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Fate and Transport of Petroleum Hydrocarbons in Soil and Ground Water at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002-2003

Scientific Investigations Report 2005-5104

U.S. Department of the Interior
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Cover photograph: View of the Big South Fork of the Cumberland River from the Honey Creek Overlook in the Big South Fork National River and Recreation Area.

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Conversion Factors, Vertical Datum, and Site-Numbering System

Multiply	By	To obtain
nanometer (nm)	3.937×10^{-8}	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	feet (ft)
kilometer (km)	0.6214	mile (mi)
square kilometer (km^2)	0.3861	square mile (mi^2)
milliliter (mL)	0.0338	fluid ounce (fl oz)
liter (L)	0.2642	gallon (gal)
micrograms per kilogram (µg/kg)	1.000×10^{-9}	pound per pound (lb/lb)
milligrams per kilogram (mg/kg)	1.000×10^{-6}	pound per pound (lb/lb)
micrograms per liter (µg/L)	6.243×10^{-8}	pound per cubic foot (lb/ft^3)
milligrams per liter (mg/L)	6.243×10^{-5}	pound per cubic foot (lb/ft^3)
liters per second (L/s)	15.85	gallon per minute (gal/min)

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

$$°F = 1.8 \times °C + 32$$

$$°C = 5/9(°F - 32)$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29); horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Site-numbering system for wells: In addition to the field site number, the U.S. Geological Survey assigns each site listed in this report a station identification number. The station identification number is used as an identifier for site data stored in the national computer data base of the U.S. Geological Survey.

The station identification number is a unique number for each site based on a latitude and longitude grid system. The number consists of 15 digits. The first 6 digits denote the degrees, minutes, and seconds of latitude; the next 7 digits denote degrees, minutes, and seconds of longitude; and the last 2 digits (assigned sequentially) identify the wells within a 1-second grid.

Site numbering system for surface-water sites: Each surface-water station in this report is assigned a unique identification number. The number is assigned when a station is first established and is retained for that station indefinitely. The station numbers indicate downstream-order position. A station on a tributary that enters between two mainstream stations is assigned a number between them. A similar order is followed in listing stations on first rank, second rank, and other ranks of tributaries.

Gaps are left in the series of numbers to allow for new stations that may be established; hence, the numbers are not consecutive. The complete number for each station such as 03540500, includes a 2-digit part number "03" plus the multi-digit downstream order number "540500." This downstream ordering system is used in most cases; however, in some cases latitude and longitude numbers are assigned to hydrologic stations as a means of identification.

Acronyms

BART	Biological activity reaction test
BISO	Big South Fork National River and Recreation Area
BTEX	Benzene, toluene, ethylbenzene, and xylene
DO	Dissolved oxygen
DRO	Diesel range organic
EPH	Extractable petroleum hydrocarbon
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
GRO	Gasoline range organic
MCL	Maximum contaminant level
NPS	National Park Service
NWQL	U.S. Geological Survey National Water Quality Laboratory
PAH	Polycyclic aromatic hydrocarbon
PBS	Phosphate buffered solution
STL	Severn Trent Laboratories
TEAP	Terminal electron acceptor processes
TPH	Total petroleum hydrocarbon
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VBW	Volatile grade blank water
VOC	Volatile organic compound
VPH	Volatile petroleum hydrocarbon
WQRL	U.S. Geological Survey Water Quality Research Laboratory

Fate and Transport of Petroleum Hydrocarbons in Soil and Ground Water at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002-2003

By Shannon D. Williams, David E. Ladd, and James J. Farmer

Abstract

In 2002 and 2003, the U.S. Geological Survey (USGS), by agreement with the National Park Service (NPS), investigated the effects of oil and gas production operations on ground-water quality at Big South Fork National River and Recreation Area (BISO) with particular emphasis on the fate and transport of petroleum hydrocarbons in soils and ground water. During a reconnaissance of ground-water-quality conditions, samples were collected from 24 different locations (17 springs, 5 water-supply wells, 1 small stream, and 1 spring-fed pond) in and near BISO. Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds were not detected in any of the water samples, indicating that no widespread contamination of ground-water resources by dissolved petroleum hydrocarbons probably exists at BISO. Additional water-quality samples were collected from three springs and two wells for more detailed analyses to obtain additional information on ambient water-quality conditions at BISO.

Soil gas, soil, water, and crude oil samples were collected at three study sites in or near BISO where crude oil had been spilled or released (before 1993). Diesel range organics (DRO) were detected in soil samples from all three of the sites at concentrations greater than 2,000 milligrams per kilogram. Low concentrations (less than 10 micrograms per kilogram) of BTEX compounds were detected in lab-analyzed soil samples from two of the sites. Hydrocarbon-degrading bacteria counts in soil samples from the most contaminated areas of the sites were not greater than counts for soil samples from uncontaminated (background) sites. The elevated DRO concentrations, the presence of BTEX compounds, and the low number of hydrocarbon-degrading bacteria in contaminated soils indicate that biodegradation of petroleum hydrocarbons in soils at these sites is incomplete.

Water samples collected from the three study sites were analyzed for BTEX and DRO. Ground-water samples were collected from three small springs at the two sites located on ridge tops. BTEX and DRO were not detected in any of the water samples, and petroleum hydrocarbons do not appear to have leached into ground water at these sites. Ground-water samples were collected from a small spring and from three auger holes at the third site, which is located in a stream valley. BTEX and DRO were not detected in these ground-water samples, and currently, petroleum hydrocarbons do not appear to be leaching into ground water at this site. Weathered crude oil, however, was detected at the water surface in one of the auger holes, indicating that soluble petroleum hydrocarbons may have leached into the ground water and may have migrated downgradient from the site in the past. The concentration of soluble petroleum hydrocarbons present in the ground water would depend on the concentration of the hydrocarbons in the crude oil at the site.

A laboratory study was conducted to examine the dissolution of petroleum hydrocarbons from a fresh crude oil sample collected from one of the study sites. The effective solubility of benzene, toluene, ethylbenzene, and total xylenes for the crude oil sample was determined to be 1,900, 1,800, 220, and 580 micrograms per liter (µg/L), respectively. These results indicate that benzene and toluene could be present at concentrations greater than maximum contaminant levels (5 µg/L for benzene and 1,000 µg/L for toluene for drinking water) in ground water that comes into contact with fresh crude oil from the study area.

Introduction

The Big South Fork National River and Recreation Area (BISO) was established in 1974 to conserve, interpret, and protect the unique resources of the Big South Fork of the Cumberland River. The National Park Service (NPS) manages BISO and has an ongoing program to protect the water resources of the area. Goals of this program include evaluating the condition of water resources and prioritizing activities to remediate any contamination of these water resources.

Approximately 300 active or abandoned oil and gas wells are located in BISO, and more than 3,000 oil and gas wells are in the Big South Fork watershed (Otton and Zielinski, 2000). Contaminants associated with oil and gas production have the potential to affect the water resources of the area. The potential contaminants associated with oil and gas production include petroleum hydrocarbons, brines and trace metals,

and in some cases naturally occurring radioactive material. Sources of these contaminants include overflowing, failing, or unlined pits; leaking tanks; leaking well heads; and interaction between ground water and petroleum or brine zones inside well bores. In 2002 and 2003, the USGS, by agreement with the NPS, investigated the effects of oil and gas production on ground-water quality at BISO with particular emphasis on the fate and transport of petroleum hydrocarbons in soils and ground water. This report is published by agreement with the NPS.

Purpose and Scope

This report presents data and results from an investigation of the effects of oil and gas production operations on ground-water quality at BISO. Objectives of this investigation included examining the extent of ground-water contamination by petroleum hydrocarbons from oil and gas production, documenting general ground-water-quality conditions in BISO, and evaluating potential natural attenuation processes such as biodegradation.

Three stages of monitoring and research activities were used to meet these objectives. During the first stage (the reconnaissance), basic water-quality data and volatile organic compound (VOC) data were collected from several locations (mostly springs) in or near BISO. During the second stage, more detailed water-quality data (including microbiological, geochemical, and additional petroleum hydrocarbon data) were collected from several of the locations sampled during the reconnaissance stage. During the third stage of the investigation, soil gas, soil, water-quality, and microbiological data were collected at three crude oil release sites in or near BISO. Little construction and lithologic data were available for wells sampled during the first two stages of the investigation, and not enough water-level data could be collected from these wells to report ground-water gradients for BISO. Site-specific hydrogeologic data were not collected as part of the investigation, and little published information specific to the geology and hydrogeology of BISO exists. Although a general description of the hydrogeology of the Cumberland Plateau section of the Appalachian Plateaus Physiographic Province is presented in the report, site-specific hydrogeologic information is not included.

Study Area

BISO includes about 506 km^2 in the rugged Cumberland Plateau section of the Appalachian Plateaus Physiographic Province in Tennessee and Kentucky (Fenneman, 1938) (fig. 1). BISO is located in parts of Fentress, Scott, Morgan, and Pickett Counties in Tennessee and McCreary County in Kentucky. Average annual precipitation near BISO (in Oneida, Tennessee) is about 140 cm (National Oceanic and Atmospheric Administration, 2002). Clear Fork and the New River meet in Tennessee to form the South Fork Cumberland River, also referred to as the Big South Fork River. The Big South Fork River flows north across the Cumberland Plateau, forming a steep-walled gorge that in places reaches a depth of 183 m (Manning, 2000), eventually flowing into the main stem of the Cumberland River in Kentucky.

The Big South Fork River watershed covers about 3,580 km^2 from its headwaters to its confluence with the Cumberland River. Within the watershed, the Big South Fork River and its tributaries drain the Cumberland Plateau. Elevations in the watershed range from over 1,060 m in the southeastern part of the watershed to around 220 m near the northern boundary. The study area for this investigation is located in the southern part of the Big South Fork River watershed (fig. 1), which contains the highest density of oil and gas production wells in the vicinity of BISO. Although all of BISO lies within the Cumberland Plateau, the southeastern part of the study area lies within the Cumberland Mountain section of the Appalachian Plateaus Physiographic Province (Fenneman, 1938) (fig. 1). The three crude oil release study sites and most of the sampling locations are located in or near the southern part of BISO (fig. 2).

The exposed geology of the study area consists predominantly of sandstones, conglomerates, shales, siltstones, and coals of Pennsylvanian age that overlie carbonates and shale of Mississippian age. The rocks of Pennsylvanian age compose the Cumberland Plateau aquifer system, which underlies BISO and the rest of the Cumberland Plateau. The sandstones have low intergranular permeability, and ground water in the aquifer occurs mostly within the fractures in the sandstones and conglomerates. The sandstone and conglomerate units are confined and separated by shale and siltstone beds of low permeability (Brahana and others, 1986). Seeps and springs, occurring where ground water intersects land surface, are common in BISO, particularly at the base of ledges and bluff shelters (Hamilton and Turrini-Smith, 1997). Commonly, springs in the Cumberland Plateau aquifer system are present at sandstone/shale contacts (Brahana and others, 1986). The only rocks of Mississippian age exposed within the study area are part of the Pennington Formation, a unit consisting of approximately 46 to 122 m of shale, siltstone, dolomite, limestone, and sandstone (Swingle and others, 1966). The Pennington Formation, which crops out in the northern part of Tennessee in the bottom of the Big South Fork River gorge, separates underlying carbonates of Mississippian age from the exposed rocks of Pennsylvanian age. The top of the Pennington Formation is considered the base of the Cumberland Plateau aquifer system. A conceptual model of ground-water occurrence and flow in BISO is shown in figure 3.

Crude Oil Release Site 1

Site 1, which is near Bear Branch in BISO (fig. 4), includes an active crude oil pumping unit and a tank battery. In 1993, a tank in an old battery was struck by lightning. Gas in the headspace of the tank exploded and about 31,800 L of crude oil were released, some of which flowed into a tributary

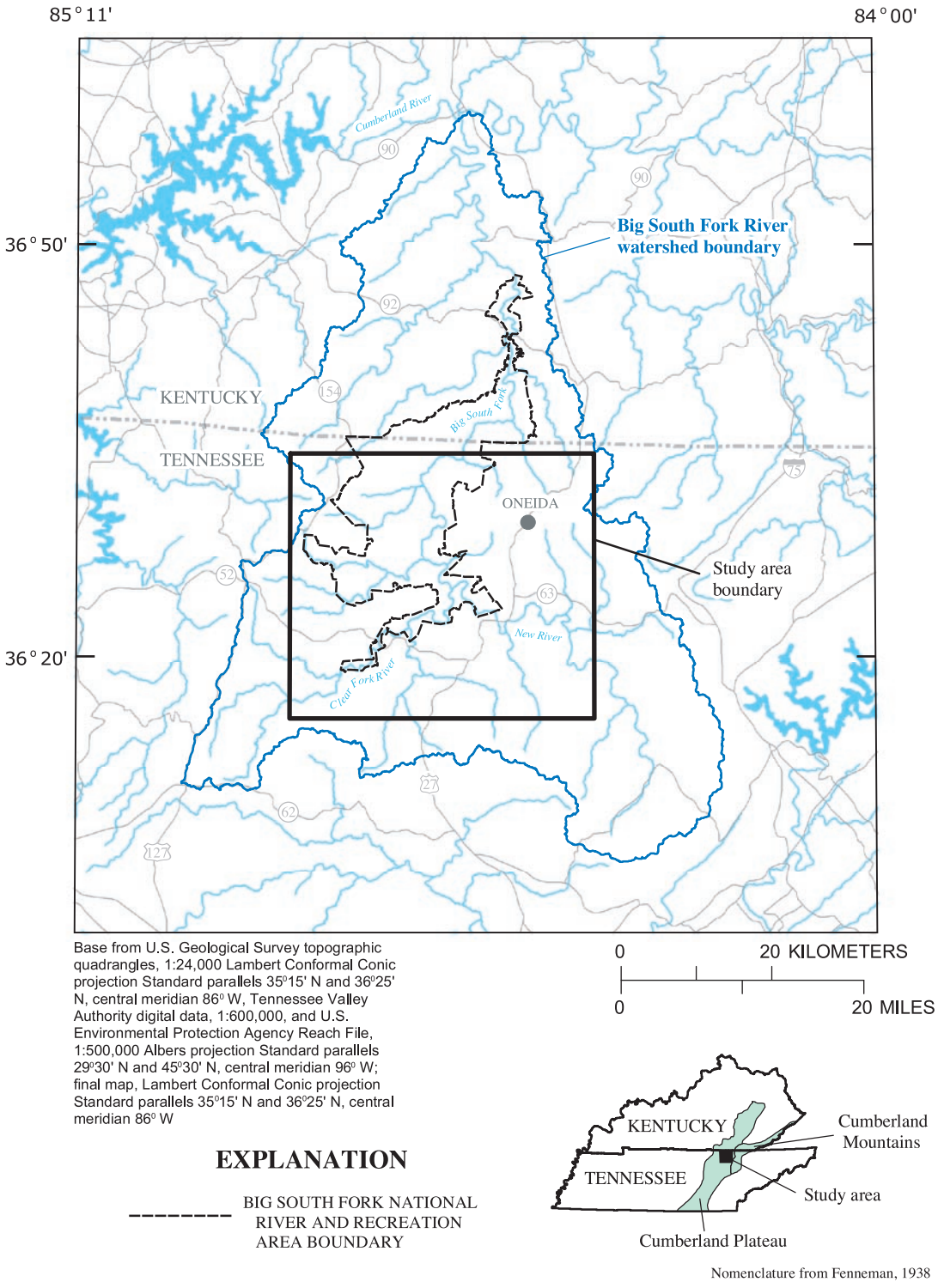

Figure 1. Location of the study area at Big South Fork National River and Recreation Area near Oneida, Tennessee.

