Prepared in cooperation with the U.S. Army, White Sands Missile Range

Geochemical Trends and Natural Attenuation of RDX, Nitrate, and Perchlorate in the Hazardous Test Area Fractured-Granite Aquifer, White Sands Missile Range, New Mexico, 1996–2006

Scientific Investigations Report 2008–5157

U.S. Department of the Interior
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Conversion Factors and Datums

Multiply	By	To obtain
inch	2.540	centimeter (cm)
foot (ft)	0.3048	meter (m)
yard (yd)	0.9144	meter (m)
mile (mi)	1.609	kilometer (km)
acre	4,047	square meter (m^2)
gallon (gal)	3.785	liter (L)
foot per day (ft/d)	0.00035	centimeters per second (cm/s)
foot per year (ft/yr)	$9.7 \mathrm{x} 10^{-7}$	centimeters per second (cm/s)
gallons per minute (gal/min)	0.0038	cubic meters per minute (m^3/min)

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Abbreviations

DS	Dissolved solids
EMRE	Electro-Magnetic Radiation Energy
Ga	Billion years before present
HTA	Hazardous Test Area
Ma	Million years before present
µg/L	Micrograms per liter
mg/L	Milligrams per liter
Nitrate	Nitrate plus nitrite as nitrogen
OB/OD	Open Burn/Open Detonation
RCRA	Resources and Conservation Recovery Act
redox	Reduction-oxidation
USGS	U.S. Geological Survey
WSMR	White Sands Missile Range
‰	Per mil

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Abstract

A fractured-granite aquifer at White Sands Missile Range is contaminated with the explosive compound RDX, nitrate, and perchlorate (oxidizer associated with rocket propellant) from the previous use of the Open Burn/Open Detonation site at the Hazardous Test Area. RDX, nitrate, and perchlorate ground-water concentrations were analyzed to examine source characteristics, spatial and temporal variability, and the influence of the natural attenuation processes of dilution and degradation in the Hazardous Test Area fractured-granite aquifer. Two transects of ground-water wells from the existing monitoring-site network—one perpendicular to ground-water flow (transect *A–A´*) and another parallel to ground-water flow (transect *B–B´*)—were selected to examine source characteristics and the spatial and temporal variability of the contaminant concentrations. Ground-water samples collected in 2005 from a larger sampling of monitoring sites than the two transects were analyzed for various tracers including major ions, trace elements, RDX degradates, dissolved gases, water isotopes, nitrate isotopes, and sulfate isotopes to examine the natural attenuation processes of dilution and degradation.

Recharge entrains contaminants at the site and transports them downgradient towards the Tularosa Basin floor through a poorly connected fracture system(s). From 1996 to 2006, RDX, nitrate, and perchlorate concentrations in ground water downgradient from the Open Burn/Open Detonation site have been relatively stable. RDX, nitrate, and perchlorate in ground water from wells near the site indicate dispersed contaminant sources in and near the Open Burn/Open Detonation pits. The sources of RDX and nitrate in the pit area have shifted with time, and the shift correlates with the regrading of the south and east berms of each pit in 2002 and 2003 following closure of the site. The largest RDX concentrations were in ground water about 0.1 mile downgradient from the pits, the largest perchlorate concentrations were in ground water about 0.15 mile downgradient from the pits, and the largest nitrate concentrations were in ground water about 0.25 mile downgradient from the pits. Strong and moderate correlation of water level and the contaminant concentrations near the source areas and low correlation outside and downgradient from the source areas indicates a diminishing of the water level/contaminant relation with downgradient flow.

Ground water was not progressively older at all locations downgradient from the Open Burn/Open Detonation site indicating multiple recharge areas. Major ion and strontium concentrations and $\delta^{2}H$ and $\delta^{18}O$ values identified similar sources of recharge waters comprising the aquifer except along the basin periphery where recharge water may be influenced by dissolution of mineral assemblages associated with ore deposits that are present along the basin margins. Ground-water ages, dissolved-solids concentrations, and calcium-strontium concentrations indicate limited or partial connectivity between fractures and contributions of uncontaminated recharge water downgradient from the site that dilutes contaminant concentrations. Changes in RDX and nitrate concentration patterns, the presence of methane, changes in carbon dioxide concentrations and $\delta^{15}N$ and $\delta^{34}S$ values, and variable reduction-oxidation conditions suggest degradation of contaminants in the downgradient direction. Estimated values of electron potential were assigned to ground water collected in October 2005 from all monitoring sites at the Hazardous Test Area. Moderate to strong reducing conditions were present upgradient from the Open Burn/Open Detonation site, at the site, and at various locations downgradient from the site, but the aquifer contained well-oxygenated water between many of the reducing areas. The spatial variability of reduction-oxidation conditions in the aquifer exemplifies the partial connectivity of the fracture system(s). Dilution of the contaminants is likely dominant where oxidizing conditions are present and degradation likely assists in naturally attenuating the contaminants in areas of reducing conditions. Substantial contaminant transport beyond the existing areal extent of the contaminants appears unlikely given the relative “stability” of contaminant concentrations from 1996 to 2006 and the ongoing processes of dilution and degradation that produce this concentration stability.

Introduction

In 2007, the U.S. Geological Survey (USGS), in cooperation with U.S. Army White Sands Missile Range (WSMR), conducted an analysis of ground-water geochemical data collected at the Hazardous Test Area (HTA). The goal was to evaluate the temporal and spatial variability of the anthropogenic compounds of RDX (explosive compound associated with C-4), nitrate, and perchlorate (oxidizer associated with rocket propellant) contaminating the fractured-granite aquifer at the Open Burn/Open Detonation site (OB/OD site) at HTA, to evaluate source characteristics, and to examine possible natural attenuation mechanisms that may have stabilized contaminant concentrations.

The Hazardous Test Area is located in southern New Mexico (fig. 1), about 25 miles (mi) east of Las Cruces and 10 mi north of WSMR Main Post. The OB/OD site is located in the northwest part of HTA (fig. 2) and consisted of two open detonation pits. The pits were excavated from native soil in 1953, and berms were constructed with native soil on all sides, except for vehicle access points. The west pit measured approximately 100 by 180 feet (ft), and the east pit was approximately 170 by 180 ft. The pits were used for the demolition of ordnance including explosives and propellants (Black and Veatch Waste Science, Inc., 1995). Most demolitions at the OB/OD site were conducted in the east pit, and the site was officially closed December 31, 2000. In 2002 and 2003, earthen berms along the southern and eastern sides of each OB/OD pit were pushed into the pits and the area regraded to the present topographic slope.

White Sands Missile Range and the USGS have been monitoring an expanding monitoring-site network at HTA (fig. 2) since 1996 under the guidance of the State of New Mexico and the guidelines of the Resources Conservation and Recovery Act (RCRA). Sampling of the HTA monitoring-site network has detected three main anthropogenic compounds: RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), nitrate (NO_3^- plus NO_2^-, reported as nitrogen), and perchlorate (ClO_4^-). RDX and nitrate have been detected in ground water from wells at the OB/OD site since regular monitoring began in 1996 and perchlorate has been detected since 1999 when monitoring of this compound began. Wells have been added to the network during the period of study to better define the areal extent of the contamination and improved analytical capabilities have provided better concentration resolution, but during the entire history of monitoring at HTA, the contaminant concentrations have remained relatively stable across the area (fig. 3).

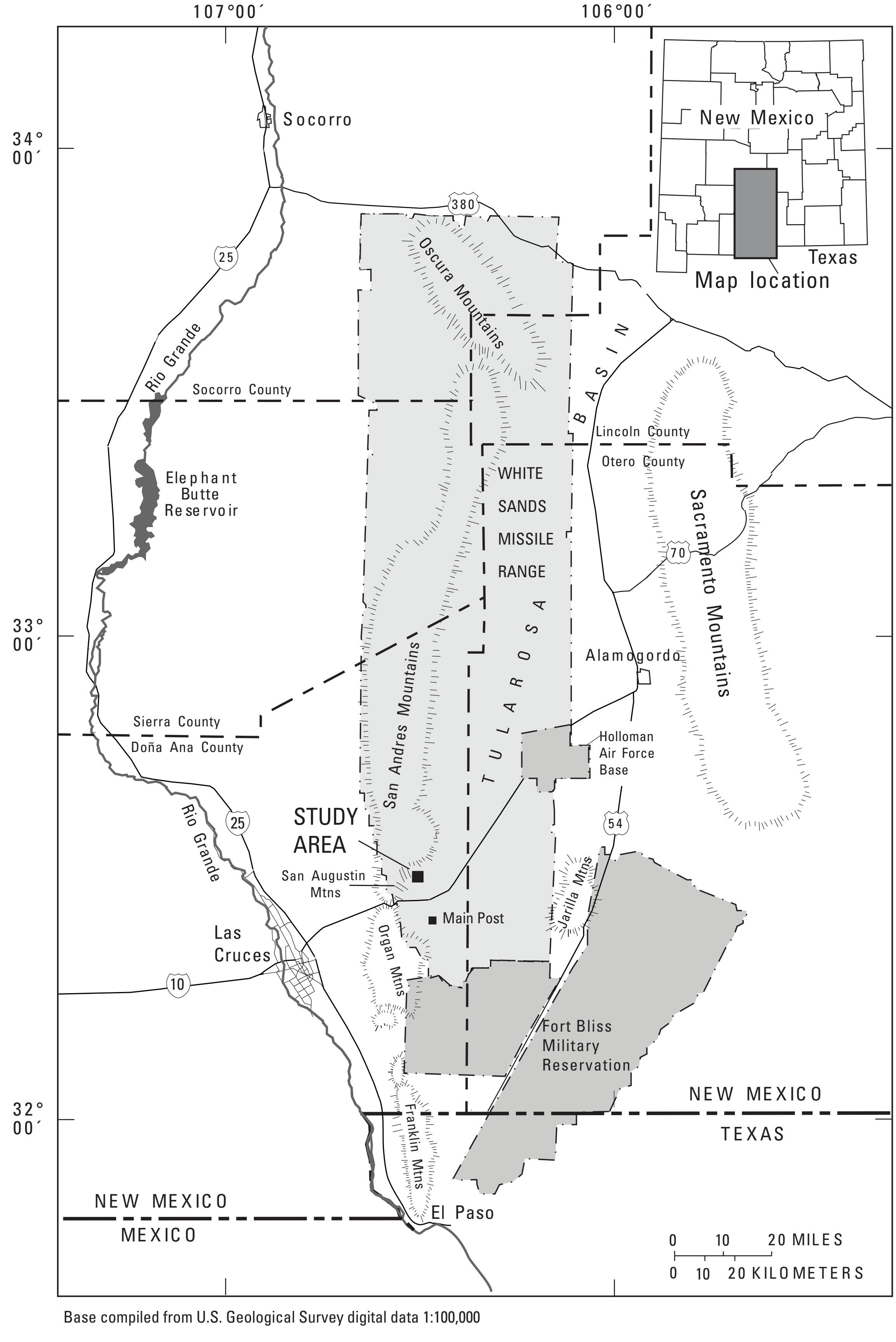
An analysis of hydraulic conductivities in fractures penetrated by monitoring wells in the OB/OD site area in 2003 (wells 10A–29) indicated a median hydraulic conductivity of 2 feet per day (ft/d) and a likely 1,000 feet per year (ft/yr) average (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The largest contaminant concentrations are spatially static (same wells continue to contain the largest contaminant concentrations), but the contaminants have been detected downgradient with addition of new wells (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Natural attenuation likely is decreasing contaminant concentrations with downgradient flow, and this decrease is balanced by a continued input of the contaminants from recharge interacting with contaminant sources in and around the pits (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Natural attenuation consists of physical, chemical, or biological processes that reduce contaminant concentrations in soil or ground water (U.S. Environmental Protection Agency, 1999). These processes can include biodegradation, dispersion, dilution, sorption, volatilization, or radioactive decay. The processes of biodegradation (degradation by microorganisms) and dispersion/dilution (dilution) are the most applicable to the nonvolatile and nonradioactive compounds of RDX, nitrate, and perchlorate.

Purpose and Scope

The purpose of this report is to examine geochemical trends and investigate the possibility of natural attenuation controlling the downgradient migration of large concentrations of the contaminants that enter the HTA fractured-granite aquifer at the OB/OD site. For purposes of this report, examination of natural attenuation processes is focused on dilution and degradation that would decrease the concentration of each contaminant with downgradient transport. This report describes the temporal and spatial concentration variability of the anthropogenic compounds of RDX, nitrate, and perchlorate as they react to recharge, ground-water flow, and likely natural attenuation processes. Data from 1996–2006 were compiled for 18 wells composing two transects extending across HTA from the existing monitoring-site network. Additional data including—water levels, dissolved oxygen, pH, RDX degradates (hexahydro-1-nitroso-,3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)), dissolved gases, major ions, trace elements, ground-water ages, stable isotopes of water, nitrogen and oxygen isotopes of nitrate, and sulfur isotopes of sulfate—for ground water at additional monitoring-site locations were used to better understand dilution and degradation processes affecting RDX, nitrate, and perchlorate concentrations in the HTA fractured-granite aquifer.

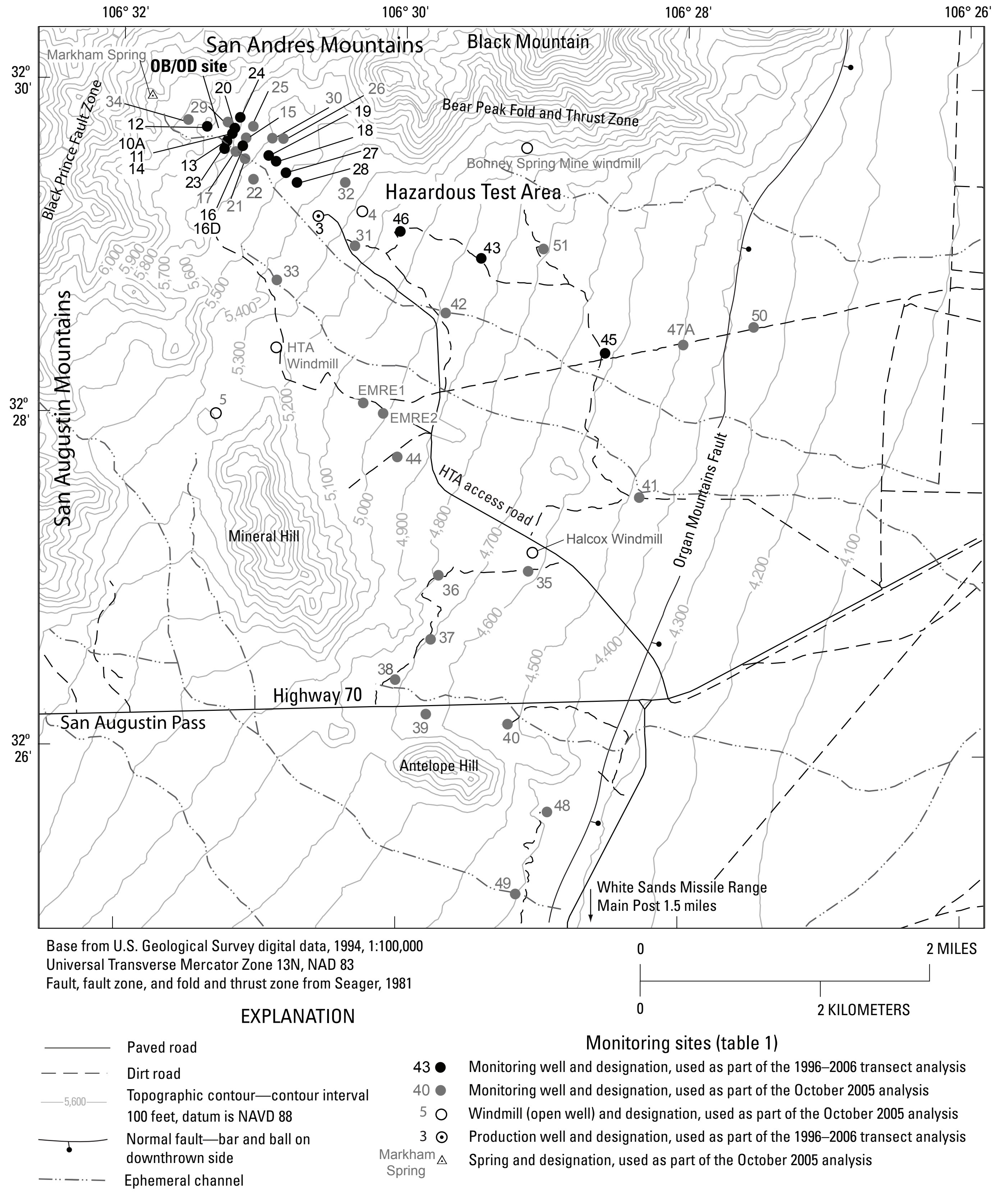
Description of the Study Area

The OB/OD site is located near the western edge of the Tularosa Basin (fig. 1) at an altitude of approximately 5,700 ft on the pediment slope of the San Augustin and San Andres Mountains. A thin soil profile consisting mostly of granite wash covers much of the terrain, but granite outcrops are visible across the surface of the pediment. Vegetation consists mostly of perennial grasses, woody brushes, yucca, prickly



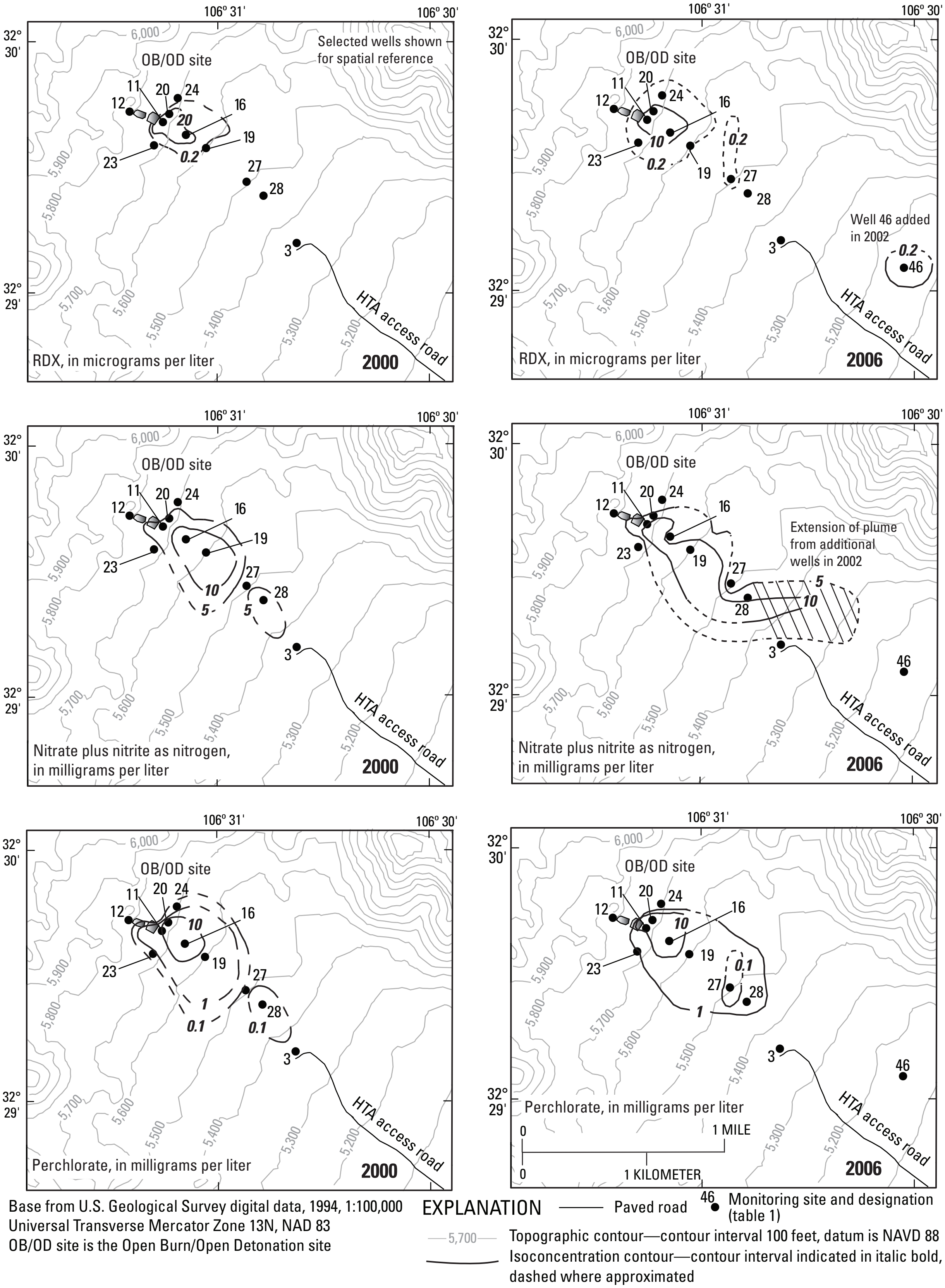
Base compiled from U.S. Geological Survey digital data 1:100,000

Figure 1. Location of White Sands Missile Range, New Mexico, and the study area.



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83
Fault, fault zone, and fold and thrust zone from Seager, 1981

Figure 2. Hazardous Test Area, Open Burn/Open Detonation (OB/OD) site, and monitoring sites, White Sands Missile Range, New Mexico.



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83
OB/OD site is the Open Burn/Open Detonation site

Figure 3. Example of relative stability of contaminant concentrations in ground water at the Open Burn/Open Detonation (OB/OD) site, White Sands Missile Range, New Mexico, 2000 and 2006 (modified from Ralph Wilcox, U.S. Geological Survey, written commun., 2003 and 2006).

pear, and barrel cactus. A series of nearly parallel ephemeral drainage channels extend east-southeast across the OB/OD site and continue through the HTA area to the valley floor of the Tularosa Basin (major ephemeral drainages shown in figure 2). The climate of the Tularosa Basin is semiarid, the basin averages less than 10 inches of precipitation per year for the interior of the basin, and average minimum and maximum temperatures range from 40 to 78°F (Western Regional Climate Center, 2007). The mountains bounding the basin average greater annual precipitation, and the eastern flank of the Organ, San Augustin, and San Andres Mountains typically receive 10 to 16 inches of precipitation per year (Waltemeyer, 2001).

Geology and Hydrology

The study area is surrounded by the San Andres Mountains to the north, San Augustin Mountains to the west, the Organ Mountains to the south, and the floor of the Tularosa Basin to the east (figs. 1 and 4). The San Augustin Mountains represent a transition from the Organ Mountains' granite batholith to the tilted and faulted, Paleozoic marine strata of the San Andres Mountains (Seager, 1981). The Hazardous Test Area is located on a pediment composed of a granite pluton of Precambrian age bounded on the north by the Bear Peak Fold and Thrust Zone, the Black Prince Fault Zone to the west, the Organ Batholith to the south, and the Organ Mountains Fault to the east (Seager, 1981) (fig. 4). The granite pluton is an eroded part of an ancient mountain or rift system formed 1.45 to 1.35 Ga that was followed by a subsequent Precambrian extensional event that emplaced diorite-diabase dikes in the area (Seager, 1981; Raatz, 2002; New Mexico Bureau of Geology and Mineral Resources, 2003). Movement of the pluton occurred during the Laramide Orogeny (80 and 40 Ma) and Rio Grande Rift deformation (35 Ma to present), and the pluton was likely rotated to its present configuration with movement along the Organ Mountains Fault, the Bear Peak Fold and Thrust Zone, and the Black Prince Fault Zone (Seager, 1981). Structural relations between the Precambrian granite pluton, the Bear Peak Fold and Thrust Zone, and the Black Prince Fault Zone indicate that Laramide deformation produced vertical uplift in a regional compressional environment (Seager, 1981). This uplift produced the current slope and configuration of this pediment basin that drains east to southeast to the floor of the Tularosa Basin.

In the study area, a thin veneer (5 to 10 ft) of well-mixed, weathered-granite alluvium and a larger-clast, granite wash overlie the weathered, upper layer of the Precambrian granite pluton (fig. 4). The surface exposure of the pediment granite of the HTA basin is densely jointed, and a combination of granular disintegration, exfoliation, and spherical weathering produces outcrops of rounded boulders, knobs, and hills (Seager, 1981). The pluton consists of two types of granite—one is gray/brown with a somewhat porphyritic texture and the other is bright red and contains abundant coarse-grained, pink, orthoclase feldspar. Diorite dikes are common in the granite outcrops, the dikes trend east to northeast at the surface, and typically range from 1 to 11-ft thick but can be as much as 100-ft thick (Seager, 1981). The principal minerals in the dikes are green amphibole and plagioclase feldspar, ranging in composition from labradorite to oligoclase (Dunham, 1935). The diorite origin is unknown but may have been emplaced in the Precambrian when diorite-diabase intrusions formed during an extensional environment (Raatz, 2002) or may be associated with the andesitic volcanism during emplacement of the Organ Batholith during the Eocene (Maciejewski, 1996).

