

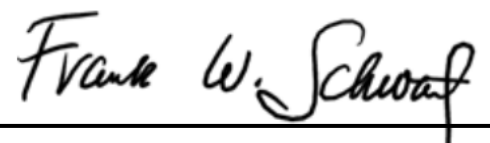
GROUND WATER CONTAMINATION OF THE
OLD O-FIELD SITE ABERDEEN PROVING GROUND MD.

Undergraduate Research Thesis
Submitted in partial fulfillment of the requirements for graduation
with research distinction in Earth Sciences
in the undergraduate colleges of
The Ohio State University

By

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The Ohio State University
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Approved by

A handwritten signature in black ink that reads "Frank W. Schwartz". The signature is written in a cursive style with a prominent initial "F" and a long, sweeping underline that extends across the width of the signature.

Franklin W. Schwartz, Project Advisor
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Abstract

The United States military is known for unsafe practices in disposing of toxic chemicals and materials. Aberdeen Proving Grounds in Maryland is no exception. One of the dumping sites located in the proving grounds is called the O-Field area. This site is located on Edgewood area of the base in a location called Gunpowder Neck. The O-Field area is only a few hundred meters east of Gunpowder River and two hundred meters south of Watson Creek. The site was set up during World War II and was used through the 1970's. The contamination at the site includes but is not limited to, lead, arsenic, DDT, organic and inorganic volatiles, PCB's, cadmium, chlorinated hydrocarbons and herbicides. This site is one of the most contaminated and dangerous sites the United States military has. Dumping at this site since the 1940s has led directly to contamination of the upper unconfined aquifer. The upper unconfined aquifer consists of alluvial sand deposits with clay lenses. The contaminated groundwater in the unconfined aquifer directly discharges into Watson Creek to the northeast. The military has made a large push to try and clean up this Old O-Field area by installing a pump and treat system. This was done to prevent the contamination of adjacent surface waters, which flow into Chesapeake Bay only a few kilometers away.

Acknowledgements

I would like to take this opportunity to thank my research professor Dr. Franklin “Frank” Schwartz for his patience and his many hours of editing, correcting and above all else the guidance that was required to complete this paper. I have learned just as much from doing this Thesis as I have while having broad topic conversations with Dr. Schwartz.

I would also like to thank Jen Campbell for driving me to my classes for many months when I injured my leg. In addition, I would like to thank Marc Rostan for his moral support and for keeping our cat Fritz aka. “The Boy” alive while I was unable to take care of him.

Introduction

During the 1970's, people of the United States were awakened to the facts of groundwater contamination, and its harmful and lasting effects. As a result, the federal government enacted new laws such as the Safe Drinking Water Act (SDWA) in 1974 and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) in 1980. CERCLA is the law that set up to deal with what we now know as Superfund Sites. This law did not only pertain to companies and individuals but also to federal agencies and departments.

Early in the 1980's, it became obvious that there were many contaminated sites that needed to be remediated (U.S. Army, 2008). Many of these sites were located on military bases where public oversight was not very intense and the naiveté of the time led to careless disposal of wastes and contamination of different areas. One of these sites is the Old O-Field area, at the Aberdeen Proving Grounds in Maryland. This site was used for military dumping with no known regulation for many years. Long-term dumping led to the contamination of surface and groundwater. This site was put on the list of Superfund Sites in 1999 due to its location near large population centers and the proximity of the Old O-Field area to the Chesapeake Bay.

This thesis has investigated some but not all the contaminants found at the site. The approach will involve comparing concentrations of common inorganic species to the natural background chemistry of groundwater in the area. In addition, the contamination concentrations will be compared to different national standards. A cation/anion balance was conducted to evaluate the quality of the actual chemical analyses. Overall, this study

provides a useful reminder of just how contaminated sites associated with military bases can be.

Site Background

Aberdeen Proving Ground

The Aberdeen Proving Grounds (APG) is located in Maryland about 32 km northeast of Baltimore. APG is a military installation operated by the U.S. Army. It covers an area of ~295 km² in Maryland, bordering Chesapeake Bay (Figure 1).

Historically, the APG was divided into two areas: the Aberdeen Area (APG-AA) and the Edgewood Area (APG-EA). The O-Field area that is the focus of the present study is located on APG-EA portion of APG (Figure 1). APG-EA is a peninsula covering an area of ~52.6 km². It is bordered by Bush River to the east, Gunpowder River to the west and to the south the Chesapeake Bay.

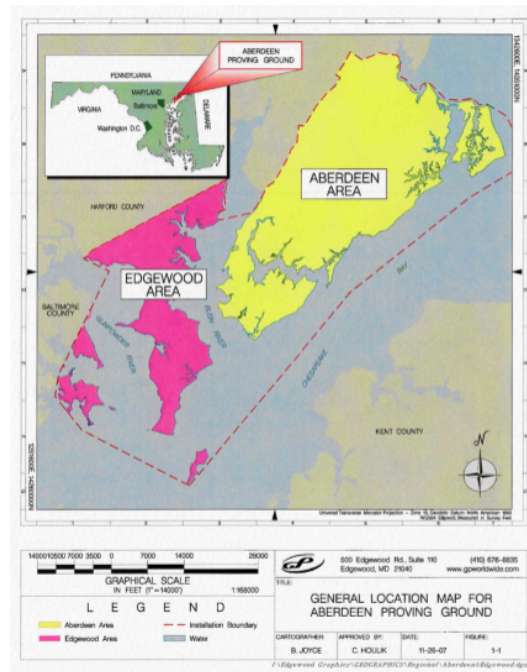


Figure 1. Map showing the overall area of the APG within Maryland and the two-main areas of APG-EA and APG-AA (U.S. Army, 2008a).

The post, which opened in 1917, has been used in different ways since its inception. Some parts of the base are used for motor vehicle testing, training military personal and the testing and production of military munitions. Currently APG is where the U.S. Army Soldier and Biological Command, U.S. Army Center for Health Promotion and Preventive Medicine, U.S. Army Medical Research Institute of Chemical Defense, U.S. Army Edgewood Chemical Biological Center, U.S. Army Chemical Materials Agency, U.S. Army Environmental Center are all located. (U.S. Army, 2008b).

The testing of motor vehicles at APG has been going on since before WW2. These tests are designed to test vehicles through rigorous durability, reliability tests (Figure 2).



Figure 2: An original Willys Overland Motor Company quarter ton 4x4 truck better known as a Jeep is shown at the APG. (source, army.mil)

Testing can also be more extreme, including that of armor testing utilizing explosives (Figure 3). Other tests involve munitions being shot at the vehicle to improve vehicle and crew survivability.



Figure 3: Mine-Resistant Ambush Protected Vehicle (MRAP) being tested with an explosive charge underneath the vehicle. (source: APGnews.com)

Shortly after APG began operating in 1917, the APG-EA was established. Historically, areas of the APG were then used for chemical, biological munitions development, testing as well as storage (U.S. Army, 2008b). During the APG-EA time of use, it was a large receiver for military waste, including low-level radioactive waste. The APG-EA also includes areas where biological, chemical munitions, and defoliants were field tested.

Not surprisingly, the variety of hazardous material and weapons being testing has led to the contamination of groundwater, surface water, sediment, and soil across the APG-EA. This contamination was caused by the field testing of munitions and the on-site disposal of hazardous materials. In some cases, munitions were used in conjunction with artillery (Figure 4) as a means of delivery (U.S. Army, 2008b).



Figure 4: Modern artillery piece being test fired at APG (“Firepower Directorate.”
Atc.army, United State. Army)

In 1917, German forces deployed chemical weapons containing mustard agents for the first time. In America, the U.S. Army began to prepare similar weapons to counter this serious threat (Figure 5).



