

In cooperation with the
U.S. Fish and Wildlife Service,
Chesapeake Bay Field Office,
Annapolis, Maryland

Ground-Water Contamination from Lead Shot at Prime Hook National Wildlife Refuge, Sussex County, Delaware

Water-Resources Investigations Report 02-4282



Cover. Oblique aerial photograph showing Broadkilm Sportsman's Club (center of photo) and Prime Hook National Wildlife Refuge, looking southwest (Refer to figure 3.)

[Photo by John Battista, U.S. Geological Survey volunteer]

U.S. Department of the Interior
U.S. Geological Survey

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by Daniel J. Soeder and Cherie V. Miller

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Conversion Factors and Vertical Datum

	Multiply	By	To obtain
inch (in.)		2.54	centimeter
foot (ft)		0.3048	meter
foot per day (ft/d)		0.3048	meter per day
mile (mi)		1.609	kilometer
square mile (mi ²)		2.590	square kilometer
acre		4,047	square meter
acre		43,559	square kilometer
square foot (ft ²)		0.0929	square meter
gallon (gal)		3.785	liter

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) by the following equation:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

Vertical Datum: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1988—a geodetic datum derived from a 1988 update of the reference geoid and first-order level nets of the United States and Canada.

In USGS standard usage, “**Altitude**” refers to height above mean sea level; “**Elevation**” refers to height above a defined reference datum. The reference datum used throughout this report is mean sea level, so in this instance the two terms are interchangeable.

Specific conductance is given in units of microsiemens per centimeter (μS/cm) at 25 degrees Celsius.

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (μg/L).

Acronyms and Abbreviations

DG	Prefix for sampling wells emplaced downgradient from the main lead shot deposits
DI	Deionized water
DZ	Prefix for sampling wells emplaced within the main “drop zone” of lead shot deposits
GPR	Ground-penetrating radar
mg/L	milligrams (10^{-3} gram) per liter
µg/L	micrograms (10^{-6} gram) per liter
mL	milliliter
µm	micrometer
NWQL	National Water-Quality Laboratory (USGS)
NWR	National Wildlife Refuge
Pb	Chemical symbol for lead
PVC	Polyvinyl chloride (plastic) pipe used for well casing
UG	Prefix for sampling wells emplaced upgradient of the lead shot deposits; sampled as a control.
USEPA	U.S. Environmental Protection Agency
USFWS	U.S. Fish and Wildlife Service (Department of the Interior)
USGS	U.S. Geological Survey (Department of the Interior)

A note on nomenclature:

Primehook and **Prime Hook**: On the USGS 7.5-minute topographic quadrangle map for Milton, Delaware, the tributary stream to the Broadkill River draining the study area is referred to as “**Primehook Creek**,” whereas the wildlife refuge is named “**Prime Hook National Wildlife Refuge**.” The name “Primehook” as a single word is an Anglicized version of an earlier, similar-sounding Dutch name meaning “Plum Point,” a local landscape feature (G. O’Shea, U.S. Fish and Wildlife Service, oral commun., 2002). Similar English adaptations of Dutch names are common in Delaware. The name was split into two words when the National Wildlife Refuge was established in 1964. This naming convention (one word for the creek and two words for the refuge) is used throughout the report.

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Abstract

Prime Hook National Wildlife Refuge is located in southeastern Delaware in coastal lowlands along the margin of Delaware Bay. For 37 years, the Broadkiln Sportsman's Club adjacent to the refuge operated a trap-shooting range, with the clay-target launchers oriented so that the expended lead shot from the range dropped into forested wetland areas on the refuge property. Investigators have estimated that up to 58,000 shotgun pellets per square foot are present in locations on the refuge where the lead shot fell to the ground.

As part of the environmental risk assessment for the site, the U.S. Geological Survey (USGS) investigated the potential for lead contamination in ground water. Results from two sampling rounds in 19 shallow wells indicate that elevated levels of dissolved lead are present in ground water at the site. The lead and associated metals, such as antimony and arsenic (common shotgun pellet alloys), are being transported along shallow ground-water flowpaths toward an open-water slough in the forested wetland adjacent to the downrange target area. Water samples from wells located along the bank of the slough contained dissolved lead concentrations higher than 400 micrograms per liter, and as high as 1 milligram per liter. In contrast, a natural background concentration of lead from ground water in a well upgradient from the site is about 1 microgram per liter. Two water samples collected several months apart from the slough directly downgradient of the shooting range contained 24 and 212 micrograms per liter of lead, respectively.

The data indicate that lead from a concentrated deposit of shotgun pellets on the refuge has been mobilized through a combination of acidic water conditions and a very sandy, shallow, unconfined aquifer, and is moving along ground-water flow-

paths toward the surface-water drainage. Data from this study will be used to help delineate the lead plume, and determine the fate and transport of lead from the source area.

Introduction

Prime Hook National Wildlife Refuge (NWR) is located along Primehook Creek and the western shore of Delaware Bay in Sussex County, Delaware, approximately 3 mi (miles) northeast of the town of Milton (figs. 1a–1b). The 9,700-acre refuge was established in 1963 and consists of approximately 7,400 acres of freshwater and tidal marsh, 1,000 acres of timber and brush, and 1,300 acres of grassland and croplands (U.S. Fish and Wildlife Service, 2000).

Large numbers of birds, including Canada geese, snow geese, black ducks, mallards, pintails, teal ducks, and wood ducks either live on the refuge year round, or pass through the area during spring and fall migrations (U.S. Fish and Wildlife Service, 2000). Because significant numbers of waterfowl use the refuge, the U.S. Fish and Wildlife Service (USFWS) was concerned about the potential environmental impact of large amounts of lead shotgun pellets deposited on the property by a shooting range adjacent to the refuge. The wildlife biologists and refuge managers were worried that the birds would ingest the lead pellets, which are approximately 1–2 mm (millimeters) in diameter, as “grit,” a single one of which could potentially kill an animal from lead poisoning (Crowley and Richardson, 2001). The USFWS was also concerned that the soil and ground water might be contaminated with lead, possibly creating paths by which it could enter the local food chain.

The USGS learned of the concerns of the USFWS in March 2000. The two agencies cooperated on an initial round of sampling in May 2000 of six shallow wells to determine if lead was present in the ground water at the site. When analysis of these samples showed the presence of lead, a second sampling round was carried out in April 2001 on 13 wells and the nearby stream. The USGS study was designed as a “field screening” to give USFWS some indication of the scope of the lead problem, and to assess where and how fast the contamination might be moving. Lead transport through shallow ground water is an unusual occur-

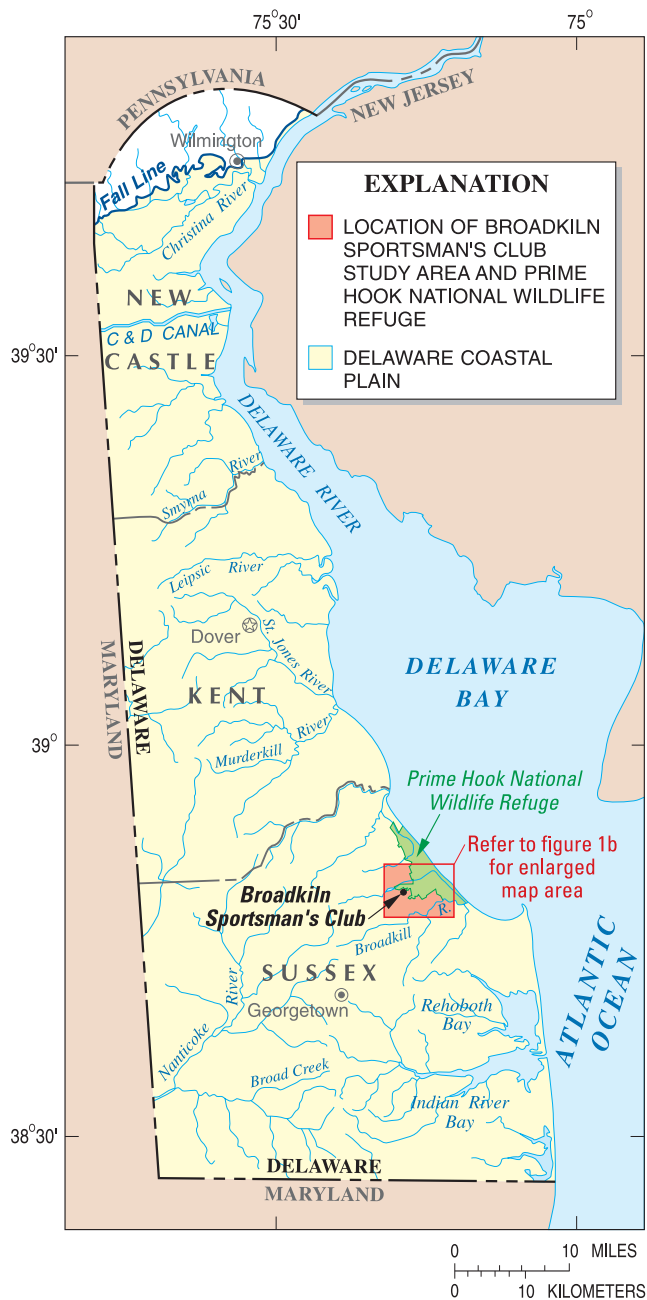


Figure 1a. Location of Prime Hook National Wildlife Refuge and the Broadkill Sportsman's Club study area, Sussex County, Delaware.

rence, as metallic lead is generally considered immobile, and the chemistry of this process was also investigated.

Background

The Broadkill Sportsman's Club (referred to in this report as "the club") was founded in 1962 in an area known as Pikes Neck, in Sussex County, Delaware. Property boundaries of Prime Hook NWR adjacent to the club were established by the USFWS in 1964. The club used five shooting ranges, each built behind a small (approximately 10 by 10 ft, or feet) concrete block bunker known as the trap house, which launched the clay targets into the air. Individual ranges had an arrangement of five angled concrete walkways behind the trap house, with shooting stations and distances marked on the walkways (fig. 2). The club members fired shotgun rounds from shooting stations on the walkways across a grassy field and toward a wooded area, intending to hit the airborne clay targets above the field. Numerous lead shotgun pellets from misses and overshot followed ballistic trajectories downrange, eventually losing velocity and/or hitting trees inside the refuge boundary and falling to the ground.

The club is located in an upland area that acts as a drainage divide for two wooded wetlands containing unnamed tributaries of Primehook Creek. The highest land elevation on the axis of the upland is about 10 ft above sea level; most of the land in the wooded wetland areas is 5 ft or less in elevation. Primehook Creek is fresh through this area, with levels controlled by a dam downstream. The Broadkill River is tidal through the refuge, but Primehook Creek behind the flow-control structure is not (G. O'Shea, USFWS, oral commun., 2000).

The part of Prime Hook NWR bordering the club downrange from the trap-shooting area consists of a forested wetland along a small, unnamed tributary or slough to Primehook Creek shown in figure 3 as the wooded area to the left of the club facility. The slough consists of a series of small, shallow ponds or pools, a few to possibly a dozen feet wide, and only a few feet deep, separated by saturated hummocks of mud, fallen trees, and organic matter. The water is nearly stagnant with very slow drainage to Primehook Creek. The size and shape of the slough varies greatly with the seasonal rise and fall of the water table, and it dries up completely on occasion. The slough is heavily forested, and is not used much by migratory fowl, which prefer open water. There are numerous small mammals, birds, amphibians, and insects that are common in and around the slough, however, and use it as a water supply. Reference to the "unnamed tributary" or "slough" in this report denotes only the Primehook Creek tributary east of the club, in the area downrange from the trap houses. No work in the western tributary, indicated on figure 3 by the wooded area to the right of the club facility, was performed by the USGS as part of this study.

