Environmental Impacts of Petroleum Production: Initial Results from the Osage-Skiatook Petroleum Environmental Research Sites, Osage County, Oklahoma

Water-Resources Investigations Report 03-4260

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

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U.S. GEOLOGICAL SURVEY

WATER-RESOURCES INVESTIGATIONS REPORT 03-4260

Prepared in cooperation with the
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Yousif K. Kharaka and James K. Otton, editors

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Menlo Park, California
2003

U.S. DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
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http://ok.water.usgs.gov/skiatook/

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Contents

Contents--continued

Contents--continued

Contents--continued

Conversion Factors

Multiply	By	To obtain
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
hectare (ha)	2.471	acre
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	0.2642	gallon (gal)
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m^3/d)	264.2	gallon per day (gal/d)
gram (g)	0.03527	ounce (oz)
kilogram (kg)	2.205	pound (lb)
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
kilopascal (kPa)	0.01	bar
meter per day (m/d)	3.281	foot per day (ft/d)
meter per kilometer (m/km)	5.27983	foot per mile (ft/mi)
meter squared per day (m^2/d)	10.76	foot squared per day (ft^2/d)

Temperature can be converted to degrees Celsius (°C) or degrees Fahrenheit (°F) by using the following equations

$$°F = (1.8 \times °C) + 32$$

$$°C = (°F - 32) / 1.8$$

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

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

Introduction and Summary

By Yousif K. Kharaka and James K. Otton

Abstract

Exploration for and production of petroleum have caused major detrimental impacts to soils, surface and ground waters, and the local ecosystems in the United States. These impacts arise primarily from the improper disposal of large volumes of saline water produced with oil and gas, from accidental hydrocarbon and produced water releases, and from abandoned oil wells that were not correctly sealed. It is important to understand the long-term and short-term effects of produced water and hydrocarbon releases from these sites in order to develop risk-based remediation plans. Remediation is particularly needed in aging and depleted fields where land use is changing from petroleum production to residential, agricultural or recreational uses.

About 20 scientists from the USGS and other governmental agencies and academia are involved in a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, organic compounds and radionuclides present in produced water, and their impacts at the Osage-Skiatook Petroleum Environmental Research (OSPER) "A" and "B" sites, located on the Osage Reservation in Osage County, Oklahoma. Stakeholders in the project include the Osage Nation, which holds the mineral rights, the Bureau of Indian Affairs with trust responsibility, and the Army Corps of Engineers, which owns the surface rights at these sites and manages adjacent Skiatook Lake. The 4250-hectare Skiatook Lake provides drinking water to local Tulsa suburban communities and a rural water district, and offers recreational fishing and boating opportunities to tens of thousands of visitors each year.

Approximately 1.5 and 1.0 hectare of land at the OSPER "A" (depleted Lester lease) and "B" (active Branstetter lease) sites, respectively, are affected by salt scarring, tree kills, soil salinization and brine and petroleum contamination due to the leakage of produced water and associated hydrocarbons from brine pits and accidental releases from active and inactive pipes and tank batteries. The leases are typical of many depleted and aging petroleum fields in Osage County, which ranks among the top oil and gas producing counties in Oklahoma with about 39,000 wells. Oil and gas production has occurred in Osage county for over one hundred years, but current production is mainly from stripper wells (averaging ~2.8 bbl/d oil and >30 bbl/d brine) that are shallow, mostly 300-700 m in depth, and produce from several sandstones of Pennsylvanian age.

Results to date show that the produced water source is a Na-Ca-Cl brine (~150,000 mg/L total dissolved solids), with relatively high concentrations of Mg, Sr, and NH_4, but low SO_4 and H_2S. With the exception of Fe and Mn, the concentrations of trace metals are low. Results also show that some and, eventually, the bulk, of inorganic salts and some dissolved organic species in the released brine from both sites will reach Skiatook Lake.

Results at the "A" site show that the salts have essentially been removed from the sandy soil which formed in a surficial layer of eolian sand, but degraded and weathered oil persists on the surface of old oil and brine pits, close to sites of old tanks, on old channels that carried oil from tanks to the oil pits and other impacted areas. Results also show a plume of high salinity water (5,000-30,600 mg/L TDS) is present at intermediate depths that extend from below the old oil and brine pits to Skiatook Lake. No liquid petroleum was found in the contaminated groundwater, but soluble petroleum byproducts, including organic acid anions and other volatile organic compounds (VOCs) are present. Results to date clearly show that significant amounts of salts from produced-water releases and petroleum hydrocarbons still remain in the soils and rocks of the impacted area after more than 60 years of natural attenuation. At the "B" site significant amounts of produced water from the two active brine pits percolate into the surficial rocks and flow towards the Skiatook Reservoir; but only minor amounts of liquid petroleum leave the brine pits and reach the Skiatook Reservoir. At both sites, results show that the chemical composition of released brines is modified further by sorption, mineral precipitation/dissolution, transpiration, volatilization and bacterially mediated oxidation/reduction reactions.

Introduction

Oil and natural gas currently are the main sources of primary energy in the USA, supplying about 63% of the energy consumption. Forecasts indicate that by 2025 natural gas and oil consumption will increase by 50% and 48%, respectively (EIA, 2003). Oil and gas production started in the USA in 1859, when the Drake's well was drilled near Titusville in Venango County, PA (Dickey, 1959). To date, a total of about 3.5 million oil and gas wells have been drilled in 36 states, but currently only about 880,000 are in production (Kharaka and Wanty, 1995; Breit and others, 2001). Petroleum production, drilling operations, and improperly sealed abandoned wells have caused major contamination of surface and ground waters and soils in energy producing states (USEPA, 1987; Richter and Kreitler, 1993; Kharaka and others, 1995; Kharaka and Hanor, 2003). Contamination results mainly from the improper disposal of some of the large volumes (currently 20-30 billion barrels per year) of saline water produced with oil and gas, and from hydrocarbon and produced water releases caused by equipment failures, vandalism, flooding, and accidents.

Prior to the institution of Federal regulations in the 1970's, produced waters, which are highly saline (TDS may exceed 350,000 mg/L dissolved solids), may contain toxic metals, organic and inorganic components, and radium-226/228 and other naturally occurring radioactive materials (NORM), were often discharged into streams, creeks, and unlined evaporation ponds causing salt scars and surface and ground water pollution (Collins, 1975; Kharaka and Thordsen, 1992; Otton and others, 1997a,b,c, 2001; Zielinski and others, 1998; Otton and Zielinski, 1999). These releases and the improper disposal of produced water are national issues that concern managers of Native American, Federal, and State lands, as well as oil and gas producers and lessees, mineral rights and lease owners, State and Federal regulators, and surface landowners (ASTM, 1999; Billingsley, 1999; Carty and others, 1997; Federal Leadership Forum, 2000; USEPA, 1987; Wilson and Frederick, 1999).

Beginning in early 2001, about 20 scientists from the USGS and other governmental agencies and academia have been conducting a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, organic compounds, and radionuclides present in produced water, and their impacts on soil, surface and ground waters and the local ecosystem at the Osage-Skiatook Petroleum Environmental Research (OSPER) "A" and "B" sites, located in Osage County, OK (fig. 1). The authors of this

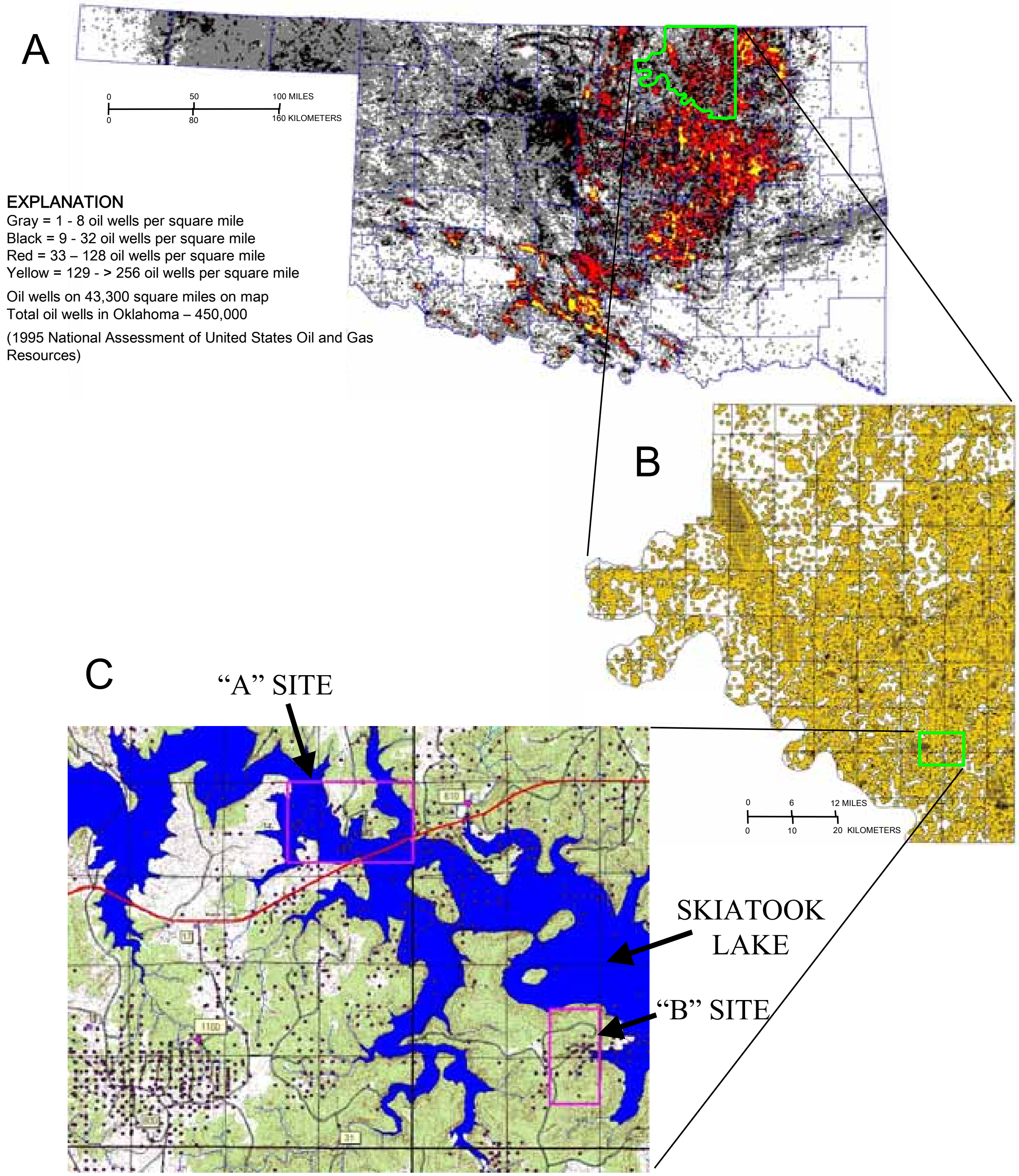

Figure 1. Distribution of petroleum wells in Oklahoma, Osage County, and the study areas. A – Location of 450,000 wells in Oklahoma; B – Location of 38,500 wells (radius of each well=1/4 mile, after Abbott, 2000) in Osage County. C – Location of many shut-in and operating wells in and near the OSPER "A" and "B" sites on Skiatook Lake.

chapter organized a special session on OSPER at the Ninth International Petroleum Environmental Conference (IPEC-9) in Albuquerque, NM, 22-25, October 2002. The session, titled “Fate and Transport of Brine and Hydrocarbon Releases in Soils and Water, Northeast Oklahoma”, attracted 10 presentations (http://ipec.utulsa.edu/). Even though reports from many of the presentations were posted at the IPEC web site, all the presenters agreed to modify their IPEC reports and or write new reports for this volume. All the reports received additional reviews and were further modified to conform to the USGS format.

Detailed studies are continuing at these two sites to evaluate the long-term and short-term effects of hydrocarbons and the dissolved and suspended constituents of produced water on soil and ground and surface waters and the natural processes that may be mitigating those effects. Results from these studies may serve to guide estimates of human and ecosystem risk at these and similar sites and the development of risk-based corrective actions by USEPA and Tribal environmental officials (Billingsley, 1999). Corrective actions are particularly needed in aging and depleted fields, where land use is changing from petroleum production to residential, recreational, agricultural or other uses (Carty and others, 1997).

OSPER “A” and “B” Sites

The two research sites, OSPER “A” and “B,” are located within the Lester and Branstetter leases, respectively, adjacent to Skiatook Lake, a 4,250-hectare reservoir completed in 1987 that provides drinking water to the local communities and is a major recreational fishery (fig. 1). The sites are located in the Central Oklahoma platform in the southeastern part of the Osage Reservation in northeastern Oklahoma (fig. 1). Both sites are in a dissected area of modest relief, with oak forests covering the slopes and tall grass present on most ridge crests. Geological mapping by Otton and Zielinski (this volume) show the area to be underlain by interbedded shale, siltstone, and sandstone. Thicker resistant sandstone units typically form the hill crests. Hill slopes are underlain by shale, siltstone, and thin sandstone beds.

Because they met our selection criteria, the OSPER sites were selected for detailed multidisciplinary investigations in June 2000, following a two-year national search effort. The geologic and climatic settings of these sites resemble those of much of the major southern mid-continent oil- and gas-producing areas of the USA. Oil and gas production has occurred in these leases for about one hundred years, resulting in impacts that include soil salinization with resultant destruction of soil textures and deep erosion, death of proximal vegetation, stress on peripheral vegetation, salinization of surface and ground waters, saturation of soils with crude oil of varying age, and weathering and dispersal of crude oil components and trace elements. An important selection criterion that was met is the fact that the sites are located on Federal lands; the Osage Nation holds the mineral rights, the Bureau of Indian Affairs (BIA) and the EPA have trust responsibility, and the Army Corps of Engineers owns the surface rights at these sites (Kharaka and others, this volume).

The OSPER “A” site, located in section 13, T22N, R10E, has an area of about 1.5 hectare that is impacted by produced water and hydrocarbon releases that occurred primarily 60-85 years ago (fig. 2). The site is underlain by 1) a surface layer of eolian sand of varying thickness (up to about 80 cm); 2) colluvium that ranges from large boulders of sandstone to thin, granule-pebble conglomerate; 3) weathered shale, siltstone, and sandstone; and

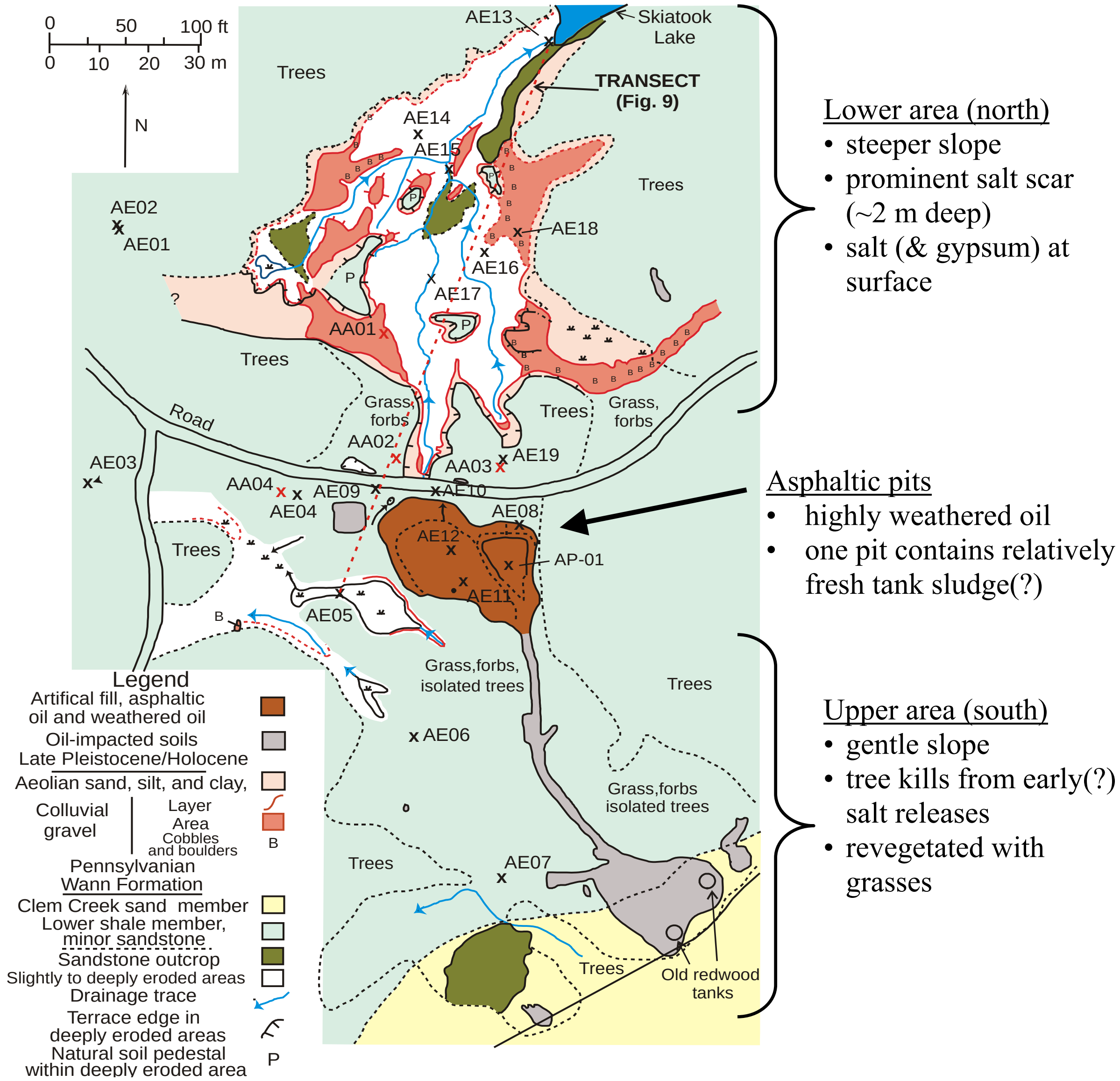

Figure 2. Geologic map of the OSPER “A” site showing the locations of the oil pits, other production features, drilled water wells and outline of the impacted areas. Note the location of the Cedar Creek arm of Skiatook Lake to the north of the site. The main arm of Skiatook Lake is just to the southwest.

