INORGANIC AND ORGANIC GROUND-WATER CHEMISTRY
IN THE CANAL CREEK AREA OF
ABERDEEN PROVING GROUND, MARYLAND

By Michelle M. Lorah and Don A. Vroblesky

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CONVERSION FACTORS AND ABBREVIATIONS

For the convenience of readers who may prefer to use metric (International System) units rather than the inch-pound units used in this report, values may be converted using the following factors:

Multiply inch-pound unit	by	To obtain metric unit
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micrometer (μm)
foot (ft)	0.3048	meter (m)
gallon (gal)	3.785	liter (L)
gallon (gal)	.003785	cubic meter (m^3)
pound, avoirdupois (lb)	4.536	kilogram (kg)

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

Water temperature, specific conductance, chemical concentration, and other chemical and physical properties of constituents (such as density, sorption, and vapor pressure) are given in metric units. Water temperature in degrees Celsius (^oC) can be converted to degrees Fahrenheit (^oF) by using the following equation:

$$^oF = 1.8\ (^oC) + 32$$

Specific conductance of water is expressed in microsiemens per centimeter at 25 ^oC (μS/cm). This unit is identical to micromhos per centimeter at 25 ^oC, formerly used by the U.S. Geological Survey.

Chemical concentration in water is expressed in milligrams per liter (mg/L), micrograms per liter (μg/L), milliequivalents per liter (meq/L), milliequivalents per kilogram (meq/kg), or micromoles per liter (μmol/L).

Molecular weight and other mass expressions are expressed in grams (g), and density is given in gram per cubic centimeter (g/cm^3). Sediment-water partition coefficients have units of milliliter per gram (mL/g). Vapor pressure is given in units of millimeter of mercury at 0 ^oC (mm Hg). Other abbreviations used include milliliter (mL) for volume measurements and micrometer (μm), which equals 1 x 10^{-6}meter, for length.

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ABSTRACT

Manufacturing of military-related chemicals and other activities have taken place since 1917 in the Canal Creek area of Aberdeen Proving Ground, Maryland, and have affected the ground-water quality. This report, which describes the first phase of a 5-year study, evaluates the distribution of inorganic and organic constituents present in the ground water in the Canal Creek area, identifies probable sources of the ground-water contaminants, and describes possible reactions affecting the organic contaminants. From November 1986 through April 1987, ground-water samples were collected once from 87 observation wells screened in Coastal Plain sediments, including 59 samples from the Canal Creek aquifer, 18 samples from the overlying surficial aquifer, and 10 samples from the lower confined aquifer.

The composition and distribution of major ions in the Canal Creek aquifer are highly variable. Samples from the Canal Creek aquifer that contain the highest dissolved-solids and chloride concentrations (maximums of 2,340 and 1,000 milligrams per liter (mg/L), respectively) are from wells located between the two creek branches where most manufacturing activities occurred.

Four samples collected from the the surficial aquifer underlying the narrow peninsula of Beach Point have distinctive sodium chloride compositions. Other samples from the surficial aquifer have either a calcium bicarbonate composition or a mixed composition.

The median dissolved-solids concentration in the lower confined aquifer (110 mg/L) is less than that in the overlying Canal Creek aquifer (164 mg/L) and surficial aquifer (286 mg/L). Chloride concentrations usually are less than the detection limit of 5 mg/L in the lower confined aquifer, suggesting that the aquifer has not been affected by inorganic wastes discharged in the Canal Creek area.

Dissolved solids and six inorganic constituents are present in concentrations that exceed the primary or secondary maximum contaminant levels (MCL's) for drinking water established by the U.S. Environmental Protection Agency. Concentrations of dissolved solids exceed the secondary MCL of 500 mg/L in six samples from the Canal Creek aquifer and six from the surficial aquifer. Elevated chloride concentrations, ranging from 290 to 1,000 mg/L, are present in three samples from the Canal Creek aquifer and in four samples from the surficial aquifer at Beach Point. In most cases, the

elevated chloride and dissolved-solids concentrations are from contamination caused by past manufacturing activities. The Beach Point samples also may be affected by intrusion of brackish water.

Excessive concentrations of iron and manganese are the most extensive water-quality problems with regard to the inorganic constituents. Both of these constituents are derived from natural dissolution of minerals and oxide coatings in the aquifer sediments. Fluoride, mercury, or chromium are present in concentrations above the MCL's in samples from four wells.

The volatile organic compounds present in the Canal Creek and surficial aquifers include chlorinated alkanes, chlorinated alkenes, and monocyclic aromatics. Samples from the lower confined aquifer do not appear to be contaminated by organic compounds. Base/neutral and acid-extractable organic compounds were not detected in any samples collected in the study area.

The chlorinated alkanes that are most widely distributed in ground water of the Canal Creek area include 1,1,2,2-tetrachloroethane and chloroform. The highest concentrations of 1,1,2,2-tetrachloroethane observed in the Canal Creek aquifer and surficial aquifer are 5,300 and 9,000 micrograms per liter (μg/L), respectively. The highest concentrations of chloroform are 460 and 66 μg/L. Other chlorinated alkanes detected in the study area include carbon tetrachloride, 1,1,2-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane.

Of the detected chlorinated alkenes, trichloroethylene and 1,2-trans-dichloroethylene are the most widespread contaminants in the Canal Creek and surficial aquifers. Vinyl chloride is present in a total of 17 samples collected from the two aquifers; tetrachloroethylene and 1,1-dichloroethylene are the least commonly detected chlorinated alkenes. The highest concentrations of trichloroethylene are 1,800 and 940 μg/L in the Canal Creek aquifer and surficial aquifer, respectively. For 1,2-trans-dichloroethylene, the highest concentrations are 1,200 and 520 μg/L. The highest concentrations of chlorinated alkanes and alkenes observed in the surficial aquifer were detected in samples collected at Beach Point.

Chlorobenzene and benzene are the only aromatics observed in concentrations significantly above the detection limits. The maximum detected concentrations of chlorobenzene (39 μg/L) and benzene (70 μg/L) in the study area were in a sample collected from the Canal Creek aquifer.

On the basis of information on past activities in the study area, some major identified sources of the volatile organic compounds include (1) their use as decontaminants and degreasers, (2) clothing-impregnating operations, (3) the manufacture of clothing impregnite, (4) the manufacture of tear gas, and (5) fuels used in garages and at the airfield.

Density, solubility, sorption affinity, and volatility are four physicochemical properties that could control reactions of the organic constituents in the ground water. The high density of most of the detected organic compounds would have aided movement of the contaminants into the aquifers by vertical sinking. The upper confining unit that overlies the

Canal Creek aquifer is missing in the outcrop area near the West Branch Canal Creek and in an area cut by a paleochannel near the East Branch Canal Creek. The Canal Creek aquifer is most susceptible to contamination at these sites because the near-surface impermeable layer is not present.

The solubilities of the volatile organic compounds found in the study area (1.1 to 16,700 mg/L) indicate that they are all moderately to highly soluble. The low organic-matter content of the aquifer sediments indicates that sorption probably is not a significant retardation mechanism for any of the volatile organics. Volatilization could only be a significant removal mechanism where the ground-water contaminants are in direct contact with an air phase, such as the soil atmosphere.

Abiotic degradation reactions include dehydrohalogenation and hydrolysis, whereas important microbially mediated reactions include reduction by hydrogenolysis or dihalo-elimination. Concentrations of 1,2-trans-dichloroethylene, trichloroethylene, chloroform, vinyl chloride, 1,1,2-trichloroethane, and 1,2-dichloroethane in the ground water may be at least partly derived from degradation reactions.

INTRODUCTION

Background

The Canal Creek area of Aberdeen Proving Ground (APG), Maryland (fig. 1), has been used to develop, test, and manufacture military-related chemicals since World War I. The chemicals produced include chlorine, mustard, tear gas, phosgene, clothing-impregnating material, chlorpicrin, white phosphorus, pyrotechnics, and arsenicals. Other relevant activities included filling of chemical munitions, landfilling of domestic waste, land disposal of production wastes, and the use of degreasing solvents on military equipment.

Evidence that activities in the Canal Creek area may have affected the environment became apparent in 1977 when white phosphorus was found in the sediments of Canal Creek (Nemeth and others, 1983). In 1984, volatile organic compounds were discovered in six standby water-supply wells, causing the Maryland State Health Department to recommend that they be shut down. Assessment of the possibility of contamination in the Canal Creek area required a study of the inorganic and organic chemistry of the ground water.

The study, which began in 1985, has a duration of 5 years. The study is divided into two phases both of which involve the installation of observation wells and the collection of samples. The objectives of the overall study include description of the hydrogeologic framework of the Canal Creek area; determination of the nature, extent, movement, and behavior of ground-water contaminants; definition, as nearly as feasible, of the contaminant sources; and evaluation of the hydrologic and hydrochemical effects of various remedial actions. This report presents and evaluates data on ground-water chemistry collected during the first phase of the study.

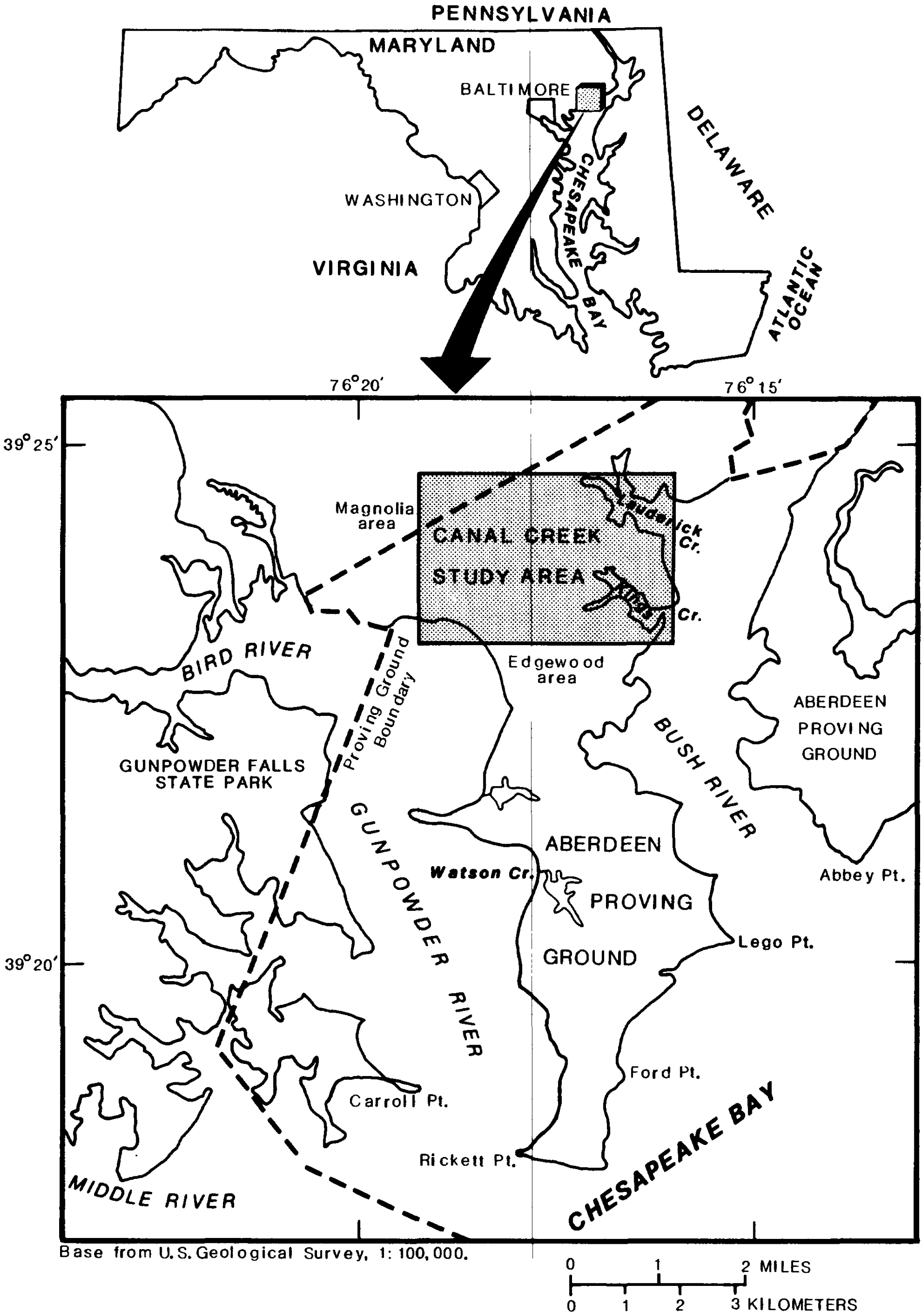


Figure 1.-- Map showing location of the Canal Creek study area.

Purpose and Scope

The purpose of this report is to (1) describe the distribution of inorganic and organic constituents present in the ground water of the Canal Creek area, identifying the major contaminants; (2) identify probable sources of the ground-water contaminants; and (3) describe the possible geochemical and physical reactions occurring among the organic contaminants in the ground water. This report presents data collected from November 1986 through April 1987 during the first phase of the 5-year study.

Ground-water samples were collected once from 87 wells to describe the distribution of constituents. The wells were screened in three aquifers, including 59 wells in the Canal Creek aquifer, 18 wells in the overlying surficial aquifer, and 10 wells in the lower confined aquifer. The three aquifers will be discussed in this order throughout the report. Thus, the results for the most extensively studied and contaminated aquifer (the Canal Creek aquifer) are presented first, whereas the results for the least studied and contaminated aquifer (lower confined aquifer) are discussed last.

Samples were analyzed for 30 inorganic constituents, for a suite of base/neutral and acid-extractable organic constituents, and for volatile organic compounds. Historical data on manufacturing locations and ground-water-head data were used to identify tentatively the probable sources of contaminants. Known physicochemical properties (for example, density, water solubility, volatility, octanol-water partition coefficients, soil-water partition coefficients) and degradation products of organic constituents were used to determine possible organic reactions.

Description of Study Area

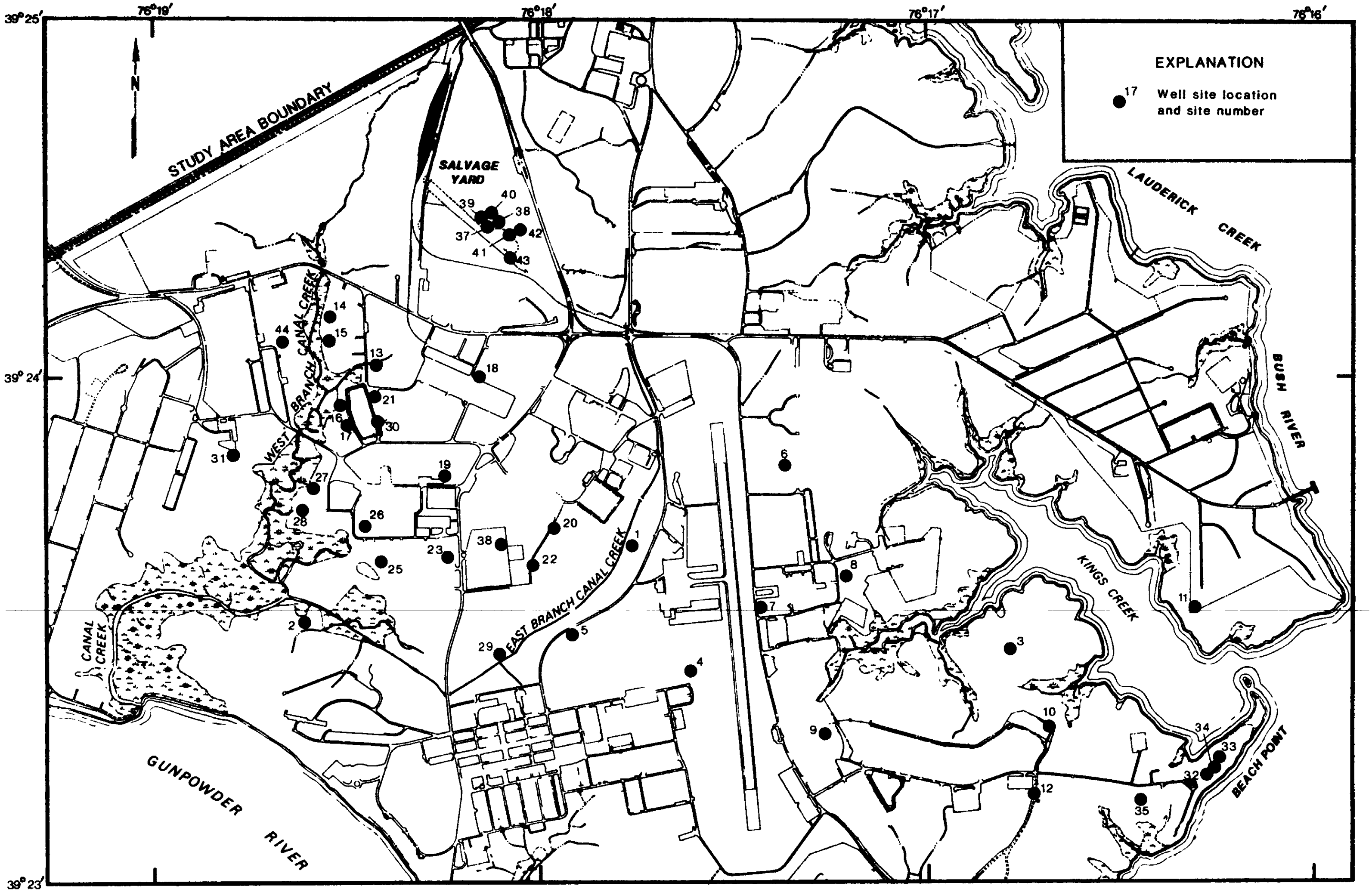
Geographic Setting

The study area, which is located in eastern Maryland, lies near the northern edge of the Atlantic Coastal Plain physiographic province. The topography of the Coastal Plain is characterized by low hills, shallow valleys, and plains. Within the Canal Creek area of APG, altitudes range from sea level to approximately 60 ft (feet) above sea level. The climate is temperate and moderately humid. Mean annual temperature is 54 degrees Fahrenheit; mean annual precipitation is 45 in. (inches) (Nutter, 1977, p.3).

The Canal Creek area of APG is bordered by two estuaries--the Bush River and the Gunpowder River--which drain to the Chesapeake Bay (fig. 1). Lauderick Creek and Kings Creek (fig. 2) discharge to the Bush River on the eastern boundary of the study area. The East and West Branches of Canal Creek, which provide surface drainage for a major part of the study area, flow into the Gunpowder River on the western boundary.

Hydrogeology

The regional geology is characterized by thick, wedge-shaped deposits of unconsolidated Coastal Plain sediments that rest unconformably on the older crystalline rocks of the Piedmont physiographic province (Owens, 1969, p. 77). The Coastal Plain sediments dip southeastward, increasing to a



Base modified from Edgewood map.
Engineering plans and services division,
Aberdeen Proving Ground, 1984.

Figure 2.-- Map showing location of well sites in the Canal Creek area.

thickness of approximately 400 ft in the study area. The unconsolidated sediments include the Potomac Group of Cretaceous age, which are overlain by the Talbot Formation of Pleistocene age. Both units consist of beds of clay, silt, sand, and gravel that were deposited in a continental environment (fluvial, channel fill, and overbank deposits). The Talbot Formation has been eroded by streams and rivers, exposing the Potomac Group.

The hydrogeology of the Canal Creek area of APG has been described from geologic data, borehole geophysical logs, and water-level measurements collected from the 87 wells installed during the first phase of this study and from 61 wells installed during the second phase (J. P. Oliveros and D. A. Vroblesky, U.S. Geological Survey, written commun., 1988). Hydraulic conductivity was determined for 15 wells by performing slug tests (J. P. Oliveros and D. A. Vroblesky, U.S. Geological Survey, written commun., 1988).

The generalized hydrogeologic section in figure 3 shows the aquifers and confining units delineated in the study area and a conceptualization of directions of ground-water flow. The sediments follow the regional trend, dipping and thickening southeastward. These hydrogeologic units were defined partly on the basis of hydrologic characteristics of the units; therefore, the boundaries between the hydrogeologic units do not necessarily correspond with contacts between geologic units. The surficial aquifer sediments are primarily composed of the Talbot Formation but are a composite of both the Talbot Formation and the Potomac Group in some areas. The upper confining unit, the Canal Creek aquifer, the lower confining unit, and the lower confined aquifer (fig. 3) are composed of Potomac Group sediments.

Geologic framework

The Canal Creek aquifer is the major aquifer in the study area (fig. 3), underlying most of the study area with a thickness ranging from 30 to 70 ft. The aquifer subcrops beneath the surficial aquifer where the upper confining unit is absent--in the Pleistocene paleochannel underlying the East Branch Canal Creek and near the West Branch Canal Creek (fig. 3). The Canal Creek aquifer and surficial aquifer are hydraulically connected in both of these areas, which extend approximately parallel to the present courses of the East and West Branches of Canal Creek. The Canal Creek aquifer crops out westward of the West Branch Canal Creek. The lower confining unit and lower confined aquifer underlie the Canal Creek aquifer (fig. 3).

The sediments of the Canal Creek aquifer, which is part of the Potomac Group, are composed primarily of coarse quartz sand and gravel containing a small percentage of dark, heavy-mineral grains. Sequences of fine sand and silt that contain an abundance of muscovite and lignite are also present in the aquifer sediments. Orange to yellow iron staining is common in sands and gravels throughout the aquifer, and some sand layers have multicolored bands of purple, red, orange, yellow, and white. Iron mineralization commonly is present as small nodules and as zones of cemented sand and gravel. Thin clay layers that are laterally extensive in places usually are composed of white to gray, dense clay.

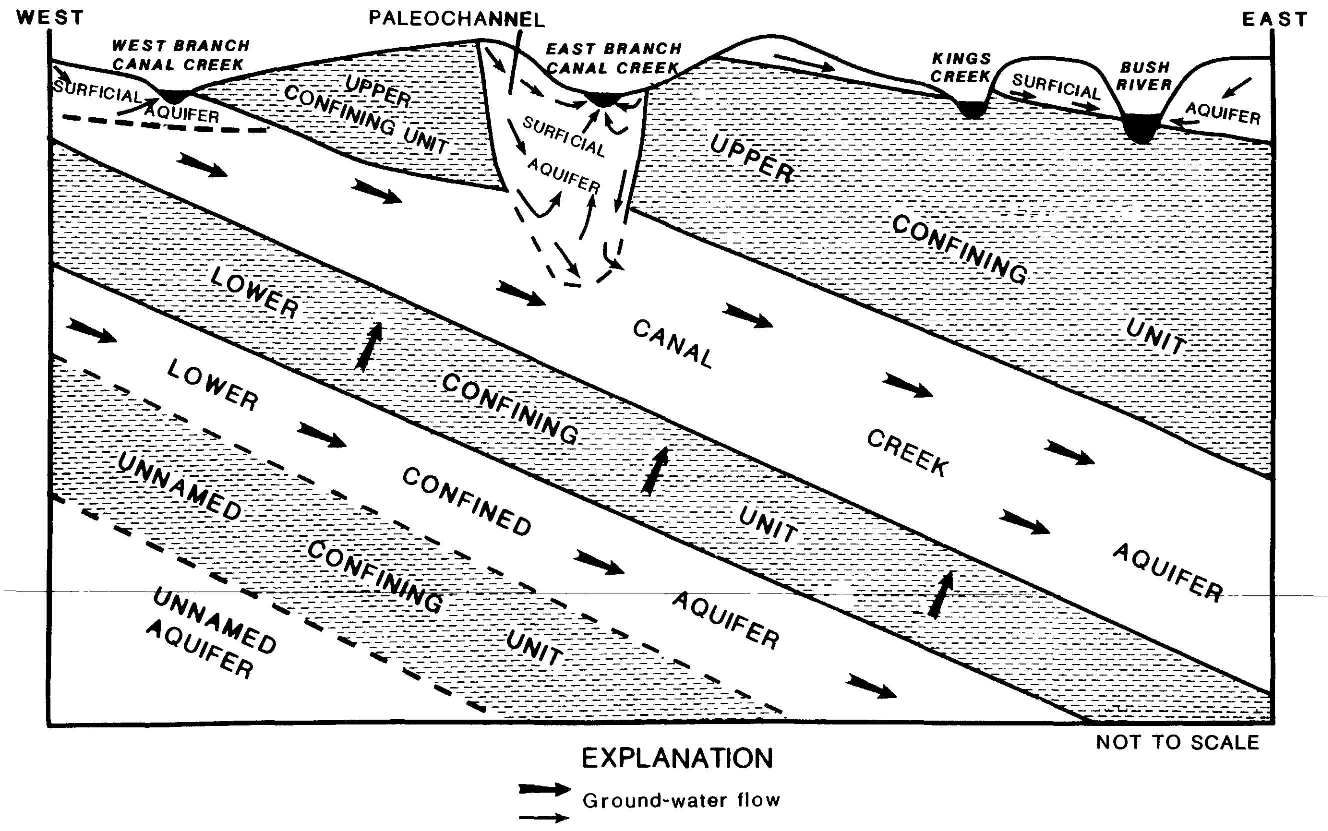


Figure 3.-- Generalized hydrogeologic section and conceptualization of directions of ground-water flow.

Because of the variable lithology of the Canal Creek aquifer sediments, the hydraulic conductivity of the aquifer also varies. The horizontal hydraulic conductivity of the aquifer ranged from 6 ft/d (feet per day) to 176 ft/d, on the basis of slug tests in 11 wells. Wells where the lowest values of hydraulic conductivity were determined generally are screened in fine to medium sand, whereas the wells where the highest values of hydraulic conductivity were determined are screened in coarse sand and gravel.

The surficial aquifer (fig. 3) is unconfined and consists of a relatively thin layer (0 to 35 ft) of discontinuous sand and gravel. Thin clay layers and stringers are also present. The surficial-aquifer sediments consist of the Talbot Formation over most of the study area; however, the sediments are a composite of both the Talbot Formation and the Potomac Group in some areas, especially where the upper confining unit crops out near the West Branch Canal Creek (fig. 3). The surficial-aquifer sediments are thickest near the West Branch Canal Creek and in the paleochannel (fig. 3). The surficial aquifer becomes more discontinuous and pinches out east and northeast of the paleochannel. Isolated parts of the surficial aquifer are present south of Kings Creek and at Beach Point (fig. 2).

The lithology of the surficial aquifer is highly variable because the sediments are composed of two geologic units in some areas and because a large part of the study area has been disturbed by excavation and landfilling. The sand members in the Talbot Formation typically are finer grained, siltier, and more muscovite-rich than the sand in the Potomac Group. Lignite and iron mineralization are common in both geologic units. In some areas disturbed by human activities, the surficial-aquifer sediments contain poorly sorted, clayey sand mixed with various fill material.

Along the West Branch Canal Creek where the surficial-aquifer sediments are dominantly of the Potomac Group, the aquifer sediments generally are coarser than sediments in the eastern half of the study area, where the Talbot Formation is dominant. The sand deposit in the paleochannel (fig. 3) is cleaner and thicker than sand found elsewhere in the surficial aquifer. The horizontal hydraulic conductivity of the surficial aquifer ranges from 11 to 44 ft/d, on the basis of slug tests performed in two wells screened in the paleochannel and in two wells located near the West Branch Canal Creek.

The upper confining unit underlies the surficial aquifer and overlies the Canal Creek aquifer (fig. 3), except where the clay has been eroded in the Pleistocene paleochannel and where the bottom of the unit crops out near the West Branch Canal Creek (fig. 3). The confining unit consists of clay in the Potomac Group with a thin veneer of clay from the Talbot Formation in some areas. Between the outcrop area and the paleochannel, the clay is relatively thin and contains a large percentage of silt and sand. East of the paleochannel, the clay thickens and becomes dense and plastic, increasing confinement of the underlying Canal Creek aquifer. The upper confining unit exceeds 100 ft in thickness in the extreme southeastern part of the study area.

The lower confining unit (fig. 3) has a distinct contact with the Canal Creek aquifer that commonly is marked by iron-mineralized nodules and iron-cemented layers that are several inches thick. The contact with the underlying lower confined aquifer is gradational. The lower confining unit has a thickness of 35 to 65 ft. Mottling of several colors is common in the clays of the lower confining unit, including dark gray, olive green, dark brown, red, and yellow. The upper part of the unit consists of dense plastic clay, whereas the lower part of the unit consists of sandy friable clay that contains a large percentage of muscovite and lignite fragments. Lenses of fine-grained sand and silt occur mostly near the bottom of the lower confining unit.

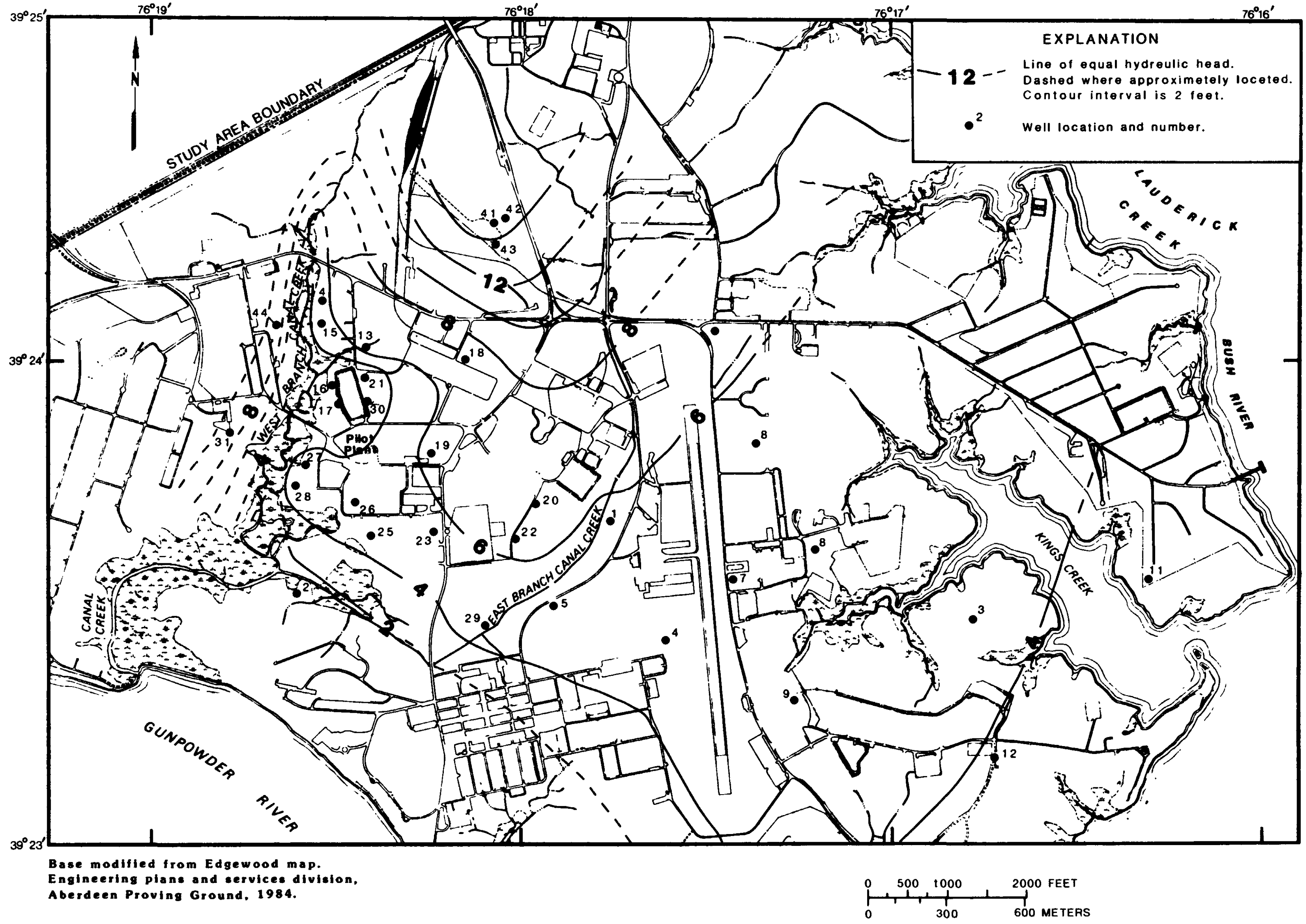
The lower confined aquifer (fig. 3) consists of fine to medium sand interbedded with clay. Although individual layers are laterally discontinuous, the lower confined aquifer as a whole appears to be continuous over the entire study area. The sand and clay layers contain abundant muscovite and lignite.

Ground-water flow

The Canal Creek aquifer contains two separate flow systems: one unconfined and part of the local flow system, and one confined and part of the regional flow system (J. P. Oliveros and D. A. Vroblesky, U.S. Geological Survey, written commun., 1988). The local flow system is present where the upper confining unit is absent near the West Branch Canal Creek and in the paleochannel near the East Branch Canal Creek (fig. 3). Both the Canal Creek aquifer and the surficial aquifer behave as a single unconfined aquifer where the upper confining unit is absent. Ground water in the local flow system of the Canal Creek aquifer discharges vertically upward to the surficial aquifer, whereas ground water in the regional flow system moves to the southeast and downdip into the deeper confined flow system (fig. 3).

The heads in the Canal Creek aquifer (fig. 4) show characteristics of local flow conditions near both branches of Canal Creek. Near the West Branch Canal Creek, large bends in the potentiometric surface of the Canal Creek aquifer indicate that heads are strongly controlled by the presence of surface water in hydraulic connection with the aquifer. In the area of the paleochannel, the potentiometric surface of the Canal Creek aquifer is only slightly affected by surface water (fig. 4). The vertical hydraulic conductivity within the paleochannel is probably lower than the horizontal hydraulic conductivity, resulting in some degree of hydrologic isolation between the Canal Creek aquifer and the surface water. An upward component of flow discharging to the surficial aquifer in the paleochannel produces a slight bend in the potentiometric surface of the Canal Creek aquifer; however, a large horizontal component of flow into the confined system subdues the response of the Canal Creek aquifer to the presence of the East Branch Canal Creek (figs. 3 and 4). Eastward of the East Branch Canal Creek, the potentiometric surface (fig. 4) is unaffected by surface water, and ground water moves in the confined regional system (fig. 3).

The Canal Creek aquifer receives recharge from three sources: (1) downward flow from the surficial aquifer; (2) upward recharge from the lower confined aquifer; and (3) precipitation infiltrating to the aquifer from updip, west and north of the study area. Recharge from the surficial aquifer occurs where the vertical head gradient is downward (unshaded zone in figure 5). The zone of insignificant recharge and discharge in figure 5 delineates where the thickness of the upper confining unit prevents downward ground-water flow.



Base modified from Edgewood map.
Engineering plans and services division,
Aberdeen Proving Ground, 1984.

Figure 4.-- Map showing distribution of hydraulic head in the Canal Creek aquifer, August 1987.

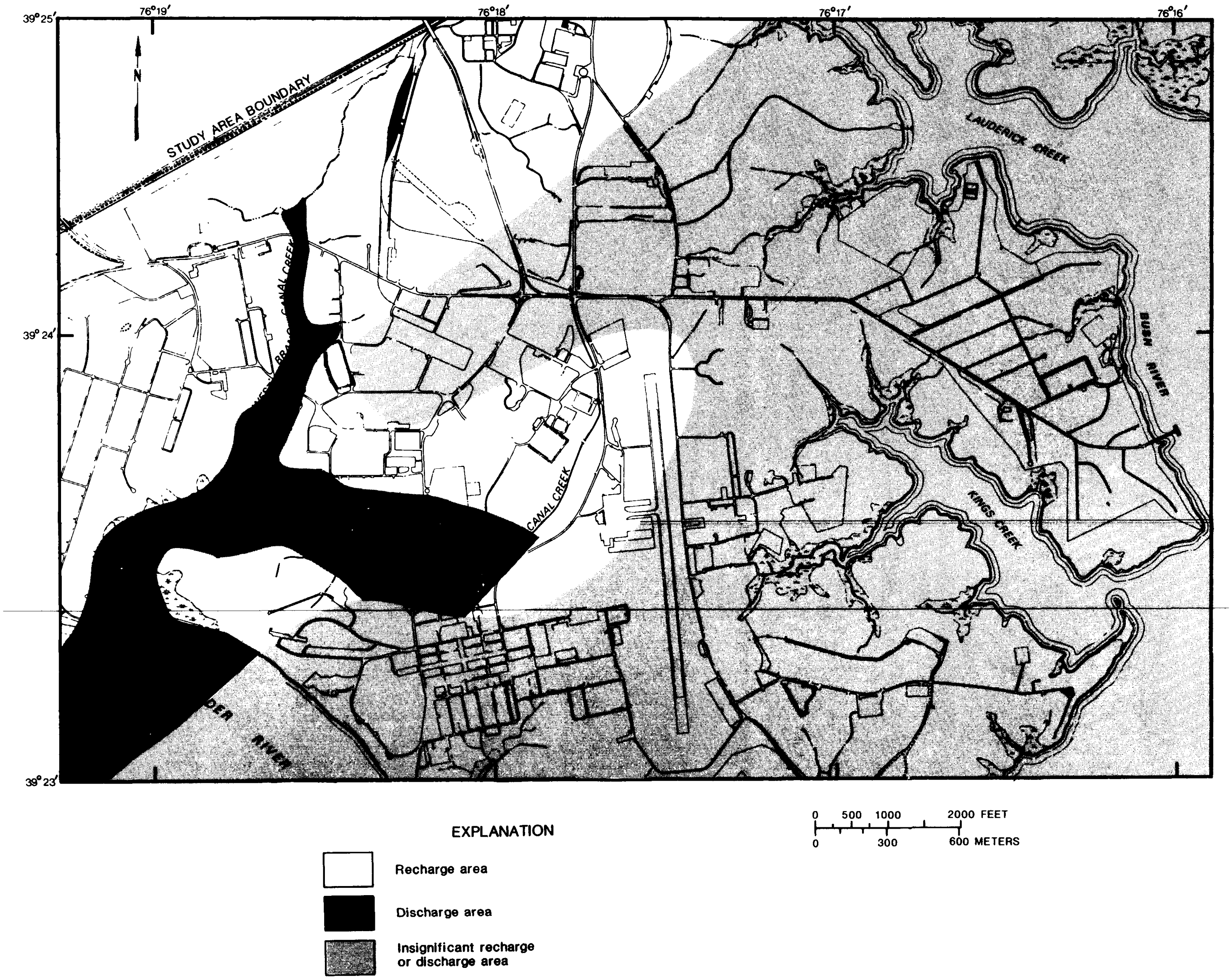


Figure 5.-- Map showing approximate location of recharge and discharge areas for the Canal Creek aquifer.

