

Ground-Water, Surface-Water, and Bottom-Sediment Contamination in the O-Field Area, Aberdeen Proving Ground, Maryland, and the Possible Effects of Selected Remedial Actions on Ground Water

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of Environmental
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By DON A. VROBLESKY, MICHELLE M. LORAH, and
JAMES P. OLIVEROS

Prepared in cooperation with the Department of
Defense, Office of Environmental Management,
Aberdeen Proving Ground, Maryland

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CONVERSION FACTORS AND VERTICAL DATUM

For readers who wish to convert measurements from the inch-pound system of units used in this report to the metric system of units, the conversion factors are listed below:

Multiply inch-pounds units	By	To obtain metric unit
inch (in.)	25.4	millimeter
inch (in.)	25,400	micrometer
inch per year (in/yr)	25.4	millimeter per year
foot (ft)	0.3048	meter
foot per day (ft/d)	0.3048	meter per day
foot per year (ft/yr)	0.3048	meter per year
foot squared per day (ft ² /d)	0.09290	meter squared per day
cubic foot per day (ft ³ /d)	0.02832	cubic meter per day
mile (mi)	1.609	kilometer
gallon (gal)	3.785	liter
gallon (gal)	0.003785	cubic meter
gallon per day (gal/d)	0.003785	cubic meter per day
pound per square inch (lb/in ²)	6.895	kilopascal

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

Water temperature, specific conductance, and chemical concentration are given in metric units. Water temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 1.8 \times (^{\circ}\text{C}) + 32$$

Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$). This unit is identical to micromhos per centimeter at 25 degrees Celsius, formerly used by the U.S. Geological Survey.

Chemical concentration in water is expressed in milligrams per liter (mg/L) and micrograms per liter ($\mu\text{g}/\text{L}$).

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Abstract

O-Field, in the Edgewood area of Aberdeen Proving Ground, Md., was periodically used for disposal of munitions, waste chemicals, and chemical-warfare agents from World War II to at least the 1950's. This disposal has resulted in contamination of ground water, surface water, and bottom sediment at the site. Contaminated ground water contains concentrations of arsenic and cadmium that exceed drinking-water maximum contaminant levels and concentrations of chloride, iron, manganese, and zinc that exceed secondary maximum contaminant levels established by the U.S. Environmental Protection Agency (1987). Dominant organic contaminants are chlorinated aliphatic compounds, aromatic compounds, and organo-sulfur and organophosphorus compounds. Surface water at the site is tidal, so that contaminant concentrations vary. Surface-water contaminants detected in nearby Watson Creek are arsenic, chlorinated aliphatic hydrocarbons, and a variety of transition metals, including mercury. Bottom sediments in Watson Creek contain arsenic, zinc, manganese, copper, lead, iron, chromium, nickel, mercury, polycyclic aromatic hydrocarbons, trichlorofluoromethane, carbon disulfide, di-*n*-octylphthalate, and 1,2-dichloroethylene.

Transport of contamination to areas outside the Proving Ground or to other areas within the Proving Ground by way of ground water is unlikely because of the localized nature of the flow system. Lateral migration of ground-water contamination is toward Watson Creek, where it discharges to surface water. Migration of ground-water contamination toward the Gunpowder River has not been observed, the possible exception being 1,4-dithiane. During periods when the contaminants in Watson Creek attain sufficient concentrations, however, the depletion mechanisms (primarily volatilization and sorption) will probably be inadequate to prevent migration of contaminated surface water to the Gunpowder River.

Assessment was performed on such remedial actions as an impermeable cap, subsurface barriers, a ground-

water drain, pumping, excavation, and no action. A digital three-dimensional ground-water flow model was used to assess possible effects of the remedial actions. Each remedial action examined has advantages and disadvantages.

Placing an impermeable cap on Old and New O-Fields may reduce the amount of leachate from the soil zone but probably will have little effect on water levels beneath the disposal areas. Complete encapsulation would impede contaminant migration but may increase the concentrations of some contaminants within the encapsulated fill that eventually could be released to the environment if the liner is breached. The subsurface barriers for Old O-Field tested by model simulation would lower water levels at Old O-Field but increase water levels at New O-Field. The subsurface barrier simulated at New O-Field would decrease water levels within the disposal trenches but increase water levels upgradient.

A ground-water drain between Old O-Field and New O-Field would lower water levels at both sites but may allow brackish surface water to move inland along the drain and recharge the aquifer during periods of extremely low ground-water levels or above-normal surface-water levels. Pumping of wells upgradient from Old and New O-Fields would lower water levels at both sites, but also would have the potential to induce the movement of contaminated ground water toward the wells during summer months.

Excavation and removal of the disposed material could increase the extent of contamination as a result of the unconventional technology required to excavate the site remotely. Model simulations indicate that pumping of downgradient wells to remove contaminated ground water would probably lower water levels within the disposal areas, but also would induce movement of water from Watson Creek into the aquifer if pumping rates were too high or not adjusted to account for seasonal water-level changes. Leaving the Old O-Field landfill in its present state would allow the continued leaching of contamination from the disposal areas and subsequent transport through the ground water.

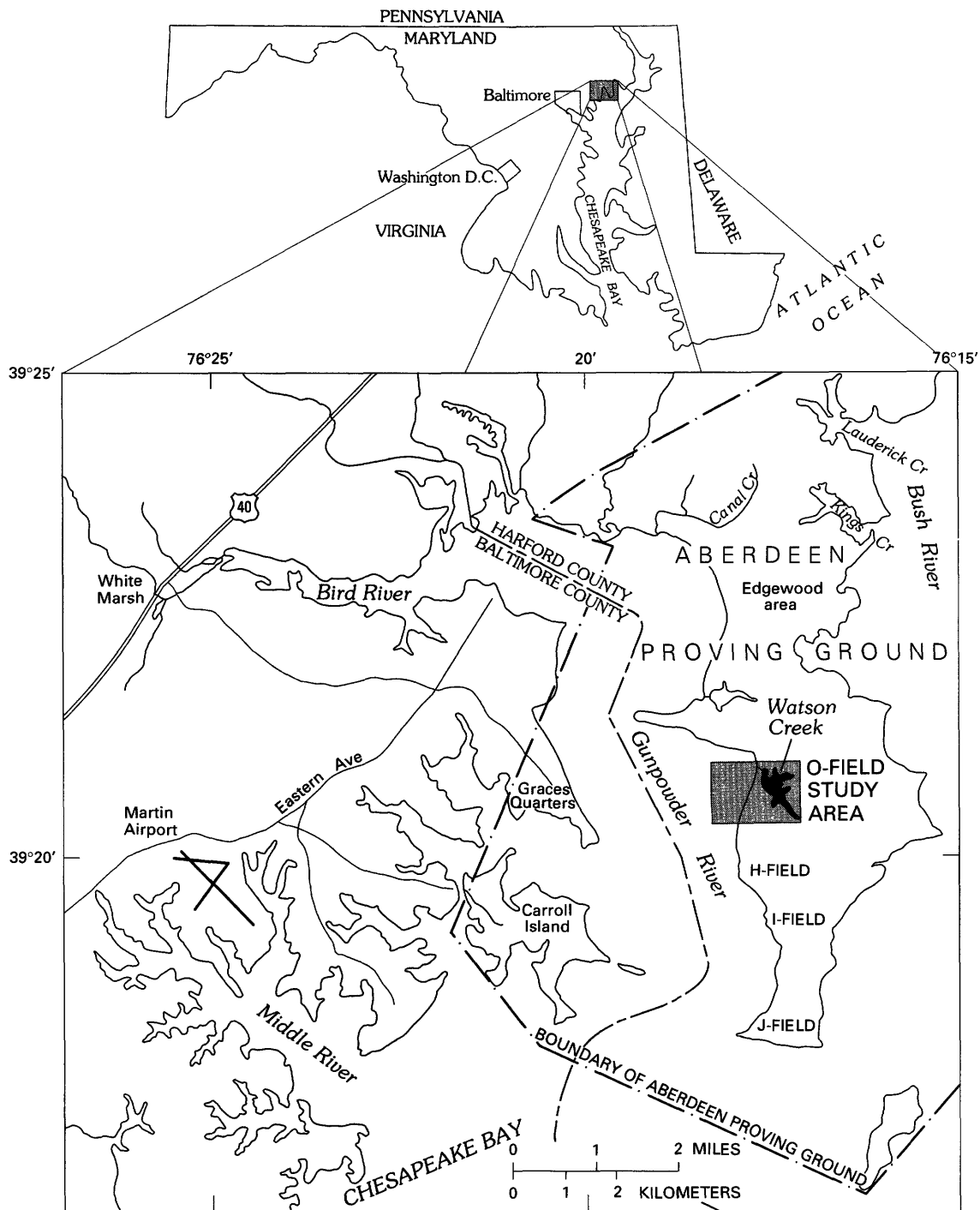


Figure 1. Location of O-Field study area in Aberdeen Proving Ground, Maryland.

INTRODUCTION

Background

O-Field (fig. 1), in the Edgewood area of Aberdeen Proving Ground, Md., was periodically used for disposal of waste material from U.S. Army operations from World War

II to at least the 1950's. The waste material consists of munitions and chemical-warfare agents. O-Field contains three sites that have been used for waste disposal: Old O-Field, New O-Field, and a small site west of Old O-Field. Analyses of ground-water samples by the Department of Defense in 1977 and 1978 indicated the presence of arsenic and chlorinated organic solvents (Nemeth and

others, 1983). Analysis of surface-water and soil samples indicated that arsenic from disposed materials at O-Field was being transported from the site by ground water and discharging into Watson Creek, a tributary of the Gunpowder River, which discharges into the Chesapeake Bay. Further investigation was required to determine if contamination was migrating to other aquifers or to the Gunpowder River. Moreover, there was a need to characterize the site hydrogeology and to assess potential remedial actions.

In March 1984, the U.S. Army Environmental Management Office of Aberdeen Proving Ground contracted the U.S. Geological Survey to conduct a hydrogeologic assessment of O-Field. On September 10, 1986, while the study was ongoing, the U.S. Environmental Protection Agency issued a Resource Conservation and Recovery Act permit to the U.S. Department of Army, Aberdeen Proving Ground to address Solid-Waste Management Units with potential to release hazardous wastes to the environment. The permit required that the hydrogeologic assessment (1) provide a framework for characterization of contaminant releases and contaminant plumes at O-Field; (2) establish an observation-well network to determine the rate and direction of ground-water movement, and the concentrations of various pollutants and indicator parameters and their spatial distribution; and (3) develop predictive systems that can be used to generate design information for selection of remedial measures. This study was fully funded by the U.S. Department of Defense through the Environmental Management Office of Aberdeen Proving Ground.

Purpose and Scope

The purpose of this report is to (1) characterize the contamination of the ground water, surface water, and bottom sediment in the O-Field area of Aberdeen Proving Ground, Md., and (2) describe the probable hydrologic and chemical effects of relevant remedial actions on the ground water at the site. The report also describes the hydrogeology at O-Field.

Two water and bottom-sediment samples were collected from Watson Creek in November 1984. A more extensive investigation of the creek and the Gunpowder River was conducted in August 1985, during which 23 water samples and 37 bottom-sediment samples (fig. 2) were collected and analyzed for inorganic and organic parameters. Thereafter, water samples from the mouth of Watson Creek and within the Gunpowder River were collected and analyzed for arsenic six times. Three water samples were collected through the ice on Watson Creek on January 29, 1988, and analyzed for volatile organics.

Water samples were collected from 11 existing wells and from 21 new wells that were installed at the site in 1985. Five additional wells were installed in 1987. Twelve core samples of aquifer material were analyzed for selected

chemical constituents, and five core samples of confining-unit material were analyzed for selected physical characteristics. The wells were sampled at approximately 3-month intervals for inorganic and organic constituents. Selected wells were sampled for a limited number of parameters on a biweekly basis from July 1986 through January 1987. Digital monitors recorded water levels at 15-min intervals on 18 wells and at two tide-gage stations for various lengths of time from April 1986 through September 1987.

Surface and borehole geophysics were used to provide information on the geology and distribution of contamination. A digital ground-water flow model was used to test hypotheses concerning ground-water movement and the hydrologic effects of various remedial actions.

Site History and Waste Characterization

Historical records of O-Field are incomplete, but the first use of the area for disposal of chemicals and explosives is thought to have been in the late 1930's. It was during that time that an explosion in a disposal pit in the Edgewood area of the arsenal forced researchers to move their disposal operations to Old O-Field (Yon and others, 1978). Excavation and utilization of unlined and uncovered disposal trenches began in 1941. The last trench was excavated in 1953, although activity at the landfill, namely, incineration and demilitarization of ordnance, continued until about 1957. The maximum depth of the trenches was at least 12 feet (ft) according to original field-survey notes of Old O-Field burial-pit locations dated September 17, 1942, book 36, located in the files of the U.S. Army Aberdeen Proving Ground Support Activity (USAAPGSA), Directorate of Engineering and Housing (DEH), Engineering Plans and Services Division (EPSD). The trenches were typically about 20 ft wide and ranged in length from about 50 to 470 ft at Old O-Field. During 1941–49, an unknown quantity, measured in tons, of chemical-filled and explosive ordnance and agent-contaminated equipment was disposed on the ground or in trenches (Yon and others, 1978). Much of the disposed material arrived in 1946, when captured foreign chemical-agent munitions were moved to Old O-Field.

Disposal at New O-Field began in 1950. Disposed material is reported to have included ordnance, contaminated material and laboratory quantities of chemical-warfare agents, and dead animals (Yon and others, 1978). The pits were about 20 ft wide and ranged in length from 40 to 150 ft. The depth of the pits is not known but is probably similar to pits at Old O-Field. New O-Field continued to be used after disposal was discontinued at Old O-Field. The primary activity in later years at New O-Field was destruction of material by burning.

Little is known regarding the small site west of Old O-Field. Ordnance, once thought to have been buried there, was later shown to have been buried within the Old O-Field

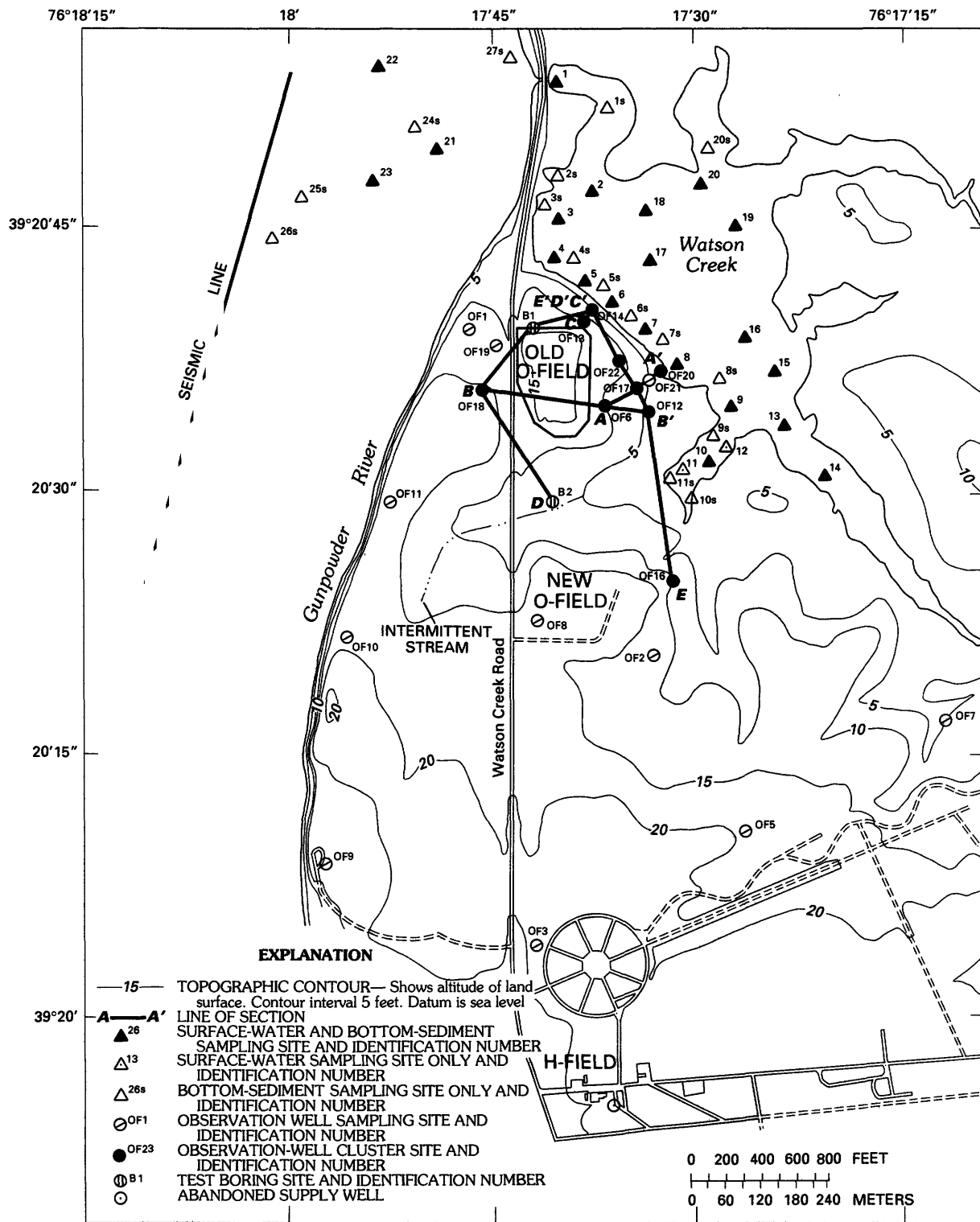


Figure 2. Locations of wells, surface-water and bottom-sediment sampling sites, marine-seismic line, and lines of hydrogeologic sections A-A', B-B', C-C', D-D', and E-E'. (Lines of section are for figs. 4-8.)

boundary (David Parks, Environmental Management Office of Aberdeen Proving Ground, written commun., 1986). Yon and others (1978) report that a truck loaded with explosives (type and quantity unknown) ignited and burned in this area.

In 1949, cleanup operations began with the goal of destroying some of the explosives. Periodically during the cleanup operation, explosions ruptured container casings. Release of chemicals to the environment, such as the overland flow of mustard agent to Watson Creek and the Gunpowder River, occurred as a result of the explosions (Dickey, 1978). In 1950, hundreds of gallons of fuel oil were placed in the trenches and ignited to burn residuals. In the years following the 1950's, dumping was limited and sporadic. Infrequent explosions continue to occur. During this investigation, the suspected ignition of a white-phosphorus munition in 1984 resulted in a fire of limited extent at Old O-Field.

Although records are incomplete, the disposed waste at New O-Field was supposed to be burned daily. In later years, new pits were excavated roughly perpendicular to the original pits. The new pits were used as burn areas for waste and are presently (1988) uncovered.

In addition to the items previously identified, a variety of decontaminating agents have been used at the site to render the chemical agents less toxic. Typical decontaminants are calcium hypochlorite, super topical bleach, sodium hydroxide (caustic soda), sodium carbonate with washing soda (soda ash), lime, and decontaminating agent noncorrosive (DANC). The DANC was mixed with tetrachloroethane as a solvent for application.

Previous Investigations

In 1976 the U.S. Army Test and Evaluation Command (TECOM) recommended an assessment of Aberdeen Proving Ground to determine the potential for off-post migration of chemical contaminants. The U.S. Department of Defense conducted a records search and recommended collection of samples from several sites, including O-Field. Observation wells were installed at O-Field in 1978. Analysis of well samples showed the presence of arsenic and chlorinated organic solvents in the ground water (Nemeth and others, 1983). Arsenic was also found in the water and bottom sediment of Watson Creek.

An additional records review (Yon and others, 1978) used available documents and personnel interviews to reconstruct a general history of site operations. The investigation found that New O-Field contained 9 disposal pits, Old O-Field contained 35 disposal pits, and there were possibly 3 additional pits on the western side of Watson Creek Road. A later review of historical survey notes showed that only one pit existed west of Watson Creek Road, and the other two suspected pits were within the

fenced area east of the road (D.M. Parks, O-Field—Modification to historical location of disposal pits: Unpublished memorandum to Installation Environmental Quality Coordinator, Aberdeen Proving Ground, Md., 5 p., 1986).

A limited resampling of O-Field ground and surface water was done by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) in 1984. The results (J.M. Murphy, Jr., USATHAMA, written commun., 1984) confirmed that ground water contained elevated concentrations of arsenic, cadmium, iron, and volatile organic compounds (VOC).

The U.S. Army Environmental Hygiene Agency (1977) conducted a surface-water quality and biological study of Watson Creek and nearby creeks. They found unusually high organic loading in Watson Creek due to lack of complete tidal flushing. They found concentrations of 24 micrograms per liter ($\mu\text{g/L}$) di-*n*-butylphthalate, 6 $\mu\text{g/L}$ 1,1,2,2-tetrachloroethane, and nonquantifiable amounts of 2,4,6-trichloroaniline, 2,4,6-dinitrotoluene, and 1,4-dithiane in Watson Creek water. Dissolved inorganic constituents exceeding chronic toxicity levels established by the U.S. Environmental Protection Agency (1987) for freshwater aquatic life in Watson Creek were zinc, copper, and lead. Copper concentrations also exceeded chronic toxicity levels for saltwater aquatic life. Mercury, selenium, and zinc were detected in muscle tissues in fish from Watson Creek but were within the established safety limits for human consumption.

ICF Technology (1987) published a feasibility study of evacuation and cleanup options for the Old O-Field area. The report used file searches, interviews, and unpublished information from this U.S. Geological Survey study to evaluate hydraulic excavation, entombment, in situ vitrification, and mechanical excavation as remedial alternatives. The methods were rated in decreasing order of feasibility as follows: (1) in situ vitrification, (2) entombment and remotely controlled mechanical excavation, and (3) hydraulic excavation.

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Many people outside the U.S. Geological Survey made important contributions to this investigation. Cynthia Couch and David Parks (Environmental Management Office of Aberdeen Proving Ground) coordinated the interaction of several different organizations during drilling. Gary Nemeth (U.S. Army Environmental Hygiene Agency) provided valuable information regarding site history and chemistry of specific chemical-warfare agents. Special thanks are also deserved by the personnel of the Technical Escort Unit at Aberdeen Proving Ground for providing safety monitoring and by the U.S. Army Corps of Engi-

neers' drillers Charles Brown, Edward Woods, and Jerome Jenkins for an outstanding job of drilling the observation wells by remote control.

METHODS

Sampling-Network Design and Numbering System

The observation-well network (fig. 2) installed at O-Field was designed to allow determination of the rates and direction of ground-water movement, the concentrations of various pollutants and indicator parameters in the ground water and their spatial distribution, and development of predictive systems that can be used to generate design information for selecting remedial actions. Eleven wells were present at the site at the time this study was initiated but, in general, were not in locations suitable for monitoring contaminant movement. Therefore, an additional 21 wells were installed at eight locations within O-Field during 1985. Most of the wells were installed as clusters, and up to four wells were used per cluster. One of the existing wells (OF6) was incorporated as part of a new cluster. Each well within the cluster was screened at a different depth to monitor vertical gradients. Most of the well screens are 2 ft long to allow approximation of a point-source sample. Selected wells contained 7-ft-long screens extending from below the water table to above the water table to allow sampling of possible floating contaminants. During the project, results from quarterly sampling of the new wells suggested the possibility that increased concentrations of contaminants might be present beyond the established well network. Therefore, an additional five wells were installed at three locations in 1987 with well screens 5 ft long. The observation-well network at New O-Field was primarily designed for reconnaissance because it was unknown whether ground-water contamination existed at the site. Consequently, only one well cluster (two wells) at New O-Field is within the contaminated area. Thus, the New O-Field wells are adequate to show the presence of contamination but not the extent.

The well numbers of ground-water sampling points at O-Field are designated by the prefix "OF" to differentiate them from several other ongoing ground-water investigations at Aberdeen Proving Ground. At sites containing more than one well, the well numbers contain letter suffixes. Suffixes were assigned to wells in alphabetical order from shallowest to deepest. Thus, well OF14A is the shallowest well, and well OF14C is the deepest well at cluster 14. An exception is well OF6. Although well OF6 is part of well cluster 6, it existed prior to this study and was monitored by the Army for several years. No suffix was assigned to the well in order to maintain consistency with labeling used in historical monitoring records.

The surface-water sampling network (fig. 2) was designed to determine whether contamination existed in Watson Creek and the Gunpowder River and to determine the extent and potential for offsite migration of such contamination. After a preliminary sampling of limited areal extent in November 1984, surface-water samples were collected from 20 sites in Watson Creek and 3 sites in the Gunpowder River in September 1985. Bottom-sediment samples were collected from 30 sites in Watson Creek and from 7 sites in the Gunpowder River in September 1985. Bottom-sediment sampling sites were more abundant than surface-water sampling sites because of the increased potential for localized contaminant concentrations in the bottom sediment. The sampling points within Watson Creek were broadly distributed to provide information for the entire main body of the creek, and were more closely spaced along the O-Field shoreline to provide information specific to O-Field discharges.

Sites where both a surface-water sample and a bottom-sediment sample were collected are designated by a site number with no suffix. Thus, the surface-water samples are numbered consecutively from 1 to 23, and bottom-sediment samples from those sites have the same number designation. However, sediment samples were also collected between several surface-water sampling sites. Sites where only a bottom-sediment sample was collected are designated by a site number with the suffix "s."

Drilling

Remote Operation

All drilling at the site was performed by the U.S. Army Corps of Engineers (COE). Encountering buried ordnance or chemical-warfare agents was a potential danger during drilling at O-Field. Extensive surveys of the predrilling site using magnetometers and metal detector scans made it unlikely that personnel would encounter such dangers. However, as an extra precaution, the COE outfitted a drilling rig to be operated remotely. The remotely controlled drilling operation required a high level of personnel protection and a highly coordinated site-management network.

Protective clothing for remote drilling at Aberdeen Proving Ground consisted of an inner garment treated with agent-resistive chemicals, nonstatic (bomb-handler's) coveralls, butyl-rubber gloves and boots, and an outer apron and coveralls, also made of butyl. Gas masks and hoods were worn during work phases involving a potential vapor hazard.

The first entry to the site each day was made by military munitions experts, who visually inspected the area and activated air-monitoring systems. The air-monitoring devices consisted of organic-vapor detectors that emitted an

alarm signal when a threshold limit was exceeded and vapor collectors that were taken to a laboratory for analysis.

When the drillers entered the site, they carried gas masks and were dressed in personnel-protection clothing. They were accompanied at all times by two military personnel trained in safety aspects of working around chemical-warfare agents and munitions. Gas masks were checked for leaks at each site entry. All groups of personnel were in radio contact with each other and with a central coordination center.

To begin the drilling operation, the drillers manually turned on the drilling rig and the air compressor and attached a 5-ft section of hollow-stem auger to the drilling rig. They then set up a closed-circuit television camera to allow the operation to be viewed on a television monitor from a Class B bombproof shelter. The shelter was located beyond the effective range of the type of munition that may have potentially been encountered. After the personnel moved to the bomb shelter, all nearby roads were blocked off. The drillers then used remote controls to activate the rig and advance the augers 5 ft into the ground. Next, the two military personnel, wearing personnel-protection clothing and gas masks, moved to the drilling rig, where they conducted a series of tests for chemical-warfare agents on the well cuttings and the borehole vapors. When the site was declared safe, the drillers were allowed to return to the drilling rig and retrieve the sample. The drillers then went back to the shelter, while the military personnel conducted tests for chemical agents on the sample. If no agent was found, the drillers returned to the rig, attached another 5-ft section of auger and began the process again.

If suspected or known unexploded ordnance was encountered, or if any of the tests by military personnel resulted in positive readings for a chemical-warfare agent, the drillers remained masked and stayed in the bomb shelter until military personnel removed the hazard. Suspected ordnance was destroyed or removed. Whenever contamination was suspected, military personnel collected samples for confirmation and decontaminated the area. When retesting produced negative readings, the drillers sealed the borehole with grout and moved to a new area. Such action was required three times during the drilling.

The potential danger of producing an airborne hazard to the drillers or to offsite areas dictated that drilling could occur only under a narrow range of weather conditions. During temperature inversions or low-wind conditions, no drilling took place because released vapors would remain near the ground and endanger onsite personnel. Similarly, if the wind direction was toward the bombproof shelter, the possibility of windborne transport of hazardous vapors toward onsite personnel required that drilling be postponed or the shelter be moved. When wind speed was too great, drilling was cancelled to eliminate the possibility of airborne transport of hazardous chemicals to offsite areas.

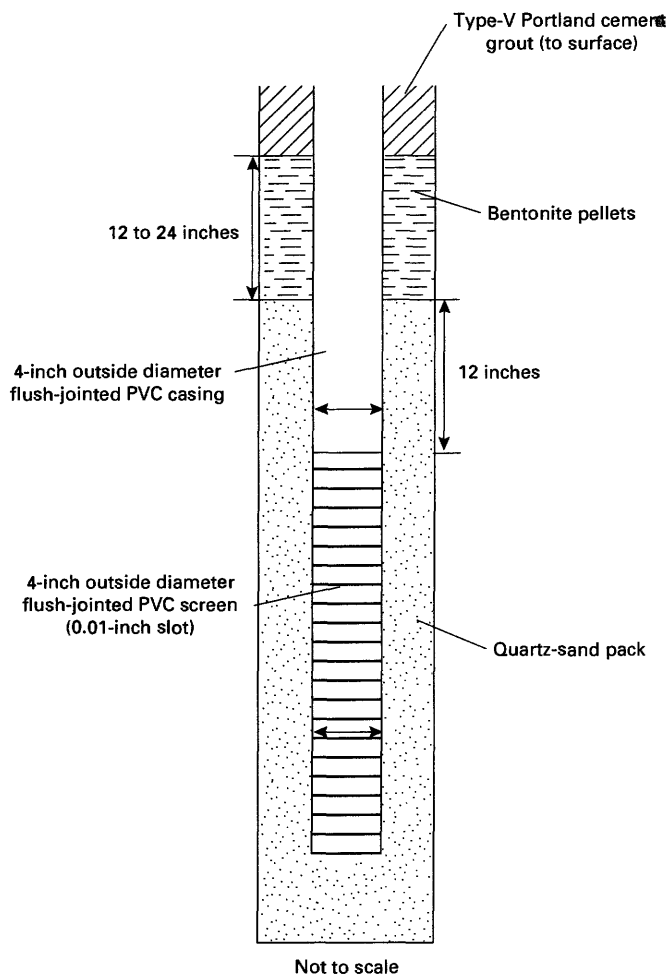


Figure 3. Typical well-screen construction.

Wells were installed using 4-inch (in.) outside diameter (od) flush-jointed polyvinylchloride (PVC) casing and screens. Screen lengths were 2 ft in areas where approximation of a point-source sample was required, 5 ft in areas generally farther from the fill, and 7 ft in wells designed to sample the surface of the water table. Continuous-slot screens with a slot size of 0.01 in. were used for all wells. The annular space outside the screen was filled with a quartz-sand pack to a height of approximately 12 in. above the top of the screen (fig. 3). A layer of bentonite pellets between 12 and 24 in. thick was placed on top of the sand pack. The remaining annular space to the surface was grouted from the bottom upward using Type V Portland cement. Augers were washed with detergent between sites. Water was not introduced into the borehole during well drilling. The wells were developed using an airlift method until the discharging water was acceptably free of suspended sediment.

Protective steel-surface casings were installed on all wells and locked to prevent vandalism. A mark placed on

the PVC casing of each well was used as a reference point for water-level measurements. The marks were surveyed to a common vertical-elevation benchmark using first-order leveling criteria.

Core Collection

Hollow-stem augers (10-in. od) were used to install the observation wells. Formation samples were taken with a core-barrel sampler that was inserted into the bottom of the auger column and advanced with the augers. The resulting samples were approximately 5 ft long by 4 in. wide. Core color, grain size, sorting, plasticity, thickness and lithology of layers, and unusual features were recorded in field books. Selected cores were collected for laboratory analysis. Undisturbed cores of confining-unit material were obtained by removing the outer 0.5 in. of core material with a clean knife, wrapping the remaining core in cheesecloth, sealing it with liquid wax, wrapping it in plastic wrap, and immediately shipping it to a contract laboratory, where analysis tests were performed for dry density, soil pH, percentage of moisture, cation-exchange capacity, permeability, liquid limit, plastic limit, and plasticity index. Samples of undisturbed aquifer material were not obtainable due to lack of cohesion. However, disturbed samples were collected from selected intervals and analyzed for concentrations of total organic carbon and total organic carbon in the size fraction less than 0.005 in., cation-exchange capacity, and concentrations of arsenic, iron, manganese, and antimony.

Hydrologic Testing

Pumping tests to determine aquifer hydraulic properties were not done at O-Field because of the requirement for offsite disposal of the contaminated water from the test and because of the possibility of forcing contaminated plume migration into previously uncontaminated areas. Instead, slug tests were done on 14 wells in the water-table aquifer and 7 wells in the upper confined aquifer. A solid slug with a displacement volume of about 1.5 gallons (gal) was used where the water column in the well was higher than 6 ft. A 3-gal slug of distilled water was used in wells with a water column of less than 6 ft. During each test, water-level data were collected with a portable, digital data logger and a 5 pounds per square inch (psi) pressure transducer. Horizontal hydraulic conductivity was calculated from the slug-test data with a method developed by Hvorslev (1951). All downhole equipment was washed several times with distilled water to prevent cross contamination between sites. The hydraulic tests were done after collection of ground-water samples.

Water-Level Measurements

Digital recorders were installed on 18 wells for various lengths of time to record water levels at 15-min intervals. The longest period of record, 18 months, was from well OF6A. Synoptic water-level measurements at all wells were made quarterly. Each measurement was repeated until two readings were identical. Water levels were manually recorded to the nearest 0.01 ft.

The data obtained from the recorders and the synoptic measurements were averaged for the period September 1, 1986, to September 1, 1987, and for the period March 1, 1986, to March 1, 1987. The values for both periods were then averaged together to determine average annual heads.

Tide-gage stations, equipped with digital recorders, were installed in the Gunpowder River and in Watson Creek to determine the tidal influence on ground-water levels. Tidal stage was recorded at 15-min intervals. A rain gage and digital recorder collected rainfall data at New O-Field. All data were stored in the U.S. Geological Survey computer network.

Ground-Water, Surface-Water, and Bottom-Sediment Sampling

Water samples were collected from selected O-Field wells five times on a quarterly basis, beginning in December 1985 and ending December 1986. Additional samples were collected more frequently from wells OF6, OF6A, and OF17A. These three wells were sampled weekly from July 22, 1986, to September 3, 1986, and then once every 2 weeks through February 5, 1987. Sampling methodology consisted of (1) purging the wells, (2) measuring field parameters, and (3) collecting, filtering, and bottling samples to be sent to the laboratory for chemical analyses.

Teflon bladder pumps with Teflon sampling tubes were permanently installed in the deeper wells (well sites OF6C, OF12C, OF13C, OF14C, OF14D, OF18C) for purging and collecting samples. The wells without bladder pumps were purged and sampled with Teflon bailers (1.5-in. od) attached to Teflon-coated stainless-steel cables. To obtain a controlled rate of sample flow, a bottom-discharge fitting with a 0.25-in. od Teflon tube, approximately 6 in. long, was attached to the bailer. The bailers were used for more than one well.

Water levels were measured at each well prior to sampling to determine the volume of water within the well. Generally, two to four well volumes of water were purged from each well, except for those wells that bailed dry after less than two well volumes were removed. For purging deep wells, the bladder pump was placed approximately 10 ft below the water surface and gradually lowered as the water level declined. The shallow wells were bailed from the top of the water column. To determine if the amount of purging

was adequate to remove the casing water, the purging methods were tested in an offsite well. The well was spiked with a known volume of salt and purged until the specific conductance declined to prespike concentrations. This test showed that removal of about 2.7 casing volumes adequately purged the casing water (Oliveros and others, 1988). The water level in the well was allowed to recover before samples were collected. Recovery periods ranged from 5 min to 4 hours.

Decontamination of bailers between wells consisted of rinsing at least three times with distilled water. After sampling the most contaminated wells, samples of the final rinse water were analyzed and showed that the rinsing was adequate to decontaminate the bailers. The same bailer was used to purge and sample a well, so the bailer was also rinsed with well water several times prior to sample collection. The possibility of cross contamination was further minimized by first sampling background wells and other sites suspected or known to be the least contaminated.

Samples were filtered and preserved in the field at the time of collection. Samples for analyses of all inorganic chemical constituents, except sulfide, were filtered through 3.9×10^{-6} in. (0.1 micrometer) membrane filters using a peristaltic pump. Before beginning sample collection at a new well, the filter stands and Tygon tubing used with the peristaltic pumps were rinsed thoroughly with distilled water and well water. The Tygon tubing was replaced frequently. To preserve the bottled samples until chemical analyses could be performed, samples for major cations and metals were treated with concentrated nitric acid, and samples for ammonia and total phosphorous were treated with sulfuric acid. Cyanide samples were preserved with sodium hydroxide.

The organic and sulfide samples were not filtered but were collected directly from the discharge tube of the bladder pump or bailer into the appropriate bottles. Samples for volatile organics were the first samples collected after well recovery. To prevent aeration of the sample, special care was used in collecting the samples for analyses of VOC's, total organic halogen (TOH), and sulfide. For VOC's, two 40 milliliter (mL) vials were filled at each well with a slow, steady stream of water and allowed to overflow several times. The inflation pressure of the bladder pump was lowered to decrease the sample discharge rate, or the bottom-discharge device was used on the bailer to obtain a slow stream of water. The glass vials were immediately sealed with Teflon-septa caps and checked for bubbles. If bubbles were seen, the vials were emptied and refilled. TOH samples were collected in the same manner in 250-mL glass bottles with Teflon-septa caps. Zinc acetate and sodium hydroxide were added to the sulfide bottles as preservatives before the bottles were filled with samples. Samples for analysis of base-neutral-acid organic compounds were collected in amber glass 3.8-liter (L) jugs.

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

Dissolved-oxygen and alkalinity concentrations, temperature, specific conductance, and pH were measured in the field. After well purging, the dissolved-oxygen concentration in each well was determined with a dissolved-oxygen meter equipped with a probe and submersible stirrer attached to the meter with a 50-ft cable. After the meter was calibrated to water-saturated air, dissolved oxygen was measured with the probe and stirrer assembly at the bottom of the well, or at 50 ft in the wells that were deeper than the cable length. For the deep wells, dissolved oxygen also was measured by pumping water from the screen depth into a jug. The jug was allowed to fill and 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 degrees Celsius ($^{\circ}\text{C}$). Temperature was also recorded from the dissolved-oxygen, pH, and conductance meters. The pH was read on a digital 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 samples were 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 conductance meter with a glass conductivity cell. By using a temperature probe with the meter, specific conductance at field-sample temperatures could be compensated automatically to a specific-conductance value at a temperature of 25°C . If the well water was turbid, the specific conductance was determined on both a filtered and an unfiltered sample.

Alkalinity titrations were performed on a 100-mL filtered sample. The sample was stirred slowly using a battery-powered magnetic stirrer, while a Hack digital titrator was used to add 0.16 normal sulfuric acid (H_2SO_4) solution to the sample until a pH end point of 4.5 was reached. Alkalinity was calculated as the end point of the cumulative volume of added acid as a function of pH.

Dissolved-oxygen meters were calibrated each day before and during sampling. The pH meters were calibrated before sampling and several times each day during sampling. The specific-conductance meters were calibrated by the manufacturer, but periodic checks were performed with standards to ensure continued calibration. Records of daily procedures, meter calibrations, and meter readings were kept in field logbooks.

For quality control and assurance, split samples were collected on at least 10 percent of the total number of wells

sampled. Split samples not showing analytical agreement were reanalyzed when possible. Two filter stands were used to simultaneously fill duplicate bottles for analysis of inorganic constituents. 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. The standards were labeled as well sites and sent with actual samples to the contract laboratory for analyses. Laboratory results agreed closely with the known concentrations of the standards. Wash blanks and a trip blank included with the field samples showed only low concentrations of common laboratory contaminants.

The contract laboratory followed the quality-assurance/quality-control program developed by USATHAMA for analysis of all the inorganic and organic constituents. Daily quality control consisted of initial calibration of the analytical instrument, additional analyses of calibration standards with each daily lot of samples, and the use of control spikes with known concentrations. During initial calibration of the analytical instruments, six standards were run at concentrations of 0, 0.5x, x, 2x, 5x, and 10x, where x is the detection limit established by USATHAMA. Besides initial calibration, one calibration standard and a blank were run with each 8-hour shift using the gas-chromatograph mass-spectrometer (GCMS) analysis of organic constituents; in most cases, seven calibration standards and a blank were run with each daily lot for analysis of inorganic constituents.

For the organic analyses, each sample was spiked with three surrogates at one of three levels of concentration. The percentage of recoveries was calculated and plotted on daily quality-control charts. The control charts, which are plots of percentage of 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 percentage of recoveries were calculated and used to set control limits for the target value. As new samples were analyzed, the percentage of recoveries of the spikes was compared with the established control limits. Warning limits to indicate that a sample may need to be reanalyzed were set at two times the standard deviation above and below the mean. For the inorganic analyses, three control spikes were added to each daily lot of samples, instead of to each sample. The percentage of recoveries of the spikes was plotted on daily quality-control charts as described for the organic analyses. Sample analyses not meeting the quality-assurance/quality-control standards were rerun or resampled if the holding time had expired.

The above procedures also applied to the surface-water and bottom-sediment samples, but collection methods were different. Surface-water samples for the August 1985 sampling were obtained from a boat. The samples were

collected from immediately below the water surface at the approximate maximum low tide and completed before the tide began moving into Watson Creek. The first samples collected were from the Gunpowder River, and later samples were collected from Watson Creek. Bottom-sediment samples were collected the following day so as not to introduce contaminants into the surface-water samples as a result of possible remobilization of sorbed species on the sediment. The samples were collected using PVC coring tubes to collect material from the upper few inches of sediment. Surface-water samples collected from the mouth of Watson Creek after August 1985 were obtained by walking out along a sandbar during low tide and collecting grab samples approximately 50 to 100 ft from the creek in the Gunpowder River.

Modeling of Ground-Water Flow

The U.S. Geological Survey modular ground-water flow model (McDonald and Harbaugh, 1984) was used to simulate ground-water movement at O-Field, Aberdeen Proving Ground. The purpose of the flow modeling was to test conceptual hypotheses regarding ground-water movement and to estimate the hydrologic effects of various remedial actions at O-Field.

The three-dimensional steady state movement of ground water through porous media may be described mathematically by the equation (McDonald and Harbaugh, 1984, p. 7)

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) - W = 0 \quad (1)$$

where:

x, y, and z are Cartesian coordinates aligned along the major axes of hydraulic conductivity K_{xx} , K_{yy} , and K_{zz} ;

h is the potentiometric head (L);

W is a volumetric flux per unit volume and represents sources and sinks of water (t^{-1});

t is time (t); and

K is hydraulic conductivity.

The flow model utilized for O-Field solves the partial differential equation using the finite-difference method in which equation 1 is replaced by a finite set of discrete points in space and time, and the partial derivatives are replaced by differences between functional values at these points (McDonald and Harbaugh, 1984, p. 8). The result is a large system of simultaneous linear equations, iteratively solved in the O-Field model by the strongly implicit procedure. The solution yields values of head at specific points in space and time.

Surface and Borehole Geophysics

The U.S. Geological Survey utilized surface-, borehole-, and marine-geophysical methods to aid in defining the hydrogeology and contaminant distribution. Gamma logs were run through the augers at each borehole to supplement the core samples and to provide geologic control in sections where sample recovery was poor. In addition, borehole gamma, spontaneous potential, and electrical resistance logs were run in two uncased test boreholes to provide deeper lithologic information.

Electromagnetic surveys were conducted at O-Field using a Geonics EM 34-3. The survey was run at spacings of 32.8 ft, 65.6 ft, and 131.2 ft, using both the horizontal- and vertical-dipole orientations. Data were collected at 100-ft intervals along 34 east-west traverses located 100 ft apart.

Seismic reflection surveys were conducted in the Gunpowder River and in nearby creeks during October 1985. In most cases, geologic information was obscured due to multiple reflections because of shallow water (6 ft) and organic-rich or tightly packed sand bottoms. However, penetration to a depth of about 150 ft was achieved along a 2,000-ft traverse, 1,400 ft offshore from Old O-Field, parallel to the shoreline (fig. 2).

DESCRIPTION OF STUDY AREA

An understanding of the ground-water hydrogeology is required to analyze the distribution and movement of ground-water contamination and to evaluate remedial actions. An understanding of the dominant surface-water currents and the distribution of bottom-sediment lithotypes in Watson Creek is necessary to describe the controls on contaminant distribution within the creek and the potential for offsite movement of contaminated surface water. This paper focuses on the ground-water hydrology at O-Field to a depth of about 120 ft, while lesser emphasis is placed on sediments between approximately 120 and 200 ft deep, and on the surface water and bottom sediments within Watson Creek and in the Gunpowder River in the vicinity of the mouth of Watson Creek.

O-Field is located on unconsolidated sand, clay, and silt of the Atlantic Coastal Plain. The Coastal Plain sediments form an eastward- to southeastward-thickening wedge-shaped body overlying a basement complex of Precambrian to Paleozoic crystalline rocks and Mesozoic rift-basin sedimentary rocks. The depth to pre-Cretaceous basement rocks at O-Field is about 650 ft (Hansen and Edwards, 1986).

The O-Field range is about 259 acres in area (fig. 1) and is bordered on the west by the Gunpowder River, on the north and east by Watson Creek, and on the south by H-Field. The topography is relatively flat, the highest elevation being about 19 ft above sea level.

Sediment samples from a depth of 48 ft at O-Field are of Quaternary age, based on pollen analysis performed by G.S. Brush (Johns Hopkins University, Department of Geography and Environmental Engineering, written commun., 1985). The sediments compose the Talbot Formation and alluvium. The Talbot Formation in the area is typically pale- to moderately-gray silt (dark brown in less weathered areas) and graywacke sand. Pebbles and gravel are common. The formation also contains localized thick beds of massive dark-gray clayey silt and abundant leaf fossils. Alluvium in the area consists of reworked sediment from the Talbot Formation or from Cretaceous sediment (Owens, 1969). Cretaceous sediment crops out approximately 1 mile (mi) north of O-Field (Owens, 1969). The depth to Cretaceous sediment at O-Field is not known.

Three aquifers are present at O-Field to a depth of about 120 ft. In this paper, the aquifers are designated, from shallowest to deepest, as the "water-table aquifer," the "upper confined aquifer," and the "lower confined aquifer." Correlation of aquifers and confining units along sections shown in figure 2 at O-Field are shown in figures 4-8. Additional aquifers occur deeper but were not investigated during this study.

Water-Table Aquifer

The water-table aquifer at O-Field is present at all locations investigated. It forms an areally extensive layer that is probably hydraulically continuous with the water table at H-Field to the south and adjoining surface waters. Saturated thickness varies seasonally as the water table rises and falls, but is typically about 10 ft.

The water-table aquifer is composed of brown to reddish-brown quartz sand interbedded with discontinuous silt and clay layers. The sand is medium grained (0.00625-0.05 in.) in the central areas near Old O-Field (sites OF6, OF18, and OF19) and becomes finer to the east and north (wells OF12B, OF13B, and OF14B) and coarser to the northeast (well OF17A) and at New O-Field (well OF16A). Adjacent to Old O-Field, on the east side, the water-table aquifer contains discontinuous layers of clay that may locally impede vertical movement of contaminants.

The soil zone at the Old and New O-Fields is composed of dark-brown clayey to sandy silt, typically about 3 ft thick. At H-Field, approximately 0.5 mi south of Old O-Field, the soil zone consists of about 6 ft of yellow clay. A dominantly sandy soil zone was found only at well site OF13B, adjacent to the north side of Old O-Field, and at wells OF18B and OF19, east of Old O-Field. The proximity of site OF13B to Old O-Field suggests that the silt may be absent due to cut and fill operations.

Estimates of horizontal hydraulic conductivities in the water-table aquifer were determined through the use of

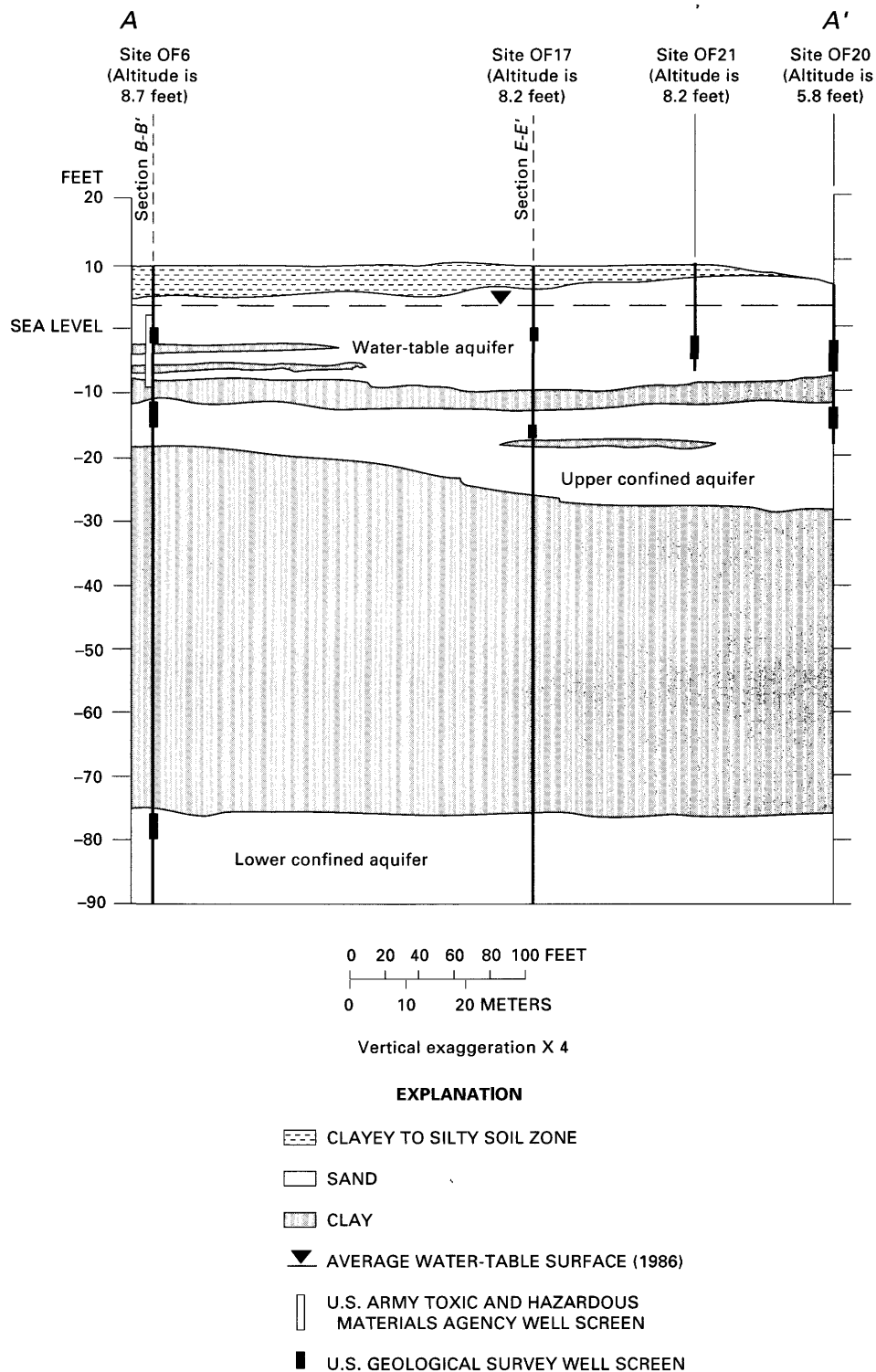


Figure 4. Hydrogeologic section A-A' from figure 2.

aquifer slug tests, as previously described, and by calibration of the digital ground-water flow model. The highest hydraulic conductivities determined by slug test (table 1) in the water-table aquifer were between 65 and about 200 feet per day (ft/d), based on data from five wells, and were

located in an area about 75 ft east of Old O-Field and extended eastward to the Watson Creek shoreline. The remaining values, less than 0.1 ft/d, are probably due, in part, to interferences during well construction, such as the collapse of fine-grained material around the screen prior to

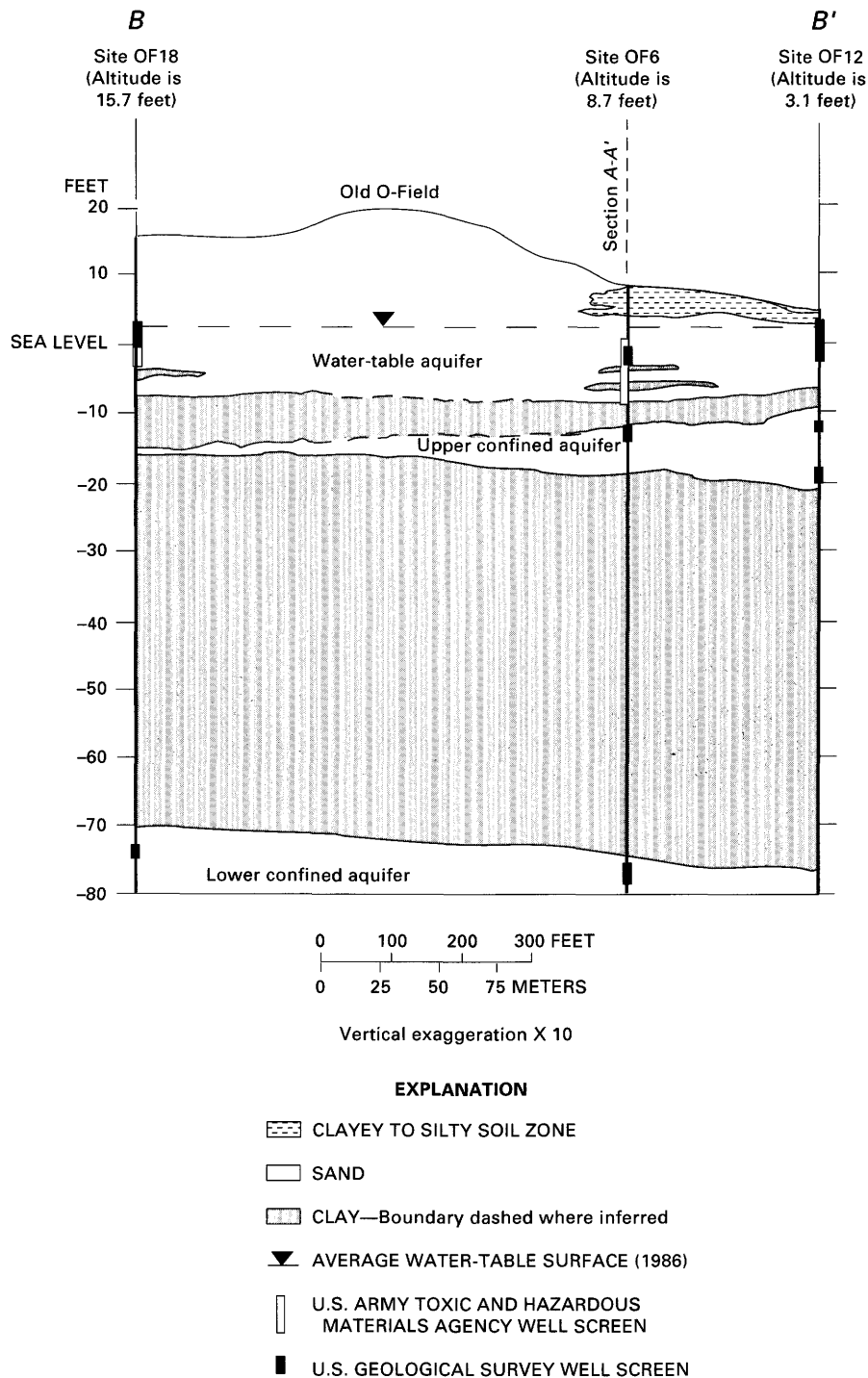


Figure 5. Hydrogeologic section *B-B'* from figure 2.

installation of the gravel pack, or to insufficient well development. However, the areas of low hydraulic conductivities found by the slug test are also areas containing, in general, finer-grained sediment than the area east of Old O-Field, where higher values were obtained. Therefore, the low values probably are partly due to the presence of finer-grained aquifer material. Model simulations suggest

that the hydraulic conductivities in the areas containing finer-grained sediment range from 4 to 30 ft/d.

