A CASE FOR BACKGROUND LEVELS OF ARSENIC IN GROUNDWATER AT THE MASSACHUSETTS MILITARY RESERVATION

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Introduction

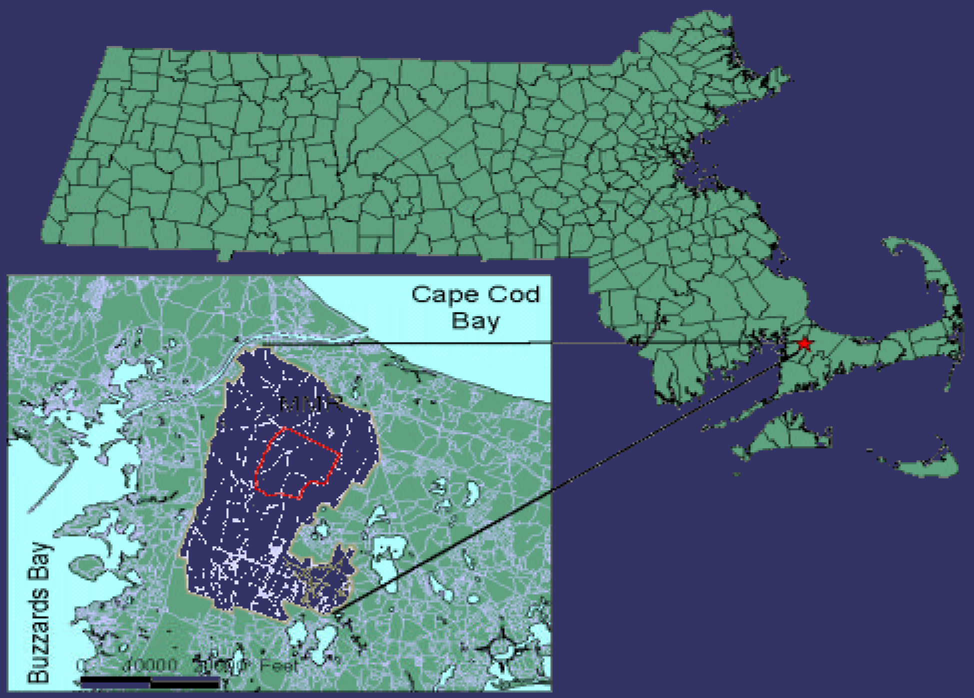
- Military training ranges under scrutiny
  - Potential impacts to ecology and environment
  - Complex issues and problems
- Major ranges receiving attention
  - Massachusetts Military Reservation (MMR) - ARNG
  - NoMan Island
  - Vieques, Puerto Rico - U.S. Navy

The Massachusetts Military Reservation (MMR) is a 21,000-acre facility located on Cape Cod, in the
County, Massachusetts . The Massachusetts Army National Guard (MAARNG) conducts training ope
Bureau (NGB). Approximately 14,000-acres of Camp Edwards constitute the Training Ranges and C
which artillery and mortars were fired during training activities. Numerous firing ranges, artillery and r
Central Impact Area lie directly over the Sagamore Lens, a major groundwater recharge area and the
apex of the Sagamore Lens located at the southeast corner of the Central Impact Area.

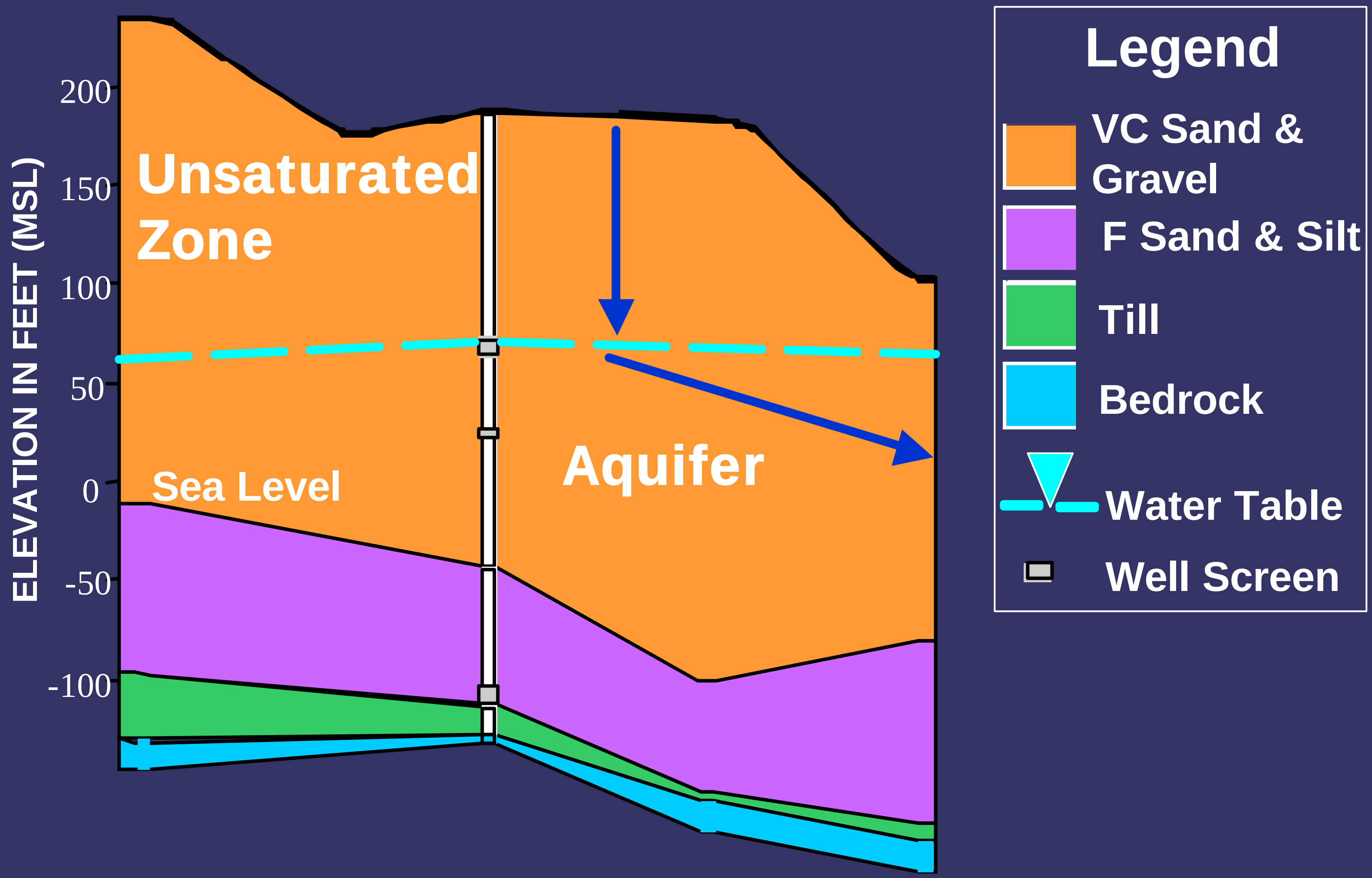
Portions of the MMR were used by the military beginning in the early 1900s; however, the majority of
Navy, U.S. Coast Guard, U.S. Air Force, MAARNG, U.S. Air National Guard, and Veterans Administra
activity at the MMR has varied over its operational history. The most intensive U.S. Army activity occ
years, the Central Impact Area has received ordnance discharged from small arms, guns, hand grena
compound used in post-WWII artillery and mortar munitions is Composition B, which is a mixture of h
primarily contained TNT as the principal explosive. The U.S. Army operated the area until about 197

Camp Edwards - Site History

- Training and Impact Areas used since 1911
- Designed to house 30,000 troops during WWII
- USEPA banned training in 1997 through an administrative order

