open fractures are mainly low angle; several low and high angle annealed fractures; well developed pyrite crystals at 71'4" along sh fractures.	BEDROCK	H SH M SV V	9 4	6 1 1	6 1 1	Py Glauco
73' TO 78'	5'	L to d gray, laminated TUFFACEOUS MUDSTONE with layers of felsic TUFF; a layer of coarse volcanics at 77'2"; well developed pyrite crystals are present on top of and at the edge surrounding crustiform pyrite; crystals especially evident on the at the intersection of low angle fractures; a long vertical annealed fracture across which there is evidence of a slight displacement of rocks.	BEDROCK	H SH M SV V 1		11	11	Py Limo Glauco
78' TO 83'	5'	L to m gray TUFFACEOUS MUDSTONE with several layers of felsic TUFF; at 80' is a CLAY layer similar to that at 63'; a vertical fracture at 82' is lined with abundant sulfides (py & cpy) and carbonates (cerussite, barite?).	BEDROCK	H SH M SV V	2	4 2 1	4 2 1	Py Cpy Cerru Barite
83' TO 88'	5'	From 83' to 84', L to m gray, laminated, TUFFACEOUS MUDSTONE; at 83.5', a h fracture marked by crustiform and disseminated pyrite; from 84' to 85'10'' is TUFFACEOUS MUDSTONE that lacks laminations and fractures, and few isolated pyrite blebs; becomes laminated at 86; crustiform / dollar-shaped pyrite near 88' along a sh fracture.	BEDROCK	H SH M SV V 1	2	1 2	1 2	Py
88' TO 93'	5'	L to m gray, laminated TUFFACEOUS MUDSTONE with layers of TUFF; at 88.5', a sh fracture is filled by a distinct unit of quartz (chalcedony) and pyrite; this 1 cm thick unit appears as several thin layers; below a layer of tuff at 92', crustifoirm pyrite along a vertical open fracture; rock may be mechanical broken near tuff layers; evidence of rock displacement across vertical annealed fracture.	BEDROCK	H SH M SV V 2	4	2 1	2 1	Py Qtz Feld Barite Clay

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BEDROCK LOG SHEET   PAGE 4 OF 6

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE
BORING ID: CH-1	CORE DIAMETER:
LOGGED BY: ABRAHAM	LATITUDE:
BEGIN DATE: 07-10-2008	LONGITUDE:
END DATE:	LAND SURFACE ELEVATION:

		LITHOLOGIC		FRATURE INFO				
INTERVAL	RECOVERY	DESCRIPTION	G/WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS
93' TO 98'	5'	M to d gray, faintly laminated TUFFACEOUS MUDSTONE with layers of felsic TUFF; rock broken up into inch-size fragments; few sulfides up to 94'8"; a vertical annealed fracture at 95' show sulfide crusts; in this interval, only two open fractures are present near the bottom.	BEDROCK	H SH M SV V	1 2	2	2	Py
98' TO 102'6"	4'6"	M to d gray, finely laminated TUFFACEOUS MUDSTONE with layers of felsic to mafic TUFF; at 98.5', a thin layer of tuff (parallel to bedding) with pyrite crystals; pyrite fills vesicles along several annealed fractures; lack fractures between 99' to 101'; a medium dip fracture at 101'8", show disseminated pyrite.	BEDROCK	H SH M SV V	12 1	5 1	5 1	Py Kaol
102'6" TO 107'	4'6"	L to m gray, laminated TUFFACEOUS MUDSTONE with layers of felsic TUFF; at 103'8", pyrite crystals line the edges of (older ?) sulfide crusts; at 105', clay and fine tuff, lacking sulfides.	BEDROCK	H SH M SV V	12 1	3 1	3 1	Py Kaol
107' TO 113'	5'	L to m gray, laminated MUDSTONE with interbedded felsic TUFF; vesicles contain sulfides; first appearance of yellowish brown (rust-like) coat along bedding partings; a 1" thick tuff at 108'8"; limonite along sh fractures.	BEDROCK	H 2 SH 3 M SV 1 V	2 4 1 1	2 4 1 1	Py Limo
113' TO 118'	5'	L to m gray, finely laminated MUDSTONE with interbedded felsic TUFF; a layer of fine CLAY at 114'; highly fractured section; FeO along sh to v fractures; sulfides along h fractures; near 118', core is highly broken into small pieces; during coring, recirculation of water was difficult due to the highly fractured interval.	BEDROCK	H SH M SV 1 V	2 12 1 2	2 12 1 2	Py Limo