The water-table aquifer derives most of its recharge from vertical infiltration of precipitation. Precipitation infiltration may be somewhat retarded by the clayey soil covering much of O-Field. Areas having dominantly sandy soil, such as at wells OF13B, OF18B, and OF19 (fig. 2),

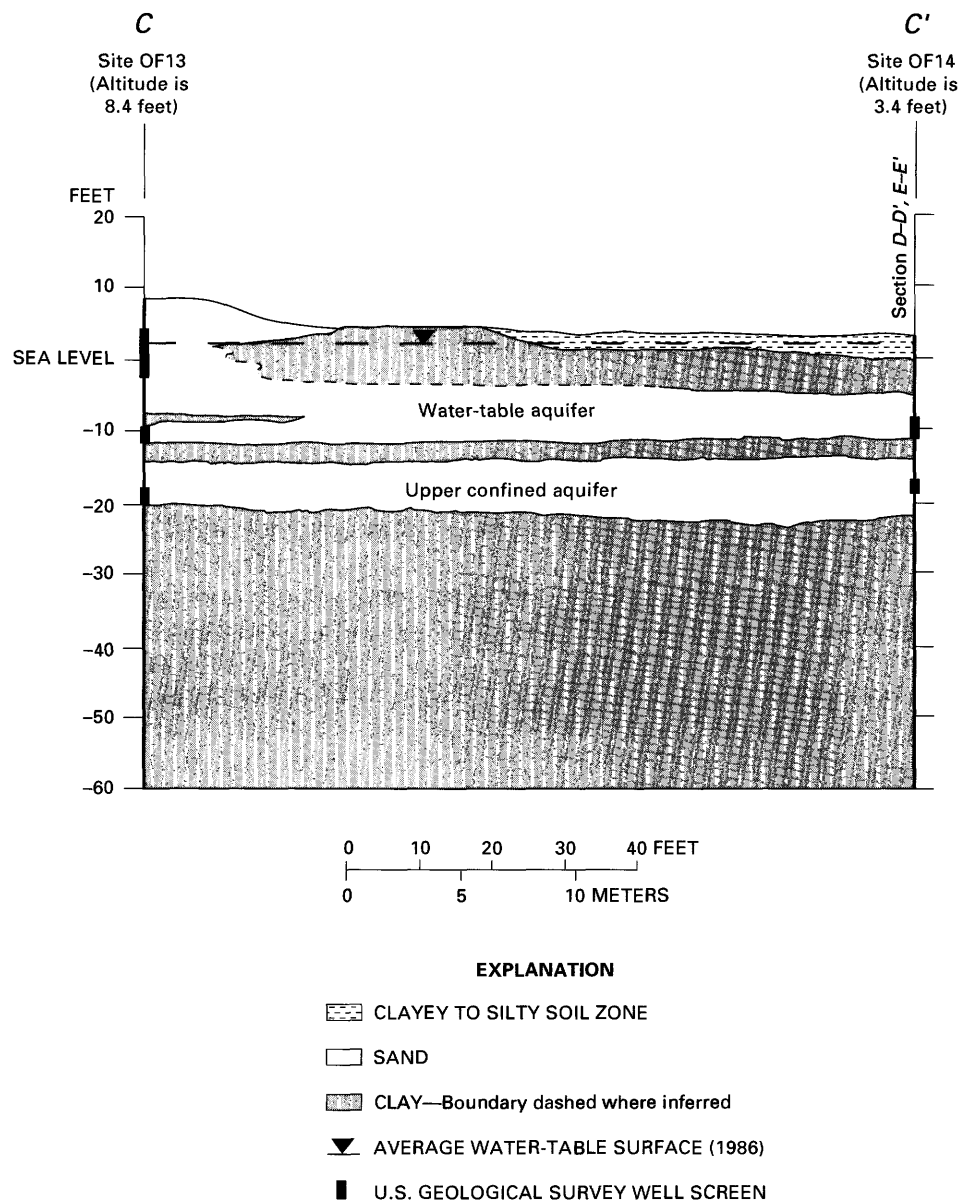


Figure 6. Hydrogeologic section C-C' from figure 2.

and areas where the soil zone has been disturbed, however, such as in the disposal areas, are areas where infiltration of precipitation may be greater. Runoff collects into short-lived ponds in some topographically low areas, such as at well OF19. The ponds provide storage that increases localized recharge of the water-table aquifer. This recharge produces ground-water mounding during the winter and spring months in areas such as at well OF19 (fig. 2).

Additional recharge to the ground water at O-Field occurs by lateral movement of ground water from H-Field. Although the soil at H-Field is probably clayey, as indicated by drillers' logs, a network of bermed, elevated roads limits rainfall runoff. The trapped precipitation probably recharges ground water by slow downward leakage through

the clayey soil or rapid infiltration through discontinuities in the clay. Ground water moves radially away from H-Field toward surface-water bodies and O-Field (fig. 9).

Ground water is also periodically recharged by Watson Creek. During occasional high tides, water from the creek moved overland to within 10 ft of well OF14B. Vertical infiltration of water from the creek into the aquifer probably occurs during such high tides. The geochemical evidence for such infiltration is discussed in the section "Ground-Water Contamination."

Ground-water discharge at O-Field primarily is to Watson Creek and the Gunpowder River. Much of the Watson Creek shoreline contains a thick marsh that is periodically submerged. Ground-water discharge along the

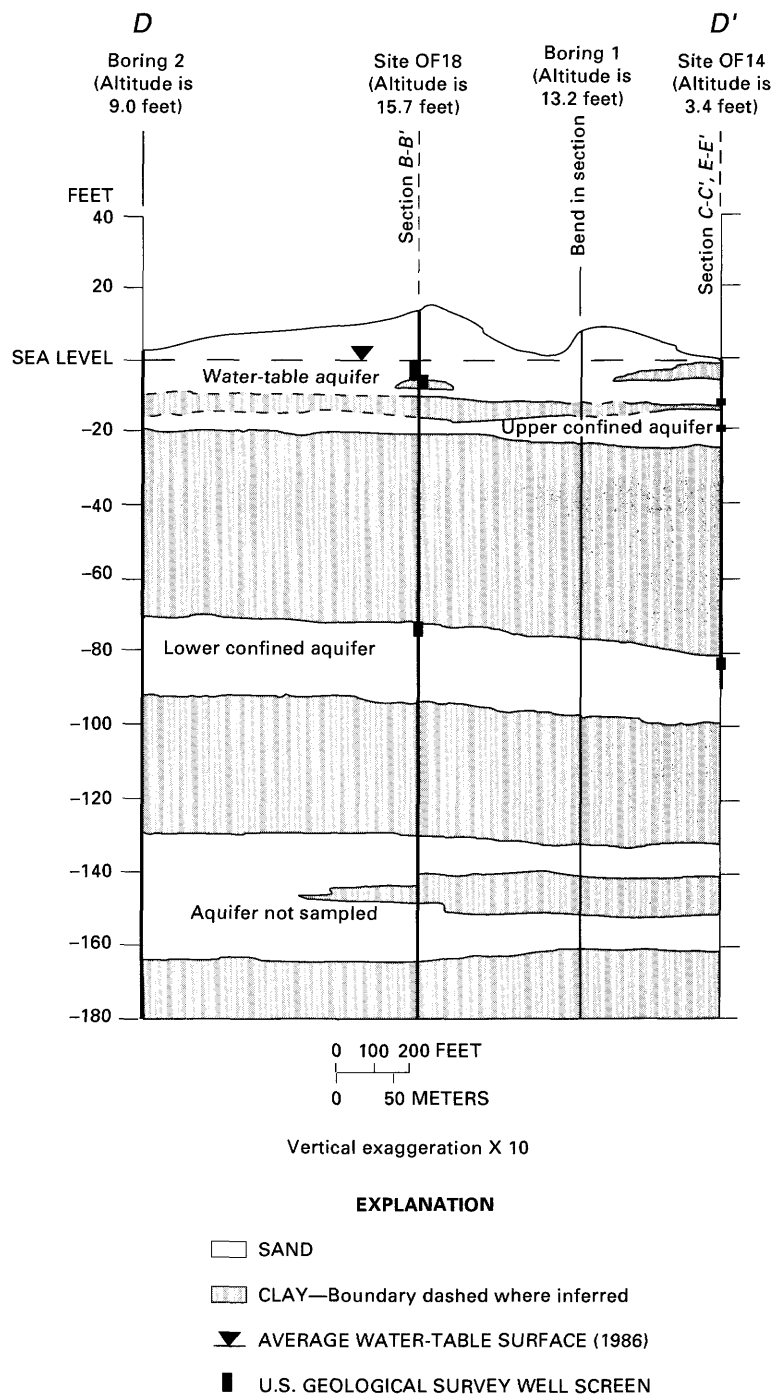


Figure 7. Hydrogeologic section *D-D'* from figure 2.

Watson Creek shoreline in the marsh areas is somewhat slower than in nonmarsh areas, due to the buildup of fine-grained sediment in the marshes. Along the Gunpowder River shoreline and the Watson Creek shoreline immediately adjacent to O-Field, the absence of marsh allows discharge of ground water to occur relatively unimpeded. The steady state horizontal ground-water velocity between the east side of Old O-Field and Watson Creek, as calcu-

lated from the ground-water flow model using a porosity of 0.3, is between about 100 and 260 feet per year (ft/yr). Ground water at O-Field also discharges to a small ephemeral stream (fig. 2) between Old and New O-Fields during periods of high ground-water levels.

Additional discharge of ground water occurs by evapotranspiration. Kozlowski (1964, p. 140) has estimated that forests in the southern United States lose as much water

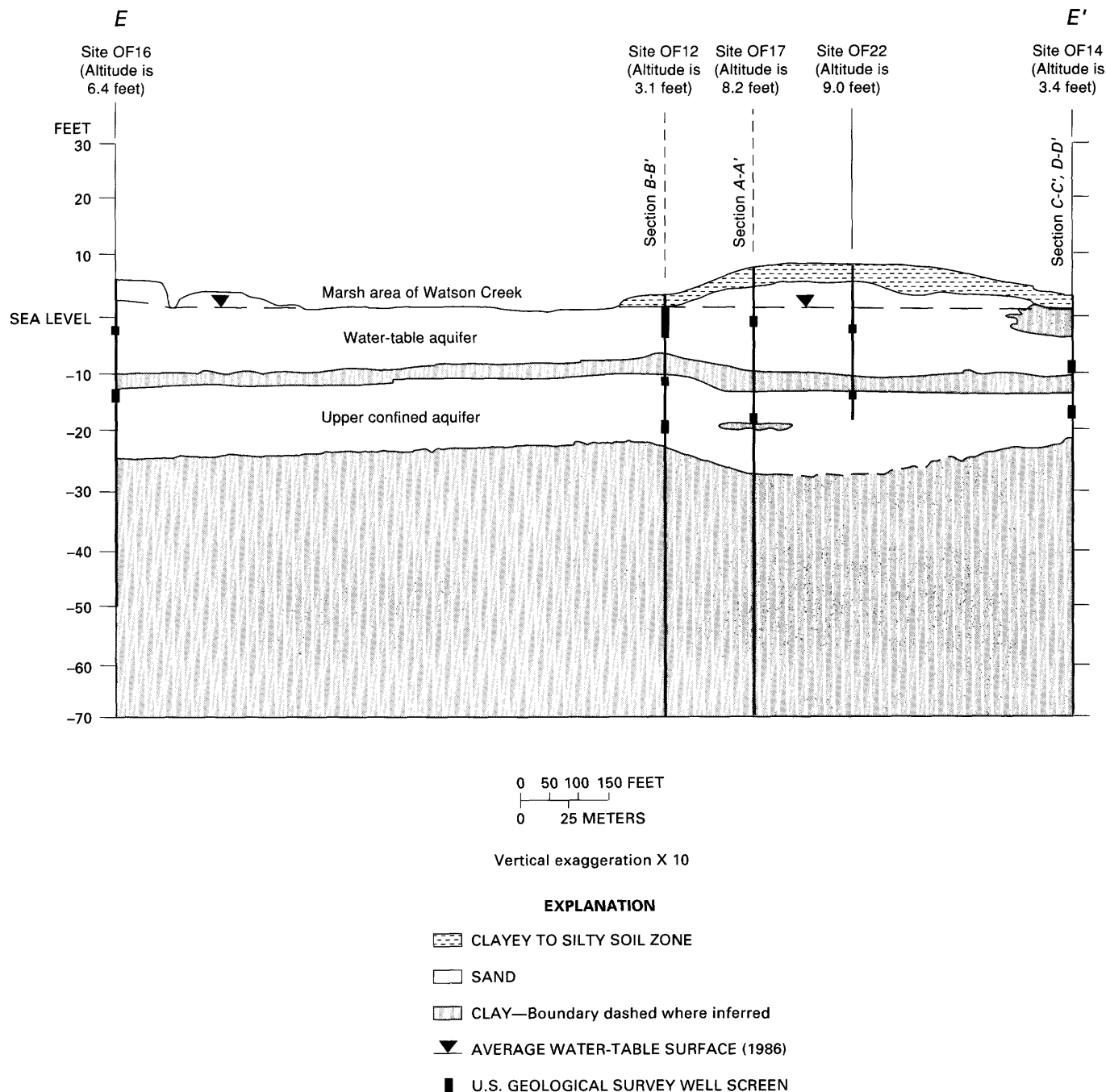


Figure 8. Hydrogeologic section E-E' from figure 2.

as 8,000 gallons per acre per day [(gal/acre)/d]. Several times that amount have been estimated to transpire from European forests (Miller, 1947). Water losses from a single silver maple tree have been estimated to be as much as 58 gallons per hour (gal/hr) during a late afternoon in July (Cummings, 1941). Lull and Axley (1958) reported that the total evapotranspiration from the soil within 5 ft of land surface in New Jersey ranged from 17 in. in bare plots to

22 in. under forested conditions between April and November. Forested areas near O-Field would be expected to behave similarly.

Ground-water levels in the water-table aquifer at O-Field varied by as much as 3 ft, depending on season, rainfall, and tidal influence. Figure 10 demonstrates that the head difference between well OF6A and well OF17A, approximately 240 ft downgradient, was substantially

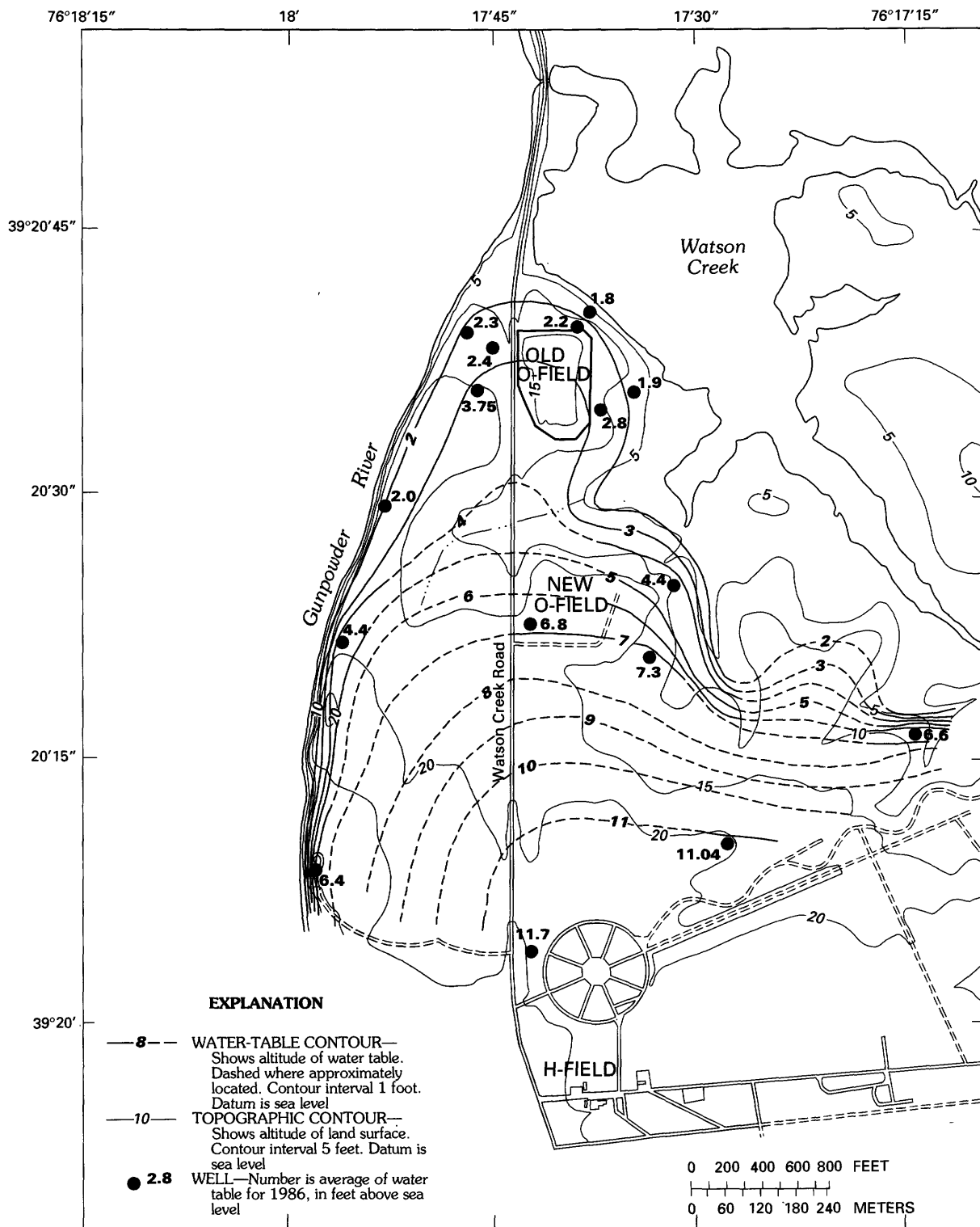


Figure 9. Altitude of the average water-table surface for 1986.

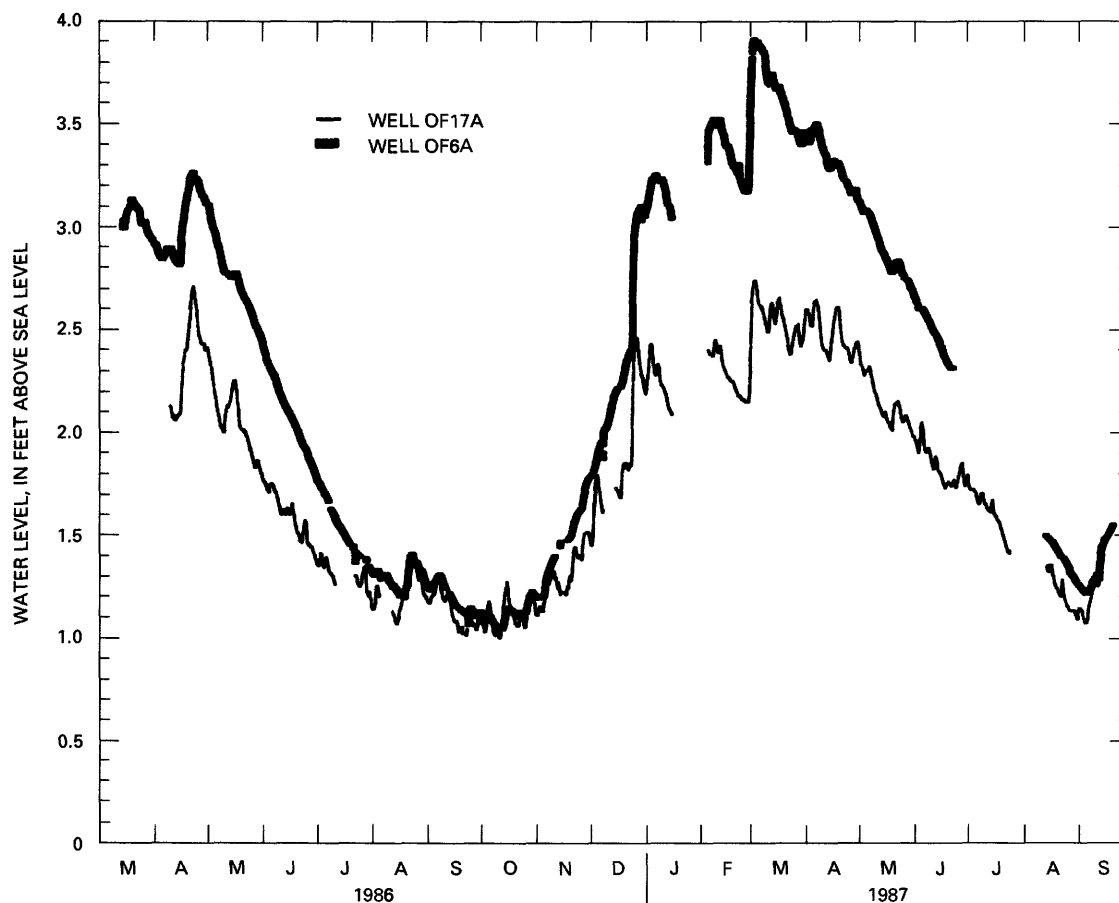


Figure 10. Water-level changes in the water-table aquifer at wells OF6A and OF17A for March 1986 to September 1987. (Data recorded at 15-min intervals.)

Table 1. Hydraulic conductivities in the water-table aquifer as determined by slug test

[All values were calculated using the Hvorslev (1951) method. ft/d, feet per day; <, less than]

Well	Horizontal hydraulic conductivity (ft/d)
OF6A	<0.1
OF12B	<.1
OF13A	<.1
OF13B	<.1
OF14B	<.1
OF16A	<.1
OF17A	202
OF18A	<.1
OF18B	<.1
OF19	<.1
OF20A	65
OF21	147
OF22A	184

greater during the winter and spring months than during the summer and fall months. In fact, during October 1986, gradients occasionally reversed (water flowed from well OF17A toward well OF6A). Thus, ground-water velocity (derived from head gradients) varied between greater than 0.2 ft/d in the winter to virtually zero during the summer of 1986 under drought conditions.

Ground-water levels at Old O-Field during the winter months rose to between 2.7 and 3.9 ft in altitude relative to sea level. The average surface altitude of Old O-Field is about 15 ft. Assuming trench depths of about 12 ft (original field-survey notes of Old O-Field burial-pit locations dated September 17, 1942, book 36, located in the files of USAAPGSA, DEH, EPSD), the seasonally high ground-water levels rose above the bottom of the disposed material.

Water-level increases in well OF6A are the result of major rainfall events, and the recessions are due to ground-water discharge to Watson Creek. In well OF17A, nearer than well OF6A to Watson Creek, the same rainfall events are recorded, but they are superimposed on a number of small-scale fluctuations that can be related to tidal changes in the creek. The tidal changes in the creek produce

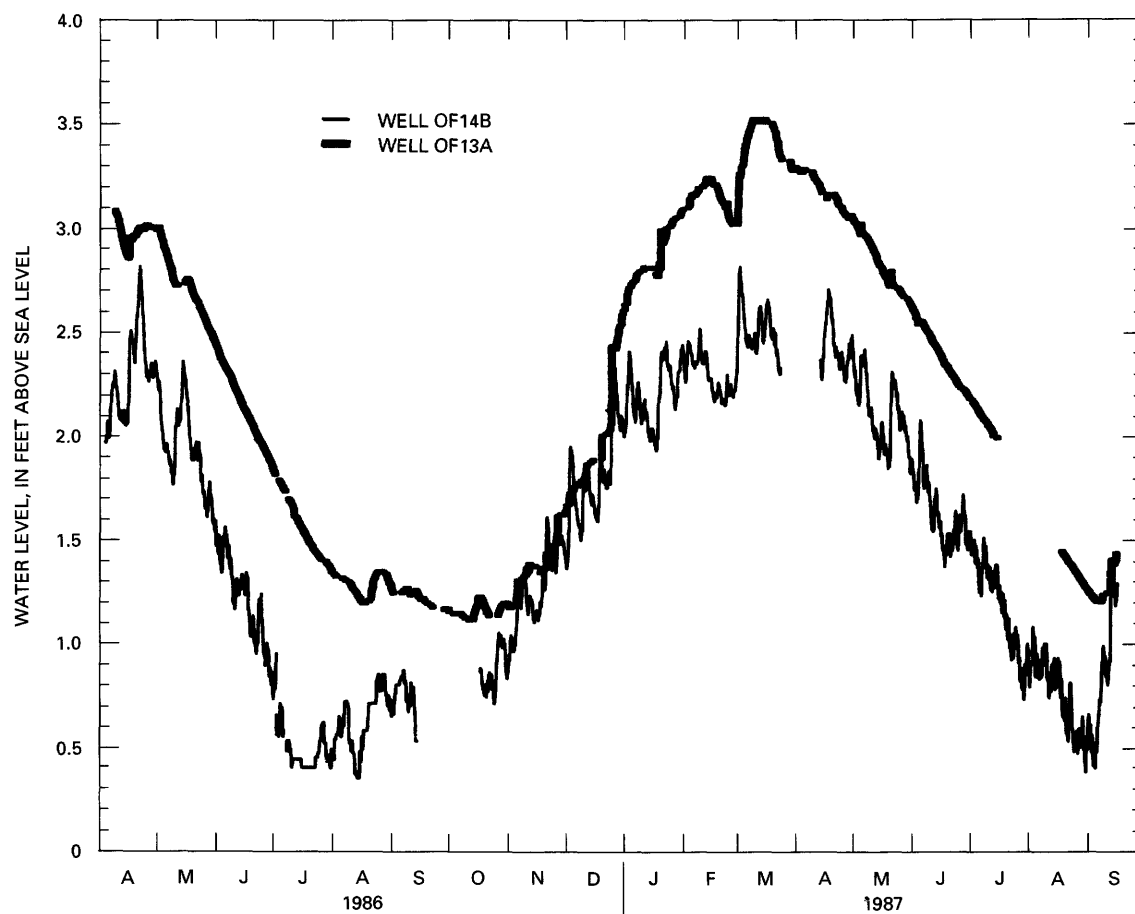


Figure 11. Water-level changes in the water-table aquifer at wells OF13A and OF14B for April 1986 to September 1987. (Data recorded at 15-min intervals.)

base-level shifts in the aquifer, raising and lowering heads inland as far as well OF17A, approximately 140 ft from the shoreline.

Similar patterns may be seen on the north side of O-Field between well OF13A (upgradient) and well OF14B (downgradient). A major difference, however, is that during the summer drought of 1986, the hydraulic gradient between the wells remained high (fig. 11). Although well OF14B is only about 30 ft from the shoreline of Watson Creek, water levels in the well, screened at an 11- to 13-ft depth, declined to about 1 ft below creek level during July 1986 (fig. 12). The decline was probably due to removal of ground water by evapotranspiration in the vicinity of well OF14B at a faster rate than it could be replaced by the combined movement of water infiltrating from the creek and water moving downgradient from well OF13A.

The drought of 1986 was apparently stressful enough to force the trees at O-Field to use ground water from the saturated zone as their primary source of moisture. Hydrographs show that water levels remained low until November, despite several rainfall events during late summer. The lack of ground-water recharge during the late summer was

probably due to resaturation of the vadose zone or to evapotranspirative stress. The trees may have prevented recharge by intercepting the vadose water or by continuing to use ground water despite the availability of vadose water. Results of field studies by Dolman (1988, p. 231) suggest that, after a drought, trees may still derive a significant quantity of water from the saturated zone, possibly reflecting an inability of the trees to quickly switch back to using water from the unsaturated zone. The clayey soil layer at O-Field apparently impeded the infiltration of water from the creek, and ground-water flow was not great enough to replace the water as quickly as it was being utilized by the trees. The influence of water infiltrating from the creek was reflected in a gradual rise in specific conductance through the summer at well OF14B. The decreased gradient between wells OF13A and OF14B during the fall months is due to decreased evapotranspiration.

Background chemistry of ground water in the water-table aquifer at O-Field (table 2) was determined primarily from analyses of water from wells OF2, OF3, OF5, and OF8. Concentrations of total dissolved solids (TDS) range from 42 to 120 milligrams per liter (mg/L). The pH is

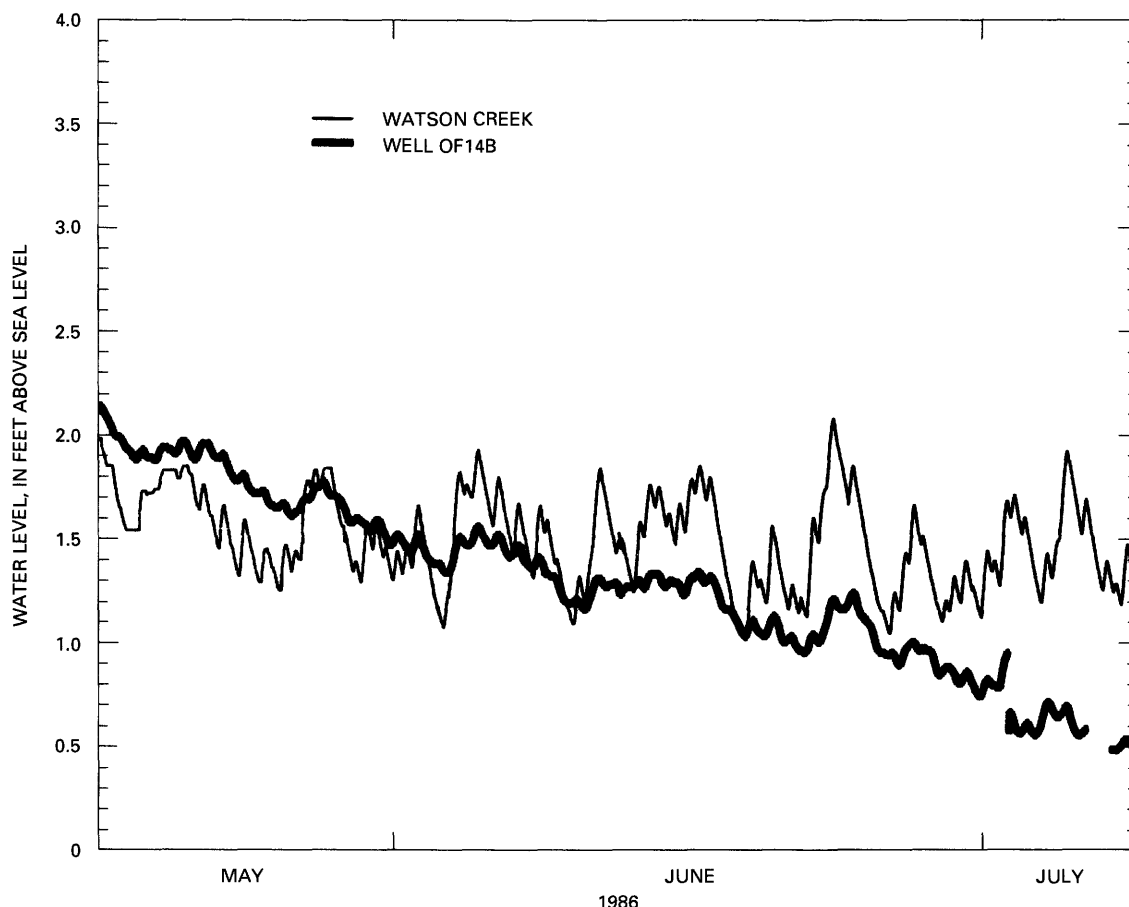


Figure 12. Water-level changes in the water-table aquifer at well OF14B and in Watson Creek for mid-May to mid-July 1986. (Data recorded at 15-min intervals.)

slightly acidic, ranging between about 4.8 and 5.7. The water contains 2 to 6.7 mg/L of dissolved oxygen. The percentages of major ions in these wells (fig. 13) indicate that the background chemistry is variable. However, calcium and magnesium are generally the dominant cations, and sulfate is the dominant anion. Potassium became the dominant cation during the drought of 1986, possibly derived from the aquifer matrix. Chloride concentrations ranged from 2.2 to 8.4 mg/L, except at well OF5, where the concentration was 23.1 mg/L. The source of the higher chloride concentration at well OF5 is unknown but is probably not related to activities at O-Field. Water from all the background wells contains less than 2 mg/L of dissolved organic carbon, which is common in natural ground water (Thurman, 1985). Low concentrations of boron (mostly <0.1 mg/L), antimony (<0.004 mg/L), and zinc (≤ 0.05 mg/L) are present in the background ground water.

The underlying confining unit is composed of black to gray or greenish-gray clay. The thickness ranges from 0.5 ft at New O-Field (well OF16B) to 5 ft at Old O-Field (well OF6C) (fig. 14). At New O-Field the clay is friable and, therefore, probably more permeable than at wells

OF17B and OF20B, east of Old O-Field, where it has greater plasticity. Leakage through the confining unit near well OF22B, northeast of Old O-Field, probably is greater than that in other areas at O-Field. Drilling logs indicate that the confining unit is composed of clayey sand interbedded with silt. The presence of contamination in the upper confined aquifer at Old O-Field and New O-Field indicates that the confining unit is leaky or is discontinuous beneath the sites due to excavation of trenches or to natural causes. The depth to the confining unit is about 25 ft below Old O-Field and about 11 ft below New O-Field. As discussed later, simulations using a three-dimensional digital ground-water flow model with a vertical hydraulic conductivity through the clay of about 0.001 ft/d below Watson Creek and between about 0.001 and 0.0001 ft/d below O-Field produce head distributions that acceptably agree with observed water-level data.

Upper Confined Aquifer

The upper confined aquifer at O-Field is present at all areas drilled and probably extends southward to H-Field.

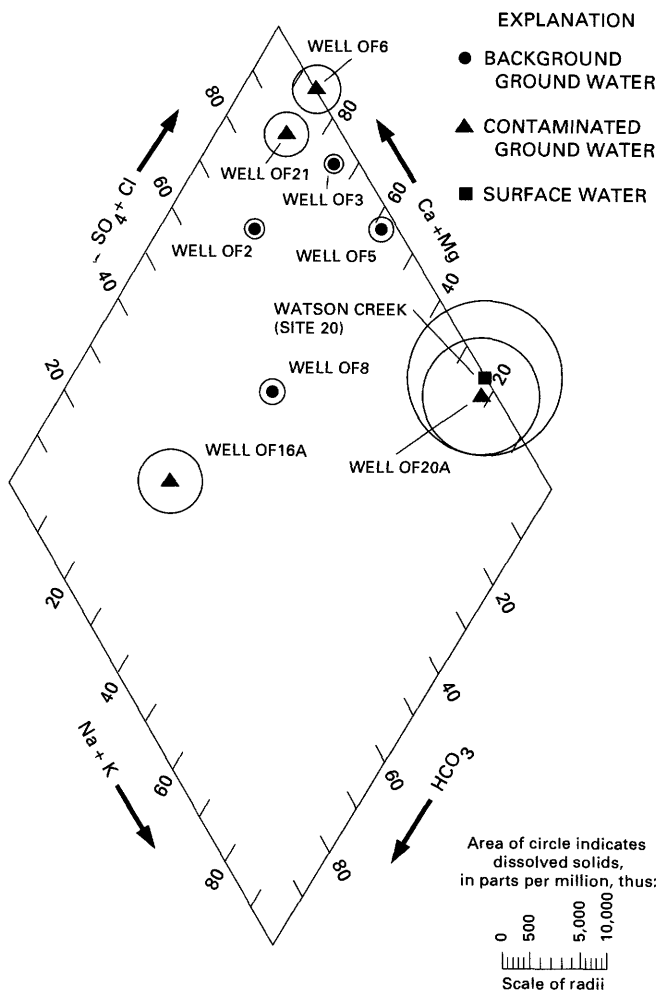


Figure 13. Percentages of dissolved major ions in Watson Creek and selected wells in the water-table aquifer, September 1987.

Table 2. Background water chemistry in the water-table aquifer from December 1985 through September 1987

[Cond., specific conductance; DO, dissolved oxygen; AmmOrN, ammonia + organic nitrogen; Phosph., phosphorous; TDS, total dissolved solids; DOC, dissolved organic carbon; fixed end point (pH 4.5); <, less than; —, no data; *, median value; pH is expressed as standard units, and specific conductance is expressed as microsiemens per centimeter. Inorganic constituents and DOC are expressed in milligrams per liter. Alkalinity is expressed as milligrams per liter of bicarbonate]

Parameter	Average	Standard deviation	Range	Number of samples
pH	5.25*	—	4.86 — 5.68	13
Cond.	105	16.4	79 — 135	12
DO	3.1	1.3	2.0 — 6.7	10
Alkalinity	7.5	7.0	0 — 23.5	11
Antimony	—	—	<.003 — .003	9
Arsenic	—	—	<.001	9
Boron	—	—	<.04 — .44	9
Calcium	4.6	2.1	2.47 — 7.4	9
Iron	1.56	4.22	.009 — 13.5	9
Magnesium	3.8	.8	2.95 — 5.8	9
Manganese	.08	.06	.024 — .22	9
Potassium	3	3.7	.17 — 12.4	9
Sodium	6.6	2.1	2.96 — 8.98	9
Silica	7.5	1.3	5.03 — 9.5	6
Zinc	.03	.02	.008 — .05	9
Chloride	7.5	5.8	2.2 — 23.1	9
Fluoride	—	—	<.1 — .19	9
Bromide	—	—	<.5	8
Sulfate	27.4	6.2	20.7 — 40	9
Sulfide	—	—	<1	1
Nitrate	—	—	<.05 — 1.08	9
Nitrite	—	—	<.05	9
AmmOrN	—	—	<.28 — .33	6
Phosph.	—	—	<.01 — .11	9
Ammonia	—	—	<.01 — .56	9
TDS	88.4	23.9	42 — 120	8
DOC	1.7	.3	1.24 — 2	5

The aquifer is thickest east of Old O-Field. It thins abruptly from 13.9 ft thick at well OF17B to 7 ft thick at well OF6B (fig. 4) near O-Field. It continues to become thinner to the west and is less than 1 ft thick at well OF18B (fig. 5). Toward the south the aquifer thickness is more uniform, being 13 ft thick at well OF12B and 12.5 ft thick at well OF16B. The depth of the aquifer, approximately 12.5 ft below sea level (fig. 15), and the presence of the overlying confining unit in wells near the Watson Creek shoreline imply that the aquifer remains confined beneath Watson Creek, at least near the shoreline. The confining unit is probably missing beneath deeper parts of the creek. Abrupt westward thinning at Old O-Field (fig. 5) implies that the aquifer does not extend beneath the Gunpowder River.

The upper confined aquifer is dominantly composed of dark-gray to brown, coarse-grained sand interbedded with gravel. Grain size decreases to the south, becoming medium grained at New O-Field (well OF16B). Interbedded layers of brown to gray clay are locally absent at a site east

of Old O-Field (well OF12B), west of Old O-Field (well OF18B), and at New O-Field (well OF16B).

Horizontal hydraulic conductivities in the upper confined aquifer were determined through the use of aquifer slug tests and, as discussed later, by calibration of a digital ground-water flow model. The horizontal hydraulic conductivities at Old O-Field determined by slug test ranged between 26 and 47 ft/d north of the fill and between 21 and 63 ft/d east of the fill (table 3). The lowest horizontal hydraulic conductivity determined by slug tests for the aquifer was 18 ft/d at New O-Field (well OF16B). Transmissivities derived from the digital flow model are only slightly lower [110–300 feet squared per day (ft²/d)] than those calculated from horizontal hydraulic conductivities using the slug test (180–600 ft²/d).

The head configuration in the upper confined aquifer (fig. 16) is similar to that in the water-table aquifer at O-Field. Recharge to the aquifer is by downward leakage of water from the overlying water-table aquifer, either slowly

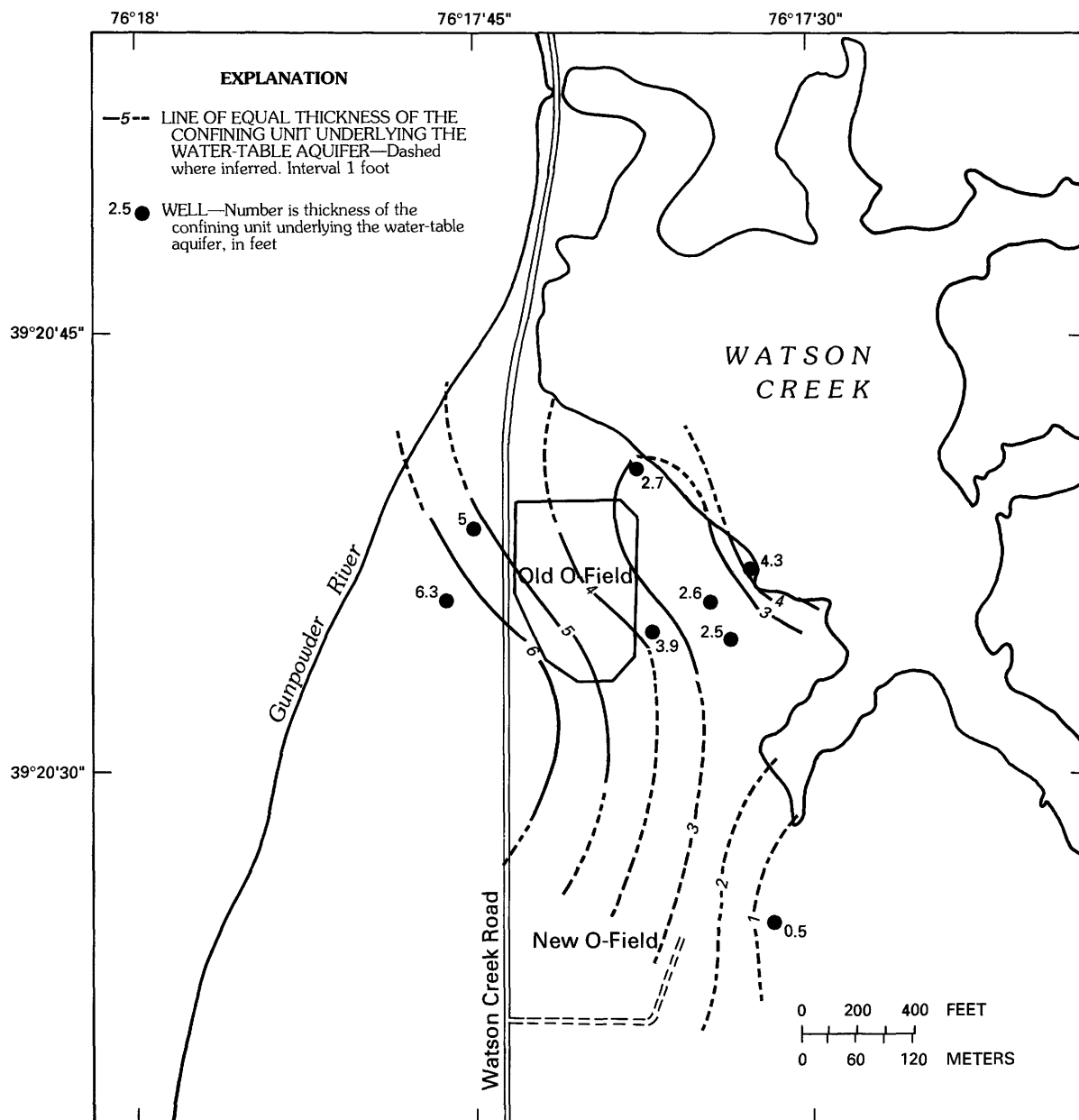


Figure 14. Thickness of the confining unit underlying the water-table aquifer at O-Field.

Table 3. Hydraulic conductivities in the upper confined aquifer as determined by slug test

[All values were calculated using the Hvorslev (1951) method. ft/d, feet per day; <, less than]

Well	Horizontal hydraulic conductivity (ft/d)
OF6B	35
OF12C	<.1
OF13C	47
OF14C	26
OF16B	18
OF17B	<.1
OF20B	21
OF22B	63

through the confining unit or more rapidly through confining-unit discontinuities. Discharge occurs in areas where the upper confined aquifer hydraulic head is greater than overlying or underlying hydraulic heads. This discharge can occur either through confining units or in areas where the aquifer is in hydraulic contact with another aquifer. Average annual head gradients for 1986 show that ground-water flow is away from Old O-Field toward Watson Creek (fig. 16).

A hydrograph of a representative well in the upper confined aquifer shows rapid, short-term water-level fluctuations of about 0.1 to 0.3 ft throughout the year (fig. 17).

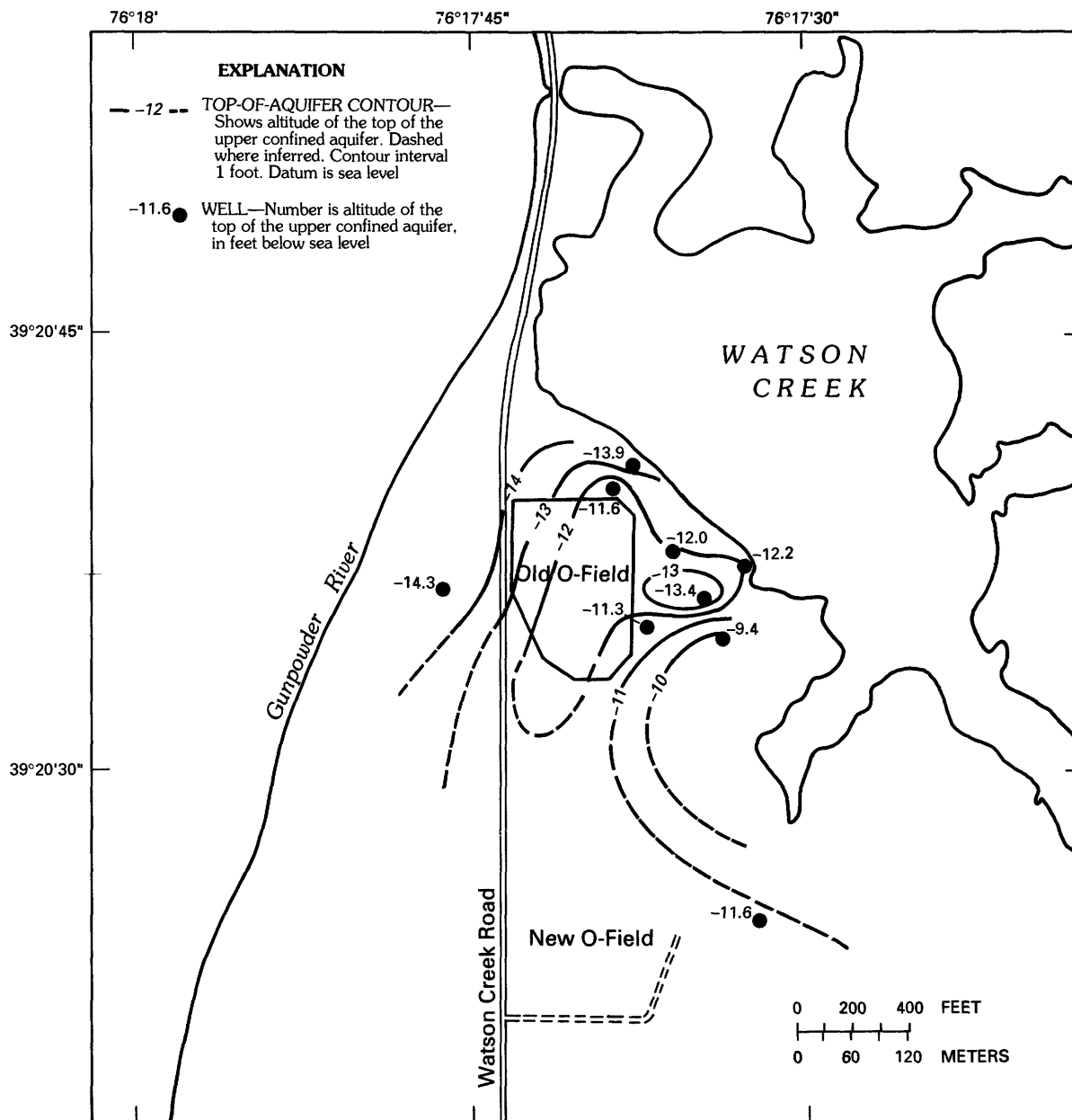


Figure 15. Altitude of the top of the upper confined aquifer at O-Field.

These fluctuations are in response to tidal changes in Watson Creek. The response is essentially instantaneous, even as far inland as well OF6B, adjacent to Old O-Field. The rapid response of the aquifer implies that the aquifer between the responding well and the creek is continuously confined. Thus, the aquifer acts as a hydraulic chamber, rapidly transmitting the increased pressure from rising tides to all confined areas. If the confining unit is missing between a particular well and the creek, the pressure might not be effectively transmitted and the well might not respond.

The hydrograph also shows several larger peaks during August 1986, coinciding with rainfall events and with water-level rises in the overlying water-table aquifer. There is an almost immediate response in the upper confined aquifer to water-level changes in the water-table aquifer. Infiltration through leaky areas in the confining unit, such as at well OF22, is not adequate to account for such rapid and major changes. It is also unlikely, based on tidal-pressure transmittal through the aquifer, that the confining unit is missing between the landfill and the creek. Therefore, the short-term rises in water level in the upper

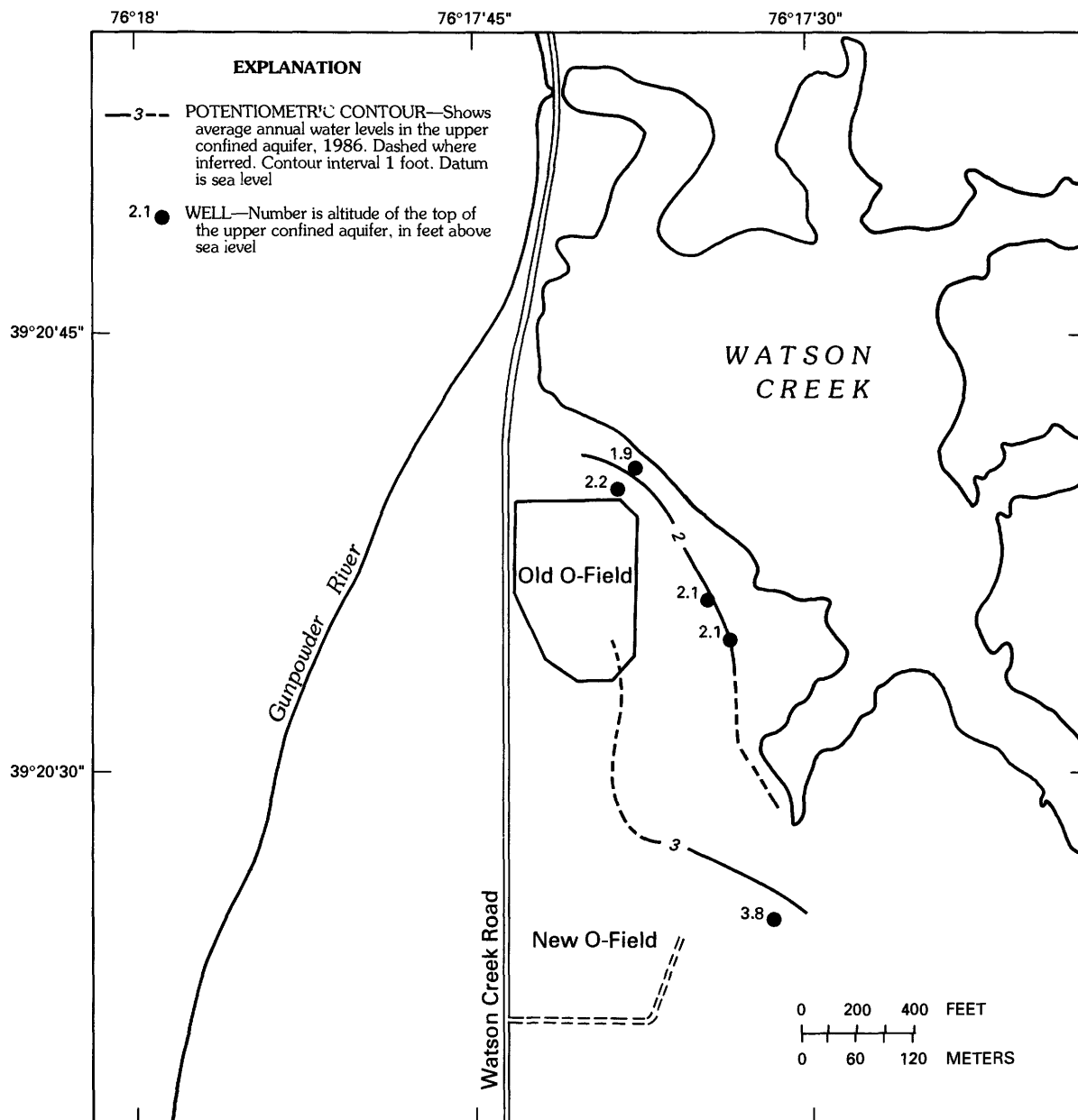


Figure 16. Average annual water levels for 1986 in the upper confined aquifer.

confined aquifer during rain events are probably largely due to pressure increases as a result of increased head in the overlying aquifer. Rainfall infiltration probably also plays a role, particularly within the Old O-Field disposal area, where excavations may have breached the overlying confining layer. Low levels of contamination in the upper confined aquifer provide evidence to suggest possible confining-layer discontinuities below the landfill.

No satisfactory background chemistry is available for the upper confined aquifer because all wells screened in the aquifer contained contamination. However, since the aquifer and the water-table aquifer are similar in lithology, they

are probably similar in background chemistry during long periods of no rainfall.