Previous Investigations

The trap-shooting range was operated from 1962–1998, until a proposed land trade with the USFWS was initiated by

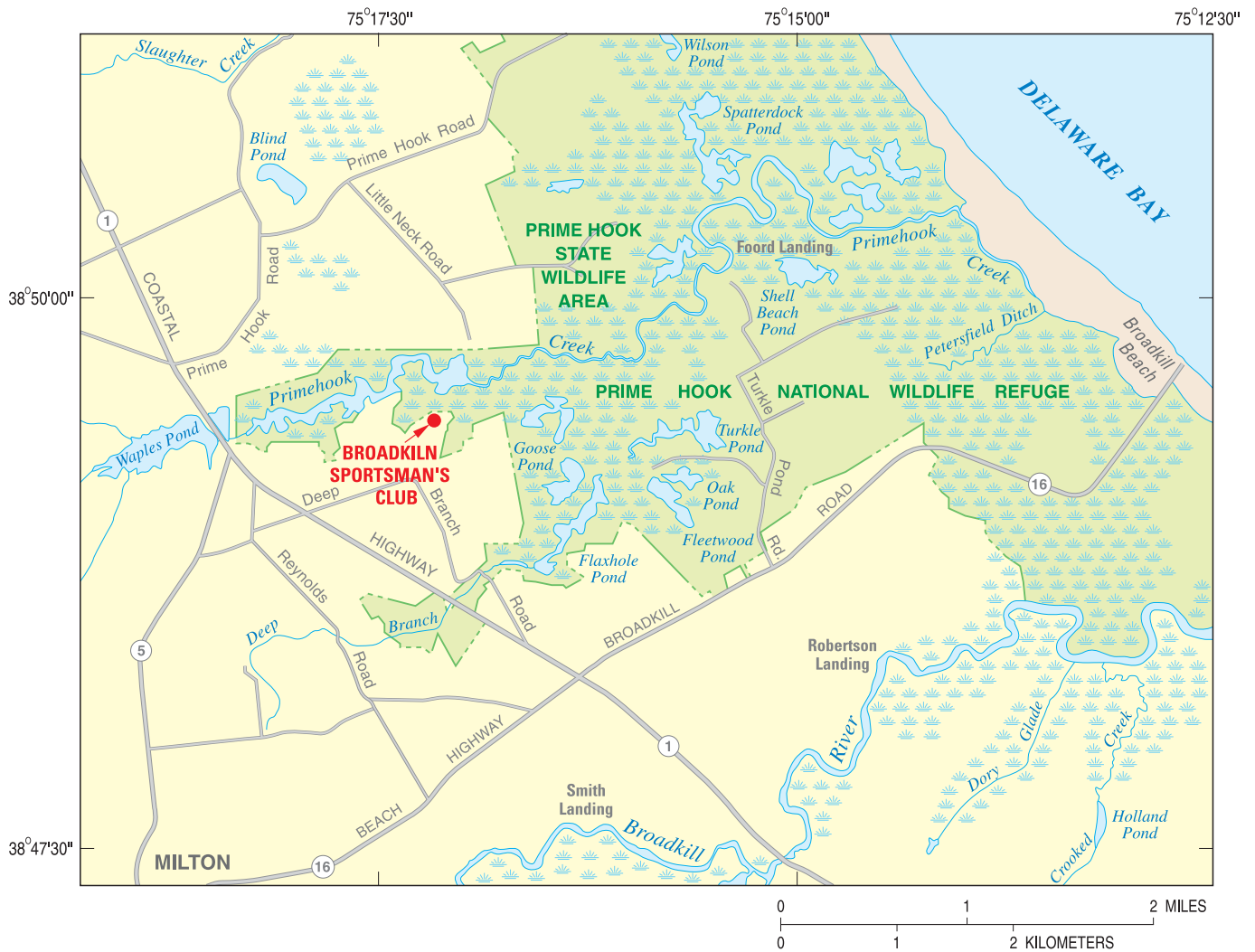


Figure 1b. Detailed view of Prime Hook National Wildlife Refuge and the Broadkill Sportsman's Club study area.

the club. As part of the proposed trade, the USFWS began a review of potential contamination of the site. In August and October 1998, USFWS personnel collected soil samples to determine the extent of lead shot deposition and lead soil concentrations on the land parcel. Results indicated that the surface soils within the shooting trajectory contained elevated concentrations of lead and high numbers of lead shotgun pellets. The USFWS ordered the club to discontinue shooting onto the refuge property, and in 2000 funded the first year of a proposed 3-year Refuge Cleanup project to delineate the magnitude and extent of soil contamination.

A preliminary assessment by a USFWS contractor concluded that lead shotgun pellets from the trap shooting range had accumulated on the refuge property in an area of about 22 acres downrange from the club (Crowley and Richardson, 2001). The highest density of pellets on the refuge was concentrated in a zone of approximately 26,200 ft² (square feet) immediately adjacent to the club property and directly downrange from the trap houses. Investigators counted as many as 57,868 lead pellets per square foot in the center of this high-density area, which is referred to as the “drop zone” in this report.



Figure 2. View of one of the five trap shooting ranges at the Broadkiln Sportsman's Club. (Shooters fired from the angled walkways at clay targets launched from the low trap house building. The tree line in the far background marks the boundary of Prime Hook National Wildlife Refuge.)

A synthetic geotextile cover was placed over the highest concentrations of lead pellets in July 2000, with the intention of preventing waterfowl and other birds from ingesting the shot as grit (fig. 4). This material is identified by Crowley and Richardson (2001) as Geotex Model 315 ST, designed to resist degradation under ultraviolet light, and rated permeable to 5 gallons per square foot per minute. The textile material was anchored in place using 18-in. (inch) steel spikes, but after deployment, it was determined that placing numerous 6-in. concrete blocks on top of the cover would help it resist wind damage.

In addition to this study, the USFWS and their contractors carried out a contaminant investigation in Primehook Creek, as well as aquatic toxicity measurements, bioaccumulation testing, and an ecological risk assessment. The risk

assessment identified the source remediation area as approximately 5 acres of both wetlands and uplands. The cleanup plan involved removal of the soil and lead pellets, grading, and reseeding (B. Crawford, USFWS, written commun., 2002).

Purpose and Scope

The purpose of this report is to provide water-quality data and interpretation to the USFWS for use in environmental risk assessment. The work was performed to analyze the spatial occurrence of lead in ground water at Prime Hook NWR, develop an understanding of the subsurface stratigraphy of the shallow aquifer system in the vicinity of the shooting range, and describe the plume of lead contamination in the study area.

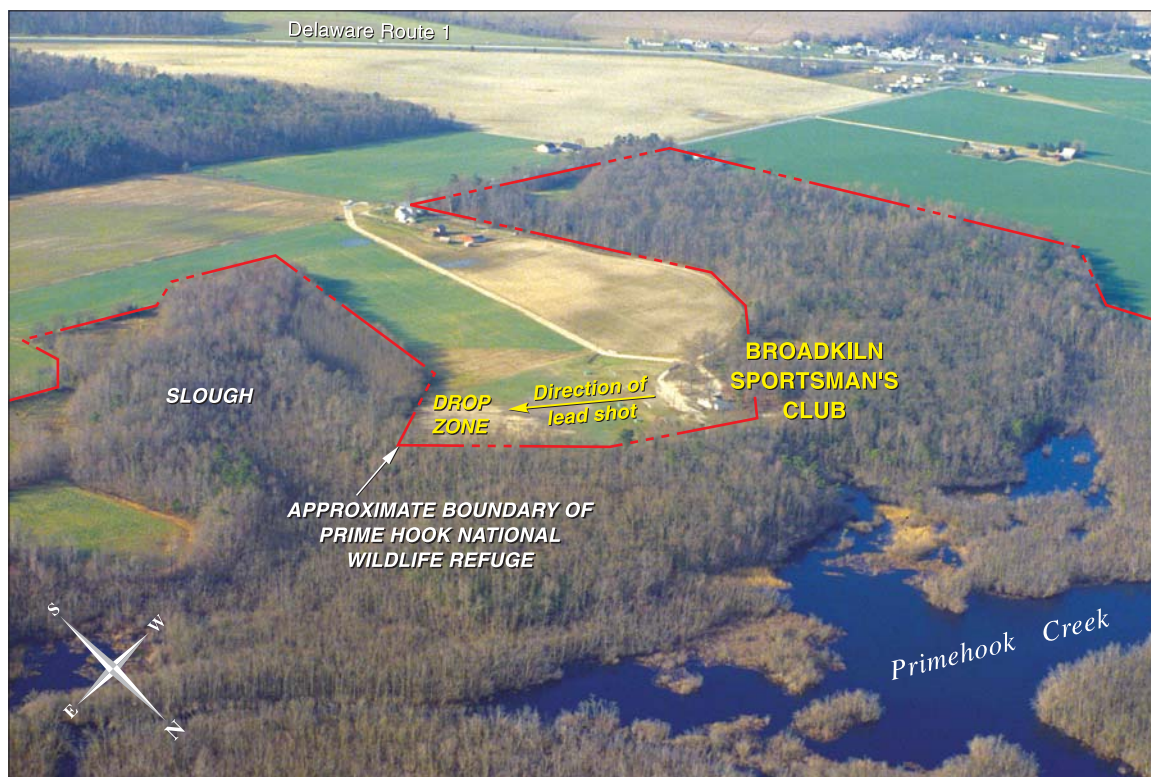


Figure 3. Oblique aerial photograph showing Broadkiln Sportsman's Club and Prime Hook National Wildlife Refuge, looking southwest.

An initial, preliminary field screening was performed to determine if lead from the shotgun pellets was present in the ground water, and subsequently, a more detailed field screening was done to try to assess the nature and extent of the contamination. The ground-water flow system also was analyzed to infer the fate and transport of lead in the ground water, and to determine the direction of movement and the potential for discharge of dissolved lead into nearby bodies of surface water.

Acknowledgments

The authors would like to thank Daniel Murphy and Sherry Krest of the U.S. Fish and Wildlife Service, Chesapeake Bay Field Office, and Barron Crawford, Annabella Larsen, and George O'Shea of Prime Hook National Wildlife Refuge for providing background information, access to the site, and assistance with some of the field

work. USGS volunteer John Battista assisted with field work and took several of the photographs used in this report. David Krantz and Joseph Beman performed coring and installed the second set of wells, using a vibracore rig loaned by the University of Delaware (UD). Beman surveyed the well locations and measured ground-water levels. Mark Nardi assembled the survey data into a GIS data base, and produced site maps. Shannon Collier of UD and David Krantz ran the ground-penetrating-radar survey, also using equipment generously loaned by UD. Michael Smigaj performed the core lithologic analysis, and Britta Hoehndorf transcribed his field notes onto a stratigraphic spreadsheet. Hoehndorf also produced the water-table map and lead concentration gradient map. The authors are grateful to all of these individuals for their help and dedication.



Figure 4. "Drop zone" of high-density pellets covered with geotextile fabric to protect waterfowl and other birds. (Cinder blocks keep the fabric from blowing away. The white building in the background is Broadkill Sportsman's Club house.)

Methods of Study

The objective of this study was to determine the presence and concentrations of lead, antimony, arsenic, and associated shotgun-pellet metal alloys, along with major ions and field parameters, in shallow ground water at Prime Hook NWR in an area downgradient from the club. To obtain the necessary data, a total of 19 shallow wells were installed on the site. Sediment cores and ground-penetrating-radar data were collected to help define the geology and geohydrology of the area. Water levels were measured to determine hydraulic gradients and flow directions, and water samples were collected for chemical analysis of lead and other compounds.