APPENDIX - I

BEDROCK LOG SHEET PAGE 5 OF 6

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION	DRILLING METHOD: WIRELINE
BORING ID: CH-1	CORE DIAMETER:
LOGGED BY: ABRAHAM	LATITUDE:
BEGIN DATE: 07-10-2008	LONGITUDE:
END DATE:	LAND SURFACE ELEVATION:

		LITHOLOGIC		FRATURE INFO				
INTERVAL	RECOVERY	DESCRIPTION	G/WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS
118' TO 123'	5'	At 118', core is highly broken up due to the highly fractured interval.; l to d gray MUDSTONE with horizontal layers of TUFF; at 188'3", evidence of oxidization and reduction (yellowish brown to blackish brown stains) on most fracture surfraces; at 12'2", pyrite crystals with hematite and limonite (on the outside); low to high angle fractures intersect.	BEDROCK	H / SH / M / SV / V	8+	4 / 4 / 1 / 1	4 / 4 / 1 / 1	Py Limo Hema Clay Qtz
123' TO 128'	4'7"	L to m gray, finely laminated MUDSTONE with layers of felsic TUFF; a 8" thick layer of coarse tuff at 124.5' is interlayered with mudstone; at 123'3", the sv fracture show alteration minerals (clay, Fe/Mn oxides).	BEDROCK	H / SH / M / SV / V	1 / 2	2 / 5 / 1 / 1	2 / 5 / 1 / 1	Py Limo Hema Clay Qtz
128" TO 133'	5'	L to m gray, laminated TUFFACEOUS MUDSTONE with layers of TUFF; mudstone shows ripple marks; FeO along sh fractures; several annealed high angle fractures filled with pyrite; at 129'7", crustiform pyrite & pyrite crystals with FeO; at 131', limonite coating and disseminated pyrite blebs; at 132'2", crustiform pyrite.	BEDROCK	H / SH / M / SV / V	10	3 / 1	3 / 1	Py Limo
133' TO 138'	5'	L to m gray, laminated MUDSTONE with layers of felsic TUFF; at 134.5', pyrite and FeO along vertical fracture; at 135'7", alteration minerals (clay, calcite, gypsum?)	BEDROCK	H / SH / M / SV / V	1	6 / 1 / 1	6 / 1 / 1	Py FeO Clay Calcite Gyps ?
138' TO 143'	5'	L to m gray, finely laminated MUDSTONE with interbedded felsic to mafic TUFF; crustiform pyrite on low angle fractures; calcite precipitate along fractures;	BEDROCK	H / SH / M / SV / V	1 / 1	8 / 2 / 1	8 / 2 / 1	Py Qtz FeO Calcite

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| BEDROCK LOG SHEET | | | PAGE 6 OF 6 | | | |

