THE EFFECT OF DROUGHT ON BENZENE CONTAMINATED UNDERGROUND STORAGE TANK SITES IN GEORGIA

by

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(Under the Direction of John F. Dowd)

ABSTRACT

Light Non-Aqueous Phase Liquids (LNAPLs) such as Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) are commonly found in petroleum products. BTEX is a major source of soil and groundwater contamination at underground storage tank (UST) sites that store gasoline and diesel fuels. Accidental releases from these sites can lead to extensive contamination plumes. Various remediation techniques and natural attenuation are used to attempt to clean up sites that have been contaminated by BTEX components. Environmental and geological conditions can influence remediation efficacy. Droughts that cause major water table fluctuations, for example, may increase the rate of natural attenuation of dissolved benzene at UST sites. This study focuses on six contaminated UST sites in Georgia. Data was compiled from reports submitted to the Georgia EPD Underground Storage Tank Management Program, and analyzes how the 2007-2009 drought and changes in groundwater levels affected benzene contamination levels.

INDEX WORDS: BTEX, Benzene, Contamination, Drought, Water Table Fluctuations, USTs, Natural Attenuation

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CHAPTER 1

INTRODUCTION

Light Non-Aqueous Phase Liquids (LNAPLs) such as benzene, toluene, ethylbenzene, and xylene (BTEX) are commonly found in petroleum products. Gasoline, for example, contains approximately 10-20% of BTEX, which is the major source of regulated soil and groundwater contamination at underground storage tank (UST) sites that store gasoline and diesel fuels. Accidental releases from these sites are among the most common causes of groundwater contamination (Kao *et al*. 2010). Once BTEX has dissolved in the groundwater, advection and dispersion can lead to extensive contamination plumes that adversely affect water supplies.

Benzene is a known carcinogen and has a low regulatory threshold level concentration of 5.0 parts per billion in groundwater. Various remediation techniques and natural attenuation are used to attempt to clean up sites that have been contaminated by BTEX components. Environmental and geological conditions can influence remediation efficacy. Droughts that cause major water table fluctuations, for example, may increase the rate of natural attenuation of dissolved benzene at UST sites.

A recent state-wide drought in Georgia started in the spring of 2006 and persisted into 2008. The peak of the drought was in 2007, and water levels did not fully recover in some places until 2009. The state climatologist classified this time period as a “severe” to “exceptional” drought. The most extreme conditions occurred in northern Georgia (Knaak, 2008). Streamflow data from 2007 and 2008 indicate that it is among one of the most severe droughts on record when compared to previous drought periods of 1925-1927, 1954-1956, 1985-1989, 1999-2002. Georgia normally receives ample rainfall that is well dispersed throughout the year, although, droughts periodically affect the region. North Georgia geology consists of fractured crystalline bedrock which cannot support high-yield municipal wells. Because this area relies heavily on surface water supplies, the water supply is susceptible to precipitation variation

(Campana 2011). The Coastal Plain is underlain by multiple layered beds of sand, clay, marl, and limestone. The layers dip and thicken coastward. Immense aquifers are found in the Coastal Plain, and recharge occurs at surface outcrops (mostly at the Fall Line.) Also, where the water table is shallow, precipitation will often percolate down through the sandy soils (Le Grand 1962). When droughts occur, water supply shortages can occur in both the Piedmont and Coastal Plain.

The water supply is just one of the elements effected by drought. Droughts can also affect water quality, as moderate climate fluctuations will often alter hydrologic regimes (Mishra and Singh 2010). The groundwater levels at one UST site in Athens, GA, for example dropped eight feet during the drought. (This site is often referred to as the original site.) Before the drought, benzene levels had been greater than 10,000 parts per billion (ppb) in several monitoring wells at the site. However, contamination levels had been dropping in the wells all during the drought, with only one eight hour enhanced fluid recovery vacuum remediation event that occurred in late 2007. Just before the wells became dry, benzene levels were in the 1,000 ppb range. In July 2008, after water levels had recovered enough to sample, BTEX contaminants were not detected or only concentrations of 50 ppb or lower were observed in any of the monitor wells. These results led to questions of how drought and water table fluctuations affect contaminated UST sites.

A review of the geology and some the processes such as the effects of water table fluctuations on contaminants, the types and severity of droughts in general, and different natural attenuation mechanisms that occurred at the original Athens site and others throughout the state during the drought led to several hypotheses of what could have caused such a drastic change in contaminant concentrations. The hypotheses for explaining decreases in contamination are 1) fluctuations in groundwater levels increase the oxygen content and increase the aerobic degradation of benzene, 2) as the water table fluctuates, some of the contaminants could become redistributed and sequestered in the soil's micropores (while this would lead to lower concentrations, it is only a redistribution of the contamination), and 3) the contamination could still be beneath the well. When the water table drops it creates a smear zone in the formation, and further water table fluctuations could lead to increased dilution and enhanced movement of the most contaminated water. Then, when the water table recovers, it may not come back up through the smear zone. In areas where the water table is shallow, clean water could also percolate down through the vadose zone leading to lower contamination concentrations.

It is probable that there is a combination and interaction of several processes that occurred and led to the decrease in benzene concentrations. It may not be possible to separate the processes and even with better site characterization it would be difficult to determine the exact progression of activities. However, this paper will look at the processes and hypotheses in more detail, and analyze six other UST sites in Georgia to examine the effects of drought and water level changes on dissolved benzene concentrations in the groundwater. Some of the factors investigated include how location, geological features, depth to the water table, and the degree of drought affect the natural attenuation of benzene. Water level data and precipitation data from several USGS sites were also used to evaluate water levels in the state during the drought.

CHAPTER 2

GEOLOGY

Geologic Provinces and Geology of Georgia

Piedmont and Blue Ridge:

The bedrock in these regions are composed of moderate to high grade metamorphic rocks such as gneisses and schists, and igneous rocks like granite. There are also at least two major northeast-trending belts of metamorphosed sedimentary rocks. The Piedmont region has gently sloping hills, and the Blue Ridge forms the North Georgia mountains of the Southern Appalachians. The water table tends to be at least 10' above the bedrock within the saprolite. The saprolite is course and does not contain much silt or clay. Porosity is about 40% which lowers with depth. The Piedmont has dendritic surface water patterns and does not correlate to underground fractures. The conventional approach of placing emphasis on the relation of groundwater to a particular formation or type of rock does not always apply in the Piedmont or Blue Ridge. All surface water is fed from local flow; there is no regional groundwater flow coming into these systems (LeGrand 1988).

Buol and Weed (1991) studied the saprolite to soil transformations in the North Carolina Piedmont which is also made up of granitic and biotite gneiss. The saprolite thickness is variable and is related to rock type and geomorphic positions, but the soil solum is frequently three feet thick and is underlain by 1 to 85 feet of saprolite. The saprolite zones above the granitic gneiss contain halloysite, gibbsite, and silicate clays. Many of these materials are recrystallized into kaolinite.

A microscopic modal analysis of the saprolite above a biotite plagioclase gneiss from samples collected in DeKalb county Georgia were found to contain 27% quartz, 35% plagioclase, 32 % biotite, 4 % muscovite, and 2% of accessory minerals. The first weathering products of biotite gneiss are gibbsite and allophane, both of which are unstable. The stable end products are kaolin materials (Grant 1963).

Soils formed over basic and or fine grained gneissic parent rocks in the Piedmont commonly contain 2:1 expanding clays. The zone most restrictive to the percolation of water tends to be near the transition from the soil solum to the saprolite (the BC transition zone). The cause of the low hydraulic conductivity in this zone is the absence of secondary structures (macropores) (Buol and Weed 1991). Another study conducted on the characterization of soils and saprolites in the Piedmont documented the hydraulic conductivities of different soil horizons. This study showed that the saturated hydraulic conductivity was largest at the top of the Bt horizon, reached a minimum at the B/C transition zone, and then increased with depth in the upper six feet of the C horizon (saprolite) (Amoozegar *et al. 1988*).

Buol and Weed (1991) also describe the porosity of weathered materials over granite. The total porosity of a column of soil and saprolite 15 feet below the land surface ranged between 52 and 47.5%. In the clayey argillic soil 18.5% of that porosity had an effective diameter of > 75 micrometers, while in the saprolite only 10-12% had pore diameters > 75 micrometers. Smaller pore sizes in the BC and C horizons could also contribute to the slower hydraulic conductivity.

Coastal Plain:

This is the area south of the Fall Line and consists of gently rolling to flat topography. The area is underlain by a wedge of unconsolidated to semi-consolidated, predominately clastic sedimentary rocks. The rocks consist mostly of sands, silts, and clays, and lesser amounts of gravel and limestone. The beds dip seaward and thickens closer to the coast. In general coarse grained sediments are closer to the up-dip limit, and clays and other fine grained sediments increase seaward. The permeability of clastic sediments is closely related to the deposition environment. Aquifers and confining beds are large, but are not uniform over the entire region. Therefore, detailed discussions have to be site specific. Recharge occurs where regional units outcrop (mostly at the Fall Line). In some areas, leakage through semi-confined layers will also occur. Most recharge to unconfined aquifers goes to local streams; only a small percentage goes into deeper confined systems (LeGrand 1962).

The Ocala Limestone makes up part of the Upper Floridan Aquifer that extends over most of Georgia’s Coastal Plain region. It is split into an upper and lower water bearing zone. The upper zone is highly weathered limestone characterized by a low permeability; it is about 40- 80 feet thick. The lower water bearing zone consists of harder, slightly weathered limestone and has a high degree of secondary permeability along fractures and joints. This zone is about 60- 80 feet thick. (Southeastern Geological Survey 1986).

The Ocala Limestone formation is overlain by 30-50 feet of undifferentiated Quaternary overburden. It is made up of fine to coarse quartz, sand, clayey sand, sandy clay, and clay. At the base of the overburden is a ten to fifteen foot thick layer of sandy clay and clayey limestone which is a residuum from the weathered Ocala Limestone. It is a zone of low permeability and serves as the upper semi-confining unit of the Upper Floridan Aquifer. The vertical hydraulic conductivity for the semi-confining clay unit is around 0.0011 feet per day. This contrasts with the overlying surficial aquifer in the overburden which has a hydraulic conductivity of 11.3 feet per day. The low permeability clays and clay rich soils are a result of prolonged chemical weathering of carbonate materials in humid climates (Warner 1997).

The Miccosukee Formation located in South Georgia and Florida is an aggregate of lenticular clayey sands and clay beds. Sediment is moderately to poorly sorted, coarse to fine grained, clayey quartz sand, and kaolinitc sandy clays. It is deeply weathered in some places and can have a thickness of up to 160 feet thick (USDA, 1989). The clays and mud are characterized as having a high plasticity, and the soils have a high content of clay minerals (Hendry and Yon, 1967). Using a sedimentary rock classification diagram and assuming the rock types in this area are claystones, sandy mudstone, and sandy claystone an estimate of the silt, sand, and clay content in the soils and saprolite could be around 0-15% silt, 10-50% sand, and 50-90% clay.

Valley and Ridge:

This region makes up the northwest corner of Georgia. Sedimentary rocks that have been folded and faulted cause long NE-SE trending valleys and ridges that give the region its name. The faults are thrust faults where sheets of limestone, sandstone, and shale have been pushed on top of each other.

The geologic unit in the southern portion of the Valley and Ridge region of Georgia, is The Rome Formation which overlies the Shady Dolomite Formation. The Shady Dolomite formation is measured to be as thick as 1000 feet in some areas. It consists of inter-bedded hematite and dolomite. Above the basal unit, the beds are all crystalline limestone and dolomite with a few thin beds of metashales. Chert and barite are common in these carbonate rocks. This formation weathers readily and most areas are covered with residual red clays (MacKallor, 1962).

The overlying Rome Formation consists of metashale with beds of metasiltstones and quartzite. It is about 2000 feet thick, and is more resistant to weathering than the Shady Dolomite. The Rome Formation is overlain by the Conasauga Formation which varies in lithology and thickness. It is at least 2000 feet thick in most places. Siltstone and dolomite shales are common. It is even more resistant to weathering than the Rome Formation. Like the other sedimentary limestone formations, the Rome and Shady Dolomite Formations contain weathered clay rich soil and saprolite materials.

Geology of the Study Sites

The sites used in this study are located in different regions of the state (Fig. 1). Each site has different geologic characteristics that make it unique (Tables 1 and 2). The attributes of the soil, saprolite, and parent material can influence percolation of precipitation down to the groundwater, the hydraulic conductivity of the groundwater movement, and can influence the fate and transport of contaminants.

The sites located in the Piedmont (Sites 4, 5, and 7) all have a similar lithology, and consist of granite and gneiss; this weathers to a clayey soil. Site 7 has a parent bedrock material of biotite gneiss. The underlying bedrock at site 4 is hornblende gneiss and amphibolite, and the parent material at Site 5 is undifferentiated granite gneiss.

The sites located in the Coastal Plain (Sites 1, 2, and 3) and the site located in the Valley and Ridge (Site 6) all have sedimentary parent rock. According to the U.S. Department of Interior U.S. Geological Survey (2013), Sites 1 and 2 are part of the Ocala Limestone Formation. Site 3 is located within the Miccosukee Formation, and Site 6 is underlain by the Rome Formation and the Shady Dolomite.