The fractured-granite aquifer at HTA is almost entirely within the granite pluton. Paleozoic marine strata—including sandstone, dolomite, shale, and limestone formations—are adjacent to the Precambrian granite along the northern perimeter across the Bear Peak Fold and Thrust Zone (Seager, 1981). Aquifer recharge likely occurs along the pediment/mountain-front interface and possibly in the ephemeral channels (Risser, 1988). Ground-water flow paths are probably tortuous because flow paths are controlled by the geometry of hydraulically conductive fractures. Boreholes drilled for installation of monitoring wells did not produce water until such a fracture(s) was penetrated, but the extent and distribution of the fractures in the study area are poorly understood. Fracture orientation is highly variable at the OB/OD site—orientation and dip of fractures were distinctly different between fractures penetrated during exploratory drilling in the east and west pits and also variable in the HTA area (Ralph Wilcox, U.S. Geological Survey, written commun. 2003).

Anthropogenic Compounds

Since 1996, contamination of ground water at HTA has been evident (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The largest concentrations have remained near and around the OB/OD pits, and contaminant concentrations in ground water at all monitoring wells have remained relatively stable (Ralph Wilcox, U.S. Geological Survey, written commun., 2003) (fig. 3). Detection of the contaminants in ground water at the site prompted WSMR personnel to authorize an investigation of soil and rock samples from the surface and subsurface in and around the OB/OD pits in 1999. RDX and other explosive compounds (1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX); 2,4,6-dintrotoluene (246-DNT); 4-amino-2,6-dinitrotoluene (426-DNT); 2,4,6-trinitrotoluene (246-TNT); and tetryl) were detected in pit-soil samples. The largest concentrations were of RDX, and HMX was the most prevalent (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The largest explosives concentrations were in surface samples collected from the west pit, particularly along the southwestern border (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Nitrate was detected in 72 of 96 soil/rock samples in the pits and 38 of 43 samples around the pits and ranged from 0.1 to 18.5 milligrams per kilogram; concentrations were larger in the west pit than the east pit (Ralph Wilcox, U.S.

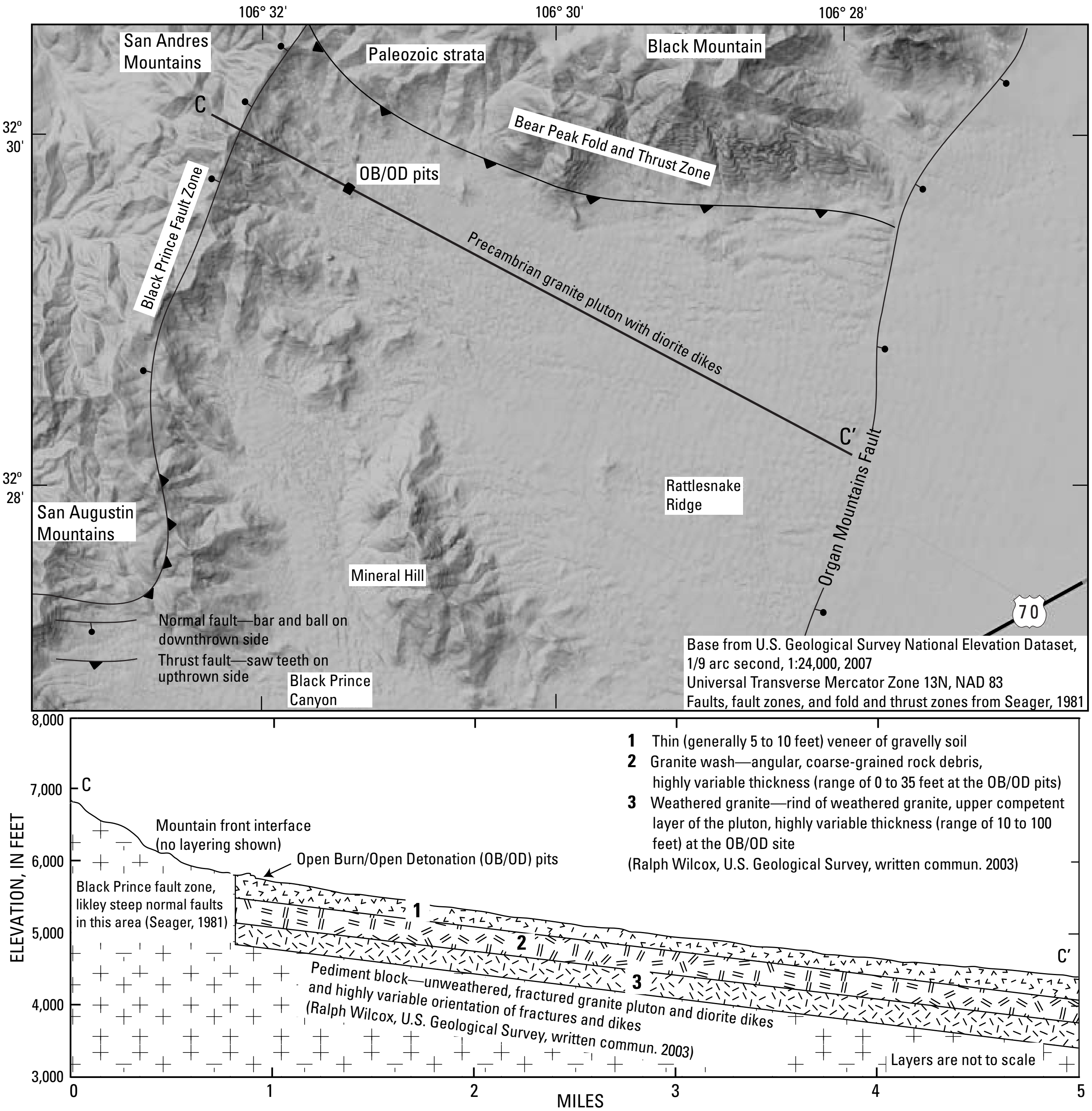


Figure 4. Geologic characteristics of the fractured-granite pluton at the Hazardous Test Area, White Sands Missile Range, New Mexico.

Geological Survey, written commun., 2003). Perchlorate was less prevalent than the explosives but was found in and around the OB/OD pits in surface and subsurface samples. Pieces of solid rocket fuel containing perchlorate have been found at the surface in and around the OB/OD pits (Ralph Wilcox, U.S. Geological Survey, oral commun., 2005). The source of contamination appears to be focused within the pits, but ordnance demolition also has scattered the source materials outside of the pits.

RDX is a highly energetic cyclic nitroamine and is a commonly used military explosive. It is soluble in water (about 38–100 mg/L possible), and sorption of RDX to soil material is variable but typically low (Seth-Smith and others, 2002). Degradation of RDX in ground water mainly occurs under anaerobic conditions and is facilitated by certain bacteria (McCormick and others, 1981; Kitts and others, 1994; Speitel and others, 2001). RDX will sequentially degrade to MNX, DNX, and TNX, and may undergo further degradation with cleavage of the ring formation to produce basic carbon and nitrogen compounds such as carbon dioxide, methane, nitrate, and ammonia (McCormick and others, 1981; Hawari and others, 2000). RDX also can degrade in oxygenated water and in the presence of select bacteria and fungus (Fournier and others, 2002; Seth-Smith and others, 2002; Thompson and others, 2005). Aerobic bacteria utilizing RDX as a nitrogen source may cause ring cleavage to produce 2,4-diazabutanal, ammonia, nitrous oxide, formaldehyde, and carbon dioxide (Fournier and others, 2002). However, other bacteria are capable of using RDX as a carbon and nitrogen source and may produce 2,4-diazabutanal, nitrate, and formaldehyde (Thompson and others, 2005).

Nitrate is stable in a range of environments, is highly soluble, and moves readily with the flow of water (Hem, 1989). The biodegradation of nitrate (denitrification) by microorganisms is most efficient in anaerobic conditions and produces nitric oxide, nitrous oxide, and nitrogen gas (Wendland and others, 1994). Degradation of nitric oxide and nitrous oxide will produce nitrogen gas as the final byproduct. Denitrification occurs readily in anaerobic conditions because nitrate is the dominant electron acceptor when oxygen is deficient (Wendland and others, 1994; Chapelle, 1993). Although the available free energy from the reduction of nitrate is similar to that of oxygen, the reduction of oxygen is more thermodynamically favorable. Additionally the activity of the denitrifying enzyme, *nitrate reductase,* is inhibited by the presence of molecular oxygen (Chapelle, 1993).

Perchlorate is used as a rocket propellant because of its strong oxidizing properties (Brown and Baohua, 2006). It is highly soluble in water (maximum of 185 grams per liter) and generally will not adsorb to soil material (Urbansky and Brown, 2002). These characteristics allow perchlorate to easily move with ground-water flow. Many bacteria in aqueous environments can use perchlorate as a reducing compound to oxidize other compounds, leading to the degradation of perchlorate to chlorate (ClO_3^-) and chlorite (ClO_2^-) (Coates and Achenbach, 2004). Further degradation results in the release of chloride and oxygen (Van Ginkel and others, 1996).

Previous Studies

No published documents are available that describe the HTA fractured-granite aquifer. From 1996–2006, the USGS provided quarterly data reports of HTA ground-water monitoring to WSMR for submission to the State of New Mexico under RCRA guidelines. All annual ground-water-level data and ground-water-quality data collected by the USGS in the HTA area from 1996–2006 are available in the USGS National Water Information System (NWISWeb at *http://waterdata.usgs.gov/usa/nwis*).

Study Methods

Contaminant data were compiled for 18 (table 1 and fig. 5) of 47 sites in the existing monitoring-site network for the period of record (1996–2006). Dissolved oxygen, pH, and water level for ground water at these wells were collected during sampling and are included in the analysis where applicable. In addition to contaminant and field data, ground-water tracer data were compiled for monitoring sites sampled in October 2005. The tracer data includes dissolved solids, trace elements, major ions, tritium-helium dating, RDX degradates (MNX, DNX, and TNX), dissolved gases, stable isotopes of water, nitrogen and oxygen isotopes of nitrate, and sulfur isotopes of sulfate (table 2). Of these tracers, only dissolved-solids and trace-element concentrations are available for all sites in the HTA monitoring network for October 2005; selected sites were sampled for analysis of the remaining tracer data. The October 2005 data represent a “snapshot” of the ground-water characteristics for interpretation of the natural attenuation processes of dilution and degradation.

The selected tracer constituents are applicable for evaluating ground-water flow paths and geochemical processes such as water-rock interaction and changes in reduction-oxidation conditions. Dissolved-solids, major-ion, and trace-element concentrations can provide general compositional characteristics and are indicators of water-rock interactions and possible reduction-oxidation conditions (Hem, 1989). Ground-water age can be determined through the analysis of radioactive isotopes, such as tritium that is incorporated into precipitation and carried to an aquifer through recharge. A more accurate method of dating than simply using tritium is the tritium-helium method, which mass balances the helium isotopes to determine the amount of ^{3}He derived from radioactive decay of ^{3}H in the water sample (Schlosser and others, 1989). The application of water isotopes ($^{2/1}$H as δ^2H and $^{18/16}$O as δ^{18}O) allows constraint of hydrologic flow paths because of the variation in isotopic composition of precipitation that may discriminate recharge areas (Genereux and Hooper, 1998). Nitrogen and oxygen stable isotope ratios of nitrate ($^{15/14}$N as δ^{15}N and $^{18/16}$O as δ^{18}O) and sulfur stable isotopes of sulfate

Table 1. Open Burn/Open Detonation Site and Hazardous Test Area study area monitoring-site information.

[USGS, U.S. Geological Survey; NAD 83, North American Datum of 1983; NAVD 88, North American Vertical Datum of 1988; ls, land surface; PVC, polyvinyl chloride; HTA, Hazardous Test Area; OB/OD, Open Burn/Open Detonation; NA, not available]

Site designation (figs. 2 and 5)	USGS site identification number	Latitude (NAD 83)	Longitude (NAD 83)	Land-surface altitude (NAVD 88)	Well depth (feet below ls)	Casing material	Screen interval (feet below ls)	Installed	Dedicated pump
Transect *A–A′*: monitoring sites perpendicular to ground-water flow—well line is southwest to northeast immediately downgradient from east pit (fig. 5)									
23	322935106311801	32 29 35.22N	106 31 17.48W	5,681.9	135	PVC	110-130	December 1999	Yes
13	322938106311601	32 29 37.13N	106 31 15.84W	5,692.1	120	PVC	95-115	March 1998	Yes
14	322939106311701	32 29 39.31N	106 31 16.69W	5,697.9	110	PVC	90-110	July 1995	No
10A	322941106311502	32 29 39.82N	106 31 15.08W	5,690.1	80	PVC	NA	June 1995	Yes
11	322941106311301	32 29 40.74N	106 31 15.04W	5,693.4	85	PVC	60-80	March 1991	Yes
20	322943106311401	32 29 42.75N	106 31 13.30W	5,701.5	100	PVC	75-95	March 1998	Yes
24	322947106311101	32 29 46.61N	106 31 10.95W	5,694.1	163	PVC	139-159	December 1999	No
Transect *B–B′*: monitoring sites parallel to ground-water flow—well line is northwest to southeast from upgradient from the OB/OD pits to the SE corner of the HTA area (fig. 5)									
12	322943106312301	32 29 43.21N	106 31 23.61W	5,757.4	155	PVC	130-150	March 1991	Yes
10A	322941106311502	32 29 39.82N	106 31 15.08W	5,690.1	80	PVC	NA	June 1995	Yes
16	322937106310901	32 29 37.77N	106 31 08.50W	5,643.3	103	PVC	78-98	March 1997	Yes
16D	322937106310902	32 29 37.50N	106 31 08.16W	5,640.1	160	PVC	134-154	March 1998	Yes
19	322935106310301	32 29 34.69N	106 31 02.79W	5,597.0	147	PVC	122-142	March 1998	Yes
18	322932106305601	32 29 31.24N	106 30 54.71W	5,538.7	130	PVC	105-125	March 1998	Yes
27	322927106305101	32 29 26.86N	106 30 51.19W	5,496.6	179	PVC	159-179	December 1999	No
28	322923106304601	32 29 23.50N	106 30 46.38W	5,453.4	149	PVC	120-140	December 1999	Yes
3	322910106303601	32 29 11.68N	106 30 37.13W	5,357.9	160	PVC	60-150	Feburary 1984	Yes
46	322906106300301	32 29 06.27N	106 30 02.51W	5,159.2	145	PVC	120-140	January 2002	Yes
43	322857106292801	32 28 57.00N	106 29 27.85W	4,956.9	99	PVC	77-97	January 2002	Yes
45	322823106283501	32 28 23.34N	106 28 34.57W	4,637.7	139	PVC	78-138	January 2002	Yes
Monitoring sites used for the snapshot analysis of data from October 2005 (fig. 2)									
4	322913106301801	32 29 13.95N	106 30 20.58W	5,269.5	72	Steel	NA	NA	Yes
5	322756106311601	32 27 55.67N	106 31 15.74W	5,360.0	122	Steel	NA	NA	No
15	322938106310801	32 29 38N	106 31 08W	5,645.1	102	PVC	77-97	July 1996	Yes
17	322936106311001	32 29 36N	106 31 10W	5,643.6	110	PVC	85-105	March 1991	Yes
21	322933106310901	32 29 33N	106 31 09W	5,621.5	110	PVC	85-105	November1999	Yes

Table 1. Open Burn/Open Detonation Site and Hazardous Test Area study area monitoring-site information.—Continued

[USGS, U.S. Geological Survey; NAD 83, North American Datum of 1983; NAVD 88, North American Vertical Datum of 1988; ls, land surface; PVC, polyvinyl chloride; HTA, Hazardous Test Area; OB/OD, Open Burn/Open Detonation; NA, not available]

Site designation (figs. 2 and 5)	USGS site identification number	Latitude (NAD 83)	Longitude (NAD 83)	Land-surface altitude (NAVD 88)	Well depth (feet below ls)	Casing material	Screen interval (feet below ls)	Installed	Dedicated pump
22	322924106310501	32 29 24N	106 31 05W	5,559.3	110	PVC	85-105	December1999	Yes
25	322943106310501	32 29 43N	106 31 06W	5,645.7	120	PVC	95-115	December1999	Yes
26	322940106305101	32 29 40N	106 30 51W	5,533.7	200	PVC	180-200	December1999	Yes
29	322944106311601	32 29 44N	106 31 16W	5,725.5	158	PVC	134-154	December1999	Yes
30	322939106305701	32 29 39N	106 30 57W	5,570.2	200	PVC	176-196	December1999	Yes
31	322902106302201	32 29 02.48N	106 30 23.94W	5,251.7	85	PVC	65-85	January 2002	Yes
32	322924106302601	32 29 24.05N	106 30 28.27W	5,343.8	75	PVC	55-75	January 2002	Yes
33	322848106305501	32 28 48.42N	106 30 56.83W	5,368.8	107	PVC	87-107	January 2002	Yes
34	322943106312801	32 29 43.48N	106 31 29.88W	5,794.9	103	PVC	83-103	January 2002	Yes
35	322704106290601	32 27 04.61N	106 29 08.01W	4,618.4	159	PVC	139-159	January 2002	No
36	322702106294401	32 27 02.71N	106 29 46.23W	4,798.5	97	PVC	77-97	January 2002	No
37	322639106294701	32 26 39.52N	106 29 49.2W	4,695.9	138	PVC	118-138	January 2002	No
38	322624106300201	32 26 24.82N	106 30 04.01W	4,723.9	119	PVC	99-119	January 2002	No
39	322612106294901	32 26 12.48N	106 29 50.73W	4,649.4	149	PVC	129-149	January 2002	No
40	322609106291401	32 26 09.26N	106 29 15.93W	4,513.6	199	PVC	179-199	January 2002	No
41	322731106281901	32 27 31.72N	106 28 21.12W	4,502.1	125	PVC	105-125	January 2002	Yes
42	322837106294301	32 28 37.33N	106 29 44.64W	4,993.5	137	PVC	117-137	January 2002	Yes
44	322745106300201	32 27 45.75N	106 30 04.4W	4,938.3	139	PVC	119-139	January 2002	No
47A	322827106280101	32 28 27.04N	106 28 03.31W	4,491.7	184	PVC	160-180	February 2003	No
48	322538106285701	32 25 37.84N	106 28 58.55W	4,406.4	159	PVC	139-159	January 2002	No
49	322508106291001	32 25 08N	106 29 11.62W	4,411.8	419	PVC	389-419	December2001	Yes
50	322834106273201	32 28 33.64N	106 27 33.38W	4,366.4	516	PVC	486-516	January 2002	Yes
51	322901106290101	32 29 00.93N	106 29 03.39W	4,834.8	145	PVC	122-142	February 2003	No

Table 1. Open Burn/Open Detonation Site and Hazardous Test Area study area monitoring-site information.—Continued

[USGS, U.S. Geological Survey; NAD 83, North American Datum of 1983; NAVD 88, North American Vertical Datum of 1988; ls, land surface; PVC, polyvinyl chloride; HTA, Hazardous Test Area; OB/OD, Open Burn/Open Detonation; NA, not available]

Site designation (figs. 2 and 5)	USGS site identification number	Latitude (NAD 83)	Longitude (NAD 83)	Land-surface altitude (NAVD 88)	Well depth (feet below ls)	Casing material	Screen interval (feet below ls)	Installed	Dedicated pump
EMRE1	322804106301701	32 28 04N	106 30 17W	5,045.2	180	PVC	155-175	December1999	Yes
EMRE2	322800106300901	32 28 00N	106 30 09W	4,996.1	100	PVC	76-95	December1999	Yes
HTA Windmill	322310106305101	32 28 24N	106 50 52W	5,214.7	NA	NA	NA	NA	
Markham Spring	322952106314401	32 29 52.32N	106 31 45.99W	6,062.2	NA	NA	NA	NA	Yes
Bonney Spring Mine Windmill	322938106291101	32 29 37.58N	106 29 10.67W	5,042.1	62	Steel	NA	NA	No
Halcox Windmill	322711106290401	32 27 11.33N	106 29 05.98W	4,642.0	37	NA	NA	NA	No

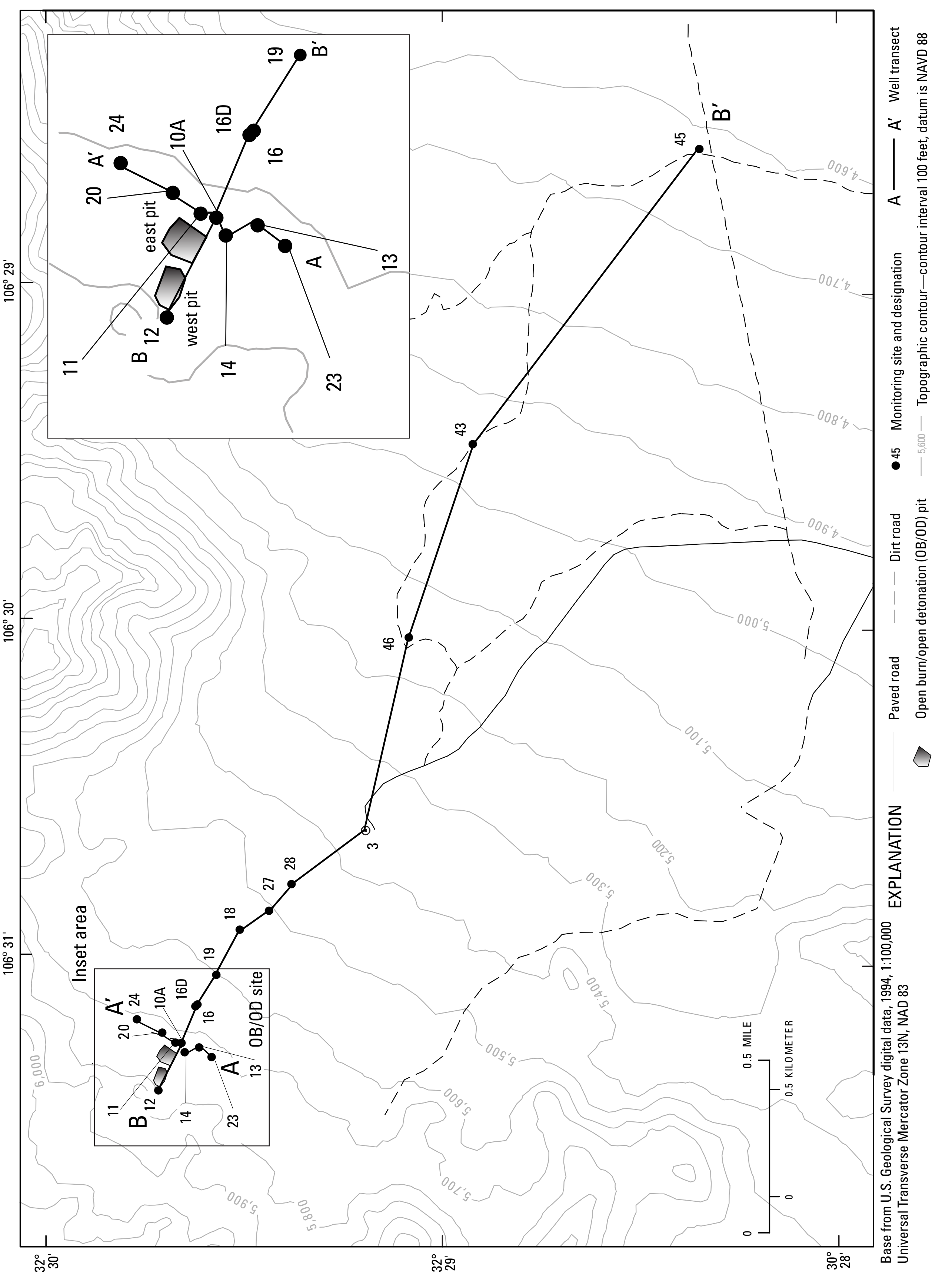


Figure 5. Location of the study’s monitoring-site transects at the Hazardous Test Area, White Sands Missile Range, New Mexico.

Table 2. Sample analytes and laboratory analysis methods.

[µg/L, micrograms per liter; mg/L, milligrams per liter; µmol/L, micromoles per liter; USGS, U.S. Geological Survey; ‰, per mil]

Constituent(s)	Description	Method/Lab code	Analytical precision
Contaminant and field data collected from 1996–2006:			
Explosives	Explosive compounds[1], including RDX and its degradates, analyzed by HPLC[1]	SW846 8330[2]	0.05 to 0.25 µg/L
Nitrate	NO_3 and NO_2 as N	MCAWW 353.2[3]	0.02 mg/L
Perchlorate	ClO_4	TestAmerica DEN LC-0024 (SW6860[2])	0.01 µg/L
Field values	Dissolved oxygen, pH	YSI 550A (+0.3 mg/L), Orion 250A+ (±0.02 pH)	±0.3 mg/L, ±0.02 pH
Tracer data collected in October 2005:			
Dissolved gases	Ar, CH_4, CO_2, He, N_2, O_2	Gas chromatography with thermal conductivity detector (Ar, He, N_2, O_2) and flame ionization detector (CH_4, CO_2)	±0.1 µmol/L
Major ions	Br, Cl, F, SO_4, Ca, Mg, Na, K	MCAWW 300.0A[3], SW846 6010B[2]	0.1 to 1 mg/L
Tritium-helium dating	$^3H/^3He$	USGS 1033 (Schlosser and others, 1989)	±0.5 years
Water isotopes	$^{2/1}H$, $^{18/16}O$	USGS 1142 (Coplen and others, 1991; Epstein and Mayeda, 1953)	±2 ‰ as δ^2H and ±0.2 ‰ $\delta^{18}O$
Nitrate isotopes	$^{15/14}N$ and $^{18/16}O$ of nitrate	USGS 2899 (Sigman and others, 2001)	±0.5 ‰ as $\delta^{15}N$ and as $\delta^{18}O$
Sulfate isotopes	$^{34/32}S$ of sulfate	USGS 1951 (Carmody and others, 1997; Glesemann and others, 1994)	±0.4 ‰ as $\delta^{34}S$
Trace elements	Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Si, Sr, Tl, U, V, Zn	SW846 6010B[2], SW846 6020[2]	0.01 to 2 µg/L

[1] RDX; HMX; tetryl; 2-amino-4,6-dinitrotoluene; 4-amino-2,6-dinitrotoluene; 1,3-, 2,4-, and 2,6-dinitrotoluene; nitrobenzene; 2-, 3-, and 4-nitrotoluene; 1,3,5-trinitrobenzene; and 2,4,6-trinitrotoluene by high-performance liquid chromatography.