In April 2000, the USGS performed an initial field reconnaissance of the site to assess possible lead contamination in the ground water. Observations of lead pellets on the surface of the drop zone showed that many were coated with a

white oxide or carbonate layer (fig. 5), while those a few centimeters down into the upper soil horizon were shiny and metallic. The absence of the coating was interpreted as evidence of corrosion, and indicated that significant amounts of lead could be dissolving from the shot. The dissolved lead might then be transported into the shallow ground water. USFWS asked the USGS to carry out ground-water sampling and metals analysis as part of the site characterization work. Water samples were collected and analyzed by the USGS in May 2000 and again in April 2001.

Well Installation

Seven drive-point well casings, each consisting of a Schedule 40 plastic (PVC) pipe, 1.5 in. in diameter and 3 ft in length, screened the entire length and fitted with a solid PVC point, were installed at Prime Hook NWR in April 2000 for initial shallow ground-water sampling. The casings were put in place using hand tools, by first clearing the ground surface of leaves, rubble, and lead shot with a shovel, and then manually digging a hole approximately a foot deep and a foot in diameter. After carefully checking the bottom of the hole to ensure that it was free of any remnant lead shot, a 2-in.-diameter, hand-operated soil auger was used to dig a round hole approximately 2 to 4 ft deep. Each casing was inserted into the hole, and a threaded steel cap on the upper end was hit several times with a sledgehammer to seat the point (fig. 6). Clean building supply sand was then placed into the annulus of the hole around the outside of the casing. Because the casings are screened over their entire 3-ft length, no attempt was made to pack off zones within the shallow soil profile penetrated by the emplacement hole. Finally, clean soil from the hand auger excavation was used to fill in the top of the hole and make it level with the ground surface. Great care was taken at every step of the installation process to ensure that no lead pellets were introduced into the hole or into the casing that might affect the results of the water sampling and metals analysis.

In April and May 2001, 12 additional wells were installed on Prime Hook NWR near the club. Using a vibro-core rig, seven wells were installed in cored holes; the remaining five were installed in hand-augered holes using the method described previously. The operational details of the vibrocore rig are discussed in a later section. After the cores were recovered, plastic pipe was inserted into the drill holes as casing to create a well for sampling. In most cases, the plastic casing was not set as deep as the total cored depth of the hole, because the deeper portions of the holes typically collapsed immediately after the core was removed. Casing was set as deeply as possible, and clean sand was packed into the annulus as it was in the hand-augered wells. Some of these later wells have screened intervals only 1 ft long, instead of the standard 3-ft screen. The shorter screens were used in selected locations to try to reduce the vertical component of the ground-water sample.

Two of the vibrocored holes were relatively deep in locations near the unnamed tributary to Primehook Creek. Both of these penetrated a dense clay layer above a coarse, clean sand. Bentonite clay was used to seal the annulus of these



Figure 5. Close-up photograph of lead shot in the drop zone at the Broadkirk Sportsman's Club with white oxide or carbonate coatings on surface pellets. (24-millimeter-diameter coin is shown for scale.)

holes where they penetrated the clay. This material swells in water, and forms an effective low permeability barrier.

Year 2000: The first well was placed upgradient and to the south of the main drop zone, in an area of the refuge that was free of visible lead pellets on the ground surface. This location was chosen as a control point to sample background levels of lead in the ground water. A second well was emplaced within the drop zone itself. This location was selected to sample the ground water directly beneath the highest concentrations of lead pellets to check for contamination. Five additional wells were then placed in various locations downgradient of the drop zone near the banks of the slough. These were intended to capture samples of any lead moving toward this surface-water body through the shallow ground water.

Year 2001: The original well in the drop zone (DZ) broke off in January 2001 when a windstorm blew the geotextile cover off the area. The plastic pipe remaining in the ground

was unsalvageable, so a new shallow well (DZ-0) was emplaced in the drop zone about 5 ft northeast of DZ. Several additional wells were installed next to existing Year 2000 sites using the vibracore rig in order to create shallow/deep well pairs (fig. 7). This was done at the upgradient site (UG, UG-1), the drop zone (DZ-0, DZ-1), and two of the downgradient sites (DG-5, DZ-2) and (DG-2, DG-7). The purpose of this type of emplacement was to collect data on the stratigraphy and lateral continuity of units across the site, as well as to investigate the depth of vertical penetration of lead in the shallow ground water. Well DZ-2 was set 10.2 ft deep near the slough, next to well DG-5, installed in 2000. DG-5 had shown a significant concentration of lead in the 2000 sampling, and emplacement of DZ-2 next to it was intended to capture a deeper part of the discharge flowpath. Coring of DZ-2 encountered a dense sandy clay from a depth of about 6 to 8 ft, with a coarse sand beneath. The 3-ft screen was set below the clay layer into this coarse sand, and



Figure 6. Seating a plastic well casing into a pre-dug hole at Prime Hook National Wildlife Refuge.

the sandy clay was sealed off with swelling bentonite. Hence, the ground water in the DZ-2 well is entirely from the deeper sand, and it is under a slightly higher pressure head than the near-surface ground water. The water level in the DZ-2 well was approximately 1.5 in. above ground surface at the time of installation.

In addition to the vibracored holes, wells were installed with the hand auger along the western bank of the slough at intervals of about 30 to 50 ft to the south of the DG-5 location. This was done in an attempt to constrain the southern boundary of the lead plume moving from the drop zone toward the tributary. The hand-augered well pair DG-8 and DG-8S, set approximately 5 ft and 2 ft deep respectively, were intended to capture deeper and shallower ground-water flowpaths in a visible discharge area or spring. DG-8 has a 1-ft screen instead of a 3-ft screen in an attempt to better isolate the slightly deeper flowpaths. Locations of all 19 wells, the trap shooting range, drop zone, and tributary are shown in the annotated aerial photo in figure 8. Construction details of the wells installed at Prime Hook NWR are summarized in table 1.

Water levels in all wells were collected during a synoptic measurement on September 24, 2001, using a Solinst water-level tape. Absolute water levels tend to be higher in the spring, when the wells were installed and sampled, but because the levels of all the wells were measured within a few hours of one another, the data provide a relatively precise “snapshot” of ground-water conditions at the time the measurement was made. To better understand ground-water behavior on a long-term basis, synoptic measurements should be repeated in different seasons under different hydrologic conditions over a period of several years. However, even a single synoptic can provide a great deal of information on the fate and transport of contaminants in ground water. Water levels from this measurement are included in table 1.

Water Sample Collection and Analysis

Water samples were collected by the USGS from 6 wells at Prime Hook National Wildlife Refuge in June 2000, and from 12 wells and the surface stream in May 2001. Additional samples were collected from the surface-water site and well DG-5 in August 2001. Sample handling was minimized to avoid contamination, and ultra-clean techniques were used. Prior to sampling, all of the sampling equipment, filters, and bottles were washed with a Liquinox detergent solution, flushed with tap water, and sequentially rinsed with a 10 percent solution of nitric acid (HNO_3), ultra-pure deionized water (DI), and three rinses of ground water just prior to sample collection. Water was collected with a peristaltic pump using Tygon tubing. Wells were purged until field parameters—pH, temperature, dissolved oxygen (DO), and specific conductance—had stabilized. Samples for the analysis of dissolved trace metals and major ions were filtered with an in-line 0.45- μm (micrometer) polycarbonate capsule filter. Samples for dissolved metals were immediately fixed with 2 mL (milliliters) of Ultrex concentrated HNO_3 per 250 mL and bagged in acid-washed zipper-lock plastic bags. Samples for the analysis of cations, silica, iron, and manganese were filtered into a separate 250-mL polyethylene bottle and fixed with 2 mL of concentrated nitric acid. Samples for anions were not fixed with acid. Whole water was collected with the peristaltic pump into a 125-mL baked amber glass bottle for the analysis of total organic carbon. Samples were shipped on ice overnight to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado. All sample collection and quality-assurance techniques for fieldwork are documented in the USGS National Field Manual (U.S. Geological Survey, 1999).

Field parameters were determined with a variety of standard probes and field meters. Orion meters were used for pH and specific conductance. A YSI dissolved-oxygen meter was used for DO. Alkalinity was determined by fixed-increment titration (U.S. Geological Survey, 1999). Water samples were collected from all wells except DG-6 and DG-7. These two holes were installed to provide a geological transect across the northern part of the site, and are located well away from the lead contamination zone. Well DG-2, located a few feet from DG-7, was sampled during the



Figure 7. Shallow/deep well pair at upgradient location, Prime Hook National Wildlife Refuge.

Year 2000 sampling round, and contained lead at concentrations below 1 $\mu\text{g/L}$, which is essentially background level. Due to financial and time constraints, wells DG-6 and DG-7 were not sampled.

Concentrations of dissolved trace metals were analyzed by direct-injection Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) with corrections for ion interferences. Documentation and quality assurance for the ICP-MS method for low-level trace-element analysis is described in Garbarino and Taylor (1994) and Garbarino (1999). Concentrations of metals in field blanks collected for this study were typically not detected except for one blank sample collected on May 23, 2001 that may have had contamination either in the blank water or in the fixing acid. This sample was recollected in August 2001 and was clean the second time. High concentrations of trace metals that were detected in the contaminated blank were within the range of background levels in the August sample, and therefore did not affect the interpretation. Analytical precision for dissolved

metals was better than ± 5 percent for samples collected at well DG-2 on June 13, 2000. Precision was not as good for a set of replicates collected from well DG-5 on May 16, 2001, possibly due to large spatial gradients in the concentrations of some metals, particularly lead, in the ground water near the drop zone. The well-purging process may have caused or exacerbated the problem by drawing water from around the well annulus where there was likely a large gradient in the concentration of lead. Analysis of a third sample from this well, collected on August 23, 2001, also indicated substantial variability in the concentrations of lead and other metals at this site. Samples for the concentrations of total organic carbon and major ions were analyzed according to USGS protocols (Wershaw and others, 1987; Fishman, 1993).