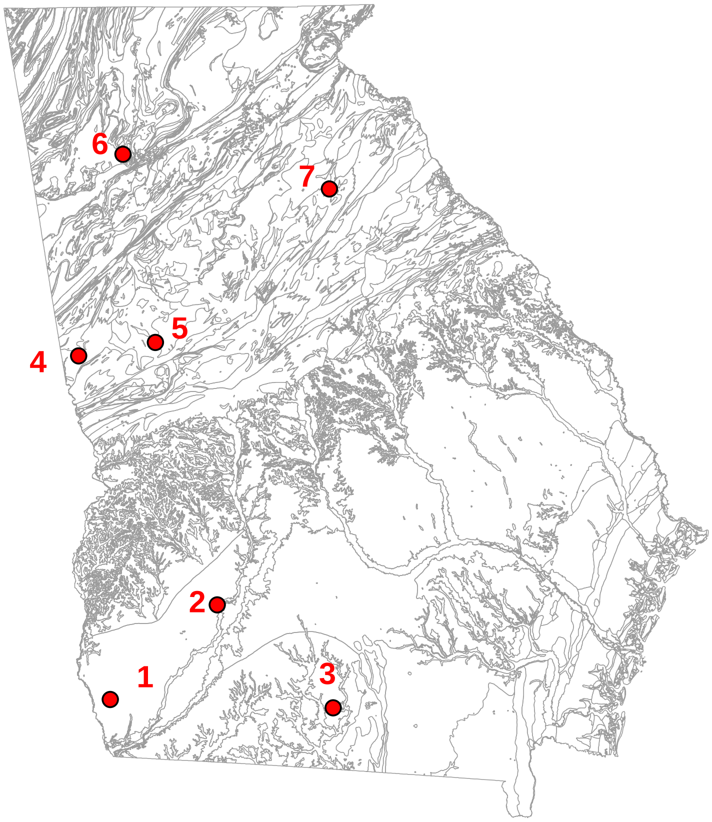

Figure 1. Geologic map of Georgia with site locations.

Table 1: Granite/ Gneiss Sites
Site 4: Hornblende Gneiss, Amphibolite
Site 5: Granitic Gneiss Undifferentiated
Site 7: Biotite Gneiss, Feldspathic Biotite Gneiss

Table 2: Limestone, Dolomite, and Sandstone Sites
Site 1: Ocala Limestone
Site 2: Ocala Limestone
Site 3: Miccosukee Formation (Clay and Mud)
Site 6: Rome Formation (Sandstone) and Shady Dolomite

Tables 1 and 2: The lithology of the geologic unit of each site.

Geology of Site 1

This site is in the Coastal Plain physiographic province, and is located in the southwestern corner of the state. The soil series at this site is TuA- Tifton sandy loam, which overlays the Ocala Limestone Formation, and has a parent material of marine deposits. The Tifton series is a well drained soil found on zero to two percent slopes (Soil Survey Staff). Soil borings from this site showed some silty sands near the surface but the majority of the profiles were sandy clay or clayey sands. The typical depth to groundwater in this area is 42 to 72 inches below ground level, and the water table at this site was shallow (about four feet). Because the water table is so shallow, monitor wells were only drilled 12-24 feet below ground level. The Ocala Limestone is a late Eocene formation. It is nearly pure limestone with occasional dolostones. The lower portion of the formation is composed of fine to medium grained fossil rich grainstone and packstone. The upper portions of the formation are more poorly sorted, and chert is common. It is fairly permeable, which allows it to form portions of the Floridan Aquifer system.

Geology of Site 2

This site is in the Coastal Plain physiographic province, and is located in the southwest portion of the state. The soil series at this site is OeB- Orangeburg loamy sand, which overlays the Dougherty Plain subsoil, and the Ocala Limestone Formation. It has a parent material of marine deposits. The Orangeburg soil series is a well-drained soil found on two to five percent slopes (Soil Survey Staff). Soil borings from this site were relatively sandy. Some borings were all clayey sands. Other profiles were sandier with well graded sands with little to no fines, and would only have intervals of more clay rich soils. The typical depth to groundwater is more than 80 inches below ground level; at this site ground water levels varied from 20-30 feet below ground level.

Groundwater moves through the Dougherty Plain subsoil, which is a flat area of karst topography. This formation is about 100 feet thick, and is characterized by sinkholes, caves, and an absence of surface streams. Below this is the Ocala Limestone. It is a late Eocene formation that is found below the Dougherty Plain residum. It is nearly pure limestone with occasional dolostones. Fine to medium grained fossil rich grainstone and packstone compose the majority of the lower portions of the formation.

The upper portions of the formation are more poorly sorted, and chert is common. It is fairly permeable, which allows it to form portions of the Floridan Aquifer system.

Geology of Site 3

This site is located in the Coastal Plain in the south central portion of Georgia. The soil series at this site is the Tifton Urban Land complex (TuB). This unit is made up of sixty percent of Tifton and similar soils, and forty percent of urban land cover. Tifton soils are well drained with a 0-5 percent slope, and a parent material of marine deposits (Soil Survey Staff). Soil borings from the site show that there are sandy silts near the surface, which become more clay rich and sandy with depth. The majority of the profiles are sandy clays or clayey sands. The underlying bedrock is the Miccosukee Formation. It is deeply weathered in some places (FL Soil Survey). This formation is a siliciclastic unit composed of grayish orange to grayish red, mottled, moderately consolidated, interbedded clay, sand and gravel of varying coarseness and mixtures (Hendry and Yon, 1967). It is characterized by high plasticity and a high content of clay minerals. The unit is relatively impermeable but is considered a part of the surficial aquifer system (Southeastern Geological Society, 1986).

Geology of Site 4

This site is in the Piedmont province, and is located in west central Georgia very close to the Alabama state line. The soil is classified as Cecil Sandy Loam (CeB). The Cecil soil series consists of deep, well drained moderately permeable soils on ridges and side slopes of the Piedmont uplands. The parent material for Cecil soils is listed as being residuum weathered from granite, gneiss, and or schist (Soil Survey Staff). The soil borings at this site show that the soils are mainly silts and clayey silts. The bedrock in the area is hornblende gneiss and amphibolite. Hornblende weathers to smectite and goethite in saprolite, and the final weathering product of amphibolite is a dark red clayey soil. (USGS, 2013).

Geology of Site 5

This site is in the Piedmont. The soil is classified as Cecil Sandy Loam- eroded (CYB2), a loamy siliceous soil. The Cecil soil series consists of deep, well drained moderately permeable soils on ridges and side slopes of the Piedmont uplands. The boring logs for this site show silty sandy clays with some borings being sandier than others. The soils are deep to saprolite and very deep to bedrock. The parent material for Cecil soils is listed as being residuum weathered from granite, gneiss, and or schist. The bedrock in the area is undifferentiated granite (Soil Survey Staff).

Geology of Site 6

This site is located in a high to average groundwater pollution susceptibility zone in the Valley and Ridge region of Georgia. Soil borings from the site show that the soils are silty clays or silts with clay and sands. The underlying geologic units are the Cambrian aged Rome Formation and the Shady Dolomite unit. The Rome Formation overlies the Shady Dolomite Formation. The Shady Dolomite consists of inter-bedded hematite and dolomite. Above the basal unit, the beds consist of crystalline limestone and dolomite with a few thin beds of metashales. Chert and barite are also common. This formation weathers readily and most areas are covered with residual red clays (MacKallor, 1963).

The overlying Rome Formation consists of metashale, siltstones and quartzite. It is more resistant to weathering than the Shady Dolomite. The Rome Formation is overlain by the Conasauga Formation which varies in lithology and thickness. Siltstone and dolomite shales are common. It is even more resistant to weathering than the Rome Formation. The Rome and Shady Dolomite Formations contain clay rich soils and saprolite.

CHAPTER 3

LITERATURE REVIEW

Droughts

"A drought is a period of drier-than-normal conditions that results in water-related problems," (USGS Drought 2001). There are several different types of drought which include meteorological, climatological, hydrological, agricultural, and socioeconomic. Because there are so many types of drought and the wide range of a drought's characteristics and impacts, it is impossible to have a single index that can adequately quantify the intensity and severity of a drought (Campana et al. 2011, Heim 2002). The type of drought that affects groundwater is a hydrological drought. It is defined as precipitation deficits over a prolonged period that affect surface or subsurface water supply, thus reducing streamflow, groundwater, reservoir, and lake levels (Heim 2002).

> "When groundwater systems are affected by droughts, first groundwater recharge and later groundwater levels and groundwater discharge decrease… Like other types of natural droughts, groundwater droughts are caused by low precipitation possibly in combination with high evapotranspiration. A lack of precipitation causes low soil moisture content which, in turn, causes low groundwater recharge. The resulting shortage in precipitation propagates through the hydrological system, causing a drought in different segments of the hydrological system (unsaturated zone, saturated groundwater, surface water). This means that the response of groundwater systems to droughts and their performance under drought conditions become increasingly important (Mishra and Singh 2010)."

In contrast to the idea that droughts affect the water table, some studies have found that the groundwater system can affect droughts. A study of drought in groundwater by Peters *et al*. (2005) states that drought characteristics are changed by the groundwater system, and that systems with different physical characteristics have different performances with respect to drought. When the distribution of droughts within different segments of the hydrological system were compared, the study found that the groundwater system causes a shift in the drought distribution from many small droughts in the recharge to fewer, but more severe droughts in the groundwater discharge.

The Effects of Water Table Fluctuations on LNAPLs

The influence of drought on BTEX contamination is unclear. In reviewing the literature, there were ample studies on the effects of water table fluctuations on LNAPLs. However, a large portion of these papers used sites or experiments where LNAPLs were floating on the water table instead of LNAPLs in the dissolved phase. Also, most of the papers dealt with short term water table fluctuations, not with long periods of drought.

“Water table fluctuation can greatly change the distribution and attenuation patterns of LNAPLs,” (Lee *et al.* 2001). There are several studies that have examined the effect of water table fluctuations on LNAPLs. Most studies show that the fluctuations help smear the LNAPL in the unsaturated zone which leads to subsequent biodegradation and enhanced dissolution. Dobson *et al*. (2007) observed the effect of water table fluctuations on LNAPLs in a lab simulated aquifer. They determined that the fluctuations affected the spatial distribution of LNAPLs within an aquifer, particularly in the vertical direction. As the water table falls, LNAPLS migrate down leaving residual amounts in the unsaturated zone. When the water table rises back up it leads to the entrapment of LNAPL and air below the water table. There was greater biodegradation of LNAPLS during a fluctuation, and it also increased the removal of dissolved LNAPLs from the system. However, it also increases the vertical extent of the source zone and increases the source zone’s transmissivity to groundwater.

During the drought most observed sites experienced small fluctuations in groundwater levels even though there was an overall decreasing trend. Reddi *et al.* (1998) observed the different characteristics between the upward and downward movements of the water table, and found that the concentration of LNAPL distribution was confined to short distances below the pool, especially when the water table was declining. Also during the downward movement, “the zone of non-zero aqueous phase concentrations was smaller than during the upward movement.” The rate of mass loss was higher during the upward movement of the water table than during the downward movement. Because of the enhanced dissolution and biodegradation, the lifetime of the LNAPL pool is expected to be shorter under fluctuating water table conditions.

Soil type and particle size also have a role in the entrapment and distribution of contaminants. Sandy soils with higher porosity can transmit water and contamination at a greater rate than a clay soil. Kampbell *et al.* (2003) preformed a study of groundwater quality during a short term drought. They found that both the concentration and detection frequency of nitrates in agricultural and septic tank land use areas were greater in sandy soils than in clayey soils. Ryan (1993) used a lab column test, and showed that the distribution of LNAPL is uniform, and that the average residual saturation is about 13% up to a particle diameter of 710 micrometers. Above that diameter, residual saturation decreases with particle size. In the same lab column test Ryan found that the distribution of contaminants was quite even as long as the medium was initially water wet, and that the distribution of trapped LNAPL is somewhat dependent on the amount that the water table is lowered between upward displacements. Soil properties can also affect LNAPL thickness, at least the thickness of free product that is observed in monitor wells. (This may or may not always reflect the conditions in the surrounding aquifer.) For a soil matrix with high porosity, the vertical movement of water and LANPL in the formation is slow and thus the gradient between the formation and monitor well tends to be small and the thickness of the LNAPL in the well is greater. For soils with a high hydraulic conductivity, the vertical movement of LNAPL and water are as fast as the water table changes in the formation. Therefore the fluctuation of LNAPL thickness in the monitor well is small (Aral and Liao 2002).

Natural Attenuation

Natural attenuation the “general term that refers to all naturally occurring physical, chemical, and biological processes that can reduce contaminant concentration or toxicity (Lee *et al.* 2001).” Sharpe (1999) adds that these processes occur “without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants." Natural attenuation depends on natural processes to degrade contaminants in soil and groundwater, and includes both non-destructive abiotic and destructive biotic processes. The mechanisms that reduce contamination concentrations include biodegradation, dispersion, dilution, sorption, volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants (McAllister and Chiang 1994; Weidemeier *et al*. 1996; Kao *et al*. 2010).

At many sites, intrinsic aerobic biodegradation by subsurface microbes is believed to be the primary natural attenuation mechanism that accounts for reduction of contaminant concentrations (Kao *et al.* 2010; Sharp 1999). This biological process is, however, dependent on the site having sufficient dissolved oxygen (DO) levels (> 1 to 2 mg/L). At these levels the microbes can utilize DO as an electron acceptor and convert the contamination to CO_2, water, and biomass (Alvarez and Illman 2006). The degradation reaction that occurs under aerobic conditions is: $C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$.

Even if DO conditions are favorable, once the degradation processes start, the organic contaminants demand high amounts of oxygen and will often deplete the DO supply, creating anaerobic conditions. However, biodegradation can occur in anaerobic conditions as well if alternative electron acceptors (i.e. nitrate, carbonate, iron (III), and sulfate) are available, and the microbes present are capable of utilizing them. These rates are usually slower than aerobic biodegradation (McAllister and Chiang 1994). One possible degradation reaction that occurs under anaerobic conditions (when chlorate acts as the electron acceptor) is: $C_6H_6 + 5ClO_3^- \rightarrow 6CO_2 + 5Cl^- + 3H_2O$.