[2] U.S. Environmental Protection Agency, 1983.

[3] U.S. Environmental Protection Agency, 1986.

($^{34/32}S$ as $\delta^{34}S$) can be indicators of possible nitrate or sulfate sources and biodegradation of nitrogen and sulfur-containing compounds (Kendall, 1998 and Canfield, 2001).

The 18 wells selected for analysis of 1996–2006 data represented two transects at the OB/OD site—one perpendicular to ground-water flow (transect *A–A´*) and one parallel to ground-water flow (transect *B–B´*). Transect *A–A´* (about 0.25 mi in length) is located immediately downgradient from the OB/OD pits and was used to examine spatial and temporal variability of the contaminants coming from the OB/OD site. Transect *B–B´* (about 3.25 mi in length) is parallel to the direction of ground-water flow with an origin upgradient from the OB/OD pits and an endpoint downgradient from the pits where contaminants have not been detected. Trend analysis consisted of graphical and statistical comparison of contaminant concentrations between wells to identify source locations, transport characteristics, and possible natural attenuation of contaminants. All non-detect values (less than method detection level) were assigned zero values. The Wilcoxon rank-sum test was used to test for differences in the contaminant concentration distributions between wells. This nonparametric test assesses whether two sets of non-normal data come from the same distribution (population) or not (Ott, 1993).

To examine aquifer properties that affect contaminant movement, a well's water level and the contaminants' concentrations were analyzed for correlation strength. With the assumption that changes in ground-water flow and contaminant concentrations are related, correlation analysis was used to test the hypothesis that changes in flow are the cause of the small temporal variability of contaminant concentrations. In addition to correlation between water level and contaminant concentrations, RDX and nitrate concentrations were analyzed for strength of correlation to examine the relation of the explosive-based contaminant sources. The nonparametric Kendall's tau rank correlation coefficient (Kendall, 1938) was used to evaluate the strength of correlation between any two variables. This method measures the degree of correlation between rankings of two groups to assess the strength of the relation.

This study implemented USGS study methods described by Lapham and others (1997), and ground-water sample collection followed USGS guidelines established by Wilde and Radtke (2005). Water levels were measured below a known, fixed altitude prior to well purging using either an electric tape or steel tape. Ground-water samples were collected from all monitoring wells using dedicated bladder pumps or a portable submersible pump. A minimum of 20 gallons was purged from each monitoring well prior to sampling. Bladder pumps were operated using compressed nitrogen during well purging and sampling. All samples were analyzed by TestAmerica, Inc., in Arvada, Colorado, except for dissolved gas and isotope samples collected in October 2005. The October 2005 dissolved-gas and isotope samples were analyzed by the USGS Dissolved Gas Laboratory (dissolved gases), Lamont-Doherty Earth Observatory at Columbia University (tritium-helium age dating), and the USGS Reston Stable Isotope Laboratory (hydrogen, oxygen, nitrogen, and sulfur stable isotopes).

Quality-assurance procedures were implemented for water-level measurements and to collect and process water-quality samples. Prior to purging, water levels were repeatedly measured with an electric tape to ensure stability and accuracy. During purging, specific conductance, water temperature, dissolved oxygen, and pH were measured in a flowthrough chamber and allowed to stabilize prior to sample collection. Stable field measurements were used to determine sufficient purge amounts for sampling formation water. After purging 20 gallons, field measurements were deemed stable if three or more sequential measurements during a minimum 10-minute period were within the following ranges: specific conductance, ±0.3 percent; temperature, ±0.2°C; dissolved oxygen, ±0.3 mg/L, and pH, ±0.1 standard unit (Wilde and Radtke, 2005).

Four types of quality-control samples were collected in the field: equipment blanks, replicates, matrix spikes, and trip blanks. One field-equipment blank was collected during each sampling round to determine the adequacy of cleaning procedures of the portable submersible pump. Two sequential replicate samples were collected at randomly selected wells to evaluate laboratory precision. One matrix-spike and one matrix-spike duplicate samples were collected to ascertain matrix interference. Trip blanks were included in all RDX sample shipments to TestAmerica, Inc. for examination of potential contamination from volatile organic compounds during transport. In addition, all laboratories used internal quality-assurance and quality-control practices including the analysis of laboratory-control and method-blank samples with submitted samples. Analysis of quality-control data did not indicate any issues with the quality of the data. Overall, concentrations in equipment and trip blanks were less than laboratory reporting levels, concentrations in replicates were within 10 percent of the environmental-sample concentrations, and matrix-spike and matrix-spike duplicate recoveries were within laboratory guidelines.

Acknowledgments

The cooperation of many individuals and organizations was essential for completion of this study. The authors acknowledge the support and help of the Environmental Compliance Unit at WSMR. In particular, Jose Gallegos who helped guide this study and provided useful insight for completion of study goals.

Geochemical Trends of RDX, Nitrate, and Perchlorate in the Fractured-Granite Aquifer

Contaminant trends in the fractured-granite aquifer at HTA can provide information concerning source location(s), transport, and natural attenuation of the contaminants. Differences in concentrations along transect *A–A´* (fig. 5) were used to identify wells closest to contaminant sources (or the largest contaminant sources) and provide information concerning the lateral dispersal of the sources. Ground-water data from wells along transect *B–B´* were used to evaluate downgradient transport and possible natural attenuation of the contaminants.

Fracture Flow in the Fractured-Granite Aquifer

Ground-water flow in the HTA fractured-granite aquifer likely occurs only in discrete fractures that intersect the upper surface of the pluton where recharge may occur. Ground water was not produced during drilling until a substantial fracture or diorite dike was penetrated during installation of all monitoring wells (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The pluton body is mostly competent with a limited amount of dikes and fractures in the vertical profile (figure 6 provides an example of the vertical profile of the upper pluton). Typically only a few water-producing fractures were identified in each borehole during drilling. Greater depth of drilling did not always penetrate an increasing number of fractures, such as well 28 (fig. 6), where an additional 125 ft of vertical penetration did not intersect any additional water-producing fractures beyond the deepest water-producing fracture at 178.5 ft below land surface. Fractures in the granite pluton dip in all directions, but the predominant orientation generally ranges from south to northeast (fig. 7). The angle of fracture dip also is variable, but clusters of fractures do appear to have similar dip angles (fig. 7). Connectivity between fractures or fracture systems is unknown, but some connectivity is assumed given the relatively smooth potentiometric surface (discussed in the following paragraph) found across HTA (fig. 8). As part of another investigation, an aquifer test in well 11 produced a small response (about 2 inches of drawdown) in the adjacent well 10A that suggests some fracture connectivity in this area (Andrew Robertson, U.S. Geological Survey, oral commun., 2008).

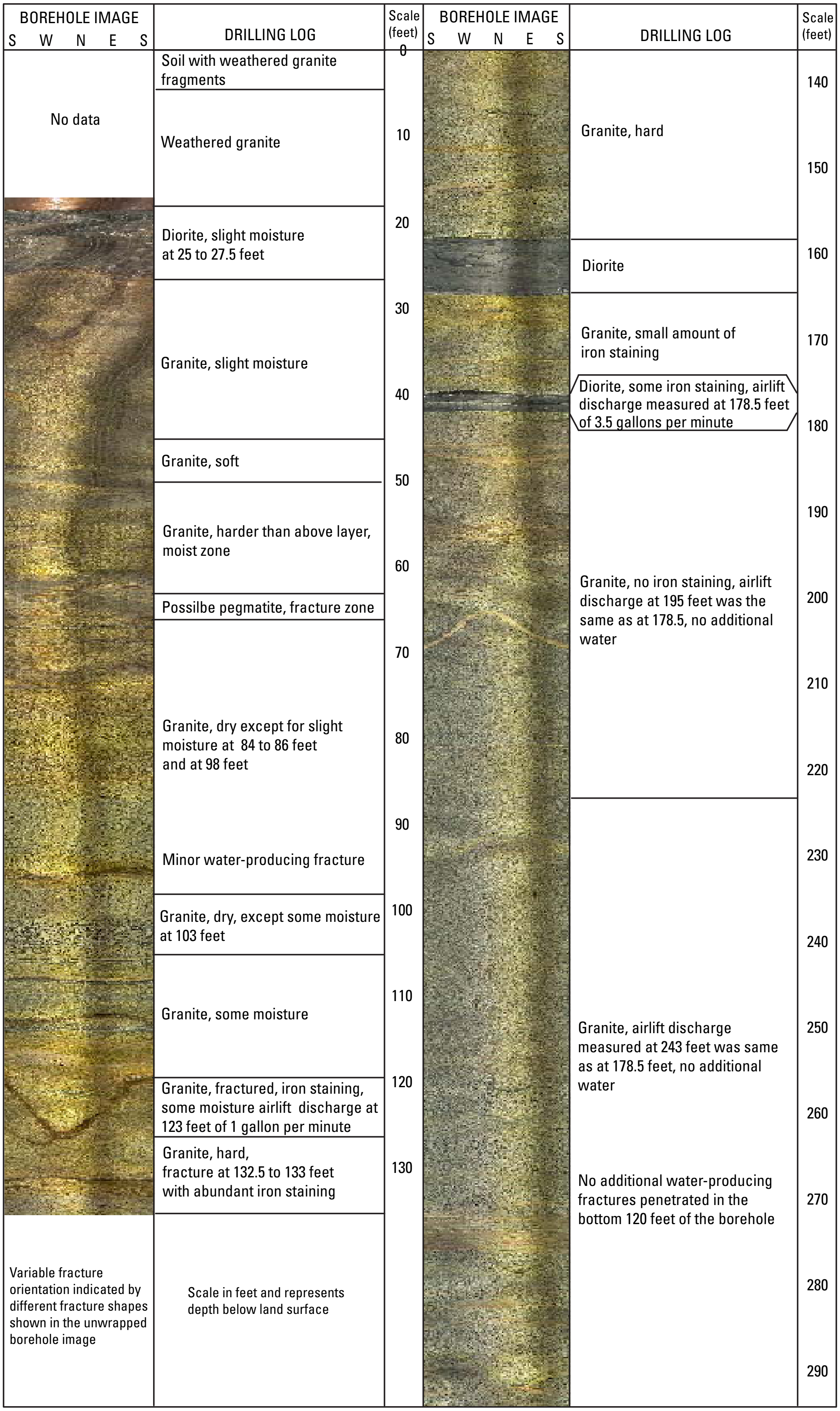


Figure 6. Borehole image and drilling log from construction of well 28 at the Hazardous Test Area, December 1999.

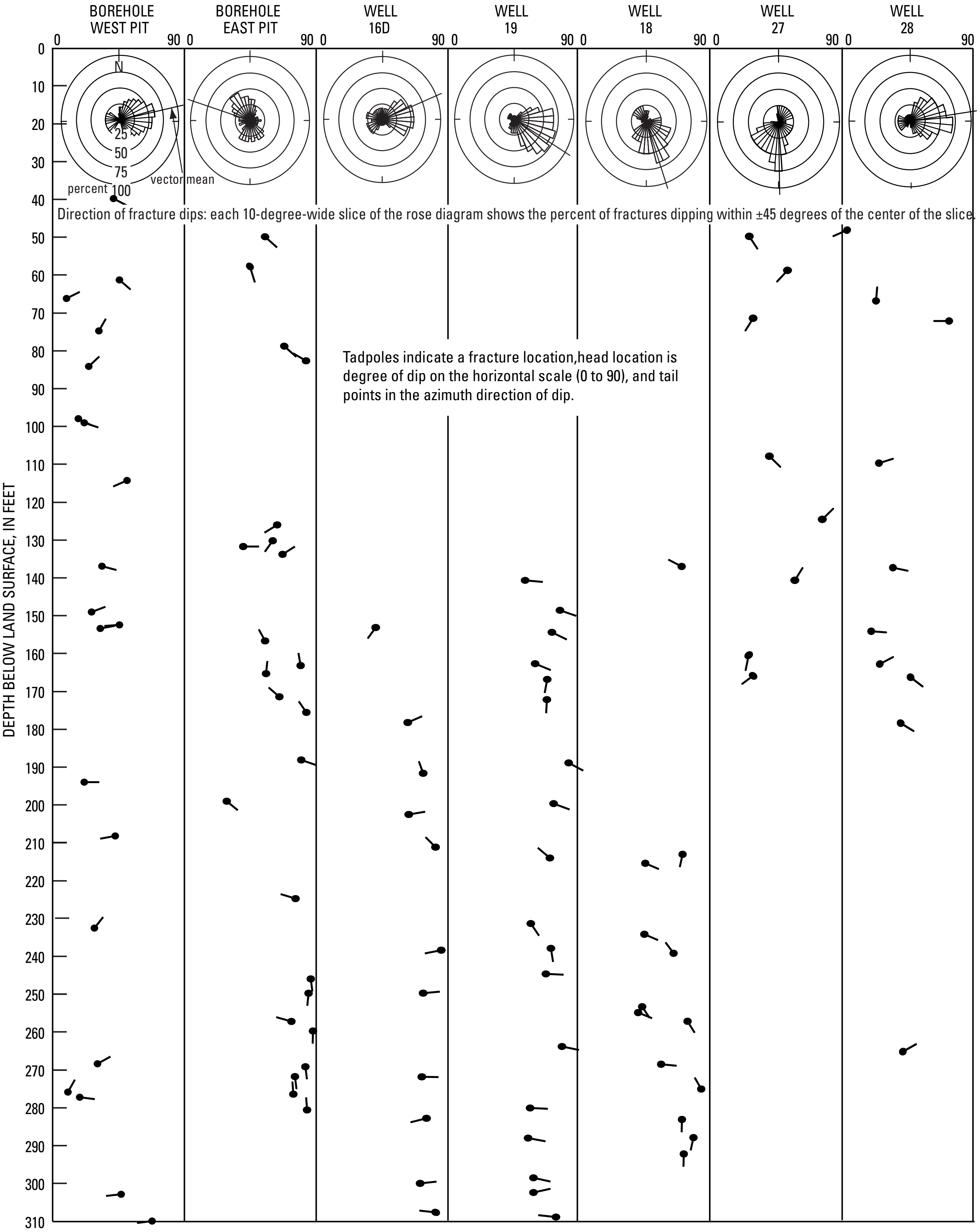


Figure 7. Fracture orientation in the granite pluton at boreholes in the Open Burn/Open Detonation pits and for selected wells downgradient from the pits.

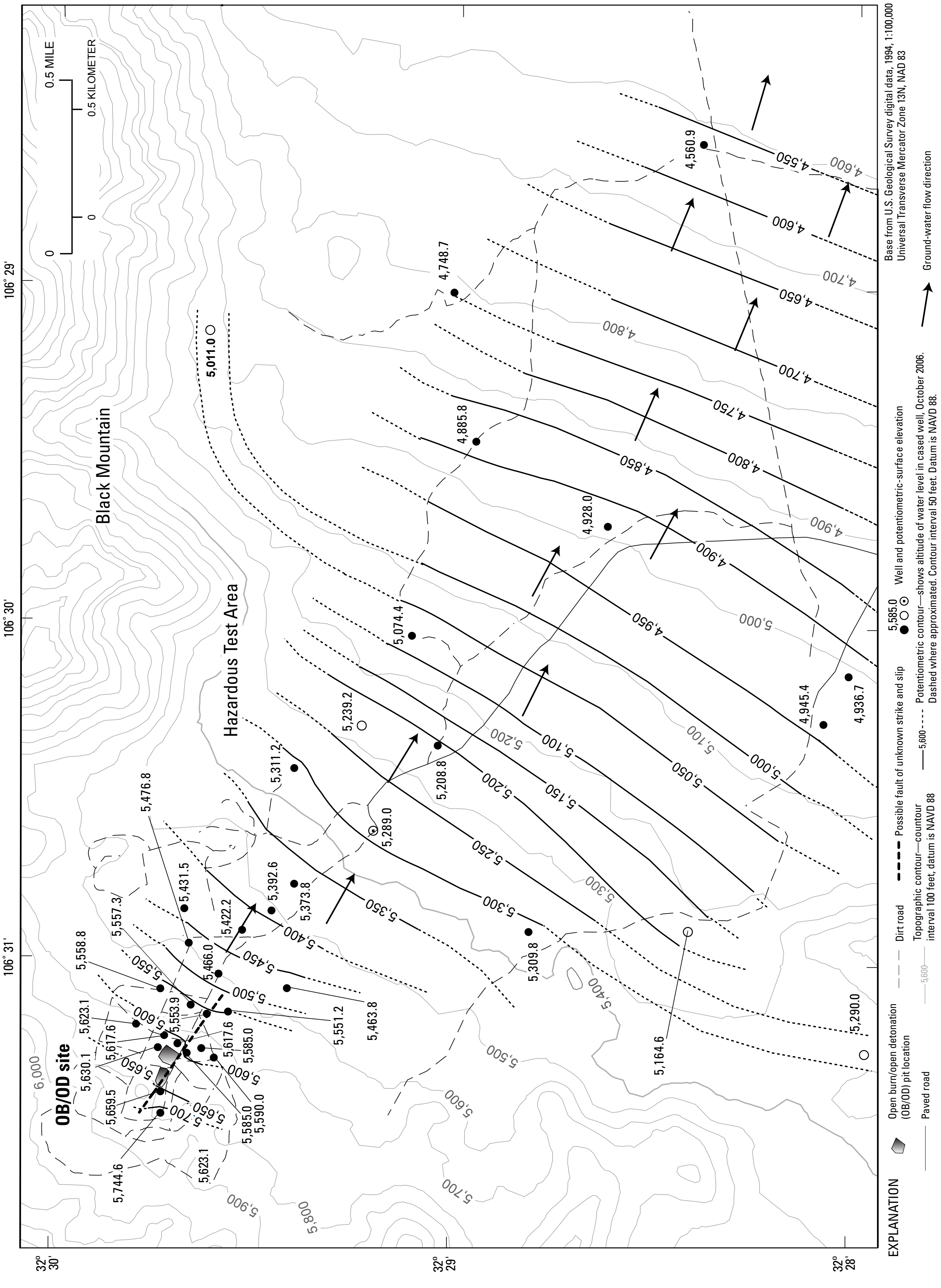


Figure 8. Potentiometric-surface contours and ground-water flow paths in the Hazardous Test Area fractured-granite aquifer, New Mexico, October 2006.

The potentiometric surface of the fractured-granite aquifer in October 2006 is parallel to the topographic gradient, and the gradient of both surfaces is about 7 percent (fig.8). Ground-water flow at the local scale will follow fracture orientation. Regional fracture connectivity would allow ground-water flow perpendicular to the potentiometric contours, which is southeastward away from the OB/OD site and towards the valley floor of the Tularosa Basin. Ground water in the fractures penetrated by monitoring wells does not have sufficient hydraulic head to reach land surface (fig. 8), but is pressurized (confined or semi-confined aquifer) and rises above the water-producing fractures in all wells. A divergence between land surface and the fractured-granite aquifer's potentiometric surface about 0.25 to 0.5 mi downgradient from the pits (fig. 9) may be an indicator of recharge variability at the mountain-front interface and OB/OD pits and disconnection of fractures penetrated by the monitoring wells. The potentiometric surface and depth to water-producing fractures were similar in this location (fig. 9). The past use of the demolition pits possibly altered fracture patterns and recharge in the pit area (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Recharge at the OB/OD pits is demonstrated by the presence of RDX and perchlorate in downgradient ground water, and recharge may have been enhanced from construction of the pits that formed catchment basins.

The potentiometric-surface irregularity at the OB/OD pits near the 5,650 and 5,600 potentiometric-surface contours is caused by a minor fault that extends through the southern part of the OB/OD site (fig. 8). Fault gouge was observed at a depth of 89 to 99 ft in the east pit (fig. 5) during exploratory drilling in 1998 (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The strike of the fault was inferred to run northwest to southeast from the east pit to a location between wells 10A and 14. The fault also may be a factor in the divergence of land surface and potentiometric surface downgradient of the pits (fig. 9) and also a factor in the variability of fracture orientation in the local area (fig. 6). Fault orientation and movement are unknown, but the lower potentiometric surface to the southwest of the fault may indicate a dip-slip direction of the fault (lower block to the southwest). The effect of the fault on the potentiometric surface does not appear to extend beyond the OB/OD site, although the lower density of wells south of the OB/OD pits inhibits detection of any influence.

The aquifer in the study area is not highly reactive to possible recharge events such as large storms (fig. 10). Mean daily-water levels did not indicate any substantial, sudden increases following such events from 2003–06. Aquifer recharge appears to be moderated by unsaturated-zone flow paths and possibly fracture geometry and density, including accessible entry points. Large precipitation accumulations in 2004 and 2006 appear to have reversed declining water levels (fig. 10). The larger response to large precipitation accumulations in well 10A suggests that most recharge likely occurs near the mountain-front interface and the response is moderated downgradient (limited recharge away from the mountain front). The lack of water-level increase in well 15 suggests limited connectivity of fractures penetrated by this well with fractures penetrated by the other wells shown in figure 10.

Contaminant Variability at the Open Burn/Open Detonation Site

RDX has been detected in ground water in all wells in transect *A–A´* (median concentrations of 2 to 60 µg/L), but the largest source appears to be located upgradient from wells 14 and 10A (fig. 11). The main source of RDX is likely within the pits but a dispersed source also is present outside of the immediate pit area. Demolition of RDX-containing material likely dispersed some of the material outside of pit boundaries. RDX concentrations along transect *A–A´* during 1998, 2000, 2003, and 2006 indicate a shift in peak RDX concentrations (fig. 12). From 1998 to 2006, peak concentrations shifted from well 14 to well 11 (about 100 yards between wells). This shift occurred in 2003 and is a result of the removal of the south and east berms of each pit in 2002 and 2003 where the berm material was pushed into the pits and the area regraded. Previous soil sampling in and around the pits detected RDX within the pits, particularly along the southwestern border (berm) of the west pit (Ralph Wilcox, U.S. Geological Survey, written commun., 2003).

Background concentrations of nitrate in ground water at HTA probably range from about 1 to 4 mg/L (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Median nitrate concentrations in ground water from wells 13, 14, 10A, 11, and 20 in transect *A–A´* range from 7 to 8 mg/L (fig. 13). The elevated nitrate concentrations in ground water at the OB/OD site originate from degradation of nitrogen-based explosives. A larger spread of nitrate concentrations across transect *A–A´* suggests a more dispersed source than RDX (fig. 13). Differences in fate and transport of RDX and the other source explosives in the natural environment can explain the differences in RDX and nitrate concentrations and spatial patterns in transect *A–A´*. In ground water, RDX tends to be more mobile than nitroaromatics such as TNT because of less sorption to soil particles (Xue and others, 1995; Yamamoto and others, 2004). Differences in soil retention could produce different rates of degradation and entrainment in ground water. HMX was the most prevalent explosive detected in soil samples collected in and around the pits (Ralph Wilcox, U.S. Geological Survey, written commun., 2003), but HMX has rarely been detected in ground water at HTA from 1996–2006 and only in wells close to the pits (10A, 11, 14, 16, 16D, and 20). This lack of HMX detection in ground water suggests degradation of HMX to nitrate prior to entrainment or prior to entering the fractures penetrated by the monitoring wells.

