The Chemical Effects on a Cape Cod Pond Due to the **Upgradient Reinjection of Carbon-Treated Groundwater**

Case Study: Snake Pond Massachusetts Military Reservation: Falmouth, Massachusetts

by

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Abstract

Snake Pond is located immediately southwest of a fuel spill groundwater plume located on the Massachusetts Military Reservation. Because a proposed extraction/reinjection well network is to be located close to the upgradient edge of Snake Pond for the purpose of plume containment, carbon-treated reinjected groundwater has the potential to be the main source of water to the pond. This fact raises concern about potential impacts to the pond ecology. The goal of this project is to assess the post-treatment effects of the proposed pump and treat system on the equilibrium chemistry of Snake Pond and assess what effects the changes may have on pond ecology. Analysis shows that inorganic species (including metals, dominant ion species, alkalinity, pH, etc.) will not be significantly altered. Because of its transparency, Snake Pond may be extremely sensitive to changes in organic carbon concentrations. The projected change in organic carbon will allow the 99% attenuation depth of UV-B radiation to penetrate 17% deeper than ambient conditions, and about 18% for UV-A radiation. Therefore, some suppression of biological activity is possible within Snake Pond due to the installation of the proposed treatment system.

Thesis Supervisor, Harold F. Hemond Director and Professor of Civil and Environmental Engineering

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1.0 Background Information

1.1 **General**

The Massachusetts Military Reservation (MMR) is located in the upper region of Cape Cod Massachusetts and borders the towns of Bourne, Falmouth, Mashpee and Sandwich (see Figure 1). Since 1911, the 34 square-mile MMR has housed Otis Air National Guard Base, US Coast Guard Air Station, and Army National Guard Camp Edwards.

During the time of MMR's heaviest military activity, the 1940s through the 1970s, Figure 1: Cape Cod Region large amounts of hazardous waste, mostly

chlorinated solvents and fuels, were generated. Common practice for many years was to dispose of such wastes by landfilling, dumping in storm drains, burning wastes in fire training areas, or just dumping them on the ground. This activity caused the MMR to be placed on the U.S. Environmental Protection Agency's Superfund National Priority List in 1989.

The MMR sits on top of the recharge area for the sole-source groundwater aquifer from which all of Upper Cape Cod draws water. Municipal and private water supplies, recreational ponds, and coastal bays of Upper Cape Cod are threatened by these contaminated groundwater plumes which contain potentially cancer causing chemicals. The MMR has 78 contaminant source areas currently identified and 10 *major* groundwater plumes moving at approximately 1.5 to 2 feet per day (see Figure 2). Within these plumes, the major contaminants of concern include trichloroethylene (TCE), tetrachloroethylene (PCE), ethylene dibromide (EDB), and benzene.

1.2 **History**

Groundwater investigations have been continuously conducted on the site since the detection of detergents by the U.S. Geological Survey (USGS) in a well used for drinking water in 1978. In 1982, the Air National Guard (ANG) initiated the Installation Restoration Program (IRP) at Otis ANG Base to identify and evaluate potential hazardous waste sites on the base. Activities initially included a historical records review, later followed by the installation of groundwater monitoring wells and an extensive groundwater, soil, surface water, and sediment sampling program. The Department of Defense (DOD) funded program has spent over \$130 million as of 1997 on investigation and cleanup at the reservation.

The following table outlines the timeline of major activities that have taken place at the MMR over the past 60 years.

Table 1: MMR History

(Reference: http://www.mmr.org)

Cleanup activities at the base, as of early 1997, focus on completing plume characterizations to define plume shapes and depths, soil testing to identify and quantify the extent of needed source area cleanup, and implementation of groundwater and soil treatment systems.

1.3 **Geology**

The topography of western Cape Cod is typified by hummocky hills, broad areas of low relief, and marshy lowlands. The main southern section of the MMR is located within a broad, southward sloping glacial outwash plain, termed the Mashpee Pitted Plain (MPP). This glacial outwash, which is the material carried from the ice as a glacier retreats by melting, may leave stranded ice masses. Kettle holes are water-filled pits that are left by dead ice blocks. The MPP is characterized by low topographic relief and an abundance of kettle hole ponds and marshes. Several valleys transect the plain in a north to south direction. The plain is bounded to the north and west by terminal moraines where the MMR exhibits irregular, hilly terrain with greater topographic relief. The ground elevation ranges from 0 to 306 feet above mean sea level (MSL).

Geology on the Upper Cape is comprised of highly permeable sands to a depth of about 300 feet, and throughout the Upper Cape, groundwater can be found 30 to 60 feet below ground surface. The glacial outwash plain, which comprises most of the MMR, consists of highly permeable sand and gravel and locally occurring lenses of lower permeability, fine grained sand, silt, and clay. These sands and gravels are commonly poorly graded: medium to coarse grained sand with well graded gravel. The predominant sediments are quartz and feldspar with surface coatings of iron oxide and occasionally manganese oxide. The well graded deposits of the Sandwich Moraine, to the north, and the Buzzards Bay Moraine, to the west, were deposited at the terminus of two adjacent glacial lobes, during the last glacial advance and retreat. The sediments of these moraines are mixtures of till, sand, silt, clay, and gravel to boulder size clasts.

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1.4 **Overview of** *Report*

A background of the site area is presented in Chapters 2 and 3. Chapter 4 describes, in detail, the methodology used to perform analytical calculations, which are presented in Chapter 5. Chapter 5 contains the key analyses of available data and provides information on existing pond surface water chemistry, groundwater chemistry, and rainwater chemistry. Chapter 6 examines the treatment train and shows how treatment will alter groundwater chemistry. Chapter 7 is a continuation of Chapter 6 and looks at expected post-treatment conditions within Snake Pond. Chapter 8 presents the summary and conclusion. Additionally, raw biological and chemical data is attached in Appendices A and B.

2.0 Background of the Fuel Spill 12 (FS-12) Study Area

2.1 **History of** *Fuel* **Spill 12**

Noting Figure 2, Fuel Spill 12 is located in the northeast corner of the plume area map. The area is partly on the MMR and partly on a bordering Christian summer camp, Camp Goodnews.

Fuel Spill 12 (FS-12) was caused by a leak in a now abandoned fuel pipeline located along Greenway Road at the MMR. The pipeline was used to transport fuels from the Cape Cod Canal to the ANG flight area. Both aviation gasoline and JP-4 jet fuel were carried in the pipeline The leak occurred in the early 1970s, and the pipeline was repaired in 1972. Contamination associated with FS-12 was first detected in 1990. Approximately 70,000 gallons of jet fuel and aviation gasoline filtered through the soil. The fuel is located near the top of the groundwater in the aquifer.

