

ARSENIC OCCURRENCE, SOURCES, MOBILIZATION, TRANSPORT AND
PREDICTION IN THE MAJOR BEDROCK AQUIFERS OF THE NEWARK
BASIN

by

MICHAEL EDWARD SERFES

A Dissertation submitted to the Graduate School-New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

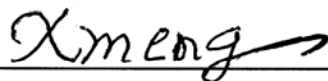
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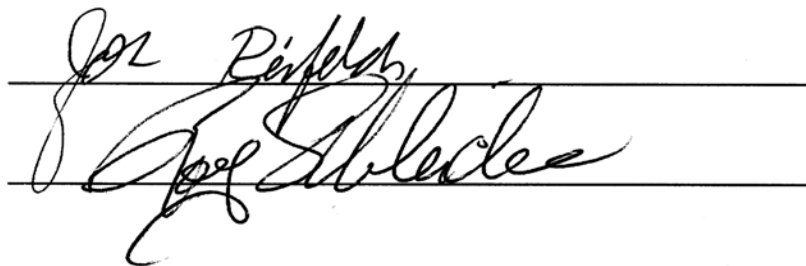
Written under the direction of

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and approved by







New Brunswick, New Jersey

October, 2005

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ABSTRACT OF THE DISSERTATION

Arsenic Occurrence, Sources, Mobilization, Transport and Prediction in the
Major Bedrock Aquifers of the Newark Basin

By MICHAEL EDWARD SERFES

Dissertation Director:
Dr. Ying Fan Reinfelder

Ground water in bedrock aquifers of the Newark Basin in New Jersey contain up to 215 $\mu\text{g/L}$ As. This basin is a Mesozoic aged half graben filled with non-marine strata and intrusive and extrusive basaltic rocks. Arsenic $> 10 \mu\text{g/L}$ in ground water mainly occur in deep lacustrine organic rich black and gray shale of the Lockatong Formation and shallow lake/playa derived red mudstone and siltstone of the younger Passaic Formation. Analyses of black shale, gray shale, and red mudstone show maximum As concentrations of 240, 50 and 14.8 mg/Kg respectively (crustal average, 1.8 mg/Kg). Electron microanalyses of pyrite in black shale confirmed that it is the major mineral source of As containing up to 4 weight percent. The oxidation of pyrite may mobilize As into ground water. The sum of REE in 16 red mudstones and siltstones (4.5 to 14.8 mg/Kg As) from the middle and upper Passaic Formation strongly correlate with As ($r = 0.95$) and moderately with Ti ($r = 0.79$) suggesting a clay association for the REE and therefore As. The congruent mobilization of As and REE from red mudstone leached using hot oxalic acid indicates that hematite is also a source of these elements. Abiotic leach experiments targeting the water-soluble fraction in red mudstone (14.8 mg/Kg As) show that As concentrations directly correlate with pulverized rock surface area, duration of water-rock contact and As

concentrations in the source rock. Also, competitive adsorption with phosphate and a pH of 8.0 maximize As concentrations in solution indicating that desorption and not dissolution is the main mobilization mechanism. Therefore, the desorption of As from clay minerals coated with early hematite is the dominant mechanism for As mobilization during water-rock contact in the red strata. Dissolution type water-bearing zones found in some red strata can supply much lithogenic As to wells intersecting them because they buffer and control aqueous pH as carbonate minerals dissolve, provide maximum surface exposure to matrix clays, and have high hydraulic conductivity and yields. The spatial distribution of arsenic concentrations in wells can be associated with identifiable geologic strata and extrapolated along strike to other areas.

PREFACE

This dissertation improves our understanding about the hydrogeochemistry of arsenic in ground water in the Newark Basin. Work on this subject started at my job with the New Jersey Geological Survey (NJGS) where I am employed as a full time research scientist/hydrogeologist. This research is directly related to water quality findings from the cooperative New Jersey Department of Environmental Protection (NJDEP) and United States Geological Survey (USGS) Ambient Ground Water Quality Monitoring Network (AGWQMN) that I manage at NJGS. From 1989 to 1998, I selected existing public, private and other wells throughout the state of New Jersey to accomplish the then main network goal of characterizing natural ground-water quality as a function of geology. In 1998 I used data from the AGWQMN and several other published reports to assess arsenic concentrations in the major aquifers in New Jersey. This preliminary assessment was conducted because nothing like it had been done before and there was growing global and national awareness and concern about adverse health impacts to people consuming arsenic contained in their well water supply. This growing concern mainly stemmed from large numbers of people in the country of Bangladesh showing observable adverse health impacts, such as dark skin discolorations called hyperkeratosis, directly related to arsenic toxicity from consuming well water containing hundreds of $\mu\text{g/L}$ As. It became immediately apparent during the 1998 assessment that ground-water in the Piedmont Physiographic province, that is mostly comprised of the Newark Basin, had higher arsenic concentrations than aquifers in other Physiographic Provinces in New Jersey. The maximum arsenic concentration observed in the basin from that data set was $19 \mu\text{g/L}$. That concentration was well below the existing Federal and State primary

drinking standard of arsenic of 50 $\mu\text{g/L}$ and although the generally higher concentrations in the basin were of scientific interest, state time and money could not then be justified to investigate the causes. However, in early 1999, a water sample collected from a residential well for the AGWQMN in the Passaic Formation in the Newark Basin had an As concentration of 57 $\mu\text{g/L}$. Interestingly, this well belongs to a co-worker who volunteered to have his well sampled. That co-worker is now managing a project to evaluate treatment technologies to lower the concentration of arsenic in residential well water and is pursuing a Ph.D. at Rutgers University investigating arsenic exposure related to well water use in the basin. At approximately the same time the well with 57 $\mu\text{g/L}$ was discovered, the United States Environmental Protection Agency (USEPA) was considering reducing the arsenic standard from 50 $\mu\text{g/L}$ to 20, 10, 5 or 3 $\mu\text{g/L}$. The combination of finding a well with 57 $\mu\text{g/L}$ arsenic in the basin and the national effort to lower the drinking water standard for arsenic allowed me to obtain NJDEP funding and manage the effort to investigate the occurrence, sources, mobilization and transport of arsenic in the major aquifers of the Newark Basin. A team of hydrogeologists, geologists and other staff from NJGS was assembled for this project. Much of the initial work conducted, and findings from that work, are described in chapter 1 of this dissertation. The cutting edge nature of this interesting and important hydrogeochemical research compelled me to pursue a Ph.D. in Geology under Dr. Ying Reinfelder in the Department of Geological Sciences at Rutgers University that focused on this work.

ACKNOWLEDGEMENTS

Many people and groups deserve recognition for their direct and indirect contributions to this project starting with all those citizen volunteers who allowed NJGS to collect samples of their well water for the initial intensive assessment described in Chapter 1 of this dissertation. People I would like to thank on a more personal level include: Dr. Ying Fan Reinfelder, Ph.D. advisor and Professor in the Department of Geological Sciences for her unwavering interest and financial support for this project. Dr. Karl Muessig, State Geologist of New Jersey in the New Jersey Geological Survey (NJGS), for recognizing the importance of this research and allowing survey resources to pursue it. Steven Spayd, NJGS, for analyzing many of the leachate samples using ICP-MS, and his perpetual and contagious enthusiasm for this project, and Dr. Gregory Herman, NJGS for sharing his knowledge of Newark Basin geology. Others people whose actions I am thankful for include my committee members Dr. John Reinfelder from the Department of Environmental Sciences at Rutgers for technical advice and NSF tuition support, Dr. Roy Schlische from the Department of Geological Sciences at Rutgers University for his thorough technical review of the geological aspects of this dissertation and Dr. Meng from Steven's Institute of Technology for his assistance leading the completion of this dissertation. Funding for supplies and analyses vital for completing this portion of the project came from CBT (Corporate Business Tax) and Indicator fund monies from the NJDEP Watershed Program and the Division of Science, Research and Technology (DSR&T) respectively. The tuition aid program at NJDEP supported my completion of this work by paying for a portion of my classes at Rutgers.

Others I would like to mention and thank for their various contributions include: John Curran and Greg Steidal from NJGS for their drilling support, John Dooley and Don Monteverde from NJGS for X-ray analysis and geologic mapping support respectively, Raymond Bousenberry from NJGS for his assistance during the Hopewell study and leach study, Samantha Magee a student intern and silver medal winner at the 2004 summer Olympics in crew for her help with the leach study while she trained in Princeton in 2003, Dr. Judy Lewis and Dr. Eileen Murphy from the NJDEP/DSR&T for their interest and initial project grant support, Dr. Jeremy Delaney from Rutgers University for microprobe support, and Zolton Szabo for stimulating discussion and some core samples and Dr. John Garbarino and Dr. Eric Vowinkle from USGS for arsenic speciation assessment support.

Last, but definitely not least, I would like to thank my wife Anne, daughter Audrey and son George for their constant support, enthusiasm and patience through the completion of this Dissertation. Without their strong and stable presence, it would not have been possible to finish this personally monumental tome. I am forever grateful to them for that gift.

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Introduction

The Newark basin is a half graben filled with continental strata and igneous rock located in Pennsylvania, New Jersey and New York (figure 1.1 and 1.2). Serfes and others (2005) measured arsenic concentrations of up to 215 $\mu\text{g/L}$ in ground water in the Newark basin in New Jersey. On February 22, 2002 the United States Environmental Protection Agency (USEPA) lowered the arsenic drinking water standard for public water supplies from 50 micrograms per liter ($\mu\text{g/L}$) to 10 $\mu\text{g/L}$ with a compliance date of January 2006 (USEPA, 2002). Estimated risks of lung or bladder cancers in individuals with lifetime exposure to drinking water with more than 10 $\mu\text{g/L}$ arsenic exceed 1 to 2 in 1000 (NAS, 1999). Human exposure to inorganic As in drinking water has been linked to internal and external cancers and non-cancer related health impacts (IARC, 1987; NRC, 2001). Arsenic in ground-water supplies is both an international and national issue with countries on all continents being affected (Smedley and Kinniburgh, 2002). The State of New Jersey is implementing a stricter arsenic standard of 5 $\mu\text{g/L}$ that will also become effective in January 2006.

Testing well water for the presence of arsenic, and the subsequent treatment of water containing unacceptable concentrations of it, are effective tools for reducing human exposure to this toxic element. However, in areas where well water testing has not been conducted, either inadvertently or in undeveloped lands, some predictive evaluation of arsenic concentrations in ground water is desirable. In theory, the prediction of aquifer vulnerability to lithogenic arsenic contamination in the Newark basin is possible if the

variables controlling its occurrence in ground water are well defined. These variables include: (a) types of major arsenic sources, (b) arsenic concentrations in and the spatial distribution of those sources, (c) active mechanisms affecting arsenic mobilization from those sources, (d) hydrogeochemical settings in which those mechanisms are triggered, and (e) mass transport and chemical mass transfer processes that control the arsenic concentration down gradient from the major sources. This dissertation addresses these variables in four chapters that focus on the following four key questions:

1. What are the spatial distribution, concentration and hydrologic and aqueous geochemical settings associated with arsenic concentrations greater than 10 $\mu\text{g/L}$ in the major bedrock aquifers of the Newark basin?
2. What are the major lithogenic sources of arsenic in those aquifers?
3. What chemical mechanisms and hydrogeologic settings favor the mobilization of arsenic from those sources?
4. What physical and chemical processes control the mass transport of arsenic in these aquifers? Can arsenic concentrations in ground water be predicted?

Most of the focus of this dissertation is in the New Jersey portion of the Newark basin. However, the formations that occur in the basin in New Jersey also occur in Pennsylvania and New York (figure 1.2). Therefore, the findings presented here should be somewhat applicable in similar geologic settings throughout the basin and other Mesozoic rift basins in eastern North America.

Chapter 1. Arsenic Occurrence in the Bedrock Aquifers of the Newark Basin:

Hydrologic and Aqueous Geochemical Setting

Introduction

The occurrence of elevated arsenic concentrations in major aquifers within the Newark basin and the potential health risks associated with consuming water containing undesirable concentrations of it, prompted me to determine the occurrence, sources, mobilization, and fate of arsenic. This chapter presents information on the spatial distribution, concentration and hydrologic and aqueous geochemical settings associated with arsenic occurrence in the major bedrock aquifers of the Newark basin.

Arsenic Sources

To effectively assess the occurrence of arsenic in the major aquifers in the basin, a preliminary identification of the potential sources is needed. I conducted the first evaluation of arsenic concentrations and spatial distribution in the basin in 1998 using data from New Jersey's Ambient Ground Water Quality Network (Serfes, 1994). The widespread nature of detectable arsenic concentrations found in the basin suggested that it was derived from dispersed non-point rather than isolated point sources of contamination. Two obvious potential non-point sources of arsenic are arsenical pesticides in agricultural areas and naturally occurring minerals containing arsenic.

Arsenical pesticides were widely used in this country, including New Jersey, from the late 1800s until the mid- to late 1900s (Murphy and Aucott, 1998). The greatest use in New Jersey was in fruit orchards (NJDEP, 1999). However, arsenical pesticides are not very water-soluble, and the arsenate binds tightly to soil particles. Studies in North Dakota, South Dakota, Wisconsin and Minnesota conclude that ground water is largely unaffected by past arsenical pesticide use (Welch and others, 2000). Therefore, arsenic from arsenical pesticide use in agricultural areas is generally not very mobile in the soils that contain it and therefore is not considered a major source of arsenic to ground water. The application of phosphate fertilizers can, however, release slugs of arsenic from those soils via competitive adsorption resulting in seasonal spikes in arsenic concentrations (Welch and others, 2000). Arsenic concentration data from wells in the basin do not support that possibility, however, as temporal analytical results from the same wells are similar and therefore steady state. Studies have demonstrated that sulfide mineral oxidation and iron oxide reduction are the most important mechanisms for mobilizing arsenic in groundwater (Welch and others, 2000). Therefore, the working hypothesis is that the arsenic in ground water in the basin is derived from natural mineral sources, not arsenic-bearing pesticides.

Arsenic Aqueous Chemistry

The occurrence, concentration and species of arsenic present in ground water are related to the locations, type and significance of the sources present and the hydrogeochemical environments in which they occur. In natural aqueous environments,

which include low temperature surface, ground water and hydrothermal waters, arsenic generally forms dissolved inorganic oxyanions (polyatomic ions that contain oxygen) of arsenite As (III), $[\text{H}_3\text{AsO}_3^0]$ below pH 9.2], and arsenate As (V), $[\text{H}_2\text{AsO}_4^-]$ at pH < 6.9 and HAsO_4^{2-} at higher pH values] (Smedley and Kinniburgh, 2002). Both species commonly occur together because the abiotic transformation from one to the other is kinetically hindered (Masscheleyn and others, 1991). However, manganese oxides, which commonly coat hydraulic conduits in the basin, are known to rapidly oxidize As(III) to As(V) (Driehaus and others, 1995; Scott and Morgan, 1995). Although not significant in most waters, organically bound arsenic such as the methylated species monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) may be produced via microbial detoxification where arsenic and organic matter occur together (Oremland and Stolz, 2003). Arsenic is particularly mobile within the pH range 6.5 to 8.5 that is commonly present in ground water and some surface waters. It can be mobile under both reducing and oxidizing conditions; however, the neutral complex arsenite is generally more mobile than the arsenate anion. The lithogenic fate of arsenic is tied to that of Fe, S and clay minerals (Stollenwerk, 2003). Therefore, iron oxides, sulfide minerals such as pyrite, and clay mineral surfaces are all potential sinks and sources of arsenic. The pH, Eh and possibly microbiological activity govern the thermodynamic stability of the species of arsenic, iron and sulfur present. Therefore, the stability of arsenic-bearing phases, and also the charge on many absorbent surfaces such as iron oxides and clays where arsenic may be adsorbed or desorbed is controlled by those variables (Welch and others, 2000).

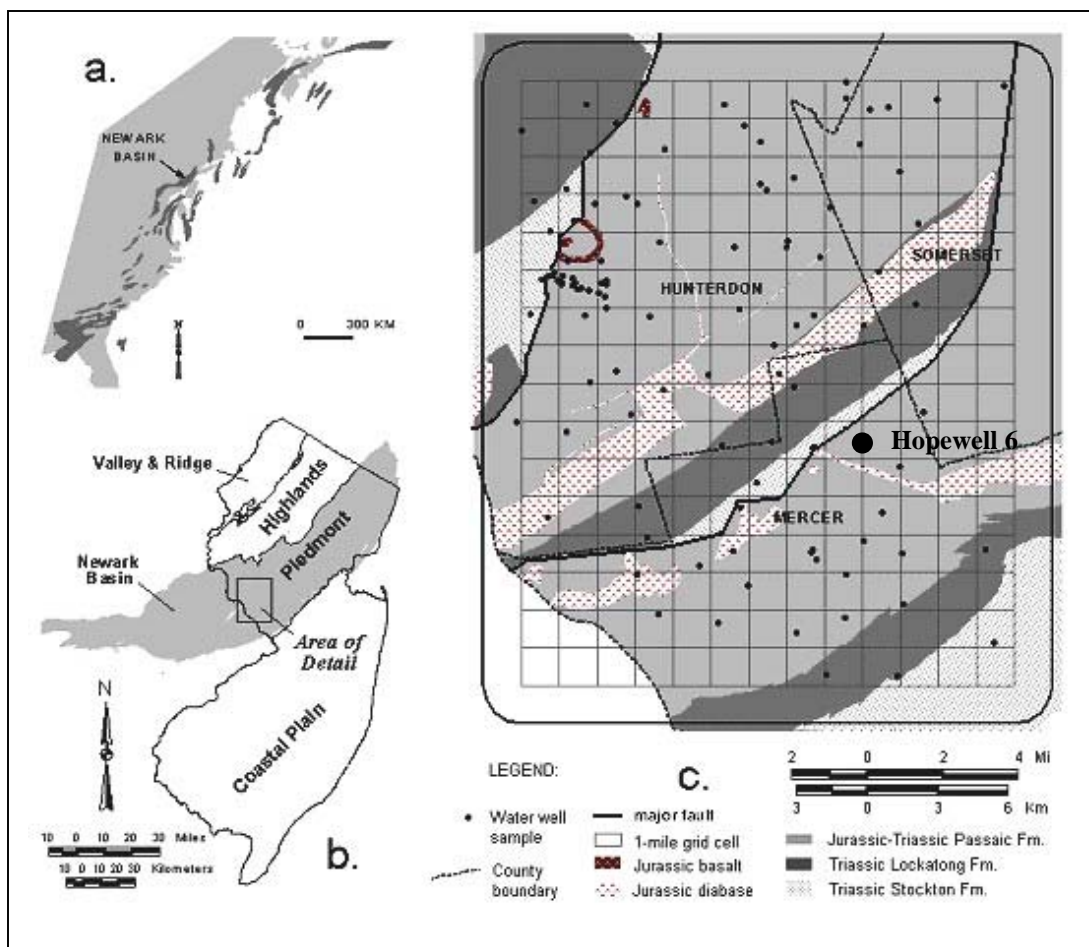


Figure 1.1 Rift basins of eastern North America and the Newark basin (modified from Schlische and others, 2002) (a). (b), Newark basin in relation to New Jersey, (c) The 520 square kilometer study area and location of wells sampled. Fifteen percent of wells sampled had greater than 10 $\mu\text{g/L}$ arsenic. The Passaic and Lockatong formations had highest occurrence and concentrations of arsenic.

The types and significance of arsenic sources and the hydrogeochemical and hydrologic settings that exist in the Newark Basin ultimately control the occurrence of arsenic in aquifers there. These sources and settings are directly related to the original depositional and diagenetic environments that preserved some primary minerals, altered others and to varying degrees controlled the formation of secondary minerals.

Information on the geologic, hydrogeologic, and hydrogeochemical settings in the basin and the analytical methods used here follows below.

Background

Geologic Setting and History

The Newark Supergroup (figure 1.1a) is present within a belt of tectonic fault-bounded extensional basins that formed along eastern North America during the Late Triassic and Early Jurassic periods (Olsen, 1980). These basins are half grabens that reflect the western limit of major brittle deformation associated with continental rifting during the opening of the Atlantic Ocean and are filled with continental strata and igneous rocks. Some of these basins are exposed at the surface and some are buried under coastal-plain and glacial sediments. Still others are located offshore. The Newark basin is the largest of the exposed basins, covering $\sim 7500 \text{ km}^2$, and extending $\sim 190 \text{ km}$ from Pennsylvania through New Jersey and into New York with a maximum width of $\sim 50 \text{ km}$ (figure 1.1b).

Northeast striking and southeast dipping border faults occur along the western edge of the Newark basin. These border faults are reactivated Paleozoic thrust faults that coalesced and underwent normal movement during the initiation of continental extension approximately 230 Ma (Schlische, 1992, and references therein). As the depth, width and length of the half graben increased, reflecting syndepositional fault movement, it filled with up to 6-8 km of fluvial and lacustrine non-marine sediments, derived from the

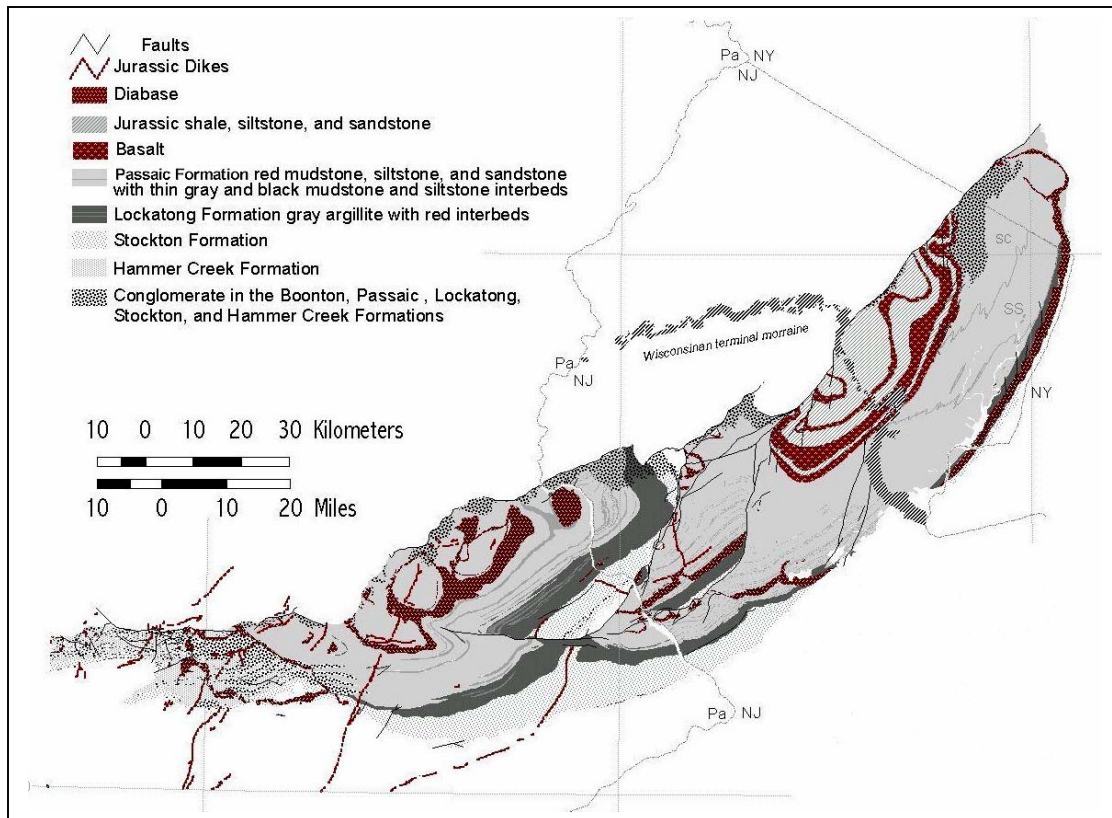


Figure 1.2. Geologic map of the Newark basin. Note large area of the Passaic Fm..

surrounding Precambrian and Paleozoic uplands, as well as mafic igneous flows and intrusions (Schlische and Olsen, 1990).

The stratigraphic and structural features of the basin are important to understand because they influence the conduit types and geometry of present hydrogeological settings. Syn-depositional rotation of the hanging walls of the northeast striking border fault and other normal fault planes resulted in increased sediment thickness adjacent to the faults and a decrease in dip from older to younger strata. The average dip is 10 to 15 degrees northwest in exposed sections. Differential movement along the boarder and major synthetic intrabasin faults produced localized folding with axes orthogonal to the

faults with more varied bedding dips and strike orientations. At approximately 201 +/- 1 Ma a short lived igneous event related to the Central Atlantic Magmatic Province (CAMP), which included the emplacement of diabase sills and dikes and basalt flows, resulted in localized contact metamorphic effects (Sutter, 1988; Olsen and Fedosh, 1988, Schlische and others, 2003). It is uncertain if the CAMP event resulted in a basin-wide versus local hydrothermal events that may have mobilized many elements, including arsenic.

Two steeply dipping and approximately northeast- and northwest- striking dominant fracture sets reflect orthogonal regional and local tectonic extension directions respectively (Schlische, 1992). Unweathered fractures are generally healed with sparry syntectonic secondary crystalline minerals (Parnell and Monson, 1995; Herman, 2001). An approximately 185 to 175 Ma tectonic compression event, attributable to the rift to-drift transition (basin inversion), produced topographic highs that set up a fault guided hydrothermal flow system, with a pre-180 Ma maximum temperature of ~ 250 °C, that circulated in the basin for 10s of millions of years (Steckler, 1993; Malinconico, 2002).

Therefore the geochemical processes associated with varying depositional, diagenetic and hydrothermal environments controlled the early fate of mobile arsenic.