Evidence that natural attenuation is occurring requires extensive data collection and site characterization. Plume characteristics such as the mass of the contaminant (is it a receding plume or a steady state plume) and D.O. concentrations, along with other monitoring data such as the extent, the rate of migration, and the distribution of the contaminant concentrations can all be used to evaluate and sometimes quantify natural attenuation (McAllister and Chiang 1994). The National Research Council lists certain 'footprints' that indicate natural attenuation of hydrocarbons is taking place. These include:

- Loss of electron acceptors- look for levels below background levels in the core of the plume;
- Generation of the products of acceptor reduction (Fe (II) and CH_4), they will be highest in the core of the plume;
- Presence of organic acids that are known intermediate products of hydrocarbon degradation; and
- An increased concentration of dissolved CO_2 and a change in alkalinity (Alvarez and Illman 2006).

Even though true evidence of natural attenuation requires a combination of factors, one simplified way to determine if aerobic biodegradation is taking place is to analyze the dissolved oxygen at the site. There is an inverse correlation between D.O. and BTEX concentrations. At sites where D.O. levels are high enough, monitor wells with the highest BTEX concentrations have the lowest D.O. levels and vice versa. Aquifer redox conditions vary within the plume. Most often conditions are highly reducing near the source, and oxygen and nitrogen are depleted. Down-gradient from the source, where contaminant concentrations are lower, groundwater is again enriched with nitrate and D.O. Thus, if D.O. levels are lower within the plume than outside the plume it is likely that natural attenuation by aerobic biodegradation is taking place (McAllister and Chiang 1994; Sharp 1999).

CHAPTER 4

METHODS

The data from the original UST site, former Prince Avenue Phillips 66 gas station in Athens, GA, was collected by All Phase Environmental as part of the Corrective Action Plan (CAP) and Monitor Only Reports as set forth by the Georgia EPD UST Management Program (USTMP). Six additional sites are evaluated in this study; they are all UST sites that have had petroleum releases from a leaking tank, dispenser island, or the product piping. The benzene contamination at these sites is in the dissolved phase, and is analyzed by collecting groundwater samples from monitor wells installed on the sites.

Data used in this study was collected by similar environmental consultants from all over the state of Georgia. The methods used by the different consultants should be comparable if they followed the Georgia EPD USTMP's guidance documents. The following is a review of the methods used to collect site data and groundwater samples.

Once contamination has been confirmed on a UST site, the EPD and the consultant work with the owner to come up with a plan that is cost effective and that will remediate the site in order to ensure the 'protection of human health and the environment.' The site's history, geology and hydrologic information are collected, and a remediation plan is proposed by the consultant and is submitted to the USTMP.

Usually the first step is to complete a Corrective Action Plan- Part A (CAP-A) which is a basic site characterization. A CAP-A is used to document release response activities, to report the magnitude of impacted media, and to summarize the proposed site investigation plans (GA DNR, 2011). There is a template that consultants must follow when filling out this report. The process starts by listing any initial abatement activities needed to prevent further release of the product and the history of the tanks and the system. The next section deals with initial site characterization. This includes the types of petroleum products released, the source of the contamination, and a list of local water resources (documenting the nearest wells and surface water bodies).

Further site characterization includes soil and groundwater analysis. Soil samples and groundwater samples are collected to determine the magnitude of soil and/or groundwater contamination. Usually at least three permanent monitor wells are installed to help find the vertical and horizontal extent of the contamination plume and to serve as permanent groundwater monitoring sample locations. Monitoring wells may not be required if soil samples taken from the worst contaminated area can be vertically delineated above the water table, and the results of a groundwater sample analyzed for BTEX, PAHs, and TPH are below the applicable water quality standards. The wells are supposed to be installed in a way that the top of the well screen lies above the water table. The wells must be placed in a triangular formation to determine the direction of groundwater flow and the hydraulic gradient. There is usually one well located at the source, one up-gradient, and one down-gradient from the source. When these wells are drilled soil boring logs are made and soil samples are also collected.

The only other geologic/hydrologic data required to be collected that has not already been mentioned is depth to groundwater, the geologic province, any unique conditions about the site, and a potentiometric map. The rest of the report is a collection of tables and figures showing the results of the lab analysis and site characteristics.

Once a CAP-A is complete, a site can be given a Monitor Only status or a CAP-B may be required for remedial activities by the GA EPD. In a monitoring only status the groundwater is sampled and BTEX contaminants are analyzed two or more times a year. No active remediation is present, and the site is only monitored to ensure that the contamination stays on the site, that it is not likely to impact other water receptors, and that it is not getting worse. Many of the sites used for this study were monitor only sites.

During a typical groundwater sampling event: Groundwater levels are measured in each well, and then a groundwater sample is collected. A minimum of three well volumes of water are removed from each well prior to sample collection to ensure that formation water is collected rather than stagnant water that has been sitting in the well since the last sample event. Samples are then collected with either a pump or a hand bailer and are placed into lab supplied 40 mL vials. All samples are preserved with HCl, and are kept cool, and a chain of custody is completed. The samples are packed in a cooler with ice, and are delivered or mailed overnight to a laboratory for analysis. The parameters tested during each sample event at every site were the same: groundwater samples from the monitor wells were analyzed for Benzene, Toluene, Ethylbenzene, and Xylenes.

All of the site data used for this investigation came from CAP-A or Monitor Only reports submitted to the GA EPD by Georgia consultants. The original plan was to use only the sites from state contractors. However, there were too many sites that could not be used due to the active remediation systems used to clean up the contamination. Also, many of the sites did not have enough of both pre and post-drought data, or had data gaps that were too large and could not give a record of site conditions during the drought. Still other sites could not be used because water levels did not fall during the drought and rise after the drought. Some of these sites showed no drops in water levels at all, and others showed an increase in water levels during the drought. Wells from the original Athens site could not be used because water levels did not recover after the drought, and the site was closed by the EPD (it was given a "No Further Action" status in 2008) before water levels had returned to pre-drought levels. The final data used for analysis in this study came from six different sites and fifteen different wells.

At each of these sites, consultants would record the sample date, the water level, and the BTEX levels observed in each well. For this study only the benzene contaminants were used during site analysis. The data was analyzed to determine if there was any correlation between benzene concentrations and groundwater levels. Line graphs depicting raw data from the consultants' reports were analyzed first; no correlations were observed. Further analysis was conducted using the following methods.

Three data points were chosen for each well. One data point was selected from before the drought, one during the drought, and one after the drought. The pre-drought data was from 2005 for all wells except for Monitoring Wells N and O from Site 6. Data from December 2004 had to be used because no samples were collected in 2005. This site underwent some changes in 2005 just before the drought. During construction the original Well N, located near the tank basin, was destroyed and a replacement well was constructed in almost the same location. Therefore, Well N data is a combination of data from both the original and replacement wells. It is unknown how this may skew the data.

The data from during the drought varied for each site, and was either from 2006, 2007, or 2008. This data point was chosen by picking the date that showed the lowest water levels for each well. The post-drought data point for each well was from 2008 or 2009. It was chosen by picking a date that showed water levels had recovered, or else was the date that had to be used due to it being the last data available or the last data available before a full remediation system was started.

Once the data points were chosen, the changes in water levels and benzene concentrations were analyzed. The fall in water level from before the drought to during the drought, and the rise of the water level from during the drought to post-drought were calculated for each well. The maximum water level change, in feet, (which ever was higher between the rise or fall) was then recorded. This was then compared to the percentage change of benzene concentrations observed in each well. The percentage change was calculated by subtracting the post-drought benzene concentrations from the pre-drought concentrations. This total was then divided by the pre-drought concentrations, and then be multiplied by 100 to determine the percentage change in the benzene contamination levels. The maximum change in water level was plotted against the benzene percentage change. The results are shown in the summary of the data in Chapter 5.

CHAPTER 5

SUMMARY OF DATA

The data used for this research project was compiled from consultant reports submitted to the Georgia EPD UST Management Program. Only sites that had data from both pre and post-drought dates (2005- 2009) were used. Sites that had free product or sites with active remediation systems in use during this time frame were not used because the objective was to observe only natural site characteristics that influenced the water and dissolved contamination levels. Six UST sites, and fifteen monitor wells that met the criteria were used in this study. (See Table 3).

Some of the sites, including the original site (Site 7), had short remediation events during the drought period. These events usually consisted of using an enhanced vapor recovery vacuum truck for several hours. Some of these shorter duration remediation events were used as baseline pilot studies for determining how effective a permanent remediation system would be. Several of the study sites did eventually have remediation systems installed; however only data from before the full system start-up were used.

For a few of the sites with full systems, the system start-up was in 2009 after at least one post-drought sample had been collected. However, Sites 2, 5, and 6 did not have any post-drought data before the remediation system was started. For this study, 2008 data, from before remediation began, was used as the post-drought data for these three sites.

Table 3: Summary of remediation events for each of the sites.

Site 1	Dec. 2007: One 24-hour EFR (Enhanced Fluid Recovery) event
Site 2	Oct. 2008: Baseline samples were taken
	April/June 2009: SVE (Soil Vapor Extraction) wells, air sparge wells, and an injection trench were constructed
Site 3	Jan. 2003: One 24-hour MPE (Multi-Phase Extraction) event
	June 2004: One 24-hour MPE event
	Nov. 2004: One 24-hour MPE event
	Dec. 2004: One 24-hour MPE event
	Nov. 2005: One 24-hour MPE event
	March 2009: One 24-hour MPE event
	May 2009: A full MPE system was started
Site 4	June 2005: One 8-hour MPE event
	April 2007: One 24 hour MPE event
Site 5	2004: Three 8-hour EFR events
	May 2008: One 8-hour ISCO/EFR (In-Situ Chemical Oxidation and Enhanced Fluid Recovery) pilot test
	July 2008: the full system start-up
Site 6	2004: Three 8-hour SVE events
	Sept. 2007: Pilot Study
	August 2008: Air Sparge/SVE system initiated
Site 7	November 2007: One 8-hour EFR event

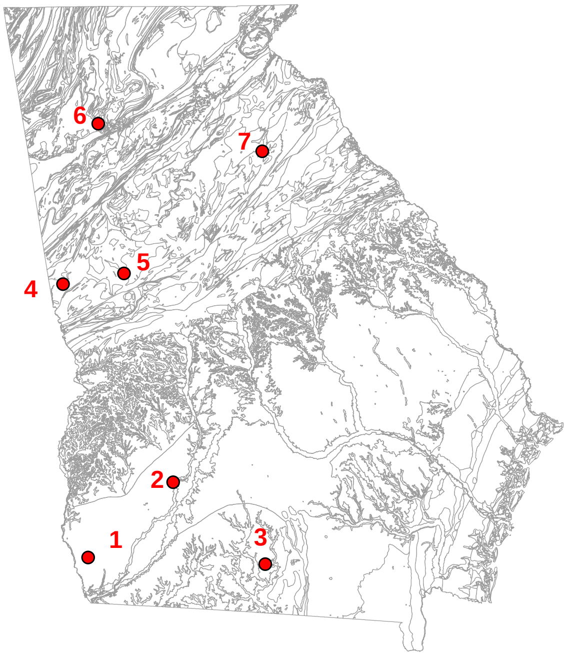

Figure 1. Geologic Map of Georgia with site locations.

Table 4: Summary of subject sites and wells. Note: Site 7 is the original site, but due to no post-drought data, wells from this site were not used in this study.

Site Number	Wells	Site Name	Address	County
1	A,B	Former Sing Station	201 South Tennille Ave. Donalsonville, GA	Seminole
2	C,D,E	Inland #412	814 N. Jefferson St. Albany, GA	Dougherty
3	F,G	Former Suwanee Swifty #272	100 East Main St. Hahira, GA	Lowndes
4	H,I	Former Kountry Korner	2972 West Point Hwy. Lagrange, GA	Troup
5	J, K, L, M	Former Clark’s Superette	1340 Hwy 76 East Gay, GA	Meriwether
6	N, O	Former Pantry #3500	301 South Erwin St. Cartersville, GA	Bartow
7*	N/A	Former Prince Ave. 66	1226 Prince Ave. Athens, GA	Clarke

Data from the monitor wells were analyzed to compare the percentage change in the benzene concentrations from before and after the drought versus the maximum water level change (feet). (See fig. 2) Two of the wells did show a significant (> 90%) decrease in benzene concentrations from before the drought to after the drought. (See Table 4) Neither the depth to groundwater nor the geologic province seemed to make a difference. One well had a shallow groundwater table, and the other was deep, and one site was located in the Coastal Plain while the other was in the Piedmont. The one factor that both wells had in common was that neither of the wells went dry during the drought.