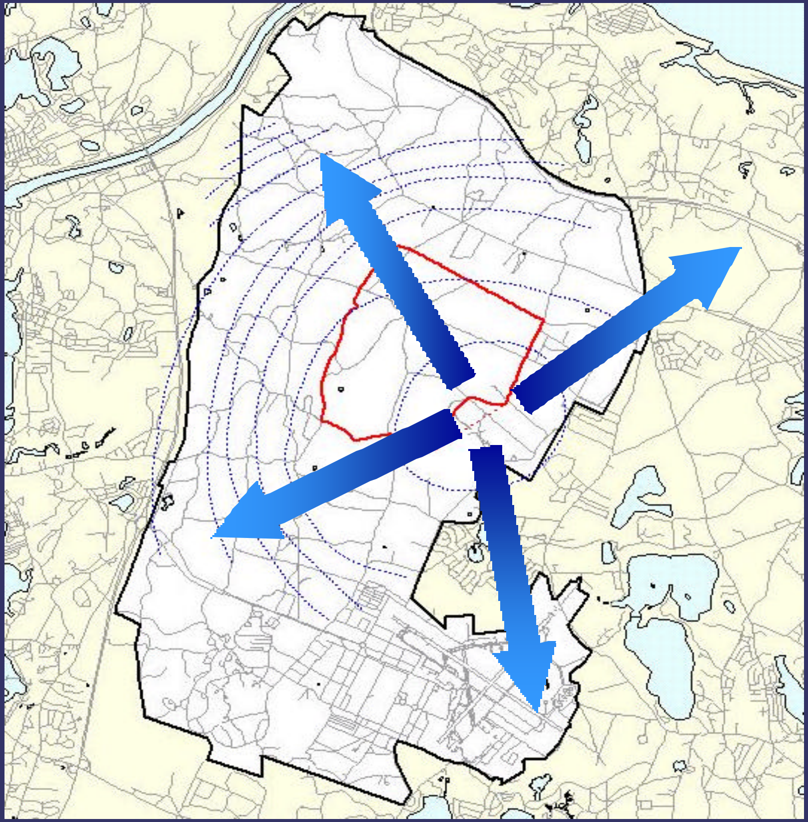


Site Lithology



The geology of western Cape Cod is comprised of glacial sediments deposited during the retreat of the Wisconsin stage of Holocene glaciation. Three extensive sedimentary units dominate the regional geology: the Buzzards Bay and Sandwich Moraines, and the Mashpee Pitted Plain. The Buzzards Bay Moraine and the Sandwich Moraine lie along the western and northern edges of Camp Edwards, respectively. The Mashpee Pitted Plain, which consists of fine to coarse-grained sands forming a broad outwash plain, lies between the two moraines. Underlying the Mashpee Pitted Plain are fine-grained, glaciolacustrine sediments and basal till at the base of the unconsolidated sediments. The Buzzards Bay Moraine and Sandwich Moraine are composed of ablation till, which is unsorted material ranging from clay particles to boulder size [boulders? ☺] deposited at the leading edge of two lobes of the Wisconsinian glacier at its furthest advance. These moraines form hummocky ridges to the west and north of the Central Impact Area. A generalized lithologic sequence for the Central Impact Area. The total thickness of unconsolidated sediments overlying bedrock varies from approximately 328 to 375 feet. The thickness of the unsaturated zone varies from 60 to 120 feet across the Central Impact Area. Conversely, the thickness of the saturated zone varies from 200 to 300 feet. A topographic bedrock high is present in the southeast corner of the Central Impact Area, in the area of the J Ranges. Another bedrock high is present in the northwest corner of the Central Impact Area.

Hydrogeologic Model



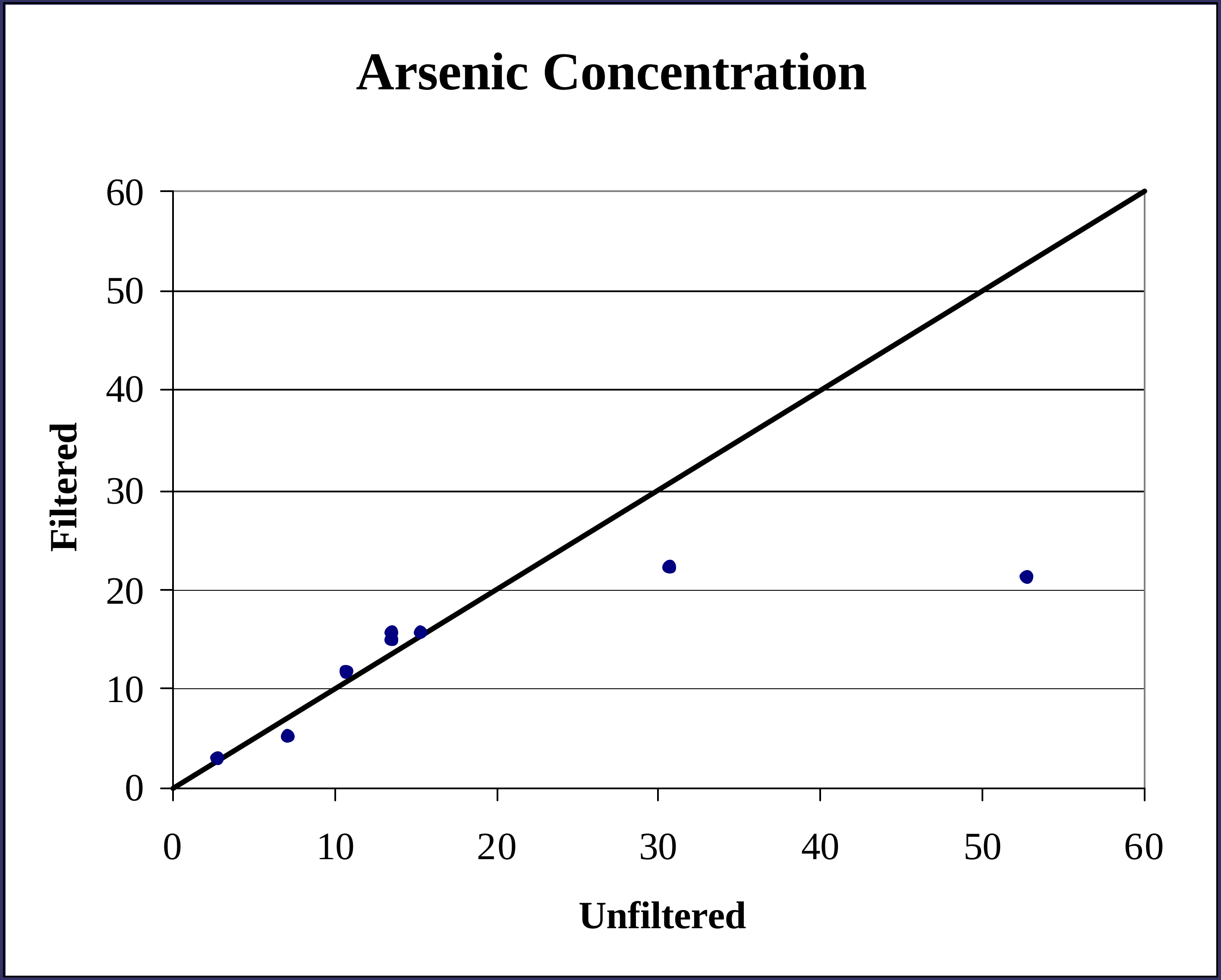
- Groundwater flow is radial with the mound to the southeast of the Impact Area
Groundwater flow is approximately one foot per day