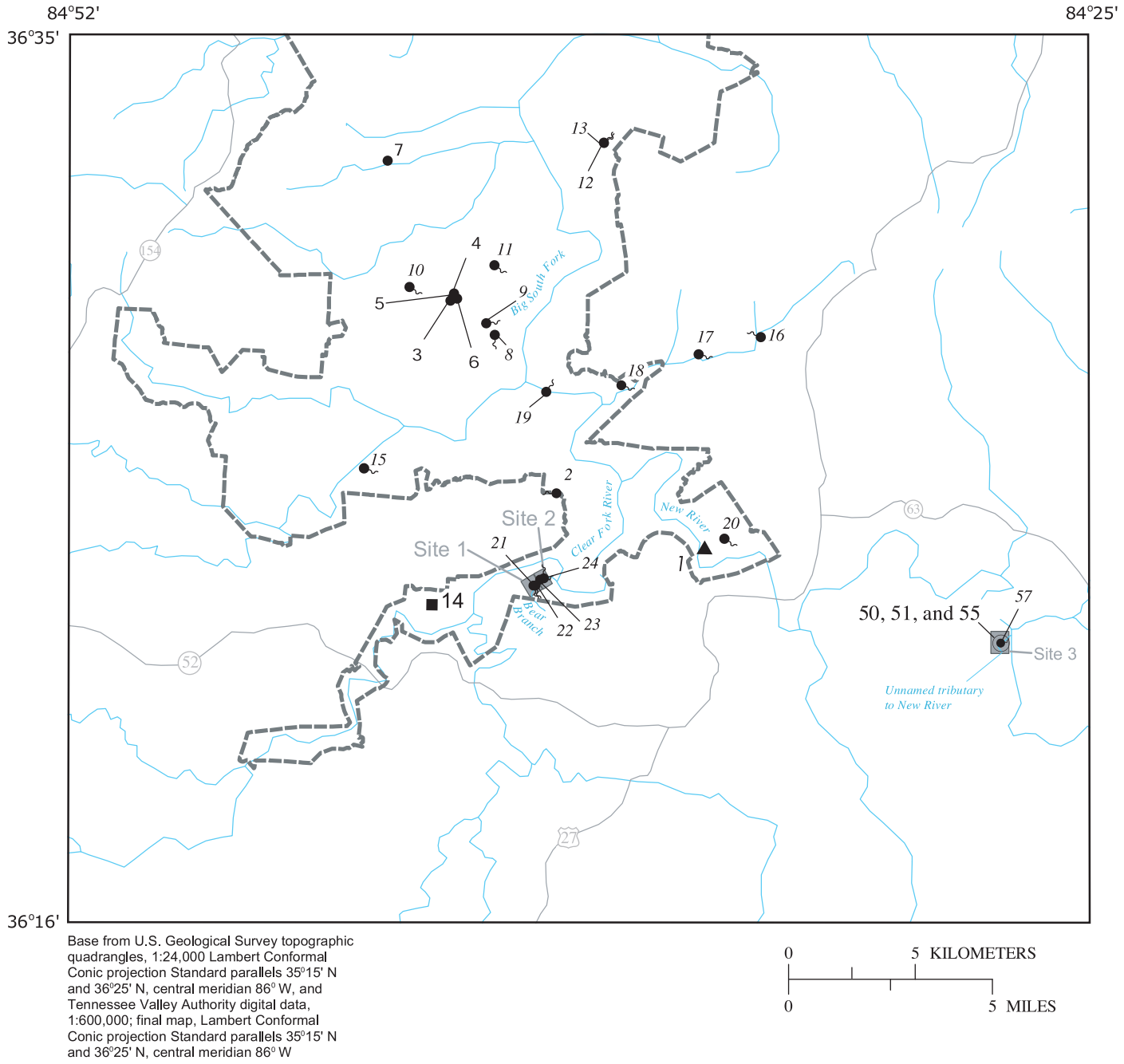

Figure 2. Locations of sites from which water samples were collected and locations of crude oil release study sites.

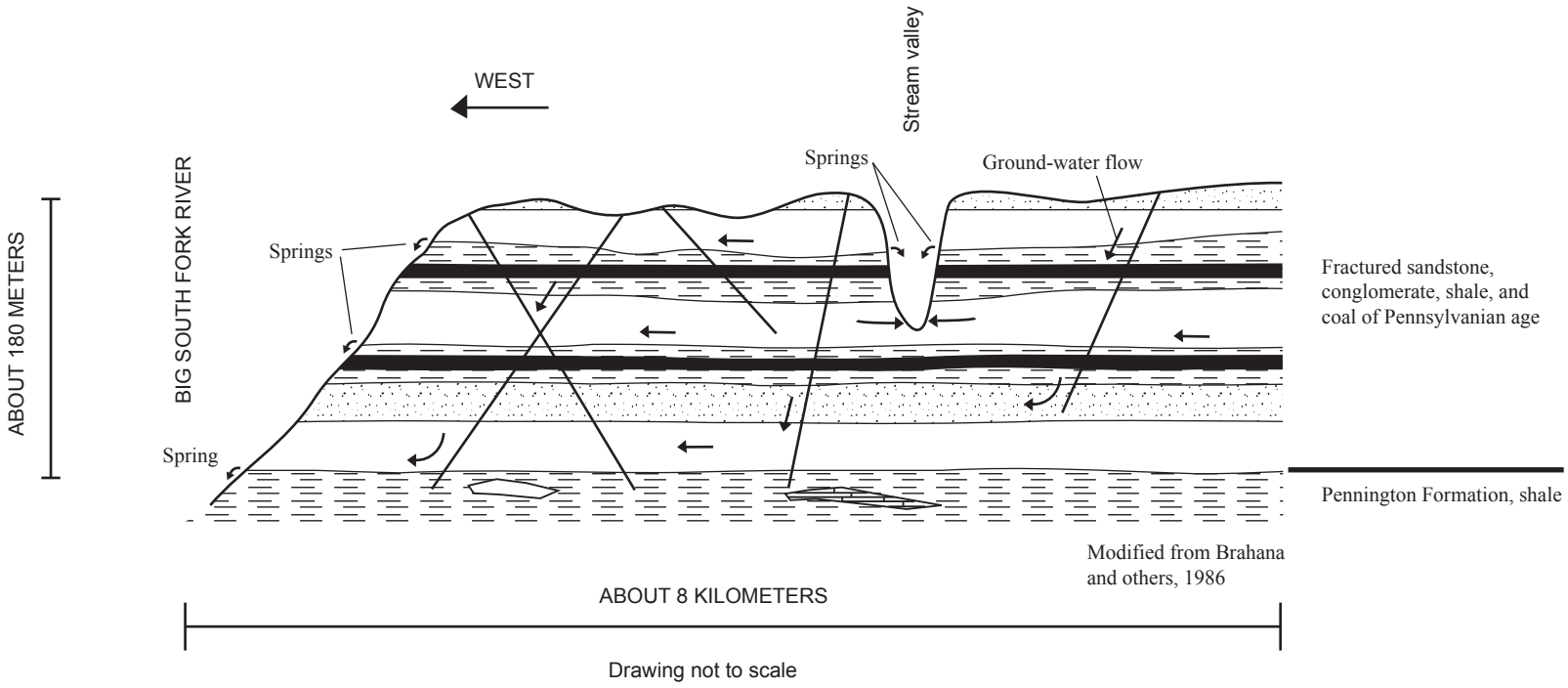

Figure 3. Conceptual model of ground-water occurrence and flow in the Big South Fork National River and Recreation Area.

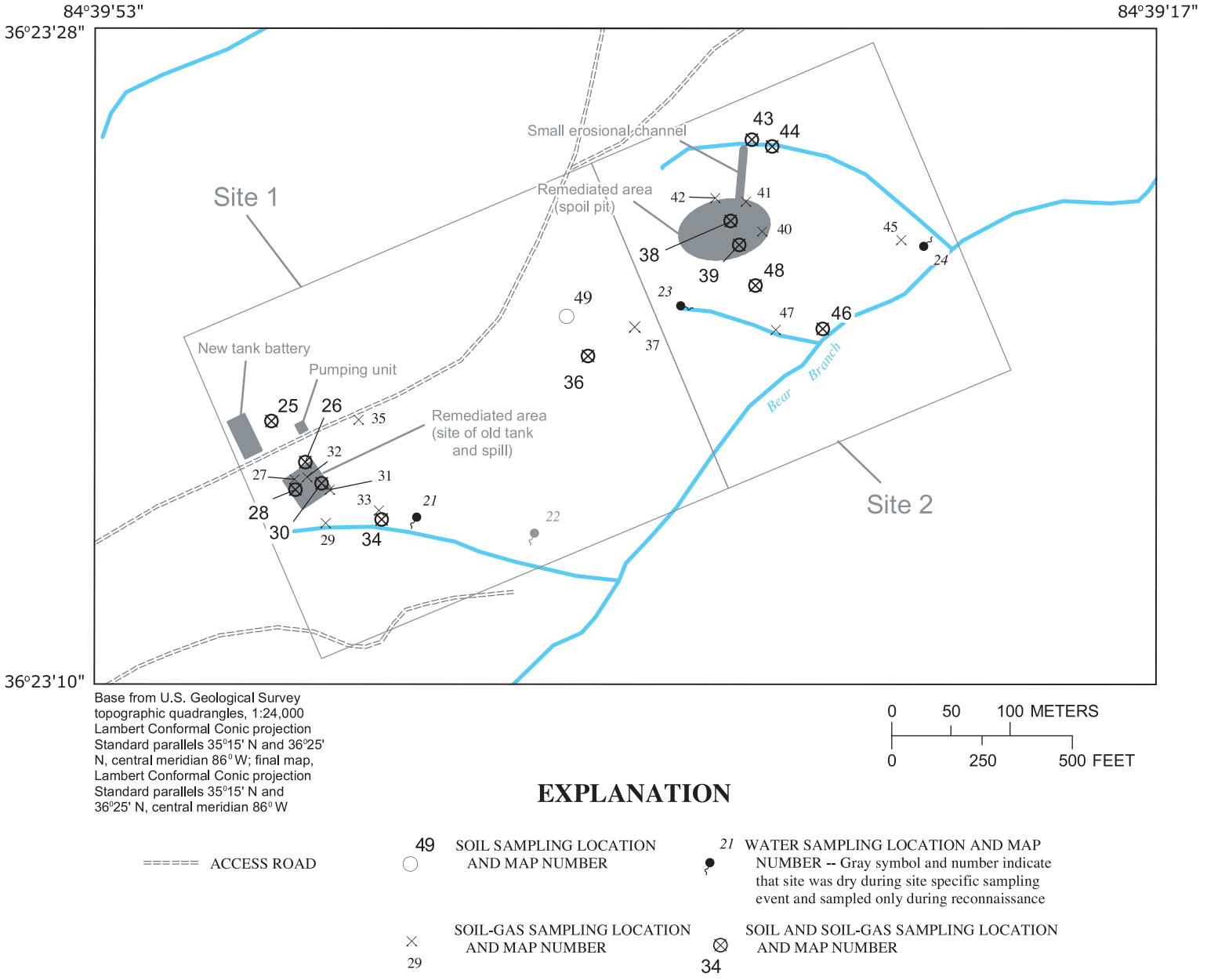

Figure 4. Sampling locations at crude oil release sites 1 and 2.

to Bear Branch. After the spill, the old tank battery was removed. Remedial activity included tilling soil near the old tank battery to a depth of 10 to 13 cm, fertilization, and planting winter wheat and winter rye (Otton and Zielinski, 2000).

This site was examined in 1999, during a study evaluating field-monitoring techniques for assessing impacts of oil and gas operations on Federal Lands (Otton and Zielinski, 2000). During the 1999 study, holes were bored about 0.5 to 1 m deep using a hand auger at the site (site BSF99-2 in Otton and Zielinski, 2000). Volatile organic compounds (VOCs) in soil gas from the auger holes or in headspace from heated bags containing soil were measured using a hand-held photoionization unit. Semisolid fragments of residual hydrocarbons and a strong hydrocarbon odor were detected in an auger hole near the southern edge of the remediated area. VOC concentrations as great as 50 mg/L were detected in the headspace from bags containing soil from that auger hole. Soil gas measured at a site located along a small dry streambed southwest of the spill site contained about 4 mg/L of VOCs. Soil gas measured at a site on the southwest side of the dry streambed contained about 1 mg/L of VOCs (Otton and Zielinski, 2000). Otton and Zielinski (2000) suggest that these data indicate that hydrocarbons are present in the subsurface along the tributary to Bear Branch.

Crude Oil Release Site 2

The second crude oil release site is located about 360 m northeast of site 1 (fig. 4) and once included a spoil pit about 30 m in diameter. Total petroleum hydrocarbon concentrations of 500 to 700 mg/kg have been detected in composite soil samples collected from the site (Otton and Zielinski, 2000). Remediation activities in 1993 and 1994 included mixing the sludge with soil, lime, and fertilizer; tilling the surface; and planting clover, winter wheat, and winter rye. The remediated area is along the crest of a ridge. A small erosional channel runs down the northwest side of the ridge to a small stream (fig. 4).