Between 1998 and 2006, the largest nitrate concentrations in transect *A–A´* shifted from well 13 to 10A, and this shift corresponds with moving of the berms in 2002 and 2003 (fig. 14). This shift corresponds to the shift in RDX concentrations that also occurred with berm regrading. The

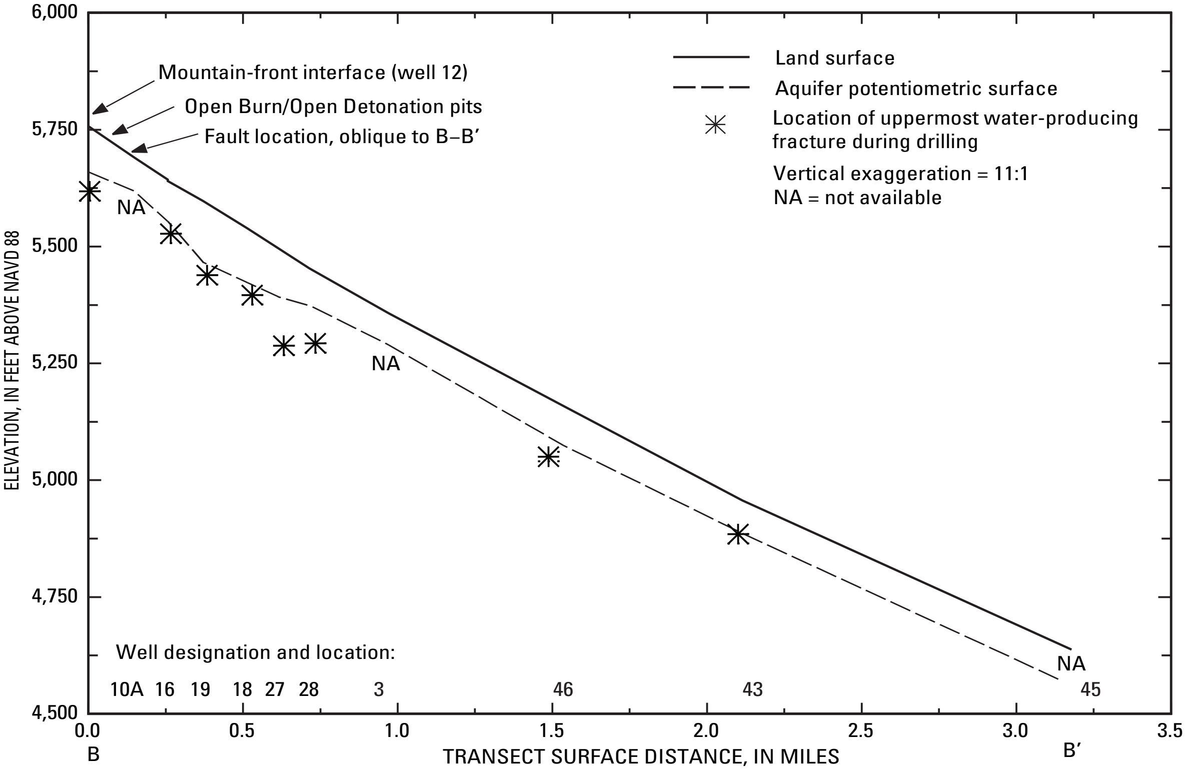


Figure 9. Vertical profile of topography and potentiometric surface at the Hazardous Test Area, transect *B–B′*, October 2006.

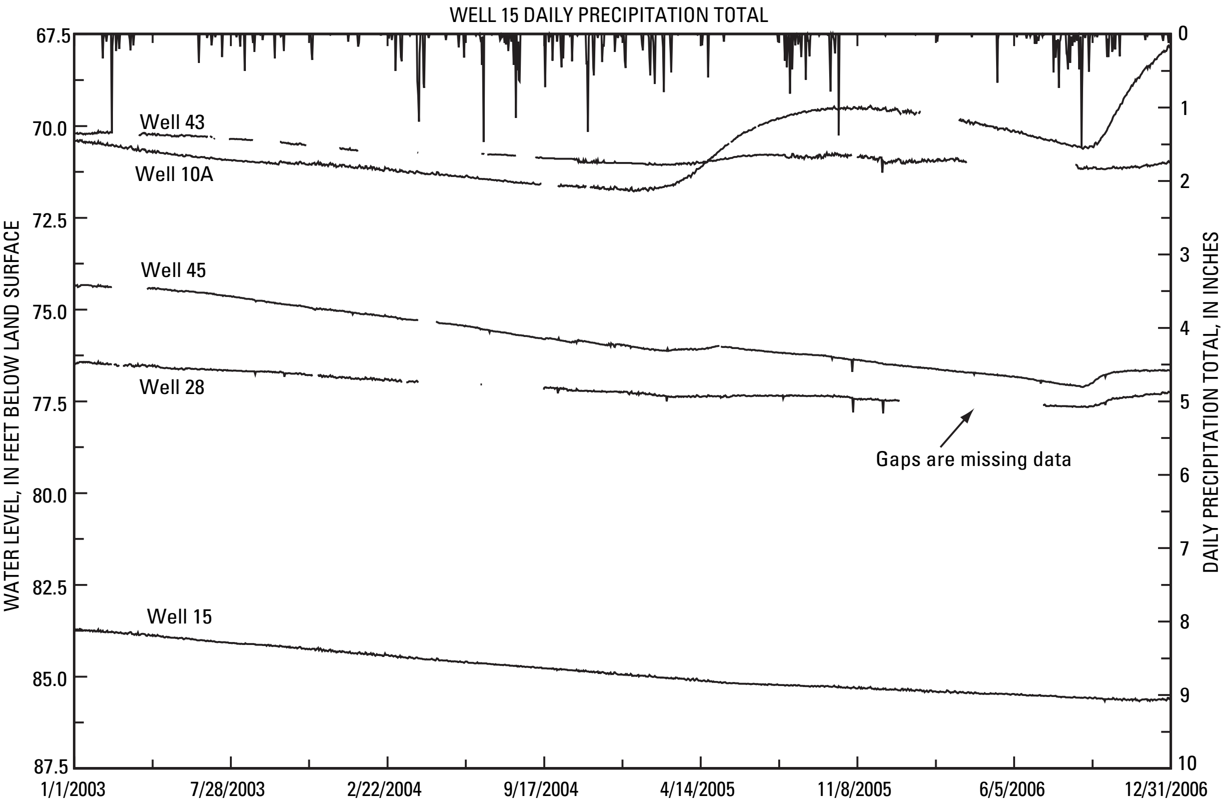


Figure 10. Mean-daily water level for select wells and daily precipitation total at well 15, Hazardous Test Area, January 2003 to January 2006.

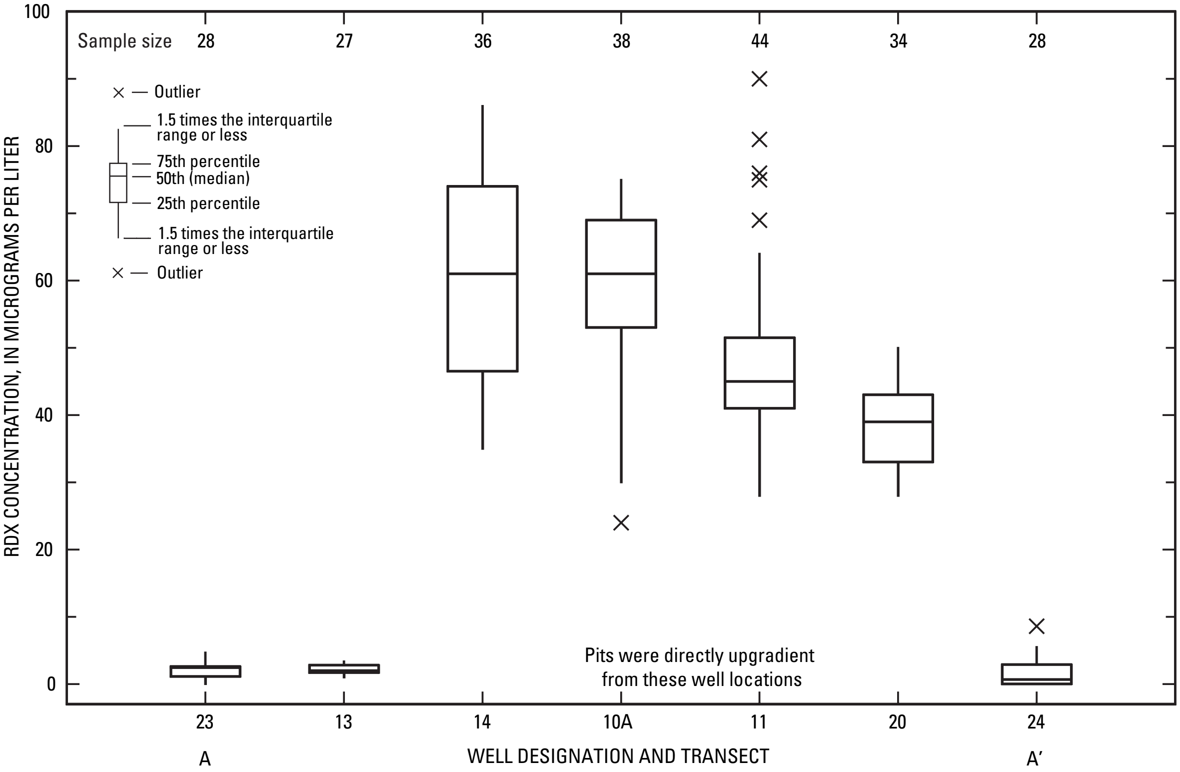


Figure 11. Spatial variability of RDX in ground water from wells in transect *A–A′* at the Hazardous Test Area, 1996–2006.

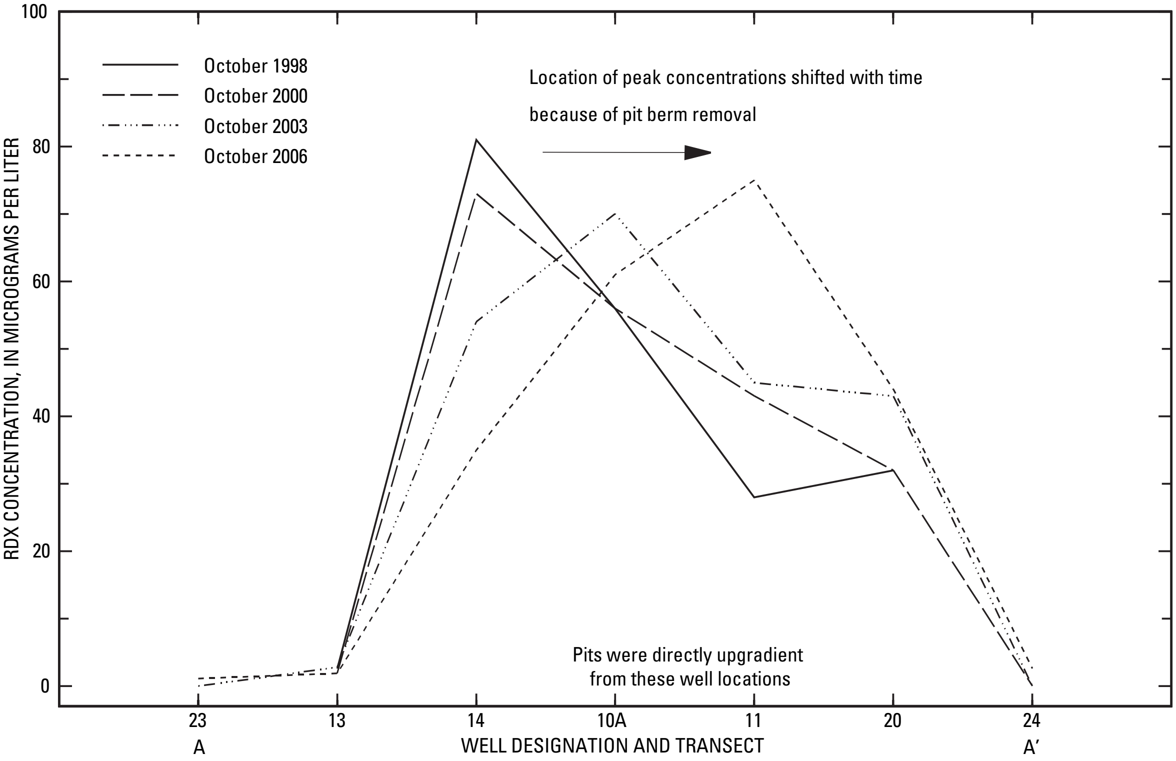


Figure 12. Temporal variability of RDX in ground water from wells in transect *A–A′* at the Hazardous Test Area.

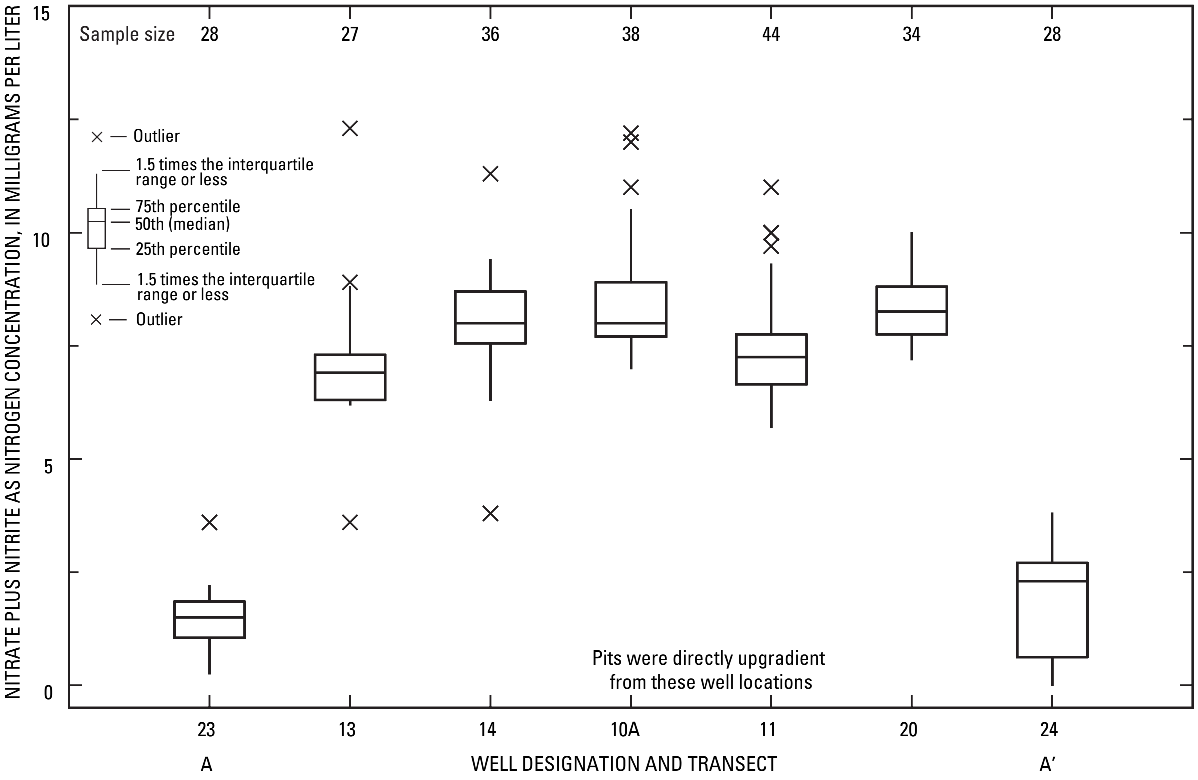


Figure 13. Spatial variability of nitrate plus nitrite as nitrogen in ground water from wells in transect *A–A′* at the Hazardous Test Area, 1996–2006.

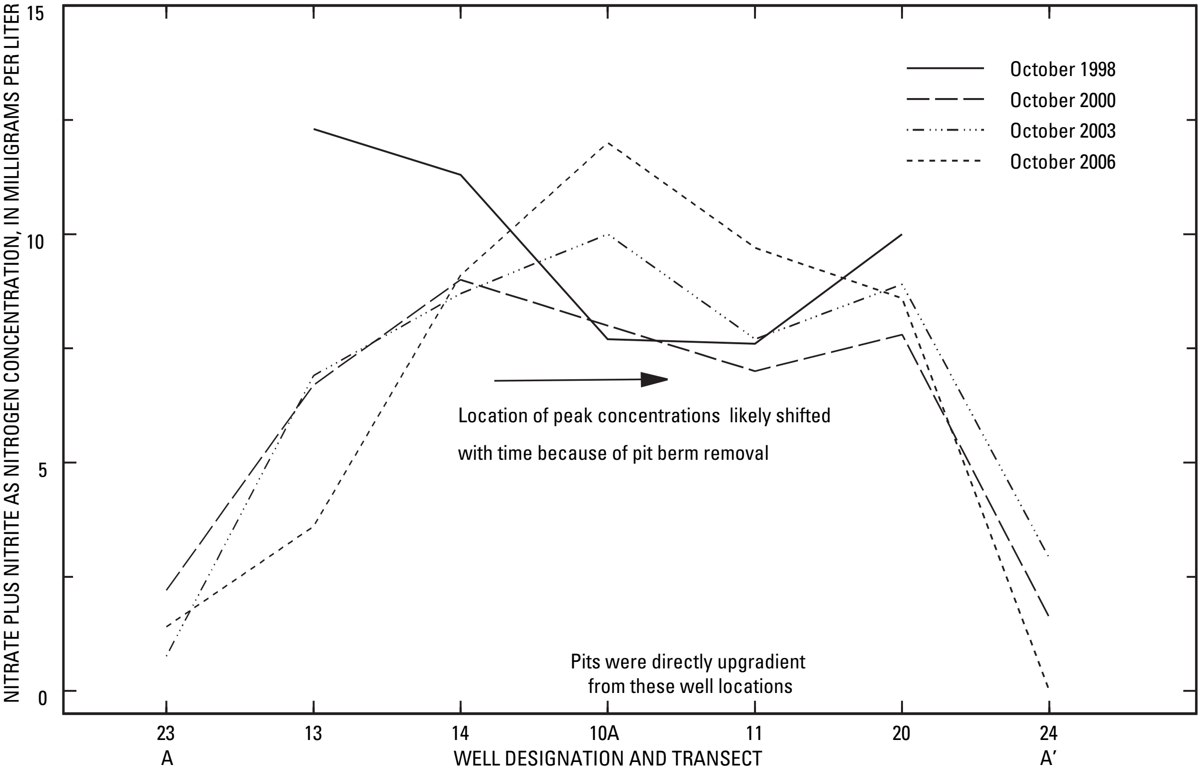


Figure 14. Temporal variability of nitrate plus nitrite as nitrogen in ground water from wells in transect *A–A′* at the Hazardous Test Area.

similarity of nitrate and RDX concentrations reacting to the berm regrading indicates similar sources or similar source locations. This shift in peak source contribution is less pronounced and traveled less distance compared to the RDX peak source. The less pronounced shift in nitrate source and the larger relative differences for RDX compared to nitrate probably is a result of the greater dispersed source of nitrate compared to RDX.

The perchlorate source location(s) appears to be more concentrated compared to RDX and nitrate sources. In transect *A–A´*, peak concentrations of perchlorate were detected in ground water from well 20, and the next largest concentrations were in ground water from wells 11, 10A, and 14; median concentrations for all wells ranged from 0.1 to 19 mg/L (fig. 15). Additionally, the source of perchlorate has not shifted during the period of record as was observed with RDX and nitrate indicating that a perchlorate source was not located at the south and east berms of each pit that were regraded in 2002 and 2003 (fig. 16). Peak concentrations across transect *A–A´* have decreased, possibly indicating a decreasing amount of source material.

Downgradient Contaminant Variability

Concentrations of RDX along the downgradient transect (*B–B´*) sharply decline in the direction of ground-water flow (fig. 17). From well 10A at the pits to well 19 (about 0.25 mi), concentrations decreased from a median of 60 µg/L to less than 0.2 µg/L. From 1998 to 2006, this downgradient decline in RDX has been stable, and the larger concentrations of RDX have not moved downgradient with ground-water flow. Recharge water continued to entrain RDX from the sources at and near the pits, but a concentrated mass of RDX has not migrated with ground-water flow during the period of study (fig. 18). The spatial stability of RDX concentrations is not a reflection of the lack of downgradient transport of RDX, because ground water in well 46 (about 1.5 mi downgradient from the pits) has contained very small concentrations of RDX since installation of the well in 2002. The apparent lack of downgradient transport of RDX likely results from natural attenuation (dilution and (or) degradation) that reduces concentrations within a short distance of the OB/OD site.

Nitrate concentrations indicate a mixed pattern in the downgradient direction, and concentrations are largest in ground water from well 19 (about 0.25 mi downgradient from the OB/OD pits) (fig. 19) where RDX concentrations are small (fig. 18). This downgradient pattern of nitrate has remained stable since 2000 and only small changes in concentrations at each well have been observed (fig. 20). The pattern of nitrate concentrations along transect *B–B´* is similar to the pattern of dissolved-oxygen concentrations (fig. 21). This pattern suggests that changes to reduction-oxidation (redox) conditions are influencing nitrate concentrations, particularly concentrations in ground water from wells 27 and 46. Ammonia has been detected at small concentrations (less than 0.1 mg/L) in only a few wells at HTA (Ralph Wilcox, U.S. Geological Survey, written commun., 2003), although if converted to ammonium (protonation of ammonia) adsorption of NH_4^+ can be substantial (Appelo and Postma, 2005) and can reduce the presence of ammonium in solution. Denitrification because of changes in redox conditions in certain fracture systems may be producing the variable downgradient pattern of nitrate at HTA, which suggests disconnected or limited connectivity between fractures radiating from the OB/OD site. The different downgradient patterns of RDX and nitrate suggest natural attenuation instead of vertical migration of the contaminants beyond the depths of the monitoring wells.

Perchlorate concentrations in ground water from wells in transect *B–B´* indicate increasing and then decreasing concentrations in the downgradient direction (fig. 22). Perchlorate concentrations were largest in ground water from wells 16 (median of 19.3 mg/L) and 16D (median of 21.0 mg/L); both wells are about 0.15 mi downgradient from the OB/OD site. Concentrations further downgradient sharply decreased with median concentrations of 0.06 and 0.95 mg/L at wells 27 and 28 (about 0.5 mi downgradient from the OB/OD site), respectively. Perchlorate was present in ground water from all downgradient wells and concentrations generally ranged from 1 to 40 µg/L at wells furthest from the OB/OD site (3, 46, 43, and 45). Perchlorate concentrations were stable in ground water along transect *B–B´* from 1999 to 2006 with minor concentration fluctuations likely from variable recharge (fig. 23).

The larger perchlorate concentrations typical of ground water from wells 16 and 16D were not detected in ground water from wells closer to the OB/OD site except for ground water from well 20. A possible link between ground water from well 20 and ground water from well 16 or 16D is difficult to ascertain (fig. 24). Perchlorate trends at these locations were similar but also indicated sufficient differences to question a possible relation. The Wilcoxon rank-sum test was used to compare the data distributions of perchlorate in ground water at well 20 with perchlorate data for wells 16 and 16D. Test results indicate no relation between perchlorate in ground water from the shallower, downgradient well 16 and well 20 (p-value of 0.55), but a likely relation between perchlorate in ground water from the deeper, downgradient well 16D and the OB/OD well 20 (p-value of 0.02). These results suggest possible fracture connectivity downgradient from the OB/OD pits (wells 16D and 20), but also downgradient fractures that are not connected or have limited connectivity with fractures penetrated by wells near the OB/OD pits (comparing wells 16 and 20). Ground water in wells 16 and 16D have the same potentiometric-surface elevation (fig. 8) that suggests recharge from the same elevation where the contaminants are entrained and no vertical hydraulic gradient between shallow and deeper fractures at this location.

Small concentrations of perchlorate (less than 10 µg/L) in ground water from HTA could or could not be from anthropogenic sources. The anthropogenic use of perchlorate is as a strong oxidizer in rocket propellants, explosives, and flares. Perchlorate has been detected in ground water in the Rio

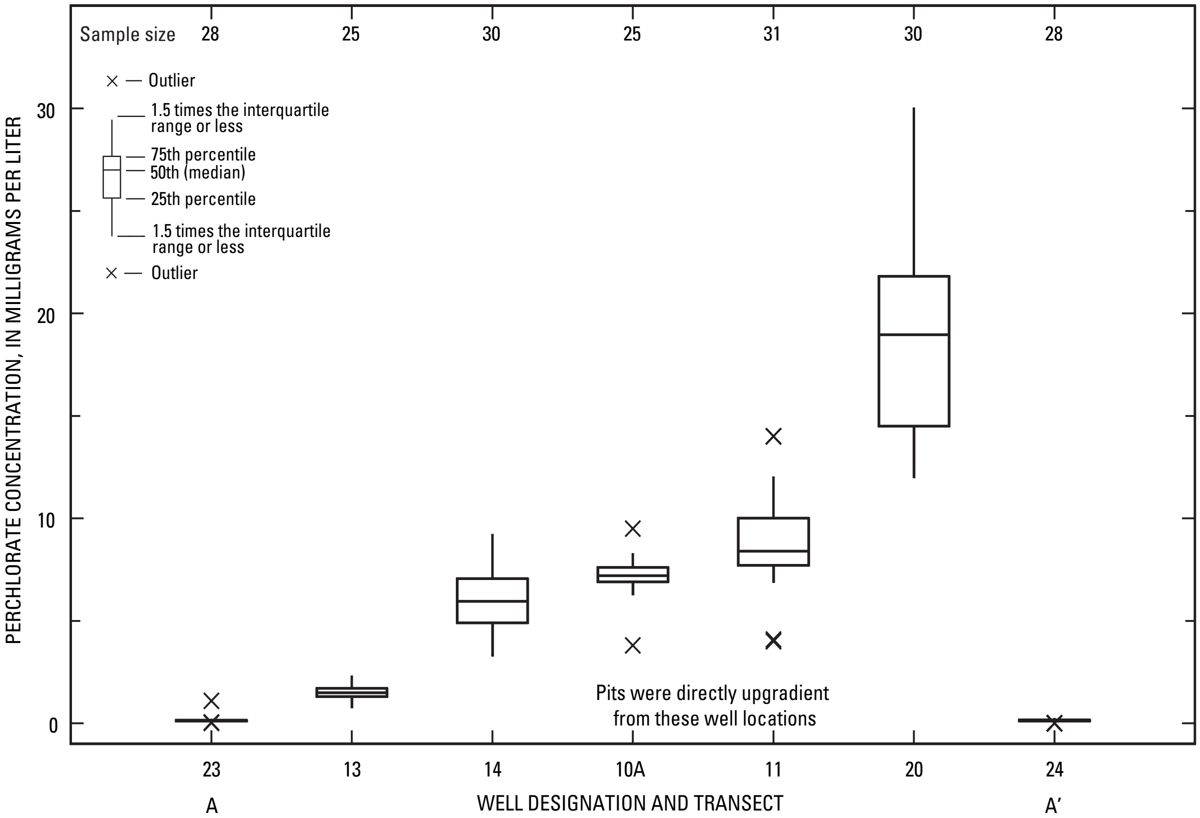


Figure 15. Spatial variability of perchlorate in ground water from wells in transect *A–A′* at the Hazardous Test Area, 1996–2006.