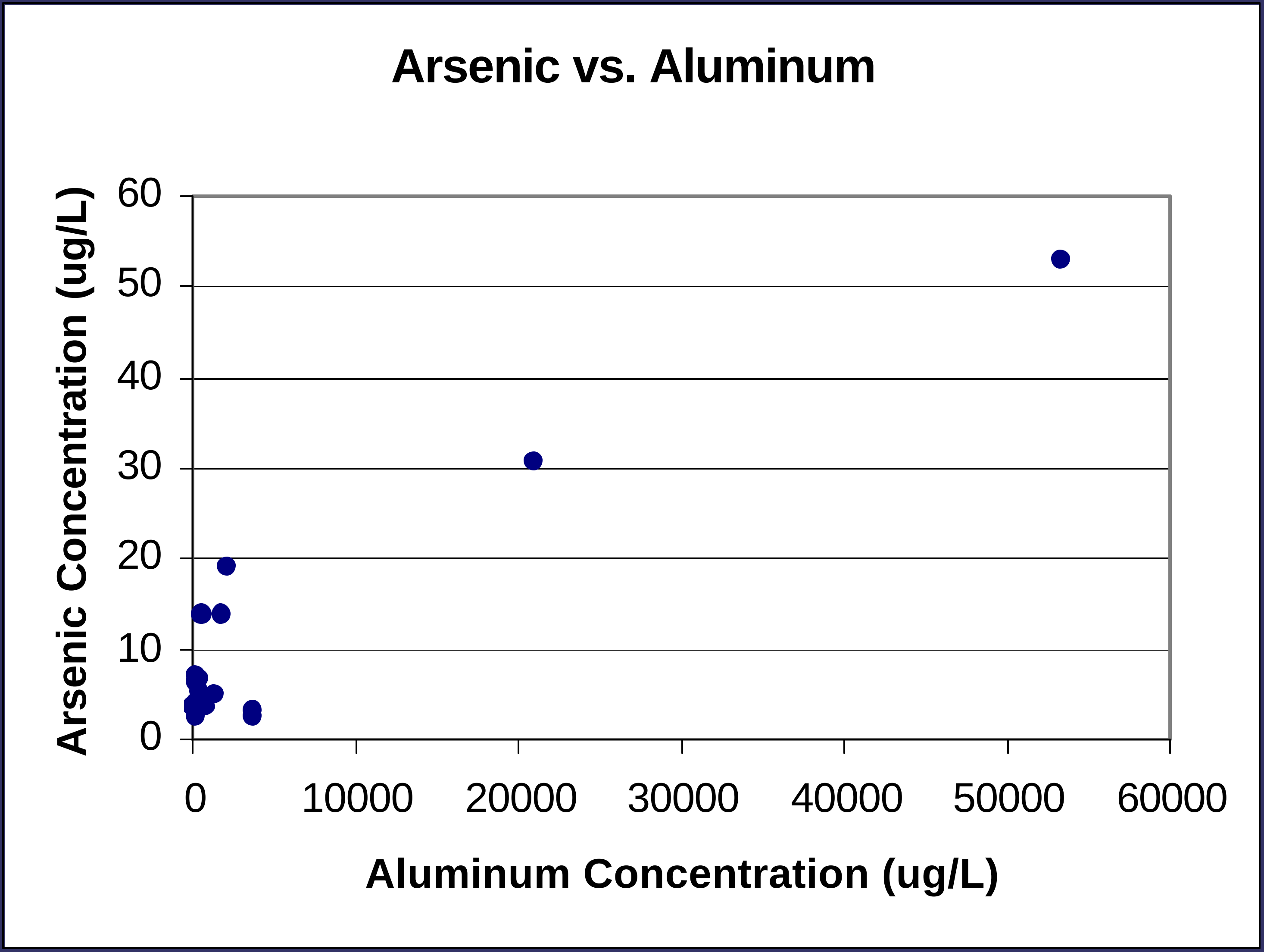
A single groundwater aquifer system underlies western Cape Cod, including Camp Edwards and the Central Impact Area. The aquifer system is unconfined (i.e., it is in equilibrium with atmospheric pressure and is recharged by infiltration from precipitation). Except on extreme slopes, surface water runoff at Camp Edwards is virtually nonexistent due to the highly permeable nature of the sand and gravel underlying the area. The high point of the water table occurs as a groundwater mound beneath the southeastern the Central Impact Area, the groundwater elevation is typically between 60 and 70 feet national geodetic vertical datum (ngvd) or approximately 100 to 120 feet below ground surface (bgs). Groundwater flow radiates outward from this mound. The ocean bounds the aquifer on three sides, and groundwater discharges into Nantucket Sound on the south, Buzzards Bay on the west, and Cape Cod Bay on the north. The Bass River in Yarmouth forms the eastern lateral aquifer boundary.

The unconsolidated deposits in the unsaturated zone consist of very coarse sand and gravel associated with topset and foreset sedimentary facies. Unconsolidated deposits within the saturated zone exhibit a coarsening upward sequence (lacustrine, bottomset, foreset, and topset sedimentary facies) consistent with a glacial depositional environment (Masterson et al. 1996). The lithologic material varies from very coarse sand and gravel at the top of the saturated zone to silt and clay at the bottom. The horizontal hydraulic conductivity of these materials is assumed to range from 125 to 350 feet/day based on grain size analysis (Masterson et al. 1996). The ratio of the horizontal to vertical hydraulic conductivity is 3:1. A layer of till (< 5 to 20 feet thick) is present on top of bedrock. The hydraulic conductivity of the till is estimated at 1 foot/day (Masterson et al. 1996). Bedrock is present at a depth of 285 to 365 feet bgs beneath the Central Impact Area and can be considered impermeable. Therefore, the bulk of regional groundwater flow is transmitted though the upper outwash units. Porosity estimates have been made for the aquifer at MMR and range from 0.30 to 0.40 based on soil lithology. The hydraulic gradient across MMR ranges from 0.008 to 0.0014 foot/foot.

Methods

- Method IM40 Soil and Groundwater
  - Soil Reporting Limit – 1.1 mg/kg
  - Soil MDL – 1.0 mg/kg
  - Groundwater Reporting Limit – 4.2 ug/L
  - Groundwater MDL – 4.0 ug/L


Arsenic Concentration
60
50
40
30
20
10
0
Filtered
0
10
20
30
40
50
60
Unfiltered



Arsenic vs. Aluminum
Arsenic Concentration (ug/L)
60
50
40
30
20
10
0
0
10000
20000
30000
40000
50000
60000
Aluminum Concentration (ug/L)

Arsenic occurs widely in the earth's crust, where it is usually associated with sulfides. Ayotte et. al. (1999) have noted that many studies have been conducted to determine the elevated levels of arsenic in groundwater throughout New England, but the definitive cause has not been identified. Munitions reported for Camp Edwards do not have any arsenic constituents.