2.2 Current Remedial Activity

The source area is currently being treated by air sparging and vapor extraction technology. This process remediates the groundwater by introducing air bubbles deep in

the ground causing the fuel to rise as a vapor. The vapor is collected and treated above ground by passing it through a catalytic oxidizer that uses heat and a metal catalyst to help cleanse the air. It then passes through activated carbon filters that rid the air of the remaining fuel compounds. Figure 3 shows an above ground photograph of the air sparging system.

 \overline{a} **Figure 3: Air Sparging System**

Over the 11-acre contaminated FS-12 site, the contaminants of concern are benzene and ethylene dibromide (EDB) (see Figure 4). The plume originating at FS-12 extends approximately 4,800 feet in length south-southeast and 2,750 feet in width. The vertical thickness varies from 60 to 130 feet at 100 to 240 feet below the ground surface

To prevent the leading edge of the plume from migrating further, an extraction/reinjection remedial system has been designed to contain the FS-12 groundwater plume. The system, which is scheduled to be installed during 1997, consists of 30 extraction wells, 30 reinjection wells, and a treatment plant for the extracted water. To develop the optimal locations for the extraction and reinjection wells, a complex series of models was constructed and evaluated (Operations Technologies Corporation, 1996) to determine which scenario would have the most efficient capture while causing minimal adverse effects on Snake Pond. The extraction/reinjection remedial system will draw the water out of the ground and remove the fuel compounds by running the water through activated carbon beds. The carbon adsorbs the fuel compounds and clean water is returned to the ground. Construction of the extraction/reinjection remedial system has already started, and system start-up is scheduled for August, 1997. See Figure 4 for a layout schematic of the extraction/reinjection well network.

2.3 Area Characterization

The FS-12 region is heavily wooded with scrub growth forest (mostly Pitch Pine). Access to this area is restricted to a single dirt road controlled by locked gates. The FS-12 aquifer surfaces in a kettle pond, specifically Snake Pond. Horizontal groundwater velocities average 0.15 ft/day. Since FS-12 is located near the top of the regional aquifer and has a substantially lower hydraulic gradient (0.0003 to 0.00067) than other Cape Cod areas, the groundwater velocity is significantly less than other locations on the MMR. The horizontal hydraulic conductivity range is about 240 to 370 ft/day (avg. $= 320$) ft/day). Vertical hydraulic conductivity range is about 15 to 190 ft/day (avg. = 75 ft/day). Transmissivity range is about 26,000 to 40,000 $\frac{\text{ft}^2}{\text{day}}$ (avg. = 35,000 $\frac{\text{ft}^2}{\text{day}}$). (Jacobs Engineering Inc., 1996)

3.0 Snake Pond

3.1 **Characteristics**

Snake Pond is located immediately southwest of the FS-12 plume. It lies in the western section of Sandwich approximately 4/10 mile west of State Route 130 and 2/3 mile northeast of Otis Air Force Base. As seen in Figure 4, some reinjection wells are located along the upgradient edge of Snake Pond.

The watershed is characterized by steep slopes and is predominantly wooded with moderate residential development to the east of the pond and light development (Camp Goodnews) on the western shore. Groundwater in the study area is unconfined with an average depth to groundwater of 70 ft. The water table is exposed at the surface of Snake Pond, delineating the southwestern boundary of the FS-12 area. There are no observed surface water inlets or outlets to Snake Pond. The general direction of groundwater flow appears to shift slightly with seasonal fluctuations in aquifer recharge, however, the groundwater generally flows to the south or southeast. During the late summer or early fall, groundwater enters Snake Pond from the northwest, north, and northeastern sides. During spring, groundwater inflow to the pond is expected to be predominantly from the northwest and north. (DEQE, 1984)

Thermal Characteristics Unstratified	
Trophic Level	Very oligotrophic
Recreational Uses	Swimming, boating, and fishing
Access	One public beach on the southern shore is accessible via Snake Pond Road; Camp Goodnews lies on the north shore

Table 2: Major Snake Pond Characteristics

(DEQE, 1984)

In 1984, an extensive survey of many lakes and ponds in the Cape Cod watershed was performed by the Massachusetts Department of Environmental Quality (DEQE), now the Massachusetts Department of Environmental Protection (DEP). This was done to obtain an adequate record of the physical and water quality characteristics of regional

Cape Cod ponds. The bathymetry and morphology of Snake Pond are provided in Figure 5. Snake Pond has a surface area of 83 acres, a mean depth of 15 feet, a maximum depth of 31 feet, and a mean width of 1,125 feet. (Operational Technologies Corporation, 1995)

3.2 Ecological Concerns

Because the proposed extraction/reinjection wells are to be located close to the upgradient edge of Snake Pond, ecologists are concerned about potential negative impacts to the pond ecosystem. Initially, the major concern of engineers, ecologists, and planners, was the hydraulic flow of the groundwater, the equilibrium plume location, and groundwater flow trajectory. Based on numerical groundwater flow models constructed by the USGS and another environmental consulting firm, P2T, there is no reason to believe that the plume will flow directly into Snake Pond under pre- or post-treatment conditions. Therefore, concern over ecological impacts shifted to the pond reaction to the possible drawdown of the water level within Snake Pond and the inflow of carbon-treated groundwater through reinjection wells.

There are many concerns, but a lack of data and funding for research, about the evaluation of ecological impacts to Snake Pond. Concerns arise because much of the carbon-treated water will be reinjected directly upgradient of Snake Pond. Currently, Snake Pond is fed by about 83-86% groundwater (17-14% rainwater). The estimated post-treatment water budget of Snake Pond is anticipated to be 14-17% rainwater, 19- 53% ambient groundwater, and 67-30% treated groundwater. Therefore, the treated groundwater has the potential to be the main source of water to the pond. Since treated groundwater has different chemistry than ambient groundwater, this could have some important effects on the physical, chemical, and biological characteristics of Snake Pond. (Walter, 1997; Dickerman, 1997)

4.0 Methodology

4.1 Overview

The goal of this project was to assess the effects of the proposed pump and treat system on the equilibrium aquatic chemistry within Snake Pond. To attain this goal, the following tasks have been performed:

- Obtained chemical species data for groundwater, surface water, and rainwater
- Performed a critical analysis of the accuracy and reliability of the data by: examining charge balances, relating measured conductivity values to the conductivity yield of measured ions, and establishing the pre-treatment equilibrium chemistry by calibrating calculated values to the measured values within Snake Pond
- Established if Snake Pond can be considered a well-mixed system by looking at spatial variations of conservative chemical ions
- Critically reviewed the literature of the proposed treatment system and determine the changes in equilibrium groundwater chemistry of the reinjected water
- Calculated the equilibrium chemistry of reinjected groundwater
- Calculated the equilibrium chemistry of reinjected groundwater and ambient groundwater mixture
- Calculated the post-treatment equilibrium concentrations of chemicals in the Snake Pond surface water
- Assessed how the changes in equilibrium chemistry may or may not affect the pond ecology and limnology

4.2 Data Collection

The first step in the methodology was to perform a literature search, which included MMR reports, engineering design reports, internal faxes/memos/emails, telephone conversations with engineers and ecologists, and analytical limnology journals/textbooks. The literature review provided an overview of the existing situation

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at the MMR, and the phone conversations with involved engineers provided insight to the current problems of interest.