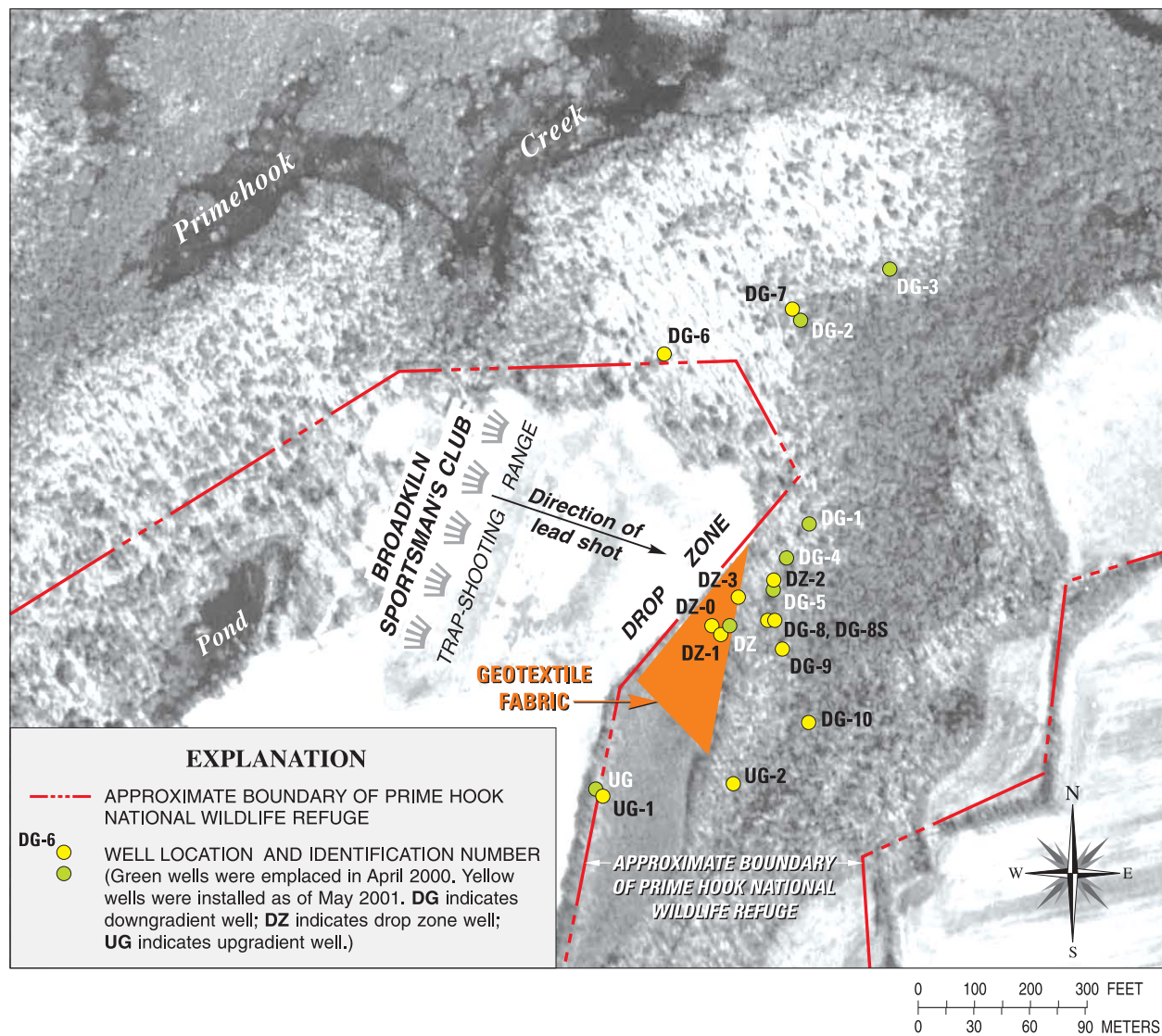


Figure 8. Aerial photograph of Broadkiln Sportsman's Club and Prime Hook National Wildlife Refuge, showing locations of all 19 wells installed at the site as of May 2001.

Table 1. *Sampling locations and well-construction data for Prime Hook National Wildlife Refuge, Sussex County, Delaware*

[ft, feet; UG, upgradient; DZ, drop zone; DG, downgradient; SW, surface water; N/A, not applicable]

Station name	Station number	Ground altitude ¹	Water altitude ^{1, 2}	Total depth (ft) ³	Screen length (ft) ⁴	Date installed	Sample date	Date of replicate
UG	384923075170901	4.80	2.63	4.22	3	20-Apr-00	13-Jun-00	16-May-01
UG-1	384923075170900	4.70	2.63	8.69	3	16-Apr-01	16-May-01	
UG-2	384923075170601	2.40	2.36	8.89	3	16-Apr-01	16-May-01	
DZ	384925075170601	3.90	no data ⁵	3.25	3	20-Apr-00	13-Jun-00	
DZ-0	384926075170601	3.90	2.41	3.12	3	24-Apr-01	18-May-01	
DZ-1	384926075170602	3.90	2.36	4.66	3	18-Apr-01	18-May-01	
DZ-2	384926075170504	2.20	2.33*	10.17	3	18-Apr-01	16-May-01	
DZ-3	384926075170603	2.60	2.30	7.58	1	19-Apr-01	18-May-01	
DG-1	384926075170401	2.80	1.96	3.51	3	20-Apr-00	13-Jun-00	
DG-2	384931075170401	2.30	1.01	2.23	3	20-Apr-00	13-Jun-00	
DG-3	384932075170201	3.15	2.71	4.01	3	20-Apr-00	13-Jun-00	
DG-4	384927075170501	2.50	2.01	4.72	1	20-Apr-00	23-May-01	
DG-5	384926075170501	2.30	2.02	1.85	3	20-Apr-00	13-Jun-00	16-May-01
DG-6	384931075170801	7.20	2.23	11.45	3	19-Apr-01	no sample	
DG-7	384932075170501	2.40	1.99	8.33	3	19-Apr-01	no sample	
DG-8	384926075170502	2.10	2.22*	4.97	1	1-May-01	23-May-01	
DG-8S	384926075170503	2.10	2.04	1.94	3	1-May-01	23-May-01	
DG-9	384925075170501	2.00	2.18*	3.08	1	1-May-01	23-May-01	
DG-10	384924075170501	2.30	2.22	3.22	1	1-May-01	16-May-01	
SW-1	01484310	1.80	1.80	N/A	N/A	N/A	16-May-01	23-Aug-01

¹ All altitudes are in feet above sea level.

² Synoptic water levels measured on 24-Sep-01.

³ Total depth is depth to bottom of casing below ground surface.

⁴ Screens are set at base of casing; DG-5, DG-2, and DG-8S are exposed above ground in shallow holes.

⁵ Casing broke off and well was abandoned before water level could be measured.

* Water under artesian pressure, slightly elevated above ground surface.

Soil and Sediment Sampling

Soil and sediment core samples were obtained from 7 of the 12 well holes installed at Prime Hook NWR in April and May 2001. The core was collected using a “vibracore” rig on loan from the University of Delaware. This soft-sediment coring rig used 4-in.-diameter thin-walled aluminum irrigation tubing as drill pipe. The tubing, which can be up to 15 ft long, was mounted vertically under a tripod-like drilling support. A vibrator designed for de-aerating concrete was attached to the upper end of the tubing using u-bolts. The intense vibration caused the tubing to cut into the ground, and a core of soft sediment was captured inside the pipe. When the pipe penetrated to sufficient depth, the vibrator was removed, and an automotive engine winch was then used to pull the pipe and core up out of the ground.

Small metal flanges riveted to the inside of the bottom end of the pipe helped keep the core inside. Details of the coring apparatus are shown in figure 9. Cores were measured, capped, and labeled before being transported to the USGS office in Dover, Delaware.

Cores were analyzed in the lab by cutting the thin aluminum pipe with a circular saw blade designed for use on aluminum house siding. The pipe was cut lengthwise, and the soft sediment core inside was then sliced with a knife. The pipe was split open, exposing the flat, cut center of the core. Core lithologic descriptions were based on standard USGS protocols (Powars, 1997), and are included in the Appendix of this report.



Flanges inside bottom of pipe to retain soft sediment core.



Core pipe was vibrated approximately 8 feet into the ground.



Tripod used to support aluminum pipe with vibrator on upper end.



Extracting the core barrel from the ground using an automobile engine winch.

Figure 9. Vibracore rig used at Prime Hook National Wildlife Refuge.

Ground-Penetrating Radar

Ground-penetrating radar (GPR) surveys were run on several transect lines across the site. The GPR equipment was generously loaned by the University of Delaware. It consists of a transmitter and receiver, each about 3 ft in length, which are placed on the ground and moved at fixed intervals along a measuring tape. A central laptop computer unit controls the radar impulses and collects the data.

Radar transects were run in both north-south and east-west directions across the site. The first transect was run from north to south from the edge of the woods into a grassy field along a line approximately 50 ft east of the trap houses. This line was 630 ft long, using 50 MHz antennas on 15-ft spacing and 1.5-ft steps. A second line was run from west to east along the southern boundary of the grassy field from the old entrance road to the edge of the woods. This transect was 590 ft long, again using the 50 MHz antennas on 15-ft spacing and 1.5-ft steps. A third GPR transect was run

eastward from the edge of the woods to the unnamed tributary, following a path that connected the UG-1 and UG-2 well sites. Because of the dense woods, the smaller 100 MHz antennas were used on a 1.5-ft spacing with 1-ft steps. Several other short transects were run in the drop zone on top of the geotextile cover, and near the trap houses.

Ground-Water Contamination

Interpretation of the lithostratigraphy indicates that the geology of this area is complex. A generalized cross section of the geologic units encountered in wells DZ-1, DZ-2 and DZ-3 is shown in figure 10. It is obvious from the cross section that the thicknesses and properties of the sediment change significantly over the relatively short distances between individual wells.

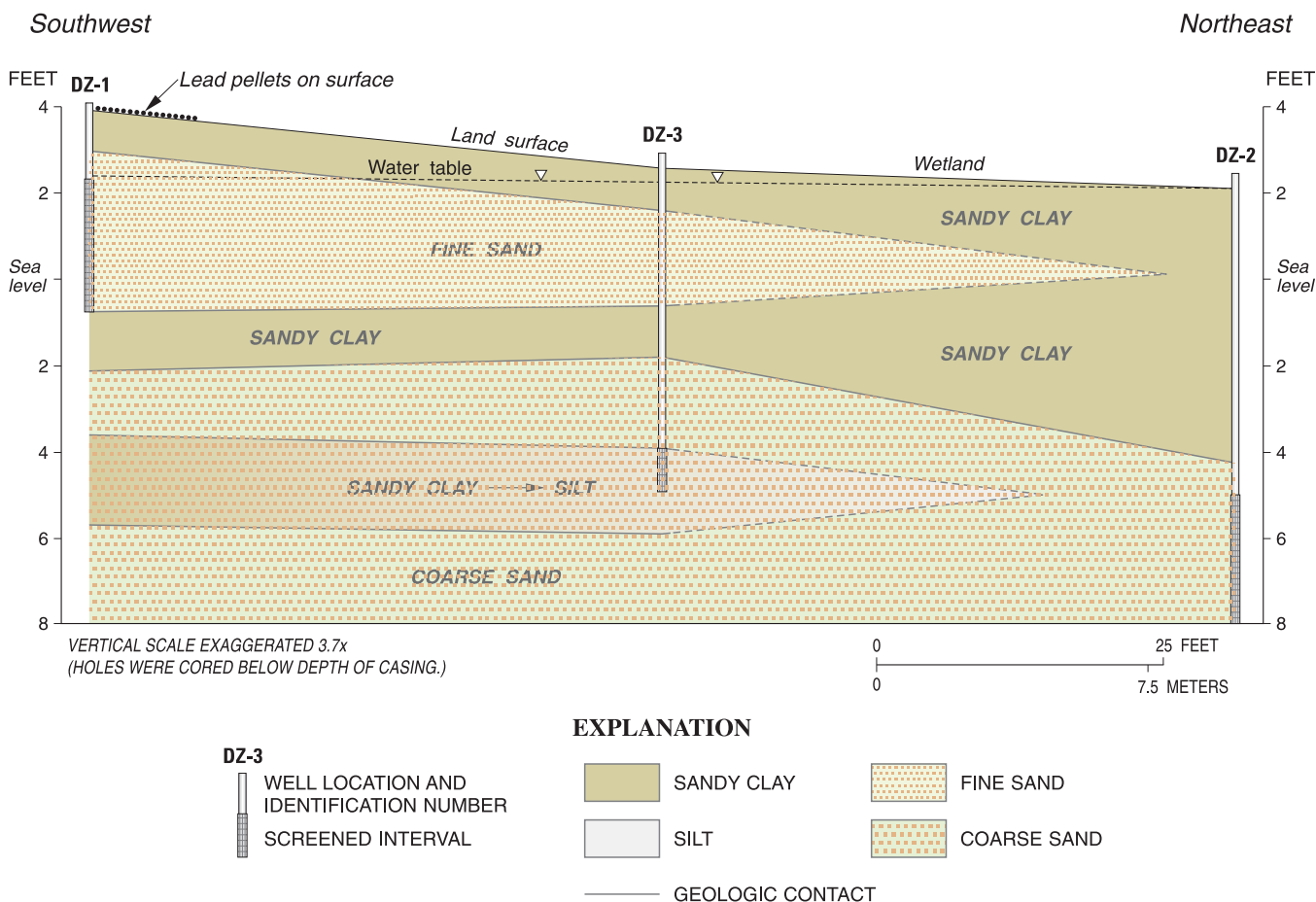


Figure 10. Generalized geologic cross section of the study area, from well DZ-1 to well DZ-2.