Figure 5: Shells being filled with mustard agent on Edgewood Arsenal Nov. 11, 1918.
 (“A Chemical and Biological History.” Apnews, Apnews.com, 5 Jan. 2017, U.S. Army photo)

Contamination Concern and Tests

In addition to munitions manufacturing and testing, contamination on APG can be attributed to the disposal methods that were used during APG's operations. One method of disposal was to release liquid chemicals and industrial waste products directly into the smaller waterbodies on APG (U.S. Army, 2008b). These water bodies include rivers such as Bush River, streams and marshland for example Canal and Kings Creek (U.S. Army, 2008b). This practice was continued up until the latter parts of the 1970's. According to Nemoff et al. (1989) if a solid waste product could be thinned either through heating of the material or through chemical dilution, the solid waste would be dumped into nearby water bodies (U.S. Army, 2008b) but details of how they did this are missing. Human waste was also disposed of by dumping in the early days of APG but this practice came to an end when a treatment plant was constructed during WW2 (U.S. Army, 2008b). The U.S. Army has found many areas that are known to be or may be contaminated across APG. These areas include O-Field, J-Field, Lauderick and Canal Creeks, Bush River, Westwood, Carroll Island (Figure 6) and other places (U.S. Army, 2008b).

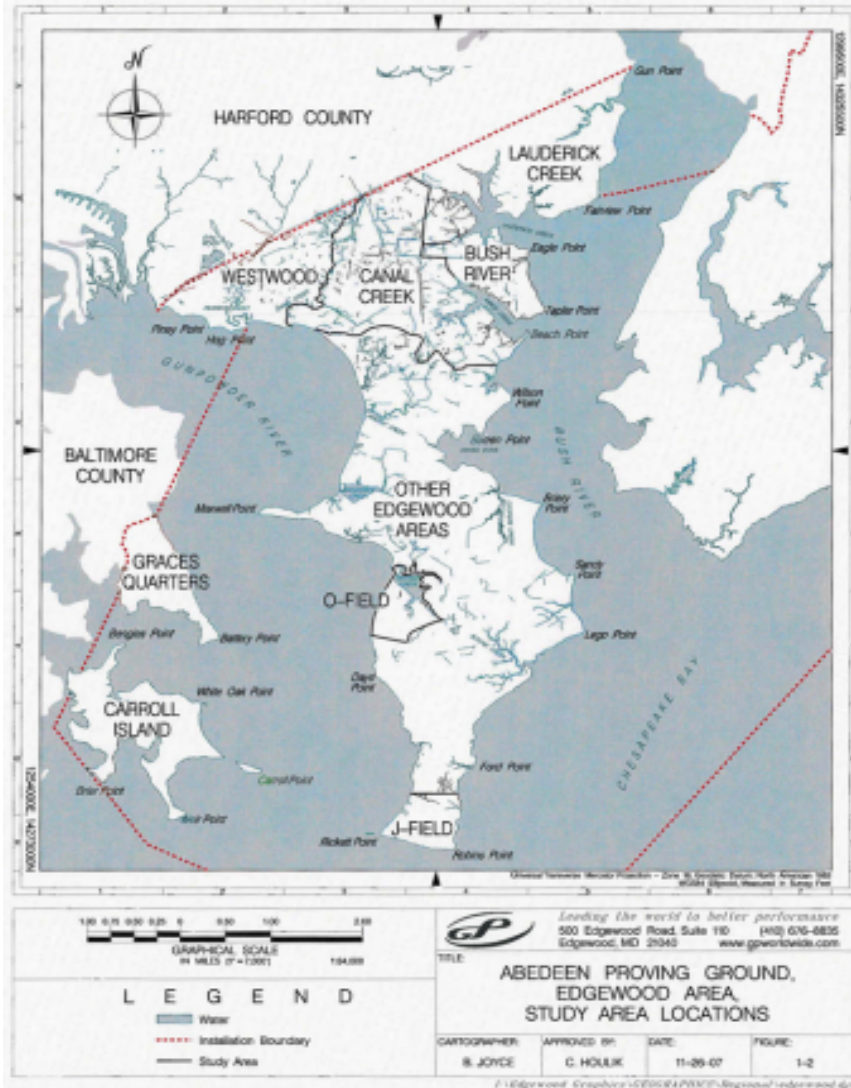


Figure 6: Areas of known contamination at Edgewood. Sourced from U.S. Army, 2008a

Topography, Land Use, Land Cover and Surface Waters

The APG is adjacent to Chesapeake Bay, and its land surface elevations range from sea level to 8 m asl. Overall, the area is flat with only minor elevation changes. A topographical map (Figure 7.) of the area shows the elevation in feet asl. Historical

military operations across the area disturbed the natural vegetation. Now the area is a mix of open fields, marsh land and light forest.

Tides

Chesapeake Bay is water body where tides occur. Downstream reaches of surface-water bodies, for example Watson Creek and Gunpowder River, experience tidal water-level fluctuations. However, the tidal fluctuations in those rivers are less than in the Chesapeake Bay and are complex due to river flow and a muted tide in the Bay Area.

Climate and Rainfall

APG has a temperate climate with an average annual temperature is 12.8 °C. Other features of the weather on an annual basis is summarized in Table 1. The hottest month on average is July with temperatures of 25 °C. January is the coldest month with an average temperature of 0.8 °C. Monthly ranges of historical high and low temperatures are summarized in Table 2. The average total annual precipitation is 1139.2 mm. Months with the highest and lowest average precipitation are July and February with precipitation amounts of 122.0 mm and 72.9 mm, respectively (Table 2).

Table 1: Historic annual averages in temperature and precipitation. sourced from usclimatedata.com utilizing data from 1981-2010

Aberdeen Proving Grounds weather averages	
Annual high temperature	17.7 °C
Annual low temperature	7.8 °C
Average temperature	12.8 °C
Average annual precipitation	1139.2 mm

Table 2: Historic temperatures and precipitation of APG by months. All measurements were recorded in °C and mm for Temperature and Precipitation respectively. This data were sourced from usclimatedata.com utilizing data from 1981–2010.

Climate Aberdeen Proving Ground - Maryland							°C °F
	Jan	Feb	Mar	Apr	May	Jun	
Average high in °C:	5.2	6.7	11.3	17.8	22.3	27.4	
Average low in °C:	-3.5	-2.7	0.9	6.8	11.6	17.2	
Av. precipitation in mm:	80	73	99	93	100	97	
Days with precipitation:	-	-	-	-	-	-	
Hours of sunshine:	-	-	-	-	-	-	
	Jul	Aug	Sep	Oct	Nov	Dec	
Average high in °C:	30.1	28.9	25.1	19.1	13.2	7.2	
Average low in °C:	20.1	19.2	14.7	8	3.5	-1.2	
Av. precipitation in mm:	112	96	115	96	87	91	
Days with precipitation:	-	-	-	-	-	-	
Hours of sunshine:	-	-	-	-	-	-	

Geology and Hydrogeologic Setting (APG)

O-Field Area

The O-Field area shown on Figure 7# below is the area of interest in the study. Historically, the name O-Field was applied to two adjacent areas, the new O-Field and the Old O-Field, the latter of which is the study area. At the O-Field area, ground elevations range generally from 1 to 6 m asl. The Old O-Field area is bordered by the Gunpowder River to the west and Watson Creek to the north and northeast. Both surface water bodies experience tidal fluctuations.

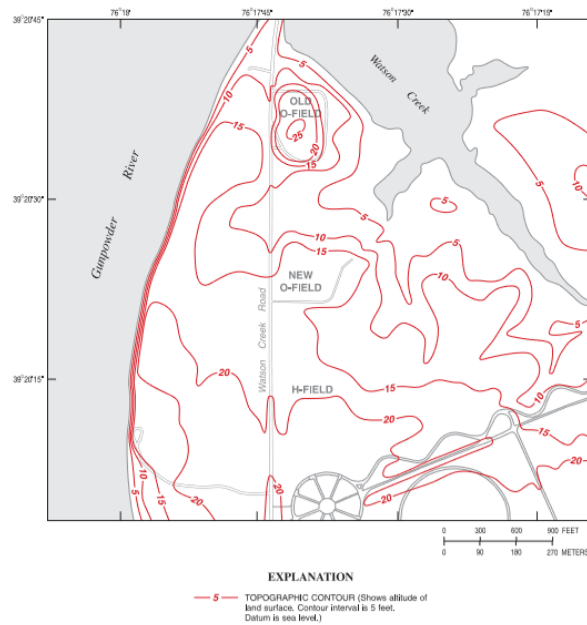


Figure 7. Topographic contour map of the O-field area all values have been given in feet above sea level. Figure taken from Banks et al., 2001

The U.S. Army used the Old O-Field area as a general disposal area for many years. Records indicate it was active as a disposal site from before World War II through the 1950s (Vroblesky et al., 1995). Both solid and liquids were disposed in lines of

trenches dug in the soil and substrate throughout the years. Waste disposal practices were rudimentary in the sense that materials were simply dumped into unlined trenches without liners, caps or other features of modern hazardous waste landfills. After dumping, flammable liquids would be poured into the pits and set alight to reduce the volume of material.