During the 1999 study, soil gas samples were analyzed at several holes augered at this site (site BSF99-7 in Otton and Zielinski, 2000). Soil gas from auger holes in or near the remediated area contained 0.1 to 0.2 mg/L of VOCs. Soil gas samples collected from auger holes along the stream, just downgradient of the erosional channel, contained between 4.7 and 13.9 mg/L of VOCs. Soil gas samples collected along the stream, just upstream from the erosional channel, contained between 0.2 and 0.9 mg/L of VOCs (Otton and Zielinski, 2000). According to Otton and Zielinski (2000), hydrocarbons likely have been transported downslope from the former spoil pit to the stream by surface flow of oil, surface flow of water carrying dissolved hydrocarbons, or shallow ground water carrying dissolved hydrocarbons.

Crude Oil Release Site 3

The third crude oil release site is located near a small unnamed tributary on the west side of New River about 8 km east of the BISO boundary (fig. 2), and includes an inactive pumping unit, two oil tanks, a pit filled with oil and water, and a brine pit (fig. 5). Of the three crude oil release sites, this was the only site at which the oil wells produced water (Otton and Zielinski, 2000). The oil- and water-filled pit is about 8 by 12 m in size and about 3 m above the flood plain of the small stream (fig. 5). Soil gas concentrations were not measured during 1999 at this site (site BSF99-3 in Otton and Zielinski, 2000). An oily sheen was noticed in a small pool of water between the pit and the stream, and visible evidence indicated that oil had spilled out of the pit and into the flood plain (Otton and Zielinski, 2000).

Petroleum Hydrocarbons

Petroleum and petroleum products are highly complex and varied mixtures. Hydrocarbons (compounds containing only carbon and hydrogen atoms) compose the majority of the components in petroleum (Weisman, 1998). Crude oil can consist of thousands of individual compounds with hydrocarbons representing from 50 to 98 percent of the total weight of crude oil (Irwin and others, 1998). When petroleum compounds such as crude oil are released into the environment, the compounds undergo physical, chemical, and biological changes collectively referred to as weathering. The degree to which various types of petroleum hydrocarbons degrade under these changes depends on the physical and chemical properties of the hydrocarbons.

Types of Petroleum Hydrocarbons

Petroleum hydrocarbons are generally divided into two groups: aliphatics and aromatics. Aliphatics include alkanes that contain single bonds between carbon atoms and have formulas of $C_nH_{2n+2,}$, alkenes, which contain one or more double bonds between atoms and have formulas of C_nH_{2n}, and cycloalkanes, which contain carbon atoms in cyclic structures. Aromatics have one or more benzene rings as part of their structure. Monoaromatics are aromatics with one benzene ring as part of their structure; polycyclic aromatic hydrocarbons (PAHs) are aromatics with two or more fused benzene rings. Monoaromatics, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), are some of the most common aromatic compounds in petroleum. Crude oil contains less BTEX than gasoline. Combining the average percentage weights for individual BTEX compounds (table 1) indicates that on average, BTEX compounds represent about 2 percent crude oil (by weight), which is consistent with data reported for crude oil samples collected from three different caverns that are used for storage in the Strategic Petroleum Reserve (U.S. Department

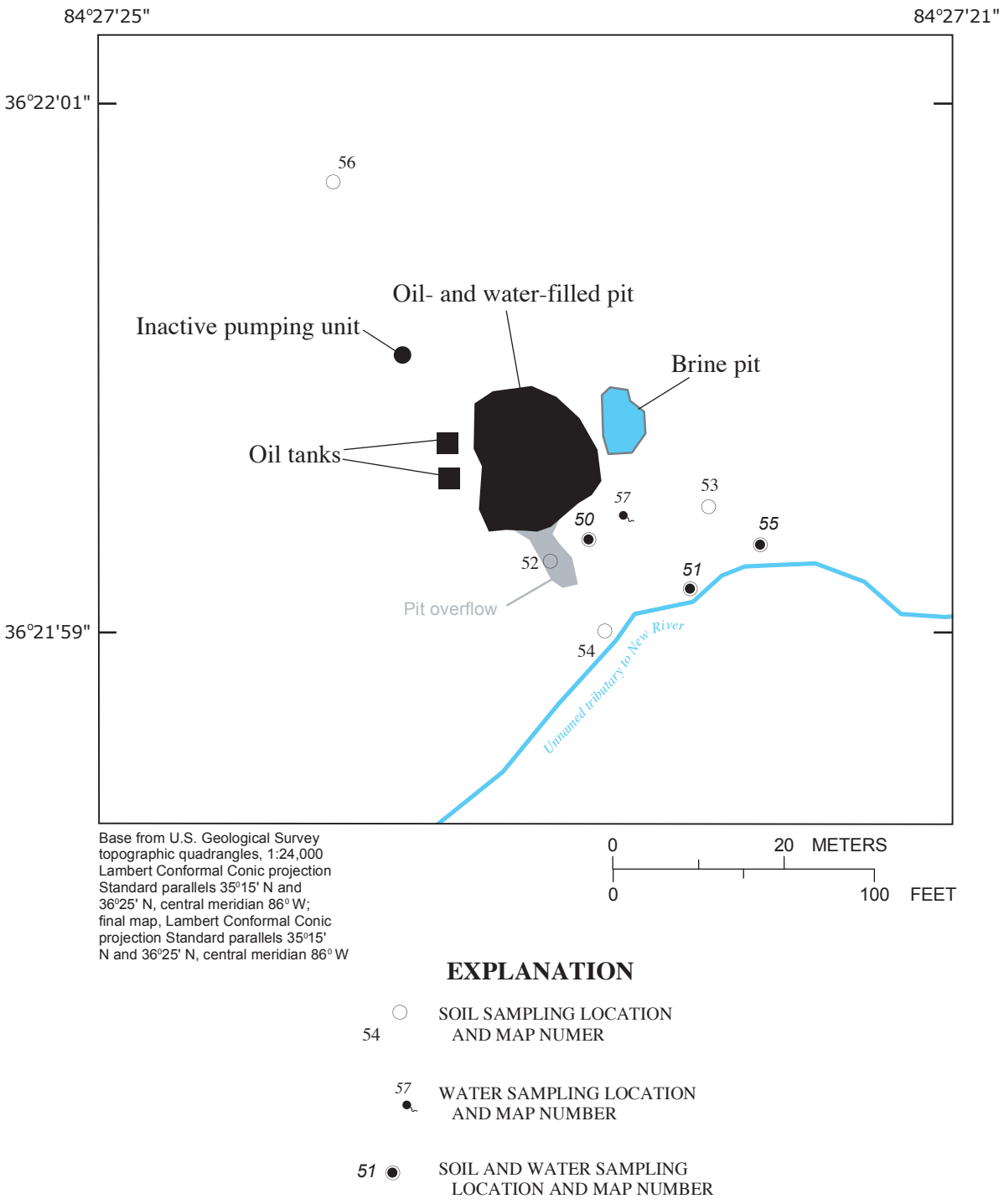

Figure 5. Sampling locations at crude oil release site 3.

Table 1. Physical, chemical, regulatory, and human health information for selected aromatic hydrocarbons.

[K_{OC}, organic carbon-water partition coefficient; L/kg, liters per kilogram; mg/L, milligrams per liter; °C, degrees Celsius; MCL, drinking water maximum contaminant level; HBL, Water Health Based Limits; --, not available]

Name	Typical amounts in crude oil[1] (in weight percent)			Physical and chemical properties						Regulatory and human health information		
	Average	Minimum	Maximum	Benzene (and total) rings	Number of carbon atoms	Molecular weight (grams)	K_{oc}[2] (L/kg)	Solubility in water[2] (mg/L at 20 to 25 °C)	Henry's law constant[2] (dimensionless at 25 °C)	MCL[3] (mg/L)	HBL[2] (mg/L)	Human carcinogenicity[3]
Benzene	0.16	0.040	0.41	1	6	78	59.0	1800	0.228	0.005	--	Yes.
Toluene	0.67	0.080	2.5	1	7	92	182	530	0.272	1	--	Not classified.
Ethylebenze	0.17	0.056	0.31	1	8	106	363	170	0.323	0.7	--	Not classified.
Total xylenes	--	--	--	--	--	--	--	--	--	10	--	Not classified.
m-Xylene	0.66	0.080	2.0	1	8	106	407	160	0.301	--	--	--
o-Xylene	0.26	0.030	0.68	1	8	106	363	180	0.213	--	--	--
p-Xylene	0.26	0.090	0.68	1	8	106	389	190	0.314	--	--	--
Naphthalene	0.069	0.033	0.092	2	10	128	2,000	31	0.0198	--	1	Possible.
Acenaphthene	0.0057	0.0057	0.0057	2	12	154	7,080	4.2	0.00636	--	2	--
Fluorene	0.020	0.0059	0.060	2 (3)	13	166	13,800	2.0	0.00261	--	1	Not classified.
Anthracene	0.0011	0.0011	0.0011	3	14	178	29,500	0.043	0.00267	--	10	Not classified.
Fluoranthene	0.00040	0.00020	0.00060	3 (4)	16	202	107,000	0.21	0.000660	--	1	Not classified.
Pyrene	0.00080	0.00040	0.0017	4	16	202	105,000	0.14	0.000450	--	--	Not classified.
Benz (a) anthracene	0.00030	0.00020	0.00070	4	18	228	398,000	0.0090	0.000140	--	0.0001	Probable.
Chrysene	0.0013	0.00070	0.0018	4	18	228	398,000	0.0016	0.00388	--	0.01	Probable.
Benzo (a) pyrene	0.00020	0.00010	0.00040	5	20	252	1,020,000	0.0016	0.0000500	0.0002	--	Probable.
Benzo (b) fluoranthene	0.00040	0.00040	0.00040	4 (5)	20	252	1,230,000	0.0015	0.00455	--	0.0001	Probable.
Benzo (k) fluoranthene	0.0016	0.0016	0.0016	4 (5)	20	252	1,230,000	0.00080	0.0000300	--	0.001	Probable.
Ideno (1,2,3-c,d) pyrene	0.00070	0.00070	0.00070	5 (6)	22	276	3,470,000	0.000022	0.0000700	--	0.0001	Probable.

[1] Potter and Simmons, 1998.

[2] U.S. Environmental Protection Agency, 1996a.

[3] U.S. Environmental Protection Agency, 2002.

of Energy, 2002). In samples from these caverns (each containing crude oil from multiple international sources), BTEX represented between 2.0 and 2.2 percent of the crude oil (by weight). Xylenes, toluene, benzene, and ethylbenzene represented 0.86 to 0.94, 0.74 to 0.81, 0.17 to 0.30, and 0.22 to 0.24 percent by weight, respectively, of the crude oil (U.S. Department of Energy, 2002). On average, crude oil contains approximately 1 percent PAHs (Irwin and others, 1998). Typically, crude oil contains high concentrations of aliphatic hydrocarbons and lower concentrations of aromatic hydrocarbons (Potter and Simmons, 1998).

Natural gas condensates also are composed primarily of aliphatic hydrocarbons; however, the condensates may contain substantial amounts of BTEX. Samples of gas condensate liquids collected from sites in New Mexico, Colorado, Wyoming, and Alberta, Canada, contained BTEX concentrations representing from 3.4 to 15.0 percent of the total condensate weight (Hawthorne and Miller, 1998). Xylenes, toluene, benzene, and ethylbenzene represented 1.8 to 5.0, 1.1 to 5.4, 0.15 to 3.6, and 0.31 to 0.63 percent, respectively, of the condensate weight. Rixey and others (1999) measured a maximum benzene concentration of 3.6 percent and mean benzene concentration of 1.0 percent (by weight) in 14 natural gas condensates, 12 of which were collected from sites in the contiguous United States.

Several aromatic hydrocarbons are known or suspected human carcinogens (table 1), and are classified as priority pollutants regulated by the U.S. Environmental Protection Agency (USEPA) (Office of the Federal Register, 2002). The BTEX compounds and 16 PAHs appear on The Clean Water Act Priority Pollutant list of 126 chemical substances (Office of the Federal Register, 2002). Benzene and PAHs are ranked sixth and ninth, respectively, on the 2001 Comprehensive Environmental Response, Compensation, and Liability Act Priority List of Hazardous Substances. This list is a prioritization of substances based on their frequency, toxicity, and potential for human exposure at sites on the National Priorities List (Agency for Toxic Substances and Disease Registry, 2001).

Cumulative concentrations of petroleum hydrocarbons commonly are referred to as total petroleum hydrocarbons (TPH). Many different analytical techniques including gravimetric, immunoassay, and gas chromatography (GC) have been used to measure TPH in soil and water. None of the techniques measure the entire range of petroleum hydrocarbons. The subsets of hydrocarbons detected by the techniques vary depending on the extraction and analytical methods used. For example, method 418.1 (U.S. Environmental Protection Agency, 1983) measures only hydrocarbons in the C6-C24 range (6 to 24 carbon atoms). The terms gasoline range organic (GRO) and diesel range organic (DRO) have been used to refer to subsets of petroleum hydrocarbons detected by some of the techniques (mostly GC techniques). The subsets of hydrocarbons detected by these methods overlap; GRO typically includes hydrocarbons in the C5-C12 range, and DRO typically includes hydrocarbons in the C9-C36 range. Volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) are additional subsets of petroleum hydrocarbons detected by GC methods. VPH hydrocarbons include C5-C12 aliphatics, BTEX, methyl tertiary-butyl ether (MTBE), naphthalene, and C9-C10 aromatics. EPH hydrocarbons include C9-C36 aliphatics and C11-C22 aromatics.

Some states use site-specific target cleanup levels for petroleum contaminated soils; however, many states have established generic cleanup levels that typically include a cleanup level for either DRO or EPH. These levels vary greatly from state to state. Cleanup levels for DRO and EPH, for example, vary from 10 to 10,000 mg/kg (Nascarella and others, 2001). Cleanup levels established by the Tennessee Department of Environment and Conservation (1998) vary from 100 to 1,000 mg/kg for EPH and from 5.0 to 100 mg/kg for benzene, depending on ground-water and soil-permeability classifications.

Transport of Petroleum Hydrocarbons

Crude oil weathering processes include adsorption of hydrocarbons to soil particles, volatilization of hydrocarbons, and dissolution of hydrocarbons in water (Barakat and others, 2001). Alkanes and alkenes tend to be more volatile than aromatics. If volatilization is the most dominant weathering process, then the loss of lower molecular weight aliphatics will be the most substantial change in the crude oil, and aliphatics may be the principal air contaminants at spill sites (Potter and Simmons, 1998).