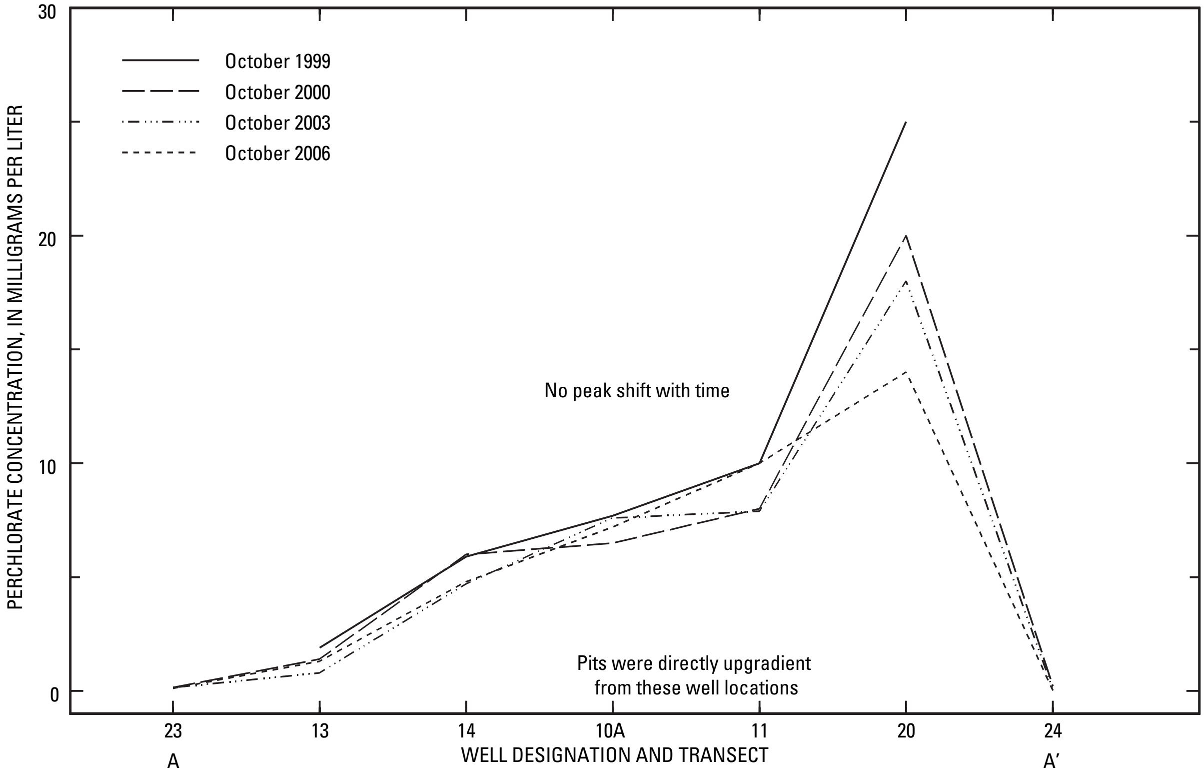


Figure 16. Temporal variability of perchlorate in ground water from wells in transect *A–A′* at the Hazardous Test Area.

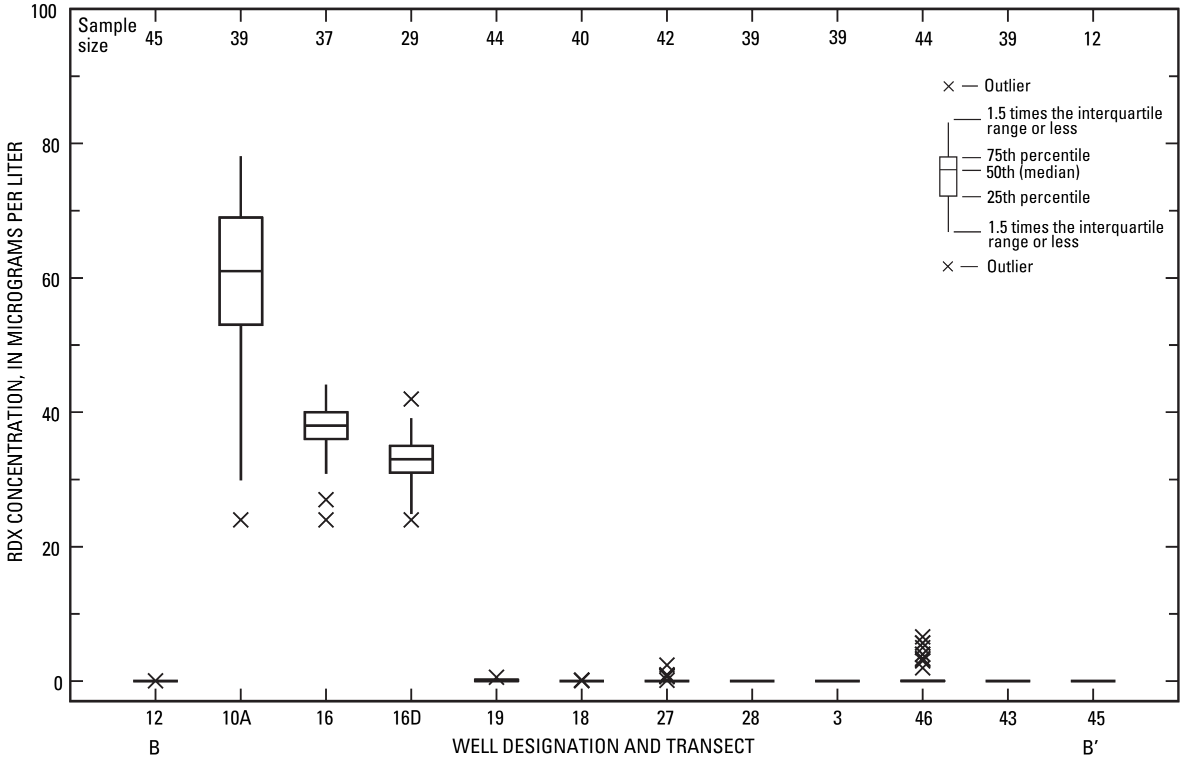


Figure 17. Spatial variability of RDX in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

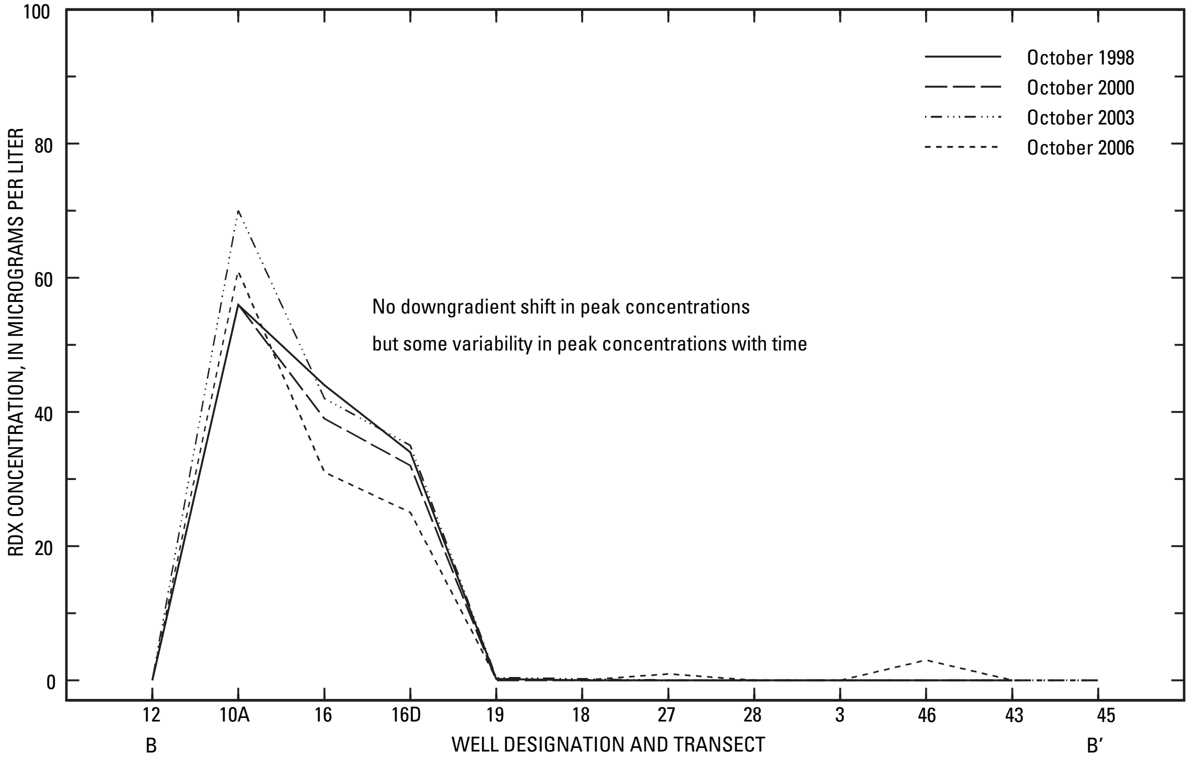


Figure 18. Temporal variability of RDX in ground water from wells in transect *B–B′* at the Hazardous Test Area.

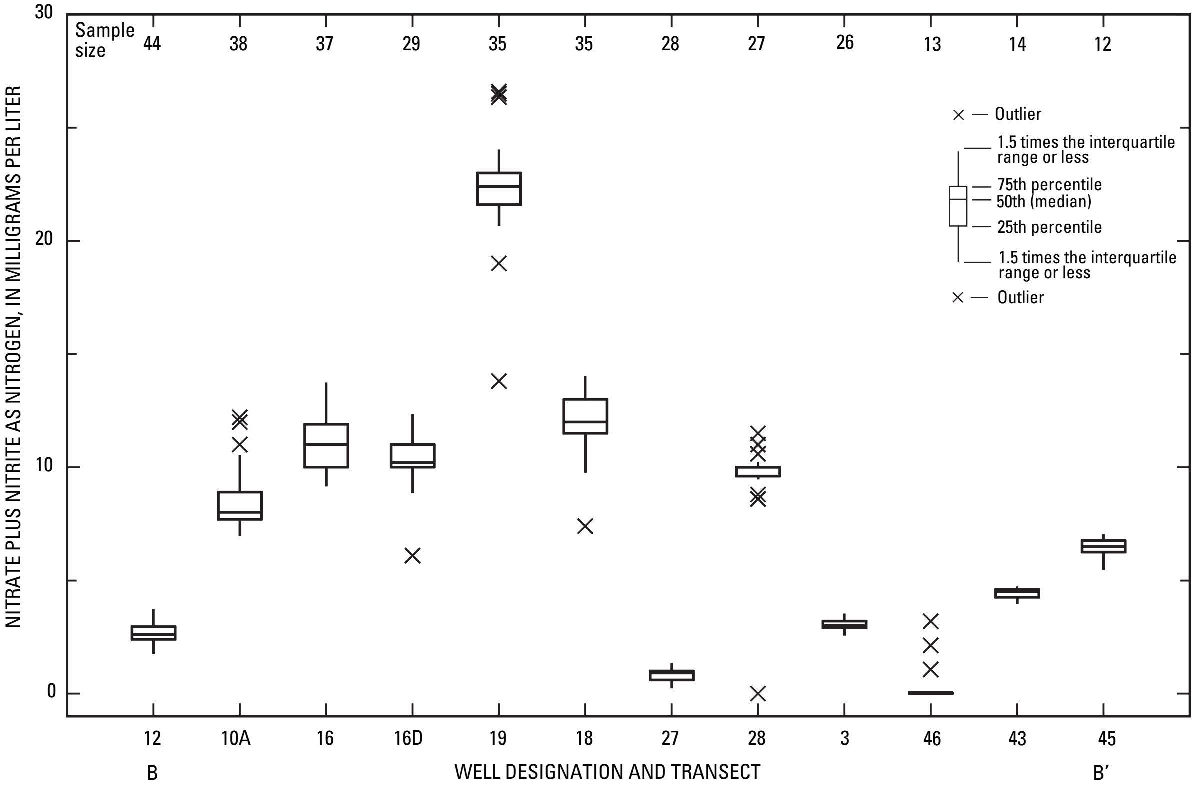


Figure 19. Spatial variability of nitrate plus nitrite as nitrogen in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

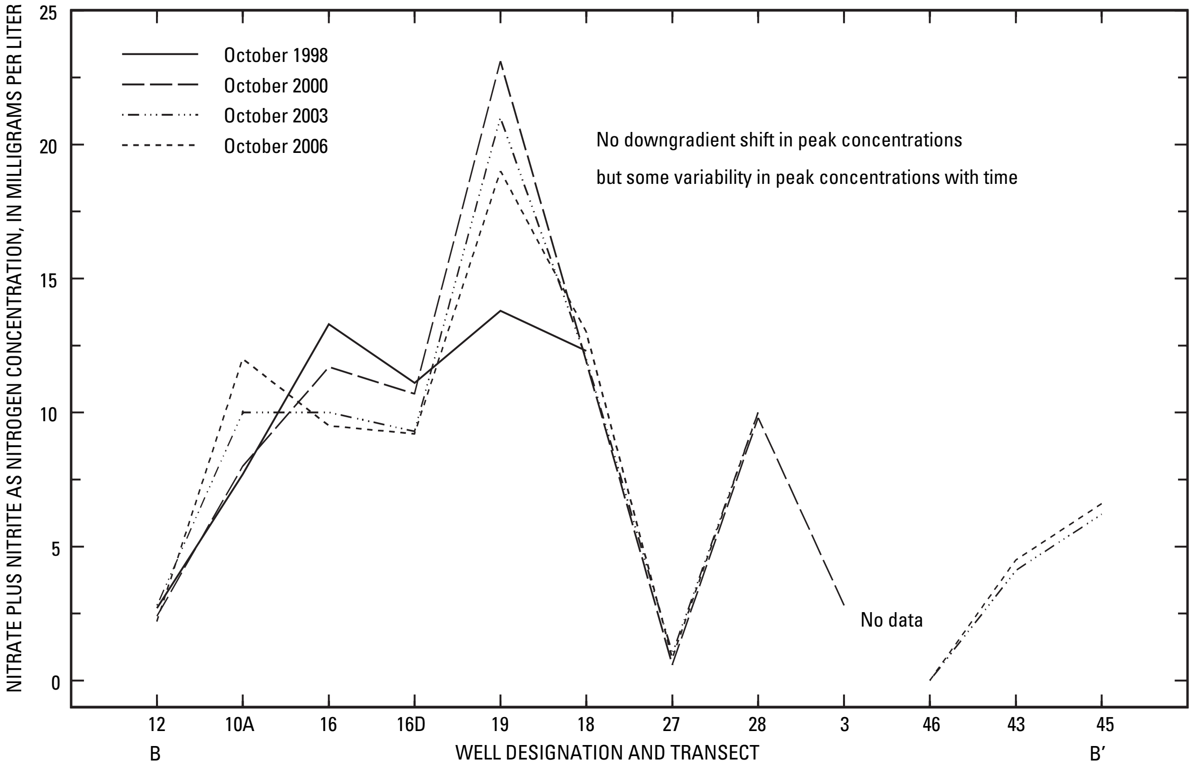


Figure 20. Temporal variability of nitrate plus nitrite as nitrogen in ground water from wells in transect *B–B′* at the Hazardous Test Area.

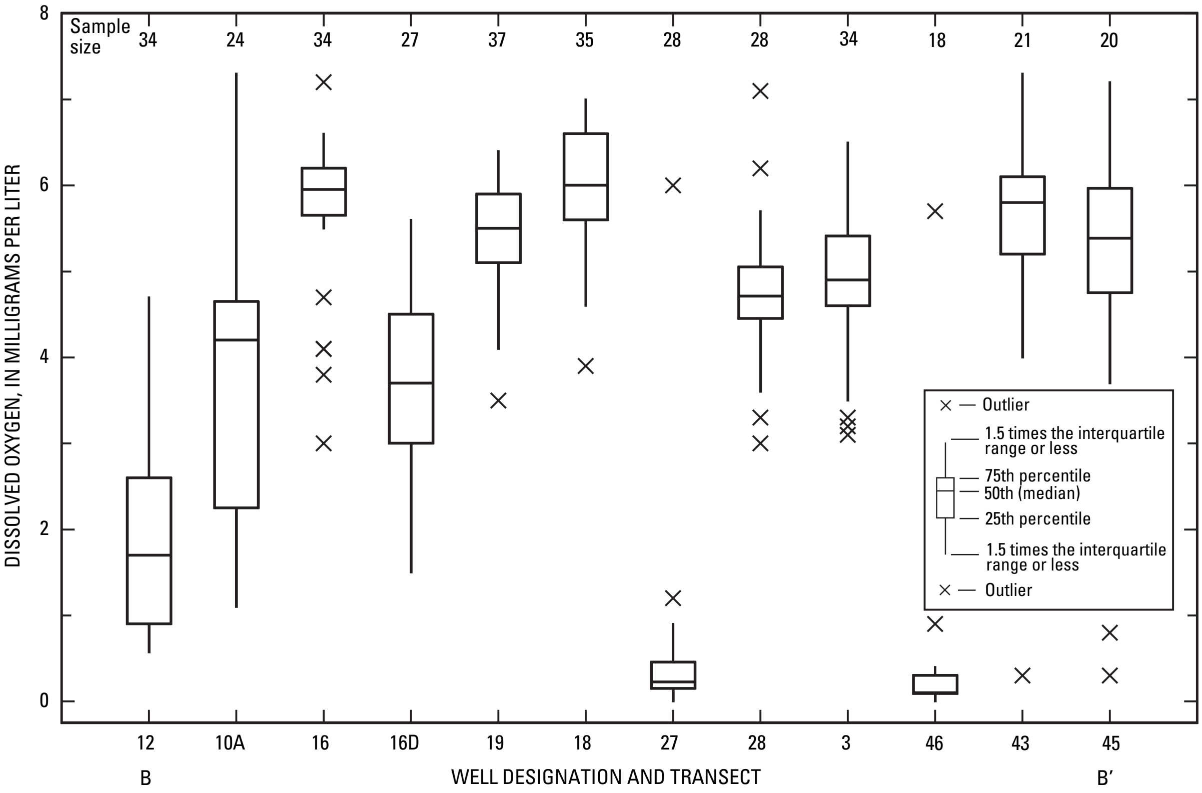


Figure 21. Spatial variability of dissolved oxygen in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

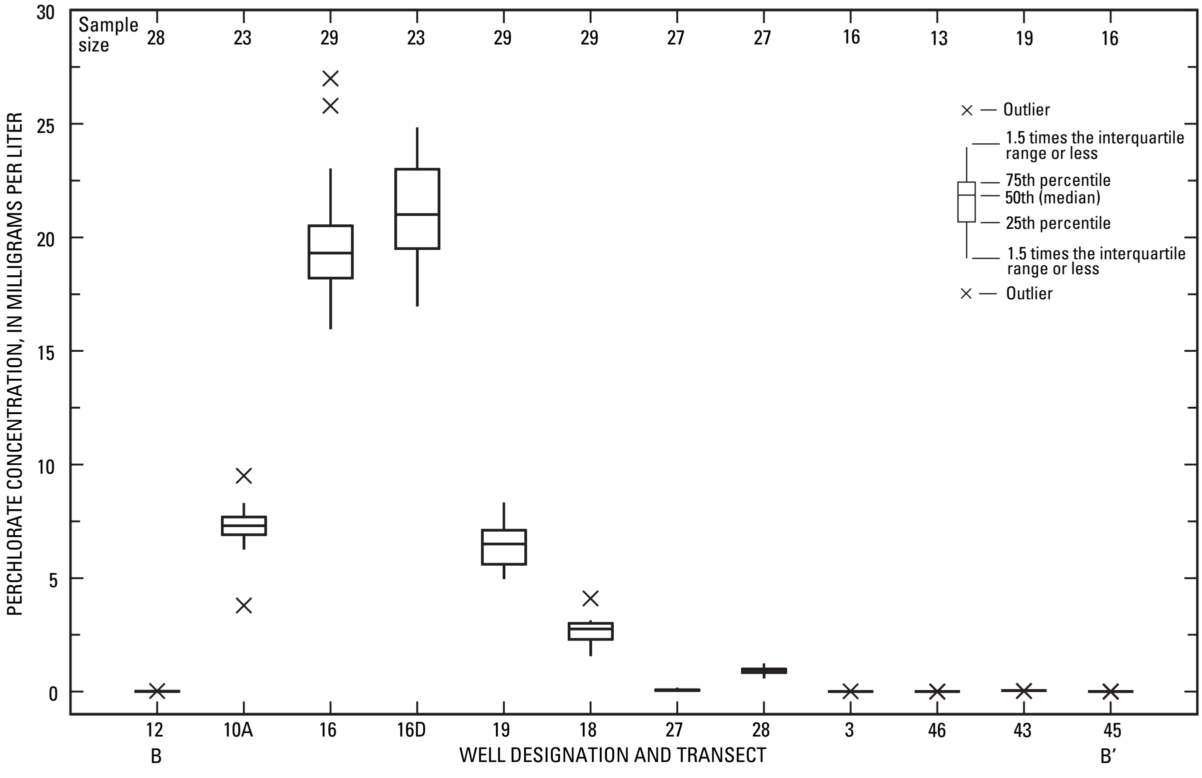


Figure 22. Spatial variability of perchlorate in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

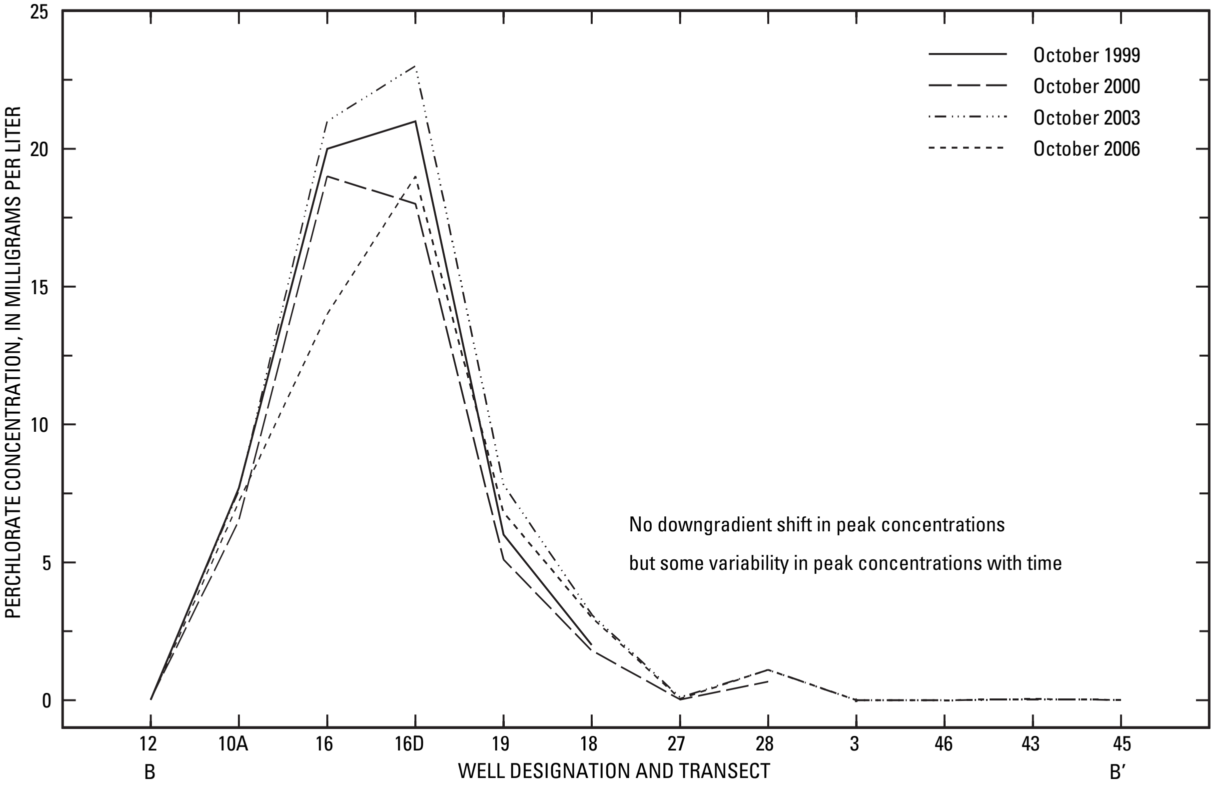


Figure 23. Temporal variability of perchlorate in ground water from wells in transect *B–B′* at the Hazardous Test Area.