A large upward head gradient exists between the lower confined aquifer and the Canal Creek aquifer, indicating that the lower confined aquifer is primarily discharging vertically to the Canal Creek aquifer within the study area. The head difference was as much as 8 ft at site 16 (fig. 2). Although the lower confining unit that separates the two aquifers is 35 to 65 ft thick, a persistent upward head gradient across the confining unit over large areas might result in a significant amount of upward ground-water flow. This recharge from the lower confined aquifer probably moves into the regional flow system of the Canal Creek aquifer (fig. 3).

Although the Canal Creek aquifer probably receives recharge from precipitation west of the study area where the aquifer crops out, most of this recharge would discharge to the West Branch Canal Creek. Recharge to the Canal Creek aquifer from north of the study area has a much greater potential to reach the regional flow system in the study area because of the direction of ground-water flow.

The primary discharge area for the Canal Creek aquifer is near the West Branch Canal Creek (fig. 5), where ground water discharges upward to the surficial aquifer and subsequently to the creek. In addition, the potentiometric surface near the West Branch Canal Creek is affected by ground-water drainage into a network of leaky sewers and storm drains. The potentiometric surface of the Canal Creek aquifer bends upgradient in one area (fig. 4), indicating convergent ground-water flow where ground water is discharging into sewers and storm drains. The ground water that flows in the regional system discharges off-site to the southeast.

Ground-water flow in the surficial aquifer is characterized mainly by local recharge and discharge with short flow paths (J. P. Oliveros and D. A. Vroblesky, U.S. Geological Survey, written commun., 1988). The surficial aquifer receives recharge from (1) direct infiltration of precipitation or surface water, (2) upward leakage from the Canal Creek aquifer, and (3) infiltration from leaky storm drains during high tides. Direct infiltration of precipitation can occur over most of the aquifer surface area. Recharge from the West and East Branches of Canal Creek during high tide may be important during drought periods when the water table is low. Recharge to the surficial aquifer from the Canal Creek aquifer occurs where an upward head gradient exists between the two aquifers, which generally is in low-lying areas near surface-water bodies.

The surficial aquifer discharges to surface water, leaky sewers and storm drains, and the Canal Creek aquifer. Discharge to surface-water bodies occurs through streambanks, bottom sediments, and marshes where an upward head gradient exists in the aquifer. Discharge into sewers and storm drains can occur when the altitude of the water table is higher than that of the bottom of the pipes; this type of discharge was evident at only one area near the West Branch Canal Creek. Much of the discharge from the surficial aquifer to the Canal Creek aquifer probably returns as recharge to the surficial aquifer at topographic lows; however, some may enter the regional flow system of the Canal Creek aquifer, providing recharge to the Canal Creek aquifer. Thus, the Canal Creek aquifer is susceptible to contamination from the surficial aquifer in the areas designated as recharge areas in figure 5.

The lower confined aquifer is mostly recharged outside the western boundary of the study area where the aquifer is relatively close to the surface. Flow from the overlying Canal Creek aquifer is unlikely to reach the lower confined aquifer under the present upward vertical gradient between the aquifers. The lower confined aquifer discharges upward throughout the study area.

Currently, pumping stresses do not affect the aquifers within the study area. However, a large amount of pumping was done during and after World War II to obtain water for manufacturing activities. Six wells, 23E-I and 23K (pl. 1), were part of the water-supply system for the Canal Creek area, and all were pumped during World War II. Wells 23H, 23F, and 23G were used to the greatest extent. A pump was installed in well 23M (pl. 1), but the well may never have been pumped for water supply. Well 23M has been used as an observation well by the U.S. Geological Survey since 1949. The data from well 23M show that the water level was approximately 20 ft lower during 1950-68. The flow system during this period probably was dominated by the cone of depression that formed around the pumped wells. Since about 1968, the water-supply wells (wells 23E-I and 23K) were not used routinely but were considered standby wells until 1984 when organic contaminants were detected in the water. Present water-level fluctuations are caused mainly by rainfall and ocean tides.

Site History

Since 1917, APG has been the primary chemical-warfare research and development center for the United States. Activities at APG include laboratory research, field testing, and pilot scale manufacturing of chemical materials. The Canal Creek area also was the location of plants for production-scale manufacturing and for chemical-munitions filling. Manufacturing and filling plants were concentrated in the area between the West and East Branches of Canal Creek (pl. 1).

A thorough research and compilation of past activities in the Canal Creek area is being conducted by Gary Nemeth of the Waste Disposal Engineering Division, U.S. Army Environmental Hygiene Agency (USAEHA), APG. A draft of the report on historical activities, titled "RCRA (Resource Conservation and Recovery Act) facility assessment, Aberdeen Proving Ground, Maryland," was completed in 1986. All historical information given in the present report was obtained from this draft report, which is referenced as "(Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986)" throughout the present report.

Plate 1 is not a complete reconstruction of the site history. Only those plants and related activities that are believed to have the greatest potential for environmental impact are included. In addition, many buildings were used for a number of widely differing operations throughout their history, and historical records are incomplete. New information is constantly being found. For example, the existence of the disposal pit east of the runway (center of plate) was not discovered until after the drilling and sample collection for the first phase of this study were completed.

Manufacturing, Filling, and Other Activities

Five major production-scale activities included the manufacturing of chlorine, mustard, chloroacetophenone (CN), and impregnite material (CC2), and the impregnating of protective clothing (pl. 1). The plants were most active during World Wars I and II (WW1 and WW2, respectively).

Chlorine was needed as a raw material for producing nearly all the chemical agents used in WW1 and WW2, and chlorine itself was used as an agent during WW1. Separate chlorine plants were built for each war. The WW2 plant was leased to a private firm to manufacture chlorine for commercial use after WW2.

Mustard, a liquid blistering agent, was manufactured at mainly the same facilities during both WW1 and WW2. The term "mustard" in historical records refers to sulfur mustard unless otherwise noted. Mustard was also produced at least once after WW2. The area of the fourth filling unit (pl. 1) contained the major buildings in which mustard was manufactured.

The chemical agent CN, which is a tear gas, was manufactured intermittently beginning shortly after WW1 and continuing through WW2. During the 1920's and 1930's, the first CN plant was operated in the area of the fourth filling unit. A second CN plant was placed in operation in 1941 in building 58 (pl. 1).

Impregnite, which is applied to clothing, provides protection by reacting with chemical agents to prevent hazardous amounts of the agents from reaching the skin. The materials N,N'-dichloro-bis-(2,4,6-trichlorophenyl) urea, abbreviated as CC2, has been the U.S. Military standard impregnite since 1924. Building 103 was used to produce impregnite beginning in 1932 on a small scale, and larger quantities were produced periodically from 1934 through WW2. In addition, CC2 production began in 1942 in the building-87 complex, commonly known as the pilot plant (pl. 1).

To produce protective clothing, CC2 has to be fixed uniformly on the cloth with a binding agent that does not interfere with the action of CC2. Chlorinated paraffin has been used as the binding agent since the 1920's. The impregnite mixture can be applied to the clothing with either an organic-solvent process or a water-suspension process. Although water suspension has been the preferred process since the end of WW2, the organic-solvent process was mainly used in the past. The first production-size clothing-impregnating unit was installed in building 103 in 1934. The largest clothing-impregnating plant in the Canal Creek area was operated in building 73 during 1942. In addition, two mobile impregnating units were used to conduct field tests of the process at Beach Point during WW2 (pl. 1).

Pilot, or experimental, manufacturing was done to gather data on manufacturing processes in support of the larger production-size activities. Thus, many of the production-scale operations were performed first on a pilot scale. In some cases, the distinction between production scale and pilot scale is unclear as some plants were operated as both. During WW1 and WW2, the experimental-plants area (pl. 1) was the location of pilot manufacturing of mustard and of arsenicals such as lewisite, adamsite, diphenylchloroarsine, and methyldichloroarsine. Pilot studies of CC2 manufacturing and clothing impregnating were largely done in building 103, but some studies also were performed in the experimental-plants area. Pilot CN studies were done in the CN plant located in the area of the fourth filling unit.

During 1942, an additional pilot plant was built east of the airfield (pl. 1). Little information is available on the plant, but pilot manufacturing of nitrogen mustard may have been done in this plant. The building-87 complex, which also was constructed in 1942, has been used for most of the pilot-production studies that have been performed since WW2 in the Canal Creek area. A large part of the research and development work in this pilot plant involved the production of nerve agents.

Munitions-filling operations have been conducted from 1918 until the present. The first, second, and third filling units (pl. 1) were operated during WW1 for filling munitions with toxic agents. The filling plant north of the first unit was used to fill smoke munitions with white phosphorus. In the 1920's and 1930's, the fourth filling unit handled CN, mustard, and other materials. Filling activities greatly increased during WW2, and many other buildings were operated as munitions-filling plants, some of which are shown on plate 1. The adamsite (DM) plant was used during WW2 for manufacturing and for filling munitions with the choking agent, adamsite. The plant was later used for a variety of mixing, filling, and loading purposes. Most filling operations since WW2 have been on a pilot scale.

Other activities that also may have affected the environment include operation of machine and maintenance shops, motorpool garages, and the airfield. Machine and maintenance shops have been located in many buildings since 1917; some of the larger shops are shown on plate 1. The machine shop labeled as building 101 actually consisted of four buildings (101A-D). Shop activities mainly consisted of fabricating metal parts for munitions and other equipment, cleaning production equipment, and metal plating.

An open lot at the north end of the airfield (pl. 1) was used as a motorpool garage and maintenance facility from WW1 until at least 1966. The main gasoline service station that has been in use since WW2 until the present also is located in this area. Aircraft maintenance facilities, or hangars, have been operated since WW1. One hangar was constructed in 1926 and another in 1943.

Waste Disposal

Organic solvents, such as carbon tetrachloride, 1,1,2,2-tetrachloroethane, and trichloroethylene, probably were the most common wastes produced in large quantities from the manufacturing, filling, and other miscellaneous activities in the Canal Creek area (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). All the major manufacturing plants (pl. 1), except for the chlorine plants, used solvents as raw materials, decontaminating agents, cleaning agents, or for all of these purposes. The most common inorganic constituents present in manufacturing wastes were chloride and sodium. Both liquid and solid chemical wastes were generated by the past operations in the Canal Creek area.

The primary method of waste disposal from WW1 until recently has been by discharge to sewer systems. The sewer lines from the majority of the manufacturing and filling plants led to the East or West Branches of Canal Creek. Exceptions include the pilot plant east of the airport, which discharged wastes to Kings Creek, and the mobile clothing-impregnating units that operated at Beach Point, which discharged wastes to the Bush River or Kings Creek. Solid wastes, such as sludges and tars, were often discharged through the sewers if the wastes could be thinned with water or held at elevated temperatures to keep them fluid.

Before and during WW2, wastes generally received little or no treatment prior to discharge. The sewer systems that received most of the manufacturing wastes were constructed of vitrified clay during WW1. The sewerlines probably would have leaked a small amount of waste even without any major cracks or other problems. Waste treatment increased after WW2 with the rising awareness of environmental concerns and regulations. During the 1940's, a new sanitary sewer system and treatment plant were constructed, but chemical wastes still went to the older system which discharged to Canal Creek. During the late 1970's or early 1980's, all discharges of untreated wastes to the creek were stopped.

Wastes that could not be put through the sewer systems were often dumped into the marshy areas along Canal Creek. Relatively thin layers of fill material have been spread inward from the edges of the swamp along most of both branches of Canal Creek. The Canal Creek channel and marsh areas were wider in the past before landfilling took place. Some of the old sewerlines discharged into areas that are now covered with fill material, such as near the mustard area. Chemical wastes including tars, sludges, and empty chemical containers have been placed in landfill areas in addition to sanitary wastes (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Photographs taken during WW1 show dumping along the east side of the West Branch Canal Creek, and large amounts of mustard are known to have been disposed of immediately south of the mustard-manufacturing area during WW1 and WW2 (pl. 1). Areas along the East Branch Canal Creek were used for landfills from the 1940's until 1972.

Several disposal pits are known to have existed in the Canal Creek area; however, few records can be found on the type of materials placed in the pits. Toxics disposal pits (#1 and #2 on pl. 1) were located near two chemical laboratories, which commonly are referred to as laboratories #1 and #2 in historical documents. Toxics included chemical agents, but the exact materials considered toxic have varied over the years. The chemical laboratory that was near pit #1 was the main research and development laboratory from 1918 through 1942. Chemical laboratory #2 also operated during the 1920's and 1930's.

The laboratories did research on most of the chemical agents produced in the area to develop and refine the manufacturing processes. Laboratory work generally produced less than several gallons of a chemical agent in a batch and most often was accomplished in glassware. Thus, the laboratories typically handled many different chemicals in small quantities. Although the laboratories also discharged liquid wastes to the sewers, the amounts probably were small compared to the manufacturing plants.

A sand pit (pl. 1) excavated during WW1 was used later as a dump site (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). This pit was the most likely disposal site for chemical-sludge wastes from the CC2 production in building 103. The pit was reportedly fairly deep and contained trucks and equipment. The sand pit is believed to have been covered in the early 1940's (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

The salvage yard (pl. 1), which also has been referred to as the G-Street dump, was used primarily as a handling and processing area for any items that were considered salvageable. Most of the material handled was scrap metal and wood. The amount of chemical waste disposal in the salvage yard probably was limited, but chemical containers often were stored temporarily in the yard. Wastes that can be seen in the area include small metal items, metal pipes, empty tanks, cars, empty 55-gal (gallon) drums, and at least 10 drums that contain unknown liquids. The salvage yard was active from the 1940's until the late 1960's; however, the area may have been used earlier as a disposal site for miscellaneous wastes. In addition, a fire-training pit, which required the use of fuels, was operated in the salvage yard from about 1972-78.

Previous Investigations

Few ground-water studies on the Canal Creek area of APG have been reported. A water-quality-monitoring program has been operating since 1966 for the area but mainly has involved the collection of surface-water and effluent samples from Canal Creek and Kings Creek (Nemeth and others, 1983). From August 1984 through May 1985, the U.S. Army Environmental Hygiene Agency (1985) also conducted a water-quality and biological study of the surface waters in the Canal Creek area. Volatile organic compounds were detected in surface-water samples from Canal Creek, including carbon tetrachloride, 1,1,2,2-tetrachloroethane, tetrachloroethylene, trichloroethylene, chloroform, 1,2-dichloroethane, and methylene chloride. The agency concluded that the concentrations of volatile organic compounds were within safe limits for aquatic and human health but appeared to be originating from an active ground-water source (U.S. Army Environmental Hygiene Agency, 1985).

Limited ground-water analyses have been reported for shallow wells installed in the Canal Creek area (Nemeth and others, 1983) and for the six standby water-supply wells (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988). The study by Nemeth and others (1983) included a survey of the soil, sediment, ground water, and surface waters of the Edgewood area of Aberdeen Proving Ground during 1977-78. Fourteen wells were installed in the Canal Creek area, which was one of five areas studied in the environmental survey. The wells were screened in surficial sand above the Canal Creek aquifer and at depths less than 35 ft below land surface. Water samples from all 14 wells were analyzed for a hydrolysis product of mustard (thiodiglycol), nerve agents, arsenic, and white phosphorus. Five or fewer ground-water samples also were analyzed for metals, various inorganic constituents, base/neutral and acid-extractable organic compounds, and volatile organic compounds.

Ground-water contamination was not detected for any of the inorganic or organic constituents, but Nemeth and others (1983) stated that the possibility of contamination could not be eliminated because of the limited number of wells sampled. The only compound of concern that was detected in this survey of the Canal Creek area was white phosphorus, which was found in the surface waters and sediment of the East and West Branches of Canal Creek.

Ground-water samples were collected from the six water-supply wells, 23E-I and 23K (pl. 1), by the Maryland State Health Department during December 1983 and March 1984 (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988). Wells 23I and 23K were sampled once during this period, and the other wells were sampled twice. The standby wells are screened in the Canal Creek aquifer, except for well 23E which is screened at several depth intervals below the Canal Creek aquifer.

Volatile organic compounds were detected in water from all the wells except 23I (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988). The lowest concentrations were observed in the deep well, 23E. In December 1983, the only volatile organic compound detected in well 23E was 1,1,2,2-tetrachloroethane (11 μg/L); however, when the well was sampled again in January 1984, only chloroform (2 μg/L) was detected. The highest concentrations were observed in well 23F (pl. 1) during both sampling periods. The major contaminant was 1,1,2,2-tetrachloroethane for which a maximum concentration of 2,300 μg/L was found. Other volatile organic compounds detected in water from the standby wells included carbon tetrachloride, tetrachloroethylene, chloroform, trichloroethylene, 1,2-trans-dichloroethylene, 1,1,2-trichloroethane, 1,2-dichloroethane, vinyl chloride, benzene, chlorobenzene, and xylenes (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988).

The six standby wells were sampled again for volatile organic compounds during March 26-28, 1985, by the U.S. Army Environmental Hygiene Agency (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988). In general, the types and concentrations of volatile organic compounds were similar to those found by the Maryland State Health Department. However, a relatively low concentration of 1,1,2,2-tetrachloroethane (13 μg/L) was detected at this time in ground water from well 23I.

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METHODS OF INVESTIGATION

Well Installation

Between April and October of 1986, 87 observation wells were drilled at 43 sites in the Canal Creek area of APG (fig. 2). The well sites were chosen on the basis of historical information regarding chemical manufacturing and waste-disposal areas (pl. 1). Well sites (fig. 2) generally consist of clusters of two to six wells, although several sites have only one well. Individual wells at a site are designated with a letter following the site number, beginning with "A" for the shallowest well. The wells range in depth from 13 to 201.5 ft below land surface and are screened in three aquifers (table 1).

Two different drilling methods were used, depending on the depth of the well. Hollow-stem augers were used to drill wells with a depth less than 120 ft. A sampling tube, with a length of 5 ft and an inner diameter of 6.25 in., was placed inside the augers to collect core samples of the sediment as the well was drilled. For wells with a depth greater than 120 ft, mud rotary drilling was done with organic-free bentonite drilling fluid. Split-spoon samples were collected from the mud holes.

Lithologic descriptions of the sediment samples and geophysical logs of the drilled holes were used to determine screen placement at each site. Gamma and electric logs were run on each mud hole, but only gamma logs could be obtained through augers. Wells were constructed of 4-in.-inner-diameter, flush-joint PVC screens and casing. Most wells were installed with 5-ft screens (table 1), and all screens have a slot size of 0.01 in. A quartz sand pack was set from the bottom of the screened interval to 2 ft above the top of the screen, and a 2- to 3-ft-thick bentonite seal was set above the sand pack. The wells were then grouted to land surface with Portland[1] Type V cement containing 4-percent bentonite.

Ground-Water Sampling

Field Methods

Water samples were collected from the 87 wells from November 19, 1986, through April 8, 1987. Because of the length of time required to sample all wells, a system was set up to minimize the sampling time for wells in a given aquifer. Wells screened in the relatively isolated flow systems of the Beach Point area and the salvage yard were sampled first (fig. 2). Second, the remaining wells screened in the surficial aquifer were sampled. The wells screened in the Canal Creek aquifer were sampled next, generally beginning at the downgradient (least contaminated) wells and moving upgradient (most contaminated). The wells in the lower confined aquifer were sampled last.

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[1] The use of brand, firm, or trade names in this report is for identification purposes only, and does not constitute endorsement by the U.S. Geological Survey.

Table 1.--Well-construction information for observation wells installed in the Canal Creek area

[S = surficial aquifer; CC = Canal Creek aquifer; LC = lower confined aquifer; -- = permit number not known; Altitude, in feet, refers to distance above or below sea level]

Well no.	Permit no.	Altitude of land surface (ft)	Drilling method	Screened depth below land surface (ft)	Aquifer
CC- 1A	HA-81-2983	8.05	auger	22- 27	S
CC- 1B	HA-81-2984	7.83	auger	47- 52	CC
CC- 1C	HA-81-2985	8.00	auger	67- 72	CC
CC- 1D	HA-81-2986	8.31	mud rotary	149-154	LC
CC- 1E	HA-81-2987	8.42	mud rotary	168-173	LC
CC- 1F	--	8.10	mud rotary	183-188	LC
CC- 2A	HA-81-2988	8.83	auger	31- 36	CC
CC- 2B	HA-81-2989	8.59	mud rotary	140-145	LC
CC- 2C	HA-81-2990	7.52	mud rotary	175-180	LC
CC- 3A	HA-81-2993	18.77	mud rotary	135-140	CC
CC- 3B	HA-81-2994	19.16	mud rotary	160-165	CC
CC- 4A	HA-81-2996	23.61	auger	78- 83	CC
CC- 4B	HA-81-2997	24.23	mud rotary	88-90, 95-99	CC
CC- 5A	HA-81-2999	17.52	auger	15- 20	S
CC- 5B	HA-81-3000	16.84	auger	54- 59	CC
CC- 5C	HA-81-3001	17.83	auger	73.5-75.5, 80.5-82.5,83-85	CC
CC- 6A	HA-81-3003	26.03	auger	58- 63	CC
CC- 6B	HA-81-3004	26.36	auger	79.5-84.5	CC
CC- 7A	HA-81-3005	28.31	auger	85- 90	CC
CC- 7B	HA-81-3006	28.04	auger	102-107	CC
CC- 8A	HA-81-3007	18.50	auger	47- 52	S
CC- 8B	HA-81-3008	18.38	auger	75- 80	CC
CC- 8C	HA-81-3009	18.10	auger	89.5- 94.5	CC
CC- 8D	HA-81-3010	21.58	auger	110-115	CC
CC- 8E	HA-81-3011	20.18	mud rotary	195.3-201.5	LC
CC- 9A	HA-81-3012	19.89	auger	8- 13	S
CC- 9B	HA-81-3013	19.87	mud rotary	118-123	CC
CC-10A	HA-81-3015	18.42	auger	12- 17	S
CC-11A	HA-81-3017	13.78	mud rotary	133-138	CC
CC-11B	HA-81-3018	13.50	mud rotary	156-161	CC
CC-12A	HA-81-3019	17.41	mud rotary	132-137	CC
CC-12B	HA-81-3020	16.50	mud rotary	160-165	CC
CC-13A	HA-81-3021	8.27	auger	24- 29	CC
CC-13B	HA-81-3022	8.29	auger	51- 56	CC
CC-14A	HA-81-3023	7.52	auger	25- 30	CC
CC-14B	HA-81-3024	7.40	auger	50- 55	CC
CC-15A	HA-81-3025	5.70	auger	19- 24	CC
CC-16A	HA-81-3027	11.74	auger	18- 23	CC
CC-16B	HA-81-3028	11.96	auger	33- 38	CC
CC-16C	HA-81-3029	11.84	auger	83- 88	LC
CC-16D	HA-81-3030	12.07	mud rotary	115-120	LC
CC-17A	HA-81-3031	10.06	auger	19- 24	CC
CC-17B	HA-81-3032	10.17	auger	30- 35	CC
CC-17C	HA-81-3033	10.29	auger	98-103	LC
CC-18A	HA-81-3034	19.80	auger	47- 52	CC
CC-18B	HA-81-3035	19.94	auger	65- 70	CC
CC-19A	HA-81-3036	28.39	auger	6- 11	S
CC-19B	HA-81-3037	28.35	auger	53- 58	CC
CC-20A	HA-81-3038	11.17	auger	11- 16	S
CC-20B	HA-81-3039	10.93	auger	25- 30	S
CC-20C	HA-81-3040	10.52	auger	54- 59	CC
CC-20D	HA-81-3041	10.78	auger	68- 73	CC
CC-21A	HA-81-3043	14.16	auger	30- 35	CC
CC-22A	HA-81-3048	11.77	auger	22- 27	S
CC-22B	HA-81-3049	11.93	auger	45- 50	CC
CC-22C	HA-81-3050	12.27	auger	65- 70	CC
CC-23A	HA-81-3051	20.35	auger	16- 21	S
CC-23B	HA-81-3052	20.43	auger	52- 57	CC
CC-25A	HA-81-3056	12.11	auger	22- 27	CC
CC-25B	HA-81-3057	12.11	auger	40- 45	CC
CC-26A	HA-81-3058	12.94	auger	15- 20	CC
CC-26B	HA-81-3059	12.97	auger	35- 40	CC
CC-26C	HA-81-3060	13.61	mud rotary	144-149	LC
CC-27A	HA-81-3061	11.39	auger	18- 23	CC
CC-27B	HA-81-3062	11.19	auger	35- 40	CC
CC-28A	HA-81-3063	10.86	auger	16- 21	CC
CC-28B	HA-81-3064	10.78	auger	45- 50	CC
CC-29A	HA-81-3065	6.52	auger	7.7-9.7,12.5-15	S
CC-29B	HA-81-3066	6.61	auger	42- 47	CC
CC-30A	HA-81-3067	21.43	auger	36- 41	CC
CC-31A	HA-81-4076	9.05	auger	25- 30	CC
CC-32A	HA-81-4046	13.33	auger	10.5- 15.5	S
CC-32B	HA-81-4047	14.05	auger	21- 26	S
CC-33A	HA-81-4048	14.27	auger	11- 16	S
CC-33B	HA-81-4049	14.18	auger	62- 67	S
CC-34A	HA-81-4045	14.61	auger	14- 19	S
CC-35A	HA-81-4044	14.17	auger	24- 29	S
CC-37A	HA-81-4043	32.14	auger	23- 28	CC
CC-38A	HA-81-4042	31.61	auger	34-39	CC
CC-39A	HA-81-4041	31.40	auger	20- 25	CC
CC-39B	HA-81-4040	31.45	auger	35- 40	CC
CC-40A	HA-81-4039	31.23	auger	26- 31	CC
CC-41A	HA-81-4038	34.61	auger	39- 44	CC
CC-42A	HA-81-4037	33.77	auger	22- 27	CC
CC-43A	--	29.99	auger	33- 38	CC
CC-44A	HA-81-4077	14.52	auger	16- 21	CC

Sampling methodology consisted of purging the wells, collecting, filtering, and bottling samples to be sent to contract laboratories, and field measurement of selected water-quality characteristics.

A minimum of two well volumes of water was purged from each well, except for those wells which became dry before removing two well volumes. The water level in the well was allowed to recover before samples were collected. Two different types of equipment were used for purging and sampling--bailers were used for the shallow wells, and a bladder pump and packer system was used for the deep wells.

Shallow wells (water column less than about 20 ft) were bailed from the top of the water column using 1.5-in.-diameter Teflon bailers attached to Teflon-coated stainless-steel cables. The water level in the well was then allowed to recover before collecting samples. To allow a controlled rate of sample flow, a bottom-discharge fitting with a 0.25-in.-diameter Teflon tube, approximately 6 in. in length, could be attached to the bailer. If the water column was greater than approximately 8 ft in the shallow wells, a stainless-steel point-source bailer, that also had a Teflon bottom-discharge device, was used to collect samples from the screened interval.

Bladder pumps and packers were used to purge and collect samples from the wells with a water-column length greater than approximately 20 ft. Use of a packer with the deeper wells greatly reduced the volume of water that had to be purged because the casing water above the screen could be sealed off. The packer was placed above the well screen, while the bladder pump was attached below the packer near the screened interval. The pumps were made of stainless steel with Teflon bladders and could be taken apart easily in the field for servicing and decontaminating. The packer was constructed of Viton. The bladder pump and packer were lowered down the well with Teflon tubing and inflated with a portable oilless air compressor.

Decontamination of the bailers, bladder pumps, and tubing consisted of rinsing at least three times with distilled water after each sampling. The bailers also were rinsed with well water several times prior to sample collection; the bladder pumps and tubing were flushed with well water during purging. The general sampling scheme, which entailed the sampling of less contaminated wells before more contaminated wells, minimized the possibility of cross-contamination between individual sites. In addition, all sampling and filtering equipment was cleaned thoroughly with laboratory detergent and rinsed with tap and distilled water before sampling wells in different aquifers.

Filtration and preservation of samples was done in the field. Samples for analyses of all inorganic chemical constituents, except sulfide, were filtered through 0.1-μm membrane filters using a peristaltic pump. Before samples from a new well were bottled, the filter stands and Tygon tubing used with the peristaltic pumps were rinsed thoroughly both with distilled water and with water from the new well. The Tygon tubing was replaced frequently. To preserve the bottled samples until chemical analyses could be performed, samples for major cations and metals were acidified to pH 2 with concentrated nitric acid; samples for ammonia, nitrite-nitrate as nitrogen, and total phosphorus were acidified to pH 2 with sulfuric acid; and, cyanide samples were treated to pH 12 with sodium hydroxide.

The sulfide and organic chemical samples did not require filtration and were transferred directly from the sampling device into the appropriate bottles. Zinc acetate and sodium hydroxide were added to the sulfide bottles as preservatives before the bottles were filled with sample. Sulfide was only collected for those wells that had a dissolved-oxygen concentration of less than about 0.5 mg/L. Samples for analysis of base/neutral and acid-extractable organic compounds (BNA's) were collected in dark-glass gallon bottles.

Special care was needed in collecting the samples for analyses of sulfide, volatile organic compounds (VOC's), and total organic halogen (TOH) to ensure minimum aeration of the sample. For VOC's, two 40-mL (milliliter) vials for each well were filled with a slow steady stream of water into the bottom of the vial and allowed to overflow several times. To obtain a slow discharge of sample into the vials, the inflation pressure was decreased on the bladder pump, and the bottom-discharge device was used with the bailers. The glass vials were sealed immediately with caps lined with a Teflon septum and checked for bubbles. If bubbles were observed, a new sample was taken. The TOH samples were collected in the same manner in 250-mL glass bottles with Teflon-lined caps.

All inorganic and organic samples were placed immediately on ice in coolers. At the end of each day, the samples were packed in the coolers and sent by overnight airfreight to laboratories for chemical analyses.

For quality control and assurance, split samples were collected on approximately 10 percent of the total number of wells sampled. Two filter stands and peristaltic pumps were used to simultaneously draw samples from the same source bottle and fill duplicate bottles for analysis of inorganic compounds. Duplicate VOC vials were filled from the same bailer. In addition, field standards consisting of known concentrations of major ions and metals were obtained from the U.S. Geological Survey National Water Quality Laboratory. These standards were labeled as well sites and sent with actual samples to the contract laboratories for inorganic analyses.

Dissolved oxygen, temperature, specific conductance, pH, and alkalinity were measured in the field. The dissolved-oxygen concentration in each well was determined with a dissolved-oxygen meter that was equipped with a probe and submersible stirrer attached to the meter with a 50-ft-long cable. After the meter was calibrated to saturated air, dissolved oxygen was measured with the probe and stirrer assembly either at the bottom of the well, or at a depth of 50 ft in wells that were deeper than the cable length. For the deep wells, dissolved oxygen also was measured by pumping water with a bladder pump from the screen depth into a 1-gal container. The discharge line from the pump was placed in the bottom of the container, and the container was kept overflowing while the meter was read.

Temperature, pH, and specific conductance were measured immediately after collection of unfiltered well water in glass beakers. Water temperature was measured with a mercury-filled glass thermometer marked in increments of 0.1 °C. Temperature also was recorded from the dissolved-oxygen, pH, and conductance meters. The pH was read on a commercial pH meter equipped with a gel-filled combination pH electrode and an automatic temperature-compensator probe. The meter was calibrated with pH 4.00 and

7.00 buffers before the sample was collected. If the pH of the sample was greater than 7.00, the meter was recalibrated with pH 7.00 and 10.00 buffers and the pH was reread on a fresh sample. Specific conductance was measured on a field/laboratory conductance meter with a glass conductivity cell. By using a temperature probe with the meter, conductance values could be automatically adjusted to a temperature of 25 °C from the sample temperature. If the well water was turbid, the conductance was determined on both a filtered and unfiltered sample.

Alkalinity titrations were performed on a 100-mL filtered sample. The sample was stirred continuously using a battery-powered magnetic stirrer while a Hach Digital Titrator was used to add sulfuric acid. Alkalinity was calculated as the inflection point of the curve generated from pH as a function of the cumulative volume of acid added.

Chemical Analyses

Two laboratories were contracted to perform all the analyses--one laboratory for the inorganic constituents and one for the organic constituents. All the inorganic and organic analyses were done by approved U.S. Environmental Protection Agency (USEPA) (1979a) methods.

Metals and major cations (calcium, magnesium, sodium, potassium) were analyzed by inductively coupled argon plasma using USEPA Method 200.7. Arsenic and mercury were determined by atomic absorption (USEPA Method 206.2 and 245.1, respectively). Two major anions, chloride and sulfate, were analyzed using a titrimetric method (USEPA Method 325.3) and a turbidimetric method (USEPA Method 375.4), respectively. Colorimetric methods were used to determine ammonia (USEPA Method 350.2), organic nitrogen plus ammonia (USEPA Method 351.3), nitrite-nitrate (USEPA Method 353.3), total phosphorus (USEPA Method 365.2), sulfide (USEPA Method 376.2), and cyanide (USEPA Method 335.2). Fluoride was measured with an ion selective electrode (USEPA Method 340.2), and the gravimetric method (USEPA Method 160.2) was used for dissolved solids.

A preliminary GC/FID (gas chromatography/flame ionization detector) scan of the BNA sample was done for each well to determine if detectable base-neutral acid organics were present. If the scan showed a concentration above the detection limit (124 µg/L), the BNA sample was analyzed for individual compounds by the USEPA Method 625 (U.S. Environmental Protection Agency, 1979a). The TOH analyses were used as a scan for the presence of volatile organic compounds. If the TOH concentration exceeded 5 µg/L, the VOC samples were analyzed by gas chromatography/mass spectrometry (GC/MS) for the suite of volatile organic compounds given by USEPA Method 624.

The contract laboratory for organic analyses followed the quality-control/quality-assurance program developed by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). Daily quality control consisted of initial calibration of the analytical instruments, additional analyses of calibration standards with each daily lot of samples, and the use of control spikes with known concentrations.

During initial calibration of all the analytical instruments, six standards were run at concentrations 0, 0.5x, 1x, 2x, 5x, and 10x, where x is the detection limit established by USATHAMA. In addition to initial calibration, one calibration standard and a blank were run with each 8-hour shift on the GC/MS.

For the organic analyses by USEPA Methods 624 and 625, each sample was spiked with three surrogates (d-chloroform, d4-1,2-dichloroethane, and d10-ethylbenzene) at one of three levels of concentrations. The percent recoveries were calculated and plotted on daily quality-control charts. The control charts, which are plots of percent recovery as a function of daily lot number or sample number for each target spike concentration, were established from previous analyses of spiked samples. The mean and standard deviation of the percent recoveries were calculated and used to set control limits for the target value. As new samples were analyzed, the percent recoveries of the spikes were compared to the established control limits. Warning limits to indicate that a sample may need to be reanalyzed were set at twice the standard deviation.

The contract laboratory for the inorganic analyses did not follow USATHAMA's program for quality control and assurance. However, the laboratory is enrolled in the Standard References Program with the U.S. Geological Survey National Water Quality Laboratory and participates in several USEPA reference programs for an additional check on quality control. After initial calibration of the instruments, the daily quality-control procedure involved analyses of a standard, a blank, a set of analytical duplicates, and a matrix spike for each inorganic constituent with each lot of samples.