4) underlying unweathered bedrock. Much of the site appears to have been impacted by early salt-water releases that killed the pre-existing oak forest. The salt-impacted soils subsequently prevented younger oak trees from colonizing much of the site except where single trees or clumps of trees found favorable conditions. The gently sloping upper part of the site is slightly eroded in places and has been mostly revegetated with grasses, forbs, sumac, and a few trees. This area drains into the main arm of Skiatook Lake just off the map to the southwest. The lower, steeper, more heavily salt-impacted portion has been eroded to depths of as much as 2 m. Seepage of salt water from a shallow sandstone aquifer continues and active salt scarring persists. This area drains into the Cedar Creek arm of Skiatook Lake to the north (fig. 2).

Drilling at the Lester Lease started in 1912, and most of the over 100,000 bbl of oil produced by 1981, was obtained prior to about 1937. Oil production, which was entirely from Bartlesville sand at depths of 450-524 m, ended about 10 years ago (BIA, unpublished lease records, 2000). Oil and produced water collected in two redwood tanks at the top of the site was transported via ditch to two roadside pits at mid-site. Remnants of decades-old produced water and hydrocarbon spills (now highly degraded and weathered oil) are scattered around the site. One pit at this site contains relatively fresh asphaltic oil and high salinity brine (Godsy and others, this volume).

The “B” site, located within the Branstetter lease in sections 29 and 32, T22N, R10E, is actively producing and has ongoing hydrocarbon releases and salt scars that have impacted an area of about one hectare. The site includes an active production tank battery and adjacent large brine pit (fig. 3), two injection well sites, one with an adjacent small pit, and an old tank battery. The large pit is about 15 m from the shoreline of the Skiatook Lake; all the other sites are within 45 m of the lake. Three salt scars that were partly “remediated” in 2000 by saline soil removal, tilling and soil amendments, extend down slope from the active tank battery, the injection well/pit, and the old tank battery site to the lakes’ edge. Two small creeks cross the northern and southern parts of the site. The upper part of the site is characterized by a thin surface layer of eolian sand mixed with sandstone-clast colluvium underlain by weathered and unweathered shale, whereas the lower part of the site is underlain by 1) a surface layer of eolian sand (20-70 cm thick); 2) colluvial apron and alluvial deposits of varying thickness comprised of sandstone pebbles, cobbles, and boulders with a fine sandy to clayey matrix; 3) weathered shale; and 4) unweathered bedrock (Otton and Zielinski, this volume).

The Branstetter lease was initially drilled in 1938 and increased activity occurred in 1947-51, when A.H. Ungerman purchased the lease. Approximately 110,000 barrels of oil were produced from the lease before water flooding for enhanced recovery began in 1953. Currently there are about 10 wells that produce 1-3 bbl/d oil, and 50-100 bbl/d brine; all the produced fluids are collected and separated in the tank battery adjacent to the large brine pit (S. Hall, oral communication, 2002). The two brine pits at this site are not lined and receive brine and hydrocarbon releases from broken pipes and tank leaks; they also receive large volumes of surface-water flow from precipitation. The brine in these pits is generally pumped into collection tanks by submersible pumps, but these occasionally fail causing filling and overflow of brine pits, as happened in November and December, 2001 for the large brine pit.

Scientific Approach

The complexity of the multiple processes operating at these sites requires a multi-disciplinary team to examine the geology, geophysics, hydrology, geochemistry, microbiology, and ecosystem dynamics to generate a credible interpretive analysis useful to the stakeholders and the scientific community. The research team for this investigation is comprised of scientists from the Geologic, Water Resources, and Biologic Resources Disciplines of the USGS and from the USEPA, BIA and local universities. This team is unique in its ability to address the relevant issues, including the fate of the contaminants and site remediation and land use.

Figure 3. View of the large brine pit , the active tank battery, and the partly remediated salt scar adjacent to Skiatook Lake at the OSPER "B" site (photo courtesy of Ken Jewell, USEPA).

Intensive investigations aimed at mapping the geology and impacted areas and other cultural features at the OSPER sites started in February 2001 (Otton and Zielinski, this volume). Water, oil and gas samples were taken from eight oil wells located in the Branstetter lease and in areas adjoining the Lester lease to characterize the crude oil and produced water contaminant sources. Water samples were also obtained from Skiatook Lake and shallow groundwater wells in the region and from brine pits, seeps and creeks in both sites (Kharaka and others, this volume). Initial surface soil sampling (0-15 cm) was conducted at site "B" in March, 2001 to determine the chemical signature of added salts and the spatial distribution of soil salinity in relation to areas of visible salt scarring (Zielinski and others, this volume). Ground electromagnetic (EM) and DC resistivity geophysical surveys were carried out in September 2001, and the data were used to interpret the subsurface distribution of saline soil, water, and bedrock at both sites (Smith and others, this volume).

A total of ~60 Geoprobe , auger and rotary wells (1-71 m deep) were drilled, cored, completed and sampled at both sites in February and March 2002. Three deep rotary wells were drilled as stratigraphic holes in nearby "unimpacted" areas. The location of the other wells were based on: (1) The presence of salt scars, excessive soil and rock erosion, brine and asphalt pits, degraded oil, dead trees and shrubs and other visible surface features; (2) results of electrical conductance, Cl, Br and SO_4 measurements on aqueous leachates from samples of shallow soil (0-15 cm) and selected soil profiles (0.5-1.7 m); and (3) results of shallow penetrating (<10 m) electromagnetic (EM) and deeper (30-60 m) DC resistivity surveys. Additional Geoprobe and auger wells were drilled at both sites in November 2002 and in March and April 2003, but results from these are not discussed in this volume.

Core samples from impacted and “pristine” areas were studied (Rice and others, this volume) using visual and microscopic description, X-ray powder diffraction of the bulk soil and clay-sized fraction, particle size analysis, cation exchange capacity, and selective extraction of iron species to establish the differences in the mineralogy, sorption of Na and other chemicals and geochemical behavior of soils impacted by saline water compared to those from unimpacted areas. A number of grab and core samples from impacted and “pristine” areas were also used by Kampbell and others (this volume) to determine a number of key parameters, including nitrates, organic matter, total petroleum hydrocarbons (TPH), conductivity, chlorides, and dehydrogenase activity (DHA - a measure of viable biomass) that are essential for the development of guidelines for stabilizing or restoring impacted areas. A series of oil, water, brine, and soil samples were characterized and analyzed for geochemical parameters that are indicative of microbial activity. Characterization of the resident microbial populations and the varying stages of weathering and biodegradation of oils were completed for a number of these samples and are reported by Godsy and others (this volume).

Based on repeated water table measurements in wells, chemical analyses of water samples, and field observations, Herkelrath and Kharaka (this volume) developed conceptual models of the hydrology and solute transport mechanisms near the major brine pit at OSPER “B” site. They propose two main mechanisms for solute transport from the waste pit to the lake. One mechanism is the relatively slow and steady flow of saline ground water from the waste pit to the lake in a near-surface aquifer. The other mechanism is relatively fast overland flow of salt-laden runoff during rainfall. Using the USGS model SUTRA, they simulated steady-state ground-water flow and solute transport from the pit to the lake. Preliminary modeling results indicated that the solute travel time from the pit to the lake in saline ground water is 2-4 years.

All the wells, other sampling sites and features were surveyed with high accuracy real-time kinematic (RTK) GPS equipment in June and July 2002. This differential correction method of surveying requires a GPS base station, a GPS rover unit and radio link between the units. The accuracy achieved is better than ±10 cm horizontally and vertically (Abbott, this volume).

Initial Summary Results

As detailed in the individual reports in this volume, a great deal has been accomplished in the last two years at the OSPER “A” and “B” sites, especially with regard to the geologic, geophysical, hydrologic and geochemical characterizations. Results to date show that impacts of produced water and associated hydrocarbons on soil and ground and surface waters at both sites and surrounding areas are widespread and pervasive. All wells show some degree of contamination from produced water and/or associated petroleum or its degradation products. Thus, it has been very difficult to obtain soil and water samples from “pristine” areas. In fact, one of the two stratigraphic wells outside the OSPER “B” site, but close to a production well, showed both oil and brine contamination and the other showed impacts from produced water. A "background" well, drilled 0.6 km to the NW of the OSPER "A" site initially (March, 2001) had freshwater (450 mg/L TDS), low DOC values and other characteristics of the pristine local groundwater; repeated sampling did not change the inorganic composition of water from this well but DOC concentrations continued to increase. Our latest (June 2003) sample from this well showed no significant change in the inorganic composition of water, but small oil globules and relatively high concentrations of DOC and BTEX were obtained.

Results of water samples from nearby oil wells, the tank battery at the "B" site, and brine pits and seeps indicate that the produced water source for both sites is/was a Na-Ca-Cl brine (~150,000 mg/L total dissolved solids), with relatively high concentrations of Mg, Sr, Fe, Mn and NH_4, but low concentrations of SO_4, H_2S and dissolved organics (Kharaka and others, this volume). Results show that the area source oils are paraffinic-naphthenic light oil (~35° API gravity), containing *n*-alkanes as the dominant components unimpacted by biodegradation. The oils at the inactive "A" site are similar although vary in stages of biodegradation. Microbial populations at both sites are degrading the water-soluble crude oil compounds. The geochemical evidence and make-up of the microbial populations at both sites indicate that the systems are slightly different but based on free energy yields, are poised at the level of iron reduction (Godsy and others, this volume). An important result from this investigation is the fact that the distribution of the high salinity groundwater plumes mapped on the basis of chemical analysis of water are in general agreement with the distribution observed from aqueous leachate data from soil and bedrock core samples as well as from the geophysical surveys.

Results at the OSPER "A" site show that the salts have essentially been removed from the sandy soil and underlying surficial sediments, but degraded and weathered oil persists on the surface of old oil and brine pits, close to sites of old tanks, on old channels that carried oil from tanks to the oil pits, and other impacted areas. Results also show a plume of high salinity water (5,000-30,000 mg/L TDS) is present at intermediate depths that extend from below the old oil and brine pits (see fig. 9, Kharaka and others, this volume) to Skiatook Lake. No liquid petroleum was found in the contaminated groundwater, but soluble petroleum byproducts, including organic acid anions and other VOCs are present. Results to date clearly show that significant amounts of salts from produced-water releases and petroleum hydrocarbons still remain in the soils and rocks of the impacted area after more than 60 years of natural attenuation.

At the "B" site significant amounts of produced water from the two active brine pits percolate into the surficial rocks and flow towards Skiatook Lake.Only minor amounts of liquid petroleum leave the brine pits and reach Skiatook Lake. Preliminary hydrologic modeling indicates that the solute travel time from the brine pit to the lake in saline ground water is slow, requiring 2-4 years. The above results and conclusions are tentative and may be modified after additional sampling from existing and new wells, tracer tests, hydrologic parameter determinations and hydrologic and geochemical modeling are completed.

Future Plans

We expect that detailed geological, geophysical, hydrologic, geochemical and ecological studies at these two sites will continue for 3-5 more years, with the emphasis shifting from site characterization to investigating the relevant hydrogeochemical processes and determining the rates of transport and degradation of solutes. Additional deep drilling, however, is needed at the OSPER"A" site to map the depth and the horizontal boundaries of the 3-D plume of high salinity water (5,000-30,000 mg/L TDS) with chemical and isotopic characteristics similar to those of the source produced water. The depth of this plume is not currently well defined; the one well that penetrates into a deeper aquifer has lower salinity (~2,000 mg/L TDS), but high Fe, Mn and dissolved organics. The horizontal plume boundaries are also not well delineated, since all wells deeper than 2 m at the site encounter the plume. Drilling at the OSPER "B" site would be mainly to investigate brine penetration below a thick (>5 m thick) shale formation.

The existing and future wells at the "A" site will be sampled to investigate the natural processes that modify the chemical composition of the groundwater plume. Processes of interest include mixing and dilution of saline groundwater with pristine groundwater and percolating water from precipitation; sorption; mineral precipitation/dissolution; evapotranspiration; and volatilization and bacterially mediated oxidation/reduction reactions. Ultimately, we plan to model the transport of reactive and conservative solutes in the shallow aquifer(s) and exchange with the Skiatook Lake water column.

The rate of salt removal from the "A" site by surface runoff is being determined by measuring the volume and chemical composition of water flowing over a weir installed close to the Skiatook Lake in a location that captures most of the surface and 'base' flow from this site following precipitation. Results to date show that the present-day natural salt-removal processes at this site are slow, thus providing a valid explanation for the fact that large amounts of salts from produced-water releases still remain in the groundwater plume after more than 65 years of natural attenuation.

It is likely that the rate of ground-water movement from the main produced-water pit at the "B" site to Skiatook Lake may be independently checked by looking at age-dependent changes in the radium-isotope composition of the produced water. A study is underway to examine changes in the Ra-228 to Ra-226 ratio between source water the pit and water in a shallow well near the lake's edge. This technique relies on the half-life differences between Ra-228 (5.75 years) and Ra-226 (about 1600 years). Most produced waters contain modest (but measurable) activities of radium.

Additional future studies would include the fate and transport of hydrocarbon degradation products, hydrocarbon-related trace elements, produced-water salts, and produced-water trace elements, especially the toxic components, including uptake and residence in soils, reservoir sediments, oak trees, and other macrobiota. Our goal is to quantify the sub-lethal effects of produced water salt and hydrocarbon releases on oak species – tree ring growth and foliar response to major and minor elements and soluble hydrocarbons. There is a proposal, not yet funded, to investigate the impacts of produced water and associated hydrocarbons on clam species and other biota in the Skiatook Lake. Finally, four plots have been planted with Bermuda grass and a selection of trees to study site restoration. We anticipate major findings from each of these investigations and tasks, and results that would be important not only to petroleum sites in the Osage County, but throughout the USA and beyond.

Acknowledgements

We are grateful to the Osage Indian Nation, to the Army Corps of Engineers and Bureau of Indian Affairs, as well as the field operators for permission to conduct research at these sites. We are grateful also for the financial support for this research provided by DOE National Petroleum Technology Office, E&P Environmental (Nancy Comstock and Dan Gurney, project coordinators). Most of the drilling at these sites has been carried out with equipment and operators from USEPA, Ada Research Laboratory (Donald Kampbell, Supervisor). James Thordsen spent considerable time and effort setting up figures and tables for all the chapters and formatting the text, including the references to meet the USGS format for WRI reports.

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Produced Water and Hydrocarbon Releases at the Osage-Skiatook Petroleum Environmental Research Sites, Osage County, Oklahoma: Introduction and Geologic Setting

By James K. Otton and Robert A. Zielinski

Abstract

The U. S. Geological Survey (USGS) is investigating the impacts of produced water and hydrocarbon releases at two research sites adjacent to Skiatook Lake in southeastern Osage County near Tulsa, Oklahoma. Site “A” is an area where produced water and hydrocarbon releases occurred primarily 65-90 years ago in an area of oak forest. The site is located in section 13, T22N, R10E near the neck of a small peninsula that extends into Lake Skiatook. The entire site is underlain by a surface layer of eolian sand and colluvium, and weathered and unweathered shale, mudstone, siltstone, clayey sandstone, and sandstone. Much of the site appears to have been impacted by early salt-water releases that killed the oak forest. The gently sloping upper part of the site is slightly eroded in places whereas the lower, steeper, more heavily salt-impacted portion has been eroded to depths of as much as 2 m. The site has been mostly to partly revegetated with forbs and grasses. However, only a few oak trees have established themselves. Oil from two redwood tanks at the south part of the site was transported via ditch to two roadside pits at mid-site. Oil spills from pipeline breaks and other tanks (no longer present) are scattered around the site. The oil in the west pit is highly weathered, but the east pit contains what appears to be relatively fresh asphaltic material.

Site “B” is located in section 29, T22N, R10E at the west end of a small bay of Lake Skiatook. The site includes an active production tank battery and adjacent large pit, two injection well sites, one with an adjacent small pit, and an old tank battery platform, all within 45 m of the lake. Hillslopes on the upper part of the site are characterized by a thin surface layer of eolian sand and sandstone clasts, underlain by weathered and unweathered shale. The lower terraced part of the site is underlain by a surface layer of eolian sand and sandy to clayey colluvium and alluvium about 1.5 m thick and weathered and unweathered shale. Three salt scars extend downslope from the active tank battery, the injection well/pit, and the old tank battery platform to the lake edge. The area underlain by shallow saline ground water is substantially larger than the salt-scarred areas. Hydrocarbons can be detected in the shallow ground water adjacent to the active pit and at the lake edge below the pit.

Introduction

In February 2001, the U. S. Geological Survey (USGS) initiated investigations of the impacts of produced water and hydrocarbon releases at two research sites adjacent to Skiatook Lake in southeastern Osage County near Tulsa, Oklahoma (figs. 1 and 2). These studies are designed to provide an in-depth understanding of the impacts of highly saline produced water and hydrocarbons on soils, vegetation, surface water and shallow ground water, and lacustrine fauna. These sites were chosen because of the similarity of the geologic and climatic setting of the sites to broad areas of the south-central U.S. oil-producing region, the presence of Federally owned lands and mineral rights under the jurisdiction of the Department of the Interior, and an adjacent public water supply and recreational fishery. Both sites are on land owned by the U.S. Army Corps of Engineers. The Osage Nation holds the mineral rights. Project results can be used to plan and evaluate cost-effective site remediation strategies, determine the rate of site restoration by natural processes, develop simple assessment techniques for other oil and gas production sites, and establish historic natural resource damage.

Both sites are in a dissected area of modest relief underlain by interbedded shale, mudstone, siltstone, and sandstone of the Pennsylvanian Wann Formation. Thick, resistant sandstone units typically form the hillcrests. Shale, mudstone, siltstone, and thin sandstone beds underlie hillslopes. Core drilling by the USGS indicates that the depth of weathering of the bedrock is about 10-25 m on the ridges and 5-6 m in small stream valleys.

These sites are located in the Cross Timbers ecosystem area of northeastern Oklahoma (Kuchler, 1964). Oak forests cover the hillslopes. The principal oak species are black jack oak (*Quercus marilandica*) and post oak (*Quercus stellata*). Grassslands and stands of oak occur on most ridge crests. Historically, this area has been used for grazing and hunting. Under natural conditions, fires control oak encroachment on grasslands.

In February and March of 2001, the sites were surveyed and mapped to characterize the local geology and cultural features. In February and March of 2002, both sites were drilled with a rotary rig, a hollow-stem auger rig, and a direct-push tool (Geoprobe).

This paper provides the geographic and geologic framework for understanding and interpreting the results of the accompanying papers that follow.

Figure 1. Location map for the Skiatook Lake area in southeastern Osage County.