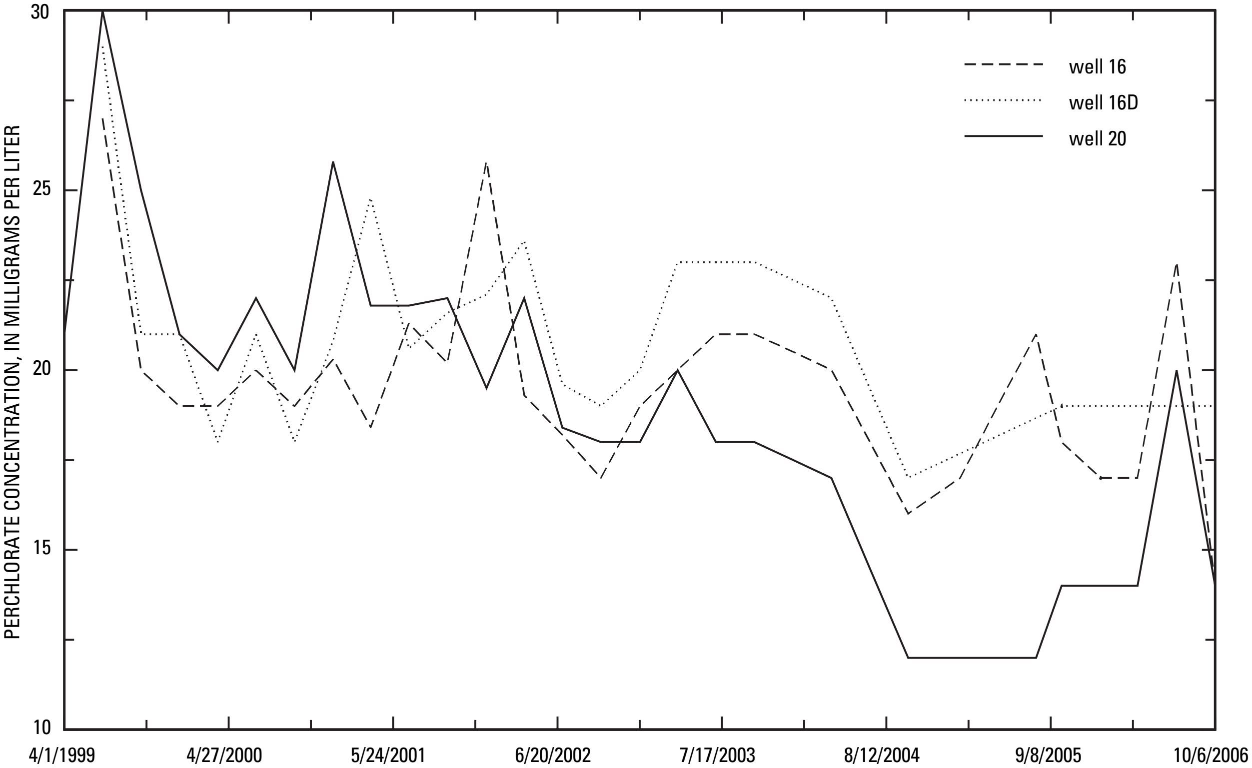


Figure 24. Perchlorate concentrations in ground water from well 20 near the Open Burn/Open Detonation site and ground water from wells 16 and 16D approximately 0.15 mile downgradient.

Grande Valley of New Mexico (Plummer and others, 2006) (ranging from 0.12 to 1.8 µg/L) and in northwestern Texas (Jackson and others, 2003) (concentrations generally were less than 5 µg/L) where no known anthropogenic source(s) exists. Further investigation of perchlorate in northwestern Texas and eastern New Mexico produced evidence that perchlorate was from a natural source (Rajagopalan and others, 2006). Atmospheric processes such as the interaction of chloride and ozone can produce perchlorate naturally (Dasgupta and others, 2005). With wet or dry deposition, perchlorate can accumulate in soil and be transported to an aquifer by recharge. The increasing analytical capability to detect perchlorate at small concentrations (0.1 µg/L or greater) has allowed the identification of naturally occurring perchlorate in arid and semiarid climates where it may accumulate in the soil (Rajagopalan and others, 2006; Rao and others, 2007). In October 2006, perchlorate was detected at HTA in ground water from many of the monitoring wells in the larger monitoring network beyond the general OB/OD area at small concentrations (1 to 2 µg/L or less). Many of these wells probably are not connected to ground-water flow paths that originate from the OB/OD site (many wells are located in areas not potentiometrically downgradient), and perchlorate at these locations may be naturally occurring.

Water Level and Contaminant Relation

Changes in water level may correlate with contaminant (RDX, nitrate and perchlorate) concentrations as an increase or decrease in recharge either dilutes or concentrates entrained contaminants. Nonparametric (Kendall's tau) correlation coefficients and the associated p-values for comparison of water levels and the three contaminants at each well indicate limited correlation, except for a few wells (tables 3 and 4). For this study, strong correlation is a tau greater than ±0.8, moderate correlation is greater than ±0.5, and low correlation is less than ±0.5 (±1 is considered perfect correlation and 0 indicates no correlation). For transect *A–A´*, water level and RDX were positively and strongly correlated for well 14 (tau of 0.81, p-value of 0.00) and moderately and negatively correlated for well 23 (tau of -0.53, p-value of 0.00). Well 14 penetrates a fracture(s) that contains ground water with the some of the largest RDX concentrations, and well 23 penetrates a fracture(s) that contains ground water with some of the smallest RDX concentrations for transect *A–A´* (fig. 11). Additionally, a positive and moderate correlation (tau of 0.51, p-value of 0.00) was present for perchlorate and water level in well 20, which contained ground water with the largest perchlorate concentrations for wells in transect *A–A´* (fig. 15). For transect *B–B´*, water level and all three contaminant concentrations were not strongly correlated (table 4). Correlation coefficients for water level and nitrate, which indicated low correlation strengths for all wells in transect *A–A´*, indicated positive and moderate strength of correlation for wells 3, 12, and 16 in transect *B–B´*. Strong and moderate correlation of water level and the contaminants near the source areas and low correlation outside and downgradient from the source(s) suggests a diminishing of the water level/contaminant relation with downgradient flow. The lessening of these relations may be a result of natural attenuation that alters contaminant concentrations and changes the relation with water level.

The correlation of RDX and nitrate concentrations was examined for similarities in contaminant sources and entrainment and transport of the two contaminants. Movement of these two contaminants in the aquifer may be similar because of their likely similar anthropogenic source (explosives). Correlation coefficients for RDX and nitrate indicate low correlation laterally (transect *A–A´*) and in the downgradient direction (transect *B–B´*) (tables 5 and 6). This lack of correlation suggests differences in source locations and possibly differences in solubility and degradation of the source explosives and nitrate within the aquifer. Nitrate is very soluble, mobile, and easily degraded under reducing conditions (Hem, 1989). RDX is more environmentally persistent compared to other explosives such as TNT (trinitrotoluene) (Spalding and Fulton, 1988). RDX and TNT were detected in soil samples collected at the OB/OD site in 1999 (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). Elevated nitrate concentrations are likely a result of entrainment and degradation of the explosive compounds detected in soil and core samples collected in and around the OB/OD pits that included RDX, HMX, DNT, TNT, and tetryl (Ralph Wilcox, U.S. Geological Survey, written commun., 2003). The recurrent detection of RDX in ground water at HTA compared to the rare detection of other explosives highlights the greater persistence of RDX compared to other explosive compounds that are present at the site. The differences in source locations, degradation, and solubility of the explosive compounds explain the low correlation between RDX and nitrate

Natural Attenuation in the Fractured-Granite Aquifer

Results of the previous section suggest natural attenuation of the contaminants in the fractured-granite aquifer. The loss of the contaminants because of vertical migration beyond the depths of the monitoring wells is unlikely. Monitoring of shallow and deeper parts of the aquifer at a single location (well 16 (shallow) and well 16D (deep)) produced equal or larger contaminant concentrations in the shallow well compared to the deeper well, and reveal that the contaminants are present throughout the vertical column and no vertical concentration gradient is present downgradient from the pits (figs. 17, 19, and 22). Additionally, no vertical hydraulic gradient is present at this location (same ground-water elevation in both wells). The sharp decreases in contaminant concentrations (figs. 18, 20, and 23) and changes to dissolved oxygen (fig. 21) suggest that natural attenuation, through dilution and degradation, is occurring downgradient from

Table 3. Kendall's tau correlation coefficients for water level and RDX, nitrate, and perchlorate in ground water from wells in transect *A–A′* at the Hazardous Test Area, 1996–2006.

[A correlation coefficient of 1 indicates a perfect, positive correlation, a coefficient of -1 indicates a perfect, negative correlation, and coefficient of 0 indicates no correlation; for this study, strong correlation is greater than 0.8, moderate correlation is greater than 0.5, and low correlation is less than 0.5; moderate and strong correlations are in bold]

Correlation with water level	Well number						
	23	13	14	10A	11	20	24
RDX: tau	**-0.53**	0.18	**0.81**	-0.18	-0.12	-0.43	-0.39
p-value	*0.00*	*0.19*	*0.00*	*0.12*	*0.23*	*0.00*	*0.00*
Nitrate: tau	0.38	0.48	0.29	-0.43	0.07	0.24	0.37
p-value	*0.00*	*0.00*	*0.03*	*0.00*	*0.52*	*0.04*	*0.00*
Perchlorate: tau	0.16	0.26	0.27	-0.01	0.21	**0.51**	0.37
p-value	*0.22*	*0.07*	*0.02*	*0.94*	*0.09*	*0.00*	*0.01*

Table 4. Kendall's tau correlation coefficients for water level and RDX, nitrate, and perchlorate in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

[A correlation coefficient of 1 indicates a perfect, positive correlation, and a coefficient of -1 indicates a perfect, negative correlation; NA, not applicable—no detections of the constituent at this well; for this study, strong correlation is greater than 0.8, moderate correlation is greater than 0.5, and low correlation is less than 0.5; moderate and strong correlations are in bold]

Correlation with water level	Well number											
	12	10A	16	16D	19	18	27	28	3	46	43	45
RDX: tau	NA	-0.18	0.15	0.02	-0.28	-0.13	-0.41	NA	NA	**-0.57**	NA	NA
p-value	*NA*	*0.12*	*0.20*	*0.85*	*0.01*	*0.14*	*0.00*	*NA*	*NA*	*0.00*	*NA*	*NA*
Nitrate: tau	**0.59**	-0.43	**0.63**	0.44	0.33	-0.47	-0.05	-0.25	**0.52**	0.21	-0.12	-0.05
p-value	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.69*	*0.06*	*0.00*	*0.20*	*0.57*	*0.84*
Perchlorate: tau	NA	-0.01	0.23	0.11	-0.33	**-0.54**	-0.04	-0.46	-0.47	0.19	-0.06	-0.34
p-value	*NA*	*0.94*	*0.07*	*0.42*	*0.01*	*0.00*	*0.78*	*0.00*	*0.00*	*0.21*	*0.72*	*0.06*

Table 5. Kendall's tau correlation coefficients for RDX and nitrate in ground water from wells in transect *A–A′* at the Hazardous Test Area, 1996–2006.

[A correlation coefficient of 1 indicates a perfect, positive correlation, a coefficient of -1 indicates a perfect, negative correlation, and coefficient of 0 indicates no correlation]

Kendall's tau correlation	Well number						
	23	13	14	10A	11	20	24
RDX/nitrate	-0.23	0.48	0.26	0.29	0.36	-0.13	-0.41
p-value	*0.06*	*0.00*	*0.03*	*0.01*	*0.00*	*0.28*	*0.00*

Table 6. Kendall's tau correlation coefficients for RDX and nitrate in ground water from wells in transect *B–B′* at the Hazardous Test Area, 1996–2006.

[NA, not applicable; A correlation coefficient of 1 indicates a perfect, positive correlation, and a coefficient of -1 indicates a perfect, negative correlation; NA, not applicable—no detections of the constituent at this well]

Kendall's tau correlation	Well number											
	12	10A	16	16D	19	18	27	28	3	46	43	45
RDX/nitrate	NA	0.29	0.05	0.03	-0.13	0.08	-0.07	NA	NA	-0.02	NA	NA
p-value	*NA*	0.01	0.65	0.81	0.25	0.33	0.55	*NA*	*NA*	0.92	*NA*	*NA*

the pits, but the effect of dilution and (or) degradation of the contaminants is difficult to ascertain because of the possible limited connectivity between fractures within the aquifer. To help evaluate the effect of natural attenuation and discriminate dilution from degradation of the contaminants, ground-water samples from select wells in the HTA monitoring network collected in October 2005 were analyzed for selected geochemical tracers (table 2).

All wells in fractures with ground water containing the contaminants have received recharge that has passed through the OB/OD site because of the presence of the contaminants, but uncontaminated recharge also is occurring outside of the OB/OD site and is likely mixing with contaminated water downgradient from the pits. This mixing of contaminated and uncontaminated water downgradient from the OB/OD site would dilute the contaminants and attenuate large downgradient concentrations. This mixing and decrease of contaminant concentrations were possibly indicated in figures 18, 20, and 23 where contaminant concentrations quickly declined after peak concentration locations. The presence of the contaminants throughout the OB/OD site and into the larger fractured-granite aquifer indicates that contaminant transport is occurring throughout the HTA, but the large concentrations (large concentrated mass) of contaminants near the OB/OD pits have not migrated with this overall contaminant transport. Decrease of the contaminant masses in solution through sorption is unlikely given the mobility of the contaminants (Anthropogenic Compounds section), so the mass is likely decreased by dilution through mixing with uncontaminated water originating outside of the OB/OD site or degradation of the contaminants such as microbially induced reduction of nitrate under hypoxic or anoxic conditions. Effects on the contaminant masses by these two processes will be further explored through an analysis of geochemical tracers.

Tritium-Helium Age Dating and Dilution

In October 2005, the apparent age of ground water from selected wells at HTA was estimated using the tritium-helium method developed by Schlosser and others (1989). Ground water in the fractured-granite aquifer is young (less than 25 years from the OB/OD pits to 3.25 mi downgradient), which suggests that contaminated recharge should have transported the contaminants throughout the downgradient aquifer. Given that the concentrations quickly decline with downgradient transport, it appears that natural attenuation processes, such as dilution, are decreasing downgradient concentrations. Within the fractured-granite aquifer, ground water was not progressively older at all downgradient locations (table 7). Younger water was present in downgradient wells (28 and 45) compared to upgradient wells (wells 19, 31, 43, and 51). Younger water in wells 28 and 45 suggests recharge is closer to these locations than upgradient wells. Fractures penetrated by wells 28 and 45 possibly receive recharge (or more recharge) from nearby ephemeral channels or mix with uncontaminated water recharged along the mountain-front interfaces along Black Mountain to the north or Mineral Hill to the south (fig. 2). Ground water in wells 28 and 45 did not contain large concentrations of the contaminants (Downgradient Contaminant Variability section). Ground water in these wells has mixed with younger, uncontaminated water and diluted contaminant concentrations and decreased ground-water ages.

Ground-Water Composition

The chemical composition of ground water (hydrochemical facies) is a response to water-rock interactions and atmospheric and anthropogenic inputs (Bullen and Kendall, 1998). Longer contact time of ground water with rock minerals will increase solute concentrations in response to dissolution reactions that are variable because of kinetic and thermodynamic properties of ground-water flow and formation minerals (Bullen and Kendall, 1998). Except for ground water along the periphery of the basin (wells 5, 40, 48, 49, and Bonney Spring Mine windmill) (fig. 2), the chemical composition of the fractured-granite aquifer at HTA was similar for most wells (mixed cation and mixed anion composition) and indicated similar water-rock interactions and recharge pathways (fig. 25). The different chemical composition of ground water in wells 5, 40, 48, 49, and the Bonney Spring Mine windmill is related to water interacting with different mineral assemblages. Ore deposits are present along the basin margins (fault zones and batholith contacts), and are particularly prevalent at San Augustin Pass (fig. 2) and northward where most of the mining in the area occurred (Seager, 1981). The Bonney Spring Mine windmill is located along the contact of the metamorphosed sedimentary rocks of the San Andres Mountains and the HTA granitic pluton in the Bear Peak Fold and Thrust Zone (fig. 4). This zone is known for zinc-lead-silver mineralization where a shale layer provided a barrier to the movement of ore fluids and mineral precipitation occurred (Seager, 1981).

Dilution

Dissolved-solids (DS) concentrations in ground water from the HTA fractured-granite aquifer in October 2005 ranged from 348 to 710 mg/L for the entire HTA monitoring network and ranged from 458 to 683 mg/L in the OB/OD site area (fig. 26). Variation in DS concentrations was a result of variable water-rock interaction (mineral differences and time of dissolution (age of water)), mixing of recharge sources, and contaminant inputs. The largest DS concentrations were north-northeast of the pits (wells 24, 25, and 29), and the smallest concentrations were south and southeast of the pits (wells 23 and 27) (fig. 26). Changes in DS concentrations across transect *A–A´* (wells 23, 13, 14, 10A, 11, 20, and 24) suggest differences in recharge upgradient from and at the OB/OD pits.

Table 7. Ground-water ages for selected wells at the Hazardous Test Area, October 2005.

[Ground-water age determined by tritium-helium method (Schlosser and others, 1989); NA, not available]

	Downgradient direction →									
Well	**12**	**11**	**16**	**19**	**28**	**31**	**43**	**51**	**45**	**41**
Approximate age (years)	NA	3.0 ±0.1	7.4 ±0.1	13.6 ±0.5	6.2 ±0.3	19.7 ±0.6	22.0 ±5	23.8 ±0.9	17.2 ±0.9	NA
Tritium units	1.43	8.59	9.82	2.93	1.41	1.56	2.17	1.04	0.84	0.71

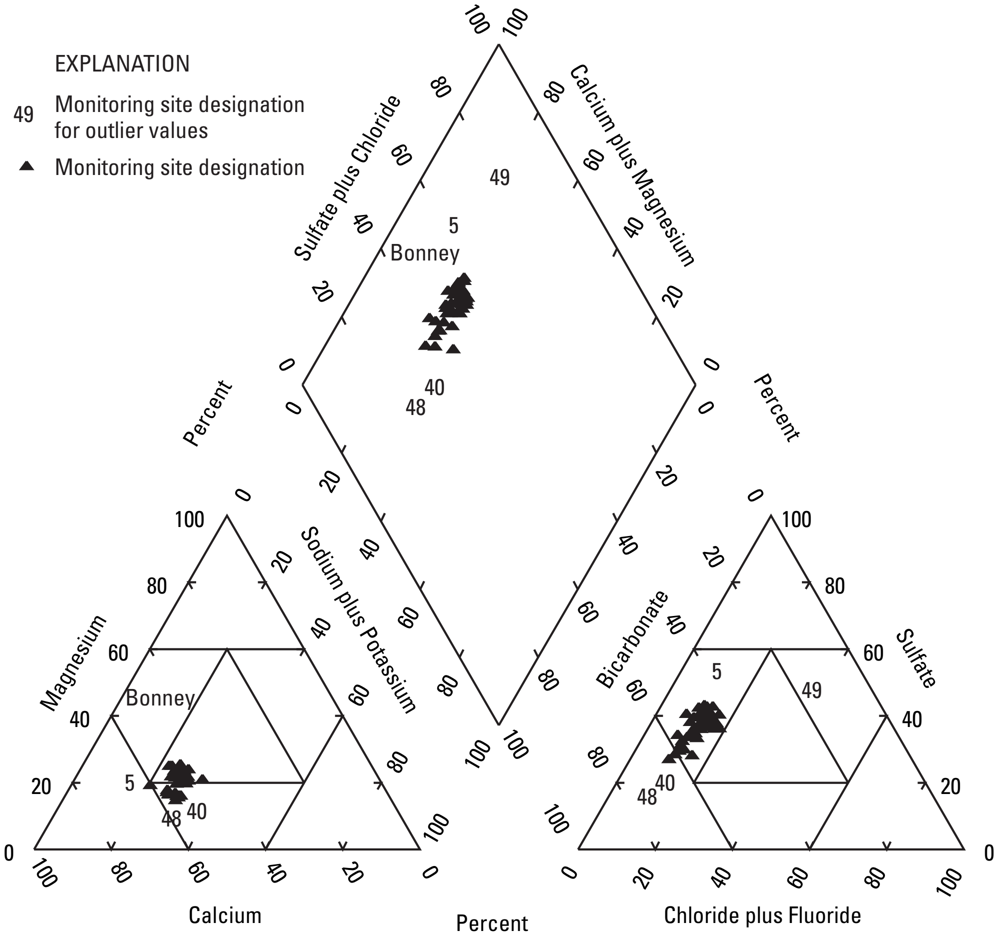
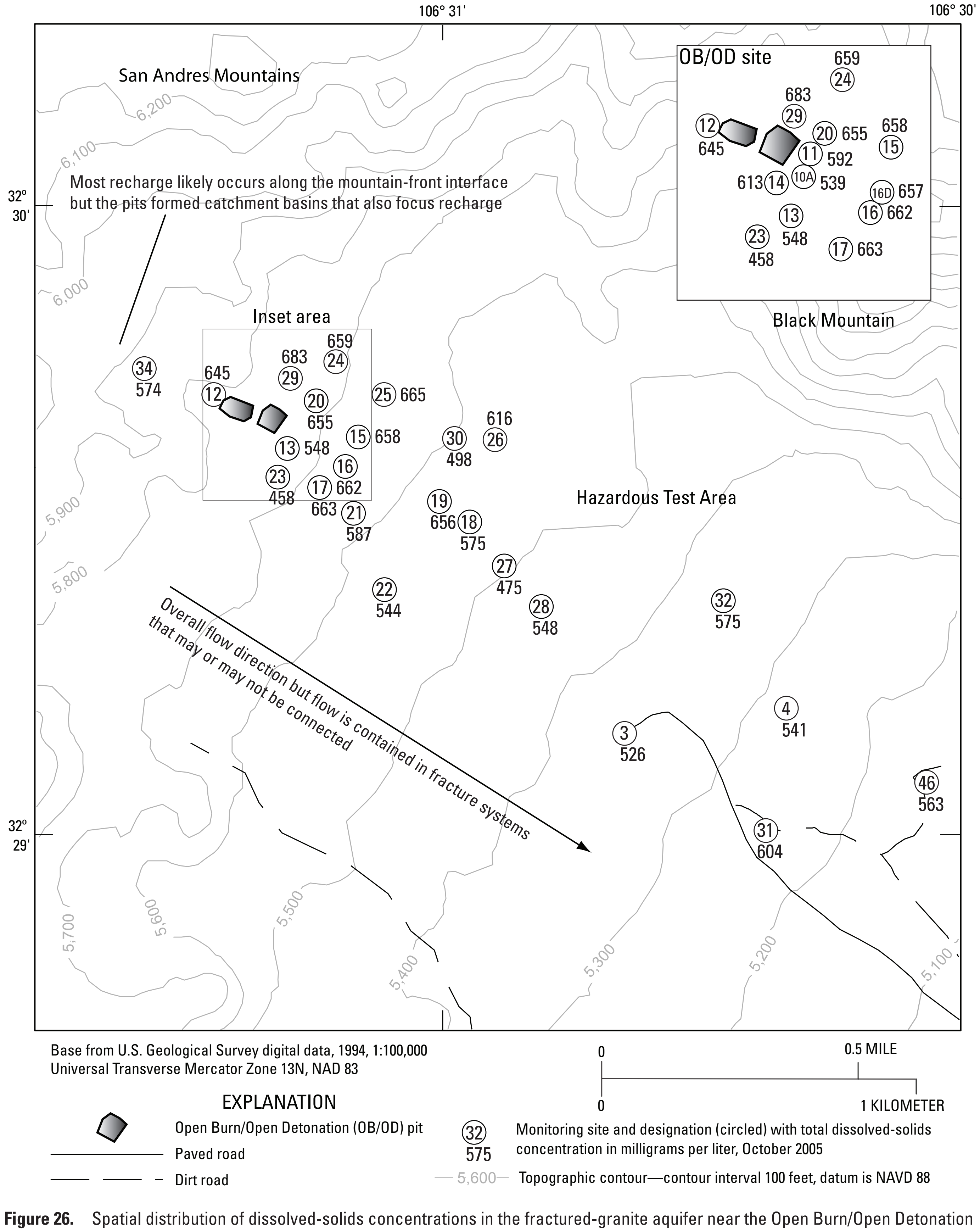


Figure 25. Piper diagram of major ion composition of ground water collected from monitoring sites in the Hazardous Test Area, October 2005.