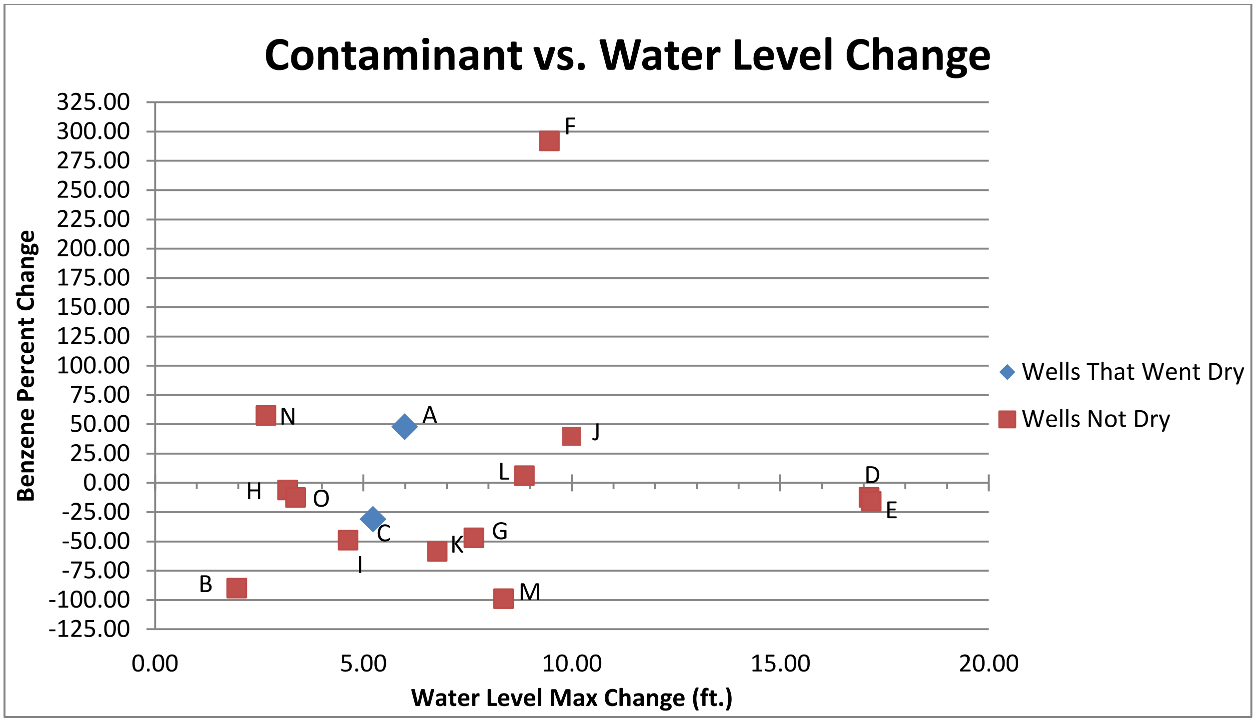

Figure 2: A plot of the wells showing the maximum water level change during the drought versus the percentage change in benzene concentrations from before the drought to after the drought. Negative percent changes represent a decrease in benzene and vice versa. For more details of the data, see Appendix B.

Table 5: Summary of the wells that had a > 90% decrease in benzene concentrations after the drought.

Site Number	**Wells**	**Geologic Area**	**Wells Went Dry?**	**Depth of Water Table (bgl)**	**Water Level Close to Full Recovery?**
1	B	Coastal Plain	No	Shallow (~4’)	Yes
5	M	Piedmont	No	Deep (~27’)	No

Summary of USGS Wells Water Level Data

Water level data from several USGS wells were used to evaluate water levels in the state during the drought. There was a general decline in water levels since 2005, with some small fluctuations, until 2008 when water levels began to recover. Water levels in the Piedmont dropped anywhere from 3 feet to 10 feet during the drought. Wells in the Coastal Plain were deeper than the Piedmont wells and the drop in water levels was more drastic. Water levels dropped ten – fifteen feet in most of the wells (USGS, 2010).

Five wells from the Piedmont region all showed similar patterns. There was a general decline in water levels since 2005, with some small fluctuations, until 2008 when water levels began to recover. Water levels dropped anywhere from three to ten feet during the drought. There was one shallow well where water levels were often above the land surface. This well showed the same overall decline during the three year period, however there was a seasonal drop where the water would recover about four feet every winter before dropping again during the summer.

Data from four wells located in the Coastal Plain were also observed. These wells are deeper than the Piedmont wells and the drop in water levels was more drastic. Water levels dropped ten to fifteen feet in most of the wells. One well, located in Laurens County (which is in the middle of the state, just below the fall line) did behave more like the wells in the Piedmont with a drop of four feet, and a general decline since 2006 and beginning to recover in 2009. Two of the wells did show a general decline in water levels since 2006, but the fluctuations were greater; the seasonal rise and fall would often be ten feet. And one well did not have an overall drop; the drastic ten foot fluctuations would always fully recover.

When water level data from the USGS wells are compared to water level data from the monitor wells at the UST sites, the time period of the water level fluctuations are similar. However, the amount of rise and fall in the monitor wells is more constant across the state than compared to the USGS wells. The fluctuations in the coastal plain monitor wells were not as drastic as the water level changes recorded in the coastal plain USGS wells. In all regions of the state the monitor well water levels changed anywhere from one to ten feet.

Summary of USGS Precipitation Data

Historical records from USGS stations that collect climate data were used to analyze Georgia's precipitation patterns from 2005-2009 (NCDC, 2012). The stations with records covering the drought period, and that were closest to the monitor well sites were chosen, with seven stations used. The amount of precipitation was given for each day of the year.

The total number of days showing precipitation, and the total amount of inches for each year were compared from each site. (See Figure 3). All sites showed the least amount of rainfall during the peak of the drought. When analyzing the total amount of rain for each year, almost every site shows a similar positive parabolic pattern. 2005 has a high amount of rainfall, 2006 has a drop in total precipitation, and by 2007 precipitation levels are at their lowest. By the end of 2008 yearly rainfall amounts rise again, and in 2009 precipitation amounts are back up to what they were in 2005. There are some variations in the sites, and there are some data gaps, but in general this rainfall pattern is common in all parts of Georgia. Two sites that varied slightly are Site 2 (Albany) and Site 3 (Valdosta): Albany, GA follows the general pattern, but the low point is in 2006 rather than in 2007, and in Valdosta, GA the 2009 rainfall amount had not recovered to the pre-drought amount.

The main differences between all the sites are how drastic the rain shortages were during the drought. Sites from the same geologic province did not always show similar amounts of rainfall or shortages. Sites from all over Georgia averaged 10- 40 inches less rain in 2007 than in 2005 and 2009. Sites from the Valley and Ridge, Piedmont, and Coastal Plain regions all varied within this range. Sites 6 and 7 in North Georgia had the greatest shortages in 2007 (31 inches, and 28 inches respectively), and the other five sites had shortages from 11-21 inches no matter what part of the state they were in. Precipitation data correlates to the State Climatologist's report (Knaak, 2008) that states that the drought was most severe in North Georgia.

When the precipitation data was compared to groundwater levels observed in the monitor wells (see Figure 3), there was little correlation. As stated above, precipitation amounts were lowest in 2007 at most sites. This was not the case with groundwater elevations. There was much more variation in the monitor wells, and 2006 or 2008 usually had the lowest recorded groundwater level elevations. Additionally, months with high amounts of rain often did not correlate with an increase in groundwater levels.

Table 6: Summary of precipitation data. The number of days of rain and the amount of rain that fell (in inches) is given for each site. *Sites 1 and 5 have data gaps in the precipitation measurements for some years.

	2005		2006		2007		2008		2009	
Site	Days of Rain	Inches	Days of Rain	Inches	Days of Rain	Inches	Days of Rain	Inches	Days of Rain	Inches
1	38*	22.20*	60*	29.68*	91	39.33	75*	51.10*	109	60.96
2	103	56.28	86	44.26	97	46.84	94	51.95	114	59.09
3	113	56.37	80	38.04	80	31.25	77	33.48	99	42.48
4	Insufficient Data									
5	117	53.63	103	32.12	105	35.13	71*	24.80*	77*	46.66*
6	72	52.69	86	43.80	77	28.15	93	39.08	120	66.29
7	114	58.45	104	40.22	83	31.50	104	36.40	125	60.23

There were some data gaps in the precipitation measurements. At Site 4 there was not sufficient data recorded, therefore it was not included. Sites 1 and 5 had several days where no precipitation data was collected. At Site 1 five months of measurements were missing in 2005, and 1 month of measurements were missing in both 2006 and 2008. While this makes it difficult to compare Site 1 with other sites, it is still possible to compare precipitation patterns during the drought (2007) and after the drought (2009) for the site because the same days were measured for these two years. There were 21.63 less inches of rain in 2007 than in 2009. At Site 5 there were data gaps in 2008 and 2009. 2008 was missing one month of measurements and 2009 had four months of measurements that were missing.

However, even though 2009 had 119 less days measured than in 2007, it still recorded more rain than the full year of 2007. 2007 had 11.53 less inches of rain than 2/3 of 2009. Also, when 2005 and 2007 are compared, which did not have any data gaps, 2007 had 18.5 less inches of rain than in 2005.

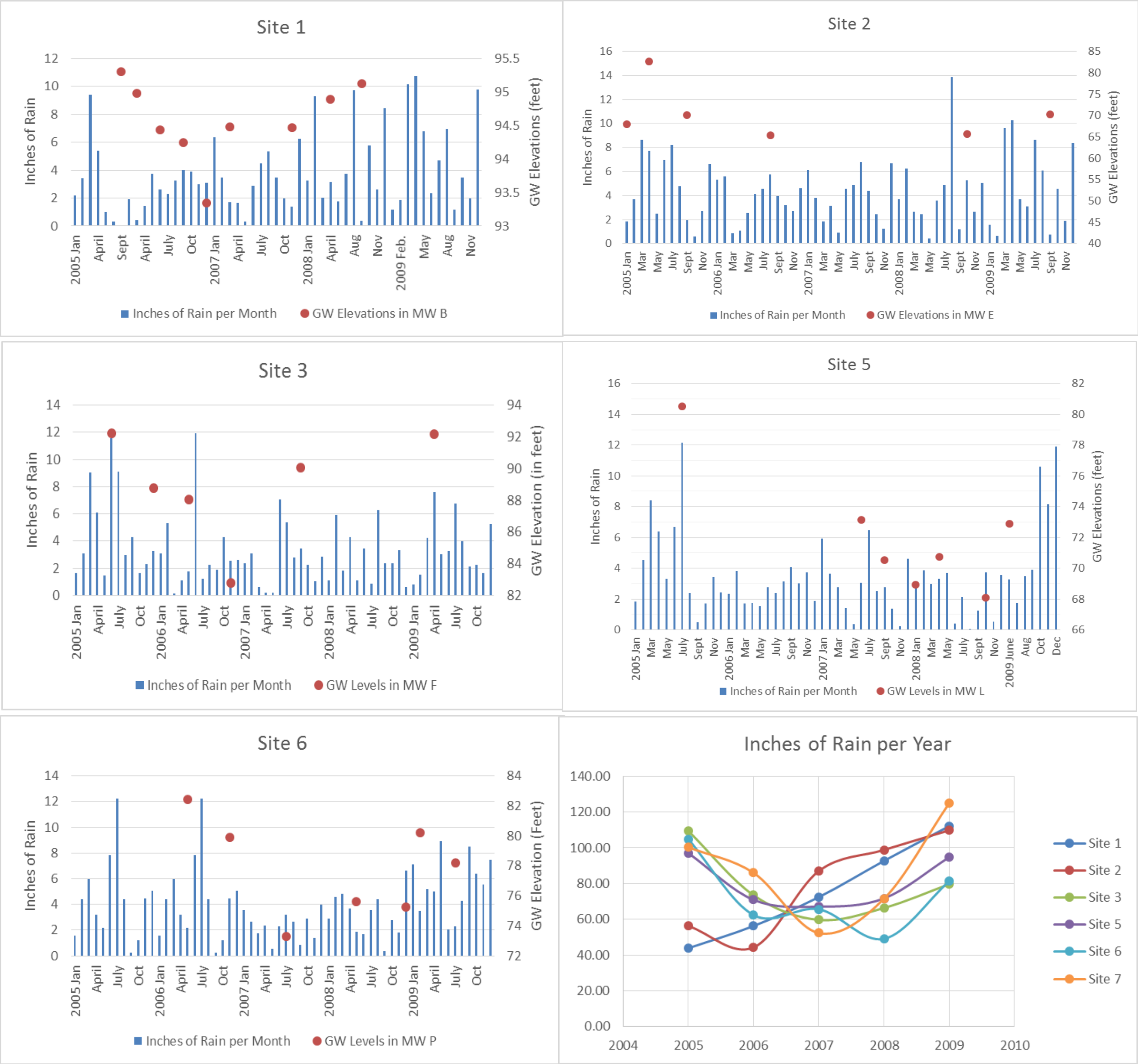

Figure 3: Precipitation data, showing the amount of rain for each site. Site 4 had insufficient precipitation data, and was not included. The groundwater levels from one monitor well at each site are also depicted. There was little correlation between precipitation and groundwater levels.

CHAPTER 6

DISCUSSION

The first part of the discussion lists general observations and hypotheses of what could be occurring at the different sites. Because not many similarities or correlations were observed for all of the data, the second part of the discussion looks at each individual site in more detail.

General Observations and Hypotheses

Site data was analyzed several ways:

- The maximum water level change during the drought versus the percentage change in benzene concentrations from before the drought to after the drought;
- Wells that went dry versus wells that did not go dry;
- The amount that the water levels recovered after the drought;
- Depth to Groundwater;
- Soil Boring Data;
- Geologic Province; and,
- Precipitation amounts from 2005-2009.

The six UST sites were categorized according to their location within the State of Georgia. We wanted to see if wells in the Piedmont behaved differently than wells in the Coastal Plain during the drought; or if the lithology of the sites made any difference. All sites have soil classifications of sandy loam or loamy sand, although there are differences in saturated hydraulic conductivity, the soil series, and the bedrock parent materials for each of the sites (Soil Survey Staff). The sites were also grouped into wells that went completely dry during the drought versus wells that did not go dry. The reason for this was to check if the wells that went completely dry during the drought had more drastic changes in contaminant concentrations once water levels recovered when compared to wells that did not go dry. Out of the sixteen wells, only two went dry during the drought; both were located in the coastal plain. One of these wells had a small decrease in benzene concentrations, and contamination levels greatly increased in the other.