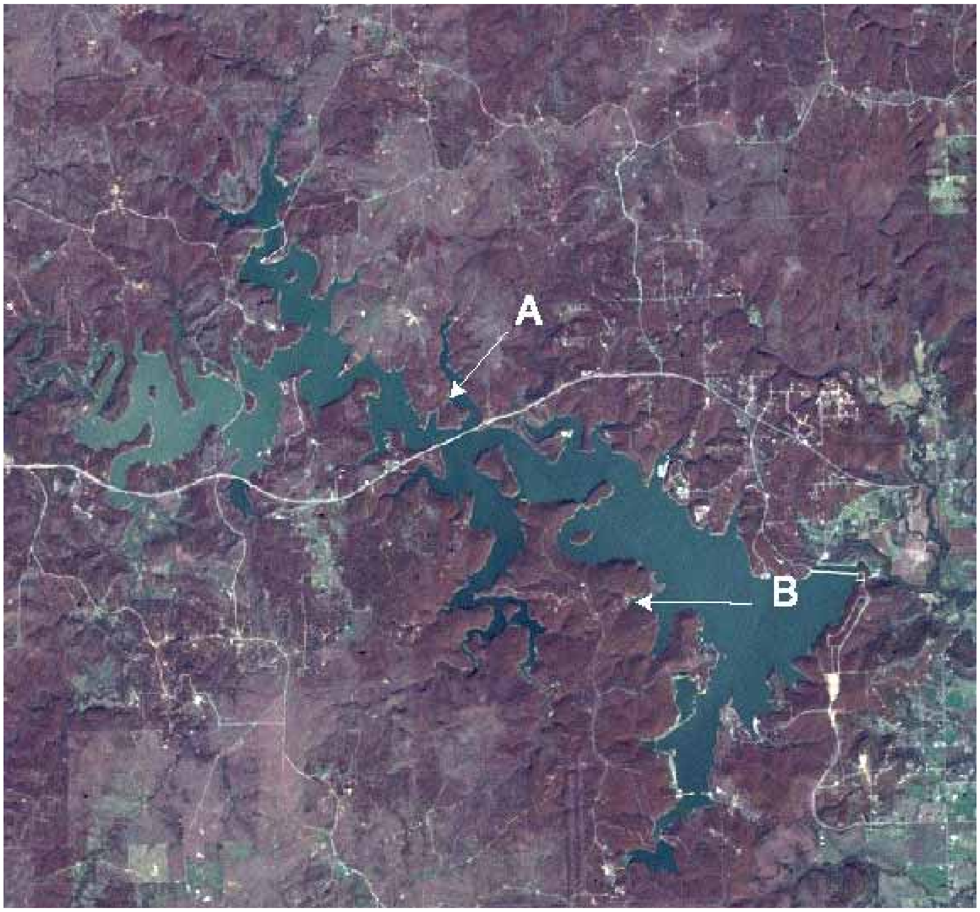

Figure 2. 1999 Landsat image of the Lake Skiatook area showing the location of research sites “A” and “B”. State Highway 20 traverses east-west across the middle of the image.

“A” Research Site

The “A” site occurs in section 13, T22N, R10E at the neck of a small peninsula that extends into Skiatook Lake between the Cedar Creek arm of the lake to the east and the main stem (Hominy Creek) (figs. 2 and 3) to the southwest. The site is characterized a mostly open area within oak forest. Vegetation mapping (fig. 4) shows that the site can be divided into two sections, one, north of the road, and the other, south of the road. The open area south of the road is vegetated by grasses, forbs, sumac, isolated oak, willow, and locust trees, and blackberry. A large sandstone outcrop area, devoid of vegetation except for lichen and mosses, lies in the southwest corner of the site. Remnants of redwood oil tanks sit on sparsely vegetated sandstone outcrop in the southeast corner. Patchy weathered asphaltic oil covers an area surrounding the tanks. Several small oak trees grow within the area of weathered asphalt. A patch of immature oak trees occurs just north of the redwood tanks.

Figure 3. 1995 aerial photo of part of section 13 showing the location of the "A" research site (outlined in white, about 140 x 230 m) adjacent to Skiatook Lake. The pencil lines are quarter-section delineations. Note the Highway 20 bridge at lower right.

A narrow corridor of weathered asphalt extends from the area around the two tanks north to two unlined pits (A and B, fig. 4). This feature follows an unlined trench (fig. 5) that appears to have been designed to carry produced fluids from the two redwood tanks to the pits. This trench cuts across the natural topographic slope, which is northwest on this part of the site. The channel splits just upslope from the two pits with one branch leading to each pit. A badly corroded pipe exits pit A through its northern berm, and this pipe likely served to allow oil to be pumped from the pit into a tanker truck. The main channel changes direction about halfway between the tank area and the pit area and it appears that oil overtopped the channel at this point and spilled onto adjacent soils (fig. 4). Pit A contains tarry or asphaltic hydrocarbon (fig. 6) on most of which which no vegetation grows. Oak trees lie to the east of the pit and a large, isolated oak tree grows just to the north of the pit berm (fig. 6). Pit B is located to the west and shares a common berm with Pit A (figs. 4 and 7). This pit contains weathered asphalt. Sparse grasses grow on much of the surface. Water ponds at the low (north) end of the pit after rainfall. Two small, low areas occur west and southwest of the two pits (fig. 4). During wet weather, the ground in these low areas is water saturated.

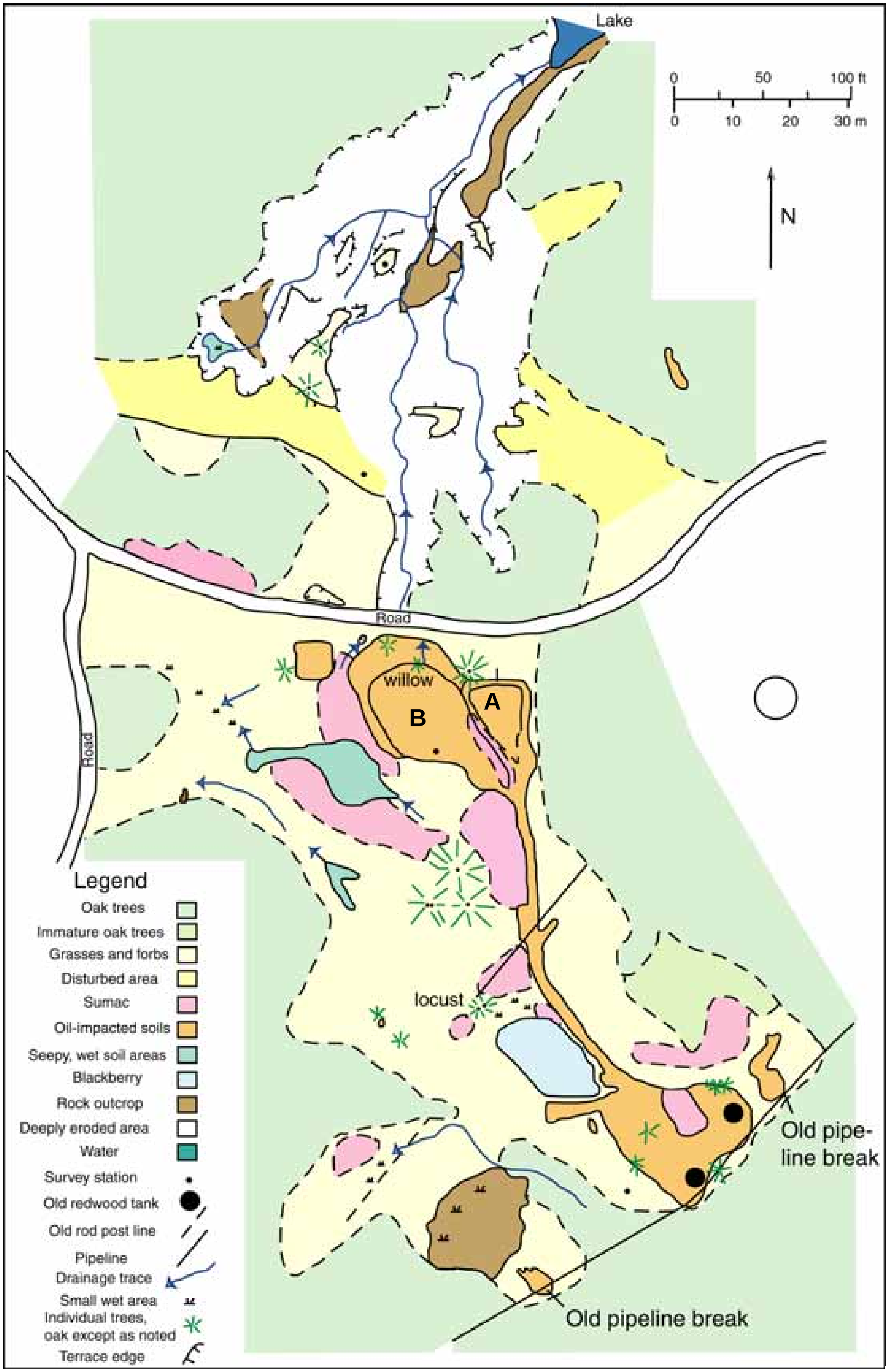

Figure 4. Vegetation map of the "A" site.

Hydrocarbons occur in soil northeast and southeast of the redwood tank area (fig. 4). Both of these oil occurrences lie adjacent to repaired breaks in a pipeline passing the site and appear to be more recent than oil associated with the tanks, based on the degree of weathering. Weathered hydrocarbons also occur in a patch of soil about 6 x 6 meters just west of pit B.

In the southern part of the site near the two redwood tanks, the soil tends to be sandy because of the sandstone outcrop and subcrop. Weathered asphaltic oil fragments, mixed with sand, have washed downslope from the redwood tank area and the area of the eastern pipeline break forming areas of sandy outwash barren of vegetation contiguous with the initial spills.

This area south of the road drains in two divergent directions (fig. 8). A drainage divide crosses this area from southeast to northwest such that most of the area south of the road drains northwestward then westward off the site, eventually into a tributary arm of the main (Hominy Creek) stem of the lake. An area adjacent to the road that includes the two pits lies north of the drainage divide. Thus the surface area around the pits appears to drain mostly northward towards the Cedar Creek arm of the lake (figs. 4 and 8).

North of the road is an area of deeply eroded and disturbed soils (figs. 4 and 9). Sparse grasses grow except where the soil salt content is high. The deeply eroded section is largely delineated by a terrace edge (fig. 4). Much of the section of disturbed soils (fig. 4) is oriented approximately east-west across the south-central part of the area north of the road. Features on the 1937 aerial photo for the site suggest that this is the trace of an older road. The road was apparently moved southward as headward erosion of two gullies impinged on the roadbed. Three soil pedestals, in which the pre-erosion soil profile is preserved, occur within the deeply eroded section (see small, irregular hachured areas in fig. 4; two pedestals are shown in fig. 10). They are capped with grasses and forbs. A small oak tree grows on one pedestal. A small promontory on which two oak trees are growing extends into the deeply eroded section from the southwest. The area is drained by several washes that coalesce to the north before leaving the site. Flow occurs in these drainages only after rainfall, although it may persist for several days in the drainage at the north edge of the site (figs. 4 and 10). Bedrock, including three outcrops of resistant sandstone ledges, is exposed in the deeply eroded section. A small wet soil area occupies the west corner of the deeply eroded section (fig. 4).

Effluorescent salt crusts are observed at various times of the year. They commonly occur on the lower part of the central sandstone outcrop (fig. 4, north central part of deeply eroded area) and on the surface of the alluvium along the channel below the central outcrop. Salts also are common around the soil pedestal in the south-central part of the deeply eroded area (fig. 11).

Figure 5. Trench with weathered asphalt between redwood tanks and pits (looking south upslope towards the location of the tanks). Note the sumac with one or two small oaks to the right and the mature oak forest in the background above the site.

Figure 6. Pit "A" with asphaltic hydrocarbons. The central part of the pit is devoid of vegetation. Sparse grasses grow in the upper part (close to the viewer).

Figure 7. Pit "B" with highly weathered hydrocarbons and sparse grasses. The photographer is standing on the berm between the two pits. The north edge of the pit berm is to the upper right. A willow tree grows just beyond this berm (see fig. 4). Sumac is growing beyond the pit to the left.

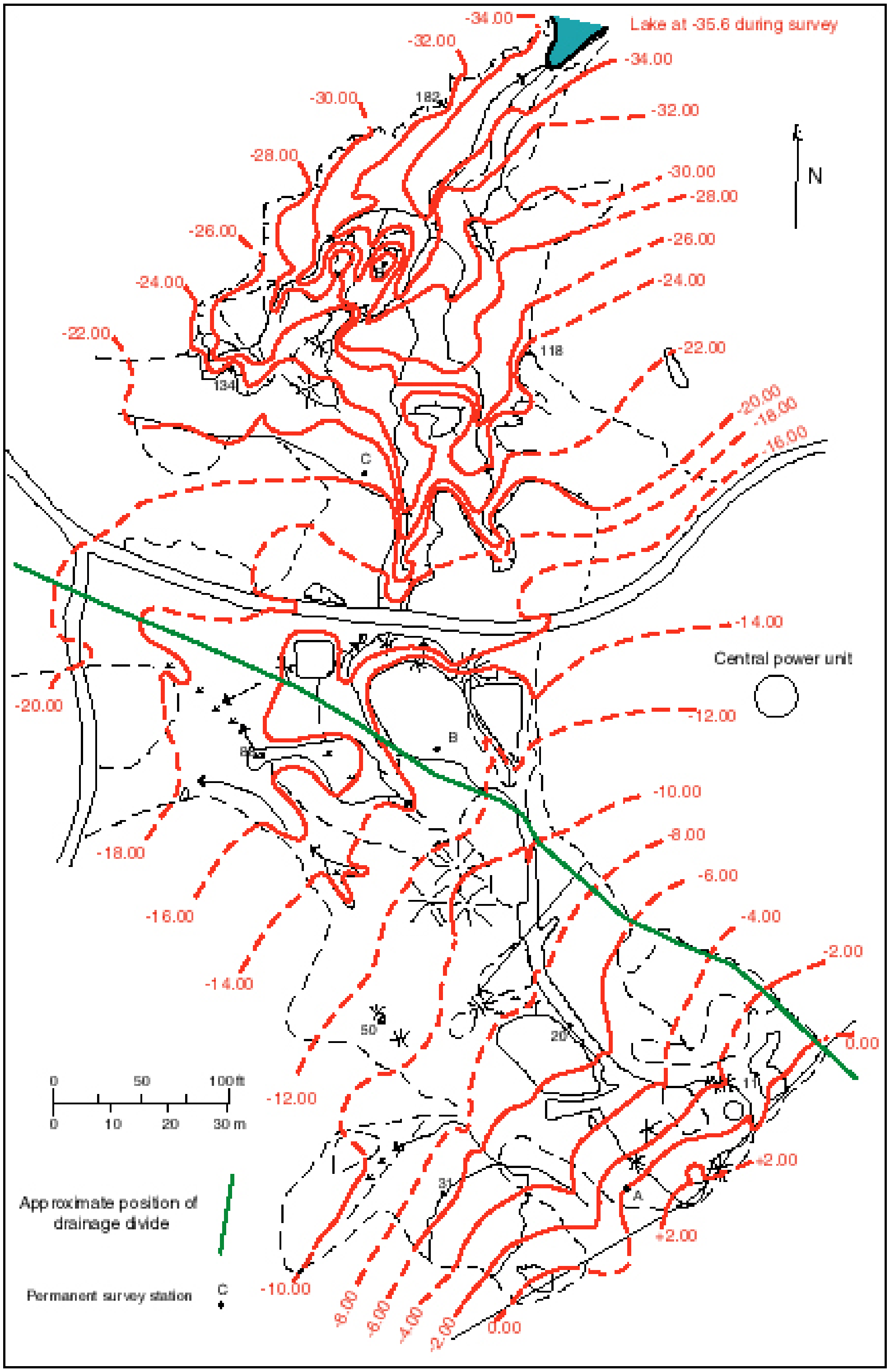

Figure 8. Topographic map of the "A" site showing the drainage divide.

Figure 9. The deeply eroded area, August 2000, from near the road looking north.

Figure 10. Surface flow disappearing below the surface of the stream alluvium within the deeply eroded area, March 10, 2001. Two soil pedestals are delineated by arrows (right and left). Sandstone bedrock outcrop is delineated by a rectangle.

Figure 11. Salt effluoresence adjacent to soil pedestal.

Lease History

The following lease history is summarized from files of the Bureau of Indian Affairs in Pawhuska, OK. Initial drilling on the lease was in late 1912 and 1913. Production is entirely from the Pennsylvanian Bartlesville Sand (local, informal name) at depths of 450-425 m. Initial oil production for some of the 1913 wells was as much as 100 barrels/day (bbls/day). However, as of July 1, 1915, aggregate oil production for 8 wells was 46 bbls/day. The most recent drilling dates from 1976 and 1977 and was designed to retrieve oil from part of the lease that was due to be flooded when the Skiatook Lake was completed (as it was in 1984).

Most wells have been plugged and abandoned, some as early as 1913. Several well sites are presently under the waters of Skiatook Lake. All of these have been plugged and abandoned. However, many of these wells were plugged prior to the 1950s with “sand pumpings”, wood, lead, rock, “heavy mud”, and “blue shale.” These had to be replugged prior to flooding of the reservoir because these materials tend to fail. The usual reason for plugging and abandoning was low production. One well, plugged in 1931, was producing 2 gallons of oil and 25 bbls of water/day. Another, plugged the same year, was producing 1.5 bbls of oil and 20 bbls water/day.

Production through 1981 was about 100,000 bbls of oil. Anecdotal reports indicate that the lease produced substantial quantities of gas that was used locally to power pumping units (Marvin Abbott, USGS, 2001, oral communication). As of 2002, one well on the lease still had a gas-fired pump. Records do not indicate that the lease was ever considered for waterflooding. At least one production well was converted to a salt-water disposal well. One initial production report notes that the oil was 35^{o} API gravity.

Geology of the “A” Site

The site is typically underlain by: 1) a surface layer of modern eolian sand or mixed eolian and slopewash sand of varying thickness (0 cm to 1 m); 2) sandy or clayey colluvium that ranges from a thin layer of granule-pebble weathered sandstone-clast conglomerate to large boulders of sandstone; 3) weathered shale, mudstone, siltstone, clayey sandstone, and sandstone; and 4) similar underlying unweathered bedrock. The eolian sand, colluvium, and the uppermost part of the weathered bedrock are exposed in the deeply eroded area and were also observed in several Geoprobe holes at the site. A more complete section of weathered bedrock down to and penetrating into unweathered bedrock was observed in auger holes.