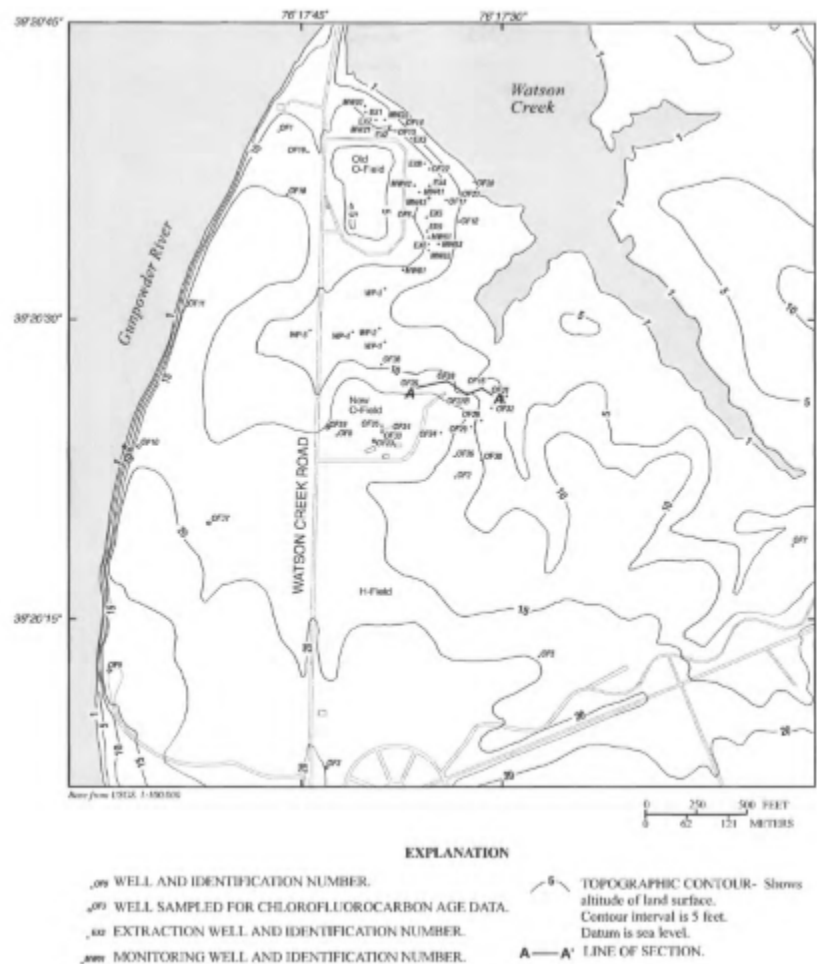


Figure 8. Well locations around the O-field Area and topographic contour lines. sourced from Banks et al., 1995.

There are no records of what solids and liquids were disposed into the unlined trenches. It is likely that materials included chemical agents used for or in the making of

chemical weapons, such as mustard gas, chemical weapons themselves, and miscellaneous contaminated materials, such as laboratory wastes, unexploded ordinance (UXO's) and dead animals (Banks et al., 1995). It should be noted that wastes were ejected out of the pits due to explosions (i.e., likely buried UXO) that occurred in 1949 (Banks et al., 1995). These explosions ejected material and UXO's also directly north into Watson creek. A fire at Old O-Field, probably from ignition of white phosphorous munitions, was reported as late as 1984 (Nemoff et al., 1989)

The burning of waste in trenches began around 1950 (Nemoff et al., 1989). Once the pits were deemed to be full, the wastes were set on fire with the help of flammable liquids such as fuel oil. After burning, fill was used to cover the trenches/pits. This material was permeable and was most likely excavated material from nearby trenches/pits. This disposal practice was used well into the 1970's.

After the explosion in 1949 at the Old O-Field area, which ejected contaminants out of the pits, 1,000 barrels of a decontaminating agent noncorrosive (DANC) were spread on and around the area to decontaminate the site. Nemoff et al. (1989) indicated that typical DANC agents could include calcium hypochlorite, super-topical bleach, sodium hydroxide (caustic soda) and lime.

Physical Hydrogeology of the O-Field Area and Hydrostratigraphic Setting

At the O-Field area, there are three aquifers present separated by two confining layers. In studies by the USGS (e.g. Nemoff et al., 1989 and Vroblesky et al., 1995), these aquifers were named informally as the water-table aquifer, the upper-confined aquifer and the lower-confined aquifer.

The water-table aquifer is an unconfined aquifer that overlies a thin confining bed. This aquifer consists of fine to coarse grained sand with discontinuous clay lenses. The thickness of the water table aquifer is between 4 and 7 m in thickness at the Field area. These sediments were deposited in a river and wetland setting during the Holocene (Vroblesky et al., 1995).

The upper confining unit occurs below the water-table aquifer. It is composed of greenish-gray clay that ranges in thickness from 0.3 to 1.5 m. This layer is thickest (0.3-1.2 m) at the Old O-Field area (Vroblesky et al., 1995). Near the New O-Field area it is < 0.3m thick. This clay unit is probably not a continuous confining layer beneath the two areas due to natural deposition and human disturbance.

Figure 9 is a west-east geological cross-section illustrating conditions close to the New O-Field area. Notice the water-table and upper confined aquifers as well as the thin upper confining unit and clay lenses within the water-table aquifer.

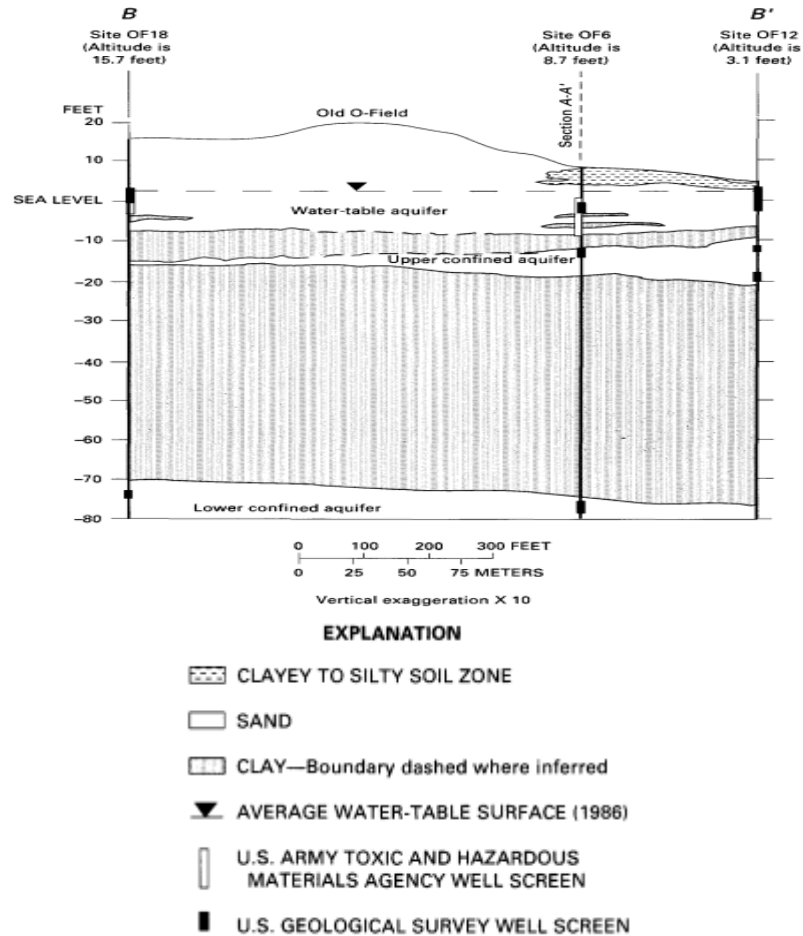


Figure 9: Short cross-section showing the hydrostratigraphic units at the old O-Field area. (Vrobley et al., 1995)