Hydrogeologic Framework

The very uppermost sediments in the sequence at the site are Holocene-age swamp deposits, consisting of organic-rich, clayey sand with thin interbeds of medium to coarse quartz sand (Ramsey, 2001). These are interpreted as swamp and stream deposits near the tributary, formed when the slough was a more active stream channel, probably during the most recent lowstand of Delaware Bay. These sediments are described in the cores as predominantly sandy clay, overlying and underlying a wedge of fine sand in well DZ-1 under the drop zone. This fine sand wedge thins toward the east in well DZ-3, and pinches out before reaching well DZ-2.

Beneath the sandy clay of the swamp deposits is a coarse, pebbly sand, interpreted as the upper part of the late Pleistocene Scotts Corners Formation. On the geologic map of the area, this unit is shown at the surface in the upland part of the neck area near the club location (Ramsey, 2001). It is overlain by the swamp deposits to the east toward the slough. The Scotts Corners Formation consists of coarse to fine sand, with discontinuous beds of clayey silt, very coarse quartz sand, and pebble gravel. It is interpreted as a transgressive unit consisting of bay, beach, and estuarine deposits formed during a previous highstand of Delaware Bay (Ramsey, 2001). The cores collected for this study penetrated a coarse sand unit, which is interpreted to be a beach-face deposit. It is continuous across the study area and dips slightly from west to east, in the direction of Delaware Bay. This coarse sand, partially confined under the Holocene sandy clay, is the apparent "artesian" unit encountered at depth in well DZ-2.

The GPR data were used to attempt to determine the lateral continuity of stratigraphic units identified in the cores. The radar data were difficult to interpret due to interference from roots, building foundations, and other structures, but do support the notion of lateral continuity in the coarse sand unit, as well as the wedge shape of some of the finer sandy clay layers, as shown in figure 10.

Results of water-level measurements in the wells in the study area show that the altitude of the water table decreases gradually from the upland areas toward the stream (fig. 11). Ground water also moves in this direction, from upland areas on the club property toward the wetland, eventually discharging into the slough, which is a tributary of Primehook Creek. Any lead mobilized in the ground water flowing under the drop zone could be expected to move toward the slough. It is important to note that dissolved lead at concentrations significantly above background levels was detected in the surface water of the slough near the seep discharge area during two different sampling rounds (May 16, 2001 and August 23, 2001).

Hydraulic gradients in the study area are generally low, averaging about 0.1 ft drop per 75 ft from the edge of the shooting range to the slough. The gradient is approximately 0.0013. A locality with a somewhat higher gradient is present along the line from the drop zone to the stream defined by wells DZ-1 to DG-5, ending at a well-defined

ground-water discharge zone on the bank of the slough near well DG-5. The highest concentrations of lead in ground water at the site were found at well DG-5.

USGS topographic maps indicate that the drainage divide on the small neck of land where the club is located lies upgradient of the drop zone. Ground water under the lead pellets in the drop zone flows east, toward the slough. Lead mobilized in this ground water will remain within the refuge boundaries and discharge into the slough. It is highly unlikely that any lead from this site will leave the boundaries of Prime Hook NWR by way of the ground water.

The results of the laboratory analyses of ground-water samples from Prime Hook NWR are shown in tables 2 and 3. Table 2 lists metals in water samples that were collected in June 2000, May 2001, and some repeat sampling in August 2001. Replicate samples and field blanks were included for quality assurance. Major ions and field parameters from the ground water at Prime Hook NWR are shown in table 3.

Low levels of lead occur naturally in ground water from Coastal Plain sediments. Contamination is defined by the degree of exceedance of these natural background levels. Lead concentrations in the wells upgradient of the drop zone were assumed to be at natural background levels. The values agreed with background lead levels from a study done in New Jersey streams (Stansley and others, 1992), indicating that a concentration of 1-2 $\mu\text{g/L}$ was reasonable for naturally occurring lead in ground water at Prime Hook. The laboratory analyses show that lead concentrations significantly above background levels were found in a number of the wells sampled at Prime Hook NWR. Concentrations of lead approximately one order of magnitude or more above background levels were found at wells DZ-0, DG-8, DG-10, and the May 2001 sample from the surface-water seep. Lead concentrations approximately two orders of magnitude or more above background levels were found at wells DZ, DZ-2, DZ-3, DG-4, DG-8S, DG-9, and the August 2001 surface-water sample. Lead concentrations three orders of magnitude or more above background levels were found in DG-5 (table 2). Water samples from the shallow/deep well pair located in the drop zone (DZ-0 and DZ-1) had nearly twice as much lead in the deeper sample compared to the shallow one. In contrast, two of the shallow/deep well pairs located along the banks of the slough in discharge areas had higher concentrations of lead in water from the shallower well. These differences in lead concentration with depth may be related to the downward or upward movement of the ground water, or could represent flow lines from different recharge areas.

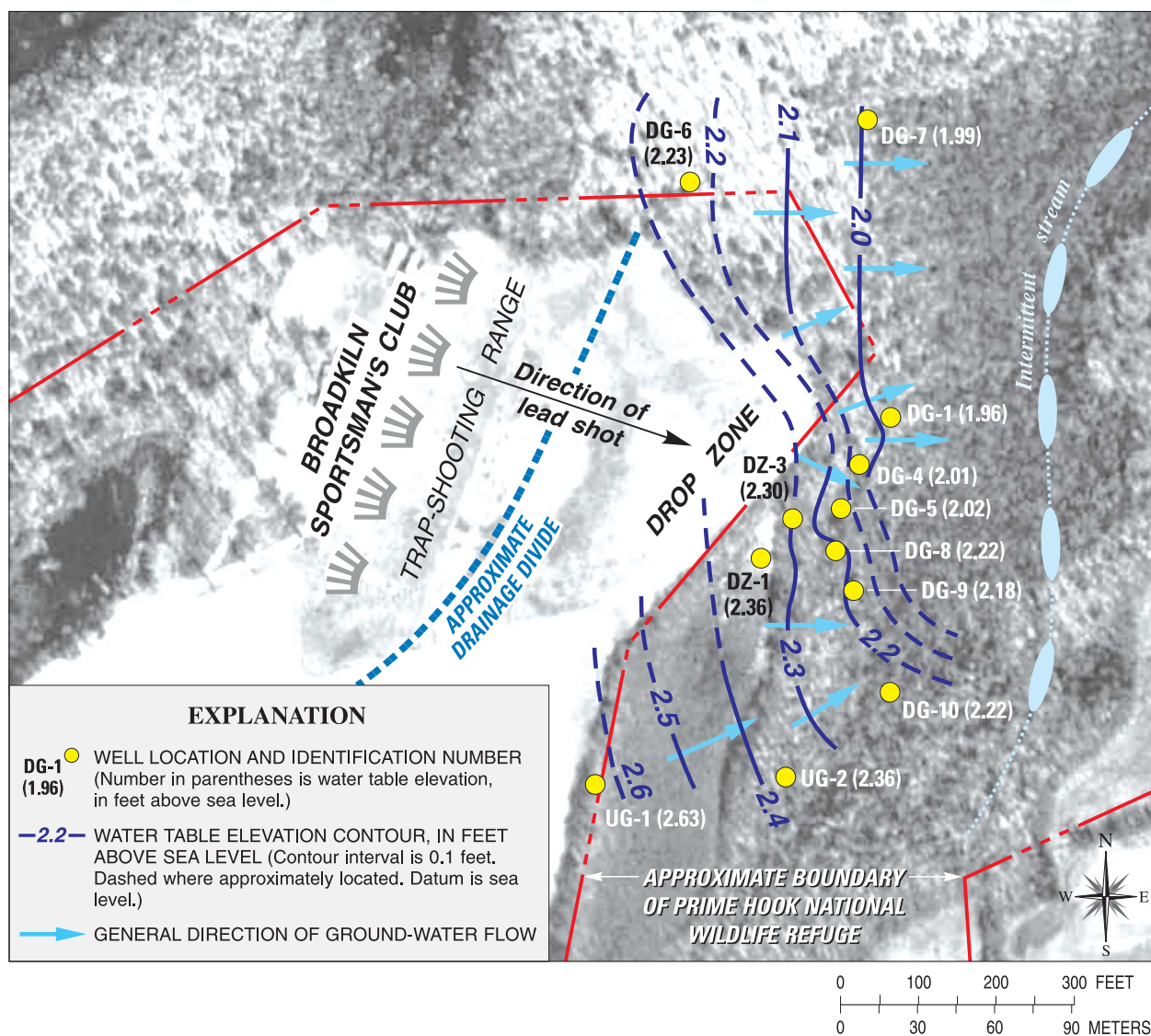


Figure 11. Aerial photograph showing the ground-water table and flow directions in the study area.

Table 2. Concentrations of dissolved metals in ground water and surface water at Prime Hook National Wildlife Refuge

[Values from replicate (rep) samples and field blanks are included for quality assurance (*in italics*). All units are in micrograms per liter. Al, aluminum; Sb, antimony; As, arsenic; Ba, barium; Be, beryllium; Cd, cadmium; Cr, chromium; Co, cobalt; Cu, copper; Fe, iron; Pb, lead; Mn, manganese; Mo, molybdenum; Ni, nickel; Ag, silver; Zn, zinc. Wells DG-6 and DG-7 were not sampled for water quality and are not included in this table; <, less than; E, estimated value; --, no data]