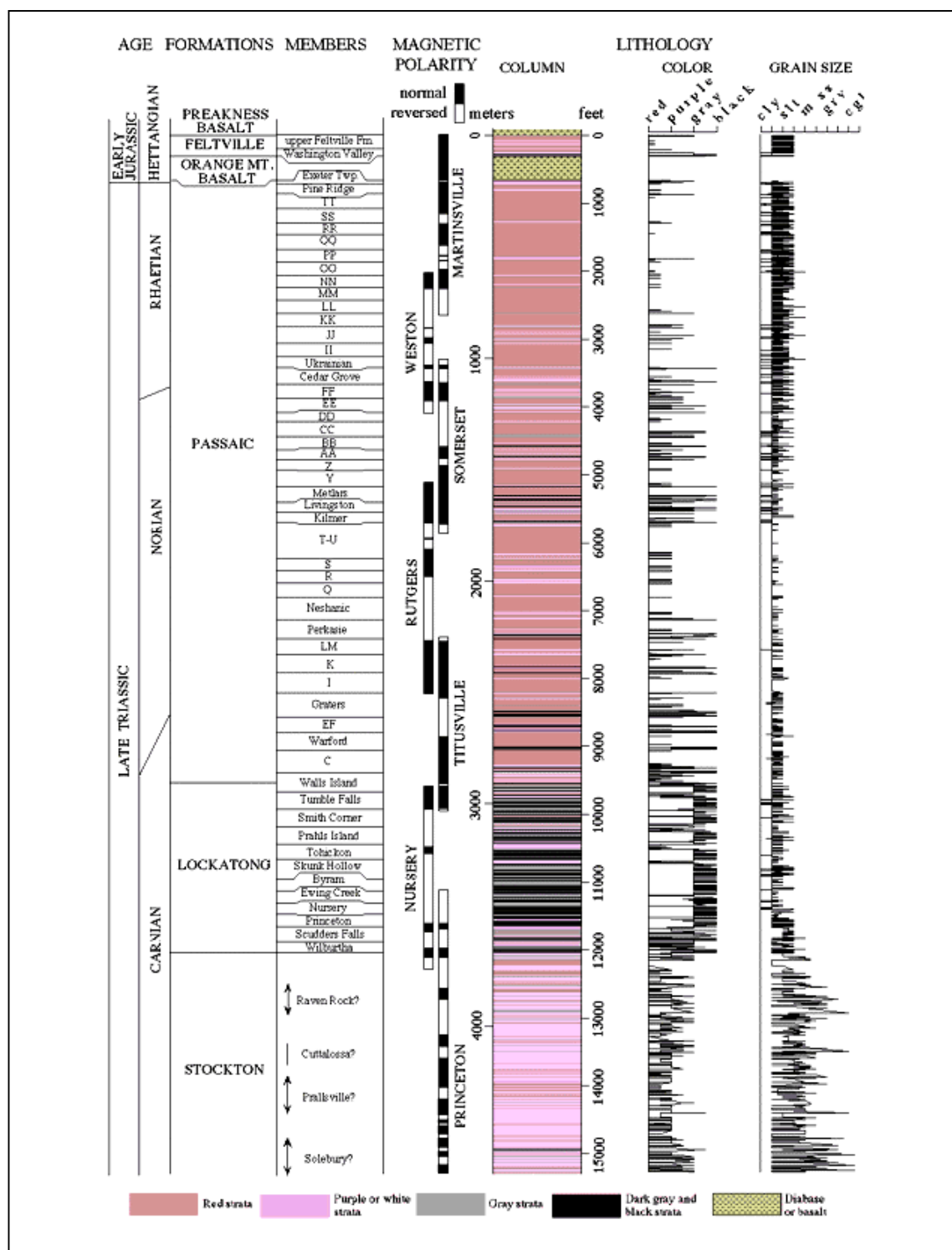


Figure 1.3. Newark basin stratigraphic column showing age, formations, members, magnetic polarity, thickness, rock color and grain size (Olsen and others, 1996).

An estimated upper limit of approximately 6 km of material was subsequently eroded from the uplifted strata, and by ~ 120 Ma the hydrothermal system was effectively shut down (Steckler, 1993; Malinconico, 2002). The surface bedrock pattern of Newark Basin strata has varied little since that time (figure 1.2). A stratigraphic column (fig. 1.3) that was compiled using data from the Newark Basin Coring Project (NBCP) shows geologic formations and members in the basin (Olsen and others, 1996). Of the ~ 7500 km² of basin exposure, 55 percent is comprised of the Passaic (4127 km²), 9 percent the Lockatong (~ 703 km²) and 12 percent the Stockton formations (~ 909 km²).

Depositional Environments

To the same degree that stratigraphy and structure have a major control on present hydrogeologic conduit types and their geometry in the Newark basin, the depositional geochemical environments and subsequent diagenetic processes that affected the stability of primary and secondary mineralogy control the hydrogeochemistry. The reactivity of these minerals during water-rock contact in the basin ground-water systems imparts a characteristic geochemical flavor to the water and in some settings also affects the occurrence of intermittent but significant dissolution type water-bearing zones. Therefore, an understanding of these depositional environments is important.

The Newark basin was hydraulically open for most of the Stockton formation and closed for the remainder of its depositional history and the sediments filling it generally have the same upland provenance (Schlische and Olsen, 1990). Stream sediment and

dissolved loads flowing into the basin were mainly derived from the flanking calc-alkaline Precambrian basement rocks with some contribution from Paleozoic rocks as conglomerates along the northwest border facies (Van Houten, 1965; van de Kamp and Leake, 1996). The Precambrian rocks included sodic-plagioclase rich granitic gneisses and schists with minor mafic varieties. Weathered mafic and sulfide minerals are likely sources of many of the metals and arsenic in the basin and sodium-rich feldspars the sodium that is particularly enriched in the Stockton, Lockatong and Passaic formations (Van Houten, 1965; Tabakh and Schreiber, 1998).

Evolving basin geometry coupled with orbitally forced climatic fluctuations controlled the long- and short-period depositional environments (Olsen and others, 1996). The basin was near the equator and exposed to cyclical wet-dry (monsoonal climate) conditions during deposition of the Lockatong and younger formations (Olsen, 1986). Varying water supply and sediment rates coupled with the dynamic tectonic basin geometry yielded the classic tripartite stratigraphy of basal fluvial (Stockton Formation) followed by deep lacustrine (Lockatong), and shallow lacustrine (Passaic) sedimentary environments (Schlische and Olsen, 1990).

The depositional environments and four major lithic groups occurring in the basin shown in figure 1.2 and table 1.1 are from oldest to youngest:

Table 1.1. Stratigraphy sequence of the Newark basin with information about the major depositional environments, lithology and secondary minerals associated with the Stockton, Lockatong and Passaic Formations.

Era	Period	Stratigraphic unit and major depositional environments	Predominant lithologies and secondary minerals (for Triassic only)
Mesozoic (Active extension, basin fills with 6 to 8 km of non-marine sediments)	Lower Jurassic (201 +/- 1 Ma)	Brunswick Group	
		Boonton Formation	Sandstone, siltstone, shale, conglomerate
		Hook Mountain Basalt	Basalt with intercalated sedimentary rock
		Towaco Formation	Sandstone, siltstone, shale, conglomerate
		Preakness Basalt	Basalt with intercalated sedimentary rock
		Feltonville Formation	Sandstone, siltstone, shale, conglomerate
		Orange Mt. Basalt	basalt
	Upper Triassic (~ 225 to 200 Ma)	Passaic Formation Thickness ~ 4000m Mostly oxic shallow lake and vegetated and dry playa mudflats with intermittent suboxic to anoxic deep lakes	Mostly red mudstone, siltstone, sandstone and conglomerate with lesser gray and black shale Secondary diagenetic and hydrothermal minerals and cements filling fractures, cavities and intergranular voids include: early and late hematite and calcite, early pyrite and late hydrothermal sulfide minerals associated with organic material, albite, k-spar, quartz, ferroan dolomite, and anhydrite/gypsum.
		Similar to upper Lockatong except mostly oxic shallow saline lake and saline mudflat with periodic suboxic to anoxic fresh and saline deep lakes	
		Lockatong Formation Thickness ~ 1150m Mostly suboxic to anoxic fresh and saline deep lake with oxic shallow saline lake and saline mudflats	Mostly gray and black mudstone with lesser red beds. Secondary diagenetic and hydrothermal minerals similar to the Passaic Formation except analcime occurs and not albite.
		Stockton Formation Thickness ~ 1200m? Mostly oxic fluvial and meandering streams and deltaic environments	Arkosic sandstone, siltstone, shale, conglomerate Secondary diagenetic and hydrothermal minerals similar to the Passaic Formation.

1. The Stockton Formation (Triassic), Alluvial and fluvial arkosic sandstone, arkosic conglomerate and red mudstone and siltstone. High-gradient braided streams, meandering streams, intermittent basin flooding, lower energy streams when basin became closed.
2. The Lockatong Formation (Triassic), Black (organic-rich), gray and red cyclical sequences of argillitic mudstone, siltstone and shale. Mainly deep anoxic lake

environments with the preservation of organic-rich detrital sediments. Periodic shallow and playa lake environments.

3. The Passaic Formation (Triassic), Cyclic sequences of red mudstone, siltstone and sandstone with intermittent gray mudstone and black shale. Shallow-water and playa lake (particularly in younger rocks) with intermittent deep anoxic lake environments.
4. The Brunswick Group (early Jurassic), Depositional environment similar to lower Passaic formation. Basalt interlayered with sedimentary rock mudstone, siltstone, sandstone and conglomerate.

The shorter period wet-dry orbital cycles of $\sim 20,000$ (Van Houten), $\sim 100,000$ and $\sim 400,000$ (McLaughlin) years are evident in the rock record of the Lockatong, Passaic and younger formations as cyclic fluctuations in color, sedimentary fabrics, and organic carbon content which are associated with various lake levels (Olsen and others, 1996). Formations, members and strata-specific hydrogeologic and geochemical environments are a reflection of cyclic depositional environments.

Hydrogeology

Ground water in the Newark basin is mainly stored in and transmitted through various interconnected conduits such as joints, faults, bedding-plane partings, solution channels and, too a lesser extent, interstitial pore spaces. Wells completed in the basin are cased through the regolith and shallow bedrock and open to various depths in the deeper bedrock. Water is supplied to the well bore from the water-bearing zones it intersects.

Well yield data from Houghton and Flynn (1988) show that the average yields are: Stockton (20.0 gpm) > Passaic (16.3 gpm) > basalt (11.8 gpm) > Lockatong (9.5 gpm) > diabase (7.4 gpm). These average yields provide indirect information about the hydraulic conductivity associated with these aquifers and potentially the relative residence time of ground water in them, with high conductivity being indicative of younger water. The water-rock contact time can potentially affect the water chemistry. The Passaic, Lockatong and Stockton formations are the three major aquifers in the basin. I next discuss their hydraulic character.

Below the shallow weathered zone, the Passaic, and probably the Lockatong, formations in the Newark basin are generally characterized as anisotropic, leaky, multi-layered aquifer systems (LMAS) with bed-parallel water-bearing zones (WBZs) sandwiched between thicker nonconductive zones (Michalski and Britton, 1997; Herman, 2001). Flow between WBZs occur as leakage via fractures that cross stratigraphic layering or as cross flow in well boreholes. Hydraulic conductivity, and therefore preference for flow, is greatest parallel to bedding strike, somewhat less in the dip direction and least perpendicular to bedding (Morin and others, 1997; Morin and others, 2000). Weathered bedrock near the surface is more hydraulically isotropic, possesses greater storage but is considered less permeable than deeper bedrock because of the clogging of potential conduits with clays (Michalski and Britton, 1997). Hydrogeologic investigations in shallow weathered sedimentary rock with dipping beds at the Oak Ridge National Laboratory facility yielded a comprehensive understanding of contaminant transport in that setting (Soloman and others, 1992; Driese and others, 2001). In the

shallow weathered zone there, near surface stormflow and deeper water-table flow are largely controlled by topography with permeable weathered WBZs acting as conduits between the two. Recharge to the deeper less weathered bedrock aquifer mainly occurs where WBZs intersect the shallow weathered zone. Although uncertainties exist, this conceptual flow model is probably accurate to some degree in the Passaic and Lockatong formations. The more coarse-grained Stockton Formation has the highest well yields of the three aquifers. This is attributed to the presence of more open fractures and intergranular pore spaces and a thicker regolith zone in the arkosic sandstones than in the fine grained rocks making up the Passaic and Lockatong formations (Rima and others, 1962). NJGS and others continue to conduct research to better understand ground-water flow characteristics in the Newark basin.

Interestingly, bedding-confined dissolution zones associated with sparry minerals (calcite, dolomite, gypsum and albite) that fill interconnected root cavities in red mudstones and siltstones of the Passaic Formation can be significant WBZs when these minerals dissolve out (Herman, 2001). This type of WBZ has been observed to carry water with high arsenic concentrations at several locations (Serfes and others, 2005).

Analytical Methods

The water-quality parameters and values in tables 1.2, 1.3 and 1.4 are for the Passaic, Lockatong and Stockton formations respectively and are described in Serfes (1994) along with a reference for the analytical methods used to obtain them. Water

samples collected from private wells for the spatial analysis of arsenic occurrence were analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS) at Environmental Health Laboratories, a New Jersey certified laboratory, in Indiana using EPA Method 200.8 - Determination of Trace Elements by Inductively Coupled Plasma - Mass Spectrometry. Aqueous samples from the Hopewell 6 case study were analyzed for arsenic and other elements at Activation Laboratories in Ancaster, Ontario in Canada using ICP-MS, ICP-OES techniques.

Whole rock geochemical analyses of all rock samples discussed in this chapter and throughout the dissertation were determined at XRAL Laboratories in Don Mills, Ontario Canada using their MER method. This Multi-method multi-element quantitative analysis uses X-ray fluorescence, ICP, Neutron Activation Analysis, ICP-MS and atomic adsorption spectrophotometry to obtain high-quality analyses on up to 64 elements. Standard procedure is to dry, crush to -2mm , riffle to a maximum split of 250g and mill in chrome steel equipment to 75μ . Silica sand cleaners were used between samples to minimize the risk of contamination from mineralized samples. Approximately 20 grams or more of each sample were sent to XRAL which more than exceeds their 5-gram minimum.

Samples were also collected for the analysis of arsenic species at select wells using opaque containers and an ethylenediaminetetraacetic acid (EDTA) preservative to minimize metal oxyhydroxide precipitation as described in Bednar and others, (2002). These samples were analyzed at the U.S. Geological Survey in Denver Colorado using a

liquid chromatograph with an anion exchange column to separate the arsenic species, As(III), dimethylarsinate (DMA), monomethylarsonate (MMA), and As(V), followed by analysis using ICP-MS to quantify species concentrations.

Aqueous Geochemical Setting

Ground-water chemistry is a function of (1) the composition of precipitation, (2) the natural and anthropogenic chemical conditions the precipitation encounters at the land surface and in the unsaturated zone, (3) the degree of water-rock contact and residence time in the aquifer, and (4) most important, the composition and mineralogy of subsurface materials that the ground-water contacts as it flows through the aquifer (Serfes, 1994). The composition and mineralogy of the subsurface materials in the Newark basin is a direct reflection of the original depositional and diagenetic environments described in table 1.1 and in the text above. The lithogenic fate of arsenic in sedimentary environments is generally tied to that of Fe and S and clay minerals. Therefore, iron oxides, sulfide minerals such as pyrite and clay mineral surfaces are all potential sinks and sources for arsenic. The aqueous geochemical environment coupled with the hydrogeologic setting control the mobilization and transport of arsenic from those sources and through the ground-water system. Chemical parameters such pH, oxidation-reduction potential and competing ions affect the stability of minerals and mineral surfaces containing arsenic. The chemical character and presence or absence of certain chemical species in ground water lends clues to the fate of minerals that could

potentially contain arsenic. Therefore, it is important to characterize the hydrogeochemical character of the major aquifers in the Newark basin.

A statistical summary of important ground-water quality characteristics in the Passaic, Lockatong and Stockton formations from Serfes, (1994) are given in tables 1.2, 1.3 and 1.4 respectively. Differences in ground-water chemistry among the three formations are related to the unique rock and mineral composition and hydrogeologic character of each. Based on the median concentrations listed in these tables, some of the more obvious differences are: (1) Waters from the Passaic Formation are highest in Ca, Mg, Cl, Li and SO₄ and specific conductivity. (2) Waters from the Lockatong Formation are highest in K, Na, Si, Fe, Mn and alkalinity and lowest in dissolved oxygen and chloride. (3) Waters from the Stockton Formation are highest in Ba and lowest in pH, specific conductivity and alkalinity.

Table 1.2. Statistical summary of water chemistry in ground water of the Passaic Formation. [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; dissolved, water filtered through a 0.45 micron filter]; min., minimum; max., maximum.

Characteristic or constituent	Number of samples	Min.	25 th percentile	Median	75 th percentile	Max.
Passaic Formation						
Characteristics						
Temperature (C)	94	9.5	12.5	13	13.5	14.5
Specific Conductivity ($\mu\text{S}/\text{cm}$)	94	155	374	450	632	2040
Dissolved Oxygen (mg/L)	94	<0.1	0.7	2.9	5	14.7
PH (standard units)	95	6	7.4	7.6	7.8	9.3
Field Alkalinity (mg/L as CaCO_3)	95	21	112	141	161	338
Major and minor dissolved constituents in mg/L						
Calcium	94	3	40	50	73	365
Magnesium	94	1.4	12	16	21	69
Sodium	94	2.1	12	15	27	270
Potassium	94	0.4	1	1.3	1.9	6.6
Chloride	94	2.8	12	18	32	110
Sulfate	94	1.1	29	44	78	1200
Silica	94	11	19	22	25	45
Trace and minor dissolved constituents in $\mu\text{g}/\text{L}$						
Barium	71	<2	27	80	205	1100
Iron	94	<3	<3	22	60	11000
Lithium	71	<4	18	24	33	100
Manganese	94	<1	<1	2	46	1600
Strontium	71	50	225	530	925	11000
Zinc	94	<3	6	18	50	740

Piper diagrams classify the hydrogeochemical type of ground water found in an aquifer by comparing the percent equivalents of the dominant cations and anions on a trilinear diagram (Back, 1960). Based on these plots, the Stockton, Lockatong and Passaic formations are all mainly calcium-magnesium-sodium-bicarbonate-type waters (Serfes, 1994). However, calcium-sulfate-type waters associated with high specific conductivity in the Passaic Fm. and sodium bicarbonate waters in the Lockatong Fm. also occur. The calcium-sulfate-type waters common in certain stratigraphic intervals in the

Passaic Formation are the direct result of the dissolution of gypsum. The high sodium in the Lockatong Formation is likely due to the dissolution of analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$).

Table 1.3. Statistical summary of water chemistry in ground water of the Lockatong Formation. [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; dissolved, water filtered through a 0.45 micron filter]]; min., minimum; max., maximum.

Characteristic or constituent	Number of samples	Min.	25 th percentile	Median	75 th percentile	Max.
Lockatong Formation						
Characteristics						
Temperature (C)	22	10.5	12.5	13	13.5	17
Specific Conductivity ($\mu\text{S}/\text{cm}$)	22	221	336	447	585	900
Dissolved Oxygen (mg/L)	22	<0.1	0.2	0.5	2.5	7.5
PH (standard units)	22	6.6	7.2	7.6	7.7	8.8
Field Alkalinity (mg/L as CaCO_3)	21	61	93	151	220	321
Major and minor dissolved constituents in mg/L						
Calcium	22	2.50	30	46	55	79
Magnesium	22	1.2	7.8	11	21	37
Sodium	22	7	12	27	35	140
Potassium	22	0.8	1.5	2.7	4.7	6.6
Chloride	22	1.7	6.2	11.5	26	70
Sulfate	22	10	17	41	62	135
Silica	23	13	20	26	34	42
Trace and minor dissolved constituents in $\mu\text{g}/\text{L}$						
Barium	21	10	33	73	153	1200
Iron	22	<3	7	19	260	2900
Lithium	21	6	9	16	25	96
Manganese	22	<2	11	26	260	790
Strontium	20	78	240	460	520	730
Zinc	22	7	12	30	170	1100

Table 1.4. Statistical summary of water chemistry in ground water of the Stockton Formation. [$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; dissolved, water filtered through a 0.45 micron filter]]; min., minimum; max., maximum.

Characteristic or constituent	Number of samples	Min.	25 th percentile	Median	75 th percentile	Max.
Stockton Formation						
Characteristics						
Temperature (C)	29	11.5	12.5	13	13.5	16.5
Specific Conductivity ($\mu\text{S}/\text{cm}$)	29	140	287	346	400	808
Dissolved Oxygen (mg/L)	29	0.1	1.0	2.9	5.1	7.7
PH (standard units)	29	5.5	6.6	7	7.6	8.6
Field Alkalinity (mg/L as CaCO_3)	29	21	85	104	145	177
Major and minor dissolved constituents in mg/L						
Calcium	29	7.8	27	36	43	47
Magnesium	29	0.27	10	13	16	25
Sodium	27	7.8	9.1	13	15	155
Potassium	29	0.8	1	1.3	1.7	302
Chloride	29	3.3	11	13	21	130
Sulfate	29	5.1	18	23	37	94
Silica	29	11	19	23	26	29
Trace and minor dissolved constituents in $\mu\text{g}/\text{L}$						
Barium	25	26	135	160	220	390
Iron	29	<3	<3	6	17	1200
Lithium	25	4	6	8	9	47
Manganese	29	<1	<1	4	40	500
Strontium	25	71	168	290	423	580
Zinc	29	<3	11	21	43	140

Spatial Occurrence of Arsenic in the Newark Basin in New Jersey

Regional Occurrence

Figure 1.4 shows the approximate (points not digitized) locations of New Jersey public-supply wells sampled in 1995 – 2000 and private wells sampled as part of the New Jersey Private Well Testing Act from September 2002 to March 2003 that have As concentrations greater than $10 \mu\text{g}/\text{L}$. Most of the wells with arsenic concentrations greater than $10 \mu\text{g}/\text{L}$ are in the Lockatong and Passaic Formations. Although preliminary,

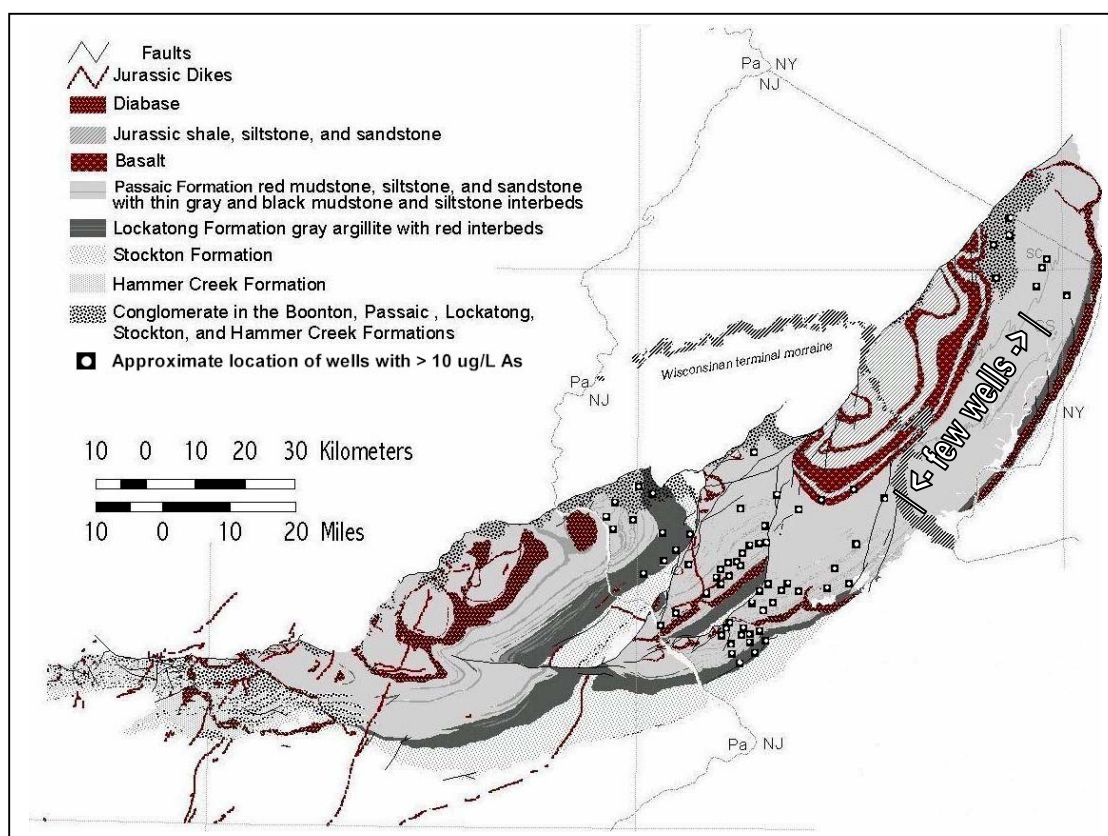


Figure 1.4. Shows the approximate (points not digitized) locations of New Jersey public supply wells sampled 1995 – 2000 and private wells sampled as part of the New Jersey Private Well Testing Act from September 2002 to March 2003, <http://www.nj.gov/dep/pwta/>, that have arsenic concentrations greater than 10 µg/L.

most of the wells in the Passaic Formation with concentrations greater than 10 µg/L appear to be associated with the Metlars, Livingston and Kilmer and older members (figure 1.4). However, wells intersecting younger members of the Passaic Formation have arsenic concentrations up to 215 µg/L. Field parameters such as pH, dissolved oxygen (DO) and specific conductivity (SC) that would aid in characterizing the hydrogeochemical environment were not collected during these regulatory samplings.

A hydrologic study by Schreffler and others (1994) in the Newark Basin in northern Bucks County Pennsylvania found wells with concentrations of As up to 28 µg/L. Out of the 35 wells with results for arsenic, four (11 percent) have arsenic

concentrations exceeding 10 µg/L. Two wells in the Passaic Formation have 24 and 28 µg/L As, one in the Lockatong Formation has 11 µg/L As, and one in the diabase has 13 µg/L As.