INORGANIC CONSTITUENTS

Analyses for 30 inorganic constituents and field measurements were obtained from 85 of the 87 wells installed in the Canal Creek area, and these data are given in table 2. Samples for inorganic analyses were not collected from two wells. Water from well 11A contained a large amount of silt which could not be filtered. Water from a broken water main flooded the area near well 35A for several days before sampling, and dilution because of the flooding was likely.

Some samples had anomalously high pH values (table 2). Reactions between the ground water and the cement used in well construction are suspected to have increased the pH. Thus, the well-water samples may not reflect the actual inorganic chemical composition of the aquifer at these sites. The suspect water samples include wells 2A, 3A, 4A, 4B, 6A, 12A, 12B, 15A, 16B, and 37A in the Canal Creek aquifer; well 34A in the surficial aquifer; and, wells 1E, 1F, 2C, 16C, and 16D in the lower confined aquifer. The potential effect of the grout on the ground water is discussed in the section on probable sources of major constituents.

Table 2.--Inorganic-chemical data for ground water in the Canal Creek area

[All concentrations are for dissolved constituents in units of milligrams per liter; (R), replicate sample; (Re), repeat sample; --, not analyzed; <, less than; °C, degrees Celsius; microsiemens/cm, microsiemens per centimeter at 25 degrees Celsius. Lead and cyanide were below detection (less than 0.05 and 0.01 milligrams per liter, respectively) in all samples]

Well no.	Sampling date	Temperature, (°C)	Oxygen	Specific conductance (microsiemens/cm)	pH (units)	Alkalinity (as HCO_3^-)	Dissolved solids	Calcium (Ca^{2+})	Magnesium (Mg^{2+})	Sodium (Na^+)	Potassium (K^+)	Sulfate (SO_4^{2-})
Canal Creek aquifer:												
CC- 1B	3-03-87	14.0	<.1	344	6.54	89	181	19	10	17	2.9	52
CC- 1C	3-03-87	13.8	<.1	271	6.02	66	156	12	6.3	19	3.0	48
CC- 2A	2-26-87	13.5	<.1	180	9.66	118	129	12	.50	8.7	30	<1.0
CC- 3A	4-08-87	12.6	1.3	666	11.34	218	254	22	.62	24	80	16
CC- 3B	4-07-87	12.1	3.2	87	5.97	34	184	5.2	1.0	6.6	1.7	8.1
CC- 4A	2-13-87	13.5	<.1	193	7.48	94	130	4.1	.81	13	29	16
CC- 4B	2-13-87	13.5	<.1	297	8.26	130	190	18	1.4	17	34	<1.0
CC- 5B	2-06-87	13.5	.2	148	5.66	22	91	6.9	1.3	20	1.9	33
CC- 5C	2-06-87	13.5	.8	382	6.69	120	246	20	1.8	25	39	13
CC- 6A	1-12-87	13.8	3.3	1,250	12.08	375	512	2.6	.08	58	190	61
CC- 6A(Re)	4-29-87	16.5	--	800	10.74	--	--	--	--	--	--	--
CC- 6B	1-12-87	13.8	2.3	258	5.84	39	170	22	8.4	11	2.0	51
CC- 7A	2-24-87	14.5	.8	191	6.06	48	110	16	2.9	18	1.2	18
CC- 7A(R)	2-24-87	--	--	--	--	--	110	4.3	2.6	17	.85	16
CC- 7B	2-24-87	14.5	<.1	299	6.88	144	150	17	4.4	17	1.7	7.0
CC- 8B	2-04-87	13.5	.9	135	5.04	10	86	4.3	1.9	13	1.6	12
CC- 8C	2-25-87	13.5	<.1	190	5.16	7	110	12	5.2	11	1.9	50
CC- 8C(R)	2-25-87	--	--	--	--	--	120	11	5.2	11	1.8	50
CC- 8D	2-25-87	13.8	<.1	140	5.71	40	80	5.0	1.8	11	2.7	8.0
CC- 9B	1-13-87	14.0	.1	244	9.44	124	143	5.7	1.2	30	28	9.2
CC- 9B(Re)	4-08-87	16.0	<.1	122	6.60	64	85	1.8	.75	16	7.6	8.4
CC-11A	4-03-87	--	--	--	--	--	--	--	--	--	--	--
CC-11B	4-03-87	13.9	.8	84	5.97	32	52	5.5	1.0	4.2	1.2	4.0
CC-12A	1-09-87	13.0	.4	132	6.82	83	84	5.8	.82	8.5	21	11
CC-12B	1-09-87	13.0	.4	268	9.71	136	162	7.6	1.9	18	50	11
CC-13A	3-04-87	13.2	2.8	2,000	4.51	<1	910	36	22	280	2.7	30
CC-13B	3-04-87	13.0	<.1	70	5.76	16	45	12	.71	6.8	4.1	<1.0
CC-14A	3-04-87	13.1	<.1	209	4.92	<1	116	5.7	3.8	23	1.2	32
CC-14B	3-04-87	13.2	<.1	95	5.15	10	59	2.1	1.2	10	.91	<1.0
CC-15A	3-04-87	12.0	2.2	341	10.65	130	165	50	.46	20	7.5	35
CC-16A	3-06-87	14.7	<.1	374	5.58	89	222	15	3.8	4.2	3.1	16
CC-16B	3-06-87	18.0	.4	604	9.94	44	403	46	4.7	56	3.5	12
CC-16B(R)	3-06-87	--	--	--	--	--	392	42	5.0	56	3.5	7.0
CC-17A	3-06-87	16.3	.3	253	5.47	13	153	9.9	4.4	27	3.8	30
CC-17A(R)	3-06-87	--	--	--	--	--	150	9.6	4.3	26	3.6	32
CC-17B	3-09-87	16.5	1.2	126	5.46	18	94	6.2	1.8	8.7	4.9	14
CC-18A	2-11-87	13.5	1.3	2,350	4.48	<1	1,300	52	27	340	2.7	7.4
CC-18B	2-11-87	13.5	<.1	98	5.74	24	75	10	4.2	6.6	2.2	5.4
CC-19B	2-10-87	13.0	<.1	125	6.57	49	80	13	1.3	4.6	4.6	<1.0
CC-20C	2-03-87	14.3	<.1	587	6.43	85	291	28	10	39	4.6	63
CC-20D	2-10-87	14.5	<.1	162	6.17	38	100	6.8	4.0	10	1.6	20
CC-21A	3-04-87	18.6	1.2	214	6.22	47	129	10	1.2	18	13	23
CC-21A(R)	3-04-87	--	--	--	--	--	125	10	1.2	19	14	22
CC-22B	2-02-87	14.0	.2	343	6.29	130	252	31	14	12	2.4	47

CC-22C	2-03-87	14.0	<.1	391	6.62	102	226	23	8.0	23	5.6	23
CC-23B	2-10-87	15.2	.1	428	6.52	188	210	28	12	23	3.5	56
CC-25A	2-27-87	15.0	<.1	386	6.21	83	234	29	8.1	26	3.5	66
CC-25B	2-27-87	15.0	<.1	463	6.36	118	233	26	8.8	34	4.9	68
CC-26A	2-27-87	12.5	<.1	274	6.58	92	168	32	3.1	15	4.2	24
CC-26A(R)	2-27-87	--	--	--	--	--	170	31	3.2	16	4.1	24
CC-26B	2-27-87	15.0	1.8	490	6.02	56	275	22	12	47	3.5	66
CC-27A	3-05-87	13.0	1.8	438	5.68	23	421	35	10	32	2.5	120
CC-27B	3-05-87	13.9	3.8	623	5.94	42	364	31	10	58	2.8	120
CC-27B(R)	3-05-87	--	--	--	--	--	370	30	10	59	2.7	120
CC-28A	3-05-87	12.0	1.3	4,280	4.88	12	2,340	33	26	730	19	190
CC-28B	3-05-87	13.4	2.4	2,110	4.78	5	1,140	17	10	340	4.1	130
CC-29B	2-10-87	13.7	<.1	235	6.54	76	150	23	.58	27	12	12
CC-30A	3-05-87	16.2	1.2	124	5.64	15	85	5.4	2.9	10	1.6	19
CC-30A(R)	3-05-87	--	--	--	--	--	89	6.8	2.8	9.7	1.5	19
CC-31A	2-19-87	13.0	5.5	156	4.58	<1	100	5.8	5.9	9.1	1.1	40
CC-37A	11-19-86	14.5	1.3	1,900	11.85	634	778	63	.04	66	250	92
CC-38A	11-21-86	13.8	<.1	310	6.56	92	134	9.3	1.3	17	28	17
CC-39A	11-19-86	14.5	1.4	313	5.74	40	203	20	3.7	30	8.3	26
CC-39B	11-19-86	12.5	1.4	89	5.22	12	62	6.5	1.3	9.7	1.2	<1.0
CC-40A	11-20-86	13.5	1.4	501	4.30	<1	357	5.0	6.8	71	1.2	120
CC-41A	11-21-86	13.6	3.6	774	6.08	44	464	17	5.7	130	5.7	200
CC-42A	11-20-86	12.5	4.4	230	5.38	15	136	14	6.8	21	2.3	36
CC-43A	11-21-86	13.0	6.8	528	6.20	105	295	39	12	52	4.2	54
CC-44A	2-19-87	9.7	2.2	214	6.62	41	140	20	5.5	7.5	2.1	31
Surficial aquifer:												
CC- 1A	3-03-87	13.9	<.1	205	6.34	100	117	16	7.0	12	2.0	7.0
CC- 1A(R)	3-03-87	--	--	--	--	--	109	14	6.8	11	6.8	18
CC- 5A	1-07-87	13.8	<.1	505	6.06	239	286	16	11	55	8.6	51
CC- 8A	2-04-87	13.7	.6	217	5.85	45	117	4.4	2.1	16	3.0	33
CC- 9A	1-06-87	13.0	.5	770	4.07	<1	558	17	22	67	1.6	54
CC-10A	1-06-87	14.1	1.1	285	5.62	27	169	8.6	6.6	29	9.4	76
CC-19A	1-07-87	12.2	<.1	261	5.98	77	178	35	6.3	3.2	6.4	96
CC-20A	1-07-87	14.0	2.9	318	6.46	102	185	28	11	16	9.2	39
CC-20B	2-02-87	14.7	3.3	412	6.36	84	236	31	11	24	7.0	48
CC-22A	2-02-87	14.0	.4	285	5.99	94	169	34	11	7.1	3.1	36
CC-23A	2-03-87	14.0	1.7	582	6.49	265	313	78	21	11	3.9	64
CC-29A	1-13-87	12.5	7.0	8,340	12.85	2,450	1,820	200	.07	65	18	<1.0
CC-32A	12-17-86	14.5	.6	1,220	5.68	37	770	31	18	190	1.9	170
CC-32B	12-17-86	14.0	.6	1,810	5.12	7	1,050	37	39	280	6.1	150
CC-33A	12-17-86	14.0	.6	617	6.24	90	370	28	12	80	3.0	74
CC-33B	12-17-86	13.2	<.1	2,160	4.44	<1	1,140	26	49	330	4.0	98
CC-34A	12-17-86	14.5	1.3	3,790	10.08	97	2,110	26	30	600	60	190
CC-35A	12-17-86	13.8	.2	364	6.66	--	--	--	--	--	--	--
CC-36A	2-19-87	11.0	.1	311	6.21	151	160	32	9.4	4.6	1.7	16
Lower confined aquifer:												
CC- 1D	3-03-87	13.7	<.1	74	6.23	37	50	3.7	1.1	4.0	1.3	9.0
CC- 1E	4-03-87	13.5	.4	3,500	11.57	297	320	5.5	.46	27.0	96	4.0
CC- 1F	3-27-87	16.0	<.1	233	10.65	143	147	39	.35	7.4	14	6.5
CC- 2B	3-24-87	13.2	.2	112	6.65	60	104	31	1.8	5.3	4.3	6.8
CC- 2C	3-26-87	14.0	3.8	1,010	12.28	236	270	44	.15	16	52	7.7
CC- 8E	4-01-87	13.8	.4	48	5.58	18	46	1.7	.64	3.4	.74	5.1
CC-16C	3-06-87	17.5	4.0	404	11.11	191	177	54	.06	5.8	6.7	6.6
CC-16D	3-27-87	16.0	1.4	221	11.02	81	116	20	.37	12	28	8.3
CC-17C	3-06-87	16.5	2.2	54	5.69	13	37	1.4	.68	2.9	.75	7.6
CC-26C	2-27-87	15.2	<.1	126	6.41	58	71	12	1.5	4.4	5.5	36

Table 2.--Inorganic-chemical data for ground water in the Canal Creek area--Continued

[All concentrations are for dissolved constituents in units of milligrams per liter; (R), replicate sample; (Re), repeat sample; --, not analyzed; <, less than; °C, degrees Celsius; microsiemens/cm, microsiemens per centimeter at 25 degrees Celsius. Lead and cyanide were below detection (less than 0.05 and 0.01 milligrams per liter, respectively) in all samples]

Well no.	Sampling date	Iron (Fe, total)	Silica	Chloride (Cl^-)	Fluoride (F^-)	Sulfide (S^{2-})	Phosphorus (P, total)	Ammonia (NH_3 as N)	Ammonia + Organic (as N)	Nitrite (NO_2^- as N)	Nitrite + Nitrate (as N)	Manganese (Mn)
Canal Creek aquifer:												
CC- 1B	3-03-87	22	3.3	15	0.80	1.2	0.04	1.2	1.2	0.02	0.07	0.62
CC- 1C	3-03-87	14	5.2	17	.88	<1.0	.01	<.20	.30	.02	.06	.77
CC- 2A	2-26-87	.06	7.6	<5	.64	<1.0	.04	<.20	.66	.01	.04	<.002
CC- 3A	4-08-87	.51	6.4	5	.50	<1.0	.08	.55	.54	--	.06	.022
CC- 3B	4-07-87	3.5	4.9	<5	.25	<1.0	.02	.12	.22	<.01	.04	.017
CC- 4A	2-13-87	1.6	4.0	<5	.38	<1.0	.02	.27	.77	<.01	.05	.14
CC- 4B	2-13-87	.05	5.3	21	.25	<1.0	.02	.23	.42	.02	.20	.089
CC- 5B	2-06-87	10	.40	9	.20	<1.0	.02	.43	1.1	<.01	.05	.16
CC- 5C	2-06-87	2.1	5.4	25	.21	1.6	.01	.42	1.6	.04	.58	.22
CC- 6A	1-12-87	.03	10	12	.17	--	.12	.58	1.3	.02	.06	<.002
CC- 6A(Re)	4-29-87	--	--	--	--	--	--	--	--	--	--	--
CC- 6B	1-12-87	1.0	8.9	21	.21	--	.02	<.20	.72	.02	.77	2.4
CC- 7A	2-24-87	15	5.2	29	.80	<1.0	.01	.48	1.1	<.01	.08	.37
CC- 7A(R)	2-24-87	14	5.2	29	.81	<1.0	.01	.45	1.0	<.01	.12	.35
CC- 7B	2-24-87	34	7.3	28	1.1	<1.0	.02	<.20	.45	.02	.19	.86
CC- 8B	2-04-87	1.8	4.9	23	.15	--	.01	<.20	.26	<.01	.12	.17
CC- 8C	2-25-87	.64	5.5	17	.72	1.6	.02	<.20	.26	<.01	.06	.26
CC- 8C(R)	2-25-87	.66	5.4	18	.78	<1.0	.01	<.20	.45	<.01	.03	.26
CC- 8D	2-25-87	11	9.2	17	.81	<1.0	.02	<.20	.60	<.01	.05	.28
CC- 9B	1-13-87	<.008	4.2	6	.27	<1.0	.01	<.20	.73	<.01	<.05	.036
CC- 9B(Re)	4-08-87	2.4	5.4	5	.22	2.0	.02	.24	.61	--	.17	.21
CC-11A	4-03-87	--	--	--	--	--	--	--	--	--	--	--
CC-11B	4-03-87	5.3	5.4	<5	.17	2.0	.03	.40	.38	.01	.08	.13
CC-12A	1-09-87	.70	5.0	<5	.13	4.4	.04	<.20	.56	.02	.06	.069
CC-12B	1-09-87	.02	5.2	<5	.17	<1.0	.02	<.20	1.2	.02	<.05	.003
CC-13A	3-04-87	.09	5.6	530	2.6	<1.0	.01	<.20	.11	<.01	.65	.37
CC-13B	3-04-87	.63	5.9	<5	.65	<1.0	<.01	<.20	<.10	<.01	.16	.034
CC-14A	3-04-87	.07	5.4	32	.62	<1.0	.02	<.20	<.10	<.01	.34	.19
CC-14B	3-04-87	1.0	4.8	20	.40	1.6	<.01	<.20	<.10	<.01	<.05	.036
CC-15A	3-04-87	.04	3.1	25	8.5	--	.04	.38	.63	<.01	<.05	.007
CC-16A	3-06-87	11	8.5	55	.62	<1.0	.03	<.20	<.50	<.01	.06	.760
CC-16B	3-06-87	.05	5.8	150	.93	<1.0	.02	<.20	<.50	.07	.22	<.002
CC-16B(R)	3-06-87	.09	5.8	140	1.1	<1.0	.01	<.20	<.50	<.01	.21	<.002
CC-17A	3-06-87	.16	6.4	27	.72	<1.0	.12	<.20	<.50	<.01	1.8	.20
CC-17A(R)	3-06-87	.09	6.1	28	.69	--	.13	<.20	<.50	<.01	1.8	.18
CC-17B	3-09-87	.13	.06	14	.72	--	.03	<.20	.16	<.01	.10	.23
CC-18A	2-11-87	.08	4.3	1,000	.38	--	.01	<.20	.77	<.01	.25	.65
CC-18B	2-11-87	.11	2.5	13	.19	<1.0	.03	<.20	.39	<.01	.24	.080
CC-19B	2-10-87	5.7	3.3	11	.16	<1.0	.01	<.20	.50	.04	.34	.16
CC-20C	2-03-87	20	3.6	60	.25	3.4	.02	.23	.44	.05	1.0	.16
CC-20D	2-10-87	9.1	3.2	16	.15	1.6	.02	<.20	<.20	<.01	.10	.53
CC-21A	3-04-87	.19	6.2	18	.73	--	.02	.27	<.10	.02	.19	.047
CC-21A(R)	3-04-87	.09	6.0	17	.81	--	.02	<.20	.12	.02	.20	.048
CC-22B	2-02-87	14	1.9	30	.21	<1.0	.02	<.20	.53	.01	2.5	2.4
CC-22C	2-03-87	8.1	<.15	40	.61	<1.0	.01	.22	.59	.01	.05	.78

CC-23B	2-10-87	30	2.8	38	.20	<1.0	<.01	<.20	.86	.01	<.03	.29
CC-25A	2-27-87	12	.35	31	1.2	<1.0	.02	.38	<.10	.02	.11	.059
CC-25B	2-27-87	17	3.6	44	1.1	--	.03	<.20	<.10	.01	.07	.79
CC-26A	2-27-87	.03	2.8	18	1.2	1.2	.01	.27	.25	<.01	.68	.026
CC-26A(R)	2-27-87	.02	5.7	18	1.3	<1.0	.01	.32	.17	<.01	.72	.026
CC-26B	2-27-87	.11	3.7	65	.80	--	.02	<.20	.14	.01	1.4	.50
CC-27A	3-05-87	.24	15	39	1.2	--	.01	<.20	.20	.02	.54	.48
CC-27B	3-05-87	6.0	8.5	94	4.2	--	.01	<.20	<.10	.01	.57	1.4
CC-27B(R)	3-05-87	6.0	8.6	85	3.6	--	.01	<.20	.12	<.01	.65	1.4
CC-28A	3-05-87	1.0	6.7	470	7.1	--	.01	.30	.27	.02	1.6	.87
CC-28B	3-05-87	1.0	6.2	240	.85	--	.01	<.20	.19	.01	1.9	1.1
CC-29B	2-10-87	.96	2.9	24	.15	<1.0	.01	.22	.35	<.01	.03	.051
CC-30A	3-05-87	2.8	5.8	15	.58	--	.01	<.20	<.10	<.01	.32	.18
CC-30A(R)	3-05-87	2.5	4.7	16	.51	--	.01	<.20	<.10	.01	.35	.18
CC-31A	2-19-87	.25	4.2	13	1.1	--	.01	<.20	.39	<.01	.44	.26
CC-37A	11-19-86	.03	5.8	19	.63	<1.0	.02	.38	1.4	.48	.83	<.002
CC-38A	11-21-86	.03	7.5	17	.13	<1.0	.02	.30	1.2	<.05	.71	.058
CC-39A	11-19-86	.09	13	49	.18	<1.0	.02	<.20	1.0	<.05	.17	.37
CC-39B	11-19-86	.16	7.8	17	.14	<1.0	.01	<.20	.50	<.05	.15	.066
CC-40A	11-20-86	.81	37	55	.29	--	.02	<.20	.88	<.05	<.05	.089
CC-41A	11-21-86	.01	8.2	76	.26	--	.02	.28	.79	.08	.26	.30
CC-42A	11-20-86	.02	8.8	36	.14	--	.02	<.20	.55	<.05	.30	.30
CC-43A	11-21-86	.02	3.2	83	.15	--	.01	<.20	.61	.05	.67	.16
CC-44A	2-19-87	.03	3.7	20	1.9	--	.03	.34	.95	<.01	1.1	.029
Surficial aquifer:												
CC- 1A	3-03-87	12	5.2	17	1.4	2.4	.02	.45	.46	.04	.06	.56
CC- 1A(R)	3-03-87	10	5.1	14	1.0	<1.0	.02	.51	.47	.04	.03	.55
CC- 5A	1-07-87	45	6.3	29	.25	1.6	.02	.42	1.0	.04	.05	1.3
CC- 8A	2-04-87	18	3.3	17	.21	<1.0	.01	<.20	.43	.01	.16	.43
CC- 9A	1-06-87	23	21	230	.15	<1.0	.01	.60	1.1	.05	.14	1.6
CC-10A	1-06-87	.03	2.7	17	.15	--	.01	<.20	.50	<.01	.82	.11
CC-19A	1-07-87	3.0	4.8	<5	.16	<1.0	.03	.79	1.7	.01	.17	.16
CC-20A	1-07-87	.07	3.4	24	.15	--	.02	<.20	.86	.02	1.4	.006
CC-20B	2-02-87	.06	2.5	44	.22	--	.02	<.20	.24	<.01	3.9	.018
CC-22A	2-02-87	.06	1.7	13	.15	<1.0	.02	<.20	.28	<.01	1.2	.026
CC-23A	2-03-87	.80	5.6	9	.30	--	.01	<.20	.45	<.01	<.03	.077
CC-29A	1-13-87	<.008	.37	5	.31	--	.03	5.5	7.4	.02	.13	<.002
CC-32A	12-17-86	.34	20	290	.25	--	.02	<.20	.98	.01	.53	.31
CC-32B	12-17-86	.10	19	420	.25	--	.06	.44	.77	<.01	.39	.42
CC-33A	12-17-86	3.0	1.4	100	.19	<1.0	.17	<.20	.67	.02	.16	.30
CC-33B	12-17-86	7.4	14	600	.30	<1.0	.02	<.20	.91	.01	.13	3.2
CC-34A	12-17-86	.09	3.9	1,000	.24	--	.02	<.20	.66	.32	.53	<.002
CC-35A	12-17-86	--	--	--	--	<1.0	--	--	--	--	--	--
CC-36A	2-19-87	13	2.8	11	.86	<1.0	<.01	.45	.58	<.01	.05	1.1
Lower confined aquifer:												
CC- 1D	3-03-87	7.9	.31	<5	1.1	<1.0	.01	<.20	<.10	<.01	.04	.21
CC- 1E	4-03-87	.13	2.7	<5	.21	<1.0	.02	.40	.31	.03	<.03	.004
CC- 1F	3-27-87	.03	4.4	<5	.25	<1.0	.06	.24	.45	.02	.20	.005
CC- 2B	3-24-87	1.1	3.6	5	.36	<1.0	.02	<.20	.46	<.05	<.05	.018
CC- 2C	3-26-87	.08	4.9	11	.30	<1.0	.02	<.20	.53	.05	<.05	.009
CC- 8E	4-01-87	4.2	4.3	<5	.15	<1.0	.02	.22	.31	.01	.09	.10
CC-16C	3-06-87	.03	4.5	<5	1.3	--	.02	<.20	<.50	.02	<.05	<.002
CC-16D	3-27-87	.45	3.7	<5	.27	<1.0	.02	.25	.26	.02	.09	.012
CC-17C	3-06-87	4.9	4.6	<5	.59	<1.0	.01	<.20	<.50	<.01	<.05	.080
CC-26C	2-27-87	4.4	14	<5	.85	1.2	.03	.20	.31	.05	.11	.16

Table 2.--Inorganic-chemical data for ground water in the Canal Creek area--Continued

[All concentrations are for dissolved constituents in units of milligrams per liter; (R), replicate sample; (Re), repeat sample; --, not analyzed; <, less than; °C, degrees Celsius; microsiemens/cm, microsiemens per centimeter at 25 degrees Celsius. Lead and cyanide were below detection (less than 0.05 and 0.01 milligrams per liter, respectively) in all samples]

Well no.	Sampling date	Arsenic (As, total)	Zinc (Zn)	Antimony (Sb)	Mercury (Hg)	Nickel (Ni)	Beryllium (Be)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Selenium (Se)
Canal Creek aquifer:												
CC- 1B	3-03-87	0.039	0.020	<0.024	<0.0002	<0.008	<0.001	0.13	<0.002	<0.006	<0.004	<0.002
CC- 1C	3-03-87	.006	.026	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 2A	2-26-87	<.005	.004	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 3A	4-08-87	<.005	.23	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.016	<.002
CC- 3B	4-07-87	<.005	.078	<.024	<.0002	<.008	<.001	<.05	<.002	.010	<.004	<.002
CC- 4A	2-13-87	<.005	.014	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.008	<.002
CC- 4B	2-13-87	<.005	.009	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.006	<.002
CC- 5B	2-06-87	<.005	.051	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 5C	2-06-87	<.005	.056	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 6A	1-12-87	<.005	.007	.074	.0006	<.008	<.001	.06	<.002	.007	.011	<.002
CC- 6A(Re)	4-29-87	--	--	--	--	--	--	--	--	--	--	--
CC- 6B	1-12-87	<.005	.026	<.024	<.0002	.028	<.001	<.05	<.002	.010	.010	<.002
CC- 7A	2-24-87	<.005	.37	<.024	.0003	<.008	<.001	<.05	<.002	.006	<.004	<.002
CC- 7A(R)	2-24-87	<.005	.033	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	.009
CC- 7B	2-24-87	<.005	.050	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 8B	2-04-87	<.005	.10	<.024	<.0002	.055	<.001	<.05	.002	<.006	.005	<.002
CC- 8C	2-25-87	<.005	.095	<.024	.0007	.070	<.001	<.05	<.002	<.006	<.004	<.002
CC- 8C(R)	2-25-87	<.005	.087	<.024	<.0002	.068	<.001	<.05	<.002	<.006	<.004	<.002
CC- 8D	2-25-87	<.005	.006	<.024	.0007	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 9B	1-13-87	<.005	<.002	<.024	.0004	<.008	<.001	.06	<.002	.006	.007	<.002
CC- 9B(Re)	4-08-87	<.005	.030	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC-11A	4-03-87	--	--	--	--	--	--	--	--	--	--	--
CC-11B	4-03-87	<.005	.11	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC-12A	1-09-87	<.005	.020	<.024	.0003	<.008	<.001	.07	<.002	<.006	.005	<.002
CC-12B	1-09-87	<.005	.010	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.014	<.002
CC-13A	3-04-87	<.005	.33	<.024	<.0002	.23	<.001	<.05	<.002	.008	.035	<.002
CC-13B	3-04-87	<.005	.17	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.008	<.002
CC-14A	3-04-87	<.005	.070	<.024	.0012	.037	<.001	<.05	<.002	<.006	.005	<.002
CC-14B	3-04-87	<.005	.032	<.024	.0004	.008	<.001	<.05	<.002	<.006	<.004	<.002
CC-15A	3-04-87	.006	.017	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.004	<.002
CC-16A	3-06-87	<.005	.034	<.024	<.0002	.012	<.001	<.05	<.002	<.006	<.004	<.005
CC-16B	3-06-87	<.005	.017	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.006	<.005
CC-16B(R)	3-06-87	<.005	.020	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.007	<.005
CC-17A	3-06-87	<.005	.074	<.024	<.0002	.050	<.001	.09	<.002	<.006	.022	<.005
CC-17A(R)	3-06-87	<.005	.064	<.024	.0015	.050	<.001	.09	<.002	<.006	.020	<.005
CC-17B	3-09-87	<.005	.43	<.024	.0014	.009	<.001	<.05	<.002	<.006	.008	<.005
CC-18A	2-11-87	<.005	.36	<.024	<.0002	.20	.003	<.05	.003	.010	.088	<.002
CC-18B	2-11-87	<.005	.033	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.008	<.002
CC-19B	2-10-87	<.005	.098	<.024	.0004	<.008	.019	<.05	<.002	<.006	<.004	<.002
CC-20C	2-03-87	.011	.009	<.024	.0004	<.008	<.001	<.05	<.002	.008	<.004	<.002
CC-20D	2-10-87	<.005	.013	<.024	.0003	.012	<.001	<.05	<.002	<.006	<.004	<.002
CC-21A	3-04-87	<.005	.027	<.024	<.0002	.014	<.001	<.05	<.002	<.006	<.004	<.002
CC-21A(R)	3-04-87	<.005	.024	<.024	<.0002	.012	<.001	<.05	<.002	<.006	<.004	<.002
CC-22B	2-02-87	<.005	.21	<.024	<.0002	<.008	<.001	.24	<.002	<.006	<.004	<.002

CC-22C	2-03-87	<.005	.019	<.024	<.0002	<.008	<.001	.08	<.002	.006	<.004	<.002
CC-23B	2-10-87	.022	.096	<.024	<.0002	<.008	<.001	.09	<.002	<.006	<.004	<.002
CC-25A	2-27-87	.011	.011	<.024	<.0002	<.008	<.001	.05	<.002	<.006	<.004	<.005
CC-25B	2-27-87	<.005	.020	<.024	<.0002	<.008	<.001	.05	<.002	<.006	<.004	<.005
CC-26A	2-27-87	<.005	.036	<.024	<.0002	<.008	<.001	1.2	<.002	<.006	.005	<.005
CC-26A(R)	2-27-87	<.005	.040	<.024	<.0002	<.008	<.001	1.5	<.002	<.006	.005	<.005
CC-26B	2-27-87	<.005	.71	<.024	<.0002	<.008	<.001	.24	<.002	<.006	<.004	<.005
CC-27A	3-05-87	<.005	.077	<.024	<.0002	.015	<.001	.13	<.002	.006	.013	<.005
CC-27B	3-05-87	<.005	.077	<.024	<.0002	.022	<.001	<.05	<.002	.053	.005	<.005
CC-27B(R)	3-05-87	<.005	.047	<.024	<.0002	.023	<.001	.09	<.002	<.006	<.004	<.005
CC-28A	3-05-87	<.005	.86	<.024	<.0002	.055	.002	.09	.005	.009	.082	<.005
CC-28B	3-05-87	<.005	1.5	<.024	<.0002	.031	<.001	.13	.005	.007	.026	<.005
CC-29B	2-10-87	<.005	.27	<.024	.0003	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC-30A	3-05-87	<.005	.072	<.024	<.0002	.043	<.001	<.05	<.002	<.006	.006	<.005
CC-30A(R)	3-05-87	<.005	.12	<.024	<.0002	.043	<.001	<.05	<.002	<.006	.005	<.005
CC-31A	2-19-87	<.005	.025	<.024	<.0002	.018	<.001	.13	<.002	<.006	.010	<.002
CC-37A	11-19-86	<.005	<.002	<.024	<.0002	<.008	<.001	<.05	<.002	.089	.008	.005
CC-38A	11-21-86	<.005	.10	<.024	<.0002	.008	<.001	.06	<.002	.013	.018	.002
CC-39A	11-19-86	<.005	.17	<.024	<.0002	.090	<.001	.05	<.002	.006	.012	<.002
CC-39B	11-19-86	<.005	.11	<.024	<.0002	.016	<.001	<.05	<.002	.006	.016	<.002
CC-40A	11-20-86	<.005	1.0	<.024	<.0002	.61	.004	.11	.003	.023	.080	.004
CC-41A	11-21-86	<.005	.091	<.024	<.0002	.014	<.001	.11	<.002	.016	.021	.003
CC-42A	11-20-86	<.005	.11	<.024	<.0002	.018	<.001	.07	<.002	.021	.034	<.002
CC-43A	11-21-86	<.005	.042	<.024	<.0002	<.008	<.001	.10	<.002	.020	.019	<.002
CC-44A	2-19-87	<.005	.008	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.007	<.002
Surficial aquifer:												
CC- 1A	3-03-87	.018	.17	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 1A(R)	3-03-87	.016	.11	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 5A	1-07-87	.007	.033	<.024	<.0002	.016	<.001	<.05	<.002	<.006	<.004	<.002
CC- 8A	2-04-87	<.005	.049	<.024	<.0002	.013	<.001	<.05	.003	<.006	<.004	<.002
CC- 9A	1-06-87	<.005	.13	<.024	<.0002	.029	.004	.11	<.002	<.006	.016	<.002
CC-10A	1-06-87	<.005	.032	<.024	<.0002	.010	<.001	.08	<.002	<.006	.005	<.002
CC-19A	1-07-87	<.005	.014	<.024	<.0002	<.008	<.001	.07	<.002	<.006	<.004	<.002
CC-20A	1-07-87	<.005	.030	<.024	<.0002	<.008	<.001	.11	<.002	<.006	.005	<.002
CC-20B	2-02-87	<.005	.27	<.024	<.0002	<.008	<.001	.24	<.002	.007	.008	.004
CC-22A	2-02-87	<.005	.092	<.024	<.0002	<.008	<.001	.06	<.002	.007	.005	.003
CC-23A	2-03-87	<.005	4.2	<.024	<.0002	<.008	<.001	.08	<.002	.015	<.004	<.002
CC-29A	1-13-87	<.005	.014	<.024	.0004	.029	<.001	<.05	<.002	.023	.026	<.002
CC-32A	12-17-86	<.005	.058	<.024	<.0002	.019	<.001	.06	<.002	.007	.013	<.002
CC-32B	12-17-86	<.005	.15	<.024	<.0002	.063	<.001	.12	<.002	.011	.013	<.002
CC-33A	12-17-86	<.005	.040	<.024	<.0002	<.008	<.001	.06	<.002	<.006	.007	<.002
CC-33B	12-17-86	<.005	.45	<.024	<.0002	.18	.004	.09	<.002	.014	.010	<.002
CC-34A	12-17-86	<.005	.046	<.024	<.0002	<.008	<.001	.22	<.002	.014	.010	<.002
CC-35A	12-17-86	--	--	--	--	--	--	--	--	--	--	--
CC-36A	2-19-87	<.005	.40	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
Lower confined aquifer:												
CC- 1D	3-03-87	<.005	.025	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	<.004	<.002
CC- 1E	4-03-87	<.005	.006	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.008	<.002
CC- 1F	3-27-87	<.005	.030	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.007	<.002
CC- 2B	3-24-87	<.005	.23	<.024	<.0002	.008	<.001	<.05	<.002	<.006	.010	<.002
CC- 2C	3-26-87	<.005	.054	<.024	<.0002	.008	<.001	<.05	<.002	<.006	.008	<.002
CC- 8E	4-01-87	<.005	.015	<.024	<.0002	<.008	<.001	<.05	.002	<.006	<.004	<.002
CC-16C	3-06-87	<.005	.015	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.006	<.005
CC-16D	3-27-87	<.005	.39	<.024	<.0002	<.008	<.001	<.05	<.002	<.006	.006	<.005
CC-17C	3-06-87	<.005	.021	<.024	.0046	.009	<.001	<.05	<.002	<.006	<.004	<.005
CC-26C	2-27-87	<.005	.040	<.024	<.0002	<.008	<.001	<.05	<.002	.010	.004	<.005

Major constituents include calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, total iron, and silica. Minor constituents, which are defined here as those inorganics that usually were present in concentrations of less than 5 mg/L, include manganese, fluoride, sulfide, total phosphorus, nitrogen species, boron, arsenic, and various trace metals. Cyanide and lead were below the detection limits of 0.01 and 0.05 mg/L, respectively, in all the samples.

The analyses of the replicate samples (table 2) generally showed slight differences in concentrations among each of the inorganic constituents, reflecting low analytical and sampling errors. The median difference between the concentration in a sample and its replicate was generally less than 5 percent for each of the major constituents. For the minor constituents, median errors between the replicate sample analyses ranged from 0 to 17 percent; the greatest difference was for zinc.