The next deeper aquifer is the so-called upper confined aquifer. It is confined on top by the upper confining unit that was discussed above. This confined aquifer is made up of dark gray to brown sand. This sand is medium to coarse grained and is interbedded with gravel and discontinuous gray clay lenses (Vrobley et al., 1995). In the upper confined aquifer at Old and New O-Field areas, grain-size fractions are present in the following proportions, 18% gravel, 63% sand, and 19% silt (ICF Kaiser Engineers, 1994). The thickness of this aquifer varies from 0.6 to 4 m depending on where the bore

holes were drilled. The upper confined aquifer is underlain by the lower-confining unit. It is a dark gray clay unit ~15.2 m thick with a grain size of 98% clay 2% sand (ICF, Kaiser Engineers, 1994). At the Old O-Field area, this clay layer is continuous and about 15.2 m thick (Nemoff et al., 1989).

The lower-confined aquifer is the deepest of the three aquifers. The datum describing this unit are extremely limited as compared the units just described. Because this unit is relatively deep with intervening confining layers, there is only a remote possibility of contamination. For this reason, the site characterization has not been concerned with this aquifer and other than merely indicating its existence.

Unit Properties

Water Table Aquifer

Step-drawdown tests were conducted by the U.S. Army Corps of Engineers (Vroblesky et al., 1995) with piezometers. Nemoff et al. (1989) assign a range of values $1.764 \times 10^{-3} - 3.881 \times 10^{-2}$ cm/s for horizontal hydraulic conductivity in their models. The average value of horizontal hydraulic conductivity is 1.06×10^{-2} cm/s. The vertical hydraulic conductivity is somewhat lower averaging 7.056×10^{-3} cm/s. In model studies (Vroblesky et al., 1995), an effective porosity of 0.4 was assigned. In WRI-00-4283 (Banks et al., 2001), a specific yield of 0.2 was used in ground water modeling. Typically, values of specific yield are less than porosity. The porosity is ~0.35, which is considered to be typical for unlithified sand (Schwartz and Zhang, 2013).

Upper confining unit

The vertical hydraulic conductivity of the upper confining unit was estimated to be 3.527×10^{-6} cm/s around the Old O-Field area (ICF Kaiser Engineers, 1994). Vroblesky et al. (1989) reported a range of 7.056×10^{-8} to 3.528×10^{-7} cm/s. This vertical hydraulic conductivity value is important because it is the primary parameter controlling the linear velocity of contaminants moving downward from the water table aquifer into the upper confined aquifer.

Upper confined aquifer

The horizontal hydraulic conductivity for this unit ranges from 6.35×10^{-3} to 2.22×10^{-2} cm/s (Nemoff et al., 1989) around the O-Field area. These values were obtained by slug testing six wells, after taking care to remove fine sediment from the well screens (Vroblesky et al., 1995). There are no specific measurements of porosity. However, given the lithology, 0.35 is a reasonable estimate.

Lower confining unit

For the lower confining unit, cores collected from six wells were tested in the laboratory to determine values of vertical hydraulic conductivity (Vroblesky et al., 1995). Values ranged from 1.658×10^{-9} to 1.658×10^{-7} cm/s with a mean value of 5.644×10^{-9} cm/s. Such values are considered to be extremely low, and typical for clays. Given the low hydraulic conductivity values and the thickness of this unit (i.e., >15 m), it is unlikely that the lower aquifer is contaminated.

Water Table Configuration and Patterns of Groundwater Flow

Studies were undertaken by the USGS to define the variability in the water table with time and patterns of groundwater flow. Figure 10 depicts variations in water levels during 1992 and 1993 in wells OF-16A and OF-16B, located slightly northeast of the New O-Field area. Both the water-table aquifer (see OF-16A) and the upper confined aquifer exhibit fluctuations close to 3 m through the year. Water-levels reach a maximum in spring and decline through summer and fall. This is a typical response reflecting annual variability in rainfall from spring through the dry fall months and decreased recharge due to water use by vegetation. The smaller fluctuations likely represent particular rain events.

In general, the water-level behavior in the two aquifer is similar, both in terms of the timing and magnitude of long and short-term fluctuations (Figure 10). Also, hydraulic heads are quite similar across the upper confining unit. This type of behavior suggests that water is able to move easily between the two aquifers and that upper confining unit is neither continuous nor effective in restricting flow.

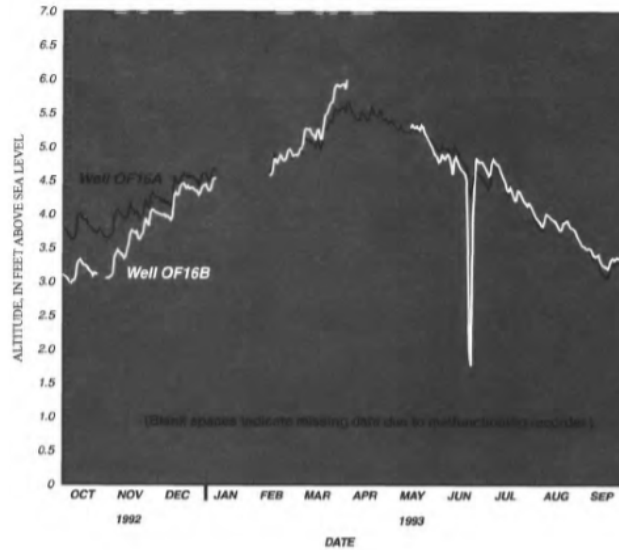


Figure 10. Hydraulic head in feet above sea level of well OF16A in the Water-Table aquifer and OF16B Upper Confined Aquifer. During Oct 1992 through to Sep 1993. (Vroblesky et al., 1995)

The water table and upper confined aquifers were instrumented with wells and piezometers. There are 31 wells in the water-table aquifer and 21 wells in the upper confined aquifer. Figure 11 is a potentiometric map design to show the pattern of groundwater flow in the water-table aquifer. In general, groundwater flows from a potentiometric high radially to water bodies around the O-field area. From a contaminant perspective, the discharge into surface here was a major concern.

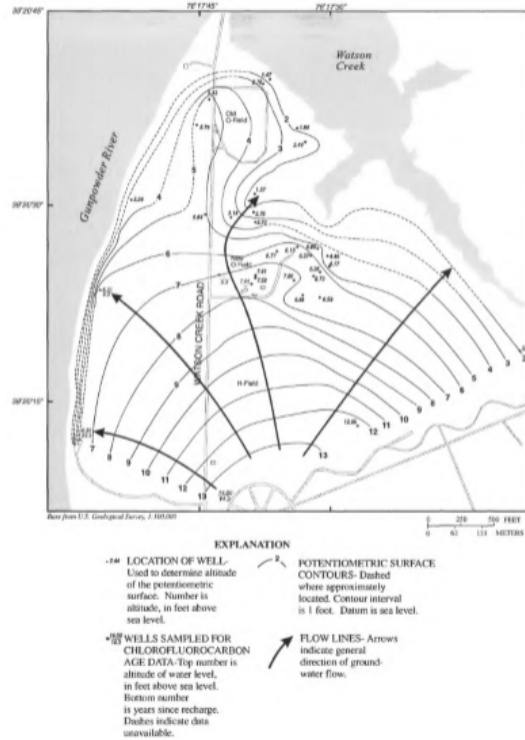


Figure 11. Potentiometric map of the O-Field Area with measurements in feet above sea level taken from June 1993. Source (Vroblesky et al., 1995)

Contaminant Hydrogeology

The history of how the Old O-field Area has been used through the years is sensitive military information that has not been made public. Thus, it is unclear as to what and how much of any material was disposed. The sensitive nature of this site also raises uncertainties concerning the depth and spatial arrangements of the trenches. It is hard to determine the timelines for disposal; or in other words what was disposed of when. Thus, only general information is provided in the USGS reports.