The key contacts for Snake Pond ecological data were Robyn Blackburn from Jacobs Engineering, Inc., Joyce Dickerman from Eco-TRET at Oak Ridge National Laboratory in Tennessee, and Bud Hoda from the Installation Restoration Program at the Massachusetts Military Reservation. Since the concerns about any possible "ecological impact" to Snake Pond are so recent (as of 1996), few data were available and the data that can be found was piecemeal, in draft form, and considered preliminary. Through the Jacobs Engineering Ecology Team, I obtained the available data via mailings, faxes, emails, and memos.

Jacobs Engineering, Inc. is conducting a baseline ecological study to characterize all ponds in the MMR region. The sampling schedule includes summer 1996, fall 1996, winter 1997, and spring 1997. The only data available to me was from the summer of 1996. This data included chemical concentrations at five locations within Snake Pond (surface water and sediment data) and at three groundwater wells immediately upgradient of Snake Pond (near the proposed reinjection system). These sampling locations are shown in Figure 7. Parameters for which data were available are shown in Table 3.

Table 3: Available Data

- Water Temperature Barium Cyanide Phosphorous
- Dissolved Oxygen Beryllium Iron Potassium
-
- Specific Conductivity Cadmium Magnesium Silver
-
- Redox Potential Chloride Nickel Sulfate
-
-
-
-
-
- pH Bromide Lead Selenium
	-
	-
	-
	-
	-
- -
- -
	-
	-
	-
	-
	-
	-
-
-
- Aluminum Cobalt Nitrate/Nitrite Zinc
	- Arsenic Copper Organic Carbon

As can be seen from Table 3, most major ions and metals are included as well as vital information on pH and organic matter. An ongoing relationship with Jacobs

- Turbidity Calcium Manganese Sodium
- Alkalinity Chromium Ammonia Vanadium
	-
	- - -
			- -

Engineering, Inc. (over the time period of 1/97 through 5/97) provided a forum to discuss their needs, new data, and my progress/ideas.

In addition to water quality data specifically in and around Snake Pond, average regional rainfall water quality data was available through the National Atmospheric Deposition Program (NADP) at Colorado State University. The NADP has rainfall sampling stations all around the United States, with the nearest one to the Massachusetts Military Reservation in Truro, MA. The data available included major ion species and pH. It was an incomplete set of chemical data, however the most important chemical ions were known. Since rainfall is a direct water source to Snake Pond, this data provided a basis to perform calculations for mixing.

4.3 Physical Modeling

It is necesary to know the percentage of treated groundwater and ambient groundwater that will be entering Snake Pond during pre- and post-treatment equilibrium conditions (see Figure 6). This project does not include any numerical groundwater modeling. However, information on physical processes can be obtained from a groundwater/surface water model and analysis of mixing processes in Snake Pond completed by Lee (1997). Using a combination of two existing physical groundwater models, which have already been developed by the USGS and P2T along with modeling by Lee (1997), ratios of rainwater/ambient groundwater/treated groundwater were obtained and subsequently used to perform chemical calculations. The important numbers for my purposes included the percentages of rainfall and groundwater that feed Snake Pond under pre- and post-treatment conditions.

4.4 Chemical Modeling

This section describes the analysis process.

Prior to conducting any chemical calculations, a rigorous evaluation of the available data must be made. This evaluation considers charge balances and continuity among individual water samples and includes calculations of specific conductivity based on available ion data. Additionally, items such as $pH/alkalinity/C_T$ (C_T is defined as "total inorganic carbon") were calculated and compared to the measured values. This comparison was used as a basis to determine the reliability of the water samples and the extent to which the analytical chemical results were accurate.

To determine if Snake Pond can be treated as a well-mixed system, spatial plots were made of the distribution of selected conservative tracer ions (Na^+, Cl^-) over the water area and depth of the pond. This analysis was used to observe if there were any

plume-like conditions or mixing patterns emanating from the groundwater inflow area of Snake Pond.

Knowing reasonable pre-treatment (existing) pond inflow percentages (groundwater and rainwater fluxes) obtained from the physical models as well as the chemical composition of groundwater and rainwater entering Snake Pond, it was determined how Snake Pond is chemically balanced. Treating the problem as an aquatic mixing problem, pH, alkalinity, and total inorganic carbon were calculated. These values were then compared to the measured chemical values. By performing this "self-check," confidence in the data is established.

Once confident of the existing conditions found at Snake Pond, it was necessary to critically evaluate the proposed pump-and-treat treatment train. Manufacturer specifications for the proposed treatment processes enabled the calculation of chemical changes in groundwater composition due to the reinjection of treated groundwater. This composition includes pH changes as well as removal of metals and organic carbon. By incorporating the expected changes with the existing data, additional calculations were performed using the *same* rainwater chemistry, *altered* groundwater chemistry, and *different* fluxes than existing conditions. The fluxes were obtained from existing USGS and P2T models as well as the model by Lee (1997).

The next series of calculations lead to the final equilibrium composition of Snake Pond. First, by treating the pond system as another mixing problem, it was possible to calculate the equilibrium of the reinjected water/ambient groundwater mixture. This follows the same chemical balance analysis as described for existing conditions, from which it is possible to calculate the post-treatment equilibrium concentrations of chemicals within Snake Pond surface water. These calculations include pH/a lkalinity/ C_{τ} as well as cationic and anionic species. The ion species concentrations were found by performing mass flux calculations. Mass fluxes were calculated by summing the

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products of the chemical concentrations and the percentage of water contribution of each source that flows into Snake Pond.

At this point, predictions were made as to the new chemistry that can be expected in Snake Pond after equilibrium has been reached. The new chemistry in Snake Pond includes pH, alkalinity, other anionic and cationic species, total inorganic carbon, and organic carbon (additional, but less important, parameters may fell of this analysis). The projected data was extended to discuss limnological issues regarding pond ecology. Topics of discussion include biological impacts, UV radiation, and overall pond productivity.

5.0 Analysis of Data

5.1 **Water Budget**

As previously mentioned, there have been several models employed to predict the long term steady-state effects of the planned extraction/reinjection system for Snake Pond. Some of the models were performed by contractors to the military who are reluctant to provide "outsiders" with data. The most helpful organization, and maybe the most reliable, was the USGS. The USGS conducted extensive modeling using MODFLOW, a finite-difference three-dimensional groundwater model (Walter, 1997). The USGS modeled a variety of sediment types in and around Snake Pond. They believe that the most reliable model is that which the outer edge of Snake Pond is treated as a coarse-grained sediment and the deeper more central part of Snake Pond is treated as a finer sediment (this model is believed by Walter **(1997)** to have a possible error of +/- 20%). Table 4 shows the rainfall and recharge rates that were used in the USGS model. These parameters were critical in determining mass flux numbers since rainfall is the governing source of water on Cape Cod. Note that Snake Pond has very steep banks and there was an assumption of no overland flow.