Six inorganic constituents and one indicator (dissolved solids) were found in concentrations that exceed the primary or secondary maximum contaminant levels, or MCL's, for drinking water established by the USEPA (1987a) under the Safe Drinking Water Act (table 3). Primary MCL's represent enforceable regulations for public water systems, whereas secondary MCL's are recommended limits for drinking water. The concentration limits for dissolved solids, chloride, iron, and manganese are secondary MCL's and are mainly to provide acceptable aesthetic and taste characteristics. However, the limits for mercury and chromium are primary MCL's for drinking water and represent levels above which there is a potential hazard to human health. For fluoride, both secondary (2.0 mg/L) and primary (4.0 mg/L) MCL's have been established (table 3). Elevated iron and manganese concentrations are the most extensive water-quality problems shown by the inorganic analyses (table 3).

Major Constituents

Distribution

Canal Creek aquifer

The ranges in concentrations of the major inorganic constituents in the Canal Creek aquifer are shown in table 4. Dissolved solids, chloride, and iron are present in concentrations above secondary MCL's for drinking water. Iron is most frequently detected in elevated concentrations (table 3).

The distribution of major ions is shown in plate 2 using Stiff diagrams. On the Stiff diagrams, cation concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) for a sample are plotted to the left of a zero vertical axis, and anion concentrations (HCO_3^-, SO_4^{2-}, Cl^-) are plotted to the right. Comparison of the size and shape of the plots reveals both the dominant ions in each well-water sample and the areal variations in the concentrations of these constituents throughout the aquifer.

Table 3.--Inorganic constituents with concentrations that exceed Federal drinking-water maximum contaminant levels

[All concentrations are for dissolved constituents in units of milligrams per liter; dashes indicate value is below the U.S. Environmental Protection Agency (1987a) standard for drinking water; MCL, maximum contaminant level; (R), replicate sample]

Well no.	Sampling date	Dissolved solids	Chloride (Cl$^-$)	Iron (Fe)	Manganese (Mn)	Fluoride (F$^-$)	Mercury (Hg)	Chromium (Cr)
Secondary MCL:		500	250	0.3	0.05	2.0	none	none
Primary MCL:		none	none	none	none	4.0	0.002	0.05
Canal Creek aquifer:								
CC- 1B	3-03-87	---	---	22	0.62	---	---	---
CC- 1C	3-03-87	---	---	14	.77	---	---	---
CC- 3A	4-08-87	---	---	.51	---	---	---	---
CC- 3B	4-07-87	---	---	3.5	---	---	---	---
CC- 4A	2-13-87	---	---	1.6	.14	---	---	---
CC- 4B	2-13-87	---	---	---	.089	---	---	---
CC- 5B	2-06-87	---	---	10	.16	---	---	---
CC- 5C	2-06-87	---	---	2.1	.22	---	---	---
CC- 6A	1-12-87	512	---	---	---	---	---	---
CC- 6B	1-12-87	---	---	1.0	2.4	---	---	---
CC- 7A	2-24-87	---	---	15	.37	---	---	---
CC- 7B	2-24-87	---	---	34	.86	---	---	---
CC- 8B	2-04-87	---	---	1.8	.17	---	---	---
CC- 8C	2-25-87	---	---	.64	.26	---	---	---
CC- 8D	2-25-87	---	---	11	.28	---	---	---
CC- 9B	4-08-87	---	---	2.4	.21	---	---	---
CC-11B	4-03-87	---	---	5.3	.13	---	---	---
CC-12A	1-09-87	---	---	.70	.069	---	---	---
CC-13A	3-04-87	910	530	---	.37	2.6	---	---
CC-13B	3-04-87	---	---	.63	---	---	---	---
CC-14A	3-04-87	---	---	---	.19	---	---	---
CC-15A	3-04-87	---	---	---	---	8.5	---	---
CC-16A	3-06-87	---	---	11	.76	---	---	---
CC-17A	3-06-87	---	---	---	.20	---	---	---
CC-17B	3-09-87	---	---	---	.23	---	---	---
CC-18A	2-11-87	1,300	1,000	---	.65	---	---	---
CC-18B	2-11-87	---	---	---	.080	---	---	---
CC-19B	2-10-87	---	---	5.7	.16	---	---	---
CC-20C	2-03-87	---	---	20	.16	---	---	---
CC-20D	2-10-87	---	---	9.1	.53	---	---	---
CC-22B	2-02-87	---	---	14	2.4	---	---	---
CC-22C	2-03-87	---	---	8.1	.78	---	---	---
CC-23B	2-10-87	---	---	30	.29	---	---	---
CC-25A	2-27-87	---	---	12	.059	---	---	---
CC-25B	2-27-87	---	---	17	.79	---	---	---
CC-26A	2-27-87	---	---	---	---	---	---	---
CC-26A(R)	2-27-87	---	---	---	---	---	---	---
CC-26B	2-27-87	---	---	---	.50	---	---	---
CC-27A	3-05-87	---	---	---	.48	---	---	---
CC-27B	3-05-87	---	---	6.0	1.4	4.2	---	.053
CC-28A	3-05-87	2,340	470	1.0	.87	7.1	---	---
CC-28B	3-05-87	1,140	---	1.0	1.1	---	---	---
CC-29B	2-10-87	---	---	.96	---	---	---	---
CC-30A	3-05-87	---	---	2.8	.18	---	---	---
CC-31A	2-19-87	---	---	---	.26	---	---	---
CC-37A	11-19-86	778	---	---	---	---	---	.089
CC-39A	11-19-86	---	---	---	.37	---	---	---
CC-40A	11-20-86	---	---	.81	.089	---	---	---
CC-41A	11-21-86	---	---	---	.30	---	---	---
CC-42A	11-20-86	---	---	---	.30	---	---	---
CC-43A	11-21-86	---	---	---	.16	---	---	---
Surficial aquifer:								
CC- 1A	3-03-87	---	---	12	.56	---	---	---
CC- 5A	1-07-87	---	---	45	1.3	---	---	---
CC- 8A	2-04-87	---	---	18	.43	---	---	---
CC- 9A	1-06-87	558	---	23	1.6	---	---	---
CC-10A	1-06-87	---	---	---	.11	---	---	---
CC-19A	1-07-87	---	---	3.0	.16	---	---	---
CC-23A	2-03-87	---	---	.80	.077	---	---	---
CC-29A	1-13-87	1,820	---	---	---	---	---	---
CC-32A	12-17-86	770	290	.34	.31	---	---	---
CC-32B	12-17-86	1,050	420	---	.42	---	---	---
CC-33A	12-17-86	---	---	3.0	.30	---	---	---
CC-33B	12-17-86	1,140	600	7.4	3.2	---	---	---
CC-34A	12-17-86	2,110	1,000	---	---	---	---	---
CC-36A	2-19-87	---	---	13	1.1	---	---	---
Lower confined aquifer:								
CC- 1D	3-03-87	---	---	7.9	.21	---	---	---
CC- 2B	3-24-87	---	---	1.1	---	---	---	---
CC- 8E	4-01-87	---	---	4.2	.10	---	---	---
CC-16D	3-27-87	---	---	.45	---	---	---	---
CC-17C	3-06-87	---	---	4.9	.080	---	.0046	---
CC-26C	2-27-87	---	---	4.4	.16	---	---	---

Table 4.--Major inorganic constituents detected in the Canal Creek aquifer

[Units are in milligrams per liter; replicate or repeat samples are not included]

Major constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Dissolved solids	58	164	45	2,340
Calcium (Ca^{2+})	58	15	2.1	63
Magnesium (Mg^{2+})	58	3.8	.04	27
Sodium (Na^{+})	58	18	4.2	730
Potassium (K^{+})	58	3.5	.91	250
Bicarbonate (HCO_3^-)	53	49	5	634
Sulfate (SO_4^{2-})	52	30	4.0	200
Chloride (Cl^-)	51	25	5	1,000
Iron (Fe, total)	57	.70	.01	34
Silica	57	5.3	.06	37

Although the major-ion composition and distribution in the Canal Creek aquifer were highly variable (pl. 2), some distinct patterns are evident. Eight well-water samples (2A, 3A, 4A, 4B, 6A, 12A, 12B, and 37A) had anomalously high concentrations of K^+ and HCO_3^-, ranging from 21 to 250 mg/L K^+ and 83 to 634 mg/L HCO_3^-. Sample 37A had the maximum concentrations of K^+ and HCO_3^- detected in the Canal Creek aquifer (table 4). With the exception of the eight wells, K^+ usually is the major cation with the lowest concentrations in the Canal Creek aquifer, as shown by its low median concentration (table 4). These eight samples also were characterized by elevated pH values, indicating that contamination by grout may be a problem. The median pH was 9.68 for the eight wells and only 6.00 for all other samples collected in the Canal Creek aquifer.

The major-ion compositions showed a distinctive sodium chloride type of water for four samples--28A, 28B, 13A, and 18A (pl. 2). The Na^+ and Cl^- concentrations in these ground-water samples, which varied from 280 to 730 mg/L and from 240 to 1,000 mg/L, respectively, were much higher than the median concentrations (table 4). The chloride concentrations in samples 13A, 18A, and 28A exceed the secondary MCL for drinking water (table 3).

The water samples that contained the highest total concentrations of major ions were from wells located between the West and East Branches of Canal Creek, where most manufacturing plants were operated. This areal distribution is shown by the generally larger size of the Stiff patterns (pl. 2) and by the high dissolved-solids concentrations (table 2) for many of the sites between the creek branches. For example, ground water from wells 13A, 18A, 28A, and 28B had dissolved-solids concentrations ranging from 910 to 2,340 mg/L which exceed the secondary standard for drinking water (table 3). In contrast, water from the farthermost downgradient well, 11B, had one of the lowest dissolved-solids concentrations (52 mg/L) observed in the Canal Creek aquifer. Sample 6A, which is from a well located east of the East Branch Canal Creek, did exceed the secondary MCL for dissolved-solids concentration (table 3); however, this sample is suspect because of its anomalous pH.

Vertical distribution of major ions also was highly variable (pl. 2). At some sites where two or more wells are screened in the Canal Creek aquifer, the inorganic constituents in the ground water differed dramatically with depth. Sites 8 and 18 provide examples. At site 8, the dominant major ions varied with increasing depth from sodium and chloride (well 8B), to calcium and sulfate (well 8C), and finally to a more mixed composition of calcium, sodium, bicarbonate, and chloride (well 8D). At site 18, the water changed from a sodium chloride type (well 18A) with a dissolved-solids concentration of 1,300 mg/L to a calcium bicarbonate type (well 18B) with dissolved-solids concentration of only 75 mg/L (pl. 2 and table 2).

This large vertical variation in the major inorganic constituents was found mainly at sites where organic contaminants were present and where thin clay lenses were present in the Canal Creek aquifer. In other ground-water studies, large changes have been recorded between samples vertically separated by as little as 3 cm (Ronen and others, 1987; Smith, R. L., and others, 1987). Chemical and microbial reactions within the contaminant plume are believed to cause these variations. Clay lenses could also cause layering of the contaminants in a plume by altering local ground-water-flow directions and velocities within the aquifer. In addition, overlapping of contaminant plumes from different sources could cause variations in the inorganic and organic composition of the water.

Surficial aquifer

The ranges in concentrations of major inorganic constituents observed in the surficial aquifer are shown in table 5, and their distribution is shown using Stiff diagrams in figures 6a and 6b. Relations between the different ground-water samples are difficult to infer because the surficial-aquifer sediments generally are not hydrologically connected. Although the five wells at Beach Point are installed in one isolated system (fig. 6b), well 33B is screened at a greater depth than the others (table 1).

Samples from six wells (1A, 20A, 22A, 23A, 29A, 36A) showed calcium bicarbonate compositions (fig. 6a). In all these well-water samples, Ca^{2+} was present in higher concentrations than Mg^{2+}, ranging from 16 to 200 mg/L Ca^{2+} compared to 0.07 to 21 mg/L Mg^{2+}. Ground water from well 29A had the maximum concentrations of Ca^{2+} and HCO_3^- observed in the surficial aquifer (table 5), and the dissolved-solids concentration exceeds the secondary MCL for drinking water (table 3).

Table 5.--Major inorganic constituents detected in the surficial aquifer

[Units are in milligrams per liter; replicate samples are not included]

Major constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Dissolved solids	17	286	117	2,110
Calcium (Ca^{2+})	17	28	4.4	200
Magnesium (Mg^{2+})	17	11	.07	49
Sodium (Na^{+})	17	29	3.2	600
Potassium (K^{+})	17	4.0	1.6	60
Bicarbonate (HCO_3^-)	15	94	7	2,450
Sulfate (SO_4^{2-})	16	59	7.0	190
Chloride (Cl^-)	16	26	5	1,000
Iron (Fe, total)	16	1.9	.03	45
Silica	17	3.9	.37	21

Four wells at Beach Point contained ground water with distinctive sodium chloride compositions (fig. 6b). Concentrations ranged from 190 to 600 mg/L Na^+ and from 290 to 1,000 mg/L Cl^-. These four samples had concentrations above the secondary MCL's for chloride and dissolved solids (table 3). Sodium was the dominant cation for the samples from wells 5A, 8A, 9A, and 33A, but the dominant anion varied in these four wells. The remaining samples from the surficial aquifer showed mixed ion compositions.

The median iron concentration for the surficial-aquifer samples (table 5) was more than six times the concentration of the 0.3-mg/L secondary MCL (table 3). Of the 17 samples collected from the surficial aquifer, 10 samples had iron concentrations that exceed the secondary MCL for drinking water (table 3).

Lower confined aquifer

Table 6 summarizes the ranges in concentrations for all major inorganic constituents detected in the lower confined aquifer. Chloride concentrations were relatively constant among the 10 wells screened in this aquifer and were generally lower than the concentrations observed in the Canal Creek aquifer or surficial aquifer (tables 4 and 5). In eight samples from the lower confined aquifer, chloride concentrations were below the detection limit of 5 mg/L (table 6). In addition, the median dissolved-solids concentration in this aquifer (110 mg/L) was lower than the median of the samples in the Canal Creek aquifer (164 mg/L) and the surficial aquifer (286 mg/L).

Table 6.--Major inorganic constituents detected in the lower confined aquifer

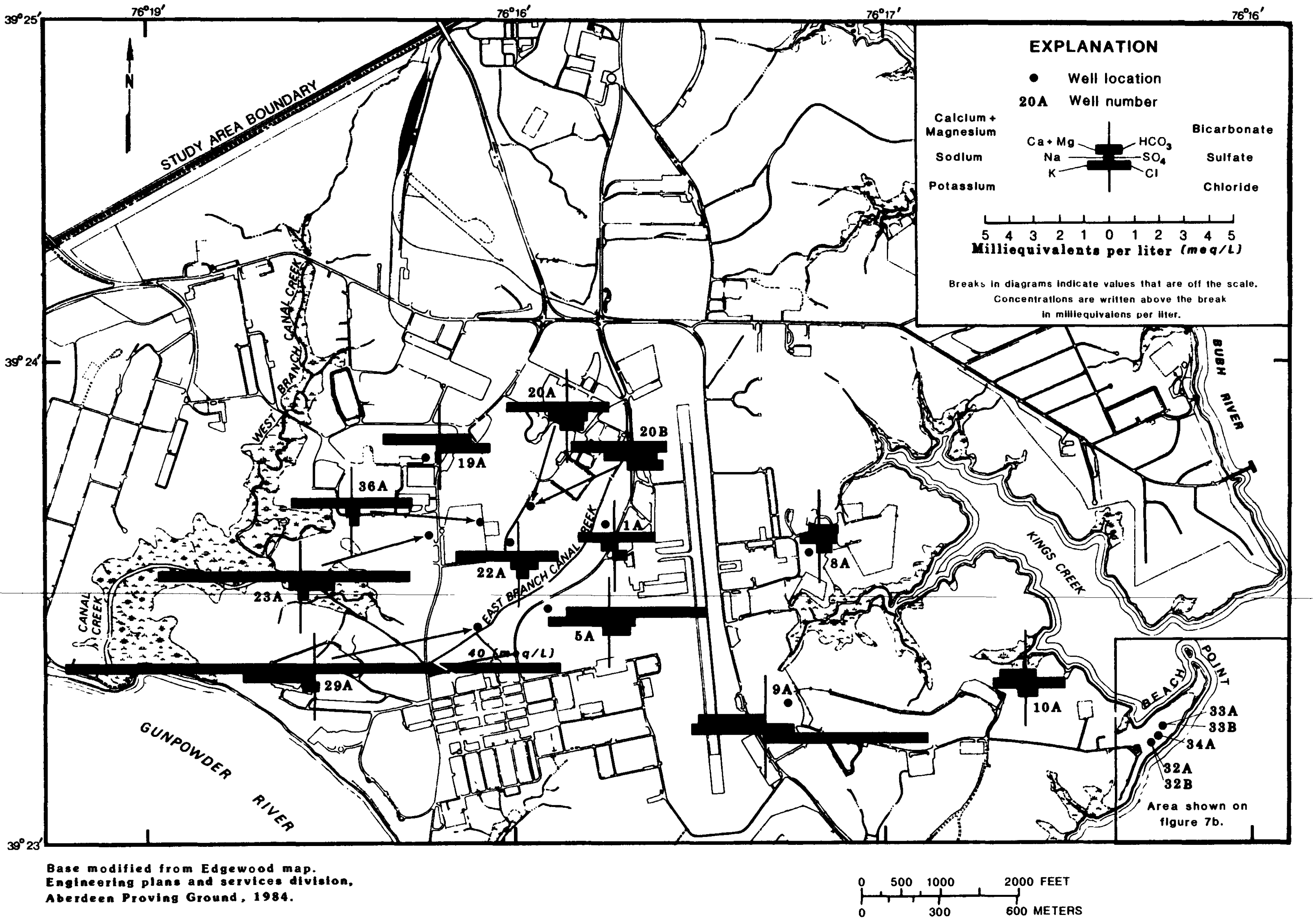
[Units are in milligrams per liter; dashes indicate that value is not known]

Major constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Dissolved solids	10	110	37	320
Calcium (Ca^{2+})	10	16	1.4	54
Magnesium (Mg^{2+})	10	.55	.06	1.8
Sodium (Na^+)	10	5.5	2.9	27
Potassium (K^+)	10	6.1	.74	96
Bicarbonate (HCO_3^-)	10	71	13	297
Sulfate (SO_4^{2-})	10	7.2	4.0	36
Chloride (Cl^-)	2	--	5	11
Iron (Fe, total)	10	.78	.03	7.9
Silica	10	4.3	.31	14

In the lower confined aquifer, iron was the only major inorganic constituent that was found in concentrations exceeding the MCL's for drinking water (table 3). Six samples contained elevated iron concentrations, ranging from 0.45 to 7.9 mg/L (table 3).

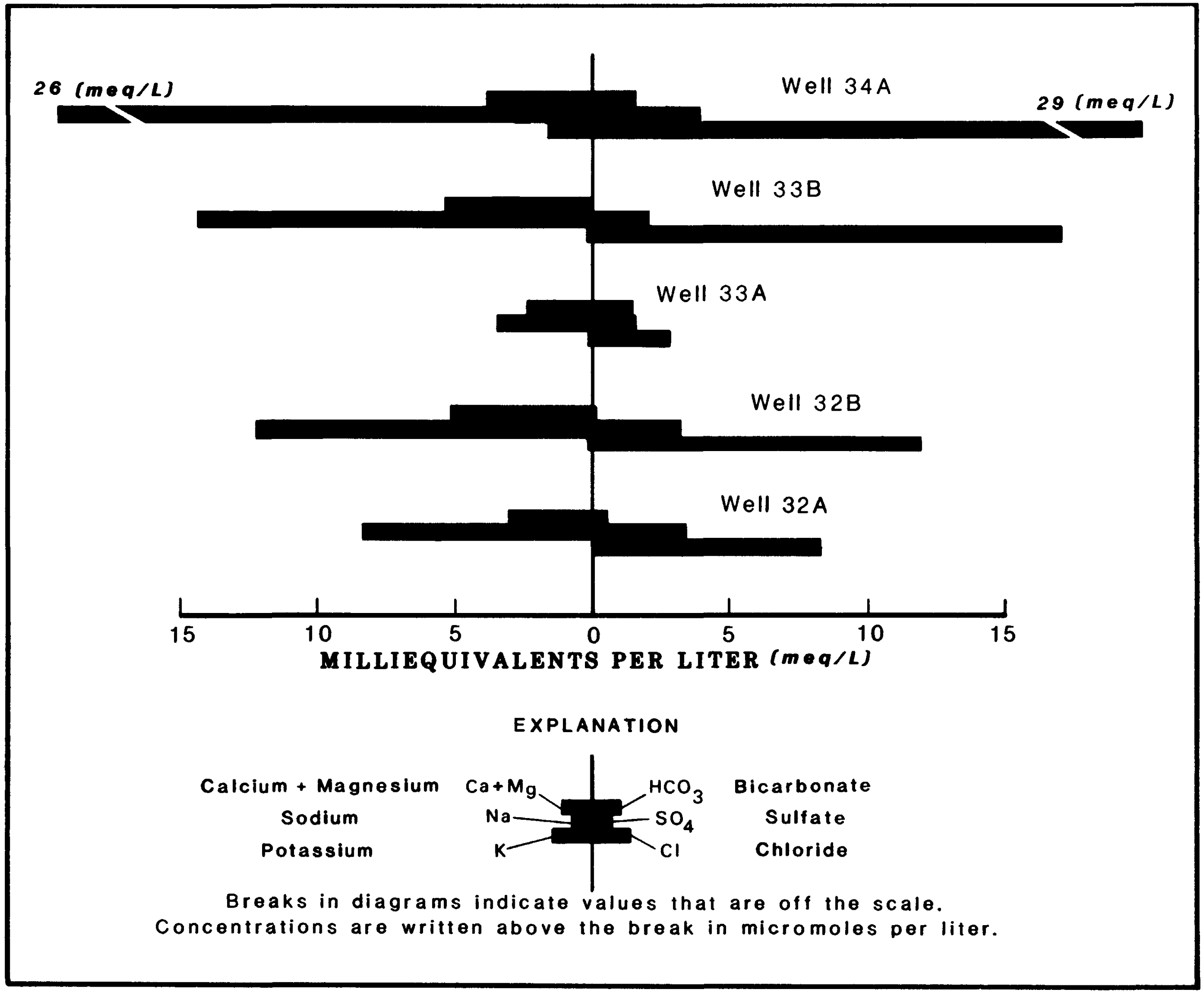
Stiff diagrams also are used to present the distribution of major ions in the lower confined aquifer (fig. 7). For 5 of the 10 ground-water samples (1F, 2B, 2C, 16C, and 16D), Ca^{2+} and HCO_3^- were the dominant major ions. The sample from well 1E showed a potassium bicarbonate composition and had the maximum concentrations of these constituents detected in the lower confined aquifer (table 6). Well water from 1E and four other wells (1F, 2C, 16C, 16D) had very high pH values that ranged from 10.65 to 12.28. These five samples with elevated pH also had elevated dissolved-solids and HCO_3^- concentrations compared to the other samples from the lower confined aquifer (table 2).

Three samples, 1D, 8E, and 17C, did not contain a distinctive suite of major ions but instead were of mixed compositions (fig. 7). Concentrations of K^+, HCO_3^-, and dissolved solids are less than the median concentrations observed for the lower confined aquifer. In addition, the low pH's of the three samples indicate that these well-water samples were not affected by reactions with the grout.



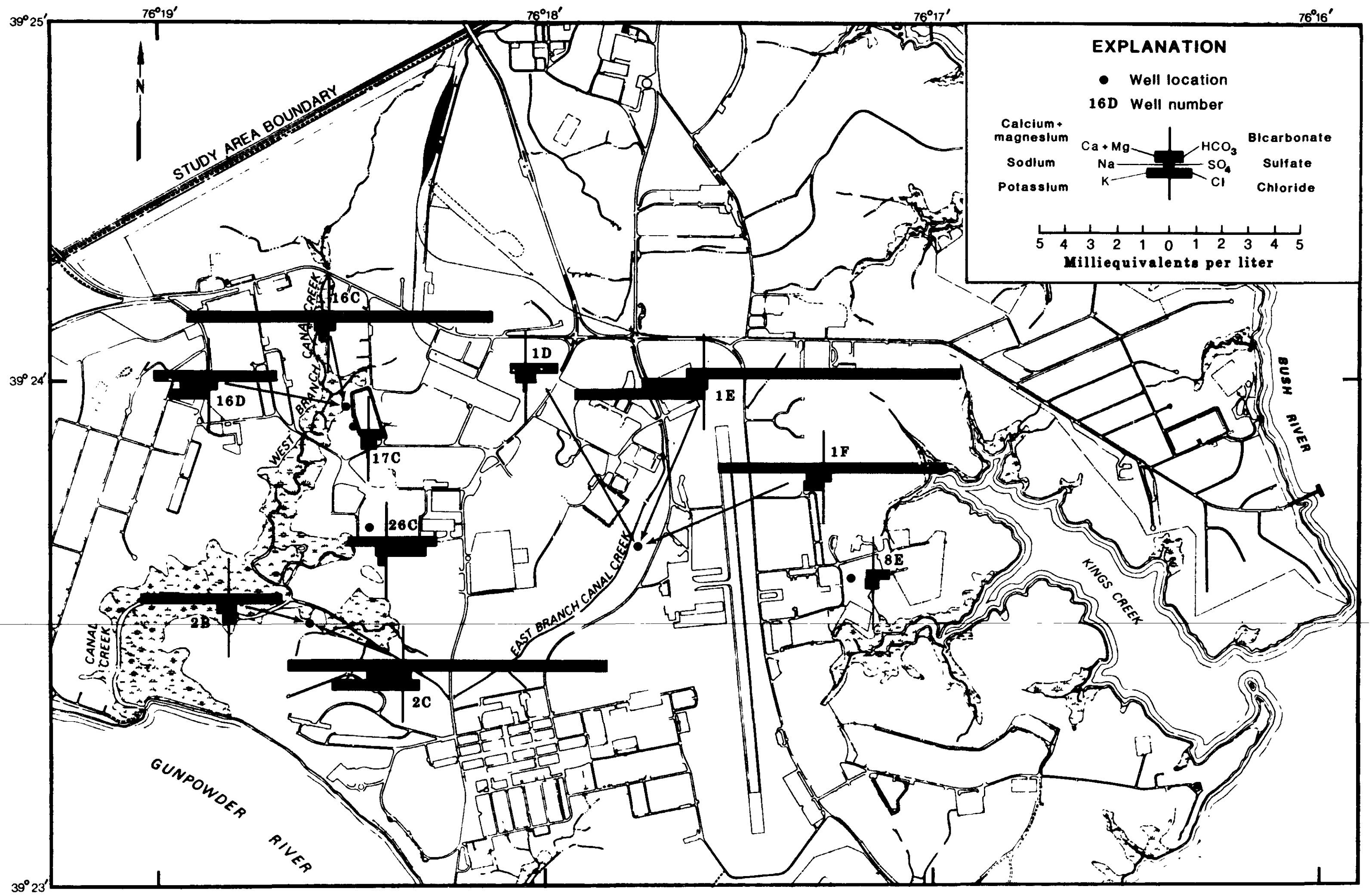
Base modified from Edgewood map. Engineering plans and services division, Aberdeen Proving Ground, 1984.

Figure 6a. -- Map with Stiff diagrams showing distribution of major ions in the surficial aquifer.



Breaks in diagrams indicate values that are off the scale.
Concentrations are written above the break in micromoles per liter.

Figure 6b. -- Stiff diagrams showing distribution of major ions in the surficial aquifer at Beach Point.



Base modified from Edgewood map.
Engineering plaes and services division,
Aberdeen Proving Ground, 1984.

Figure 7. -- Map with Stiff diagrams showing distribution of major ions in the lower confined aquifer.

Probable Sources

Well grout

The samples that contained elevated pH's are believed to have been affected by reactions with the cement used to create a seal above the screen in the monitoring wells. Contact between the ground water and the grout can occur if the well is not constructed properly and is known to yield samples with anomalously high pH (Walker, 1983; Williams and Evans, 1987). Elevated K^+ and HCO_3^- concentrations were often associated with the high pH's observed in ground water in the Canal Creek area.

Cement is a highly alkaline material that is composed mainly of calcium oxide and silicon dioxide. Magnesium, potassium, sodium, and sulfur oxides also are present in smaller amounts (Neville, 1981; Williams and Evans, 1987). Bentonite, which was added to the cement, consists predominantly of the clay mineral montmorillonite but can contain other clay minerals in amounts as high as 50 percent (Hurlbut and Klein, 1977, p. 403; Williams and Evans, 1987). Sodium, calcium, and potassium can be present on the cation-exchange sites of the clay minerals.

To test the effect of grout on water chemistry, samples were collected from well 41A--an uncontaminated well where water has a relatively low pH of 5.97--and mixed with the Portland Type V cement and bentonite used in well construction. The excess water from the hardening cement slurry was filtered and analyzed for Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, and Cl^-. The cement-slurry sample was collected about 1 hour after mixing. The cement-slurry water showed extremely high concentrations of K^+ (1,500 mg/L) and HCO_3^- (2,140 mg/L). Concentrations in the well water before mixing with the cement were only 3.1 mg/L K^+ and 59 mg/L HCO_3^-. In addition, the pH rose from 5.97 in the untreated well water to 12.64 when cement was added.

The wells suspected of reacting with the grout are similar in chemical composition to the cement-slurry water, as shown in the Piper diagram of figure 8. However, some differences in inorganic composition are seen between the cement-slurry water (41G) and the well-water samples suspected of reactions with the grout. The cement-slurry water contained higher concentrations of calcium and sulfate than the potentially grout-affected samples and a relatively lower percentage of potassium and bicarbonate (fig. 8).

The cement-slurry data were input into the geochemical model WATEQF (Plummer and others, 1976), and the results showed that sample 41G was supersaturated with respect to calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and two magnesium carbonates, artinite ($Mg_2(OH)_2CO_3 \cdot 3H_2O$), and huntite ($CaMg_3(CO_3)_4$). With time, precipitation of these minerals would decrease the calcium, magnesium, and sulfate concentrations in the grout-affected wells, explaining the difference in composition between the cement-slurry sample and these wells. Because a chemical sink for potassium does not exist, potassium concentrations would increase relative to the other major cations in the grout-affected wells. The concentration of magnesium in the ground water from well 41A did decrease when it was mixed with the cement; the initial water from well 41A contained a magnesium concentration of 5.2 mg/L, whereas the cement-slurry water contained a concentration of 0.34 mg/L.

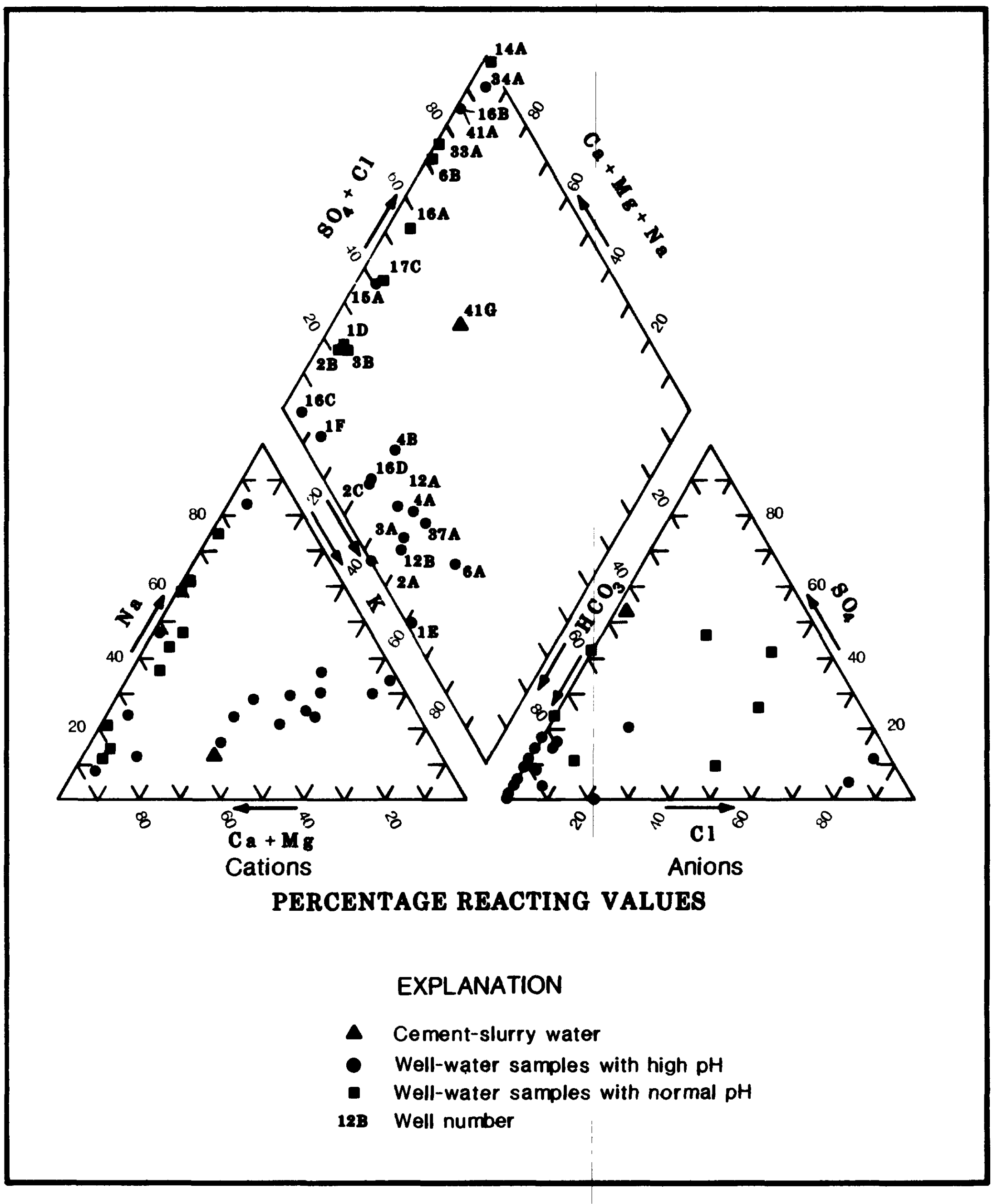


Figure 8.-- Piper diagram showing comparison of major-ion composition of water in wells believed to be affected by grout and wells not affected by grout.

Seven well-water samples showed anomalously high pH but did not have elevated K^+ concentrations. These samples include water from wells 1F, 2C, 15A, 16B, 16C, 16D, and 34A. Although samples from wells 2C and 16D did have high enough concentrations of K^+ to plot in the same composition range as the other grout-affected samples on the Piper diagram (fig. 8), samples 1F, 15A, 16B, 16C, and 34A showed a much lower percentage of K^+. Possibly, mineral precipitation has not been as extensive in these wells as in those enriched in K^+. Another possibility is that grout effects are diminished by a second source of major ions, such as from contamination.

Dissolved solids, chloride, and sodium

The concentrations of dissolved solids exceeded the secondary drinking-water MCL of 500 mg/L in 11 well-water samples, including samples from 5 wells in the Canal Creek aquifer and from 6 wells in the surficial aquifer (table 3). These elevated concentrations of dissolved solids could be caused by (1) intrusion of natural brackish-water into the aquifer, (2) high concentrations of inorganic compounds associated with contaminants discharged or dumped in the study area, or (3) reactions between the ground water and the grout used in well construction. Elevated chloride concentrations were associated with elevated dissolved-solids concentrations in seven well-water samples (table 3). High sodium concentrations also were associated with elevated chloride and dissolved-solids concentrations.

Chloride and sodium have numerous anthropogenic sources in the Canal Creek area. Both Cl^- and Na^+ were present in wastes generated by many manufacturing processes, including the production of chlorine, mustard, impregnite (CC2), and the arsenicals made in the experimental-plants area (pl. 1). Chlorine manufacturing could be a large source of Cl^- and Na^+ because rock salt was used as a raw material and both solid and liquid wastes contained these ions.

In addition, decontamination activities could have introduced a source of Na^+ and Cl^-. Caustic, or sodium hydroxide (NaOH), was one of the most commonly used decontaminants and is highly soluble in water. Chlorinated lime, or bleach ($CaCl(OCl) \cdot 4H_2O$), and calcium hypochlorite ($Ca(OCl)_2$) are decontaminating agents that would yield chloride (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). However, the environmental effect of these inorganic chlorinating agents is thought to be localized and short term. Chloride also could be released into the ground water during the breakdown of chlorinated organic contaminants, such as mustard and chlorinated organic solvents.

Analyses from the Canal Creek aquifer at wells 6A and 37A show anomalously high pH values and high HCO_3^- and K^+ concentrations, indicating that reactions with grout are a problem in these wells (fig. 8). For wells 13A and 18A, the high Na^+ and Cl^- concentrations mainly contribute to the elevated dissolved-solids concentrations. The low pH (4.48 to 4.51) and alkalinity (less than 1 mg/L) eliminate grout reactions as a problem, whereas the location of the wells (fig. 2) and directions of ground-water flow (fig. 4) eliminate the possibility of brackish-water intrusion. Therefore, it is most likely that the inorganic constituents are associated with discharge of contaminants in the study area. High concentrations of volatile organic compounds also were detected in samples 13A and 18A.