Spatial Analysis of Arsenic Occurrence in the Central Newark Basin

In 1999-2000, the NJGS used a Geographic Information System to conduct a detailed spatial analysis and investigation on the occurrence of arsenic in ground water as a function of bedrock lithology. The study is a 200 square mile (518 km²) region in western New Jersey where high concentrations of arsenic in well water are present (Figure 1.1c). A grid-based approach using square-mile cells, and random selection within blocks, assured that the sampling was spatially distributed within the study area rather than being mainly clustered in high-population areas if a simple random approach was used (Alley, 1993). The goal was to collect a representative well-water sample and field parameter data: pH, DO, SC, and temperature (T) from at least one domestic well per cell. We obtained untreated mainly from outside taps after water had flowed for at least 15 minutes and field parameters stabilized. I obtained three well records per cell for a total of 600 well records total by conducting a well record search using the New Jersey Department of Environmental Protection Division of Water Supply database. Generally, I used the most recent well records in each cell to simplify the determination of the property owner. We sent letters requesting volunteers for this project to the well owners and sampled the first respondents. Out of the 200 cells, 94 volunteers were found. We

also conducted cluster sampling in two areas where at least one well had an arsenic concentration greater than 40 $\mu\text{g/L}$.

Sample Results

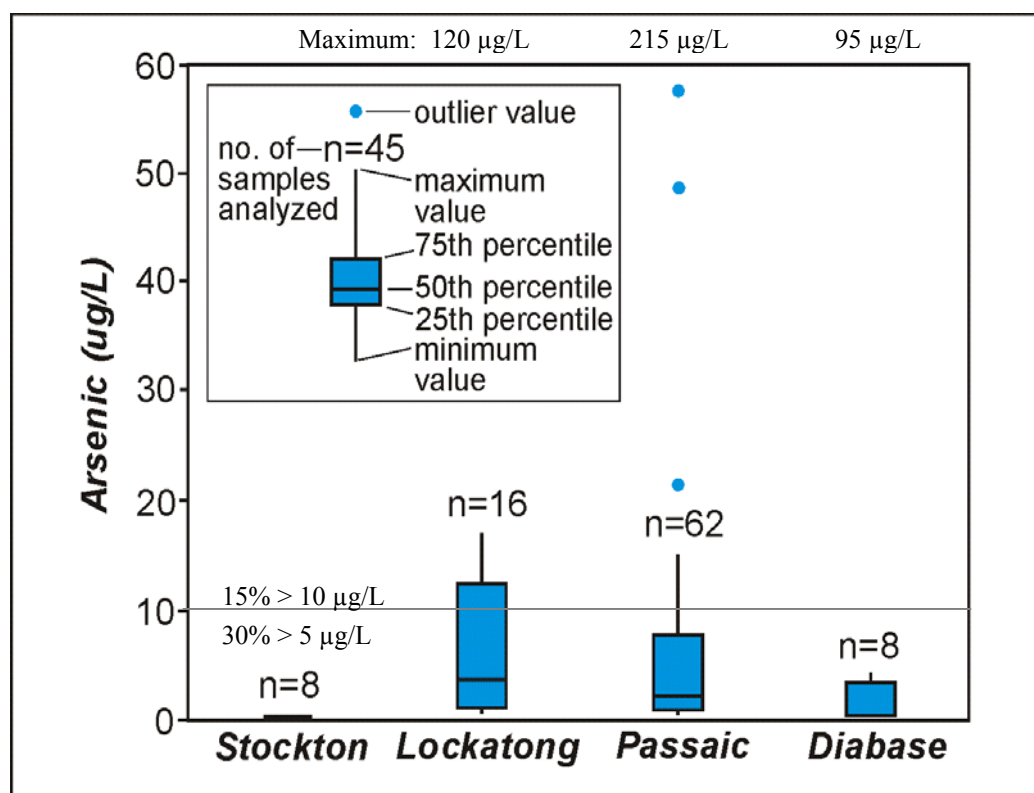


Figure 1.5. Box and pin diagrams summarize the arsenic concentration results from the 1999-2000 initial investigation. Maximum concentrations of arsenic found subsequent to the initial data are also shown.

Of the 94 wells sampled, 15 percent have arsenic concentrations exceeding 10 $\mu\text{g/L}$ (figure 1.5). Well water from the Passaic and Lockatong formations have the highest arsenic concentrations and frequency of occurrence (Serfes and others, 2005). The Passaic Formation is much more aerially extensive of the two and therefore the number

of wells impacted by concentrations of arsenic exceeding than the drinking water standards are greater (figure 1.2 and 1.3).

Based on the results of pH and dissolved oxygen (DO) concentrations taken at the time of the sample, arsenic concentrations greater than 10 µg/L in the Passaic Formation generally have pH values ranging from 7.5 to 8.2 and low dissolved oxygen (DO) concentrations (DO < 3 mg/L) (Figure 1.5). Arsenic concentrations greater than 40 µg/L are associated with suboxic concentrations (DO < 1.0 mg/L) and a pH of about 8 in the Passaic Formation. These values fall into the lower and upper percentiles respectively for that formation (table 1.2). However, in the Lockatong Formation, 15 of 16 samples have DO < 3 mg/L and 11 are < 1 mg/L regardless of the arsenic concentration (table 1.6). Also, the pH at which the highest arsenic concentrations occur is not as well defined. The low DO is characteristic of this formation and is related to the more anoxic nature of the organic-rich and pyritic deep-water lake strata (table 1.3). The geochemical nature of the Passaic and Lockatong formations defined during the arsenic reconnaissance study is comparable to that given in tables 1.2 and 1.3. Subsequent sampling also identified areas in the Newark basin where some wells have even higher concentrations than found in the original reconnaissance. Several wells in diabase near the contact with sedimentary rock in the southwestern part of the basin in New Jersey have up to 95 µg/L arsenic. Approximately 10 miles east of those wells, a well in the Lockatong Formation has up to 120 µg/L arsenic. Also, wells drawing water from a sulfide mineralized zone in the Passaic Formation under a basalt flow in the north-central Newark basin in New Jersey have arsenic concentrations up to 215 µg/L.

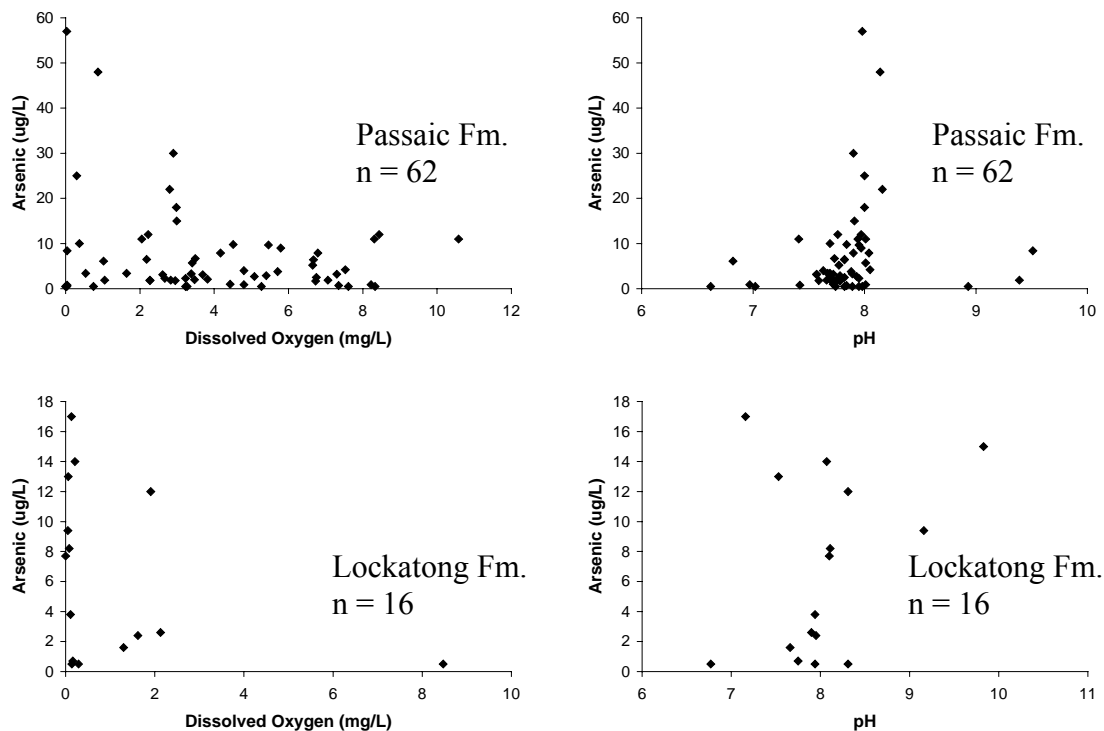


Figure 1.6. Arsenic versus dissolved oxygen and pH in ground water in the Passaic and Lockatong Formations in the western Newark Basin in New Jersey.

Ground water collected from a 400-foot deep public-supply well (Hopewell 6) in the Passaic Formation in Hopewell Borough, New Jersey, has consistently had an arsenic concentration of $45 \pm 5 \mu\text{g/L}$ since it was installed in 1995. Samples collected periodically over months and years from other wells in an arsenic treatment study in the Newark basin generally also have had less than a 20 percent variation in arsenic concentrations (Steven Spayd, New Jersey Geological Survey, personal communication). These temporally consistent concentrations indicate that a steady-state geochemical condition exists between ground water and the rock matrix it flows through. The few exceptions are several wells with high arsenic concentrations open in and under diabase and basalt that show large concentration fluctuations. There appears to be an association

between precipitation events and decreasing concentrations in these wells likely reflect a more open fracture network than in the sedimentary rocks of the Passaic and Lockatong formations.

The results from arsenic species analysis showed that arsenic in ground water in the Passaic Formation is predominantly arsenate even under suboxic conditions (Table 1.5). One explanation for the occurrence of the oxidized arsenic species in the Passaic Formation could be reactive contact with Mn-oxide coatings that I identified on a

Table 1.5. Arsenic speciation in 9 private residential wells in the Passaic Formation. Concentrations in $\mu\text{g/L}$.

Species	Well 1	2	3	4	5	6	7	8	9
As total	22.3	31.8	61.9	39.8	19.5	5.2	40.5	9.7	22.7
As + 3	0.3	0.1	0.5	1.6	<0.1	<0.1	0.3	<0.1	0.2
As + 5	22.0	31.4	59.6	37.9	19.2	4.9	39.9	9.3	22.5
MMA	<0.1	0.1	0.4	<0.1	0.1	<0.1	0.1	0.2	<0.1
DMA	<0.1	0.2	0.4	0.2	0.2	0.2	0.2	0.2	<0.1

bedrock fracture surface in the Passaic Formation using energy dispersion spectroscopy (EDS). Manganese oxides are known to rapidly oxidize arsenic from As (III) to As (V) (Driehas and others, 1995; Scott and Morgan, 1995). Arsenic species analyses of 23 public-supply wells in the Passaic Formation known to have elevated arsenic concentrations showed the same (Steven Spayd, New Jersey Geological Survey, personal communication). However, Arsenite (As III) was the dominant species in two private and two public wells in the Lockatong Formation where it comprised over 63 percent of total arsenic concentrations that ranged from 11.9 to 45.0 $\mu\text{g/L}$ in the four wells. Water from those wells also had a hydrogen sulfide odor indicating strong reducing conditions. The

methyalted arsenic species monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) were all less than 0.5 µg/L.

Case Study: Hopewell 6

History

Hopewell 6 (HW 6) is a 400-foot-deep (121.92 m), public supply well in Hopewell Borough, Mercer County, New Jersey that was installed in the Passaic Formation in 1995 to meet the boroughs growing water supply demands (figure 1.1 and 1.7). In December 1995, a 72-hour pump test was conducted using a 400-foot-deep, 6-inch-diameter (0.1524 m), observation well (well 1) located about 75 feet (22.86 m) northeast and along strike with HW 6 and a 300-foot-deep (91.44 m), 6-inch-diameter, observation well (well 2) that is about 300 feet to the north and down dip of HW 6. All of these wells have a 50-foot-deep (15.24 m) steel casing and are open from the bottom of the casing to the bottom of the well. The results of the test showed that the aquifer has heterogeneity, anisotropy, with the greatest draw down along strike, has leaky boundaries, and that HW 6 can produce 140 gallons per minute without any detrimental impact to other nearby producing wells. Non-pumping deep local flow is expected to parallel strike and follow topography. Therefore, deep ground water flows from the diabase uplands in the southwest, down valley along the strike of bedding to the northeast where it eventually discharges to local streams (figure 1.7). Most of the recharge to the stratabound water-bearing zones intersecting these wells is expected to occur up valley

where the beds outcrop below the regolith. A water-quality analysis of HW 6 conducted in November 1995 yielded an arsenic concentration of 44 $\mu\text{g/L}$. This concentration has generally varied by less than 20 percent since that time. The well was only operated for a few years when the borough stopped using it because of the high arsenic concentrations.

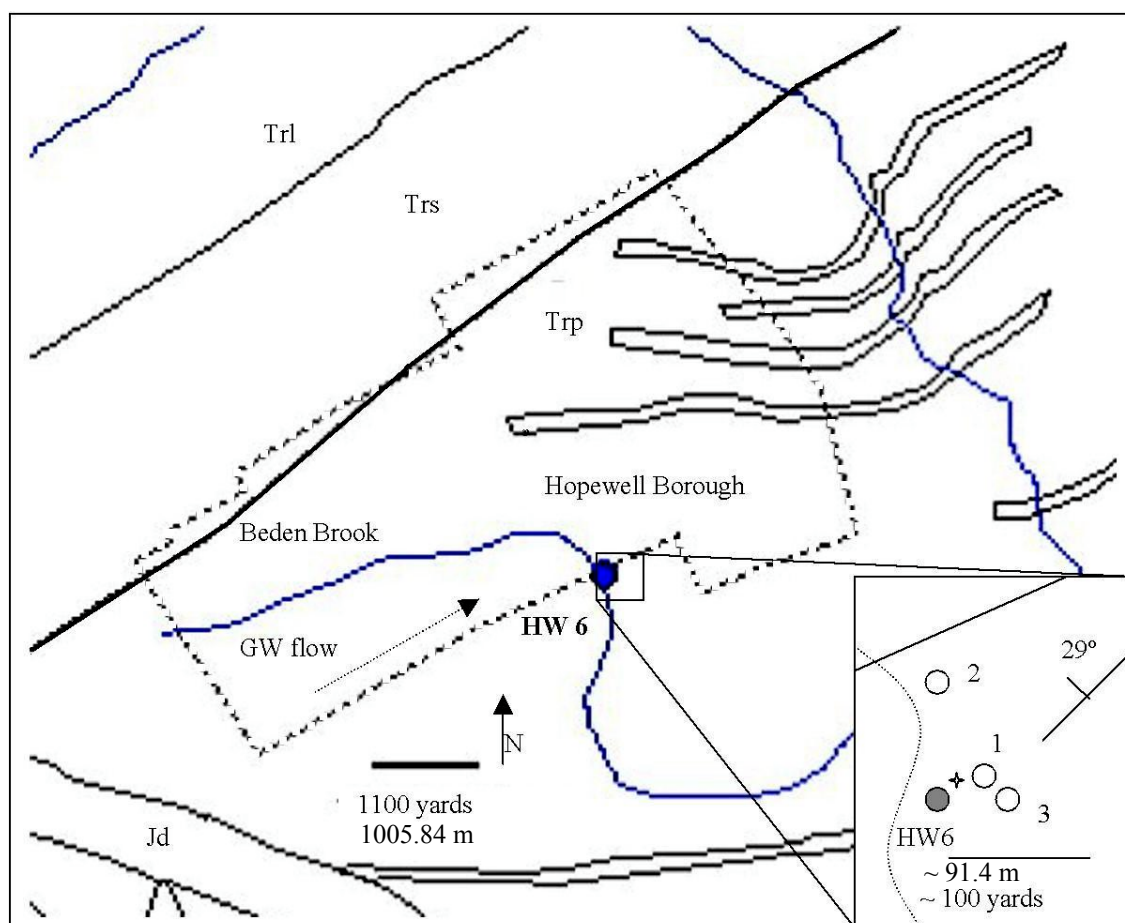


Figure 1.7. Geologic map showing the location of the 400 foot deep public supply well Hopewell 6 (HW 6) and the approximate locations of the associated observation wells 1, 2 and 3, the local strike and dip (N65E, 29NW), Borough boundary, stream and 400' core (+). Passaic (Trp), Lockatong (Trl) and Stockton (Trs) Formations, diabase (Jd). Regional location shown in figure 1.1.

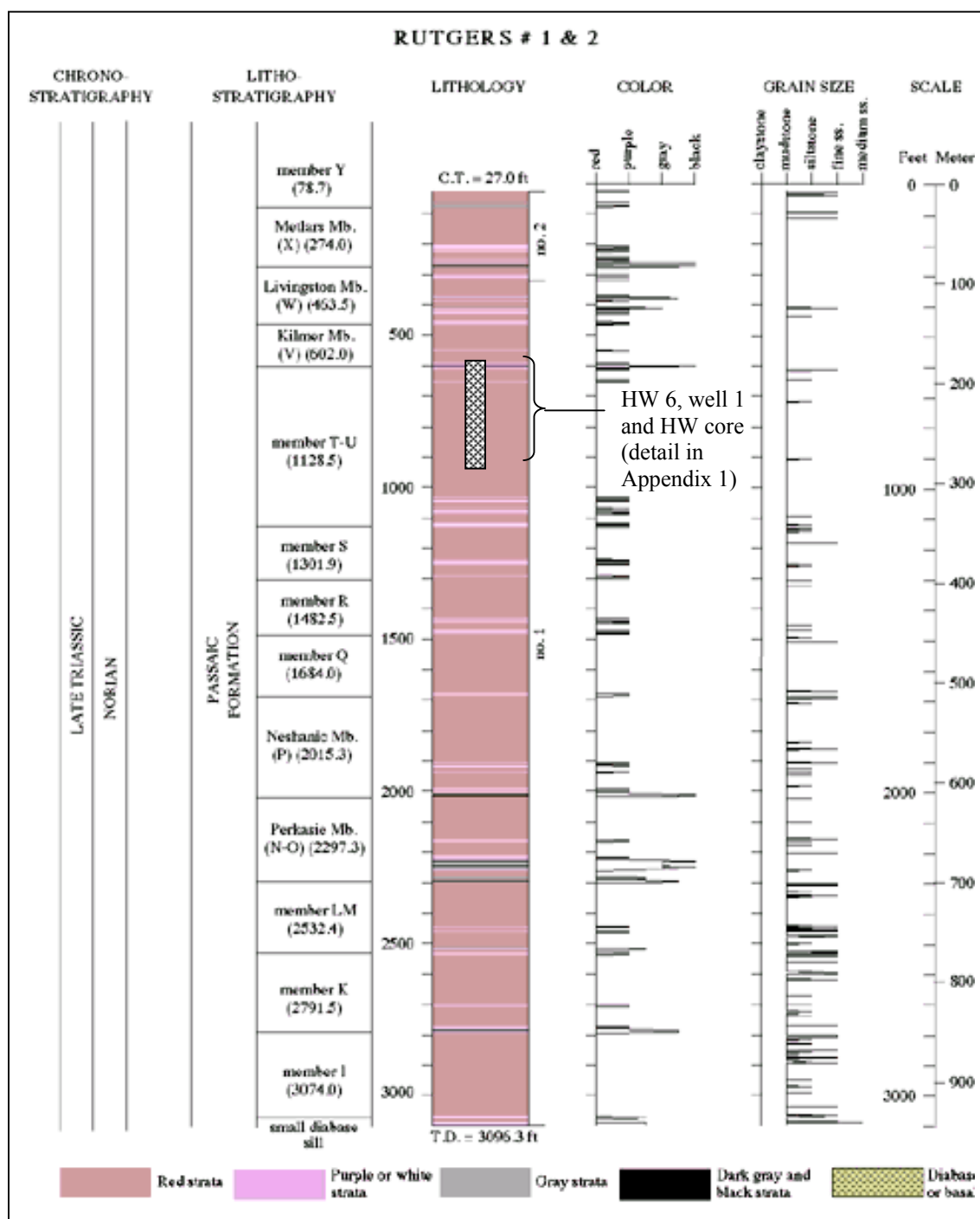


Figure 1.8. Stratigraphic column of the Rutgers 1 and 2 cores, see figure 3, from the Newark Basin Coring Project (Olsen and others, 1996). Showing ages, formation, members, magnetic polarity, thickness, rock color and grain size. Strata intersected by wells HW 6, obs.well 1, and the 400 foot core are corrected for the 29 degree dip.

In 1999 the NJGS collected a 400-foot long rock core approximately 50 feet

(15.24 m) from HW 6 to investigate the structural features associated with the water-bearing zones related to the hydraulics of that well (Herman, 2001). An optical televiewer in well 1 related features in the core with those in the well. Down-hole geophysical logging assessed flow. This core intersected the pyritic black and gray shale of the Kilmer Member and the older T-U member that is mainly red mudstones and siltstones (figure 1.8 and Appendix 1). An important finding of that investigation was that the major water flow into well 1, and therefore HW 6, is in the same stratigraphic interval as mineral-dissolution cavities present in the core (figure 1.9). I analyzed the whole rock geochemistry of select rock samples from the HW-core, shown in table 2.3; arsenic μ concentrations in the pyritic black shale are higher than in the gray or red mudstones and siltstones. The microanalysis of pyrite in the black shale showed that concentrations of arsenic ranged up to 3000 mg/Kg (Serfes, 2005). These findings stimulated a tentative hypothesis that the pyrite in the black shale was the source arsenic to HW 6. However, to test the initial hypothesis proposed in 2001, I planned an intensive investigation of the hydraulics and hydrochemistry of HW 6 in September 2002.



Figure 1.9. Examples of sparry minerals filling fractures and root cavity and other voids in HW 253 and 359 and dissolution-type-water bearing zones HW 324 and 359. Samples are from the HW core. Images from Herman (2001).

During September of 2002 the NJGS installed a 35-foot-deep (10.67 m) shallow well (well 3) less than 100 feet (30.48 m) and slightly up dip from HW 6 as part of the ongoing investigation of arsenic in ground water. This well has a steel casing to a depth of 10 feet (3.048 m) and is open to the black and gray shale from approximately 16 to 24 feet (4.88 to 7.31 m) to below the ground surface. A field parameter sounding of well 3 was conducted approximately one month after installation evaluated pH and redox

Table 1.6. Field parameter sounding of well 3 (35 feet deep with 10 foot casing and 2 foot stick up) conducted 10/2/02. Meter (Horiba X-22) held at depth until readings steady. 10 feet is 3.048 m.

Rock Color	Casing	Purple-Red	Black-gray	Gray-purple	Red
Depth (feet)	10.92	15.92	18.92	24.92	33.92
Well 3					
Characteristics					
Temperature (C)	17.8	16.2	15.3	14.2	12.7
Specific Conductivity (µS/cm)	330	410	430	440	520
Dissolved Oxygen (mg/L)	0.0	0.0	0.0	0.0	0.09
PH (standard units)	6.56	6.80	6.95	6.96	7.06
Oxidation-reduction potential (mvolts)	-47	-84	-95	-94	-4

variations with depth (table 1.6).

From September to November of 2002 the NJGS conducted a hydrologic and water-quality investigation of HW 6 and the adjacent observation wells to assess where and in what water-bearing zones the arsenic is being transported. As part of this investigation, single hydraulic packers along with transducers collected hydraulic head data and isolated zones in the well borehole for water-quality sample collection. I also collected field water-quality parameter data and samples for age dating using CFCs and for comprehensive chemical analyses (table 1.7). Semi-quantitative well yield testing evaluated variations in yield within the well bore. Most of the hydraulic testing related to

HW 6 took place in well 1 because the pump could not easily be removed from the public supply well. Because HW 6 and adjacent well 1 are along strike and drilled to the same depth, the comparison seemed reasonable.

Table 1.7. Select results from Hopewell intensive investigation 9/2002–11/2002. All samples were collected during that period except well 1 (9/14/01). Hydraulic packer used on wells 1 and 2. Samples were not filtered. CFC analyses were conducted at the University of Miami Tritium Laboratory using their prescribed syringe technique. Field parameters determined using Horiba X-22 and Hach Alkalinity titration. Chemical analyses conducted at Activation Laboratories in Ancaster, Canada. No measurement taken (--). Sample interval is in feet below grade (10 feet is 3.048 m).

Well (p, if packer used)	6	1	1p	1p	1p	1p	2	2p	2p	3
Sample Interval – Top (feet)	50	50	50	50	50	291	50	50	60	10
Sample Interval - Bottom	400	400	60	400	291	400	300	60	300	35
Hopewell intensive investigation										
CFC 11, 12, 113 model age										
Age +/- 2 years	21	23	--	--	--	--	22	--	--	30
Characteristics										
Temperature (C)	14.4	13.4	12.9	13.9	--	--	12.9	12.9	13.6	15.4
Specific Conductivity (µS/cm)	380	420	530	430	--	--	339	390	330	380
Dissolved Oxygen (mg/L)	0.0	0.0	0.0	0.21	--	--	3.62	1.45	2.3	0.0
PH (standard units)	7.87	7.71	7.43	7.65	--	--	7.79	8.0	7.47	7.25
ORP (mvolts)	105	31	-61	128	--	--	--	108	130	-44
Field Alkalinity (mg/L as CaCO ₃)	142	150	203	127	111	94	--	101	99	115
Major and minor dissolved constituents in mg/L										
Calcium	49.4	59.1	80.4	52.8	47	50.1	28.9	44.5	37.4	83.9
Magnesium	14.3	16.3	30.1	17	16.8	12.9	15.6	21	16.5	23.6
Sodium	18.6	24.4	14.1	23.6	19	24.6	9.7	12.7	10.7	15.5
Potassium	1.17	1.04	1.59	1.07	1.18	0.88	0.97	1.15	1.1	1.61
Chloride	8.7	11.2	25.1	11.9	12.4	10.2	12.6	18.8	11.9	15.2
Sulfate	43.4	40.3	29.5	49.2	25.4	38.5	22.1	24.2	21.5	30.2
Silica	11.3	11.9	11.7	10.5	11.0	11.3	10.8	11.6	12.2	10.0
Strontium	2.56	2.58	0.95	2.53	1.79	2.40	1.15	1.26	1.13	0.49
Nitrate	1.73	1.11	0.59	0.71	1.46	1.57	--	3.01	2.26	.52
Phosphorous (ND = <0.04)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trace and minor dissolved constituents in µg/L										
Arsenic	41.9	33.8	3.01	29.4	27.3	36.4	9.2	7.03	8.5	1.06
Barium	133	136	226	149	170	109	153	165	170	372
Iron	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Manganese	1.2	0.5	38.1	<0.5	2.4	0.7	<0.5	3.4	0.2	303
Molybdenum	14.7	16.4	18.2	16.5	12.9	23.2	1.9	1.5	1.5	17.2
Uranium	4.85	2.09	1.93	1.65	1.59	1.33	0.92	0.83	0.80	1.67
Zinc	48.7	<0.5	381	39.3	44.9	52.8	<0.5	54.5	26.0	2.0

Summary of Findings with Discussion

Hydraulics

1. Hydraulic head measurements in wells 1 and 2 above and below packers showed a downward vertical gradient. This is indicative of a topographically controlled head being transmitted down dip in the stratabound water bearing zones that have an opposing orientation to the slope.
2. The hydraulic yields in well 1 are approximately the same from 50 to 291 feet (15.24 to 88.70 m) as from 291 to 400 feet (15.24 to 121.92 m). Therefore, the yields are higher in the deeper strata.
3. Observations in core samples show an increase in dissolution zones in the deeper strata (figure 1.8). This is consistent to the finding that yields increase with depth.