Station name	Date	Al	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Ag	Zn
UG	6/13/2000	<16	<1	<0.9	63.1	<1	<1	<0.8	2.11	<1	--	1.12	89.6	<1	1.36	<1	<4
UG	5/16/2001	1	0.07	--	73.8	<0.06	0.06	<0.8	0.6	<0.2	<10	0.8	41.5	<2	0.34	<1	<1
UG-1	5/16/2001	--	<0.05	<0.2	--	--	--	--	--	--	410	1.91	132	--	2.61	--	--
UG-2	5/16/2001	--	0.14	E 0.2	--	--	--	--	--	--	20	6.25	76.5	--	3.02	--	--
DZ	6/13/2000	<19	9.61	1.3	67.7	<1	<1	<0.8	1.52	<1	--	392	78.9	<1	<1	<1	<4
DZ-0	5/18/2001	3	0.43	--	23.5	E 0.04	1.01	<0.8	1.81	E 0.2	2,180	7.56	--	<2	0.52	<1	3
DZ-1	5/18/2001	--	0.4	1.5	--	--	--	--	--	--	3,160	14.4	120	--	1.07	--	--
DZ-2	5/16/2001	12	17	--	118	0.07	0.22	<0.8	1.05	<0.2	800	529	67.9	<2	1.6	<1	5
DZ-3	5/18/2001	--	13.9	11	--	--	--	--	--	--	550	491	67.9	--	1.35	--	--
DG-1	6/13/2000	154	1.96	5.2	15.7	<1	<1	0.9	2.1	<1	--	1.42	43.4	<1	1.26	<1	5
DG-2	6/13/2000	<41	<1	<2	17.1	<1	<1	<0.8	1.54	<1	--	<1	19.1	<1	<1	<1	<5
DG-2 rep	6/13/2000	<44	<1	<2	16.7	<1	<1	<0.8	1.49	<1	--	<1	18.1	<1	<1	<1	<5
DG-3	6/13/2000	628	<1	2.6	37.3	<1	<1	2.2	2.02	<1	--	1.55	20.3	<1	2.53	<1	9
DG-4	5/23/2001	--	1.58	0.2	--	--	--	--	--	--	50	131	12.2	--	0.82	--	--
DG-5	6/13/2000	--	--	--	--	--	--	--	--	--	--	965	--	--	--	--	--
DG-5	5/16/2001	60	51.8	--	35.4	E 0.04	0.8	<0.8	0.93	0.3	540	1,010	19	<2	1.46	<1	8
DG-5 rep	5/16/2001	53	59.9	--	39	E 0.03	0.5	<0.8	0.91	<0.2	590	777	19	<2	0.86	<1	6
DG-5	8/23/2001	--	65	--	--	--	--	--	--	--	--	1,420	--	--	--	--	--
DG-8	5/23/2001	--	5.54	1.2	--	--	--	--	--	--	220	11.3	43.9	--	2.43	--	--
DG-8S	5/23/2001	--	22.9	22	--	--	--	--	--	--	270	357	35	--	1.6	--	--
DG-9	5/25/2001	--	2.78	0.2	--	--	--	--	--	--	<10	112	39.6	--	2.33	--	--
DG-10	5/16/2001	--	0.7	E 0.2	--	--	--	--	--	--	E 8.7	7.77	36.5	--	1.65	--	--
Surface-Water Seep	5/16/2001	25	10.9	--	150	0.08	0.12	<0.8	3.08	<0.2	170	23.7	53.5	<2	0.98	<1	5
Surface-Water Seep	8/23/2001	--	22.8	--	--	--	--	--	--	--	--	212	--	--	--	--	--
Field Blank	6/13/2000	<5	<1	<2	<1.0	<1	<1	<0.8	<1.00	<1	--	<1	<1.0	<1	<1	<1	<1
Field Blank	5/16/2001	<1	<0.05	--	<1.0	<0.06	<0.04	<0.8	<0.1	<0.2	<10	<0.08	<1	<2	<0.06	<1	<1
Field Blank	5/23/2001	--	0.09	<0.2	--	--	--	--	--	--	--	1.44	--	--	0.06	--	--
Equipment Blank	8/23/2001	--	0.14	--	--	--	--	--	--	--	--	0.09	--	--	--	--	--
Field Blank	8/23/2001	--	<0.05	--	--	--	--	--	--	--	--	<0.08	--	--	--	--	--

Table 3. Major ions and field parameters in water samples from Prime Hook National Wildlife Refuge

[Concentrations are in milligrams per liter (mg/L), µS/cm, microsiemens per centimeter; <, less than; E, estimated value; --, no data]

Station name	Date	Temperature, degrees Celsius	Specific conductance (µS/cm)	Dissolved oxygen (mg/L)	pH	Total organic carbon (mg/L as C)										Silica (mg/L as SiO ₂)
						Calcium (mg/L as Ca)	Magnesium (mg/L as Mg)	Sodium (mg/L as Na)	Potassium (mg/L as K)	Bicarbonate (mg/L as HCO ₃)	Chloride (mg/L as Cl)	Sulfate (mg/L as SO ₄)	Fluoride (mg/L as F)			
UG	6/13/2000	15.2	157	3.0	5.6	--	--	--	--	--	--	--	--	--	--	--
UG	5/16/2001	13.0	173	2.0	5.9	14.10	6.76	2.2	6.83	16	15.4	15.6	<2	3.3	3.3	8.9
UG-1	5/16/2001	12.0	146	4.6	5.0	7.16	7.79	2.6	3.39	--	10.2	18.4	<2	8.9	11.8	11.8
UG-2	5/16/2001	13.4	191	3.3	4.8	4.94	9.67	6.8	5.36	--	17.3	23.1	<2	--	--	--
DZ	6/13/2000	20.6	32	2.5	5.1	--	--	--	--	--	--	--	--	--	--	--
DZ-0	5/18/2001	17.2	37	1.3	5.2	1.89	0.50	2.6	0.55	6	2.8	3.6	<2	5.4	5.4	4.4
DZ-1	5/18/2001	16.4	66	1.7	5.3	3.26	1.11	2.7	2.27	18	3.4	6.1	<2	4.4	10.7	7.9
DZ-2	5/16/2001	12.8	88	3.1	5.3	2.95	4.59	2.3	2.68	--	4.4	21.9	<2	10.7	7.9	7.9
DZ-3	5/18/2001	--	81	2.2	5.3	2.77	3.76	1.8	2.00	3	3.0	21.9	<2	--	--	--
DG-1	6/13/2000	16.0	111	<0.1	5.8	--	--	--	--	--	--	--	--	--	--	--
DG-2	6/13/2000	16.3	95	1.9	5.2	--	--	--	--	--	--	--	--	--	--	--
DG-3	6/13/2000	15.3	84	5.7	5.0	--	--	--	--	--	--	--	--	--	--	--
DG-4	5/23/2001	14.4	106	3.0	6.0	3.54	1.27	3.3	2.03	10	5.3	8.9	<2	5.8	--	--
DG-5	6/13/2000	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DG-5	5/16/2001	14.8	67	1.4	5.5	3.70	1.37	4.1	2.87	23	6.6	0.6	<2	8.2	8.0	8.0
Replicate	5/16/2001	--	--	--	--	3.67	1.34	4.2	3.18	--	6.4	0.8	<2	--	--	--
DG-5	8/23/2001	23.1	82	2.0	5.5	--	--	--	--	27	--	--	--	--	--	--
DG-8	5/23/2001	15.0	144	3.0	6.1	15.90	3.94	3.3	2.22	32	6.4	21.8	<2	7.9	9.1	10.4
DG-8S	5/23/2001	16.1	94	1.9	5.6	6.19	3.98	2.7	2.16	15	5.5	16.9	<2	9.1	10.4	9.5
DG-9	5/25/2001	15.2	152	6.0	6.4	7.44	6.78	6.4	3.98	4	16.2	0.8	<2	10.4	9.5	9.5
DG-10	5/16/2001	13.5	149	1.1	6.4	6.30	5.22	8.5	3.46	8	12.8	3.3	<2	--	--	--
Seep	5/16/2001	14.9	128	<1.0	6.0	4.60	5.72	6.8	3.15	30	15.9	3.1	<2	11.5	--	--
Seep	8/23/2001	25.5	68	0.5	5.7	--	--	--	--	16	--	--	--	--	--	--
Blank	5/16/2001	--	--	--	--	<0.01	<0.01	<0.1	<0.09	--	<0.1	<0.1	<2	<0.5	<0.5	<0.5

Changes in lead concentration over time at two sites indicate a large degree of variability in ground-water levels and chemistry. The lead content in water collected from the surface-water seep increased by nearly an order of magnitude between the sample collected in May 2001, and the follow-up sample collected in August 2001. Wetter conditions and higher water volumes in May may have diluted the lead concentration, whereas during the low-flow period in August, it was much more concentrated. Antimony in these samples showed an increase as well, doubling in concentration in August compared to May.

Another temporal change might be present between well DZ, emplaced in the drop zone in 2000, and well pair DZ-0/DZ-1, emplaced in 2001. The drop zone was covered with a geotextile fabric a few weeks after shallow well DZ was emplaced and sampled to prevent migratory waterfowl from landing in the area and ingesting the lead shotgun pellets as grit. Concentrations of lead in samples from well DZ collected in 2000 were nearly 50 times higher than those collected at nearby well DZ-0 in 2001 from the same depth. Although the geotextile barrier was permeable to rainwater, it is possible that the material still reduced infiltration and may have limited additional lead from making its way from the pellets into the ground water. This could explain the reduced lead concentrations in the more recently collected water samples, although natural variability in the ground-water system also could be a factor.

The mobility of lead depends upon the metal's corrosion or passivation behavior in each geochemical environment. The oxidation of metallic lead is rapid under normal environmental conditions, but the oxidized lead reacts readily with other species to form insoluble precipitates that coat and passivate the surface of the metal. Available literature on environmental lead commonly cites examples such as lead bullets found on Revolutionary War or Civil War battlefields that have been well-preserved under an oxide or carbonate coating for sometimes hundreds of years (Rimstidt and Craig, 2000). The mobility of lead, however, is controlled by processes that may override the passivation. Low pH, in particular, is suspected of being a major agent in the increased solubility of the lead carbonate hydrocerussite.

Relatively low pH was found in the shallow ground water at Prime Hook NWR. Values in the range of about 4.8 to 6.4 were common during the field sampling. The acidic conditions are responsible for dissolving the lead carbonate off the pellets. Because of the apparent lack of buffering capacity and adsorption sites in the silica-rich sediments, the dissolved lead was mobilized and moved into the ground water. Many of the stratigraphic horizons are sandy, with little or no clay or iron oxide coatings that could trap and hold the lead. Once lead was in the ground water, however, it is possible that its solubility was enhanced by the formation of dissolved organic-carbon complexes. Total organic carbon in the water samples ranged from approximately 1 to 34 mg/L.

Concentrations of dissolved iron were relatively high in many of the Prime Hook ground-water samples, up to 2 or

3 mg/L. High iron concentrations are not unusual in ground waters from the Delaware Coastal Plain, and these values appear to represent natural background levels. At a number of locations in the sediment cores, iron hydroxides were found in abundance, commonly at contacts between sand and clay layers. This could potentially be the result of iron oxide precipitation at oxidation-reduction boundaries, but it is more likely that these iron-stained layers represent episodes of subaerial exposure or ancient soil horizons (Ramsey, 2001). An active geochemical boundary may result in the precipitation of lead at the same locations as the iron, or the lead may simply be captured by pre-existing iron oxide deposits in the sediments. The detailed chemical analysis of the sediments required to investigate this hypothesis was beyond the scope of this study. Once the drop zone is remediated and the source area removed, the lead in the ground-water system may eventually be naturally attenuated as the system flushes out. However, some of the lead also may be immobilized as it becomes bound to iron oxides at the margins of the sand units, making the natural attenuation process very lengthy.

A map view of interpolated lead concentrations in the ground water is shown in figure 12, based on data from table 2. The highest concentration of lead is in the vicinity of well DG-5, which is in a discharge area near the slough. The ground water appears to be actively transporting lead to this point. A lower concentration of lead surrounds this core region, with the axis of the concentration oriented from the drop zone toward well DG-5. On the basis of existing data, this is the most well-defined plume of lead contamination in the ground water at Prime Hook NWR.

Lower concentrations of lead in the ground water are spread out, and appear to be oriented in a direction more parallel than perpendicular to the banks of the slough. One reason for this may be a wider areal distribution of source pellets in fewer numbers on the ground in locations that are still downrange, but outside of the main drop zone. Lead may be moving into the ground water just as readily, but in lower initial concentrations because of a more sparse pellet count. Also, the ground-water table map in figure 11 shows that the hydraulic gradient is lower in the area to the south of the drop zone. This lower gradient, combined with the seasonal rise and fall of the water table, may average out the concentration of lead over a broad area, instead of transporting it in a directional manner as it does at well DG-5. A conceptual model of ground-water flow and transport of the lead from the drop zone to the stream is shown in cross section in figure 13. Ground water discharging into the slough is carrying lead into the surface water.