Bedrock Geology

Lithology

The bedrock units (figs. 12 and 13) mapped at the surface at the “A” site are part of the Pennsylvanian Wann Formation (Gardner, 1957). The sandstone in the uppermost part of the site near the redwood tanks (figs. 12 and 13) is herein mapped as the lower part of the Clem Creek Sandstone Tongue of the Wann Formation whereas the underlying rocks which are locally exposed in the lower part of the site belong to the lower shale member which here is comprised of beds of shale, siltstone, clayey sandstone, sandstone, and mudstone.

The lowermost part of the Clem Creek sand forms the sandstone outcrop in the southwest corner of the open area (fig. 12). Patches of sandstone interspersed with thin sandy soil occur around the two redwood tanks showing that the Clem Creek sand also underlies the tanks.

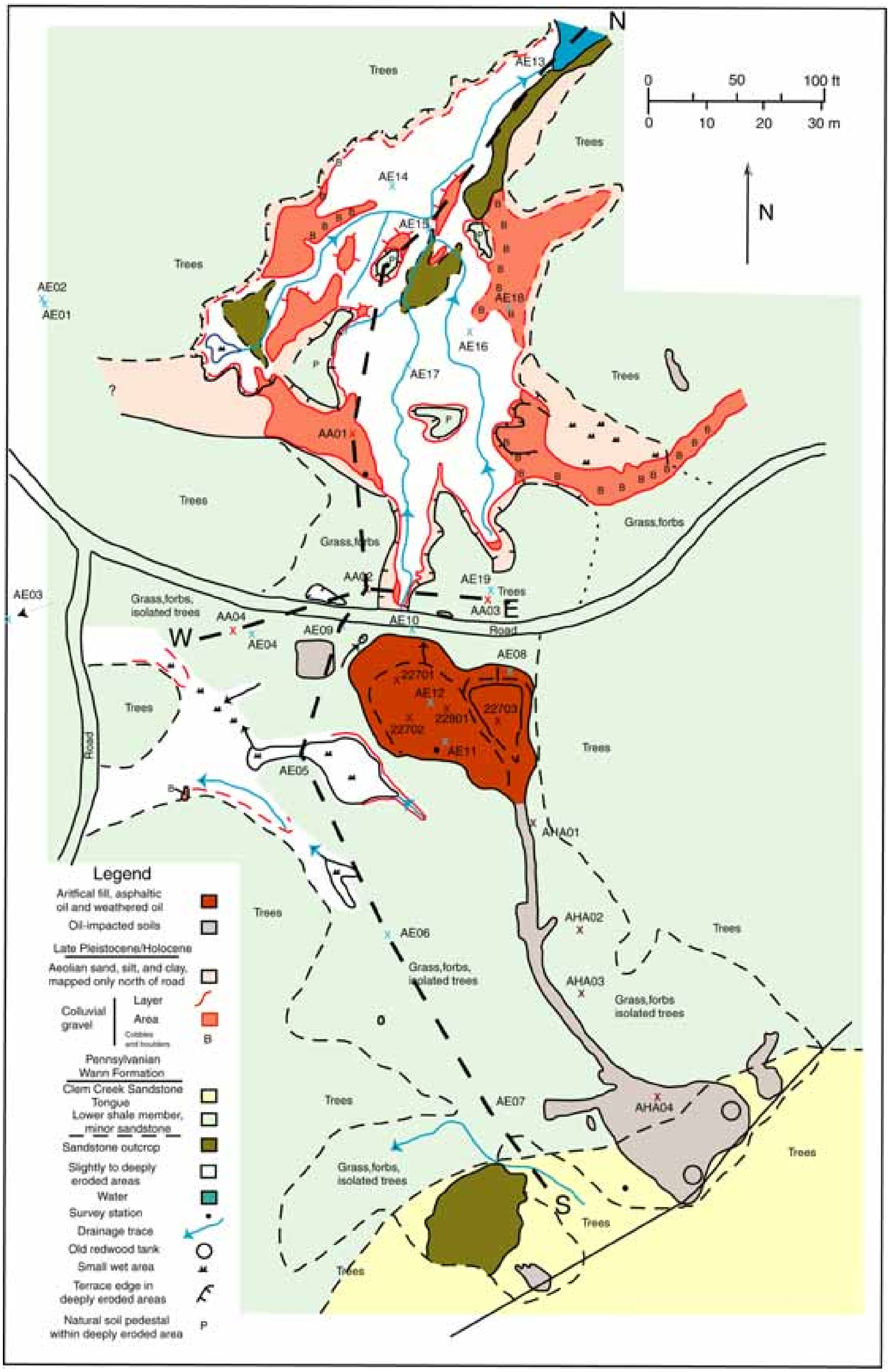

Figure 12. Geology of the “A” site showing locations of drillholes and cross sections.

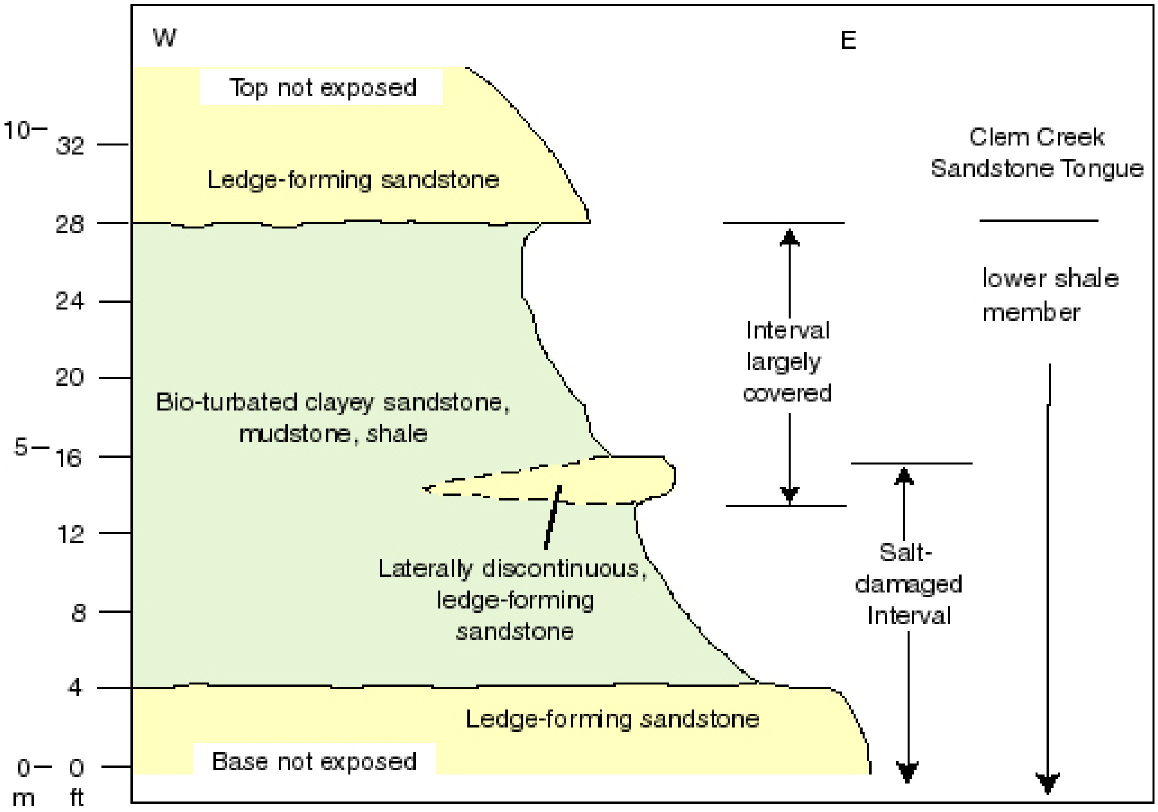

Figure 13. Generalized bedrock section at "A" research site. Thicknesses are estimated from contour map. Section is part of the Pennsylvanian Wann Formation (Gardner, 1957).

The contact between the Clem Creek tongue and the underlying sequence is not exposed on the site, but can be recognized by a gentle break in slope at the low, north edge of laterally discontinuous exposures of nearby sandstone.

Bedrock is not exposed between outcrop of the Clem Creek Sandstone Tongue near and southwest of the redwood tanks and the road that traverses the site. Shallow auger holes south of the road (AE05, 06, 07, fig. 12) show that the bedrock in this area is comprised mostly of clayey sandstone, with lesser sandy shale and siltstone. A single large sandstone boulder occurs in the gently eroded area west of the pits ("B", fig. 12). It is unclear whether this is a colluvial boulder derived from sandstone outcrops upslope or outcrop of an underlying resistant sandstone layer within the bedrock.

North of the road, in the deeply eroded area, clayey sandstone, mudstone, shale, siltstone, and sandstone crop out. All units are weathered and most units form poor exposures except in some of the deeper gullies. Resistant sandstone ledges crop out in three areas: the west edge, the center, and the north part of the deeply eroded area (fig. 12). The outcrop at the west edge consists of cross-bedded sandstone. The weathered surface is mottled grayish orange, yellow gray, and olive gray[1]. Small surface pits weather moderate yellow brown.

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[1] Colors used here and elsewhere are derived from the "Rock Color Chart" published by the Geological Society of America.

The resistant sandstone outcrop in the center is exposed in a deep gully where it is underlain by less resistant clayey sandstone and sandy mudstone. It consists of thickly bedded sandstone. Small pits pockmark most exposed sandstone surfaces. Pits up to about 10 cm across have formed locally in the weathered surface. Broken surfaces are very light gray to light gray in color whereas the weathered surfaces are typically mottled very light gray and dark yellow orange to moderate yellow brown, occasionally moderate red to gray red. The small pits coincide with vertical burrows whose cross-sections can be seen on some weathered surfaces or on freshly broken rock.

The sandstone outcrop to the north consists of thickly bedded sandstone, which is very light gray to light gray on freshly broken surfaces. It weathers dark yellow orange to moderate yellow brown, occasionally moderate red to gray red. This outcrop is weakly pitted in exposures near the lake and at the south end of the outcrop. Except for the intervening patch of overlying colluvium and eolian sand, this outcrop would be continuous with the sandstone in the center.

To the southeast of the deeply eroded area is an arcuate zone of large flat slabs of sandstone up to 3.6 m across mapped as part of the colluvium (ENE-trending, light reddish brown area marked by a string of "B"s in fig. 12). These sandstone slabs dip gently downslope along the length of the exposure. Many are contiguous, but in some places gaps occur between slabs. These sandstone slabs are interpreted as large pieces of a well-indurated bed that have weathered from the outcrop, have been undercut by erosion of the less-resistant underlying sediment, and have moved downslope. If so, the sandstone bed from which these slabs are derived may lie beneath the overlying surficial cover a few meters upslope. It appears that this sandstone bed does not extend westward across the width of the research site as no sandstone ledge is exposed along strike in the deeply eroded area where gullies extend southward towards the edge of the road (fig. 12).

The bedrock units exposed at the surface in the deeply eroded area persist in the subsurface and were observed in Geoprobe and auger holes as portrayed in figures 14 and 15. Figure 14 is an east-west cross section along the road through augerholes AA04, AA02, and AA03. These three augerholes intercepted sandstone, clayey sandstone, mudstone, and shale. Some thin coaly beds were intercepted in AA04. The sections are dissimilar enough between the three holes that no correlation from one hole to the next seems reasonable. Unweathered bedrock was intercepted in AA02 and AA04 at depths of 14.4 m and 4.6 m, respectively. AA03 did not penetrate unweathered bedrock.

Figure 15 is a north-south cross section that extends from the sandstone outcrop area north to a point close to the lake. All holes south of the road are shallow. Thus, bedrock information is limited in that part of the cross section.

Structure

The sedimentary section on the peninsula is everywhere very gently dipping, and the regional dip is on the order of 1-2^{o} to the west (Gardner, 1957). Locally in the Skiatook Lake area, however, the section is faulted and gently folded. Small domal structures occur in the section that are often the locus of oil accumulation in the subsurface.

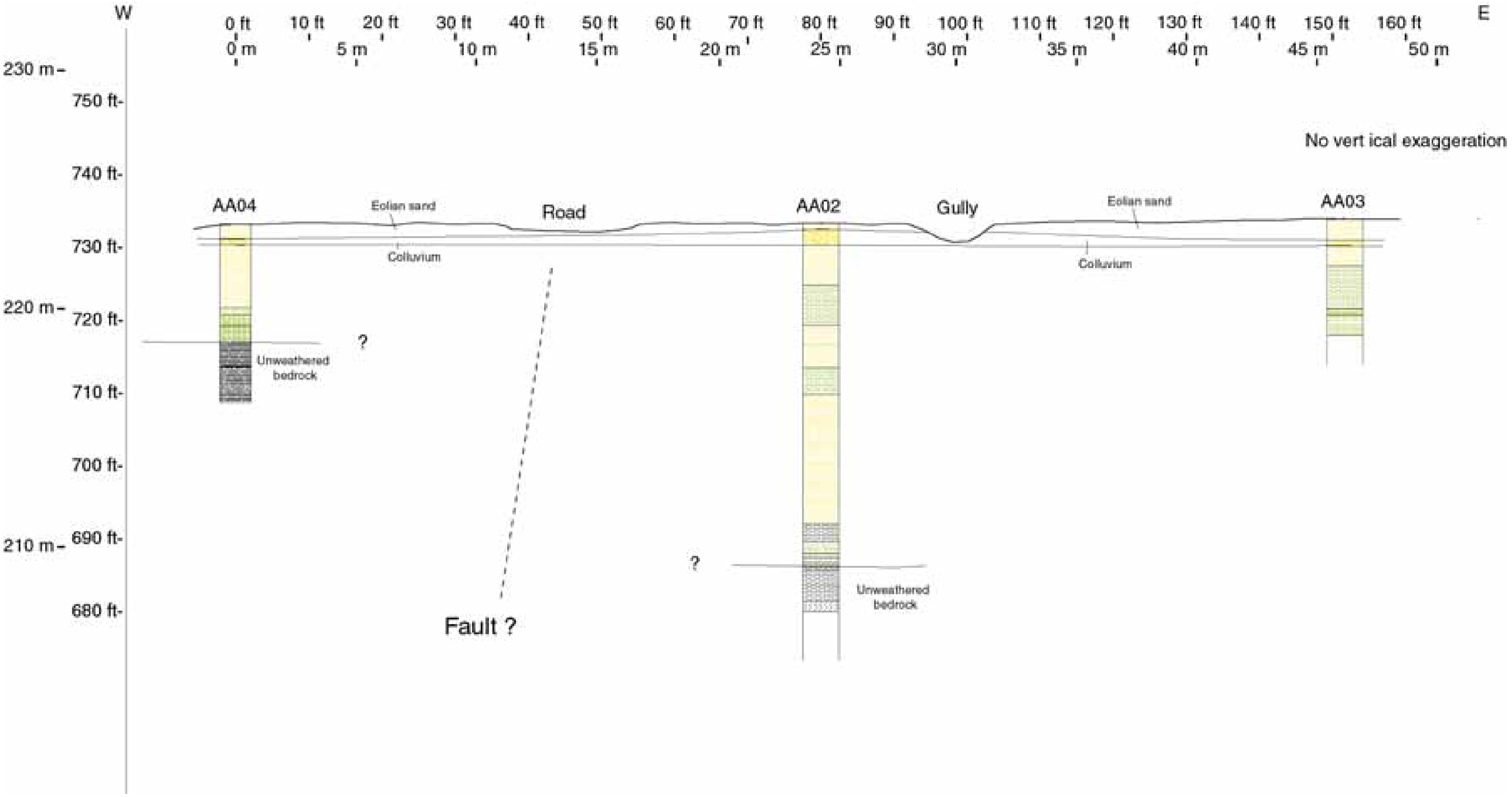


Figure 14. East-west cross section along the road showing thin surficial sediments and underlying bedrock. Note change in depth of weathering between hole AA04 and AA02. See figure 12 for location of cross section.

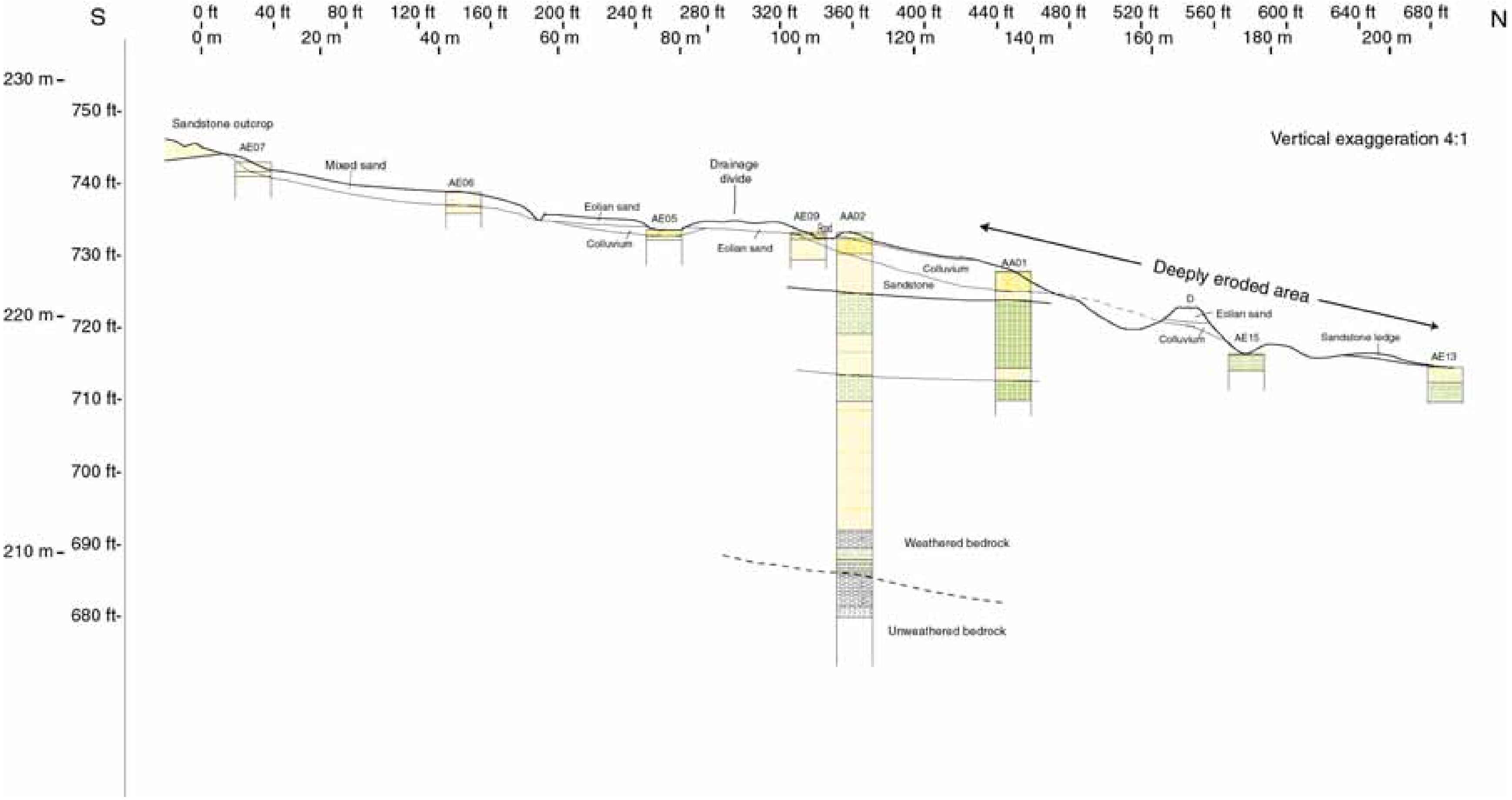


Figure 15. North-south cross section extending from the sandstone outcrop area north to a point close to the lake showing surficial sediments and underlying bedrock. See figure 12 for location of cross section.