Water Chemistry

1. As a general statement, all of the well water is classified as the calcium bicarbonate type, which is characteristic of the Passaic Formation. A comparison of water quality from HW6, and wells 1 and 2 (table 1.8) with that for similar type wells in the Passaic Formation (table 1.2), indicates that generally all of the chemical parameters from these wells fall between the 25th and 75th percentiles for the Passaic Formation except for a lower DO in HW 6 and well 1, a slightly higher pH and Sr concentration in all, and a lower Si concentration in all. Also,

HW 6 and well 1 have very high As concentrations whereas well 2 has a concentration approximately 4 times lower but higher than most of the wells sampled during the reconnaissance study (figure 1.5).

2. Arsenic concentrations are highest in HW 6 and well 1. They increase with well depth in well 1 and are much lower in well 3 that intersects the black and gray strata that have the highest whole-rock concentrations of arsenic (tables 1.6 and 1.8). Therefore, the arsenic is entering HW 6 and well 1 via the deep high yielding dissolution zones in the red mudstones and not from the shallow black/gray shale zone as originally hypothesized.
3. Wells HW 6, 1 and 3 are suboxic to anoxic whereas well 2 has a DO concentration similar to the median for the Passaic Formation (tables 1.2 and 1.8)
4. The field parameter measurements taken during a sounding of well 3 showed that the water in this well is generally reducing compared to the other wells and that the water adjacent to the black/gray shale is the most reducing (tables 1.7 and 1.8).
5. The ground-water chemistry in well 1 when open only from 50 to 60 feet (15.24 to 18.29 m) is similar to well 3 which is open from 10 to 35 feet (15.24 to 10.67 m). Both have a much lower oxidation reduction potential, lower As, Sr, and SO_4 , concentrations, a lower pH, and higher Ca, Mg, Ba and Mn concentrations than
6. the other wells (table 1.8). These chemical conditions suggest that pyrite is stable in the more reduced environment but carbonate minerals are not at the lower pH. The lower Sr concentration may indicate that Sr is associated with Ca in gypsum (CaSO_4) rather than in calcite (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$). Not

surprisingly, the alkalinity is higher in the shallow zones of well 1, 203 mg/L at 50 to 60 feet (15.24 to 18.29 m) than in the deeper, 94 mg/L when open from 291 to 400 feet (15.24 to 121.92 m).

7. Age of ground water using CFCs was approximately 22 years in HW 6 and wells 1 and 2. Ground water in well 3, which is much shallower, had a model age of 30 years. The older age of water in well 3 is probably reflective of a lower permeability compared to the water bearing zones intersected by the deeper wells.
8. The deeper zones in well 1 have a much higher As, Sr, and SO₄, higher pH and lower alkalinity and Mn concentrations.
9. All of the wells have nitrate values indicative of anthropogenic impacts. All of the beds intersected by these wells outcrop in former and current agricultural fields.

These findings clearly demonstrate that arsenic concentrations can vary considerably between adjacent wells unless they intersect the same strata. Wells that mainly intersect high-yielding WBZs that are transporting elevated concentrations of arsenic have unacceptable concentrations in their water supply.

Findings and Conclusions

The results from the reconnaissance sampling of private wells in a 200-square-mile (518 km²) study area in the Newark basin in New Jersey, the intensive study at HW6 and other related work provide the following findings and conclusions.

1. Of the three major formations, the Passaic and Lockatong formations have the highest arsenic concentrations with more than 15 percent of the wells exceeding 10 and 30 percent 5 µg/L As.
2. Arsenic concentrations in some individual wells sampled multiple times over periods of months and years have generally varied by less than 20 percent indicating a steady state geochemical condition.
3. Work at HW6 showed that arsenic concentrations can vary considerably between adjacent wells unless those wells intersect the same WBZs that transport arsenic.
4. Ground water in the Lockatong Formation is characterized by low DO: 15 of 16 samples have DO < 3 mg/L and 11 are < 1 mg/L regardless of the arsenic concentration. Also, the pH at which the highest arsenic concentrations occur is not well defined and ranges from 7 to 10. Arenite (As III) is the dominant species.
5. Ground water with arsenic concentrations greater than 10 µg/L in the Passaic Formation in the Newark basin are characterized by:
 - ◆ similar Ca-Mg,-Na bicarbonate type water as in most ground water in the Passaic Formation.

- ◆ dissolved oxygen concentrations < 3.0 mg/L
- ◆ arsenate, As (V), (HAsO_4^{2-}) > 95 % arsenic total (table 1.5).
- ◆ pH range between 7.5 to 8.2 .
- ◆ generally low iron and manganese concentrations.
- ◆ average sulfate and total dissolved solids concentrations for the Passaic Formation.

6. Commonalties among wells in the Passaic Formation with > 20 $\mu\text{g/L}$ arsenic are:

- ◆ pH of approximately 8.0.
- ◆ DO usually < 1.0 mg/L.
- ◆ an association with dissolution zones formed by the solution of secondary calcite calcite +/- dolomite +/- gypsum in interconnected voids.

In chapters 2 and 3, I explore sources and the mobilization of arsenic in the shallow-water lake/playa derived red mudstone and siltstone that comprise most of the Passaic Formation and the black organic-rich deep-water lake shale that comprises most of the Lockatong Formation.

Chapter 2. Major Lithogenic Sources of Arsenic in the Newark Basin: Early Fate with Implications for Modern Ground-Water Quality

Introduction

In theory, the prediction of aquifer vulnerability to lithogenic arsenic contamination in the Newark basin is possible if the variables controlling its occurrence in ground water are well defined. These variables include: (a) types of major arsenic sources, (b) arsenic concentrations in and the spatial distribution of those sources, (c) mobilization mechanisms affecting those sources, (d) hydrogeochemical settings in which those mechanisms are triggered, and (e) mass transport and chemical mass-transfer processes that control the arsenic concentration down-gradient from the major sources. This chapter mainly addresses variables (a) and (b), and focuses on these key questions:

1. What are the major lithologic sources of arsenic in the Newark basin?
2. Is it possible to determine the spatial distribution and concentrations of those sources?

I use two approaches to address these questions. First, I present and interpret arsenic and other element concentrations from the analyses of whole rock samples, minerals and leachate from experiments using pulverized rock. Although this geochemical characterization is revealing, it is somewhat limited because of the small number of samples in comparison to the size and geochemical diversity of the basin

itself. Second, in an attempt to resolve that limitation, I construct a conceptual model of the geochemical cycle and ultimate lithogenic fate of arsenic in the depositional, diagenetic and hydrothermal environments existing in the basin during the Mesozoic Era.

Background

Arsenic Geochemistry and Occurrence

Arsenic is a heavy metalloid element with atomic number 33 and has only one natural isotope with atomic mass number 75. It has five valence states in the natural environment: -3, -1, 0, +3 and +5 (Jones and Nesbitt, 2002). Arsenic ranks fifty-second in crustal abundance and has an average crustal concentration of 1.8 mg/Kg or parts per million (ppm), (Demayo, 1985). Arsenic occurs at crustal concentrations in many rock-forming minerals because it can substitute for Si^{4+} , Al^{3+} , Fe^{3+} and Ti^{4+} in their structures (Smedley and Kinniburgh, 2002). Geological processes can enrich some rock types with arsenic (table 2.1). Relative to igneous rocks, arsenic concentrations are significantly higher in fine-grained and organic-rich sedimentary rocks and their metamorphic equivalents. Black pyritic shale generally has arsenic concentrations on the high end of the range. Iron-oxide-rich rocks also have higher concentrations relative to igneous rocks. Ore bodies containing rock with arsenic bearing minerals such as arsenopyrite can have extremely high concentrations of arsenic but their occurrence is very localized and therefore not considered further here.

Table 2.1. Arsenic concentration ranges in various rock types (Boyle and Jonasson, 1973)

Rock type	Number of samples	Arsenic concentration range in mg/Kg	Average in mg/Kg
Basalt	78	0.2 to 113	2.3
Granite	116	0.2 to 15	1.3
Slate and Phyllite	75	0.5 to 143	18.1
Shale and Argillite	116	0.3 to 500	14.5
Coals ¹	Not given	0.3 to 35,000	Not given
Iron rich rocks	45	1 to 2900	Not given

¹Belkin and others (2000); Palmer and Klizas (1997)

The fate of arsenic is closely tied to the geochemical cycles of iron and sulfur and the occurrence of clay minerals (Stollenwerk, 2003). Chemical, physical and microbiological processes active in depositional, diagenetic and hydrothermal sedimentary environments can enrich secondary solid phases with coincident mobile arsenic. This enrichment is intimately tied to the aqueous chemistry of arsenic and that of the authigenic phases that concentrate it into their crystalline structures or as an absorbed impurity. In oxidizing environments, aluminum and manganese may also play a defining role if quantities are significant in comparison to iron (Sullivan and Aller, 1996, Manning and Goldberg, 1997). In unconsolidated sediments, arsenic is generally highest in the finer grained mud and clay fractions associated with ferric oxides or pyrite and organic material (Smedley and Kinniburgh, 2002). Clays can also adsorb arsenic at their oxide-like edges (Welch and others, 1988). It logically follows that the reduction of iron oxides and the oxidation of sulfide minerals such as pyrite are considered the most significant mechanisms for the mobilization of into ground water (Welch and others, 2000).

Under aerobic conditions where oxides are stable, dissolved arsenic can readily adsorb to Fe, Al and Mn oxides, particularly iron oxides because of their ubiquitous

occurrence, and therefore it concentrates on and in them in surface and subsurface environments (Smedley and Kinniburgh, 2002). Concentrations of arsenic in hematite and ferric oxyhydroxides can range up to 160 and 76,000 mg/Kg respectively (Baur and Onishi, 1969; Pichler and others, 1999). Other anion-forming elements that may also be adsorbed to iron oxides include V, B, F, Mo, Se, U, Cr, Re and P (Smedley and Kinniburgh, 2002). Metal ions exposed on the oxide surfaces complete their coordination shells with OH groups that bind or release H^+ depending on the pH (Strum, 1992). The pH dependent density of the surface functional groups OH_2^+ , OH, and O^- make up the active binding sites and affect the overall surface charge of the absorbent. Therefore, at pH values below the adsorbents point of zero charge (PZC), pH at which the net surface charge is zero, the surface is dominated by OH_2^+ and above it O^- yielding a net positive and negative charge respectively. The complexation of arsenite and arsenate at the metal-oxide surface is mainly associated with ligand exchange with those functional groups. The anion arsenate ($H_2AsO_4^-$) is more strongly retained at lower pH values when the net surface charge is positive and arsenite ($H_3AsO_3^0$) at higher pH values (Wilkie and Hering, 1996). Experimental work using goethite as an absorbent showed that the adsorption of As(V) is more favorable than As(III) below pH 5-6, and above pH 7-8 As(III) has a greater affinity for to adsorb onto the solid (Dixit and Hering, 2003). Both arsenic species mainly form bidentate binuclear surface complexes (Manning and others, 1998, Sun and Doner, 1996). Similar to oxide minerals, the Al ions exposed at clay mineral edges can also form inner sphere complexes with adsorbed arsenic (Foster, 1999).

The nucleation and growth of pyrite occurs in anoxic environments where sulfide and ferrous iron are stable. Arsenic is a chalcophile element (sulfur loving) that substitutes for sulfur in the structure of pyrite (Savage and others, 2000). Other chalcophile elements that are sometimes associated with arsenic in sulfide minerals include Cu, Zn, Sb, Pb, Sn, Cd, Hg, and Ag (Morse and Luther, 1999; Smedley and Kinniburgh, 2002). Arseniferous pyrite is generally the most ubiquitous arsenic bearing sulfide mineral and micron-scale spot concentrations are up to 8.5 and 9.97 weight percent in sedimentary and hydrothermal pyrite, respectively (Kolker and others, 1998; Plumlee 1989).

Microorganisms are ubiquitous in surface and subsurface environments (including hydrothermal), and have the potential to dramatically alter the geochemistry and mineralogy of their surroundings (Mojzsis and others, 1996; Lovely and Chapelle, 1995). The biogeochemical cycle of arsenic overlaps that of iron and sulfur and therefore all three direct the fate of arsenic. Microbial aerobic oxidation and anaerobic respiratory reduction (energy generating) processes can catalyze energetically possible but kinetically hindered redox reactions, thereby changing the valence, and therefore species and behavior, of inorganic and organic elements. Heterotrophic oxidizing, chemoautotrophic oxidizing and dissimilatory respiring microorganisms have been identified that can catalyze the rate of arsenic, iron and sulfur chemical equilibrium (Oremland and Stolz, 2003; Glasauer and others, 2003; Moore and others, 1988; Canfield, 1989). These microbial-mediated reactions affect the mobility of arsenic and

the stability of the pyrite and iron-oxide and oxy-hydroxide minerals to which it is bound.

Authogenic Minerals

Secondary or authogenic minerals are the products of reactions involving residual or mobile reactants derived from pre-existing minerals that are susceptible to chemical weathering. Arsenic can become enriched in some authogenic minerals and can become sources of arsenic to ground water when these minerals are later exposed to the aqueous environment. Minerals such as clays that were derived from the weathering of minerals in the crystalline host rock can adsorb As and other element species. Other secondary minerals such as iron oxides and pyrite are also sinks for mobile arsenic. Because they may only be stable within very narrow geochemical ranges, they can later become sources if conditions change. Many workers have evaluated the paragenetic sequence of authogenic minerals, that make up the sedimentary cements, in the Newark Basin (Oshchudluk and Hubert, 1988; Smoot and Simonson, 1994; Parnell and Monson, 1995; van de Kamp and Leake, 1996; Tabakh and Schreiber, 1998). Based on their work, table 2.2 summarizes the general succession of authogenic minerals occurring before and after the formation of authogenic microcline (K-spar) sedimentary cements dated at less than or equal to 196 \pm 1 Ma (Kunk and others, 1995). Synsedimentary and early diagenetic

hematite, after iron-oxyhydroxide, and pyrite are likely sinks for arsenic and many metals. Arsenic associated with iron-oxyhydroxides in areas of evaporative concentration (brines) occurs in modern intercratonic basins (Welch, 1998). Early diagenetic hematite associated with clayey rims occurs in sandstone in the Stockton, Passaic and Feltville formations (Oshchudlak and Hubert, 1988). Low-temperature pyrite readily forms in lakes with organic-rich sediments and incorporates available arsenic into its structure (Berner, 1984; Morse and Luther, 1999). Sulfide minerals present at oxic/reducing geochemical boundaries in Mesozoic rift basins are related to the transport and precipitation of scavenged metals and nonmetals in hydrothermal fluids (Smoot and Robinson, 1988). The significance of diabase intrusions (~ 200 Ma) versus the topographically driven (< 195 Ma) associated hydrothermal activity is controversial. Steckler and others (1993) and Malinconico (2002) presented evidence of a post-igneous heating event in which waters flowed down along the border faults into the deeper Stockton Formation where they were heated to ambient temperatures of up ~ 250 °C before flowing up along intrabasin faults and into lower-temperature permeable beds. Regardless of the causes for hydrothermal fluids in the Newark Basin, experimental studies to evaluate hot water (up to 500 °C)-rock interactions demonstrated that significant quantities of As, Sb, Se and S could be leached from greywacke (Ewers, 1977). Hematite formed during the hydrothermal event(s) could have acted as both a source and sink for metals and arsenic.

Table 2.2. General paragenetic sequence of authogenic minerals in the Newark Basin based on the work of Oshchudluk and Hubert, 1988; Smoot and Simonson, 1994; Parnell and Monson, 1995; van de Kamp and Leake, 1996; Tabakh and Schreiber, 1998.

Formation 225 to 200 Ma	Synsedimentary to early diagenetic		K-spar age ~ 196 Ma	Late diagenetic (hydrothermal association, 100 to 250 °C)		
Passaic	Calcite, early hematite ¹	Pyrite ² , Albite	K-spar +/- Quartz	Fe-dolo., anhydrite	Bitumen ³ ; Fe, Cu, Pb, Zn sulfides ²	Calcite, barite, Late hematite
Upper Lockatong	Calcite, early hematite ¹	Pyrite ² , Analcime	K-spar +/- Quartz	Fe-dolo., anhydrite	Bitumen ³ ; Fe, Cu, Pb, Zn sulfides ²	Calcite, barite, Late hematite
Lower Lockatong	Calcite, early hematite ¹	Pyrite ² , Albite	K-spar +/- Quartz	Fe-dolo., anhydrite	Bitumen ³ ; Fe, Cu, Pb, Zn sulfides ²	Calcite, barite, Late hematite
Stockton	Calcite, early hematite ¹	Pyrite ² , Albite	K-spar +/- Quartz	Fe-dolo., anhydrite	Bitumen ³ ; Fe, Cu, Pb, Zn sulfides ²	Calcite, barite, Late hematite

¹ oxidizing environment, iron oxides formed coatings on surface sediments such as clay minerals.

² reducing environment, associated with deposited organic-rich (black and gray strata), remobilized organic material or relict organic matter in root cavities.

³ organic matter (non-mineral) mobilized from black or gray strata into intergranular pores and vein openings. Created disseminated reducing zones for sulfide mineralization.

Previous Geochemical Evaluations

The results of several geochemical evaluations of trace elements in the Newark and other Mesozoic rift basins in eastern North America were studied by Dean, 1988. Evaluation of trace metal versus inorganic constituents and organic carbon concentrations in black and gray shale showed that the metals (Cr, Cu, Ni, V, Y, and Zn) are generally associated with the inorganic clay fraction (Al₂O₃ association) and not the organic-carbon fraction. Another conclusion from that study was that although background concentrations of Cu are associated with the inorganic clay fraction, rocks in the Passaic Formation in the Newark basin with the highest concentrations of copper are associated with the highest organic-carbon content. The Cu-mineralized zones are associated with the sediment hosted stratabound copper sulfide mineralization that is widespread in the eastern Mesozoic basins (Robinson, 1985). A more comprehensive study by van de

Kamp and Leake (1996) focused on sodium enrichment in the Newark basin rocks, correlated TiO_2 (clay-indicator element) with Ba, Co, Cr, Ni, Rb, Y, Zn, Zr and Al_2O_3 and concluded that all but Ba and Rb are associated with illite in the Stockton and Passaic formations. These trace metals are inferred to have been concentrated in evaporative lake brines before being adsorbed or incorporated in primary and secondary minerals. They also concluded that, because of the lack of clay minerals in the Lockatong Formation, particularly in the analcime-rich strata, enriched metals such as Co, Cr, Cu, Ni, and Zn must be associated with oxides and sulfides. From a geochemical perspective, the Lockatong Formation is distinctly different than the Stockton and Passaic formations. Although Dean (1988) provided the range of arsenic concentrations in black and gray shale, arsenic was not statistically correlated with other chemical constituents in either report.

Stratabound red-bed type copper deposits, and lesser zinc and lead deposits, associated with sulfide minerals have been recognized in the Newark basin for over 100 years (Kummel, 1901). Preserved organic material related to paleo-root structures in fluvial sandstone, and lacustrine sandy mudstones underlying laminated black shales host these post-depositional deposits in the Newark and other Mesozoic basins (Smoot and Robinson, 1988). Arsenic concentrations exceeding background values by an order of magnitude are in some instances also associated with these deposits. The metals in these sulfide minerals may have originated in hydrothermal brines that flowed through fault conduits and into more porous strata where they precipitated out as mainly pyrite and chalcocite (Cu_2S), (but may include chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and native

copper) when encountering organic material (Smoot and Robinson, 1988). Smoot and Robinson (1988) conducted lithostratigraphic and geochemical studies of two black and gray mudstones units separated by red beds at the Culpeper Crushed Stone quarry in Stevensburg Virginia to evaluate sulfide mineral associations in the host rock and centimeter scale associations of Ag, As, Cu and Zn concentrations. Base-metal sulfides (sphalerite, chalcopyrite, bornite and minor galena) to occur as disseminations and replacements in fracture fillings in a zone of up to 4m thick in association with root-disrupted mudstones that underlie black, organic-matter-rich strata. Concentrations of arsenic locally exceed 200 parts per million relative to ~ 10 ppm background in the red-bed un-mineralized strata. A centimeter-scale stratigraphic profile of metal concentrations shows that elevated arsenic and other metals may or may not correlate well with each other. An analogous evaluation by Malinconico (2002) in the Ukrainian and Cedar Grove members of the Passaic Formation in the Newark basin also showed variable correlations between arsenic and other metals. It does appear that a post-depositional metal mobilization and precipitation event associated with hydrothermal fluids, permeable fractures and strata, and organic matter occurred in a number of basins in the Newark Supergroup (Robinson, 1985; Smoot and Robinson, 1988). The variable metal associations in the host rock are likely related to differences in their mobility and the dominant sulfide minerals occurring in any location.

The source of Cu and other metals in these deposits may be the hematite that cements the red beds (e.g., Rose and others, 1986). However, the occurrence of a bleached zone in purple/red shale at the base of the Orange Mountain Basalt may suggest

otherwise (Sclar and Moses, 1991); this zone is associated with native copper and contains enriched concentrations of Ca, Na, K, Rb, Sr, Ba, Y, Cu, As, B and CO_3 and is depleted in Fe relative to the purple/red shale. The proposed mechanism for the bleaching and element enrichment is the reductive dissolution of the hematitic cements via an oxidation reaction with sulfide contained in hydrothermal fluids. The reaction that produced immobile native copper and mobile ferrous iron and sulfate is thermodynamically most favorable below 220 °C. Arsenic and many or all of the elements enriched in the bleached zone are not associated with the removed hematite.

Analytical and Leach Experiment Methods

The whole rock geochemical analysis methodology is described in the Analytical Methods section of Chapter 1 of this dissertation.

Pulverized (95% by weight was less than the -80-mesh size fraction ($< 180 \mu$)) red mudstone and siltstone samples HW-3033 and HW-394 from the HW-core were leached using doubly distilled water, and a sequential 0.11M acetic acid, CH_3COOH , (exchangeable procedure) and 0.01M oxalic acid, $\text{HOOC}\text{COOH} \cdot 2\text{H}_2\text{O}$, (reducible procedure) following modified procedures and information in Rauret and others, 1999 and Panias and others, 1999. The leachate, unleached solid samples and post-leach solids, designated HW-3033L and HW-394L, were analyzed using methods described in the Analytical Methods section of Chapter 1 of this dissertation. The major goal of the reducible procedure using oxalic acid was to dissolve as much hematite as possible to

assess its potential as an arsenic source. The reducible procedure is based on a method described in Panias and others, 1996 because it involves the reductive dissolution of iron oxides (hematite). Also, unlike sulfuric or hydrochloric acid, which can also dissolve hematite, oxalic acid will not increase the concentration of sulfate or interfere with the analytical determination of arsenic using ICP-MS such as chloride will do.

The reducible leach procedure started by using 500 ml of 0.01M oxalic acid to 20 grams of pulverized rock sample in a 600 ml Pyrex beaker. After one-hour at 90 to 100 °C, the mixture is decanted into a Pyrex funnel containing a qualitative lab filter paper. The filter residue is air dried and then recovered via scraping and returned to the beaker for a total of 5 rounds as per the above. The leached residual rock material is analyzed for whole rock geochemical analyses and compared to that of the unleached solid to evaluate element concentration differences.

Findings: Sources of Arsenic in the Newark Basin

Lithochemistry

Arsenic concentrations from whole rock geochemical analyses of rocks from the Stockton, Lockatong and Passaic Formations are shown in figure 2.1. Black shale and gray mudstone from the Passaic and Lockatong Formations have the highest arsenic concentrations with some pyrite rich portions of black shale exceeding 200 ppm (Szabo and others, 1997; Serfes and others, 2005). The Stockton Formation and red mudstone

and siltstone of the Passaic Formation generally have much lower concentrations of arsenic. Arsenic concentrations in ground water are highest in the Lockatong and Passaic formations, and this section focuses on the geochemistry of arsenic in the cyclic deep-lacustrine and shallow-lacustrine/playa mudstone strata.