Background Water Chemistry

The background water chemistry for the water table aquifer at the O-field area was found by in USGS WSP (Water-Supply Paper) report 2399 (Vroblesky et al., 1995). Their study looked at the chemistry of groundwater sampled from wells between December 1985 and September 1987 to find a general background of the water in the water table water at the O-field area. The water-table aquifer was found to have a TDS of 42–120 mg/L, pH of 4.8–5.7 and dissolved oxygen (DO) of 2–6.7 mg/L. A more extensive list can be found below in table 3. These data will be used to compare contamination to the background water of the O-field area.

Table 3. Attributes and constituents in the background water in their respective units. The samples were collected from December 1985 to September 1987. DOC is dissolved organic carbon; AmmOrN is ammonia + organic nitrogen. Alkalinity is given in mg/L of bicarbonate. pH uses the standard pH scale. Specific conductance has units of microsiemens/cm. All other inorganic constituents are given in mg/L (Vroblesky et al., 1995)

Parameter	Average	Standard Deviation	Range	n
pH	5.25*	—	4.86-5.68	13
Cond.	105	16.4	79-135	12
DO	3.1	1.3	2.0-6.7	10

Alkalinity	7.5	7	0-23.5	11
Antimony	—	—	<0.003- 0.003	9
Arsenic	—	—	<0.001	9
Boron	—	—	<0.04- 0.04	9
Calcium	4.6	2.1	2.47-7.4	9
Iron	1.56	4.22	0.009- 13.5	9
Magnesium	3.8	0.8	2.95-5.8	9
Manganese	0.08	0.06	0.024- 0.22	9
Potassium	3	3.7	0.17-12.4	9
Sodium	6.6	2.1	2.96-8.98	9
Silica	7.5	1.3	5.03-9.5	6

Zinc	0.03	0.02	0.008- 0.05	9
Chloride	7.5	5.8	2.2-23.1	9
Fluoride	—	—	<0.1-0.19	9
Bromide	—	—	<0.5	8
Sulfate	27.4	6.2	20.7-40	9
Sulfide	—	—	<1	1
Nitrate	—	—	<0.05- 1.08	9
Nitrite	—	—	<0.05	9
AmmOrN	—	—	<0.28- 0.33	6
Phosphorous	—	—	<0.01- 0.11	9
Ammonia	—	—	<0.01- 0.56	9

TDS	88.4	23.9	42-120	8
DOC	1.7	0.3	1.24-2	5

Initial Assessments of Groundwater Contamination

It was early in 1970s with the initial discoveries of serious contamination at Love Canal near Niagara Falls New York when America woke up to the possibilities of serious contamination at many sites. In 1976, the Army began initial studies to identify locations across the APG-EA where UXOs and other hazards materials were located (U.S. Army, 2008b). The investigation utilized historical documents to discover areas where hazardous materials might be located. After the completion of the study in 1985, the EPA proposed that the APG-EA should be placed on the National Priorities List (NPL) (U.S. Army, 2008b). The purpose of the NPL in the U.S. and its territories is to designate sites are known or may be releasing hazardous contaminant into the environment. This list also includes sites that have national priority for further study. These sites are also commonly referred to as Superfund sites. In many cases, these are orphan sites where the original companies etc. causing the problems are no longer in business.

The dumping of wastes at APG-EA has led to the contamination of local soils, groundwater, river sediments, wetland sediments, and the local flora and fauna. Investigations by the U.S. Army found chlorinated organic solvents and high arsenic levels (Nemoff et al., 1989). Studies conducted by the U.S. Army Toxics and Hazardous

Materials Agency (USATHAMA) at the Old O-Field Area, determined that contamination was present in the water-table aquifer and in both the upper and lower confined aquifers.

Site investigations began with U.S. Army Environmental Hygiene Agency in 1985 (Vroblesky et al., 1995), In 1989, the Environmental Protection Agency (Nemoff et al., 1989) conducted studies to determine the toxicity of the ground water at the Old O-Field area. The APG-EA was officially put on the NPL in 1990.

Pump and Treat Remediation

In 1990, the USGS conducted a remedial investigation feasibility study of the O-Field area (Vroblesky et al., 1995) determined that the optimum remedy involved the installation of an engineered cap that would minimize water flows through the waste dumped at the site and the use of pumping wells to control the plumes found to be discharging into nearby water bodies. More specifically, a pump and treat system was installed in 1992 to prevent dissolved contaminants from the Old O-Field area from entering through the subsurface into Watsons creek (Vroblesky et al., 1995).

Groundwater extraction wells were emplaced along the northern and eastern sides of the hazardous waste dump. Contaminated groundwater moving away from the site is intercepted by the cones of depression of these wells and plume migration is effectively stopped. The contaminated water pumped from the wells is transported through a piping system to a treatment facility built on site (U.S. Army, 2008a). The essential features of

the remediation system at the Old O-Field area included the engineered surface liner, the system of pumping wells, and the waste-water treatment plant (Figure 12).

The treatment plant is designed to remove organic and inorganic contaminants. The treated water is then discharged into Gunpower River west of the Old O-Field area. Later on, a Permeable Infiltration Unit was used on the Old O-Field area (U.S. Army, 2008a) to mitigate the likelihood of explosive events from the UXO's and to reduce vapor release of gasses. Five-year reviews are also to be conducted on this site as are enforcement of restrictions on site access to the O-Field area and to Watson Creek areas especially for hunters and fishermen.



Figure12. This figure from Google Earth shows the Old O-Field area, the pumping wells for the remediation system and the treatment facility. Major water bodies shown are Watson Creek and Gunpowder River. The photo was taken on 5/25/2013.

Description of the Geochemical Data

The data on water chemistry comes from the summary in Nemoff et al., (1989), Table 5 for the period from December 1985 to September 1987. The table summarizes the measured concentrations organic and inorganic constituents.

One of the objectives of this study was to examine the overall quality of the chemical measurements through a cation anion balance. In essence, the test can detect errors in the analyses that would cause the sum milliequivalents of cations to be different than the anions. Due to the age of the data, no electronic copies of the data could be obtained other than the full USGS report. Thus, all data was transcribed from the USGS report 89-238 to an excel spread sheet by hand. Checks for accuracy and errors were regularly conducted after each set of well data was completed. This included visual checks and mathematical checks to minimize error with further checks conducted by the research advisor.

Determination of Cation Anion Balances

The data were transcribed into an Excel spreadsheet to facilitate the determination of the cation anion balances. Any samples for which results were missing data necessary for the calculation were not used. This screening significantly reduced the number of analyses that were available for each well was necessary to obtain an accurate and consistent results.

To calculate the cation anion balance for a water sample first requires the concentrations tabulated as mg/L to be converted to meq/L. This conversion uses the following equation (Schwartz and Zhang 2003):

$$meq/L = \frac{mg/L}{formula\ wt\ (mg)/charge}$$

where mg/L is the reported concentration of the species, e.g., Ca²⁺, formula wt is the formula weight for Ca and charge is the charge of the ion (i.e., 2 for Ca²⁺). To illustrate this calculation, consider a Ca²⁺ concentration of 8.52 mg/L reported for OF1 12/6/1985

$$0.425\ meq/L = \frac{8.52\ mg/L}{40.08\ (mg)/2}$$

Once the concentration conversion to meq/L was complete for each usable sample, they were then separated into cations and anions. The positively charged cations for each sample are added up to provide the total cations in meq/L. The total of anion concentrations for each of the samples as meq/L is also determined. An example of this calculation can be found in Schwartz and Zhang, 2003; p. 373.

These steps above can be applied to concentrations of cations and anions. For the more common constituents, there are also simple conversion factors to easily convert mg/L to meq/L. These factors are also provided by Schwartz and Zhang (2003). Once the total cation and total anions are calculated for a set of sample data, the cation anion balance can be calculated as follows:

$$Cation\ Anion\ Ratio = \frac{\Sigma cations(meq/L)}{\Sigma anions(meq/L)}$$

Ideally, the cation anion ratio for a high-quality water sample should be 1. In other words, the sum of the cations should equal the sum of the anions, meaning the sample is electrically neutral. Such perfection never occurs in practice so a water sample is considered to acceptable if the ration falls between 0.95 and 1.05 (Schwartz and Zhang, 2003). These balance calculations are evaluated in the following section to evaluate the quality of the water samples.