Data from the monitoring wells was analyzed to compare the percentage change in the benzene concentrations from before and after the drought versus the maximum water level change (feet). (See Figure 2) There were two wells that had a greater than or equal to 90% decrease in benzene. The wells are from two different sites, and have different characteristics (See Table 4). We looked at these wells to see if anything about the sites were similar, or for anything that would explain why there was such a drastic drop in benzene concentrations in these wells after the water levels recovered. However, there were not many correlations between the sites. One of the wells that had a drastic drop in benzene is located in the Piedmont, and the other well is located in the Coastal Plain. Surprisingly neither of these wells went dry during the drought. One of the wells has a deep groundwater table with depths greater than 20 feet below ground level, and the other well has a shallow groundwater table (4 -12 feet below ground level). There are too many differences between the sites and not enough site characterization or geochemical or biological analyses to make any conclusions about what caused benzene levels to drop so much in these wells.

Another factor considered for all of the wells was how much the water level recovered after the drought, and if that made a difference in lowering benzene concentrations. Most of the water levels in the wells recovered about the same amount as they dropped. However there were some exceptions, water levels at Sites 2 and 5 never fully recovered- the water levels stayed lower than they were before the drought. There was no apparent relationship between recovery levels and benzene concentrations. For example, the monitoring wells from Site 5 all showed an eight to ten foot decrease in water levels that never recovered after the drought. However, benzene concentrations in Wells J and L showed an overall increase and wells K and M showed an overall decrease. Well M was also one of the wells that had a 90 percent or greater decrease in benzene from the drought to after the drought. Even though the water level patterns were similar, the benzene concentrations were different. Additionally, at all of the sites where water levels made an almost full recovery to pre-drought conditions, there were some wells that showed an overall increase in benzene and some wells that showed an overall decrease in benzene concentrations.

Even though there were no major patterns or correlations between water levels and benzene concentrations, the majority of the wells did show an overall decrease in contamination levels from before the drought to after the drought. With the limited data that was available from the EPD reports, it is hard to determine what caused the significant drop in benzene concentrations in two of the wells. It could be that normal natural attenuation processes were at work, and the decreases would have occurred whether there was a drought or not. However, natural attenuation alone would likely explain the two wells that showed such a drastic change between pre- and post- drought benzene concentrations. We did not have enough data to analyze if the drought and fluctuations in water levels increased the natural attenuation processes. Therefore three proposed hypotheses about what could be causing the decrease in benzene concentrations are described below.

One hypothesis as to why there were such drastic drops in benzene in some of the wells is that the fluctuation in water levels could have increased the oxygen content in groundwater and in turn increased the aerobic degradation of benzene. This biodegradation commonly leads to certain geochemical transitions at gasoline contaminated sites. Anaerobic conditions often exist close to the source where the hydrocarbon concentration (and consequently the electron acceptor demand) is highest. With greater distance from the source the hydrocarbon concentrations are lower, and the electron acceptors are replenished from the cleaner groundwater. The electron accepting conditions transition through several reducing zones before reaching aerobic conditions again near the outer edges of the contamination plume (Alvarez and Illman 2006). Gelman and Binstock (2008) completed a natural attenuation study of BTEX in a shallow coastal aquifer, and found similar conditions. In close proximity to the source, conditions were highly reducing and DO and nitrate were almost completely consumed. Dissolved Mn and Fe were present in the water, confirming that biodegradation was taking place. Further down-gradient the electron acceptor concentrations increased and the iron (a metabolic by-product) was no longer present.

This could explain the contamination decrease in some of the wells and not others. The sites that did not have a drop in benzene may not have had enough DO or enough other electron acceptors in the groundwater for biodegradation to occur. One simplified way to determine if natural attenuation occurs more when water tables are lowered would be to analyze the DO levels and measure geochemical parameters that indicate biodegradation is occurring (increased CO_2 and shifts in electron acceptors) pre and post-drought. The GA EPD does not require any of these parameters to be tested for and are not included in site characterizations. Further research and more in-depth site characterizations would be needed to determine if there is an increased potential for the aerobic degradation of benzene due to drops in the water table.

Another hypothesis as to what happened to the contamination during the drought in the wells that went dry is that the contamination could still be beneath the well. When the water table drops it brings the contamination down with it, and it creates a smear zone in the formation along the well casing and beneath the well if the well went completely dry. While the water tables are low, there are still small fluctuations in the water levels that can lead to increased dilution and enhanced movement of the most contaminated water further along in the contaminant plume. Also, if the water table drops to a higher zone of hydraulic conductivity, the most contaminated water could move further away from the source. These activities could somewhat decrease the amounts of contamination. When the water table recovers, it may not always come back up through the bottom of the well, and cleaner water from the formation above the smear zone could be coming back into the well. In the areas where the water table is shallow, clean water can percolate down through the vadose zone. In these scenarios, the water in monitor wells after the drought would never come into contact with the contaminated soil or smear zone beneath the well, and the samples could show low or none of the contamination that was found there previous to the drought.

One other hypothesis of what could be occurring at the sites to decrease benzene concentrations is that when the water table fluctuates, some of the contamination could become ‘frozen’ in the soil’s micropores. When the water table falls some the water gets left behind in the unsaturated zone formation.

Water moves out of the large pores and eventually some of the contaminated water gets trapped in the micropores. This could lead to lower contamination concentrations. The benzene that is trapped will slowly diffuse back into the larger pores, but this concentration is minute. While this may lead to lower contamination concentrations, the contaminants have merely been relocated, and have not been removed or attenuated.

Physical processes such as dilution/dispersion, sorption, and volatilization can result in plume attenuation. Dispersion and dilution are mixing processes that reduce the contaminant concentrations. Sorption is when contaminants partition from the aqueous phase to a solid medium. It is a general term used to describe several mechanisms where a contaminant may partition to a surface or onto a solid matrix. They are classified as: adsorption, absorption, and precipitation reactions (Alvarez and Illman 2006). These processes may greatly decrease the concentrations and the mobility of the contaminants, but does not remove them from the ground.

In contrast, if conditions are right, some of the contaminants that get sequestered in the micropores could become volatized. This occurs as the contaminants are drawn into the capillary fringe. As water levels drop and the vadose zone becomes drier, any contaminants that get drawn into the capillary fringe can volatize into the pore spaces of the vadose zone and subsequently into the atmosphere. Volatilization is the process where contaminants are removed from the soluble groundwater plume, through the capillary fringe, and into the vapor phase within in the unsaturated zone. This process usually does not account for more than 5-10% of the total mass loss of benzene. However, it may be more significant if the water table is shallow or highly fluctuating (Kao *et al.* 2010; McAllister and Chiang 1994).

In all likelihood, there is a combination and interaction of several processes that occur at the sites that lead to changes in benzene concentrations. It would be hard to determine the exact progression of activities at each site even with better site characterizations. However, the second part of the discussion will examine each site in more detail to develop site specific hypotheses on the effects of drought on the attenuation of benzene concentrations.

Site Specific Hypotheses

Site 1   Wells A, B
Former Sing Station
201 South Tennille Ave.
Donalsonville, GA; Seminole County

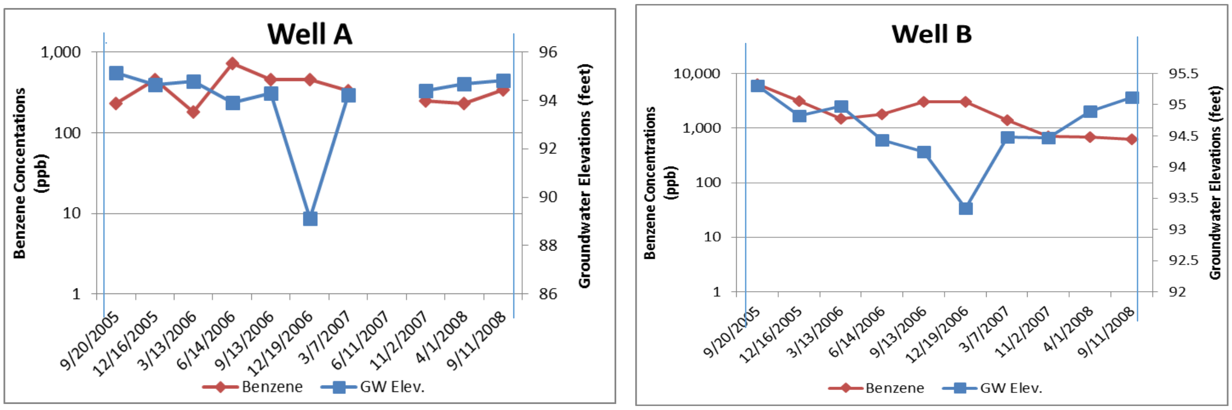

Figure 4: Benzene concentrations versus groundwater levels in monitor wells A and B. Further analysis of this data (see Appendix C) showed that benzene levels increased by 47.83 percent and that the maximum change in groundwater levels was 5.99 feet in Monitor Well A. Monitor Well B showed a benzene decrease of 90 percent and maximum groundwater level change of almost 2 feet.

This site is in the Coastal Plain physiographic province, and is located in the southwestern corner of the state. Soil borings from this site showed some silty sands near the surface but the majority of the profiles were sandy clay or clayey sands.

There was one 24 hour vacuum remediation event conducted on this site in Dec. 2007. However, there was not much change in contamination concentrations after the event. The remediation event should not have impacted the data analysis for this site. The water level in Well A dropped 5.99 feet, and the well went dry during the drought. Well A was one of the shallower wells at the site with a depth of 12 feet. Once water levels came back up, Benzene concentrations had dropped 100 ppb. However during the last sample event recorded, benzene levels had increased back up to the same level as just before the well went dry resulting in a 47.83 percent increase. Well B did not go dry during the drought; this well was 25 feet deep. Water levels only dropped two feet and later recovered. Benzene dropped from 6,300 to 630 ppb, a 90 percent change.

It is interesting how differently the two wells from this site behaved. The major difference is the change in benzene concentrations. Benzene increased in Well A, but Well B was one of the seven wells that had a drastic decrease in benzene concentrations (90% drop). Well B was closer to the source than Well A. One possible reason for the drastic drop in Well B and not in Well A would be that the geochemical conditions closer to the source were more highly reducing and therefore more conducive for aerobic biodegradation. However, if aerobic biodegradation depends on water table fluctuations to increase oxygen levels, then the changes in Well B water levels would not likely produce much oxygen.

As discussed in the general hypotheses section, just the act of the water level dropping and then fluctuating could lead to higher oxygen levels which could lead to increased degradation of contamination levels. This did not occur in Well B. Water levels showed a steady decrease all during 2006 in Well B, but only dropped two feet. In 2007 water levels began to steadily increase; there was not much fluctuation in this well. In general, conditions near the source of contamination are more highly reducing until the dissolved oxygen levels are depleted. Therefore, aerobic biodegradation activities may have occurred, perhaps just not for as long than if water levels were fluctuating and replenishing DO levels. Natural attenuation may account for a portion of the drop in benzene levels, but does not likely explain the entire 90 percent decrease.

The steady decrease in water levels would have allowed for contamination to be left behind in the unsaturated zone. As the sandy soils dried out, some of the contamination may have been volatized from the large pores, however the clay content increased with depth at this site. The sandy clays would likely have less capillary fringe action, and there would be more discontinuous fine pores where the contamination could become sequestered. When this occurs it could lead to seemingly lower benzene concentrations, however the contamination would still remain in the system. To get such a drastic drop in benzene concentrations in Well B, a combination and perfect interaction of processes would have needed to occur.

Even though Well A went dry, benzene levels increased. This shows that the hypothesis of the contamination staying below the well after it has gone dry may not be applicable, at least at this site. Contamination levels in this well were never as high as Well B or any of the other sites. Benzene levels do not fluctuate much in this well. In fact benzene was steadily decreasing before and after the well went dry, and even after water levels started to recover after the drought. It was only the last sample event that showed a slight increase in contamination. Even though concentrations only went up by 110 ppb from before the drought (and also from the previous sample event) this was still a 47 percent increase over all. It is unclear what causes small re-bounds in benzene concentrations after having a year with a decreasing trend.

<u>Site 2 Wells C, D, E</u>

Inland #412
814 N. Jefferson St.
Albany, GA; Dougherty County

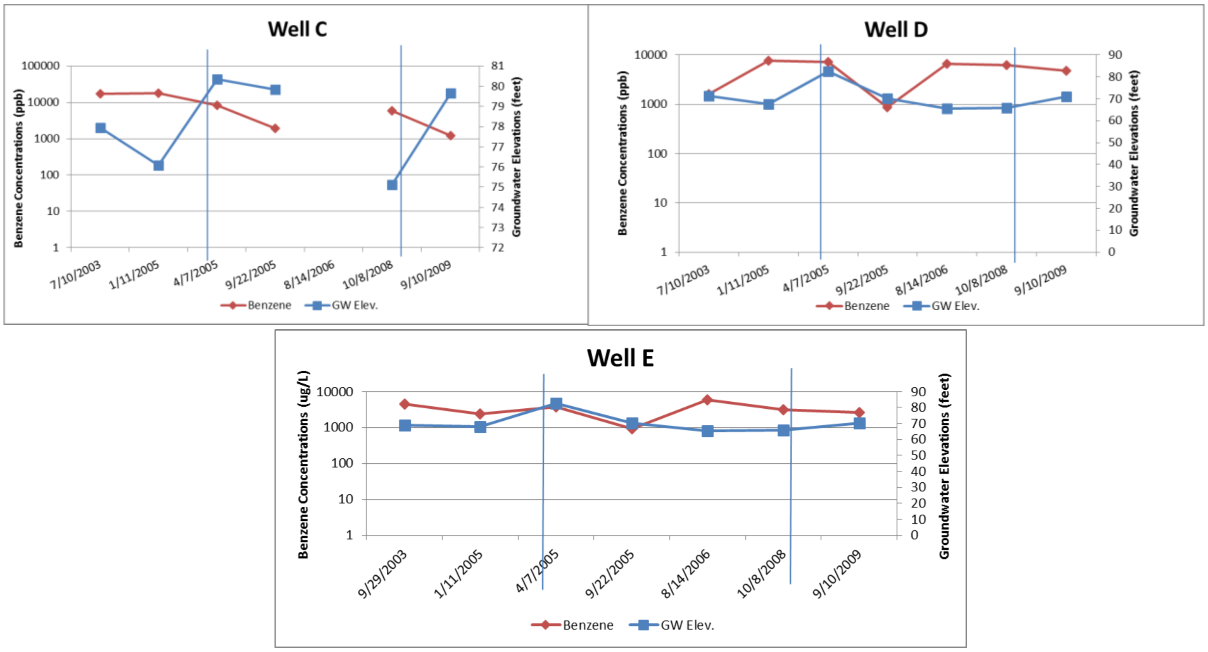

Figure 5: Benzene concentrations versus groundwater levels in monitor wells C, D and E. Further analysis of this data (see Appendix C) showed that benzene levels dropped 30.95 percent and that the maximum change in groundwater levels was 5.23 feet in Monitor Well C. Monitor Well D and E showed a benzene decrease of 12.5 and 15.8 percent respectively and both had a maximum groundwater level change of approximately 17 feet.