At all locations in the O-Field area where drilling extended below the upper confined aquifer, the lithology of the underlying confining unit is consistent. The black to dark-gray clay is friable near the top and becomes increasingly plastic toward the bottom. Leaf and stem fossils were locally abundant, typically associated with fine-grained vivianite (an iron-phosphate mineral). The top of the clay is found at a depth of 20 to 39 ft below land surface (figs. 4–8). The thickness ranges from 48.5 to 55.5 ft (fig. 18) at Old O-Field. The top of the clay is eroded into a trough,

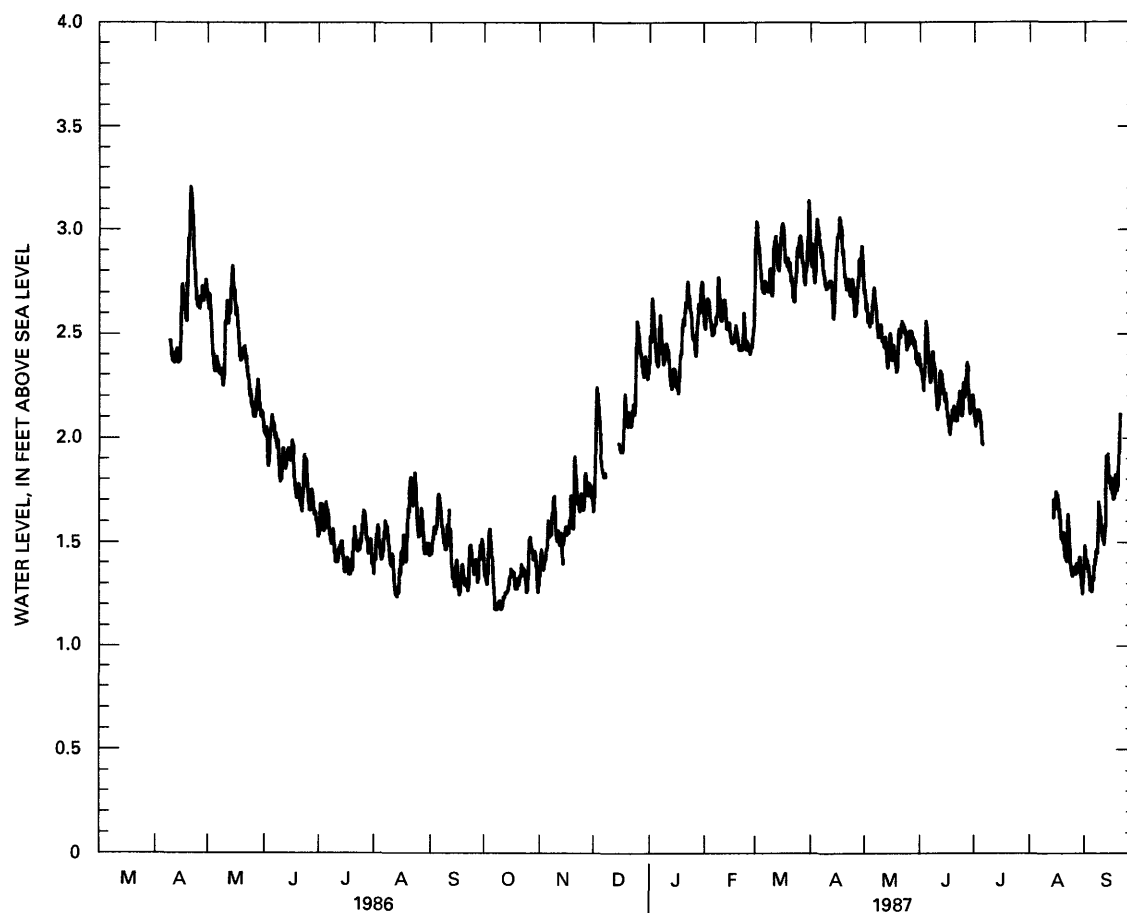


Figure 17. Water-level changes in the upper confined aquifer at well OF6B for April 1986 to September 1987.

Table 4. Laboratory-determined properties of undisturbed core samples from the confining unit below the upper confined aquifer at wells OF18C and OF13C

[ft/d, feet per day; g/mL, grams per milliliter; meg/100 g, milliequivalent per 100 grams]

Parameter	Horizon (feet below sea level)				
	Well OF18C			Well OF13C	
	6-7	11-12	20-21	24-25	29-30
Dry density (g/mL)	1.704	1.798	1.405	1.481	1.236
Soil pH	5.9	5.75	5.38	4.64	5.06
Cation exchange capacity (meg/100 g)	3.842	8.906	10.478	8.557	21.829
Percentage of moisture	12.9	4.9	21.3	35.9	52.3
Hydraulic conductivity (ft/d)	6.8×10^{-6}	4.7×10^{-6}	1.6×10^{-5}	1.6×10^{-4}	4.7×10^{-4}
Liquid limit	57	37	27	69	172
Plastic limit	37	21	18	43	108
Plasticity index	20	16	9	26	64

trending toward the southwest through Old O-Field. A palynological investigation (G.S. Brush, Johns Hopkins University, Department of Geography and Environmental Engineering, written commun., 1985) indicates that the upper part of the clay is no older than Pleistocene. Samples were not collected from the lower part of the clay.

The results of laboratory analysis for physical properties of five samples collected near the top of the clay are shown in table 4.

Exploratory borings west of O-Field, across the Gunpowder River, show that the clay is absent at Graces Quarters and present at Carroll Island (fig. 1) (Scott W.

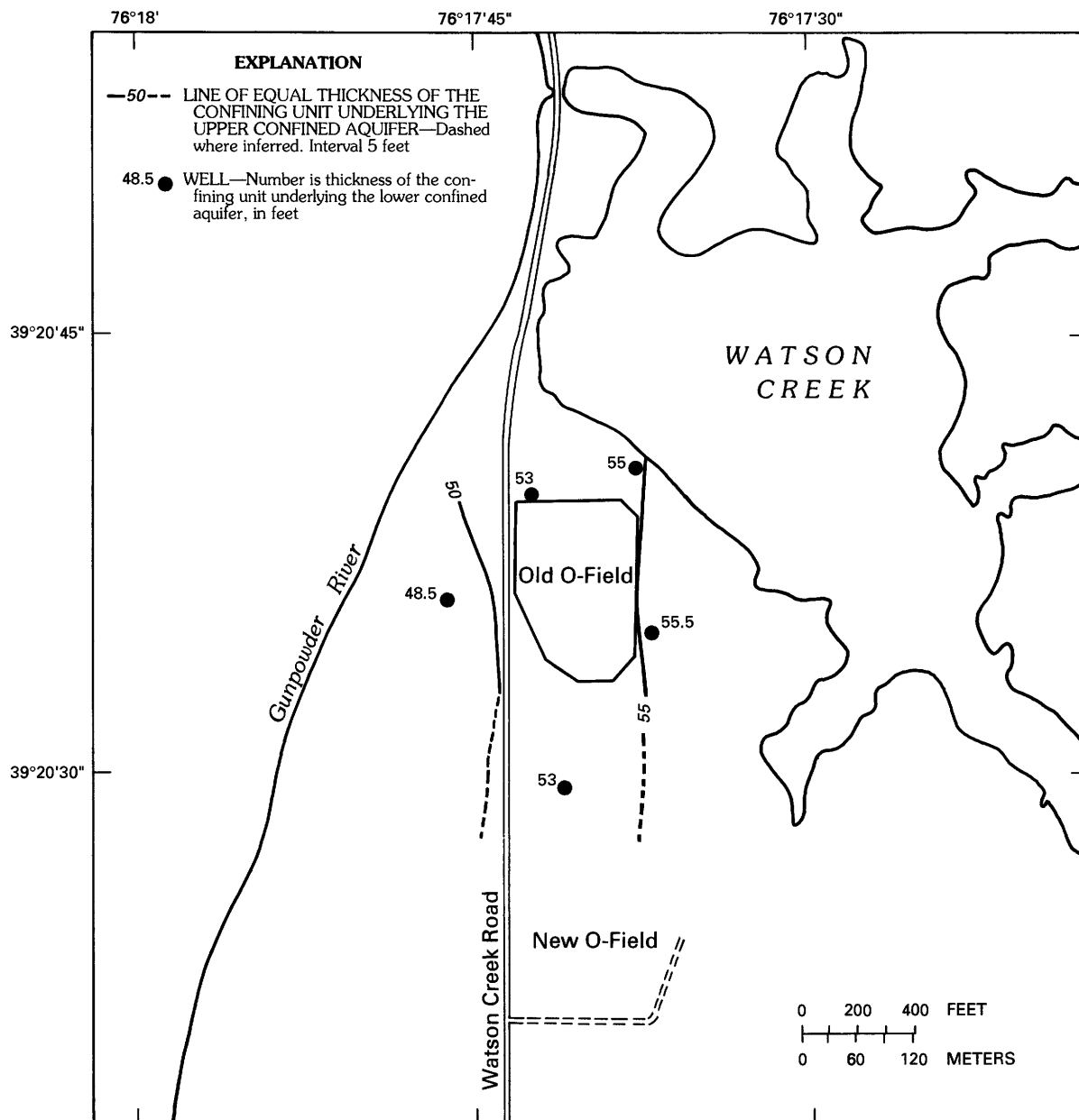


Figure 18. Thickness of the confining unit underlying the upper confined aquifer.

Phillips, U.S. Geological Survey, oral commun., 1987). The clay does not extend far to the south of O-Field. The log of an abandoned water-supply well at H-Field, about 1/2 mi south of O-Field, shows clay at approximately the same altitude, but the driller's log indicates that it is white in color: the white clay is clearly of a different lithology. The clay layer below O-Field also cannot extend far to the north because older sediments (Cretaceous) crop out approximately 1 mi north of O-Field (Owens, 1969). Therefore, the clay is situated in a trough trending northeast to southwest through O-Field.

Although the clay is not areally extensive to the north and south, the extent, thickness, and low permeability are probably adequate to prevent contaminant migration or substantial water movement across the confining unit. Moreover, a clay found at the same horizon in the abandoned supply well at H-Field implies the presence of a more-or-less continuous confining unit between O-Field and H-Field, although the lithologies of the two clays are different.

The trend of the trough exactly corresponds to an area in the Bush River (fig. 1) where the river abruptly alters

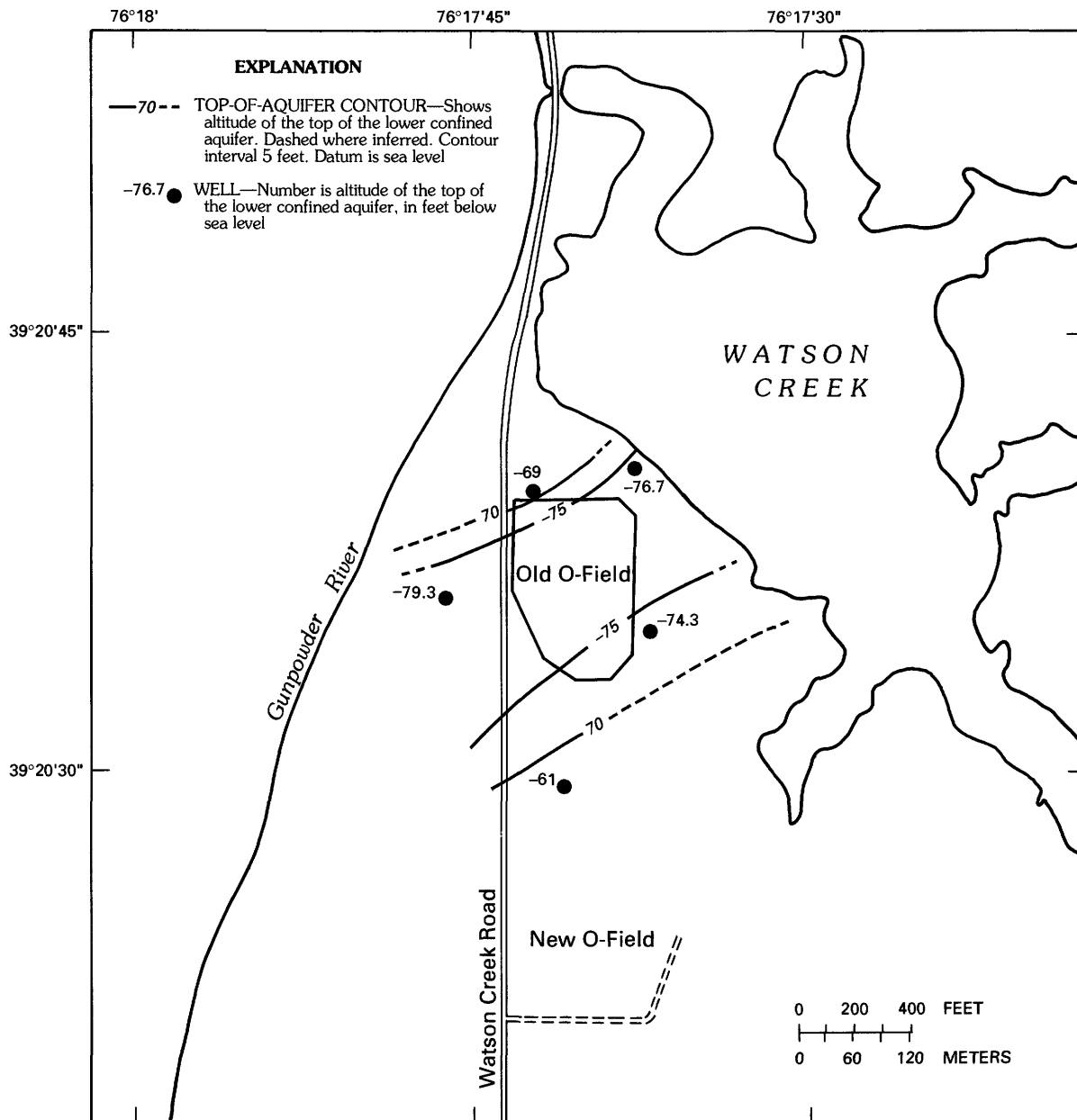


Figure 19. Altitude of the top of the lower confined aquifer.

direction. The trough is a paleochannel, possibly representing the ancestral Bush River or Susquehanna River. It extended southward through what is now O-Field and Carroll Island. A possible explanation for the lithology is that abandonment of the channel allowed fine-grained sediment to settle out of suspension, resulting in the thick layer of clay present today.

Lower Confined Aquifer

Two investigative borings and three observation wells penetrate the lower confined aquifer. It is about 20 ft thick

at a depth of approximately 80 ft (fig. 19). The extent of the aquifer is not known with certainty; however, it is at approximately the same depth as an aquifer of similar thickness at H-Field. Because the overlying clay is probably not of the same lithology as the corresponding clay at H-Field, it is likely that the sand immediately underlying the clay is also of a different lithology. However, the fact that the lower confined aquifer and the aquifer at H-Field are at approximately the same horizon implies that they may be hydraulically continuous.

No samples of the aquifer material could be obtained, —but the grinding behavior of the augers during drilling

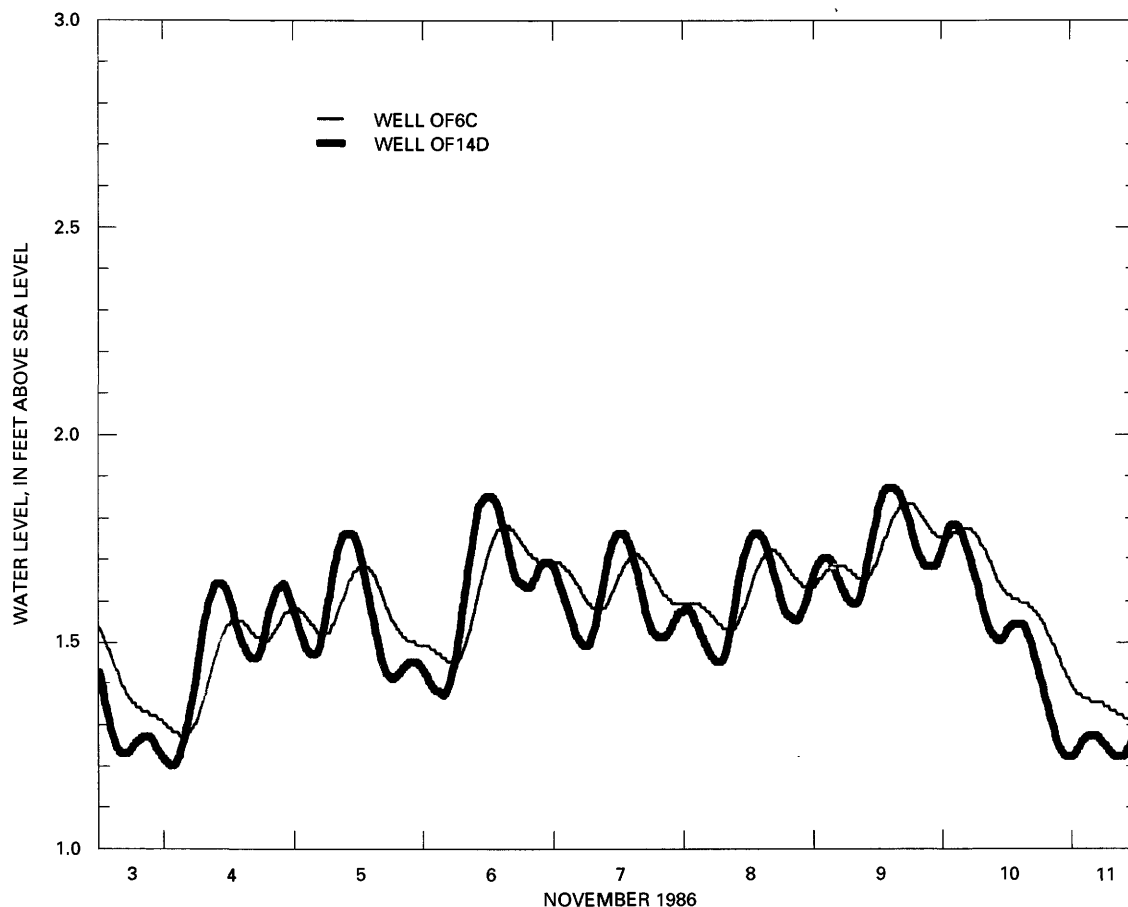


Figure 20. Water-level changes in the lower confined aquifer in wells OF6C and OF14D for November 3 to November 11, 1986.

implies that gravel is present. Downhole gamma, spontaneous-potential, and resistance logs likewise imply a highly permeable layer.

The head gradient in the lower confined aquifer varies, commonly changing direction with each tidal cycle (fig. 20). Wells OF18C and OF6C behave similarly, but heads in well OF14D undergo larger changes in amplitude, primarily because well OF14D is closer to areas of tidal change than wells OF18C and OF6C. The response of the aquifer to tidal cycles is caused by loading and unloading of pressure differences as the tide changes. The pressure changes are transmitted rapidly through the aquifer because it is confined.

The average hydraulic gradient, determined by comparing hydrographs, was extremely low [2.8×10^{-4} feet per foot (ft/ft)] toward the west-northwest during November 1986. The gradient direction may indicate that water from the aquifer is discharging through the confining unit, which may be channelized and locally thin or missing at places beneath the river, into the Gunpowder River. Alternatively, the gradient direction may be related to the head distribution in the overlying aquifers.

The heads are typically higher in the lower confined aquifer than in the upper confined aquifer. Therefore, even in the unlikely case that there are circuitous pathways for downward contaminant migration through the confining unit between aquifers, the hydraulic gradient would oppose all such flow except for the possible downward migration of dense organic solvents.

Ground water in the lower confined aquifer at O-Field is unsuitable for drinking purposes; the poor quality probably is due to natural causes. Concentrations greater than the EPA secondary maximum contaminant levels (SMCL's) for drinking water (U.S. Environmental Protection Agency, 1987) were found for iron and manganese. Specific-conductance values were 918 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) at well OF14D and 592 $\mu\text{S}/\text{cm}$ at well OF6C during the first sampling, but decreased to between about 200 and 300 $\mu\text{S}/\text{cm}$ thereafter. Alkalinity ranged from about 140 to 185 mg/L as bicarbonate.

Although the pH is near neutral (about 6.5–6.8), the water in the aquifer has a low redox potential, as evidenced by the lack of oxygen and the presence of sulfide (2.7 mg/L) and ammonia (2.75 mg/L). A sediment sample from the

aquifer contained a large concentration of organic carbon [95.68 milligrams per gram (mg/g) total], so the low redox conditions may be due to degradation of naturally occurring organic compounds. Although mean iron (16.8 mg/L) and manganese (0.544 mg/L) concentrations exceed the SMCL's for drinking water (0.3 and 0.05 mg/L, respectively) (U.S. Environmental Protection Agency, 1987), the concentrations are not unusual in such a reducing environment. They are probably, therefore, due to natural dissolution of iron and manganese grain coatings.

A number of other organic compounds present in low concentrations were cyclohexanol (1 µg/L), 1,4-dithiane (3 µg/L), methyl naphthalene (1 µg/L), acetone (14 µg/L), 1-pentene (5 µg/L), and 2-butanone (7 µg/L). One organic compound found in somewhat higher concentrations was 1,4-dioxane (53 µg/L in well OF6C). The compound is commercially used as a solvent for such organic products as paint and varnish. It also was found in well OF12A (water-table aquifer) and well OF12B (upper confined aquifer) at concentrations of 3 and 2 µg/L, respectively. No information was found on the tendency of 1,4-dioxane to form naturally.

Dissolved arsenic was present (maximum of 0.0044 mg/L), but the concentrations were below the 0.05 mg/L maximum contaminant level (MCL) for drinking water (U.S. Environmental Protection Agency, 1987). Sorbed arsenic (2.49 µg/g) was also found in sediment that may be of the lower confined aquifer. The sediment sample was a sidewall scraping, so the depth associated with the sample is not known with certainty.

The aquifer materials at H-Field and O-Field are at approximately the same depth, suggesting that the former supply well at H-Field is screened in the lower confined aquifer. Although the H-Field well contained many of the organic compounds found in the aquifer at O-Field, most also were found in the associated method blank and may represent laboratory contamination. Sulfur (S_8) also was found in the aquifer at H-Field, but 1,4-dioxane and arsenic were not.

Despite the unsuitability of the water in the lower confined aquifer for drinking purposes, the continuity, thickness, and density of the overlying confining unit combined with the net upward hydraulic gradient make it unlikely that O-Field operations degraded water quality in the lower confined aquifer. The conditions found in the aquifer at O-Field, therefore, probably represent background quality.

No samples of the sediments underlying the lower confined aquifer were collected. However, geophysical logs of boreholes that extend beneath the lower confined aquifer indicate that the underlying confining unit is about 48 ft thick and overlies an aquifer about 10 ft thick. Below this aquifer, clayey material extends for about 47 ft before reaching the next sand layer.

Surface Water

Old O-Field is bordered on three sides by streams: Watson Creek to the north and east and the Gunpowder River to the west. New O-Field is bordered by Watson Creek to the north. Watson Creek has a 2,180-acre watershed and discharges to the Gunpowder River. A series of dams constructed at the mouth of the creek to enlarge the surface-water body for wildlife habitats restricts tidal flushing and causes high organic loading in the creek (U.S. Army Environmental Hygiene Agency, 1977).

Tidal amplitudes in the Gunpowder River are typically between 0.5 and 2.0 ft (fig. 21). Extreme tides occur occasionally, depending upon wind direction and moon orientation. Watson Creek tidal amplitudes, which are controlled by Gunpowder River tides, are typically less than 0.4 ft. When the tide is lower in the Gunpowder River than in Watson Creek, water flows out of the creek and continues to do so until the incoming tide is greater in the Gunpowder River than in the creek. Watson Creek flow then reverses. If the incoming tide in the Gunpowder River does not reach the altitude of the culvert (hereafter called the mouth of the creek in this report) connecting Watson Creek to the river, water continues to flow out of the creek. Thus, Watson Creek regularly misses tidal cycles of the Gunpowder River. Similarly, if the low tide in the Gunpowder River is above creek level at the mouth of the creek, water continues to flow into the creek throughout the river's low-tide cycle. Mean altitude of Watson Creek was about 1.5 ft relative to sea level during the period from April 1986 to April 1987.

Water currents within Watson Creek vary, depending on winds and tidal cycles. The geomorphology of Watson Creek and short-term observations suggest that the dominant incoming currents follow the path shown in figure 22. The water enters through the mouth of the creek, moves through a narrow inlet (approximately 125–175 ft wide), is deflected by a bend in the channel toward the southwest, and enters the main body of the creek, where water is deflected slightly southeast by a small island toward the shoreline of Old O-Field. The shoreline deflects water movement to the east, where the current begins to circulate water to the rest of the creek in a generally counterclockwise direction.

In the main body of Watson Creek, outgoing tidal water does not move along a primary path of current flow as does the incoming tidal water. It moves instead from all points within the creek toward the inlet in a more or less uniform fashion (fig. 23). Once within the inlet, the water essentially follows the same path as the incoming tides.

Maximum current velocity in Watson Creek is at the mouth, often producing standing waves. Water movement is slower through the inlet. Velocities decrease substantially within the main body of the creek but still produce small waves between the inlet and the O-Field shoreline. Currents in the main body of the creek are typically gentler during the

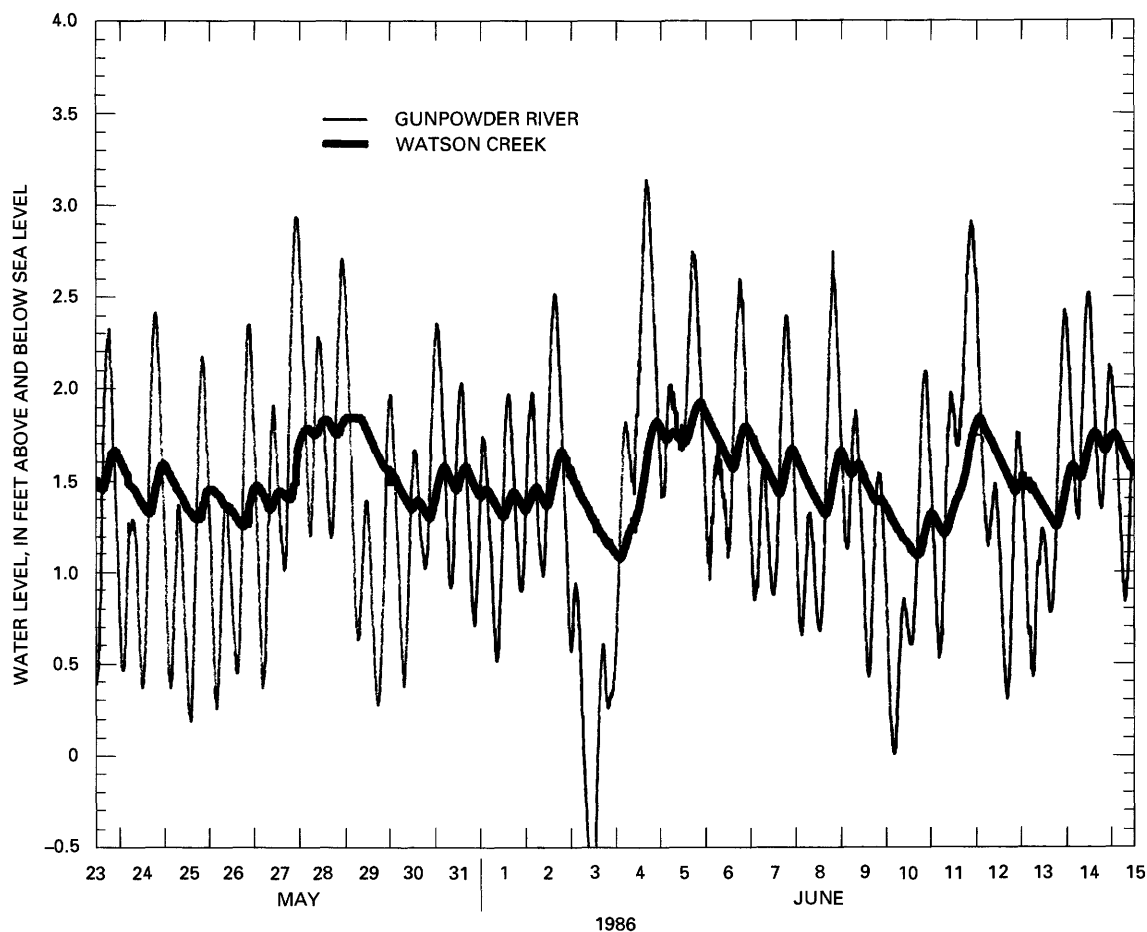


Figure 21. Tidal changes in the Gunpowder River and Watson Creek for May 23 to June 15, 1986.

outgoing tides because the velocity distribution of the water is more uniform. However, the convergence of flow lines for outgoing water at the point where the main body of the creek connects to the comparatively narrow inlet indicates that the point is an area of increased velocity.

Some areas within the creek rarely experience enough current to mobilize fine-grained particulate matter. The tributaries of Watson Creek and the extreme western edge of the main body of the creek are areas of particularly quiescent water. The western edge of the creek is outside the dominant paths of outgoing current and is sheltered from incoming current by a small shoal between the inlet and Old O-Field. Wind-induced currents are similarly minimal along the western edge of the creek because it is protected by a landmass to the south and by thick stands of marsh grass to the west and north.

The lithology of the bottom sediment within Watson Creek is controlled by current-velocity distributions within the creek. Coarse-grained materials are found in areas where current velocities are insufficient to transport them and yet sufficient to transport the fine-grained material. Organic-rich fine-grained material settles out of suspension in areas of quiescence.

Tidal currents in the Gunpowder River are such that its bottom sediments consist of sand. The sand is coarser along the shoreline due to wave action. At the mouth of Watson Creek, where the current is high, the sediment is entirely medium- to coarse-grained sand and gravel (fig. 24). Within Watson Creek, the tract along the path of incoming tidal current is dominantly sand near the inlet and organic-rich sand farther along the flow path, where the current is reduced. Bottom sediment within the creek tributaries and along the western edge of the main creek body consists of a layer of organic detritus, approximately 6 in. thick (U.S. Army Environmental Hygiene Agency, 1977). The inside (western) edge of the curved channel in the creek inlet also contains fine-grained material as bottom sediment. The sediment grain size and channel curvature indicate that the inside edge is an area of deposition.

GROUND-WATER CONTAMINATION

In addition to the previously discussed information regarding past disposal practices, knowledge of the distribution and general chemistry of the specific contaminants is

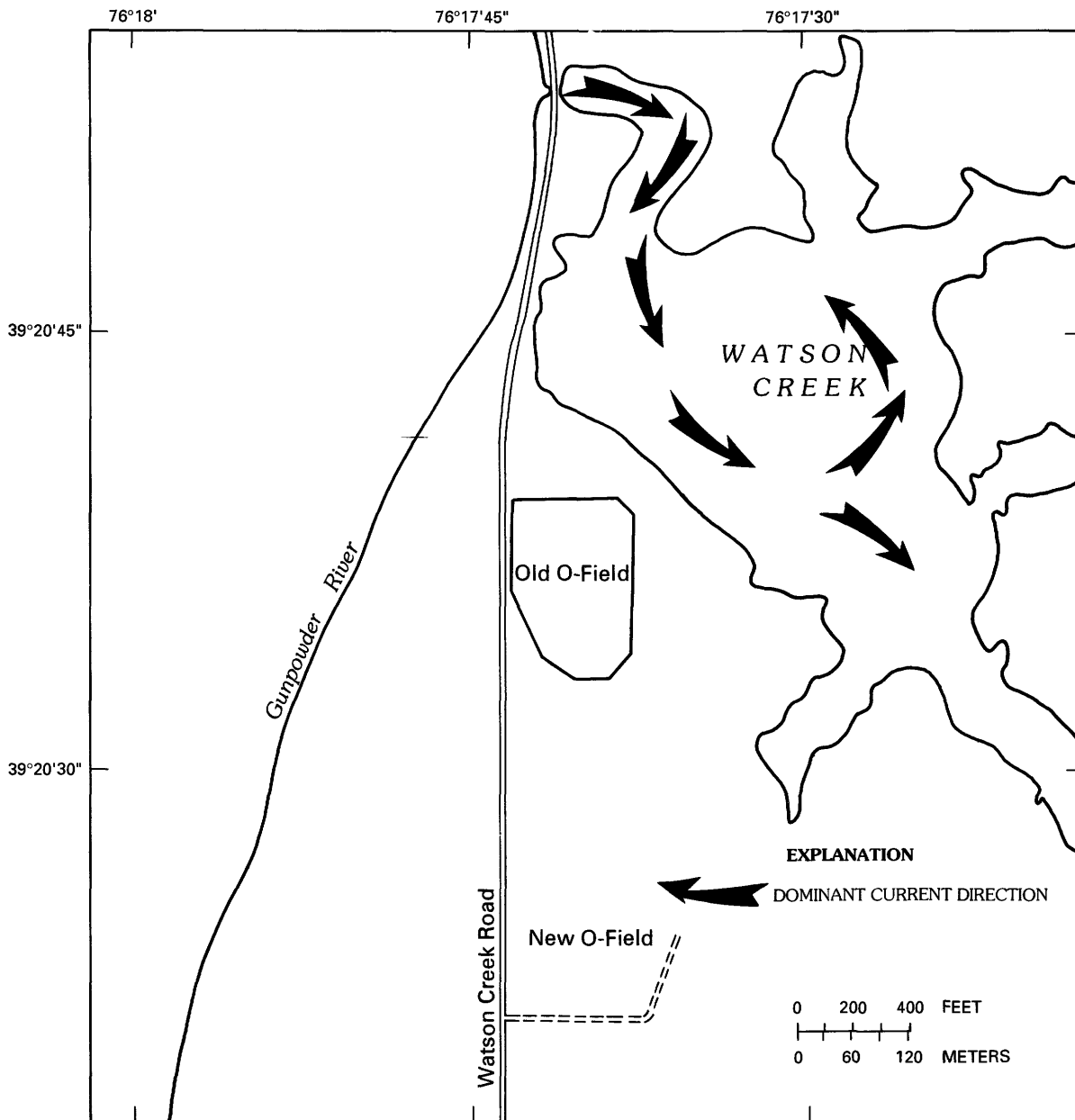


Figure 22. Observed current directions of the surface water during incoming tidal cycles in Watson Creek.

necessary to understand the probable fate and source of the contaminants and to evaluate probable chemical effects of various remedial actions. Dissolved oxygen and pH control the chemistry of several of the contaminants at O-Field. Alkalinity and specific conductance are important indicators of ground-water contamination at the site.

The ground water at O-Field contains both inorganic and organic contaminants. Inorganic contaminants that exceeded MCL's established by the U.S. Environmental Protection Agency (1987) were arsenic and cadmium. Those that exceed SMCL's were chloride, iron, manganese, and zinc. Dominant organic contaminants are chlorinated

aliphatics, aromatics, and organosulfur and organophosphorus compounds. Of the organic contaminants for which primary drinking water standards have been established (U.S. Environmental Protection Agency, 1987), benzene, carbon tetrachloride, trichloroethylene, and vinyl chloride are present at excessive concentrations. Major areas of contamination are northeast and east of Old O-Field and north of New O-Field, between the disposal areas and Watson Creek. Well OF19, adjacent to the disposal pit west of Old O-Field, contained higher-than-background concentrations of iron, manganese, potassium, sodium, sulfate, ammonia, and TDS. Specific conductance, pH, and

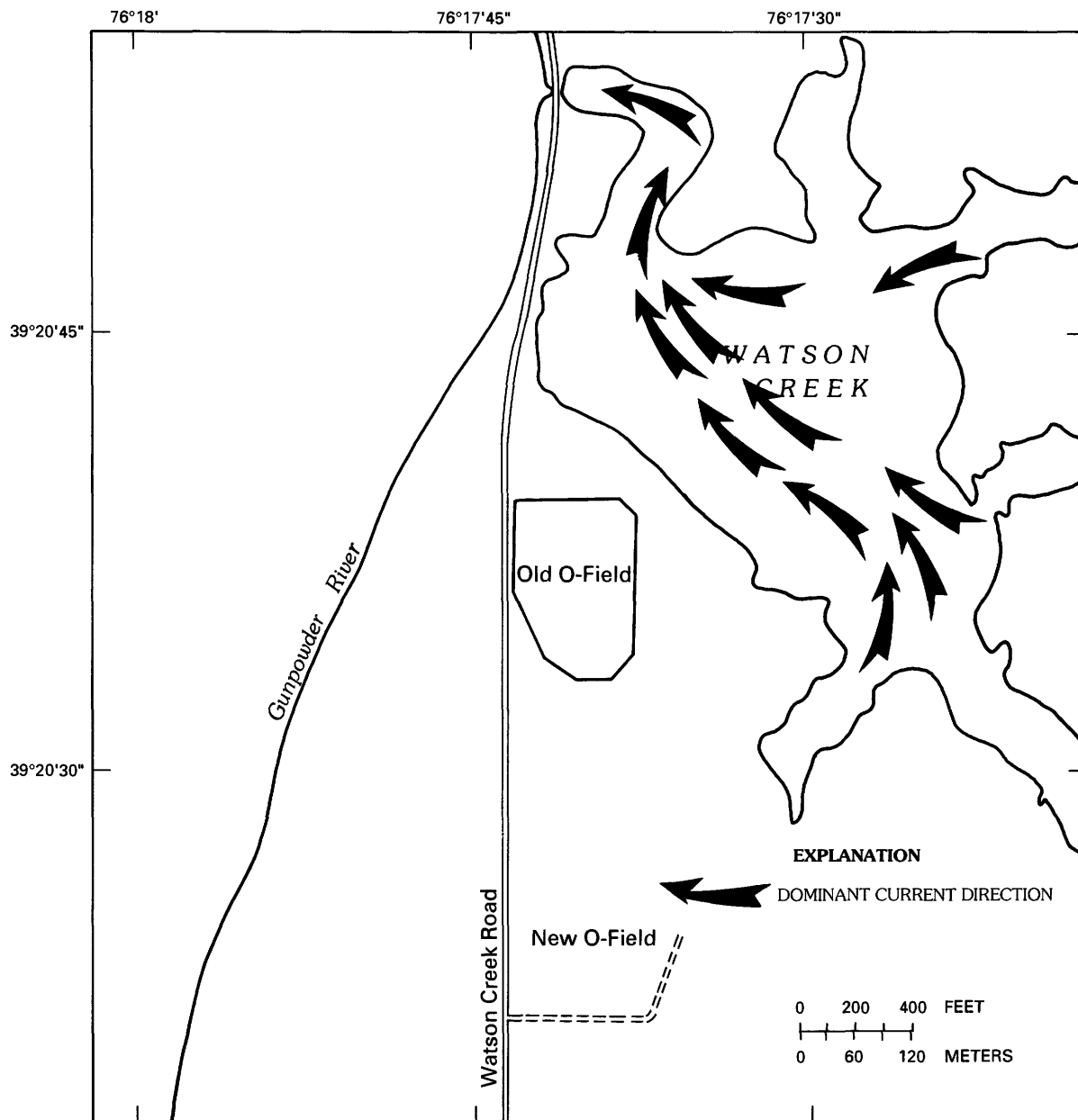


Figure 23. Observed current directions of the surface water during outgoing tidal cycles in Watson Creek.

alkalinity concentration in well OF19 were also higher than background. Of these, only iron and manganese concentrations exceeded SMCL's (U.S. Environmental Protection Agency, 1987) and none exceeded MCL's. No organic contaminants were detected.

Both the water-table aquifer and the upper confined aquifer contain contaminated ground water. In general, the highest concentrations of contaminants are found in the water-table aquifer. Concentrations of iron, tetrachloroethylene, methylene chloride, toluene, and benzene, however, are higher in the upper confined aquifer than in the

water-table aquifer at New O-Field. Although relatively low concentrations of organic contaminants are found in water samples from the lower confined aquifer, hydraulic gradients and the lithology and thickness of the overlying confining unit make it unlikely that O-Field operations have contaminated the lower confined aquifer. Therefore, the organic compounds may represent contaminants introduced in the laboratory or during drilling.

The distribution of individual dissolved species in the ground-water contamination at Old O-Field varies areally. For example, the concentrations of arsenic and organic

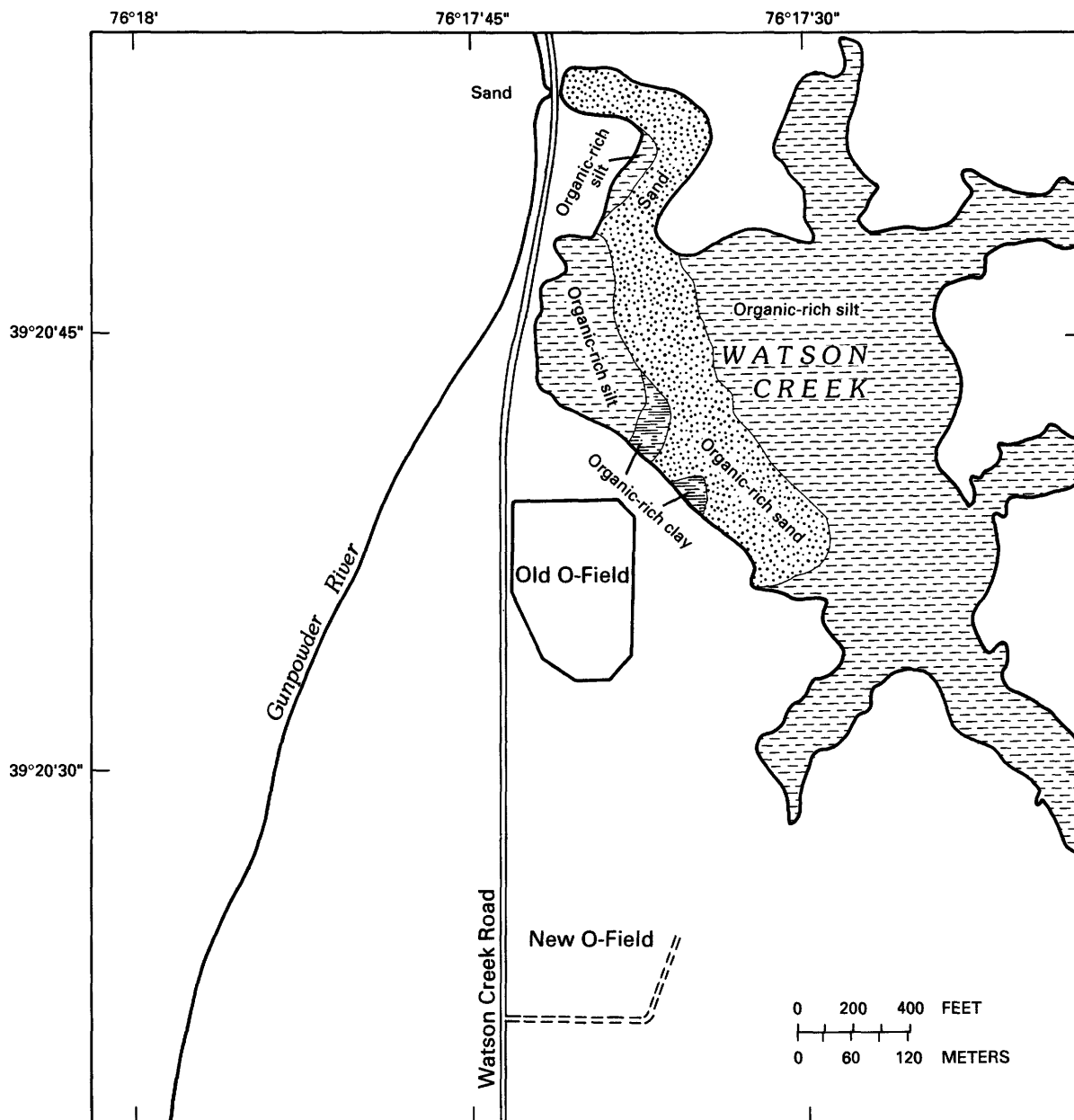


Figure 24. Lithology of bottom sediments in Watson Creek and the Gunpowder River.

contaminants are highest along the western side of the disposal area. However, iron is present as two distinct plumes, one along the eastern side and one along the northeastern side of the disposal area, and chloride concentrations are greatest along the northeastern side and near the Watson Creek shoreline, east of Old O-Field. The distribution may be the result of inhomogeneously distributed waste types within the disposal area. The areal distribution of contaminants at New O-Field cannot be evaluated because of the limited number of wells at the site.

Dissolved Oxygen, Alkalinity, pH, and Specific Conductance

Contaminated ground water at O-Field has a broad range of values for alkalinity concentration, pH, and specific conductance. The reason for the variability is that differing types of ground-water contamination occur both laterally and vertically, affecting changes in alkalinity, pH, and specific conductance. The two major types of ground-water contamination related to O-Field activities are

inorganic contamination (primarily by arsenic, iron, and manganese) and organic contamination (primarily by aromatic compounds, chlorinated aliphatic hydrocarbons, and sulfur and phosphorus compounds). One type of contamination present that is not related to O-Field activities is naturally occurring brackish-water intrusion near the shoreline of Watson Creek.

Dissolved oxygen is typically absent in most contaminated ground water at O-Field but present in uncontaminated ground water. Much of the depletion is probably due to use of oxygen during microbial degradation of organic contaminants. A considerable amount of oxygen is required by bacteria to aerobically biodegrade certain organic compounds, particularly aromatic compounds (Barker and others, 1987, p. 69). Organic compounds present at O-Field that are subject to aerobic degradation include benzene, toluene, xylene, aniline, and chlorinated aromatics.

The vertical variation in alkalinity, pH, and specific conductance is most obvious at wells OF6 and OF6A—two wells within the same cluster, but screened at different depths within the water-table aquifer (fig. 4). Well OF6A is screened at a depth of 9.5 to 11.5 ft below land surface, in dominantly organic contamination. The screen is immediately above a localized and discontinuous clay lens 1 ft thick. Well OF6, which existed at the site prior to this study, is screened at a depth of 8 to 18 ft below land surface in dominantly inorganic contamination. The screen is open above and below the clay lens. Well OF6 contained water that had a consistently lower pH than did well OF6A (median of 4.54 compared with 5.3), as well as lower specific conductance (mean of 741 compared with 1,164 $\mu\text{S}/\text{cm}$) and alkalinity (typically absent in well OF6; mean of 106 mg/L in well OF6A). The actual differences probably are greater but are masked in well OF6 by mixing effects within the well screen of water from above and below the clay. Dissolved-oxygen concentration was higher in some samples from well OF6 than from well OF6A.

One possible explanation for the abrupt vertical variation in concentrations at wells OF6 and OF6A is that the organic contamination detected in the ground water primarily is related to the application of chemical-warfare-agent decontaminants to the land surface. The decontaminants were sometimes highly alkaline materials, so that the upper part of the water table would be expected to be higher in alkalinity and pH than the deeper water. Moreover, the thin clay may locally limit vertical mixing. Downgradient from wells OF6 and OF6A, at well OF17A, the clay lenses are absent (fig. 4). Thus, the water sampled at well OF17A is probably a mixture of the two water types sampled at wells OF6 and OF6A.

At certain areas in the water-table aquifer along the Watson Creek shoreline, specific conductance is higher in the ground water than in the contaminated ground water near the disposal area. Values of 5,140 $\mu\text{S}/\text{cm}$ at well OF14A and 6,190 $\mu\text{S}/\text{cm}$ at well OF20A are due to

infiltration of brackish water from the creek. The average specific conductance measured in Watson Creek was 9,460 $\mu\text{S}/\text{cm}$. Inorganic ion ratios demonstrate that the ground water in wells OF14A and OF21 closely resembles that in Watson Creek (fig. 13).

Contaminated ground water in the upper confined aquifer contained no dissolved oxygen during the period of record between December 1985 and September 1987. The pH ranged from about 5.7 to 6.7. Specific conductance was highest near Old O-Field (greater than 1,000 $\mu\text{S}/\text{cm}$ along the northern side and from 500 to 650 $\mu\text{S}/\text{cm}$ along the southeastern side). Specific conductance decreased away from the fill, from 560 to 800 $\mu\text{S}/\text{cm}$ along the northern side to about 180 $\mu\text{S}/\text{cm}$ along the southeastern side, at the Watson Creek shoreline. Specific conductance in the upper confined aquifer at New O-Field ranged from about 320 to 640 $\mu\text{S}/\text{cm}$.

The most alkaline ground water in the upper confined aquifer was in well OF16B at New O-Field, ranging from about 120 to 200 mg/L as bicarbonate. Alkalinity at Old O-Field ranged from 25 to 125 mg/L.

Arsenic

Arsenic (As) is present in the ground water at O-Field in concentrations exceeding MCL's established by the U.S. Environmental Protection Agency (1987) for drinking water (0.05 mg/L). The highest concentration measured was 2.24 mg/L in well OF6 (in the water-table aquifer) during March 1986. The arsenic plume in the water-table aquifer is most concentrated at the southeastern edge of Old O-Field and decreases in concentration as it moves northeastward to Watson Creek (fig. 25). Vertical variations in concentration exist within the water-table aquifer. Well OF6A, screened above a localized clay lens (fig. 4), contained less arsenic than well OF6, a well drilled prior to this study and screened both above and below the clay. Thus, arsenic concentrations near the fill at Old O-Field are most concentrated near the base of the water-table aquifer.

Elevated concentrations of arsenic are also present in the upper confined aquifer but at lower concentrations than in the water-table aquifer. The maximum concentration measured in the upper confined aquifer was 0.092 mg/L at well OF17B during December 1986. Elevated arsenic concentrations in the upper confined aquifer appear to be confined to a narrow area in Old O-Field, extending from well OF6B to well OF17B.

The highest arsenic concentration measured at New O-Field was 0.011 mg/L in the water-table aquifer during July 1986. Only two wells are located downgradient from the New O-Field disposal area, one in the water-table aquifer (well OF16A) and one in the upper confined aquifer (well OF16B). Arsenic is not a major contaminant in the existing wells at New O-Field. The maximum arsenic

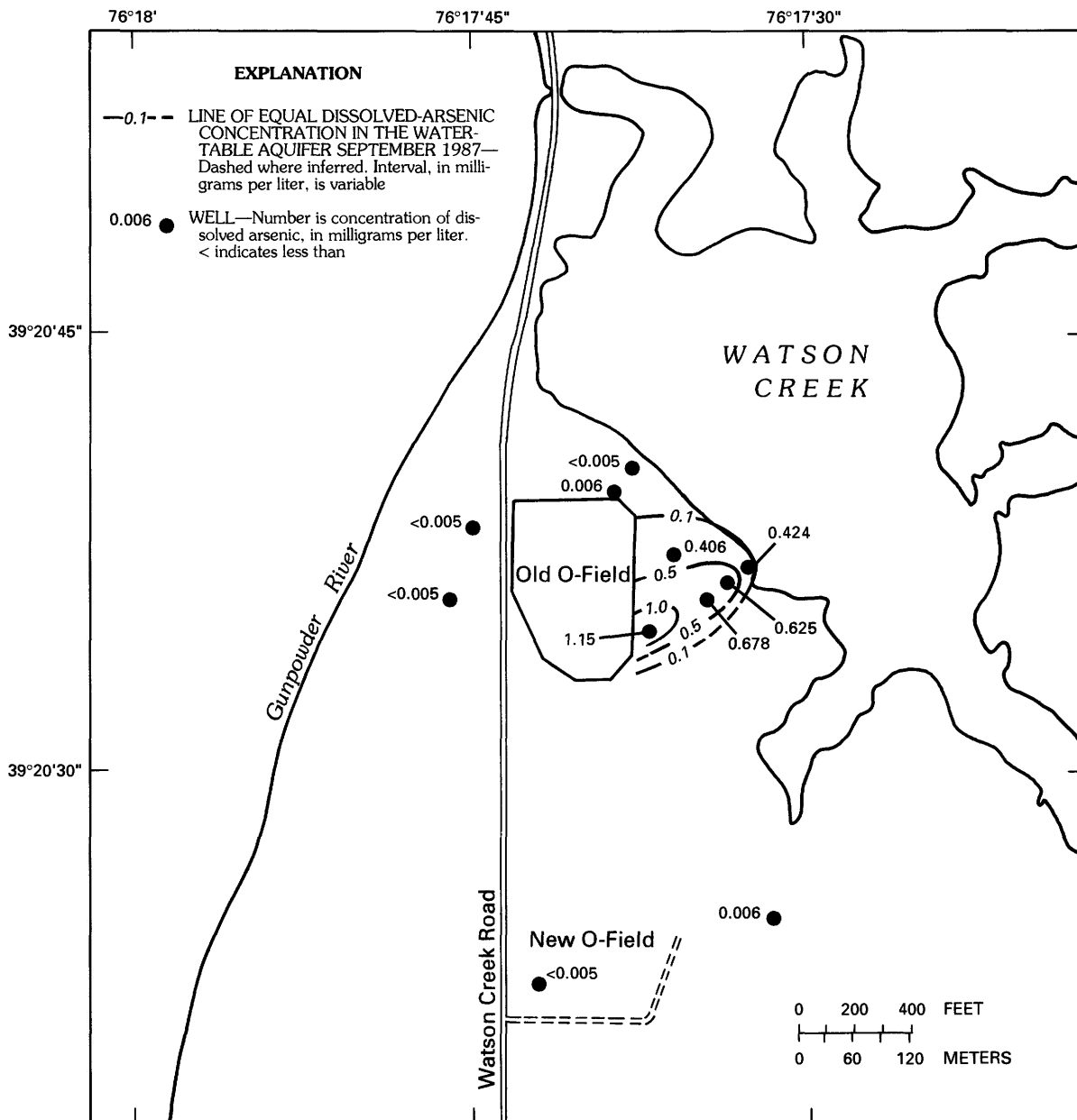


Figure 25. Distribution of dissolved arsenic in the water-table aquifer, September 1987.

concentration in the lower confined aquifer was 0.004 mg/L (well OF14C in July 1986). Arsenic contamination elsewhere at New O-Field, however, cannot be ruled out.

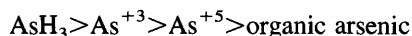
Organic arsenic was also present in the ground water at O-Field. Concentrations of 0.016, 0.047, and 0.023 mg/L were found in the water-table aquifer at wells OF6, OF6A, and OF17A, respectively, during September 1986. The September 1986 sample for well OF14B (water-table aquifer) did not contain organic arsenic, but a replicate sample from that well contained 0.003 mg/L organic arsenic. Low concentrations of organic arsenic were also

found in the upper confined aquifer (0.0016 mg/L, in well OF17B).

Arsenic may be present in ground water as inorganic and organic forms. Inorganic forms are arsenic acid (H_3AsO_4), arsenous acid (H_3AsO_3), arsenic sulfide (HAsS_2), arsenic metal (As), and arsine gas (AsH_3). The oxidation states of arsenic in each of these species is +5, +3, +3, 0, and -3, respectively (Ferguson and Gavis, 1972). Common organic forms of arsenic include methane arsenic acid [$\text{CH}_3\text{AsO}(\text{OH})_2$], dimethylarsinic acid [$(\text{CH}_3)_2\text{AsOOH}$], dimethylarsine [$(\text{CH}_3)_2\text{AsH}$], and tri-

methylarsine [(CH₃)₃As], the oxidation states of which are +3, +1, -3, and -3, respectively.

Reduced forms of arsenic are both more mobile and more toxic than oxidized forms. Fowler and others (1979) show the relation between speciation and toxicity, from most to least toxic, as



The oxidation of arsenite (containing trivalent arsenic) to the less mobile and less toxic arsenate (containing pentavalent arsenic) has been shown to occur naturally in a variety of environments. Abiotic conversion of trivalent arsenic [As⁺³] to pentavalent arsenic [As⁺⁵] can be induced by relatively slow reactions with iron oxides or by more rapid reactions with manganese oxides (Huang and others, 1982, p. 320; Oscarson and others, 1983). Biotic transformation may occur by microbial demethylation of trimethylarsine oxide to cacodylate, methane arsonate, and, eventually, arsonate (Woolson, 1982).