No data were collected from the far side of the slough because the area is virtually inaccessible. Although it is possible that lead traveling along deeper, confined flowpaths could be present in ground water east of the slough, this was beyond the range of the investigation. The issue of ecological concern for the USFWS was whether or not lead was getting into the surface water of the intermittent stream, and hence potentially into the biota. Because the shallow

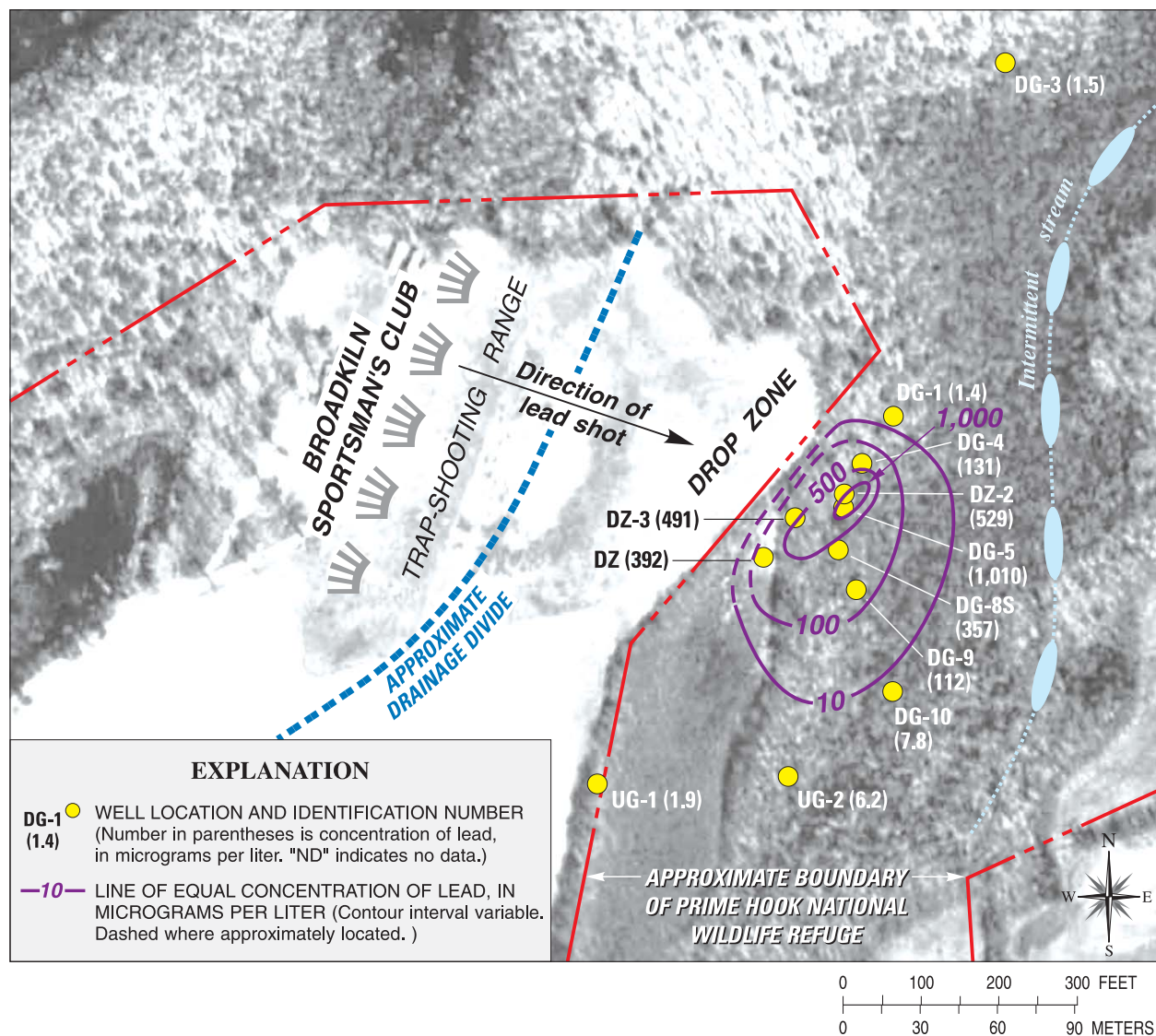


Figure 12. Interpolated lead concentrations in ground water at Prime Hook National Wildlife Refuge.

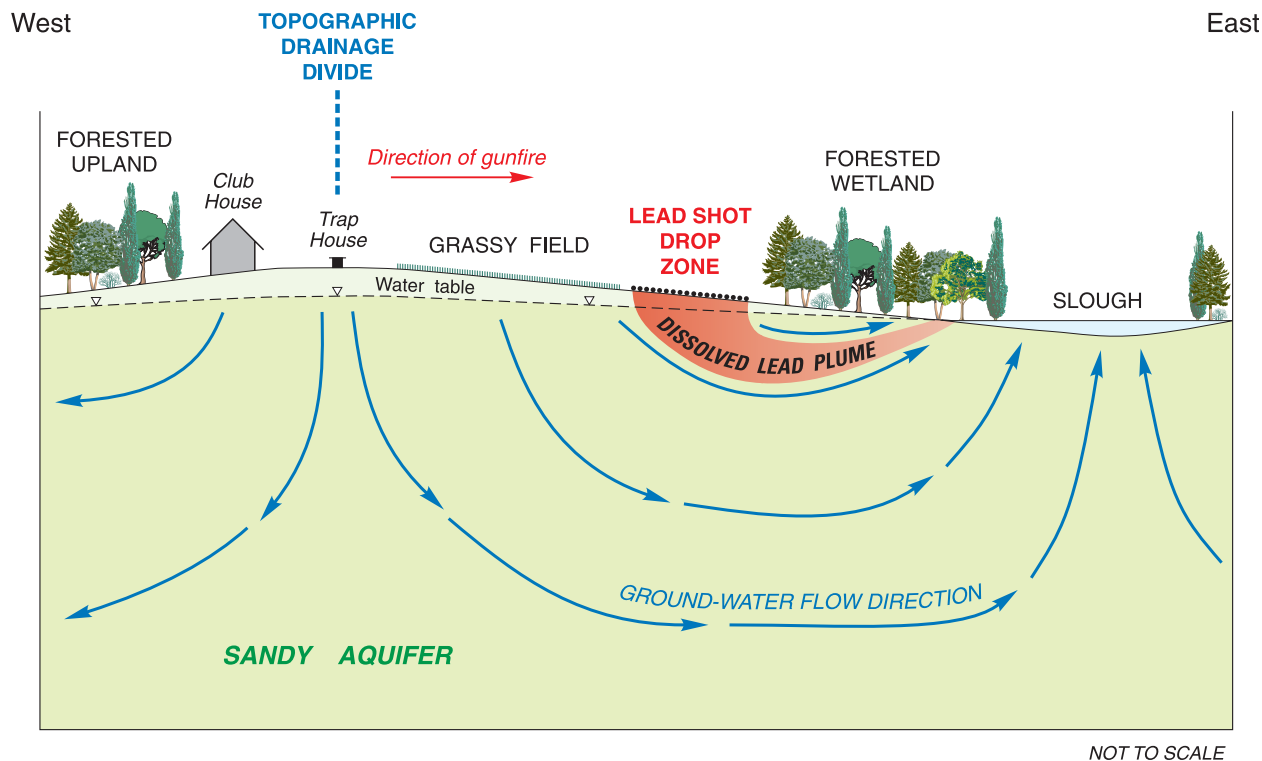


Figure 13. Conceptual model of ground-water flow and contaminant transport in the study area.

ground water in this area is not used for water supply, if lead is indeed present in ground water east of the slough, it is likely to remain there.

Ground-Water Traveltime

The well-defined plume of dissolved lead now being discharged into the slough formed within the last 37 years, after shooting began in the early 1960s. This indicates that if the source area is cleaned up, the lead may eventually flush out of the ground water. Some lead may have been deposited on clays or in iron-rich zones along the flowpaths, however, and could take a relatively long time to clear out of the system.

A rough estimate of ground-water traveltime (GWTT) at the Prime Hook NWR site can be derived from the head contours and some estimates of sediment properties. The following assumptions were used for this calculation:

1. The range of hydraulic conductivity in fine sand can be quite variable. Numbers taken from Freeze and Cherry (1979) estimate it to be between 1 and 50 ft/day (feet per day). There is a fairly large error range associated with this estimate, but it is reasonable as an order of magnitude.
2. Porosity of the aquifer is assumed to be 25 percent (0.25) for compacted, uncemented sand (Heath, 1983).
3. Hydraulic gradient is approximately a 0.1-ft drop per 75 ft from the edge of the shooting range to the slough. The gradient is approximately 0.0013.
4. These estimates apply only to the unconfined surficial aquifer. There are insufficient data from the partially confined aquifer in the coarse beach-face sand at depth to estimate GWTT.

Calculations:

Estimated ground-water velocity (Heath, 1983)

$$v = (K/n) \times dh/dl,$$

where

v	=	velocity,
K	=	hydraulic conductivity,
n	=	porosity, and
dh/dl	=	hydraulic gradient.

For

K	=	1 to 50 ft/day,
n	=	0.25, and
dh/dl	=	0.0013,
v	=	0.0052 to 0.26 ft/day.

The estimated time of ground-water travel, assuming the distance from the drop zone to the discharge area is about 200 ft, would range from approximately 800 to 38,000 days (26 months to 104 years). The 37-year maximum limit on the transport time of the present contamination fits into this range.

Ground water traveling from farther upgradient off the shooting range itself would likely be moving along a longer, deeper flow path through the semiconfined, coarse sand beach face, as indicated by the higher hydraulic heads measured in this unit. It is possible that there may be some downward leakage or percolation into this sand from the overlying system, contributing to the relatively high concentrations of lead in the deeper samples. Most of the ground water in this beach face sand would have entered it from upgradient, on the club property, however, not by infiltrating through the drop zone.

Actual traveltimes for contaminants transported by the ground water may be significantly longer than those for the water alone, due to retardation factors such as adsorption in the sediments. An assessment of the potential for natural attenuation would require an in-depth analysis of the sediment geochemistry, and a better understanding of the site geology and hydrology. Due to the low hydraulic gradient and the opportunity for lead to interact and bond with sediments, it may actually take a considerable amount of time for the system to naturally attenuate. After the source area is remediated, periodic, long-term monitoring of metals in the ground water downgradient of the source and in the discharge areas would provide data on the performance of natural attenuation in the ground-water system.

Summary and Conclusions

The Broadkiln Sportsman's Club in Sussex County, Delaware, northeast of the town of Milton, operated a trap shooting range adjacent to Prime Hook National Wildlife Refuge for a period of 37 years. Lead shotgun pellets from misses and overshoot accumulated on the refuge within a forested wetland downrange, in numbers as high as 57,868 pellets per square foot. Because of acid rain and low pH conditions in the wetland, the lead dissolved and infiltrated into the ground water. The metal is being transported down-gradient along shallow flowpaths, and discharging into an unnamed tributary of Primehook Creek. Lead concentrations in the ground water near a discharge zone into the unnamed tributary range from 10 to 1,000 times above natural background levels.