This site is in the Coastal Plain physiographic province, and is located in the southwest portion of the state. Soil borings from this site were relatively sandy. Some borings were all clayey sands. Other profiles were sandier with well graded sands with little to no fines, and would only have intervals of more clay rich soils. Groundwater levels at this site varied from 20-30 feet below ground level.

The release at this UST site dates back to 1994 when a leak in the product piping was discovered. The piping was fixed, free product was no longer detected after the 2003 and 2004 remediation events, and as of October 2009 the remediation system seemed to be reducing BTEX concentrations, and the USTs were still in use.

In 2003 there was an AS/SVE pilot test. In Dec. 2004 there was a MPE event, but due to poor results they discontinued with this, and just monitored the site through 2006. Active remediation was proposed and in Oct. 2008 they took baseline samples of all the wells. SVE wells, air sparge wells, and an injection trench were constructed, and then in April/June 2009 active remediation began. All of the data used in this study is from before the startup of the remediation system. Water levels never recovered in any of the monitor wells before the remediation system was started. This could impact data analysis, because no true post-drought data was used. This, and other site anomalies are taken into account during this site discussion.

The three wells used from this site are close to the UST tank basin and the original source of the leak; they are at the center of the contamination plume. Wells D and E are deep monitoring wells, which explains the difference between water level fluctuations in these wells from those in Well C. Well C is almost thirty-two (32) feet deep, and had a maximum groundwater level change from before the drought to after the drought of approximately five feet. In contrast, Wells D and E are fifty-nine and seventy feet deep respectively. The maximum groundwater change was seventeen feet in both of these wells.

Precipitation amounts were high in March (more than 8 inches) and in three days in April 2005 just before the sample event (almost 5 inches). There were other months with high precipitation amounts, however they did not lead to such a spike in groundwater levels. (See Figure 3). Because the spike was mainly seen in the deeper wells, perhaps these wells receive recharge from a different area than the shallow well, and the precipitation amounts just before the sample event did make a difference, and at least in part, led to the high groundwater levels during the April 2005 sample event.

The seventeen foot maximum change in groundwater levels in the deep wells is one of the irregularities that occurs at this site. During the April 2005 sample event, water levels were high in all wells. In Wells D and E there was a spike, where the water had risen fifteen feet in the four months since the previous sampling event. Five months later at the next sample event, the water levels had dropped back down twelve feet. In Well C the groundwater levels were the highest they had ever been in April 2005. Groundwater levels had not dropped as drastically as in the deep wells at the next sample event; it had only dropped one half foot. However, one year later, in 2006, the shallow well was dry. In 2008 when water had come back into the well, water levels were still low. The groundwater did not have time to recover from the drought before the remediation system was started.

Another irregular pattern at this site was the behavior of the contamination. In the deep wells, there was a major decrease in benzene concentrations in September 2005 that correlates with the water levels dropping back to a normal range following the spike in water levels in April. However, by the following sample event in 2006, benzene levels had gone back up. Other than this one major decrease, benzene levels do not change much in Well D. In Well E there is more of a correlation between benzene and groundwater fluctuations until 2006. After the decrease in benzene concentrations, water levels continued to drop, but benzene levels went back up. Well C benzene patterns are different from the deep wells. In 2005 benzene levels had dropped drastically at each sample event; concentrations had decreased from 18,000 to 1,900. In 2006 the well was dry, and by the next sample event in 2008 after water levels had increased, benzene levels had increased as well. Benzene concentrations were then 5,800 micrograms per liter.

Even though Well C went dry during the drought, benzene levels did not drastically decrease. In fact, benzene levels were higher after the well had been dry than they were just before the well became dry. Therefore, as in Site 1, this shows that the hypothesis of contamination staying below a well after it has become dry may not be applicable.

The sandy soils where fine pores are discontinuous, and the lack of constant water table fluctuations that allows for low capillary fringe action and for the unsaturated zone to dry out as the water table drops may give this site ideal conditions for contaminants to become sequestered in the micropores. If there is not much capillary fringe action that volatizes the contaminants, then the contaminants are likely to be partitioned onto the surface of soils within the fine pores. Dispersion and migration from the fine pores can take a long time, and could lead to an apparent decrease in contaminant concentrations, but the contaminants have not been removed from the ground.

Site 3 Wells F and G
Former Suwanee Swifty #272
100 East Main St.
Hahira, GA; Lowndes County

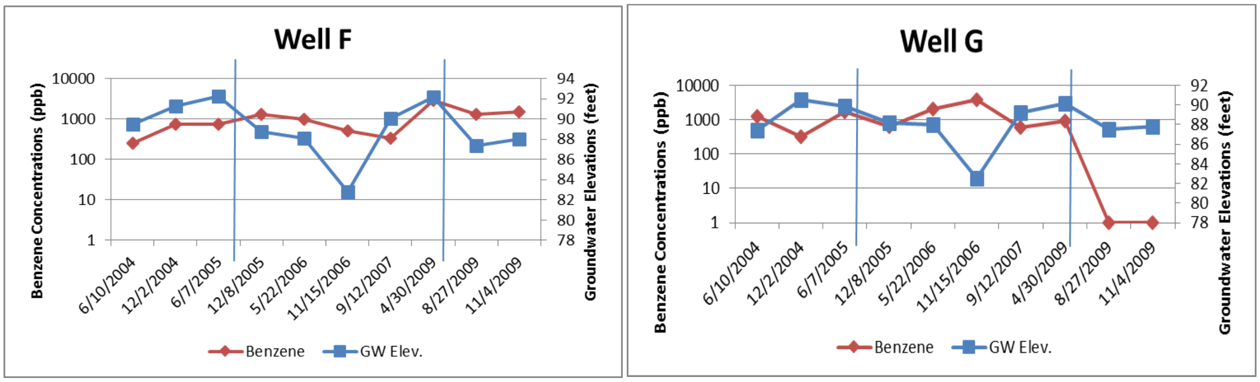

Figure 6: Benzene concentrations versus groundwater levels in monitor wells F and G. Further analysis of this data (see Appendix C) showed that benzene levels increased 292 percent and that the maximum change in groundwater levels was 9.39 feet in Monitor Well F. Monitor Well G showed a benzene decrease of 47 percent and had a maximum groundwater level change of approximately 7.65 feet.

This site is located in the Coastal Plain in the south central portion of Georgia. Soil borings from the site show that there are sandy silts near the surface, which become more clay rich and sandy with depth. The majority of the profiles are sandy clays or clayey sands.

There have been several eight hour EFR events at this site: Jan. 2003, June 2004, Nov. 2004, Dec. 2004, and Nov. 2005. In March 2008 the EPD approved installation of an EVR system, and start-up began in May 2009. (The data used is all from before the system start-up.)

The water table is shallow, and typically varied from 4 to 12 feet below ground level. During the drought water levels in both wells dropped seven to nine feet. Neither well went dry, and water levels recovered after the drought. Benzene increased by 2,160 ppb in Well F and decreased by 800 ppb in Well G.

It is unclear why these two wells behaved so differently. The beginning concentrations pre-drought were both about the same; yet benzene concentrations increased in one well and decreased in the other well. In Well F that showed an increase in contamination overall, benzene levels steadily decreased from the end of 2005 all during the drought until 2009 when contamination levels suddenly increased. In Well G that had decreased benzene concentrations over all, benzene levels were steadily increasing from the end of 2005 until Nov. 2006. Then by 2007 benzene levels had dropped 3,300 ppb.

In late 2006 there was a major drop in groundwater levels in both wells. In Well F benzene levels continued to decrease during the drop and as water levels began to recover. It was not until later that the increase in benzene occurred. In Well G benzene levels began to decrease after the major drop in groundwater as the water levels began to recover. As the water levels dropped, benzene increased, and as the water levels recovered, benzene decreased. However, in 2009 benzene levels had increased in both wells at the last sample event before the start-up of the remediation system.

Precipitation data could explain the low levels of groundwater in 2006, however 2007 had even lower amounts of rain, yet during the 2007 sample event groundwater levels had recovered from the major drop. This dip in groundwater levels is an anomaly for this site, and seems to have affected benzene concentrations, at least in Well G.

The capillary fringe action may be higher at this site due to water table fluctuations. This could lead to some contamination being volatized into the vapor phase. Additionally, the water table fluctuations could lead to increased dilution and movement of the contamination plume further down gradient. Also, the water table is shallow at this site and the soils are relatively sandy. Therefore, clean water could percolate down from the surface or from higher in the formation as it flows into the wells which could further dilute the benzene concentrations.

These factors could explain the decrease in contamination concentrations in Well G, and the decreasing trend in Well F. However, they would not explain the sudden spike in benzene levels in Well

F that caused that well to have almost a 300% increase from before the drought to after the drought. One of the possible reasons for the difference in concentrations in Well F and the differences between the two wells could result from a 'fingering' of the contaminant, and the difference in mixing that occurs when the water table changes.

Site 4   Wells H, I
Former Kountry Korner
2972 West Point Hwy.
Lagrange, GA; Troup County

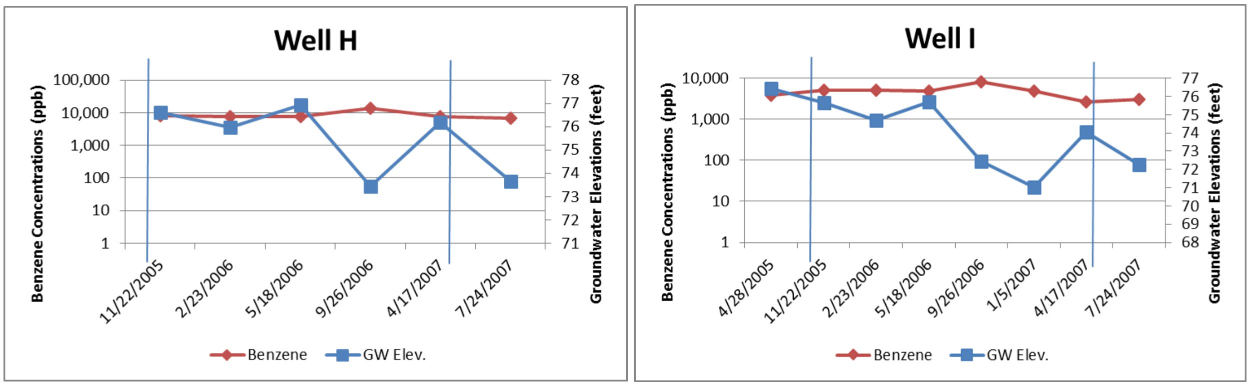

Figure 7: Benzene concentrations versus groundwater levels in monitor wells H and I. Further analysis of this data (see Appendix C) showed that benzene levels decreased 6 percent and that the maximum change in groundwater levels was 3.18 feet in Monitor Well H. Monitor Well I showed a benzene decrease of 49 percent and had a maximum groundwater level change of approximately 4.63 feet.

This site is in the Piedmont province, and is located in west central Georgia very close to the Alabama state line. The soil borings at this site show that the soils are mainly silts and clayey silts

The nearest water supply well and the nearest surface water are both within 500 feet. The site is located in close vicinity to a groundwater divide and recharge occurs mostly from precipitation. Percolation is limited to non-paved areas. Another recharge source for the site is septic systems. There are two small spring fed creeks which serve as groundwater discharge areas. The groundwater flow is SE toward one of these creeks. Even though the surface topography slopes west the groundwater gradient is to the east/southeast.

It is important to note that the "post-drought" data for this site is from 2007. While this may impact data analysis the last sample event used in analysis (4/17/2007) did show a recovery of ground-water levels. Water levels dropped three to four feet, and never fully recovered in either well. Benzene concentrations dropped 500 ppb, a six percent change, in Well H. In Well I, benzene dropped 2,500 ppb, which was a forty nine percent change since before the drought.

It is also important to note that the percent change analysis uses the April 2007 sample event as the post-drought data rather than the July 2007 sample event. This is because there was an increase in water levels in April whereas in July water levels had decreased again. However, Figure 7 shows that during the last sample event in July 2007, Well H had a decrease in benzene levels and Well I had an increase in benzene levels. This data would change the percent change analysis so that Well H would have had a greater percentage of change and Well I would have had a lower percentage of change in benzene concentrations.