Reduction of arsenate to arsenite and methylated forms may also occur naturally (Ferguson and Gavis, 1972; Wood, 1974). McBride and Wolfe (1971) characterize the microbially mediated sequence as arsenic acid → arsenous acid → methane arsinic acid (MAA) → dimethylarsinic acid (DMAA) → dimethylarsine → trimethylarsine.

Arsenic may be removed from solution by coprecipitation with or sorption onto metal-ion hydroxides (Pierce and Moore, 1980) and sorption onto aluminum hydroxides (Anderson and others, 1975; Holm and others, 1979). Coprecipitation of arsenic may occur with phosphate minerals, but in a study of phosphate pebbles in Florida, Stow (1969) showed that arsenic has a greater affinity for iron than for phosphate. As⁺³ also has a strong affinity for sulfur, readily sorbing or coprecipitating with sulfur oxides.

The degree of sorption onto metal oxides and hydroxides varies with the types of competing ions and the type of oxide present. Pakholkor and others (1980) found that sorption onto iron hydroxide is greater in the presence of sodium chloride or sodium sulfate than in the presence of fluoride. They also found that the sorptive capacity of granulated metal-oxide hydrates decreases in the order Fe(OH)₃ > Al(OH)₃ > MnO₂·nH₂O. The preference for sorption onto iron is caused primarily by the positive charge of iron oxides in typical aquifer systems, allowing the oxides to sorb anions, such as arsenic. Manganese oxides are negatively charged over a broader pH range than are iron oxides (Drever, 1982, p. 79), so manganese oxides preferentially sorb cations.

Variations in pH may result in complexation that affects sorption. Galba (1972) found that calcium ions may reduce sorption by forming CaHAsO₄ at pH > 7 to 11 or Ca₃(AsO₄)₂ at pH > 11. Thanabalsingam and Pickering (1986) found that in acidic environments, humic acid may contribute more to the retention process than clays and some

hydrous oxides, but increasing pH (pH > 5) results in less sorption, due to enhanced deprotonation of weak acids and competition from hydroxide for anion exchange sites.

Speciation also substantially affects sorption. Sorptive studies by Frost and Griffin (1977) demonstrated that the amount of As⁺³ retained on clay was less than the amount of As⁺⁵. Thanabalsingam and Pickering (1986) produced similar results for sorption onto humic acids. Maximum sorption of As⁺⁵ occurred in the pH range where H₂AsO₄⁻ was the dominant species. Maximum sorption for As⁺³ involved As₃O₅⁻ and H₂AsO₃⁻. They found that the affinity sequence for sorption on organic anion exchange sites (for example, humic acid) is H₂PO₄⁻ > H₂AsO₄⁻ > SO₄⁻² > CO₃⁻² for As⁺⁵ and H₂PO₄⁻ > H₃AsO₃ > F⁻ > SO₄⁻² > CO₃⁻² for As⁺³. The results agree with those of Pierce (1981), who reports that phosphate strongly competes with arsenates for sorption sites on the hydrous oxides of iron, aluminum, and manganese. Thus, the addition of phosphate may displace sorbed arsenic on humic acids.

Species of organic arsenic typically are more mobile than the inorganic species. Reece and others (1984) have shown that arsenate is more strongly bound to soil than is organic arsenic because arsenate has three hydroxyl groups to one for the organic species tested. Moreover, leaching is inversely proportional to the number of hydroxyl radicals on the arsenic atom. Other factors that influence leaching are the total number of binding sites (anion exchange capacity) and the amount of arsenic available.

Because arsenic toxicity and mobility depend on the oxidation state of the ion, and because oxidation and reduction reactions typically are microbially mediated, the microbial population in ground water at O-Field was examined to determine the role of microbes in altering arsenic at the site. Preliminary results suggest that bacteria in the ground water at wells OF6 and OF17A do not directly transform, precipitate, or volatilize arsenic (J.L. Zelibor, M.W. Doughten, and others, Testing for bacterial resistance to arsenic in monitoring-well water by the direct viable counting method: Unpublished report on file in the U.S. Geological Survey District Office, Towson, Md., 1986). Nevertheless, arsenic transformations appear to be occurring. Arsenic near the fill at well OF6 was entirely trivalent. Arsenic in wells OF6A and OF6B was 91 and 96 percent trivalent in December 1985. However, at the downgradient wells OF17A and OF17B, arsenic was only 79 percent and 88 percent trivalent, respectively. Thus there appears to be oxidation of some of the As⁺³ to the less hazardous, less mobile As⁺⁵.

Arsenic variations with time showed little relation to variations in iron or sulfate at wells OF6A and OF17A, suggesting that coprecipitation and sorptive reactions with iron or sulfide were not dominant processes at those locations. Because sulfate is a major component (concentrations as high as 176.5 mg/L at well OF6) of the

contamination and arsenic is in the trivalent state, there should be a strong affinity for sorption or coprecipitation with metal sulfides.

Control of arsenic solubility by sulfide may occur in the ground water at O-Field at certain times. Sulfide was not present in the ground water during the March 1986 sampling but was present during the September 1987 sampling. Arsenic sorption or coprecipitation with metal sulfides may occur during such times, but the attenuated arsenic probably is remobilized when more oxidizing conditions return.

For the most part, arsenic probably moves through the aquifer relatively unaffected by attenuation reactions. By the time ground water discharges to Watson Creek, much of the arsenic is still in the unoxidized, highly toxic trivalent form.

If arsenic is sorbed onto aquifer grain coatings within the fill area, then dissolution of those grain coatings can remobilize arsenic. Increases in dissolved phosphate may put arsenic into solution by preferential exchange at sorption sites. Such increases in dissolved phosphate are produced by the hydrolysis of white phosphorus, a major component of the waste, to phosphoric acid. White phosphorus degrades explosively when exposed to air, but if enough moisture is present, the hydrolysis of white phosphorus may increase the dissolved arsenic concentration.

The arsenic at O-Field resulted from the disposal of arsenicals in the Old O-Field landfill. Examples of possible arsenicals disposed at Old O-Field are lewisite $[(\text{ClCH}_2\text{CH})_2\text{AsCl}]$, mustard-lewisite mixtures, phenyldichloroarsine $(\text{C}_6\text{H}_5\text{AsCl}_2)$, ethyldichloroarsine $(\text{C}_2\text{H}_5\text{AsCl}_2)$, methyldichloroarsine $(\text{CH}_3\text{AsCl}_2)$, diphenylchloroarsine $[(\text{C}_6\text{H}_5)_2\text{AsCN}]$, adamsite $[\text{C}_6\text{H}_4(\text{AsCl})(\text{NH})\text{C}_6\text{H}_4]$, and diphenylcyanoarsine $[(\text{C}_6\text{H}_5)\text{AsCN}_2]$ (U.S. Departments of the Army and Air Force, 1975).

Cadmium

Cadmium (Cd) concentrations were less than, or at, detection levels (0.002 mg/L) in most wells but exceeded MCL's (U.S. Environmental Protection Agency, 1987) for drinking water (0.01 mg/L) in the water-table aquifer at well OF14A (0.021 mg/L) during December 1985. Other wells containing detectable cadmium were well OF17A (0.007 mg/L), well OF13B (0.003 mg/L), well OF14B (0.003 mg/L), well OF6 (0.002 mg/L), and well OF13C (0.002 mg/L). A distribution map is not shown for cadmium because it was present in appreciable concentrations only at well OF14A (0.021 mg/L). Analysis for cadmium in well OF14A was performed only for the December 1985 samples because the well was destroyed soon after by frost heaving. Because of the low concentrations in the remaining wells, cadmium was not analyzed in subsequent samplings. The subsequent samplings, however, showed that concentrations of some constituents varied greatly over time.

Cadmium is a relatively more mobile ion than the other heavy metals. It may be transported in solution as organic or inorganic complexes and as hydrated cations. At pH values less than about 9, Cd^{+2} is by far the dominant cadmium ion in solution (Weber and Posselt, 1974). In organically polluted water, cadmium may be present as complexes with humic acids (Callahan and others, 1979, p. 9-5) or with other natural complexing agents. The complexes may remain stable down to pH 3 (Guy and Chakrabarti, 1976). The tendency of ligands to complex with cadmium appears to follow the order, humic acids $> \text{CO}_3^{-2} > \text{OH}^- \geq \text{Cl}^- > \text{SO}_4^{-2}$ (Callahan and others, 1979, p. 9-1).

Cadmium can be removed from solution by sorption onto mineral surfaces and organic materials and by sorption onto or coprecipitation with hydrous metal oxides (Callahan and others, 1979, p. 9-7). Sorption may increase with the presence of anions, particularly humic acids. The increase probably is caused by sorption of complexes formed from the anions and cadmium (Huang and others, 1977). Sorption also tends to increase with increasing pH.

Sorbed cadmium may be released from sorption sites under certain conditions. The desorption is strongly pH dependent, increasing as the pH drops below about 6 (Huang and others, 1977). Increases in salinity have also been reported to mobilize sorbed cadmium (Helz and others, 1975).

Cadmium in the ground water at O-Field undergoes sorption and desorption reactions. In some areas, sharp vertical interfaces exist between water of differing pH, such as at wells OF6A and OF6, where pH values of 4.37 and 6.21 were measured only a few feet apart. A thin clay separates the differing water types at the wells, but the clay layer does not extend farther along the flow path. In the downgradient areas, seasonal and tidal fluctuations in water level periodically shift the horizons of the low-pH and high-pH zones. Moreover, increases in salinity in ground water near the shoreline, due to infiltrating creek water, may be sufficient to desorb cadmium bound to the sediment. Thus, cadmium may be cycled between dissolved and sorbed phases.

Although the highest concentrations of cadmium in the ground water at O-Field are at a well (OF14A) in an area subject to periodic recharge of brackish water from Watson Creek, the creek water and bottom sediments contain concentrations of cadmium that are less than detectable (detection limit 0.002 mg/L for water and 0.2 mg/g for sediment). Thus, infiltration of surface water is not a direct source of cadmium. Cadmium is not a component of chemical-warfare agents, and it is unlikely that cadmium occurs naturally in greater than trace amounts in the sediments at O-Field. Cadmium was used in metal-plating operations at Aberdeen Proving Ground during World War II, however, and plating residue or waste may have pro-

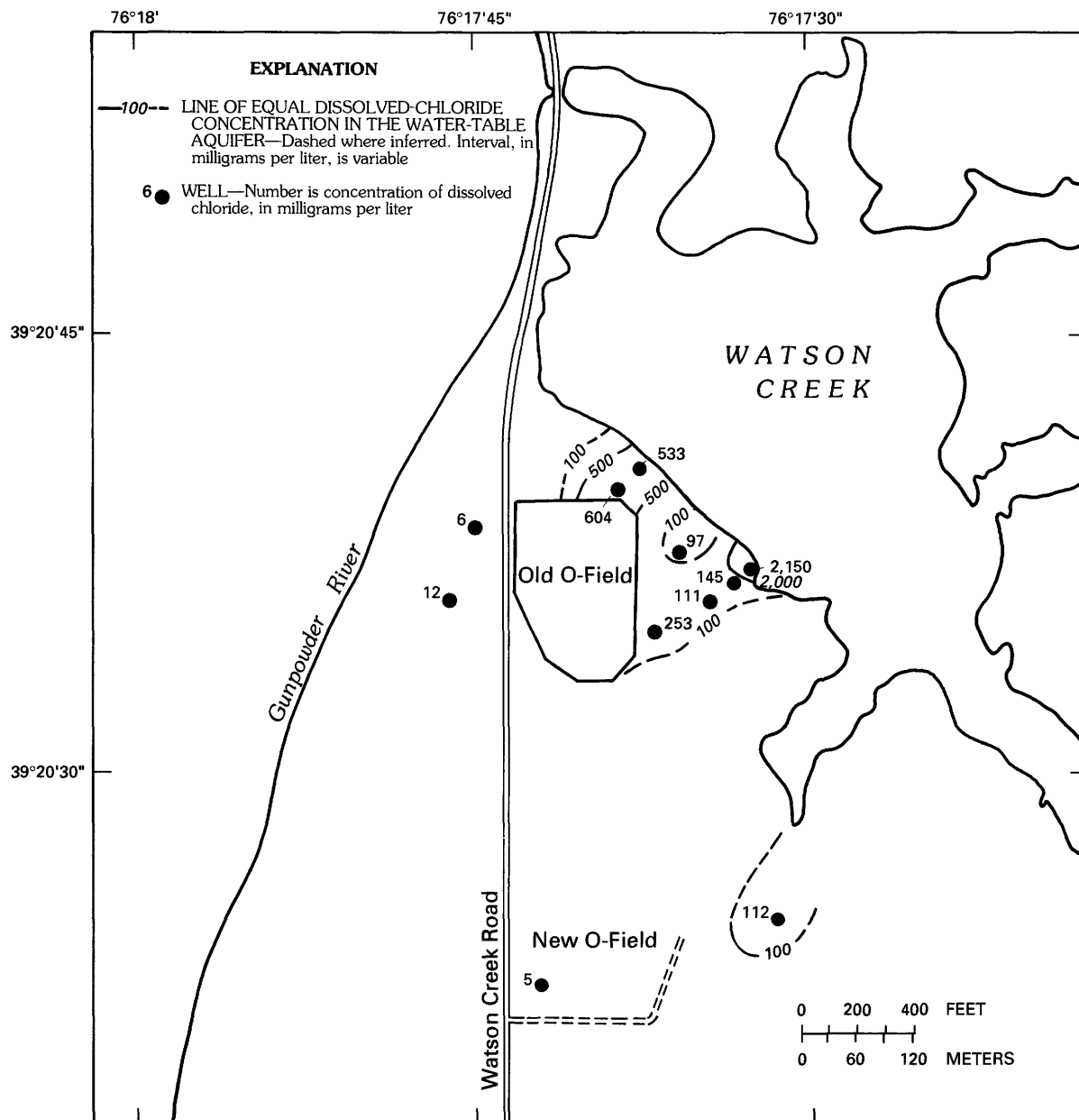


Figure 26. Distribution of dissolved chloride in the water-table aquifer, September 1987.

vided a source. Cadmium also may be derived from the disposal of cadmium-plated metals or cadmium-rich alloys.

Chloride

Chloride is present in the water-table aquifer at O-Field in concentrations exceeding the U.S. Environmental Protection Agency (1987) SMCL's for drinking water (250 mg/L). The maximum concentration measured was 2,150 mg/L, believed to be the result of naturally occurring infiltration of brackish water from Watson Creek. The maximum concentration believed related to activities at

O-Field was 623 mg/L at well OF13B during September 1986.

At Old O-Field, the water-table aquifer is contaminated between the disposal area and Watson Creek. Maximum concentrations of chloride are found near the northeastern and southeastern corners of the disposal area and near the Watson Creek shoreline (fig. 26) and appear to be associated with the observed paths of ground-water flow away from the disposal area (fig. 9). Chloride concentrations at New O-Field are above background (7.5 mg/L average concentration) but not above SMCL's for drinking water (U.S. Environmental Protection Agency, 1987).

Chloride also is present in concentrations above SMCL's in the upper confined aquifer at well OF13C (maximum concentration of 533 mg/L). Elevated chloride concentrations, but not greater than SMCL's for drinking water (U.S. Environmental Protection Agency, 1987), also are present downgradient from well OF13C.

The lower confined aquifer contains chloride in concentrations of less than 45 mg/L except at well OF14D, where the concentrations were 344 and 330 mg/L during the first and second sampling runs, respectively. The increased levels may have been introduced as a result of drilling through the overlying aquifer, which contains elevated chloride concentrations. The well development and presampling purge may not have been adequate to remove contaminants from the aquifer. After two additional sampling runs, the concentrations decreased substantially and, thereafter, remained below 45 mg/L. Thus, if cross contamination occurred during drilling, the introduced contaminants probably were removed, at least within the accuracy of the analytical methods.

Chloride salts are highly soluble, are not substantially sorbed onto mineral surfaces, do not substantially enter into redox reactions, have no major biochemical roles, and generally are not complexed by other ions at low to moderate chloride concentrations (Hem, 1985, p. 118). Inhibition of chloride movement by cation-exchanging clay minerals that are tightly compressed at depth (White, 1965) has not been observed in shallow ground water. Therefore, chloride movement in shallow ground water generally is controlled by hydrodynamic processes rather than by sorption or chemical reactions.

Although the chloride ion is essentially unreactive, some of the reactions that produce chloride may have significance for other dissolved ions. One possible source reaction is the hydration of chlorine (American Water Works Association, 1971, p. 189). Calcium hypochlorite [$\text{Ca}(\text{OCl})_2$] reacts with acids, liberating chlorine. In water, chlorine forms a mixture of hypochlorous (HOCl) and hydrochloric (HCl) acids, the reaction being nearly complete above a pH of about 4. The HCl further dissociates to liberate chloride. Between a pH of 6.0 and 8.5, hypochlorous almost completely dissociates to hypochlorite ions (OCl^-). Chlorine is a strong oxidizer, having a higher Eh-stability field than that of water. Therefore, the introduction of chlorine into an aqueous system not only will liberate chloride ions but also will raise the oxygenation state of the system, causing reduced forms of redox-dependent species, such as iron, sulfur, nitrogen, arsenic, manganese, and reduced inorganics, to oxidize.

The production of hypochlorite as a result of decontamination operations involving bleaching agents could have oxidized ions subject to redox reactions. Iron and manganese probably precipitated as mineral coatings, possibly accompanied by coprecipitation of arsenic. However, the effects from the increased oxidation state would have

been short lived. Microbial metabolism of organic contaminants would be expected to renew the anaerobic conditions and redissolve the mineral coatings. The hypochlorite also may have oxidized disposed metal. Chloride in the aquifer at O-Field is nonreactive and will not sorb onto mineral or organic matter.

Some chloride in the ground water at O-Field originated from the disposal of chlorinated chemical-warfare agents, examples of which are phosgene, diphosgene, mustard, lewisite, phenyldichloroarsine, ethyldichloroarsine, methyldichloroarsine, diphenylchloroarsine, adam-site, chloracetophenone, and O-chlorobenzyl malononitrile. A possibly more significant source, however, is related to the use of chlorinated decontaminating agents. Chlorine is in a readily soluble form in most chlorinated decontaminating agents, so it probably flushes through the flow system after a relatively short time, either as chloride or hypochlorite. A more persistent source of chloride is the tetrachloroethane in the decontaminating agent DANC. The continuing presence of tetrachloroethane at the site attests to its persistence. As is discussed in the section on chlorinated aliphatic hydrocarbons, tetrachloroethane at O-Field is degrading to lesser chlorinated species, releasing chloride as a reaction product.

The elevated concentrations of chloride in the ground water near the shoreline have a different source. Ion-ratio plots (fig. 13) of well water and surface water at O-Field show that the shallow ground water along the edge of Watson Creek at wells OF14A and OF20A is similar to the water in Watson Creek but differs from most other areas at O-Field. The chemical composition of ground water at wells OF14A and OF20A, therefore, appears to be the result of ground water mixing with water infiltrating from Watson Creek. During high tides, the tide water rises faster than the water table. Tidal water moves overland a short distance and infiltrates. Once in the ground water, it cannot move out as quickly as the tide because it must move through the aquifer, so it remains as a slug of brackish water. The effect is probably more pronounced during periods of extreme tides.

Iron and Manganese

Dissolved iron (Fe) and manganese (Mn) in the water-table aquifer, the upper confined aquifer, and the lower confined aquifer at O-Field are present at concentrations exceeding the SMCL's for drinking water established by the U.S. Environmental Protection Agency (1987) (0.3 mg/L iron and 0.05 mg/L manganese). The maximum concentrations of iron and manganese measured near O-Field were in water samples from the water-table aquifer (245 mg/L in well OF20A and 17.4 mg/L in well OF13B, respectively). At Old O-Field, concentrations of iron and manganese in samples from the water-table aquifer are

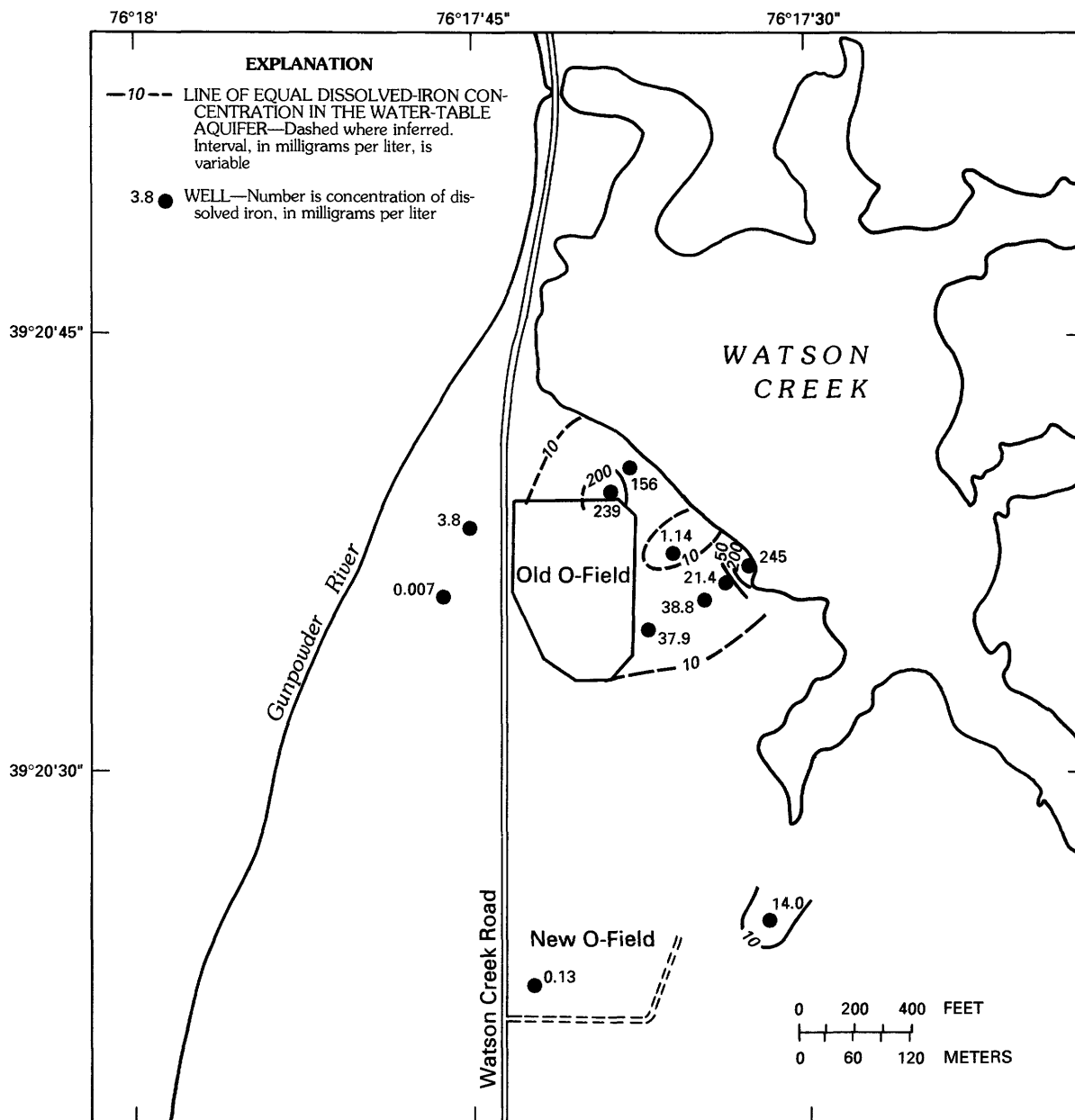


Figure 27. Distribution of dissolved iron in the water-table aquifer, September 1987.

elevated between the disposal area and Watson Creek (fig. 27). Maximum concentrations of iron and manganese were found near the northeastern and southeastern corners of the disposal area and near the Watson Creek shoreline. As with chloride and arsenic, a vertical variation of iron and manganese occurs within the water-table aquifer at wells OF6 and OF6A. Iron and manganese are consistently more concentrated in the shallower well OF6A (average of 47.8 mg/L and 4.3 mg/L, respectively) than in the deeper well OF6 (average of 38.6 mg/L and 1.1 mg/L, respectively).

A similar distribution of iron and manganese occurs in the upper confined aquifer at Old O-Field. The highest

concentrations are northeast of the fill (242 mg/L iron in September 1987, and 4.71 mg/L manganese in September 1986). A plume with lower concentrations also extends from the east side of the fill (69.6 mg/L iron and 1.69 mg/L manganese, in July 1986). The maximum concentration in the lower confined aquifer was 30.1 mg/L iron in well OF14D during September 1986, and 0.866 mg/L manganese in well OF6C during December 1985.

Elevated concentrations of iron and manganese are also present at New O-Field. The maximum concentration of iron measured in the water-table aquifer was 30.7 mg/L (March 1986). The highest concentration measured in the

upper confined aquifer was 63.7 mg/L (December 1985). The highest concentration of manganese was 1.41 mg/L in the water-table aquifer (September 1986) and 0.862 mg/L in the upper confined aquifer (September 1987).

Oxidation of iron and manganese is strongly related to the Eh and pH of the solution, and reduction of these species is strongly related to microbial activity. Figure 28 shows the Eh and pH conditions under which various forms of iron are stable in the iron-sulfur-carbonate system. The shaded areas show conditions under which the most stable iron species exist in solid phase. The most common form of iron in solution is the Fe^{+2} ion. In highly acidic and oxygenated water, Fe^{+3} , FeOH^{+2} , and $\text{Fe}(\text{OH})_2^+$ can be present, but the total activity of these species in equilibrium with ferric hydroxide is less than 10 $\mu\text{g/L}$ above a pH of 4.8 (Hem, 1985).

Ferrous complexes (Fe^{+2}) are highly mobile in solutions within their Eh/pH stability field but may be rapidly oxidized to ferric (Fe^{+3}) forms under higher Eh or pH conditions. Above a pH of about 4.8, ferric iron is relatively insoluble; therefore, if ferrous iron is oxidized to ferric iron by increasing the Eh or pH, the iron will become less stable in solution and may precipitate, typically as grain coatings. Similarly, the grain coatings may be redissolved by microbial reduction of the iron to Fe^{+2} .

Under certain conditions, ferrous iron may remain stable in solution outside its stability field. Ferrous complexes with organics may be considerably more resistant to oxidation than free ferrous ions (Hem, 1985).

Manganese chemistry is more or less analogous to iron chemistry, but there are several notable differences. Manganese is stable as an ion (Mn^{+2}) over a broader range of Eh and pH conditions. Sulfide has a less pronounced effect and carbonate a more pronounced effect on manganese precipitation than on iron precipitation.

Hydrous oxides of iron and manganese have high affinities for sorption of heavy metals. The sorptive capacities of iron and manganese are controlled primarily by Eh and pH. At higher pH, the amount of sorbed hydrogen ion decreases, leaving the hydrous oxides with net negative charges and increasing the potential for cation sorption. Manganese oxide is anionic over a broader pH range than is iron oxide (Drever, 1982, p. 79); therefore, manganese has a higher cation-sorptive capacity at moderate pH than does iron. At low pH, increased protonation leads to a net positive surface charge, essentially eliminating the potential for cation sorption but increasing the potential for anion sorption. Microbial reduction, and subsequent dissolution of the hydrous oxides, returns the sorbed ions to the aqueous phase.

The dissolved-oxygen concentration in ground water at the site varies with time, so the stability of dissolved iron also would be expected to vary. During oxic periods, iron is unstable in the aqueous ferrous (Fe^{+2}) form and can precipitate as amorphous iron minerals on the aquifer

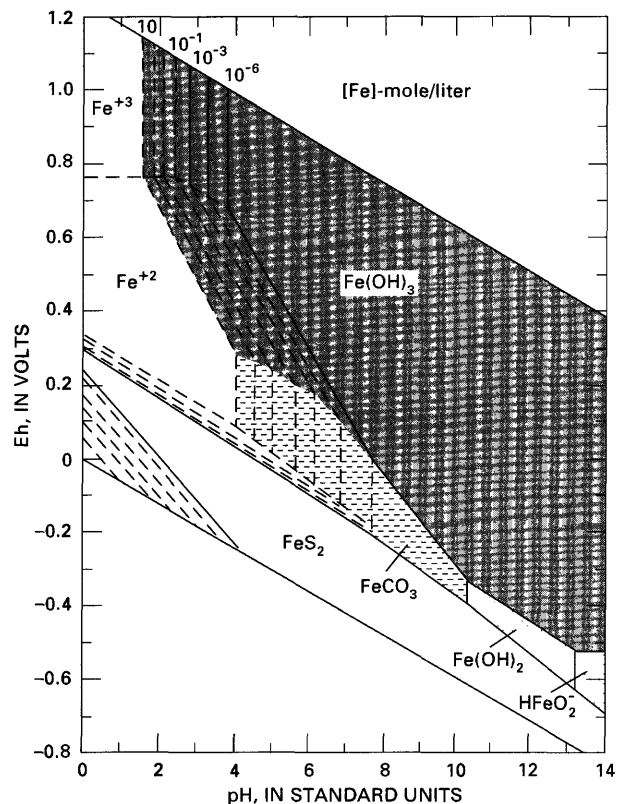


Figure 28. Solubility of dissolved iron in relation to pH and Eh at 25°C and 1 atmosphere. Total dissolved sulfur 10^{-4} M; bicarbonate species 10^{-3} M (Hem, 1967).

matrix. During anoxic periods, the iron may be returned to solution by microbial reduction. Thus, the rate of movement would be expected to be slower for iron than for water.

Iron and manganese will continue to be present in elevated concentrations in ground water at O-Field as long as iron and manganese grain coatings and organic ground-water contamination exist at the site and conditions are suitable for microbial reduction of iron and manganese. Movement from the fill area toward Watson Creek will probably be somewhat slower for iron and manganese than for water because of precipitation and dissolution of oxyhydroxide phases. In the mixing zone near the shoreline where brackish-water intrusion has occurred, precipitation reactions should occur. During periods of minimum intrusion, microbial reduction of iron and manganese can return those species to solution (producing locally elevated concentrations in ground water). Evidence for the local increase in dissolved iron concentrations in the mixing zone is shown in figure 29. Chloride concentrations increase from well OF21, through the mixing zone at well OF20A, to Watson Creek. Dissolved iron concentrations, however, are highest within the mixing zone at well OF20A. The concept is one

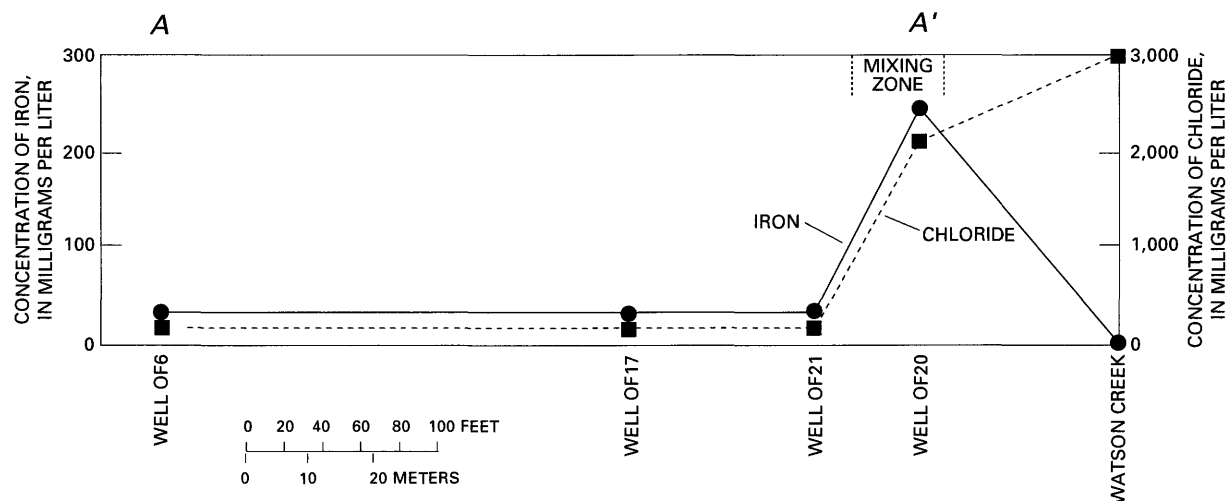


Figure 29. Concentrations of iron and chloride in the water-table aquifer along hydrogeologic section A-A', September 18, 1987.

of an oscillating redox boundary, through which iron and manganese are intermittently discharging to Watson Creek. The broader range of Eh/pH stability for manganese indicates that manganese can be expected to be more mobile than iron under such variable redox conditions.

The dominant source of iron and manganese in the ground water is probably microbial reduction and dissolution of naturally occurring iron- and manganese-rich grain coatings. Another potential source is the partial oxidation ($\text{Fe}^0 \rightarrow \text{Fe}^{+2}$) of disposed metal in the presence of hypochlorite-based decontaminants. Although the reaction would be expected to proceed to complete oxidation (Fe^{+3}), the generation of Fe^{+2} as an intermediate product implies the possibility of Fe^{+2} release to the ground water.

Zinc

Zinc (Zn) is present in the water-table aquifer at O-Field in concentrations exceeding the SMCL for drinking water (5 mg/L) established by the U.S. Environmental Protection Agency (1987), but only in well OF14A. Only two samples were collected from well OF14A before it was destroyed by frost heaving. The sample from December 1985 contained a zinc concentration of 7.89 mg/L, and the sample from March 1986, 4.31 mg/L. Concentrations of zinc at other areas around the fill (wells OF6, OF6A, OF17A, OF21, and OF22) generally were from 1.0 to 2.18 mg/L, higher than background (<0.1 mg/L). The former H-Field supply well also contained anomalously high zinc concentrations (1.64–2.09 mg/L), although not exceeding SMCL's. Zinc concentrations elsewhere in the lower and upper confined aquifers were less than 0.5 mg/L.

Zinc solubility depends on pH and the number and types of competing ions. Below a pH of 8, zinc is present as

the Zn^{+2} ion and becomes increasingly soluble as pH declines. Above a pH of about 8, solubility of zinc is substantially reduced. Zinc is least soluble at a pH of about 9.5 (Hem, 1972). The principal limiting factors on the solubility of zinc are the presence of sulfur and carbon dioxide. At a pH greater than 6, the solubility of zinc is decreased by at least an order of magnitude by the increase in the partial pressure of carbon dioxide from $10^{-3.5}$ to 10^{-2} bar (Mann and Deutscher, 1980), resulting in the precipitation of zinc carbonate. Sulfur limits the solubility by allowing sphalerite (ZnS) to precipitate (Hem, 1972). There is also some evidence that zinc can coprecipitate with calcium as carbonate and phosphate (apatite) (Wedepohl, 1978), sorb onto clay minerals (Krauskopf, 1956) and onto manganese or iron oxide and hydroxide surfaces (Jenne, 1968), and be complexed by organic material of low solubility (Hem, 1972).

The pH conditions at well OF14A dictate that the most stable form of zinc is the Zn^{+2} ion. At the low pH (4.5–4.6) in well OF14A, competition with other ions should not have a major control over zinc solubility. Zinc should be highly soluble, therefore, and move at approximately the same rate as ground water toward Watson Creek.

Zinc is a relatively common element in the environment. The acidic pH of ground water on the northern side of Old O-Field (well OF14A) is sufficient to dissolve zinc. Slightly elevated zinc values were also found in low-pH water in wells on the eastern side of Old O-Field (well OF6, 2.18 mg/L; well OF17A, 1.97 mg/L). Zinc concentrations were higher on the northern side of the fill (well OF14A) than on the eastern side (well OF6), although the pH was lower at well OF6 than at well OF14A. The geology of both sites appears similar, so the high zinc concentrations probably are the result of something other than dissolution of aquifer material.

Zinc oxide is a major component (46.66 percent by weight) of a smoke munition termed "HC mixture," which also contains aluminum and hexachloroethane (U.S. Departments of the Army and Air Force, 1975). Chlorinated organic compounds were present at well OF14A in trace amounts; however, hexachloroethane is poorly soluble in water. The low solubility coupled with periodic dilution from infiltration of water from Watson Creek near well OF14A are probably adequate to reduce hexachloroethane to concentrations that are less than detectable. Therefore, the most likely source of the elevated zinc concentrations north and east of Old O-Field is the disposal of HC mixture. The elevated concentrations at well OF14A may have resulted from the disposal of HC mixture in the immediate vicinity of the well. Zinc also may have been derived from the dissolution of aquifer materials and metals containing zinc.

The former H-Field supply well contains steel well casing. The high zinc concentration (2.09 mg/L) in the well, therefore, may be derived from preferential dissolution of the casing.

Additional Inorganic Constituents

Several other inorganic constituents were analyzed in the ground water. Additional inorganic parameters that were monitored quarterly were ammonia, antimony, boron, bromide, calcium, fluoride, magnesium, nitrate, nitrite, phosphorus, potassium, sodium, silica, sulfate, sulfide, total Kjeldahl nitrogen (TKN), and TDS. The percentages of major ions shift along the ground-water flow path from being dominantly a chloride-type water to higher percentages of bicarbonate (HCO_3^-) (fig. 30). Flow paths shown in figure 30 are from well OF13C to well OF14C and from well OF6B through well OF17B to well OF20B. The shift in major-ion percentages is toward the percentage value at well OF12C. The shift may be the result of mixing water from near Old O-Field with the less contaminated down-gradient water, or it may represent increased bicarbonate production along the flow path due to biodegradation of organic contamination.

Some inorganic constituents were analyzed only once because they were not detectable or were present at concentrations less than MCL's or SMCL's established by the U.S. Environmental Protection Agency (1987). Those not detectable at the concentration shown in parentheses were beryllium (0.001 mg/L), lead (0.005 mg/L), mercury (0.0002 mg/L), selenium (0.003 mg/L), and cyanide (0.005 mg/L).

Copper concentrations were less than the detection limits (0.004 mg/L) in most wells and were below the SMCL's (U.S. Environmental Protection Agency, 1987) for drinking water (1.0 mg/L) at well OF6 (0.156 mg/L), well OF14A (0.022 mg/L), and well OF17A (0.088 mg/L).

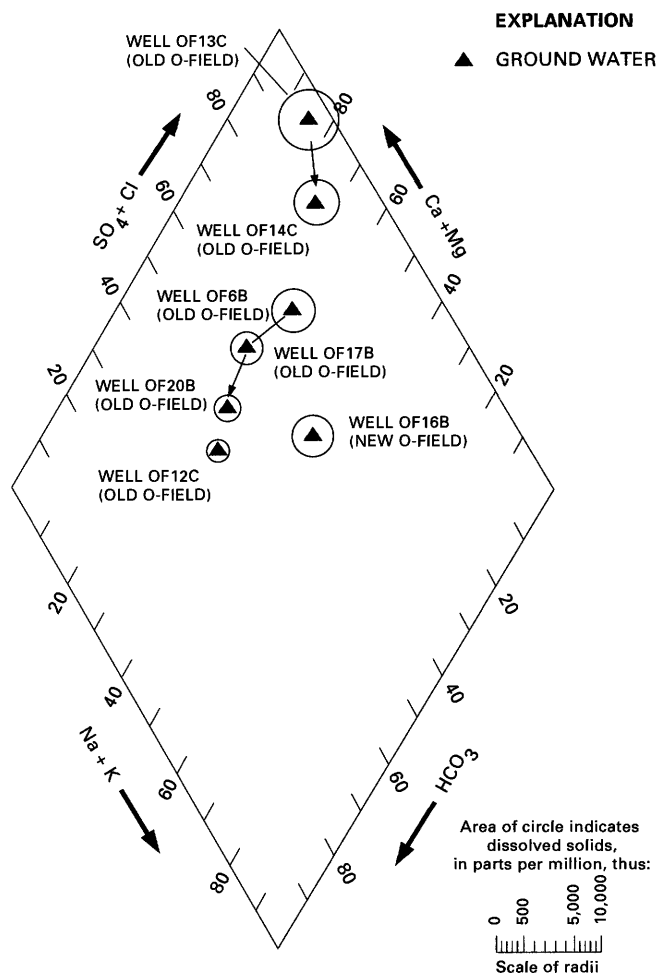


Figure 30. Percentages of dissolved major ions in the upper confined aquifer, September 1987.

Chromium concentrations were less than detection limits (0.004 mg/L) in most wells and were present at concentrations below MCL's (U.S. Environmental Protection Agency, 1987) for drinking water (0.05 mg/L) in well OF13B (0.01 mg/L) and well OF14B (0.01 mg/L). Therefore, copper and chromium were deleted from subsequent sampling analyses. However, samples for copper and chromium should be collected and analyzed occasionally to determine if concentrations increase.

Nickel concentrations varied across the site. The maximum measured concentrations in December 1985 were 0.09 mg/L at well OF14A, 0.031 mg/L at well OF12A, and 0.21 mg/L at well OF6. The remaining concentrations varied from less than detectable limits (0.004 mg/L) to 0.016 mg/L. Nickel was detected in background wells at concentrations of as much as 0.013 mg/L.

Boron concentrations are highest in the immediate area around Old and New O-Fields. Concentrations above 1.0 mg/L were present in the water-table aquifer at wells OF6, OF6A, OF13B, OF14B, and OF17A. The maximum

concentration in the water table was 7.85 mg/L in well OF14B at Old O-Field during March 1986. Concentrations greater than 1.0 mg/L also were present in the upper confined aquifer at wells OF13C, OF14C, OF16B, and OF17B. The highest concentration recorded in the upper confined aquifer was 9.62 mg/L in well OF13C at Old O-Field during March 1986, but had decreased to 0.15 mg/L in September 1987. Boron concentrations in the lower confined aquifer were less than 1.0 mg/L.

Antimony is present in the ground water at O-Field in concentrations exceeding 0.01 mg/L. The highest concentration measured in the water-table aquifer was 0.1 mg/L in well OF12A at Old O-Field during March 1986; however, there is some uncertainty in the value. The concentration during the prior quarterly measurement was only 0.0136 mg/L. Frost heaving has since destroyed the well, so further measurements to verify the data are unavailable.

Ground water in the water-table aquifer consistently contained greater than 0.01 mg/L concentrations of antimony for the period from December 1985 to August 1986 in the area adjacent to Old O-Field (wells OF6, OF6A, and OF13B) and in the downgradient wells northeast of Old O-Field (well OF14B). Well OF14A (water-table aquifer) also contained concentrations greater than 0.01 mg/L during December 1985 and March 1986, but was destroyed by frost heaving before additional data could be collected. The highest concentrations at wells OF6 (0.015 mg/L) and OF6A (0.0219 mg/L) were found during August 1986. At well OF13B, the highest concentration was 0.023 mg/L, during March 1986. After the August 1986 sampling, concentrations declined to less than detectable levels in the water-table aquifer and remained so for the rest of the year. By September 1987, however, antimony concentrations rose to 0.044 mg/L in well OF13B and 0.028 mg/L in well OF14B.

The only antimony concentration greater than 0.01 mg/L in the upper confined aquifer was along the northeastern edge of Old O-Field at well OF13C (0.0214 mg/L in December 1985). The highest concentration measured at New O-Field was 0.011 mg/L in August 1986 in the water-table aquifer.

Chlorinated Aliphatic Hydrocarbons

Aliphatic compounds are saturated or unsaturated, open-chain or cyclic compounds, not containing a benzene ring. In the ground water at O-Field, the chlorinated aliphatics are dominantly represented by chlorinated ethanes and ethylenes (table 5).

The major areas of ground-water contamination by chlorinated aliphatics at the site are in the water-table aquifer along the eastern side of Old O-Field (fig. 31) and at New O-Field. Comparison of the water-quality data from wells OF6 and OF6A at Old O-Field indicates that concen-

trations of the higher-chlorinated species are greater near the top of the water-table aquifer than deeper in the aquifer.

The upper confined aquifer at Old O-Field contains lower concentrations of chlorinated aliphatic compounds than does the corresponding water-table aquifer. Similarly, the water-table aquifer at New O-Field contains higher concentrations of vinyl chloride and 1-2-dichloroethylene than does the upper confined aquifer. However, the upper confined aquifer at New O-Field contains higher concentrations of tetrachloroethylene than are found in the water-table aquifer at New O-Field.

The lower confined aquifer contained trace concentrations of methylene chloride (maximum of 13.9 µg/L in July 1986 at well OF6C) and chloroform (1.6 µg/L in June 1986 at well OF18C), but they were also present in the laboratory method blanks. Trichloroethylene was detected in only one well (well OF18C) during one out of three samplings. The concentration (1.4 µg/L) was close to the detection limit (1.3 µg/L) and was also present in the corresponding laboratory blank. Thus, the detected chlorinated aliphatic compounds in the lower confined aquifer probably represent analytical error.

Chlorinated aliphatic hydrocarbons are generally hydrophobic but may be moderately to highly soluble, depending on the species and amount of organic carbon in the aquifer. Thus, they can exist in water-saturated soil systems as a free product or in an aqueous solution. A series of laboratory experiments by Schwillie (1988) provided valuable insight into the behavior of both the free product and dissolved forms. Schwillie's experiments demonstrated that because chlorinated aliphatic compounds are denser than water, the free product moves downward through the unsaturated zone to the capillary fringe or to a low-permeability layer at a rate faster than water. If the amount of the product is small, downward movement may then cease. With increasing amounts of the product, enough pressure head may build up to allow the product to penetrate the water-bearing zone or the low-permeability layer. The required pressure becomes greater as pore size decreases until the pore size becomes so small that vertical movement ceases.

The movement of the free product in the saturated zone is downward. Lateral dispersion is relatively unaffected by ground-water velocity; however, Schwillie's experiments showed a narrowing of the plume in high-permeability zones and lateral spreading in less permeable zones. When the free product intercepts an impermeable layer, it typically will follow the downgradient slope of the layer even when the slope is in a direction different from ground-water movement. Thus, the free product will collect in depressions on the impermeable layer.

Not all of the free product necessarily will sink to the bottom of the aquifer even in major spills. Schwillie (1988) has shown that halogenated aliphatic hydrocarbons tend to

Table 5. Maximum concentrations of chlorinated aliphatic hydrocarbons detected at O-Field, and sampling dates and well numbers

[$\mu\text{g/L}$, micrograms per liter]

Constituent	Maximum detected concentration ($\mu\text{g/L}$)	Date	Well
Old O-Field water-table aquifer			
1,1,2,2-Tetrachloroethane	33,000	April 1988	OF6A
Chloroform	15,000	September 1987	OF6A
Trichloroethylene	3,860	September 1987	OF6A
Tetrachloroethylene	2,397	September 1986	OF6A
Methylene chloride	2,430	October 1986	OF17A
1,2-Dichloroethane	2,420	October 1986	OF6
1,2- <i>trans</i> -Dichloroethylene	2,290	October 1986	OF6A
Vinyl chloride	2,200	December 1986	OF14B
Carbon tetrachloride	750	September 1987	OF6
1,1,2-Trichloroethane	55	September 1986	OF6A
Old O-Field upper confined aquifer			
1,2- <i>trans</i> -Dichloroethylene	488	September 1987	OF13C
Vinyl chloride	272.5	September 1987	OF6B
Chloroform	150	July 1986	OF6B
Trichloroethylene	53	September 1986	OF6B
Methylene chloride	32	December 1985	OF17B
1,2-Dichloroethane	16	December 1985	OF17B
1,1,2,2-Tetrachloroethane	5.8	December 1986	OF13C
1,1,2-Trichloroethane	5.8	December 1986	OF13C
Tetrachloroethylene	4.2	September 1986	OF6B
New O-Field water-table aquifer			
1,2- <i>trans</i> -Dichloroethylene	10,350	September 1987	OF16A
Vinyl chloride	7,244	September 1986	OF16A
Methylene chloride	65	December 1986	OF16A
Tetrachloroethylene	28	March 1986	OF16A
Trichloroethylene	2.3	September 1986	OF16A
1,1,2,2-Tetrachloroethane	1.8	September 1986	OF16A
1,2-Dichloroethane	1.6	September 1986	OF16A
New O-Field upper confined aquifer			
Vinyl chloride	988	September 1986	OF16B
Tetrachloroethylene	580	December 1985	OF16B
1,2- <i>trans</i> -Dichloroethylene	504	March 1986	OF16B
Methylene chloride	462	March 1986	OF16B
Trichloroethylene	287	December 1986	OF16B
1,1,2,2-Tetrachloroethane	68	March 1986	OF16B
Chloroform	16	March 1986	OF16B
1,2-Dichloroethane	9	December 1985	OF16B
1,1,2-Trichloroethane	6	December 1986	OF16B

move by capillary action and may be retained in intergranular areas in amounts of about 0.3 to 5 percent by volume following the passage of the organic liquid. Part of the product remains in the unsaturated zone in the corners of pores and as films on grain surfaces. Another part is left disseminated in the saturated zone as discontinuous, irregularly shaped bodies of the product, showing no tendency for further movement. The disseminated product in the saturated and unsaturated zones constitutes the residual saturation of the flow system.

The action of water on the product in pools and residual saturation can spread contamination beyond the

immediate vicinity of the spill. Water is a stronger wetting agent than chlorinated aliphatic hydrocarbons, so the addition of water either as rainfall infiltration or the rising water table will displace the chlorinated organic compounds in the unsaturated zone from their sorption sites, resulting in remobilization. Moreover, chlorinated aliphatic hydrocarbons in contact with water will partially go into aqueous solution due to the moderate to high solubilities. Once in solution, chlorinated aliphatic hydrocarbons do not typically achieve the concentrations necessary to cause substantial density sinking. Instead, the dissolved part moves laterally with ground-water flow.

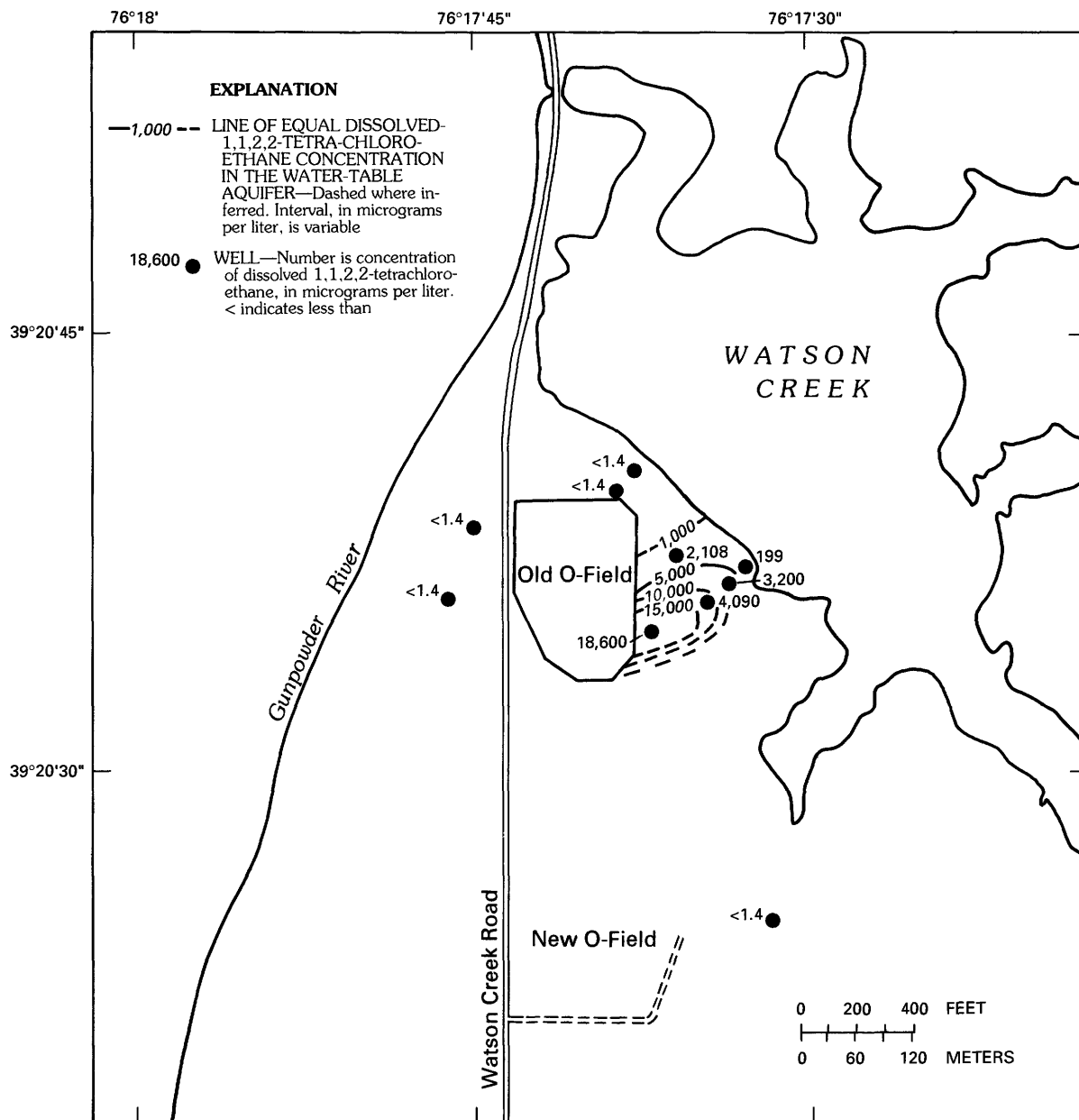


Figure 31. Distribution of 1,1,2,2-tetrachloroethane in the water-table aquifer, September 1987.

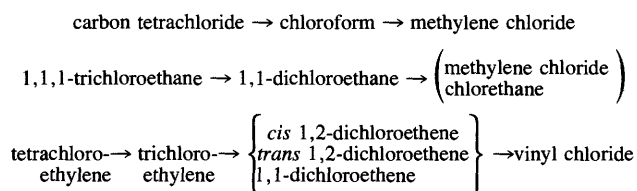
Dissolved chlorinated aliphatic hydrocarbons also may be derived from the large surface area of the disseminated product in the saturated zone. Water moving across the surface of product pools on impermeable layers will likewise dissolve chlorinated hydrocarbons. The concentrations derived from dissolution of the product in the saturated zone are related to ground-water velocity. At low velocities, the contact time between the water and the product is increased, so aqueous concentrations increase. Higher velocities result in lower aqueous concentrations but flush the product through the aquifer more quickly.

Individual chlorinated aliphatic hydrocarbons vary in their ability to be mobilized and transported by ground water. The variations primarily are due to differences in solubility. Therefore, an environmental mobility factor can be assigned to individual chlorinated aliphatics to describe their relative movement in ground water (Roy and Griffin, 1985). For example, the solubilities (Verschueren, 1983) of tetrachloroethylene (150 mg/L at 20°C), trichloroethylene (1,000 mg/L at 20°C), and 1,1,1-trichloroethane (700 mg/L at 20°C) indicate moderate mobility, whereas methylene chloride (13,200 mg/L at 20°C) is highly mobile.

Chlorinated aliphatic hydrocarbons are volatile, so they have a tendency to form a vapor phase and disperse into the atmosphere. The rate of volatilization in a soil zone depends on numerous factors, including but not limited to air temperature, humidity, wind speed, soil type, temperature, moisture, and the vapor pressure of the compound. The aqueous volatility of an organic compound is determined by dividing the vapor pressure of the compound by its solubility (Canter and others, 1987). Thus, if its aqueous solubility is high, a compound may have a high vapor pressure and still remain unvolatilized in the soil or water.