An initial round of sampling by the U.S. Geological Survey in cooperation with the U.S. Fish and Wildlife Service was done in May 2000 on six shallow wells to determine if lead was present in ground water at the site. When analysis of these samples showed the presence of lead, a second sampling round was carried out in April 2001 on 13 wells and the nearby stream. The U.S. Geological Survey study was designed as a "field screening" to give the U.S. Fish and Wildlife Service some indication of the scope of the lead problem, and to assess where and how fast the contamination might be moving.

Most of the ground-water movement at the site is lateral, from the upland areas near the club toward the slough. The near-surface geology consists of gently eastward-dipping beach face and foreshore sand units from a previous high-stand of Delaware Bay, overlain by swamp deposits consisting of clayey sand. Discontinuous clay layers and lenses occur throughout, several with pronounced iron-oxide stains indicating potential oxidation-reduction boundaries.

The highest concentrations of lead are present in a fairly narrow plume in an area of higher than average hydraulic gradients. Lower concentrations of lead are present in ground water throughout a broader area of the site. The lead is mobilized by low pH precipitation and ground water, and transported into a silica-rich sand with little capacity for buffering. The lead may eventually be trapped in iron-oxide rich layers in sands and clays.

Planned cleanup of the site by the U.S. Fish and Wildlife Service includes physical excavation and removal of the pellet-contaminated soil, offsite disposal, grading, and revegetation of the area. Once the source area is remediated, the lead may eventually be flushed out of the ground water, but additional ground-water monitoring data would be needed to assess the potential for natural attenuation in this system.

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Appendix. Prime Hook core lithologic descriptions

(Lithology by Michael Smigaj, U.S. Geological Survey; transcription by Britta Hoehndorf, U.S. Geological Survey.)

[UPPER CASE terms represent the major sediment type present. Depths are given as cm (centimeters) below land surface. Depths to the top of the water in the well, mean sea level, bottom of casing, and base of core are noted. Cores are deeper than the bottom of the well casing, because the lower parts of the holes typically collapsed between the removal of the core and the insertion of the plastic casing.]

Well DG-6: Depth below land surface

0 cm	Sandy clay, organic-rich, tan brown
8 cm	clayey SAND, fine to medium, tan to brown (plant root extending to 34 cm depth)
48 cm	clayey SAND, fine to medium, tan to brown, fine scattered gravel decreasing downward
82 cm	clayey SAND, fine to medium, tan-light gray to tan-gray
140 cm	clayey Sand, fine to medium, light tan with fine gravel
145 cm	clayey Sand, fine, light tan-gray
151 cm	- water level in well -
157 cm	CLAYEY SILT, light tan to light gray
163 cm	sandy CLAY, light tan
172 cm	2nd core (debris, collapse)
183.5	SAND, medium to coarse, opaque to white; gravel, fine to coarse, opaque, white to gray
219.5	- mean sea level -
220.5	sandy CLAY, tan to gray; with coarse sand and gravel, clayey gray stringer
294.5	CLAY, light gray to gray; with fine sand, yellow-orange at base
305.5	sandy CLAY, yellow-orange
349 cm	- bottom of well casing -
367.5	SAND, fine to medium, opaque, yellow-orange stained, with some clay
371.5	sandy CLAY, gray; with cherty gravel, fine to medium
379.5	yellow-orange clayey SAND, fine to medium, opaque; with fine gravel at base
390 cm	light gray and yellow-orange clayey SAND, fine to medium, opaque
397 cm	sandy CLAY, light gray
435.5	sandy CLAY, light gray; sand coarsens downward near base
475.5	clayey SILT, light gray
477.5	sandy CLAY, light gray
508.5	CLAY, light yellow-orange to yellow-orange, with stringers of coarse sand
524.5	sandy CLAY, light gray
539.5	fine to coarse sandy CLAY, light gray; sand coarsens downward
543.5	Peat, base of core

Well DG-7: Depth below land surface

0 cm	sandy light tan to light gray CLAY, fine white to black gravel at base
12.5	- water level in well -
38 cm	light gray, clayey fine SAND
53 cm	light tan-gray, clayey fine SAND, scattered fine gravel near top
71 cm	light tan-gray clayey, fine to medium SAND, coarsening downward
73 cm	- mean sea level -
96 cm	light tan to tan-gray sandy CLAY
136 cm	dark tan clayey, fine to medium SAND, some fine gravel
156 cm	yellow-tan clayey, fine to medium SAND
162 cm	gray and yellow-orange clayey, fine to medium SAND, some fine gravel

Appendix. Prime Hook core lithologic descriptions—Continued

Well DG-7: Depth below land surface—Continued

191 cm	yellow-tan to tan-brown, fine to coarse SAND
198 cm	dark tan-gray clayey, fine to medium SAND, with fine gravel
254 cm	- bottom of well casing -
298 cm	gray clayey, fine to medium SAND, some coarse, fine gravel throughout with gravel base
355.5	tan-gray clayey, fine to medium SAND, with fine gravel, more clay at bottom, with mottled white-gray to tan-brown streaks
380 cm	light tan-brown clayey; fine to coarse SAND, darker tan-brown clay at base
393 cm	light tan-gray clayey, fine to coarse SAND, some fine gravel
413 cm	light tan-gray clayey, fine SAND; some light tan and orange-brown streaks
465.5	fine sandy, gray, light tan, orange-brown mottled CLAY, fine gravel at base
485 cm	fine, some coarse, sandy light tan-gray CLAY, some fine gravel
593 cm	light gray to orange-tan clayey fine SAND, fine gravel at base
598 cm	light tan, orange-tan CLAY, with fine sand
602 cm	light gray clayey, fine SAND, with fine gravel
612 cm	sandy, light tan to tan CLAY
635 cm	gray to light tan clayey fine to coarse SAND, some fine gravel
641 cm	light gray, light tan, tan-orange stratified clayey, fine to coarse SAND
731 cm	light tan-gray, fine to medium SAND
739.5	base of core

Well DZ-1: Depth below land surface

0 cm	fine to medium sandy, tan-gray CLAY
4 cm	fine to medium sandy, tan-gray SILTY-CLAY
30 cm	gray to brownish-tan, clayey fine to medium SAND
47 cm	- water level in well -
62.5	tan-gray clayey, fine to coarse SAND, with fine gravel
118 cm	- mean sea level -
122.5	tan-brown clayey, fine SAND
127.5	clayey, white to gray, fine to medium SAND, fining upward
140 cm	light tan, fine sandy CLAY, stratified bands of tan-gray and yellow-orange clay
142 cm	- bottom of well casing -
186 cm	tan-brown, clayey fine to coarse SAND, with fine gravel
191 cm	clayey, white-gray, fine to medium SAND, fining upwards
195.5	clayey, white fine SAND, stratified, with fine gravel
228.5	dark tan-brown, fine sandy CLAY
233 cm	light tan-gray, fine sandy CLAY
237 cm	tan-gray, fine sandy CLAY
241 cm	light-tan, fine sandy CLAY
244.5	dark tan, fine sandy CLAY, some coarse sand
252 cm	light gray, fine sandy CLAY (compact)
264.5	light gray, fine sandy CLAY (loose)

Appendix. Prime Hook core lithologic descriptions—Continued

Well DZ-1: Depth below land surface—Continued

271.5	orange-tan, fine sandy CLAY
278.5	light tan, fine sandy CLAY
294 cm	light tan, clayey fine to coarse SAND, with fine gravel
306 cm	light tan, clayey, fine SAND
319.5	base of core

Well DZ-2: Depth below land surface

+3.96	- water level in well - (elevated nearly 4 cm above ground surface)
0 cm	fine sandy, dark gray silty CLAY, (plant root extending down)
11.5	fine sandy, gray CLAY, clasts of yellow-orange clay and fine to medium gravel
67 cm	- mean sea level -
91.5	fine sandy, light gray to tan-gray CLAY
139 cm	fine sandy, gray and orange-tan CLAY
144.5	fine sandy gray CLAY
148.5	fine sandy, light to dark gray CLAY, clasts of light gray silt, occasional fine gravels
196.5	tan-gray, clayey fine SAND, occasional fine gravel
310 cm	- bottom of well casing -
395 cm	light to dark tan, clayey, fine to coarse SAND, some fine to coarse gravel
441 cm	base of core

Well DZ-3: Depth below land surface

0 cm	fine sandy, gray to tan-gray CLAY, occasional fine gravel
9.144	- water level in well -
36 cm	tan-gray, clayey, fine to coarse SAND, with some fine to coarse gravel
79.248	- mean sea level -
102 cm	fine to medium sandy, tan-gray CLAY, with reddish-brown clay at base
112.5	tan-gray SILT
122 cm	fine sandy gray CLAY, some reddish-brown clay
145.5	tan-gray, clayey fine SAND, with fine to coarse gravel
198.5	gray to light gray SILT, reddish-brown at upper contact
219.5	fine sandy, light gray to gray SILT; sand increasing downward
231.01	- bottom of well casing -
251.5	tan-gray, clayey fine to coarse SAND, sand coarsens downward with a decrease in clay
357.5	fine sandy, tan-gray CLAY
377.5	fine sandy, dark tan-gray CLAY
384 cm	fine sandy, tan-gray CLAY
387.5	fine sandy, dark tan-gray CLAY
392.5	fine to coarse sandy, tan-gray CLAY
427.5	fine sandy, yellow-orange CLAY, with fine to coarse gravel at upper contact, decreasing downward
438.5	fine to medium sandy, tan-gray CLAY, fine gravel, dark gray clay clast near base
509.5	base of core

Appendix. Prime Hook core lithologic descriptions—Continued

Well UG-1: Depth below land surface

0 cm	orange-brown, silty-clayey coarse SAND and fine gravel
47 cm	orange-brown, clayey fine to medium SAND, fine to medium gravel
63.1 cm	- water level in well -
77.5	sandy, orange-brown SILT and CLAY, gray clay clasts throughout
94 cm	sandy, gray, orange SILT
121 cm	sandy, orange-brown CLAY, with gray silt stringers
131.5	yellow-orange, clayey fine Sand, with fine gravel
143.3	- mean sea level -
202 cm	sandy, yellow-orange silty CLAY
250.5	orange-brown clay, mottled with gray SILT
265 cm	- bottom of well casing -
309.5	sandy, orange-brown CLAY, with fine chert
313.5	orange-brown CLAY, mottled with gray silt
351.5	orange-brown CLAY, darkening to base
362.5	base of core

Well UG-2: Depth below land surface

0 cm	sandy, dark gray SILT, with organic plant root
1.3 cm	- water level in well -
9 cm	fine sandy gray SILT, with orange-brown clay
61 cm	reddish-brown, fine to medium SAND, coarsening downward with fine gravel at base
73 cm	- mean sea level -
83.5	light tan-gray, clayey fine to medium SAND, some coarse sand
176.5	tan, yellow-orange, clayey fine to medium SAND
267 cm	sandy, tan to yellow-orange CLAY, with coarse sand
271 cm	- bottom of well casing -
305.5	sandy, light tan to yellow-orange CLAY, with fine gravel and clay clasts
320.5	sandy, tan to yellow-orange CLAY, stratified, with fine gravel
339.5	orange-brown SILT
344.5	yellow-orange CLAY
348.5	light tan-gray CLAY, with coarse gravel
360 cm	tan-yellow, fine to medium SAND, traces of coarse sand and fine gravel at base
427 cm	light tan, medium SAND, with fine gravel and coarse chert at base
487 cm	light tan, medium to coarse SAND
504.5	white to gray, medium SAND
507 cm	tan to yellow, medium stratified SAND, fining upward
526.5	iron stained, fine SAND (0.5 cm layer)
527 cm	clayey, medium to coarse stratified, yellow to tan SAND
534.5	base of core