PROJECT: MORGAN MILL GW MONITOR & RESEARCH STATION   **DRILLING METHOD:** WIRELINE

BORING ID: CH-1   **CORE DIAMETER:**

LOGGED BY: ABRAHAM   **LATITUDE:**

BEGIN DATE: 07-10-2008   **LONGITUDE:**

END DATE: 09-09-2008   **LAND SURFACE ELEVATION:**

		LITHOLOGIC		FRATURE INFO				
INTERVAL	RECOVERY	DESCRIPTION	G/WATER ZONE	DIP ANGLE	# ANNEALED	# OPEN	H2O BEARING	MINERALS
143' TO 145'	2'	L to m gray, finely laminated MUDSTONE with interbedded TUFF; relatively few fractures	BEDROCK	H SH M SV V		1 1	1 1	Py FeO
145' TO 150'	5'	L gray, finely laminated MUDSTONE; calcite lines fractures – well developed crystals along vertical fractures but as precipitate along low angle fractures; pyrite disseminated.	BEDROCK	H SH M SV V	3	5 1	5 1	Py Calcite FeO Qtz
150" TO 153'5"	3'5"	L to m gray, laminated MUDSTONE; three h fractures at 150', 151'7" and 153'4" and one distinct annealed vertical fracture; at 151'7" and 153'4", calcite crystals, disseminated pyrite and quartz; drill bit broke to pieces during coring at this depth. **END OF CORING.**	BEDROCK	H SH M SV V	1	3	3	Py Calcite FeO Qtz

APPENDIX - II

Appendix II. Chemical characteristics of private water-supply wells sampled near the Morgan Mill Station, Union County, North Carolina.