Chlorinated aliphatic hydrocarbons can be transformed by a variety of biotic or abiotic mechanisms. The transformations can be divided into four types of reactions: substitution, dehydrohalogenation, oxidation, and reduction (table 6).

Microbial populations may play a significant role in mediating dehalogenation reactions. Parsons and Lage (1985) have shown in a laboratory (under conditions of neutral to acid pH, reductive potential, and the absence of oxygen and light) that reductive dehalogenation of tetrachloromethane, tetrachloroethane, and 1,1,1-trichloroethane produced trichloromethane, dichloroethane, and 1,1-dichloroethane, respectively. Field studies by Wood and others (1981) have shown that anaerobic microbes may transform parent compounds into the following daughter compounds:



In general, the type of reaction that a particular halogenated aliphatic hydrocarbon will undergo depends on the number and type of halogen substituents. With increased numbers of attached halogens, or with increasing substitution of bromine for chlorine as the halogen, the electrophilicity and oxidation state of the compound increase, making the compound more susceptible to dehydrohalogenation and reduction and less susceptible to substitution and oxidation. The less halogenated the compound, the faster the rate of oxidation (Vogel and others, 1987). Parsons and Lage (1985) have shown in a laboratory (under conditions of neutral to acid pH, reductive potential, and the absence of oxygen and light) that chlorinated alkenes tend to be more resistant to biotransformation than the chlorinated alkanes.

The use of chlorinated aliphatic hydrocarbons at O-Field probably left droplets of solvent sorbed to the soil and aquifer matrix in the disposal area. The amount of vertical movement through the unsaturated zone depends largely on the amount of the product disposed and the

permeability of the soil. If sufficient amounts were disposed, then the free product probably moved downward through the water-table aquifer until it reached an impermeable layer. Because chlorinated aliphatics are moderately soluble, part of the free product could have gone into solution and began moving with ground water. The sorbed portion would have then become a continuing source for additional dissolved solvent. Once in the ground-water flow system, much of the solvent was not in contact with an air-water interface, so volatilization would have been of limited effectiveness in removing solvent from the ground-water system.

Tetrachloroethylene and 1,1,2,2-tetrachloroethane behave somewhat differently in the ground water near Old O-Field, suggesting a possible difference in source. During the drought period between March and July 1986, the concentrations of chlorinated ethylenes at well OF6A decreased, while the concentration of 1,1,2,2-tetrachloroethane increased (fig. 32). Moreover, the molar ratio of reactant to products increased (fig. 33), suggesting the input of higher chlorinated species relative to breakdown products.

Rainfall in late August and early September 1986 raised water levels slightly. Tetrachloroethylene concentrations increased and 1,1,2,2-tetrachloroethane concentrations decreased slightly. The molar ratio of reactants to products continued to increase. The rapid increase in concentrations after the late August and early September rains and the increased molar ratio imply that tetrachloroethylene was leached from the soil zone in the immediate vicinity of the well. However, the decrease in 1,1,2,2-tetrachloroethane concentrations implies a different major source, probably from within the Old O-Field trench area. Thus 1,1,2,2-tetrachloroethane was probably moving out of the fill in the ground water as a slug of contamination, possibly as a result of water levels and rain that were higher than normal in March and April. Concentrations of 1,1,2,2-tetrachloroethane and reactant/product ratio at well OF6A increased further as the slug continued to move toward the well.

Although the bulk of 1,1,2,2-tetrachloroethane probably was derived from within the disposal area, a lesser amount may also have been leached from the soil zone and added to the contamination moving from O-Field. The concentration decrease during the rainfall of late August and early September was less than would be expected if dilution and dispersion were the only factors. For example, during late September to mid-October 1986, the recession slope of 1,1,2,2-tetrachloroethane concentrations, due to degradation (as discussed below), was greater in the absence of rain than during the rainy period. The implication is that the decreasing concentrations during the rainy period were somewhat stabilized by the input of additional tetrachloroethane from the soil zone.

Table 6. Abiotic and biotic reactions of halogenated aliphatic compounds

[From Vogel and others, 1987]

Reactions	Examples
I. Substitution (a) solvolysis, hydrolysis $RX + H_2O \rightarrow ROH + HX$ (b) conjugation and other nucleophilic reactions $RX + N^- \rightarrow RN + X^-$	$CH_3CH_2CH_2Br + H_2O \rightarrow CH_3CH_2CH_2OH + HBr$ $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$
II. Dehydrohalogenation $\begin{array}{c} \quad \\ -C-C- \\ \quad \\ X \quad H \end{array} \rightarrow \begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + HX$	$CCl_3CH_3 \rightarrow CCl_2CH_2 + HCl$
III. Oxidation (a) α-hydroxylation $\begin{array}{c} \\ -C-X \\ \\ H \end{array} + H_2O \rightarrow \begin{array}{c} \\ -C-X \\ \\ OH \end{array} + 2H^+ + 2e^-$ (b) halosyl oxidation $\begin{array}{c} \\ -C-X \\ \end{array} + H_2O \rightarrow \begin{array}{c} \\ -C-X^+O^- \\ \end{array} + 2H^+ + 2e^-$ (c) epoxidation $\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + H_2O \rightarrow \begin{array}{c} \diagup \quad O \quad \diagdown \\ C \quad \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} + 2H^+ + 2e^-$ (d) biohalogenation (alkenes) $\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + X^- + H_2O \rightarrow \begin{array}{c} \diagup \quad OH \quad X \\ C-C \\ \diagdown \quad \quad \\ \quad \quad +H^+ \end{array} + 2e^-$	$CH_3CHCl_2 + H_2O \rightarrow CH_3CCl_2OH + 2H^+ + 2e^-$ $CH_3CHCl_2 + H_2O \rightarrow CH_3CHClCl^+O^- + 2H^+ + 2e^-$ $CHClCCl_2 + H_2O \rightarrow CHClOCCl_2 + 2H^+ + 2e^-$ $CH_2CH_2 + Cl^- + H_2O \rightarrow CH_2OHCH_2Cl + H^+ + 2e^-$
IV. Reduction (a) hydrogenolysis $RX + H^+ + 2e^- \rightarrow RH + X^-$ (b) dihalo elimination $\begin{array}{c} \quad \\ -C-C- \\ \quad \\ X \quad X \end{array} + 2e^- \rightarrow \begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + 2X^-$ (c) coupling $2RX + 2e^- \rightarrow R-R + 2X^-$	$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$ $CCl_3CCl_3 + 2e^- \rightarrow CCl_2CCl_2 + 2Cl^-$ $2 CCl_4 + 2e^- \rightarrow CCl_3CCl_3 + 2Cl^-$

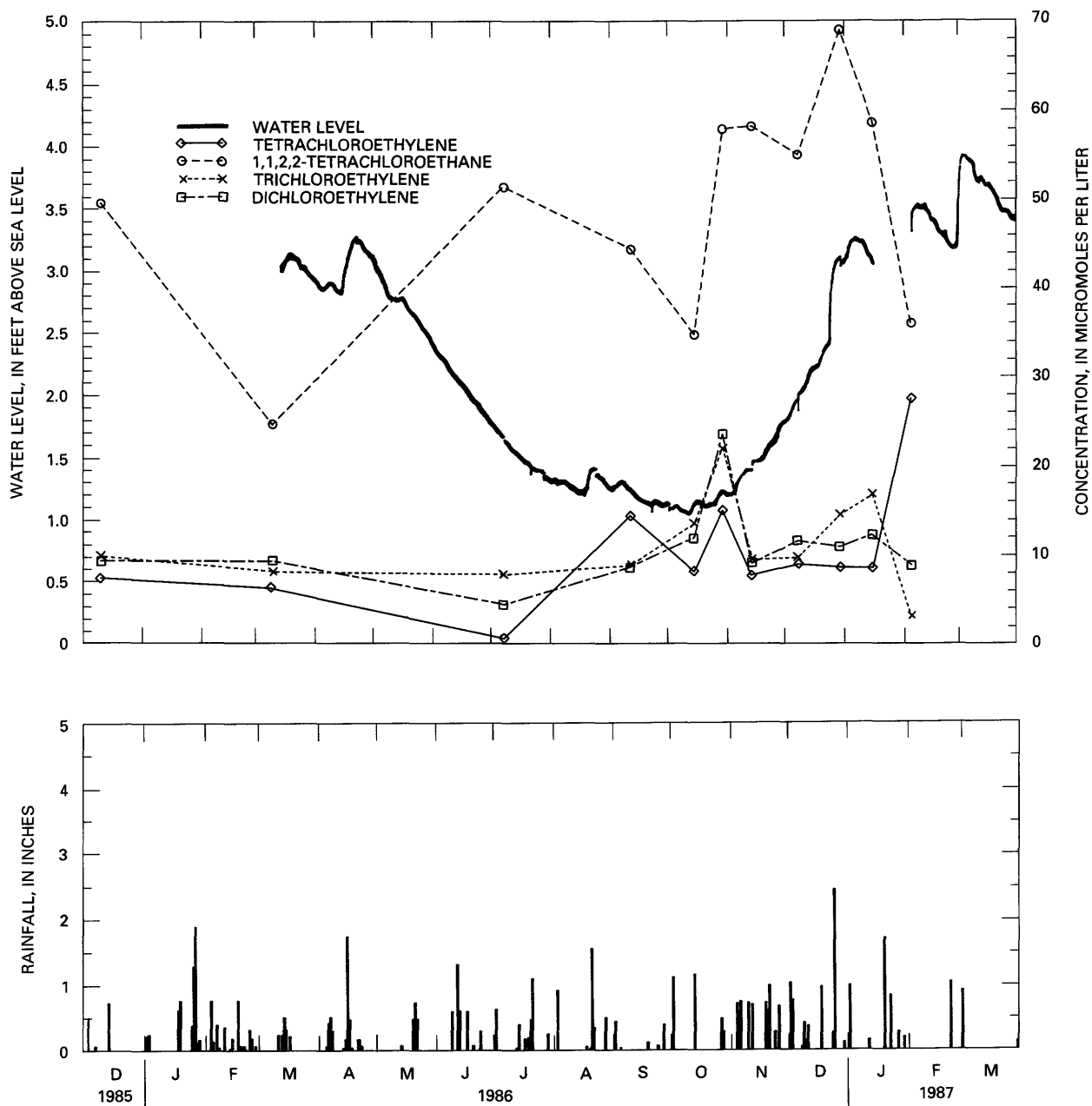


Figure 32. Changes in the concentration of selected chlorinated aliphatic hydrocarbons and in the water level at well OF6A, and rainfall for December 1985 to March 1987.

The decrease in reactant/product ratio at well OF6A during the essentially rainless period in early October probably reflects dehalogenation of tetrachloroethylene and tetrachloroethane. Concentrations of both reactants and products increased after a small rainfall in late October 1986, possibly due to leaching, but apparently not enough to increase the reactant/product ratio. In early November 1986, however, a period of sustained rainfall (4.3 in. over a 10-day period) decreased concentrations by dilution, but increased reactant/product ratios, probably due to the input of additional reactant from the soil zone. A dry period in

late November allowed the reactant/product ratios to decrease. Additional rain in late December abruptly increased the ratios.

At well OF17A, downgradient from well OF6A, similar examination of the data shows that somewhat different processes occurred. During the period from March to August 1986, concentrations were increasing at well OF6A but were decreasing at well OF17A throughout the summer (fig. 34). Also, unlike well OF6A, the reactant/product ratios in well OF17A decreased throughout the summer (fig. 35), indicating dehalogenation. In the

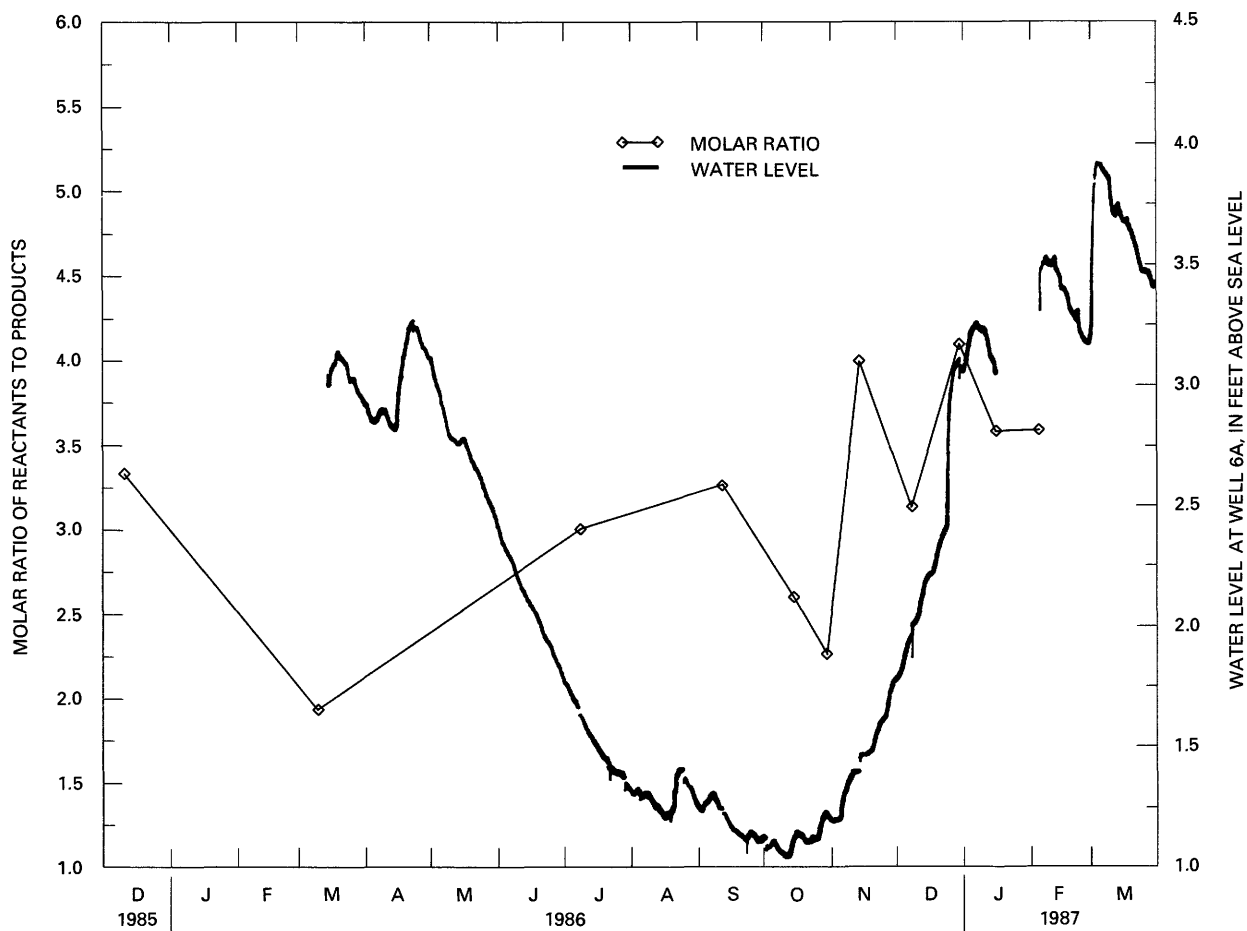


Figure 33. Changes in the molar ratio of selected chlorinated aliphatic reactants to products and changes in the water level at well OF6A for December 1985 to March 1987. Reactants are tetrachloroethylene; 1,1,2,2-tetrachloroethane; trichloroethylene; and 1,1,2-trichloroethane. Products are vinyl chloride; 1,2-dichloroethane; and 1,2-dichloroethylene.

essentially dry period around mid-October, tetrachloroethane decreased at well OF6A but increased at well OF17A, while the reactant/product ratio continued to decline. The increase was probably due to the lateral migration of a small pulse of contaminant that had also been undergoing dehalogenation. Finally, when the November rains produced abrupt increases in tetrachloroethane and reactant/product ratios at well OF6A, a similar response occurred more than a month later at well OF17A, due to traveltime.

The chemical evidence supports the hypothesis that chlorinated aliphatic hydrocarbons are leached during rain events from within the fill area of Old O-Field and in the vicinity of well OF6A. Velocity determinations of contaminant movement are difficult because the pulse seen at well OF17A may not be the same contamination at well OF6A for the previous months. Contaminant may be leaching from the soil zone somewhere between the two wells rather than in the immediate vicinity of well OF17A because recharge events produced no abrupt increases in concentra-

tions. The data also suggest that between rainfall events, reactions are actively dehalogenating higher chlorinated aliphatics to lower chlorinated aliphatics.

Calculations of retardation factors for the chlorinated aliphatic hydrocarbons at O-Field indicate that the amount of fine-grained organic carbon (less than 0.01 percent) present below the soil zone is insufficient to produce significant sorption; therefore, the dissolved chlorinated aliphatic hydrocarbons probably will travel at about the same rate as ground water.

Chemical analysis of ground-water samples collected on February 5, 1987, and September 21, 1987, showed an increase in 1,1,2,2-tetrachloroethane concentrations at wells OF6A and OF17A from 6,050 $\mu\text{g/L}$ and 1,991 $\mu\text{g/L}$, respectively, to 18,000 $\mu\text{g/L}$ and 14,100 $\mu\text{g/L}$, respectively, in the water-table aquifer (fig. 36). The increase was higher than any detected since sampling began in December 1985. The period between the two samplings was marked by an increase in ground-water levels near Old O-Field

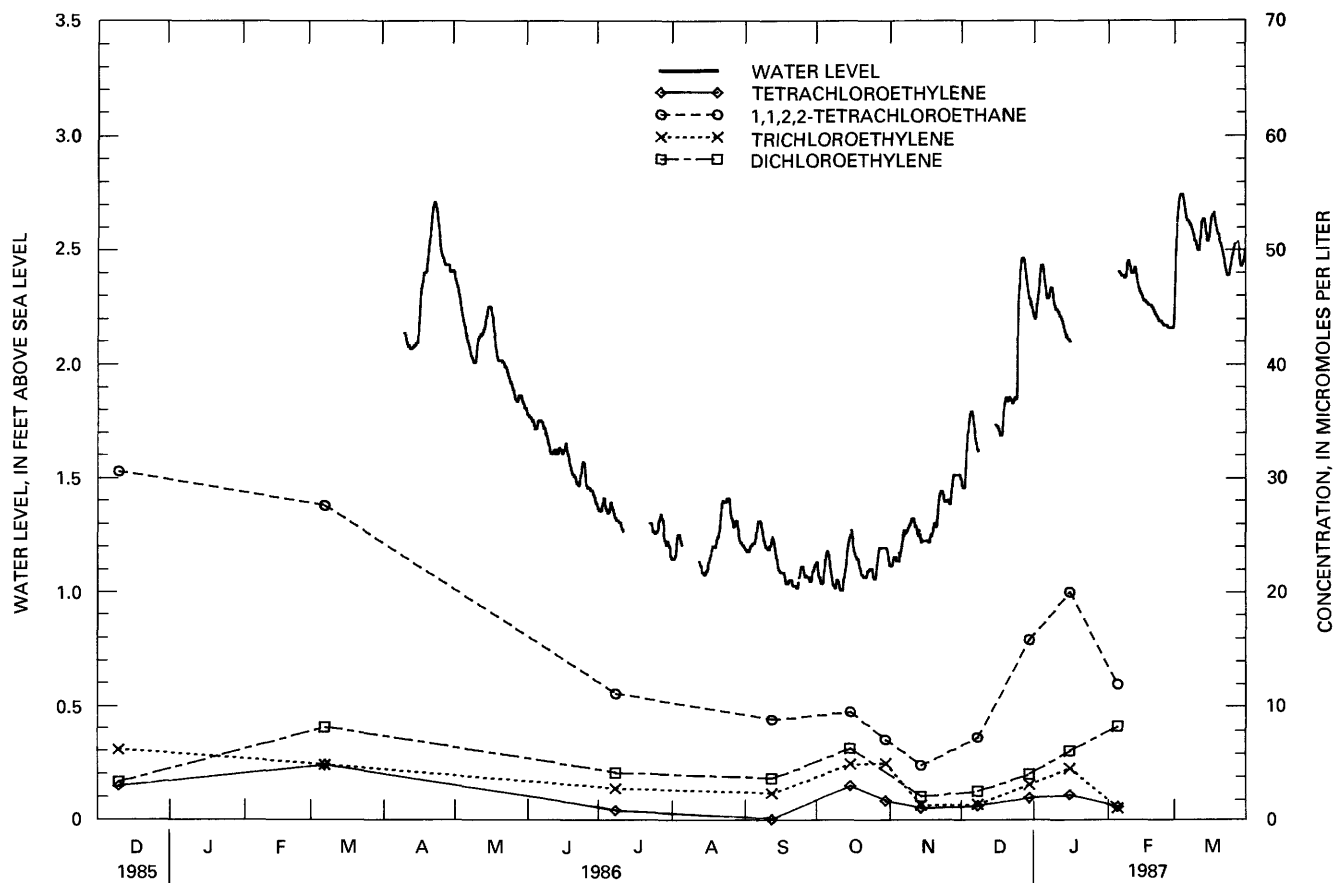


Figure 34. Changes in the concentration of selected chlorinated aliphatic hydrocarbons and changes in the water level at well OF17A for December 1985 to March 1987.

approximately 0.6 ft higher than during the previous winter (fig. 10). It is likely that the increase in concentration of 1,1,2,2-tetrachloroethane is due to leaching of product from within the trench area of Old O-Field as a result of high ground-water levels and rainfall. Thus, the elevated concentrations detected in September 1987 appear to represent the movement of a pulse of 1,1,2,2-tetrachloroethane away from Old O-Field. On April 15, 1988, the concentrations were lower, possibly because the pulse was between wells or because of rainfall effects. Possible rainfall effects include dilution of the contamination or depression of the plume beneath a veneer of freshwater overlaying the contamination. The highest concentrations, however, were at well OF17A, 260 ft downgradient from well OF6A (fig. 36). Further migration of the pulse was apparent during the October 15, 1988, sampling, when the highest concentrations were at well OF21, 340 ft downgradient from well OF6A (fig. 36).

Based on the previous discussion, dehalogenation of chlorinated aliphatic hydrocarbons is occurring at O-Field; therefore, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, and chloroethane are probably related, in part, to the same initial contaminant, namely, 1,1,2,2-

tetrachloroethane. The decontaminant DANC, used extensively at O-Field, had 1,1,2,2-tetrachloroethane as the major solvent. Degreasing solvents also were disposed at O-Field (G. Nemeth, U.S. Army Environmental Hygiene Agency, written commun., 1988), so another potential source of chlorinated aliphatic compounds is as primary components of disposed solvent. Trichloroethylene was a commonly used solvent at Aberdeen Proving Ground for degreasing operations and may have been disposed at O-Field.

Tetrachloroethylene is unlikely to have been generated by transformations from other species under the conditions at O-Field and, therefore, was also probably part of the original waste. The lesser-chlorinated ethylenes probably were generated by transformation reactions, such as hydrogenolysis, hydrolysis, or dehydrohalogenation of trichloroethylene or tetrachloroethylene. Part of the dichloroethylene may have been produced by dihaloelimination of tetrachloroethane (table 6). Vinyl chloride at Old O-Field may be partly due to the dehalogenation of higher-chlorinated ethanes or ethylenes.

The presence of carbon tetrachloride in the ground water at O-Field may be due to disposal of CNB, a variety

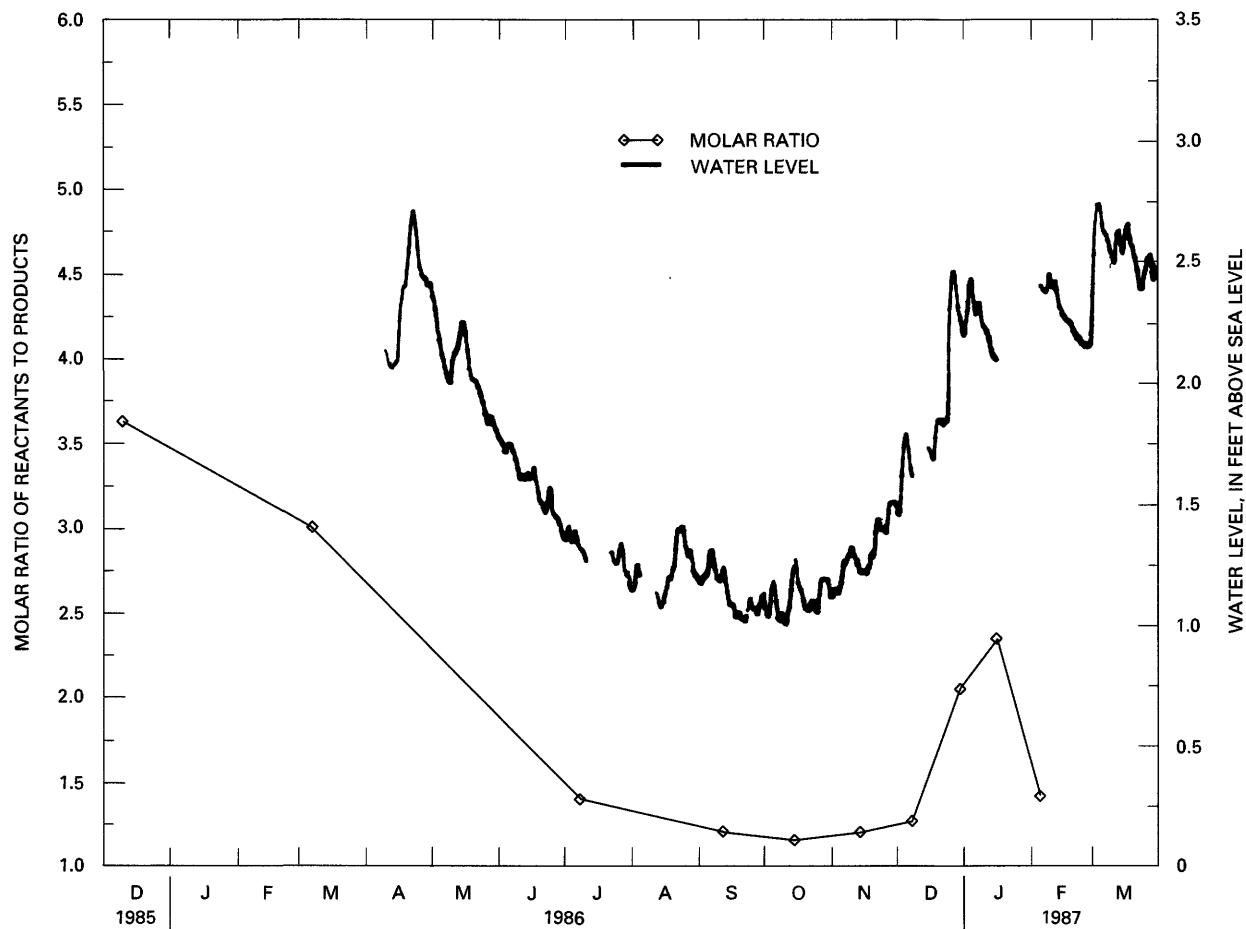


Figure 35. Changes in the molar ratio of selected chlorinated aliphatic reactants to products and changes in the water level at well OF17A for December 1985 to March 1987. Reactants are tetrachloroethylene; 1,1,2,2-tetrachloroethane; trichloroethylene; and 1,1,2-trichloroethane. Products are vinyl chloride; 1,2-dichloroethane; and 1,2-dichloroethylene.

of tear gas composed of 10-percent chloroacetophenone, 45-percent benzene, and 45-percent carbon tetrachloride. Carbon tetrachloride was commonly used at Aberdeen Proving Ground to clean up spills, so disposal of raw product may have occurred. Carbon tetrachloride was also used in solution with bleach or chlorine as decontaminating agents (Mankowich and others, 1970), but the major period of use preceded the time that O-Field was in operation (Gary Nemeth, U.S. Army Environmental Hygiene Agency, oral commun., 1988).

Methylene chloride is a breakdown product of all of the chlorinated aliphatic volatiles. Its presence, therefore, is probably due to degradation of higher-chlorinated species. It is also a common laboratory contaminant.

Aromatic Compounds

Aromatic compounds are organic molecules containing a benzene ring. At O-Field the most concentrated

aromatic compound detected was benzene. It occurred in two plumes emanating from Old O-Field and one from New O-Field (fig. 37). The maximum concentration observed was 6,040 $\mu\text{g/L}$ during October 1986 at well OF6A. Other aromatic compounds and their maximum detected concentrations in the water-table aquifer were toluene (2,400 $\mu\text{g/L}$ in well OF6 during October 1988), C3 alkyl benzene (1,854 $\mu\text{g/L}$ in well OF6A during December 1985), chlorobenzene (430 $\mu\text{g/L}$ in well OF6A during September 1987), and ethylmethylbenzoic acid (116 $\mu\text{g/L}$ at well OF6A in December 1985). Dominant aromatic compounds in the upper confined aquifer at Old O-Field were benzene (950 $\mu\text{g/L}$ at well OF6B in September 1987) (fig. 38), chlorobenzene (213 $\mu\text{g/L}$ in well OF6B during December 1987), and toluene (13.5 $\mu\text{g/L}$ at well OF6B during September 1987).

Aromatic compounds also present in the water-table aquifer at New O-Field (well OF16A) were benzene and toluene (maximum concentrations measured were 32.7

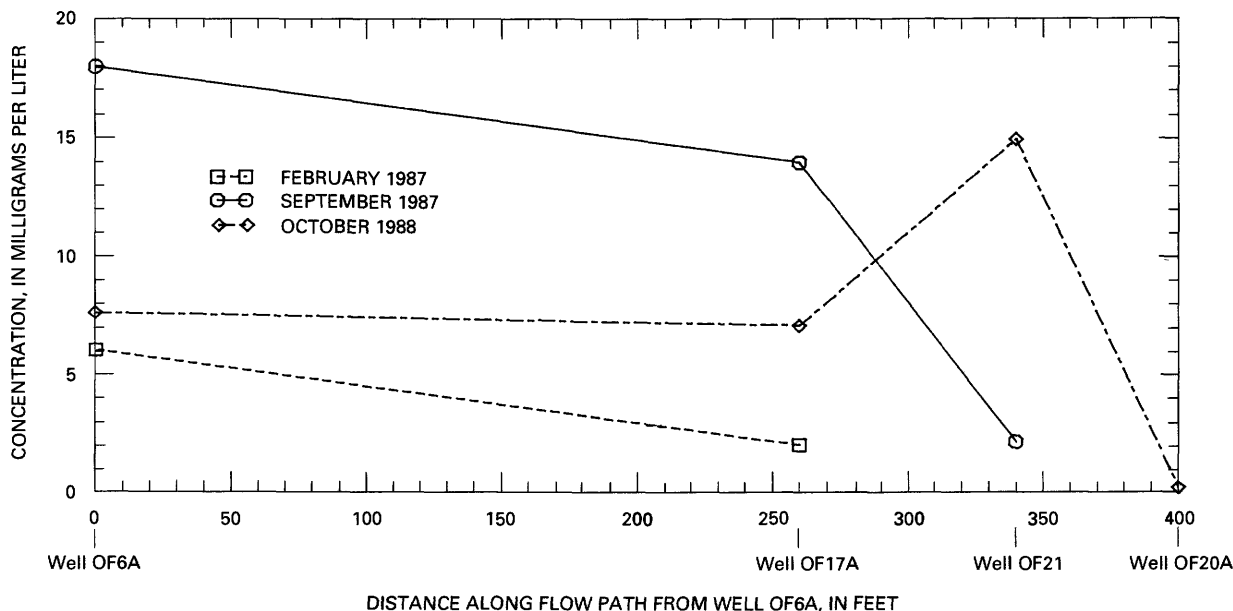


Figure 36. Changes in concentrations of 1,1,2,2-tetrachloroethane with time along flow path from well OF6A to well OF20A.

µg/L in September 1987 and 28.6 µg/L in July 1986, respectively). Additional compounds tentatively identified with a GCMS library search in December 1985 were dichlorophenol (not 2,4-) (23 µg/L), ethyl-2-methylbenzene (21 µg/L), 3,5-dichloroaniline (20 µg/L), trichloroaniline (19 µg/L), chloroaniline (16 µg/L), and 1-ethyl-2-methylbenzene (9 µg/L). These additional compounds were not present at Old O-Field.

Aromatic compounds present in the upper confined aquifer at New O-Field (well OF16B) and their maximum concentrations were toluene (49 µg/L in July 1986), benzene (48 µg/L in December 1986), and chlorobenzene (16.7 µg/L in July 1986). Additional compounds tentatively identified using a GCMS library search in December 1985 were aniline (26 µg/L), xylene (21 µg/L), diphenyl methane (7 µg/L), dimethyl benzoic acid (6 µg/L), trichloroaniline (2 µg/L), an isomer of trimethyl benzene (2 µg/L), and xylene (2 µg/L). These additional compounds were not present at Old O-Field.

The wells immediately adjacent to Old O-Field (wells OF6, OF6A, OF13A, and OF13B) and wells at New O-Field (wells OF16A and OF16B) were sampled for 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene, and 2,6-dinitrotoluene during December 1986. Only TNT was detectable and was found only in well OF6 (22.1 mg/L). Samples were collected from wells OF20A, OF20B, OF21, OF22A, and OF22B during September 1987 and analyzed for a broader suite of nitroaromatics. The nitroaromatics tested were 1,3,5-trinitro-1,3,4-triazacyclohexane (RDX), 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, tetryl, and nitrobenzene, as well as the constituents from the December

1986 sampling. The only compound detected was 1,3-dinitrobenzene in the water-table aquifer. Concentrations of 1,3-dinitrobenzene were 71.8 mg/L at well OF22A, 23.3 mg/L at well OF21, and 4.6 mg/L at well OF20A.

The lower confined aquifer was found to contain 38 µg/L benzene, but only in well OF6C and only during one sampling run. Benzene was not detected in samples from well OF6C (July 1986) during the other four sampling periods nor in samples from the other two wells in the aquifer during any of the five sampling periods.

Aromatic hydrocarbons vary in solubility and mobility. Aqueous solubilities are 1,780 mg/L (30°C) for benzene, 500 mg/L (20°C) for chlorobenzene, 175 (20°C) to 198 mg/L (25°C) for xylene; and 515 mg/L (20°C) for toluene (Verschueren, 1983). In saturated soil-water systems, benzene is considered to be highly mobile, chlorobenzene moderately mobile, xylene moderately (o-xylene) to poorly mobile (m-xylene and p-xylene), and toluene moderately mobile (Roy and Griffin, 1985).

Benzene, xylene, and toluene readily biodegrade when oxygen is present in shallow ground-water systems. Laboratory experiments by Barker and others (1987) showed that benzene was somewhat more persistent and that the degradation produced phenolic and acidic breakdown products. Other classical microbial breakdown products of monoaromatics are catechols and cresols (methyl phenol), benzoic and various hydroxybenzoic acids, and benzaldehyde (Gibson, 1978). Considerable oxygen is required for aerobic degradation of benzene, xylene, and toluene (Barker and others, 1987), so the species tend to be more persistent in anaerobic conditions.

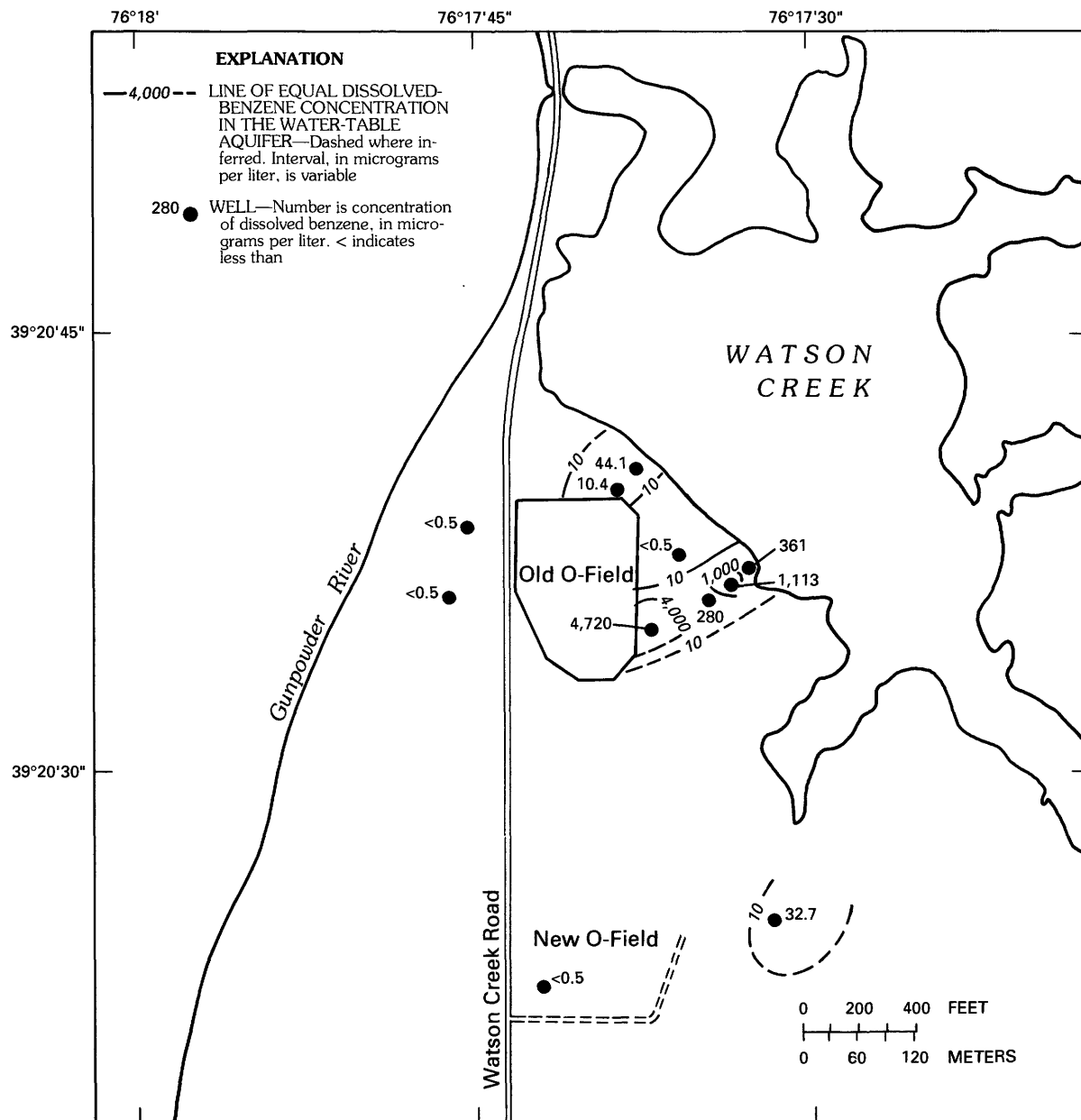


Figure 37. Distribution of benzene in the water-table aquifer, September 1987.

Chlorobenzenes have been observed to occur under aerobic but not anaerobic conditions (Bouwer and McCarty, 1984). The degradation is slower than for alkyl aromatics, possibly due to difficulty in cleaving the chlorine bond (Schwarzenbach and others, 1983). Possible degradation products are chlorinated phenols and catechols.

Phenolic compounds are anionic, and their solubility is, therefore, higher than uncharged organics and increases with pH due to increased deprotonation. The negative charge causes the anionic organics to be repelled from the negatively charged clay surfaces. Therefore, phenolic compounds are generally not sorbed onto the aquifer matrix except for limited sorption onto sediment organic matter

(Chiou, 1981). There is some evidence, however, to suggest phenolic degradation by anaerobic bacteria (Ehrlich and others, 1982).

The nitrobenzenes can be persistent in ground water. Hydrolysis of the nitrobenzenes under ambient environmental conditions is unlikely (Fieser and Fieser, 1956), and oxidation does not appear to be a major reaction for the nitrobenzenes. Substitution by nitro groups decreases the electron density of aromatic rings (Fieser and Fieser, 1956), reducing the susceptibility to attack by molecular oxygen and hydroxyl radicals. TNT concentrations in ground water, however, may be limited by microbial degradation under aerobic conditions (McCormick and others, 1976;

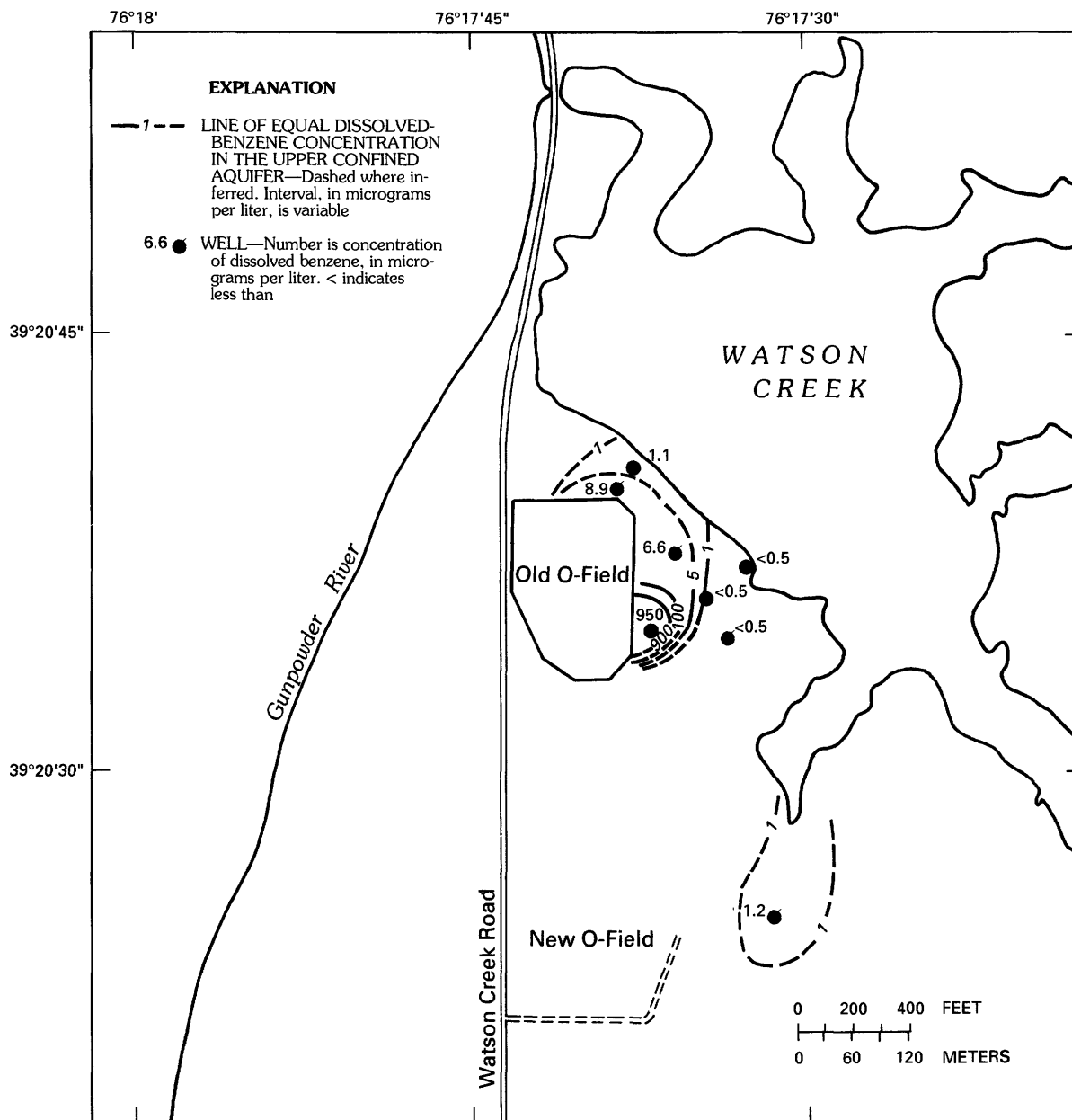


Figure 38. Distribution of benzene in the upper confined aquifer, September 1987.

Spangord and others, 1980), by sorption onto sands (Spangord and others, 1980), or both (Spalding and Fulton, 1988).

The degradation of TNT produces a series of compounds resulting from the reduction of one or more of its nitro groups and a series of coupling products of these groups (Won and others, 1974). Examples of breakdown products are 2,6-dinitro-4-hydroxylaminotoluene and 2-6-dinitro-4-aminotoluene. A laboratory study by Dacre and Rosenblatt (1974) showed that TNT eventually can be broken down completely by microbial action to succinic acid, various amino acids, and carbon dioxide.

Benzene and toluene probably have played a role in producing the anaerobic conditions present in the ground water at O-Field. The considerable amount of oxygen required to degrade them may have been enough to utilize dissolved oxygen faster than it could be recharged.

Once the oxygen is depleted, degradation is slow, if it occurs at all. Therefore, biodegradation of aromatic organic compounds probably is limited in the anaerobic ground water at Old and New O-Fields. Benzene would be expected to migrate through the aquifer at about the same rate as ground water. The major depletion mechanism probably is volatilization at the air-water interface.

Chlorobenzene would be expected to be mobile in ground water because of the low (<0.01 percent) organic carbon content of the aquifer. However, degradation probably will be slow because it may not be able to compete adequately with nonchlorinated aromatics for available oxygen.

The TNT contamination does not extend farther downgradient than the vicinity of well OF6. However, 1,3-dinitrobenzene occurs only in the downgradient wells. The difference may mean that TNT transport is limited by microbial degradation in the oxygenated water at well OF6.

Benzene and toluene are contaminants that may result from disposal of petroleum products. As part of the cleanup operations at O-Field, munitions, chemicals, and contaminated materials were burned. During 1950, the burning involved pumping hundreds of gallons of fuel oil into the pits at Old O-Field (Dickey, 1978). The entire field was then sprayed with fuel oil and ignited. It is likely that some of the fuel oil seeped into the ground before it could burn, and, once several inches in the ground, it may have avoided destruction by the fire. This operation was most likely a major source of fuel components in the ground water. Burning operations continued in later years at New O-Field; however, the amount of fuel used at any one time probably was not as great because the amount of material to be destroyed was less. Additional benzene contamination may have occurred from degradation of CNB (U.S. Departments of the Army and Air Force, 1975).

The density of benzene is less than that of water. Its presence in the upper confined aquifer, therefore, is not due to density settling from the water-table aquifer. Hydrologic evidence discussed earlier suggests that the confining unit beneath the water-table aquifer may be discontinuous beneath the Old O-Field fill area. Thus, the presence of benzene as a major organic contaminant in the upper confined aquifer may be due to excavation of trenches through the confining layer and disposal of fuel into the trenches.

Alternatively, the elevated benzene concentrations (950 µg/L during September 1987) in the upper confined aquifer at well OF6B may have been introduced during drilling. The same site also contained the highest concentration of benzene in the water-table aquifer. This source is unlikely, however, because the well was thoroughly purged for sampling five times between December 1985 and September 1987, and no decrease in concentration with time was observed. Instead, the highest concentration was found during the last sampling.

The presence of nitroaromatics (TNT and 1,3-dinitrobenzene) is due to disposal of explosives at Old O-Field. The 1,3-dinitrobenzene may represent a microbial degradation product of TNT or a manufacturing impurity. The presence at New O-Field of dichlorophenol, trichloroaniline, and several derivatives may be due to the use of herbicides.

Organosulfur and Organophosphorus Compounds

A variety of chemical-warfare agents and munitions products disposed at Old O-Field are organic compounds containing sulfur or phosphorus groups. Therefore, selected ground-water samples were tested for various organosulfur and organophosphorus chemical-warfare agents and degradation products in September 1987. The analysis showed the presence of methyl phosphonic acid in the water-table aquifer at New O-Field (well OF16A) and Old O-Field (well OF20A) at concentrations greater than 10,000 µg/L (not quantifiable due to interferences with other constituents). Methyl-*bis*(1-methylethyl)-ester phosphonic acid, a related product, was also found in the water-table aquifer at New O-Field (32 µg/L in December 1985). Contaminants tested for in September 1987, but not detected, were mustard agent (detection limit 0.03 µg/L), nerve agent GD (detection limit 0.003 µg/L), nerve agent GB (detection limit 0.0003 µg/L), nerve agent VX (detection limit 0.002 µg/L), ethylmethyl phosphonic acid (detection limit 400 µg/L), isopropyl methyl phosphonic acid (detection limit 400 µg/L), P-methylphosphonic acid (detection limit 400 µg/L), and chlorovinylarsonic acid (detection limit 40 µg/L).

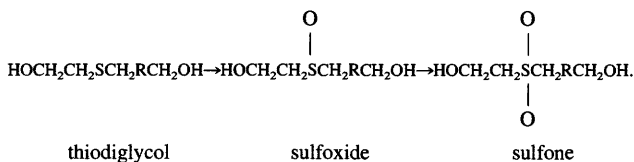
Thiodiglycol, an indicator of mustard-agent degradation, was not found at New O-Field but was found in the ground water north and east of Old O-Field. The highest concentrations in the water-table aquifer were detected near the fill at wells OF6 and OF6A (both 1,000 mg/L). Farther downgradient, at well OF17A, the concentration was 100 mg/L and at well OF21 was 200 mg/L. The ground water at well OF22A, immediately adjacent to Watson Creek along the same flow path, contained 10 mg/L. Well OF13B, screened in the water-table aquifer along the north side of Old O-Field, also contained thiodiglycol (10 mg/L), as did the downgradient well OF14B (5 mg/L).

Thiodiglycol was present in the upper confined aquifer east of Old O-Field. Concentrations ranged from 2 mg/L at wells OF17B and OF22B to 1 mg/L at well OF20B.

A GCMS library search to tentatively identify unknown constituents detected during analysis of samples collected during December 1985 revealed the presence of a number of cyclic sulfur-containing compounds. The dominant species was 1,4-dithiane, present in the water-table aquifer at well OF6A (5,154 µg/L), well OF6 (4,634 µg/L), well OF14B (1,132 µg/L), well OF17A (927 µg/L), well OF13B (58 µg/L), well OF14A (40 µg/L), and in the otherwise uncontaminated well OF18A (32 µg/L). Low concentrations (9 mg/L) of 1,4-dithiane were found in well OF19; in the upper confined aquifer at Old O-Field in wells OF17B (150 µg/L), OF6B (130 µg/L), OF14C (8 µg/L), and OF12B (3 µg/L); and in the lower confined aquifer at wells OF18C (9 µg/L) and OF6C (3 µg/L). No 1,4-dithiane was found at New O-Field. Other sulfur compounds

detected and tentatively identified were thiirane, thioxane, 3,5-methyl-1,2,4-trithiolane, 1,3-dithiolane-2-thione, thiophene, oxathione, dithione, 6-methyl-1,3-oxathiane, and carbon disulfide.

In general, sulfides are readily oxidizable to sulfoxides or sulfones (Streitwieser and Heathcock, 1981, p. 811). For thiodiglycol, the reaction would be



Thiols are readily oxidized to disulfides in the presence of mild oxidizing agents. Under reducing conditions, the weak disulfide bond may be converted back to the thiol. Reactions can also occur at the hydroxide ends of the compound. The acid-dissociation constant (pK_a) for thiodiglycol has not been published, but values for a number of typical alcohols (Streitwieser and Heathcock, 1981, p. 238) are greater than 10.0. Therefore, if thiodiglycol behaves similarly, the hydroxide groups should be undissociated and uncharged in acidic ground water, and the potential for electrostatic sorption onto aquifer material would be limited.

Little information is available on the behavior of methylphosphonic acid in soil and water, although it is reportedly very soluble (Rosenblatt and others, 1975) at dissociation contents of 2.38 and 7.74 (Crofts and Kosolapoff, 1953). Thus, it should have a net negative charge in slightly acidic water.

The high solubility and probable lack of an electrostatic charge on thiodiglycol under the pH conditions in the ground water at O-Field imply that it will probably migrate through the ground water relatively unimpeded by aquifer-matrix reactions and discharge into Watson Creek. The high solubility and probable negative charge on methyl phosphonic acid in the ground water at O-Field imply that it should behave similarly. Redox reactions have occurred among the sulfur compounds, as evidenced by the presence of 1,3-dithiolane-2-thione. The presence of bis(thio)bis-6-methyl-1,3-oxathiane may indicate that 1,4-dithiane is undergoing similar oxidations. Increased oxidation rates should occur as the sulfides are transported into more oxygenated water. Wells OF18A and OF18B are west of the ground-water divide at Old O-Field, so the low concentrations of 1,4-dithiane present in the wells may be moving toward the Gunpowder River.

Methyl phosphonic acid, present at New O-Field, is a degradation product of the nerve agent GB (Rosenblatt and others, 1975). An intermediate hydrolysis product, isopropyl methyl phosphonic acid, is particularly resistant to further hydrolysis but will hydrolyze to methyl phosphonic acid in the presence of heat and a strong acid (Rosenblatt

and others, 1975). Because acids were disposed of at New O-Field and the area was used to incinerate waste, the methyl phosphonic acid may be due to incineration of GB in the presence of disposed acids.

Thiodiglycol is produced by hydrolysis of mustard (Rosenblatt and others, 1975). In contact with water, mustard dissolves at a slow rate, but once in solution, the hydrolysis to thiodiglycol is rapid. It is unlikely that thiodiglycol was generated by a process other than hydrolysis of mustard. Because thiodiglycol is highly mobile, its presence in high concentrations near the fill indicates that mustard is still present and hydrolyzing within the fill.

Compounds 1,4-dithiane, 1,4-thioxane, and possibly thiophene are thermal degradation products of mustard (Nemeth and others, 1983). The remaining sulfur-containing cyclic compounds are similar in structure to the thermal degradation products and, therefore, probably have the same origin. The presence of 1,4-dithiane west of Old O-Field at wells OF18A and OF18B may indicate that contaminated ground water from Old O-Field was moving through the area, but the lack of other characteristic contaminants argues against that source. Thermally degraded mustard may have been dispersed into that area or generated in that area, providing a 1,4-dithiane source.

SURFACE-WATER CONTAMINATION

The surface water of Watson Creek contains the dissolved constituents arsenic, mercury, transition metals, and chlorinated aliphatic hydrocarbons, which may be related to activities at O-Field. Offsite transport of arsenic to the Gunpowder River was detected during only one of seven samplings. Transport of chlorinated aliphatic hydrocarbons to the mouth of Watson Creek was detected during a period when an ice covering on the creek prevented volatilization, and no samples were collected from the Gunpowder River during the period of ice cover. However, the cold water temperatures and low turbulence at the time of sampling suggest that chlorinated aliphatic hydrocarbons also may have been transported to the Gunpowder River.

Water samples collected from Watson Creek in March 1989 showed the presence of a variety of chlorinated aliphatic hydrocarbons. The contaminants appear to be related to a pulse or pulses of chlorinated solvent that apparently leached from Old O-Field to the ground water and migrated to Watson Creek as a result of above-normal ground-water levels in 1987.