Annual Rainfall	47 in/yr.	
Evaporation from Pond	31 in/yr.	
Recharge for Pond	16 in/yr.	
\cdot \sim \mathbf{r} \sim \sim \sim $\sqrt{ }$	\sim \sim \sim	

Table 4: USGS Rainfall/Recharge Relationship

Recharge Elsewhere in Cape Cod Aquifer 1 22 in/yr. (Walter, 1997)

The rounded results of the USGS MODFLOW model are as presented in Table 5. Additionally, the results for the P2T model are provided (Dickerman, **1997).** Although the exact flow values are unavailable for the P2T model, it can clearly be seen that the results are vastly different from the USGS results. This is due to different recharge

assumptions and different methods of accounting for boundary conditions. For more information on this issue see Lee (1997)

Since the post-treatment conditions have a greater *total* flow in the case of the **USGS** model, there would have to be a change in pond elevation to accommodate the increased water volume. Therefore, the **USGS** estimated a total *average* rise in the water level of Snake Pond of 0.2 feet. However, since there is a natural seasonal fluctuation of over one foot, this should not have a substantial impact on the ecology of Snake Pond (Dickerman, **1997).** The P2T model estimated that the post-treatment conditions will have the same *total* flow as pre-treatment conditions, and P2T assumes that the Snake Pond water surface may be treated as a constant head boundary (there is some debate over this issue); no fluctuation can occur at a constant head boundary.

Currently, Snake Pond is fed about **83-86% by** groundwater (14-17% rainwater). The estimated post-treatment water budget of Snake Pond is anticipated to be 14-17% rainwater, **19-53%** ambient groundwater, and **67-30%** treated groundwater. The wide range of these numbers reflects the wide variety of results obtained from the different models. Note that the treated groundwater has the potential to be the main source of water to the pond.

5.2 Rainfall Analysis

This section deals with analyzing the available rainwater data. All rainwater data was obtained through the World Wide Web database of the National Atmospheric Deposition Program (NADP) of Colorado State University. With the reasonable assumption that this data is representative of the whole Cape Cod Region, some calculations were performed. The following data is averaged over the 1995 summer season for samples taken at the Truro, MA rainwater sampling station:

Ion	Molar Concentration	
$\overline{\text{Ca}^{2+}}$	$10^{-5.90}$	
Mg^{2+}	$10^{-5.84}$	
$\overline{K^+}$	$10^{-6.29}$	
Na^+	$10^{-4.93}$	
$\overline{\text{NH}_4}^+$	$10^{-4.93}$	
NO ₃	$10^{-4.67}$	
\overline{CI}	$10^{-4.89}$	
$[SO_4^2]$	$10^{-4.83}$	

Table 6: Available Summer 1995 Chemical Rainfall Data

It is important to note again that these are *average* summer readings for the year of 1995. At other locations in the state, or during other seasons, these chemical parameters may vary.

Assuming that the rainwater is in equilibrium with the atmosphere, alkalinity and carbonate species were calculated as follows:

Cons tan ts:

Partial Pressure, $P_{CO_2} = 10^{-3.5}$ atm Henry's Constant, $K_{H(CO_2)} = 10^{-1.5} \frac{M}{atm}$ Equilibrium Expressions: $H_2CO_3^* \Leftrightarrow HCO_3^- + H^+$ K = 10^{-6.35} $HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$ K = 10^{-10.33} (1) (2)

Calculations:

$$
\left[H_{2}CO_{3}*\right] = \left[P_{CO2}\right] \cdot \left[K_{H}\right] = \left(10^{-3.5} \text{atm}\right) \cdot \left(10^{-1.5} \frac{\text{M}}{\text{atm}}\right) = 10^{-5.0} \text{M}
$$
\n(3)

$$
\frac{\left[\text{HCO}_3^-\right]\text{H}^+}{\left[\text{H}_2\text{CO}_3^-\right]} = 10^{-6.35} \Rightarrow \left[\text{HCO}_3^-\right] = \frac{\left[10^{-6.35}\right]\text{I}0^{-5.0}}{\left[10^{-4.41}\right]} = 10^{-6.94} \tag{4}
$$

$$
\frac{\left[CO_3^{2-}\prod H^+\right]}{\left[HCO_3^{-1}\right]} = 10^{-10.33} \Rightarrow \left[CO_3^{2-}\right] = \frac{\left[10^{-10.33}\prod 10^{-6.94}\right]}{\left[10^{-4.41}\right]} = 10^{-12.86}
$$
\n(5)

In systems with only carbonate alkalinity, alkalinity is equal to the negative of the TOTH (Total Hydrogen)mass balance equation (Morel and Hering, **1993)**

Alkaliniky (Alk) = -[H +]+ [OH-]+ [HCO 3-]+ 2[C0 ³ 2- Assu ming that [OH- [HCO3- and [CO 32-]are negligible (eq.4 and 5): Alk = -[H+]= -10-4 41M **(6)**

Also, total inorganic carbon is equal to the sum of the carbonate species:

$$
C_{\tau} = [H_2CO_3 *] + [HCO_3^-] + [CO_3^{2-}]
$$

Assuming that
$$
[HCO_3^-]
$$
 and
$$
[CO_3^{2-}]
$$
 are negligible:

$$
C_{\tau} = [H_2CO_3 *] = 10^{-5.0} \text{ M}
$$
 (7)

To summarize, the most important equilibrium characteristics of the rainwater are:

- $pH = 4.41$
- Total Inorganic Carbon, $C_T = 10^{-5.0}$ M
- Alkalinity = $-10^{-4.41}$ M

5.3 Reliability of Chemical Data

Since the Massachusetts Military Reservation is an EPA listed Superfund site, all sampling is supposed to be carefully checked for reliability. This is done by hired chemical analyst companies using the guidelines found in a set of frequently updated EPA documents. The references are commonly known as the Environmental Protection Agency document *National Functional Guidelines.* In this text, one can find information on *qualifiers* that are used to show: if data follows trends, concentrations truly show up as "non-detect," or if a data point "spike" is an error or not.

To evaluate the "completeness" of the individual water samples, charge balance calculations were performed. Using measured values for specific conductivity and the dominant ion species, a calculation can be done based on the *Standard Methods* technique (Eaton *et al.,* 1996). The technique was used on each individual sampling location. For example, at location SNAKEPD-01 (see Figure 7), a complete set of data (see Table 3) was analyzed. Also, see Appendix B for a complete list of raw sampling data. Groundwater was not analyzed in this way due to the fact that the measured values of conductivity were so erratic; in other words, there were no reliable control checks for reality.