Well	Date Sampled	Sample ID	Analysis*	Field pH	Field ORP mV	Field DO mg/L	Field SC µS/cm	Ag µg/L	Al µg/L	As µg/L	As(III) µg/L	Ba µg/L	Ca mg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe µg/L	K mg/L	Mg mg/L	Mn µg/L	Na mg/L	Ni µg/L	Pb µg/L	Se µg/L	Zn µg/L	NO3+NO2 mg/L	TOC mg/L	SO4 mg/L	Cl mg/L	Alk mg/L
Se-1	8/6/2008	A08589	Total	7.5	-229	0.85	306	<5.0	51	39	na	13	44	<1.0	<10	2.2	<50	0.30	5.5	<10	15	<10	<10	10	<10	4.4	na	9.9	14	84
Se-2	8/6/2008	A08590	Dis	na	na	na	na	<5.0	<50	38	na	12	44	<1.0	<10	2.4	<50	0.30	5.5	<10	15	<10	<10	10.0	<10	na	na	na	na	na
Mr-1	8/6/2008	A08592	Total	7.3	-225	0.84	374	<5.0	<50	44	na	31	60	<1.0	<10	6.6	<50	0.37	6.9	<10	18	<10	<10	8.3	<10	2.7	na	15	1.8	120
Mr-2	8/6/2008	A08594	Dis	na	na	na	na	<5.0	<50	43	na	31	59	<1.0	<10	6.9	<50	0.39	6.9	<10	18	<10	<10	8.2	<10	na	na	na	na	na
Mr-3	8/6/2008	A08596	Spec	na	na	na	na	<5.0	<50	n/a	9.6	30	59	<1.0	<10	5.2	<50	0.40	6.9	<10	18	<10	<10	7.7	<10	na	na	na	na	na
Lg-1	8/14/2008	A08601	Total	7.2	-226	1.03	301	<5.0	<50	31	na	<10	44	<1.0	<10	12	<50	0.29	5.5	<10	16	<10	<10	<5.0	110	4.4	na	10	24	91
Lg-2	8/14/2008	A08602	Dis	na	na	na	na	<5.0	<50	29	na	<10	43	<1.0	<10	10	<50	0.38	5.5	<10	16	<10	<10	<5.0	110	na	na	na	na	na
He-1	8/14/2008	A08603	Total	7.3	-270	0.17	595	<5.0	<50	77	na	33	82	<1.0	<10	8.4	<50	0.47	11	170	35	<10	<10	5.3	<10	2.2	<2	10	110	140
He-2	8/14/2008	A08605	Dis	na	na	na	na	<5.0	<50	76	na	33	81	<1.0	<10	7.8	<50	0.50	11	160	35	<10	<10	<5.0	<10	na	na	na	na	na
Wk-1	8/14/2008	A08606	Total	6.8	-246	0.39	564	<5.0	<50	34	na	29	100	<1.0	<10	2.1	<50	0.39	9.2	<10	20	<10	<10	7.6	<10	1.8	<2	11	58	180
Wk-2	8/14/2008	A08609	Dis	na	na	na	na	<5.0	<50	35	na	31	100	<1.0	<10	2.2	<50	0.42	9.5	<10	21	<10	<10	7.1	<10	na	na	na	na	na
Wk-3	8/14/2008	A08610	Spec	na	na	na	na	<5.0	590	n/a	7.4	28	96	<1.0	<10	<2.0	<50	0.44	9.2	<10	21	<10	<10	7.8	13	na	na	na	na	na
Wk-4	8/14/2008	A08611	P-T	na	na	na	na	<5.0	<50	<5.0	na	<10	0.13	<1.0	<10	16	<50	0.26	<0.10	<10	150	<10	<10	5.8	22	na	na	na	na	na
Cn-1	8/12/2008	A08698	Total	7.3	-207	0.44	467	<5.0	<50	20	na	<10	66	<1.0	<10	<2.0	<50	0.45	9.4	<10	21	<10	<10	22.0	<10	4.4	na	13	48	140
Cn-2	8/12/2008	A08700	Dis	na	na	na	na	<5.0	<50	18	na	<10	70	<1.0	<10	2.9	<50	0.38	9.9	<10	23	<10	<10	26.0	<10	na	na	na	na	na