Less than 5 percent of crude oil will dissolve in water (Irwin and others, 1998). Aromatic hydrocarbons, especially BTEX, tend to be the most water-soluble fraction of crude oil and other petroleum compounds. Benzene (10 times more soluble than ethylbenzene or xylenes) is the most water soluble of the BTEX compounds (table 1). BTEX compounds also are the most volatile of the aromatic compounds and are considered to be VOCs.

BTEX compounds have the lowest soil organic carbon sorption coefficients (K_{oc}) of the most common aromatic hydrocarbons (table 1). K_{oc} is the ratio of the amount of a compound sorbed to the organic matter component of soil or sediment to the amount of the compound in the aqueous phase at equilibrium, and has been used as one variable in predicting the mobility of a compound from soil to ground water. Benzene (K_{oc} of 59) is considered to be highly mobile in soil, toluene (K_{oc} of 182) is considered to be moderate to highly mobile in soil, and xylenes (K_{oc} of 363 to 407) are considered to be moderately mobile in soil (U.S. Environmental Protection Agency, 1995).

Benzene often is the main ground-water contaminant of concern at petroleum release sites because of its high toxicity and mobility (as compared to other petroleum hydrocarbons). Plumes of benzene and other BTEX compounds have been detected in ground water near crude oil spills. At a site in Bemidji, Minn., benzene concentrations as great as 6.8 mg/L

were detected in ground-water samples collected 16 years after 1.7 million L of crude oil were spilled in 1979 (Cozzarelli and others, 2001).

Most PAHs, because of their low volatility, are classified as semivolatile organic compounds. In general, PAHs do not easily dissolve in water and are more likely to partition into sediments and soils rather than into ground water because of their low solubilities and high K_{oc}s. As a result, transport of PAHs tends to be associated primarily with erosion of contaminated soils and sediments. PAHs sorbed to sediments may potentially affect aquatic communities downstream of contaminated sites (Irwin and others, 1998). The potential for colloid-facilitated transport of PAHs in ground water also has been documented. Geochemical changes caused by oil degradation mobilized a small amount of iron-rich colloids at the Bemidji, Minn., spill site and contributed to the transport of PAHs over great distances (Ryan and others, 1999). Some PAHs such as naphthalenes are more volatile and more water soluble than most PAHs (table 1), and can pose a threat to ground-water resources (Goerlitz and others, 1985).

O'Reilly and others (2001) estimated potential dissolved concentrations of crude oil hydrocarbons (aromatics) in water and compared the estimated concentrations to maximum contaminant levels (MCLs) and water health based limits (HBLs) recommended by the USEPA. O'Reilly and others (2001) used published composition data for 69 crude oils, Raoult's law, and published hydrocarbon solubility data to estimate the maximum dissolved concentrations (effective solubility) of benzene and 13 PAH compounds in water exposed to crude oil. MCLs were available for only benzo(a)pyrene and benzene. The estimated maximum dissolved concentration for benzo(a)pyrene [3.3×10^{-4} µg/L] was well below the MCL of 0.2 µg/L for benzo(a)pyrene; however, the estimated maximum dissolved concentration for benzene (27,000 µg/L) was well above the MCL of 5.0 µg/L for benzene. The estimated maximum dissolved concentrations did not exceed any of the recommended HBLs for the other PAHs examined (O'Reilly and others, 2001). Benzene concentrations may be greater than MCLs at gas condensate spill sites or sites where crude oil containing more than 300 mg of benzene per kg of oil (0.03 percent by weight) has been released (Rixey and others, 1999).

Biodegradation of Petroleum Hydrocarbons

Biodegradation is a major weathering process of crude oil and an important natural attenuation process. Rates of biodegradation vary with different microbial populations, hydrocarbons, and geochemical and hydrological conditions present in the subsurface. Nearly all soils and sediments have populations of bacteria and other organisms capable of degrading petroleum hydrocarbons (Kennedy and others, 2000; Potter and Simmons, 1998; U.S. Environmental Protection Agency, 1999; Wiedemeier and others, 1995). Hydrocarbon-degrading bacteria can be present in low numbers in unpolluted environments; however, microbial populations can adapt and reach high densities after coming into contact with released petroleum compounds (Wisconsin Department of Natural Resources, 1994). Generally, petroleum hydrocarbons and other organic molecules with abundant carbon-hydrogen bonds are good food sources (electron donors) because they contain high-energy electrons.

Soil and ground-water bacteria use a variety of natural electron acceptors in the degradation process. The use of these final electron acceptors is not arbitrary but is based on energy transfer efficiency and availability (Montgomery and others, 1994). The most common inorganic electron acceptor in ground water is dissolved oxygen (DO). Once DO has been depleted, bacteria will preferentially use the next most efficient electron acceptor—usually this is nitrate (NO_3^-) or insoluble manganese (Mn^{4+}). After NO_3^- and Mn^{4+} have been depleted, the bacteria will use ferric iron (Fe^{3+}), followed by sulfate (SO_4^{2-}), and carbon dioxide (CO_2), respectively. During the reduction of these electron acceptors CO_2, ammonia (NH_3), soluble manganese (Mn^{2+}) and iron (Fe^{2+}), sulfide (S^{2-}), and methane (CH_4) are produced.

Bacteria responsible for biodegradation commonly are categorized by their terminal electron acceptor processes (TEAP). Types of bacteria include aerobic bacteria, which use DO as their TEAP, nitrate-reducing bacteria, iron- and manganese-reducing bacteria, sulfur-reducing bacteria, and methanogenic bacteria. *Pseudomonas* bacteria are free-swimming aerobic bacteria known to degrade BTEX (Chapelle, 2000).

Biodegradation rates for the various types of petroleum hydrocarbons depend on the TEAP occurring. The sequence of preferential electron acceptor processes has been shown to cause zones of different electron-accepting processes dominating in different redox zones in contaminant plumes (Godsy and others, 1999). Geochemical and microbiological data can be used to delineate the zones and to obtain information on possible degradation rates. Biodegradation rates of low to moderate weight aliphatic, alicyclic, and aromatic hydrocarbons can be high if ideal conditions are present. Resistance to biodegradation typically increases as the molecular weight of the hydrocarbon increases (Wiedemeier and others, 1995).

At the Bemidji, Minn. crude oil spill site, microorganisms have degraded BTEX compounds in the ground water, and biodegradation has slowed the movement of BTEX compounds (Cozzarelli and others, 2001). Many of the soluble hydrocarbons are degraded in an anoxic zone that has developed downgradient of the oil body, but benzene has been more recalcitrant under anoxic conditions and has migrated farther downgradient than other BTEX hydrocarbons (Eganhouse and others, 1996). Field studies at a crude oil spill site in India indicated that up to 75 percent of the hydrocarbons present could be biodegraded within a year if the proper geochemical and microbial consortia are present (Gogoi and others, 2003).

Multiple lines of evidence generally are needed to demonstrate biodegradation processes at contaminated sites (National Research Council, 1993; Wiedemeier and others,

1995). The lines of evidence used to examine biodegradation of petroleum hydrocarbons include (1) chemical data that indicate decreasing concentrations of petroleum hydrocarbons, (2) geochemical data that indicate depletion of electron acceptors, and (3) laboratory or field microbiological data that indicate the bacteria present at a site can degrade petroleum hydrocarbons (U.S. Environmental Protection Agency, 1997).

Methods

Various methods were used to gather information for the investigation. To provide background information on oil and gas production operations in BISO and to aid in the selection of sampling locations for the investigation, oil and gas well records were obtained from State and Federal agencies, and an inventory of available water wells and springs in BISO was compiled from information provided by NPS. During the first stage of the investigation (the ground-water-quality reconnaissance), water samples were collected from springs, wells, and a few surface-water sites. Water samples collected during the reconnaissance were analyzed for physical properties (temperature, DO, pH, and specific conductance), VOCs, and selected types of bacteria. During the second stage of the investigation, additional water samples were collected from selected reconnaissance sites to obtain additional information on background water-quality conditions. Samples collected during the second stage of the investigation were analyzed for physical properties, geochemical indicators, VOCs, DRO, and selected types of bacteria. During the third stage of the investigation, soil gas, soil, water, and crude oil samples were collected to evaluate the fate and transport of petroleum hydrocarbons at the crude oil release sites. Soil gas samples were analyzed for VOCs. Soil samples were analyzed for VOCs, DRO, and selected types of bacteria. Water samples were analyzed for physical properties, geochemical indicators, VOCs, DRO, and selected types of bacteria. A fresh crude oil sample collected from an active production well at one of the release sites was used during a laboratory study examining the dissolution of petroleum hydrocarbons into water.

Sample Collection and Preservation

Water samples were collected from 29 sites during the investigation. Water samples were collected from springs close to the surface discharge points. Samples typically were collected by dipping containers into springs. Some springs were enclosed and samples were collected from discharge pipes coming from the springs. Water samples were collected from wells after the wells had either been pumped for several hours or after measurements of temperature, DO, specific conductance, and pH had stabilized. Samples were collected from a spigot closest to the well head. Water samples were collected from auger holes by using bailers. Samples for selected geochemical indicators were filtered and acidified following methods described by Wilde and others (1999).

Water samples for VOCs were collected in 40-mL glass vials and acidified following methods described by Wilde and others (1999). Quality-control procedures for VOC sampling included the collection of duplicate samples and trip blanks. Water samples analyzed for DRO organics using field screening methods were collected in 40-mL glass vials. Duplicate samples for laboratory analysis of DRO were collected in glass containers provided by the laboratory. Water samples for microbiological analysis were collected in sterilized glass containers. All water samples were stored at approximately 2 °C (degrees Celsius) until analyzed.

Soil gas surveys were performed using methods described by USEPA (1996b). A 0.95-cm-diameter hole was driven into the ground to a depth of about 1.2 m using a slam bar. A 0.64-cm-diameter stainless steel probe was inserted into the hole, and the hole was sealed by tightly packing soil into the top of the hole. An air sampling pump and Teflon tubing was used to purge the probes and to transfer soil gas samples to 1-L Tedlar bags (U.S. Environmental Protection Agency, 1994c).

Hand augers were used to obtain soil samples from selected depths below land surface. Soil samples for field screening of petroleum hydrocarbons were collected using methods described by Hewitt and Myers (1999) and were preserved using method 5035 (U.S. Environmental Protection Agency, 1996c). Modified 10-mL syringes were used to transfer approximately 5 g of soil to a preweighed sample vial (40-mL VOC vial) that contained 1 g of sodium biosulfate preservative and 20 mL of volatile grade blank water (VBW). The vial was then sealed and weighed. Duplicate soil samples for laboratory analysis of VOCs were collected in EnCore samplers (U.S. Environmental Protection Agency, 1996c). Soil samples analyzed for DRO using field screening methods were collected in 40-mL glass vials. Duplicate samples for laboratory analysis of DRO and for percent moisture were collected in glass containers provided by the laboratory. Soil samples for microbiological analysis were collected in sterilized glass containers. All soil samples were stored at approximately 2 °C until analyzed.

A crude oil sample was collected from a production well at site 1. The crude oil sample was collected from a valve at the pumping unit. The sample was collected in a 40-mL VOC vial and was stored at approximately 2 °C. The sample was used during a laboratory study to examine the dissolution of BTEX from crude oil.

Physical Properties and Geochemical Analyses

Physical water-quality properties such as temperature, specific conductance, and pH were measured in the field using water-quality meters and methods described by Wilde and Radtke (1998). The probes for the water-quality meters were placed directly in the water body, if possible. If the probes

could not be placed in the water body, samples were collected in clean containers, the probes were placed in the containers, and measurements were made.

Geochemical data were collected using titrametric or spectrophotometric methods described by the Hach Company (1992) and included alkalinity, DO, NO_3^-, NH_3, Fe^{2+}, SO_4^{2-}, S^{2-}, and chloride, and total iron concentrations. Water-quality meters were calibrated following procedures described by the Hach Company (2001). Quality control procedures during spectrophotometric analyses included the analysis of blanks and quality control standards as described by the Hach Company (1992).

Selected duplicate water samples were sent to the USGS Water Quality and Research Laboratory (WQRL) in Ocala, Fla. WQRL used methods I-2540-85, I-2545-85, and I-2522-85 (Fishman, 1993) to analyze for nitrite (NO_2^-), NO_2^- plus NO_3^-, and NH_3, respectively. WQRL used method I-2057-85 (Fishman and Friedman, 1989) to analyze for SO_4^{2-} and chloride and method 200.7 (U.S. Environmental Protection Agency, 1994a) to analyze for Fe^{2+}.

Petroleum Hydrocarbon Analyses

Soil gas, soil, and water samples were screened for VOCs using a portable GC and methods described by Williams and Farmer (2003). The sample injection methods described in Williams and Farmer (2003) were modified for soil gas and soil samples. Soil gas samples were injected into the GC through the analysis port following methods described by USEPA (1994b). Soil samples were purged using a Sentex 40-mL Vial Purge System. This system contained two needles that were inserted into septa-capped sample vials. The longer needle extended to the bottom of the vial and was used to purge samples; the shorter needle extended only into the top of the vial and was used to transfer purged VOCs from the headspace of the vial to the trap located in the GC.

Analytical standards containing 50 mg/L each of benzene, ethylbenzene, toluene, o-xylene, m-xylene, and p-xylene, naphthalene, and methyl tertiary butyl ether were used to prepare calibration standards. Analytical runs of about 8 minutes were used to screen for BTEX and other VOCs in soil gas, soil, and water samples. VOCs were tentatively identified as being BTEX compounds if the retention time of the compound was within 5 percent of the retention time of the BTEX compound. VOCs tentatively identified may or may not have actually been a BTEX compound because many VOCs have similar retention times. Concentrations of unidentified VOCs were estimated by comparing the peak areas of these compounds to a calibration curve created using peak areas for BTEX compounds. The concentrations of tentatively identified BTEX compounds and unidentified VOCs were summed to obtain an estimated total concentration for the VOCs detected. The capacity of the portable GC to measure VOCs has been evaluated by the USEPA Superfund Innovative Technology Evaluation (SITE) Program (Einfeld, 1998).

Duplicates of selected soil samples and water samples were sent to the USGS National Water Quality Laboratory (NWQL) and to Severn Trent Laboratories (STL), both in Denver, Colorado. NWQL used gas chromatography/mass spectrometry (GC/MS) methods (Connor and others, 1998) to analyze for BTEX compounds in water. STL used methods 5035 and 8260B (U.S. Environmental Protection Agency, 1996c) to prepare and analyze soil samples for BTEX compounds. STL measured percent moisture in soil samples by using method 160.3 (U.S. Environmental Protection Agency, 1983).