Within Snake Pond, a total of six surface water samples were taken: one sample at each of the five sampling locations taken at different depths with a duplicate sample at sampling location number one. Conductivity measurements taken were compared to calculated ones. Calculated values were obtained using values for λ , equivalent conductance of the *i*th ion, that were taken from *Standard Methods, Section 2510: Conductivity.* Table 7 summarizes the results, and the calculations are shown in Table 8.

Sample Identification	Measured Conductivity $(\mu mho/cm)$	Calculated Conductivity $(\mu mho/cm)$
SNAKEPD-01	65	62
SNAKEPD-01D	65	
SNAKEPD-02	65	
SNAKEPD-04	65	
SNAKEPD-05	64	
SNAKEPD-03	65	

Table 7: Specific Conductivity Results for Surface Water Samples

As can be seen from Table 7, the calculated conductivity values are reasonably close to the measured ones. This was evidence that the above samples are complete (except SNAKEPD-03). Note that for sample SNAKEPD-03 (see Table 8), the values of measured and calculated conductivity do not match. This is obviously due the fact that several important parameters were not sampled for: Na^+ , and SO_4^2 , and, therefore, conductivity could be computed accurately.

Another form of "back of the envelope" calculations were conducted to verify if the measured alkalinity was reasonable based on the ion concentrations of strong acids and strong bases. The following equation is a governing equation for the definition of alkalinity:

Alkalinity = (Concentration of Strong Bases) - (Concentration of Strong Acids)

\nAlkalinity =
$$
C_B - C_A
$$

\n(8)

The following is a sample calculation for groundwater sample GMW-10 (all concentrations are in molar values):

Alkalinity =
$$
2[Ca^{2+}] - [Cl^-] + 2[Mg^{2+}] + [K^+] - 2[SO4^{2-}] + [Na^+]
$$

($[H^+]$ and $[NO_3^-]$ are negligible) (9)

$$
10^{-3.86} = 2[10^{-4.48}] - [10^{-3.51}] + 2[10^{-4.08}] + [10^{-4.67}] - 2[10^{-4.18}] + [10^{-3.59}]
$$

$$
10^{-3.86} \neq 10^{-4.16}
$$

(note that the value for alkalinity is obtained by converting 6.9 mg/l as CaCO₃ to eq./l)

The failure for these two values to match can easily be explained. As can be seen in the above calculation, chloride and sodium are the dominant species. Since alkalinity has a magnitude much less than these dominant ions, this method of calculation produces

large error and uncertainty. A small fluctuation in chloride and sodium would dominantly alter alkalinity, causing the probability of the calculated alkalinity to exactly match the measured alkalinity to be virtually zero. A 27% error of either sodium or chloride concentrations would be necessary to reconcile the observed difference.

Many other similar calculations were performed with all of the individual surface water and groundwater samples, all having the same results: no exact matches between measured and calculated values for alkalinity. The calculation shown on the previous page was the closest match of all attempts to verify alkalinity in this way! Some of the results even showed opposite signs (positive vs. negative alkalinity). Since the reported measured values for alkalinity were reasonable for a groundwater and surface water, they will be accepted as true; this will be seen more clearly in Section 5.6.

The presence of organic acids (mostly humic acids) can severely affect alkalinity can be severely affected (Hemond, 1990). Since the concentrations of TOC in Snake Pond surface water $(< 1.1$ mg/l) and the surrounding groundwater $(< 0.2$ mg/l) are so small, organic acid effects are negligible. If TOC were concentrations of tens of mg/1 or greater, then organic acids would alter alkalinity values.

5.4 Mixing of pH, Alkalinity, and C_T

In this groundwater/surface water environment, it can safely be assumed that the dominant form of alkalinity is carbonate alkalinity. Table 9 outlines the ranges and average values of pH, C_T , and alkalinity found in individual groundwater and surface water samples at Snake Pond. Note in Table 9 that alkalinity in the groundwater samples for Snake Pond exceed surface water alkalinity values (as would be expected). Also, variations in rainwater, since it only comprises a small fraction of the water entering Snake Pond, have less of an impact. This is a typical scenario for alkalinity relationships between surface water, groundwater, and rainwater.

	pH	Alkalinity
		(equivalents/liter)
Ambient Groundwater	$4.87 - 6.82$	$10^{4.02} - 10^{-3.50}$
	$(\text{avg.} = 5.25)$	$(\text{avg.} = 10^{-3.77})$
Ambient Surface Water	$6.64 - 7.29$	$10^{-4.21} - 10^{-4.02}$
	$(\text{avg.} = 6.85)$	$(\text{avg.} = 10^{-4.15})$
Rainwater	4.41	$-10^{-4.41}$

Table 9: Range of pH and Alkalinity Values Found

Results from the USGS groundwater model suggest a groundwater and surface water mixture of **17%** rainwater and 83% groundwater. Therefore, using this mixture ratio and the pH and alkalinity ranges found in groundwater and rainwater, it was attempted to explain the surface water chemistry and validate the measured values. Direct rainfall input is fairly easy to quantify since the rainfall and recharge in the Upper Cape Cod region are widely known and accepted (Advanced Sciences, Inc., 1995).

By knowing the alkalinity, pH, and total inorganic carbon of groundwater and rainwater, as well as knowing the mixing ratios, it was possible to predict the parameters present in the surface water. Therefore, calculations were performed using the "end of the range" (upper and lower) values for groundwater, pH, and alkalinity. This would predict an acceptable range of values that might be found in the surface water.

Sample calculation:

Groundwater: $pH = 4.87$, alkalinity = $10^{-4.02}$ equivalents/liter Rainwater: $pH = 4.41$, alkalinity = $-10^{4.41}$ equivalents/liter

Groundwater:

Alkalinity (Alk) =
$$
- [H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]
$$

\nAssuming that $[OH^-]$ and $[CO_3^{2-}]$ are negligible:

\n $[HCO_3^-] = Alk + [H^+] = 10^{-3.96} \, \text{M}$

$$
H_2CO_3^* \Leftrightarrow HCO_3^- + H^+ K = 10^{-6.35}
$$
\n
$$
HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ K = 10^{-10.33}
$$
\n(11)

$$
HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ K = 10^{-10.33}
$$

$$
\begin{aligned}\n\left[H_{2}CO_{3} * \right] &= \frac{\left[HCO_{3} - H^{+} \right]}{\left[K\right]} = 10^{-6.35} \\
&\Rightarrow \left[H_{2}CO_{3} * \right] = \frac{\left[10^{-3.96} \text{ } \frac{\left[10^{-4.87} \right]}{\left[10^{-6.35} \text{ } \frac{\left[10^{-2.48} \text{ } M \right]}{\left[
$$

Now it is possible to mix 83% groundwater with 17% rainwater: C_T and alkalinity are conservative and follow mass balance laws.