Results

Cation / Anion Balance

The mean value of the calculated balance of the Old O-Field area was found to be 0.932. with a Standard Deviation of 0.215. Generally, the check of the cation/anion balance is less satisfactory than is expected. The mean value itself is outside the +/- 5% value normally considered to be the range for acceptability. There could be several reasons for this result. First, the water analyses mostly considered constituents commonly comprising a so-called routine water analysis. In water that is contaminated there may be species that contribute significantly to the balance charge but were not analyzed e.g., organic ions. Second, it is not clear whether constituents known to change with time, e.g., bicarbonate, Fe, were analyzed in a timely manner or preserved. Finally, some samples completely out of balance, might reflect transcription errors or analytical errors. With so many of the studies unreleased due to security reasons, it is impossible to come to a definitive conclusion.

Severity of Contamination

The severity of contamination in groundwater at the Old O-Field area is examined through a comparison of the water quality data to commonly accepted metrics including Maximum Contaminant Level (MCLs) (Schwartz and Zhang, 2003) and background water quality. The EPA defines an MCL as:

“The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs (Maximum Contaminant Level Goals) as feasible using the best

available treatment technology and taking cost into consideration. MCLs are enforceable standards”.

All of the standards are expressed as mg/L, which for most water samples is equal to concentrations expressed as parts per million (ppm) . Note that MCLs only exist for the most hazardous of constituents in groundwater. MCLs do not exist for most of the common constituents in groundwater.

I also make use of another set of standards which are guidelines (i.e., unenforced) for drinking water. These are referred to as the National Secondary Drinking Water Regulations (NSDWRs). The EPA describes these as follows:

“National Secondary Drinking Water Regulations set non-mandatory water quality standards for 15 contaminants. EPA does not enforce these "secondary maximum contaminant levels" (SMCLs). They are established as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color, and odor. These contaminants are not considered to present a risk to human health at the SMCL” (EPA, web)

The following sections compare contaminant concentrations and pH for samples collected from the various aquifers in the old O-Field area. Values are compared to MCL, SMCL and estimates of the constituent concentrations under background conditions.

pH

According to the EPA's SMCL, the pH for drinking water should fall in the range 6.5 to 8.5. The background concentrations of groundwater at the O-Field areas found by USGS (Vroblesky et al., 1995), had pH values ranging from 4.86-5.68, with an average of pH 5.25.

Overall, the pH of samples collected from the water table aquifer is below the SMCL of 6.5-8.5 pH (Figure 14). The background pH that was found by USGS (Vroblesky et al., 1995) is in the middle of the measurements pH 5.3. There is a high range of averages for well pH's, the lowest average is pH 4.5 and the highest average is pH 6.4.

The upper confined aquifer has higher pH with less variability within the aquifer as compared to the water table aquifer. The background water pH found by USGS (Vroblesky et al., 1995) is lower than the measurements observed with a pH of 5.3. Background water does not meet SMCL, falling below the lower limit of 6.5 pH (Figure 14). Overall, the pH of groundwater in the water table aquifer is somewhat lower and more variable than in the upper confined aquifer. This may be an indication that groundwater in the water table aquifer is more contaminated than the underlying aquifer.

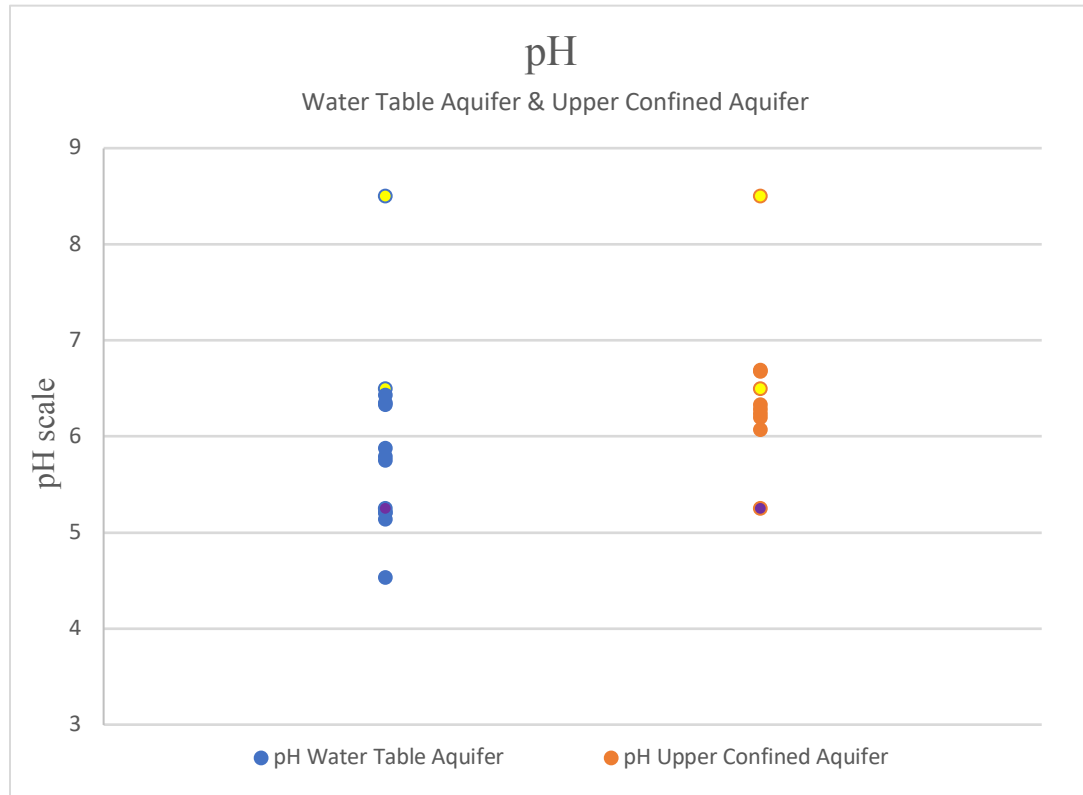


Figure 14. Average pH of each well from which samples were collected. The blue circles represent values for the water table aquifer and the orange circles represent values for the upper confined aquifer. The circles with a yellow fill represent the SMCL upper and lower limits of 8.5 and 6.5, respectively. The purple filled circles indicate the pH of background water.

Chloride

The SCML for chloride is 250 mg/L. There is not a MCL available for this contaminant. The evaluation of background water chemistry of Old O-Field area was found by USGS (Vrobley et al., 1995), indicated range for Cl from 2.2 to 23.1 mg/L with an average of 7.5 mg/L.

The chloride concentrations from sampling wells completed in the water table aquifer are highly variable with a range exceeding two-orders-of-magnitude (Figure 15). Some sample values for chloride are close to the background concentration of 7.5 mg/L but the majority is much higher. The SMCL for chloride is 250 mg/L and there is one average value found from well OF20A indicating a concentration of one order-of-magnitude higher average than the SMCL.

The chloride averages in the upper confined aquifer well samples are less variable with a range larger than one order of magnitude (Figure 16). Some samples averages for chloride are near the background of 7.5 mg/L but the majority are much higher. The SMCL for chloride is 250 mg/L and none of the averages exceeds the SMCL. It is likely therefore that water table aquifer has higher chloride values due to contamination. The upper confined aquifer may have chloride concentrations that are influenced by Chesapeake Bay.

Iron

The SMCL for iron is 0.3mg/L. There is no MCL for the concentration of iron. The background water chemistry of Old O-Field area was found by USGS (Vroblesky et al., 1995) to range 0.009–13.5 mg/L with an average of 1.56 mg/L. The data were analyzed by utilizing the averages for each well over their respective sampling periods.

Iron in the water table aquifer has a very high variability with a range of about 3.5 orders of magnitude (Figure 15). The SMCL of 0.3 mg/L is exceeded by every well

average except that from well OF13A with an average of 0.11 mg/L. The highest iron concentration is ~245 mg/L which is about 3 orders of magnitude larger than the SMCL.