Samples from wells 28A and 28B also contained organic compounds, and the elevated concentrations of dissolved solids, Na^+, and Cl^- could again be associated with contamination. Chlorine was manufactured near site 28. Rock salt was stored in tanks near the WW2 chlorine plant, which was operated until 1968 (pl. 1). Waste disposal was through sewerlines to the West Branch Canal Creek. Brine sludge was piped first to settling and disposal tanks before being discharged to the sewer (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). These storage, settling, and disposal tanks once surrounded the area of site 28.

Brackish-water intrusion from the tidal Canal Creek also is a possibility at site 28, which is located in a marshy area of the West Branch Canal Creek (fig. 2). However, if the ground water at site 28 is affected by infiltration of brackish water, the ground water at nearby site 27 would be expected to show similar elevated concentrations of Na^+ and Cl^-. The concentrations in samples 27A and 27B were considerably lower than those from site 28 (pl. 2).

Samples from six wells screened in the surficial aquifer had concentrations of dissolved solids exceeding the secondary MCL (table 3). The elevated dissolved-solids concentration in well 9A is caused mainly by high Cl^- and Na^+ concentrations. This shallow well is screened from 8 to 13 ft below land surface and is located near the intersection of several roads. Salt used for road deicing could be a source of the dissolved solids, as the well was sampled during the winter on January 6, 1987, four days after a snowstorm.

Water from well 29A, which also exceeded the secondary MCL for dissolved solids (table 3), had extremely high HCO_3^- and Ca^{2+} concentrations. The major-ion composition does not indicate that either reactions with grout or intrusion of brackish water occurred. Most likely, the high dissolved-solids concentration is derived from the fill material in which the well is screened along the East Branch Canal Creek. The well water was analyzed for surfactants as a possible source, but concentrations were less than the detection limit of 10 μg/L.

The four other wells in the surficial-aquifer system from which concentrations exceed the dissolved-solids secondary MCL (table 3) are located on Beach Point, a narrow peninsula bordered by Kings Creek and Bush River. The major-ion compositions showed a distinctive sodium chloride type for these samples (fig. 6b). The water samples, especially from well 33B, also were contaminated with volatile organic compounds. Thus, both brackish-water intrusion and contamination could be sources of the elevated concentrations of inorganic constituents. In addition, the sample from well 34A had a higher pH and K^+ concentration than samples from the other wells on Beach Point, showing that reaction with the grout may be a problem in this well.

Because chloride and sodium were common wastes discharged during past operations in the Canal Creek area, the low chloride and dissolved-solids concentrations observed in the lower confined aquifer (table 6) indicate that the ground water was not affected by inorganic wastes. Water samples from the lower confined aquifer that showed the highest concentrations of dissolved solids were also samples that were suspected of reacting with the grout. Chloride concentrations, which would not be affected by grout, were low in all the samples. In addition, the distribution of chloride in the Canal Creek aquifer showed the highest concentrations in the area between the West and East Branches Canal Creek (pl. 2). Most of the manufacturing and waste-disposal activities occurred in this area. In contrast, the farthermost downgradient samples from the Canal Creek aquifer (3A, 3B, 11B, 12A, 12B) had chloride concentrations of less than 6 mg/L (table 2).

Iron

Of the 85 samples from the Canal Creek area, ground water from 48 wells had concentrations that exceed the secondary MCL for iron (table 3). Most of the 48 wells are screened in sediments of the Potomac Group, and ground water from the Potomac Group generally is higher in iron than is water in most other aquifers of the Maryland Coastal Plain (Otton and Mandle, 1984, p. 29). The abundant iron-bearing minerals in the sediments, such as hematite, limonite, and siderite, are a major natural source of iron. Iron-oxide coatings are widespread in the Potomac sands, producing mottled or variegated hues of maroon, yellow, purple, and brown (Glaser, 1969, p. 7). The amount of iron that will go into solution is highly variable, depending on the oxidation potential and pH of the water (Hem, 1985, p. 77). Otton and Mandle (1984, p. 29) found a median iron concentration of 7.2 mg/L and a maximum of 73 mg/L in 23 ground-water analyses from the Potomac Group in the upper Chesapeake Bay area. The median iron concentration for ground water in the Canal Creek area was lower, ranging from 0.70 mg/L in the Canal Creek aquifer to 1.9 mg/L in the surficial aquifer, and a maximum iron concentration of 45 mg/L was detected (tables 4 to 6).

Minor Constituents

Distribution

Canal Creek aquifer

Of the minor constituents detected in the Canal Creek aquifer (table 7), only fluoride, sulfide, the nitrogen species, manganese, zinc, and boron reached concentrations greater than 1.0 mg/L. Fluoride is the only minor constituent that was detectable in all 58 samples collected from the Canal Creek aquifer. Organic nitrogen, which is a reduced form of nitrogen, was the most common nitrogen species detected. Organic-nitrogen concentrations were obtained by subtracting the ammonia concentration from the ammonia + organic nitrogen concentration in table 2. Phosphorus, arsenic, antimony, mercury, nickel, beryllium, cadmium, chromium, copper, and selenium were present in concentrations usually lower than 0.1 mg/L and commonly less than detection limits (table 7).

Manganese, fluoride, and chromium were found in elevated concentrations in the Canal Creek aquifer (table 3). Manganese was detected in concentrations above the secondary MCL for drinking water more frequently than the other minor inorganic constituents (table 3). The median manganese concentration in the Canal Creek aquifer (table 7) was above the secondary MCL of

Table 7.--Minor inorganic constituents detected in the Canal Creek aquifer

[Units are in milligrams per liter; replicate or repeat samples are not included; dashes indicate that value is not known]

Minor constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Fluoride (F^-)	58	0.54	0.13	8.5
Sulfide (S^{2-})	9	1.6	1.2	4.4
Phosphorus (P)	55	.02	.01	.12
Ammonia (NH_3) (as N)	22	.32	.12	1.2
Organic nitrogen (as N)	41	.51	.10	1.2
Nitrite (NO_2^-) (as N)	28	.02	.01	.48
Nitrate (NO_3^-) (as N)	52	.17	.03	2.5
Manganese (Mn)	54	.18	.003	2.4
Arsenic (As)	6	.011	.006	.039
Zinc (Zn)	56	.063	.004	1.5
Antimony (Sb)	1	--	--	.074
Mercury (Hg)	13	.0004	.0003	.0014
Nickel (Ni)	24	.025	.008	.61
Beryllium (Be)	4	.004	.002	.019
Boron (B)	22	.09	.05	1.2
Cadmium (Cd)	5	.003	.002	.005
Chromium (Cr)	21	.009	.006	.089
Copper (Cu)	34	.010	.004	.088
Selenium (Se)	4	.004	.002	.005

0.05 mg/L. Fluoride concentration (table 3) was above the secondary MCL for drinking water in one well (13A) and above the primary MCL in three wells (15A, 27B, 28A). Chromium was detected in elevated concentrations in two well-water samples (27B, 37A).

The maximum boron concentration in the Canal Creek aquifer was found in water from well 26A (1.2 mg/L) and was more than an order of magnitude higher than the median concentration (table 7). The anomalous boron concentration in sample 26A was confirmed by analysis of a replicate sample (1.5 mg/L for

26A(R) in table 2). Although the USEPA has not set a secondary MCL for boron concentrations in drinking water, boron is known to be toxic to some plants in concentrations as low as 1.0 mg/L (Hem, 1985, p. 129). Building 58, north of site 26 (pl. 1), is presently leased by a chemical company that manufactures zinc borates for fire retardants and uses both borax and boric acid (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Surficial aquifer

Fluoride, organic nitrogen, and zinc were found in samples from all 17 wells screened in the surficial aquifer (table 8). Phosphorus, nitrate, nitrite, manganese, boron, and copper were present in more than 60 percent of the samples. Concentrations of chromium, nickel, ammonia, arsenic, beryllium, selenium, mercury, cadmium, and sulfide were less than the detection limits in more than half of the samples. Sample 29A, which is from a well screened at the water table and located near horse pastures along the East Branch Canal Creek (fig. 2), showed the maximum concentrations of the nitrogen species. Antimony was not detected in any of the wells screened in the surficial aquifer.

Twelve of the seventeen samples from the surficial aquifer contained manganese concentrations above the secondary MCL for drinking water (table 3). All other minor constituents detected were below the primary and secondary MCL's established for drinking water.

Lower confined aquifer

Fluoride, nitrogen species, phosphorus, manganese, zinc, and copper were common minor inorganic constituents in the lower confined aquifer (table 9) as they were in the Canal Creek aquifer and the surficial aquifer. However, one or more of the constituents sulfide, mercury, nickel, cadmium, and chromium were present in only 3 or fewer of the 10 samples collected from the lower confined aquifer. Nickel, cadmium, and chromium concentrations were equal to or slightly higher than the detection limits for these constituents (table 2). Arsenic, antimony, beryllium, boron, and selenium were not detected in any of the samples. In general, the lower confined aquifer was found to have lower concentrations of the minor inorganic constituents than those found in the Canal Creek and surficial aquifers (tables 7 to 9).

Manganese and mercury were detected in elevated concentrations in samples from the lower confined aquifer (table 3). The median manganese concentration of 0.018 mg/L was lower than the median concentrations found in the other two aquifers (0.18 and 0.31 mg/L). However, manganese concentrations in the lower confined aquifer did exceed the secondary MCL for drinking water (0.05 mg/L) in four of the samples (table 3). The mercury concentration detected in sample 17C, 0.0046 mg/L is more than twice the primary MCL allowed in drinking water. Mercury did not exceed the limit in any other samples collected in the Canal Creek area.

Probable Sources

Probable sources for the minor constituents that were found in concentrations exceeding the drinking-water limits will be discussed. These include manganese, fluoride, mercury, and chromium (table 3).

Table 8.--Minor inorganic constituents detected in the surficial aquifer

[Units are in milligrams per liter; replicate samples are not included; dashes indicate that value is not known]

Minor constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Fluoride (F^-)	17	0.24	0.15	1.4
Sulfide (S^{2-})	2	--	1.6	2.4
Phosphorus (P)	16	.02	.01	.17
Ammonia (NH_3) (as N)	7	.45	.42	5.5
Organic nitrogen (as N)	17	.53	.01	1.9
Nitrite (NO_2^-) (as N)	11	.02	.01	.32
Nitrate (NO_3^-) (as N)	15	.15	.01	3.9
Manganese (Mn)	15	.31	.006	3.2
Arsenic (As)	2	--	.007	.018
Zinc (Zn)	17	.058	.014	4.2
Antimony (Sb)	0	--	--	--
Mercury (Hg)	1	--	--	.0004
Nickel (Ni)	8	.024	.010	.18
Beryllium (Be)	2	--	.004	.004
Boron (B)	12	.08	.06	.24
Cadmium (Cd)	1	--	--	.003
Chromium (Cr)	8	.012	.007	.023
Copper (Cu)	11	.010	.005	.026
Selenium (Se)	2	--	.003	.004

Manganese

Manganese concentrations are above the secondary MCL of 0.05 mg/L in samples from 58 wells in the Canal Creek area (table 3). Ground water containing greater than 0.05 mg/L manganese is fairly common in Harford County (Nutter, 1977, p. 31). Manganese probably is derived from a natural source. Although manganese is not an essential constituent of any of the more common silicate rock minerals, it can substitute for iron, magnesium, or calcium in silicate structures. Manganese is similar to iron in that both metals commonly are present as oxide coatings on sediments and can go into solution with changing pH and redox conditions in the ground water (Hem, 1985, p. 85).

Table 9.--Minor inorganic constituents detected in the lower confined aquifer

[Units are in milligrams per liter; dashes indicate that value is not known]

Minor constituent	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected
Fluoride (F^-)	10	0.33	0.15	1.3
Sulfide (S^{2-})	1	--	--	1.2
Phosphorus (P)	10	.02	.01	.06
Ammonia (NH_3) (as N)	5	.20	.24	.40
Organic nitrogen (as N)	6	.16	.01	.53
Nitrite (NO_2^-) (as N)	7	.02	.01	.05
Nitrate (NO_3^-) (as N)	5	.07	.04	.18
Manganese (Mn)	9	.018	.004	.21
Arsenic (As)	0	--	--	--
Zinc (Zn)	10	.028	.006	.39
Antimony (Sb)	0	--	--	--
Mercury (Hg)	1	--	--	.0046
Nickel (Ni)	3	.008	.008	.009
Beryllium (Be)	0	--	--	--
Boron (B)	0	--	--	--
Cadmium (Cd)	1	--	--	.002
Chromium (Cr)	1	--	--	.010
Copper (Cu)	7	.007	.004	.010
Selenium (Se)	0	--	--	--

Fluoride

Four ground-water samples, all of which were collected from the Canal Creek aquifer, had fluoride concentrations greater than the MCL's for drinking water (table 3). The elevated concentrations (2.6 to 8.5 mg/L) were found in wells located along the West Branch Canal Creek, including 13A, 15A, 27B, and 28A (fig. 2).

One possible natural source of fluoride is dissolution of mineral particles that contain fluoride and are widespread in resistate sediments (Hem, 1985, p. 121). Minerals that contain fluoride include fluorite, apatite, some micas, and amphiboles such as hornblende. However, it does not seem likely that a natural source in the sediments would produce such a localized effect in concentrations of fluoride in ground water.

One possible anthropogenic source of fluoride is from production of methyldifluoroarsine (CH_3AsF_2), which is abbreviated MF, M_5, or MD-2 (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). MF was produced and tested as an experimental chemical agent between 1927 and 1928. Waste products must have contained fluorinated compounds because hydrofluoric acid and sodium fluoride were used in the process. A relatively small amount of waste, however, would have been generated because only about 500 lb (pounds) of MF was produced. The exact location of the production plant is unknown, but it probably was in one of the buildings in the experimental-plants area near the West Branch Canal Creek (pl. 1).

Two nerve agents, Sarin (GB) and Soman (GD), also contain fluoride and may be a more probable source for the ground-water contamination. A hydrolysis product of these nerve agents is hydrofluoric acid. The pilot plant north of site 27 was used to manufacture nerve agents since WW2 (pl. 1). When the agent GB was manufactured during 1951-57, hydrofluoric acid was used in the process. Wastes were discharged through the sewer to the nearby West Branch Canal Creek.

The most likely source of the elevated fluoride concentrations in samples from wells 27B and 28A is the use of rock salt in chlorine manufacturing at the WW2 plant (pl. 1). Fluoride was a common impurity in the rock salt (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986), which was stored in tanks near site 28. Brine made from the rock salt was treated with soda ash to precipitate impurities. Sludge from the brine-treatment process was piped first to settling and disposal tanks before being discharged to the sewer. The tanks and sewer discharge point were located in the vicinity of sites 27 and 28. The ground water at these sites also contained elevated sodium and chloride concentrations that probably were derived from the rock salt and brine.

Mercury

The mercury concentration in water from well 17C, which is screened in the lower confined aquifer, exceeds the primary MCL of 0.002 mg/L (table 3). Although detectable mercury concentrations were present in several other samples, none are above the MCL. No other inorganic constituents which could present a health hazard in drinking-water supplies were detected in the lower confined aquifer.

Downward infiltration of contaminants from the Canal Creek aquifer is highly unlikely. The screened interval of well 17C is from 98 to 103 ft below land surface, and approximately 36 ft of clay overlie this deep aquifer. In addition, hydraulic heads are higher in the lower confined aquifer than in the Canal Creek aquifer so that ground water would not flow downward from the Canal Creek aquifer under current conditions (J. P. Oliveros and D. A. Vroblesky, U.S. Geological Survey, written commun., 1988).

Possibly, the water from well 17C was contaminated with mercury during sampling or during transport of the bottles to the laboratory. Mercury is a volatile compound that can be easily lost from solution and migrate through polyethylene sample bottles (Avotins and Jenne, 1975; Bothner and Robertson, 1975; Matsunaga and others, 1979). Water from wells 17A and 17B, which are in the same cluster as well 17C but screened in the Canal Creek aquifer, had mercury concentrations of 0.0015 and 0.0014 mg/L, respectively (table 2). Except for the sample from well 17C, mercury concentrations in the two samples from wells 17A and 17B are higher than in other ground-water analyses from the study area and are about three times greater than background concentrations in natural waters. Klein (1972) estimated the background level of mercury in river and ground water to be on the order of 0.05 µg/L. Bottles for sample 17A and the replicate 17A(R) were collected on the same day as the samples from well 17C and shipped in the same cooler. Thus, the mercury contamination in sample 17C may have been caused by mercury volatilization from the 17A bottles during shipping.

A study of the estuaries in the Canal Creek area found mercury in the sediment of Canal Creek in concentrations of 0.381 to 6.00 µg/g (micrograms per gram), or 381 to 6,000 µg/L (U.S. Army Environmental Hygiene Agency, 1985). The maximum concentration was found near site 17. Because mercury tends to sorb readily on a variety of materials, bottom and suspended sediments are likely to contain higher concentrations of mercury than the water itself.

Two references to mercury have been found in the historical records for the Canal Creek area (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Chlorine manufacturing by a private firm that leased the WW2 plant used a mercury cell process, and mercury was present in the waste products. The manufacturer leased the WW2 chlorine plant (pl. 1) from shortly after WW2 until 1968. Mercuric chloride was used as a catalyst in the production of lewisite on a small experimental scale during late 1941 to early 1943. Only about 3 percent of the mercuric chloride was lost from solution in making a batch of lewisite, and the catalyst solution was reused. The experimental production plant was located in building 644 (pl. 1), which is south of site 17. Present head data for the Canal Creek aquifer do not indicate either plant as a likely source for the mercury at site 17 (fig. 4); however, natural flow directions would have been greatly altered during the period of heavy pumping. The chlorine plant, which used a greater amount of mercury and is closer to site 17, would be a more likely source than the lewisite manufacturing.

Chromium

Samples from 27B and 37A were found to contain concentrations of chromium greater than the primary MCL for drinking water (table 3). Both wells are screened in the Canal Creek aquifer but lie along separate flow paths (fig. 4). Site 37 is in the salvage yard, where various metal objects have been deposited and could possibly be a source of chromium. Samples from the other wells in the salvage yard (fig. 2) also contained chromium, with concentrations ranging from 0.006 to 0.023 mg/L. Concentrations of chromium in natural waters commonly are less than 0.010 mg/L (Hem, 1985, p. 138).

Another possible source of chromium in the Canal Creek area is from metal-plating operations. Machine shops were located near site 27 in building 88 and in the building-101 complex (pl. 1). Metal shavings from the building-101 shop, which was used throughout WW2, were placed in large piles on the ground south of the building.

ORGANIC CONSTITUENTS

Sixteen volatile organic compounds, including chlorinated alkanes, chlorinated alkenes, and aromatics, were identified in the ground water of the Canal Creek area of APG. Tables 10 and 11 list all the organic-chemical data collected, and tables 12 and 13 summarize the ranges of concentrations detected for each organic compound. All 87 observation wells were sampled for organic constituents; however, the water from well 35A probably was diluted because of flooding from a nearby broken water main, as mentioned previously.

Ten volatile organic compounds for which analyses were performed were not identified in any of the wells. The 10 compounds (and their detection limits) are bromoform (<3.2 µg/L), chlorodibromomethane (<2.0 µg/L), chloroethane (<3.5 µg/L), 2-chloroethyl vinyl ether (<5.9 µg/L), dichlorobromomethane (<1.2 µg/L), 1,2-dichloropropane (<1.5 µg/L), 1,3-dichloropropylene (<1.5 µg/L), methylbromide (<1.5 µg/L), methylchloride (<1.6 µg/L), and 1,1,1-trichloroethane (<1.2 µg/L). In addition, base/neutral and acid-extractable organic compounds (BNA's) were not detected in any of the samples.

The chlorinated alkanes and alkenes also can be referred to as halogenated or chlorinated aliphatic compounds. Aliphatic hydrocarbons are straight-chain molecules composed only of hydrogen and carbon. To form chlorinated aliphatics, chloride replaces one or more of the hydrogen atoms in the structure of the compound. The chlorinated alkanes are saturated aliphatic compounds because each carbon atom is bonded covalently to four other atoms by single bonds (fig. 9). Alkenes are unsaturated aliphatics containing carbon-carbon double bonds.

The structure of aromatic compounds is characterized by a benzene ring (fig. 9). Benzene consists of a cyclic arrangement of six carbon atoms with a single hydrogen atom bound to each carbon. One or more of the hydrogen atoms can be replaced in the benzene ring to form other monocyclic aromatic compounds, such as toluene and chlorobenzene (fig. 9).

The major organic contaminants detected in ground water of the Canal Creek area were chlorinated alkanes and alkenes. Aromatic volatile compounds were less widespread and generally appeared in lower concentrations. Total organic halogen (TOH) measures the halogen (chlorine, bromine, fluorine) concentration associated with volatile organic compounds. Because chlorinated volatile organic compounds were the major organic compounds found in the Canal Creek area, the TOH concentration can be used as an indicator of organic contamination in each sample (table 10). Duplicate TOH analyses were performed by the laboratory for most samples, and TOH was calculated for all samples using the concentrations of chlorinated volatile compounds measured by USEPA Method 624 (U.S. Environmental Protection Agency, 1979a).

Organic contaminants were detected only in the Canal Creek aquifer and in the surficial aquifer. Of the 59 wells sampled in the Canal Creek aquifer, only 10 samples (not including replicate or repeat samples) had TOH concentrations less than the detection limit of 5 μg/L; three samples of the 18 wells screened in the surficial aquifer contained TOH concentrations less than 5 μg/L. In contrast, the TOH concentration in all 10 samples from the lower confined aquifer generally were less than 5 μg/L (table 10). One sample from the lower confined aquifer, collected from well 2B, did contain a TOH concentration of 8 μg/L, but the organic compounds that were detected most likely are derived from laboratory contamination of the sample.

Toluene, ethylbenzene, and especially methylene chloride were found in low concentrations in several of the samples from the lower confined aquifer; however, these volatile organic compounds commonly are used in analytical laboratories and often appeared in the method blanks (table 11). For example, methylene chloride concentrations in the laboratory blanks were as high as 21.5 μg/L (table 11). Toluene, ethylbenzene, and methylene chloride generally were the only volatile organic compounds observed in the laboratory method blanks. Although the blank concentration was subtracted from the sample concentration before reporting the values in table 10, the low concentrations of methylene chloride in some samples still may be attributable to laboratory contamination and/or analytical error.

Errors in the analyses of the sample replicates were largest for concentrations of toluene, ethylbenzene, and methylene chloride (table 10). For example, the methylene chloride concentration was 55 μg/L in the sample from well 27B but 330 μg/L in the replicate sample 27B(R); the sample from well 30A had a methylene chloride concentration of 35 μg/L, whereas the replicate sample 30A(R) had a concentration of 7.5 μg/L. In addition, toluene, ethylbenzene, and methylene chloride often appeared in low concentrations in one sample but were below detection in the replicate sample.

With the exception of these three compounds, the difference in the concentrations of the volatile organic compounds between a sample and its replicate generally ranged from 0 to 44 percent with a median error of 14 percent. This median error is relatively low, considering the large degree of error that could be introduced during sampling, shipping, and analysis because of the volatile nature of the compounds.

Table 10.--Organic-chemical data for ground water in the Canal Creek area

[All concentration units are in micrograms per liter; <, less than; --, not analyzed;
#, sample was diluted; *, below blank concentration; (R), replicate sample; (Re), repeat sample.
Chemical abbreviations: CT = carbon tetrachloride, CF = chloroform, MC = methylene chloride,
1122-PCA = 1,1,2,2-tetrachloroethane, 112-TCA = 1,1,2-trichloroethane]

Well no.	Sampling date	Date of analysis	Toluene	Benzene	Ethyl-benzene	Chloro-benzene	CT	CF	MC	1122-PCA	112-TCA
Canal Creek aquifer:											
CC- 1B	3-03-87	3-14-87	<0.4	<0.5	2.9	<0.6	<1.5	<0.8	5.1*	3.1	<1.6
CC- 1C	3-03-87	3-18-87	1.6	<.5	9.1	<.6	<1.5	<.8	3.1*	14	<1.6
CC- 2A	2-26-87	3-06-87	<.4	<.5	.9*	<.6	<1.5	<.8	4.6	6.9	<1.6
CC- 3A	4-08-87	4-13-87	3.6	<.5	1.8	<.6	<1.5	2.9	2.7*	<1.4	<1.6
CC- 3B	4-07-87	4-14-87	<.4	<.5	3.3	<.6	<1.5	<.8	5.3	<1.4	<1.6
CC- 4A	2-13-87	2-28-87	<.4	<.5	1.7	<.6	<1.5	<.8	1.9*	<1.4	<1.6
CC- 4B	2-13-87	2-28-87	<.4	<.5	<.4	3.0	<1.5	<.8	2.4*	5.3	<1.6
CC- 5B	2-06-87	2-20-87	--	--	--	--	--	--	--	--	--
CC- 5C	2-06-87	2-28-87	<.4	<.5	<.4	<.6	<1.5	1.2	1.8*	<1.4	<1.6
CC- 6A	1-12-87	1-21-87	<.4	<.5	<.4	<.6	<1.5	6.5	4.3*	<1.4	<1.6
CC- 6A(Re)	4-29-87	5-18-87	<.4	<.5	2.3*	<.6	<1.5	2.8	4.0*	<1.4	<1.6
CC- 6B	1-12-87	1-21-87	<.4	<.5	.4*	<.6	14	10	2.7*	40	<1.6
CC- 7A	2-24-87	3-06-87	<.4	1.5	<.4	4.4	<1.5	2.9	2.6	14	<1.6
CC- 7A(R)	2-24-87	3-06-87	<.4	<.5	2.8	3.5	<1.5	2.8	1.2	19	<1.6
CC- 7B	2-24-87	3-06-87	<.4	<.5	1.8	3.5	<1.5	3.8	4.4	360	<1.6
CC- 8B	2-04-87	2-28-87	<.4	40	<.4	1.6	460	12	1.6*	650	79
CC- 8C	2-25-87	3-06-87	2.0	<.5	<.4	<.6	<1.5	12	6.1*	280	<1.6
CC- 8C(R)	2-25-87	3-06-87	2.4	<.5	3.0	<.6	<1.5	12	22	240	<1.6
CC- 8D	2-25-87	3-06-87	<.4	<.5	1.8	<.6	<1.5	10	5.6*	320	<1.6
CC- 9B	1-13-87	1-21-87	<.4	<.5	2.4*	<.6	<1.5	<.8	3.9*	<1.4	<1.6
CC- 9B(Re)	4-08-87	4-14-87	<.4	<.5	<.4	<.6	<1.5	<.8	6.0	<1.4	<1.6
CC-11A	4-03-87	4-13-87	3.9	<.5	2.7	<.6	<1.5	<.8	4.3*	<1.4	<1.6
CC-11B	4-03-87	4-14-87	<.4	<.5	1.8*	<.6	<1.5	<.8	5.5	<1.4	<1.6
CC-12A	1-09-87	1-15-87	--	--	--	--	--	--	--	--	--
CC-12B	1-09-87	1-20-87	<.4	<.5	<.4	<.6	<1.5	<.8	3.1*	<1.4	<1.6
CC-13A	3-04-87	3-18-87	<1.2#	<1.5#	<1.2#	<1.8#	<4.5#	<2.4#	7.1*	380	<4.8#
CC-13B	3-04-87	3-14-87	<.4	<.5	<.4	<.6	<1.5	1.4	3.2*	81	<1.6
CC-14A	3-04-87	3-17-87	<.4	2.0	1.9*	9.8	<1.5	4.1	4.9*	28	<1.6
CC-14B	3-04-87	3-17-87	<.4	4.2	2.9	<.6	<1.5	<.8	13*	11	<1.6
CC-15A	3-04-87	3-17-87	<.4	<.5	<.4	<.6	<1.5	<.8	13*	<1.4	<1.6
CC-16A	3-06-87	3-20-87	<8.0#	<10#	<8.0#	32	<30#	78	<22#	<22#	<32#
CC-16B	3-06-87	3-20-87	<4.0#	<5.0#	8.0	<6.0#	<15#	<8.0#	12	<14#	<16#
CC-16B(R)	3-06-87	3-20-87	1.9	<.5	2.3*	<.6	8.5	4.5	.7	<1.4	<1.6
CC-17A	3-06-87	3-20-87	<8.0#	<10#	<8#	<12#	160	40	<22#	460	<32#
CC-17A(R)	3-06-87	3-20-87	.5	<.5	8.6	<.6	180	38	7.1	460	<1.6
CC-17B	3-09-87	3-20-87	3.4	<.5	2.5*	<.6	38	30	1.7	200	<1.6
CC-18A	2-11-87	2-27-87	<.4	<.5	1.8*	<.6	<1.5	3.4	3.7*	280	<1.6
CC-18B	2-11-87	2-27-87	<.4	<.5	3.3	<.6	<1.5	12	3.4*	550	<1.6
CC-19B	2-10-87	2-18-87	<.4	<.5	<.4	<.6	<1.5	11	4.2*	5.4	<1.6
CC-20C	2-03-87	2-28-87	<.4	<.5	1.0	<.6	<1.5	6.1	2.1*	7.7	<1.6
CC-20D	2-10-87	2-18-87	<.4	<.5	<.4	<.6	<1.5	13	2.5	2.0	<1.6
CC-21A	3-04-87	3-14-87	<.4	<.5	<.4	<.6	120	13	1.9*	170	<1.6
CC-21A(R)	3-04-87	3-14-87	<.4	<.5	3.2	<.6	<1.5	11	3.1*	180	<1.6

CC-22B	2-02-87	2-27-87	<.4	<.5	3.1	<.6	<1.5	<.8	3.3*	<1.4	<1.6
CC-22C	2-03-87	2-28-87	<.4	<.5	<.4	<.6	<1.5	<.8	<1.1	<1.4	<1.6
CC-23B	2-10-87	2-27-87	<.4	<.5	1.0*	<.6	<1.5	<.8	4.4*	<1.4	<1.6
CC-25A	2-27-87	3-07-87	<.4	<.5	9.1	<.6	<1.5	<.8	3.0*	91	<1.6
CC-25B	2-27-87	3-07-87	7.5	<.5	2.6*	<.6	<1.5	<.8	2.2*	4.2	<1.6
CC-26A	2-27-87	3-20-87	<.4	<.5	1.7*	<.6	480	150	1.4	25	<1.6
CC-26A(R)	2-27-87	2-20-87	<.4	<.5	4.6	<.6	500	170	3.2*	<1.4	<1.6
CC-26B	2-27-87	3-14-87	2.1	70	3.2	39	190	330	5.4*	110	<1.6
CC-27A	3-05-87	3-18-87	<8.0#	<10#	<8.0#	<12#	<30#	<16#	<22#	3,300	<32#
CC-27B	3-05-87	3-19-87	5.9	<.5	<.4	<.6	36	79	55	48	<1.6
CC-27B(R)	3-05-87	3-20-87	6.9	<.5	1.7	<.6	39	92	330	56	<1.6
CC-28A	3-05-87	3-18-87	<.4	<.5	1.8	<.6	340	460	8.3*	81	<1.6
CC-28B	3-05-87	3-18-87	<.4	<.5	3.0	<.6	240	170	9.7*	53	<1.6
CC-29B	2-10-87	2-18-87	<.4	<.5	<.4	12	<1.5	<.8	3.2*	<1.4	<1.6
CC-30A	3-05-87	3-19-87	<2.0#	<2.5#	<2.0#	<3.0#	260	34	35	510	6.5
CC-30A(R)	3-05-87	3-18-87	<1.6#	<2.0#	1.7	<2.4#	250	27	7.5*	470	5.6
CC-31A	2-19-87	3-05-87	<.4	<.5	1.5*	<.6	<1.5	<.8	14	<1.4	<1.6
CC-37A	11-19-86	12-03-86	<.4	<.5	<.4	<.6	<1.5	4.0	2.2*	<1.4	<1.6
CC-38A	11-21-86	12-04-86	<.4	<.5	<.4	<.6	<1.5	1.9	14	1.9	<1.6
CC-39A	11-19-86	12-03-86	<.4	<.5	<.4	<.6	<1.5	4.0	4.0*	5,300	73
CC-39B	11-19-86	12-03-86	<.4	<.5	<.4	<.6	<1.5	2.9	1.0	7.8	<1.6
CC-40A	11-20-86	12-04-86	<.4	<.5	<.4	<.6	<1.5	1.4	28	<1.4	<1.6
CC-41A	11-21-86	12-05-86	--	--	--	--	--	--	--	--	--
CC-42A	11-20-86	12-09-86	--	--	--	--	--	--	--	--	--
CC-43A	11-21-86	12-05-86	--	--	--	--	--	--	--	--	--
CC-44A	2-19-87	3-05-87	<.4	<.5	3.0	<.6	<1.5	24	16	<1.4	<1.6
Surficial aquifer:											
CC- 1A	3-03-87	3-07-87	<.4	<.5	5.1	<.6	<1.5	<.8	2.4*	31	<1.6
CC- 1A(R)	3-03-87	3-14-87	<.4	<.5	1.9	<.6	<1.5	<.8	2.8*	41	<1.6
CC- 5A	1-07-87	1-20-87	<.4	<.5	<.4	<.6	<1.5	<.8	1.0	<1.4	<1.6
CC- 8A	2-04-87	2-18-87	--	--	--	--	--	--	--	--	--
CC- 9A	1-06-87	1-08-87	1.1	<.5	<.4	14	<1.5	<.8	3.1*	<1.4	<1.6
CC-10A	1-06-87	1-08-87	<.4	<.5	<.4	<.6	88	20	4.7*	<1.4	<1.6
CC-19A	1-07-87	1-20-87	<.4	<.5	<.4	<.6	<1.5	<.8	0.8	<1.4	<1.6
CC-20A	1-07-87	1-20-87	<.4	<.5	<.4	<.6	<1.5	<.8	3.4*	<1.4	<1.6
CC-20B	2-02-87	2-27-87	<.4	<.5	1.8*	<.6	<1.5	6.0	2.6*	10	<1.6
CC-22A	2-02-87	2-27-87	<.4	<.5	2.0	<.6	<1.5	5.5	2.8*	2.1	<1.6
CC-23A	2-03-87	2-28-87	<.4	<.5	<.4	<.6	<1.5	<.8	1.8*	<1.4	<1.6
CC-29A	1-13-87	1-21-87	.5	2.0	.5	22	<1.5	6.8	3.3*	<1.4	<1.6
CC-32A	12-17-86	1-08-87	<.4	<.5	<.4	<.6	<1.5	66	3.5*	<1.4	<1.6
CC-32B	12-17-86	1-08-87	<.4	<.5	<.4	<.6	<1.5	52	5.0*	<1.4	<1.6
CC-33A	12-17-86	1-08-87	<8.0#	<10#	<8.0#	<12#	<30#	<16#	<22#	1,300	<32#
CC-33B	12-17-86	1-08-87	<20#	<25#	<20#	<30#	<75#	<40#	<55#	9,000	80
CC-34A	12-17-86	1-08-87	2	<2.5#	<2.0#	<3.0#	<7.5#	8.0	<5.5#	8.0	<8.0#
CC-35A	12-17-86	1-07-87	<.4	<.5	<.4	<.6	<1.5	1.4	0.4	<1.4	<1.6
CC-36A	2-19-87	3-05-87	<.4	<.5	1.1*	<.6	<1.5	<.8	7.5	<1.4	<1.6
Lower confined aquifer:											
CC- 1D	3-03-87	3-20-87	2.0	<.5	<.4	<.6	<1.5	<.8	2.7*	1.2*	<1.6
CC- 1E	4-03-87	4-13-87	11	<.5	<.4	<.6	<1.5	<.8	1.6*	<1.4	<1.6
CC- 1F	3-27-87	4-05-87	1.0	<.5	2.6	<.6	<1.5	<.8	3.4	<1.4	<1.6
CC- 2B	3-24-87	4-05-87	<.4	<.5	2.8	<.6	<1.5	<.8	9.4	<1.4	<1.6
CC- 2C	3-26-87	4-05-87	3.3	<.5	1.5	<.6	<1.5	<.8	2.4	<1.4	<1.6
CC- 8E	4-01-87	4-13-87	<.4	<.5	<.4	<.6	<1.5	<.8	1.9*	<1.4	<1.6
CC-16C	3-06-87	3-19-87	<.4	<.5	2.8	<.6	<1.5	<.8	7.4	<1.4	<1.6
CC-16D	3-27-87	4-05-87	7.0	<.5	<.4	<.6	<1.5	<.8	2.3*	<1.4	<1.6
CC-17C	3-06-87	3-20-87	<.4	<.5	3.3*	<.6	<1.5	<.8	2.7	<1.4	<1.6
CC-26C	2-27-87	3-07-87	<.4	<.5	2.5*	<.6	<1.5	<.8	2.8*	<1.4	<1.6