The sandstone bedrock ledge in the northern part of the deeply eroded area extends southwest to the outcrop in the center of the deeply eroded area, interrupted only in one area by overlying uneroded colluvium and eolian sand. Along its extent, the upper contact appears to rise in altitude from about –35 feet with respect to datum to about –29 feet with respect to datum (figs. 8 and 12). If so, this information suggests a local southeasterly dip for this sandstone bed, although the strike and dip are not measurable without at least one additional reference point because the outcrop is so linear. In the central sandstone outcrop, one bedding surface in the lower part of the exposure shows a series of filled fractures, the most prominent of which are oriented 040°, approximately parallel to the trend of the sandstone outcrop. These fractures may be related to a local structural feature, such as a small fault or the crest of a small anticline or both. The transition from weathered bedrock to unweathered bedrock in both AA04 and AA02 takes place where the section is changing from dominantly sandstone to dominantly shale (fig. 14). This transition is offset about 10 m vertically between the two holes. A fault may be inferred between AA04 and AA02. The apparent dip on the sandstone beds at the surface in the deeply eroded area may represent drag on a normal fault

Specific structural interpretations cannot yet be drawn from the exposures in the deeply eroded area or from the drillhole data and mapping of the rest of section 13 may have to be completed to determine whether faults or small folds are present.

Surficial Geology

The surficial deposits consist of colluvium, eolian sand, and mixed eolian sand and sandy slopewash. These units are exposed in the deeply eroded area north of the road and in the more gently eroded areas west and southwest of the two pits south of the road (fig. 12). The colluvium ranges from a thin layer of weathered granule-pebble sandstone-clast conglomerate to large boulders of sandstone within a sandy matrix. The weathered granule-pebble sandstone-clast conglomerate is the most widespread facies, occurring in the gently eroded areas west of the pits and around most of the margin of the deeply eroded area. These granule to pebble beds blanket parts of the deeply eroded area forming small terraces (figs. 8 and 12) adjacent to some of the stream channels. The granule to pebble colluvium and overlying eolian sand are well exposed in the soil pedestal in the north-central part of the deeply eroded area (fig. 16). Locally, a clayey colluvial facies is present. This facies consists of isolated sandstone clasts in a clayey matrix comprised of weathered shale. It appears to consistently underlie the sandy granule-pebble colluvium, but additional exposures need to be documented to confirm that relationship.

The boulder beds in the colluvium occur downslope from outcrop or subcrop of resistant sandstone beds on the northwest and northeast sides of the deeply eroded area (marked by “B” in the northern part of fig. 12). The boulders that occur about 10-15 m north-northeast of the sandstone outcrop at the west edge of the deeply eroded area (fig. 12) are identical in appearance (presence of crossbeds, color and weathering characteristics) to the sandstone in the outcrop and thus are inferred to have been derived from it. A train of sandstone cobbles and boulders is also exposed in the small scarp along the northeast edge of the deeply eroded area. These boulders resemble the sandstone slabs found to the southeast (discussed above) and may be derived from that outcrop/subcrop area.

Throughout the central and northern parts of the site, eolian sand forms a discrete layer that mantles the underlying colluvium and is widely exposed at the surface in areas around and within the deeply eroded area (figs. 12, 14, 15, and 16). It is composed of very well sorted, fine to very fine sand grains. Thin pebbly layers and isolated sandstone pebbles occur within the lower part of the eolian sand suggesting that the eolian sand has been locally reworked by slopewash, since the sandstone pebbles are derived from upslope exposures of weathered bedrock. An A soil horizon, characterized by stained fine sand, is developed in the upper part of the eolian sand layer (fig. 16). In the south part of the site, the eolian sand appears to be mixed with sand derived from weathering of the sandstone bedrock exposed there.

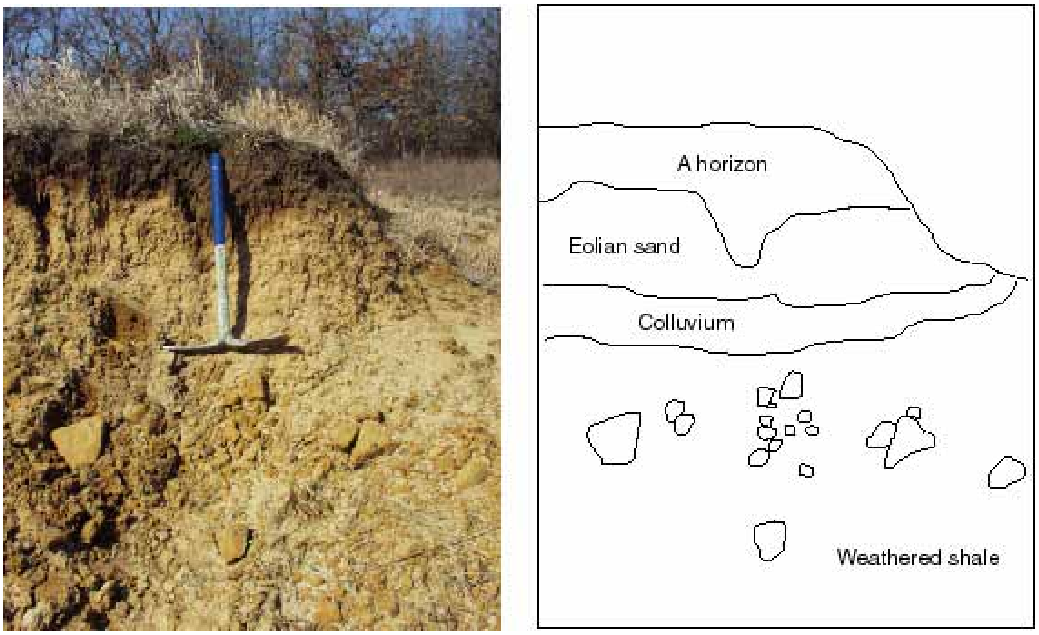


Figure 16. Stratigraphic section exposed in a soil pedestal within the deeply eroded area. The pick is 0.65m long. Sandstone clasts below the pick are eroded from the colluvial layer.

Hydrology

During wet periods such as early March 2001, water flows across the surface in small drainage ways and water-saturated ground occurs at the surface at several localities within the research site Most of the drainage ways and saturated localities are marked in blue or with a marsh symbol on figures 4 and 12. Present, but not mapped in figure 12, is modern alluvium that occupies the valley floor under the main channel for a few tens of meters upvalley from the lake. Based on the observed textures of the units exposed in the deeply eroded area and the location of wet places, it seems likely that the colluvium and the eolian sand are the most permeable units on the site. Among the bedrock units, it seems likely that the sandstone beds are the most permeable. Following rainfall, water seeps from the sandstone outcrop in the center of the deeply eroded area days after the rest of the site has dried up (fig. 10). Ephemeral salt crusts form on the lower parts of the sandstone outcrop and on the surface of the alluvium as drying occurs.

“B” Research Site

The “B” site occurs in the southeast corner of 28, T22N, R11E in southeastern Osage County about 5.3 km southeast of the “A” site. It consists of a mostly open area on a hillslope and terrace at the west end of a small bay off the main part of Skiatook Lake. Two small streams feed into the bay to the north and south of the research site. The open area is surrounded by mature oak forest that covers the adjacent hillslopes. Access roads cross the site and traces of an older roadbed marked by limestone gravel occur in the central part of the site. The open area is occupied mainly by grasses and forbs, cut and fill, pits, salt scars and a few isolated oak trees and a few small groves of oaks (figs. 18 and 19).

At least three tank batteries have been constructed at this site. An active tank battery and adjacent pit about 26 m across occur in the south part of the site. A salt scar extends from the east edge of the pit berm down to the lake (figs. 18 and 19). An old tank battery site, presently (2002) marked by a flat graded area with some piles of rubble, occurs in the central part of the site (fig. 19). A second salt scar extends down to the lake from the east edge of this graded area. Two tanks were removed in 1999. A tank, injection well, and pit about 10 m across occur in the north part of the site and a third salt scar extends downslope towards the lake from the east edge of the pit berm (fig. 19). This salt scar terminates in a shallow pit separated from the lake by a low berm. An additional injection well occurs on the northeast part of the site across the north creek (fig. 19).

Oil-saturated soils occur on the hillslope to the west of the southern tank battery. They are associated with breaks in two pipelines (unmapped) that traverse the upper part of the site. Another area of oil-saturated soil occurs just east of the pit adjacent to the southern tank battery. The 1960 aerial photo suggests that a tank that predates the present pit was located at this site. Three small areas of oil-saturated soils are located near the stream in the northern part of the site. They are also near old pipeline breaks.

The salt scars below the 3 tank batteries were remediated in the fall of 1999 by removing 15 cm of salty surface soil, replacing it with clean soil, covering the areas with straw, and seeding with winter wheat (G. Berschue, U.S. Army Corps of Engineers, 2001, oral commun.). Salt crusts are common on the remediated areas and have also been observed in a barren patch of saline ground near the lake’s edge (fig. 19). Growth of planted grasses was reasonably successful the first growing season (2000), but most of the grasses have since died, especially below the active pit.

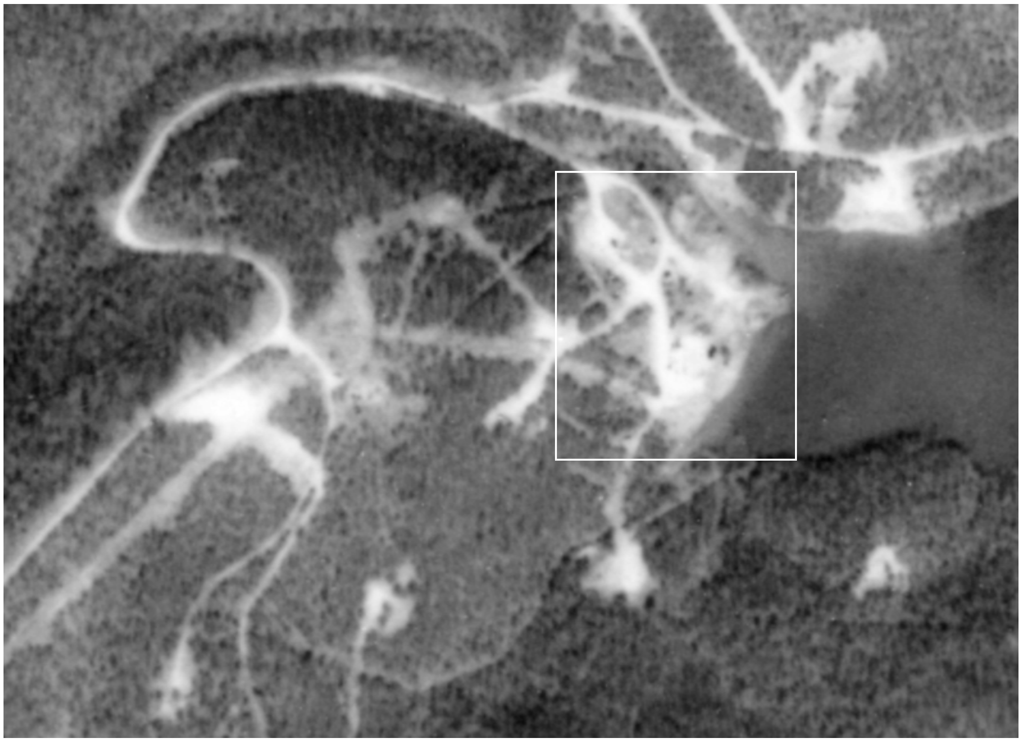
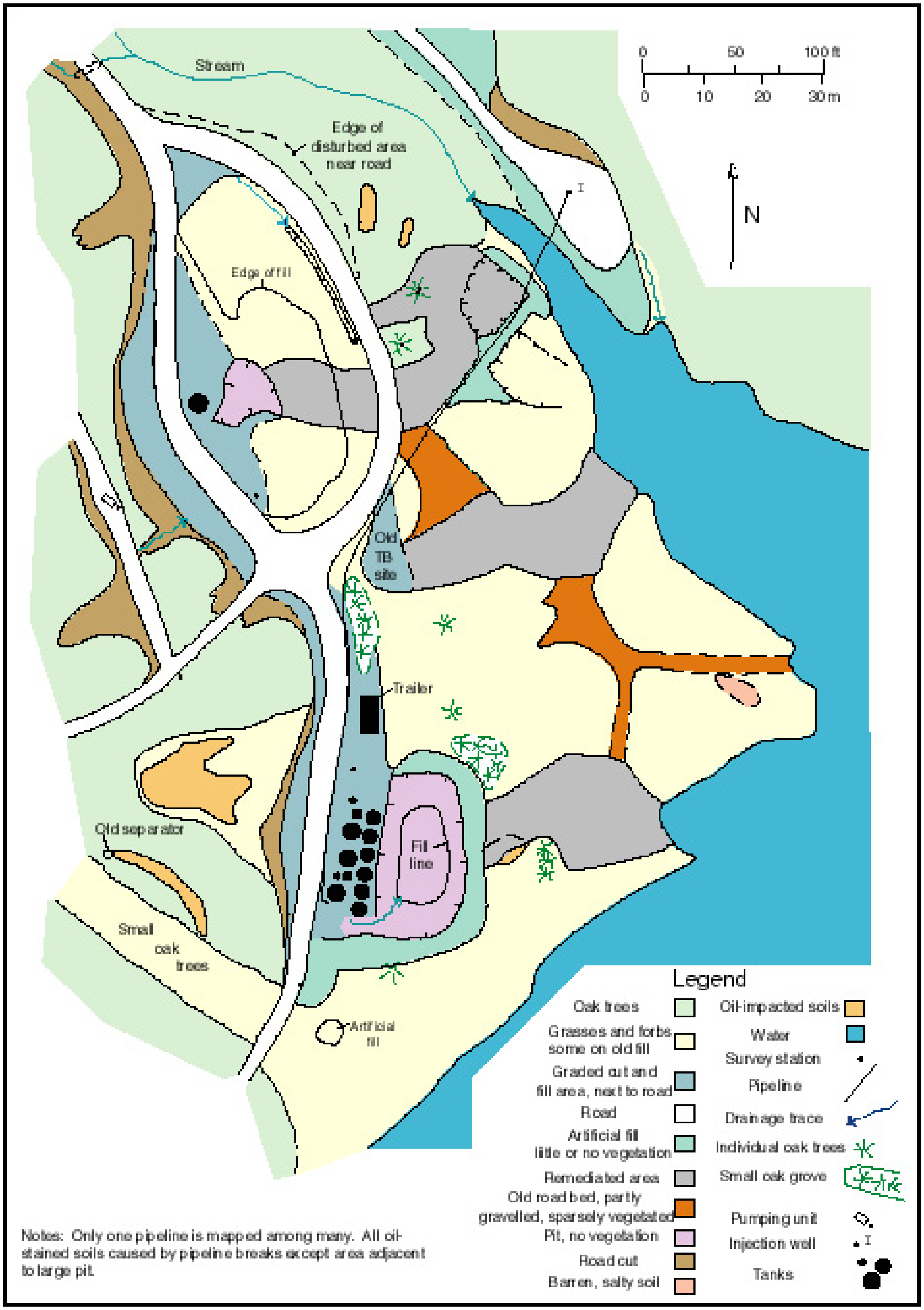


Figure 17. Aerial photo (1995) of the "B" research site at west end of small bay (outlined in white).

Figure 18. Aerial view of grassy area with active tank battery, pit, salt scar, and Skiatook Lake, south part of site "B." The lake level is above the normal pool elevation. Photo by Ken Jewell, U.S. Environmental Protection Agency, Ada, Oklahoma.



Notes: Only one pipeline is mapped among many. All oil-stained soils caused by pipeline breaks except area adjacent to large pit.

Figure 19. Features and vegetation map, "B" research site.