Soil and water samples were analyzed for DRO compounds using SiteLAB field screening methods, which incorporate fluorescence-based analytical techniques (SiteLAB Corporation, 2001). Aromatic hydrocarbons absorb light energy of specific wavelengths (excitation wavelengths) and emit light energy at longer wavelengths (emission wavelengths) (Tetra Tech EM Inc., 2001). Because fluorescence increases with hydrocarbon concentration, fluorometers equipped with specific excitation and emission filters can measure specific types of aromatic hydrocarbons. Monoaromatic compounds such as BTEX have emission wavelengths of about 280 nanometers (nm), two- to three-ring aromatics have an emission wavelength of approximately 330 nm, and aromatics with greater than three rings have an emission wavelength of approximately 380 nm (California Environmental Protection Agency, 1997). Emission filters with a bandwidth between 275 and 285 nm can be used to measure GRO petroleum hydrocarbons, and emission filters with a bandwidth between 300 and 400 nm can be used to measure DRO petroleum hydrocarbons (Tetra Tech EM Inc., 2001).

The SiteLAB method uses methanol to extract hydrocarbons from soil or water samples (SiteLAB Corporation, 2001). The soil extraction process is similar to that used for enzyme immunoassay techniques in USEPA SW-846 method 4030 (Greason, 1997). Hydrocarbons were extracted from samples using methods described by the SiteLAB Corporation (2001). Methanol-extracted solutions were diluted if necessary and analyzed using a fluorometer (Turner Designs TD-700). The fluorometer was equipped with a clear quartz mercury vapor lamp with a predominant emission of 254 nm wavelength (Turner Designs 10-046), an excitation filter with a bandwidth of 254 (Turner Designs 10-038R), an emission filter with a bandwidth from 300 to 400 nm (Turner Designs 10-069R), and a red sensitive photomultiplier tube detector (185 to 870 nm). With this configuration, the fluorometer was capable of detecting aromatic DRO compounds up to C40 molecular weight (Greason, 1997).

Quality-control procedures include the analysis of calibration standards and equipment blanks. Calibration standards containing known concentrations (0.1 to 5 mg/L) of DRO were purchased from SiteLAB (DRO C10-C40 aromatics standard kit). Equipment blanks were used to account for any interference from the methanol and disposable plastic containers and materials used during the extraction procedure (Greason, 1997). The Massachusetts Department of Environmental

Protection (MDEP) evaluated SiteLAB methods and volatile and extractable petroleum hydrocarbon methods used by 29 laboratories. The MDEP evaluation determined that the SiteLAB field method produced results of similar accuracy to that of the laboratory methods (Kinney, 1998). The USEPA Environmental Technology Verification Program also has evaluated SiteLAB methods for measuring TPH in soil. The USEPA evaluation determined that the SiteLAB method exhibited good accuracy and precision and is a reliable field measurement method for TPH in soil (Tetra Tech EM Inc., 2001). Selected duplicate soil samples and water samples were analyzed by STL for DRO using method 8015B (U.S. Environmental Protection Agency, 1996c).

Microbiological Analyses

Semi-quantitative biological activity reaction tests (BARTs), described by Cullimore (1993), were used to examine water and soil samples for the presence of viable bacteria. BARTs consist of a capped sample vial containing a floating ball and crystallized selective medium attached to the floor of the vial. After water samples are added to the BART container, the floating ball restricts the entry of oxygen into the sample below creating selective growth conditions for any bacteria present. The selective culture medium varies for different types of bacteria. During this study, BARTs for total aerobic heterotrophic bacteria, denitrifying bacteria, iron-related bacteria, SO_4^{2-}-reducing bacteria, fluorescing *Pseudomonas*, and slime forming bacteria were used. Bacterial activity is detected by looking for specific growth activities and reactions associated with each type of BART. Growth activities include the formation of clouds, slimes, and gels. Reactions include color changes, development of gasses, and precipitation of dissolved constituents. The rates at which these activities and reactions occur can sometimes be used to quantify bacteria populations (Droycon Bioconcepts Inc., 2003).

Membrane filtration plate counts were used to quantify hydrocarbon- (crude oil and diesel) degrading bacteria in soil and water samples. Bacteria were extracted from soil samples by placing 50 g of soil in 200 mL of sterile homogenization buffer and agitating in a blender for 1 minute. The mixture was placed in an ice water bath for 1 minute. This procedure was repeated three times. The mixture was centrifuged at 640 times the force of gravity for 15 minutes at 4 °C. The supernatant was transferred to a sterile 250-mL tube and centrifuged at 15,000 g for 20 minutes at 4 °C. The above steps were repeated two times using the original 50-g soil sample. The resulting bacterial pellet was suspended in 10 mL of sterile phosphate buffered solution (PBS).

Water samples and bacteria solutions extracted from soil samples were serially diluted (into 100 mL of sterile PBS) eight times using a 0.1 dilution factor each time. Three replicates were prepared for each dilution. All three sets of replicates were filtered [47-mm (millimeter) diameter, 0.4-mm pore size filters] and a set of replicates was placed on one of three types of agar plates. The first type of plate was used to quantify crude oil degrading bacteria and consisted of Bushnell-Haas broth (Bushnell and Hass, 1941) containing 1 percent agar and 100 microliters (µL) of p-iodonitroterazolium violet solution and 500 µL of crude oil spread on top of the solidified broth. The second type of plate was used to quantify diesel-degrading bacteria and consisted of Bushnell-Haas broth containing 1 percent agar and 100 µL of p-iodonitroterazolium violet solution and 500 µL of diesel fuel spread on top of the solidified broth. The third type of plate was used to quantify total heterotrophic bacteria and contained tryptic-soy agar. The p-iodonitroterazolium violet solution consisted of 3 milligrams (mg) of p-iodonitroterazolium violet dissolved into 3 mL of sterilized distilled water.

A positive control was prepared by filtering a solution containing *Pseudomonas aeruginosa* and placing these filters onto the various agar plates. A negative control was prepared by filtering an undiluted bacteria extraction from one of the sampling locations and a solution containing *Pseudomonas aeruginosa* and placing these filters onto plates of Bushnell-Haas broth containing 1 percent agar and 100 µL of p-iodonitroterazolium violet. The plates were incubated at 25 °C and then evaluated, and bacteria were counted at 48 and 72 hours.

Crude Oil Dissolution Study

Crude oil samples from site 1 were placed in volatile blank water (VBW) to monitor the dissolution of BTEX and other soluble petroleum hydrocarbons from the crude oil. Three replicates were created, each containing 3 mL of crude oil in 1-L glass bottles containing VBW and a stir bar. The bottles were sealed with solid Teflon-lined caps and were placed on stir plates. After 4 days of stirring, water samples were removed from two of the bottles and analyzed for BTEX and other VOCs. After 6 additional days of stirring, a water sample was removed from the third bottle and analyzed to determine if additional dissolution of BTEX and other VOCs had occurred. Water samples were analyzed using the methods previously described for environmental water samples.

Ground-Water Quality and Potential Natural Attenuation

This investigation had three stages of monitoring and research activities. The ground-water-quality reconnaissance was completed during June 2002. During the reconnaissance, water samples were collected from 24 locations (17 springs, 5 water-supply wells, 1 small stream, and 1 spring-fed pond) in and near BISO (fig. 2). More detailed water-quality sampling was completed during July 2002. During this second stage of the investigation, additional water samples were collected from three springs and two wells sampled during the

reconnaissance. Sampling at the three crude oil release sites (the third stage of the investigation) occurred from September 2002 through February 2003.

Ground-Water-Quality Reconnaissance

In June 2002, water samples were collected from 17 springs, 5 water supply wells, 1 small stream, and 1 spring-fed pond in and near BISO. The reconnaissance and sampling was conducted during a relatively dry period. Total monthly precipitation in the vicinity of BISO for April through June 2002 was below average (National Oceanic and Atmospheric Administration, 2002). Most of the springs located and sampled during the reconnaissance were small. Estimated discharges ranged from less than 0.02 to 0.13 L/s (table 2). The specific conductance of water samples from springs generally ranged from 8 to 45 µS/cm (microsiemens per centimeter) with one exception. The highest specific conductance in a water sample collected from a spring was 105 µS/cm at sampling location 17, which is a spring that emerges from the top of a shale layer. The specific conductance of water samples collected from wells generally ranged from 30 to 42 µS/cm, but water from one well had a specific conductance of 460 µS/cm. DO concentrations in water samples ranged from 0.8 to 10.7 mg/L. Most samples were well oxygenated. Only two samples contained less than 5 mg/L of DO, and only two samples had a specific conductance greater than 50 µS/cm (table 2). The sample containing the least DO (0.8 mg/L) and the highest specific conductance (460 µS/cm) was from a water-supply well (sampling location 7) near a stream that is about 6 km northwest of and about 200 m lower in elevation than the location of the other wells sampled.

BTEX compounds were not detected in any of the water-quality samples collected during the reconnaissance of ground-water-quality conditions in BISO (table 2). BTEX detection limits for the portable GC used to screen the water samples ranged from 0.5 to 1 µg/L. The lack of BTEX detections in ground-water samples from various locations indicates that contamination of ground-water resources by dissolved petroleum hydrocarbons in BISO is probably not widespread.

Background Water-Quality Conditions

Sampling locations 2, 3, 7, 15, 16, and 18 from the reconnaissance were selected for additional water-quality sampling to obtain additional information on water quality away from areas of oil and gas production. Samples were collected in July 2002, when total monthly precipitation for the area was again below average (National Oceanic and Atmospheric Administration, 2002). Samples were again analyzed for physical properties and VOCs to determine if any temporal variations existed in ground-water-quality conditions (table 3). Water samples could not be collected from sampling location 2 because this spring was dry during the sampling on July 30 and 31, 2002. Most samples were well oxygenated, generally ranging from 6.4 to 7 mg/L of DO. Specific conductance generally ranged from 13 to 40 µS/cm. Once again, the sample containing the least DO (2.8 mg/L) and the highest specific conductance (384 µS/cm) was collected from sampling location 7. BTEX compounds were not detected in any of the additional water-quality samples collected in July 2002 (table 3).

The water samples collected during July 2002 also were analyzed for geochemical indicators, DRO, and selected bacteria. Dissolved NH_3, Fe^{2+}, and S^{2-} concentrations were not detected in any of the water samples collected from sites 3, 7, 15, 16, and 18 (table 4). DRO compounds were not detected in any of the water samples from these sites (table 4). The detection limit for the field screening method used to analyze for DRO was 0.10 mg/L. Bacteria associated with the biodegradation of petroleum hydrocarbons were detected in several of the water samples collected at sampling locations 3, 7, 15, 16, and 18 during July 2002 (table 5).

Crude Oil Release Site 1

Water, soil gas, and soil samples were collected at site 1 during September and December 2002. The samples were analyzed to evaluate potential contamination and biodegradation at the site. Although total monthly precipitation in the area for September and December 2002 was above average, both months were preceded by below average precipitation (National Oceanic and Atmospheric Administration, 2002). Both springs at site 1 (sampling locations 21 and 22) were dry when soil gas and soil samples were collected during September 2002 (table 3). On December 3, 2002, the spring at sampling location 22 was still dry; however, a small amount of flow was discharging from the spring at sampling location 21 (water samples had to be collected in a cup for measurement of physical properties). Water collected at location 21 had a specific conductance of 34 µS/cm (table 3) with low concentrations for dissolved NO_3^-, NH_3, Fe^{2+}, SO_4^{2-}, S^{2-}, and DRO. The dissolved chloride concentrations were 5.4 to 7.4 mg/L (table 4). Water samples from sampling location 21 analyzed using field screening methods did not contain detectable concentrations of BTEX or DRO (tables 3 and 4). BTEX compounds also were not detected in a duplicate water sample from sampling location 21 analyzed by STL (table 3).

Soil gas samples were collected at 13 sampling locations (numbers 25 through 37) at site 1 during September 2002 (table 6). The greatest number of VOCs (16) and the highest estimated total VOC concentrations (about 40 µg/L) were detected in a soil gas sample from location 26 (table 6). This sample was collected near the old tank battery location and is within the area that was remediated after the spill in 1993 (fig. 4). At least seven VOCs were detected in every soil gas sample collected at site 1 (table 6). Many of these detected VOCs had GC retention times near the retention times for BTEX compounds. Estimated total VOC concentrations for the other soil gas samples collected at this site ranged from about 1 to about 2.7 µg/L (table 6). These estimates represent

Table 2. Physical properties and volatile organic compound data for water samples collected during the ground-water-quality reconnaissance, June 2002.