Table 10.--Organic-chemical data for ground water in the Canal Creek area--Continued

[All concentration units are in micrograms per liter; <, less than; --, not analyzed;
#, sample was diluted; *, below blank concentration; (R), replicate sample; (Re), repeat sample.
Chemical abbreviations: 12-DCA = 1,2-dichloroethane, 11-DCA = 1,1-dichloroethane,
PCE = tetrachloroethylene, TCE = trichloroethylene, 11-DCE = 1,1-dichloroethylene,
12-tDCE = 1,2-trans-dichloroethylene, VC = vinyl chloride, TOH-1 = total organic halogen,
TOH-2 = total organic halogen, lab duplicate, TOH-calc. = total organic halogen, calculated]

Well no.	Sampling date	Date of analysis	12-DCA	11-DCA	PCE	TCE	11-DCE	12-tDCE	VC	TOH-1	TOH-2	TOH-calc.
Canal Creek aquifer:												
CC- 1B	3-03-87	3-14-87	3.9	<1.0	<1.5	250	4.4	1,200	100	--	--	1,200
CC- 1C	3-03-87	3-18-87	6.2	<1.0	<1.5	160	2.0	620	36	--	--	620
CC- 2A	2-26-87	3-06-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	10
CC- 3A	4-08-87	4-13-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 3B	4-07-87	4-14-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 4A	2-13-87	2-28-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	13	8	<5
CC- 4B	2-13-87	2-28-87	1.9	<1.0	<1.5	<1.3	<1.9	120	11	72	82	100
CC- 5B	2-06-87	2-20-87	--	--	--	--	--	--	--	<5	<5	--
CC- 5C	2-06-87	2-28-87	3.8	<1.0	<1.5	130	<1.9	220	25	280	280	280
CC- 6A	1-12-87	1-21-87	<1.5	<1.0	<1.5	3.6	<1.9	<1.6	<1.3	270	270	9
CC- 6A(Re)	4-29-87	5-18-87	<1.5	<1.0	<1.5	5.5	<1.9	<1.6	<1.3	--	--	<5
CC- 6B	1-12-87	1-21-87	<1.5	<1.0	<1.5	10	<1.9	<1.6	<1.3	50	49	65
CC- 7A	2-24-87	3-06-87	2.1	<1.0	<1.5	21	<1.9	160	10	110	110	160
CC- 7A(R)	2-24-87	3-06-87	1.9	<1.0	2.9	19	<1.9	140	7.6	96	100	140
CC- 7B	2-24-87	3-06-87	4.3	<1.0	<1.5	50	<1.9	360	51	360	430	630
CC- 8B	2-04-87	2-28-87	2.7	<1.0	<1.5	1,800	<1.9	250	18	620	660	2,700
CC- 8C	2-25-87	3-06-87	6.1	<1.0	<1.5	<1.3	<1.9	66	41	280	280	320
CC- 8C(R)	2-25-87	3-06-87	6.2	<1.0	<1.5	49	<1.9	68	31	270	270	350
CC- 8D	2-25-87	3-06-87	4.3	<1.0	<1.5	<1.3	<1.9	160	35	340	400	410
CC- 9B	1-13-87	1-21-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 9B(Re)	4-08-87	4-14-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-11A	4-03-87	4-13-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-11B	4-03-87	4-14-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-12A	1-09-87	1-15-87	--	--	--	--	--	--	--	<5	<5	--
CC-12B	1-09-87	1-20-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	16	16	<5
CC-13A	3-04-87	3-18-87	<4.5#	<3.0#	<4.5#	26	<5.7#	<4.8#	<3.9#	--	--	340
CC-13B	3-04-87	3-14-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	69
CC-14A	3-04-87	3-17-87	<1.5	<1.0	<1.5	2.1	<1.9	<1.6	<1.3	--	--	32
CC-14B	3-04-87	3-17-87	<1.5	<1.0	<1.5	1.8	<1.9	<1.6	<1.3	--	--	10
CC-15A	3-04-87	3-17-87	<1.5	<1.0	<1.5	2.3	<1.9	<1.6	<1.3	--	--	<5
CC-16A	3-06-87	3-20-87	990	<20#	26	300	<38#	670	140	--	--	1,600
CC-16B	3-06-87	3-20-87	<15#	<10#	<15#	98	<19#	15	<13#	--	--	100
CC-16B(R)	3-06-87	3-20-87	3.6	<1.0	3.5	110	<1.9	11	<1.3	--	--	89
CC-17A	3-06-87	3-20-87	<30#	<20#	<30#	100	<38#	<32#	<26#	--	--	650
CC-17A(R)	3-06-87	3-20-87	9.0	<1.0	<1.5	87	<1.9	8.6	<1.3	--	--	670
CC-17B	3-09-87	3-20-87	6.1	<1.0	<1.5	23	<1.9	21	<1.3	--	--	270
CC-18A	2-11-87	2-27-87	<1.5	<1.0	<1.5	<1.3	<1.9	1.4*	<1.3	220	230	240
CC-18B	2-11-87	2-27-87	<1.5	<1.0	<1.5	<1.3	<1.9	5.6	<1.3	520	480	480
CC-19B	2-10-87	2-18-87	<1.5	1.1	<1.5	<1.3	<1.9	<1.6	<1.3	14	14	14
CC-20C	2-03-87	2-28-87	<1.5	<1.0	<1.5	<1.3	<1.9	2.7	<1.3	31	24	14
CC-20D	2-10-87	2-18-87	<1.5	1.1	<1.5	3.8	<1.9	55	1.7	67	63	57
CC-21A	3-04-87	3-14-87	<1.5	<1.0	<1.5	2.2	<1.9	<1.6	<1.3	--	--	260
CC-21A(R)	3-04-87	3-14-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	160

CC-22B	2-02-87	2-27-87	<1.5	<1.0	<1.5	<1.3	<1.9	220	27	130	130	170
CC-22C	2-03-87	2-28-87	<1.5	<1.0	<1.5	<1.3	<1.9	52	<1.3	38	31	38
CC-23B	2-10-87	2-27-87	<1.5	<1.0	<1.5	7.5	<1.9	160	22	110	100	140
CC-25A	2-27-87	3-07-87	<1.5	<1.0	28	99	<1.9	30	<1.3	--	--	200
CC-25B	2-27-87	3-07-87	<1.5	<1.0	<1.5	13	<1.9	91	<1.3	--	--	81
CC-26A	2-27-87	3-20-87	<1.5	<1.0	3.5	<1.3	<1.9	<1.6	<1.3	--	--	600
CC-26A(R)	2-27-87	2-20-87	<1.5	<1.0	3.5	<1.3	<1.9	<1.6	<1.3	--	--	620
CC-26B	2-27-87	3-14-87	4.0	3.1	100	6.2	2.8	7.4	<1.3	--	--	690
CC-27A	3-05-87	3-18-87	<30#	<20#	<30#	410	<38#	38	<26#	--	--	3,200
CC-27B	3-05-87	3-19-87	<1.5	<1.0	<1.5	12	<1.9	4.8	<1.3	--	--	160
CC-27B(R)	3-05-87	3-20-87	<1.5	<1.0	<1.5	12	<1.9	6.0	<1.3	--	--	460
CC-28A	3-05-87	3-18-87	3.9	<1.0	22	34	<1.9	3.4	<1.3	--	--	800
CC-28B	3-05-87	3-18-87	<1.5	<1.0	32	22	<1.9	3.0	<1.3	--	--	470
CC-29B	2-10-87	2-18-87	<1.5	<1.0	<1.5	6.0	<1.9	32	25	47	48	47
CC-30A	3-05-87	3-19-87	9.5	<5.0#	<7.5#	86	<9.5#	<8.0#	<6.5#	--	--	780
CC-30A(R)	3-05-87	3-18-87	8.0	<4.0#	<6.0#	67	<7.6#	<6.4#	<5.2#	--	--	710
CC-31A	2-19-87	3-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	2.4	<1.3	8	7	14
CC-37A	11-19-86	12-03-86	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-38A	11-21-86	12-04-86	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	14
CC-39A	11-19-86	12-03-86	<1.5	<1.0	<1.5	570	2.5	290	2.5	--	--	5,200
CC-39B	11-19-86	12-03-86	<1.5	<1.0	<1.5	83	<1.9	<1.6	<1.3	--	--	74
CC-40A	11-20-86	12-04-86	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	22
CC-41A	11-21-86	12-05-86	--	--	--	--	--	--	--	17	--	--
CC-42A	11-20-86	12-09-86	--	--	--	--	--	--	--	33	--	--
CC-43A	11-21-86	12-05-86	--	--	--	--	--	--	--	14	--	--
CC-44A	2-19-87	3-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	43	36	35
Surficial aquifer:												
CC- 1A	3-03-87	3-07-87	<1.5	<1.0	<1.5	16	<1.9	11	1.6	--	--	47
CC- 1A(R)	3-03-87	3-14-87	<1.5	<1.0	<1.5	16	<1.9	9.1	<1.3	--	--	54
CC- 5A	1-07-87	1-20-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	55	59	<5
CC- 8A	2-04-87	2-18-87	--	--	--	--	--	--	--	<5	<5	--
CC- 9A	1-06-87	1-08-87	<1.5	<1.0	<1.5	3.0	<1.9	<1.6	<1.3	16	16	7
CC-10A	1-06-87	1-08-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	120	120	98
CC-19A	1-07-87	1-20-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	15	17	<5
CC-20A	1-07-87	1-20-87	<1.5	<1.0	<1.5	41	<1.9	<1.6	<1.3	51	50	33
CC-20B	2-02-87	2-27-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	40	74	14
CC-22A	2-02-87	2-27-87	<1.5	<1.0	4.2	<1.3	<1.9	8.0	<1.3	29	30	16
CC-23A	2-03-87	2-28-87	<1.5	<1.0	<1.5	<1.3	<1.9	9.7	<1.3	19	19	7
CC-29A	1-13-87	1-21-87	<1.5	<1.0	<1.5	1.3	<1.9	2.1	6.4	68	73	23
CC-32A	12-17-86	1-08-87	<1.5	<1.0	<1.5	1.7	<1.9	<1.6	<1.3	210	200	60
CC-32B	12-17-86	1-08-87	<1.5	<1.0	<1.5	3.1	<1.9	<1.6	<1.3	190	200	49
CC-33A	12-17-86	1-08-87	<30#	<20#	64	250	<38#	<32#	<26#	1,000	1,000	1,300
CC-33B	12-17-86	1-08-87	<75#	<50#	<75#	940	<95#	520	<65#	6,100	6,100	8,800
CC-34A	12-17-86	1-08-87	<7.5#	<5.0#	<7.5#	380	<9.5#	<8.0#	<6.5#	400	400	310
CC-35A	12-17-86	1-07-87	<1.5	<1.0	<1.5	1.9	<1.9	4.9	<1.3	27	18	5
CC-36A	2-19-87	3-05-87	<1.5	<1.0	1.7	3.4	<1.9	<1.6	<1.3	12	13	10
Lower confined aquifer:												
CC- 1D	3-03-87	3-20-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 1E	4-03-87	4-13-87	<1.5	<1.0	<1.5	<1.3	<1.9	3.9	<1.3	--	--	<5
CC- 1F	3-27-87	4-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 2B	3-24-87	4-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	8
CC- 2C	3-26-87	4-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC- 8E	4-01-87	4-13-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-16C	3-06-87	3-19-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-16D	3-27-87	4-05-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-17C	3-06-87	3-20-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5
CC-26C	2-27-87	3-07-87	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3	--	--	<5

Table 11.--Organic-chemical data for method blanks

[All concentration units are in micrograms per liter; chemical abbreviations: CT = carbon tetrachloride, CF = chloroform, MC = methylene chloride, 1122-PCA = 1,1,2,2-tetrachloroethane, 112-TCA = 1,1,2-trichloroethane, 12-DCA = 1,2-dichloroethane, 11-DCA = 1,1-dichloroethane, PCE = tetrachloroethylene, TCE = trichloroethylene, 11-DCE = 1,1-dichloroethylene, 12-tDCE = 1,2-trans-dichloroethylene, VC = vinyl chloride]

Date of analysis	Toluene	Benzene	Ethyl-benzene	Chloro-benzene	CT	CF	MC	1122-PCA	112-TCA	12-DCA	11-DCA	PCE	TCE	11-DCE	12-tDCE	VC
12-03-86	<0.4	<0.5	<0.4	<0.6	<1.5	<0.8	3.9	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
12-04-86	<.4	<.5	<.4	<.6	<1.5	<.8	4.2	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
1-07-87	.4	<.5	<.4	<.6	<1.5	<.8	4.0	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
1-08-87	<.4	<.5	<.4	<.6	<1.5	<.8	6.0	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
1-20-87	<.4	<.5	<.4	<.6	<1.5	<.8	3.4	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
1-21-87	<.4	<.5	<.4	<.6	<1.5	<.8	6.5	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
2-18-87	<.4	<.5	<.4	<.6	<1.5	<.8	5.0	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
2-27-87	<.4	<.5	1.8	<.6	<1.5	<.8	8.9	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
2-28-87	<.4	<.5	<.4	<.6	<1.5	<.8	3.4	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-05-87	<.4	<.5	1.5	<.6	<1.5	<.8	1.6	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-06-87	<.4	<.5	1.5	<.6	<1.5	<.8	6.3	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-07-87	<.4	<.5	<.4	<.6	<1.5	<.8	13.7	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-14-87	<.4	<.5	1.8	<.6	<1.5	<.8	13.1	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-17-87	<.4	<.5	2.0	<.6	<1.5	<.8	13.7	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-18-87	<.4	<.5	1.3	<.6	<1.5	<.8	11.9	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-19-87	<.4	<.5	1.5	<.6	<1.5	<.8	21.5	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
3-20-87	<.4	<.5	4.3	<.6	<1.5	<.8	5.7	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
4-05-87	<.4	<.5	1.4	<.6	<1.5	<.8	2.8	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
4-13-87	.8	<.5	1.5	<.6	<1.5	<.8	7.2	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
4-14-87	<.4	<.5	2.2	<.6	<1.5	<.8	5.2	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3
5-18-87	<.4	<.5	2.3	<.6	<1.5	<.8	12.0	<1.4	<1.6	<1.5	<1.0	<1.5	<1.3	<1.9	<1.6	<1.3

Table 12.--Organic contaminants detected in the Canal Creek aquifer, and comparison of their concentrations to Federal drinking-water maximum contaminant levels

[Units are in micrograms per liter; MCL is maximum contaminant level as established by the U.S. Environmental Protection Agency (1987b); replicate or repeat samples are not included; dashes indicate that value is not known]

Organic compound	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected	Well no. (for max. conc.)	MCL
Chlorinated alkanes:						
Carbon tetrachloride	11	190	14	480	CC-26A	5
Chloroform	32	11	1.2	460	CC-28A	--
Methylene chloride	16	5.4	1.0	55	CC-27B	--
1,1,2,2-tetrachloroethane	34	67	1.9	5,300	CC-39A	--
1,1,2-trichloroethane	3	73	6.5	79	CC- 8B	--
1,2-dichloroethane	14	4.2	1.9	990	CC-16A	5
1,1-dichloroethane	3	1.1	1.1	3.1	CC-26B	--
Chlorinated alkenes:						
Tetrachloroethylene	6	27	3.5	100	CC-26B	--
Trichloroethylene	30	24	1.8	1,800	CC- 8B	5
1,1-dichloroethylene	4	2.6	2.0	4.4	CC- 1B	7
1,2-trans-dichloroethylene	28	60	2.4	1,200	CC- 1B	--
Vinyl chloride	15	25	1.7	140	CC-16A	2
Aromatics:						
Benzene	5	4.2	1.5	70	CC-26B	5
Chlorobenzene	8	7.1	1.6	39	CC-26B	--
Toluene	8	3.5	1.6	7.5	CC-25B	--
Ethylbenzene	18	3.0	1.0	9.1	CC-25A	--

In 1987, the USEPA established National Primary Drinking Water Regulations for eight volatile organic compounds (U.S. Environmental Protection Agency, 1987b). The established MCL's, which are enforceable standards, are shown in tables 12 and 13 for six volatile organic compounds detected in the Canal Creek area. Of the six compounds, only 1,1-dichloroethylene was found in lower concentrations than the MCL. Although MCL's have not been set for all the compounds, the 16 volatile organics in tables 12 and 13 have been identified as priority pollutants by USEPA because of their persistence in the environment, their prevalent use in the United States, and their known or suspected toxicity to humans (U.S. Environmental Protection Agency, 1979a). It should be noted that USEPA Method 624 actually gives the total of 1,2-_trans_-dichloroethylene and 1,2-_cis_-dichloroethylene and that 1,2-_cis_-dichloroethylene is not a priority pollutant.

The distribution and possible sources for the volatile organic compounds observed in the Canal Creek aquifer and in the surficial aquifer are discussed in this report. However, the results of the second phase of the study are needed to better define the sources and extent of contamination. Multiple sources for many of the organic compounds existed in the Canal Creek area of APG. Defining the sources also is complicated by the many ways contaminants could have been released to the environment, including (1) spills of chemicals on the surface, (2) discharge of wastes through sewers to the swamps and creeks, (3) disposal of solid wastes in the swamps and creek, (4) leaking of wastes through the sewerlines, and (5) disposal of wastes in

Table 13.--Organic contaminants detected in the surficial aquifer, and comparison of their concentrations to Federal drinking-water maximum contaminant levels

[Units are in micrograms per liter; MCL is maximum contaminant level as established by the U.S. Environmental Protection Agency (1987b); replicate or repeat samples are not included; -- indicate that value is not known]

Organic compound	Number of samples in which constituent detected	Median concentration detected	Minimum concentration detected	Maximum concentration detected	Well no. (for max. conc.)	MCL
Chlorinated alkanes:						
Carbon tetrachloride	1	--	--	88	CC-10A	5
Chloroform	8	7.4	1.4	66	CC-32A	--
Methylene chloride	4	.9	.4	7.5	CC-36A	--
1,1,2,2-tetrachloroethane	6	21	2.1	9,000	CC-33B	--
1,1,2-trichloroethane	1	--	--	80	CC-33B	--
1,2-dichloroethane	0	--	--	--	--	5
1,1-dichloroethane	0	--	--	--	--	--
Chlorinated alkenes:						
Tetrachloroethylene	3	4.2	1.7	64	CC-33A	--
Trichloroethylene	11	3.4	1.3	940	CC-33B	5
1,1-dichloroethylene	0	--	--	--	--	7
1,2-trans-dichloroethylene	6	8.8	2.1	520	CC-33B	--
Vinyl chloride	2	--	1.6	6.4	CC-29A	2
Aromatics:						
Benzene	1	--	--	2.0	CC-29A	5
Chlorobenzene	2	--	14	22	CC-29A	--
Toluene	3	1.1	.5	2.0	CC-34A	--
Ethylbenzene	3	2.0	.5	5.1	CC- 1A	--

dump areas and pits. In addition, historical records of manufacturing processess, materials used, and wastes generated are incomplete. Finally, present directions of ground-water flow may not accurately reflect source areas because head gradients would have been altered and possibly reversed during the period of heavy pumping from 1950-68.

Many of the organic compounds could have both a primary and secondary source. Direct use of a compound and disposal as a waste product in the study area could provide a primary source, whereas product degradation is considered a secondary source. Primary sources are discussed in the probable sources section; secondary sources are discussed in the section on geochemical reactions.

Chlorinated Alkanes

Distribution

Canal Creek aquifer

For the 59 wells sampled in the Canal Creek aquifer, chloroform and 1,1,2,2-tetrachloroethane were the most widespread chlorinated alkanes, appearing in samples from 32 and 34 wells, respectively, in concentrations above the detection limits (table 12). Carbon tetrachloride, methylene chloride, and 1,2-dichloroethane were found in 11 to 16 samples. Only three samples contained 1,1,2-trichloroethane or 1,1-dichloroethane.

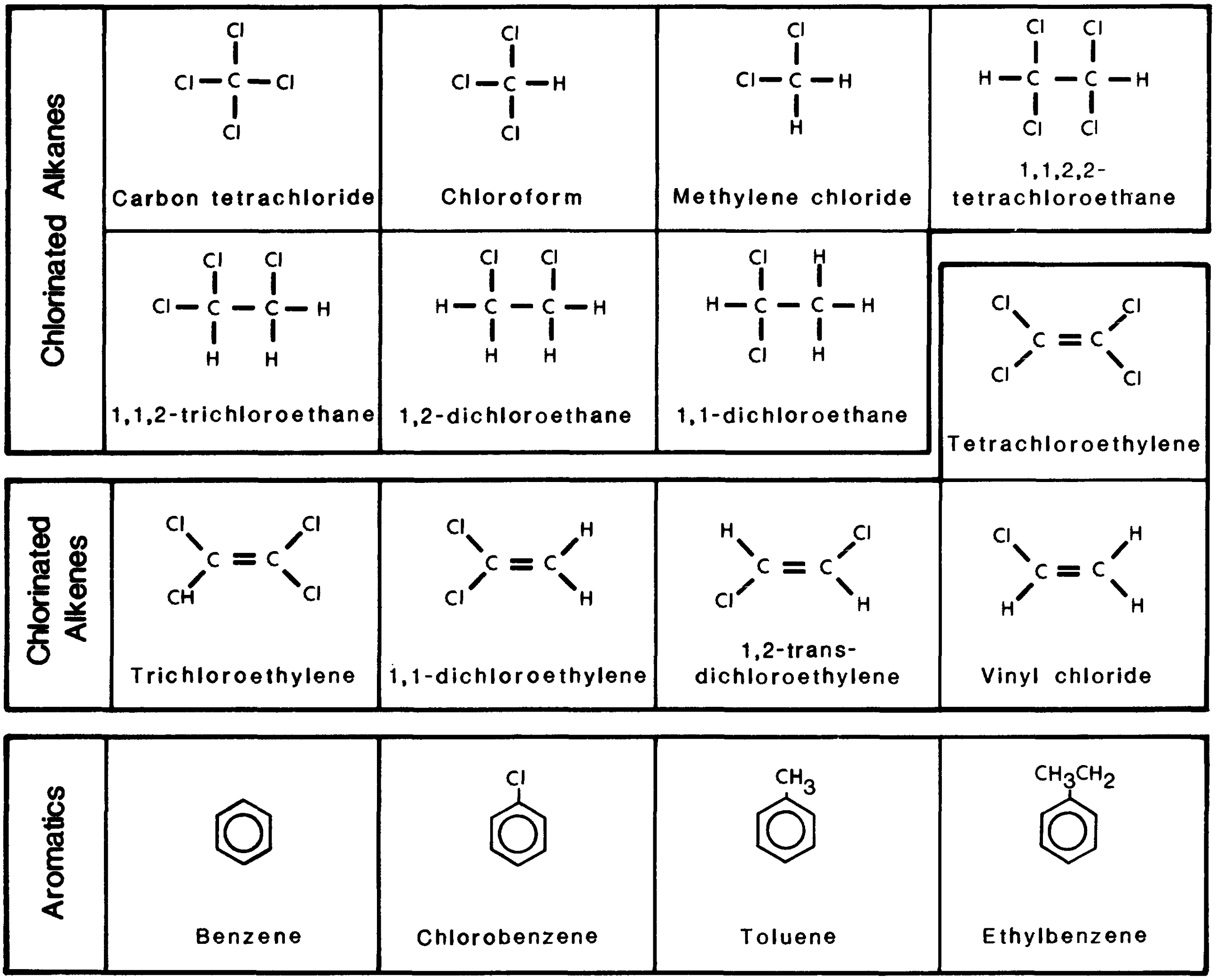


Figure 9.-- Structural diagrams of the organic constituents detected in ground water in the Canal Creek area.

Horizontal bar graphs, which are similar to the Stiff diagrams plotted for the major inorganic constituents, are used to show the distribution of the more common organic contaminants found in the Canal Creek aquifer (pl. 3). Chlorinated alkanes are plotted in micromoles per liter (μmol/L) to the left of the zero vertical axis, and chlorinated alkenes are to the right. Some samples are not plotted on plate 3 because organic concentrations were too low for the patterns to be discerned easily.

Methylene chloride is not shown on plate 3 because it generally appeared in only low concentrations (median of 5.4 μg/L) and could be the result of laboratory contamination. The maximum concentration of methylene chloride in the Canal Creek aquifer was 55 μg/L at well 27B (table 12); the replicate sample for 27B had a methylene chloride concentration of 330 μg/L (table 10). This discrepancy was the largest observed between the replicate analyses for any of the organic compounds.

The maximum concentration of 1,1,2,2-tetrachloroethane in the Canal Creek aquifer (5,300 μg/L) was seen in the sample from well 39A (table 12), which is in the salvage yard (pl. 3). High concentrations were also found along the West Branch Canal Creek in wells near the pilot plant (13A, 17A, 17B, 21A, and 30A) and south of the pilot plant, especially at well 27A. In addition, 1,1,2,2-tetrachloroethane was the major organic contaminant at site 18. Eastward of the East Branch Canal Creek, only samples from sites 7 and 8 had 1,1,2,2-tetrachloroethane as a major contaminant.

Although chloroform was as widespread as 1,1,2,2-tetrachloroethane, chloroform was present in lower concentrations (table 12). The highest concentrations of chloroform also were found along the West Branch Canal Creek, especially at wells 26A, 26B, 28A, and 28B. Chloroform was the major organic constituent in samples from wells 19B and 44A, but the concentrations were relatively low (11 and 24 μg/L, respectively).

Except for the sample from well 8B, all the samples that contained carbon tetrachloride are from wells located along the West Branch Canal Creek. Ten samples were from three sites surrounding the pilot plant (17, 21, and 30) and from sites 26, 27, and 28 (pl. 3).

The sample from well 16A had a 1,2-dichloroethane concentration of 990 μg/L, the maximum concentration observed in the ground water of the Canal Creek area (tables 12 and 13). With the exception of the sample from well 16A, 1,2-dichloroethane was present in the Canal Creek aquifer in concentrations that are only slightly above the detection limit (1.5 μg/L). Concentrations of 1,1-dichloroethane also were low, reaching a maximum of 3.1 μg/L in the Canal Creek aquifer (table 12).

Concentrations of 1,1,2-trichloroethane were higher than those of the two dichloroethane compounds, except for the 1,2-dichloroethane concentration in 16A (table 12). The samples from wells 8B and 39A contained 79 and 73 μg/L of 1,1,2-trichloroethane, respectively. One sample from a well near the pilot plant, 30A, had a lower concentration of 6.5 μg/L.

Vertical distribution of the chlorinated alkanes in the Canal Creek aquifer was highly variable. For the sites where more than one well is screened in the aquifer, concentrations of the major chlorinated alkanes generally decreased with depth. These sites include 8, 13, 14, 16, 17, 25, and 28 (pl. 3). In contrast, concentrations of the alkanes were found to increase in the deep wells at sites 6, 7, and 18 compared to the shallow wells.

The specific types of chlorinated alkanes present in the ground water also changed with depth in some well clusters. For example, the sample from well 27A had 3,300 μg/L of 1,1,2,2-tetrachloroethane, which was the only alkane. The sample from well 27B, which is screened about 12 ft below 27A, had a much lower concentration of 1,1,2,2-tetrachloroethane (48 μg/L), but also contained carbon tetrachloride (36 μg/L), chloroform (79 μg/L), and methylene chloride (55 μg/L).

Surficial aquifer

For the 18 samples collected in the surficial aquifer, the most widely distributed alkanes were 1,1,2,2-tetrachloroethane and chloroform, which were present in six to eight well-water samples (table 13). These two chlorinated alkanes also were the most extensive contaminants in the Canal Creek aquifer. Methylene chloride, carbon tetrachloride, and 1,1,2-trichloroethane were present in one to four of the samples. The median methylene chloride concentration (table 13) is not significantly higher than the concentrations measured in the laboratory blanks (table 11). Thus, methylene chloride concentrations probably are caused by laboratory contamination and analytical error. Concentrations of 1,2-dichloroethane and 1,1-dichloroethane were below the detection limit in all the samples from the surficial aquifer.

The horizontal bar diagrams in figures 10a and 10b show the distribution of chlorinated alkanes in the surficial aquifer. Samples from six wells in the surficial aquifer--5A, 8A, 9A, 19A, 35A, and 36A--had low TOH concentrations of less than or equal to 10 μg/L (table 10) and are not shown in figures 13a and 13b. Methylene chloride was the only organic constituent detected in the ground-water samples from wells 5A and 19A.

The highest concentrations of chlorinated alkanes in the surficial aquifer were observed in samples from Beach Point (table 13 and fig. 10b). The concentration of 9,000 μg/L of 1,1,2,2-tetrachloroethane, found in the sample from well 33B at Beach Point, was the maximum concentration observed among the 87 samples collected in the Canal Creek area (tables 12 and 13). Less 1,1,2,2-tetrachloroethane (1,300 μg/L) was found in well water from 33A, which is screened at a shallower depth in the same cluster as 33B. The concentrations of 1,1,2,2-tetrachloroethane are significantly higher in samples from wells 33A and 33B than those in all other surficial-aquifer samples (fig. 10a and 10b). In addition, water from well 33B was the only sample from the surficial aquifer that had detectable 1,1,2-trichloroethane (80 μg/L).

The maximum chloroform concentration in the surficial aquifer (66 μg/L) also was observed at Beach Point, but at site 32 rather than site 33 (fig. 10b). Samples from 33A and 33B did not contain chloroform; however, the detection limits were higher than usual (<16 and <40 μg/L chloroform) because the samples had to be diluted to analyze for the 1,1,2,2-tetrachloroethane (table 10).

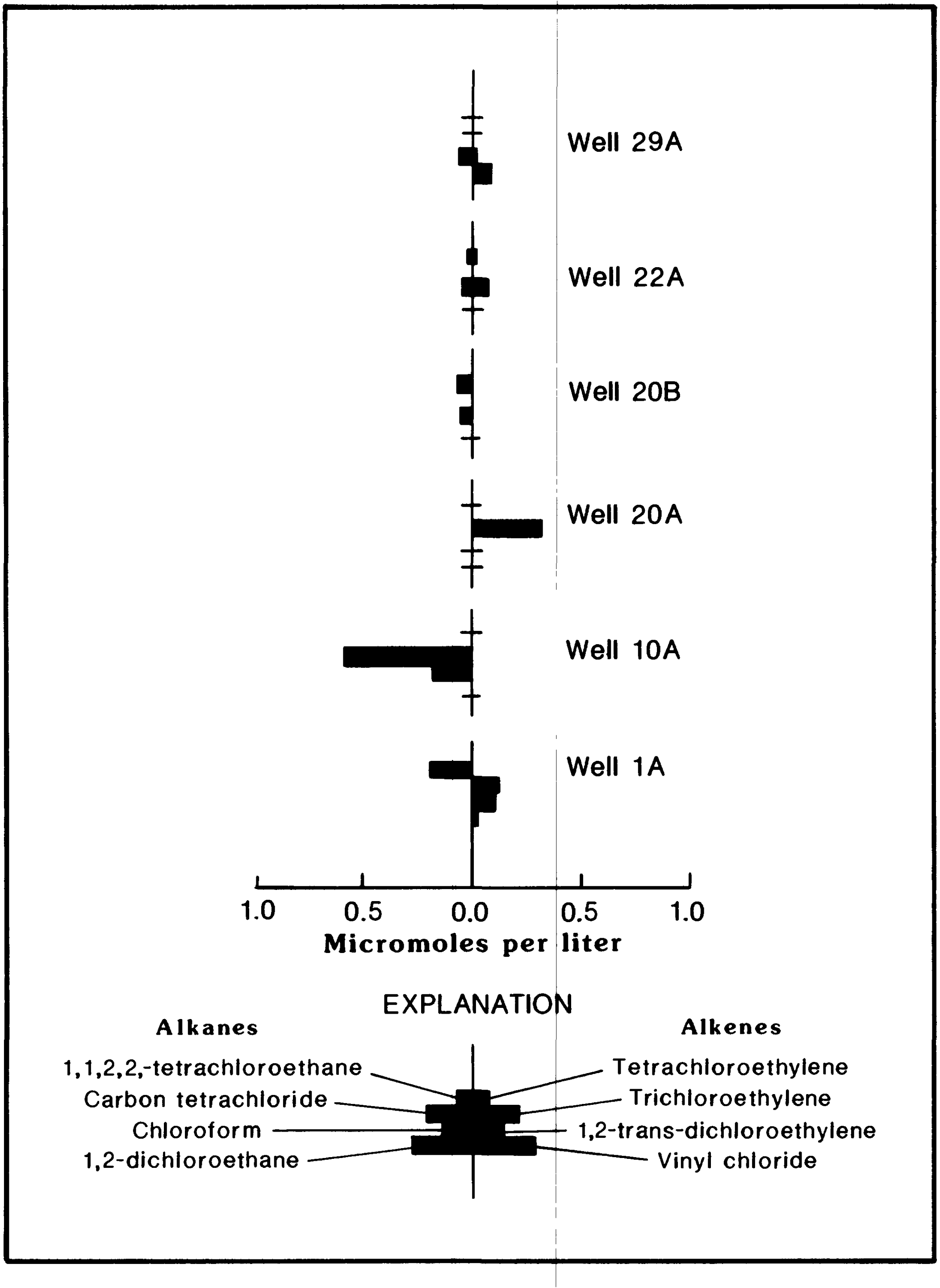


Figure 10a.-- Stiff diagrams showing distribution of specific organic constituents in the surficial aquifer.

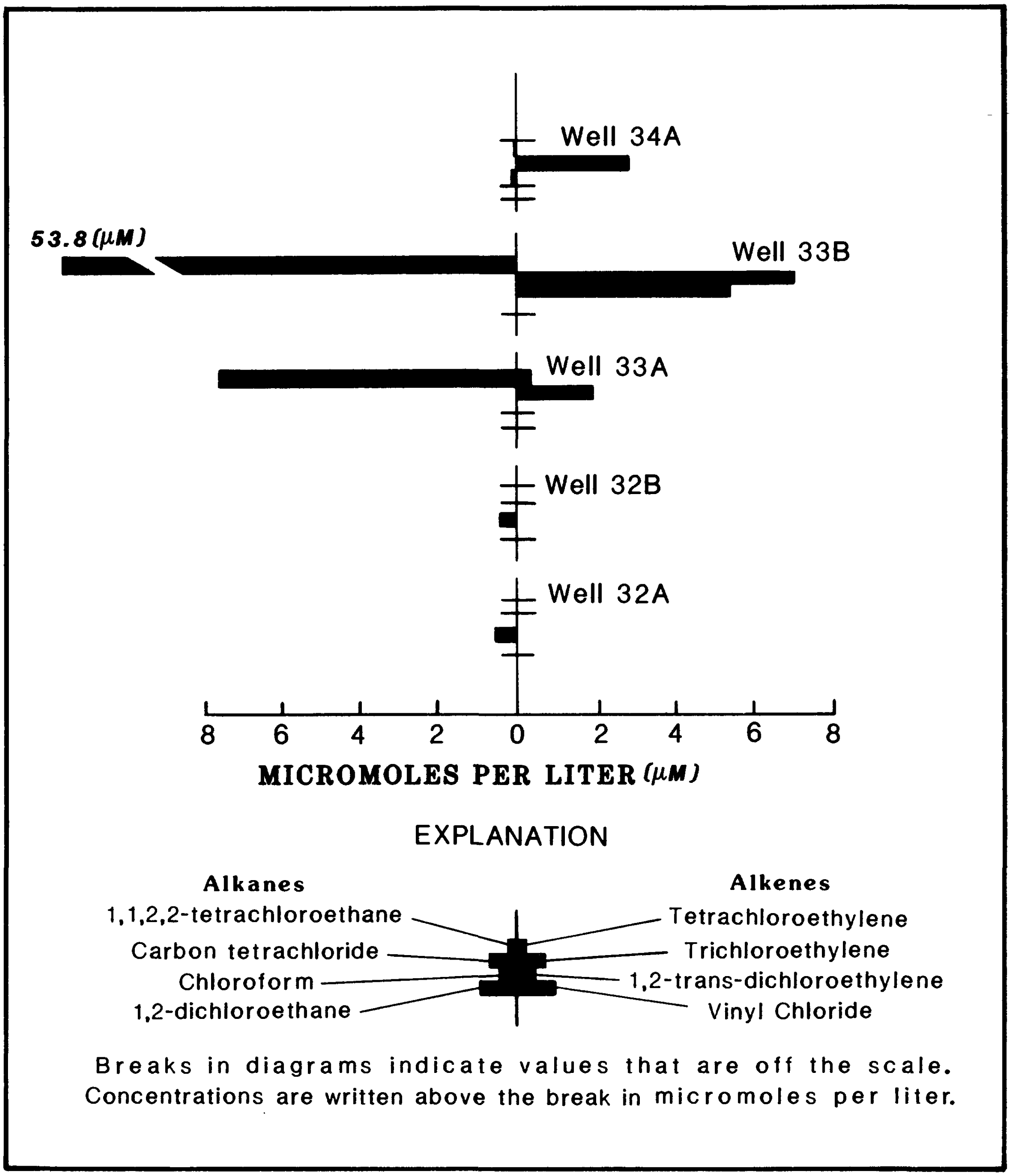


Figure 10b.--Stiff diagrams showing distribution of specific organic constituents in the surficial aquifer at Beach Point.