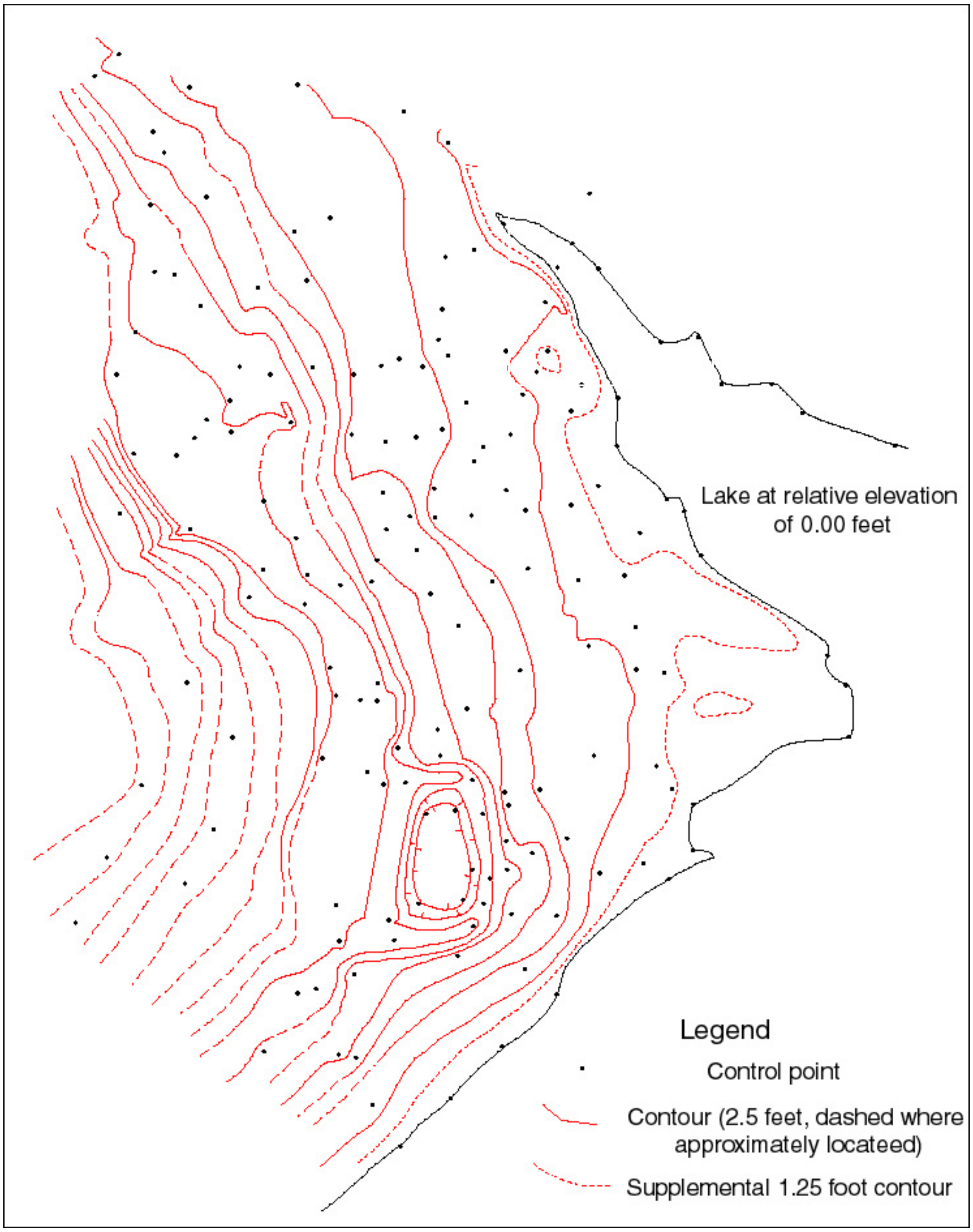


Figure 20. Topographic map of the “B” research site

The entire site slopes generally eastward towards the lake or the small creek (fig. 20). The lower parts of the site adjacent to the lake and north stream form a gently sloped terraced area. During lowstands of the reservoir, it is apparent that the north and south stream channels are incised below the level of this terrace.

Lease History

As with the “A” site, the following lease history is summarized from files of the Bureau of Indian Affairs in Pawhuska, OK. This lease was initially drilled in 1938.

Production began in 1939. The initial target was the Bartlesville Sand (local name). The productive unit proved to be the Cleveland Sand (local name). The Cleveland Sand occurs at depths of 260-305 m below the surface. Oil is localized by a small, northeast-trending dome with about 10 m of structural relief. The initial production was solution-gas driven. Waterflooding was initially investigated in 1948 and began in late 1951 when a single salt-water disposal well was drilled into the productive unit and used to test the potential for waterflooding. A full-fledged waterflood was proposed in March 1953 and began shortly thereafter. In January 1953, there were 10 producing wells on the lease averaging 21 bbls/day total oil production. Through January 1953 the lease had produced a little less than 110,000 bbls of oil. Production continues today at approximately 10 bbls/day for the lease (S. Hall, lease operator, oral commun., 2002).

Geology of the "B" Site

The entire site is underlain by bedrock composed of 1) near-surface weathered shale, and minor siltstone and sandstone and 2) similar underlying unweathered bedrock. Eolian sand and sandstone-clast colluvium of varying thickness cover bedrock on the hillslopes and thicker eolian sand, colluvium, and alluvium cover bedrock in the terraced area adjacent to the lake (fig. 21).

Bedrock Geology

Lithology

The bedrock units mapped at the surface at the "B" research site are part of the Pennsylvanian Wann Formation (Gardner, 1957). The lower shale member of the Wann underlies the entire area of figure 21. Thick sandstone beds of the Clem Creek Sandstone Tongue crop out upslope west of the map area and are the likely source of many of the sandstone clasts that occur in the colluvium and alluvium at the site.

The shale is well exposed in the road cut on the hillslope west of the northern tank and injection well. The upper 0.5 meters of the shale weathers moderate red orange to moderate red brown and grades downward to weathered shale that is light olive gray, yellow gray, and, locally, very dark yellow orange in color.

Two to three thin sandstone beds, in aggregate probably less than 1 meter thick, occur in the site area. They crop out in the bottom of the north streambed just upstream from the lake (fig. 21). From there to the east, their trace is covered by alluvium and fill, but beyond the fill area the sandstones can be observed as large blocks of sandstone float along the steep hillslope at the edge of the lake. Similar sandstone crops out on the west side of the active pit. This sandstone can be traced southward into trees south of the site area. It is uncertain whether the sandstone beds in the stream bottom are the same as the sandstone beds exposed in the pit.

In all outcrop and float areas, the sandstone is very fine-grained, light olive gray on fresh surfaces, and weathers moderate yellow brown, dark yellow brown, dark yellow orange, and moderate red orange. It is well cemented and has very well-developed joints spaced 10-50 cm apart that cause the sandstone to break up into slabs 12-20 cm thick and as much as 1.8 m long.

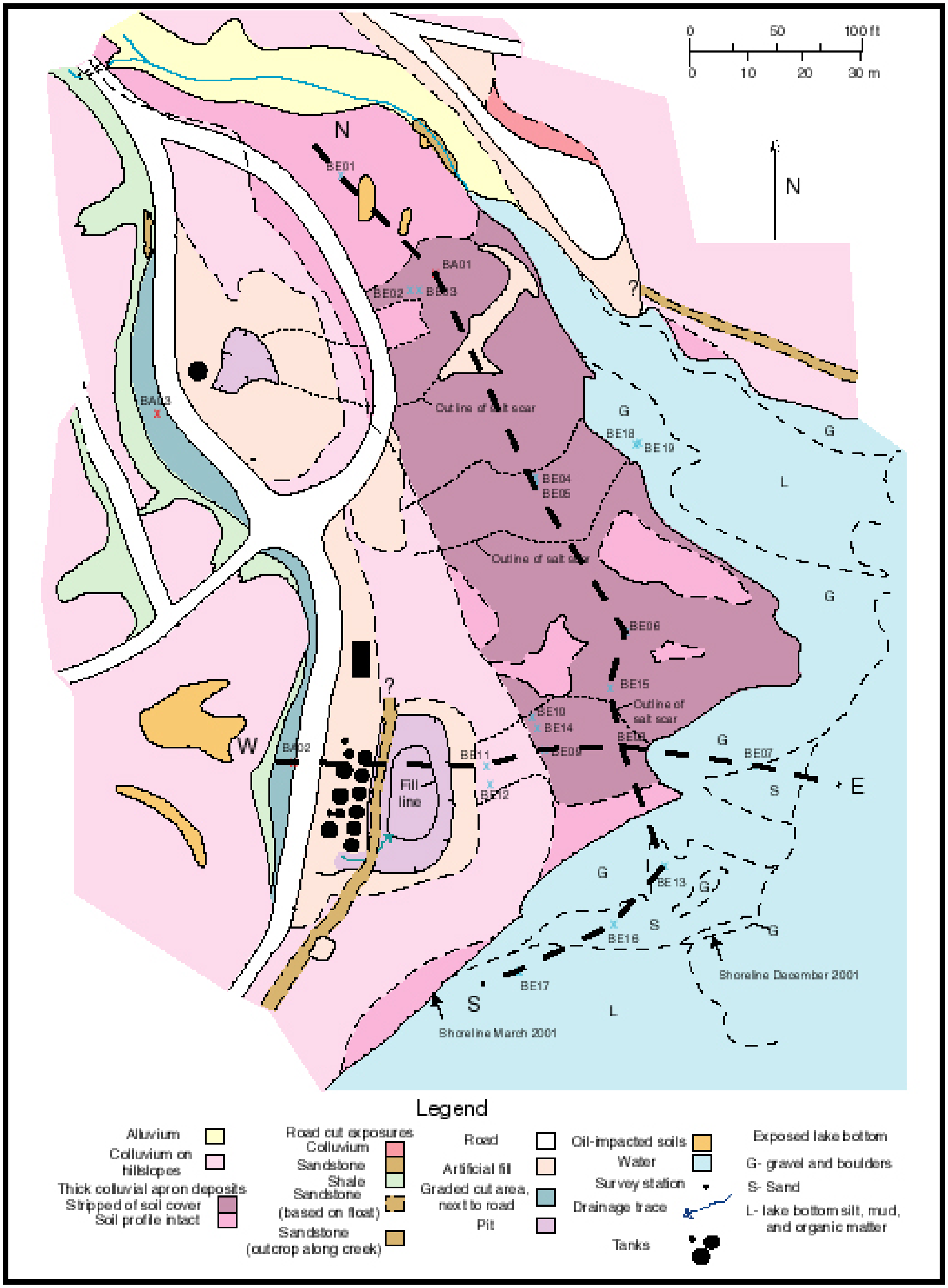


Figure 21. Geologic map of the "B" research site showing geology of the exposed lake bottom and locations of drillholes and cross sections.

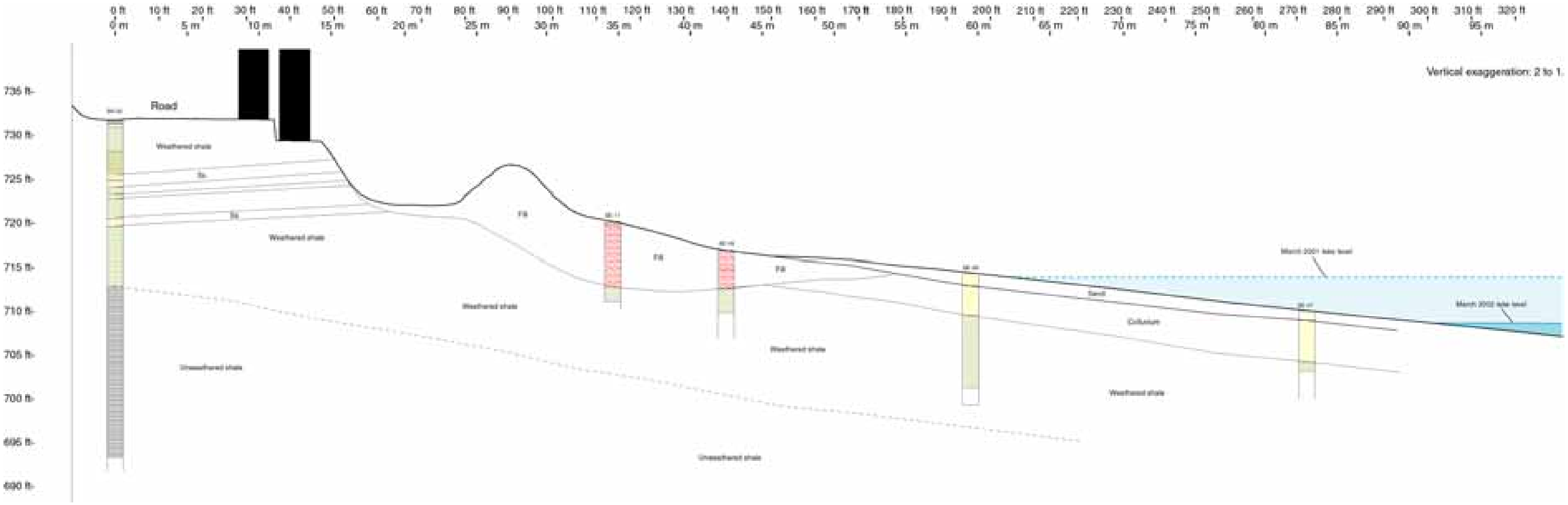


Figure 22. East-west cross section through the active tank battery down to the lake. See figure 21 for location of cross section.

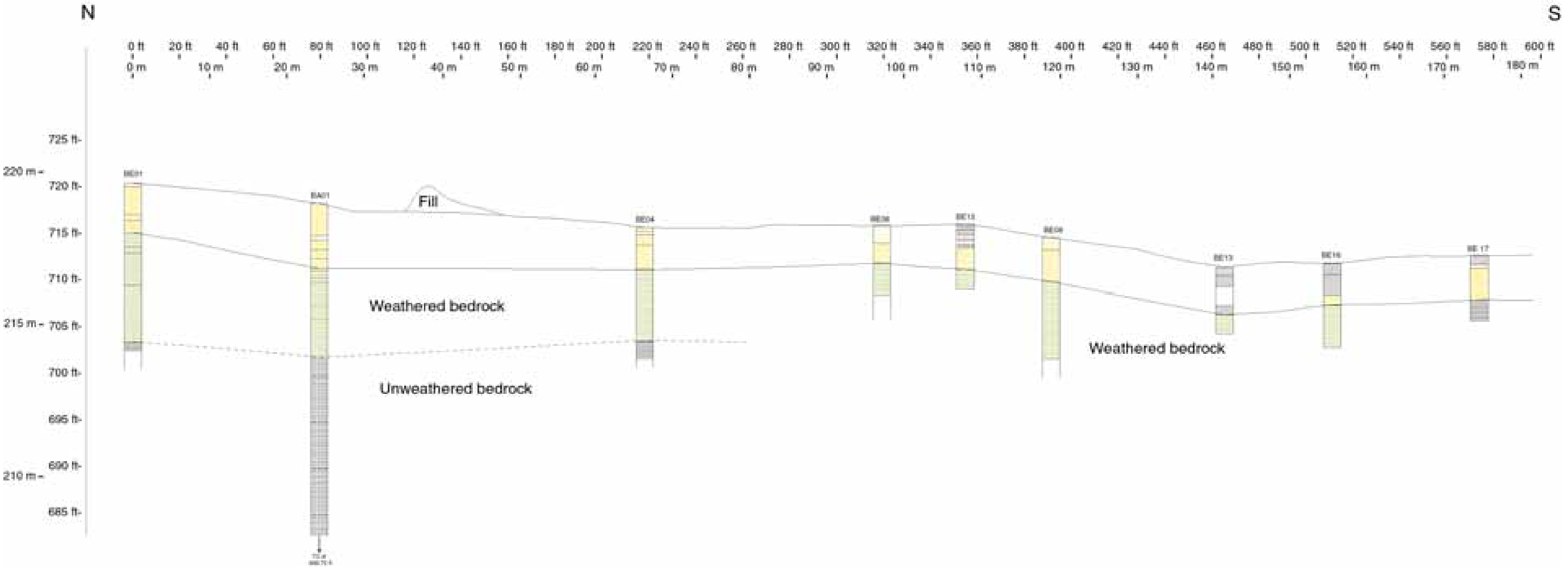


Figure 23. North-south cross section through surficial sediments underlying the terrace. See figure 21 for location of cross section.

The shale and thin sandstone beds were encountered in three augerholes (BA01, 02, and 03, fig. 21) and in the lowermost part of several Geoprobe holes (fig. 21). The bedrock geology observed in these holes is portrayed in figures 22 and 23. The thin sandstones observed in the west wall of the active pit can be correlated with sandstones at depth in augerhole BA02 (fig. 22). In all three augerholes, several very thin sandstones 2-5 cm thick were observed, some of them water bearing. The thickness of weathered bedrock ranges from 3-5.5 m. The sandstones and shales in unweathered bedrock are varying shades of gray. Thin concretionary beds typically less than 1 cm thick are common in the shale.

Exposed sandstone beds on the bluffs around the site dip gently westward, although exposures within the site are insufficient to establish the local dip.

Surficial Geology

The surficial deposits overlying the shale and sandstone consist of colluvium, eolian sand, and alluvium (along the creek to the north). On the steep hillslopes west of the three tank battery sites (fig. 21), the colluvium is relatively thin and does not form a discrete layer, but rather colluvial material occurs as scattered granules, pebbles, cobbles, and boulders of sandstone within a matrix of clayey eolian sand. These sandstone clasts sometimes rest directly on the underlying weathered bedrock and sometimes lie within or on the surface of the sandy layer.

Colluvium is much thicker (1 m, or more) on the steep southeast-facing hillslope northeast of the north creek adjacent to the injection well pad. Angular granules, pebbles, cobbles and boulders of sandstone in a sandy matrix are exposed in the road cut at the edge of the cut and fill area surrounding the injection well north of the creek (fig. 21).

Low on the hillslopes below the tank batteries is a break-in-slope (fig. 20) below which is a terrace underlain by a thicker section of colluvium and overlying eolian sand. This section averages 1.5-1.8 m thick (fig. 23). The colluvium varies from pebbles, cobbles and boulders of sandstone in a matrix of clayey to silty sand to clayey, shale-clast colluvium with only scattered sandstone clasts. The sandstone clasts in the sandy facies are usually friable and often have a thick oxidation rind.

The eolian sand layer overlying this colluvium is comprised of very fine-grained sand to clayey and silty very fine grained sand as much as 55 cm thick. The sand is very well sorted. A dark yellow brown soil horizon has formed in the upper part of it. The lower part of the eolian sand layer is dark yellow orange in color and includes granules and small pebbles of weathered sandstone suggesting some reworking of the sand, probably by slope wash. This layer erodes readily and has been stripped from much of the site (fig. 21), probably by erosion that followed road building and erosion after salt-water saturation of the soil below the tank batteries.

The alluvium along the creek is composed of sand and gravel with abundant large cobbles and boulders of sandstone. At least one terrace occurs within the mapped alluvium. Near the lake, the creek has cut down to sandstone bedrock (fig. 21) and a stream-cut terrace edge about 0.75 m high composed of 0.45 m of weathered shale and 0.3 m of overlying colluvium is exposed.

During lowstands of the reservoir (see below), lake bottom sediments are exposed (fig. 21). Areas of gravel and boulders, sand, and lake bottom silt and clay occur. The gravel, boulders, and sand represent sediment reworked from the alluvium and colluvium by wave action. Abundant leaf litter is mixed with the lake bottom silt and clay.