Wm-1	8/12/2008	A08698	Total	6.7	-149	2.55	298	<5.0	<50	7.2	na	<10	40	<1.0	<10	9.5	<50	0.69	7.8	<10	17	<10	<10	<5.0	<10	7.2	na	10	27	77
Wm-2	8/12/2008	A08703	Dis	na	na	na	na	<5.0	<50	7.3	na	<10	39	<1.0	<10	15	<50	0.64	7.7	<10	16	<10	<10	<5.0	18	na	na	na	na	na
R-1	8/12/2008	A08704	Total	7.4	-146	2.32	290	<5.0	63	15	na	<10	40	<1.0	<10	<2.0	<50	0.32	6.3	<10	14	<10	<10	<5.0	<10	4.8	na	20	22	85
R-2	8/12/2008	A08706	Dis	na	na	na	na	<5.0	<50	15	na	<10	41	<1.0	<10	<2.0	<50	0.35	6.2	<10	13	<10	<10	<5.0	<10	na	na	na	na	na
Oe-1	8/12/2008	A08707	Total	7.1	-192	0.42	538	<5.0	<50	16	na	<10	78	<1.0	<10	2.9	<50	0.48	12	<10	24	<10	<10	<5.0	13	3	na	10	100	130
Oe-2	8/12/2008	A08711	Dis	na	na	na	na	<5.0	<50	16	na	<10	79	<1.0	<10	2.7	<50	0.45	12	<10	24	<10	<10	<5.0	14	na	na	na	na	na
Sh-1	8/14/2008	A08632	Total	6.6	-201	0.75	214	<5.0	<50	<5.0	na	<10	23	<1.0	<10	17	<50	0.61	7.3	11	11	<10	<10	<5.0	24	1.1	na	23	12	53
Sh-2	8/14/2008	A08637	Dis	na	na	na	na	<5.0	<50	<5.0	na	23	23	<1.0	<10	17	<50	0.59	7.3	11	11	<10	<10	<5.0	25	na	na	na	na	na
Re-1	8/18/2008	A08440	Total	7.6	-233	0.37	598	<5.0	<50	59	na	53	69	<1.0	<10	4.4	<50	0.49	12	100	51	<10	<10	8.1	<10	0.24	<.02	20	73	170
Re-2	8/18/2008	A08446	Dis	na	na	na	na	<5.0	<50	58	na	53	69	<1.0	<10	4.8	<50	0.45	12	100	50	<10	<10	7.9	<10	na	na	na	na	na
Tm-1	8/18/2008	A08441	Total	6.9	-175	1.38	1161	<5.0	<50	32	na	16	150	<1.0	<10	9.1	<50	0.62	28	<10	63	<10	<10	6.1	<10	5.3	<.02	20	270	190
Tm-2	8/18/2008	A08437	Dis	na	na	na	na	<5.0	<50	32	na	17	150	<1.0	<10	7	<50	0.63	28	<10	65	<10	<10	6.6	14	na	na	na	na	na
Bg-1	8/18/2008	A08443	Total	7.1	-209	0.48	615	<5.0	<50	14	na	14	73	<1.0	<10	3.2	<50	0.58	17	<10	38	<10	<10	8.5	<10	3.9	<.02	20	90	150
Bg-2	8/18/2008	A08446	Dis	na	na	na	na	<5.0	<50	14	na	14	74	<1.0	<10	3.8	<50	0.58	17	<10	38	<10	<10	8.8	<10	na	na	na	na	na
Bg-3	8/18/2008	A08440	Spec	na	na	na	na	<5.0	<50	n/a	<5.0	14	74	<1.0	<10	<2.0	<50	0.60	18	<10	38	<10	<10	8.2	<10	na	na	na	na	na
Bg-4	8/18/2008	A08444	P-T	na	na	na	na	<5.0	<50	<5.0	na	<10	4.3	<1.0	<10	<2.0	<50	0.39	1	<10	15	<10	<10	<5.0	12	na	na	na	na	na
Mr-1	8/19/2008	A08453	Total	7.2	-251	0.23	705	<5.0	<50	20	na	10	96	<1.0	<10	<2.0	<50	0.53	14	<10	35	<10	<10	<5.0	<10	5	4.3	20	20	140