Iron concentrations in the upper confined aquifer had a range of about an order-of-magnitude. The SMCL of 0.3 mg/L is exceeded in every well sampled, and even the background of 1.56 mg/L. The highest iron concentration is 98.4 mg/L which is about 2.5 orders of magnitude larger than the SMCL. All averages greatly exceed the background iron concentrations (Figure 16). It is likely that the high iron concentrations are being facilitated by anoxic conditions created by the presence of organic compounds and the low pH.

Sulfate

Sulfate has a SMCL of 250 mg/L and has no MCL. The background concentration for groundwater ranged from 20.7 to 40 mg/L with an average of 27.4 mg/L. The data were analyzed by utilizing the averages for each well over their respective sampling periods.

The Water Table Aquifer has concentrations of sulfate lower than the SMCL level of 250 mg/L (Figure 15). The background concentration for sulfate (i.e., of 27.7 mg/L) is generally lower than most of the concentration averages found by sampling the wells.

The Upper Confined Aquifer has concentrations of sulfate lower than the SMCL level of 250 mg/L (Figure 16). The concentration values determined for several of the samples are all lower than background (27.7 mg/L). The lower sulfate concentrations

here could be due to lowering of concentrations via sulfate reduction reactions in association with organic contaminants.

TDS (Total Dissolved Solids)

The SMCL for TDS is 500 mg/L with no MCL. The background TDS for the Old O-Field area was found by USGS (Vroblesky et al., 1995), to have a range of 42–120 mg/L and an average of 85.4 mg/L.

TDS in the water table aquifer to be highly variable over a range of about 1.5 orders of magnitude (Figure 15). The SMCL is 500 mg/L with the highest TDS found to be 3230 mg/L at OF20A. All the concentration in wells exceeded the background TDS of 85.4 mg/L.

The TDS in the upper confined aquifer has a variability of about 1 order of magnitude (Figure 16). The SMCL is 500 mg/L and none of the well averages exceed 500mg/L. The background amount of 85.4 mg/L is exceeded by every well average.

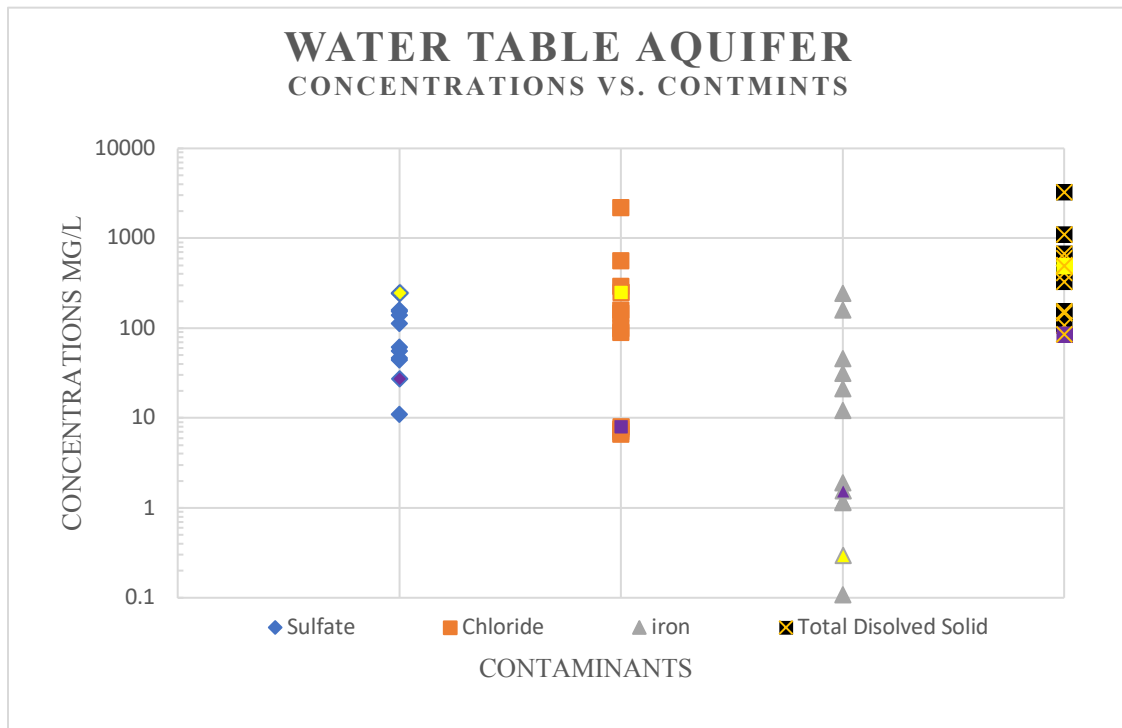


Figure 15. Concentrations in mg/L for sulfate, chloride, iron and TDS in groundwater from the water table aquifer, plotted on a logarithmic scale. The yellow symbols for each contaminant are EPA's SMCL, the purple symbols for each contaminant are the background water chemistry of the O-field area.

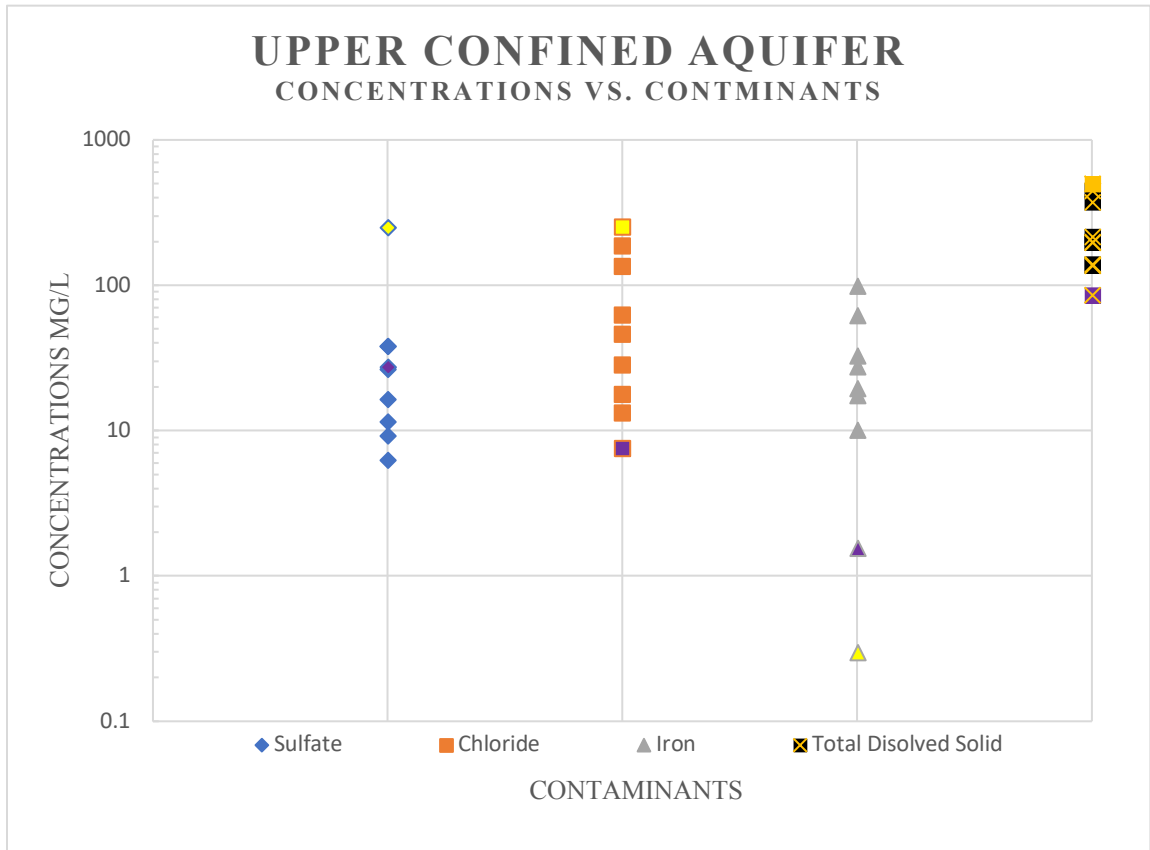


Figure 16. Concentrations in mg/L for sulfate, chloride, iron and TDS in groundwater from the upper confined aquifer, plotted on a logarithmic scale. The yellow symbols for each contaminant are EPA's SMCL, the purple symbols for each contaminant are the background water chemistry of the O-field area.