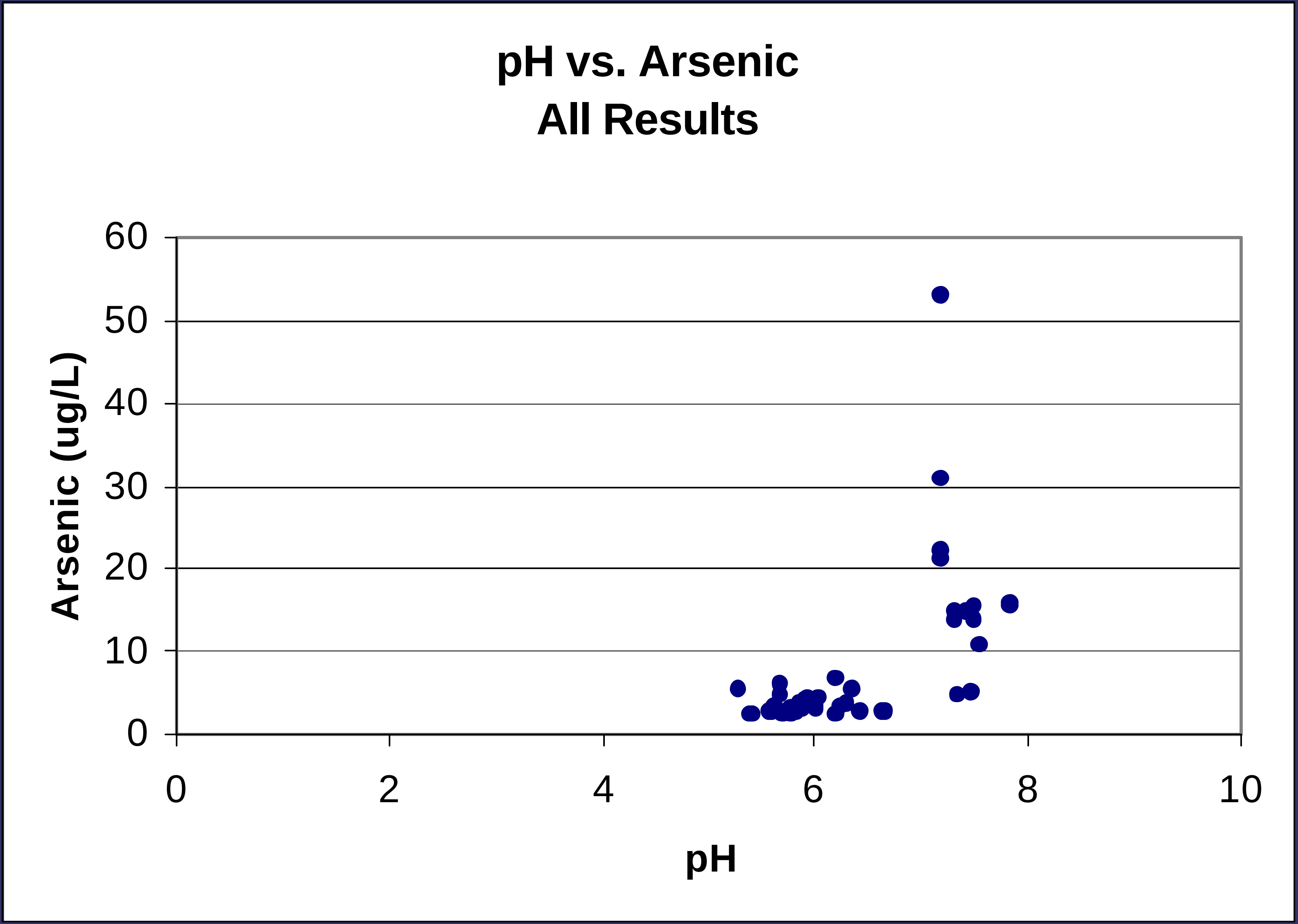
The mean arsenic concentration in the Central Impact Area is 7.74 ug/L with a maximum concentration of 52.8 ug/L. The current USEPA MCL is 50 ug/L, although the USEPA is proposing a new value of 10 ug/L. Korte (1990) reports that naturally occurring arsenic is common in alluvial aquifers of the U.S. In unconsolidated aquifers of the New England Coastal Basin, 7.5 percent of samples exceed the USEPA MCL of 50 ug/L (Ayotte, et. al., 1999). The frequency of detection for the unfiltered samples collected in the Central Impact Area that exceed the arsenic MCL of 50 ug/L is 6.7 percent , which is consistent with the New England Coastal Basin study. Andreae (1980) reports that rain from terrestrial air masses averages 0.46 ug/L arsenic. Thus, nearly one quarter of the arsenic present in groundwater at Camp Edwards can be attributed to precipitation alone.

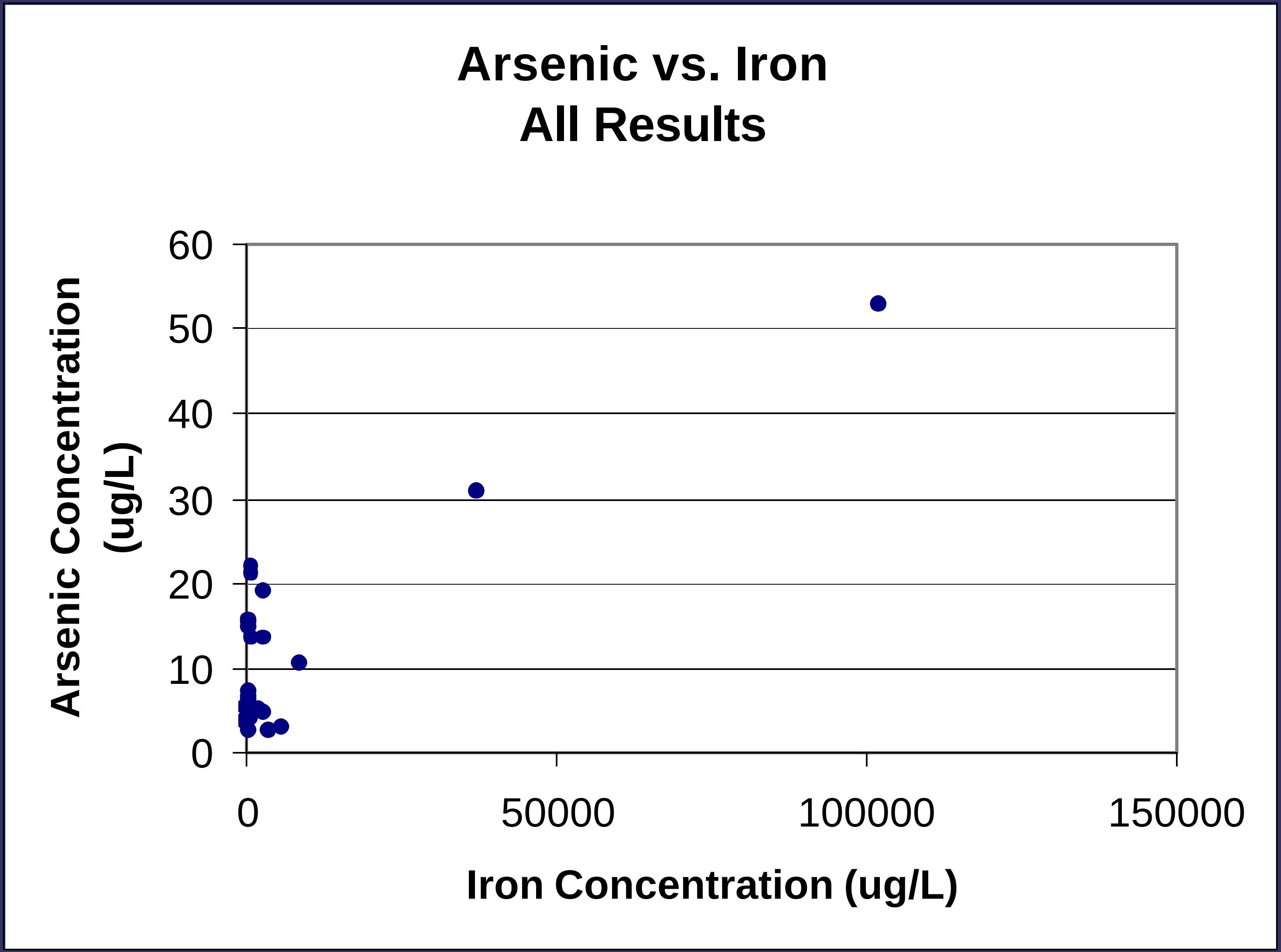
All of the arsenic values greater than 10 ug/L occurred at 58MW0010A and MW-7M1. The concentrations at MW-7M1 are influenced by the amount of iron and possibly aluminum and manganese suggesting a turbidity issue. The highest unfiltered arsenic concentrations coincided with an exceptionally large amount of iron and aluminum in the unfiltered samples. The concentration of aluminum and iron is above the solubility limit for these two metals at the Eh and pH conditions for this sample. It is clear the unfiltered sample collected on September 7, 1999 is an anomalous sample, which is not reflective of aquifer conditions at this location. It is likely a iron or manganese particulate containing arsenic sorbed onto the surface was present in the unfiltered sample. Upon acidification of the sample for preservation purposes the arsenic went into solution and was thus analyzed. The turbidity level has also been declining from a high of 286 NTUs on January 23, 1998 to non-detect on August 8, 2000. Arsenic was not detected in the August 8, 2000 sampling event. The other three wells screened at this location MW-7S, MW-7M2, and MW-7D have not had elevated arsenic levels. The data would suggest a zone with higher arsenic levels which is associated with a higher concentration of iron and manganese present in the aquifer matrix as will be discussed below.