Only RDX peaked in concentration near the pits (fig. 18), but the peak RDX concentrations are at the microgram per liter scale and would not substantially contribute to the DS milligrams per liter concentrations. Nitrate concentrations peaked near well 19 and perchlorate concentrations peaked near well 16 and 16D, and DS concentrations in this area are larger than DS concentrations in ground water from wells along the eastern and southern boundaries of the OB/OD pits. The influx of contaminants appears to have increased DS concentrations downgradient from the pits, but a diluting influence is evident downgradient from well 19. DS concentrations in ground water from well 18, 27, and 28 are substantially lower than DS concentrations in ground water from wells 15, 16, 16D, 17, and 19. This decrease in DS concentrations is likely because of dilution from another recharge source that was suggested by the decrease in contaminant concentrations (Downgradient Contaminant Variability section) and ground-water ages.

A linear trend of calcium and strontium concentrations indicates differences in mineral dissolution and mixing of



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83

Figure 26. Spatial distribution of dissolved-solids concentrations in the fractured-granite aquifer near the Open Burn/Open Detonation Site in the Hazardous Test Area, October 2005.

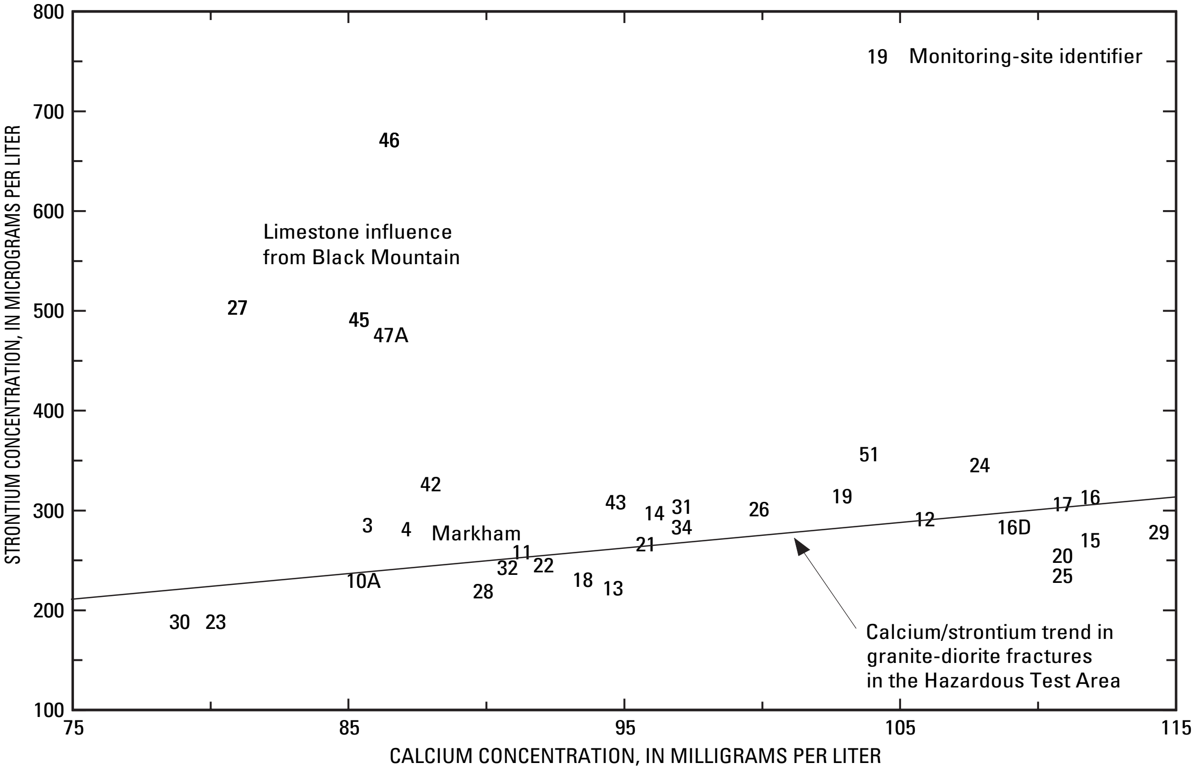


Figure 27. Strontium and calcium concentrations in ground water from monitoring sites in the Hazardous Test Area, October 2005.

various recharge and flow paths (fig. 27). Ground water from wells 27, 45, 46, and 47A is influenced by dissolution of other mineral assemblages not representative of the granite-diorite minerals that compose the granitic pluton. Larger concentrations of strontium relative to calcium can indicate dissolution of limestone (Bierman and others, 1998), which is abundant in the San Andres Mountains and at Black Mountain along the northern perimeter of the HTA fractured-granite aquifer. Recharge water from this area appears to cross the Bear Peak Fold and Thrust Zone and merge with select fractures in the HTA fractured-granite aquifer. The strontium/calcium indicator of mixing of contaminated and uncontaminated water near well 27 agrees with interpretation of the ground-water ages and DS concentrations that suggested a similar influence by well 28.

Degradation and Changes to Carbon Forms

Biodegradation of organic compounds, such as RDX and other explosives, can affect ground-water physical and chemical properties (Fetter, 1999). The degradation of RDX and other explosives likely contributes various byproducts to ground water in the fractured-granite aquifer that may be visible at or downgradient from the large RDX concentrations, or the degradation of the RDX and other explosives may alter ground-water chemistry such as the change in dissolved oxygen visible in figure 21. Degradation of RDX and other explosives would consume oxygen and produce degradates (such as MNX, DNX, and TNX for RDX) or final byproducts (such as nitrate, methane, carbon dioxide, or nitrogen gas) (McCormick and others, 1981; Hawari and others, 2000).

Some of the indicators of RDX degradation in the HTA fractured-granite aquifer include the presence of RDX degradates, RDX/nitrate/nitrogen-gas pattern, the presence of methane, and changes in carbon dioxide concentrations. Certain RDX degradates were detected in ground water collected in October 2005 from a few wells near and downgradient from the pits. MNX was detected in ground water from wells 10A, 11, and 29; DNX was detected in ground water from wells 23 and 46; and TNX was not detected. The presence of these compounds in the fractured-granite aquifer indicates degradation of RDX near its source location(s) and downgradient from the pits. The lack of degradates further downgradient indicates degradation to simpler chemical forms such as nitrate or dilution. In the downgradient direction, the largest RDX concentrations were in ground water from well 10A (fig. 18) followed by downgradient decreases to near nondetection levels by well 19. This pattern was opposite of the downgradient nitrate pattern that indicated an increasing nitrate concentration from well 12 to the largest nitrate concentration in ground water from well 19 (fig. 20). This inverse pattern from the OB/OD pits to well 19 suggests a contribution of nitrate to ground water from the degradation of RDX. The likely degradation of RDX can only account for a small part of the increase in nitrate, which suggests additional nitrate inputs. These other nitrate inputs may be related to the degradation of other explosive compounds—such as HMX, DNT, TNT, and teryl—that have been detected in soil samples in and around the pits but are rarely detected in ground water and only at wells near the OB/OD pits, including wells 10A, 11, 13, 14, 16, 16D, 20, and 24. It is possible that other fractures not represented by the upgradient wells are transporting nitrate from degraded explosives to this location.

During October 2005, ground-water samples from selected wells were analyzed for dissolved gases including nitrogen, methane, and carbon dioxide. An inverse relation was present for nitrogen gas and nitrate concentrations in ground water from wells in transect *B–B´*, indicating denitrification and formation of nitrogen gas (fig. 28). Denitrification typically occurs under anaerobic conditions where nitrate is reduced by microbes to nitrogen gas (Stumm and Morgan, 1996). Small dissolved-oxygen concentrations were present in ground water at wells 12, 27, and 46 (fig. 21), which corresponds to wells with the largest nitrogen gas concentrations and the smallest nitrate concentrations (fig. 28).

Methane was detected in ground water from wells 26 and 46 (2 of the 12 samples collected for gas analysis from wells in the OB/OD pits area or downgradient from the pits), but only the detection of methane in ground water from well 46 appears to correlate with degradation that also has increased nitrogen-gas concentrations and decreased nitrate and oxygen concentrations in ground water at this location. The USGS geochemical model PHREEQC (version 2.13.1) was used to estimate carbon-dioxide concentrations (partial pressures) for ground water from selected wells where water temperature, pH, dissolved oxygen, and alkalinity were determined for the October 2005 samples. Results were cross validated against carbon dioxide concentrations measured as part of the dissolved gas analyses for selected wells. Carbon dioxide concentrations likely increased in ground water downgradient from the OB/OD pits from well 10A (0.33 millimoles per liter) to well 16D (0.62 millimoles per liter). This increase in carbon dioxide (CO_2) over this distance corresponds to the decrease in RDX ($C_3H_6N_6O_6$) over this same distance (fig. 18).

Natural Attenuation and Chloride

Chloride is considered a conservative element that may be used for tracing source waters and flow paths (Drever, 1997), but the addition of anthropogenic chloride to the aquifer from degradation of perchlorate adds to the uncertainty of the chloride source at each location. Perchlorate likely is degrading within the soil and ground water thereby producing artificially large and variable perchlorate and chloride concentrations in the aquifer downgradient from the OB/OD site. The relation of chloride to chloride plus perchlorate (in millimoles per liter) for ground water from

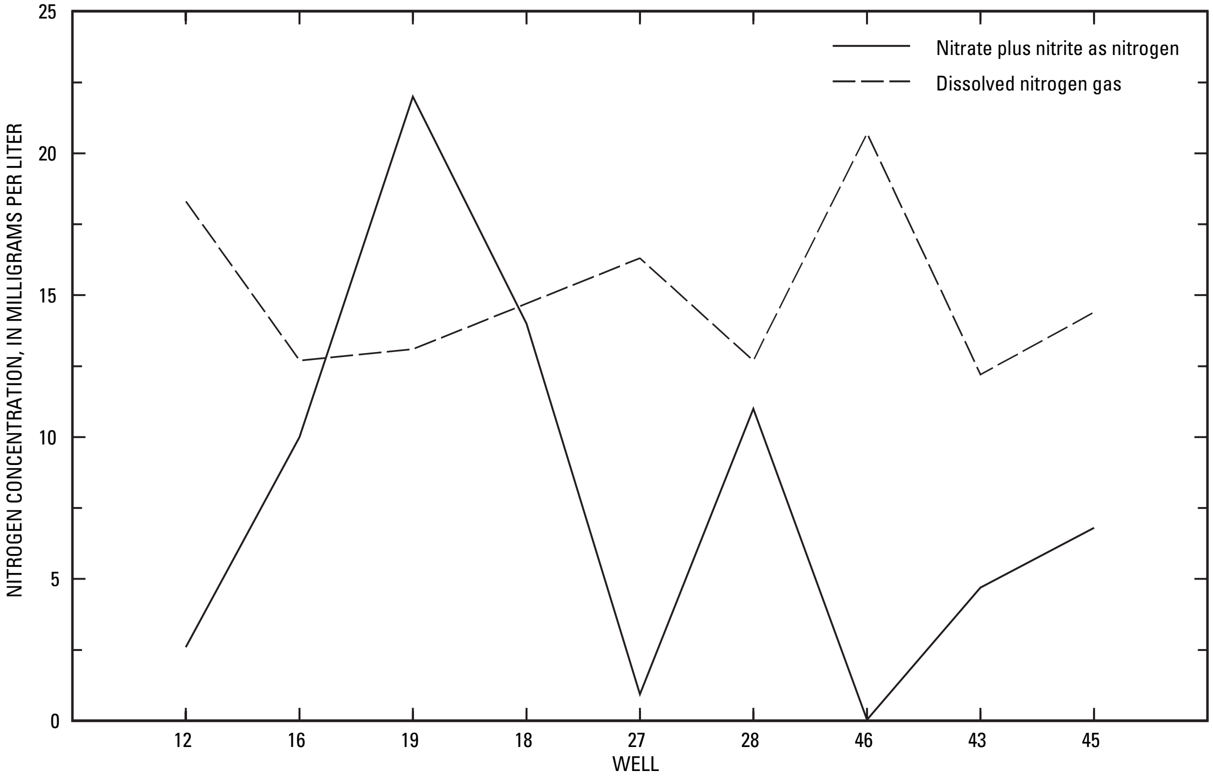


Figure 28. Nitrate plus nitrite as nitrogen and dissolved nitrogen gas concentrations in ground water from selected wells in transect *B–B´* at the Hazardous Test Area, October 2005.

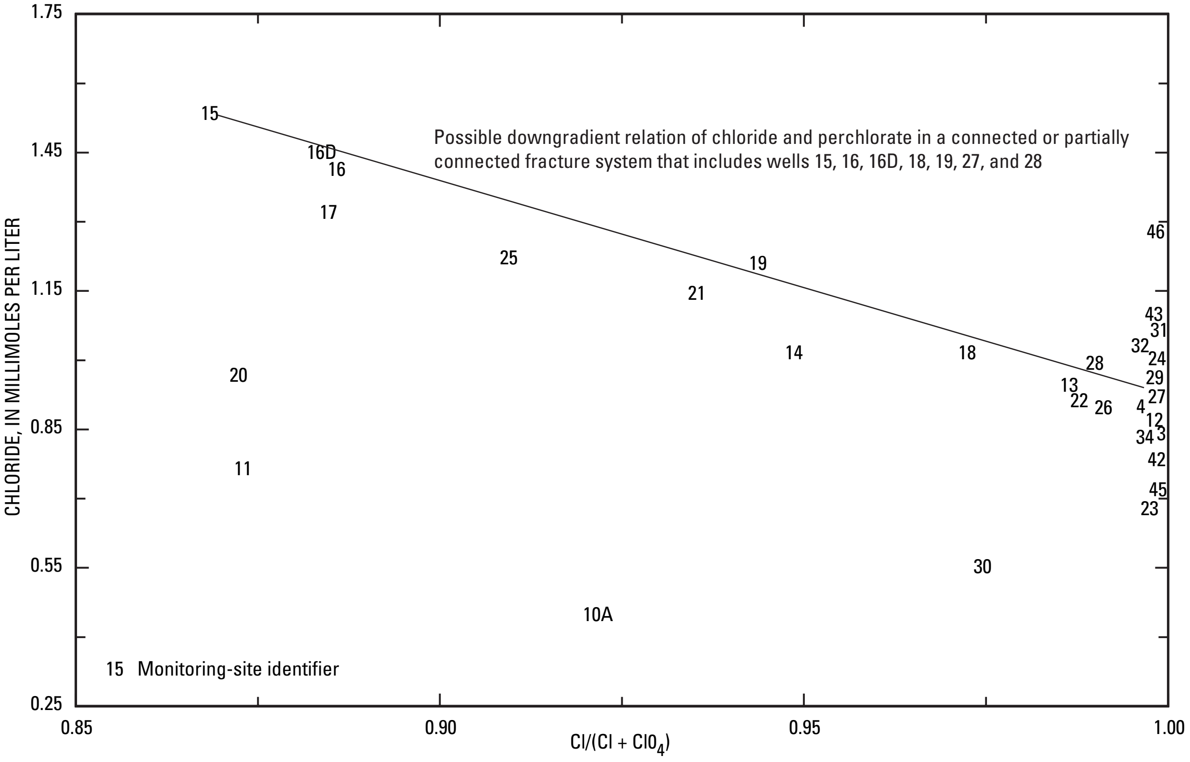


Figure 29. Perchlorate (ClO_4) and chloride (Cl) relations in ground water from selected wells in the Hazardous Test Area, October 2005.

wells at and downgradient from the OB/OD site provides a means of visualizing the degradation of perchlorate and changes to chloride concentrations. The largest perchlorate concentrations relative to chloride concentrations were present in ground water from wells 11, 15, and 20 near the OB/OD pits (fig. 29). The larger chloride concentration in ground water from well 15 suggests an additional chloride input along with entrainment of perchlorate from the OB/OD site. Ground water in well 15 possibly represents entrainment of perchlorate from the OB/OD site but also the entrainment of additional chloride from the OB/OD site that may be a result of the degradation of additional perchlorate at the surface or in the vadose zone. Ground water from wells 11 and 20 near the pits indicates a relatively large input of perchlorate but no corresponding input of additional chloride, which indicates a different source pathway than ground water in well 15.

Downgradient from the OB/OD pits, perchlorate concentrations decline in ground water from all wells as indicated by the increasing chloride to chloride-plus-perchlorate ratio (fig. 29), and this decline was strongly visible in transect *B–B′* (fig. 22). Chloride concentrations generally decline in the downgradient direction but concentrations are more variable because of the initial upgradient chloride contribution, which further highlights the likelihood of disconnected or partially connected fracture systems. Wells 15, 16, 16D, 18, 19, 27 and 28 may represent a connected or partially connected fracture system and changes to perchlorate and chloride may provide insight to natural attenuation processes. The effect of degradation is unknown but dilution is visible in this system of wells. If this was a closed system that did not receive additional recharge, chloride concentrations would increase with the degradation of perchlorate but the opposite effect is visible. Chloride concentrations declined with decreasing perchlorate concentrations indicating dilution of chloride and either dilution and (or) degradation of perchlorate.

Stable Isotopes

The δ^2H and $\delta^{18}O$ values for October 2005 samples collected from selected wells at HTA indicate similar isotope ratios (small range of δ^2H and $\delta^{18}O$), although ground water from the southern part of the study area (wells 37, 40, 41, and 45) did contain slightly less depleted values (fig. 30). Stable isotopes of water are temperature dependent and similar isotopic values indicate similar source waters (Eby, 2004). The slightly less depleted isotopic values in ground water from selected wells may be a result of different recharge elevations or seasonal differences. Seasonal differences are related to temperature effects such as differences in evaporation prior to recharge or different isotopic values when comparing winter or summer precipitation (Eby, 2004). Ground water in wells near the OB/OD site contained a slight variation of isotope ratios that may be a result of the mixing of waters from different recharge areas that have a slightly different isotopic

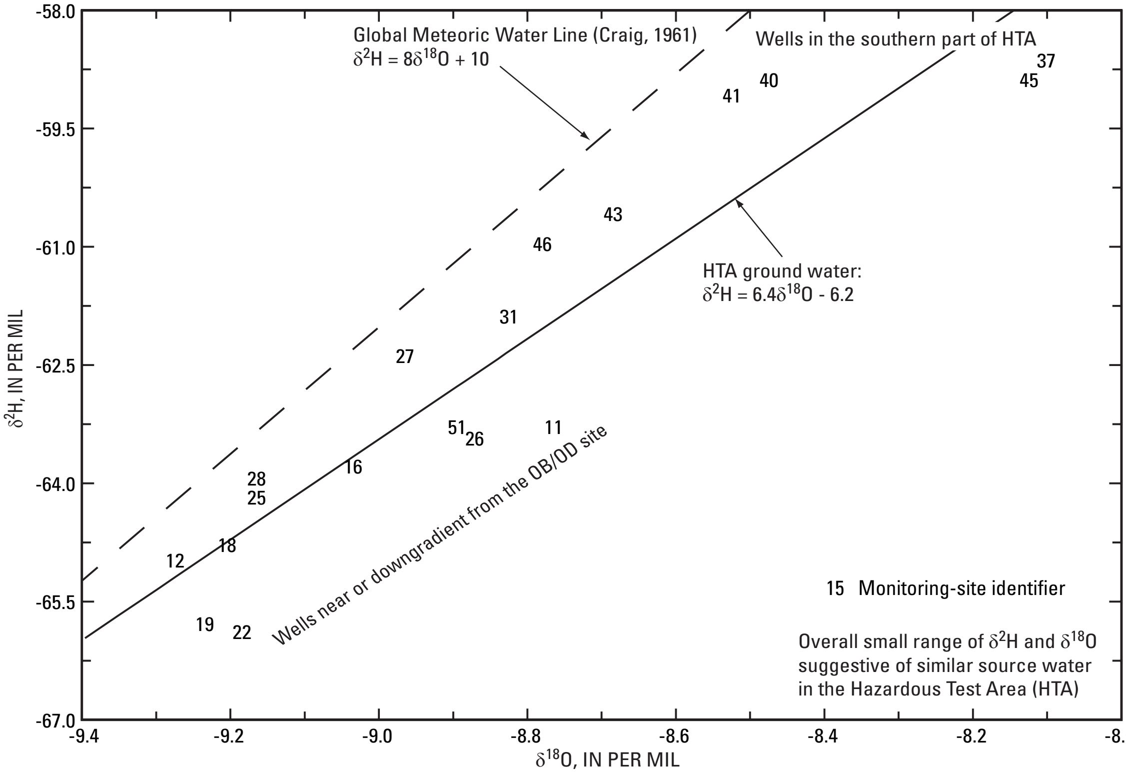


Figure 30. δ^2hydrogen and δ^{18}oxygen for ground water collected from selected wells in the Hazardous Test Area, October 2005.

value because of temperature effects. Ground water at the downgradient locations may receive a mix of recharge from the San Augustin Mountains and San Andres Mountains (wells 41 and 45) or some local contributions such as from around Mineral Hill (wells 37 and 40), which may produce a slightly different isotopic signature than just San Augustin recharge. These results partially correspond to calcium/strontium results (fig. 27) where ground water from downgradient wells 27, 45, and 46 indicated a likely limestone-water interaction. Limestone is only present in the San Andres Mountains (Black Mountain) in the study area.

Denitrification and sulfate reduction will increase (enrich the heavier isotope) $\delta^{15}N$ and $\delta^{18}O$ values for residual nitrate and $\delta^{34}S$ values for residual sulfate as the lighter isotopes are more quickly reduced (Eby, 2004). The $\delta^{15}N$ and $\delta^{18}O$ values of nitrate were heaviest in ground water from wells 12 (upgradient from the pits), 26 (east of the pits), and 43 (downgradient from the pits) (fig. 31). The lightest nitrogen and oxygen isotope ratios of nitrate were in ground water from wells 19 and 11 (near the OB/OD pits). Sulfate in ground water from wells 12 and 24, upgradient and north of the OB/OD pits, contained the lightest $\delta^{34}S$ values, and sulfate in ground water from well 46, downgradient from the OB/OD pits, was the heaviest (fig. 32).

The differences in $\delta^{15}N$ and $\delta^{18}O$ values in nitrate are probably the result of mixing of naturally occurring nitrate and nitrate derived from explosives at the OB/OD site along with the effect of denitrification of the mixed nitrate pool (overall mass available for geochemical reactions). Nitrate derived from natural organic material typically contains a $\delta^{15}N$ greater than zero and as much as 9‰ (Fogg and others, 1998; Komor and Anderson, 1993). The $\delta^{15}N$ values of nitrogen and oxygen in nitrate derived from RDX have not been determined, but nitrogen used in the production of explosives likely is similar to atmospheric nitrogen (0‰) given the atmospheric source for nitrogen-based explosives. Coffin and others (2001) determined $\delta^{15}N$ values for TNT ranging from 3 to 6‰. The $\delta^{15}N$ values for nitrate degraded from explosives may be smaller than $\delta^{15}N$ of the source compound because the lighter isotope is preferentially removed from the explosive compound during degradation. For these reasons, $\delta^{15}N$ of nitrate degraded from explosives likely is lighter (smaller) than $\delta^{15}N$ of nitrate from natural organic sources. The lightest $\delta^{15}N$ and $\delta^{18}O$ values in ground water were located at wells 11 and 19 where some of the largest nitrate concentrations were measured. Ground water from well 12 (upgradient from the OB/OD site) contained the heaviest $\delta^{15}N$ and $\delta^{18}O$ values, which indicates a mostly natural source of nitrate. The heavier $\delta^{15}N$ and $\delta^{18}O$ values for ground water from wells 26 and 43 indicate denitrification of the mixed nitrate pool.