[USGS, U.S. Geological Survey; º, degrees; ´, minutes; ˝, seconds; L/s, liters per second; ºC, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; <, less than; --, no data]

Sampling site number	Type of site	USGS number	Sampling date	Physical properties					Volatile organic compound data (micrograms per liter)				
				Estimated discharge (L/s)	Temperature (ºC)	Specific conductance (µS/cm)	pH (standard units)	Dissolved oxygen (mg/L)	Benzene	Toluene	Ethylbenzene	m-Xylene and p-Xylene	o-Xylene
1	Stream	3408510	06/11/2002	<0.02	18.0	32	6.6	8.3	<0.5	<0.5	<0.5	<1	<1
2	Spring	362515084390501	06/11/2002	<0.02	15.5	9	5.9	9.5	<0.5	<0.5	<0.5	<1	<1
3	Well	362916084415901	06/12/2002	--	17.5	30	5.7	7.9	<0.5	<0.5	<0.5	<1	<1
4	Well	362925084415301	06/12/2002	--	15.0	34	6.0	8.8	<0.5	<0.5	<0.5	<1	<1
5	Well	362920084415401	06/12/2002	--	16.0	42	6.0	7.0	<0.5	<0.5	<0.5	<1	<1
6	Well	362919084414701	06/12/2002	--	15.5	38	6.1	7.8	<0.5	<0.5	<0.5	<1	<1
7	Well	363215084433801	06/12/2002	--	16.0	460	9.1	0.8	<0.5	<0.5	<0.5	<1	<1
8	Spring	362839084404601	06/12/2002	<0.02	15.0	19	4.8	9.3	<0.5	<0.5	<0.5	<1	<1
9	Spring	362849084410401	06/12/2002	<0.02	15.5	45	7.1	10.6	<0.5	<0.5	<0.5	<1	<1
10	Spring	362939084430401	06/12/2002	<0.02	15.5	32	6.4	9.1	<0.5	<0.5	<0.5	<1	<1
11	Spring	363007084404901	06/13/2002	<0.02	17.5	16	5.1	6.7	<0.5	<0.5	<0.5	<1	<1
12	Spring	363238084375401	06/13/2002	<0.02	13.5	12	4.8	8.1	<0.5	<0.5	<0.5	<1	<1
13	Spring	363237084375401	06/13/2002	<0.02	18.0	17	6.2	9.5	<0.5	<0.5	<0.5	<1	<1
14	Pond	362249084422201	06/24/2002	0.00	24.0	45	5.7	1.7	<0.5	<0.5	<0.5	<1	<1
15	Spring	362544084442201	06/24/2002	0.06	17.0	17	5.9	9.5	<0.5	<0.5	<0.5	<1	<1
16	Spring	362833084333901	06/25/2002	0.02	15.5	45	5.5	9.7	<0.5	<0.5	<0.5	<1	<1
17	Spring	362811084352901	06/25/2002	0.13	17.5	105	6.4	8.6	<0.5	<0.5	<0.5	<1	<1
18	Spring	362728084371801	06/25/2002	0.03	16.0	34	7.1	9.8	<0.5	<0.5	<0.5	<1	<1
19	Spring	362719084392301	06/25/2002	0.06	18.5	18	6.3	8.1	<0.5	<0.5	<0.5	<1	<1
20	Spring	362413084344401	06/25/2002	0.09	15.5	15	4.7	7.7	<0.5	<0.5	<0.5	<1	<1
21	Spring	362315084394201	06/12/2002	<0.02	17.5	8	5.8	8.7	<0.5	<0.5	<0.5	<1	<1
22	Spring	362314084393801	06/12/2002	<0.02	14.5	14	5.9	7.5	<0.5	<0.5	<0.5	<1	<1
23	Spring	362320084393301	06/12/2002	<0.02	16.5	12	7.0	10.7	<0.5	<0.5	<0.5	<1	<1
24	Spring	362322084392501	06/12/2002	<0.02	15.0	18	5.6	5.4	<0.5	<0.5	<0.5	<1	<1

Table 3. Physical properties and volatile organic compound data for water samples collected after reconnaissance, July 2002 - February 2003.

[L/s, liters per second; µS/cm; microsiemens per centimeter; mg/L, milligrams per liter; --, no data; <, less than]

Sampling location	Type of location	Sampling date	Type of analysis	Physical properties					Volatile organic compound data (micrograms per liter)				
				Estimated discharge (L/s)	Temperature (°C)	Specific conductance (µS/cm)	pH (standard units)	Dissolved oxygen (mg/L)	Benzene	Toluene	Ethylbenzene	m-Xylene and p-Xylene	o-Xylene
3	Well	07/31/2002	Field	--	19.5	31	5.9	6.6	<0.5	<0.5	<0.5	<1	<1
7	Well	07/31/2002	Field	--	14.0	384	8.4	2.8	<0.5	<0.5	<0.5	<1	<1
15	Spring	07/30/2002	Field	0.04	18.5	13	6.9	7.0	<0.5	<0.5	<0.5	<1	<1
16	Spring	07/30/2002	Field	<0.02	17.5	40	5.9	6.9	<0.5	<0.5	<0.5	<1	<1
18	Spring	07/30/2002	Field	<0.02	18.0	32	6.5	6.4	<0.5	<0.5	<0.5	<1	<1
Site 1													
21	Spring	09/03/2002	--	Dry	--	--	--	--	--	--	--	--	--
21	Spring	12/03/2002	Field	<0.02	--	34	5.7	--	<0.5	<0.5	<0.5	<1	<1
21	Spring	12/03/2002	Laboratory	--	--	--	--	--	<0.2	<0.2	<0.2	<0.2	<0.2
22	Spring	09/03/2002	--	Dry	--	--	--	--	--	--	--	--	--
22	Spring	12/03/2002	--	Dry	--	--	--	--	--	--	--	--	--
Site 2													
23	Spring	09/03/2002	Field	<0.02	--	11	7.3	5.4	<0.5	<0.5	<0.5	<1	<1
23	Spring	09/03/2002	Laboratory	--	--	--	--	--	<0.2	<0.2	<0.2	<0.2	<0.2
23	Spring	12/03/2002	Field	<0.02	--	9	6.4	--	<0.5	<0.5	<0.5	<1	<1
24	Spring	09/03/2002	--	Dry	--	--	--	--	--	--	--	--	--
24	Spring	12/03/2002	Field	<0.02	--	16	5.7	--	<0.5	<0.5	<0.5	<1	<1
24	Spring	02/19/2003	Field	<0.02	--	--	--	--	<0.5	<0.5	<0.5	<1	<1
Site 3													
50	Auger hole	12/10/2002	Field	--	--	3,440	6.8	--	<0.5	<0.5	<0.5	<1	<1
51	Auger hole	12/10/2002	Field	--	--	7,600	6.0	--	<0.5	<0.5	<0.5	<1	<1
51	Auger hole	12/10/2002	Laboratory	--	--	--	--	--	--	--	--	--	--
55	Auger hole	12/10/2002	Field	--	--	577	4.7	--	<0.5	<0.5	<0.5	<1	<1
55	Auger hole	12/10/2002	Laboratory	--	--	--	--	--	<0.2	<0.2	<0.2	<0.2	<0.2
57	Spring	02/19/2003	Field	<0.02	--	--	--	--	<0.5	<0.5	<0.5	<1	<1

Table 4. Geochemcial and diesel range organic compound data for water samples collected after reconnaissance, July 2002 - February 2003.

[$CaCO_3$, calcium carbonate; N, nitrogen; Fe, iron; SO_4, sulfate; S^{2-}, sulfide; Cl, chloride; mg/L, milligrams per liter; --, no data; <, less than]

Sampling location	Type of location	Sampling date	Type of analysis	Geochemical data								Diesel range organics (mg/L)
				Alkalinity (as $CaCO_3$)	Nitrate, dissolved (as N)	Ammonia, dissolved (as N)	Iron, total (mg/L as Fe)	Iron, dissolved (mg/L as Fe)	Sulfate, dissolved (mg/L as SO_4)	Sulfide, dissolved (mg/L as S^{2-})	Chloride, dissolved (mg/L as Cl)	
3	Well	07/31/2002	Field	8.9	0.7	<0.01	0.02	<0.01	<1	<0.001	0.6	<0.10
7	Well	07/31/2002	Field	160	0.1	<0.01	0.09	<0.01	19	<0.001	5.0	<0.10
15	Spring	07/30/2002	Field	4.0	0.1	<0.01	<0.01	<0.01	<1	<0.001	0.7	<0.10
16	Spring	07/30/2002	Field	2.9	1.8	<0.01	0.03	<0.01	<1	<0.001	3.6	<0.10
18	Spring	07/30/2002	Field	12	0.2	<0.01	0.02	<0.01	<1	<0.001	0.5	<0.10
Site 1												
21	Spring	09/03/2002	--	--	--	--	--	--	--	--	--	--
21	Spring	12/03/2002	Field	0.40	0.1	0.04	0.07	0.02	<1	0.002	5.4	<0.10
21	Spring	12/03/2002	Laboratory	--	<0.02	<0.01	--	0.03	1.2	--	7.4	
22	Spring	09/03/2002	--	--	--	--	--	--	--	--	--	--
22	Spring	12/03/2002	--	--	--	--	--	--	--	--	--	--
Site 2												
23	Spring	09/03/2002	Field	1.1	<0.1	<0.01	0.01	<0.01	<1	<0.001	0.9	1.7
23	Spring	09/03/2002	Laboratory	--	<0.02	<0.01	--	0.01	0.4	--	--	<0.25
23	Spring	12/03/2002	Field	1.1	<0.1	<0.01	0.01	0.01	<1	0.001	0.5	<0.10
24	Spring	09/03/2002	--	--	--	--	--	--	--	--	--	--
24	Spring	12/03/2002	Field	1.5	0.1	0.01	0.05	0.01	<1	0.003	0.8	<0.10
24	Spring	02/19/2003	Field	--	--	--	--	--	--	--	--	--
Site 3												
50	Auger hole	12/10/2002	Field	--	--	--	--	--	--	--	--	40
51	Auger hole	12/10/2002	Field	63	0.2	2.00	31.2	25.2	58	0.013	4,000	<0.10
51	Auger hole	12/10/2002	Laboratory	--	<0.02	0.68	--	28.9	59	--	2,590	--
55	Auger hole	12/10/2002	Field	0.28	0.0	0.23	0.26	0.02	190	0.011	22.3	<0.10
55	Auger hole	12/10/2002	Laboratory	--	--	--	--	--	--	--	--	--
57	Spring	02/19/2003	Field	--	--	--	--	--	--	--	--	--

Table 5. Summary of results from biological activity reaction tests (BARTs), July 2002 - December 2002.

[NA, not applicable; D, duplicate sample; SFB, slime-forming bacteria; IRB, iron-related bacteria; SRB, sulfate-reducing bacteria; DNF, denitrifying bacteria; HB, heterotrophic bacteria; PBS, sterilized phosphate buffer solution; some BARTs are capable of detecting additonal types of bacteria, these detections are shown in parentheses]

Crude oil release site	Sampling location	Type of sample	Sampling date	Slime-forming bacteria BART	Iron-related bacteria BART	Sulfate-reducing bacteria BART	Denitrifying bacteria BART	Heterotrophic bacteria BART
NA	3	Water	07/31/2002	Positive for SFB	Negative for IRB (Heterotrophic bacteria) (Anaerobic bacteria)	Negative for SRB (Possibly anaerobic bacteria)	Positive for DNF	Positive for HB Aerobic
NA	7	Water	07/31/2002	Positive for SFB	Positive for IRB (Heterotrophic bacteria) (Enteric bacteria) (Possibly anaerobic bacteria)	Positive for SRB Dense slime bacterial and SRB consortium (Possibly anaerobic bacteria)	Positive for DNF	Positive for HB Aerobic
NA	15	Water	07/30/2002	Positive for SFB	Negative for IRB (Heterotrophic bacteria) (Possibly anaerobic bacteria)	Negative for SRB (Possibly anaerobic bacteria)	Negative for DNF	Positive for HB Aerobic
NA	16	Water	07/30/2002	Positive for SFB	Negative for IRB (Heterotrophic bacteria) (Possibly anaerobic bacteria) (Possibly *Pseudomonads* and enteric bacteria)	Negative for SRB (Possibly anaerobic bacteria)	Negative for DNF	Positive for HB Aerobic
NA	18	Water	07/30/2002	Positive for SFB	Positive for IRB (Heterotrophic bacteria) (Enteric bacteria) (Possibly anaerobic bacteria)	Negative for SRB (Possibly anaerobic bacteria)	Negative for DNF	Positive for HB Aerobic
1	21	Water	12/03/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Negative for IRB	Negative for SRB	Positive for DNF	Positive for HB Aerobic
2	23	Water	09/05/2002	Positive for SFB	Negative for IRB	Negative for SRB (Anaerobic bacteria)	Negative for DNF	Positive for HB Possibly anaerobic
2	24	Water	12/03/2002	Positive for SFB (Fluorescing *Pseudomonads*)	Negative for IRB	Negative for SRB	Negative for DNF	Positive for HB Aerobic

Table 5. Summary of results from biological activity reaction tests (BARTs), July 2002 - December 2002.—Continued

[NA, not applicable; D, duplicate sample; SFB, slime-forming bacteria; IRB, iron-related bacteria; SRB, sulfate-reducing bacteria; DNF, denitrifying bacteria; HB, heterotrophic bacteria; PBS, sterilized phosphate buffer solution; some BARTs are capable of detecting additonal types of bacteria, these detections are shown in parentheses]

Crude oil release site	Sampling location	Type of sample	Sampling date	Slime-forming bacteria BART	Iron-related bacteria BART	Sulfate-reducing Bacteria BART	Denitrifying bacteria BART	Heterotrophic bacteria BART
1	25	Soil	09/05/2002	Positive for SFB	Slightly positive for IRB	Negative for SRB	Negative for DNF	Positive for HB Possibly anaerobic
1	28	Soil	09/05/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Positive for IRB (Anaerobic bacteria)	Positive for SRB Complex bacterial consortium	Negative for DNF	Positive for HB Possibly anaerobic
1	28 D	Soil	09/05/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Positive for IRB (Anaerobic bacteria)	Positive for SRB Complex bacterial consortium	Negative for DNF	Positive for HB Possibly anaerobic
1	34	Soil	09/05/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Positive for IRB (Anaerobic bacteria)	Positive for SRB Dense slime bacterial and SRB consortium (Anaerobic bacteria)	Positive for DNF	Positive for HB Possibly anaerobic
2	38	Soil	12/03/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Negative for IRB	Positive for SRB Dense slime bacterial and SRB consortium	Positive for DNF	Positive for HB Aerobic
2	46	Soil	12/03/2002	Negative for SFB	Negative for IRB	Negative for SRB	Negative for DNF	Positive for HB Aerobic
3	50	Water	12/10/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Negative for IRB (Anaerobic bacteria) (Enteric bacteria)	Positive for SRB Complex bacterial consortium	Negative for DNF	Positive for HB Aerobic
3	50	Soil	12/10/2002	Positive for SFB (*Pseudomonads* and enteric bacteria)	Negative for IRB	Positive for SRB Dense slime bacterial and SRB consortium	Positive for DNF	Positive for HB Aerobic
NA	Control	PBS	09/05/2002	Negative for SFB	Negative for IRB	Negative for SRB	Negative for DNF	Negative for HB
NA	Control	PBS	12/10/2002	Negative for SFB	Negative for IRB	Negative for SRB	Negative for DNF	Negative for HB

Table 6. Volatile organic compound data for soil gas samples, September and December 2002.