Arsenic occurs in groundwater as an arsenate As(V) or arsenite As(III) and thus is expected to be dissolved and mobile. Differentiation of the type of arsenic is important because As(III) is 25 to 60 times more toxic than As(V) (Morrison et al. 1989). In addition, As(V) is much less mobile than As(III). Based on the Eh, pH data the majority of the groundwater samples from the Central Impact Area fall within the As(V) stability field as expected for an oxidizing groundwater environment (Brookins, 1988).

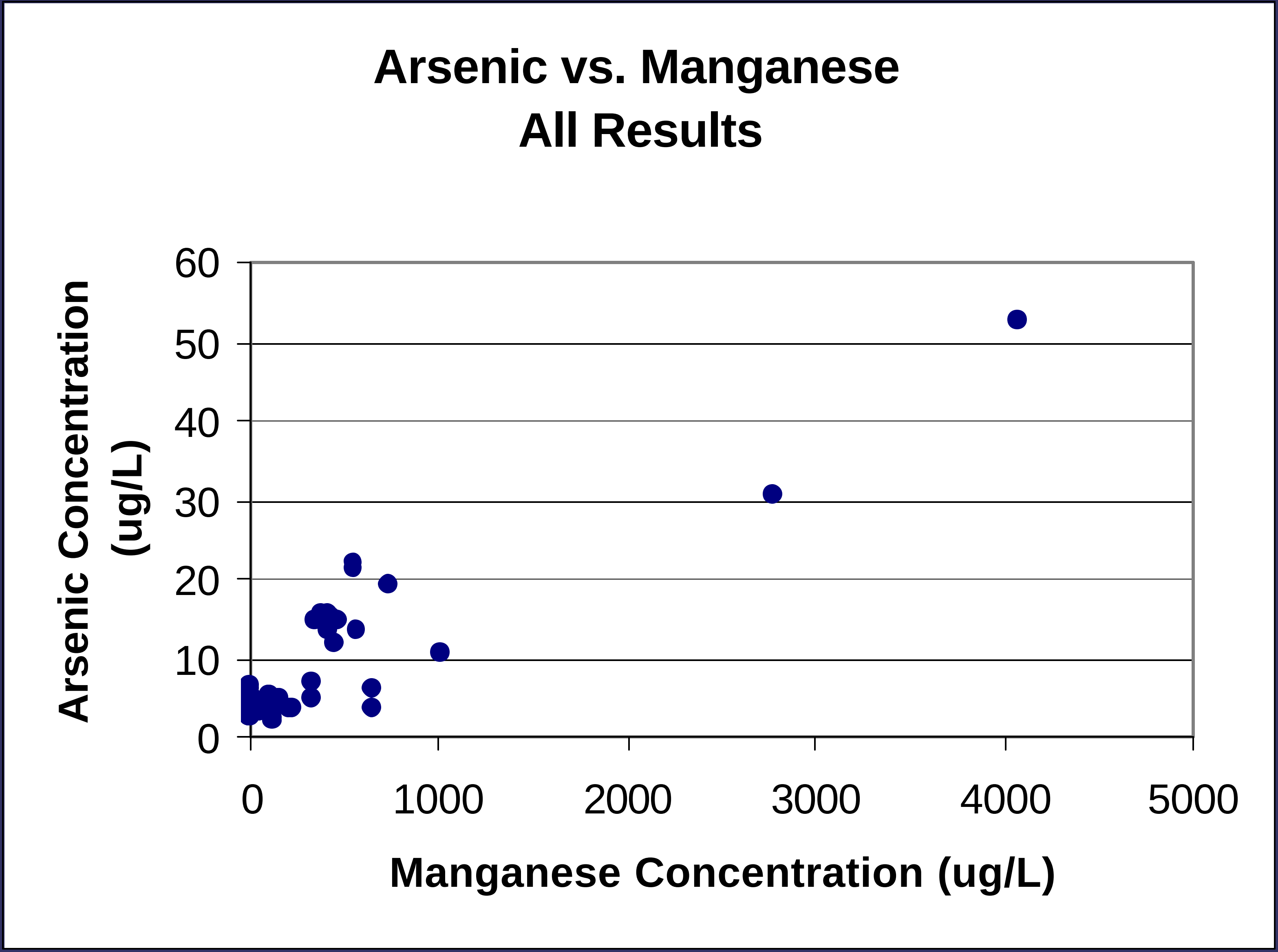
The presence of copper can limit arsenic's solubility to approximately 200 to 400 mg/L (Hem, 1989). Also the sorption of metal arsenates on iron and manganese can also limit arsenic solubility. In the absence of a relationship between the concentration of arsenic with pH, aluminum, iron, or manganese it can be safely assumed that arsenic is present as a dissolved species (Hem, 1989). A relationship does exist between the arsenic concentration and the pH, aluminum and manganese concentrations in groundwater for MMR. As the pH of the groundwater increases so does the concentration of arsenic. As the aluminum and manganese concentrations increase so does the arsenic concentration. The relationship is less clear between arsenic and iron. Korte (1990) indicates that arsenic is expected to be adsorbed to iron oxides. Considering arsenic's chemistry it is also likely that arsenic will be strongly adsorbed to aluminum and manganese oxides as well. The elevated aluminum concentrations in the groundwater samples can be explained by the presence of suspended solids. It appears the elevated arsenic concentrations can also be explained by the presence of suspended solids with arsenic being adsorbed to manganese oxide particulates. A comparison of filtered versus unfiltered samples, indicating non-agreement between the two at the higher unfiltered arsenic concentrations. There is good agreement at concentrations up to 17-18 ug/l, indicating that arsenic in these samples is likely present in the dissolved form. If the arsenic were dissolved as predicted by its geochemical stability field, all the data points would plot on the line. When the unfiltered groundwater samples, with high particulate matter, are acidified following the USEPA preservation protocols the reduced pH releases arsenic from iron and manganese oxyhydroxides into solution (Xu et. al., 1991).