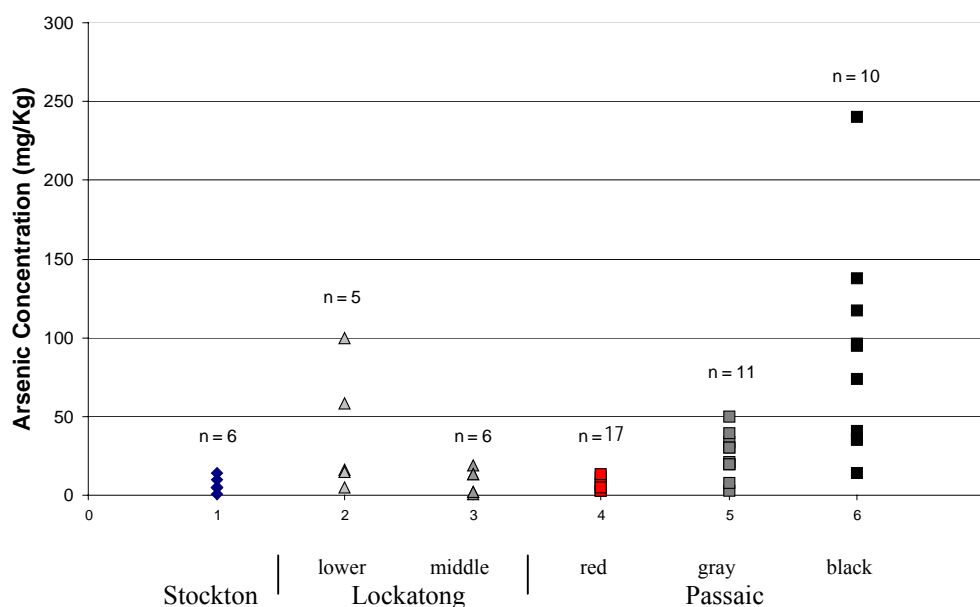


Figure 2.1. Arsenic whole rock concentration from the 3 major formations in the Newark Basin. Data from: Serfes and others, 2005, table 2.3, Malinconico, 2002, Szabo and others, 1997.

Although black and gray shale in the Passaic Formation have the highest concentrations of arsenic, red beds (including purple beds) comprise ~ 97.5 % of the Passaic Formation and are volumetrically and spatially the most abundant strata in the Newark basin at ~ 53 % of the total (figures 1.2, and 1.3.). Water from many wells intersecting red strata in the Passaic Fm. have unacceptable As concentrations and, since these beds comprise a larger area of the basin than the Lockatong Formation (~ 9 % of

basin), the number of affected wells are greater. Thus, most of the following information and discussion will focus on the geochemical character of the red beds in the Passaic Fm.

The geochemical data in table 2.3 show the concentration variations of select chemical parameters in samples from the 400-foot-long (121.92 m) HW-core (figure 1.8 and appendix 1) containing the Kilmer Member and older massive red mudstone of the T-U member in the middle Passaic Formation.

Table 2.3. Analytical results from 12 whole rock geochemical analyses of black and gray shale and red shale mudstone from core (HW) in the Kilmer and T-U members of the middle Passaic, and 3 samples from one core (SS) one 1 from another (M) in the upper Passaic Formation. Rock color: black and gray, shale; red, mudstone/siltstone.

Core/Depth	Rock color	mg/Kg		Percent by weight			
		As	REE ⁽³⁾	Fe ₂ O ₃ ⁽²⁾	S	Ti	C-organic
HW-26	black	95	112.1	4.91	1.82	0.436	0.43
HW-28.5	gray	18	150.8	6.19	0.57	0.543	0.23
HW-29.5	red	10.0	209.60	8.94	0.02	0.81	0.07
HW-30-33 ¹	red	4.50	167.18	8.47	0.17	0.72	0.06
HW-33	red	7.0	184.27	7.45	0.05	0.72	0.05
HW-83.6	red	5.1	167.68	5.71	0.00	0.63	<0.05
HW-144	red	12.1	254.07	8.74	0.02	0.90	<0.05
HW-161	red	10.4	235.93	8.10	0.02	0.89	<0.05
HW-213.4-214 ¹	red	11.1	249.46	8.84	0.02	0.89	<0.05
HW-225.6	red	10.3	241.10	8.65	0.00	0.89	<0.05
HW-286	red	11.0	229.00	7.36	0.02	0.80	0.04
HW-334	red	11.7	246.88	8.72	0.02	0.83	<0.05
HW-392-393 ¹	red	14.8	255.50	8.91	0.02	0.85	<0.05
HW-394	red	13.0	248.56	8.34	0.01	0.87	0.03
SS-96.5	red	11.1	235.17	8.47	0.02	0.88	0.05
SS-144-145 ¹	red	9.6	230.52	8.83	0.02	0.9	0.06
SS-147	red	8.6	208.65	6.5	0.02	0.89	0.08
M-1127	red	4.5	169.59	4.76	0.04	0.81	<0.05

¹Composite sample

²Iron reported as Fe₂O₃ regardless of actual oxidation state of Fe

³REE, sum of the rare earth elements concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

This core was collected adjacent to the 400-foot-deep (121.92 m) public-supply well, HW 6, with $\sim 45 \mu\text{g/L}$ of arsenic. Also included in table 2.3 are the results from four samples from the upper Passaic Formation. Three samples are from a core (SS), from unidentified members between JJ and SS in figure (1.3), collected adjacent to a private well with $\sim 57 \mu\text{g/L}$ of arsenic and one is from just below the Orange Mountain Basalt in the Martinsville core (M), of the Newark Basin Coring Project. The sample from the Martinsville core is in the same stratigraphic horizon as a well with $215 \mu\text{g/L}$ of arsenic, but is not adjacent to it.

The black and gray shale HW-26 and HW-28.5 in table 2.3 have the highest arsenic, sulfur and organic carbon contents in the HW core. Arsenic in these and other black and gray shale units are mainly associated with pyrite (Serfes and others, 2005). This association with pyrite is discussed further in the next section.

The red mudstone and siltstones from the HW, SS and M cores (table 2.3) have lower arsenic concentrations, trace amounts of organic matter, and generally very little sulfur compared to the black and gray shale. However, HW-30-33 that is just below the black and gray shale has 0.17 percent S and a Cu concentration of 2430 mg/Kg , not shown. This copper enrichment is stratigraphically similar to others in the Newark and other Mesozoic rift basins (Robinson, 1985; Smoot and Robinson, 1988). Although interesting, the copper enrichment does not appear to be associated with an arsenic enrichment and is therefore beyond the scope of this dissertation.

Because well water drawn from the red strata can have very high As concentrations, the geochemical association of arsenic with mineral phases in these strata is important to understand. As a first attempt to determine these relationships, I conducted linear correlation analysis (table 2.4) of As, REE (sum of the rare earth elements concentrations in mg/Kg of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), Fe₂O₃, S, Ti, Cu, Pb and Zn from the 16 red mudstone and siltstone listed in table 2.3.

Table 2.4. Multielement correlation analysis showing the correlation coefficient, r , for 8 select elements from the 16 red mudstones and siltstones shown in table 3.

Element	mg/Kg					Weight percent		
	As	REE	Cu	Pb	Zn	Fe ₂ O ₃	S	Ti
As	1	0.95	-0.46	-0.31	0.54	0.68	-0.51	0.67
REE	0.95	1	-0.45	-0.25	0.52	0.70	-0.51	0.79
Cu	-0.46	-0.45	1	-0.28	0.08	0.12	0.95	-0.37
Pb	-0.31	-0.25	-0.28	1	-0.62	-0.64	-0.13	0.18
Zn	0.54	0.52	0.08	-0.62	1	0.85	-0.02	0.24
Fe ₂ O ₃ %	0.68	0.70	0.12	-0.64	0.85	1	0.04	0.47
S %	-0.51	-0.51	0.95	-0.13	-0.02	0.04	1	-0.38
Ti %	0.67	0.79	-0.37	0.18	0.24	0.47	-0.38	1

These analyses show that the sum of REE in the 16 samples strongly correlate with As ($r = 0.95$ or $r^2 = 0.90$) and moderately strongly with Ti ($r = 0.79$ or $r^2 = 0.62$). Both REE and Ti are geochemical indicators of clay minerals in fine-grained sedimentary rocks (Conde, 1991; van de Kamp and Leake, 1996). The contribution of REE from zircon and apatite in shales is generally considered less important than clay control (Conde, 1991). Therefore, As appears to be related to clay minerals. Figure 2.2 shows the covariance of REE with As.

The REE concentrations in red mudstone and siltstone range from approximately 165 to 255 mg/Kg (Figure 2.2). Within an As concentration range of 5 to 12 mg/Kg the increase in the REE concentration is proportional. However, above and below that concentration range there appears to be no correlation between arsenic and REE.

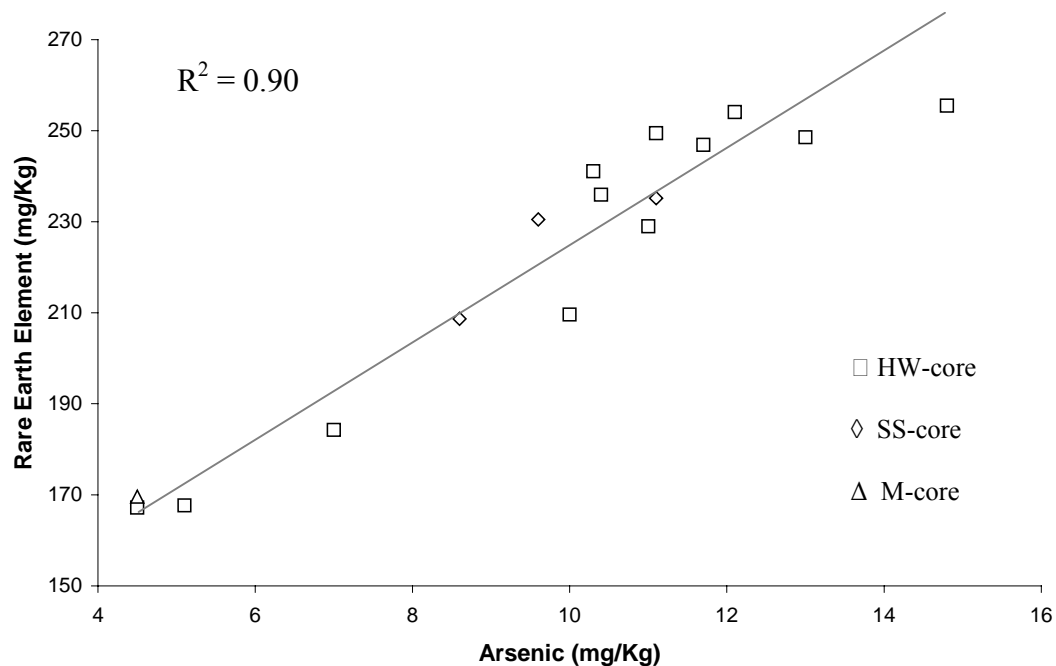


Figure 2.2. Shows the correlation of the sum of REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) to arsenic in the 16 red mudstones and siltstones (table 2.3) that are from the upper 2/3 of the Passaic Formation.

Black and Gray Shale: Mineral Sources of Arsenic

The fine-grained nature of shale, mudstone and siltstone make the geochemical characterization of all except the coarser individual minerals difficult. Electron microprobe analysis of black and gray shale in the Warford Member of the lower Passaic Formation (core sample provided by Zoltan Szabo, USGS) and the Kilmer Member of the middle Passaic, HW-core identified the mineral pyrite (FeS_2) as the major source of arsenic in both (Figure 2.3). These two black shale units have measured

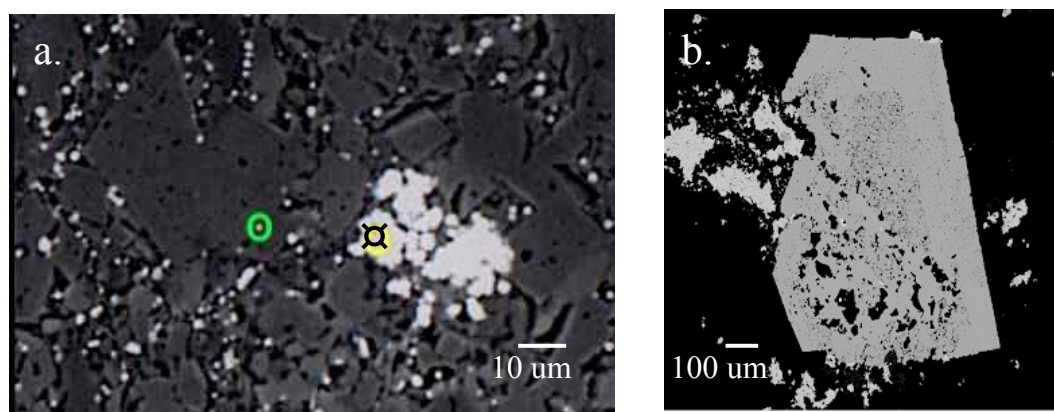


Figure 2.3. Scanning electron micrograph of (a) black shale from the Warford Member of the lower Passaic Formation in the Newark basin in New Jersey. Pyrite (bright) in a calcite matrix (dark). Arsenic concentrations in pyrite, 11,500 (o) and 15,860 (x) mg/Kg. Large pyrite in (b) with chalcopyrite (lightest) in dark matrix is from the Kilmer Member in the lower Passaic Formation. Arsenic concentrations in some pyrite range up to 3000 mg/Kg.

maximum arsenic concentrations in pyrite of 40,000 and 3000 mg/Kg, respectively.

Arsenic concentrations vary considerably within and between pyrite grains, and smaller grains generally had higher concentrations than larger grains. Pyrite cores and small micron sized grains were observed to have the highest concentrations of arsenic and rims around the cores the lowest (Figure 2.4). For example, the pyrite grain with 4-weight

percent arsenic was less than two microns in diameter. This suggests that most of the mobile arsenic was readily incorporated into pyrite early on as it nucleated and grew. Under sulfide reducing conditions, the nucleation and growth of low-temperature pyrite occurs in the deep lake sediments and can act as a sink for many metals and arsenic (Berner, 1984). I therefore conclude that the early diagenetic nucleation and growth of

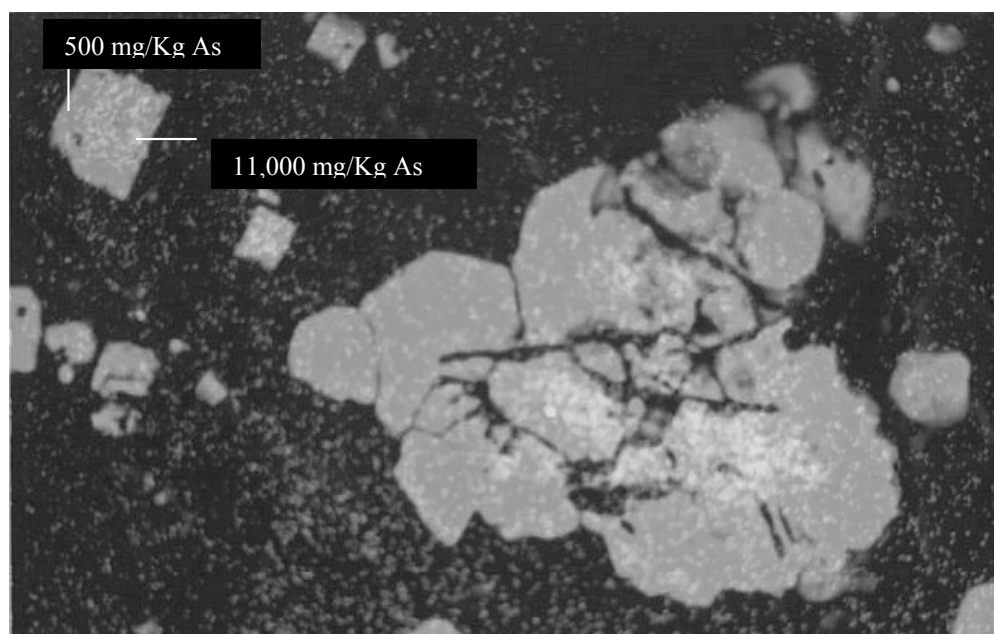


Figure 2.4. Arsenic element map of pyrite (bright) in black shale from the Warford Member of the lower Passaic Formation in the Newark basin in New Jersey. Arsenic detentions shown as white dots on pyrite. Higher densities of white dots indicate a higher arsenic concentration.

pyrite in the anoxic deep lake sediments was associated with the scavenging of most of the available mobile As. The subsequent growth of pyrite was associated with pore fluids depleted in As and therefore the rims have lower concentrations of it. Some late-stage mobilization and enrichment of As in sulfide minerals occurred during the hydrothermal event(s) (Smoot and Robinson, 1988).

Hydrogeochemical investigations to evaluate pyrite as a source of As to ground water are ongoing.

Red Mudstone: Mineral Sources of Arsenic

Multielement correlation analyses of red mudstone and siltstone in tables 2.3 and 2.4 show that REE correlate strongly with As and Ti. As mentioned previously, many workers have concluded that the abundance of REE in shale is associated with clay mineral content and that coarser grained fractions are relatively depleted in these elements (McLennan, 1989; Conde, 1991; Henderson, 1996). However, early hematite mineral coatings and late hydrothermal hematite are ubiquitous in these rocks and iron oxides are common sources of As to ground water (table 2.2). Correlation analysis results in table 2.4 show moderate relationships between REE and Fe_2O_3 of $r = 0.70$, and As and Fe_2O_3 or $r = 0.68$. Because of the fine-grained nature of many minerals in these rocks and the dispersed character of arsenic within them, their analysis and examination using standard analytical techniques such as the electron microprobe is much more limited than with arsenic enriched pyrite in black shale. To further investigate the association of arsenic to clay, hematite and possibly other minerals in these rocks, I conducted leach experiments using a composite sample (HW-3033) of red mudstone from 30 to 33 feet (9.14 to 10.06 m) with an average arsenic concentration of 4.5 mg/Kg and a sample (HW-394) from 394-feet (120.09 m) with 13 mg/Kg arsenic as described in table 2.3. Table 2.5 shows minerals generally present in the red mudstones and siltstones of the Passaic Formation. Interestingly, water samples from high-yielding water-bearing zones

intersecting the 300 to 400 foot (91.44 to 121.92 m) interval in HW6, a 400-foot-deep (121.92 m) well adjacent to the HW-Core, have arsenic concentrations ($\sim 45 \mu\text{g/L}$) about 9 times higher than from the 10 to 100 foot (3.05 to 30.48 m) interval ($\sim 5 \mu\text{g/L}$).

The results in table 2.6 show the whole rock compositions of unleached and leached-residual samples after exposure to a sequential leach of acetic acid followed by oxalic acid as described in the methods section and in the references below table 2.6. I conducted an acetic acid leach procedure to evaluate element associations with the acid soluble carbonate minerals (appendix A). Chemical analysis of the acetic acid leachate (table a.1 in the appendix) show that although the carbonate phases dissolved, the arsenic concentration is very low indicating that those phases are not a source of arsenic to ground water. Leachate from subsequent water-soluble leach experiments I performed on a pulverized sparry void and vein fill minerals extracted from red mudstone in the HW-core show a similar result with an As concentration of $< 0.5 \mu\text{g/L}$ in the leachate. Thus, the soluble sparry carbonate and sulfate minerals are not sources of arsenic.

The hot oxalic acid leach targeted the reducible fraction that includes hematite. Because both acetic and oxalic acid will react with carbonate minerals, the results in table 2.6 are actually independent of the acetic acid leach. For comparison purposes, all results in table 2.6 are normalized to silica because of its high bulk concentration and the general stability of silicate minerals when exposed to organic acids. Some destabilization of the weaker silicate mineral surfaces can occur however.

Table 2.5. General mineral composition of fine-grained red rocks in the Passaic Formation mainly after van de Kamp and Leake (1996) but also Van Houten (1956); Oshcudlak and Hubert (1988). Actual mineral percentages can vary in individual rocks.

Mineral	Formula	~ %
Quartz	SiO ₂	29.6
Plagioclase	(Na, Ca) AlSi ₃ O ₈	30.4
Microcline	KAlSi ₃ O ₈	< 5.0
Anhydrite/Gypsum	CaSO ₄	<1.0
Calcite	CaCO ₃	2.9
Ferroan Dolomite	(Ca, Mg)CO ₃ ·(Fe, Mn) CO ₃	<1.0
Hematite	Fe ₂ O ₃	8.0
Illite	(H ₃ O, K) _y (Al ₄ ·Fe ₄ ·Mg ₄ ·Mg ₆)(Si _{8-y} ·Al _y)O ₂₀ (OH) ₄	25.5
Chlorite	(Mg, Fe ²⁺ , Fe ³⁺) ₆ AlSi ₃ O ₁₀ (OH) ₈	3.5

I use an arbitrary element stability scale related to the percent loss in table 2.6 to discuss the data associated with this experimental technique. The less abundant elements Na, K and S show greater stability than silica therefore an artificial increase in concentration is reflected by a negative value. A loss of < 0 percent is considered extremely stable, 0 to 10 percent is stable, > 10 to 20 is moderately stable, > 20 to 40 is unstable, > 40 to 60 is very unstable and > 60 is extremely unstable under the conditions of this procedure.

I first discuss elements reported in weight percent for both samples. K and Na are extremely stable to stable indicating that albite and microcline were unreactive. Ca, Mg and Sr are very to extremely unstable as calcite and ferroan dolomite are extremely reactive when exposed to these acids. Of the three, Mg is most stable, probably because

of its association with the more stable clay minerals illite and chlorite. Si, Al and Ti are stable suggesting that minerals containing these phases, such as the clays and feldspars, are not very reactive. S is extremely stable in HW-3033 but extremely unstable in HW-394. This may indicate that sulfur in HW-3033 is associated with sulfide minerals and in HW-394 it is mainly associated with more soluble anhydrite. Fe unstable in both and is assumed to be associated with the reductive dissolution of hematite. Manganese and phosphorous are both extremely unstable. Mn is more likely associated with dolomite than hematite because the percent loss is more similar to Ca, Sr and Mg than Fe. P is predicted to be associated with apatite, which is apparently very unstable in oxalic acid because it was not detected in leachate from the acetic acid procedure.

Of the minor and trace elements reported in mg/Kg, Cu is extremely stable in both samples. The concentration of Cu in HW-3033 is over 2000 mg/Kg and is likely bound as a sulfide mineral because this sample is less than 10 feet (3.05 m) away from gray and black beds that contain chalcopyrite and pyrite. Pb, Zn, Mo and As are all very to extremely unstable. Because sulfide minerals appear not to be very reactive, these elements are most likely adsorbed or absorbed impurities associated with clay minerals or hematite. The REE, V and U are moderately stable to unstable and are predicted to be associated with the clay minerals and/or hematite.

Table 2.6. Whole-rock geochemical results from the sequential extraction of red mudstone using acetic acid (exchangeable fraction) followed by oxalic acid (reducible fraction).

Element	HW-3033 fresh ¹	HW-3033 leached ²	Percent loss ³	HW-394 fresh ¹	HW-394 leached ²	Percent loss ³
weight %						
Potassium	4.88	5.74	-3.9	4.30	4.30	9.3
Sodium	2.60	3.03	-3.0	3.67	4.28	-5.8
Calcium	3.32	2.94	97.1	1.56	0.11	97.1
Magnesium	4.43	2.7	46.1	3.03	1.91	42.8
Silicon	47.96	54.28	0.0	52.46	57.85	0.0
Aluminum	18.90	20.31	5.0	19.71	20.10	7.5
Sulfur	0.17	0.22	-14.4	0.03	0.01	69.8
Iron	8.47	7.66	20.1	8.13	6.96	22.4
Manganese	0.08	0.02	77.9	0.12	0.03	77.3
Titanium	0.72	0.80	1.8	0.81	0.84	6.0
Phosphorous	0.16	0.01	94.5	0.17	0.01	94.7
mg/Kg						
Strontium	201	78.5	65.5	153.5	93.9	78.5
Copper	2430	2556	7.0	12.80	14.20	-0.6
Zinc	130	80.5	45.3	122.1	63.2	53.1
Lead	14	1	94.0	11	7	42.3
Vanadium	133	136	9.6	142	130	17.0
Molybdenum	2	<1	> 50	2	<1	>50
Sum REE	167.18	157.99	16.5	237.51	195.95	25.2
Uranium	2.82	2.57	19.5	3.37	2.82	24.1
Arsenic	4.5	3	41.5	13	7.2	49.8

¹ original pulverized whole rock sample with > 95 % < 80 mesh.

² sequential extraction: 1st, acetic acid (0.11 molar) solution and pulverized rock, 40:1 solution: rock, was shaken for 16 hours; 2nd hot (90 – 100 C) oxalic acid (0.01 molar) The results from these extractions are given in the appendix.

³ sample results are normalized to silicon because it has a high concentration and silicate minerals are generally stable using these extractions.