Biologically mediated sulfate reduction is considered a strong reduction indicator because the reduction of oxygen,

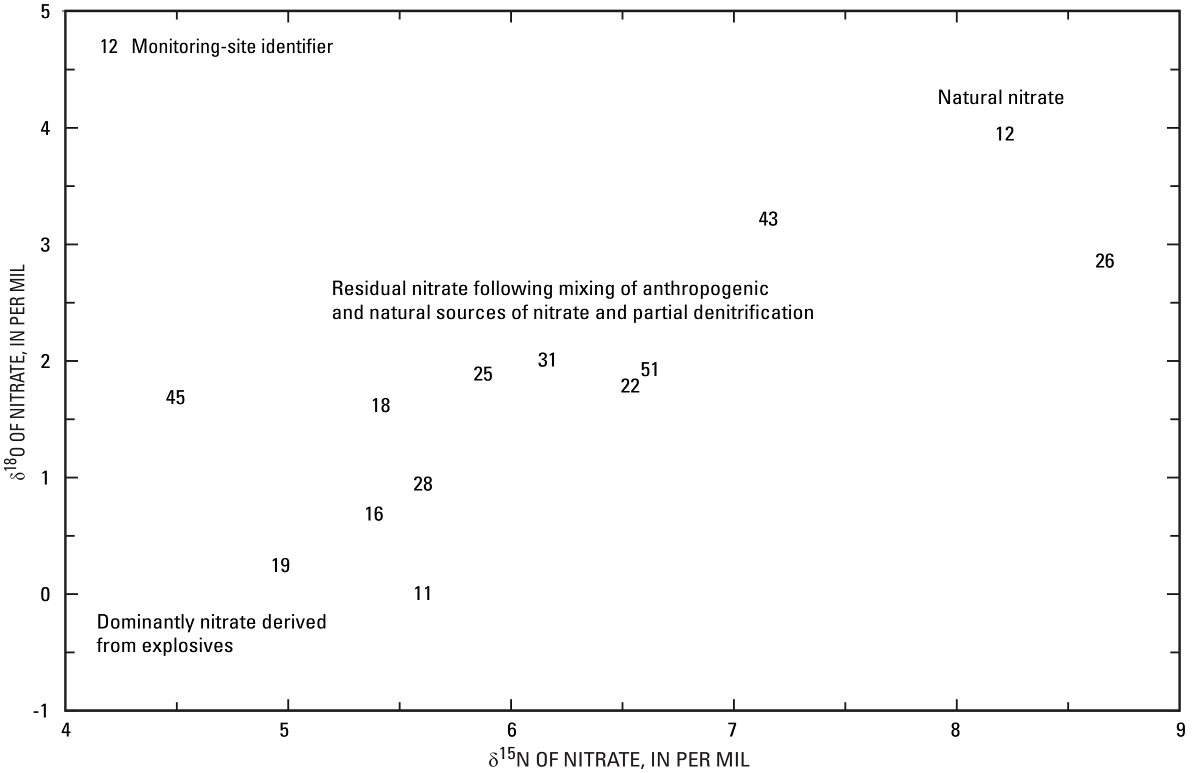


Figure 31. δ^{15}nitrogen and δ^{18}oxygen values of nitrate in ground water from selected wells in the Hazardous Test Area, October 2005.

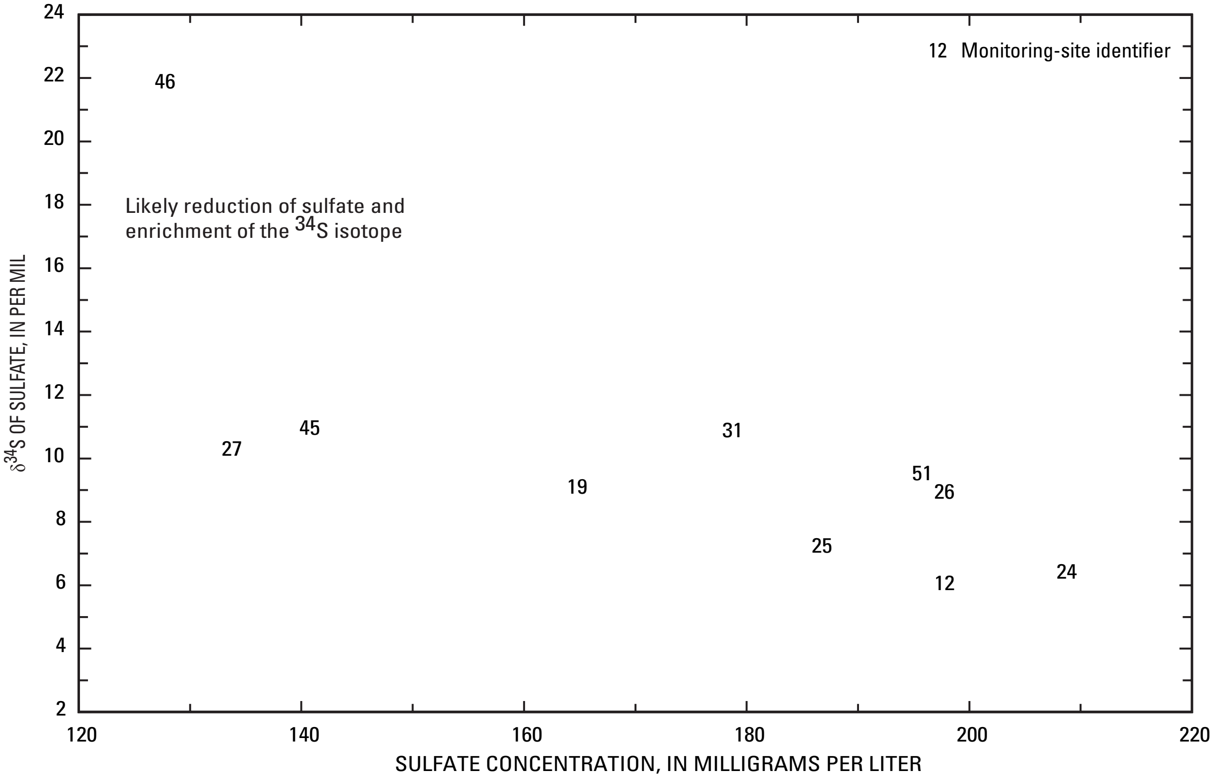


Figure 32. Sulfate concentrations and δ^{34}sulfur values for sulfate in ground water from selected wells in the Hazardous Test Area, October 2005.

nitrate, manganese, iron, and organic matter generally will occur prior to reduction of sulfate because of the increased energy necessary for the reduction reaction (inversely described by the electron activity of the solution) (Stumm and Morgan, 1996). Sulfur isotopes of sulfate were only measured in ground water from a few wells, but the limited results suggest an inverse relation between sulfate concentrations and $\delta^{34}S$ values (fig. 32). This inverse relation likely is the result of sulfate reduction that decreased the sulfate concentration and increased the isotopic ratio for the residual sulfate. The likelihood of sulfate reduction suggests strong reducing conditions in parts of the aquifer.

The aroma of hydrogen sulfide (reduced sulfur form) was detected by the authors in ground water from downgradient wells 23, 24, 36, 40, 46, and 48 during the study period of 1996–2006, which further suggests downgradient reducing conditions and likely degradation of the contaminants in the aquifer. Sulfate reduction is not a continuous process in the aquifer and likely fluctuates according to inputs and oxygen consumption. Hydrogen sulfide has been detected in ground water from well 24 but not during the October 2005 sampling. Sulfate concentrations and sulfur isotopes of sulfate in ground water from well 24 from the October 2005 sampling also do not indicate sulfate reduction compared to sulfur isotope data from the other wells (fig. 32). Additionally, hydrogen sulfide has been detected in ground water from well 34 but not well 12. This difference in reducing conditions in the two upgradient wells (located within 200 yards of each other) suggests different fracture systems radiating from the mountain-front interface above the OB/OD site (assuming a closed fracture system and no loss of hydrogen sulfide gas if these two wells penetrated the same system).

Reduction-Oxidation Sequence

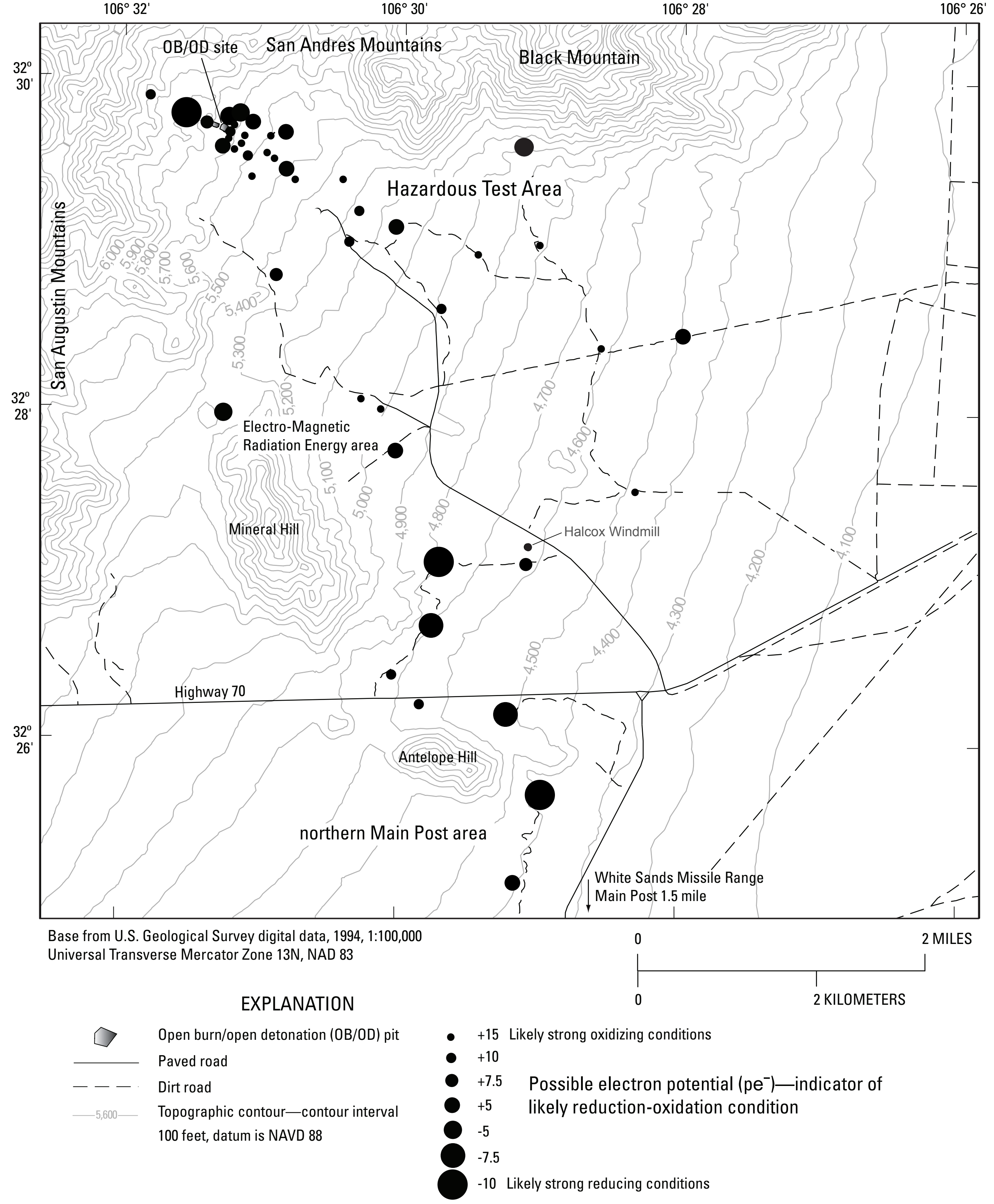
The introduction of anthropogenic organic compounds into a closed or semi-closed ground-water system can induce a sequence of redox reactions. This redox sequence is microbially mediated and results from the relative ease of certain compounds to provide energy to the microbes (Stumm and Morgan, 1996). The redox sequence generally consists of the following major reactions in order of increasing reducing conditions: oxygen consumption (respiration), denitrification, manganese reduction, fermentation (organic matter reduction), iron reduction, sulfate reduction, and methane fermentation (Stumm and Morgan, 1996). Contaminant concentrations and isotope ratios indicate that ground water at HTA is undergoing redox reactions, and ground water at specific wells is undergoing various reduction processes that can be used to indicate a position in the overall redox sequence.

Using the redox sequence, estimated values of pe^- (electron potential, log $\{e^-\}$) were assigned to ground water collected in October 2005 from all wells in the larger monitoring network that contained data for dissolved oxygen, nitrate, manganese, iron, sulfate, and bicarbonate. These values were used to estimate the strength of reducing and oxidizing conditions at HTA (fig. 33). Values of pe^- were assigned using median values of the reduction processes over their known range as presented in Stumm and Morgan (1996). For example, a pe^- value of +15 was assigned to ground water from a well that indicated aerobic conditions and no visible reduction indicators such as increased manganese or iron concentrations, as opposed to a pe^- value of -7.5 where sulfate reduction is likely occurring as indicated by a smaller sulfate concentration. Seven possible pe^- values were assigned: no apparent reduction in dissolved oxygen concentrations (+15), likely reduced oxygen concentrations (+10), reduced nitrate concentration (+7.5), increased manganese concentration (+5), increased iron concentration (-5), decreased sulfate concentration (-7.5), and increased bicarbonate concentration from carbon dioxide production (-10). Values assigned to ground water at the individual wells do not convey known electron potentials but are estimates of redox strength based on available data for comparison of ground water in and around HTA.

Spatial variability of redox conditions at HTA (fig. 33) supports the conclusion of disconnected or partially connected fractures within the aquifer with variable hydraulic conductivities. Moderate to strong reducing conditions are present upgradient from the OB/OD site, at the OB/OD site, and at various locations downgradient from the pits, but well-oxygenated water also is located between many of the reducing locations. Such changes in redox conditions with downgradient flow in a connected aquifer system would require substantial re-oxidation of the ground water, which is unlikely given the mostly closed nature of the fractured-granite aquifer at HTA. The clustering of reducing conditions around the OB/OD pits also suggests biodegradation of the contaminants and the subsequent influence on redox conditions in ground water. Strong reducing conditions along the periphery of the basin (near Black Mountain, Antelope Hill, and Mineral Hill) may be an effect of sulfide-mineral dissolution in the mineralized zones described in the Ground-Water Composition section.

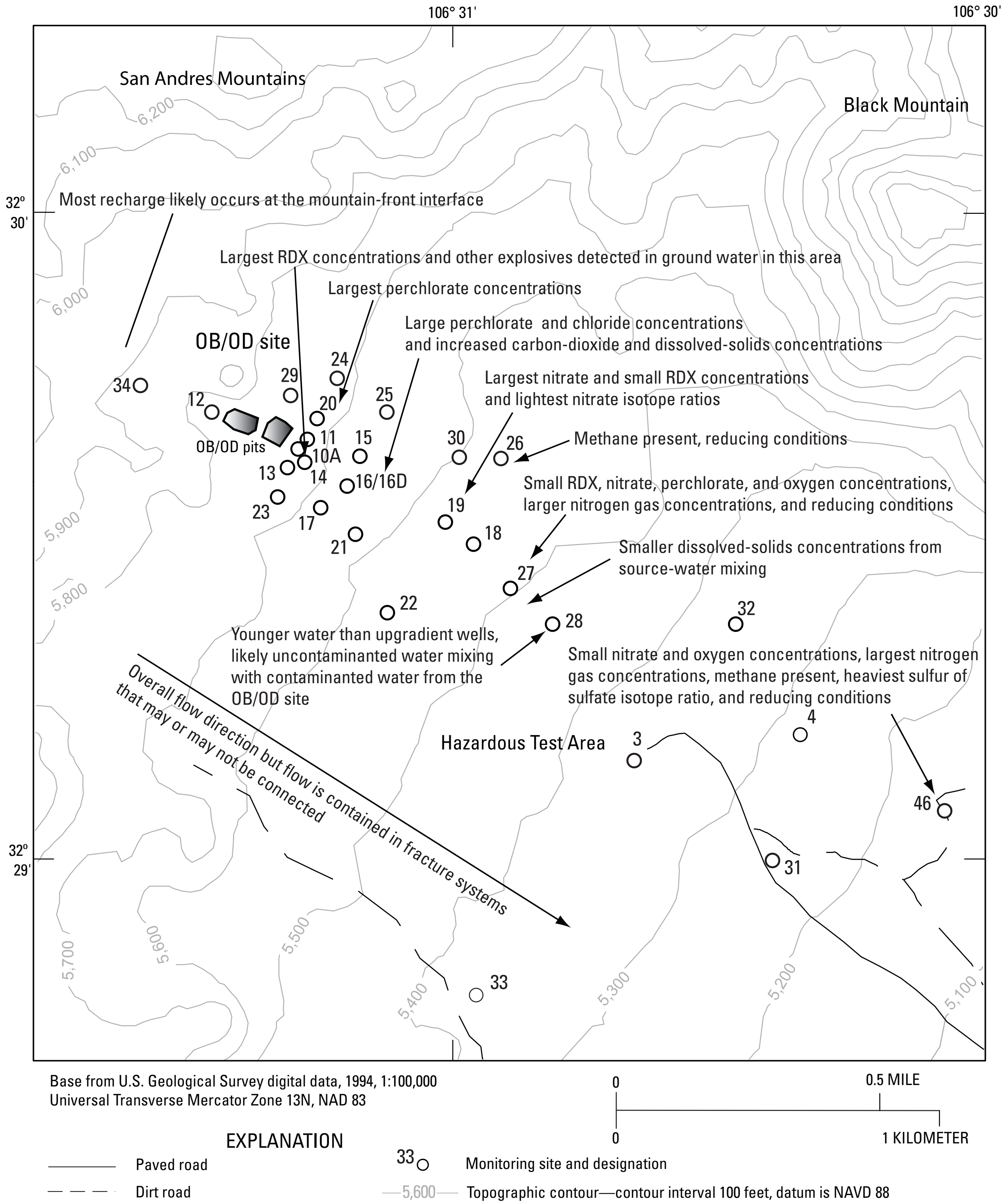
Summation of Natural Attenuation Indicators

Various indicators of natural attenuation described in this report present discrete evidence of dilution and degradation of the contaminants in the HTA fractured-granite aquifer. Individually, these indicators only suggest natural attenuation, but combined, a distinct and fully evident picture of natural attenuation is more apparent. Figure 34 spatially presents the major indicators for natural attenuation with downgradient ground-water flow from the OB/OD site. The spatial summation of natural attenuation indicators describes partially disconnected fracture systems and natural attenuation of the contaminants with downgradient flow. Dilution of the contaminants is dominant where oxidizing conditions are present as described in the Reduction-Oxidation Sequence section above. Degradation assists in naturally attenuating the contaminants in areas of reducing conditions given the



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83

Figure 33. Possible reduction-oxidation conditions (relative electron potential values) for ground water at the Hazardous Test Area, Electro-Magnetic Radiation Energy area, and northern Main Post area, October 2005.



Base from U.S. Geological Survey digital data, 1994, 1:100,000
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Figure 34. Spatial pattern of contamination of the Hazardous Test Area fractured-granite aquifer near the Open Burn/Open Detonation site and indicators of natural attenuation that reduce contaminant concentrations in the downgradient direction, October 2005.

greater likelihood of contaminant degradation under anaerobic conditions. Substantial contaminant transport beyond the existing areal extent of the contaminants appears unlikely given the relative “stability” of contaminant concentrations from 1996–2006 and the ongoing processes of dilution and degradation that produce this concentration stability.

Summary

In 2007, the U.S. Geological Survey, in cooperation with U.S. Army White Sands Missile Range, conducted a study of ground-water geochemical data collected at the Hazardous Test Area at White Sands Missile Range from 1996–2006 to evaluate temporal and spatial variability of RDX (explosive compound associated with C-4), nitrate, and perchlorate (oxidizer associated with rocket propellant) contaminating the fractured-granite aquifer. Contamination of the aquifer was a result of the use of the Open Burn/Open Detonation site at the Hazardous Test Area, and the goal of the analysis was to examine natural attenuation mechanisms that appear to have induced stability in the areal extent of the contaminant concentrations in ground water.

The Hazardous Test Area is located in southern New Mexico, about 25 miles east of Las Cruces and 10 miles north of White Sands Missile Range Main Post. The Open Burn/Open Detonation site is located in the northwestern part of the Hazardous Test Area and consisted of two open detonation pits. The pits were used for ordnance demolition, were closed in 2000, and partially regraded in 2002 and 2003. The Hazardous Test Area aquifer is almost entirely within a fractured, Precambrian-granite pluton that contains diorite dikes. Most aquifer recharge likely occurs along the mountain-front interface and in ephemeral channels. Two transects of ground-water wells from the existing monitoring-well network—one perpendicular to ground-water flow (transect *A–A´*) and another parallel to ground-water flow (transect *B–B´*)—were selected to examine source characteristics and the spatial and temporal variability of the contaminant concentrations. Ground-water samples collected in 2005 from a larger sampling of wells than the two transects were analyzed for various tracers including major ions, trace elements, RDX degradates, dissolved gases, water isotopes, nitrate isotopes, and sulfate isotopes to examine the natural attenuation processes of dilution and degradation.

Ground water in the fractures penetrated by monitoring wells is pressurized in the closed or semi-closed system, and the potentiometric surface parallels land topography except immediately downgradient from the pits. An anomaly in the potentiometric surface near the Open Burn/Open Detonation site is caused by a minor fault that runs through the southern part of the site. Recharge entrains contaminants at the site and transports them downgradient towards the Tularosa Basin floor through a poorly connected fracture system(s). RDX in ground water from wells at the Open Burn/Open Detonation site indicates a source near the pits but also a dispersed source outside of the immediate pit area. The main source of RDX has shifted with time, and the shift in peak concentrations correspond with the regrading of the south and east berm areas of each pit in 2002 and 2003 following site closure. A larger dispersal pattern and larger nitrate concentrations compared to RDX indicate a larger source area of degrading explosive compounds that produce elevated nitrate concentrations in the aquifer. The dispersed nitrate source did shift with time and corresponded with berm regrading. The source of perchlorate appears to be more concentrated compared to RDX and nitrate sources, and the source location of perchlorate has not shifted with time.

From 1996–2006, RDX, nitrate, and perchlorate concentrations in ground water downgradient from the Open Burn/Open Detonation site have been relatively stable. Natural attenuation (dilution and (or) degradation) appears to be reducing contaminant concentrations within 0.5 mile downgradient from the site. Largest RDX concentrations were located within 0.1 mile of the pits (wells 10A, 11, and 14). The largest nitrate concentrations were present in ground water about 0.25 mile downgradient from the pits (well 19). Perchlorate concentrations were largest in ground water from wells 16 and 16D (about 0.15 mi downgradient from the pits), and perchlorate concentrations quickly declined further downgradient. There is limited correlation between changes in water levels and contaminant concentrations and between the concentrations of the explosives-related contaminants of RDX and nitrate except at the largest contaminant concentration locations.

Ground water was not progressively older at all locations in the downgradient direction, and age-dating results may be evidence of disconnected or partially connected fractures and downgradient recharge and mixing of contaminant and uncontaminated waters. Dissolved-solids concentrations in ground water in the Open Burn/Open Detonation site area were largest north-northeast of the pits, concentrations increased immediately downgradient from the pits because of contaminant inputs, and concentrations then decreased likely because of dilution from downgradient flow mixing. Major ion and strontium concentrations and δ^2H and δ^{18}O values identified similar sources of recharge waters to the aquifer except along the basin periphery where recharge water may be influenced by dissolution of mineral assemblages associated with ore deposits that are present along the basin margins. Some recharge appears to be crossing the Bear Peak Fold and Thrust Zone from the San Andres Mountains and mixing within certain fractures as indicated by calcium, strontium, and δ^2H and δ^{18}O values. The RDX degradates of MNX and DNX were present in ground water in a few wells near and downgradient from the pits in October 2005. In the downgradient direction, the largest RDX concentrations were in ground water from well 10A followed by downgradient decreases to near nondetection levels by well 19. This pattern was opposite of the downgradient nitrate pattern that indicated an increasing nitrate concentration from well 12 to the largest nitrate concentration in ground water from well 19. This inverse pattern from the Open Burn/Open Detonation pits to well 19 suggests a contribution of nitrate to ground water from the degradation of RDX. The likely degradation of RDX can only account for a small part of the increase in nitrate, which suggests additional nitrate inputs. These other nitrate inputs may be related to the degradation of other explosive compounds—such as HMX, DNT, TNT, and teryl—that have been detected in soil samples in and around the pits but are rarely detected in ground water and only at wells near the Open Burn/Open Detonation pits, including wells 10A, 11, 13, 14, 16, 16D, 20, and 24.

Nitrogen-gas and nitrate concentrations in ground water from downgradient wells showed an inverse relation and indicated degradation of nitrate at certain locations in the aquifer. The presence of methane and changes in likely carbon-dioxide concentrations in ground water from certain wells suggest reducing conditions and degradation of the contaminants. The perchlorate and chloride relation indicates perchlorate degradation at the Open Burn/Open Detonation pits and dilution of perchlorate and chloride downgradient from the pits. The lightest $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in ground water were located at wells 11 and 19 where the largest nitrate concentrations were present. Ground water from the background well (12) contained the heaviest $\delta^{15}N$ and $\delta^{18}O$ values because of a natural nitrate source. The lighter $\delta^{15}N$ and $\delta^{18}O$ values for ground water in downgradient wells suggest denitrification of the mixed nitrate pool. Sulfate concentrations and $\delta^{34}S$ values also indicate redox changes and reduction downgradient from the Open Burn/Open Detonation pits.

Estimated electron potential values were assigned to ground water collected in October 2005 from all wells at the Hazardous Test Area that contained data for dissolved oxygen, nitrate, manganese, iron, sulfate, and bicarbonate. Moderate to strong reducing conditions were present upgradient from the Open Burn/Open Detonation site, at the site, and at various locations downgradient from the site, even though the aquifer contained well-oxygenated water between many of the reducing locations. The spatial variability of reducing conditions in the aquifer exemplifies disconnected or partially connected fractures and natural attenuating conditions with downgradient flow. Dilution of contaminants is dominant where oxidizing conditions are present and biodegradation assists in naturally attenuating the contaminants in areas of reducing conditions. Substantial contaminant transport beyond the existing areal extent of the contaminants appears unlikely given the relative “stability” of contaminant concentrations from 1996–2006 and the ongoing processes of dilution and degradation that produce this concentration stability.

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