Hydrology

The stream at the northern edge of the site drains a small basin to the northwest and feeds into the waters of the cove. A second stream occurs south of the site (see fig. 17) and drains another small basin. Surface hydrology within the site has been altered substantially by the roads, cut and fill areas, pits, and erosion channels that originate in disturbed areas upslope from the site. Water tends to follow these artificial drainageways. Water ponds in a small ditch along the dirt road northeast of the north tank battery during wet periods.

The relatively thick section of colluvium and alluvium beneath the terrace represents a major pathway for subsurface movement of produced water releases from the pit towards the lake.

The elevation of the lake surface varies in response to water input, evaporation and other losses, and releases by the U.S. Army Corps of Engineers. The normal pool elevation is 218 m above sea level. During the course of this study the pool elevation has varied from a little over normal pool (fig. 19) to as low as 215.5 m. The lake surface elevation has an impact on the local hydrology in that it affects the local base level for ground water and surface water flow. Areas of ground water seeps are exposed under lowstand conditions.

Conclusions

Research sites “A” and “B” on Lake Skiatook provide excellent opportunities to study the impacts of produced water and hydrocarbon releases on soils, surface water, ground water, and the ecosystems they support. Site “A” is the older site where production activities ceased perhaps 65-70 years ago and the site has been partly reclaimed by natural processes. A salt scar persists on the lower part of the site north of the road and erosion continues. The upper part of the site has limited initial and continuing erosion although weathered asphalt mixed with sand is eroding from oil spill areas near the two tanks and moving downslope. These areas are devoid of vegetation. Pit “A”, with relatively fresh-appearing asphalt, is devoid of vegetation in the main part of the pit, but some grasses are starting to colonize the upper margin. Pit “B” has a greater level of colonization by grasses although the north end of the pit, which frequently has ponded water, remains devoid of vegetation. Tree-ring chronology and geochemical studies of oak trees within and adjacent to the open area may lead to a better understanding of the site history and impacts.

Movement of fluids in the subsurface of site “A” is likely to occur primarily in the relatively thin colluvium and overlying eolian sand. The persistence of vegetated pedestals within the deeply eroded area, even one pedestal that weeps salts, suggests that the salts can bypass the root zone of plants where the eolian sand and colluvium are thick enough. The upper part of the weathered bedrock may be storing and slowly releasing salt accumulated while an active source was present. The sandstone outcrop in the middle of the deeply eroded area continues to weep substantial amounts of salt suggesting that this sandstone may be a significant pathway for saline fluids in the weathered bedrock.

The two pits are an apparent source of salt for the deeply eroded area. Two gullies are eroding headward towards the position of these two pits (fig. 21). Headward erosion in other directions suggests that other sources of salt may have originally been present at site “A”, but the direct evidence is now missing. The variable pitting and mottled very light gray to red, orange, and brown colors observed in the sandstone outcrops at this site are typical of salt-damaged sandstone observed by the authors at oil production sites throughout eastern Osage County.

Site “B” has recent releases of produced water and hydrocarbon. This site provides an opportunity to evaluate the transport of produced water salts and hydrocarbons to Lake Skiatook. Aside from the physical impacts of road construction and site preparation through cut and fill, the salt scars below the three tank battery sites are the most visible impacts, although substantial erosion of the surface soil layer from much of the terrace area has occurred between the three salt scars. Isolated low soil pedestals are found within this terrace area suggesting that parts of the terrace were isolated from the causes of erosion (roads or shallow saline groundwater).

The colluvium and alluvium beneath the terrace area is a likely pathway for transport of produced water. The amount of clay in the colluvium varies across the site suggesting that sandy colluvial facies are likely to have higher permeability and be a preferred pathway. The upper part of the weathered shale bedrock may store salts to some degree, but the shale would seem to be a barrier to downward movement of contaminants except where fracture permeability is significant. The thin sands and the concretionary beds may offer some pathways for fluid movement especially where they are fractured.

A grove of small oak trees grows adjacent to the edge of the active pit berm. These trees are apparently hydrologically isolated from salt and hydrocarbon releases from the pit. Study and monitoring of these trees may lead to further insights regarding history and ecosystem impacts at this site.

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Preliminary Geophysical Characterization of Two Oil Production Sites, Osage County, Oklahoma – Osage-Skiatook Petroleum Environmental Research Project

By Bruce D. Smith, Robert J. Bisdorf, Robert J. Horton, James K. Otton, and Ray S. Hutton

Abstract

Ground electromagnetic (EM) and dc resistivity geophysical surveys were used to interpret the subsurface distribution of salinized soil, water, and bedrock at two oil production sites (A and B) on Skiatook Lake in southeastern Osage County, Oklahoma and to characterize the larger scale geologic and hydrologic setting. EM measurements were made on grids of about 1000 m^2 using a very shallow penetrating (less than 10 m) electromagnetic geophysical system (EM31). At site A, high subsurface conductivities (more than 100 millisiemens/meter, mS/m) found immediately down slope from disposal ponds extended down the local drainage to below the normal pool elevation 231 m of nearby Lake Skiatook. At site B, three areas of high subsurface electrical conductivity were clearly associated with three salt scars and extended in the subsurface below the normal level of Skiatook Lake. DC resistivity soundings were made in and around the two sites in order to characterize deeper (30-60 m) electrical properties of the subsurface lithology and ground water. These soundings and borehole electrical logs show that the shale that dominates the local lithology is moderately resistive (20 to 100 ohm meters). The shale is clearly distinguishable from sandstone interbeds of higher resistivity and saline water bearing horizons of much lower resistivity.

Introduction

Ground geophysical surveys were done at the Osage Skiatook Petroleum Environmental Research project (OSPER) sites “A” and “B” in late September of 2001. Otton and Zielinski (this volume) describe the location, geologic setting, and oil production history of the study area. The near-surface lithology at site A is sandstone, mudstone, clayey sandstone, and shale, at site B it is mostly shale with minor siltstone and sandstone. Surface salt scars caused by release of salt water as part of past oil production activities are present at both areas. Oil production at the “A” site began in 1913 whereas it began in 1937 at the “B” site. Currently only site B is still producing. Geophysical work for the OSPER project has focused on the characterization and mapping of the subsurface geology and hydrology at each site and the surrounding area. Electrical geophysical logging has been done in two core drill holes at site B.

Methods

Both electromagnetic (EM) induction and galvanic dc resistivity survey methods were used at each site. Though each of these methods is very effective in subsurface mapping, both were affected to varying degrees by conductive metal, primarily tanks and flow lines from production operations. Electrical properties of rocks can be measured in resistivity (ohm meter) or conductivity (siemens). The latter quantity should not be confused with conductance measurements of water, which are commonly expressed in microsiemens/cm (µs/cm), and are not a measure of the volume electrical conductivity but the point-to-point conductivity. Normal borehole geophysical resistivity logs are commonly expressed in ohm meters. Geophysical terrain conductivity systems commonly measure millisiemens, which can be related to ohm meters as:

$$1/(1000^{*}\ \text{ohm meter}) = 1\ \text{millisiemens}.$$

In sedimentary rock, the bulk electrical conductivity is controlled by the porosity and conductance of the pore fluid. A porous rock containing water with a high conductance will also have a high electrical conductivity or a low resistivity. Thus electrical geophysical methods are popular in mapping plumes of saline water (Sharma, 1997). Other earth materials such as clays, siltstones, and shales can have high electrical conductivities. Therefore, high electrical conductivity is not uniquely correlated with poor water quality (high total dissolved solids, TDS).

DC resistivity sounding methods are commonly used in ground water exploration and characterization (Sharma, 1997). An electrical current is applied directly into the ground through electrodes and the resulting voltage is measured with a second set of collinear electrodes. We used a Schlumberger array where current electrodes were expanded from less than 1 meter to a maximum spacing of about 100m. Shorter current spacing was used when pipes and other metal objects interfered with larger spacings. Borehole logging contracted to Century Geophysics at site B used a "normal resistivity" method, which also induces a direct current into the earth.

The electromagnetic (EM) induction method uses a wire loop as a transmitter and another loop as a receiver. The electromagnetic field in the transmitter induces a current to flow in the earth (in proportion to the electrical conductivity) that creates a secondary electromagnetic field that is detected by the receiver. We used an EM31 system that has loops separated by 3.1 m. McNeill (1980) discusses the principles of this geophysical system. In the normal surveying geometry the transmitter and receiver loops are horizontal coplanar (vertical magnetic dipole, VMD) According to McNeill (1990), measurements with this coil configuration have a depth of exploration to about 4.5m. The measurement system can be rotated so the coil system is vertical coplanar (horizontal magnetic dipole, HMD), in which case the depth of exploration is about 2.3m.

Geophysical Surveys at Site A

DC Resistivity Soundings

The location of four dc resistivity soundings made at the site is shown in figure 1. Sounding number seven is located at the south end of the prominent salt scar discussed by Otton and Zielinski (2003). The digitized field measured apparent resistivities, interpreted subsurface

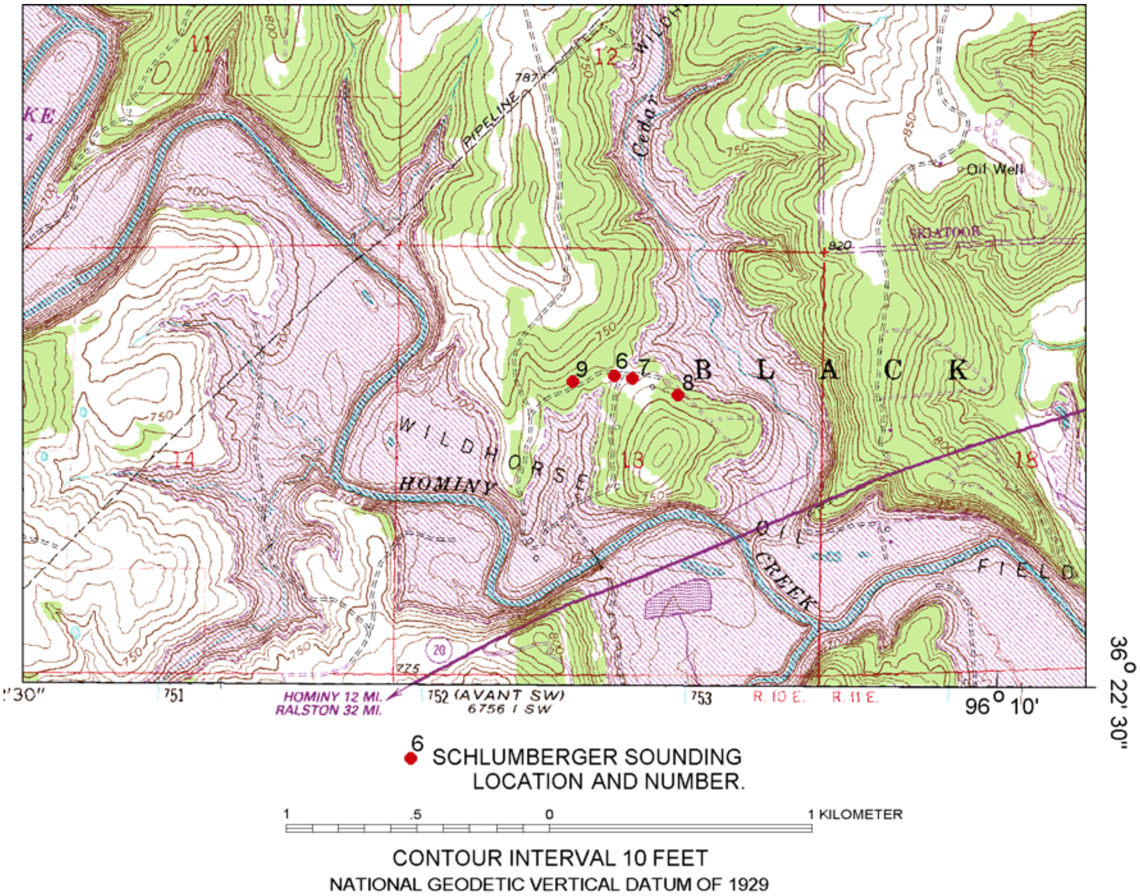

Figure 1. Location map of Schlumberger dc soundings at the "A" site. Figure 1 of Otton and Zielinski (this volume) gives the general location of study areas.

layer resistivities, and computed apparent resistivities for sounding 7 are shown in figure 2. Note that the x-axis of figure 2 represents both the distance between current electrodes for the measurement of apparent resistivity and depth of the layered earth in meters. The y-axis represents both the observed apparent resistivity and the interpreted layer resistivity. Sounding number 7 shows layers of very low resistivity, less than 10 ohm meters (100 mS/m). This interpreted low resistivity (high conductivity) zone from 1.5 to 8 m is due to saline waters that have caused the salt scaring rather than the presence of conductive clays. This interpreted subsurface zone correlates with high conductivities mapped in the EM31[1] survey. The interpreted low resistivities do not extend to depth suggesting that the saline waters have not come from a source at depth directly beneath the sounding. This interpretation agrees well with nearby auger drill holes AA04 and AA02, which identified saline water in sandstone at depths of 1.5 to 8 m.

The interpreted subsurface conductivities from the dc resistivity soundings are shown as a cross section in figure 3. The edge of the saline water layer is interpolated between soundings 7 and 8 to the east. There is a pronounced decrease in interpreted subsurface conductivity for sounding 9 in comparison to sounding 6. On possible interpretation is that westward extension of high subsurface conductivity in the sandstone is terminated at a fault contact with relatively less permeable shale.

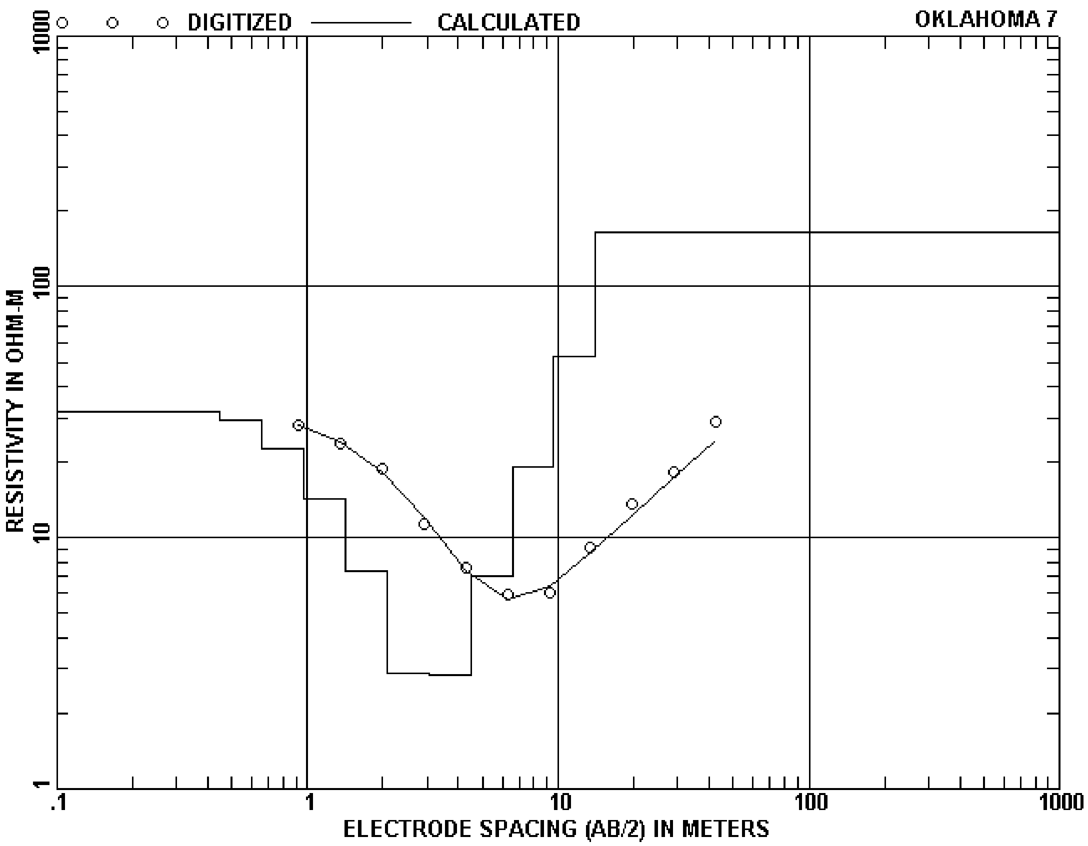

Figure 2. Plot of apparent resistivity as a function of electrode separation (m) and interpreted subsurface resistivity as a function of depth (m) for dc sounding 7. Circles indicate digitized field observations. The solid line that resembles a stair step is the layered earth resistivity model as a function of depth that produces the best-fit theoretical solution (smooth solid line).

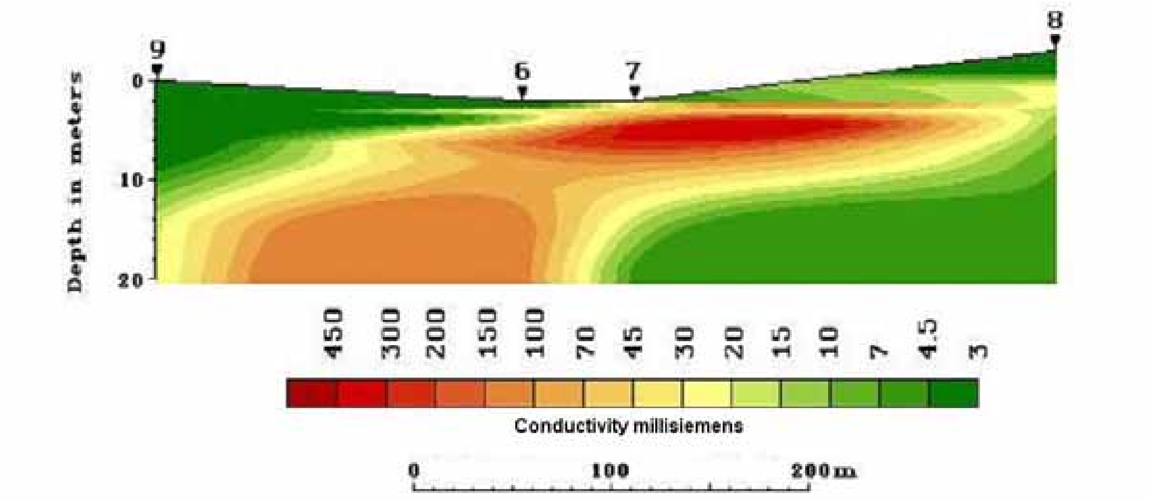

Figure 3. Electrical cross section from interpreted Schlumberger dc soundings at site A shown as conductivity in millisiemens per meter.