Alkalinity = (0.83)
$$
\cdot
$$
 [Groundwater] + (0.17) \cdot [Rainwater]
Alkalinity = (0.83) \cdot [10^{-4.02}] – (0.17) \cdot [10^{-4.41}] = 10^{-4.14}

$$
C_{T} = (0.83) \cdot [\text{Groundwater}] + (0.17) \cdot [\text{Rainwater}]
$$
\n
$$
C_{T} = (0.83) \cdot [10^{-2.47}] + (0.17) \cdot [10^{-5.0}] = 10^{-2.55} \text{M}
$$
\n(14)

The new pond water now equilibrates with the atmosphere:

$$
P_{CO_2} = 10^{-3.5} \text{ atm}
$$

\n
$$
K_H = 10^{-1.5} \frac{M}{\text{atm}}
$$

\n
$$
[H_2CO_3 *] = 10^{-5.0} M
$$

\nAlkalinity =
$$
[HCO_3^-] = 10^{-4.14}
$$

\n
$$
[H^+] = \frac{[K][H_2CO_3 *]}{[HCO_3^-]} = \frac{[10^{-6.35}][10^{-5.0}]}{[10^{-4.14}]} = 10^{-7.21}
$$
 (15)
\n
$$
pH = 7.21
$$

The preceding calculations were also performed for other pH and alkalinity scenarios, and the results are listed in Table **10:**

Groundwater)			
Scenario	Resulting pH	Resulting Alkalinity (equivalents/liter)	
Groundwater pH = 4.87, Alk. = $10^{-4.02}$	7.21	$10^{-4.14}$	
Groundwater pH = 4.87 Alk. = $10^{-3.50}$	7.75	$10^{-3.60}$	
Groundwater pH = 6.82 Alk. = $10^{-4.02}$	7.21	$10^{-4.14}$	
Groundwater pH = 6.82 Alk. = $10^{-3.50}$	7.75	$10^{-3.60}$	

Table 10: Calculated pH and Alkalinity Values for Snake Pond (83% Groundwater)

Up to this point, it has been shown that the individual samples appear internally consistent (i.e. calculated conductivities of major ions match pretty well with the measured ones). However, it has not been seen if alkalinity is a reliable value since Equation 8 does not justify an alkalinity value. Therefore, as will be seen later in Section 5.6, the measured alkalinities are shown to be reasonable values for the existing pretreatment conditions. This provides confidence in the provided water quality data. So, in order to put together a chemical composite of the Snake Pond surface water, it is important to see if Snake Pond is well-mixed.
5.5 Chemical Mixing Within the Pond

By examining the conservative species in a pond, namely $Na⁺$ and Cl, it can be determined if a pond acts as a well-mixed tank or if it appears that a plume of chemicals is entering from the upgradient edge. Plume-like conditions would be observed by a chemical gradient from high concentration to low concentration from north to south. If it is found that Snake Pond is well-mixed, then it is a reasonable assumption to mathematically average concentrations from all sample points to create a representative value of the whole pond.

Figure 8 shows Na⁺ and Cl- concentrations in relation to sampling locations and depth. This data is accompanied by a schematic of Snake Pond. As can clearly be seen from the table, **Cl-** is virtually constant through all of the surface water and groundwater $(\approx 11 \text{ mg/l})$. Also, the concentration of Na⁺ is virtually constant $(\approx 5.7 \text{ mg/l})$. Since the concentrations are constant throughout the pond, the results show that Snake Pond can be treated as well-mixed. This supports the fact that the pond is unstratified. Therefore, when performing future alkalinity and ion calculations, an average value of the samples will be used as a representative pond value.

5.6 Summary of Available Data

Using the results described in the preceding sections, a chart was compiled of available data. The summary, shown in Table 11, includes the average measured values of surface water and groundwater recorded in micro-equivalents per liter along with the standard deviation of the dominant ion species. Additionally, it includes the average values of other cations, anions, organic carbon, temperature, dissolved oxygen, and pH. These numbers are probably only accurate to two significant figures. More significant figures are shown, but are not reliable, hence, the often large standard deviation.

There is also a record of alkalinity values that were measured, a comparison value of alkalinity calculated using Equation 8, and a final comparison of calculated alkalinity assuming the measured average pH is accurate and the surface water is in equilibrium with the atmosphere. Along with alkalinity, a record of measured specific conductivity and a comparison value using the method outlined in Section 5.3 is listed.

There is a column titled "Method"; this refers to the methodology used to derive the number immediately to the right. Five terms are used to describe method:

- **1.** Average: *Average* means that the mean value was taken over a series of data points.
- 2. Below **Detect:** *Below Detect* means that the chemical species was undetectable in the water sample, and the lowest measurable value was listed. This implies that the actual concentration of the chemical was something less than the number listed.
- 3. Given: *Given* is simply a single number that was obtained from literature, or *given* can be a known constant.
- 4. **Fixed:** *Fixed* is a constant value that is directly due to an environmental constant (i.e. K_H)
- **5. Calculated:** *Calculated* means that some equation method described in this report was used.

Table 11: Summary of Data Major Ions Calcium Chloride

Method

Rainwater

p equivalent/liter 2.50 12.98

Given Given

Copper Cyanide Iron Lead Manganese **Mercury** Nickel Phosphorus, Dissolved Orthophosphate Selenium Silver Thallium Vanadium Zinc

Suspended Solids Total Dissolved Solids Total Organic Carbon

One result reported in Table 11 provides assurance that the given data is reliable. Notice that, when back-calculating the partial pressure of $CO₂$ using average given alkalinity and pH for surface water and groundwater, it was found that the partial pressures are $10^{-3.45}$ atm and $10^{-1.44}$ atm in surface water and groundwater respectively. These values are very much representative of typical values found in the environment. So, with this final verification, the given data was shown to be reasonably accurate.

5.7 **Chemical Budget**

By using existing groundwater and rainwater data, predictions for pre-treatment conditions ware calculated (using the 83%/17% ratio) and compared to the measured surface water concentrations in Table 11.

This comparison, shown in Table 12, is crucial in seeing if simple mixture calculations between groundwater and rainwater is enough to predict surface water. The difference between the calculated and the actually measured surface water concentration represents an additional source or sink within Snake Pond.

Table 12: Comparison of Data

Surface Water

83% AMB GW / 17% RW (USGS)

The majority of calculated chemical species are reasonably close to the measured values. For an analysis of this type, these order-of-magnitude comparisons are considered reasonably accurate. The major changes that are observed, namely total organic carbon, need to be further explained.