There is no pattern in the detections of arsenic either spatially or with depth to suggest arsenic is a contaminant in groundwater at Camp Edwards (Figure 5-26). The elevated arsenic concentrations appear to be partly a function of particulates present in the groundwater samples. The lower concentrations likely represent the ambient groundwater quality. There is no evidence that arsenic measured in groundwater samples indicates contamination resulting from military training activities.


pH vs. Arsenic
All Results
Arsenic (ug/L)
60
50
40
30
20
10
0
0
2
4
6
8
10
pH

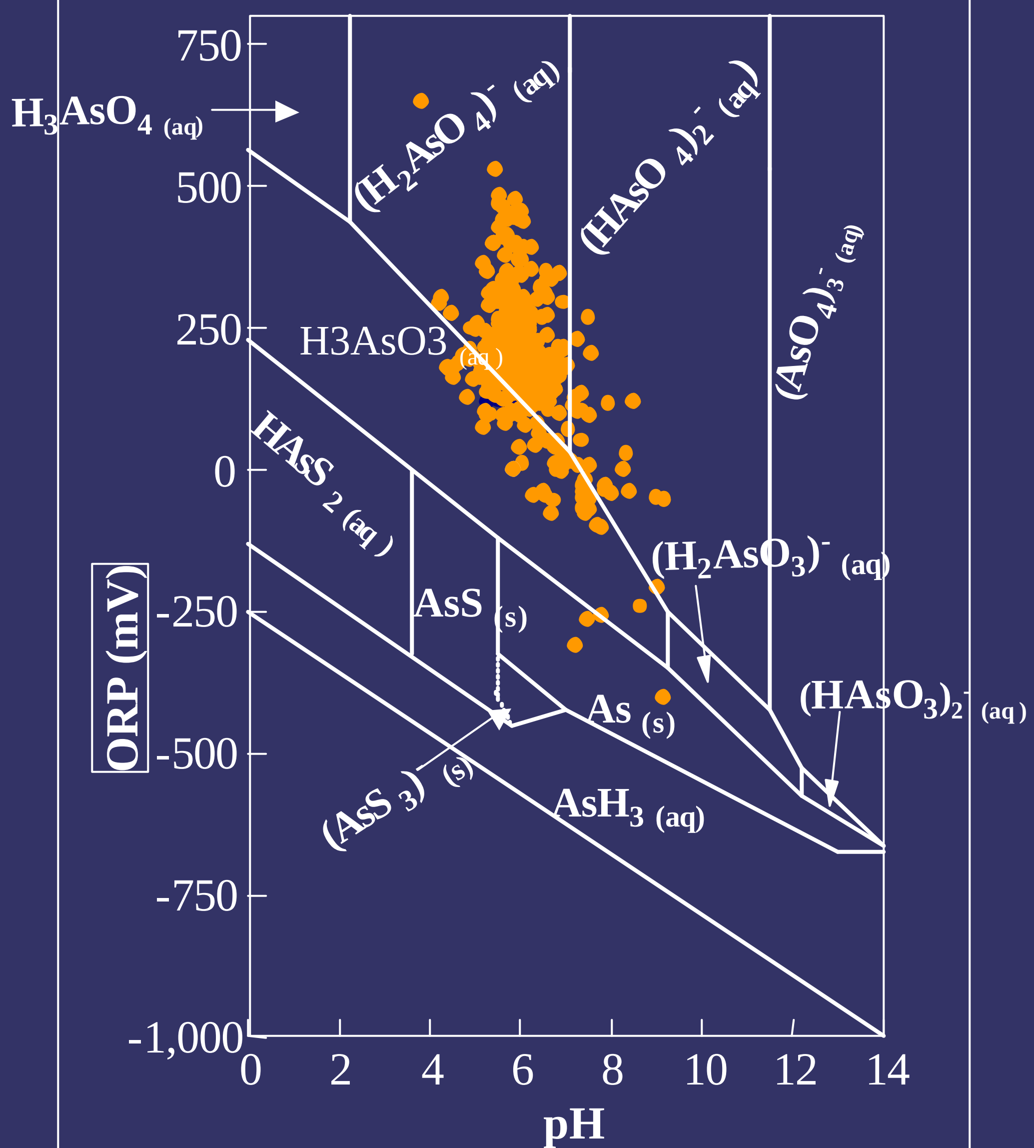


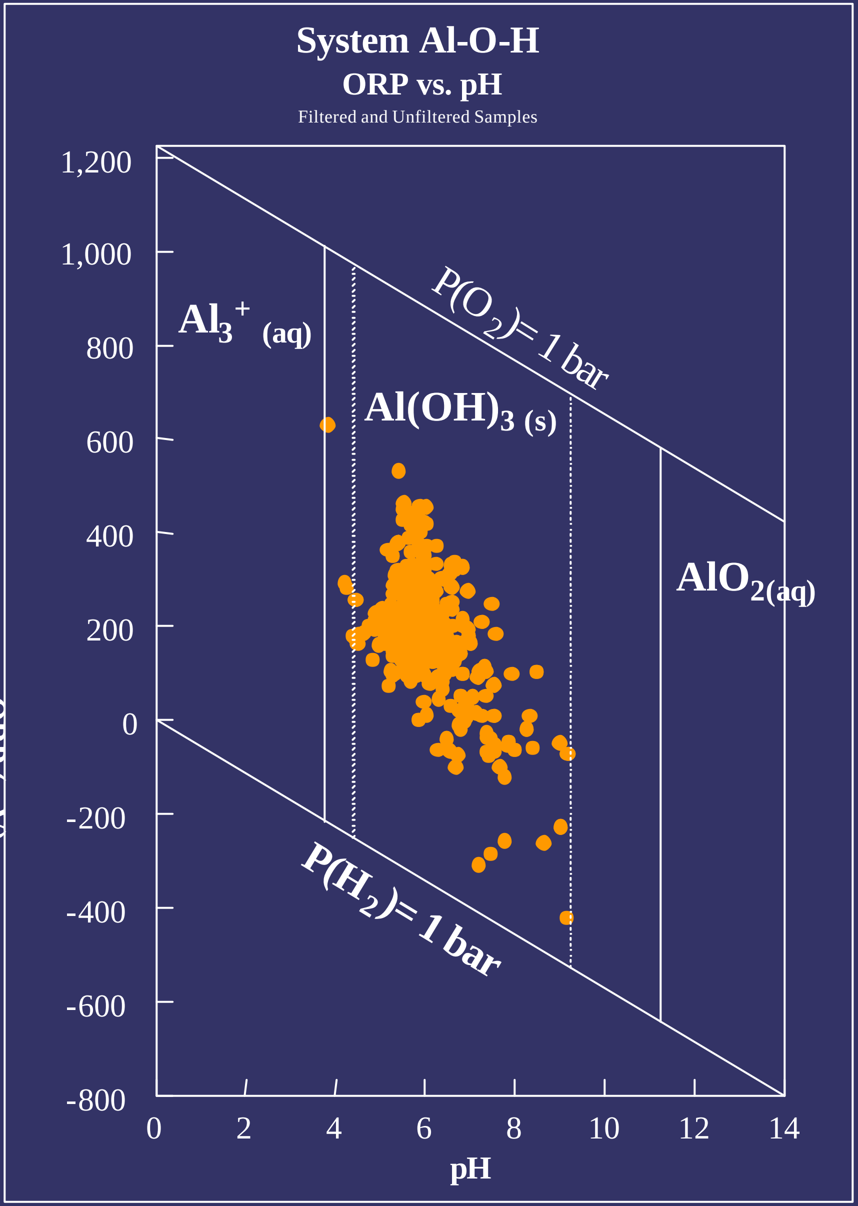
Arsenic vs. Iron
All Results
Arsenic Concentration (ug/L)
60
50
40
30
20
10
0
0
50000
100000
150000
Iron Concentration (ug/L)



Arsenic vs. Manganese
All Results
Arsenic Concentration (ug/L)
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
Manganese Concentration (ug/L)