Discussion of As sources in red mudstone and siltstone

Correlation analysis in table 2.4 showed that arsenic in the red mudstone and

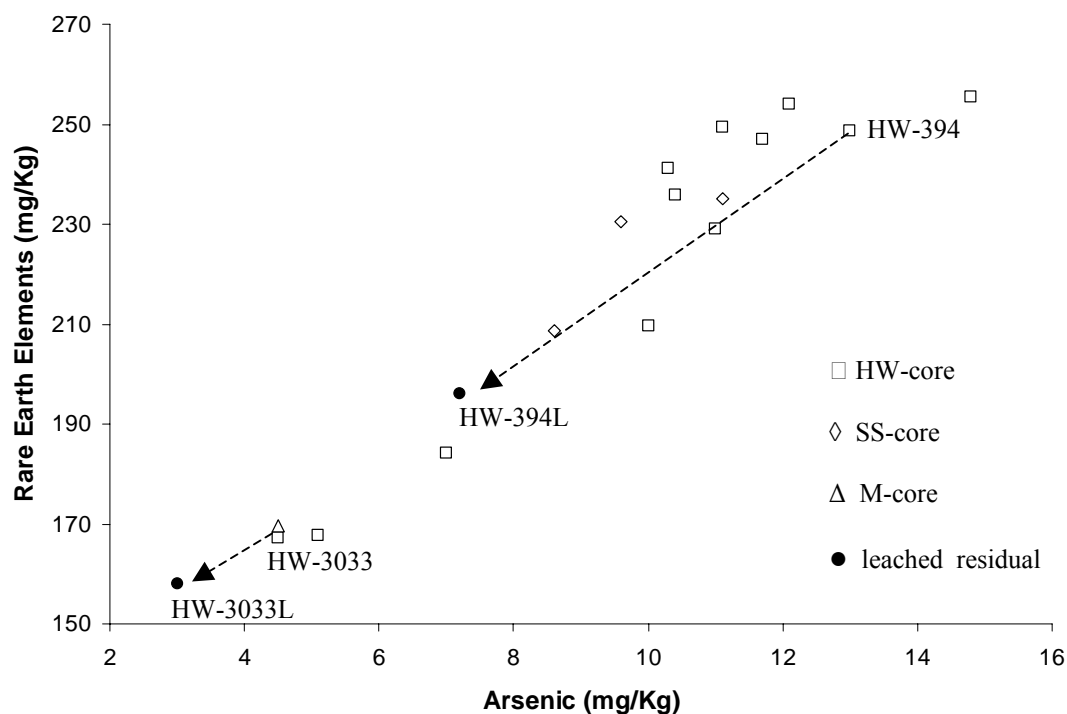


Figure 2.5. Shows the correlation of REE to arsenic in the 16 red mudstones and siltstones from table 2.3. Arrow from unleached HW-394 and HW-3033 to leached samples HW-394L and HW-3033L.

siltstone of the Passaic Formation has a strong geochemical association ($r \geq 0.8$) with REE and a moderate association with iron (r between 0.5 – 0.8). Much Fe, REE and As became mobile during the oxalic acid leach procedure indicating that hematite was unstable and may also be a source of REE and arsenic. Figure 2.6 shows leached residual samples of HW30-33 and HW394 compared to REE versus As in red mudstones and siltstones from the HW-core. Both REE and As were mobilized in proportion to each

during the leach procedure. This is evident because the trend lines of the leached residuals of HW-394 and HW-30-33 closely follow the nearly linear trend of the unleached samples in figure 2.6. Two hypotheses consistent with that observation are: (1) that only clay minerals are a source of arsenic and (2) REE and/or clay minerals associated with hematite coatings are sources. In regard to the first hypothesis, the congruent loss of REE from illite and/or chlorite may be explained by competitive effects due to the abundant free Fe^{2+} released during the reductive dissolution of hematite effectively competing with REE for surface sites on clays. Surface adsorption of REE onto clays and other lithogenous materials and significant buildup on clay surfaces associated with saline waters in marine to non-marine rocks occurs (Della Valle, 1980; Fleet, 1984). The high surface area of clays makes them particularly effective sinks for REE. All the REE have a 3+ oxidation state in nature except for Eu which can also have a charge of 4+ and 3+ respectively. REE are more mobile in acid aqueous environments, particularly hydrothermal ones, than in more alkaline ones (Michard, 1989). The hot oxalic acid leach solution simulates an acidic low temperature hydrothermal environment. Arsenic may similarly be released via competitive adsorption with the oxalate anion (HC_2O_4^-). However, it is not known if the release of REE and As via competitive affects would be proportional to each other as observed. Interestingly, the dissolution of hematite cements would expose more clay surface area thereby increasing the mobilization of As and REE into the leachate.

The second hypothesis assumes that clays in association with hematite coatings are the major source of arsenic and REE. Two generations of hematite are present in

these rocks: early hematite associated with the depositional environment and late hematite formed during the late-stage hydrothermal event. Many workers (Oshchudluk and Hubert, 1988; van de Kamp and Leake, 1996; Tabakh and Schreiber, 1998) have noted hematite coatings on detrital minerals. Late hematite is more than seven times more abundant in sandstone of the Passaic Formation than early hematite (Oshchudluk and Hubert, 1988). Therefore, the iron in the late hematite would mask the statistical correlation between Fe_2O_3 in the early hematite and As, REE and Ti. Iron-oxide coatings associated with clay minerals are known to increase their adsorptive capacity relative to non-coated grains (Lin and Puls, 2000; Foster, 2003). If this iron-oxide rind contained much of the total REE and As, then the reductive dissolution of it during the hot oxalic acid leach procedure would mobilize these elements in proportion to their bulk concentration, as was observed. Therefore, I infer that clay minerals and the early hematite that coats them are the major source of arsenic in the red mudstones and siltstones of the Passaic Formation.

Discussion

Newark basin strata accumulated in three major depositional/geochemical environments: fluvial, shallow lake/playa and deep lake. These depositional environments transitioned temporally and, to some degree spatially, with each other; however a dominant environment defines each formation. The Newark rift basin has tripartite stratigraphy with mostly fluvial/deltaic depositional environments in an early open basin (Stockton Formation) followed by deep lake in a narrow closed basin

(Lockatong Formation) and then shallow lake/playa in a wide closed basin (Passaic Formation) (Schlische and Olsen, 1990). Major syndepositional, early diagenetic and late diagenetic hydrothermal mineral sinks for arsenic include clay minerals and early-hematite mineral coatings associated with fluvial and shallow lake/playa red mudstone, siltstone and sandstone, and low-temperature and hydrothermal pyrite that nucleated and grew early in deep anoxic lake sediments and during the subsequent hydrothermal event. I discuss the fate of arsenic in each of these environments below.

Fluvial environments

Although fluvial environments occurred periodically throughout the basin-fill history of the Newark Basin, they dominated during the deposition of the Stockton Formation. The whole-rock concentrations of arsenic in figure 2.1 show that the mostly fluvial strata of the Stockton Formation have a range similar to the red mudstone in the Passaic Formation. This suggests that the early hematite coatings on detrital minerals making up these rocks were sinks for arsenic as they were in the red mudstone. Arsenic concentrations in ground water associated with these rocks is low relative to that in the Lockatong and Passaic formations (Serfes and others, 2005). This may be the result of a lower median pH, 7.0 versus 7.6 in the Lockatong and Passaic formations, that would retard the desorption of arsenic into solution. Also, the Stockton Formation has the greatest yield of the three formations in part due to the predominance of deeper and higher permeable near surface fractures that would presumably result in less water-rock contact surface area (Rima, 1962; Szabo and others, 1997; Herman, 2001).

Shallow lake/playa environments

Shallow lake/playa depositional environments predominate the upper 2/3 of the Passaic Formation with the lower 1/3 having a greater predominance of deep lake environments more similar to but much less abundant than the Lockatong Formation. The correlation of arsenic with REE in unleached and leached red mudstone in figure 2.5 is interpreted to indicate that As is associated with clay minerals coated with early diagenetic hematite. This interpretation is supported by findings in hydraulically open and closed alluvial basins in the semi-arid southwestern United States (e.g.: Robertson, 1989; Welch and Lico, 1998). Some of these basins are modern analogs of the Newark basin's hydrogeochemical setting that existed in the shallow lake/playa environments associated with vegetated mudflats that had shallow water tables fresh enough to support plant growth (Smoot and Olsen, 1994). Ground water in alluvial basins in Arizona have arsenic concentrations of up to 1300 $\mu\text{g/L}$ (Robertson, 1989). Arsenic occurs as arsenate (HAsO_4^{-2}) in these oxic ground waters and concentrations are controlled by pH and redox conditions that affect the stability of iron oxyhydroxide and the adsorption-desorption of arsenic from it. Aqueous arsenic is associated with red clay beds containing up to 88 mg/Kg of As. Although the concentration of arsenic and anions and oxyanions such as F, V, Se and Mo are associated with iron oxyhydroxides, ubiquitous clay minerals such as montmorillonite may also play a role (Robertson, 1989). Another example occurs around the Carson River in the Carson Desert in Nevada where concentrations of As and U locally exceed 1000 $\mu\text{g/L}$ in shallow ground water (Welch and Lico, 1998). These high concentrations are interpreted to be the result of evaporative concentration of Carson

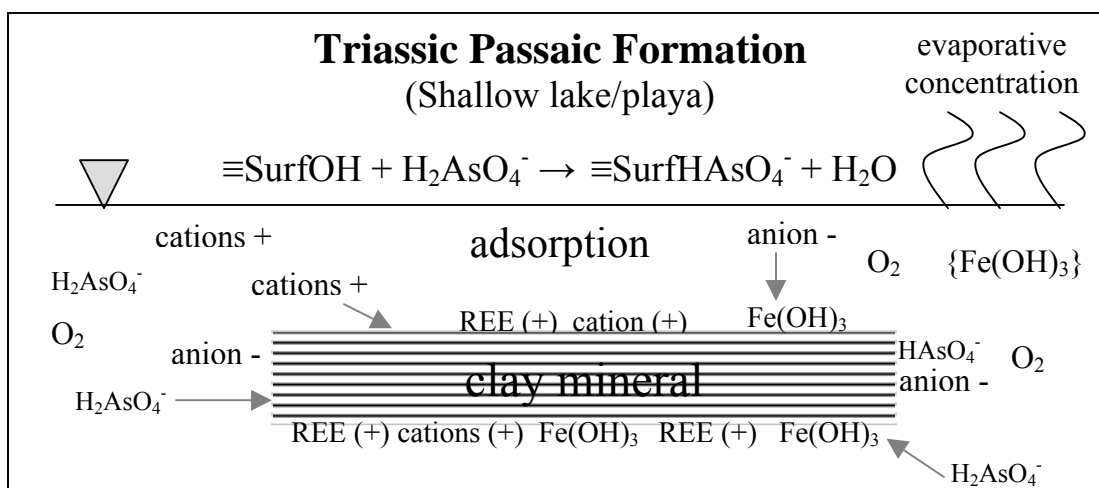


Figure 2.6. Fate of arsenic in red mudstones and siltstones in the Passaic Formation. In the Triassic, evaporative concentration induces arsenic and other anions onto clay edges and cations onto basal planes (Foster, 1999). Precipitated coatings of Fe(OH)_3 on clays and other particles may have enhanced the adsorption of ions (Lin and Puls, 2000; Foster, 2003).

River water because concentrations of As and U correlate positively with Cl. Arsenic and U are associated with adsorption onto and the stability of iron oxide phases. The association of arsenic with clay and hematite in red mudstone and siltstone in the Newark basin and the existence of modern analogs indicates that the syndepositional and early diagenetic adsorptive enrichment of As, REE and other elements onto clays and iron oxyhydroxide coatings is reasonable (figure 2.6). The evaporative concentration of As in the playa environments likely enhanced its adsorption onto those phases.

Deep Lake Environments

During the wet part of the climate cycle, lake-water levels increased. If they were deep enough to maintain anoxic bottom conditions, organic material was preserved giving the lithified sediment a black color. Under sulfide reducing conditions, the nucleation and growth of low-temperature pyrite occurs in the deep lake sediments and

can act as a sink for many metals and arsenic (Berner, 1984). Pyrite cores and small micron sized grains were observed to have the highest concentrations of arsenic and rims around the cores the lowest. My interpretation of these observations is that most of the mobile arsenic was readily incorporated into pyrite early as it nucleated and grew (Figure 2.4).

Hydrothermal Events

Hydrothermal activity during the intrusion of diabase dated by Sutter (1988) at $\sim 202 \pm 1$ Ma and during the younger tectonic inversion event that created a topographically driven hydrothermal flow system between approximately 190 and 180 Ma (Malinconico, 2002). However, the significance of one event versus the other for transporting arsenic, metals and other elements on local and basin wide scales is unclear. The mobilization and precipitation of As, Cu, Pb, and Zn into sulfide minerals during these event(s) apparently preceded the precipitation of hydrothermal hematite (table 2.2). As shown in table 2.4, only Zn has a strong correlation with Fe in the red mudstones. The precipitation of the pervasive late hematite cements occurred at approximately 179Ma and produced a basin wide secondary magnetic signature (component B) coincident with normal polarity (Witte and others, 1991). This short lived chemical precipitation of hematite may have resulted when iron rich intrastratal fluids mixed with somewhat alkaline and oxygen rich thermal waters. Intrastratal Fe was mobilized from the chemical decomposition of iron-bearing minerals such as biotite Oshchudluk and Hubert, 1988). Note that the 179 Ma age of this magnetic signature is currently under debate and may be

revised 10s of millions of years older (Paul Olsen, Personal Communication). The strong association of As with REE and REE with Ti suggests a clay association (table 2.4). The moderate to weak correlation of As with Fe, and the increase in As and Y concentrations in bleached mudstone due to the reductive dissolution and loss of hematite cements (4.0 reduced to 0.5 weight percent hematite) as noted by Sclar and Moses (1991) strongly suggests that hydrothermal or late hematite is not a major source of As in red mudstones.

Prediction

If the geochemistry of the geologic members and associated strata in the Newark basin are laterally consistent, then the prediction of the spatial distribution and concentration of arsenic in black/gray shale and red mudstone and siltstone may be theoretically possible. Because sediment source areas and depositional environments within the basin appear to have been temporally similar with some spatial variation, at least on some local scale it is reasonable to expect this consistency. Evidence to support that assumption is lacking, however, and additional work to verify it is needed.

Conclusions

1. The major lithogenic sources of arsenic in the Newark basin are early diagenetic low temperature and late diagenetic hydrothermal pyrite in anoxic sediments and detrital

and early diagenetic clay minerals that are coated with early hematite in more oxic sediments.

2. The early fate of arsenic was controlled by the geochemical character of the depositional environment that resulted from climatic cycle variations coupled with the tectonic evolution of the basin. Post-deposition hydrothermal activity appears to have mobilized some As in some locations.
3. In the Lockatong and Passaic formations arsenic concentrations are highest in the pyritic gray and black shales. In the red mudstones of the upper 2/3 of the Passaic Formation that I studied, arsenic concentrations are associated with REE and therefore presumably the clay content of the rock itself. Early hematite that coats clay and other minerals enhanced the adsorption of arsenic. The existing evidence suggests that the late hematite cements associated with the hydrothermal event are not a major source of arsenic but may be a minor source.
4. Semi-quantitative prediction of arsenic concentrations in rocks of the Newark basin may be possible on some spatial scale. However, an understanding of the specific hydrogeologic and aqueous geochemical conditions associated with arsenic mobilization and transport are required to predict arsenic concentrations in ground water.

Chapter 3. Mobilization of Arsenic from Clay Minerals in Red Mudstone and Siltstone to Ground Water in the Passaic Formation of the Newark Basin

Introduction

This chapter focuses on understanding the mobilization mechanisms affecting the release of arsenic to ground water from the clay-rich red mudstone and siltstone of the Passaic Formation. My original working hypothesis for arsenic source and mobilization in the Passaic Formation centered on the pyrite-rich black and gray shale that is intercalated with the predominant red strata. However, I subsequently found that many wells with elevated arsenic concentrations intersect water-bearing zones comprised of only red strata, and therefore that strata was suspected of being a source of arsenic to ground water. Based on the correlation between REE and arsenic discussed in chapter 2, the major source of arsenic in red mudstone and siltstone in the Passaic Formation is clay minerals such as illite and chlorite that are coated with early hematite. To evaluate the mobilization character of arsenic from these minerals in red mudstone and siltstone, I present and discuss the chemistry of the water-soluble fraction (leachate) from water-rock leach experiments. The rock samples used in these experiments are mainly from the 400-foot (121.92 m) HW-core that contains red, gray and black mudstone and siltstone collected adjacent to the 400-foot (121.92 m) public supply well (HW6) that consistently has 45 +/- 5 µg/L arsenic.

I next briefly discuss and dismiss two alternative hypotheses for arsenic mobilization in the red strata of the Passaic Formation. One is that mobile arsenic is associated with the dissolution of soluble sparry minerals such as calcite, dolomite and gypsum in the ground-water conductive-voids. I conducted water soluble leach experiments using sparry mineral material from void fillings and a vein from the 254-254.5 (~ 77.42 m) and 309-310 foot (~ 94.18 m) sections of the HW-core, respectively, in a similar manner to those described in this chapter for red mudstone and siltstone. Leachate from those experiments yielded arsenic concentrations of $<1.0 \mu\text{g/L}$ in both the void and vein fill material indicating they are not a likely source of arsenic to ground water. The second hypothesis is that arsenic mobilization is the result of the reductive dissolution of ubiquitous hematite. This possibility is not supported by field data since aqueous iron concentrations are very low in wells with elevated arsenic concentrations in the Passaic Formation. For example, Hopewell 6 with $45 \pm \mu\text{g/L}$ As has an Fe concentration $< 0.5 \mu\text{g/L}$ (table 1.8) and I measured an Fe concentration of $< 5 \mu\text{g/L}$ As in a residential well with $57 \mu\text{g/L}$ As that is in the upper Passaic Formation. If hematite is dissolving, iron concentrations should be higher.

Field Observations

The field observations presented here (chapter 1 of this dissertation and Serfes and others, 2005) are from reconnaissance sampling of private wells in a 200 square mile (518 km^2) study area in the Newark basin in New Jersey (figure 1.1). This study showed that of the three thickest formations, the Passaic and Lockatong have the highest arsenic

concentrations with more than 15 percent of the wells exceeding 10 µg/L As. Assessment of potential mobilization mechanisms active in the Passaic Formation are based on identified natural sources and geochemical observations associated with well water containing elevated arsenic concentrations. Arsenic concentrations in some individual wells sampled multiple times over periods of months and years have generally varied by less than 20 percent indicating a steady-state geochemical system. Ground water with arsenic concentrations greater than 10 µg/L in the Passaic Formation in the Newark basin are characterized by:

1. Similar Ca-Mg,-Na bicarbonate type water as most ground water in the Passaic Formation
2. Dissolved oxygen concentrations (DO) < 3.0 mg/L (figure 3.1)
 - Note: DO usually < 1.0 mg/L if As > 20 µg/L
3. Arsenate, As (V) > 95 % arsenic total
4. pH range between 7.5 to 8.2 (figure 3.1)
 - Note: pH of approximately 8.0 if As > 20 µg/L
5. Generally low iron and manganese concentrations
6. Average sulfate and total dissolved solids concentrations for the Passaic

Also, an association with dissolution zones formed by the solution of secondary calcite +/- dolomite +/- gypsum in interconnected voids is observed in several wells with high As concentrations investigated for this study.

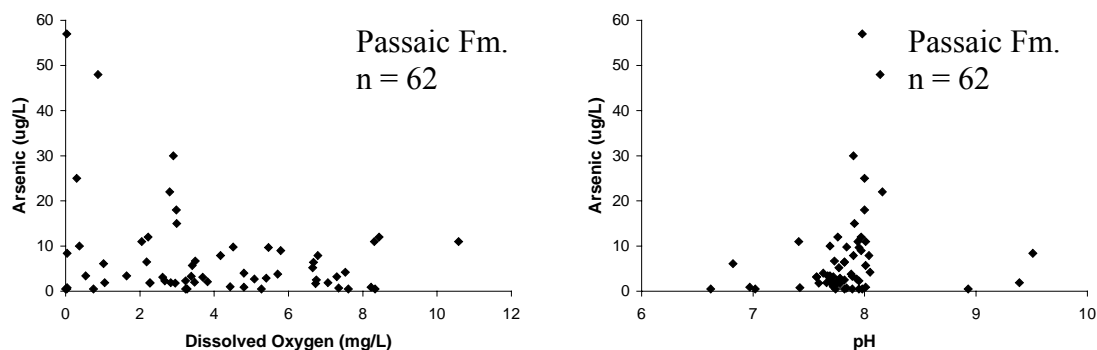


Figure 3.1. Arsenic versus dissolved oxygen and pH in ground water in the Passaic and Lockatong formations in the western Newark basin in New Jersey.

Materials and Methods

I conducted leach experiments using a mixture of pulverized rock and doubly distilled deionized water to evaluate the mobilization potential of arsenic from the sedimentary bedrock making up the Passaic Formation. The rock samples used in these experiments are from the 400-foot (121.92 m) long HW-core. For the first leach experiment I used samples of black, gray and red shale and siltstone from between 18 and 31 feet (5.49 to 9.45 m) in depth in the HW-core to compare As mobility between the different rock types. When pulverized into a powder, over 95 percent of these samples passed through a 80 mesh screen. The leach procedure and results are described in more detail below. I conducted subsequent leach experiments to evaluate mobilization mechanisms and master variables affecting arsenic mobilization. For most of these experiments I used red mudstone from 392 to 393 feet (~ 119.48) ~ in depth in the HW-core (14.7 mg/Kg) and, when pulverized, over 75 percent passed through a 80 mesh

screen. The pulverized rock was thoroughly mixed to ensure comparability between sample results.

A general description of the procedure I used follows. Pulverized rock samples and doubly distilled deionized water are mixed in 250 ml Nalgene Erlenmeyer flasks for these experiments. Samples are agitated for a prescribed period dependent on the goals of the experiment using a Burrell Wrist Action Shaker. Immediately following agitation, all samples are centrifuged for one-half hour at up to 3600 rpm using an International Equipment Company 4B centrifuge and filtered through a 0.45-micron Gelman filter to remove any remaining suspended particulates. The filtered samples of leachate are placed into 120 ml Nalgene sample containers for transport to the laboratories. No preservatives are used. All arsenic analyses are conducted using ICP-MS with a minimum detection limit of 0.3 µg/L or less. Other elements were analyzed using ICP-MS, ICP-OES and ion chromatography at Activation Laboratories in Ancaster, Ontario in Canada. Some samples were analyzed using ICP-MS at the Environmental and Occupational Health Sciences Institute/New Jersey Department of Environmental Protection Analytical Center at Rutgers University. Whole rock geochemical analysis is described in the Analytical Methods section in chapter 1 of this dissertation.

Arsenic Leach Potential of Red, Gray and Black Mudstones and Siltstones

I conducted an evaluation of the potential for arsenic to become mobile during water-rock contact using red, gray and black mudstone and siltstone in the Passaic

Formation. Samples of red (4.5 mg/Kg As), gray (12.6 mg/Kg As), and black (52.4 mg/Kg As) strata from between 18 and 31 feet (5.49 to 9.45 m) in the HW-core were used. Pyrite is ubiquitous in the black shale and I analyzed point concentrations of up to 3000 mg/L of arsenic using electron microprobe techniques (Serfes, 2005). Over 95% by weight of pulverized rock in all these samples is less than the -80-mesh size fraction. In this experiment I exposed 500 grams of pulverized rock to 500 ml of doubly distilled deionized water for 1 hour per week for 20 weeks following the Accelerated Weathering of Solid Materials procedure outlined in ASTM (2001).

Evaluating Whole-Rock Arsenic Concentration Versus Arsenic Mobilization

I compare the concentration of arsenic in six samples of pulverized red mudstone and siltstone from two rock cores in the Passaic Formation, the HW-core and one collected adjacent to a private well with 57 $\mu\text{g/L}$ arsenic, with the concentration of arsenic in leachate from these rocks. I mixed 5 grams of pulverized rock with 200ml of doubly distilled deionized water and agitated the mixture for 16 hours as per a modified version of the BCR Technique described in Rauret and others (1999).

Evaluating Surface Area Versus Arsenic Mobilization

To evaluate the concentration of arsenic in the water soluble fraction as a function of surface area I mixed 5, 10, 20, 40, 80 and 160 grams of pulverized red mudstone (HW 392-393) containing 14.8 mg/Kg arsenic with 200ml of doubly distilled deionized water.

These samples were agitated for 16 hours as per a modified version of the BCR Technique described in Rauret and others (1999).

Evaluating Arsenic Mobilization at Various pH Values and in the Presence of $\text{Na}_2\text{H}_2\text{PO}_4$

I conducted an evaluation of arsenic concentration versus stable pH in the aqueous leachate to better understand the mechanisms associated with the mobilization of arsenic in the natural ground-water system. Stabilized pH values of 8.0, 8.5 and 9.0 were maintained using a 50 micromolar bicine, $\text{C}_6\text{H}_{13}\text{NO}_4$, buffer solution ($\text{pK}_a = 8.35$). A 50 micromolar hepes, $\text{C}_8\text{H}_{17}\text{N}_2\text{SO}_3$, buffer solution ($\text{pK}_a = 7.55$) maintained pHs of 6.5, 7.0 and 7.5. Initially, each sample contained 5 grams of sample HW392-393, containing 14.8 mg/Kg arsenic, with 200 ml of DDW. This initial mixture was agitated for two hours to allow the solution to reach pseudo equilibrium with the solid. Each sample was then titrated up to the target pH values using KOH. If the target pH was exceeded, HCl was added to lower and thereby adjust the pH to the target value. This procedure took approximately one hour. The pH-adjusted samples were then agitated for an additional 21 hours for a total of 24 hours of contact time. In order to assess the competitive desorption of arsenic from the rock material I also used a solution containing 50 micromolar of NaH_2PO_4 buffer ($\text{pK}_{a2} = 7.21$) adjusted to a pH of 7.5.

Kinetic Study: Arsenic Mobilization as a Function of Time

To evaluate the rate that arsenic goes into solution I conducted a kinetic study using 5 grams of sample HW 392-393 per 200-ml doubly distilled deionized water with contact times of 9.6, 96, 960 and 10,760 minutes. Samples were continually agitated during this study. No pH buffers were used.

Results

Arsenic Leach Potential of Red, Gray and Black Mudstones and Siltstones

Table 3.1 gives the arsenic concentrations, pH and specific conductivity in the leachate samples. Average arsenic concentrations in leachate of $\sim 6 \mu\text{g/L}$ from the red is greater than $\sim 3 \mu\text{g/L}$ from the black samples which is greater than $\sim 1 \mu\text{g/L}$ from the gray mudstone and siltstone. Microscopic examination of pyrite in the pulverized black shale (52.4 mg/Kg, As) showed that it had not oxidized after 20 weeks and therefore presumably was not contributing arsenic to the leachate. The arsenic concentrations in the leachate versus the week the sample was collected are shown in figure 3.2. The observation that the red siltstone leached higher concentrations of As than the black and gray shale prompted me to consider the red strata as a source of arsenic to ground water in some hydrogeologic settings.

Table 3.1. Shows pH, specific conductivity (SC) in us/cm, and arsenic (As) concentrations in $\mu\text{g/L}$ during the 20 week leach procedure for red, black and gray pulverized sedimentary rock.