Total organic carbon is an interesting quantity which is highly dependent on the biological activity of the pond. The detection limit for total organic carbon (TOC) is 0.2 mg/l, however, a typical groundwater value in the Cape Cod sandy aquifer is 0.15 mg/l, so 0.15 mg/l was assumed as a representative value for this site. The surface water has a known concentration of TOC of 0.68 mg/1. So, it can be seen that Snake Pond biological activity is a major and dominant contributor to TOC concentration in the surface water. If the groundwater provides only 0.12 mg/l, it is clear that the majority (0.56 mg/1) of TOC comes from pond activity.

Other less important observations are:

Chloride: This is shown to be higher in the surface water than calculated. This could easily be attributed to the windblown chloride from the ocean.

Metals: It can easily be seen that many of the measured surface water concentrations are less than those calculated for groundwater. This can be primarily attributed to settling.

It is important to note that for future comparisons, the model system to compare is the *calculated* system are *not* the measured one. This is so that the *relative* losses are found and used for comparison purposes. To be more explicit: the *calculated* values for post-treatment conditions need to be compared to the *calculated* pre-treatment (as opposed to the *actual* measured surface water values). This is because the calculated values do not match exactly, however, they were earlier shown to be reasonably accurate. Therefore, we will calculate the *relative* losses within Snake Pond.

6.0 Expected Changes in Groundwater Chemistry

6.1 **FS-12 Treatment Train**

The treatment train planned for use to treat the leading edge of the plume is a carbon adsorption system (see Figure 9). The design objective is to remove all VOCs, EDB, and semi-volatiles.

The treatment process consists of the extracted groundwater entering a holding tank, while a metered flowrate is released and treated with $KMnO₄$ and NaOH. The flow than enters a greensand filter, from which sediment is removed to a sedimentation tank and disposed of, and the remaining groundwater is transported to the UV/oxidation system. After UV/oxidation treatment, the groundwater enters the granular activated carbon filter beds where the contaminants of concern (namely EDB and benzene) are adsorbed to carbon granules. After the treatment is completed, the water enters another holding tank, from which it is reinjected into the ground through an extensive network of reinjection wells (see Figure 4).

6.2 Inorganic Compounds

The following information on chemical changes due to the treatment train process was taken from Jacobs Engineering Group, Inc. (1996).

Since the influent water will be heated as it undergoes treatment, the treatment plant effluent will be approximately 2.2⁰ F (1.2⁰ C) warmer, on average, than the ambient groundwater. This value was estimated based on the power input from pumps and the UV/oxidation system.

The pH of the treatment plant effluent will be near neutral (pH 7), and will be somewhat higher that the slightly acidic ambient groundwater (4.87 - 6.82). Massachusetts Department of Environmental Protection (DEP) regulations require that the pH of injected groundwater be between 6.5 and 8.5. Therefore, a base caustic (NaOH) will be added to increase the pH to the DEP regulated levels. The caustic addition for pH control will add about 0.3 mg/l of alkalinity (measured as $CaCO₃$).

Nitrogen (in the form of ammonia, nitrates, and nitrites) will not be significantly removed by the treatment plant unit operations. One may argue that the oxidation of NH_4^- to NO_3^- will be a sink for ammonia. However, since NH_4^+ and NO_3^- were found to be at below detectable concentrations in both surface water and groundwater, the loss due to oxidation will be negligible. Likewise, dissolved inorganic anions, inorganic carbon, and phosphate concentrations will not be substantially reduced during treatment. Thus no significant changes in Snake Pond were anticipated for these compounds.

Total dissolved solids (TDS) will be added to the water through the use of caustic for pH control. Caustic addition will increase the TDS by about 0.3 ppm. The TDS in a nearby well is 34 ppm. If the TDS at FS-12 is about the same as that well, then the increase would be about 1%. If iron and manganese are precipitated, the increase would be less.

The greensand filters will remove 90% of the iron and manganese. The carbon beds will nearly completely remove the lead.

The following parameters are expected to have little or no impact by the treatment system, and should not be changed in Snake Pond.

- Inorganic compounds (other than $Na⁺$ used in pH control)
- Ammonia (not present in detectable amounts in the groundwater)
- Hardness
- Dissolved Inorganic Carbon
- Soluble Reactive Phosphate

6.3 Organic Compounds

An anticipated 100% of total organic carbon (TOC) will be removed by the activated carbon. It is difficult to quantify the changes of TOC in Snake Pond directly because of the difficulty in quantifying the biological activity. Also, through the use of treatment plant filters, TSS should be reduced by over 90%.

6.4 Summary of Ambient Groundwater and Reinjected Groundwater Composite

Table 13 shows the difference between the reinjected groundwater and the ambient groundwater. Aligned next to the previously seen ambient groundwater composite, the effect of the treatment train on groundwater chemistry can seen by comparing these two columns.

 \sim

It can be clearly seen from Table 13 that there are not many outstanding changes in the groundwater composites. The major change of concern was the pH of the reinjected groundwater being altered to 7.0 and the TOC concentration being altered to 0.0 mg/l. These specific issues will be addressed in more detail in Chapter 7.

7.0 Changes Expected in Surface Water Chemistry

7.1 Mixing of pH, Alkalinity, and C_T

As done for pre-treatment conditions, two composite sample scenarios of Snake Pond surface water were calculated (see Table 14) by performing ratio calculations as well as pH/alkalinity/ C_T calculations. Table 14 is the expected post-treatment relative surface water chemistry in Snake Pond based on the two groundwater models that have been proposed by USGS and P2T. The two post-treatment predictions can be compared against the pre-treatment predictions.

The first set of data are from the calculated pre-treatment condition, detailed earlier. The respective header is 83% AMB GW / 17% RW (USGS). The next header, which states 30% TR GW / 53% AMB GW / 17% RW (P2T), is the representative composite when the P2T model is applied. The final header, which states 67% TR GW */* 19% AMB GW / 14% RW (USGS), is the representative composite when the USGS model is applied. The referenced percentages are from Table 5.

The difference between the two post-treatment scenario models and the pretreatment model, is taken to be the overall effect on Snake Pond surface water. By using the two models (P2T and USGS) for comparison, this study covers a wide range of possible flux scenarios.

Close observation of the results shown in Table 14 do not show any startling results. pH, which was original a concern, turns out not to change at all due to equilibration with the atmosphere. Also, ion concentrations are not significantly altered. TOC reduction may still be a concern.

7.2 UV-B Penetration

Total organic carbon was also a major concern of ecologists. One might say, by looking at the bottom of Table 14, that when assuming the P2T model is correct, TOC is reduced from 0.12 mg/l to 0.03 mg/l. That is a *75%* reduction! But, by recalling that the bulk on TOC comes from biological activity in Snake Pond, it can easily be reconciled that a 0.09 mg/l drop in TOC is not as drastic. Assuming that dissolved organic carbon is equal to TOC, it can be said that the pre-treatment concentration of DOC in Snake Pond is 0.68 mg/l and the post-treatment DOC concentration is 0.59 mg/l (0.68 mg/l - 0.9 mg/l).