[VOCs, volatile organic compounds; µg/L; micrograms per liter]

Crude oil release site	Sampling location	Sampling date	Number of VOCs detected	Total peak area for all VOCs detected	Estimated total concentration of VOCs detected (µg/L)
1	25	09/04/2002	14	19,230,000	2.1
1	26	09/04/2002	16	932,700,000	40
1	26 (duplicate)	09/04/2002	14	874,100,000	36
1	27	09/04/2002	12	7,915,000	1.0
1	28	09/04/2002	12	18,230,000	1.6
1	29	09/04/2002	14	32,420,000	2.2
1	30	09/04/2002	9	25,950,000	2.2
1	30 (duplicate)	09/04/2002	11	39,620,000	2.7
1	31	09/04/2002	14	28,770,000	2.3
1	32	09/04/2002	11	37,840,000	2.3
1	33	09/04/2002	12	18,990,000	1.5
1	34	09/04/2002	10	34,700,000	2.6
1	35	09/04/2002	8	19,820,000	1.4
1	36	09/04/2002	9	21,730,000	1.8
1	37	09/04/2002	7	10,460,000	1.0
2	38	09/04/2002	16	58,470,000	4.9
2	38	12/03/2002	5	208,200	0.10
2	39	12/03/2002	15	4,117,000	0.84
2	40	12/03/2002	4	12,230	<0.10
2	41	12/03/2002	2	42,490	<0.10
2	42	12/03/2002	2	24,010	<0.10
2	43	12/03/2002	2	89,520	<0.10
2	44	12/03/2002	1	8,674	<0.10
2	45	12/03/2002	2	27,570	<0.10
2	46	12/03/2002	3	1,698,000	0.25
2	47	12/03/2002	3	36,880	<0.10
2	48	12/03/2002	2	11,390	<0.10

the total concentration of the VOCs detected, not the total concentrations of all VOCs that may have been present in the sample. Short, 8-minute GC scans were used to screen only those VOCs with retention times similar to those for BTEX compounds. This may be one reason that the soil gas concentrations detected during this investigation were much lower than concentrations detected during the 1999 study by Otton and Zielinski (2000), when a sample collected near sampling location 28 (fig. 4) had 50 mg/L of VOCs, and a sample collected near sampling location 29 (fig. 4) had 4 mg/L of VOCs.

Soil samples were collected from various depths at sampling locations 25, 26, 28, 30, 34, and 36 at site 1 in September 2002 (fig. 4, table 7). Samples were collected from several depths (approximately 0.2, 0.5, 0.7, and 0.9 m below land surface) at sampling location 25, which is between the new tank battery and the pumping unit, and topographically upgradient from the remediated area (fig. 4). Using field screening methods, benzene (2.3 µg/kg) was tentatively identified in a soil sample collected from 0.9 m below land surface at sampling location 25 (table 7). Benzene also was tentatively detected in soil samples collected from sampling location 26 (7.7 µg/kg) and from sampling location 28 (1.2 and 3.4 µg/kg) both of which are in the remediated area. Benzene was not detected in duplicate samples analyzed by the laboratory (table 7). Laboratory detection limits for benzene ranged from 5.3 to 14 µg/kg (variations in detection limits for the same compound were caused by differences in amounts of soil analyzed). Based on the laboratory results, the compound tentatively identified as benzene was likely some other VOC with a retention time similar to that of benzene. Additional BTEX compounds were detected by the field screening methods in soil samples from sampling location 25; however, an estimated concentration (less than the reporting limit) of 1.0 µg/kg of toluene was detected by STL in a duplicate collected from 0.5 m below land surface (table 7). Toluene probably was not detected in soil samples analyzed using the field screening methods because the detection limit for toluene ranged from 1.69 to 2.87 µg/kg for soil samples from sampling location 25.

Toluene and other BTEX compounds (at concentrations of about 45 to about 200 µg/kg) were tentatively identified in soil samples collected from sampling location 26 (table 7). Toluene and other BTEX compounds were not detected by STL in a duplicate soil sample from sampling location 26 (table 7); therefore, the compounds tentatively identified as BTEX compounds were probably other VOCs with GC retention times similar to the BTEX compounds. The highest estimated total concentration of VOCs detected at site 1 (760 µg/kg) was for a soil sample collected from sampling location 26 (table 7). BTEX compounds were not detected by field screening or laboratory methods in soil samples collected from other sampling locations (30, 34, and 36) at site 1 (table 7).

Elevated DRO concentrations [greater than soil cleanup levels established by TDEC (1998) for EPH] were detected in soil samples from site 1. DRO concentrations of about 2,400 mg/kg were detected in soil samples from sampling location 26 by using the field screening methods and by STL (table 7). Elevated DRO concentrations (930 to 1,500 mg/kg) also were detected at location 28 (table 7), the other sampling location in the formerly remediated area (fig. 4). All soil samples collected outside of the remediated area contained DRO concentrations less than 100 mg/kg (table 7).

Microbiological tests indicated that petroleum-degrading bacteria were present in soil samples at site 1. A wide variety of bacteria often associated with the biodegradation of petroleum hydrocarbons were detected in soil samples from sampling locations 25, 28, and 34 (table 5) by using BARTs. Slime-forming (*Pseudomonads* and enteric), denitrifying, and

Table 7. Volatile and diesel range organic compound data for soil samples, September 2002 - February 2003.

[LS, land surface; mg/kg, milligrams per kilogram; --, no data; <, less than; J, estimated concentration less than the reporting limit; VOCs can only be tentatively identified by the field analytical techniques used during this study. Compounds identified by field analysis as BTEX compounds may actually be other VOCs with similar retention times]

Sampling location	Sampling date	Sampling depth (meters below LS)	Type of analysis	Moisture in sample (percent)	Volatile organic compound results (micrograms per kilogram)					Diesel range organics (mg/kg)
					Benzene	Toluene	Ethylbenzene, m-xylene, and p-xylene, total	o-Xylene	Estimated total for all VOCs detected	
Crude oil release site 1										
25	09/05/2002	0.2	Field	--	<0.88	<1.8	<7.0	<7.0	36	26
	09/05/2002	0.5	Field	--	<0.87	<1.8	<7.0	<7.0	130	2.6
	09/05/2002	0.5	Laboratory	12.0	<5.7	1.0 J	<5.7	<2.8	110	<4.5
	09/05/2002	0.7	Field	--	<0.85	<1.7	<6.9	<6.8	22	0.50
	09/05/2002	0.9	Field	--	2.3	<1.8	<7.2	<7.2	--	--
	09/05/2002	0.9	Field	--	<1.4	<2.9	<11	<11	290	0.50
26	09/05/2002	0.6	Field	--	7.7	45	220	<7.6	530	2,500
	09/05/2002	0.6	Laboratory	13.0	<5.7	<5.7	<2.9	<2.9	760	2,400
28	09/05/2002	0.5	Field	--	1.2	<1.4	<5.5	<5.5	35	930
	09/05/2002	0.5	Field	--	3.4	<1.4	<6.4	<6.4	52	1,500
30	09/05/2002	0.5	Field	--	<0.98	<2.0	<7.8	<7.8	94	8.7
	09/05/2002	0.5	Laboratory	6.0	<5.3	<5.3	<2.7	<2.7	76	11
34	09/05/2002	0.2	Field	--	<1.3	<2.7	<10.6	<10.6	140	4.8
	09/05/2002	0.2	Laboratory	10.0	<14	<14	<6.8	<6.8	110	<4.5
36	09/05/2002	0.5	Field	--	<0.85	<1.4	<6.8	<6.8	110	3.2
Crude oil release site 2										
38	12/04/2002	0.6	Field	--	2,500	400	150	45	16,000	3,000
	02/19/2003	0.6	Field	--	36	22	<26	<26	250	--
	02/19/2003	0.6	Laboratory	15.0	<5.9	<5.9	<5.9	<3.0	840	--
39	12/04/2002	0.6	Field	--	130	<13	<2.7	<26	1,700	4,200
43	12/04/2002	0.6	Field	--	1.5	1.5	<2.7	<2.7	37	12
44	12/04/2002	0.2	Field	--	0.86	4.7	<2.4	<2.4	7.5	20
46	12/04/2002	0.5	Field	--	<0.71	2.2	<2.5	<2.9	2.7	<0.20
48	12/04/2002	0.5	Field	--	1.4	<1.5	<2.6	<2.9	4.6	<0.20
49	02/19/2003	0.6	Field	--	<0.64	<1.3	<2.8	<2.6	<2.8	--
Crude oil release site 3										
50	02/19/2003	0.5	Field	--	2.1	3.0	<3.2	<3.2	5.1	--
	02/19/2003	0.5	Laboratory	27.0	2.1J	2.6J	<3.4	<3.4	830	--
	12/09/2002	0.6	Field	--	4.9	4.5	4.3	<2.1	11	58
	12/09/2002	1.2	Field	--	7.9	5.1	5.0	<2.0	32	130

Table 7. Volatile and diesel range organic compound data for soil samples, September 2002 - February 2003.—Continued

[LS, land surface; mg/kg, milligrams per kilogram; --, no data; <, less than; J, estimated concentration less than the reporting limit; VOCs can only be tentatively identified by the field analytical techniques used during this study. Compounds identified by field analysis as BTEX compounds may actually be other VOCs with similar retention times]

Sampling location	Sampling date	Sampling depth (meters below LS)	Type of analysis	Moisture in sample (percent)	Volatile organic compound results (micrograms per kilogram)					Diesel range organics (mg/kg)
					Benzene	Toluene	Ethylbenzene, m-xylene, and p-xylene, total	o-Xylene	Estimated total for all VOCs detected	
Crude oil release site 3—Continued										
51	12/09/2002	0.8	Field	--	<0.58	<1.2	<2.3	<2.3	2.1	0.90
52	12/09/2002	0.9	Field	--	8.7	2.4	<2.7	<2.7	37	53
53	12/09/2002	0.8	Field	--	<0.68	<1.4	<2.7	<2.7	1.3	1.4
54	12/09/2002	0.2	Field	--	<0.41	<0.81	<1.6	<1.6	1.6	3,400
	12/09/2002	0.6	Field	--	<0.60	3.9	<2.4	<2.4	44	32
55	12/09/2002	0.6	Field	--	<0.49	6.6	<2.0	<2.0	170	<0.20
56	02/19/2003	0.6	Field	--	<0.64	<1.3	<2.6	<2.6	0.93	--

heterotrophic bacteria also were detected in water samples collected from the spring at sampling location 21 in December 2002 (table 5).

Viable bacteria colonies were detected in membrane filtration plates containing petroleum (diesel or crude oil), growth media, and environmental samples (water or soil extraction solutions). Counts of 3,600, 3,800, and 1,800 col/100 mL (colonies per 100 milliliters of sample) for total heterotrophic, crude oil-degrading, and diesel-degrading bacteria, respectively, were detected in the water sample from the spring at location 21. These results indicate that bacteria detected in water and soil samples at the study sites were able to use petroleum hydrocarbons (from crude oil or diesel) as their primary growth substrate.

Bacteria were not present on control plates containing petroleum, growth media, and sterile water, verifying that the procedure used to sterilize the petroleum samples was successful. Bacteria also were not present on control plates containing only growth media and environmental samples, verifying that possible impurities in the growth media were not being used as a primary growth substrate.

The elevated DRO concentrations detected in soil samples at sampling locations 26 and 28 and the presence of unidentified VOCs in soil gas (sampling location 26) and soil samples (sampling locations 25, 26, 34, and 36) indicate that biodegradation of petroleum hydrocarbons at study site 1 is incomplete. The detection of toluene in one of the soil samples indicates that BTEX compounds may be present at low concentrations at the site. Only a few ground-water samples (from one small spring) could be collected; however, BTEX and other soluble petroleum hydrocarbons do not appear to be leaching into shallow ground water at site 1.

Crude Oil Release Site 2

Water, soil gas, and sediment samples were collected to evaluate potential contamination and biodegradation at site 2. Two small springs are located at site 2. The spring at sampling location 24 (fig. 4) was dry on September 3, 2002, but was sampled during December 2002 and February 2003 (table 3). The spring at sampling location 23 was sampled during September and December 2002. Concentrations of constituents used to characterize ground-water geochemistry were all low or below detection limits (table 4). BTEX compounds were not detected in any of the water samples collected from the two springs (table 3), and DRO concentrations were less than 2 mg/L in all of the water samples (table 4).

Soil gas samples were collected from 11 sampling locations at site 2 (fig. 4, table 6). During December 2002, the greatest number of VOCs (15) and the highest estimated total VOC concentrations (0.84 µg/L) were detected in a soil gas sample from sampling location 39 (table 6). This location is near the south side of the former spoil pit that was remediated in 1993 and 1994 (fig. 4). Sampling location 46, near the confluence of the small stream south of the remediated area and Bear Branch (fig. 4), contained the second highest estimated total VOC concentration (0.25 µg/L). The remainder of the soil gas samples collected at the site contained estimated VOC concentrations of 0.10 µg/L or less. VOC concentrations in the soil gas sample collected from sampling location 38 in September 2002 were substantially higher than in December 2002. The estimated total VOC concentration was 4.9 µg/L with 16 compounds detected in the September 2002 soil gas sample from location 38. Only five VOCs (estimated total of 0.10 µg/L) were detected in the December 2002 soil gas sample

(table 6). None of the soil gas samples collected in December 2002 at site 2 contained VOC concentrations as high as those in the soil gas sample collected from sampling location 38 in September 2002; VOC concentrations in the September 2002 sample from sampling location 38 were similar to those detected at site 1.

Soil samples were collected from sampling locations 38, 39, 43, 44, 46, 48, and 49 during December 2002 and February 2003 (table 7). VOCs, tentatively identified as BTEX compounds based on GC retention times, were detected in soil samples collected from sampling locations 38, 39, 43, 44, 46, and 48 during December 2002 (table 7). The greatest VOC concentration (estimated total of 16,000 µg/kg) was detected in a soil sample from sampling location 38 (table 7). During February 2003, additional soil samples were collected from sampling location 38 and were analyzed using field screening methods and by STL. These subsequent concentrations were lower than in December 2002, and STL did not detect BTEX compounds in the soil sample from sampling location 38, indicating that the VOCs detected by the field screening methods were not BTEX compounds.

An elevated DRO concentration of about 4,200 mg/kg was detected in a soil sample collected from 0.6 m below land surface at sampling location 39 using field screening methods (table 7). An elevated DRO concentration (3,000 mg/kg) also was detected in soil collected from 0.6 m below land surface at sampling location 38, near the center of the remediated area (table 7, fig. 4). DRO concentrations were less than 100 mg/kg (table 7) in all soil samples collected from locations downgradient of the former spoil pit/remediated area including locations 43 and 44 (fig. 4). Locations 43 and 44 are along the stream bank just downstream of the small erosional channel that Otton and Zielinski (2000) documented as being a possible path for the transport of hydrocarbons from the former spoil pit.