Arsenic

A water sample collected from Watson Creek in November 1984 contained 0.08 mg/L arsenic near the northeastern shoreline of Old O-Field (site 6), and another sample contained 0.02 mg/L arsenic at the mouth of the

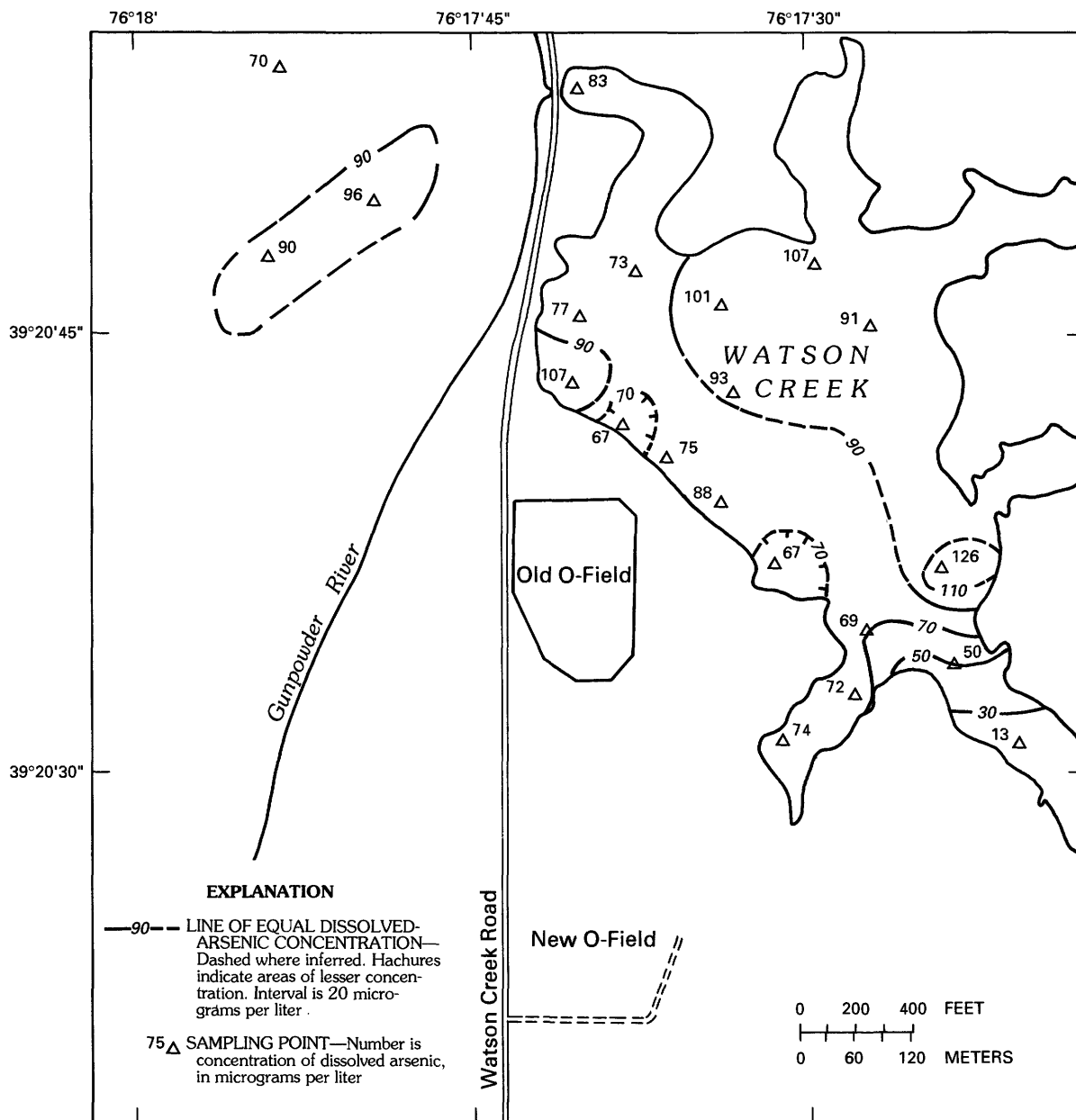


Figure 39. Distribution of dissolved arsenic in Watson Creek and the Gunpowder River, August 1985.

tributary leading to New O-Field (site 9). A more extensive investigation conducted in August 1985 detected similar concentrations of arsenic. Concentrations during the August 1985 sampling ranged from 0.013 to .126 mg/L within Watson Creek. Elevated concentrations coincide, in general, with areas of dominantly fine-grained bottom sediment and with areas of elevated arsenic concentrations in the bottom sediment. Concentrations within the tract (fig. 39) are locally higher at surface-water site 7 (fig. 2), immediately offshore from the area of Old O-Field containing the highest known concentrations of arsenic in ground water (fig. 25). The lowest concentrations were found along a

tract extending from the mouth of the creek to the O-Field shoreline and then southeastward (fig. 39). The path of relatively low concentrations corresponds, in general, to the area along which incoming tides are channeled into a more or less uniform flow direction (fig. 23), although the samples were collected at low tide.

Dissolved-arsenic concentrations in the Gunpowder River during the August 1985 sampling ranged from 70 to 96 $\mu\text{g/L}$ near the mouth of the creek. Subsequent sampling over a 1-year period did not detect the presence of arsenic.

Arsenic chemistry in surface water is subject to the same controls as those discussed for ground water. The

exchange of arsenic between dissolved and sorbed states, however, would be expected to occur more often in surface water, due to more rapid environmental changes. Aggett and O'Brien (1985, p. 235) found the exchange in Lake Ohakuri, New Zealand, to be cyclic and driven by seasonal changes in dissolved oxygen. Similar changes occur in the Chesapeake Bay. Large portions of the bay become anoxic during the summer. The anoxic conditions typically build in bottom waters during April and May and diminish beginning in October and November (Officer and others, 1984). Sanders (1985) has shown that the changes are accompanied by changes in dissolved-arsenic speciation. During the winter, the only arsenic species in bay water is arsenate. During the summer, substantial amounts of arsenite and methylated arsenic are present. Sanders was able to show a correlation between methyl arsenic and phytoplankton, suggesting that the methylated forms are due to biotic reduction. His data also imply that arsenite is present as a result of abiotic reduction.

The shallow and restricted nature of Watson Creek makes it vulnerable to variations in chemistry. Temperature changes, biologic activity, rainfall, and tidal cycling would be expected to subject arsenic to repeated transformations between the oxidized and reduced forms and to accompanying sorption and desorption reactions. Temperature changes exert an influence on arsenic by reducing the solubility of dissolved oxygen during the summer. The reduced amount of oxygen available during the summer is further drained by microbial degradation of the abundant organic matter in Watson Creek (U.S. Army Environmental Hygiene Agency, 1977). Release of bound arsenic may then occur by desorption or dissolution of the metal-oxide sorbent.

Rainfall events have the potential to cause both desorption and resorption of arsenic. Rainfall may wash sediment into the creek as surface runoff. If the sediment is contaminated with arsenic, desorption may occur, particularly during the warm summer months when the oxygen content of the creek would be expected to be lower. Alternatively, if the oxygenated summer rainwater sufficiently increases the oxygen content of Watson Creek water, resorption of arsenic may occur.

A major role of Watson Creek tidal cycling in relation to arsenic chemistry appears to be the redistribution of sediment by tidal currents. Fine-grained sediment is removed from areas having strong currents and deposited in more quiescent areas. The fine-grained material is typically rich in iron, manganese, and organics and has a large surface area available for sorption. Thus, sorption and desorption reactions probably occur to the greatest extent in quiescent areas of the creek.

The dissolved arsenic concentrations in the surface water at O-Field are the result of several factors. Based on the occurrence of dissolved arsenic in the Chesapeake Bay (Sanders, 1985), transport of naturally occurring or anthro-

Table 7. Maximum concentrations of additional selected inorganic constituents in the surface water of Watson Creek and the Gunpowder River, August 1985

[mg/L, milligrams per liter; <, less than]

Constituent	Maximum concentration (mg/L)
Alkalinity	960
Beryllium	<.001 (not detected)
Boron	1.02
Cadmium	.019
Chloride	3,180
Chromium	<.004 (not detected)
Copper	.0025
Iron	.082
Lead	<.01 (not detected)
Magnesium	274
Manganese	.874
Mercury	.00038
Nickel	.011
Potassium	78.6
Selenium	.94
Silica	1.98
Sodium	1,881
Sulfate	960
Total dissolved solids	6,574
Total suspended solids	44

pogenic arsenic into Watson Creek from the Chesapeake Bay and the Gunpowder River probably occurs, but at negligible concentrations. Other possible sources are overland transport of arsenic-contaminated sediment, ground-water discharge of arsenic contamination, or dissolution of arsenic from naturally occurring deposits.

The distribution of dissolved arsenic corresponds closely with the distribution of fine-grained bottom sediment, also containing arsenic. The relation implies that dissolution processes play a role; however, a locally elevated concentration (25 $\mu\text{g/g}$) at surface-water site 7s, adjacent to the area of arsenic contamination in the ground water at Old O-Field, suggests that discharge of contaminated ground water also is a factor. The elevated concentrations detected in August 1985 may have resulted from overland runoff from the heavy rainfall that occurred the night before sampling. The failure to obtain similarly high concentrations in eight subsequent samplings suggests that the events producing concentrations as high as those found during August 1985 are not common, or are of too short a duration to have been detected by subsequent samplings.

Additional Inorganic Constituents

Several other inorganic constituents were tested in the water in Watson Creek during August 1985. The constituents and their maximum concentrations are shown in table 7.

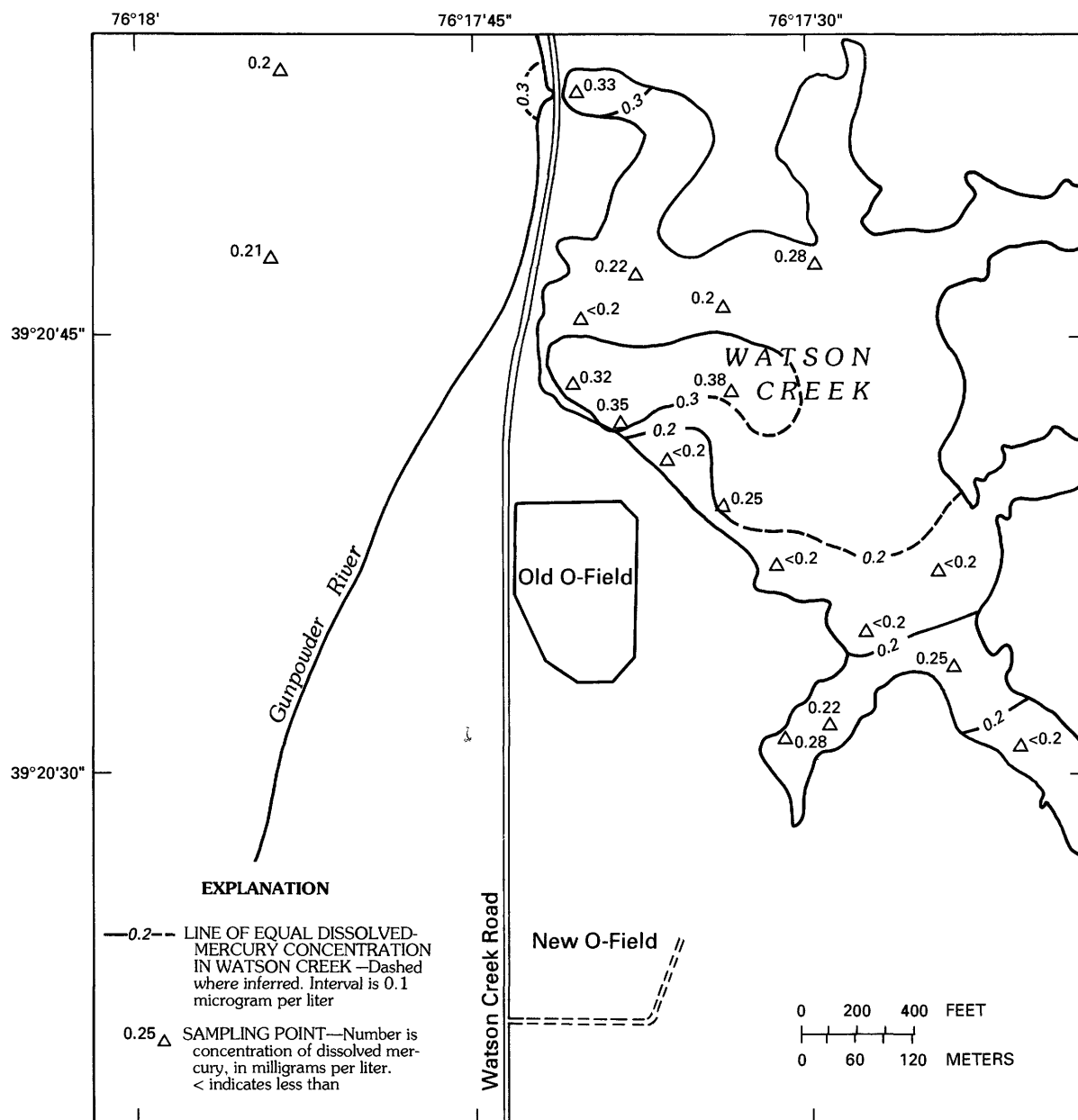


Figure 40. Distribution of dissolved mercury in Watson Creek and the Gunpowder River, August 1985.

Dissolved-mercury concentrations typically were around 0.2 to 0.28 $\mu\text{g/L}$ (fig. 40). The maximum value (0.38 $\mu\text{g/L}$) was from the center of Watson Creek. Concentrations between 0.30 and 0.35 $\mu\text{g/L}$ were measured at the mouth of the creek and along the northern shoreline of Old O-Field at sites 4s and 5s. Mercury solubility is low (about 25 $\mu\text{g/L}$) (Hem, 1970), so mercury chemistry and possible sources for the metals are discussed in the section entitled "Bottom-Sediment Contamination."

Chlorinated Aliphatic Hydrocarbons

Chlorinated aliphatic hydrocarbons were not found in Watson Creek during the November 1984 or the August 1985 sampling. However, methylene chloride (15.8 $\mu\text{g/L}$) was found at site 6 (fig. 2) but not in the corresponding method blank during September 1987. Contaminants also were found during January 1988 in samples collected through holes chipped in the 6-in.-thick layer of ice that

covered the creek. Samples were collected 20 and 50 ft offshore from Old O-Field and from the mouth of the creek, on the Watson Creek side. The surface-water sample near Old O-Field contained 1,1-dichloroethylene (260 µg/L), 1,2-trans-dichloroethylene (130 µg/L), 1,2-dichloroethane (120 µg/L), chloroform (96 µg/L), 1,1,2,2-tetrachloroethane (90 µg/L), vinyl chloride (47 µg/L), and trichloroethylene (34 µg/L). The sample taken from the mouth of Watson Creek contained 1,1,2,2-tetrachloroethane (20 µg/L) and chloroform (4 µg/L).

Water samples collected from Watson Creek in March 1989 showed the presence of 1,1,2,2-tetrachloroethane (49.8 µg/L), total 1,2-dichloroethylene (11.6 µg/L), 1,2-dichloroethane (9.3 µg/L), chloroform (7.6 µg/L), trichloroethylene (6.5 µg/L), tetrachloroethylene (4.2 µg/L), and vinyl chloride (3.4 µg/L) at site 7s (fig. 2). Only one sample of the creek was collected during March 1989, so the distribution of the surface-water contamination was not determined.

The reactions involving chlorinated aliphatic hydrocarbons in surface water are, in general, the same as those in ground water; however, the primary fate in surface-water systems is typically volatilization. Laboratory studies by Dilling and others (1975) indicate that volatilization rates are little affected by the presence of other material (clay, limestone, sand, salt, peat moss, and kerosene), suggesting that the sorptive process cannot efficiently compete with solute evaporation. The studies showed 50-percent volatilization of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene in less than 90 min of stirring at 200 revolutions per minute at 25°C.

A major factor affecting chlorinated aliphatic hydrocarbons in surface water at O-Field is probably volatilization. Watson Creek typically has less than detectable concentrations of chlorinated aliphatic hydrocarbons. However, during the January 1988 sampling, the creek was frozen. The ice covering prevented loss to the atmosphere by volatilization, so the hydrocarbons were transported to the mouth of the creek. Although no samples were collected in the Gunpowder River, the low turbulence and cold water temperatures at the mouth of the creek at the time of sampling suggest that low concentrations of chlorinated aliphatic hydrocarbons may have been transported to the Gunpowder River during the time that the creek was frozen. Although chlorinated aliphatic hydrocarbons were not detected in the Gunpowder River during the study period, the presence of those compounds in Watson Creek indicates the potential for contaminant transport from the creek to the river.

The source of the chlorinated aliphatic hydrocarbons in surface water at O-Field is related to ground-water discharge of contaminants from O-Field. Chlorinated aliphatic hydrocarbons have been found in the ground water

extending from Old O-Field to the beach at Watson Creek (fig. 31).

The chlorinated aliphatic hydrocarbons detected in Watson Creek in March 1989 appear to be related to a pulse or pulses of chlorinated solvent that leached from the Old O-Field disposal area during a period when ground-water levels were higher than normal in 1987. The contaminants moved through the ground water toward Watson Creek during 1987–88 (fig. 36). The chlorinated aliphatic hydrocarbons in the creek, therefore, probably represent the arrival of the migrating ground-water contamination at the discharge area in Watson Creek. Although the extent of ground-water contamination at New O-Field is not known with certainty, the fill is old enough that, based on the ground-water velocities suggested by flow modeling efforts, contamination probably is also discharging into Watson Creek.

BOTTOM-SEDIMENT CONTAMINATION

The bottom sediment in Watson Creek contains certain constituents that appear to be related to disposal operations at O-Field, specifically arsenic, transition metals, mercury, polycyclic aromatic hydrocarbons, as well as a variety of other organic compounds. To a large extent, the areal distribution of constituents in the bottom sediment of Watson Creek potentially related to O-Field operations depends on currents, sediment type, water chemistry, proximity to the area of ground-water contamination at O-Field, and chemistry of the constituents. An understanding of these controls is necessary to evaluate the potential for offsite transport of contaminants.

Arsenic

The distribution of arsenic in the bottom sediment (fig. 41) during August 1985 closely corresponded to the observed distribution of currents (figs. 22 and 23) and bottom-sediment lithology (fig. 24) in Watson Creek. Arsenic was most concentrated in areas of typically quiescent water and organic-rich, fine-grained bottom sediment, such as along the western edge of the creek and within its tributaries. Arsenic concentrations were lowest in areas of higher current velocities and areas with a dominantly sandy bottom. An exception is an area of locally high concentrations (greater than 10 µg/g) (fig. 41) in the sandy sediment at sites 7 and 7s (fig. 2), adjacent to the area of arsenic-contaminated ground water at Old O-Field (fig. 25).

Arsenic chemistry in the bottom sediment is subject to the same controls as those discussed in the sections on ground water and surface water. In addition, bottom sediment may contain vertical chemical gradients, controlled by differing redox states. Solid phases of arsenic, copper, and

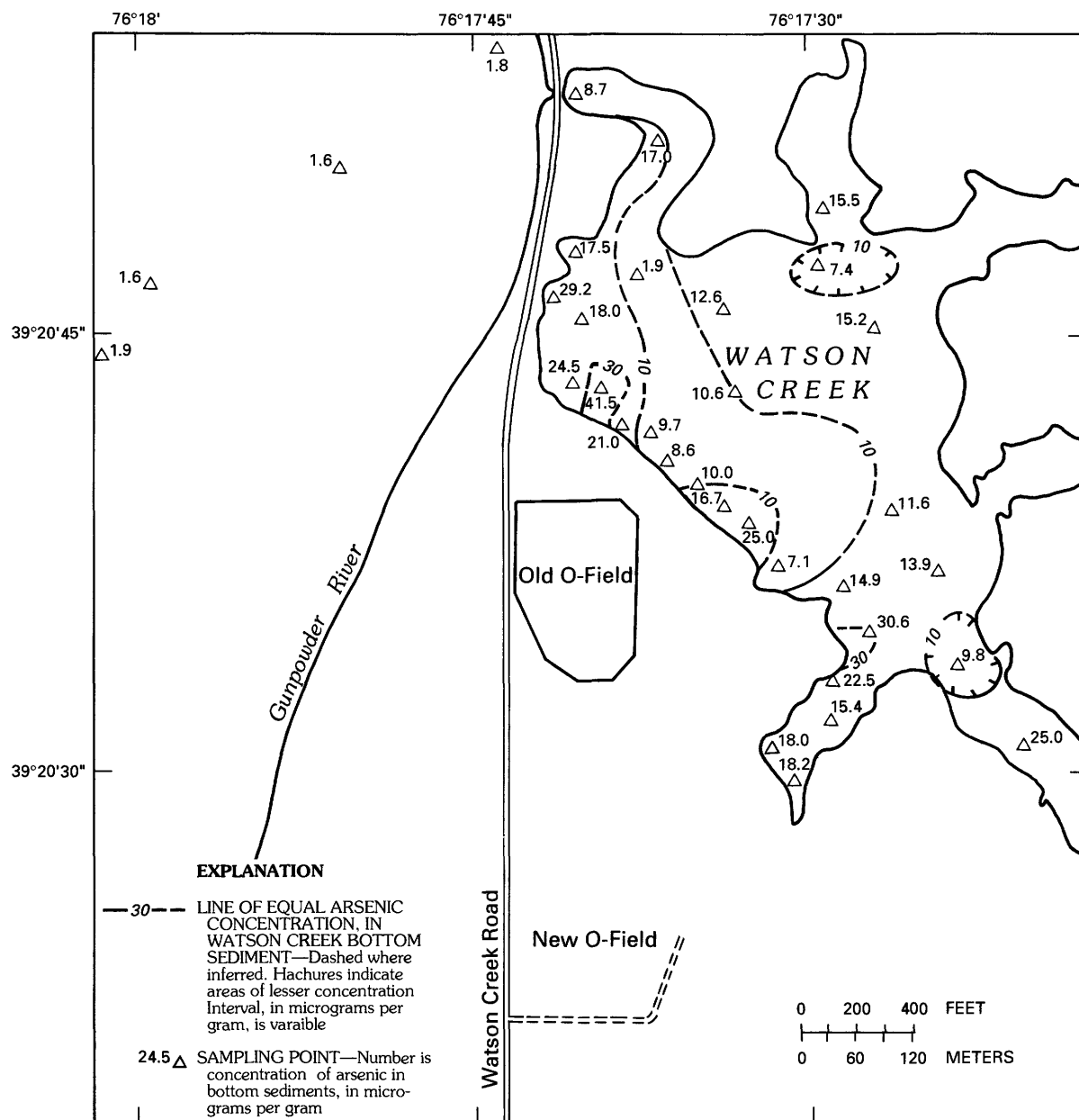


Figure 41. Distribution of arsenic in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

zinc have been shown to change from dominantly oxyhydroxide and organic phases in the more oxidized layers to sulfide phases in the more reduced layers (Moore and others, 1988, p. 435).

Both dissolved and particulate forms of arsenic are present in Watson Creek, suggesting that neither form is thermodynamically unstable enough to allow either to dominate. Thus, the sorption and desorption controls discussed for surface water may shift arsenic between dissolved and sorbed phases in the creek. The potential exists for transport of arsenic to the Gunpowder River in particulate form.

However, outgoing currents in Watson Creek are weak, so transport of particulate arsenic to the Gunpowder River probably is rare in the absence of sediment disturbance.

Arsenic in bottom sediments at O-Field may be partly derived from natural sources (Sanders, 1985). Groundwater discharge of arsenic from Old O-Field also appears to be a source, as implied by the locally elevated arsenic concentrations (16.7 and 25 $\mu\text{g/g}$) in sediment adjacent to the area of Old O-Field that contains the highest concentrations of arsenic in the ground water. A potential source for

the elevated concentrations (24.5 and 29.2 $\mu\text{g/g}$) along the western edge of the creek, adjacent to Watson Creek Road, is an, as yet, undetected plume of contamination north of Old O-Field. However, transport of contaminated sediment from elsewhere in the creek and deposition of the sediment along the western edge of the creek are recurring processes and are probably adequate to account for the distribution. Arsenic-contaminated sediment transported to the creek by rainfall runoff is an additional potential source.

Transition Metals

Transition metals are those elements of the periodic table that exhibit properties of metals and nonmetals. In this report, the term "transition metal" refers only to the elements and complexes of iron, manganese, lead, chromium, nickel, copper, zinc, and cadmium. Cadmium was the only trace metal sampled that was not found in detectable concentrations (2.0 $\mu\text{g/g}$) in the bottom sediments. Mercury usually is considered a transition metal, but is discussed separately in this paper because it is subject to different controls on solubility.

All of the transition metals present in sediment samples from surface-water bodies at O-Field were more concentrated in bottom sediments in the creek than in bottom sediments in the Gunpowder River in August 1985. Maximum concentrations detected are listed in table 8.

The distributions of bottom-sediment transition metals were similar, as represented by iron (fig. 42), manganese (fig. 43), copper (fig. 44), and chromium (fig. 45). All showed an approximate inverse relation to sediment grain size. Concentrations tended to be lower in the creek along the path of incoming tidal currents, where the sediment was sandy (fig. 24); in the inlet; in the main body of the creek; and, in general, along the Watson Creek shoreline. Concentrations were relatively higher in tributaries and at the extreme western edge of the main creek area, where the sediments consisted of fine-grained organic detritus.

Although transition metals in the bottom sediments were, in general, less concentrated along the Old O-Field shoreline than elsewhere in Watson Creek, there were also areas of locally elevated concentrations along the Old O-Field shoreline. One of these areas (bottom-sediment location 7s) was immediately downgradient from an area of iron (fig. 27) and manganese contamination in the ground water at Old O-Field in wells OF20A, OF21, OF17A, and OF6A.

Distribution maps for zinc, lead, and nickel are not shown because their distributions were similar to those of the other transition metals. They, too, were locally concentrated at bottom-sediment location 7s. Zinc concentrations were 240 to 236 mg/g at sites 7s and 7, respectively, compared with less than 50 $\mu\text{g/g}$ at adjacent sites 6s and 8. Lead concentrations at site 7s and 7 were about 30 $\mu\text{g/g}$, but

Table 8. Maximum concentrations of transition metals detected in bottom sediment in Watson Creek and the Gunpowder River, August 1985

[$\mu\text{g/g}$, micrograms per gram]

Constituent	Maximum concentration ($\mu\text{g/g}$)
Chromium	39.4
Copper	66.7
Iron	40,370
Lead	47.9
Manganese	379
Nickel	37.5
Zinc	394

were less than 11 $\mu\text{g/g}$ at adjacent sites 6s and 8. Nickel concentrations exceeded 20 $\mu\text{g/g}$ at sites 7s and 7, but were less than 10 $\mu\text{g/g}$ at sites 6s and 8.

Another area of locally high concentrations along the Old O-Field shoreline was at bottom-sediment sampling site 4s. Unlike site 7s, site 4s is located in an area where the bottom sediment is composed of fine-grained organic detritus, and so would be expected to contain relatively higher concentrations. No wells exist immediately inland from site 4s, so the relation to ground-water contamination was not evaluated.

Iron and manganese chemistry is subject to the same controls in bottom sediments as in ground water. The other transition metals are controlled mainly by reactions involving iron and manganese and exhibit a particularly strong affinity for sorption onto iron-oxide or manganese grain coatings (Jenne, 1968). Other reactions, typically less important, are complexation with organic substances, ion exchange, and chemical precipitation. Ion exchange may produce significant attenuation, but the competing effects of calcium, sodium, hydrogen, and potassium often remobilize metals on exchange sites. Chemical precipitation of trace metals is strongly pH dependent, the maximum precipitation occurring at neutral to high pH (Canter and others, 1987, p. 155). The association of transition metals with organic material, as a result of cation exchange or complexation, typically results in immobilization. However, the transition metals may be remobilized by further ion exchange or by biodegradation of the organic sorption site.

In general, reactions of transition metals tend to favor immobilization of the metal. Therefore, transition metals usually are more concentrated in sediment than in the associated water. Fine-grained sediments have a larger surface area available for sorption than do coarse-grained sediments, so higher concentrations of transition metals would be expected to be associated with fine-grained sediment than with coarser-grained sediment (Horowitz, 1984).

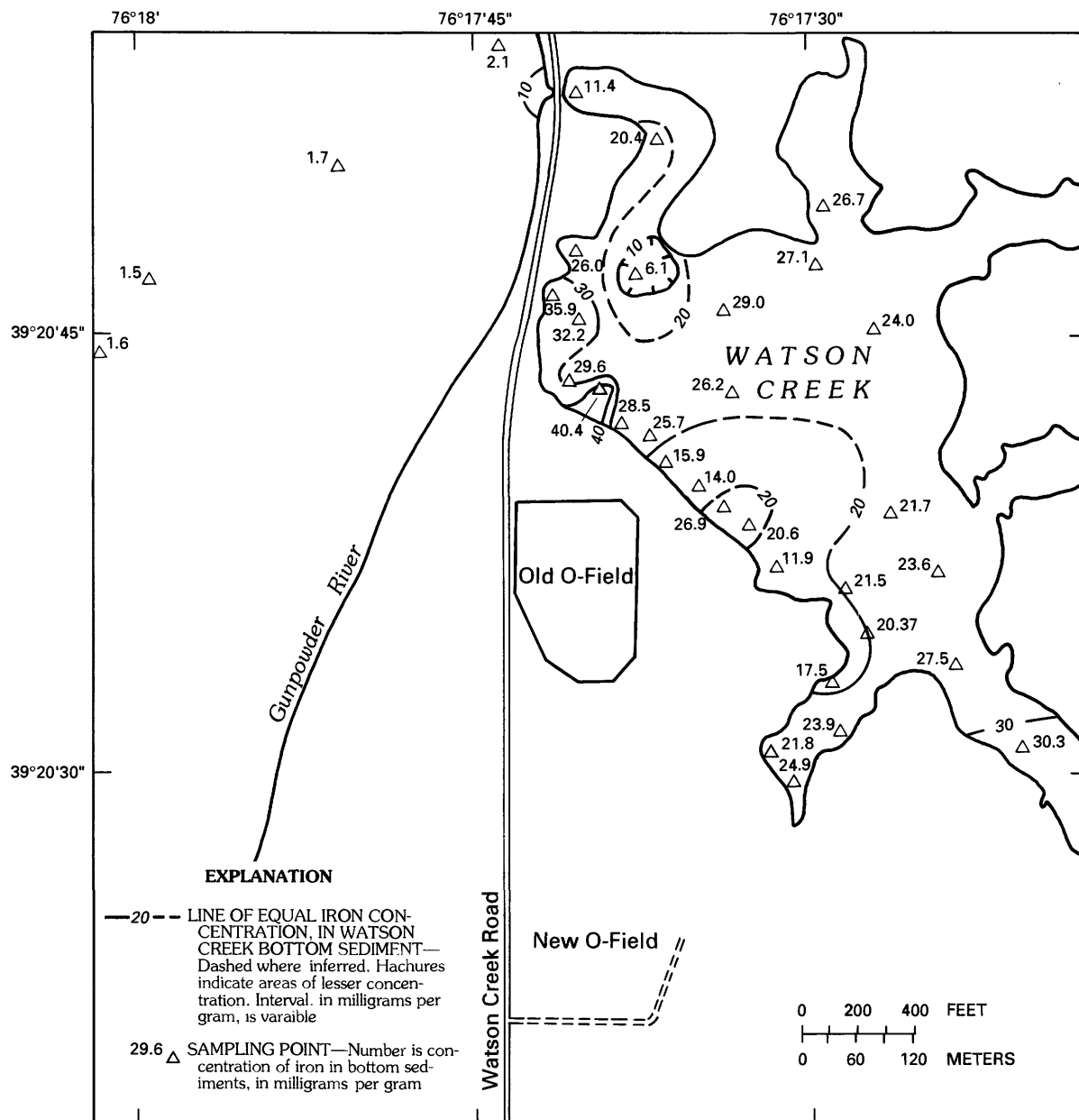


Figure 42. Distribution of iron in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

Iron is a component of the ground-water contamination. Discharge of contaminated ground water to Watson Creek moves dissolved iron into an environment of higher pH and dissolved oxygen. The higher oxygenation state of water in Watson Creek would be expected to cause iron precipitation as amorphous oxyhydroxides on grain coatings and organic particulate matter. Dissolved manganese may be transported farther because of its greater stability, before precipitating. The iron and manganese precipitates may then become sites for sorption and coprecipitation reactions involving other trace metals.

Sorption reactions involving transition metals preferentially occur on fine-grained material because of the increased surface area available for reactions. Thus, transition metals tend to become more concentrated in the sediment-size fraction most easily transported by current. Incoming tidal currents, therefore, redistribute metal-rich fine-grained sediment to eastern parts of the creek and into tributaries. Outgoing tidal currents transport this sediment westward, where it would be expected to collect in depositional areas, such as north of Old O-Field and along the western bank of the tidal inlet.

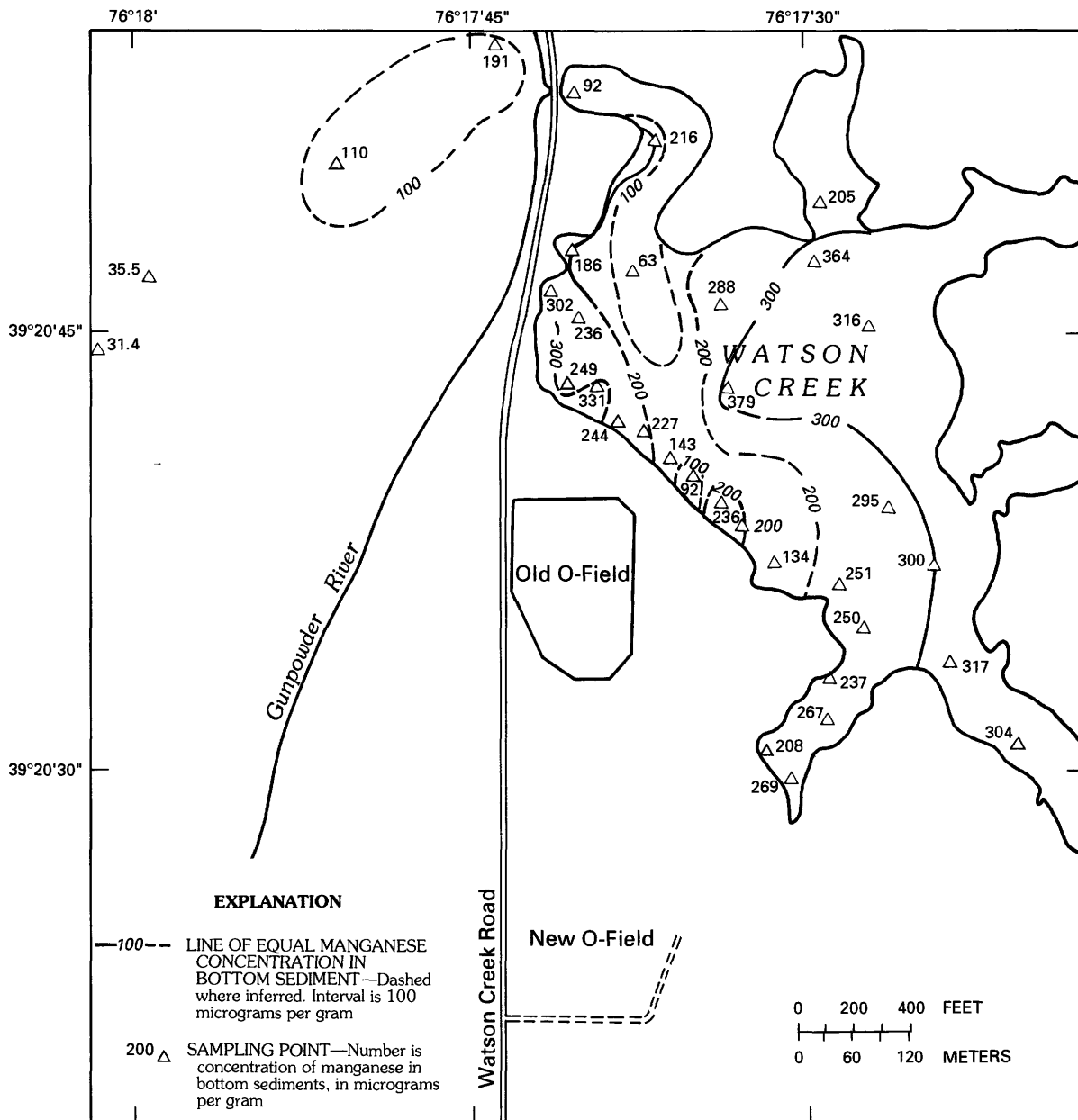


Figure 43. Distribution of manganese in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

The precipitates of iron and manganese hydroxides would be expected to scavenge transition metals from solution. Moreover, transition metals are probably redistributed by currents within the creek and shifted between dissolved and solid phases. The tendency for dissolution of solid phases would be expected to be greater during periods of lower dissolved oxygen content in the surface water, for example, during summer months. The discharge of contaminated ground water and the accompanying precipitation of iron and manganese oxyhydroxides also may scavenge transition metals already present in the creek.

Concentrations of transition metals in the tributary leading to New O-Field are, for the most part, not substantially greater than in other tributaries to Watson Creek. An exception is zinc. The highest concentration of zinc (394 $\mu\text{g/g}$) in the bottom sediment was located within the tributary, immediately offshore from New O-Field. The second highest concentration (381 $\mu\text{g/g}$), however, was in the Watson Creek inlet, not far from the mouth. Thus, unlike Old O-Field, contamination from New O-Field does not appear to have left a recognizable signature of transition metals in Watson Creek sediment.

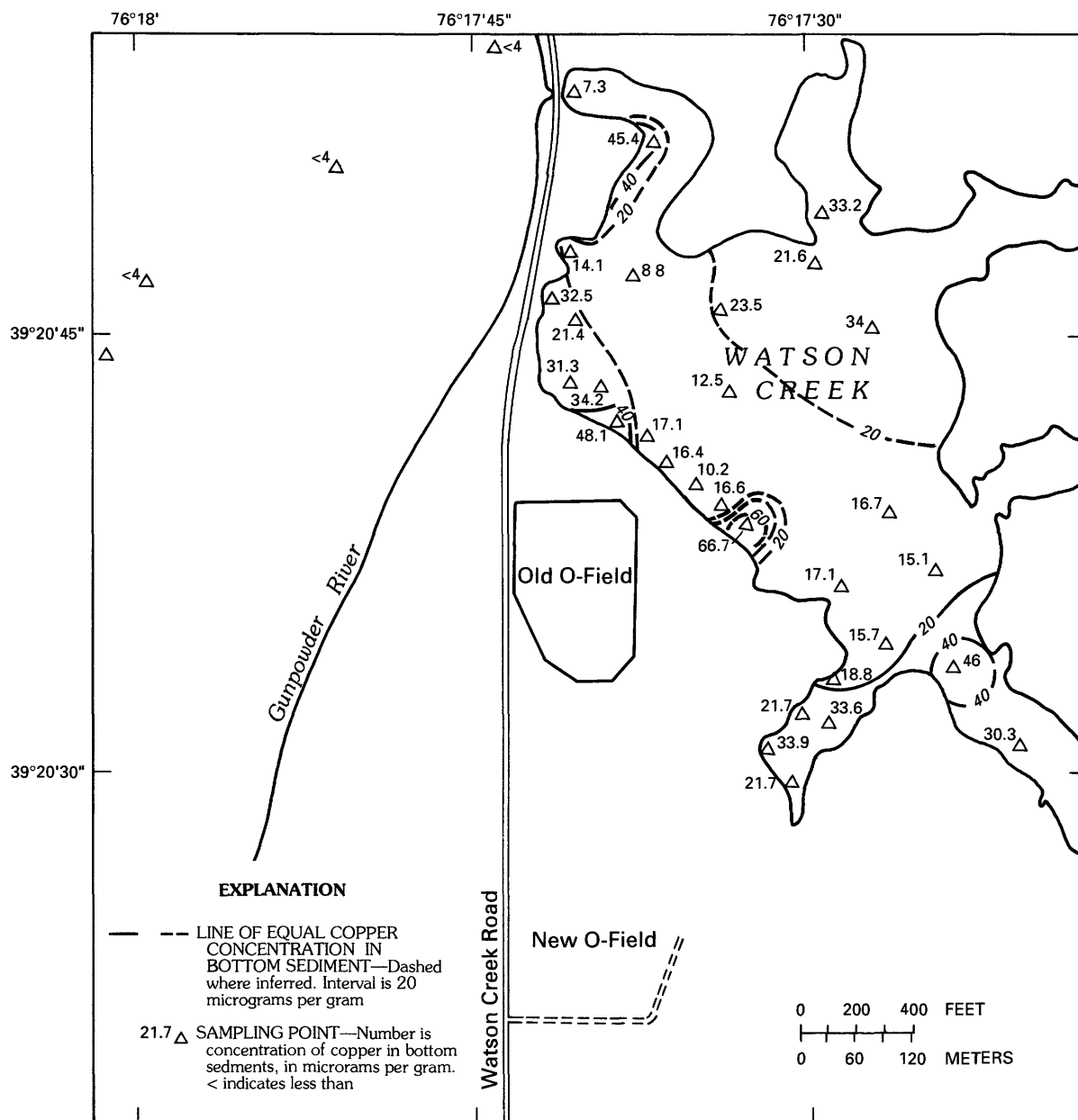


Figure 44. Distribution of copper in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

The area of locally elevated concentrations of transition metals in the bottom sediment at site 7s is of interest because it was within the zone of sandy sediment (fig. 24), where sorption onto grain coatings would be expected to be markedly less than in the finer-grained material, and to be about the same as in adjacent areas of similarly sandy material. One explanation is that site 7s is an area where transition-metal contamination had been discharged, either by overland flow or by ground-water discharge. Iron and manganese contamination in the ground water is present inland from site 7s, implying that site 7s is an area of

contaminated ground-water discharge to Watson Creek from O-Field.

Potential sources for the transition metals are residues from metal-plating operations and metal disposal at O-Field. Zinc oxide is a major component of the smoke agent HC and probably was disposed at O-Field.

The elevated concentrations of transition metals found in Watson Creek tributaries and in the northeast and western parts of the creek are associated with fine-grained organic-rich sediment. Concentrations would be expected to be naturally higher in this material than in the sandy

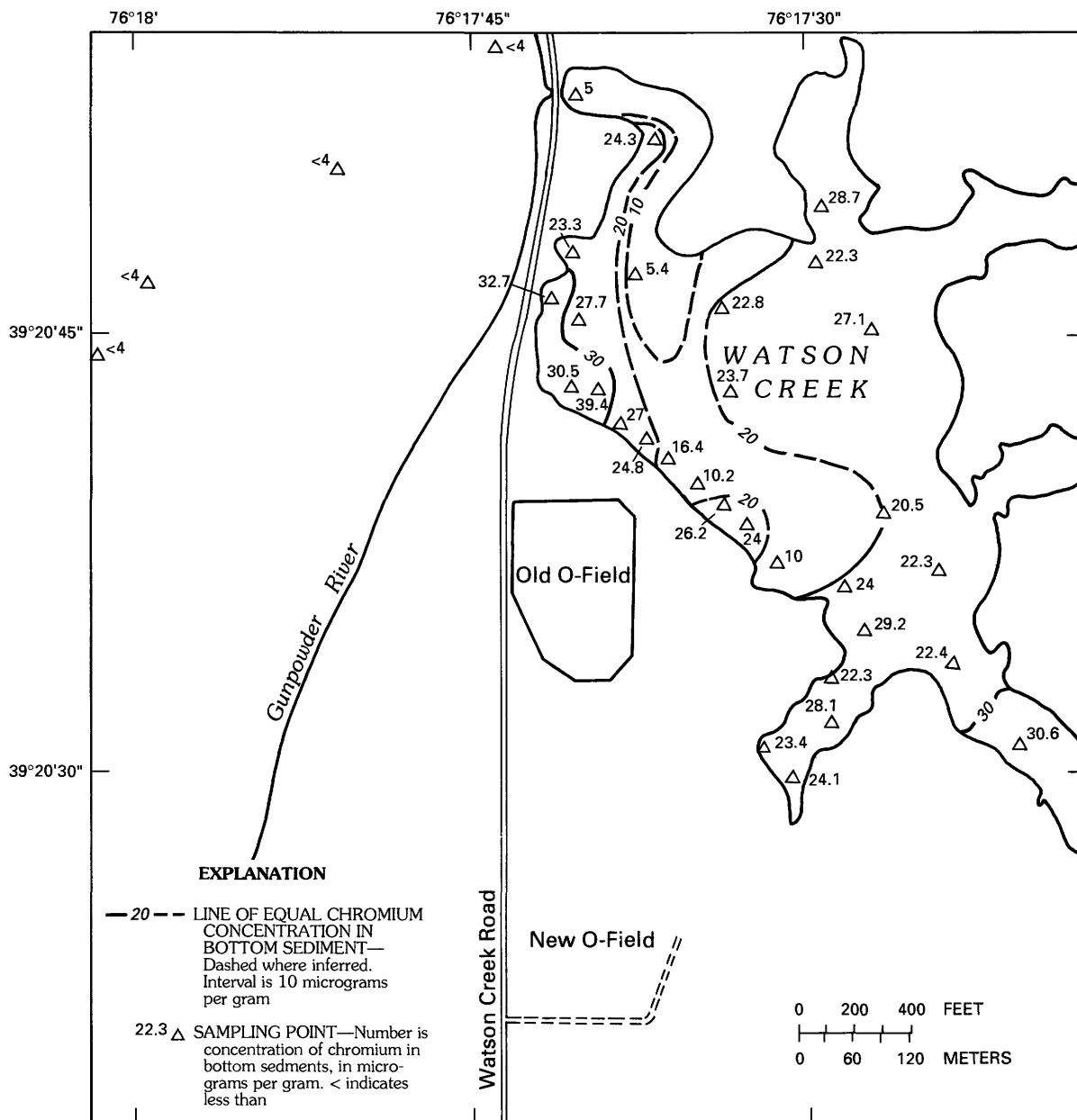


Figure 45. Distribution of chromium in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

material found along the Old O-Field shoreline. It is, therefore, uncertain whether the concentrations in that area represent naturally occurring material or current-induced redistribution of transition-metal contamination.

Mercury

Mercury (Hg) was not detectable in the bottom sediments of the Gunpowder River in August 1985. Concentrations within Watson Creek were mostly at or near detection limits (0.2 $\mu\text{g/g}$), but were higher ($>0.4 \mu\text{g/g}$) in

localized areas (fig. 46). The highest concentrations were found in the creek tributaries (0.57 $\mu\text{g/g}$) and on either side of the path of incoming tide at the area where the inlet enters the main part of the creek ($>0.8 \mu\text{g/g}$). Concentrations ranging from less than 0.2 to 0.45 $\mu\text{g/g}$ were found along the shoreline of Old O-Field. The four samples from the Gunpowder River contained less than 0.2 $\mu\text{g/g}$ of mercury.

Mercury may be present in the environment in three different oxidation states. The most oxidized form is the mercuric ion (Hg^{+2}), the most reduced form is elemental mercury, and the intermediate form is the mercurous ion (Hg_2^{+2}). Between pH 5 and 9 in a moderately oxidizing

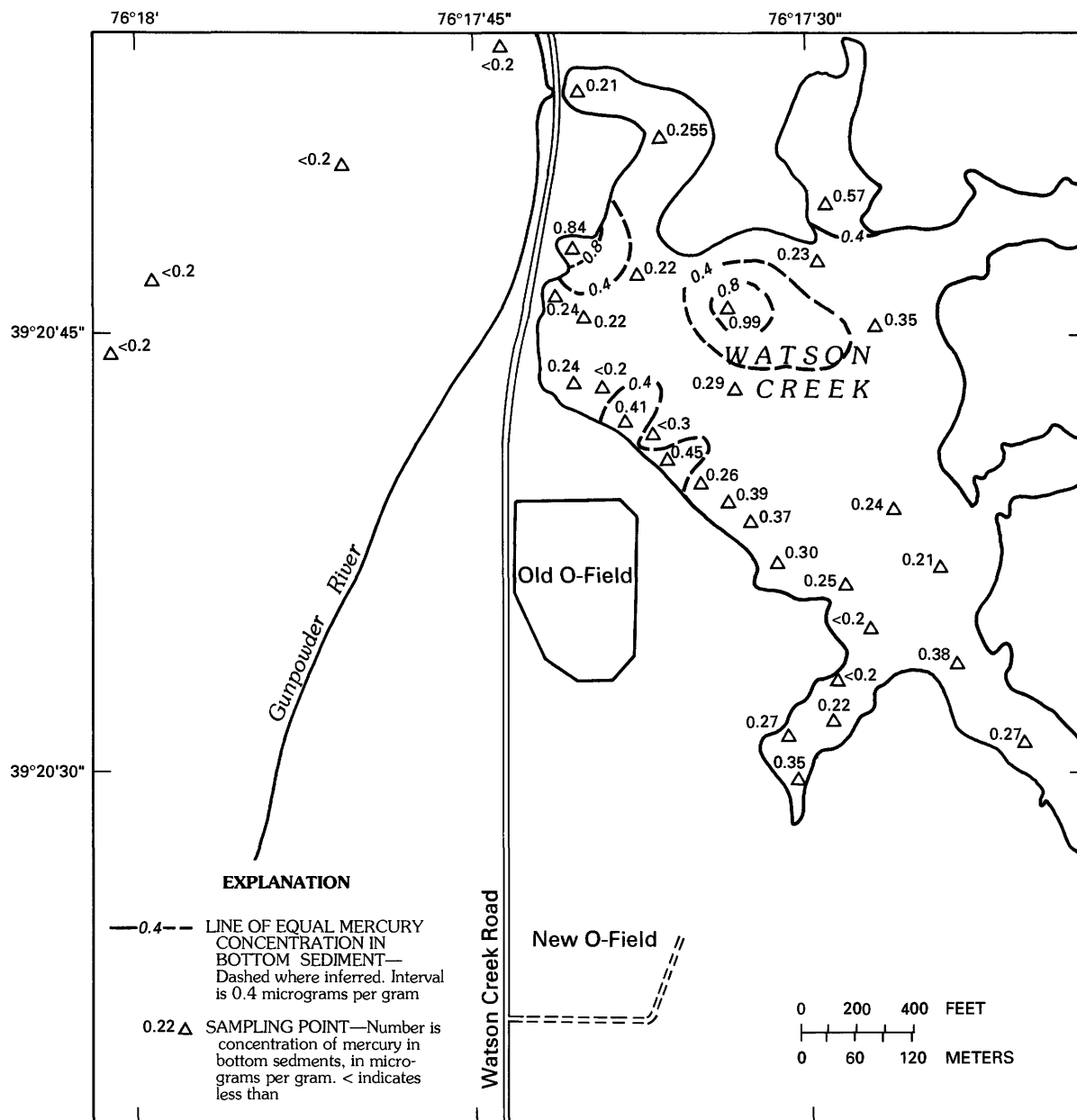


Figure 46. Distribution of mercury in bottom sediments in Watson Creek and the Gunpowder River, August 1985.

environment, mercury solubility is low (about 25 $\mu\text{g/L}$), and most of the mercury is in its elemental form (Hem, 1970, p. 21). The elemental form is a liquid at ordinary temperatures and can, to some extent, escape from surface water and sediment by volatilization. If sulfur is present under more reducing conditions, mercury may precipitate as cinnabar (HgS). The solubility of cinnabar is extremely low ($<0.002 \mu\text{g/L}$) (Hem, 1970).

The solubility of mercury increases under the more oxidizing conditions of aquatic environments rich in chlo-

ride, due to the formation of uncharged or anionic complexes with chloride. Complexes with ammonia also may enhance mercury solubility, but the occurrence of the complex is generally limited to solutions containing more than 100 mg/L of ammonia (Hem, 1970, p. 23).

The affinity of mercury for organics results in the formation of a number of methylated forms of mercury. Wood and others (1968) found that bacterial methylation of mercury typically produces dimethyl mercury as the ultimate product, but also may produce methyl mercury when

an excess of mercuric ion exists. At low pH, such as is sometimes found in the anaerobic bottom sediments of lakes, the poorly soluble dimethyl mercury dissociates to the soluble and toxic methyl mercury form (Greenson, 1970, p. 32). As methyl mercury in solution, it increases in toxicity, mobility, and availability for ingestion into aquatic life. Methylation also can enhance the volatilization of mercury (Callahan and others, 1979).

Mercury's affinity for organics also results in sorption onto sediment organic matter. The sorption appears to be relatively independent of pH (Ramamoorthy and Rust, 1976) and so dominantly controlled by organic matter that little of the sorption is associated with inorganic oxide components of the sediment (MacNaughton and James, 1974). Reimers and Krenkel (1974) found that inorganic mercury is bound strongly enough by sediments to be transported by sedimentary mobilization.

Mercury typically is not present in large amounts as dissolved species in surface water. Controls on aqueous concentrations appear to affect the tendency of mercury to be lost by volatilization to the atmosphere and to be sorbed onto reduced sediments. An additional control may be the removal of mercury from water by aquatic organisms (Hem, 1970, p. 21). Mercury sorbed onto sediments can be remobilized if the system becomes oxygenated. Mercury scavenged by aquatic organisms also can be returned to the aqueous system if the organisms die and decay.

Most of the mercury in surface water at O-Field probably is in the particulate form because of either reduction to metallic mercury, precipitation as sulfide, sorption onto inorganic and organic sorbates, complexation with particulate organics, or sorption and ingestion by aquatic life. Sulfur is present locally in the bottom sediment (32.0 $\mu\text{g/g}$ at site 4s) (fig. 2), suggesting that precipitation as mercuric sulfide could be occurring.

Offsite transport of mercury has not been documented at O-Field; however, the potential exists for offsite transport as low concentrations in dissolved form or as sediment load during storm transport. Although the solubility of mercuric sulfide is extremely low, the potential exists for bacterial processes in the sediment to oxidize the sulfide to sulfate, releasing Hg^{+2} to the water.

Mercury was a component used in prototype manufacturing of lewisite during World War II. Both liquid and solid wastes from the operation may have contained mercury. Although the wastes typically were discharged to surface-water bodies or swamps near the manufacturing areas to the north, some were probably disposed of at Old O-Field (G. Nemeth, U.S. Army Environmental Hygiene Agency, oral commun., 1988). Mercury also was used at Aberdeen Proving Ground for a short time in electrolysis cells for the production of chlorine and sodium hydroxide, but the production predated the disposal operations at O-Field.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAH's) were detected in bottom sediments during November 1984. The compounds and their concentrations were naphthalene (35.8 $\mu\text{g/kg}$ at site 6 and 34.3 $\mu\text{g/kg}$ at site 9), phenanthrene (65.1 $\mu\text{g/kg}$ at site 6 and 53.3 $\mu\text{g/kg}$ at site 9), and fluoranthene (30 $\mu\text{g/kg}$ at site 6 and 27.2 $\mu\text{g/kg}$ at site 9).

PAH's have low aqueous solubilities and high octanol-water coefficients (Karickhoff and others, 1979). They, therefore, partition onto sediments and organic matter and tend to bioaccumulate. Volatilization is not significant for PAH's, biodegradation is slow (Gardner and others, 1979), and photolytic degradation appears not to be an important fate process unless the PAH's are present in oil slicks or in shallow, low-turbidity water with a low content of dissolved organic matter (Callahan and others, 1979). Therefore, PAH's in the bottom sediment tend to be persistent contaminants.

Biodegradation of PAH's results in increased substitution of alkyl groups (Harrison and others, 1975), which increases the potential for further degradation of the substituted ring. For example, phenanthrene, a bottom-sediment PAH detected in Watson Creek, consists of three orthofused benzene rings. Substitution of OH groups on positions 3 and 4 of the rings increases the molecule solubility and allows further degradation to a dihydroxy-naphthalene. In a similar way, the dihydroxy-naphthalene further degrades to an α -hydroxy-muconic semialdehyde.