The water levels and benzene concentrations at this site seem to be inversely correlated. Benzene levels are highest during the drought when there was less rain. There is even a spike in benzene levels in September 2006, which is when groundwater levels first showed a major decrease.

Because this site's recharge occurs mostly from precipitation, perhaps after the drought when water levels were increasing, there was enough clean water percolating down from the surface and from higher in the formation to dilute the benzene contamination. As with Site 4, the capillary fringe action may be higher at this site due to water table fluctuations which could lead to some contamination being volatized. Additionally, the water table fluctuations and percolation of fresh water could lead to increased DO levels. Both of these wells are close to the contamination source. While increased aerobic biodegradation may not usually occur near the source because DO levels are depleted faster there, anaerobic biodegradation could be occurring. Another source of recharge at this site is the septic system. Increased nitrates could be acting as alternative electron acceptors which would allow anaerobic biodegradation to also occur.

<u>Site 5   Wells J, K, L, M</u>
Former Clark's Superette
1340 Hwy 76 East
Gay, GA; Meriwether County

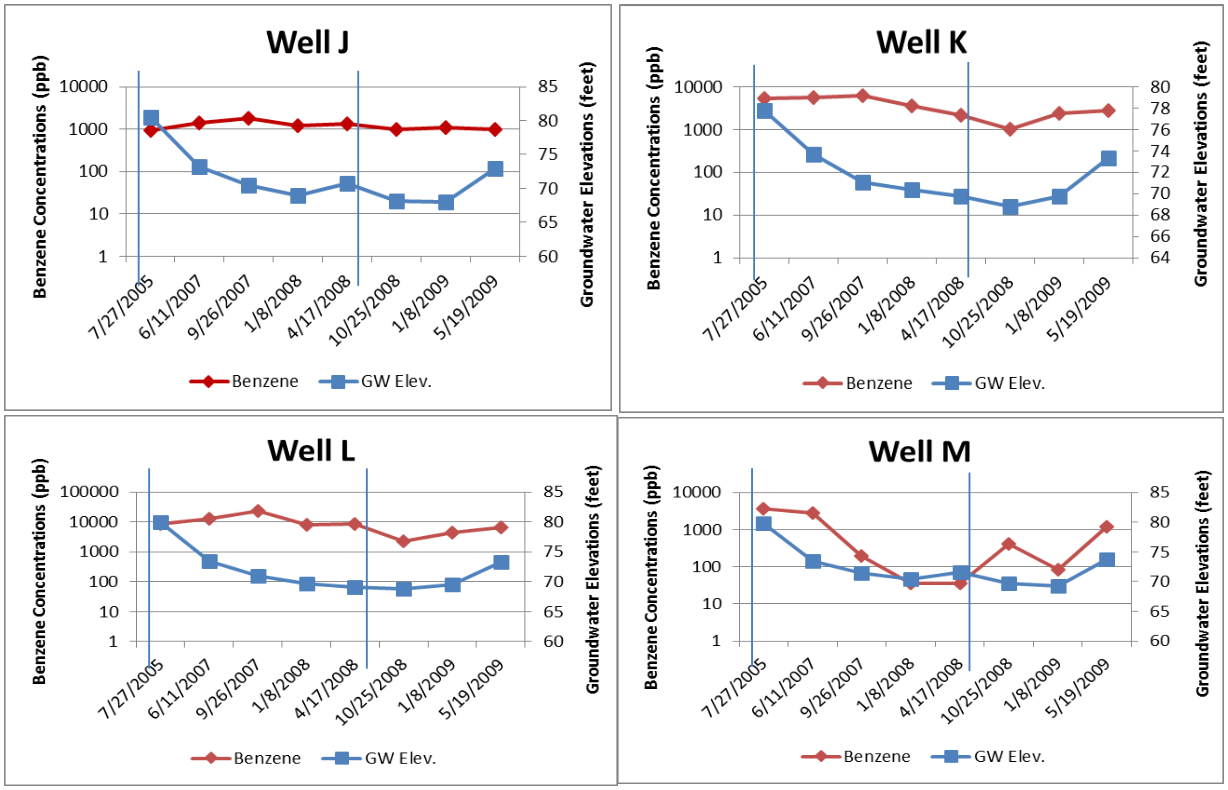

Figure 8: Benzene concentrations versus groundwater levels in monitor wells J, K, L and M. Further analysis of this data (see Appendix C) showed that benzene levels increased 39.78 percent in Well J and 6 percent in Well L. The maximum groundwater level change in these wells was 10 feet and 8.86 feet respectively. Monitor Well K showed a benzene decrease of 58.49 percent and had a maximum groundwater level change of 6.77 feet. Monitor Well M was one of the wells that had a major decrease in benzene concentrations, and dropped 99.03 percent; the maximum change in groundwater levels was 8.36 feet.

This site is in the Piedmont. The boring logs for this site show silty sandy clays with some borings being sandier than others.

In May 2008 an eight hour pilot test was performed. A remediation system (ISCO/EFR) was started for the site in July 2008. The data used is all from before either of these remediation events. Groundwater levels in all of the wells were decreasing during most of the drought.

Wells K and L are deep wells (approximately 50 feet below ground level) and Wells J and M and shallower (approximately 25 feet below ground level.) Water levels dropped about seven to ten feet in all of the wells, and steadily decreased all during the drought. Water levels slightly recovered in Wells J and M before the remediation system was started. However, water levels in Wells K and L did not begin to recover before remediation began. This may affect data analysis for these two wells. Benzene concentrations went up in Well J, and dropped drastically in Well M. Well M was one of the wells that had almost a 100% decrease from before the drought to after the drought. Benzene levels in this well dropped all during the drought and correlated with the dropping groundwater levels.

Groundwater patterns were similar in all wells, however the benzene concentrations varied between wells. Wells J and K did not show much change in benzene concentrations, however Well L showed a spike in benzene concentrations in 2007 before dropping back down and having only minor changes overall. Benzene levels in Well M were the most different, and had an almost one hundred percent (100%) decrease before the remediation ever began. Concentrations dropped from 3,700 ppb to 36 ppb.

Well M is one of the shallow wells and is closest to the former tank basin. The other wells are down gradient from Well M and the tank basin. If the contamination plume is mobile and moving away from the source (and Well M), then this could explain why there is a continuous decrease in benzene concentrations. Decreasing water levels with no water table fluctuations could allow contaminants to be partitioned to the sandier soils in Well M as the unsaturated zone dries out. These two actions combined could explain the large decrease in benzene concentrations in Well M.

The data from Wells K and L seems to confirm the hypothesis of the migration of the plume away from Well M. These two wells are right next to each other about 50 feet down gradient from Well M, and both showed a steady increase in benzene concentrations from 2005 to 2007. However, is unknown why Well L had an increase in benzene and Well K had a decrease in benzene in 2008 just before remediation began. The location and depth of the wells and the dropping groundwater levels in the wells are similar; the only difference seems to be that Well L had slightly sandier soils than Well K. Perhaps the clays in Well K allow for more contamination to partition to the soil surfaces than to the sands in Well L.

It may be misleading for Wells J and L to have an overall increase in benzene concentrations. Neither of the wells had major changes in benzene concentrations, and if slightly different sample dates were used, then the percent change analysis could have had different outcomes form these wells. Because there was not much recharge of groundwater before the remediation started, it is unknown how benzene concentrations may have reacted as more groundwater came back into the system post-drought.

Site 6 Wells N, O
Former Pantry #3500
301 South Erwin St.
Cartersville, GA; Bartow County

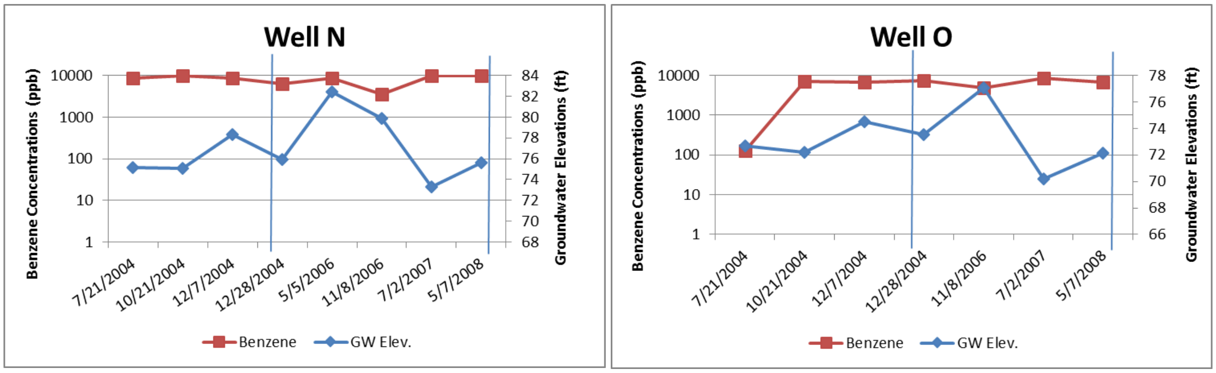

Figure 9: Benzene concentrations versus groundwater levels in monitor wells N and O. Further analysis of this data (see Appendix C) showed that benzene levels increased 57.48 percent and that the maximum change in groundwater levels was 2.66 feet in Monitor Well N. Monitor Well O showed a benzene decrease of 12.58 percent and had a maximum groundwater level change of 3.37 feet.

This site is located in a high to average groundwater pollution susceptibility zone in the Valley and Ridge region of Georgia. Soil borings from the site show that the soils are silty clays or silts with clay and sands.

This site underwent some changes in 2005 just before the drought. Site maps show that the layout of the property has changed. In 2004 the store was near the northwest corner of the site with the tank basin and one dispenser island located just southeast of the store. Eventually (likely in 2005) the store was torn down and a new store was built along the western property line of the site. The original tanks were removed from the ground in 2005 and were replaced during construction using the same tank basin. Three dispenser islands under a canopy replaced the area of the old store.

During construction the original Well N, located near the tank basin, was destroyed and a replacement well was constructed in almost the same location. Therefore, Well N data is a combination of data from both the original and replacement wells. It is unknown how this may skew the data.

In Sept. 2007 there was an AS/SVE pilot test. In May 2008 they took baseline samples, and the system started up in Aug. 2008. All data used are from before the system start up.

During the drought water levels dropped nine feet in Well N and seven feet in Well O. The water only recovered two feet before they started the remediation system after the drought. Well N had a 57.48% increase, and Well O had a 12.58% decrease in benzene. Benzene and groundwater levels showed an inverse relationship during the drought in Well O. Water levels decreased and benzene levels increased. During the last sample event as water levels begin to increase, Well O continues the inverse relationship with a decrease in benzene, but Well N benzene levels showed no change.

Well O is down-gradient from the source. Perhaps geochemical parameters and water table fluctuations allowed for increased natural attenuation. Most often conditions are highly reducing near the source where aerobic biodegradation is taking place, and oxygen and nitrogen are depleted. Down-gradient from the source, where contaminant concentrations are lower, groundwater is again enriched with nitrate and D.O. allowing attenuation to continue. This could explain why there was a decrease in Well O, but not in Well N.

Perhaps Well N did not have much change in contamination concentrations because it is closer to the tank basin and the source of contamination. Well N showed some decreases in benzene levels, but they would always increase again. Aerobic biodegradation may have lowered contamination levels, but then the levels increased again once the DO and electron acceptors were depleted near the source. The fine silty clay soils near the source could also be slowly leeching contamination into the plume further increasing benzene levels. At the end of the drought, not enough time had passed for groundwater levels to fully recover before remediation began and no recharge had percolated down to the aquifer adding clean water to dilute the contamination.

CHAPTER 7

FURTHER RESEACH AND CONCLUSIONS

This research paper attempted to use Georgia EPD UST site data to determine how the long term drought in 2006 and 2007 affected BTEX contamination levels. The Georgia EPD Underground Storage Tank Management Program regulates all of the UST sites in Georgia. If there is ever a petroleum release, and contamination is confirmed, the EPD wants to ensure that the contamination does not harm the environment or the health of humans. Site assessments, corrective action plans, and monitoring reports are used to study and document site conditions. If droughts or other climatic or environmental anomalies can significantly alter site conditions and the amounts of BTEX or other groundwater quality parameters, it would be in the regulatory agency's interest to understand these effects.

There were not many correlations between water levels and benzene concentrations. No generalizations or assumptions could be made from the data used in this study other than each site should be evaluated with site specific data.

One factor that may have affected data analysis is the limited quantity of data, and the selection process of which three sample events to use for pre-, during-, and post-drought analysis. Some of the sites had limited data with data gaps of one or two years in between sample events. Pre-drought data had to be from 2004 for some sites, while other sites used data from 2005. Trying to compare sites is already complicated, therefore when trying to compare data from different points in time, it becomes even more difficult.

Comparing sites from different time periods may be difficult, but analysis of each individual site could be as equally challenging. Once the three data points were chosen for a site, the same sample event dates had to be used for each well on the site. There were a couple of wells where the original data points could not be used because not all the wells had been sampled on that date. This occurred for Site 1. By choosing a date common to both wells, Well A data changed from having a decrease in benzene concentrations when using the original sample event data, to having an overall increase in benzene. This caused speculation as to the validity of any of the data. By choosing a slightly different point in time, the results could be different for any of the wells at any of the sites. Also, some sites had remediation systems that started before water levels had completely recovered from the drought. Data from before the remediation began had to be used so that only natural processes and changes in benzene concentrations were evaluated. However, by not using true post-drought data from when groundwater levels had recovered, the results may still have been skewed.