	Red			Black			Gray		
Week	pH	SC	As	pH	SC	As	pH	SC	As
1	7.7	1200	5.52	7.6	5600	3.27	7.5	3000	0.97
2	7.8	260	7.81	7.7	2700	2.07	8.1	440	1.16
3	7.8	230	6.60	7.9	1460	3.09	8.1	360	1.34
4	8.1	202	7.66	8.1	496	3.11	8.3	358	1.30
5	8	192	7.58	8.2	322	3.71	8	301	1.35
6	8.1	189	6.61	8.1	356	3.36	8	391	1.13
7	7.4	218	6.50	7.5	377	2.93	7.7	422	0.97
8	7.2	167	7.18	8.2	185	3.31	8	204	1.00
9	7.5	185	6.06	7.6	286	2.95	8	291	1.11
10	7.6	166	6.58	7.1	258	2.83	7.3	355	0.91
11	7.2	157	5.57	7.5	269	2.66	7.4	383	0.86
12	7.5	177	5.45	7.8	249	2.73	7.8	307	0.90
13	7.2	173	5.21	8	251	2.42	8	330	0.53
14	7.5	163	5.90	7.4	245	2.77	7.7	344	0.85
15	8.1	173	5.29	6.9	231	2.40	8.1	306	0.89
16	8.1	160	--	7.7	215	--	8.1	281	--
17	7.9	150	4.68	7.9	181	2.56	8.1	282	0.59
18	7.6	168	--	7.5	224	--	7.7	328	--
19	8	167	--	8.2	172	--	8	265	--
20	7.5	161	4.01	8	175	2.24	7.8	246	0.51

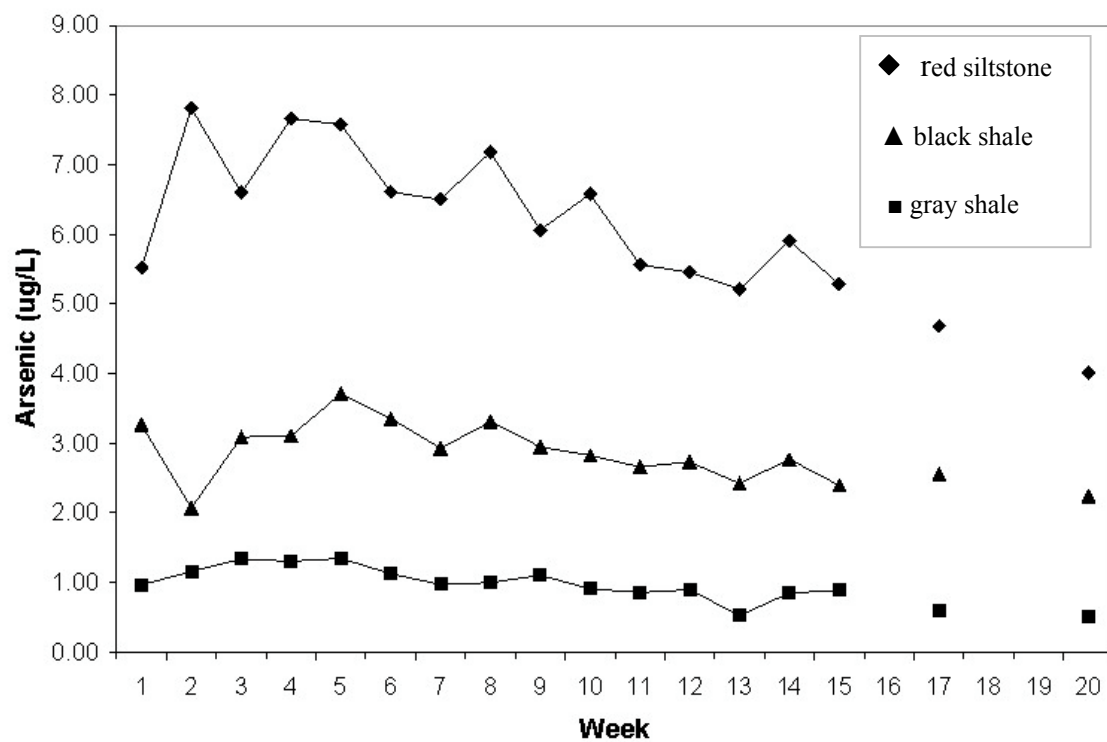


Figure 3.2. Arsenic concentration in leachate versus week of sample collection.

Evaluating Whole Rock Arsenic Concentration Versus Arsenic Mobilization

Table 3.2 and figure 3.3 show arsenic concentrations in pulverized rock from six separate samples of red mudstone and siltstone and in the associated leachate after a 16-hour leach procedure. These data show that there is a strong linear correlation, $r = 0.81$, between arsenic concentrations in the rock and that in the leachate.

Table 3.2. Concentrations of arsenic in pulverized rock from six separate red mudstones and siltstones and associated leachate after 5-grams of pulverized rock was mixed with 200 ml of doubly distilled deionized water and agitated for 16-hour.

Rock mass (grams)	Arsenic rock (mg/Kg)	Arsenic leachate ($\mu\text{g/L}$)
5	4.5	2.05
5	9.6	4.13
5	11.1	4.67
5	11.1	13.5
5	13	12.3
5	14.8	14.3

The graph of whole rock concentrations of arsenic in red mudstone and siltstone versus that in leachate shows a positive trend (figure 3.4).

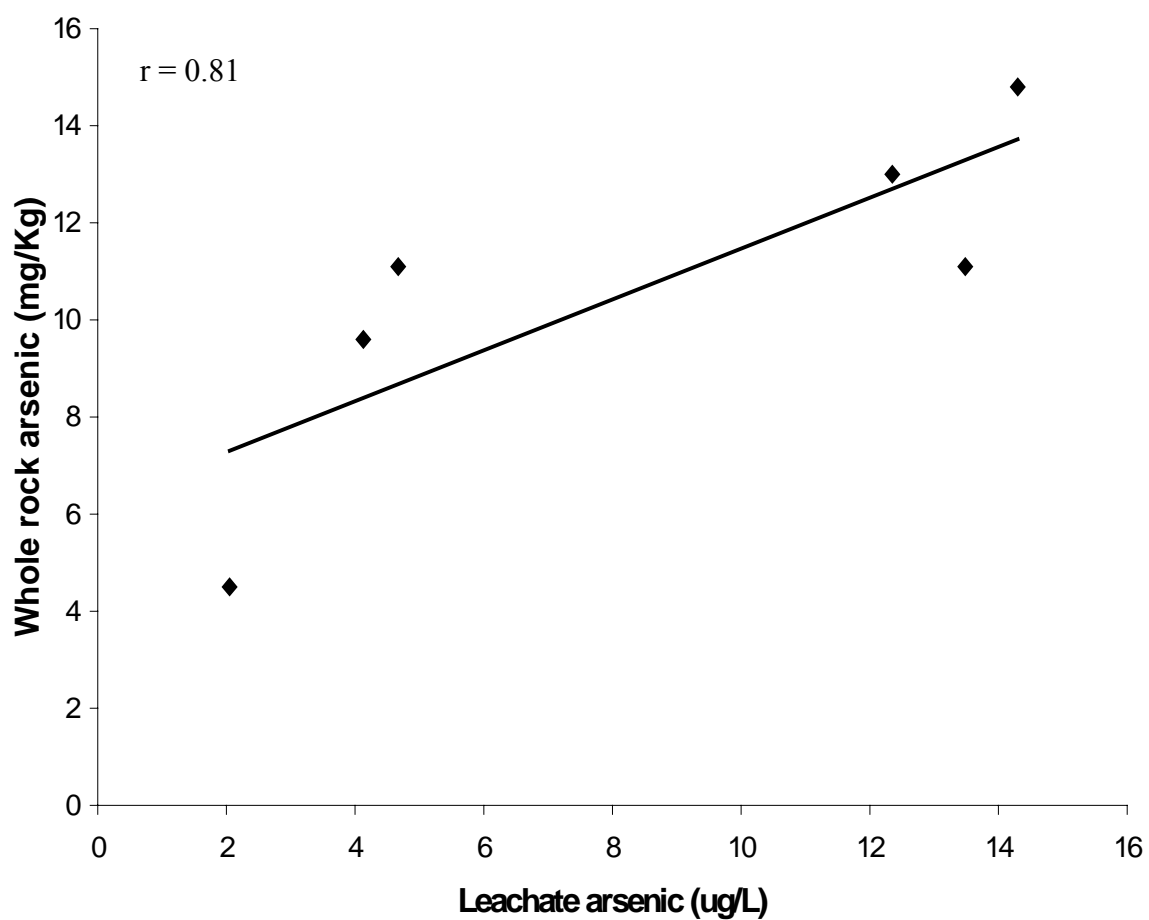


Figure 3.3. Whole rock arsenic concentrations versus leachate arsenic concentrations for six samples using 5-grams of pulverized rock to 200 ml of doubly distilled deionized water followed by a 16-hour agitation procedure.

Evaluating Surface Area Versus Arsenic Mobilization

Table 3.3 provides data from the evaluation of rock surface area versus arsenic mobilization in aqueous solution. Arsenic concentrations in leachate ranged from 14.3

Table 3.3. Mass of pulverized rock (red mudstone, 392-393) in 200 ml of doubly distilled deionized water used in 16-hour agitation procedure. The leachate pH, specific conductivity (SC) in us/cm and arsenic (As) concentrations are listed.

Rock mass (grams)	pH	SC (us/cm)	Arsenic (µg/L)
5	8.16	30	14.3
10	7.59	35	19.2
20	7.58	46	25.0
40	7.60	75	52.6
80	7.45	110	74.4
160	7.40	185	103

µg/L for a pulverized rock to water ratio of 1:40 to just over 103 µg/L for a ratio of 0.8:1 for a 16 hour exposure time (figure 3.4). The trend of arsenic concentrations versus surface area is shown in figure 3.5. A relative surface area of 1 is equal to a 1:40 rock to water ratio. The variation of arsenic concentration to relative surface area (RSA) in these experimental results can be described by the power function:

$$\text{As } (\mu\text{g/L}) = 13.164(\text{RSA})^{0.604}$$

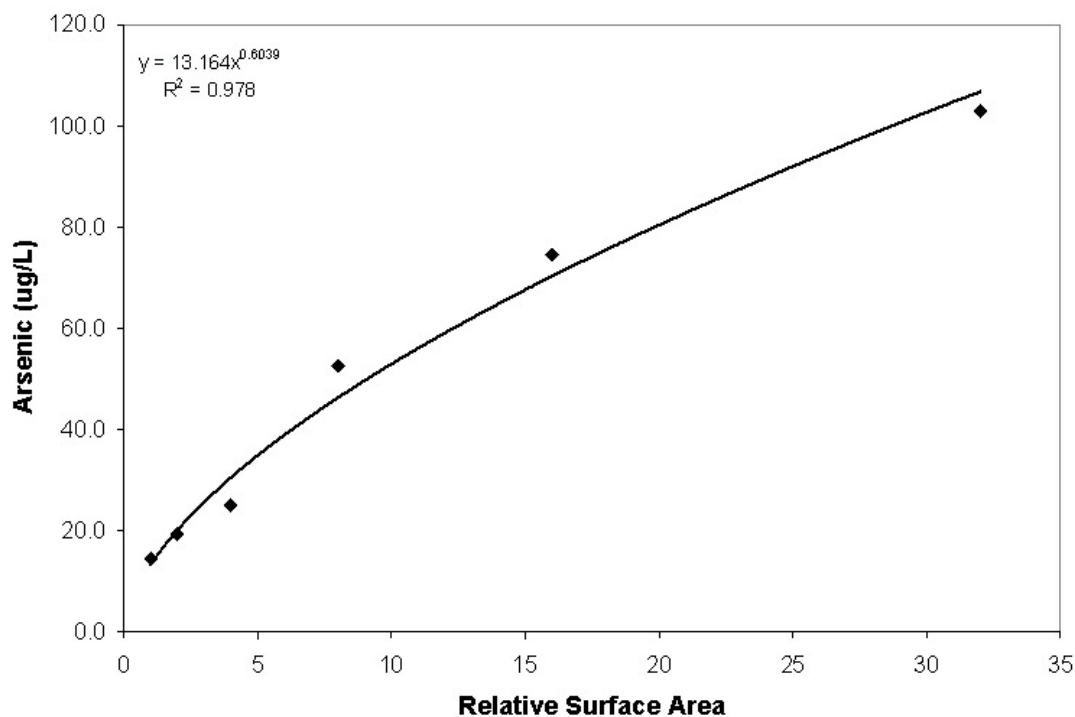


Figure 3.4. Arsenic concentrations versus relative surface area of pulverized rock. A relative surface area of 1 is equal to a 1:40 rock to water.

Evaluating Arsenic Mobilization at Various pH Values and in the Presence of

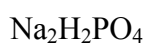


Table 3.4 lists data from the leach experiments that assessed arsenic mobilization versus pH and the competitive ion phosphate. All final leachate pH values were within

Table 3.4. Lists buffers used to stabilize the pH in a mixture of 200 ml of doubly distilled deionized water and 5 grams of pulverized rock, the buffered pH of the leach experiments, the final leachate pH after 24 hours, and the As concentration.

Buffer	Buffered pH	Final pH	Arsenic ($\mu\text{g/L}$)
Hepes	6.5	6.55	6.9
Hepes	7.0	7.02	5.6
Hepes	7.5	7.52	12.2
NaH_2PO_4	7.5	7.53	30
Bicine	8.0	7.98	16.7
Bicine	8.5	8.49	12.6
Bicine	9.0	9.00	15

0.05 of the original KOH adjusted pH. Arsenic mobilization clearly increased from a pH of 6.5 to 8.0 and then decreases slightly at greater pH values (figure 3.5). The maximum arsenic concentration at a pH of 8.0 is 16.7 $\mu\text{g/L}$. The NaH_2PO_4 buffer (50 micromolar) was adjusted to pH 7.5 and yielded an arsenic concentration of 30 $\mu\text{g/L}$, that is, ~ 2.5 times more than in the non-phosphate sample at the same pH. This indicates that competitive ions such as phosphate can enhance the mobilization of arsenic from these rocks.

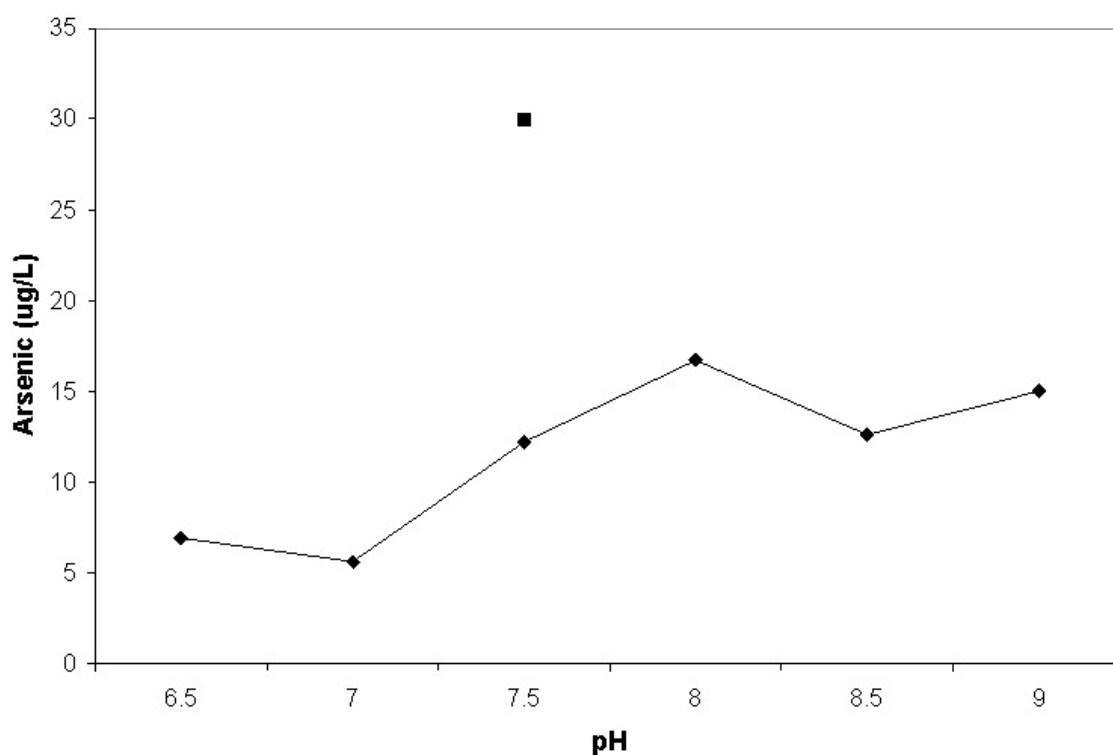


Figure 3.5. Arsenic concentration versus pH using bicine and hepes buffers. NaH_2PO_4 buffer results shown by (■).

Kinetic Study: Arsenic Mobilization as a Function of Time

Table 3.5 and figure 3.6 give results from leach experiments assessing arsenic mobilization as a function of time. It must be noted that this is an unconstrained experimental assessment because master variables such as pH and ionic strength are not controlled. Therefore, this is a cursory examination of the rate of arsenic mobilization from red mudstone.

Table 3.5. Results from kinetic experiment showing contact time of 5 grams of pulverized red mudstone (HW 392-393) in 200 ml doubly distilled deionized water and the, pH, specific conductivity and arsenic concentration after agitation.

Contact time (hours)	pH	Conductivity (us/cm)	Arsenic ($\mu\text{g/L}$)
0.16	6.23	16	1.9
1.6	7.00	20	2.5
16	7.95	35	12.9
179	8.25	55	22.7

Arsenic mobilization as a function of time can be described mathematically by the equation:

$$\text{As}(\mu\text{g/L}) = 3.12\text{Ln}(\text{hours}) + 4.87$$

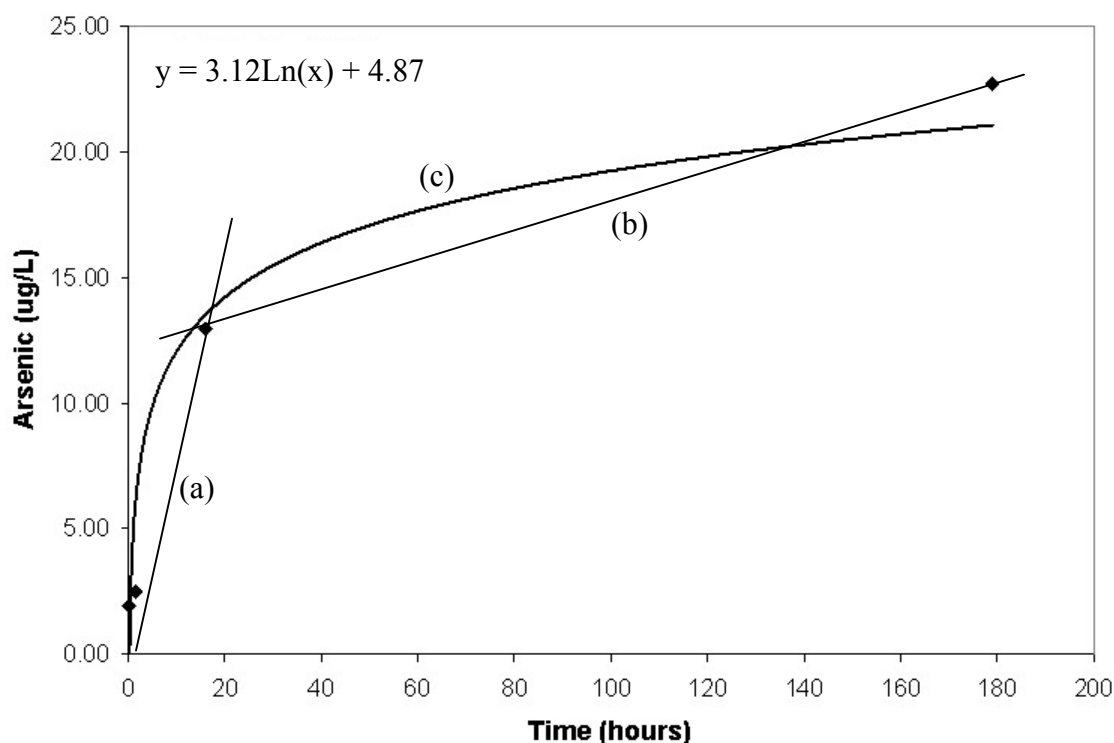


Figure 3.6. Arsenic concentration versus contact time. (a) Steep slope indicates rapid initial desorption of As. (b) Less steep slope shows slower As desorption and a more steady state geochemical condition. (c) Is the best-fit curve illustrating the time dependent mobilization of As.

Discussion

The result of leach experiments using pulverized red mudstone and siltstone demonstrate that arsenic concentrated on hematite-coated clay minerals in shallow lake/playa deposits can be readily mobilized into dilute aqueous solutions. These experiments are thought to simulate ground water–rock contact in the Passaic aquifer, and therefore the results yield clues to the mobilization character and mechanisms in the natural setting. Results of the first leach experiment I conducted are shown in table 3.1

and figure 3.2 and reveal that red strata can be significant sources of arsenic to ground water. Several speciation analyses using an anion exchange resin technique developed by Dr. Xiaoguang Meng, School of Engineering, Stevens Institute of Technology and based on Fricklin, 1983, performed during the 20-week leach experiment showed that the arsenic being leached from the red siltstone was dominantly arsenate, As(V). This is not surprising considering the oxic nature of the hematite-rich red mudstone and siltstone. Furthermore, Serfes and others (2005) showed that ground water in the Passaic is dominantly As(V) (Serfes and others, 2005). In addition to the oxic nature of this sedimentary rock, other factors favor As(V) over As(III). Lin and Puls (2000) determined that arsenite (H_3AsO_3^0) that adsorbs onto clay minerals is eventually oxidized to arsenate (H_2AsO_4^-). Also, manganese oxides rapidly oxidize As(III) to As(IV) (Driehaus and others, 1995; Scott and Morgan, 1995). Therefore, the oxic depositional environment, potential oxidation of arsenite (H_3AsO_3^0) to arsenate on clay surfaces and the occurrence of manganese oxides coating open fractures and voids in the Passaic Formation explain the predominance of arsenate in the aquifer.

The concentration of arsenic in leachate is directly proportional to that in the pulverized rock it is in contact with (figure 3.3). The slightly erratic concentration associations shown in this graph (figure 3.3) may be due to the variable exposure of arsenic-rich surfaces between these different rocks. However, in the aquifer, the concentration of arsenic in ground water appears to be proportional to the concentration of arsenic in the rock it contacts. For consistency, subsequent leach experiments I performed used a red mudstone associated with WBZs transmitting water with greater

than 45 $\mu\text{g/L}$ arsenic and having an arsenic concentration of 14.8 mg/Kg (HW 392-393). The results of the relative surface area versus arsenic mobilization (figure 3.4) illustrate that the degree of water-rock contact is directly and positively related to the arsenic concentration in the leachate. This indicates that water-rock contact along the flow path in the aquifer favors greater arsenic mobilization and therefore concentration in ground water. The pH dependence of arsenic mobilization demonstrated in (figure 3.5) is similar to that from field data collected from private wells (figure 3.1) with maximum mobilization at a pH of approximately 8.0. I interpret the maximum mobilization of As at pH 8.0 to indicate that the surface of goethite/hematite, with a point of zero charge of ~ 7.8 to 8.5, is controlling the arsenic concentration in solution via adsorption-desorption reactions (Stumm, 1992). Arsenic desorbed from early hematite coatings on clays and/or adsorbed onto early and late hydrothermally derived late hematite cements are possible mechanisms for the pH dependent control of aqueous As concentrations. The competitive nature of arsenic mobilization with phosphate from these rocks is also evident in figure 3.5, with an almost 250 percent increase in mobilized arsenic from the non-phosphate buffered sample at the same pH. However, analyses of ground water from wells in the Passaic Formation from this study yielded <0.04 mg/L phosphate. Serfes (1994) also reported low concentrations of phosphate in ground water in the Newark basin. Therefore, dissolved phosphate is not a major control on As concentrations in the Passaic Formation. However, the pH and competitive-dependent arsenic mobilization noted in this aquifer material indicates that desorption, not dissolution of soluble phases, is the major release mechanism of soluble As.

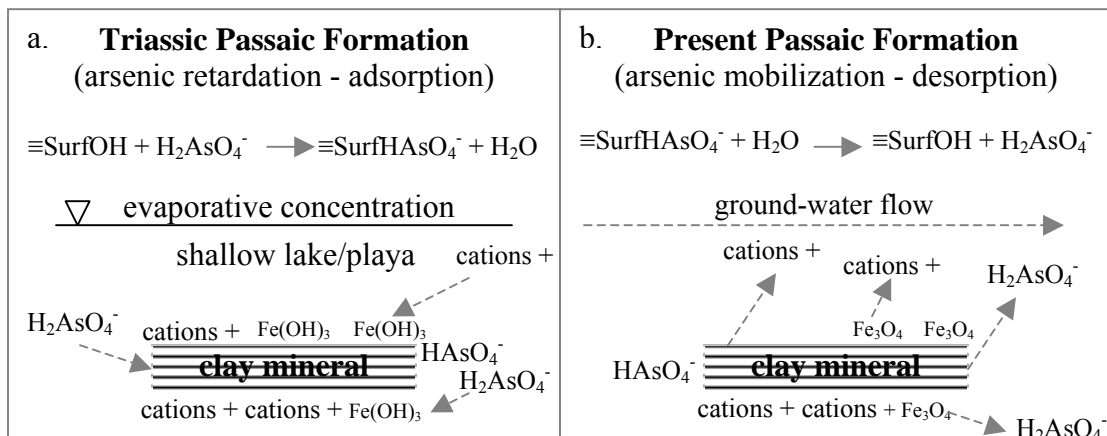


Figure 3.7. Fate of arsenic in red mudstones and siltstones in the Passaic Formation. In the Triassic (a.), evaporative concentration induces arsenic and other anions onto clay edges and cations onto basal planes. Iron oxy-hydroxide coatings will enhance adsorption. At present (b.), arsenic and other anions and cations adsorbed onto clays and hematite (recrystallized $\text{Fe}(\text{OH})_3$) coatings are now mobilized into dilute ground water during water-rock contact.