Figure 10: Graph of UV-B Penetration vs. Depth (Williamson *et al.,* **1996)**

(Williamson *et al.,* **1996)** developed empirical equations to calculate the depth of 1% **UV-B** penetration as a direct function of DOC concentration (see Figure **10).** It was found that a strong dependence of attenuation depth on DOC below the 1 - 2 mg/l DOC range suggests that **UV** (type **A** and B) attenuation in low **DOC** lakes is **highly** sensitive to even small changes in DOC (see Figure 10). Changes in climate, lake hydrology, acid deposition, and other environmental factors that alter DOC concentrations in lakes may

be more important that stratospheric ozone depletion in controlling DNA-damaging UV radiation environments in lakes.

Many dissolved organic matter (DOM) compounds are absorbers of harmful UV-B radiation. UV-B has been known to have a negative impact on many components of freshwater ecosystems including bacteria, phytoplankton, zooplankton, and fish, some of which are utilized as a heterotrophic food source. Additionally, DOM compounds that absorb UV light have been known to speed up or slow down nutrient cycling and primary productivity. One could say that the DOC acts as a sunscreen to the pond system. (Williamson *et al.,* 1996)

The empirical model used to predict 1% attenuation depths for UV was developed from UV radiation, chlorophyll, and DOC on 65 glacial lake sites in North and South America. The core equation to calculate a coefficient for downwelling radiation are as follows:

for UV-B:
\n
$$
K_{d320} = 2.09[DOC]^{1.12}
$$
 (r² = 0.87, N = 63) (16)

for UV-A:
\n
$$
K_{d380} = 0.83[DOC]^{1.16}
$$
 (r² = 0.92, N = 62) (17)

where DOC is expressed in mg/l.

Then, to predict the depth, Z, below the lake/pond surface, the following equation was used:

$$
Z_{a\lambda} = 4.605 \, \text{K}_{d\lambda}^{-1} \tag{18}
$$

When applying this method of analysis to the Snake Pond data, it was found that the pre-treatment UV-B penetration depth is 3.39 meters, and the post-treatment UV-B penetration depth is 3.98 meters (a difference of 0.59 meters). Remember that the mean depth of Snake Pond is only 4.6 meters.

The same analysis applied for UV-A reveals a similar impact. It was found that the pre-treatment UV-A penetration depth is 8.68 meters, and the post-treatment UV-A penetration depth is 10.23 meters (a difference of 1.55 meters). Noting that the maximum depth of Snake Pond is *9.45* meters, Snake Pond will be completely exposed to UV-A radiation (for 1% attenuation).

8.0 Summary and Conclusions

This analysis shows that it si possible that there will be a negative impact on Snake Pond due to the installation of the proposed treatment system, primarily because of reduced DOC (see Williamson *et al.,* 1996). A closer look at Table 13 shows that inorganic species (including metals, dominant ion species, alkalinity, pH, etc.) will not be significantly altered. However, the change in organic carbon, may alter the ecology of Snake Pond.

pH, which was initially a concern, is not changed appreciably. This is due to the fact that the pond will equilibrate with the atmosphere. So, regardless of the high or low pH in the groundwater, alkalinity is a conservative substance that will govern the resultant pH in Snake Pond surface water.

Noting that many inorganic species will not be significantly changed, it is worth discussing TOC/DOC issue. TOC is physically and chemically complex. It contains colloidal and particulate fractions of detritus. Very approximately, carbon comprises about 50% by mass of the DOM. The remainder is due to oxygen and hydrogen, with lesser amounts of nitrogen, phosphorous, and sulfur. In systems dominated hydrogeologically by fluxes of groundwater, the groundwater may be the dominant TOC source, especially in more oligotrophic systems. Note that Snake Pond is very oligotrophic. DOM also changes the biological availability of many metals to algae, zooplankton, or even fish by complexation. Thus, the presence of DOM can make some metals less toxic or make some metals more toxic. (Williamson *et al.,* 1996)

Since Snake Pond has very low concentrations of organic carbon, and is shallow relative to the UV-B and UV-A penetration depth of this oligotrophic pond, there may be some significant impact on plankton communities (a heterotrophic food source), vegetation, and overall pond productivity (according to Williamson *et al.,* 1996). It is difficult, however, to quantify to what extent this will happen. If Snake Pond had

ambient TOC/DOC concentrations of several mg/1, then, I would conclude that this effect could be neglected. It is difficult to quantify the extent of biological damage that will be seen. The 1% attenuation depth is not necessarily the important fraction where biota begin to die. 1% is, however, an accepted index for measuring light penetration. An ongoing field of study involves assesing which specific planktonmic, bacteria, and other aquatic inhabitants are influenced by increasing UV radiation. For more informantion on this see Moeller (1994) or Karentz *et al.* (1994). I feel that Snake Pond is very sensitive to the DOC parameter.

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Appendices

Appendix A: Biological Data

This is a summary of the results of a biological survey was conducted by Jacobs Engineering, Inc. conducted on 10/22/96 (Jacobs Engineering Group, Inc., 1996).

Vegetation Found

- rose coreopsis (Coreopsis rosea)
- tickle grass (Agrostis scabra)
- panic grass (Panicum lanuginosum)
- narrow-leaved goldenrod (Euthamia galetorum)
- young pitch pines along pondshore
- steeplebush
- meadowsweet
- brambles (Rubus flagellaris and Rubus hispidus)
- little bluestem (Schizycarium)
- bushclover (Lespedeza capitatum)

Amphibian/Reptiles Found

- adult bullfrogs
- eastern painted turtles

Odonates Observed (on several different dates)

- civil bluet (Enallagma civile)
- little bluet (E. minisculum)
- steam bluet (E. exulans)
- calico pennant (Celithemis elisa)

Fish Species Occurrence

- American eel (Anguilla rostrata)
- Brown bullhead (Ameiurus nubulosus)
- White sucker (Catostomus commersoni)
- * Banded killfish (Fundulus diaphanus)
- Golden shiner (Notemigonus crysolecas)
- Largemouth bass (Nucrioterys salmoides)
- * Smallmouth bass (Mocropterus dolomeuie)
- * Bluegill (Lepomis macrochirus)
- Pumpkinseed (Lepomis gibbosus)
- Yellow Perch (Perca flavescens)
- White Perch (Morone americana)
- Chain pickerel (Esox niger)

Appendix B: Chemical Data

The following series of data sheets are the raw data provided by Jacobs Engineering, Inc. used to perform the analyses done in this report.

Note that the DO/pH/temp etc. profiles were collected at approximately 3 meter intervals.

Sampling Depths:

 $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ and $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ and $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$