For the other surficial-aquifer samples, water from wells 1A and 10A had relatively high concentrations of chlorinated alkanes (fig. 10a). The compound 1,1,2,2-tetrachloroethane was the only chlorinated alkane present in the ground water at 1A (fig. 10a) and in the underlying Canal Creek aquifer at this site (pl. 3). Concentrations of 1,1,2,2-tetrachloroethane were higher in water from well 1A (31 μg/L) than in water from the deeper wells 1B and 1C. Carbon tetrachloride was present in one sample, from well 10A, at a concentration of 88 μg/L (table 13). Carbon tetrachloride and chloroform were the only organic contaminants found in this water-table well.

Probable Sources

Primary sources are the only known sources for 1,1,2,2-tetrachloroethane and carbon tetrachloride because higher chlorinated compounds that could degrade to these constituents were not disposed of in the study area. However, both primary and secondary sources are possible for chloroform and 1,2-dichloroethane, and only secondary sources are known for methylene chloride, 1,1,2-trichloroethane, and 1,1-dichloroethane. Secondary sources are discussed in the section on degradation reactions.

1,1,2,2-tetrachloroethane

Two major uses of 1,1,2,2-tetrachloroethane in the Canal Creek area could have introduced this solvent to the ground water: (1) decontamination and equipment cleaning, and (2) protective-clothing impregnating. The decontaminant DANC, which is an abbreviation for Decontaminating Agent, Non-Corrosive, consisted of an organic chlorinating compound mixed with 1,1,2,2-tetrachloroethane. The DANC solutions typically contained 90 to 95 percent by weight of this solvent, and the solution ingredients were not mixed until ready for use (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). The 1,1,2,2-tetrachloroethane commonly was mixed with 1,3-dichloro-5,5-dimethylhydantoin as the chlorinating agent in DANC but also was used in solution with other compounds. DANC was used to decontaminate mustard, lewisite, the nerve agent VX, and other agents that can be destroyed by chlorination. Production of these agents and filling of munitions might have required the use of DANC for cleaning spills and equipment. Manufacturing plants were largely concentrated in the area by the West Branch Canal Creek where 1,1,2,2-tetrachloroethane was found in the ground water at many sites (pls. 1 and 3).

Mustard and impregnite (CC2) manufacturing were two of the most extensive operations in the APG area (pl. 1) and produced large amounts of waste that discharged to or were dumped in the swamp by the West Branch Canal Creek. During WW2 mustard production, both 1,1,2,2-tetrachloroethane and carbon tetrachloride were often used in decontaminating and cleaning solutions. These solvents would have been discharged with the production wastes. The WW2 mustard plant operated from 1940-43, and the quantity of mustard produced was reported to be 34,803,927 lb (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). About 400,000 lb of mustard also was produced after WW2 in late 1949 to early 1950. Sewer wastes discharged to the swamp a short distance from building 644 (pl. 1). Solid materials, including gummy mustard from bad batches, were probably dumped in the nearby swamp (Gary Nemeth, U.S. Army Environmental Hygiene, written commun., 1986).

During impregnite manufacturing, filters and other equipment commonly were cleaned with 1,1,2,2-tetrachloroethane. The amount of 1,1,2,2-tetrachloroethane used was approximately 9 to 10 percent of the quantity of CC2 manufactured. The total WW2 production of CC2 was 2,897,582 lb (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986), requiring about 289,700 lb of the solvent during this time alone. The production plant in the building-87 complex discharged wastes to the upper part of the West Branch Canal Creek, whereas the plant in building 103 discharged wastes to the lower part (pl. 1).

The CC2 manufacturing at the building-87 complex, or the pilot plant, is a more likely source than mustard production for the 1,1,2,2-tetrachloroethane found in the ground water at sites 17, 21, and 30. Mustard manufacturing and disposal occurred farther downgradient from the pilot plant. Both CC2 and mustard production could be sources of this chlorinated alkane at sites 25, 26, 27, and 28 (pl. 3). The upper confining unit crops out in the area of sites 25, 26, 27, and 28 near the West Branch Canal Creek. Thus, a clay bed is not present near the surface to impede movement of contaminants into the aquifer.

In the pilot plant at building 87, various nerve agents also have been produced, including VX. The solvent 1,1,2,2-tetrachloroethane could have been used in decontaminating and cleaning, contributing to the concentrations found at sites 17, 21, and 30.

Site 18, where 1,1,2,2-tetrachloroethane was present in high concentrations in the ground water (pl. 3), is downgradient from a disposal pit (pit #2 on pl. 1). Agents from a chemical laboratory, including mustard, were buried in the pit (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986) and may have been decontaminated with DANC. In addition, munitions were filled with miscellaneous toxic chemicals in buildings near site 18 (pl. 1), and these plants could have been another source of contaminants. Although historical records do not mention the use of 1,1,2,2-tetrachloroethane in these filling plants, the solvent could have been used for cleaning equipment and to control spills.

The inorganic and organic constituents found in the ground water at site 13 are similar to those found at site 18, suggesting that the source of contamination for the two sites may be the same. Sodium and chloride concentrations were anomalously high at both sites (pl. 2), and 1,1,2,2-tetrachloroethane was the major organic contaminant (pl. 3). Additional data are needed to verify this hypothesis, however.

The solvent 1,1,2,2-tetrachloroethane was selected as having the best characteristics for binding impregnite (CC2) to protective clothing (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). In the process for impregnating clothing, approximately 85 percent of the solution was solvent. The first production-size impregnating unit was located in building 103 where CC2 also was manufactured (pl. 1). Wastes from this impregnating plant, which began operation in 1934, would have been another major source of 1,1,2,2-tetrachloroethane in the ground water near the West Branch Canal Creek.

Another impregnating plant that was operated in building 73 discharged wastes through sewerlines to the East Branch Canal Creek (pl. 1). Storage tanks of 1,1,2,2-tetrachloroethane were located at the western side of the building, and some drums of the solvent were stored on a concrete platform along the southern side of the building (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Solvent was received by tank cars or in 55-gal drums at the platform. About 1,024,000 lb of 1,1,2,2-tetrachloroethane was used during the 278 days that the plant operated in 1942. Ideally, only small quantities of waste should have been generated by the impregnating plant. However, the 1,1,2,2-tetrachloroethane rapidly corroded the aluminum used to construct the mixing tanks and the solvent-recovery system. During the final months of operation, the solvent-recovery rate was only about 36 percent (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Much of the lost solvent was discharged to the sewer with cooling water, although some probably was lost as vapor to the air. On one occasion, the failure of a mixing tank released 2,000 gal of impregnating solution into the sewer (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). A large part of the solvent released from this plant would have been in liquid form as raw product instead of in solution in water.

This impregnating plant probably was the source of the 1,1,2,2-tetrachloroethane detected in the surficial and Canal Creek aquifers at site 1 and in the Canal Creek aquifer at sites 7 and 8 (pl. 3 and fig. 10a). Two factors would have enhanced the movement of the solvent into the ground water. First, a dam constructed in WW2 (pl. 1) created a reservoir in the creek at the sewer-discharge point. This reservoir would have promoted sinking of the heavy raw-product form of the solvent to the streambed near site 1 and reduced loss of the solvent by volatilization. Secondly, the Pleistocene paleochannel had eroded the upper confining unit at site 1 (fig. 3) so that migration of the solvent into the surficial aquifer and the Canal Creek aquifer was not impeded by a clay layer. Water at site 8, which is downgradient of sites 1 and 7, showed the highest concentrations of 1,1,2,2-tetrachloroethane in this area, indicating that this contaminant moved with time from site 1 to site 8. High concentrations of 1,1,2,2-tetrachloroethane were detected in samples from the standby well 23F near site 1 (pl. 1) between December 1983 and March 1985 (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988). This contamination may have been part of the plume that has since migrated toward site 8. The heavy ground-water pumping during 1950-68 is believed to have created a cone of depression and slowed movement of the contaminants during this period.

Ground water from site 6 near the East Branch Canal Creek also contains 1,1,2,2-tetrachloroethane, but directions of ground-water flow show that it is unlikely that contamination at site 6 is related to contamination at sites 1 and 8 (fig. 4). Especially during the period of heavy pumping, ground-water flow northward from site 1 would have been improbable. The source of the solvents probably was located to the northwest of site 6, but additional data are needed to identify this source.

The high concentrations of 1,1,2,2-tetrachloroethane in the Beach Point samples (fig. 10b) most likely are also related to clothing-impregnating activities. During 1943, mobile plants were moved to Beach Point, and experimental studies of the CC2-impregnating process were conducted. One plant consumed about 100,000 lb of 1,1,2,2-tetrachloroethane during field testing (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Most wastes were discharged to the Bush River or Kings Creek, and wastes from the laboratory sinks were discharged to small pits dug next to the mobile units. Additionally, solvent spills could have released 1,1,2,2-tetrachloroethane to the environment, and less than 7 ft of clay that could impede downward movement of contaminants overlie the surficial aquifer at Beach Point.

An extremely high concentration of 1,1,2,2-tetrachloroethane (5,300 µg/L) also was found in water from well 39A located in the salvage yard. Spills or leaks of solvent from containers are likely to have occurred during temporary storage and handling of chemicals during the time the salvage yard operated. Some drums that contain unknown liquids still are present in the area.

Carbon tetrachloride

Carbon tetrachloride contamination could be related to its use as (1) a decontaminating and cleaning agent, (2) a raw material in impregnite (CC2) manufacturing, (3) a solvent in experiments of the clothing-impregnating process, and (4) a raw material in chloroacetophenone (CN) manufacturing. The plants that used carbon tetrachloride for production of chemicals were located near the West Branch Canal Creek, but documentation on areas where this solvent was used for decontaminating and cleaning is more difficult to find. Chlorine or bleach dissolved in carbon tetrachloride were common decontaminating agents.

Chlorine in solution with carbon tetrachloride was used often to decontaminate equipment and spills during WW2 mustard manufacturing (pl. 1). About 110 gal of carbon tetrachloride were needed to decontaminate a mustard reactor after a "wild run" (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). If the sensitive conditions required for the mustard reaction were not controlled properly, a "wild run" occurred resulting in the formation of a gummy mass of mustard from sulfur precipitation. The carbon tetrachloride and mustard commonly were washed into the sewer that discharged to the West Branch Canal Creek or were dumped in the marsh (pl. 1).

One of the first processes used to manufacture impregnite involved washing the reaction mixture with either carbon tetrachloride or alcohol. This process was used on a small scale during 1926-31 in the experimental-plants area, probably in building 643 or 622 (pl. 1). Wastes were discharged to the nearby swamp and creek (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Building 622 was located near sites 27 and 28 where high concentrations of carbon tetrachloride were found in the ground water.

The mobile plants that were operated during WW2 to study the clothing-impregnating process used carbon tetrachloride in some experiments. At least some of these tests were performed in and near building 103 and could be another source of carbon tetrachloride at sites 26, 27, and 28 (pl. 1).

The tear gas CN commonly was mixed with other compounds. One mixture produced was CNB which contained 10 percent CN, 45 percent benzene, and 45 percent carbon tetrachloride; another mixture contained 38.5 percent chloroform and 38.5 percent chlorpicrin (CNS). The CN plant in building 58 (pl. 1) produced more than 1.5 million lb of CN during 1941-44, and much of this CN was used to form CNB and CNS. Raw materials, including carbon tetrachloride, were stored in tanks near the building, and 55-gal drums and 1-ton containers of raw materials and finished products were stored temporarily in open areas around the plant (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). The main sewer where wastes and spills were discharged was a 12- or 15-in.-diameter concrete line extending southward from the plant (pl. 1). The acidic wastewaters dissolved the bottom of the sewerline, and the problem was not discovered until 1942. The sewer was then replaced with a terra-cotta line (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Most probably, the carbon tetrachloride contamination in the Canal Creek aquifer at site 26 resulted largely from the CN wastes seeping through the concrete sewer and from spills on the land surface. Westward ground-water flow (fig. 4) also could have spread carbon tetrachloride to sites 27 and 28. In addition, operating procedures at the plant specified that CN that precipitated from leaky containers was to be buried with soda ash at least 100 ft from the building. Thus, buried CNB mixtures could be an additional source of carbon tetrachloride at sites 27 and 28 because burial was most likely in the swamp west of the plant (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Again, the lack of a near-surface confining bed in this area would have increased the susceptibility of the ground water to contamination.

Activities in the pilot plant of the building-87 complex (pl. 1) were the most likely source of carbon tetrachloride found at sites 17, 21, and 30. Since the pilot plant was constructed in 1942, numerous activities have taken place there that could have required the use of chlorinated solvents, including production of CC2, pilot production of chemicals, detoxification of chemical agents, and filling of munitions with chemical agents. One reference to carbon tetrachloride was found in the manufacturing procedure for the chemical agent GB, or isopropylmethylphosphonofluoridate. Carbon tetrachloride was used in the product column cooler. Building 84, which is located on the eastern side of the pilot plant (pl. 1), was used to fill munitions and degrease bomb bodies during and after WW2. Mustard and CNB were two agents used in the munitions filling. Spills of CNB could have introduced carbon tetrachloride into the ground water. Carbon tetrachloride could also have been used to decontaminate spills and equipment in both the pilot plant and building 84.

Near the East Branch Canal Creek, the impregnating plant in building 73 and the munitions-filling plants (pl. 1) could have been a source of carbon tetrachloride. Only water from well 8B showed a high concentration of this solvent in the Canal Creek aquifer underlying the eastern portion of the study area. The carbon tetrachloride could be associated with the plume of 1,1,2,2-tetrachloroethane from the impregnating plant; however, historical records do not indicate use of carbon tetrachloride in the plant. Many toxic chemicals, including mustard, white phosphorus, CN, and chlorpicrin, were handled at the second and third filling plants. Carbon tetrachloride may have been used in decontamination. Wastes from the filling plants discharged to the East Branch Canal Creek (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Another possible source could have been derived from the use of carbon tetrachloride as a metal degreaser in the garage and hangars near the East Branch Canal Creek.

During WW2, another pilot-plant facility was constructed near Kings Creek (pl. 1). Site 10 (fig. 2), where carbon tetrachloride was detected as the major contaminant in the surficial aquifer, is located near these buildings. Nitrogen mustard may have been produced there during the early 1940's; otherwise, little is known about activities at this plant (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Chloroform

The CN plant in building 58 (pl. 1) required chloroform as a raw material to make CNS. The CNS solution contained 38.5 percent chloroform. Chloroform was received in steel drums that each held approximately 650 lb (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). This plant, which had a leaky sewer, most likely contributed both the chloroform and carbon tetrachloride to the ground water at sites 26, 27, and 28. Chloroform also can have a secondary source from degradation reactions.

1,2-dichloroethane

Although 1,2-dichloroethane can be formed from degradation of other compounds, the anomalously high concentration in well 16A suggests a primary source of the solvent in this area. One possible source could be from the filling of FM (titanium tetrachloride) smoke munitions. Although FM munitions usually contained only titanium tetrachloride, the filling for some training munitions was mixed partly with 1,2-dichloroethane because of the high cost of titanium tetrachloride (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Some FM was stored in drums for use as screening smoke instead of being used as filling in munitions. Building 84 on the eastern side of the pilot plant was a munitions-filling plant during WW2. Mustard, phosgene, CN agents, and some smoke materials are known to have been handled in this building.

Chlorinated Alkenes

Distribution

Canal Creek aquifer

Trichloroethylene and 1,2-trans-dichloroethylene were the most prevalent alkenes in the Canal Creek aquifer and were detected in 30 and 28 of the samples, respectively (table 12). Vinyl chloride was found in 15 samples, and tetrachloroethylene and 1,1-dichloroethylene were the least commonly detected chlorinated alkenes. Concentrations of 1,1-dichloroethylene, which were much lower than concentrations of the other chlorinated alkenes (table 12), were not significantly greater than the detection limit of 1.9 μg/L (table 10). The distribution of these alkenes, except for 1,1-dichloroethylene, is shown on plate 3.

The trichloroethylene concentration of 1,800 µg/L, which was detected in the sample from well 8B, was the maximum concentration observed from the 59 wells sampled in the Canal Creek aquifer (table 12). Trichloroethylene concentrations were also high (100 µg/L or greater) at site 1 near the East Branch Canal Creek, at sites 16, 17, and 27 along the West Branch Canal Creek, and at site 39 in the salvage yard (pl. 3).

The median 1,2-trans-dichloroethylene concentration of 60 µg/L was greater than the median observed for the other chlorinated alkenes. The maximum 1,2-trans-dichloroethylene concentration was found in the ground water at well 1B (table 12). Elevated concentrations of 1,2-trans-dichloroethylene and trichloroethylene were found in some of the same samples from the Canal Creek aquifer, including sites 1, 8, 16, and 39 (pl. 3). In addition, high concentrations of 1,2-trans-dichloroethylene were present at site 7, which lies on a flow path between sites 1 and 8, and at sites 4, 5, 22, and 23 near the East Branch Canal Creek.

The maximum concentration of vinyl chloride for the Canal Creek aquifer was found at well 16A near the West Branch Canal Creek (table 12). Except for the sample from well 16A, vinyl chloride was observed in the Canal Creek aquifer only at sites located near the East Branch Canal Creek (sites 1, 4, 5, 7, 8, 22, 23, and 29 in pl. 3). Unlike vinyl chloride, tetrachloroethylene was observed in the Canal Creek aquifer only at sites located near the West Branch Canal Creek. These sites include 16, 25, 26, and 28 (pl. 3).

Some general comparisons can be made between the distribution of chlorinated alkanes and chlorinated alkenes in the Canal Creek aquifer. Chlorinated alkene concentrations showed that these compounds were the dominant organic contaminants at sites near the East Branch Canal Creek, such as sites 1, 4, 5, 7, 20, and 22 (pl. 3). In contrast, the chlorinated alkanes generally appeared in the highest concentrations at sites located along the West Branch Canal Creek and including the area surrounding the pilot plant. Two exceptions include the ground water from well 16A and at site 8 that contained high concentrations of chlorinated alkanes and alkenes. Neither chlorinated alkanes nor alkenes were observed at the farthermost downgradient wells in the Canal Creek aquifer. The total organic halogen concentrations in ground water at these downgradient sites (sites 3, 9, 12, and 11) were less than 5 µg/L (table 10).

The vertical distribution of both types of aliphatic compounds was characterized mainly by a decrease in concentration with depth at each well cluster. Vertical changes in the alkane concentrations were discussed in a preceding section. For well clusters 1, 16, 17, 22, 27, 28, and 39, the concentrations of chlorinated alkenes were lower in the deepest well in the Canal Creek aquifer (pl. 3). The alkene concentrations were higher in the deep wells only at sites 6 and 7. The vertical distribution was variable at clusters 8 and 25 (pl. 3).

Surficial aquifer

Trichloroethylene, which was the dominant chlorinated alkene found in the surficial aquifer, was present in 11 samples (table 13). The trichloroethylane concentration in five of these samples can be seen on figures 10a and 10b; trichloroethylene also was present in low concentrations in samples from wells 9A, 29A, 32A, 32B, 35A, and 36A (table 10). Concentrations of 1,2-trans-dichloroethylene, tetrachloroethylene, and vinyl chloride were detected in six or fewer of the samples. The concentration of 1,1-dichloroethylene was below the detection limit in all 18 samples collected from the surficial aquifer. Samples from wells 8A, 5A, 10A, 19A, and 20B did not contain any detectable chlorinated alkenes.

Some ground-water samples from Beach Point showed significantly higher detected concentrations of trichloroethylene, 1,2-trans-dichloroethylene, and tetrachloroethylene than did the other samples from the surficial aquifer (figs. 10a and 10b). The maximum concentration of trichloroethylene (940 μg/L) was found in the sample from well 33B at Beach Point, and high concentrations of trichloroethylene also were observed in samples from wells 33A and 34A (fig. 10a). The maximum concentration of 1,2-trans-dichloroethylene (520 μg/L) also was found at well 33B at Beach Point, whereas the maximum concentration of tetrachloroethylene (64 μg/L) was found in the sample from well 33A at the same site.

Although the concentration of tetrachloroethylene was below the detection limit in the sample from well 33B, some could be present in the ground water because the sample was diluted in the laboratory for analysis and consequently the detection limit for tetrachloroethylene was raised to 75 μg/L (table 10). In addition, vinyl chloride was not detected in the Beach Point samples, but the laboratory detection limits again were high for the samples from site 33 (table 10).

In addition to the Beach Point samples (fig. 10b), samples collected from the surficial aquifer near the East Branch Canal Creek showed relatively high concentrations of chlorinated alkenes (figs. 2 and 10a). The sample from well 20A had a trichloroethylene concentration of 41 μg/L, and the sample from well 1A had a concentration of 11 μg/L 1,2-trans-dichloroethylene. Trichloroethylene was the only organic contaminant detected at well 20A. Tetrachloroethylene was detected in a sample from well 22A at a low concentration of 4.2 μg/L, and vinyl chloride was found in samples from wells 1A and 29A in low concentrations (1.6 and 6.4 μg/L, respectively).

Concentrations of chlorinated alkenes generally were lower in the surficial aquifer than the concentrations observed in the underlying Canal Creek aquifer at the same sites (pl. 3 and fig. 10a). For example, the 1,2-trans-dichloroethylene concentration in the sample from well 1A was 11 μg/L, whereas concentrations were as high as 1,200 μg/L (sample from well 1B) in the Canal Creek aquifer at this site.

Probable Sources

Probable primary sources of the chlorinated alkenes are discussed in this section, whereas secondary sources are discussed in the section on degradation reactions. Some primary sources are identified for tetrachloroethylene, trichloroethylene, and vinyl chloride.

Tetrachloroethylene

During the WW2 testing of the clothing-impregnating process, tetrachloroethylene was used in experiments. Some tests were performed in building 103 (pl. 1), and some were performed using the mobile impregnating units. The tetrachloroethylene observed in the Canal Creek aquifer at sites 25, 26, and 28 could have resulted from these experiments. Tetrachloroethylene also was found in the ground water at Beach Point (site 33). Mobile impregnating units are known to have operated in this area during 1943, although it is not known if tetrachloroethylene was used in any of the tests. Although other references to tetrachloroethylene have not been found in historical records, it may have been used as a degreaser on equipment.

Trichloroethylene

Trichloroethylene was used mostly as a degreaser on equipment and metal parts. Therefore, sources for this solvent are widespread, including any of the manufacturing plants, munitions-filling plants, machine and maintenance shops, and the airfield. Information on the machine and maintenance shops has shown that trichloroethylene is the chlorinated solvent that has been used most commonly since WW2 (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

The pilot plant near the West Branch Canal Creek is one likely source area for the trichloroethylene found at nearby sites, such as at sites 16, 17, and 30 (pl. 1). Trichloroethylene was handled at the plant for several purposes during production of methyldichlorophosphine (SW), which was an intermediate compound for manufacturing nerve agents. Production of SW occurred during the 1950's as part of pilot manufacturing of the nerve agents GB and VX. The major components of the plant were constructed outside to the south of the main building in the 87 complex because of safety considerations for workers. Trichloroethylene was circulated through the recycling columns for cleaning, and the solvent was used in testing the final purification system. Because SW is very reactive with water or water vapor in the air, SW was drained into trichloroethylene when the production system was emptied for cleaning or repairing (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). The method of waste disposal is not known; however, operating procedures indicated that chemical spills should be flushed into the sewer with large amounts of water. The main sewerline extends westward from the pilot plant and slightly south of site 16 toward the creek.

Munitions filling also occurred in the pilot plant and in building 84 near the pilot plant (pl. 1). Cleaning and degreasing of the metal parts of the munitions probably were done using trichloroethylene at least occasionally (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Metal parts including bomb bodies were degreased in building 84 between WW2 and the mid-1960's.

The first, second, and third filling units could have been a source of trichloroethylene for sites near the East Branch Canal Creek (sites 1, 5, 7, 8, and 20). Wastes from these plants generally discharged to sewers leading into this branch of the creek.

Three major machine and maintenance shops could have contributed large amounts of solvents to ground water in the area near both branches of Canal Creek by spills or discharge of wastes into the sewer system. These buildings include (1) building 103, which was a machine shop between WW1 and WW2; (2) the building-101 complex, which operated during and after WW2; and (3) building 88, which operated from 1922 until the mid-1960's (pl. 1). The period of greatest activity in these three shops was during manufacturing of metal parts for munitions during WW2. Building 88 was the main shop after WW2. During the mid-1960's, the production-type shop activities were moved to building 60, which operated until 1975 (pl. 1). Although present hydraulic-head data for the Canal Creek aquifer (fig. 4) indicate that flow directions are mainly toward the West Branch Canal Creek from these machine shops, the heavy pumping that occurred until 1968 probably would have caused ground-water contaminants to flow toward sites 1, 20, and 22. High concentrations of trichloroethylene and possible degradation products such as 1,2-trans-dichloroethylene are found at these sites (pl. 3).

Degreasing solvents used at the airfield probably were disposed of through the sewer system until recent times (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). The sewer discharged to the adjacent East Branch Canal Creek, and the wastes could have provided another source for the trichloroethylene found at site 1. Solvents from the hangar and motorpool garage located west of site 6 could be sources of the trichloroethylene found in the ground water at this site.

Because of the widespread use of trichloroethylene upgradient of sites 1, 7, and 8, the chlorinated alkenes observed along this flow path might be unrelated to the 1,1,2,2-tetrachloroethane, which probably was derived from the clothing-impregnating operations in building 73 (pl. 1). Trichloroethylene and its degradation products, including 1,2-trans-dichloroethylene and vinyl chloride, were found in high concentrations at these sites (pl. 3). Records of the clothing-impregnating operations did not indicate use of trichloroethylene.

The sand pit located directly north of site 23 could be another source of trichloroethylene (pl. 1). Very little information has been found on the materials placed in this pit or on the period it was used. Sludges from impregnite manufacturing are thought to have been dumped in this pit (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986); however, the chlorinated alkanes which were raw materials for the impregnating process were not observed in ground water at site 23. Chlorinated alkenes were the only organic compounds found at this site.

Spills or leaks from chemical containers handled in the salvage yard are the only known source of contamination near site 39. A partly filled drum near site 39 has a label indicating that it originally contained trichloroethylene. Because significant concentrations of volatile organic compounds were detected in the salvage yard only in the samples from site 39, the contamination at the salvage yard may be localized.

Vinyl chloride

The only known primary source of vinyl chloride is from lewisite production. Lewisite was manufactured in the experimental-plants area (buildings 642 and 644) in 1925 and again from 1940-43 (pl. 1). Vinyl chloride was a by-product of the process. Analyses of crude lewisite reportedly showed the presence of approximately 3 percent vinyl chloride. Vinyl chloride dissolved in the crude product would have been removed during distillation. Liquid wastes, including bad batches of lewisite, were discharged to the West Branch Canal Creek, and solid wastes probably were dumped or buried in the swamp (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). However, vinyl chloride was not observed in any samples from the wells located near the experimental-plants area (pl. 3).

Aromatics

Distribution

Canal Creek aquifer

Aromatic compounds were the least common organic contaminants in the Canal Creek aquifer. Of the 59 samples collected in this aquifer, ethylbenzene was detected in 18 samples; chlorobenzene and toluene were detected in 8 samples; and benzene was present in 5 samples (table 12).

Although ethylbenzene was the most widely distributed aromatic compound, concentrations ranged only from 1.0 to 9.1 μg/L. These low concentrations probably are not significant because ethylbenzene is a common laboratory contaminant (table 11). For the replicate samples, ethylbenzene often was detected in one sample but not the other (table 10). The same problems existed for toluene, which was detected in concentrations of only 1.6 to 7.5 μg/L (table 12).

Chlorobenzene and benzene were detected in higher concentrations than were the other aromatics. The greatest concentrations of chlorobenzene were found in samples from wells 16A and 26B (table 10), both of which are located near the West Branch Canal Creek (fig. 2). Well 26B contained the maximum concentrations of both benzene (70 μg/L) and chlorobenzene (39 μg/L) in the Canal Creek area (table 12). The benzene concentration also was high (40 μg/L) in the sample from well 8B; however, benzene concentrations were below the detection limit in samples from wells 8C and 8D, which are in the same well cluster as well 8B in the Canal Creek aquifer (table 10).

Surficial aquifer

In the surficial aquifer, chlorobenzene was the only aromatic compound detected in concentrations significantly above the detection limits (table 13). Chlorobenzene concentrations were 14 μg/L in a sample from well 9A and 22 μg/L in a sample from well 29A. Chlorobenzene was the major organic contaminant in both of these isolated water-table wells.

Probable Sources

Benzene

The production of CN in building 58 (pl. 1) probably was the major source for benzene found in the ground water at well 26B. The reaction of benzene with chloroacetylchloride was used to produce CN, and the CN was then removed from the benzene by fractional distillation. When the mixture CNB, which contained 45 percent benzene, was manufactured, distillation was not needed. Benzene was received in tank cars and stored in tanks directly north of site 26. Benzene was pumped to smaller tanks for use inside the plant. The production of CN was inefficient, sometimes requiring benzene in quantities 100 percent greater than theoretical (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Although some benzene would have been lost as vapor, much was discharged with the wastewaters. Spills, leaky storage tanks, and the leaky sewerline probably have released benzene to the ground water.

Production of the arsenical diphenylchloroarsine (DA) required the use of benzene to control foaming during reactions. In the early 1920's and 1930's, this arsenical was manufactured south of site 26 in the experimental-plants area (pl. 1). Benzene was stored in tanks in the southern part of the experimental-plants area by building 643. Open sewers carried wastes to the swamp by Canal Creek (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986).

Benzene also was used in reaction solutions for the production of a type of nitrogen mustard called tris(2-chloroethyl)amine. This mustard was manufactured on an experimental scale in 1943. The location of the plant is unknown but probably was in the experimental-plants area or in the pilot plant constructed near Kings Creek (pl. 1).

Two possible widespread sources of benzene include (1) the munitions-filling plants and (2) the fuels used at garages, gas stations, and the airfield. Spills of CNB during filling of munitions would have released benzene. Building 84 was used for CNB filling, and ground water at site 16 near this plant contains benzene. The munitions-filling plants, garage, and airfield near the East Branch Canal Creek could have been sources of the benzene found at site 8.

Chlorobenzene

Chlorobenzene was used in the plants for protective-clothing impregnating (Gary Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1986). Quality control of the impregnating process was maintained by checking the concentrations of constituents in the reaction solutions and by checking the impregnite concentration on clothing samples. These analyses required the use of chlorobenzene as a solvent. The impregnating plant in building 73 by the East Branch Canal Creek could have been a source for the chlorobenzene found at site 8. The impregnating unit to the east of site 26 in building 103 could have introduced chlorobenzene into the ground water at this site (pl. 1).

In addition, chlorobenzene was a raw material in the production of the arsenical DA. This plant, which was located in the experimental-plants area, was discussed in the preceding section on benzene.

Chlorobenzene in sample 29A from the surficial aquifer could be derived from material in the fill in which well 29A is partly screened. A chemical laboratory located immediately east of site 9 has been operated from 1942 to the present (1988). The laboratory may have handled chlorobenzene in small quantities as a solvent and could be a source for the low concentrations detected in the surficial aquifer at well 9A.

Geochemical and Physical Reactions

Identification of Possible Reactions from Physicochemical Properties of Organic Constituents

The chlorinated alkanes, chlorinated alkenes, and monocyclic aromatic hydrocarbons that were identified as ground-water contaminants in the Canal Creek area generally can be characterized as immiscible with water. However, these organic compounds are moderately to highly soluble in water (table 14) relative to the low concentration limits set for drinking water (tables 12 and 13). They can exist in water-saturated sediments as a free product or dissolved in water. Because all the observed organic contaminants are volatile, they also can exist in the vapor phase in the unsaturated zone. The physicochemical properties of the organic compounds (table 14) largely control the reactions that could occur in the ground water, thereby affecting the migration and distribution of the individual chlorinated aliphatic and aromatic organic compounds.

Density

The density of organic compounds greatly affects the movement of free product into the ground water. Much of the waste discharged or dumped during past production-related activities in the Canal Creek area would have included dense chlorinated hydrocarbons as free product, such as 1,1,2,2-tetrachloroethane, trichloroethylene, and carbon tetrachloride. Solvent spills and use of decontaminants, such as DANC, also could have released free product to the environment. The organic contaminants detected in the ground water of the Canal Creek area include dense chlorinated hydrocarbons, characterized by a density greater than that of water (1.00 gram per cubic centimeter). Only four of the less widespread contaminants (vinyl chloride, benzene, toluene, and ethylbenzene) have low densities (table 14).

From a series of laboratory experiments, Schwille (1988) demonstrated that the high density of chlorinated solvents causes the free product to move downward at a faster rate than water through the unsaturated zone to the capillary fringe or to a low-permeability layer. Downward movement may then cease if the amount of free product is small. However, if a large solvent spill occurs, enough pressure head may develop to allow the free product to penetrate the water-bearing zone or the low-permeability layer. The required pressure increases as the pore size decreases until the pore size becomes so small that vertical movement ceases (Schwille, 1988).

Table 14.--Chemical formulas and physicochemical properties of organic compounds detected in ground water in the Canal Creek area

[Density, vapor pressure, and solubility data are for a temperature of 20 degrees Celsius (°C) unless otherwise noted; K_{ow} is the octanol-water partition coefficient; K_{oc} is the organic carbon sediment-water partition coefficient; g/mole, grams per mole; g/cm^3, grams per cubic centimeter; mm Hg, millimeters of mercury; mg/L, milligrams per liter; mL/g, milliliters per gram]

Compound	Formula	Molecular[a] weight (g/mole)	Density[a] (g/cm^3)	Vapor[a] pressure (mm Hg)	Solubility[a] (mg/L)	log K_{ow}	K_{oc} (mL/g)
Chlorinated alkanes:							
Carbon tetrachloride	CCl_4	153.8	1.59	90	800	[a]2.64	[b]232
Chloroform	$CHCl_3$	119.4	1.49	160	8,000	[a]1.97	[c]44
Methylene chloride	CH_2Cl_2	84.9	[f]1.33	349	16,700/25 °C	[d]1.25	[b]25
1,1,2,2-tetrachloroethane	$C_2H_2Cl_4$	167.9	1.60	5	2,900	[d]2.56	[c]118
1,1,2-trichloroethane	$C_2H_3Cl_3$	133.4	1.44	19	4,500	[d]2.17	[c]56
1,2-dichloroethane	$C_2H_4Cl_2$	99.0	1.25	61	8,690	[d]1.48	[c]14
1,1-dichloroethane	$C_2H_4Cl_2$	99.0	1.17	180	5,500	[d]1.79	[c]30
Chlorinated alkenes:							
Tetrachloroethylene	C_2Cl_4	165.8	1.63	14	150/25 °C	[a]2.60	[b]303
Trichloroethylene	C_2HCl_3	131.5	1.46	60	1,100/25 °C	[d]2.29	[b]152
1,1-dichloroethylene	$C_2H_2Cl_2$	96.9	1.22	500	[d]400	[d]1.48	[c]65
1,2-trans-dichloroethylene	$C_2H_2Cl_2$	96.9	1.26	200/14°C	600	[d]1.48	[c]59
Vinyl chloride	CH_2CHCl	62.5	0.91/15°C	2,660/25°C	1.1/25 °C	[d]0.60	--
Aromatics							
Benzene	C_6H_6	78.1	0.88	76	1,780	[a]2.13	[e]83
Chlorobenzene	C_6H_5Cl	112.6	1.11	8.8	500	[a]2.84	[b]318
Toluene	$C_6H_5CH_3$	92.1	0.87	22	515	[a]2.69	[b]242
Ethylbenzene	$C_6H_5CH_2CH_3$	106.2	0.87	7	152	[a]3.15	[b]622

[a] Verschueren (1983)

[b] Roy and Griffin (1985, p. 242)

[c] Schwille (1988, p. 130-131)

[d] U.S. Environmental Protection Agency (1979b)

[e] Lyman and others (1982, p. 4-24)

[f] Weast (1983, p. C-372)

Lateral dispersion of the free product is relatively unaffected by ground-water velocity. When the free product intercepts a relatively impermeable layer, the solvent typically will follow the slope of the layer even when it is in a different direction from ground-water flow (Schwille, 1988). The free product will tend to collect in depressions on the impermeable layer.

Not all of the dense free product will necessarily sink to the bottom of an aquifer even in major spills. Instead, part of the product remains in the unsaturated zone as droplets in pore spaces and as films on grain surfaces. Another part remains in the saturated zone as disseminated, irregular-shaped bodies of free product that show no tendency for further movement (Schwille, 1988).