The slope of line (a) in figure 3.6 shows that the concentration of arsenic in the leachate increased rapidly during the first 16 hours of the kinetic leach experiment. This is interpreted to represent surface reaction rate control. The slope of line (b) is less than (a) indicating that the rate of release of exchangeable arsenate (H_2AsO_4^-) is decreasing and approaching a steady state. The approach of steady state is interpreted to indicate that the concentration of arsenate in solution is high enough to impart transport control to the reaction rate. Ground water dated in a 400 foot (121.92 m) and 35 foot (10.67 m) deep well adjacent to the HW-core yielded ages of 22 +/- 2 years and 30 +/- 2 years, respectively, using CFCs concentrations. Ground water dated for this project from two other wells in the Passaic Formation with elevated arsenic concentrations yielded ages of 26 +/- 2 years and > 50 years. The desorption of arsenic in a matter of hours (figure 3.6) and the relatively much older ground water from the five wells indicate that a temporal steady state concentration will exist in the natural ground-water system.

Based on the findings in this dissertation, the fate of arsenic in the Passaic Formation in the Newark Basin is now better understood. The Late Triassic depositional environments associated with the upper 2/3 of the Passaic Formation were mainly fresh-water oxic vegetated shallow lake and dry playa mudflats (Smoot and Olsen, 1994), which subsequently lithified into red hematite cemented rock. Intermittent suboxic deep lake environments deposited sediments that eventually lithified into organic-rich pyritic gray and black mudstones. During the drying cycle in the oxic environments, evaporative concentration of soluble elements occurred, making shallow lakes and ground water less fresh. Voids, such as root cavities, associated with these vegetated mudflats sometimes contain trapped fine-grained clays and silts (Smoot and Olsen, 1994). At mineral specific saturation concentrations, evaporite minerals were precipitated in voids cavities (van de Camp and Leake, 1996). Mobile elements in the brines, that included metals and arsenic, adsorbed onto mineral surfaces such as clays and the syndepositional/early diagenetic iron-oxyhydroxides that coated them and other minerals (figure 3.7a). The strong correlation between REE and arsenic in whole rock samples of red mudstone and siltstone indicate an arsenic-clay association (chapter 2). It is these syn-depositional and early diagenetic environments that mainly controlled the sedimentary facies, mineralogy and major and trace element distributions. Subsequent diagenesis and the movement of hydrothermal fluids through the basin locally redistributed many of the elements and replaced evaporite minerals with sparry minerals such as calcite, dolomite, gypsum and albite in intrastratal voids. The subsequent dissolution of these sparry minerals create significant WBZs in the host rock (Herman, 2001).

Based on the results of the leach experiments, arsenic mobilization to ground water in red strata in the Passaic Formation are controlled by the following master variables: (1) pH, (2) arsenic concentration in the red strata, (3) degree of water-rock contact, (4) competing ions, and (5) duration of water-rock contact. Of the five master variables, the first three are most relevant to the natural system as major competing ions such as phosphate are lacking and ground water is generally decades to possibly centuries old. Red-beds in the Passaic Formation contain stratigraphic flow zones where secondary, sparry, carbonate and sulfate minerals are dissolved by the recharge and transmission of weakly acidic ground water. These zones are likely sources for the mobilization and transport of lithogenic As (figure 7b). Sparry minerals in these zones buffer and control aqueous pH by dissolution and thereby provide increasing surface exposure of matrix clays. They possess high hydraulic conductivity and supply high yields to wells intersecting them. If the arsenic concentrations in the aquifer matrix material are high, I expect that wells intersecting these zones will supply water with high arsenic concentrations.

I also expect variables affecting the aqueous geochemistry at any point along a stable ground water flow path to be somewhat temporally stable. Therefore, it is not surprising that steady state arsenic concentrations, which are controlled by the first three master variables, occur in most wells in the Passaic Formation.

Conclusions

Results from the leach experiments showed that As concentrations in the aqueous leachate directly correlate with the surface area of water-rock contact, concentration of arsenic in the source rock and duration of contact. Competitive ions such as phosphate and a pH of 8.0 maximize As concentrations in solution indicating desorption and not dissolution as the master mobilization mechanism. Maximum mobilization of arsenic at pH 8.0 is consistent with field observations and suggests that the adsorption/desorption of arsenic on hematite/goethite surfaces, with a point of zero surface charge of ~ 8.0 to 8.5, moderates its concentration in solution. Therefore, at a pH of approximately 8.0, desorption from the clay and early hematite sources is greatest and adsorption onto the late hematite source is the least. Red-beds in the Passaic Formation contain stratigraphic flow zones where secondary, sparry, carbonate and sulfate minerals are dissolved by the recharge and transmission of weakly acid ground water. These zones are likely sources for lithogenic As in wells intersecting them because they buffer and control aqueous pH, provide maximum surface exposure to matrix clays, and provide high hydraulic conductivity and yields to wells intersecting them.

Chapter 4. Summary of Dissertation Findings with Implications for Arsenic Transport, Concentration Prediction and Needs for Further Work Associated with Ground Water in the Passaic and Lockatong Formations

Introduction

This dissertation focused on answering the following four key questions.

1. What are the spatial distribution, concentration and hydrologic and aqueous geochemical settings associated with arsenic concentrations greater than 10 $\mu\text{g/L}$ in the major bedrock aquifers of the Newark basin?
2. What are the major lithogenic sources of arsenic in those aquifers?
3. What chemical mechanisms and hydrogeologic settings favor the mobilization of arsenic from those sources?
4. What physical and chemical processes control the mass transport of arsenic in these aquifers? Can arsenic concentrations in ground water be predicted?

The summary below briefly describes the findings in chapters 1 through 3 as they relate to questions 1, 2 and 3 above. A conceptual model of arsenic transport and a discussion concerning the prediction of arsenic concentrations in ground water in the Lockatong and Passaic Formation in the Newark basin follows. The final section lists and briefly discusses needs for further work identified during this dissertation work.

Summary

My hypotheses concerning what and how natural sources of arsenic are contaminating ground water in the Newark basin continue to evolve but are much more supported by observations and experimentation than those prior to this work. The updated hypotheses are based on findings from well-water samples, whole rock and mineral geochemical analyses and leach experiments. Well-water reconnaissance sampling discussed in chapter 1 showed that the Lockatong and Passaic formations have the highest percent of wells exceeding 10 $\mu\text{g/L}$. Maximum concentrations of arsenic measured in black, gray and red mudstones and siltstones in the Lockatong and Passaic formations are 240, 50 and 14.8 mg/Kg respectively. One of my first important discoveries during this work was that pyrite associated with black and gray mudstone and siltstone in the Basin contained up to 4-weight percent arsenic. Because of that finding, black/gray shale were originally hypothesized by me to be the major source of arsenic to ground water in both the Lockatong and Passaic formations. In the Passaic Formation, large masses of red beds are intercalated with lesser masses of pyrite-rich gray and black units. In accordance with the original hypothesis, complex flow paths from the black units to wells intersecting only the red units are required to explain elevated arsenic concentrations found in those wells. Because of the hematite-rich nature of the red beds, and the untenable nature of the flow paths required to support some black to red bed flow in some locations, hematite in the red units also became a suspected source of arsenic. Subsequent analysis of whole-rock geochemical data from red beds in the Passaic Formation, discussed in chapter 2, revealed that arsenic has a strong positive correlation with rare earth elements (REE) and

a moderate correlation with iron. Because clay minerals are associated with REE in fine-grained sedimentary rock, I concluded that the As is also associated with clay minerals. However, I also explored the possibility that hematite could also be a source of arsenic by leaching pulverized red strata with hot oxalic acid to reductively dissolve that phase. I found that arsenic and REE are released congruently and concluded that hematite is also a source. Because As is associated with clay, and early hematite coats the clay minerals, I concluded that the major hematite source of As is the early rather than the more abundant late hydrothermal hematite. This conclusion should be validated using sophisticated analytical techniques such as laser-ablation ICP-MS. Another potential source in red beds that was also explored are the soluble sparry (white) minerals such as calcite, dolomite and gypsum that fill interconnected voids in some strata and produce highly permeable zones when they dissolve out (Herman, 2001). Leach experiments showed that these sparry minerals are not significant sources of arsenic to ground water. Although the arsenic in ground water in the Passaic Formation may be associated with clay minerals, pyrite in the Lockatong Formation may still be the ultimate source there. However, clay minerals in the Lockatong Formation may also be a source of arsenic to ground water. More work is needed to evaluate this possibility. The Passaic Formation has the highest measured arsenic concentration in ground water of 215 $\mu\text{g/L}$ and numerically has more wells with unacceptable concentrations because of its greater areal exposure. Therefore, most of the work to assess the mobilization of arsenic in chapter 3 focused on the red mudstone and siltstone of the Passaic Formation.

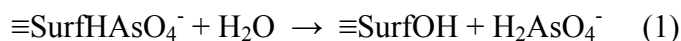
Results from the leach experiments demonstrated that arsenic concentrations in the aqueous leachate directly correlate with the surface area of water-rock contact, the concentration of arsenic in the source rock and the duration of contact. Competitive ions such as phosphate and a pH of 8.0 maximize arsenic concentrations in solution indicating desorption and not dissolution as the master mobilization mechanism. A maximum arsenic concentration at pH 8.0 is consistent with field data and suggests that hematite/goethite, with a point of zero charge of ~ 7.8 to 8.5, moderates the As concentration via adsorption-desorption reactions. Some red units in the Passaic Formation contain strata bound flow zones where secondary, sparry, carbonate and sulfate minerals are dissolved by the recharge and transmission of weakly acidic ground water forming an interconnected anastomosing conduit network. These zones are likely sources for lithogenic arsenic in wells intersecting them because they buffer and control aqueous pH, provide maximum surface exposure to matrix clays, and provide high hydraulic conductivity and yields to wells intersecting them. Models describing the transport of As in the Passaic and Lockatong formations in the Newark basin must be based on these findings.

Transport of Arsenic in the Lockatong and Passaic Formations

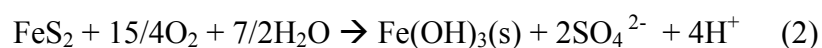
Figure 4.1 shows conceptual models summarizing arsenic sources, mobilization and transport in black/gray shale and red mudstone and siltstone. These models are representative of the Passaic Formation with mostly red units and the Lockatong formation, consisting of mostly black/gray strata. According to the leaky, multi-layered

aquifer system flow model of Michalski and Britton (1997), the advective flow in the Passaic is assumed to be mostly stratabound and anisotropic. This model is assumed to also reflect flow in the multi-layered stratigraphy of the Lockatong Formation. Both model flow paths in figure 4.1 start with dilute, acidic, oxygen-bearing recharge water infiltrating the aquifers.

In the red strata, the dissolution of sparry minerals such as calcite and iron/manganese bearing dolomite in the water bearing zones, raise the pH and release reduced Fe and Mn that can react with and lower the concentration of dissolved oxygen. The removal of these phases also provides fresh clay surfaces for water contact. Results from the leach experiments described in chapter 3 indicate that the arsenic concentrations along the flow path are mainly a function of the arsenic concentration in the rock with which the water is in contact with, the degree of that water/rock contact and the aqueous pH. Although not explored in this dissertation, the concentration of dissolved oxygen, the oxidation-reduction potential and microbes found in these natural aqueous systems may also play a role in arsenic mobilization. Arsenic adsorbed to the hematite-coated clay minerals during the Mesozoic is released into solution via desorption ($\equiv\text{Surf}$, refers to a mineral surface):



In the black/gray strata, pyrite will be oxidized during exposure to oxic recharge waters following the generally accepted overall reaction (e.g.: Howard, 1998):



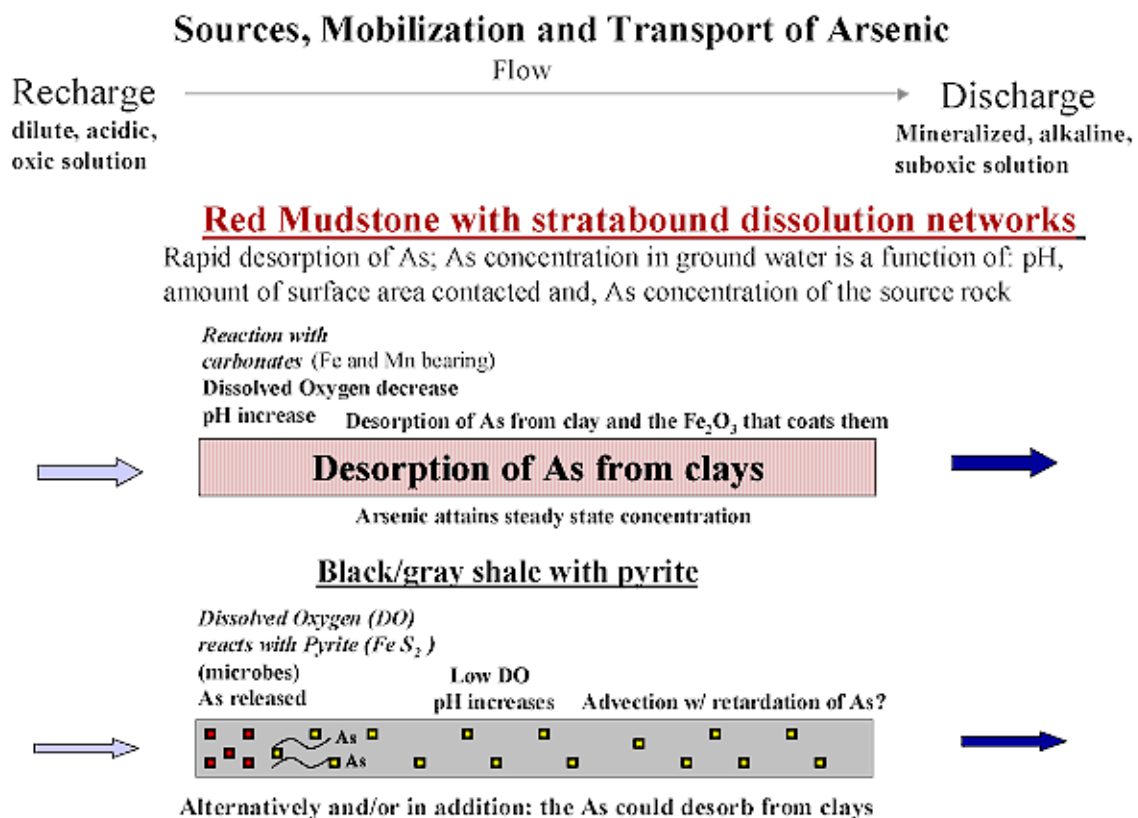


Figure 4.1. Hypothetical sources, mobilization and transport of arsenic in the black/gray shale of the Lockatong Formation and red mudstone and siltstone of the Passaic Formation.

Arsenic contained in the pyrite will then be available for mobilization if the geochemical conditions are favorable. If pyrite is the major source of arsenic to ground water in the black/gray shale, the mobilization of it is expected to occur only when the pyrite is oxidized at the start of the flow path when dissolved oxygen is available. Down gradient from that zone, dispersion, retardation via adsorption and possibly mineral precipitation would decrease aqueous arsenic concentrations. If clays are also a source of arsenic to ground water, desorption from them along the flow path will also occur.

Prediction of the Spatial Concentration of Arsenic in Ground Water

Indirect and direct approaches can be used to predict the spatial concentration of arsenic in ground water. The indirect approach requires identifying the types and spatial distribution of geologic sources of arsenic and understanding the mobilization mechanisms, geochemical environments and ground-water flow characteristics in the hydrogeologic setting of interest. As mentioned above, the arsenic concentration along the ground-water flow path is mainly a function of the arsenic concentration in the rock it contacts, the degree of water/rock contact and the aqueous pH. If these variables are known, it is theoretically possible to predict steady-state arsenic concentrations in ground water in the red beds of the Passaic Formation. Each of these variables is discussed below.

The occurrence of fine-grained red mudstone versus coarser-grained siltstone or sandstone may be an indicator of higher arsenic concentrations in rock because the clay content is expected to be greater. The high-resolution stratigraphic information provided by the Newark Basin Coring Project includes rock-type designations such as claystone, mudstone, siltstone and sandstone (see figure 1.8 for example) throughout the entire length of cores (Olsen and others, 1996). However, the HW-core rocks are classified as mudstones using the Newark Coring Project designations and have arsenic concentrations ranging from 7 to 14.8 mg/Kg. This large range indicates that using rock-type designations alone as a predictive tool for whole rock As concentrations would be crude

at best. However, if the arsenic concentration within individual stratum is approximately laterally consistent, and that concentration is known, then prediction is possible. If it can be shown that this assumption is true, this approach could be attempted by conducting whole rock geochemical analysis on thousands of feet of core at a predetermined frequency. The sampling frequency would have to be determined by quantifying the As concentration variation within the strata. The usefulness of this approach to evaluate arsenic concentrations in the red strata is questionable however until the work necessary to verify its validity is conducted. Determining the lateral and vertical variation of As concentrations within the strata comprising the Passaic Formation would be very expensive and is therefore a limitation. Another limitation of the indirect approach is that it is difficult to envision being able to accurately predict the amount of exposed surface area within the strata bound hydraulic conduits ground water flows through or the spatial variation of aqueous pH in the stratabound water-bearing zone of interest. Therefore, without quantification of the master variables affecting the occurrence of arsenic in ground water, the indirect approach alone is not feasible for the intended application.

The direct approach requires accurately plotting arsenic in well water concentration data from public and private wells on a geologic map and identifying areas and possibly geologic members (see figure 1.3) that have concentrations greater than selected target values. Theoretically, geologic members associated with elevated arsenic in ground-water concentrations in an area with significant data control could be extrapolated into areas lacking such control because similar geochemical conditions are likely to exist. Limitations to this approach are the availability of well-water arsenic

concentration data and the accuracy of geologic mapping at the member scale. Because of privacy issues, the private well testing act data compiled by the NJDEP/Bureau of Safe Drinking Water, which is the largest dataset with arsenic in well water concentrations, is not presently available, even to others within the NJDEP. In addition to that limitation, basin wide geologic mapping at the member scale has not been conducted everywhere. In the northeastern part of the basin the geologic facies change in the Passaic Formation. This change is reflected in coarser-grained lithologies and less black/gray shale marker beds to aid in identifying geologic members. Therefore, accurately relating arsenic concentration data with geologic members in all areas may be difficult and not necessarily applicable because of lateral facies changes. Work is currently underway to obtain the Private Well Testing Act data and to more accurately map geologic members in some areas in New Jersey.

Need for Further Work

Further work that will lead to a better understanding of the sources, mobilization and prediction of As in ground water in the Passaic and Lockatong formations in the Newark basin include:

1. Verifying the major hematite source of As in the Passaic Formation. This could be accomplished by using analytical techniques such as laser ablation ICP-MS to quantify low level As concentrations in early hematite coating clays and other minerals and comparing it to that in late hydrothermal hematite.

2. Determine if pyrite is the major source of As to ground water in the Lockatong Formation. Although pyrite is the major mineral source of As in the black and gray shale, it has not been proven to be the major source of As found in ground water associated with these rocks. Work to verify the major natural As source(s) contaminating ground water in the Lockatong Formation is needed.
3. Determine what role the oxidation-reduction potential (ORP) of ground water in the Passaic and Lockatong formations has on the mobilization of As. It is possible that the destabilization of metal oxide surfaces as a function of ORP could affect the adsorption and desorption of As in solution.
4. Determine the microbiological control(s) of As mobilization and speciation in the Passaic and Lockatong formations.
5. Test the validity of extrapolating the spatial distribution of As concentrations in well water along the trend of geologic strata into areas where no control exists. If it can be shown that this approach can be used to predict As concentrations in ground water a useful As in ground water probability map can be constructed throughout much of the Newark basin.



Appendix 2

Sequential Extraction of Red Mudstone (HW-394): leachate chemistry

Methods

To assess the potential release of arsenic from red mudstone, I analyzed and evaluated the leachate chemistry from water-soluble and a sequential leach using acetic and oxalic acid was analyzed and evaluated. Sample HW-394 (red mudstone) with 13 mg/Kg As was pulverized and 95% by weight was less than the -80 mesh size fraction. This pulverized material was exposed to doubly distilled deionized water (DDW) to evaluate the water-soluble fraction as well as to a separate sequential acetic and oxalic acid extraction to evaluate the acid exchangeable and reducible fractions respectively. The water-soluble extraction procedure used doubly distilled deionized water as the leachant, and for comparison purposes, followed the BCR Technique described for acetic acid which follows. The acid extractable procedure used 0.11M acetic acid solution, a 40 to 1 leachant to sample ratio, and an agitation time of 16 hours as per the BCR Technique described in Rauret and others, 1999. The reducible leach procedure reductively dissolves iron oxides (hematite) (Panias and others, 1996) and uses a 0.01M oxalic acid solution. The reducible procedure followed the acid exchangeable procedure using the same leached rock material and is therefore sequential. The reducible leach solution and pulverized rock, ~ 20:1, is heated 1 hour at 90 to 100 °C, the beaker is then decanted and leachate filtered through qualitative lab filter, the residue is air dried and returned to the

beaker for a total of 5 rounds. The water soluble and exchangeable samples were centrifuged immediately after agitation at up to 3600 rpm for at least one-half hour. All samples were filtered through a 0.45-micron filter to remove suspended particulate. Samples were analyzed using ICP-MS, ICP-OES and ion chromatography at Activation Laboratories in Ancaster, Ontario in Canada.

Results: water soluble and sequential extraction procedure

The composition of leachate from water soluble and sequential leach using acetic and oxalic acid HW-394 is presented in table A-1. Solutes from the water-soluble extraction represent the most readily dissolved and desorbed fraction of the rock material. The solute to sample ratios of 40:1, 20:1 and 5:1 by weight represent relative water to rock surface areas of 1, 2 and 8 times respectively. Although the pulverization process likely broke mineral lattices thereby exposing elements to leaching that would otherwise be tied to the crystalline structure and therefore not labile, the concentration variations as a function of surface area are informative. Sulfate and calcium are probably mostly associated with anhydrite with some of the calcium and magnesium associated with calcite and dolomite. Most of the remaining elements are assumed to have gone into solution via desorption from the iron-coated clay minerals illite and chlorite. All solute concentrations, including arsenic, increase significantly at the solute to sample ratio of 5 to 1.

The concentration of Ca and Mg in the acid exchangeable leachate fraction is dramatically increased from the water soluble indicating that carbonate minerals are dissolved and more metal cations such as Cu, Zn and Pb are desorbed due to the lower pH conditions. The increased iron and magnesium are probably related to the dissolution of ferroan dolomite. Arsenic is assumed not to have been released from the carbonates because of the low concentrations usually associated with those minerals. Also, leachate from experiments using sparry mineral material filling voids and veins in the HW-core had $< 0.5 \mu\text{g/L}$ As. However, if arsenic was released during this extraction it may have a chemical affinity to adsorb on hematite and clay surfaces at the equilibrated pH of ~ 4.2 after 16 hours of contact time.

The oxalic acid or reducible sequential leach clearly dissolved some of the hematite and weaker silicate minerals. Although the arsenic concentration of $93.5 \mu\text{g/L}$ in solution is higher than $17.8 \mu\text{g/L}$ in the water extractable leach with the same leachant to sample ratio, it is not significantly higher given the large amount of iron that went into solution. Therefore, it is assumed that arsenic is not significantly associated with the bulk of the hematite and is more likely associated with the clay fraction and the early hematite that coats it. It is interesting to note that there was a significant increase in the phosphate concentration suggesting that the mineral apatite, which occurs in the Passaic Formation, was dissolved. This may have released the additional arsenic into solution. Because of the aggressive attack of oxalic acid on hematite and the weaker silicates (clay surfaces?) it is further assumed that adsorption onto these phase would be limited even at a pH of ~ 2.0 .

Table A2.1. Leach study results from red mudstone core sample HW-394 (13 mg/Kg).

Element (µg/L)	Water soluble extraction ¹			Sequential Extraction ²	
	Doubly distilled water: sample (weight) Equilibrated pH range: 7.0 to 8.4			Exchangeable Acetic acid ³	Reducible Oxalic acid ⁴
	40:1	20:1	5:1	40:1	20:1
Potassium	7,060	6,310	13,040	12,600	8,930
Sodium	1,510	1,840	5,920	3,690	5,520
Calcium	4,230	3,790	4,920	226,000	39,900
Magnesium	877	897	1,442	51,000	74,200
Strontium	188	212	299	1470	268
Silicon	2,820	2,850	4,340	<20,000	81,900
Aluminum	155	129	391	7,250	81,000
Sulfate	2,910	3,590	8,620	4,870	5,930
Iron	12	15	162	14,800	108,200
Manganese	1.3	1.5	3.8	13,700	1,810
Titanium	1.0	1.1	5.9	11	389
Copper	1.8	1.0	16.2	171	113
Zinc	2.9	3.4	74.8	949	689
Lead	0.07	0.14	0.55	19	90
Vanadium	8.3	9.5	14.9	<10	178
Molybdenum	9.8	15	52.4	<10	30
Sum REE	0.22	0.44	0.93	187.66	439.73
Uranium	0.12	0.14	0.37	4.7	7.42
Phosphorous	<0.02	<0.02	<0.02	<0.02	9,220
Arsenic	12.3	17.8	39.3	15	93.5

¹ doubly distilled water and pulverized rock shaken for 16 hours, no adjustments.

² acetic acid leach followed by hot oxalic acid leach using same pulverized rock samples.

³ acetic acid (0.11 molar) solution and pulverized rock was shaken for 16 hours.

⁴ hot (90 – 100 C) oxalic acid (0.01 molar) solution and pulverized rock heated 1 hour, note that sample was taken during 2nd of 10 sequential reducible extraction rounds.

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Curriculum Vita

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Education

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Lehigh University, Bethlehem, PA	Geological Sciences	MS.	1984
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Recent Professional Experience

Research Scientist 1, New Jersey Geological Survey, NJ	2000 - present
Adjunct Professor, Bucks County Community College, PA	1993 - present
Supervising Geologist, New Jersey Geological Survey, NJ	1991 - 2000

Publications (selection of 10)

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