Discussion

The cation/anion balance results suggest a slight excess in anions water chemistry. This bias is unusual in that ideally one will expect the mean to be 1.00 with some spread due to small errors. As mentioned, this difference could be due to the large amounts of contaminants some of which may not have been measured. Another reason might be due to the presence of positively charged organic compounds that were not included in the cation/anion balance.

The pH of the well measurements in the water table aquifer were not all within the range of background water. This indicates that the contamination has changed the pH of the ground water. Due to the distribution, it is not clear if the overall pH is changing at the present time to become more basic. What is clear is that a rather pronounced spatial variability of pH is being measured. It is likely that this variability could be caused by spatial heterogeneity in the loading of the hazardous waste dump at the Old O-field.

The pH in the upper confined aquifer is higher than the background pH, but the variance of the measurements was very small. The reason for the rise in pH from the background water chemistry is not known. What is known is that in this rain fed systems pH has risen to near SMCL levels.

The species of interest in the water table have been shown to have a large variability in concentrations. This suggest that there is significant variability caused by different sources or transport within the aquifer. The iron possibly originates from the degradation of steel barrels, UXO shells, and other steel items in the waste. Thus, the

large concentration of dissolved iron at the site is not surprising. This is exactly what the data shows with measurements many orders of magnitude above the SMCL and the background water chemistry. It is likely that the combination of the low pH of the groundwater and reducing conditions caused by the large concentrations of organic compounds is an important contributing factor.

It is also known that there were chemical UXOs buried at the site. Some of these agents have led to an increase over the background concentration of chloride, which is an ingredient in many chemical munitions developed at the APG-EA in its early days. It is known that such materials were disposed of in Old O-Field area. Sulfate was found to exceed its background concentration but does not exceed the SMCL. This result was unexpected due to the diverse collection of contaminants placed into the ground at the site. It could be that concentrations were higher in the past but declined due to the reduction of sulfate by bacteria.

The elevated TDS content of groundwater in the water table aquifer was to be expected. Indeed, the data show a large increase in TDS over the background water and in some cases concentrations that exceed the SMCL of 500 mg/L. Before the cap was installed, recharge had ready access to the various wastes, many of which could dissolve given the weakly acid groundwater.

The concentrations of the species of interest in groundwater in the upper confined aquifer appear less elevated relative the natural background. Nevertheless, the groundwater there appears to be contaminated. The average concentrations of sulfate are considerably less than the SMCL and are all close to concentrations indicated for the

natural background water. Chloride concentration levels are elevated above the background concentration but do not surpass the SMCL. Measured concentrations of chloride suggest somewhat lower levels of contamination in this aquifer. TDS is elevated well above the background level but does not surpass the SMCL. Where the upper confined aquifer does differ greatly from the other species is in terms of iron concentrations. Iron exceeds the SMCL and background concentrations. Perhaps reducing groundwater may mobilize naturally occurring iron in the sediments.

There is no doubt that the water table aquifer is more contaminated as compared to the upper confined aquifer. However, the USGS and military treat the upper confined aquifer as an isolated and confined aquifer. With the elevated measurements of species over the natural background and a water chemistry that is closer in many ways to the water table aquifer, it does not look to be the case. Before human disturbances on the site the upper confined aquifer was probably more confined than now. After multiple explosions on the site, other disturbances (e.g., trenching), the thin upper confining layer is probably less effective. Now, I do not think that the two aquifers isolated from one another anymore.

Conclusions

This purpose of this thesis was to examine a case study of contamination at the Aberdeen Proving Ground in Maryland with a focus on groundwater. The study specifically examined historical water quality data from wells and piezometers at the Old O-Field area, a site with buried ordinance and other hazardous warfare agents.

Part of the investigation involved an assessment of the quality of the routine water analyses that were undertaken by the USGS and environmental companies working at the site. The overall approach involved the calculation of cation/anion balances for all publicly available data collected by and tabulated by the USGS (Nemoff et al., 1989). My analysis determined that the cation/anion balance was biased towards an excess of anions relative to the cations. With the information provided, it was not possible to determine the specific cause of the imbalance.

The analysis of the extent of contamination of the water table aquifer and upper confined aquifers involved comparing the results of chemical analyses of wells and piezometers installed at the site to (i) background water chemistry established for the site, and (ii) common regulatory standards used for this purpose, MCL and SMCLs. The results of the analyses indicate contamination of the Old O-Field area. In the cases of the constituents of interest pH, chloride, iron, sulfate and TDS were present at concentrations above background. Iron was the most striking because it was shown to be orders of magnitude higher than EPA's SMCL and background water chemistry. The analysis was hindered by the absence of available information on organic contaminants, which were

problematic at this site. Thus, the overall severity of contamination at the site could not be fully determined because of this data gap.

The study specifically examined the extent of contamination in the water table aquifer compared to the deeper the upper confined aquifer. Contamination was evident in both aquifers but muted in the upper confined aquifer compared to the water table aquifer. I concluded that the confining layer separating these two aquifers was not effective in controlling the downward spread of contamination. However due to the similarities of the concentrations of parameters and species in the two aquifers, it is likely that the aquifers are coupled and should not be treated as independent from one another at the Old O-Field area.

Suggestions for Future Work

This thesis leaves yet more questions to be answered. In the future a researcher would want to file more Freedom of Information Act Requests targeting the multiple five-year reviews that the U.S. Army has conducted to acquire more data that is not currently publicly available. This would make it easier to assess contamination levels through time. Someone may also want to do an on-site testing of the ground water. On site testing will be challenging due to the restricted access on base and on the Old O-Field site. If on site tests could be conducted further research could compare the contamination levels over time and have a more updated data set for other researchers to utilize.

Appendix

Appendix I

Empirical results of the cation anion balance.

Cation/Anion ratio	0.931541446
Standard Dev.	0.215087696
Norm Distribution	0.624864503
n	118

Appendix II

Data from the water table aquifer that was used to create Figure 15 and pH values used in Figure 14. The pH values are using the pH scale. For sulfate, chloride, iron and TDS all values are the well average values expressed in mg/L.

Water Table Aquifer Averages Per Well					
Wells	pH	Sulfate	Chloride	Iron	TDS
OF6A	5.79	113.24	286.17	45.76	669.58
OF12A	5.21	140.5	157.5	1.9	602
OF13A	5.14	44.1	6.57	0.11	108.17
OF14B	5.88	11.07	549.88	159.33	1097.83
OF17A	4.53	153.8	88.36	31.36	328.71
OF18A	5.21	55.8	7.96	1.17	155
OF19	6.35	47	6.99	12.17	146
OF20A	6.43	245	2150	245	3230
OF21	5.75	61.2	145	21.4	411
OF22A	6.33	160	97	1.14	496
SMCL	6.5-8.5	250	250	0.3	500
BWC	5.25	27.7	7.5	1.56	85.4

Appendix III

Data from the Upper confined aquifer that were used to create Figure 16 and pH values used in Figure 14. The pH values are using the pH scale. For sulfate, chloride, iron and TDS all values are the well average values expressed in mg/L.

Upper Confined Aquifer Averages Per Well					
Wells	pH	Sulfate	Chloride	Iron	TDS
OF6B	6.28	6.28	134.02	62	371.3
OF12B	6.68	11.55	13.05	10.04	135.8
OF14C	6.08	16.3	184.1	98.38	444.8
OF17B	6.3	9.23	45.68	32.75	214.7
OF18B	6.2	37.8	17.6	19.44	198.7
OF20B	6.69	26.5	28	17.5	139
OF22B	6.2	38	62	27.5	196
SMCL	6.5-8.5	250	250	0.3	500
BWC	5.25	27.4	7.5	1.56	85.4

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