The water in Watson Creek typically contains suspended fine-grained material, so photolytic degradation probably is not an important process. The PAH's will probably biodegrade with time, but the relative lack of PAH's with alkyl groups suggests that the process will be slow, and the PAH's will be persistent in the bottom sediment. The low solubility of PAH's will prevent them from being transported offsite in solution. There is potential for offsite transport as sediment load; however, the unusually thick layer of fine-grained organic sediment in Watson Creek (U.S. Army Environmental Hygiene Agency, 1977) implies that bulk transport of sediment from distal points in Watson Creek to the Gunpowder River is not a common occurrence. Thus, transport of contaminated sediment offsite also is probably minimal.

PAH's can occur as a result of high-temperature ($>700^\circ\text{C}$) pyrolytic reactions, such as forest fires or municipal incineration, or as a result of petroleum spills. Forest fires and petroleum spills are both documented at O-Field. It is sometimes possible to differentiate between the two sources by examining the types of PAH's present. PAH's having a pyrolytic origin tend to contain a larger percentage of unsubstituted isomers (Pancirov and Brown, 1977). PAH's derived from petroleum constitute a homologous series that contains more methyl- and higher alkyl-substituted isomers than parent compounds, such as pyrene.

The lack of substituted isomers in Watson Creek sediment implies that the PAH's were derived from pyrolysis of organic matter as a result of fires. However, it also is possible that the more-soluble alkyl-substituted isomers partitioned into the aqueous phase, preferentially removing them from the sediment. Preferential bioaccumulation of higher homologs, preferential biodegradation of lower homologs, or preferential vaporization of lower homologs also may have occurred, further disrupting the isomer balance (Laflamme and Hites, 1978).

Additional Organic Constituents

A variety of other organic compounds were detected in samples of the bottom sediment of Watson Creek. Samples from November 1984 showed the presence of carbon disulfide (16 µg/kg at site 6), trichlorofluoromethane (98 µg/kg at site 6 and 53 µg/kg at site 9), 1,2-dichloroethylene (0.2 µg/kg at site 9), and di-*n*-octylphthalate (6.82 µg/kg at site 6).

Carbon disulfide is an organic solvent sometimes used in herbicides. The herbicides periodically applied to O-Field could create a potential source for carbon disulfide. An additional potential source is the breakdown of sulfur-containing munitions and chemical agents. Disulfides can be produced by reduction of thiols and thiones, some of which are products of mustard gas degradation. Carbon disulfide is moderately soluble (2,300 mg/L at 22°C) (Verschueren, 1983, p. 240), so partitioning onto the bottom sediment should be minimal.

Trichlorofluoromethane and 1,2-dichloroethylene are subject to the same types of chemical controls as other chlorinated aliphatics. Trichlorofluoromethane is comparatively soluble (1,100 mg/L at 25°C), so it probably is not strongly partitioned onto the sediment phase. Potential sources of trichlorofluoromethane are fluoride-containing nerve agents, spray cans, polyurethane foams, cleansing compounds and solvents, and fire extinguishers.

Phthalates are common laboratory contaminants. Di-*n*-octylphthalate did not show up in the method blank, although several other phthalates did. Phthalate in Watson Creek should readily sorb onto suspended sediment or bottom material. Volatilization is not a major control on phthalate chemistry, so the phthalate should remain with the sediment, probably coupled with slow biodegradation.

PROBABLE EFFECTS OF SELECTED REMEDIAL ACTIONS ON GROUND WATER

The three-dimensional, digital ground-water flow model of McDonald and Harbaugh (1984) was used to simulate steady state ground-water flow in the upper two aquifers at O-Field as an aid in evaluating the hydrologic

effects of selected remedial actions. The general approach to calibration of the model involved varying the simulated recharge and the horizontal and vertical hydraulic conductivity to produce different models, each of which incorporated essentially the same hydraulic heads observed in the study area. By keeping the model input variations within a hydrologically reasonable range of values, a series of simulations were developed that bracketed the range of values of error of the input data.

Description of Ground-Water Flow Model

The flow model (McDonald and Harbaugh, 1984) used to simulate ground-water movement in the O-Field area consisted of two layers that simulated the water-table aquifer: an underlying confining unit and the upper confined aquifer. The model was used in a quasi-three-dimensional mode—that is, lateral flow was simulated within the layers, and vertical flow was simulated between the layers. The area was divided into a block-centered rectangular grid system. Each grid block, or cell, represents a prism of aquifer material within which the hydraulic properties are assumed to be uniform. For a block-centered grid, the model calculates a head value at the center of each cell.

The model grid consists of 61 columns oriented southwest to northeast and 66 rows oriented northwest to southeast (fig. 47). The grid is variably spaced. Cell size in this model varies from 20 ft in areas of interest at O-Field to 2,375 ft at the opposite end of the grid. Changes in cell size were limited to no more than 1.5 times larger or smaller than the size of the adjacent cell.

Simulation of ground-water flow requires that the system under study be enclosed by boundaries that correspond to hydrogeologic features at which some characteristic of ground-water flow is defined. Examples of boundary conditions are specified head (of which constant head is a special case) and specified flux (of which no-flow, head-dependent flux, free-surface, and seepage-face boundaries are special cases) (Franke and others, 1984). Therefore, the grid extends beyond O-Field to H-Field and I-Field to the south (fig. 47) to coincide with identifiable hydrogeologic features for which boundary conditions could be reasonably defined. Lateral boundaries of the flow system vary and are specific to each of the two aquifers modeled.

The water-table aquifer in the modeled area is bordered at most locations by surface-water bodies that can be modeled under steady state conditions as constant heads. Ground water drains to Watson Creek in the northeastern part of the modeled area, to the Gunpowder River in the northwestern to southwestern part, to tributaries of the Bush River in the southeastern part, and to a marsh between I-Field and J-Field in the southern part (fig. 47). The surface-water bodies are simulated as constant heads of 1.5 ft, the approximate average tidal level based on several

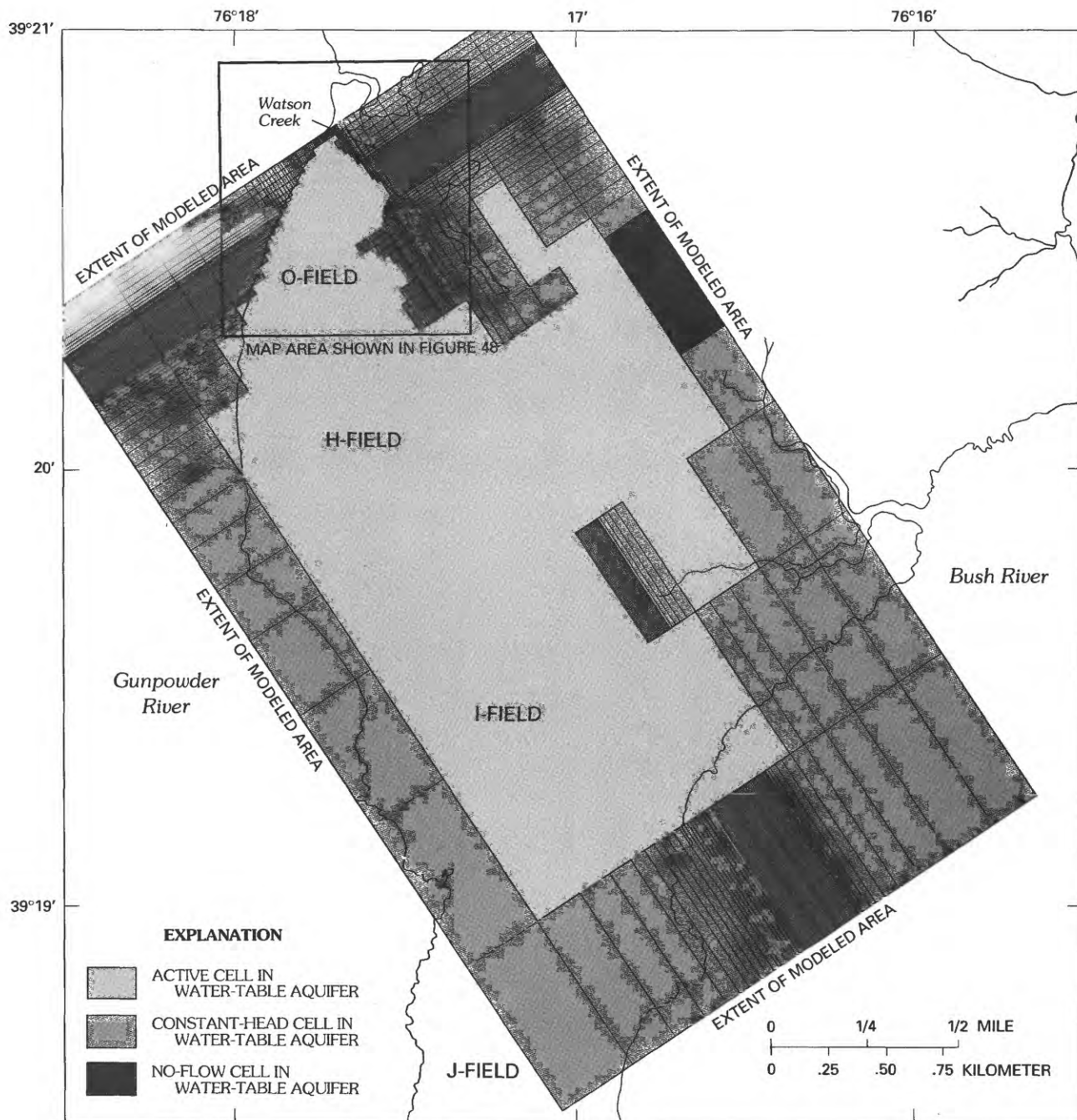


Figure 47. Finite-difference grid used for ground-water flow model and simulated model boundaries used in the water-table aquifer.

months of data from tide gages in Watson Creek and the Gunpowder River. The water-table aquifer is, therefore, bounded along most of its shoreline by constant-head cells (fig. 47).

The water-table aquifer extends beyond the modeled area at two locations. One of the locations is along the narrow strip of land between Watson Creek and the Gunpowder River (fig. 48), near the inlet to Watson Creek.

However, at this edge of the modeled area, ground-water flow is parallel to the model boundary because of tidally induced movement of ground water between the Gunpowder River and Watson Creek. The northern edge of the model between the Gunpowder River and Watson Creek is, therefore, simulated as a no-flow boundary (fig. 48). The other area where the water table extends beyond the modeled area is the eastern side of H-Field (fig. 47), where

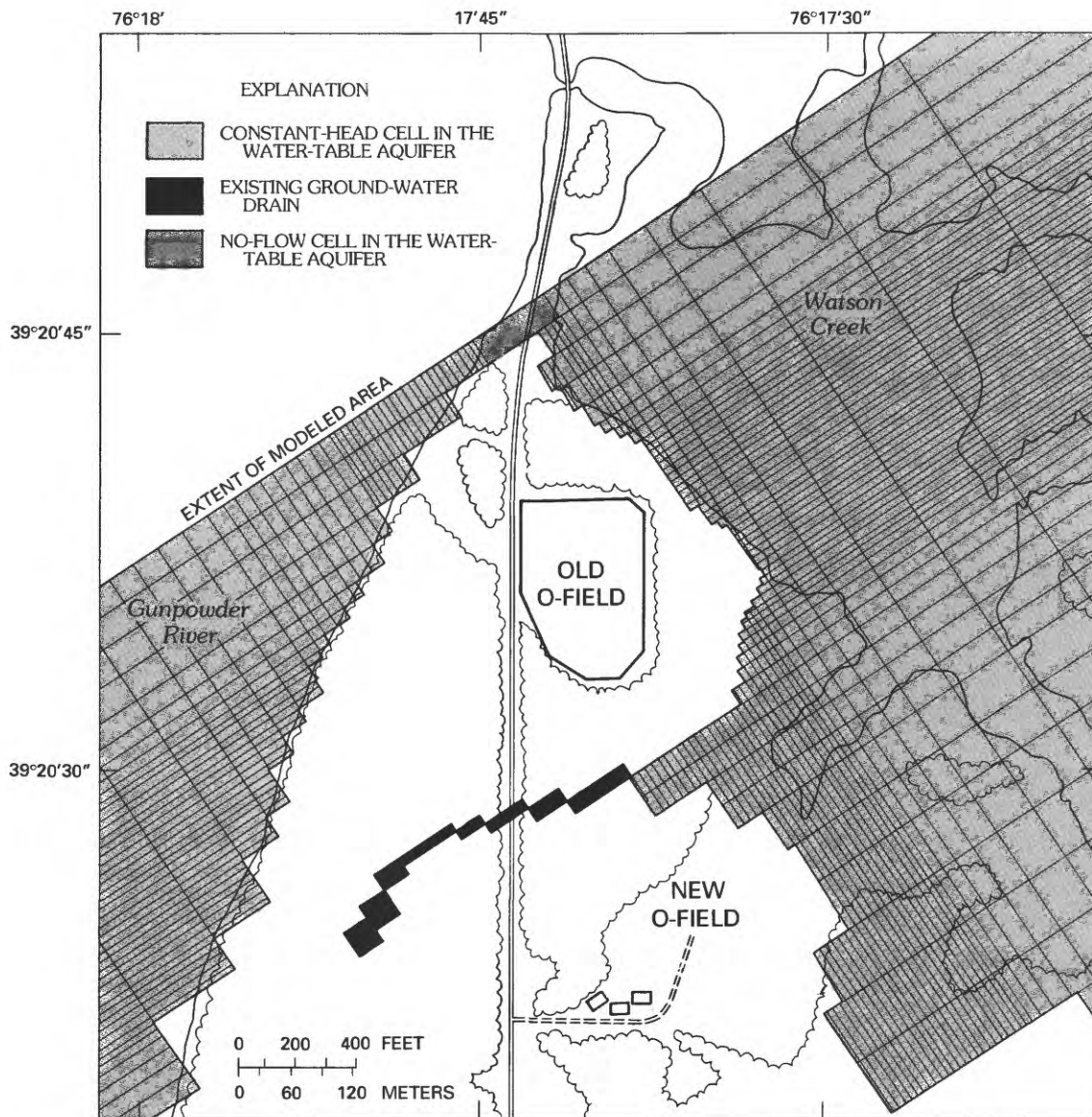


Figure 48. Finite-difference grid superimposed on O-Field.

ground water drains to tributaries of Watson Creek in the north and to tributaries of the Chesapeake Bay to the south. The landmass of H-Field trends to the east and then northeast, narrowing to approximately 1,500 ft wide (fig. 47). The northeastern boundary of the model was chosen at the narrowest part. At that point, ground water is almost certainly flowing to surface-water bodies in the northwest and southeast and flowing parallel to the model boundary, so a no-flow boundary was used. The no-flow boundary condition remained valid during simulation of remedial scenarios (water-level changes did not occur at the boundary).

An intermittent stream (fig. 2) between Old O-Field and New O-Field acts as an area of ground-water discharge for the water-table aquifer during periods of high ground-water levels. Throughout much of the year, the stream is dry. The stream is simulated in the model as a drain (fig. 48) that can act as a zone of ground-water discharge when water levels are above the base of the drain. When water levels fall below the base of the drain, vertical leakage through the drain ceases.

The upper boundary of the O-Field modeled area is the top of the water table, simulated as a free-surface boundary (water levels are free to fluctuate). The lower

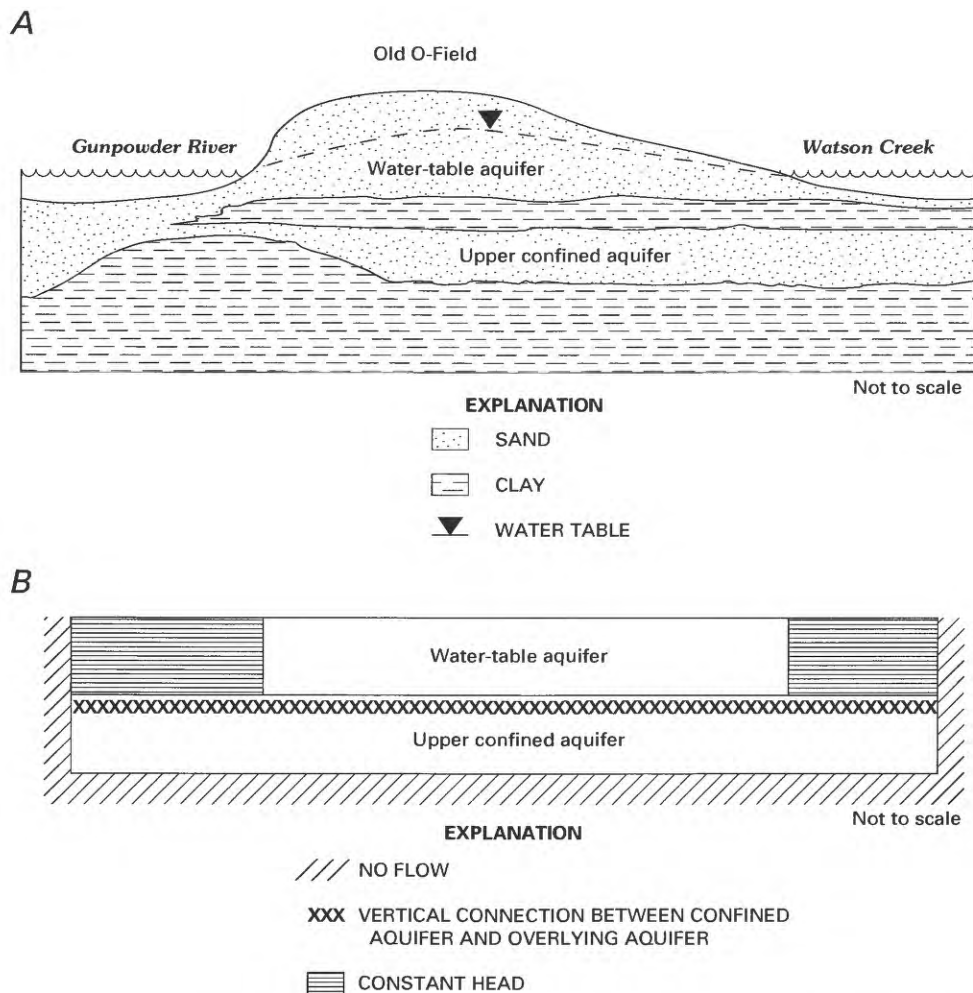


Figure 49. (A) Generalized hydrogeologic section and (B) schematic representation of model layers and boundaries.

boundary of the modeled area coincides with the top of a 50-ft-thick layer of dense clay below the upper confined aquifer. The low permeability and continuity of the clay justify its use as a no-flow boundary for the purposes of this report.

The upper confined aquifer is bounded on the top by a confining unit (fig. 49), separating it from the water-table aquifer and from surface-water bodies. Leakage through the confining unit is controlled by its vertical hydraulic conductivity (fig. 50), simulated as 2×10^{-4} ft/d over most of the modeled area, based on typical values for clay (Freeze and Cherry, 1979) and on model calibration. Somewhat higher values were used in the vicinity of well OF22 (2×10^{-3} ft/d), where borehole data indicate that the confining unit probably is leakier, and within parts of Old O-Field (2×10^{-2} ft/d) where the confining unit is leaky or absent.

The confining unit between the two aquifers is probably at a depth of about 10 ft below the bottom of Watson Creek (fig. 4). The probable low potential for

Watson Creek to have extensively eroded the creek bed implies that the upper confined aquifer is at least partially confined beneath Watson Creek (fig. 49). The aquifer was, therefore, modeled as confined beneath the creek and extending across the creek. In the Gunpowder River, the Bush River, and the Chesapeake Bay, extensive reworking of sediment probably removed the confining unit and left relatively permeable material in its place (fig. 49). Therefore, a relatively low value for vertical hydraulic conductivity (1×10^{-3} ft/d) was assigned to the confining unit below Watson Creek, and a high value (2×10^2 ft/d) representative of a typical sand (Freeze and Cherry, 1979, p. 29) was assigned to the confining unit below the Gunpowder River, the Bush River, and the Chesapeake Bay.

The lateral boundaries in the simulation of the upper confined aquifer were assumed to coincide with the edge of the model grid and were specified as no-flow boundaries (fig. 51). The relatively high value for vertical hydraulic

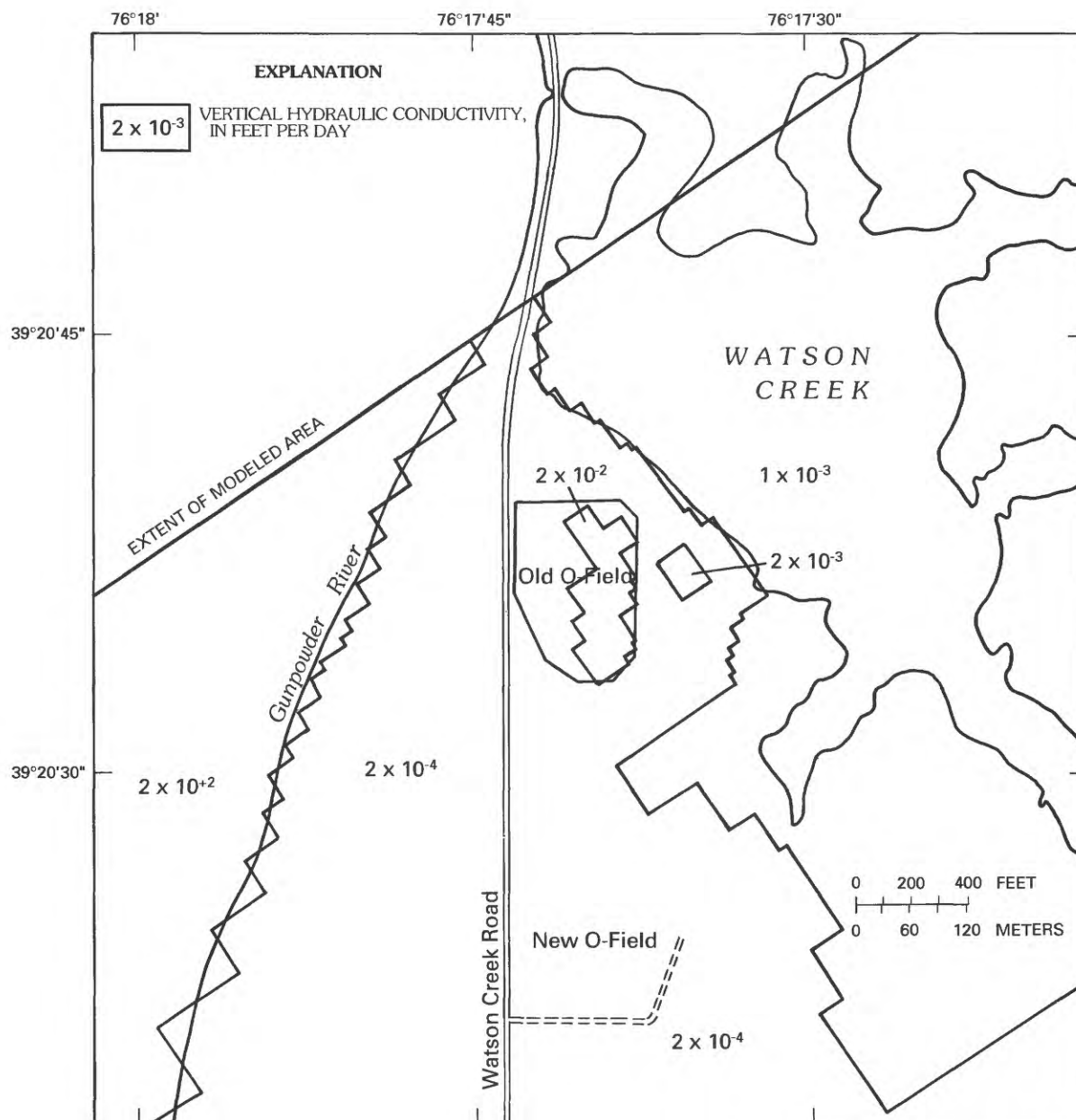


Figure 50. Distribution of vertical hydraulic conductivity in the confining unit separating the water-table aquifer from the upper confined aquifer used in model simulations. (Number is value in feet per day.)

conductivity of the overlying confining unit in areas beneath the Gunpowder River, the Bush River, and the Chesapeake Bay allowed the heads in the upper confined aquifer at those cells to closely approximate the overlying constant head and to be relatively unaffected by water-level changes in other parts of the aquifer. The Gunpowder River, the Bush River, and the Chesapeake Bay, therefore, are effectively the lateral boundaries for the upper confined aquifer.

The lateral boundary of the upper confined aquifer east of H-Field (fig. 47) is a no-flow boundary placed sufficiently far from O-Field to have negligible effects on

simulations within the O-Field area. The lateral boundary for the upper confined aquifer north of Old O-Field is based on the geologic data from well OF4 (fig. 48), located near the Watson Creek inlet. The log of the well (Nemeth and others, 1983, p. PA-6) shows the presence of clayey sand and sand-clay mixtures at the same horizon as the upper confined aquifer, indicating that the aquifer is absent at well OF4. No information is available on the horizontal extent of the less permeable material at well OF4. However, the material is located within a major linear paleochannel that trends northeast-southwest. Sedimentary facies within the

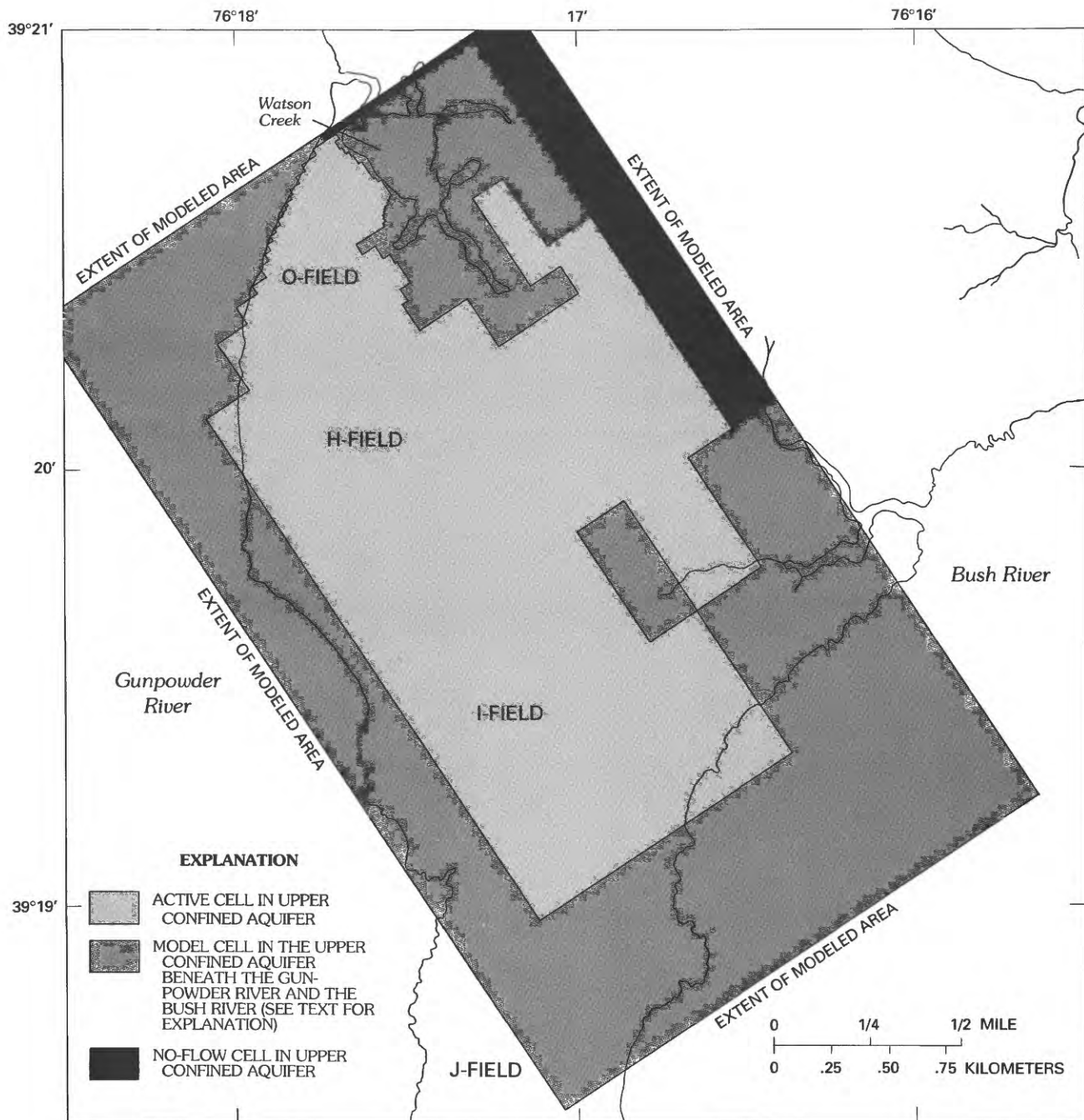


Figure 51. Boundaries of simulated ground-water flow model used in the upper confined aquifer.

paleochannel should have more or less the same trend as the paleochannel, as evidenced by the southwestward-trending linear body of black clay within the confining unit underlying the upper confined aquifer. It is reasonable to expect the same trend for the poorly permeable material at well OF4. The boundary for the upper confined aquifer is, therefore, considered to be between Old O-Field and well OF4 and to trend northeast-southwest. It is simulated as a row of no-flow cells.

Stresses on System

Recharge to the water-table aquifer at O-Field is primarily from vertical infiltration of rainfall within the O-Field area. Typical values for rainfall in areas near O-Field are about 39 to 47 inches per year (in/yr) (U.S. Department of Commerce, 1964). Most of the rainfall is lost as runoff, trapped in the soil zone, or used by plants, so only part is captured as ground-water recharge. Johnston

(1977) estimated that the rate of ground-water recharge in central and southern Delaware is about 13.5 in/yr. The similarity of O-Field to Delaware with respect to geology, climate, topography, and vegetation suggests that the value also is applicable to ground-water recharge at O-Field. Therefore, 13.5 in/yr was used in the O-Field flow model to simulate average annual recharge into sandy soil zones.

In much of the O-Field area, the soil zone is clayey. In those areas, however, head changes in the water-table aquifer in response to rainfall indicate that recharge does occur, although somewhat less than in the sandy areas. Thus, a recharge value (12 in/yr) slightly lower than the simulated average annual recharge (13.5 in/yr) was used to simulate recharge in areas where the soil zone is clayey.

O-Field is separated from the nearest areas of major ground-water use by the Gunpowder River, which acts as a hydrologic boundary. The nearest pumped well is at H-Field, approximately 0.5 mi south of O-Field. The H-Field well is screened in an aquifer deeper than those considered in the model and is pumped only for short periods to wash vehicles. Therefore, the effects of pumpage by the well were not addressed in this model.

Discharge of ground water from the modeled area is by flow to adjacent surface-water bodies and by evapotranspiration to the atmosphere. Evapotranspiration is included in the source term as a net loss of recharge on the basis of the work of Johnston (1977, p. 17).

Calibration

Preliminary calibration of the steady state ground-water flow model was achieved by setting the average annual recharge at a constant value and adjusting the model coefficients, primarily horizontal hydraulic conductivity of the water-table aquifer, within a reasonable range of values. Adjustments of input data were made until simulated heads acceptably matched the average annual heads observed over a 2-year period by synoptic manual measurements and continuous water-level recorders. A match was considered acceptable if the simulated and average annual heads agreed within about 0.5 ft. Average annual heads were determined for September 1, 1986, to September 1, 1987, and for March 1, 1986, to March 1, 1987. The heads used for calibration were the average of these two periods. Once an acceptable match between simulated and average annual heads was obtained, the model was considered to be a reasonable approximation of the ground-water system.

In the second part of the model calibration, the model was adjusted to simulate a period of elevated ground-water levels, as represented by the water levels measured on April 22, 1986. Hydrographs (figs. 10, 11, and 17) show that ground-water levels rose rapidly between about November 1986 and January 1987. Although minor fluctuations in water levels continued to occur thereafter, the approximate average water levels remained fairly constant until late

April 1987, before declining. The general stability in water levels between about mid-January to late April 1987 implies that the period was one of more or less steady state conditions and can be represented by the April 1987 data. The April 1986 data were used for the model simulations because more wells were available in 1986 and because the similarity in water levels between the April 1986 and April 1987 data implies that the steady state assumption is also valid for the period represented by April 1986.

For the second part of the calibration, the two parameters held constant were the horizontal hydraulic conductivity of the water-table aquifer and the horizontal transmissivity in the upper confined aquifer obtained from the average annual head calibration. Recharge was then uniformly increased until the simulated heads acceptably matched heads measured on April 22, 1986, a period of relatively high ground-water levels. Horizontal hydraulic conductivity and transmissivity were then adjusted slightly to obtain an improved match. The new values were incorporated into the original model to ensure that the changes did not produce major disagreements between measured average annual heads and simulated heads. The model was considered calibrated when horizontal hydraulic conductivity and transmissivity distributions were obtained that provided an acceptable match (within about 0.5 ft) to measured heads under average annual conditions (figs. 52 and 53) and during a period of elevated water levels (figs. 54 and 55) (represented by April 22, 1986, data).

The solution obtained by the above methods does not constitute a unique combination of reasonable model inputs. Several alternative solutions to the steady state model were generated by varying both recharge and horizontal hydraulic conductivity by the same factor. The range of solutions considered to be within acceptable limits was defined by recharge estimates and by field measurements of horizontal hydraulic conductivity using slug tests. Although the amount of recharge used in the model probably is a good approximation, uncertainty in the actual value implied that actual recharge may have been as much as 16 in/yr or as little as 9 in/yr during the timeframe over which the simulated heads were measured. Therefore, recharge was increased to 16 in/yr, and horizontal hydraulic conductivity was uniformly increased by the same percentage. The resulting head configurations still closely matched measured heads, so the new recharge/hydraulic-conductivity relation was considered to bracket the range of error on the high-flow end of the solution series. A similar approach was used to provide an error bracket on the low-flow end of the solution series by changing recharge to 9 in/yr and adjusting horizontal hydraulic conductivity accordingly. The error brackets enclosed the range of solutions considered acceptable during simulations of remedial actions.

The horizontal hydraulic conductivity used for model simulation is close to that obtained by slug tests at O-Field. The highest field-determined horizontal hydraulic conduc-

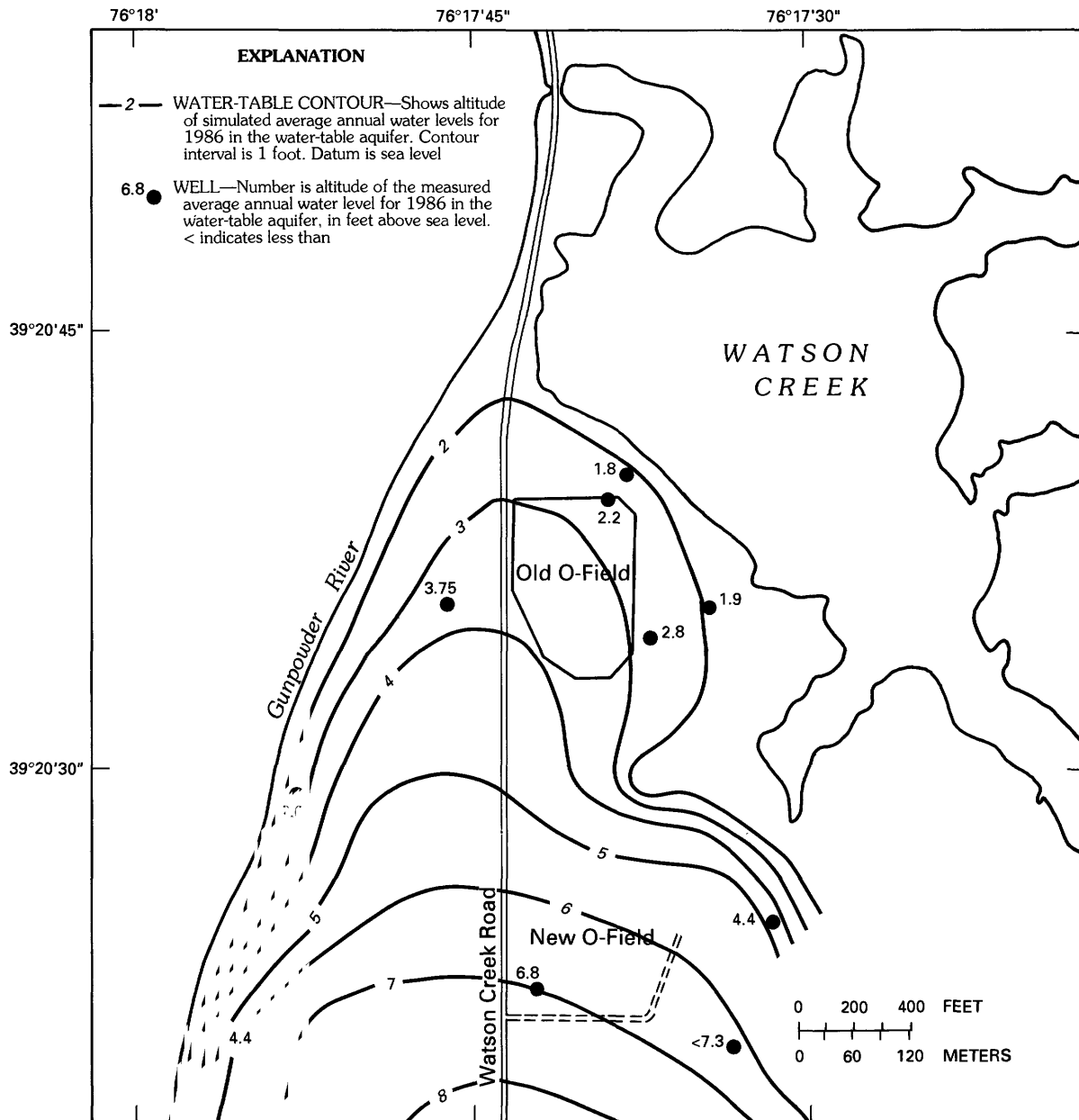


Figure 52. Relation of simulated to measured average annual heads in the water-table aquifer, 1986.

tivities (63–202 ft/d based on data from five wells) (table 3) were in the water-table aquifer in an area about 75 ft east of Old O-Field and extending eastward to Watson Creek. The area is simulated in the model using a horizontal hydraulic conductivity of 110 ft/d. Elsewhere in the water-table aquifer, field-determined horizontal hydraulic conductivities were less than 0.1 ft/d (based on nine wells tested). The low values are probably due partly to the inability of the well-development techniques to adequately remove the fine-grained sediment, which was introduced during well drilling, from the screened interval. Low values of measured horizontal hydraulic conductivity, however, generally

tend to be in areas where the sand is finer grained than that in the area east of Old O-Field, where higher hydraulic conductivities were obtained. Therefore, the remaining modeled area of the water-table aquifer was simulated using lower horizontal hydraulic conductivities (5–75 ft/d) (fig. 56).

Discharge to Watson Creek, and recharge from the creek to the aquifer, are controlled by a row of relatively low values of horizontal hydraulic conductivity bordering the creek, representing the stream-bottom sediment. Discharge to the Gunpowder River and the Chesapeake Bay in most places is through a clean beach sand, so in most areas,

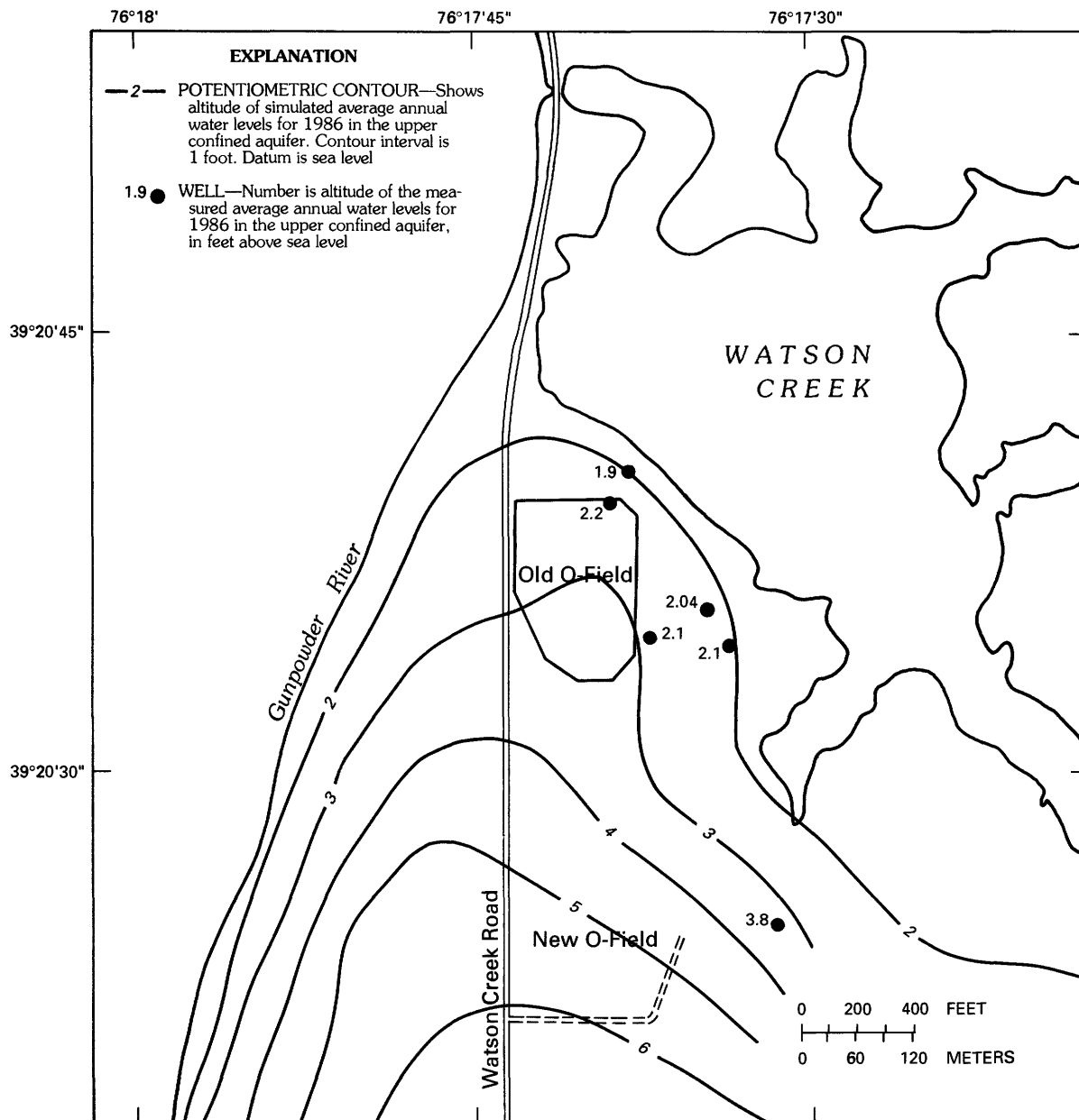


Figure 53. Relation of simulated to measured average annual heads in the upper confined aquifer, 1986.

higher values of horizontal hydraulic conductivity were used to represent water movement between the water-table aquifer and the river and bay. The average annual velocity of ground water in the water-table aquifer derived from the model using a porosity of 0.3 percent was about 255 ft/yr in the area of ground-water contamination between the eastern side of Old O-Field and Watson Creek.

The horizontal hydraulic conductivities derived by slug test in the upper confined aquifer ranged from 18 to 63 ft/d (table 3). Direct conversion to transmissivity produces values of about 180 to 600 ft²/d; however, the derived conductivities are only valid for the screened interval,

which typically was installed in the coarse-grained material. Therefore, the transmissivities estimated from slug-test data are probably higher than actual values. Most areas of the upper confined aquifer were simulated using transmissivities from 110 to 300 ft²/d; 600 ft²/d was assigned to the aquifer beneath the Gunpowder River and the Chesapeake Bay; and 40 ft²/d was assigned to a small area southwest of O-Field, where the aquifer thins considerably (fig. 57).

Sensitivity

The flow model was calibrated to conditions of average annual recharge and rerun under differing values of

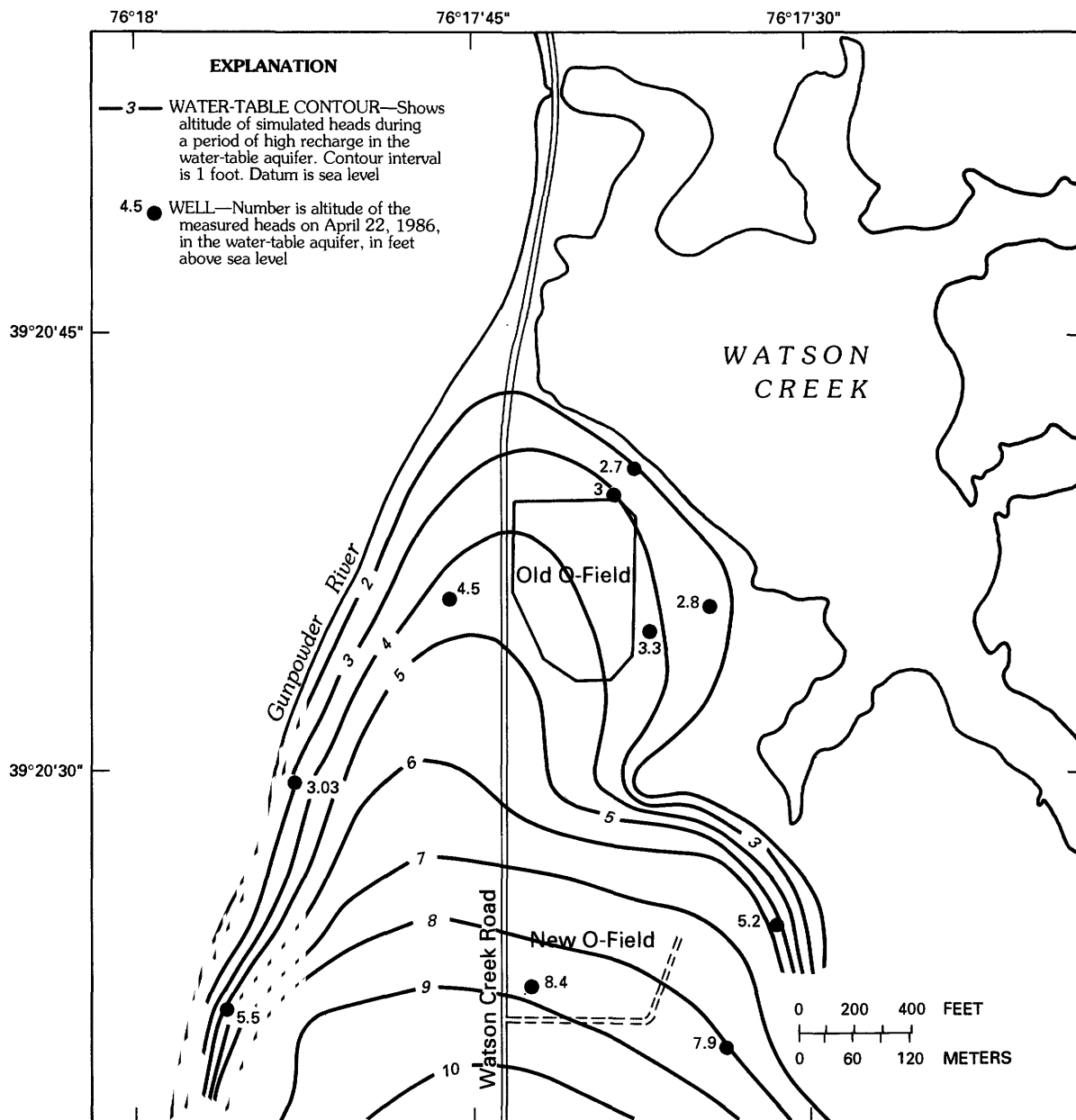


Figure 54. Relation of simulated heads during a period of elevated recharge to heads measured on April 22, 1986, in the water-table aquifer.

recharge, vertical hydraulic conductivity of the confining unit, horizontal hydraulic conductivity of the water-table aquifer, and transmissivity of the upper confined aquifer to determine the sensitivity of the model to those inputs. The analysis showed that heads in the water-table aquifer are relatively unaffected by increases of 10 times the calibrated values or decreases of 0.01 times the calibrated values in vertical hydraulic conductivity of the confining unit. Changes in transmissivity of the upper confined aquifer of 0.1 to 5 times the calibrated values also have little effect on water-table aquifer heads. The effects of changes in vertical

hydraulic conductivity and transmissivity on water levels are more pronounced in the upper confined aquifer than in the water-table aquifer.

Simulated water levels in both aquifers, however, are sensitive to changes in horizontal hydraulic conductivity and recharge in the water-table aquifer. Decreasing water-table hydraulic conductivity by an order of magnitude increased water-table heads by 6 ft at Old O-Field, 10 ft at New O-Field, and 29 ft near the center of the modeled area. Water levels in the upper confined aquifer responded similarly, rising 3 ft at Old O-Field, 8 ft at New O-Field,

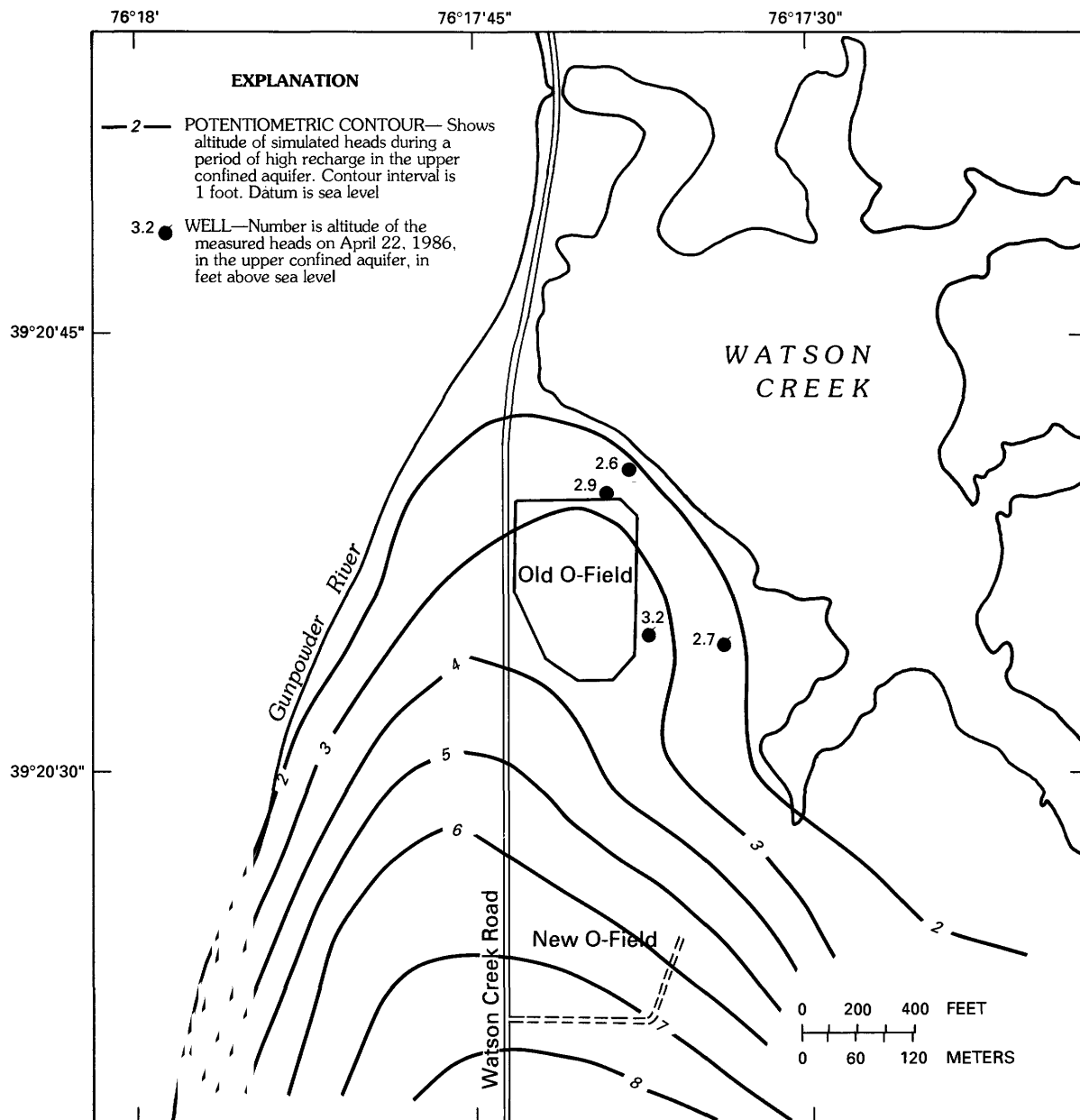


Figure 55. Relation of simulated heads during a period of elevated recharge to heads measured on April 22, 1986, in the upper confined aquifer.

and 27 ft near the model center. Increasing horizontal hydraulic conductivity by a factor of 10 resulted in water-table drawdowns of 2 ft at Old O-Field, 4 ft at New O-Field, and 9 ft near the center of the model. The change decreased water levels in the upper confined aquifer by 1.6 ft at Old O-Field, 3 ft at New O-Field, and 8 ft near the model center.

Decreasing recharge by an order of magnitude produced approximately the same results as those obtained from increasing hydraulic conductivity by an order of magnitude. Increasing recharge by 3.5 in/yr increased heads

in the water-table aquifer by approximately 1 ft at Old O-Field and 2 ft at New O-Field. Simulated water levels in the upper confined aquifer increased about 0.5 ft at Old O-Field and 1 ft at New O-Field. The analyses indicate that the model is most sensitive to increases in recharge and least sensitive to changes in vertical hydraulic conductivity of the confining unit and transmissivity of the upper confined aquifer.