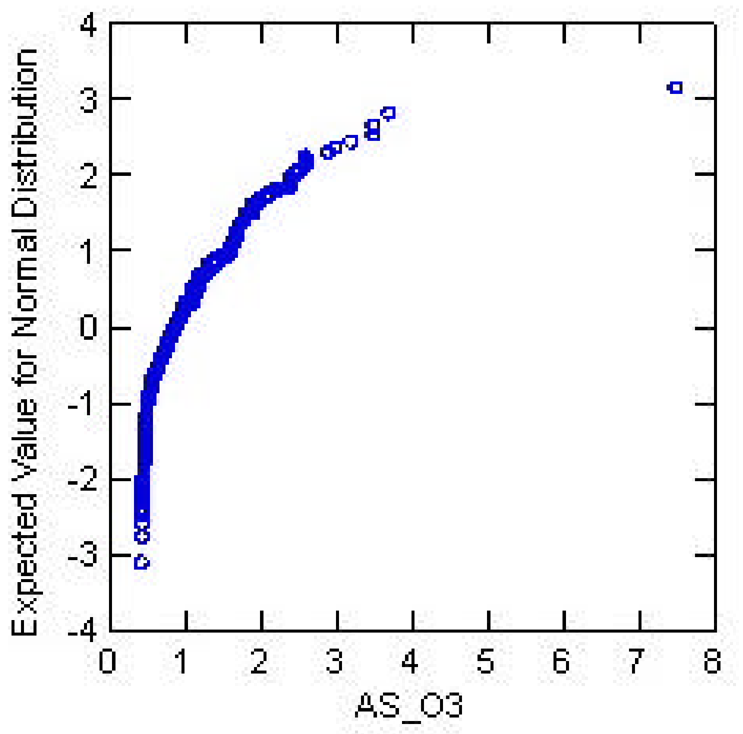
System As-O-H-S
ORP vs. pH
Filtered and Unfiltered Samples



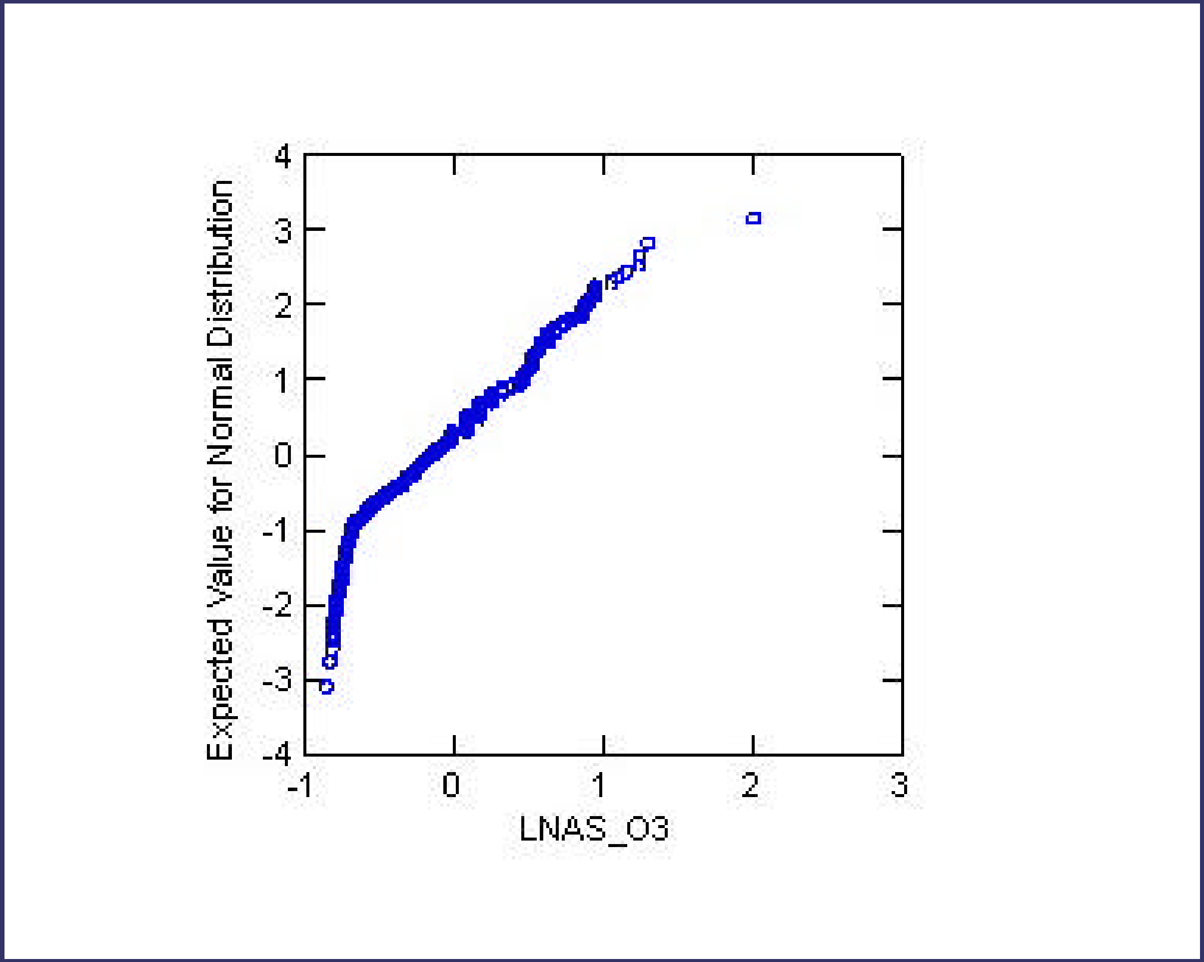


System Al-O-H
ORP vs. pH
Filtered and Unfiltered Samples
1,200
1,000
800
600
400
200
0
-200
-400
-600
-800
ORP (mV)
0
2
4
6
8
10
12
14
pH
Al3+ (aq)
Al(OH)3 (s)
AlO2(aq)
P(O2)= 1 bar
P(H2)= 1 bar