Disseminated free product in the unsaturated zone may be remobilized if infiltrating rainfall or a rising water table causes additional water movement through the soil. The water, which is a stronger wetting agent, will displace the dense organic compounds from their sorption sites. In addition, free product in both the unsaturated and saturated zones can be further transported in aqueous solution. Water moving across pools of free product that collected on impermeable layers and across disseminated free product will partially dissolve the chlorinated organic compounds. Dissolution of disseminated free product can cause release of the organic compounds into the ground water long after the bulk of the contaminant plume has passed.

Once in solution, the chlorinated hydrocarbons typically do not achieve the extreme concentrations necessary to cause density sinking (Schwille, 1988, p. 102). The dissolved organic compound instead moves in the direction of ground-water flow. The concentrations derived from dissolution of free product in an aquifer are partly related to the ground-water-flow velocity. At low velocities, the resulting long contact time between the water and the organic compound allows concentrations to increase. Increased velocities result in decreased aqueous concentrations, but the contaminants spread relatively quickly.

The distribution of organic compounds in the surficial aquifer at Beach Point demonstrates the behavior of dense chlorinated hydrocarbons. The 1,1,2,2-tetrachloroethane and trichloroethylene in the ground water (fig. 10b) probably resulted from spills on the surface during testing of the clothing-impregnating process. Yet, the highest contaminant concentrations were observed in the deepest well installed on Beach Point, well 33B, showing that the dense free products moved downward to at least 67 ft below land surface (table 1). Clay layers that are from 22.2 to 24.0 ft and from 25.2 to 28.0 ft below land surface did not stop vertical movement of the solvents.

In two regions of the study area where large amounts of dense chlorinated hydrocarbons were discharged, a surficial clay that would normally impede sinking of the dense, free products into the Canal Creek aquifer are not present. One area is located where the upper confining unit crops out near the West Branch Canal Creek. Sites 16, 17, 25, 26, 27, and 28 are in the outcrop area, and water samples from these sites contain high concentrations of dense chlorinated hydrocarbons (pl. 3). Free product remaining in the unsaturated zone could still be a source of dissolved solvent to the Canal Creek aquifer in this area.

The second area is near well cluster 1 where a paleochannel had eroded the upper confining unit (fig. 3). The low concentrations of 1,1,2,2-tetrachloroethane observed in the Canal Creek aquifer (pl. 3) and in the surficial aquifer at site 1 (fig. 10a) may have resulted from dissolution of disseminated free product that was left behind as the bulk of this contaminant moved downgradient toward site 8. At site 8, the upper confining unit consists of dense clay that is about 48 ft thick. Thus, the contamination found in the ground water at site 8 must have entered the Canal Creek aquifer upgradient in an unconfined area, such as near site 1.

The 35- to 65-ft-thick clay layer beneath the Canal Creek aquifer, the lower confining unit (fig. 3), seems to have acted as an effective barrier against further vertical sinking of the dense chlorinated solvents into the lower confined aquifer. The 10 wells screened in the lower confined aquifer were uncontaminated (table 10).

Solubility

The mobility in ground water of the individual chlorinated aliphatic compounds and the aromatic compounds is largely controlled by their solubility in water (table 14). The solubility of organic compounds and their tendency to sorb to sediments are interrelated. Highly soluble compounds are distributed more quickly in ground water because their movement is less likely to be retarded by sorption onto sediments than are compounds with low solubility (Vershueren, 1983, p. 8). Water solubility also can indicate the susceptibility of the organic compounds to other transformation processes such as hydrolysis, volatilization, and biodegradation.

The solubility of the volatile organic compounds detected in ground water of the Canal Creek area varies greatly, ranging from 1.1 mg/L at 25 °C for vinyl chloride to 16,700 mg/L at 25 °C for methylene chloride. Highly soluble compounds, such as methylene chloride, are distributed most quickly in ground water. The moderately to highly soluble nature of the volatile organic compounds indicate that they are capable of causing concentrations in ground water that greatly exceed the MCL's established for drinking water. All the volatile organic compounds detected in the Canal Creek area were present in concentrations much lower than their solubility concentrations; however, concentrations did exceed MCL's that have been established for some of the compounds (tables 12 and 13).

Hansch and others (1968) found a linear relation between the aqueous solubility of organic compounds and their octanol-water partition coefficients (K_{ow}). This coefficient is the ratio of the concentration of a compound in the immiscible organic solvent, octanol, to the concentration in an equal volume of water. Thus, compounds with a low K_{ow} (log $K_{ow} < 1$) tend to be more hydrophilic, or more soluble in water. The octanol-water partition coefficients indicate that the organic compounds in ground water of the Canal Creek area are hydrophobic to variable degrees (table 14).

Sorption affinity

For concentrations typically encountered in natural waters, the affinity of organic compounds for the soil or sediment phase can be described by the linear sorption isotherm (Freeze and Cherry, 1979, p. 403; Schwarzenbach and Westall, 1981),

$$s = K_d \, c, \tag{1}$$

where s is the amount of the organic solute adsorbed to the solid phase (in milligrams per kilogram), K_d is the slope of the sorption isotherm (in milliliters per gram), and c is the equilibrium concentration of the organic solute in aqueous solution (in milligrams per liter). The constant K_d is called the distribution coefficient. Laboratory experiments have shown that many organic compounds, including several halogenated hydrocarbons (Chiou and others, 1979; Wilson and others, 1981) and benzene (Rogers and others, 1980), follow a linear adsorption isotherm.

Numerous studies have reported that organic matter in the solid phase is a better sorbent for hydrophobic organic compounds than are mineral surfaces (Lambert, 1968; Chiou and others, 1979; Karickhoff and others, 1979; Schwarzenbach and Westall, 1981). Mineral surfaces, which typically are hydrophilic, bind preferentially to water. In contrast, organic matter in sediments and soils has a pronounced hydrophobic character that would attract nonpolar, hydrophobic organic compounds.

Thus, the distribution coefficient, K_d, has been found to correlate well with the fraction of organic carbon (f_{oc}) in the soil or sediment

$$K_{oc} = K_d / f_{oc} \tag{2}$$

where K_{oc} is the organic carbon sediment-water partition coefficient and f_{oc} is defined as mass organic carbon (in grams) per unit mass dry soil (in grams). Three assumptions are inherent in equation (2) (Roy and Griffin, 1985):

1. Adsorption can be described by a linear isotherm, or in other words, a dilute system exists.
2. The partitioning between the solid and aqueous phase has reached equilibrium.
3. All sorption occurs on the organic matter in the solid phase.

Empirical methods of estimating K_{oc} have been developed on the basis of direct correlations between K_{oc} and either the octanol-water partition coefficient (K_{ow}) or the solubility of the organic solute (Karickhoff and others, 1979; Roy and Griffin, 1985; Schwarzenbach and Giger, 1985).

To estimate the amount of sorption in ground water of the Canal Creek area, K_{oc} values were compiled from the literature (table 14), and the organic-carbon content of the aquifer sediments was analyzed (table 15). Laboratory experiments by Schwarzenbach and Westall (1981) demonstrated that most sorption of organic solutes occurs in the fraction of the sediment finer than 125 μm. Thus, the fraction of organic carbon in the aquifer material was calculated by analyzing the total organic-carbon content in the size fraction finer than 125 μm and multiplying by the amount of this sediment in a unit mass of the total sediment sample.

The aquifer sediments contain an extremely low fraction of organic material (table 15), indicating that sorption onto organic matter in the sediments could not be a significant retardation mechanism for the organic contaminants found in the Canal Creek area. The median f_{oc} in the Canal Creek aquifer, based on 32 sediment samples, was only 0.000026. In the surficial aquifer, the median f_{oc} was 0.000065 based on 12 samples. Schwarzenbach and Westall (1981) found that estimates of K_d based on the organic-carbon content of sediments were only accurate for f_{oc} values greater than 0.001. They observed little sorption by organic-poor sediments in laboratory experiments and concluded that nonpolar organic compounds would be mobile in such media.

Possibly, some sorption could be occurring on mineral surfaces in the sediment. Several researchers have shown that sorption of nonpolar organic compounds onto mineral surfaces, especially clay minerals, could be an important process in aquifer sediments with a low organic-carbon content (Schwarzenbach and Westall, 1981; Roy and Griffin, 1985; Curtis and others, 1986; Estes and others, 1988).

Volatility

All the organic compounds found in the ground water of the Canal Creek area are volatile, indicating that they will tend to partition from the aqueous to the vapor phase and diffuse across an air-water interface. The factors that control volatilization include vapor pressure, aqueous solubility, and environmental conditions such as temperature, wind speed, and humidity (Lyman and others, 1982, p. 15-1; Smith, J. A., and others, 1987). Henry's Law constant, which is defined as vapor pressure divided by the solubility, gives an indication of the relative volatility of individual organic compounds from solution. As Henry's Law constant increases, the tendency for a compound to volatilize increases. Thus, compounds with a high vapor pressure and low solubility would tend to be the most volatile.

On the basis of its vapor pressure and solubility, vinyl chloride is the most volatile organic contaminant detected in ground water in the Canal Creek area (table 14). However, volatilization could only be a significant removal mechanism for the organic ground-water contaminants in the unsaturated zone or at the water table where the water is in contact with an air phase. Volatilization would have decreased the amount of organic contaminants that reached the ground water from a solvent spill or waste discharge.

Identification of Possible Degradation Reactions

A variety of degradation reactions in ground water can transform the dissolved chlorinated aliphatic and aromatic compounds found in the Canal Creek area. These include two reactions that generally are abiotic, hydrolysis and dehydrohalogenation, and two types of reactions that mostly are mediated by microorganisms in ground water, oxidation and reduction

Table 15.--Analyses of aquifer sediments for total organic carbon and for percentage of sediment finer than 125 micrometers, and calculated values of the fraction of organic carbon in the sediment

[ft, feet; µm, micrometers; g/g, grams per gram]

Well no.	Sample depth (ft below land surface)	Total organic carbon in size fraction finer than 125 µm (g/g)	Percent sediment in size fraction finer than 125 µm	Fraction organic carbon in sediment (f_{oc}) (g/g)
Canal Creek aquifer sediments:				
CC- 1B	45-50	2.42×10^{-4}	3.21	7.77×10^{-6}
CC- 3A	132-134	4.87×10^{-4}	11.6	5.63×10^{-5}
CC- 3B	159-161	1.26×10^{-4}	10.6	1.33×10^{-5}
CC- 4A	79.5-83.5	2.29×10^{-4}	12.7	2.90×10^{-5}
CC- 4B	87-89	3.47×10^{-4}	8.05	2.79×10^{-5}
CC- 5C	70-75	4.70×10^{-4}	8.47	3.98×10^{-5}
CC- 8B	74-79	3.28×10^{-4}	5.10	1.67×10^{-5}
CC- 9B	114-122	1.48×10^{-3}	11.0	1.63×10^{-4}
CC-11A	134-136	7.88×10^{-5}	16.7	1.31×10^{-5}
CC-11B	156-160	3.91×10^{-4}	20.8	8.13×10^{-5}
CC-13A	24-29	4.72×10^{-4}	1.46	6.89×10^{-6}
CC-13B	49-54	5.79×10^{-4}	6.49	3.76×10^{-5}
CC-15A	22-27	5.30×10^{-4}	4.39	2.32×10^{-5}
CC-16A	19-24	3.18×10^{-4}	11.6	3.68×10^{-5}
CC-17A	19-24	7.24×10^{-5}	33.0	2.39×10^{-5}
CC-17B	24-29	1.82×10^{-4}	5.13	9.34×10^{-6}
CC-19B	54-59	7.23×10^{-4}	4.74	3.43×10^{-5}
CC-25A	19-24	3.46×10^{-4}	15.1	5.22×10^{-5}
CC-27A	19-24	4.53×10^{-4}	18.4	8.34×10^{-5}
CC-27B	29-39	1.39×10^{-3}	7.60	1.06×10^{-4}
CC-28A	15.8-18.5	1.67×10^{-4}	12.2	2.04×10^{-5}
CC-29B	43.7-48.7	7.09×10^{-4}	7.23	5.13×10^{-5}
CC-30A	34-39	8.52×10^{-5}	9.10	7.75×10^{-6}
CC-31A	24-29	5.71×10^{-4}	2.21	1.26×10^{-5}
CC-37A	24-29	2.92×10^{-4}	12.6	3.67×10^{-5}
CC-38A	37-39	1.86×10^{-4}	8.76	1.63×10^{-5}
CC-39A	24-27	4.89×10^{-4}	8.69	4.25×10^{-5}
CC-39B	34-39	2.49×10^{-4}	5.56	1.39×10^{-5}
CC-40A	24-29	4.34×10^{-4}	25.3	1.10×10^{-4}
CC-41A	39-44	2.61×10^{-4}	5.13	1.34×10^{-5}
CC-42A	26.5-29	2.30×10^{-4}	7.88	1.81×10^{-5}
CC-43A	29-34	2.01×10^{-4}	6.79	1.36×10^{-5}
Surficial aquifer sediments:				
CC- 1A	20-25	4.11×10^{-4}	5.34	2.19×10^{-5}
CC- 5A	14-19	9.75×10^{-4}	7.88	7.68×10^{-5}
CC-10A	9-14	6.99×10^{-4}	5.96	4.17×10^{-5}
CC-19A	4-9	1.85×10^{-3}	20.6	3.82×10^{-4}
CC-20A	4-9	2.57×10^{-4}	4.87	1.25×10^{-5}
CC-20A	9-14	1.98×10^{-3}	8.36	1.66×10^{-4}
CC-22B	41.5-43.5	4.22×10^{-4}	12.6	5.33×10^{-5}
CC-23A	14-19	1.29×10^{-4}	9.33	1.20×10^{-5}
CC-32A	9-14	1.23×10^{-3}	1.08	1.33×10^{-5}
CC-33A	11.5-12.1	8.73×10^{-4}	40.6	3.55×10^{-4}
CC-34A	14-19	1.23×10^{-3}	6.70	8.24×10^{-5}
CC-35A	14-19	1.59×10^{-3}	8.76	1.39×10^{-4}

(Vogel and others, 1987). Oxidation/reduction reactions can occur abiotically in the presence of transition metals, such as iron, to transfer electrons. However, the electron acceptors and donors used to oxidize and reduce organic compounds are most commonly derived from biological systems (Vogel and others, 1987). Microorganisms are ubiquitous in ground water (Alexander, 1981), and their need for energy, carbon, and other essential nutrients is the driving force behind biotic reactions (Smith, J. A., and others, 1987). In general, abiotic reactions occur at a slower rate than microbially mediated reactions, but abiotic reactions can still be significant depending on ground-water-flow velocity (Vogel and others, 1987).

Hydrolysis and dehydrohalogenation reactions

During hydrolysis of chlorinated aliphatic compounds, the organic molecule reacts with water, forming a new carbon-oxygen bond and cleaving a carbon-halogen bond (fig. 11). Thus, a halogen is replaced by a hydroxyl group to produce an alcohol (Lyman and others, 1982, p. 7-1). Further hydrolysis to acids or diols can occur if the alcohols still contain a halogen (Vogel and others, 1987). Hydrolysis rates can be accelerated by catalysts such as microbially derived enzymes and clays. For example, aerobic bacteria isolated from a contaminated soil were found to catalyze the transformation of 1,2-dichloroethane to chloroethanol (Vogel and others, 1987).

Hydrolysis of the monocyclic aromatic contaminants detected in the Canal Creek area is unlikely at normal ground-water temperatures. The attack of the water molecule or hydroxide ion on the benzene ring would be impeded by the negative charge density of the ring (U.S. Environmental Protection Agency, 1979b, p. 71-3). Chlorobenzene is converted into phenol by hydrolysis only at temperatures greater than 300 °C (U.S. Environmental Protection Agency, 1979b, p. 72-3).

Dehydrohalogenation reactions can occur only with chlorinated alkanes that contain more than one carbon atom. The reaction produces an alkene. Dehydrohalogenation consists of removal of a halogen from one carbon atom and simultaneous or subsequent removal of a hydrogen atom from an adjacent carbon (fig. 11). No reports of mediation or catalysis by microorganisms have been found for the dehydrohalogenation reaction (Vogel and others, 1987).

In general, as the number of halogen atoms in an aliphatic compound increases, hydrolysis reaction rates tend to decrease, whereas dehydrohalogenation rates tend to increase (Vogel and others, 1987). Thus, hydrolysis is more likely to occur than dehydrohalogenation for dichlorinated alkanes, such as 1,2-dichloroethane. Dehydrohalogenation may be more important for polychlorinated alkanes, except for those compounds containing only one carbon atom such as carbon tetrachloride (Vogel and others, 1987).

The half-life data in table 16 are grouped under both hydrolysis and dehydrohalogenation reactions because of some uncertainty in the actual mechanism at 20 °C (Vogel and others, 1987). Rates usually are measured at high temperatures in aqueous solutions that contain high concentrations of organic solvents and then extrapolated to lower temperatures. In some cases, hydrolysis may prevail at one temperature and dehydrohalogenation at another. Reported rates and reaction products often vary significantly for individual compounds. Thus, caution is needed in using reported rates and half-lives.

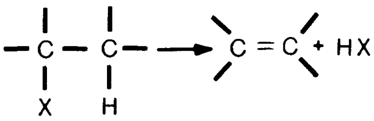
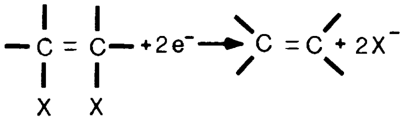
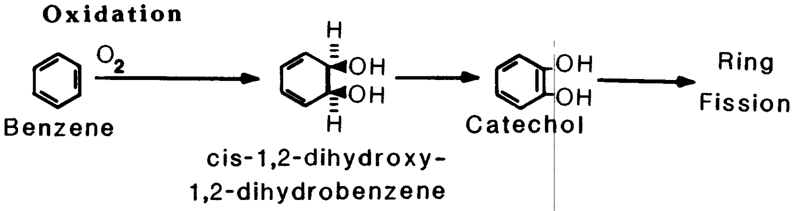
General Reactions	Examples
Halogenated Aliphatic Compounds:	
I. Hydrolysis $RX + H_2O \rightarrow ROH + HX$	$C_2H_4Cl_2 + H_2O \rightarrow C_2H_4ClOH + HCl$ 1,2-dichloro ethane → chloroethanol
II. Dehydrohalogenation 	$CCl_3CH_3 \rightarrow CCl_2CH_2 + HCl$ 1,1,2-trichloro-ethane → 1,1-dichloro ethylene
III. Reduction (a) hydrogenolysis $RX + H^+ + 2e^- \rightarrow RH + X^-$ (b) dihalo-elimination 	$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$ carbon tetrachloride → chloroform $CHCl_2CHCl_2 + 2e^- \rightarrow CHClCHCl + 2Cl^-$ 1,1,2,2-tetrachloroethane → 1,2-trans-dichloroethylene
Monocyclic Aromatic Compounds:	
I. Oxidation 	

Figure 11.-- Chart showing types of degradation reactions possibly affecting the organic constituents in ground water in the Canal Creek area.

Table 16.--Reported half-lives of abiotic hydrolysis or dehydrohalogenation of some chlorinated aliphatic compounds

[Half-lives are at 20 degrees Celsius; from Vogel and others, 1987, p. 725]

Compound	Half-life (years)
Chlorinated alkanes:	
Carbon tetrachloride	7,000
Chloroform	1.3; 3,500
Methylene chloride	1.5; 704
1,1,2,2-tetrachloroethane	0.8
1,1,2-trichloroethane	170
1,2-dichloroethane	50
Chlorinated alkenes:	
Tetrachloroethylene	0.7; 6
Trichloroethylene	0.9; 2.5

For the compounds detected in the ground water of the Canal Creek area, the short half-lives for 1,1,2,2-tetrachloroethane, tetrachloroethylene, and trichloroethylene (table 16) suggest that abiotic degradation reactions could be important in decreasing the concentrations of these organic contaminants. In addition, dehydrohalogenation reactions are important as a possible secondary source of chlorinated alkenes. Dehydrohalogenation rather than hydrolysis probably would be the significant abiotic reaction for 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane. Dehydrohalogenation of 1,1,2,2-tetrachloroethane would produce trichloroethylene. Dehydrohalogenation of 1,1,2-trichloroethane occurs at a much slower rate than 1,1,2,2-tetrachloroethane (table 16) and produces 1,1-dichloroethylene. Thus, trichloroethylene and a relatively lower amount of 1,1-dichloroethylene in the ground water of the Canal Creek area could be partly derived from abiotic degradation reactions.

Oxidation and reduction reactions

Chlorinated aliphatic compounds have a higher oxidation state than the monocyclic aromatic compounds. Thus, chlorinated aliphatics are more susceptible to reduction than to oxidation, and the aromatics are more susceptible to oxidation reactions than to reduction reactions (Wilson and McNabb, 1983; Vogel and others, 1987). In general, the more chlorine atoms attached to an aliphatic compound, the faster the reduction rate will be (Vogel and others, 1987).

Chlorinated aliphatics can be microbially reduced by two types of reactions, hydrogenolysis and dihalo-elimination (fig. 11). Hydrogenolysis entails the sequential replacement of chlorine atoms by hydrogen atoms and has been observed only under anaerobic conditions (Vogel and others, 1987).

Field and laboratory studies have shown that anaerobic bacteria in ground water are able to degrade parent compounds into the following daughter compounds (Wood and others, 1985):

carbon tetrachloride --> chloroform --> methylene chloride

tetrachloroethylene --> trichloroethylene --

{cis-1,2-dichloroethylene}
-->{trans-1,2-dichloroethylene} --> vinyl chloride
{1,1-dichloroethylene}

1,1,1-trichloroethane --> 1,1-dichloroethane --> chloroethane.

Methylene chloride also has been observed as a biodegradation product of tetrachloroethylene and 1,1,1-trichloroethane (Wood and others, 1985). Hydrogenolysis of 1,1,2,2-tetrachloroethane to 1,1,2-trichloroethane has been reported under anaerobic conditions (Bouwer and McCarty, 1983). Further reduction to 1,1-dichloroethane or 1,2-dichloroethane is possible (Vogel and others, 1987). Wood and others (1985) have shown that biodegradation of either trichloroethylene of tetrachloroethylene resulted in the production of cis- over trans-1,2-dichloroethylene by a factor of 25 to 1 or more. The analysis reported as 1,2-trans-dichloroethylene in the present study is actually the total of both isomers of dichloroethylene.

Dihalo-elimination involves the loss of two halogen atoms from adjacent carbons on a polyhalogenated alkane, forming an alkene (fig. 11). Thus, 1,1,2,2-tetrachloroethane could be reduced to cis- or trans-1,2-dichloroethylene; and, 1,1,2-trichloroethane could be reduced to vinyl chloride (Vogel and others, 1987). Dihalo-elimination reactions have been observed under aerobic conditions, unlike hydrogenolysis reactions.

Water in the majority of the wells contaminated with organic compounds in the Canal Creek area had dissolved-oxygen concentrations that were low (less than 1.0 mg/L) or below detection limits (table 2). The presence of sulfide in some of the ground-water samples also indicates anaerobic conditions (table 2). Because biotic hydrogenolysis reactions are known to occur only in anaerobic conditions, the polychlorinated aliphatics would be more resistant to degradation in areas where dissolved oxygen is present in the ground water. Some of the highest dissolved-oxygen concentrations were found at sites 27 and 28 (1.3 to 3.8 mg/L) near the outcrop area of the Canal Creek aquifer. Recharge of oxygenated precipitation to the aquifer may inhibit degradation of the chlorinated aliphatics in this area.

Methylene chloride, 1,1,2-trichloroethane, and 1,2-trans-dichloroethylene are ground-water contaminants detected in the Canal Creek area, but primary sources for these compounds could not be determined from historical reports of manufacturing and other operations. Instead, these compounds probably are derived from the secondary source of degradation of parent compounds, except for methylene chloride which could be derived largely from laboratory contamination.

The daughter compound 1,2-trans-dichloroethylene was one of the most widespread contaminants in the Canal Creek aquifer and appeared in high concentrations (pl. 3), indicating that degradation reactions are occurring in the ground water. Reduction of tetrachloroethylene and trichloroethylene, both of which had primary sources in the Canal Creek area, could produce 1,2-trans-dichloroethylene by hydrogenolysis. In addition, some of this daughter compound could be produced from dihalo-elimination reactions under aerobic or anaerobic conditions.

Although some primary contaminant sources in the Canal Creek area were identified for trichloroethylene, chloroform, 1,2-dichloroethane, and vinyl chloride, an additional source of these compounds may exist from degradation reactions. Distinguishing between a primary or secondary source of these compounds is difficult. Trichloroethylene may have mainly primary sources because it was used extensively as a solvent in the study area. Known uses of tetrachloroethylene, which could be one parent compound for trichloroethylene, are more limited. Probably, a relatively small part of the trichloroethylene is produced by hydrogenolysis of tetrachloroethylene. A significant percentage of the chloroform found at sites 26, 27, and 28 probably was introduced to the ground water from the CN-manufacturing operations near the West Branch Canal Creek (pl. 1) rather than from a secondary source. Except for well 16A where concentrations of 1,2-dichloroethane were anomalously high, this compound is most likely derived from degradation of 1,1,2,2-tetrachloroethane. Vinyl chloride was detected only in ground water where high concentrations of 1,2-trans-dichloroethylene also were found (pl. 3 and figs. 10a, 10b). This fact indicates that vinyl chloride is derived mainly from the sequential reduction of tetrachloroethylene or trichloroethylene by hydrogenolysis.

Degradation of benzene and chlorobenzene, which are the major aromatic contaminants in the Canal Creek area, has been observed by microbial oxidation under aerobic conditions. Bacteria initially oxidize aromatics by oxygenases to form a dihydrodiol with a *cis*-configuration (fig. 11). Further oxidation leads to the formation of catechols and finally to enzymatic fission of the aromatic ring (Cerniglia, 1984, p. 101; Dagley, 1984).

Barker and others (1987) found that benzene readily degraded in a shallow sand aquifer when dissolved-oxygen concentrations were high (greater than 1 mg/L). Several researchers have shown that chlorobenzene is more resistant to microbial attack than is benzene, possibly because of the difficulty in cleaving the chlorine bond (Gibson and others, 1968; U.S. Environmental Protection Agency, 1979b, p. 72-6). Anaerobic degradation of benzene and chlorobenzene generally has not been observed in field or laboratory studies (Schwarzenbach and Giger, 1985; Barker and others, 1987). However, recent experiments by Major and others (1988) have demonstrated that benzene can be biodegraded under anaerobic conditions if nitrate were added to act as an electron acceptor.

Low dissolved-oxygen (0.5 to 1.8 mg/L) and nitrate (0.09 to 1.4 mg/L) concentrations were found at the sites where benzene and chlorobenzene were detected (wells 9A, 8B, and 26B in table 2). This suggests that degradation was not occurring or was limited. However, previous microbial oxidation of these aromatics may have been a significant process in reducing the dissolved-oxygen concentrations at these sites.

SUMMARY AND CONCLUSIONS

Many activities since 1917 in the Canal Creek area of Aberdeen Proving Ground, Maryland, may have affected the environment. These activities include manufacturing of chemical agents on an experimental and production scale, filling of chemical munitions, fabrication and cleaning of military equipment, and field testing of chemicals. Organic solvents, chloride, and sodium probably were the most common wastes generated in large quantities. The primary method of waste disposal until about the late 1970's was the discharge of untreated liquid wastes through sewerlines leading to the West and East Branches of Canal Creek and the dumping of solid wastes in swampy areas along the creek.

To assess the possibility of ground-water contamination in the Canal Creek area, ground-water-chemical data were collected from November 1986 through April 1987 as part of the first phase of a 5-year study. This report (1) describes the distribution of inorganic and organic constituents present in ground water in the Canal Creek area, (2) identifies probable sources of ground-water contaminants, and (3) describes possible geochemical and physical reactions among the organic contaminants. Ground-water samples were collected from 87 observation wells screened in unconsolidated Coastal Plain sediments, including 59 samples from the Canal Creek aquifer, 18 samples from the overlying surficial aquifer, and 10 samples from the lower confined aquifer.

The major-ion composition and distribution in the Canal Creek aquifer are highly variable. Samples from the Canal Creek aquifer that contain the highest dissolved-solids and chloride concentrations are from wells located upgradient between the two creek branches, where manufacturing activities mainly took place. In this area, maximum dissolved-solids and chloride concentrations are 2,340 and 1,000 mg/L, respectively. In contrast, water from the farthermost downgradient well (11B) has dissolved-solids and chloride concentrations of 52 and less than 5 mg/L, respectively.

Four water samples collected from the surficial aquifer at Beach Point, a narrow peninsula surrounded by Kings Creek and Bush River, have distinctive sodium chloride compositions. Other surficial-aquifer samples have either a calcium bicarbonate composition or a more mixed composition.

The median dissolved-solids concentration in water from the lower confined aquifer (110 mg/L) is lower than the median in water from the Canal Creek aquifer (164 mg/L) and the surficial aquifer (286 mg/L). In addition, chloride concentrations are usually below the detection limit of 5 mg/L in the lower confined aquifer, suggesting that the aquifer has not been affected by inorganic wastes discharged in the Canal Creek area.

Anomalously high pH values (6.82 to 12.28) were detected in a total of 16 samples from the three aquifers. Elevated concentrations of potassium and bicarbonate commonly are associated with the elevated pH values. These well-water samples are believed to have been affected by reactions between the ground water and the grout used in well construction and do not reflect the actual inorganic composition of the aquifer water.

Dissolved solids, two major inorganic constituents, and four minor inorganic constituents are present in concentrations that exceed the drinking-water MCL's established by the USEPA. Concentrations of dissolved solids exceed the secondary MCL of 500 mg/L in 12 samples--6 samples from the Canal Creek aquifer and 6 from the surficial aquifer. Elevated chloride concentrations, ranging from 290 to 1,000 mg/L, are present in three samples from the Canal Creek aquifer and in four samples from the surficial aquifer at Beach Point. In most cases, the elevated chloride and dissolved-solids concentrations are derived from contaminants released during past activities. The Beach Point samples also are probably affected by intrusion of brackish water.

Iron is the only major inorganic constituent that is found in all three aquifers in concentrations above the USEPA MCL's for drinking water. Iron is derived from natural dissolution of iron-bearing minerals in the sediments and iron-oxide coatings on grains. Manganese, which also is derived from natural dissolution of minerals and oxide coatings, is the most extensive water-quality problem found for the minor inorganic constituents. Four samples from the Canal Creek aquifer, all collected from wells located near the West Branch Canal Creek, contain elevated fluoride concentrations (2.6 to 8.5 mg/L). The two most probable sources of fluoride include wastes from the production of fluorinated nerve agents and from chlorine manufacturing which used rock salt containing fluoride. Mercury and chromium occur in concentrations above the primary MCL's in samples from one and two wells, respectively.

Sixteen volatile organic compounds, including chlorinated alkanes, chlorinated alkenes, and monocyclic aromatics, are present in water samples from the Canal Creek and surficial aquifers. However, the low concentrations of methylene chloride, toluene, and ethylbenzene probably are the result of laboratory contamination of the samples. These three compounds are commonly used in analytical laboratories and appeared in the method blanks. Total organic halogen concentrations, which provide an estimate of the total amount of chlorinated volatile organic compounds in each sample, are greater than 5 μg/L in 49 samples from the Canal Creek aquifer and in 15 samples from the surficial aquifer. Water samples from the lower confined aquifer do not show any evidence of organic contamination except for low concentrations of methylene chloride, toluene, or ethylbenzene in a few samples. Base/neutral and acid-extractable organic compounds were not detected in the three aquifers.

The chlorinated alkanes that are distributed most widely in the Canal Creek aquifer include 1,1,2,2-tetrachloroethane and chloroform, which are present in 34 and 32 samples, respectively, of the 59 samples collected. The maximum concentration of 1,1,2,2-tetrachloroethane in the Canal Creek aquifer (5,300 μg/L) was from a well in the salvage yard. The highest concentration of chloroform (460 μg/L) appears in the Canal Creek aquifer from a well located near the West Branch Canal Creek. Other alkanes present in the Canal Creek aquifer (and their maximum concentrations) include methylene chloride (55 μg/L), carbon tetrachloride (480 μg/L), 1,1,2-trichloroethane (79 μg/L), 1,2-dichloroethane (990 μg/L), and 1,1-dichloroethane (3.1 μg/L).

In the surficial aquifer, the highest concentrations of chlorinated alkanes generally appear in the Beach Point samples--1,1,2,2-tetrachloroethane (9,000 μg/L), 1,1,2-trichloroethane (80 μg/L), and chloroform (66 μg/L). The most widespread alkanes in the surficial aquifer are 1,1,2,2-tetrachlorethane and chloroform.

Information on past activities in the study area indicates that one or more major sources exist for the chlorinated alkanes: (1) from use as a decontaminant and in cleaning equipment, (2) from the process used to impregnate protective clothing, (3) from use as raw materials in the manufacture of impregnite material, and (4) from use as raw materials in the manufacture of the tear gas chloroactophenone.

Of the detected chlorinated alkenes, trichloroethylene and 1,2-trans-dichloroethylene are the most widespread contaminants in the Canal Creek aquifer, appearing in 30 and 28 samples, respectively. Vinyl chloride is present in 15 samples; tetrachloroethylene and 1,1-dichloroethylene are the least commonly detected chlorinated alkenes in the Canal Creek aquifer. The maximum concentrations of trichloroethylene (1,800 μg/L) and 1,2-trans-dichloroethylene (1,200 μg/L) in the Canal Creek aquifer are seen in samples from wells located near the East Branch Canal Creek. In the surficial aquifer, the greatest contamination by chlorinated alkenes is seen at Beach Point--trichloroethylene (940 μg/L), 1,2-trans-dichloroethylene (520 μg/L), and tetrachloroethylene (64 μg/L).

Trichloroethylene probably is derived from its past use as a degreaser on equipment and metal parts in machine shops, in filling and manufacturing plants, in garages, and in aircraft hangars. Tetrachloroethylene was used experimentally in clothing-impregnating operations. The other alkenes probably have only secondary sources from degradation reactions.

Chlorobenzene and benzene are the only aromatics observed in the Canal Creek aquifer in concentrations significantly above the detection limits, and they are present in eight or fewer samples. The maximum detected concentrations of chlorobenzene (39 μg/L) and benzene (70 μg/L) occur in the same sample from near the West Branch Canal Creek. Only chlorobenzene (22 μg/L) is found in the surficial aquifer in concentrations significantly above detection limits.

The production of chloroacetophenone required benzene as a raw material and is probably the major source for benzene in the ground water. Other possible sources include fuels from the garages and airfield. Chlorobenzene in the Canal Creek aquifer could be derived from its use as a solvent for quality-control analyses in the clothing-impregnating plants and use as a raw material in the production of an arsenical.

Density, solubility, sorption affinity, and volatility are four physicochemical properties that could control reactions among the organic constituents in the ground water. Most of the detected organic contaminants have higher densities than water in their free-product form, and many of the wastes discharged in the study area would have contained solvents as free product rather than dissolved in water. Their high density would have aided in movement of the contaminants into the aquifers by vertical sinking.

Two areas where large amounts of wastes were discharged are especially susceptible to contamination because a near-surface clay layer does not exist to impede vertical movement of contaminants: (1) the outcrop area of the upper confining unit, located near the West Branch Canal Creek; and (2) an area near the East Branch Canal Creek where a paleochannel has eroded the surface clay.

Solubility varies greatly for the volatile organic compounds found in the Canal Creek area (1.1 to 16,700 mg/L). The compounds are moderately to highly soluble, and the solubility concentrations are much greater than the low concentrations (2 to 7 μg/L) established by the USEPA as MCL's in drinking water for several volatile organic compounds.

Sorption probably is not a significant retardation mechanism for any of the volatile organic compounds found in the Canal Creek and surficial aquifers because of the low organic-carbon content of the aquifer sediments. The amount of sorption that could occur was estimated using the measured fraction of organic carbon associated with the aquifer sediments and organic carbon sediment-water partition coefficients found in the literature.

The organic contaminants are all volatile to some extent. However, volatilization could only be a significant removal mechanism where the ground-water contaminants are in direct contact with an air phase, such as in the unsaturated zone.

Abiotic half-lives for 1,1,2,2-tetrachloroethane, tetrachloroethylene, and trichloroethylene indicate that dehydrohalogenation or hydrolysis could be important degradation reactions for these compounds. The abiotic degradation of 1,1,2,2-tetrachloroethane could result in the production of trichloroethylene in the ground water.

The chlorinated alkanes and alkenes can be degraded by microbially mediated reduction reactions, including hydrogenolysis and dihalo-elimination reactions. The widespread contaminant 1,2-trans-dichloroethylene, for which sources could not be found from historical reports on manufacturing and other activities in the Canal Creek area, probably is produced from reduction of parent compounds such as tetrachloroethylene, trichloroethylene, and 1,1,2,2-tetrachloroethane. Concentrations of trichloroethylene, chloroform, vinyl chloride, 1,1,2-trichloroethane, 1,2-dichloroethane, and methylene chloride in the ground water may be at least partly derived from reduction reactions.

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