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APPENDIX -II

October 2009

Well	Date Sampled	Sample ID	Analysis*	pH	ORP mV	DO mg/L	SC µS/cm	Ag ug/L	Al ug/L	As ug/L	As(III) ug/L	Ba ug/L	Ca mg/L	Cd ug/L	Cr ug/L	Cu ug/L	Fe ug/L	K mg/L	Mg mg/L	Mn ug/L	Na mg/L	Ni ug/L	Pb ug/L	Se ug/L	Zn ug/L	NO3+NO2 mg/L	TOC mg/L	SO4 mg/L	Cl mg/L	Alk mg/L
Mc-2	8/19/2008	AB0407	Diss	na	na	na	na	<5.0	<50	20	na	10	97	<1.0	<10	2.6	<50	0.52	14	<10	35	<10	<10	<5.0	<10	na	na	na	na	na
Dk-1	8/19/2008	AB0408	Total	7.1	-253	0.17	1069	<5.0	<50	15	na	100	160	<1.0	<10	3.3	<50	0.83	22	240	54	11	<10	<5.0	<10	4	<.02	26	41	210
Dk-2	8/19/2008	AB0410	Diss	na	na	na	na	<5.0	<50	15	na	100	160	<1.0	<10	5.6	<50	0.92	22	230	53	11	<10	<5.0	13	na	na	na	na	na
Kr-1	8/20/2008	AB0480	Total	6.9	-291	0.25	1206	<5.0	<50	<5.0	na	77	180	<1.0	<10	<2.0	2200	0.65	35	780	66	<10	<10	<5.0	<10	<.02	na	150	180	190
Kr-2	8/20/2008	AB0483	Diss	na	na	na	na	<5.0	<50	<5.0	na	93	160	<1.0	<10	<2.0	1600	0.77	34	590	63	<10	<10	<5.0	<10	na	na	na	na	na
Ge-1	8/20/2008	AB0452	Total	6.7	-265	0.25	461	<5.0	<50	6.7	na	14	59	<1.0	<10	<2.0	4500	0.60	15	840	39	<10	<10	<5.0	<10	<.02	na	70	38	95
Ge-2	8/20/2008	AB0456	Diss	na	na	na	na	<5.0	<50	6.3	na	17	67	<1.0	<10	<2.0	4800	0.64	17	910	47	<10	<10	<5.0	<10	na	na	na	na	na
Ge-3	8/20/2008	AB0458	Spec	na	na	na	na	<5.0	620	6.5	na	14	59	<1.0	<10	<2.0	4500	0.62	15	850	39	<10	<10	<5.0	<10	na	na	na	na	na
Hi-1	8/19/2008	AB0454	Total	6.9	-278	0.16	269	<5.0	<50	<5.0	na	<10	39	<1.0	<10	<2.0	1500	0.42	5.9	480	15	<10	<10	<5.0	<10	0.04	0.05	20	120	77
Hi-2	8/19/2008	AB0455	Diss	na	na	na	na	<5.0	<50	<5.0	na	<10	40	<1.0	<10	<2.0	1400	0.41	6	490	15	<10	<10	<5.0	<10	na	na	na	na	na
De-1	8/19/2008	AB0461	Total	7.3	-279	0.27	460	<5.0	<50	<5.0	na	63	74	<1.0	<10	2.4	470	0.47	7.6	370	22	<10	<10	<5.0	<10	0.02	na	46	32	120
De-2	8/19/2008	AB0453	Diss	na	na	na	na	<5.0	<50	<5.0	na	62	73	<1.0	<10	6.8	<50	0.45	7.5	360	22	<10	<10	<5.0	<10	na	na	na	na	na
Jn-1	8/19/2008	AB0455	Total	7.1	-277	0.18	375	<5.0	<50	<5.0	na	<10	<10	<1.0	<10	3.7	57	<0.10	<0.10	<10	91	<10	<10	<5.0	<10	<.02	0.05	95	150	79
Jn-2	8/19/2008	AB0456	Diss	na	na	na	na	<5.0	<50	<5.0	na	<10	0.17	<1.0	<10	<2.0	<50	<0.10	<0.10	<10	93	<10	<10	<5.0	39	na	na	na	na	na
Hh-1	8/21/2008	AB0464	Total	6.8	-240	0.4	821	<5.0	<50	<5.0	na	49	100	<1.0	<10	<2.0	1700	0.88	13	740	61	<10	<10	<5.0	13	0.08	na	94	120	140
Hh-2	8/21/2008	AB0467	Diss	na	na	na	na	<5.0	<50	<5.0	na	48	100	<1.0	<10	<2.0	510	0.90	13	700	62	<10	<10	<5.0	<10	na	na	na	na	na
Le-1	8/21/2008	AB0470	Total	6.9	-238	0.41	325	<5.0	<50	<5.0	na	<10	49	<1.0	<10	2.1	<50	0.58	4.6	610	17	<10	<10	<5.0	<10	0.72	na	26	20	98
Le-2	8/21/2008	AB0456	Diss	na	na	na	na	<5.0	<50	<5.0	na	<10	50	<1.0	<10	2.4	<50	0.60	4.6	610	17	<10	<10	<5.0	29	na	na	na	na	na
Sn-1	8/21/2008	AB0452	Total	6.1	-141	2.43	185	<5.0	<50	<5.0	na	<10	16	<1.0	<10	3.1	<50	0.65	5.7	200	14	<10	<10	<5.0	11	0.82	na	19	18	33
Sn-2	8/21/2008	AB0456	Diss	na	na	na	na	<5.0	<50	<5.0	na	<10	16	<1.0	<10	3.5	91	0.64	5.7	230	13	<10	<10	<5.0	16	na	na	na	na	na

* Dissolved samples represent samples filtered through a 0.45 micron filter.

* Speciated samples represent samples filtered through a 0.45 micron filter and an As speciation filter to determine As(III) concentration.

* Post-Treatment samples represent samples collected following a treatment system at the residence.