A wide variety of bacteria often associated with the biodegradation of petroleum hydrocarbons was detected in soil samples collected from sampling location 38. Slime-forming bacteria were detected in both of the springs (sampling locations 23 and 24) at site 2 and fluorescing *Pseudomonads* also were detected in the spring at sampling location 24 (table 5). Crude oil-degrading and diesel-degrading bacteria were detected in water samples collected from the spring at sampling location 24 on December 3, 2002. Using the membrane filtration plate counts, 4,900, 450, and 4,300 colony forming units (cfu)/100 mL of total heterotrophic, crude oil-degrading, and diesel-degrading bacteria, respectively, were detected in a water sample from the spring. Soil samples from sampling location 49, a background location at site 1, contained 77 diesel- and 110 crude oil-degrading bacteria per gram of wet soil. Soil samples from sampling location 38, one of the more contaminated locations at sites 1 and 2, contained 28 diesel- and 67 crude oil-degrading bacteria per gram of wet soil.

The elevated DRO concentrations detected in soil samples, the presence of unidentified VOCs in soil samples, and the low numbers of petroleum-degrading bacteria in contaminated soils indicate that biodegradation of petroleum hydrocarbons at study site 2 is incomplete. Only six groundwater samples (from two small springs) could be collected; however, BTEX and other soluble petroleum hydrocarbons do not appear to be leaching into shallow ground water at site 2.

Crude Oil Release Site 3

Site 3 represents conditions that exist where a site has not been actively remediated for hydrocarbon contamination. This site is the only site where water is produced from the oil well. Water and soil samples were collected at site 3 during December 2002 and February 2003 (table 3). Total monthly precipitation for December 2002 and February 2003 was above normal (National Oceanic and Atmospheric Administration, 2002 and 2003). Soil gas samples were not collected because of the high water table and wet conditions encountered at the site.

Water samples were collected from three auger holes and one spring at the site. Auger holes were drilled using hand augers to obtain soil samples; water was encountered and the auger holes were extended about 0.5 m below the water surface. Water was encountered at about 1.5 m below land surface at sampling location 50, about 1.2 m below land surface at sampling location 51, and about 0.6 m below land surface at sampling location 55. About three volumes of water were purged from the auger holes, and water samples were collected using bailers. Water samples collected from sampling locations 50, 51, and 55 had the highest specific conductance of any of the water samples collected at all three sites (table 3), and the highest concentrations of dissolved iron, sulfate, and chloride were detected in water samples from the auger holes at site 3 (table 4). The elevated specific conductance and chloride concentrations at site 3 are likely the result of releases of brine from the wells and tanks. BTEX compounds were not detected in any water samples collected from site 3. A spring (sampling location 57, fig. 5), about 5 m northeast of sampling location 50, was dry during the sampling in December 2002. The spring was flowing, and a water sample was collected in February 2003. BTEX compounds were not detected in the water sample from the spring.

Soil samples were collected from sampling locations 50 through 55 in December 2002 (table 7). BTEX compounds (benzene and toluene) tentatively were identified at concentrations ranging up to 8.7 µg/kg in soil samples analyzed using field screening methods (table 7). During February 2003, additional soil samples were collected from sampling location 50, and one sample was sent to STL to determine if the detected VOCs actually were BTEX compounds. Benzene and toluene were detected in the soil sample analyzed by STL (table 7), indicating that the VOCs detected in the soil sample from sampling location 50, and most likely the VOCs detected in other soil samples, were BTEX compounds.

DRO concentrations detected in soil samples from site 3 ranged from <0.2 to about 3,400 mg/kg (table 7). Weathered crude oil was observed at the water surface in the auger hole

at sampling location 50. DRO concentrations in water samples from locations downgradient of sampling location 50 (sampling locations 51 and 55) were less than 0.10 mg/L (table 4).

Bacteria often associated with the biodegradation of petroleum hydrocarbons were detected in soil and water samples collected from sampling location 50 (table 5). Crude oil-degrading and diesel-degrading bacteria were detected in soil samples collected from sampling location 50 (one of the more contaminated locations at site 3) on December 10, 2002. Using the membrane filtration plate counts, 18,000, 160, and 78 cfu per gram of wet soil of total heterotrophic, crude oil-degrading, and diesel-degrading bacteria, respectively, were detected in soil samples collected from sampling location 50. These bacteria counts were lower than counts for soil samples from a background location at site 3 (sampling location 56). Total heterotrophic, crude oil-degrading, and diesel-degrading bacteria counts of 140,000, 220, and 970 cfu per gram of wet soil, respectively, were detected in soil samples from sampling location 56.

The elevated DRO concentrations detected in soil samples, the presence of BTEX compounds in soil samples, and the low numbers of petroleum-degrading bacteria in contaminated soils indicate that biodegradation of petroleum hydrocarbons at study site 3 is incomplete. The detection of weathered crude oil at sampling location 50 indicates that crude oil has percolated down through the soil to shallow ground water (only a few meters below land surface) at the site. The crude oil does not appear to have migrated horizontally in ground water based on the low DRO concentrations in water samples collected downgradient of sampling location 50.

BTEX compounds were not detected in ground-water samples; however, benzene may have leached into ground water and may have migrated downgradient from the site in the past. The concentration of benzene and other soluble petroleum hydrocarbons present in the ground water would depend on the concentration of these hydrocarbons in the crude oil at the site. High chloride concentrations (table 4) detected in water samples from sampling location 51 indicate that brine likely has migrated downgradient from the well, tanks, and pit.

DRO data for soil samples collected from sampling location 54 may indicate surface transport of petroleum hydrocarbons away from this site. The highest DRO concentration (3,400 mg/kg) was detected in a shallow (0.2-m-deep) soil sample collected from sampling location 54. Location 54 is near the stream where visible evidence indicates that crude oil and water have overflowed the large pit at site 3. The DRO concentration in a sample from 0.6 m below land surface at sampling location 54 was less than the concentration in the shallow sample (table 7). Based on these data, petroleum hydrocarbons sorbed to sediment may be reaching the stream by overland transport. The elevated DRO concentrations at the other two sites and the erosional channel at site 2 indicate that the potential exists for overland transport of petroleum hydrocarbons from other crude oil-contaminated sites in the study area. Petroleum hydrocarbons such as PAHs, if present in suspended or bed sediments, could possibly affect aquatic communities downstream of contaminated sites.

Crude Oil Dissolution Study

Dissolution of BTEX compounds from crude oil was detected during the crude oil dissolution study. BTEX compounds were detected in water samples removed from all three of the 1-L glass bottles containing VBW and crude oil from site 1. Water from replicates 1 and 2, which were stirred for 4 days, contained slightly greater concentrations of BTEX than water from replicate 3, which was stirred for 10 days (table 8). The lack of increase in dissolved BTEX concentrations from day 4 to day 10 indicates that the BTEX dissolved in water was in equilibrium with BTEX in the crude oil. Using the average of the three replicates, the maximum dissolved concentrations (effective solubility) of BTEX compounds in water exposed to crude oil from site 1 ranged from 220 µg/L for ethylbenzene to 1,900 µg/L for benzene (table 8).

The effective solubility values for BTEX compounds from the crude oil sample were used to determine if contact with crude oil in the study area might cause BTEX concentrations in ground water to exceed drinking water MCLs. The effective solubility for benzene (1,900 µg/L) was substantially less than maximum effective solubility for benzene (27,000 µg/L) reported by O'Reilly and others (2001); however, the effective solubility was substantially above the MCL of 5 µg/L for benzene in drinking water (table 8). The effective solubility of toluene (1,800 µg/L) also was above the MCL of 1,000 µg/L for toluene in drinking water (table 8). The effective solubility of ethylbenzene (220 µg/L) and total xylenes (580 µg/L) were less than MCLs for drinking water (table 8). Results from the crude oil hydrocarbon dissolution study indicate that benzene and toluene concentrations greater than drinking water MCLs may be present in ground water that comes into contact with fresh (unweathered) crude oil from the study area. Releases of crude oil or natural gas condensate at sites in stream valleys may have the greatest potential for benzene and toluene contamination of ground water because of the shallow depths to ground water commonly found at these sites.

Table 8. Results from the crude oil hydrocarbon dissolution study.

[µg/L, micrograms per liter; MCL, drinking water maximum contaminant level; effective solubility was calculated using averages from the three replicates; water/crude oil solutions were stirred for 4 days in replicates 1 and 2 and for 10 days in replicate 3]

Name	Dissolved concentration in water samples (µg/L)			Effective solubility (µg/L)	MCL (µg/L)
	Replicate 1	Replicate 2	Replicate 3		
Benzene	1,900	2,000	1,700	1,900	5
Toluene	1,900	1,900	1,600	1,800	1,000
Ethylbenzene	250	250	170	220	700
m- and p-Xylene	300	300	180	260	--
o-Xylene	370	370	230	320	--
Total xylenes	--	--	--	580	10,000

Summary

Approximately 300 active or abandoned oil and gas wells are located in BISO, and more than 3,000 oil and gas wells are present in the Big South Fork watershed. In 2002 and 2003, the USGS investigated the effects of oil and gas production operations on ground-water quality at BISO with particular emphasis on the fate and transport of petroleum hydrocarbons in soils and ground water. Three stages of monitoring and research activities were performed during the investigation. The first stage consisted of a reconnaissance of the general ground-water-quality conditions in BISO. The second stage included more detailed characterization of ground-water-quality conditions at a few of the reconnaissance sampling locations. The third stage of the investigation included additional sampling at three crude oil release sites in and near BISO to evaluate the fate and transport of petroleum hydrocarbons.

When petroleum compounds such as crude oil are released into the environment, the compounds undergo physical, chemical, and biological changes. The degree to which the various types of petroleum hydrocarbons degrade depends on the physical and chemical properties of the hydrocarbons. Monoaromatics, such as BTEX, are some of the most common aromatic compounds in petroleum. BTEX compounds are the most soluble aromatic compounds and have the lowest K_{oc} of the most common aromatic hydrocarbons. Because of the high degree of toxicity and mobility of benzene (compared to other petroleum hydrocarbons), it is commonly the main ground-water contaminant of concern at petroleum release sites. Benzene concentrations may be of concern (greater than MCL) at gas condensate spill sites or sites where crude oil containing more than 0.03 percent benzene (by weight) has been released.

During the ground-water-quality reconnaissance, samples were collected from springs, wells, and a few surface-water locations in various parts of BISO. Water samples collected during the reconnaissance were analyzed for physical properties (temperature, DO, pH, and specific conductance), VOCs, and selected types of bacteria. During the second stage of the investigation, additional water samples were collected and analyzed for physical properties, geochemical conditions, VOCs, DRO, and selected types of bacteria. During the third stage of the investigation, soil gas, soil, water, and crude oil samples were collected to evaluate the fate and transport of petroleum hydrocarbons at three crude oil release sites. Soil gas samples were analyzed for VOCs. Soil samples were analyzed for VOCs, DRO, and selected types of bacteria. Water samples were analyzed for physical properties, geochemical indicators, VOCs, DRO, and selected types of bacteria. A crude oil sample collected from an active oil production well at one of the release sites was used during a laboratory study examining the dissolution of petroleum hydrocarbons from the oil into water.

BTEX compounds were not detected in water samples in either the reconnaissance stage or the second stage of the investigation. During the reconnaissance, water samples were collected from 24 sampling locations (17 springs, 5 water-supply wells, 1 small stream, and 1 spring-fed pond) in or near BISO. BTEX compounds were not detected in any of the samples collected during the reconnaissance, indicating that contamination of ground water by dissolved petroleum hydrocarbons is not widespread in BISO. During the second stage of the investigation, additional water samples were collected from three springs and two wells sampled during the reconnaissance. BTEX and DRO were not detected in any of the water samples collected during the second stage of the investigation.

Elevated DRO concentrations (as great as 2,400 mg/kg) detected in soil samples and the presence of unidentified VOCs in soil gas and soil samples indicate that biodegradation of petroleum hydrocarbons at site 1 is incomplete. The detection of toluene (1.0 µg/kg) in a lab-analyzed soil sample indicates that BTEX compounds may be present at low concentrations at the site. Only a few ground-water samples (from one small spring) could be collected; however, BTEX and other soluble petroleum hydrocarbons do not appear to be leaching into ground water at site 1.

DRO concentrations (as great as 4,200 mg/kg) detected in soil samples, the presence of unidentified VOCs in soil samples, and the low petroleum-degrading bacteria counts found in contaminated soils indicate that biodegradation of petroleum hydrocarbons at site 2 is incomplete. Only a few ground-water samples (from two small springs) could be collected; however, BTEX and other soluble petroleum hydrocarbons do not appear to be leaching into ground water at site 2.

Elevated DRO concentrations (as great as 3,400 mg/kg) detected in soil samples, the presence of BTEX compounds in soil samples, and the low petroleum-degrading bacteria counts found in contaminated soils indicate that biodegradation of petroleum hydrocarbons at site 3 is incomplete. Collection of soil and ground-water samples indicate that crude oil has percolated down through the soil to shallow ground water only a few meters below land surface at site 3.

The crude oil does not appear to have migrated horizontally in ground water based on the low DRO concentrations detected in water samples from downgradient locations at site 3. BTEX compounds were not detected in ground-water samples; however, benzene may have leached into ground water and may have migrated downgradient from site 3 in the past. The concentration of benzene and other soluble petroleum hydrocarbons present in the ground water would depend on the concentration of these hydrocarbons in the crude oil at the site. Elevated chloride concentrations detected in water samples collected from auger holes at site 3 indicate that brine likely has migrated downgradient from the well, tanks, and pits.

The elevated DRO concentrations in shallow soil samples at all three sites, the erosional channel at site 2, and visible evidence of overflow of oil and water from the pit at site 3 indicate the potential for overland transport of petroleum hydrocarbons from crude oil-contaminated sites in the study

area. Petroleum hydrocarbons such as PAHs, if present in suspended or bed sediments, could possibly affect aquatic communities downstream of contaminated sites.

During the crude oil hydrocarbon dissolution study, the effective solubility of benzene in water exposed to crude oil from site 1 was substantially above the MCL of 5 µg/L for benzene in drinking water. The effective solubility of toluene (1,800 µg/L) also was above the MCL of 1,000 µg/L for toluene in drinking water. The effective solubility of ethylbenzene (220 µg/L) and total xylenes (580 µg/L) were less than MCLs for drinking water. Results from the crude oil hydrocarbon dissolution study indicate that BTEX concentrations greater than drinking water MCLs may be present in ground water that comes into contact with fresh (unweathered) crude oil from the study area. Releases of crude oil or natural gas condensate at sites in stream valleys may have the greatest potential for benzene and toluene contamination of ground water because of the shallow depths to ground water commonly found at these sites.

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