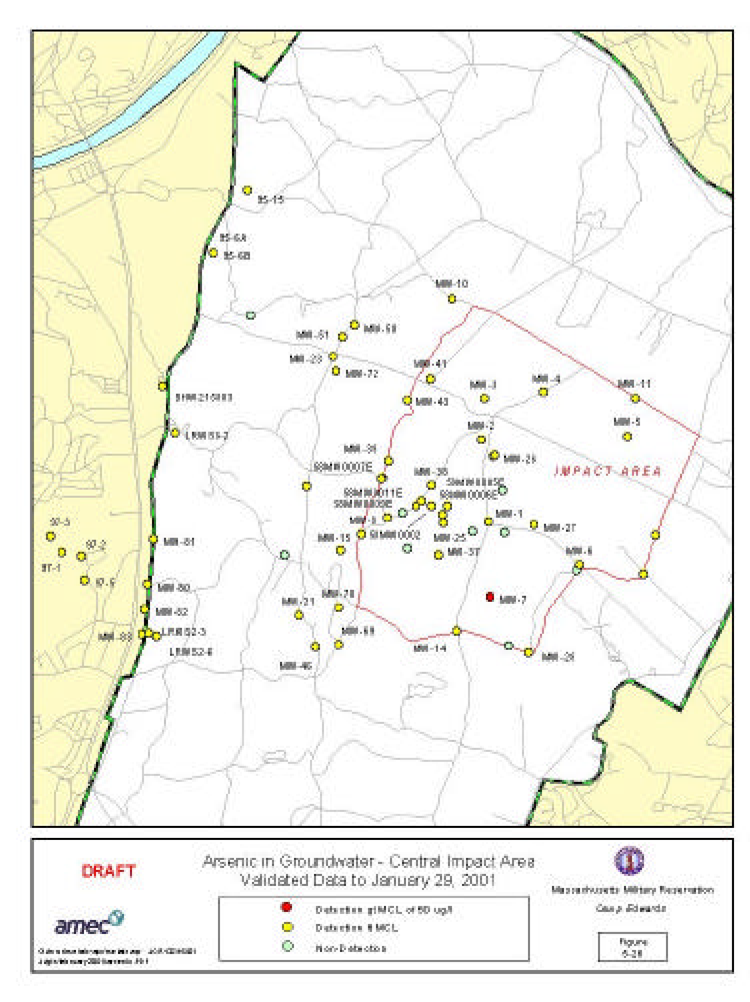
Distribution of Arsenic in Surface Soil



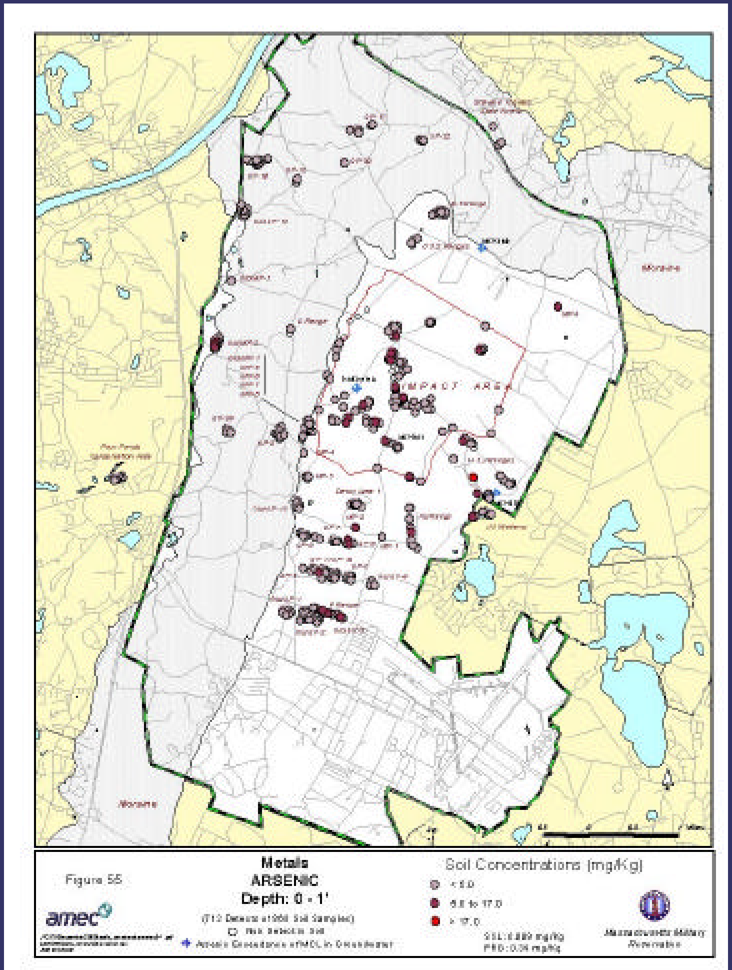
Natural Log Distribution of Arsenic in Surface Soil



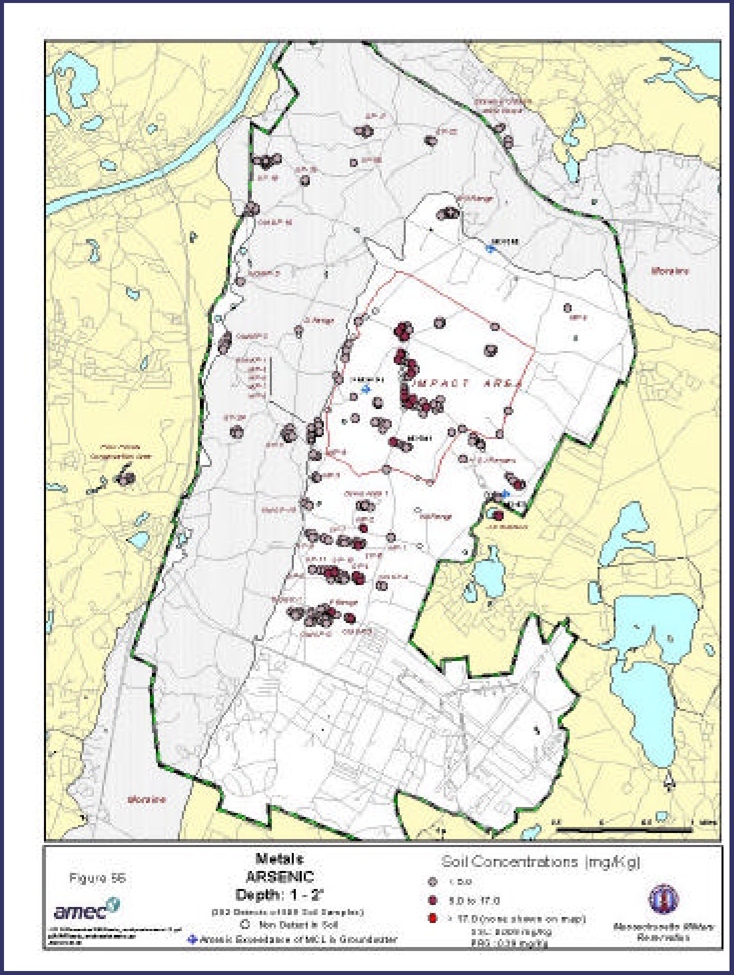
Arsenic Distribution in Groundwater



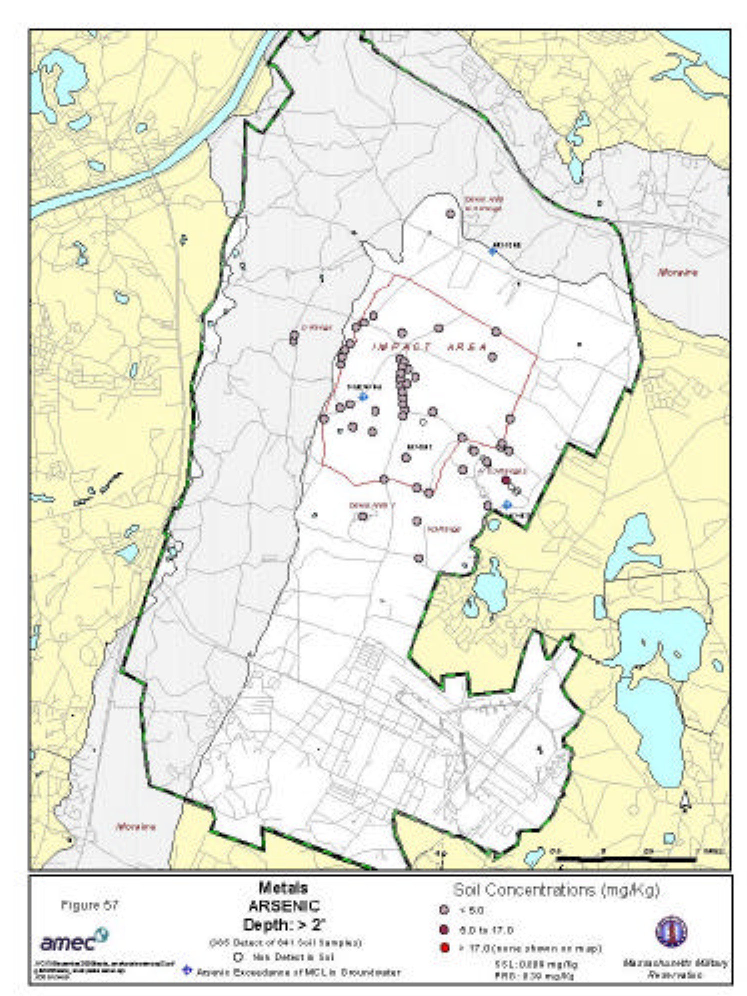
Arsenic Distribution in Surface Soil (0-1 feet)



Arsenic Distribution in Surface Soils (1-2 feet)



Arsenic Distribution in Soil (Greater 2 feet)



Conclusions

There is no data spatially or with depth to suggest that arsenic is a groundwater contaminant at Camp Edwards. The elevated arsenic concentrations appear to be partly a function of particulates present in groundwater samples. The lower concentrations likely represent the ambient groundwater quality. There is no evidence that arsenic measured in groundwater samples indicates contamination resulting from military training activities. There is no evidence of arsenic hotspots present in soil corresponding with elevated levels in groundwater.