Perhaps better site studies and characterization with more data would be helpful in reaching more conclusive results. The frequency of the sample dates and monitoring of the sites was only a few times per year. These frozen snapshots of the site conditions do not give an accurate picture of what is occurring at each site. A more constant monitoring program would be needed for further research. The EPD reports also varied in how detailed the consultants were in characterizing each site. Better and more consistent aquifer characterization is needed for each site. At a minimum a researcher would like to have the soil type, particle size, hydraulic conductivity, DO levels, pH, conductivity, the oxidation redox potential (ORP) and groundwater temperature for each well. If individual studies were conducted at each site by the same researcher with the specific objective of determining the effects of drought on benzene contamination, a more in depth idea of what was going on during the drought could possibly be obtained.

One important factor that was not considered during this research paper was to determine how much natural attenuation is occurring at the study sites. Natural attenuation calculations would have been included in this study if more data had been available for each site. DO levels would be especially important to monitor because it is needed for aerobic biodegradation to occur. Further plume characterization would be needed, and there are certain criteria that could be monitored and used to determine if natural attenuation is taking place. If site conditions are right for natural attenuation, the fluctuating water tables and drought conditions may not have been a major contributing factor in the decreased BTEX concentrations. Or in contrast, if estimated natural attenuation rates could have been compared to what actually occurred at a site, the data may have led to the conclusion that natural attenuation is enhanced by fluctuating groundwater levels.

Another idea for further research would be to design and conduct an experiment in a laboratory where different variables could be controlled. The 'site' conditions would be known, and could be made to simulate any type of situation. The water table fluctuations and the effects they have on the contamination could be observed more constantly and easily. None of the laboratory experiments assessed during the literature review for this report simulated a long term drought or considered LNAPLs that were already in the dissolved phase.

This research has shown that there are many factors to consider when trying to determine the effects of drought on benzene contamination. There are too many aspects that make each site unique. The location within Georgia, i.e. the geologic province, topography, and even the underlying bedrock will influence site conditions. The depth to groundwater, soil properties, and the type of recharge at each site could affect how severe the drought is at each site and how groundwater fluctuates within the wells. This in turn affects the dispersion and attenuation rates of benzene contaminants. These are just some of the known factors that impact site conditions; without thorough subsurface investigations it is impossible to know what is going on at a site. Furthermore, droughts are complex and their severity can vary from region to region. The exact effects the drought had on each of the sites and the site conditions are more unknown factors that are site specific. Therefore it has been difficult to compare sites, and it is easy to understand why there were not many similar behaviors observed between the sites during the drought. Even with better site characterization and further studies, it would be difficult to determine the exact effects of drought on BTEX concentrations.

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APPENDIX A

LIST OF ABREVIATIONS

AS- Air Sparge, a remediation technique

BGL- below ground level

BTEX- Benzene, Toluene, Ethylbenzene, Xylenes

CAP (A or B) - Corrective Action Plan (part A or B)

DO- Dissolved Oxygen

EFR- Enhanced Fluid Recovery vacuum remediation event

EVR- Enhanced Vapor Recovery vacuum remediation event

GA EPD- Georgia Environmental Protection Division

HCl- Hydrochloric Acid

ISCO- In-Situ Chemical Oxidation, type of remediation

LNAPL- Light Non-Aqueous Phase Liquids

mg/L- milligrams per liter, equivalent to parts per million

mL- milliliters

MPE- Multi- Phase Extraction, type of vacuum remediation

MW- Monitor Well

NFA- No Further Action status

PAHs- Polynuclear Aromatic Hydrocarbons

ppb- Parts per billion, equivalent to micrograms per liter (ug/L)

SVE- Soil Vapor Extraction, type of vacuum remediation

TPH- Total Petroleum Hydrocarbons

USDA- United States Department of Agriculture

USGS- United Stated Geological Survey

UST- Underground Storage Tanks

USTMP- Underground Storage Tank Management Program, a division of the GA EPD

APPENDIX B

ANALYSIS OF DATA

The following tables show portions of the analyses completed for each site. For each well, three dates were chosen to compare ground water levels and benzene concentrations from before, during, and after the drought. The benzene percent difference from before to after the drought and the maximum water level change was calculated for each well. This data was used to create Figure 2.

Well #	Date	WL Pre	WL Dur.	WL Post	WL Chg. (Fall)	WL Chg. (Rise)	B Pre	B Dur.	B Post	B Chg.	B % Diff.	Max WL Change
Site 1												
MW-A	9/20/05	95.13			-5.99	5.69	230			110	47.83	5.99
	12/19/06		89.14					450				
	9/11/08			94.83					340			
MW-B	9/20/05	95.3			-1.96	1.78	6300			-5670	-90.00	1.96
	12/19/06		93.34					3000				
	9/11/08			95.12					630			
Site 2												
MW-C	4/7/2005	80.35			-5.23	n/a	8400			-2600	-30.95	5.23
	8/14/06		0					n/a				
	10/8/08			75.12					5800			
MW-D	4/7/05	82.56			-17.13	0.3	7200			-900	-12.50	17.13
	8/14/06		65.43					6600				
	10/8/08			65.73					6300			
MW-E	4/7/05	82.56			-17.18	0.31	3800			-600	-15.79	17.18
	8/14/06		65.38					5800				
	10/8/08			65.69					3200			
Site 3												
MW-F	6/7/05	92.23			-9.46	9.39	740			**2160**	291.89	9.46
	11/15/06		82.77					520				
	4/30/09			92.16					2900			
MW-G	6/7/05	89.83			-7.34	7.65	1700			-800	-47.06	7.65
	11/15/06		82.49					3900				
	4/30/09			90.14					900			
Site 4												
MW-H	11/22/05	76.62			-3.18	2.76	8100			-500	-6.17	3.18
	9/26/06		73.44					14000				
	4/17/07			76.2					7600			
MW-I	11/22/05	75.64			-4.63	3.03	5100			-2500	-49.02	4.63
	1/5/07		71.01					5000				
	4/17/07			74.04					2600			

Well #	Date	WL Pre	WL Dur.	WL Post Dr.	WL Chg. (Fall)	WL Chg. (Rise)	B Pre	B Dur.	B Post Dr.	B Chg.	B % Diff	Max WL Change
Site 5												
MW-J	7/27/05	80.52			-10	0.21	930			**370**	39.78	10
	9/26/07		70.52					1800				
	4/17/08			70.73					1300			
MW-K	7/27/05	77.8			-6.77	-1.23	5300			-3100	-58.49	6.77
	9/26/07		71.03					6200				
	4/17/08			69.8					2200			
MW-L	7/27/05	79.9			-8.86	-1.9	8300			**500**	6.02	8.86
	9/26/07		71.04					24000				
	4/17/08			69.14					8800			
MW-M	7/27/05	79.77			-8.36	0.2	3700			-3664	-99.03	8.36
	9/26/07		71.41					200				
	4/17/08			71.61					36			
Site 6												
MW-N	12/28/04	75.94			-2.66	2.33	6350			**3650**	57.48	2.66
	7/2/07		73.28					10000				
	5/7/08			75.61					10000			
MW-O	12/28/04	73.55			-3.37	1.97	7550			-950	-12.58	3.37
	7/2/07		70.18					8400				
	5/7/08			72.15					6600			

APPENDIX C

SITE DATA

The following tables are a summary of the original data for each site collected from the consultants' CAP-A and Monitoring Only reports submitted to the Georgia EPD USTMP. Benzene levels are shown in ppb, and the groundwater elevations are corrected to an arbitrary 100 foot bench mark at ground level. This data was used to create Figures 4 through 9.

Site 1			
Well #	Date	Benzene	GW Elev.
Well A MW-6	9/20/2005	230	95.13
	12/16/2005	450	94.65
	3/13/2006	180	94.78
	6/14/2006	720	93.91
	9/13/2006	450	94.3
	12/19/2006	450	89.14
	3/7/2007	330	94.23
	6/11/2007	NS	NS
	11/2/2007	250	94.4
	4/1/2008	230	94.68
	9/11/2008	340	94.83
Well B TMW-3	9/20/2005	6,300	95.3
	12/16/2005	3,100	94.82
	3/13/2006	1,500	94.98
	6/14/2006	1,800	94.43
	9/13/2006	3,000	94.24
	12/19/2006	3,000	93.34
	3/7/2007	1,400	94.48
	11/2/2007	700	94.47
	4/1/2008	690	94.89
	9/11/2008	630	95.12

Site 2			
Well #	Date	Benzene	GW Elev.
Well C mw-5	10/17/1999	25000	72.77
	4/4/2002	FP	73.2
	7/10/2003	17000	77.93
	1/11/2005	18000	76.09
	4/7/2005	8400	80.35
	9/22/2005	1900	79.82
	8/14/2006	NS	NS
	10/8/2008	5800	75.12
	9/10/2009	1200	79.66
Well D DW-1	10/14/1999	9100	62.94
	4/4/2002	878	65.26
	7/10/2003	1600	71.18
	1/11/2005	7600	67.61
	4/7/2005	7200	82.56
	9/22/2005	860	70.21
	8/14/2006	6600	65.43
	10/8/2008	6300	65.73
	9/10/2009	4800	70.95
Well E DW-2	8/13/2003	5000	72.46
	9/29/2003	4420	68.84
	1/11/2005	2400	67.94
	4/7/2005	3800	82.57
	9/22/2005	930	70.17
	8/14/2006	5800	65.38
	10/8/2008	3200	65.69
	9/10/2009	2600	70.32

Site 3			
Well #	**Date**	**Benzene**	**GW Elev.**
Well F mw-3	1/20/1998	1400	NS
	8/9/1999	788	88.71
	6/7/2000	392	87.14
	1/12/2001	426	91.38
	10/8/2001	1029	87.77
	4/4/2002	1400	91.08
	10/11/2002	512	88.25
	4/10/2003	817	94.7
	11/18/2003	428	89.64
	6/10/2004	252	89.51
	12/2/2004	750	91.27
	6/7/2005	740	92.23
	12/8/2005	1300	88.78
	5/22/2006	980	88.06
	11/15/2006	520	82.77
	9/12/2007	330	90.08
	4/30/2009	2900	92.16
	8/27/2009	1300	87.34
	11/4/2009	1500	88
Well G mw-7	6/7/2000	206	86.64
	1/12/2001	1180	90.93
	10/8/2001	375	87.33
	4/4/2002	390	91.5
	10/11/2002	785	87.68
	4/10/2003	365	94.85
	11/18/2003	645	88.96
	6/10/2004	1290	87.44
	12/2/2004	320	90.51
	6/7/2005	1700	89.83
	12/8/2005	650	88.18
	5/22/2006	2000	88.03
	11/15/2006	3900	82.49
	9/12/2007	600	89.18
	4/30/2009	900	90.14
	8/27/2009	1	87.48
	11/4/2009	1	87.8

Site 4			
Well #	**Date**	**Benzene**	**GW Elev.**
Well H MW-3	1/25/2005	11,000	75.79
	8/12/2005	9,300	NS
	11/22/2005	8,100	76.62
	2/23/2006	7,600	75.98
	5/18/2006	7,700	76.95
	9/26/2006	14,000	73.44
	1/5/2007	NS	72.51
	4/17/2007	7,600	76.2
	7/24/2007	6,600	73.66
Well I MW-10	4/28/2005	3,800	76.46
	11/22/2005	5,100	75.64
	2/23/2006	5,200	74.71
	5/18/2006	4,900	75.72
	9/26/2006	8,200	72.45
	1/5/2007	5,000	71.01
	4/17/2007	2,600	74.04
	7/24/2007	3,000	72.25

Site 5			
Well #	**Date**	**Benzene**	**GW Elev.**
Well J MW-7S	7/27/2005	930	80.52
	6/11/2007	1400	73.16
	9/26/2007	1800	70.52
	1/8/2008	1200	68.91
	4/17/2008	1300	70.73
	10/25/2008	970	68.08
	1/8/2009	1100	67.99
	5/19/2009	1000	72.88
Well K MW-13D	7/27/2005	5300	77.8
	6/11/2007	5500	73.68
	9/26/2007	6200	71.03
	1/8/2008	3500	70.35
	4/17/2008	2200	69.8
	10/25/2008	1000	68.78
	1/8/2009	2400	69.78
	5/19/2009	2800	73.3
Well L MW-15D	7/27/2005	8300	79.9
	6/11/2007	13000	73.47
	9/26/2007	24000	71.04
	1/8/2008	8000	69.62
	4/17/2008	8800	69.14
	10/25/2008	2300	68.78
	1/8/2009	4300	69.47
	5/19/2009	6500	73.33
Well M MW-18	7/27/2005	3700	79.77
	6/11/2007	2800	73.44
	9/26/2007	200	71.41
	1/8/2008	36	70.49
	4/17/2008	36	71.61
	10/25/2008	420	69.75
	1/8/2009	85	69.31
	5/19/2009	1200	73.76

Site 6			
Well #	**Date**	**Benzene**	**GW Elev.**
Well N mw-3r	5/5/2006	8430	82.41
	11/8/2006	3600	79.89
	7/2/2007	10000	73.28
	5/7/2008	10000	75.61
	12/3/2008	7300	75.24
	2/24/2009		80.19
	7/8/2009	5600	78.18
	1/22/2010	4000	83.01
	7/16/2010	4000	78.08
Well O mw-5	7/21/2004	130	72.68
	10/21/2004	7100	72.22
	12/7/2004	6900	74.5
	12/28/2004	7550	73.55
	5/5/2006	NS	NS
	11/8/2006	4900	77.05
	7/2/2007	8400	70.18
	5/7/2008	6600	72.15
	12/3/2008	6100	70.93
	2/24/2009	NS	73.24
	7/8/2009	2600	74.9
	1/22/2010	2300	79.86
	7/16/2010	1800	78.28