The lower boundary of the model was also tested to determine model sensitivity. Simulations of a three-layer system, which included the lower confined aquifer,

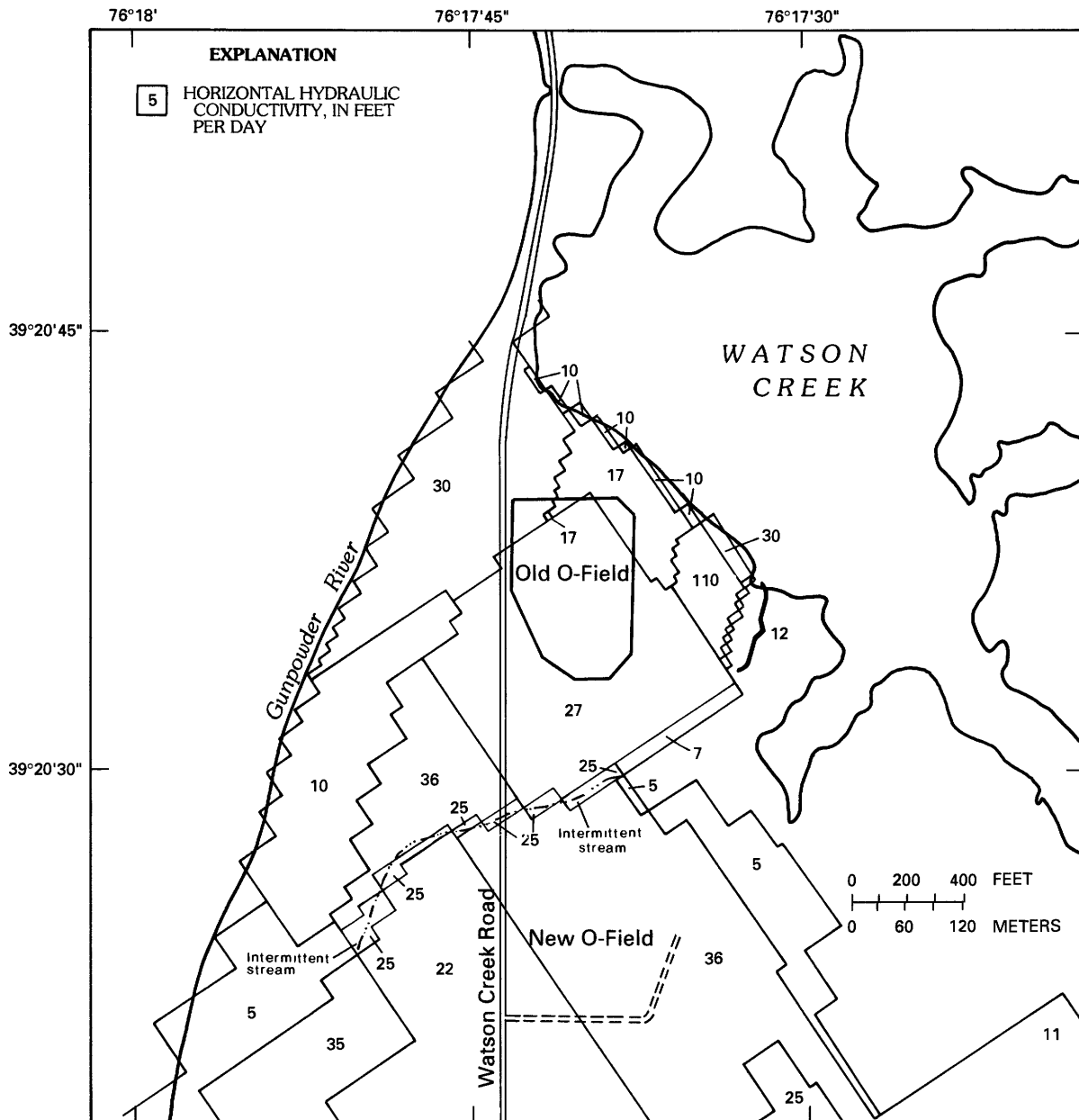


Figure 56. Distribution of horizontal hydraulic conductivity used in the model for the water-table aquifer. (Number is value in feet per day.)

demonstrated that head changes in the lower confined aquifer produced negligible change in water level in the upper confined aquifer. Thus, simulation of the ground-water system as a two-layer system is considered adequate to represent O-Field hydrology.

Remedial Actions

The three-dimensional digital flow model of the area developed using the computer code of McDonald and Harbaugh (1984) was used to evaluate the hydrologic

effects of selected remedial actions at O-Field. The remedial actions examined were (1) installation of an impermeable cap, (2) installation of subsurface barriers, (3) installation of a ground-water drain, (4) ground-water pumping to control water levels, (5) ground-water pumping to recover contaminants, (6) excavation and removal, and (7) no action. The locations of simulated caps, subsurface barriers, the ground-water drain, and wells are shown in figure 58.

The remedial actions were evaluated primarily on the basis of their ability to lower ground-water levels within the disposal areas and to limit lateral or vertical movement of

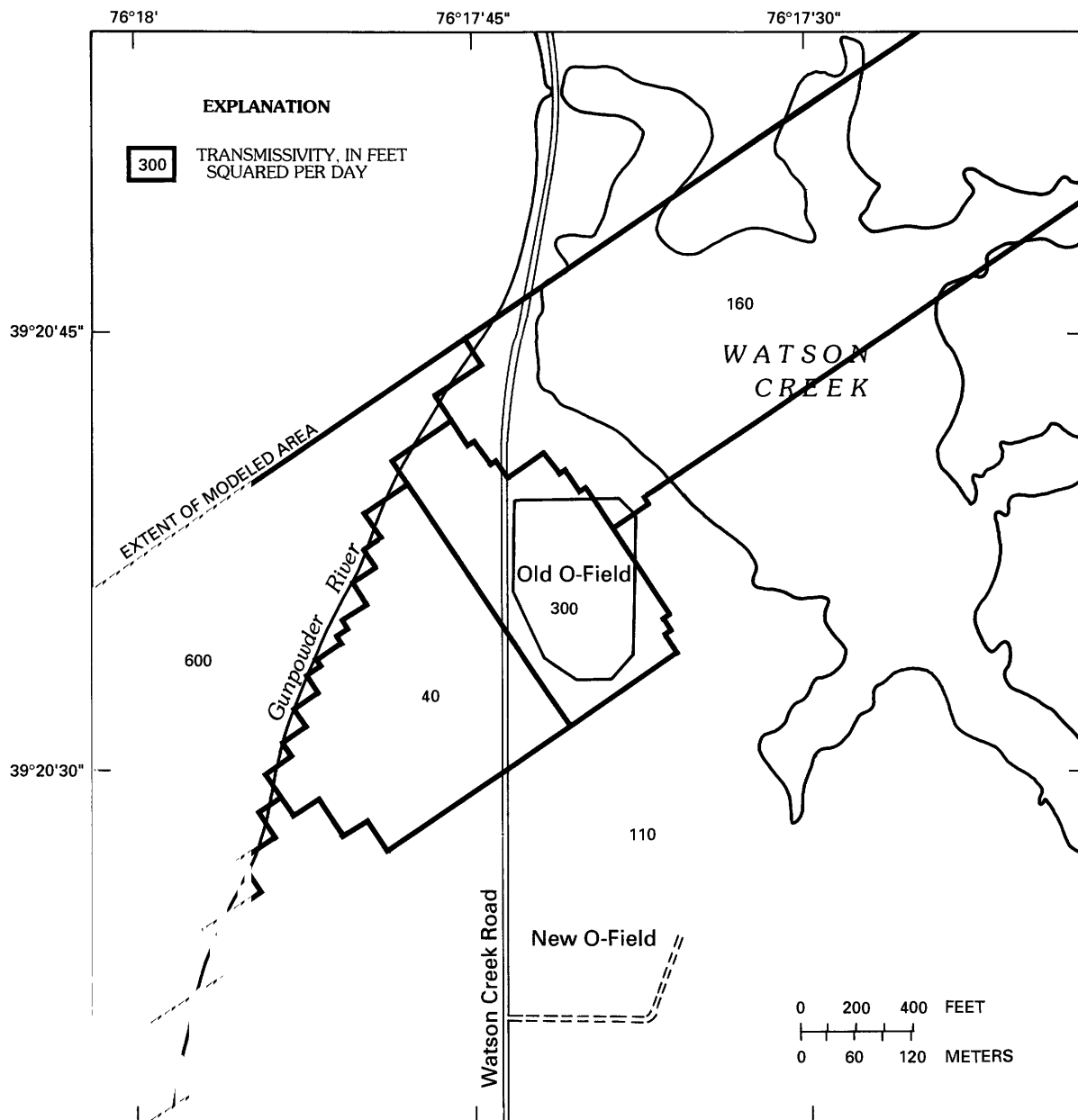


Figure 57. Simulated distribution of transmissivity used in the model for the upper confined aquifer. (Number is value in feet squared per day.)

water through the disposal areas. Leaching of contamination from within the landfill can occur both by downward infiltration of rainwater and by ground water moving through contaminated areas. The amount of ground-water decline necessary to limit contaminant leaching is uncertain; however, the pulse or pulses of 1,1,2,2-tetrachloroethane that moved from the Old O-Field disposal area toward Watson Creek during 1987 and 1988 probably leached from the disposal area as a result of ground-water levels that were higher than normal in March–May 1987. The ground water

near the disposal area in the spring of 1987 was 0.7 ft higher at well OF6A and 0.4 ft higher at well OF13A than during the previous spring (figs. 10 and 11). The ground-water levels during the spring of 1986 were 2 ft higher than during the summer and also appear to have leached contamination from Old O-Field, but in lesser concentrations. Thus, water-level declines within Old O-Field of about 1 ft during periods of seasonally high water levels may be enough to make a difference in the amount of contamination leached from the disposal area. The discussions of remedial-action

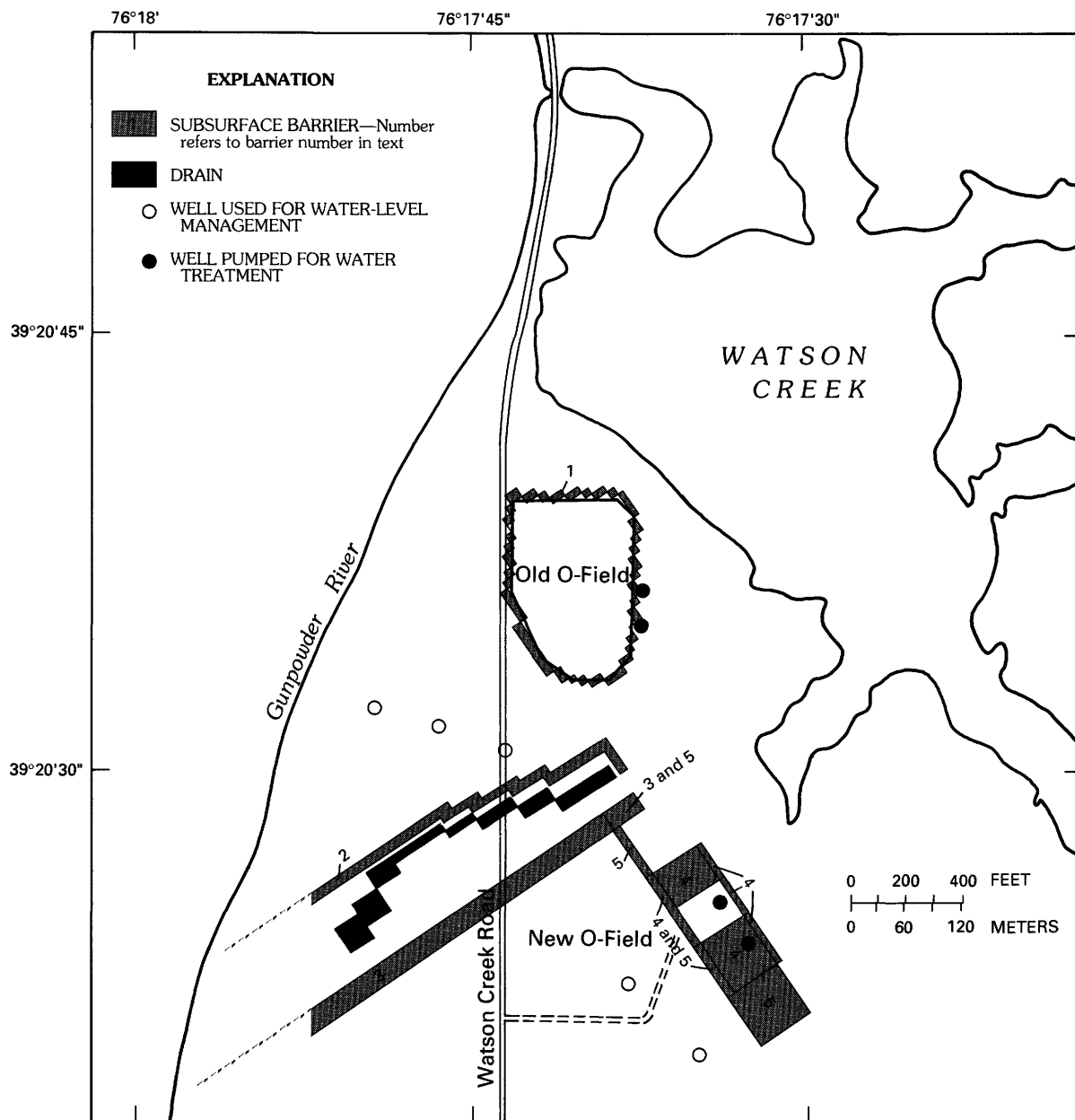


Figure 58. Sites of simulated remedial actions.

simulations concentrate on the water-table aquifer because it contains the greatest contamination and has the greatest potential for discharge to surface water.

All of the remedial actions evaluated using the flow model were simulated under steady state conditions of average annual rates and relatively high rates of recharge as represented by the April 22, 1986, water levels (figs. 54 and 55). For each recharge scenario, the remedial actions were simulated under a range of conditions that bracketed the probable uncertainty in the model input of recharge and hydraulic conductivity. Thus, when ranges of model results

are presented, they represent an estimate of the uncertainty of the solution.

One uncertainty not represented by the error brackets is that of the extent of contamination at New O-Field. The chemical information available from within the contamination at New O-Field is limited to one well cluster. Therefore, hydrologic evaluations of the remedial simulations concentrate on water-level changes in the area of documented disposal trenches. If contamination exists upgradient from the known trench area, then some of the remedial actions, particularly subsurface barriers, could increase the

extent of contamination. More information is needed on the distribution of contamination at New O-Field to provide the necessary information for management decisions concerning remedial measures at the site.

Impermeable Cap

Impermeable caps are designed to prevent infiltration of precipitation into landfills, the intent being to lower aquifer heads within the fill and reduce the amount of contaminant mobilization from the unsaturated zone. The hydrologic effects of one impermeable cap over Old O-Field and one over New O-Field were simulated using the flow model. The impermeable caps were represented by areas of no ground-water recharge. The boundaries of the cap at Old O-Field were considered to be the same as those of the Old O-Field fill area. The cap at New O-Field encompassed the disposal trenches, covering an area of about 2.5 acres.

Flow-model simulations indicate that installing an impermeable covering on Old O-Field would have only moderate effect on water levels within the fill. The maximum water-level reduction within the fill would be about 0.5 ft under average annual conditions and about 0.7 ft during periods of high ground-water levels represented by the April 22, 1986, heads. The simulated cap at New O-Field had even less effect on water levels. The maximum water-level reduction produced at New O-Field was about 0.3 ft. Ground-water velocities appear to be sufficient to compensate for the recharge water intercepted by the coverings.

Although the hydrologic effects of an impermeable covering on Old and New O-Fields are relatively small, the covering may have an effect on the amount of contaminants leached from the soil zone by rainfall events. Water has a stronger wetting ability than chlorinated aromatic hydrocarbons, so that the infiltration of precipitation is sufficient to desorb the organics from aquifer grains (Schwille, 1988, p. 52). Ideally, the fill covering should reduce or prevent such infiltration, consequently retarding both organic and inorganic contaminants in the soil zone. However, during exceptionally rainy periods, the rise in ground-water levels within the fill because of lateral flow may be sufficient to resaturate contaminated areas and mobilize contaminants.

Subsurface Barriers

Subsurface barriers to ground-water flow may be used at hazardous-waste landfills for a variety of purposes, including reduction of the amount of lateral ground-water flow recharging the fill from offsite and encapsulation of contaminated areas (when combined with an impermeable cap). The barriers are most effective when they extend vertically through the entire saturated thickness of an aquifer and are seated into a low-permeability boundary.

The thick, dense clay of the confining unit underlying the upper confined aquifer provides such an underlying boundary.

Three configurations of subsurface barriers at Old O-Field and two configurations at New O-Field (fig. 58) were simulated using the model. All of the barriers were simulated as extending through both of the modeled aquifers to the top of the dense clay layer underlying the upper confined aquifer at a depth of about 25 ft. The barriers were assumed to be 5 ft thick and to have a horizontal hydraulic conductivity of 0.001 ft/d. Horizontal hydraulic conductances were calculated to account for the fact that the walls did not compose an entire model cell. The simulations assume that recharge does not occur over the area of the cells representing the barriers.

Barrier 1 surrounds Old O-Field and approximately coincides with the Old O-Field fence (fig. 58). The simulation of barrier 1 assumes that the fill is also covered with a cap to prevent infiltration. Thus, barrier 1 constitutes full encapsulation of Old O-Field.

The primary goal in simulating barriers 2 and 3 was to determine if effective site control could be exercised by operations far enough from Old O-Field to substantially reduce the potential explosive and chemical hazards that might be encountered during excavations. The purpose of the barriers is to reduce the amount of water entering O-Field from offsite in an effort to lower heads within fill areas. Barrier 2 is located on the Old O-Field side of an intermittent stream that acts as a ground-water drain during periods of seasonally high ground water, and barrier 3 is located on the New O-Field side of the same stream (fig. 58). Barriers 2 and 3 were simulated both with and without an impermeable cap over Old O-Field.

Encapsulation of New O-Field was simulated in the same way as Old O-Field and is represented by barrier 4 (fig. 58). Barrier 5 at New O-Field is located in the same area as the upgradient part of barrier 4, but extends farther northwest and southeast. Barrier 5 was simulated both with and without an impermeable cap over New O-Field.

Barrier 1, complete encapsulation of Old O-Field, provides the most effective control of water movement through the Old O-Field fill area. In addition to isolating the fill hydrologically, the modeled flow simulations indicate that water levels would also decline outside the fill in the vicinity of well OF6A, where soil-zone contamination by chlorinated solvents is suspected. The amount of simulated head decline at well OF6A ranges from about 0.4 to 0.6 ft under average annual conditions and averages about 0.5 ft. During periods of seasonally high ground water, as represented by the April 22, 1986, heads, the water table would decline by about 0.6 to 1.0 ft at well OF6A. Ground-water rises on the upgradient side of the barrier would be about 0.4 ft.

Barrier 2 cuts off subsurface flow from the south to Old O-Field. The barrier allows the water to discharge

instead to the intermittent stream between Old O-Field and New O-Field. The wall simulated a slight water-level rise at New O-Field (0.4 ft under average annual conditions and from 0.4 to 1.4 ft during periods of seasonally high ground-water levels). Maximum water-level declines at Old O-Field would be about 0.3 ft under average annual conditions and from 0.3 to 1.6 ft during periods of seasonally high ground water. Using barrier 2 in conjunction with capping Old O-Field would have no effect on water levels at New O-Field, but would change maximum water-level declines at Old O-Field to 0.7 ft under average annual conditions and to about 0.9 ft during periods of seasonally high ground water.

Barrier 3 also cuts off subsurface flow from the south into Old O-Field, but it would allow the intermittent stream to act as a drain for Old O-Field ground water. Barrier 3, in comparison with barrier 2, would produce greater head declines at Old O-Field and greater head rises at New O-Field. Maximum water-level declines at Old O-Field would be 0.4 to 0.55 ft under average annual conditions and 0.4 to 1.8 ft during periods of seasonally high ground-water levels. Water levels would increase at New O-Field by about 1.7 ft under average annual conditions and by 2.3 to 3.3 ft during periods of seasonally high ground water. Capping Old O-Field would change the water-level declines to 0.67 to 0.8 ft under average annual conditions and 0.86 to 1.0 ft during periods of seasonally high ground water.

As with Old O-Field, complete encapsulation of the New O-Field trenches (barrier 4) would provide the most effective control of water movement through the trench area; however, model simulations also showed water-level rises of about 0.8 ft immediately upgradient from the barrier. Barrier 5 would produce substantial water-level declines (about 2.5 ft under all conditions) in the trench area at New O-Field. Barrier 5 in combination with an impermeable cap would produce drawdowns of about 3.5 ft under average annual conditions and about 4.5 ft during periods of seasonally high ground water. In addition to lowering water levels in the trench area, however, barrier 5 would also produce an increase in water levels of about 2 ft on the upgradient side of the barrier.

Complete encapsulation provides a greater degree of short-term aquifer protection than the other simulated barriers; however, the concentrations of some contaminants may increase in solution within the encapsulated fill. In the absence of oxygenated recharge, degradation of aromatic hydrocarbons probably will produce anoxic conditions within the encapsulated fill. Once conditions become sufficiently anoxic, biodegradation of the aromatics will slow. Biodegradation of chlorinated aromatic hydrocarbons within the fill would be expected to continue. Iron, manganese, and a number of relatively insoluble trace metals can be mobilized once more efficient electron acceptors are depleted. At Old O-Field, arsenic sorbed onto iron or manganese grain coatings may be mobilized but would

probably reprecipitate as sulfides. Therefore, unanticipated failure of the subsurface barriers by chemical degradation or design problems may result in release of some contaminants in higher concentrations than are now present in the ground water. The potential for such problems can be reduced by encapsulation in combination with pumped wells within the fill, so that contaminated ground water can be treated and infiltrating water can be removed.

Concentrations of contaminants outside the fill would be expected to decrease within about 3 years, on the basis of an average annual ground-water velocity of about 255 ft/yr. However, continued desorption of organic and inorganic contaminants from the soil zone and the aquifer matrix outside the encapsulated area probably will result in the continued production of low concentrations of contaminants.

The upgradient subsurface barriers 2 and 3 may decrease the amount of contamination added to the ground water during periods of high water levels at Old O-Field. The amount of contamination would be further decreased by installation of an impermeable covering over the fill; however, increased water levels at New O-Field probably would result in increased leaching of contaminants there, particularly if barrier 3 was used.

The upgradient subsurface barrier 5 may produce a decrease in contaminant leaching from the trench area at New O-Field. If the barrier was used in combination with an impermeable cap, the effectiveness would be further increased. Contaminant leaching from the saturated zone, however, probably would continue. Moreover, if contaminants exist in the unsaturated zone upgradient from the proposed barrier, the water-level rise would probably increase leaching on the upgradient side of the barrier.

Ground-Water Drain

Drains or interceptor trenches require the excavation of a trench below the water table. Drain pipes can be placed in the trench, or the trench can be backfilled with gravel or left open. The goal is to produce a continuous area in which the water table is lowered along the length of the drain. The drain may be active (pumped) or passive (gravity flow). At O-Field, an upgradient drain would intercept uncontaminated ground water moving from the south toward O-Field, with the intent of lowering the water table in the vicinity of Old O-Field.

The drain considered here is passive, in that water removal occurs by gravity flow to Watson Creek. The location of the drain coincides with a natural drain between Old O-Field and New O-Field (fig. 58). In model simulations, the effectiveness of the natural drain was enhanced by lowering the drain bottom to the average stage of Watson Creek, approximately 1.5 ft above sea level during the period of record.

Model simulations indicate that the deepened drain between Old O-Field and New O-Field would produce drawdowns at both sites of 0.8 to 0.9 ft under average annual conditions and from 0.9 to 1.0 ft during periods of seasonally high ground-water levels as represented by the April 22, 1986, heads. A ground-water divide would develop between the drain and the Old O-Field fill approximately 125 ft southeast of the fill. Water northeast of the divide would continue to flow toward the fill, but water south of the divide would flow toward the drain. The ground-water contamination beneath and east of Old O-Field would not be induced to flow toward the drain. The addition of an impermeable covering on Old O-Field would further increase simulated reductions in water level beneath the fill to about 1 ft under average annual conditions and to about 1.3 ft during periods of seasonally high ground water.

The lowering of heads in both Old O-Field and New O-Field could decrease leaching of contaminants from the soil zone. Continued leaching of contaminants may occur as a result of infiltration of rainfall and during periods when the water levels are high enough to mobilize contaminants. An impermeable covering would aid in reducing mobilization of unsaturated-zone contaminants. Ground-water contaminants beneath New O-Field, Old O-Field, and the area east of Old O-Field would probably continue to migrate along their present flow paths rather than be diverted toward the drain.

A potential disadvantage of the drain is that, during dry summer periods when ground-water levels are below those of the surface water, brackish surface water may enter the drain and move inland. The drain could then act as a losing stream and recharge parts of the water-table aquifer with brackish surface water. If the surface water contains contamination from O-Field, then the movement of water from the streams into the water table would transport contamination to that part of the water-table aquifer. The contamination would be localized, and increased ground-water gradients during periods of higher ground-water levels would cause the contamination to flow back toward the drain. There is also the possibility that an effect of mixing ground water with infiltrated brackish water could locally reduce permeability by the precipitation of iron.

Water-Level Management by Control of Pumpage

Water-level management by controlling pumpage using wells upgradient from contaminated areas was simulated. The goal of such control is to lower water levels within the fill areas without reversing water levels sufficiently to induce movement of contaminants toward uncontaminated areas of the site. Three pumped wells upgradient from Old O-Field and two pumped wells upgradient from New O-Field (fig. 58) were simulated separately. The hydrologic effects of the wells were examined under simulated pumping scenarios of 2,900, 5,800, 10,000, and

21,600 gallons per day (gal/d) per well. The pumpage was simulated both with and without impermeable coverings on the respective disposal areas.

Simulated pumping of the Old O-Field wells at a rate of 2,900 gal/d produced drawdowns at Old O-Field of about 0.4 ft for both average annual conditions and conditions of seasonally high ground water as represented by the April 22, 1986, heads. Simulated drawdowns at New O-Field were less than 0.1 ft. The pumpage did not produce a reversal of ground-water gradient.

Simulated pumpage of 5,800 gal/d produced 0.7 to 1.0 ft of drawdown at Old O-Field under average annual water-level conditions and about 0.9 ft during periods of seasonally high ground water. The pumpage produced a ground-water divide between Old O-Field and the wells. The location of the divide varied within the model-error brackets from the edge of the fill under average annual water-level conditions to 250 ft southeast of the fill during periods of seasonally high water levels. The proximity of the divide to the fill in most of the simulations implies that the pumpage may induce contaminant flow from the fill toward the wells during periods of lower than normal recharge.

Providing a cover for Old O-Field at pumpage of 2,900 gal/d would increase the amount of drawdown beneath the fill to about 0.8 ft under average annual and seasonally high water-level conditions. Combining the cover with upgradient pumpage of 5,800 gal/d would produce drawdowns beneath Old O-Field of 1.1 and 1.4 ft under average annual and seasonally high water-level conditions, but also would produce a gradient reversal near the fill. Simulated removal of water from the line of wells at rates of 10,000 and 21,600 gal/d with and without covers on the disposal areas would exceed the recharge to the aquifer.

A similar approach with the upgradient New O-Field wells showed that pumpage of 2,900 gal/d would not substantially lower water levels within the trench area, even with an impermeable cap on the trenches. Pumping at a rate of 5,800 gal/d would produce drawdowns in the trench area of about 0.5 ft or less. The pumpage, in combination with an impermeable covering, would increase drawdowns in the trench area to about 0.6 to 1 ft. Pumping 10,000 and 21,600 gal/d would produce drawdowns of about 1 ft and about 2.3 to 3.5 ft, respectively, but both also would produce substantial changes in directions of ground-water flow either at or close to the disposal trenches. The gradient reversals would be intensified with the addition of an impermeable covering. Thus, the increased pumping rates could induce the movement of contaminants toward the wells.

The water-level decline beneath Old O-Field and New O-Field produced by low pumping rates (2,900 gal/d at both sites and 5,800 gal/d at New O-Field) could result in a reduction in the release of contaminants to ground water. However, at higher pumping rates, some model simulations within the range of error demonstrated the possibility of

inducing contaminant migration into previously uncontaminated areas. The extent of the cones of depression could be monitored by installing observation wells between the pumped site and the disposal area. The distribution of ground-water contamination at New O-Field must be determined before the potential for pumpage-related, contaminant-transport reversals can be evaluated.

Excavation

Excavation and removal of the waste material from O-Field is a particularly hazardous undertaking because of the likelihood of encountering munitions containing explosives and chemical-warfare agents. ICF Technology (1987) examined possible excavation techniques for Old O-Field and determined that the most practical methods were hydraulic excavation and remotely controlled mechanical excavation. Hydraulic excavation involves the use of remotely controlled water cannons or jets to wash the soil, munitions, and other debris into a defined area where they can be more easily removed. Excess water would be collected in a settling pond, pumped offsite for treatment, and reused for hydraulic excavation. Remotely controlled mechanical excavation involves the operation of machinery, such as a cable-controlled plow or dragline, a remotely controlled excavator, or a horizontal mining machine.

The short-term hydrologic effects of excavating O-Field depend on the excavation methodology used. Hydraulic excavation would introduce amounts of water into the subsurface that probably could not be recovered by the methods proposed. Thus, ground-water mounding likely would occur in the vicinity of the excavation. Excavation by remotely controlled equipment would have a minimal effect on ground-water levels. However, dewatering operations might be required if excavations extend into the saturated zone.

Long-term water-level changes caused by excavation and backfilling of Old O-Field will probably be minimal. Model simulations of Old O-Field encapsulation suggest that, even if the excavations are backfilled with clay, the average annual head decline would not be more than about 0.5 ft at Old O-Field and about 0.9 ft at New O-Field.

As with the hydrologic effects, the probable chemical effects of excavation depend on the method used. Although any disturbance of the disposal area can potentially release contamination by rupturing containers or by exposing contaminated surfaces to the effects of weather, the operation of remotely controlled excavation equipment would be expected to have a substantially less severe impact on the ground-water chemistry than would hydraulic excavation. The strong surface-wetting ability of water compared with that of many of the organic contaminants (Schwille, 1988) means that the jetted water from the hydraulic excavation could desorb a variety of organic contaminants from the soil zone and aquifer matrix. Further solution of both organic

and inorganic contaminants could occur simply from the hydraulic breakup of congealed chemicals into a broadly disseminated mass that is susceptible to hydrolysis. Much of the generated aqueous contamination could then enter the ground water. Thus, hydraulic excavation has the potential of releasing contaminants in concentrations far exceeding those presently in the ground water.

Whichever method of site excavation is used, an initial increase in the concentration of ground-water contamination would be expected. Contaminant concentrations in the ground water would be expected to decline gradually. However, continued desorption of both inorganic and organic contaminants from the aquifer matrix may continue to add low concentrations of contaminants to the ground water.

Treatment of Pumped Water

Pumping contaminated ground water for treatment requires the placement of pumped wells at strategic locations within the contamination plume. The existing observation wells at Old O-Field are probably inadequate to function as withdrawal wells, primarily because of their size and location. The effectiveness of pumped wells in recovering contamination from the water-table aquifer at New O-Field cannot be determined because the distribution of ground-water contamination at the site is not known with certainty.

The feasibility of using wells to remove ground-water contaminants was tested by simulating separately two wells adjacent to the southeastern side of Old O-Field and two wells adjacent to the northeastern side of New O-Field disposal trenches (fig. 58). The hydrologic effects of pumping were simulated under pumping scenarios of 2,900, 5,800, 10,000, and 21,600 gal/d per well. The pumpage was simulated both with and without an impermeable covering on the respective disposal areas.

Simulated pumping of the downgradient wells at a rate of 2,900 gal/d produced a drawdown of about 0.5 ft beneath Old O-Field and from 0.5 to 0.8 ft at the trenches in New O-Field. The simulated pumping did not produce a cone of depression large enough to intercept the entire contaminant plume east of Old O-Field. The limited amount of information on contaminant distribution at New O-Field does not allow evaluation of the amount of contaminant that would be captured.

Simulated pumpage of 5,800 gal/d at Old O-Field lowered water levels below the fill by about 0.7 ft both under average annual water-level conditions and during periods of seasonally high ground-water levels as represented by the April 22, 1986, heads. The pumpage produced a cone of depression large enough to intercept the entire contaminant plume east of the fill. However, the pumping rate under average annual water-level conditions produced a ground-water divide approximately 50 ft inland

from Watson Creek. The proximity of the divide to Watson Creek implies that maintaining the pumping rate through the summer could induce movement of surface water into the aquifer and toward the wells. One solution is to adjust pumping rates seasonally and to monitor the cone of depression by installing observation wells between Watson Creek and the pumped wells. Simulated pumping at 5,800 gal/d from the two wells adjacent to New O-Field did not induce surface-water infiltration into the aquifer, but infiltration during dry summers cannot be ruled out.

The drawdowns and radii of contaminant interception would be increased by the addition of impermeable caps over Old O-Field and New O-Field. With a cap, pumping the Old O-Field wells at 2,900 gal/d would be adequate to intercept most ground-water contamination at Old O-Field under average annual water-level conditions, but not under conditions of seasonally high ground-water levels as represented by the April 22, 1986, heads. Average drawdowns of about 1 ft would be produced below both Old and New O-Field.

The cone of depression produced by pumping the Old O-Field wells at 5,800 gal/d would be sufficient to intercept the bulk of contaminated ground water east of the fill; however, it would induce movement of Watson Creek water into the aquifer if the rate was maintained under average annual water-level conditions. Average drawdowns beneath the fill would be between 1.3 and 1.4 ft. The model simulations indicate that higher pumping rates at Old O-Field either would exceed the recharge rate of the aquifer or induce movement of surface water into the aquifer throughout much of the year.

Simulated drawdowns at the New O-Field trenches ranged from 1.1 to 1.8 ft for pumpage of 5,800 gal/d. Pumpage at New O-Field of 10,000 gal/d would produce water-level declines of about 2.5 to 3.5 ft under average annual water-level conditions and about 2.2 to 3.5 ft during periods of seasonally high ground-water levels, as represented by the April 22, 1986, heads. The simulations did not show inducement of infiltration of creek water, but the proximity of the hydraulic-gradient reversal to the creek implies that infiltration probably would be induced if the pumping rate was maintained during the dry summer months. Higher pumping rates either would exceed the recharge rate of the aquifer or induce movement of surface water into the aquifer throughout much of the year.

Contaminant concentrations in the ground water at Old and New O-Field would be expected to decline as a result of pumpage at an appropriate rate. The increase in ground-water velocity could accelerate the rate of solution of sorbed organic contaminants or free products beneath the fill. Pulses of contamination may still be generated as a result of infiltration of rainfall or by water levels rising into the base of the landfill, but the pulses could be intercepted by the wells before discharging to surface water. Thus, renovation of the ground water and contaminated aquifer

matrix could be greatly accelerated by the pumpage. Even at accelerated hydrolysis rates, however, contamination beneath the sites probably is extensive enough to continue production of low concentrations of contaminants in the ground water. Moreover, desorption of organic and inorganic species from the aquifer matrix outside the fill, as less contaminated water begins to enter the plume area, also may contribute low concentrations of contaminants to the ground water. Thus, the required duration for such pumpage cannot be stated with certainty. At pumping rates sufficient to induce brackish-water intrusion from Watson Creek, increased TDS and chloride concentrations will result, and aquifer permeability may decrease as a result of iron precipitation.

No Action

The no-action alternative assumes that the disposal areas and contaminated ground water will be left in their present condition. If no remedial actions are performed at the disposal areas, ground-water levels will continue to rise during some winter and spring months to above the base of disposed materials. The rate of ground-water movement will continue to be an average of about 0.9 ft/d at Old O-Field and about 0.7 ft/d (on the basis of model simulations and using a porosity of 0.3 percent) at New O-Field.

If the disposal sites are allowed to remain in their present condition, contaminant transport will continue. Because large amounts of chlorinated solvent are believed to exist within the fill area in the soil zone or as a free product in subsurface pools, rainfall could continue to displace solvent from the soil zone, and increased ground-water velocities during periods when ground-water levels are higher than normal would probably continue to dissolve parts of subsurface organic-solvent pools. Mobilization and transport of inorganic contaminants from the fill area would also be expected to continue.

Continued movement of solute from the fill area is expected. Arsenic will probably coprecipitate with iron oxyhydroxides upon entering the creek. Transport of arsenic and other sediment-associated contaminants to the Gunpowder River could occur during periods of high turbidity in the creek, such as those after a heavy rain. Transport of arsenic from the creek to the Gunpowder River also could occur if dissolved arsenic, from either ground-water transport or desorption, reaches sufficient concentrations, as for example, after a period of increased contaminant discharge from ground water.

Volatilization and sorption onto organic sediment would be expected to be important depletion mechanisms for volatile organic compounds entering Watson Creek from the ground water throughout much of the year. During periods when the surface of the creek is frozen, however, volatilization will be minimal, and transport of volatiles to the Gunpowder River is likely to occur. Moreover, if

contaminants within the creek attain sufficient concentrations during other times of the year, the depletion mechanisms may be inadequate to prevent transport of contaminants to the Gunpowder River.

Increased contaminant movement from O-Field could result from rupture or rusting of drums or ordnance casings. Such events also could introduce previously undetected contaminant species.

SUMMARY AND CONCLUSIONS

O-Field, in the Edgewood area of Aberdeen Proving Ground, Md., has been used periodically for disposal of waste material during and since World War II. The material consists of munitions, waste chemicals, and chemical-warfare agents. O-Field contains three sites that have been used for waste disposal: Old O-Field, New O-Field, and a small site west of Old O-Field. Investigation of ground water at O-Field and of the adjacent surface water by the U.S. Geological Survey shows that O-Field operations have contaminated both those water sources and the bottom sediment of Watson Creek.

O-Field is located on unconsolidated sand, clay, and silt deposits of the Atlantic Coastal Plain. Three aquifers are present at O-Field to a depth of about 120 ft. In this report, the aquifers are designated, from shallowest to deepest, the "water-table aquifer," the "upper confined aquifer," and the "lower confined aquifer." Additional aquifers are present at greater depth but were not investigated during this study.

The water-table aquifer consists of fine- to coarse-grained sand interbedded with discontinuous clay lenses. Recharge is primarily from rainfall, although some results from infiltration of brackish surface water, particularly during periods when tides are higher than normal. Ground water discharges by evapotranspiration to the atmosphere and by lateral flow to Watson Creek and the Gunpowder River. Seasonal variations in rainfall and evapotranspiration result in water-level differences of as much as 3 ft in the water-table aquifer at Old O-Field. Background wells in the aquifer contain 60 to 100 mg/L TDS; calcium and magnesium are the dominant cations, and sulfate is the dominant anion. Background pH is 4.8 to 5.7.

The water-table aquifer is underlain by a confining unit composed of black to greenish-gray clay. The thickness of the confining unit is about 5 ft in the Old O-Field area and about 0.5 ft at New O-Field. The presence of contamination in the underlying aquifer at Old O-Field and New O-Field implies that the confining unit is discontinuous or leaky beneath the sites.

The upper confined aquifer at O-Field consists of dark-gray to brown, medium- to coarse-grained sand interbedded with gravel and discontinuous clay lenses. The aquifer is probably confined beneath parts of Watson Creek. Recharge to the aquifer is by leakage of water from the

overlying water-table aquifer either slowly through the confining unit or more rapidly through confining-unit discontinuities. Discharge is by upward leakage through the confining unit to the water-table aquifer in downgradient areas and by leakage to surface-water bodies. Water-level fluctuations in the upper confined aquifer are primarily a hydrostatic-pressure response to fluctuations of water levels in the water-table aquifer and surface water.

A dense, black to dark-gray clay layer approximately 50 ft thick underlies the upper confined aquifer at O-Field. The clay is continuous beneath O-Field but is absent 1 mi north and 1/2 mi south of O-Field; however, it does extend southeastward at least as far as Carroll Island. A white clay of differing lithology is present south of O-Field at H-Field at about the same depth as the dark clay at O-Field, implying that the white clay functions with the dark clay as a continuous confining unit.

Recharge and discharge areas of the lower confined aquifer are not known with certainty; however, the average hydraulic gradient is toward the west-northwest. Ground water in the lower confined aquifer at O-Field is unsuitable for drinking purposes because of excessive concentrations of iron, manganese, and sulfide, probably the result of natural chemical conditions.

No sediment samples were collected from the confining unit underlying the lower confined aquifer. However, geophysical logs of boreholes penetrating the confining unit indicate that it is about 48 ft thick and overlies an aquifer about 10 ft thick. Below the 10-ft-thick aquifer, clayey material is about 47 ft thick.

Old O-Field is bordered by surface water on three sides: Watson Creek to the north and east and the Gunpowder River to the west. New O-Field is bordered by Watson Creek to the north. The bottom sediment in the Gunpowder River is dominantly sand, but the bottom sediment in Watson Creek is sand in some areas and organic-rich fine-grained material in other areas. The lithology of the bottom sediment in Watson Creek is controlled by current-velocity distributions within the creek. Coarse-grained material is found in areas where current velocities are sufficient to suspend and transport the fine-grained material. Organic-rich detritus and fine-grained material settle out of suspension in areas of quiescence.

Ground-water contamination is present at both Old O-Field and New O-Field in the water-table aquifer and the upper confined aquifer. Well OF18A (water-table aquifer), west of Old O-Field, contained 1,4-dithiane (32 µg/L), which may be moving toward the Gunpowder River; however, other contaminants were absent.

Contaminated ground water in the water-table aquifer at Old O-Field contains concentrations of arsenic and cadmium in excess of U.S. Environmental Protection Agency MCL's. Chloride, iron, manganese, and zinc are present at concentrations exceeding the U.S. Environmental Protection Agency SMCL's. Organic contaminants detected

are thiodiglycol, 1,3-dinitrobenzene, 2,4,6-trinitrotoluene, 1,1,2,2-tetrachloroethane, chloroform, 1,4-dithiane, benzene, trichloroethylene, tetrachloroethylene, 1,2-*trans*-dichloroethylene, C3 alkyl benzene, dichloroethane, methylene chloride, carbon tetrachloride, chlorobenzene, toluene, and a variety of sulfur-containing compounds.

Contaminated ground water in the upper confined aquifer at Old O-Field contains concentrations of arsenic in excess of U.S. Environmental Protection Agency MCL's and concentrations of chloride, iron, and manganese in excess of SMCL's. Organic contaminants are thiodiglycol, benzene, 1,2-*trans*-dichloroethylene, vinyl chloride, chloroform, 1,2-dichloroethane, 1,4-dithiane, 1,1,2,2-tetrachloroethane, trichloroethylene, methylene chloride, chlorobenzene, and toluene.

Ground water in the water-table aquifer at New O-Field contains concentrations of iron and manganese exceeding SMCL's. Organic contaminants detected were 1,2-*trans*-dichloroethylene, vinyl chloride, benzene and several alkylated benzenes, toluene, and methylene chloride. The water-table aquifer at New O-Field also contains a number of organic compounds not present at Old O-Field: chloro-, 3,5-dichloro-, and trichloroaniline; xylene; dichlorophenol (not 2,4); 1-ethenyl-2-methylbenzene; phosphonic acid; and methyl-*bis*(1-methylethyl)ester.

The upper confined aquifer at New O-Field also contained detectable ground-water contamination. Inorganic constituents exceeding U.S. Environmental Protection Agency SMCL's were iron and manganese. Organic contaminants detected were vinyl chloride, tetrachloroethylene, 1,2-*trans*-dichloroethylene, methylene chloride, trichloroethylene, 1,1,2,2-tetrachloroethane, toluene, benzene, chlorobenzene, and chloroform. Aromatic compounds not detected at Old O-Field or in the water-table aquifer at New O-Field but present in the upper confined aquifer at New O-Field were aniline, dimethyl benzoic acid, and a trimethyl benzene isomer.

Chloride moves through the ground water relatively unaffected by reactions with the aquifer matrix. Additional chloride is being generated along the flow path by degradation of chlorinated aliphatic hydrocarbons.

The behavior of several contaminants is dependent on Eh and pH conditions in the ground water. Arsenic is oxidizing from arsenite to the less mobile and less toxic arsenate as it moves along the flow path. Arsenic probably precipitates as sulfides during anoxic periods but can be remobilized when periods of high rainfall increase the amount of dissolved oxygen. Iron and manganese may precipitate as oxyhydroxides during oxic conditions and redissolve when conditions become anoxic. The broader Eh/pH-stability range of manganese means that manganese remains more mobile than iron under these variable redox conditions. As sorption sites precipitate or dissolve in response to variations in Eh/pH conditions and microbial

activity, cadmium would also be expected to undergo sorption/desorption reactions.

Zinc solubility depends on pH, but at low pH (4.5-4.6) in the water sample from the well containing elevated zinc content, zinc is soluble and can move at approximately the same rate as ground water. The dominant species of antimony at the given pH should be Sb^{+5} , which typically can sorb onto the aquifer matrix to some extent. Therefore, dissolved antimony would be expected to move somewhat more slowly than ground water.

Chlorinated aliphatic hydrocarbons appear to be leached during rain events from the unsaturated zone within the Old O-Field fill area and immediately east of the fill area. The leached contaminants enter the ground water, where they undergo dehalogenation. The dehalogenation reactions are reflected by the decreasing of reactant/product molar ratios. Sorption onto aquifer material is not believed to be an important process at O-Field because insufficient amounts of fine-grained organic carbon are present below the soil zone.

Biodegradation of aromatic hydrocarbons at O-Field apparently has been a factor in producing the anoxic conditions in the ground water. Once the oxygen is utilized, however, biodegradation of the aromatics slows. Thus, biodegradation of the aromatics would be expected to be significant only after major recharge events, when oxygenated water is added to the flow system. During anoxic periods in the ground water, the primary depletion mechanism probably is volatilization at the air-water interface.

Trinitrotoluene mobility is probably limited by microbial degradation in the oxygenated water near well OF6. Thiodiglycol probably moves through the aquifer relatively unimpeded and discharges into Watson Creek.

The distribution of individual dissolved species in the contaminated ground water at Old O-Field is aerially variable. Arsenic and organic contaminants are most concentrated along the northeastern side of the disposal area. However, iron is present in two distinct plumes, one along the eastern side and one along the northeastern side of the disposal area, and chloride concentrations are greatest along the northeastern side and near the Watson Creek shoreline, east of Old O-Field. The spatial distribution of contaminants at New O-Field cannot be evaluated because of the limited number of wells at the site.

The primary causes of ground-water contamination at O-Field are waste disposal and operations involving organic-solvent-based decontamination. Chloride contamination in the ground water at O-Field is due partly to the dehalogenation or chlorinated organics and partly to direct disposal of bleaching agents used for decontamination. Additional chloride contamination occurs in localized areas near the shoreline as a result of brackish-water infiltration from Watson Creek during periods of exceptionally high tides. Arsenic contamination has resulted from disposal and subsequent degradation of arsenic-based chemical-warfare

agents. Iron and manganese are derived partly from the degradation of buried waste metal at O-Field and partly from leaching and dissolution of iron- and manganese-rich grain coatings in the aquifer. Zinc, detected at concentrations greater than U.S. Environmental Protection Agency SMCL's at only one well, may have resulted from the degradation of waste-smoke munitions or from dissolution of aquifer materials and metals containing zinc. The presence of cadmium is related to disposal of metal-plating residues and (or) degradation of cadmium-plated metals and cadmium-rich alloys.

The use of solvent-based decontaminating agents appears to have been the primary source of much of the chlorinated aliphatic hydrocarbon contamination detected at O-Field. Many of the aromatic contaminants in the ground water at the site resulted from the burning of waste in combination with large quantities of fuel oil. Nitrobenzenes at the site probably are attributable to the disposal of explosives. Other organics, such as thiodiglycol, 1,2-dithiane, and methyl phosphonic acid, are likely degradation products of chemical-warfare agents.

Contamination related to O-Field activities has also been detected in the water and bottom sediments of Watson Creek. Arsenic and chlorinated aliphatic hydrocarbons in the surface water appear to be related to O-Field operations. Mercury and a variety of transition metals are also present.

Samples of bottom sediment from Watson Creek contained arsenic, zinc, manganese, copper, lead, iron, chromium, nickel, and mercury. Organic constituents detected in the bottom sediment were several polycyclic aromatic hydrocarbons, trichlorofluoromethane, carbon disulfide, di-*n*-octylphthalate, and 1,2-dichloroethylene.

The distribution of inorganic contaminants in both the surface water and the bottom sediment of Watson Creek is largely a function of current-induced transport of bottom sediment. Incoming tides generate current velocities high enough to suspend the fine-grained material from the bottom sediment and transport it to more quiescent areas, where it is redeposited. In general, arsenic and the transition metals have a relatively high affinity for sorption or precipitation with the fine-grained fraction of sediment. The highest concentrations of arsenic and the trace metals generally are associated with areas of fine-grained bottom sediment. An exception is immediately offshore from an area of contaminated ground water at Old O-Field. Anomalously high concentrations of trace metals are found in the bottom sediment of that offshore area, despite its dominantly sandy nature. The proximity to ground-water contamination suggests that it is in a zone where contaminated ground water is discharging to Watson Creek.

The PAH's in the bottom sediment will probably biodegrade with time, but the relatively low concentrations of degradation products imply that this is a slow process. The slow degradation of the PAH's and their affinity for sorption mean that they will be persistent in the bottom

sediment. Phthalates probably undergo a similar fate. Volatilization and transport of aqueous phases are important mechanisms for carbon disulfide, trichlorofluoromethane, and 1,2-dichloroethylene.

The inorganic constituents in Watson Creek are partly related to disposal operations at O-Field. With the possible exception of mercury, their presence also may be due to dissolution of naturally occurring minerals. The relative lack of substituted isomers of PAH's implies that the PAH's were derived from pyrolysis of organic matter as a result of fires. However, a similar isomer relationship could have developed from disposal of petroleum-based products if the more soluble alkyl-substituted isomers partitioned into the aqueous phase, preferentially removing them from the sediment.

Ground-water transport of contamination offsite or to other areas onsite is unlikely. A 50-ft-thick layer of clay below O-Field at a depth of about 25 ft restricts the downward migration of contaminants. Lateral migration of contamination is toward Watson Creek. The creek provides a low-energy environment, where fine-grained precipitates of arsenic and iron can settle out of suspension. Volatilization would be expected to be the primary depletion mechanism within the creek. Migration of contaminants through the ground water toward the Gunpowder River has not been observed, except possibly for 1,4-dithiane.

The predicted effects of selected remedial actions on ground water were examined as part of this investigation. The methods of evaluation were flow-model analysis and extrapolation of known or suspected chemical processes to determine hydrologic and contaminant responses to stresses on the flow system as a result of remediation measures. The flow model used is a three-dimensional finite-difference model that simulates steady state ground-water flow in the water-table aquifer and in the upper confined aquifer.

The analyses indicate that covering the Old O-Field landfill with an impermeable cap would lower water levels beneath the fill by less than 1 ft. However, the reduction of precipitation infiltration into the unsaturated zone at the fill could decrease the amount of contaminant leaching.

Complete encapsulation of Old O-Field by seating a low-permeable subsurface barrier into the thick clay layer underlying the fill, and covering the fill with an impermeable cap, would provide short-term aquifer protection; however, the concentrations of some contaminants are likely to increase in solution within the encapsulated fill. Failure of the encapsulating walls due to chemical degradation or design may increase the concentrations of some contaminants in the ground water.

Subsurface barriers upgradient from Old O-Field and from the trenches at New O-Field also were examined. The barriers resulted in water-level declines below Old O-Field of about 1 ft, but they also produced increases in water level at New O-Field. Thus, while potentially reducing the

amount of contaminant leaching by ground water from Old O-Field, the barriers also may increase the amount of leaching at New O-Field.

The subsurface barrier at New O-Field reduced water levels by about 2.5 ft at the disposal trenches. The reductions increased to 3.5 to 4.5 ft with the addition of an impermeable covering; however, the barrier also increased water levels by about 2 ft on the upgradient side. Limited information is available on the extent of contamination at New O-Field, so the potential cannot be evaluated for contaminant leaching after the water level rises upgradient from the barrier.

Deepening an existing intermittent stream that drains to Watson Creek was also tested as a remedial action. Model simulations show that use of a deep drain to intercept water moving into Old O-Field from the south lowered water levels in the water-table aquifer beneath both Old O-Field and New O-Field. A ground-water divide would develop between the drain and Old O-Field. Thus, contaminant movement from Old O-Field toward the drain probably would not occur. During periods of low ground-water levels or high surface-water levels, brackish surface water could enter the drain and move inland. The drain would then act as a losing stream, recharging parts of the water-table aquifer with brackish surface water.

The model also was used to test the effectiveness of pumping upgradient wells to manage water levels within disposal areas. Three pumped wells upgradient from Old O-Field and two upgradient from New O-Field were simulated and evaluated separately. At a simulated pumping rate of 5,800 gal/d at the Old O-Field wells, 0.7 to 1.0 ft of drawdown would occur beneath Old O-Field. The drawdown would increase by about 0.5 ft if the pumping was simulated with the addition of an impermeable covering over the fill. This remedial action could decrease contaminant leaching; however, at those pumpage rates, some model solutions within the range of error indicated that contaminants would be induced to migrate to previously uncontaminated areas.

A similar approach for the upgradient New O-Field wells showed that pumpage of 2,900 gal/d would not substantially lower water levels within the disposal area, even with an impermeable cap on the trenches. Pumping at a rate of 5,800 gal/d would produce drawdowns in the disposal area of about 0.5 ft or less. The pumpage simulated in combination with an impermeable covering would increase drawdowns in the trench area to about 0.6 to 1 ft. Pumping 10,000 and 21,600 gal/d would produce drawdowns of about 1 ft and 2.3 to 3.5 ft, respectively, but both rates would produce hydraulic-gradient reversals extending up to or close to the disposal trenches. The hydraulic-gradient reversals would be intensified with the addition of an impermeable covering. Thus, the higher pumping rates may induce the movement of contaminants toward the wells.

The hydrologic and chemical effects of excavating and removing the fill material at O-Field would depend on the excavation technique used. The two techniques determined by a separate study as being the most practical are hydraulic excavation and remotely controlled mechanical excavation. Hydraulic excavation, involving the use of remotely controlled water cannons to wash the waste material into a central collection area, would produce ground-water mounding at the fill and potentially could release contaminants in concentrations exceeding those presently in the ground water. Although any disturbance of the disposal area can potentially release contamination by rupturing containers or exposing contaminated surfaces to the effects of weather, the operation of remotely controlled excavation equipment would be expected to have a substantially less severe impact on the ground-water chemistry than would hydraulic excavation. Although excavation probably would result in an initial increase in ground-water contaminant concentrations, the long-term effect would be a gradual lowering of contaminant levels. Continued desorption of inorganic and organic contaminants from the aquifer matrix, however, will continue to produce low concentrations of contaminants.

Pump-and-treat remediation of ground-water contamination at Old O-Field and New O-Field was examined using the ground-water flow model to simulate two pumped wells downgradient from the disposal areas. Simulated pumpage of 2,900 gal/d under conditions of average annual recharge would be sufficient to intercept the bulk of ground-water contamination at Old O-Field if the landfill were covered with an impermeable cap, but not if the cap were absent. This rate would not be adequate during the winter, when ground-water levels are higher than normal. Increased pumping of 5,800 gal/d would be sufficient during the winter but could induce movement of water from Watson Creek into the aquifer if the rate is maintained under conditions of average annual recharge.

Simulated drawdowns at the New O-Field trenches ranged from 1.1 to 1.8 ft at a pumpage of 5,800 gal/d at the site. Pumpage at New O-Field of 10,000 gal/d would produce water-level declines of about 2.5 to 3.5 ft under average annual recharge conditions and about 2.2 to 3.5 ft during a period of seasonally higher ground-water levels. The simulations predict that induced infiltration of water from the creek would not occur, but the nearness of the cone of depression to the creek implies that infiltration could be induced if the pumping rate was maintained during periods of below-normal ground-water levels. Increased pumping rates either would exceed the recharge rate of the aquifer or induce movement of surface water into the aquifer through-out much of the year.

If no remedial actions are taken at O-Field, mobilization and transport of organic and inorganic contaminants will continue, primarily because of seasonal and recharge-induced water-level rises above the base of the buried

contamination. The ground-water contaminants will continue to discharge to Watson Creek. If the contaminants in the creek attain sufficient concentrations, then the depletion mechanisms may be inadequate to prevent contaminant migration from the creek to the Gunpowder River.

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