EM31 Survey

The survey grid was constructed using measuring tape and compass. Points on the grid were tied to survey points used for geologic mapping (Otton and Zielinski, this volume). A surveying GPS system with better than .1 m accuracy (Abbott, this volume) was used to geographically position the geophysical survey grid. Survey lines were measured North-South every 10 m along an East-West baseline. A few fill-in lines were surveyed at 5 m. Stations along the lines were measured every 1 m. Apparent conductivity measurements were made with both the vertical and horizontal magnetic dipole (VMD and HMD) configuration. Figure 4 shows the conductivities for the VMD configuration (4.5 m). Results from the shallower (2.5 m) HMD configuration are not shown because survey results are much the same. This result is consistent with the 1.5 to 8 m depth of saline water observed in auger drill holes.

High measured conductivities from 100 mS to nearly 200 mS are located entirely north of the East-West road through the middle of site A. The conductivity highs are undoubtedly the result of shallow saline waters, which probably contributed salts to the area of the salt scar. Probably sources of the saline water are the impoundment ponds located immediately south of the road (fig. 4). High conductivities are located further to the northwest than might be expected if these ponds were the only source of saline waters. Older temporary impoundment areas may also have been located further to the north during past oil production.

The high subsurface conductivities shown in figure 4 end before the drainage enters Skiatook Lake. One shallow (1.6m) well near the lakeshore contains saline water of 12,000 TDS (Kharaka and others, this volume). This well is located at the terminus of the salt-scarred area and probably receives salts originated from the high conductivity, presumably contaminated area indicated in figure 4.

Geophysical Surveys at Site B

DC Resistivity Survey

DC soundings were made along a 3-km-long E-W line that included site B (fig. 5). Sounding #1 is located near a 76-m rotary-drill hole (BR01) that was designed to define the lithology above site B and to evaluate the dc sounding that was done before the drilling. The first 10 m of the hole is weathered sandstone that measured about 500 ohm meters (2 mS) on the normal resistivity geophysical borehole logs. From 10 m to about 30 m, the lithology is predominantly sandstone of resistivity that varies from 50 to 100 ohm meters (20 to 10 mS). The natural gamma logs show some clay rich zones less than 2 m thick within the sandstone that have low neutron porosity and resistivities of about 50 ohm meters (20 mS). Shale occurs below the sandstone to the bottom of the hole where there is a small “marker sandstone” less than 2 m thick. Neutron porosity of the shale is much lower that the sandstone indicating that the shale is very tight and not a good aquifer. The actual formation resistivities cannot be accurately interpreted from these logs since a caliper log was not done. The sandstone portion of the drill holes are more likely to wash out which can have unpredictable effects on the normal resistivity log measurements.

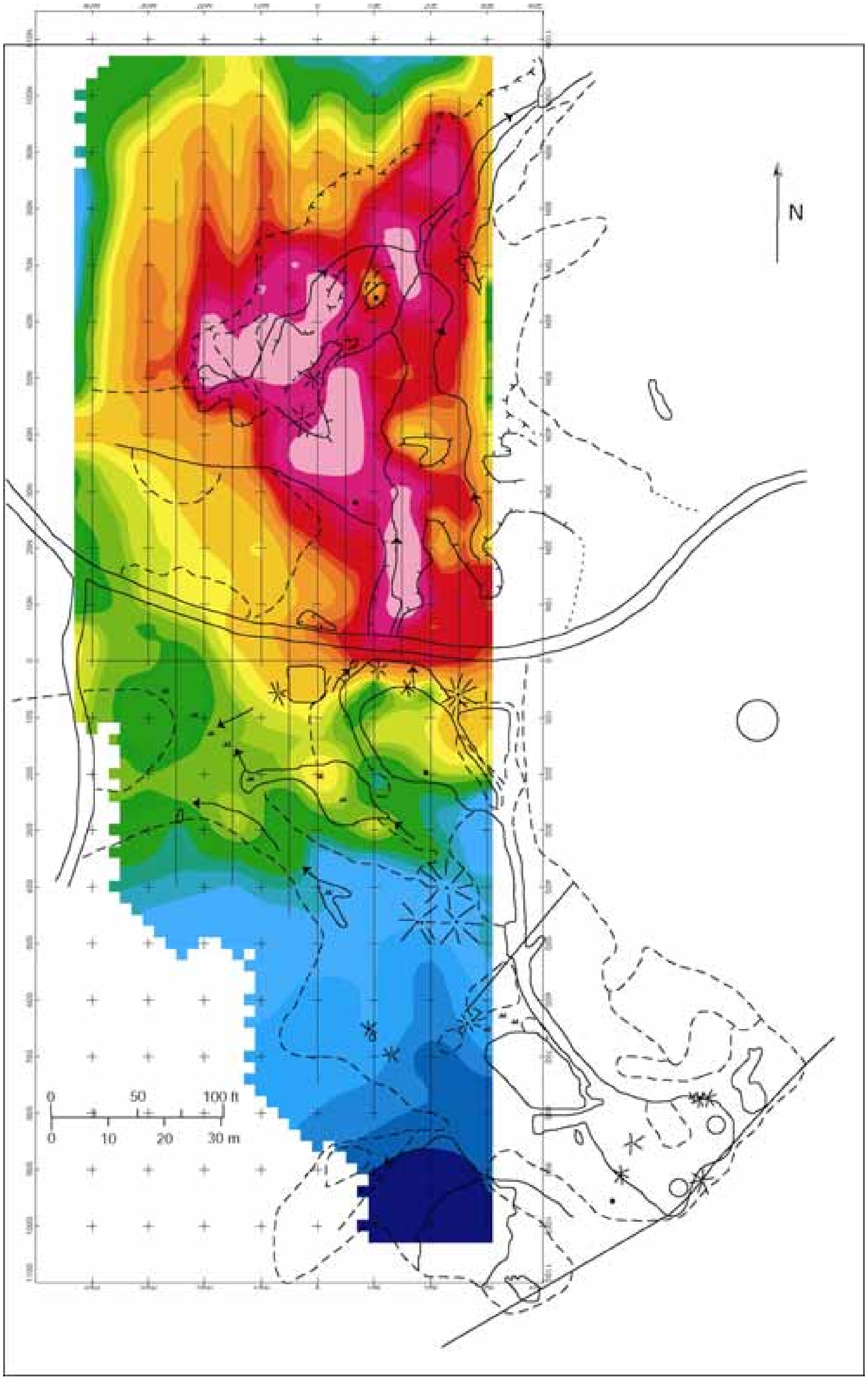

Figure 4. EM31 conductivity map for the vertical magnetic dipole (4.5 m depth of penetration) of site A at the OSPER study area. The solid lines show the 10m survey grid. Linework on the map shows features from the site geologic map (Otton and Zielinski, this volume). High conductivities are shown in the warmer colors (red and pink) and low conductivities are shown in cooler colors (green and blue).

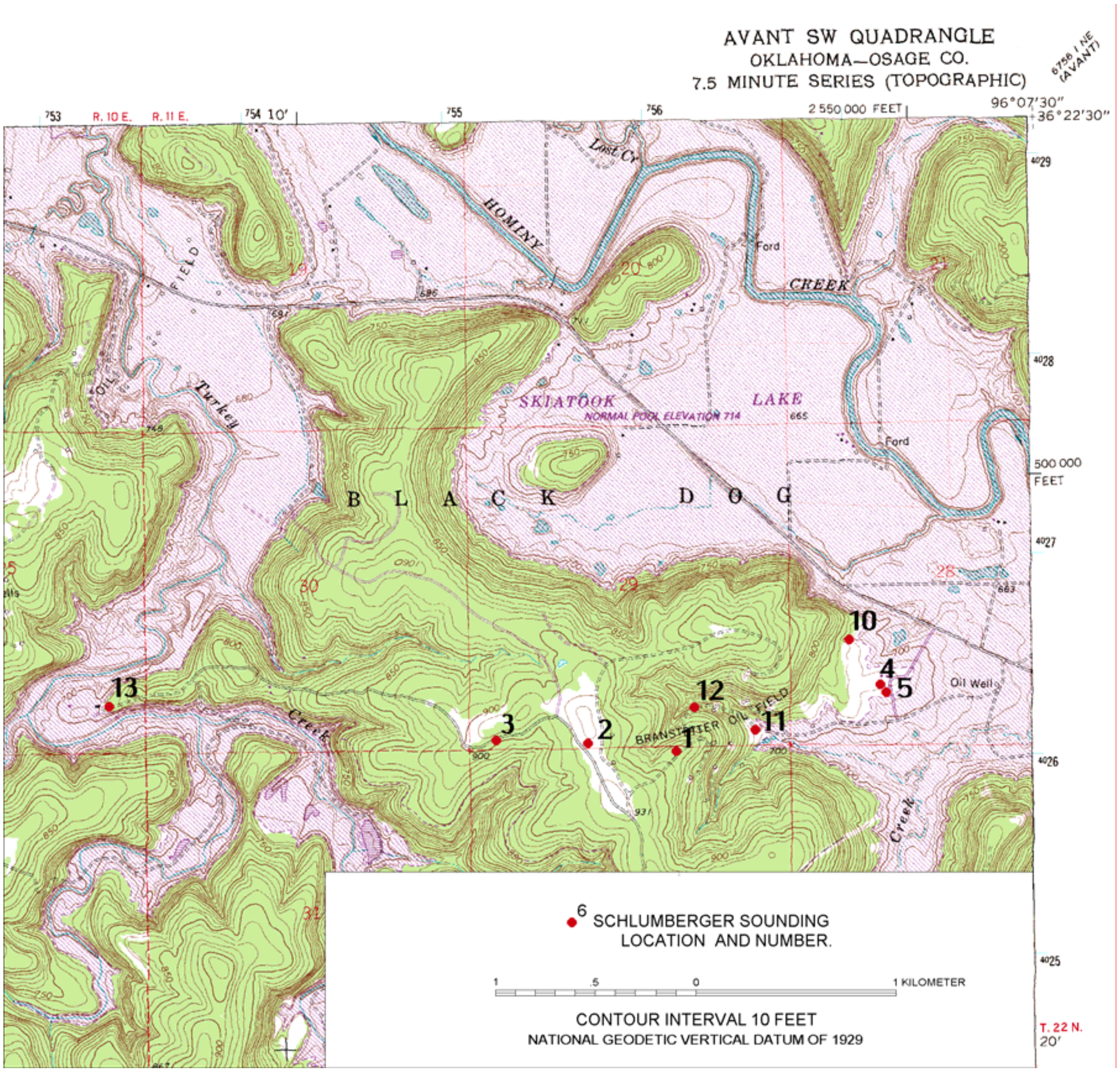

Figure 5. Location map of Schlumberger dc soundings at OSPER study site B. Figure 1 of Otton and Zielinski (this volume) gives the general location of study areas. Sounding number 11 is at study site B.

Interpreted subsurface resistivities for DC sounding #1 (fig. 6) are similar to the resistivity values (100 ohm meter) of the normal borehole log. Plotting conventions for figure 6 are the same as discussed for figure 2. The high resistivity weathered zone (1 – 10 m) has interpreted resistivities of 1000 ohm meters with a thickness of a few meters. The apparent sandstone unit thickness of 30 m agrees well with the observed lithology in the nearby drill hole but the last 20 m a lower resistivity than the upper part of the underlying shale. The lower resistivity may be due to brackish ground water within the sandstone unit. BR01 is screened at 15 –18 m where no water has been observed. The well is also screened at 26-31 m where the waters had a TDS of around 2,000 mg/l but increased in June of 2002 to 9,000 TDS (Kharaka and others, this volume).

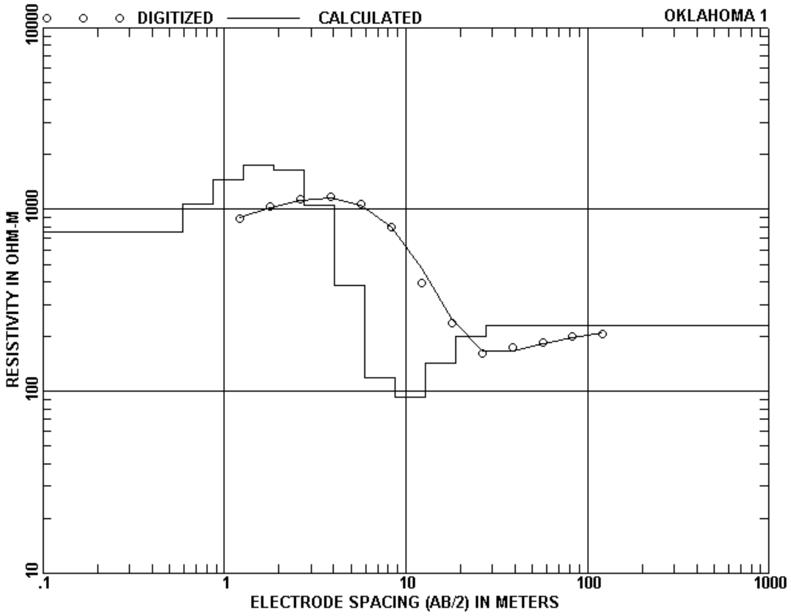

Figure 6. Plots of apparent resistivity as a function of electrode separation and interpreted subsurface resistivity as a function of depth in meters for dc sounding 1. Circles indicate digitized field observations. The solid line that resembles a stair step is the layered earth resistivity model as a function of depth that produces the best-fit theoretical solution (smooth solid line).

DC soundings 13, 10, and 5 were made at the lake edge in October 2001, when the lake was about 1.8 m below the normal pool elevation. Both the sounding near study site B (numbers 5 and 10) and away from the site (number 13) show that at the lake edge there is a subsurface shallow high conductive zone (fig. 7). This could be caused by shallow brackish water in the formation at lake level. At this time the interaction between lake water and ground water has not been studied, but additional electrical studies could shed light on this relationship.

DC sounding number 11 was made near geoprobe hole BE04 (a direct push probe) located on one of the salt scars at site B (Otton and Zielinski, this volume). The interpreted sounding (fig. 8) shows that there is a near-surface zone of extremely low resistivity (less than 3 ohm meters 330 mS/m) at 0.6 – 2.0 m depth. The low resistivity (high conductivity) is caused by saline water that is observed in this and other shallow boreholes. The saline waters are only 1-2 m thick, suggesting that the shale bedrock acts as an effective confining layer, and that the saline waters have not penetrated the shale.

EM31 Survey

Ground conductivity measurements were made at 1 m intervals along grid lines trending northwest-southeast and spaced 10 m apart. Measurements were made with both vertical magnetic dipole (VMD, 5.5 m depth of exploration) and horizontal magnetic dipole (HMD, 2.25 m depth of exploration) orientations. Figure 9 shows the conductivity map for the horizontal magnetic dipole. The northwestern-most salt scar (fig. 9) does not have an associated area of

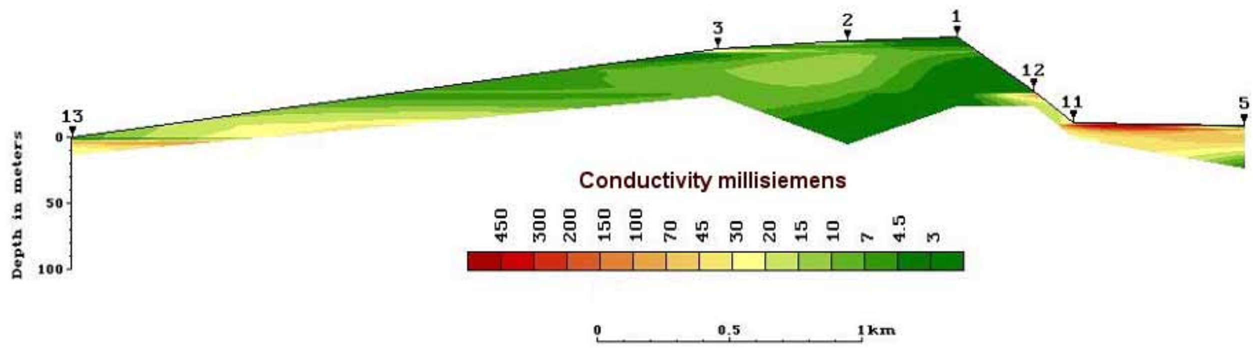

Figure 7. Electrical cross section from interpreted Schlumberger dc soundings (see fig. 5) shown as conductivity in millisiemens per meter. Sounding number 11 is at site B.

high subsurface conductivity. Metal pipes cause the conductive anomaly in this area. This area of the oil production facility also is the location of a salt-water injection well (Otton and Zielinski, this volume) for the complex.

The middle salt scar (fig. 9) has a subsurface conductivity high that is slightly offset from the center of the scar. The area of very saline shallow water is near geoprobe hole BE04, discussed previously. The zone of saline water trends northeast toward the creek and lakeshore. At the time the ground survey was done, the lake level was below normal. It does not appear that the very high salinity plume would extend under the lake. However, it should be noted that high conductivities occur along the stream channel, which is normally below lake level.

The southeastern salt scar (fig. 9) is down slope from an active pit (shown in gray) that temporarily stores both brine and hydrocarbons from the adjacent tank battery. The salt scar is likely due to brines in this pit. Very high concentrations of salt are found in the colluvium just southeast of the berm around the pit, and at times, very high TDS (several thousand mg/l) have been observed at the base of the berm. The highest subsurface conductivity associated with the southeastern salt scar was measured in an area that is normally submerged when the lake is at normal level.

Figure 10 shows the VMD conductivity data (5.5 m depth of penetration) and geologic features superimposed on a 1960 aerial photograph that was geographically registered (Abbott, 2003) to the survey area. There are two areas (indicated by “1” and “2” in fig. 10) at the southeast part of site B that were associated with oil production in 1960 was taken, but are now below the normal lake level. In February of 2002 the lake level was still low and exposed parts of the two areas. A relic portion of a berm was noted at the circular feature labeled “1” (fig. 10). One possible interpretation of the circular features on the photograph is that the darker area (“2” in fig. 10) was a holding pond for hydrocarbons. The lighter feature (“1” in fig. 10) may have been a holding pond for brine. If this is the case then the much higher conductivities in this area might be a remnant plume from this storage area. The berm may have also served to retard the flow of more recent brine release from the existing storage pit.

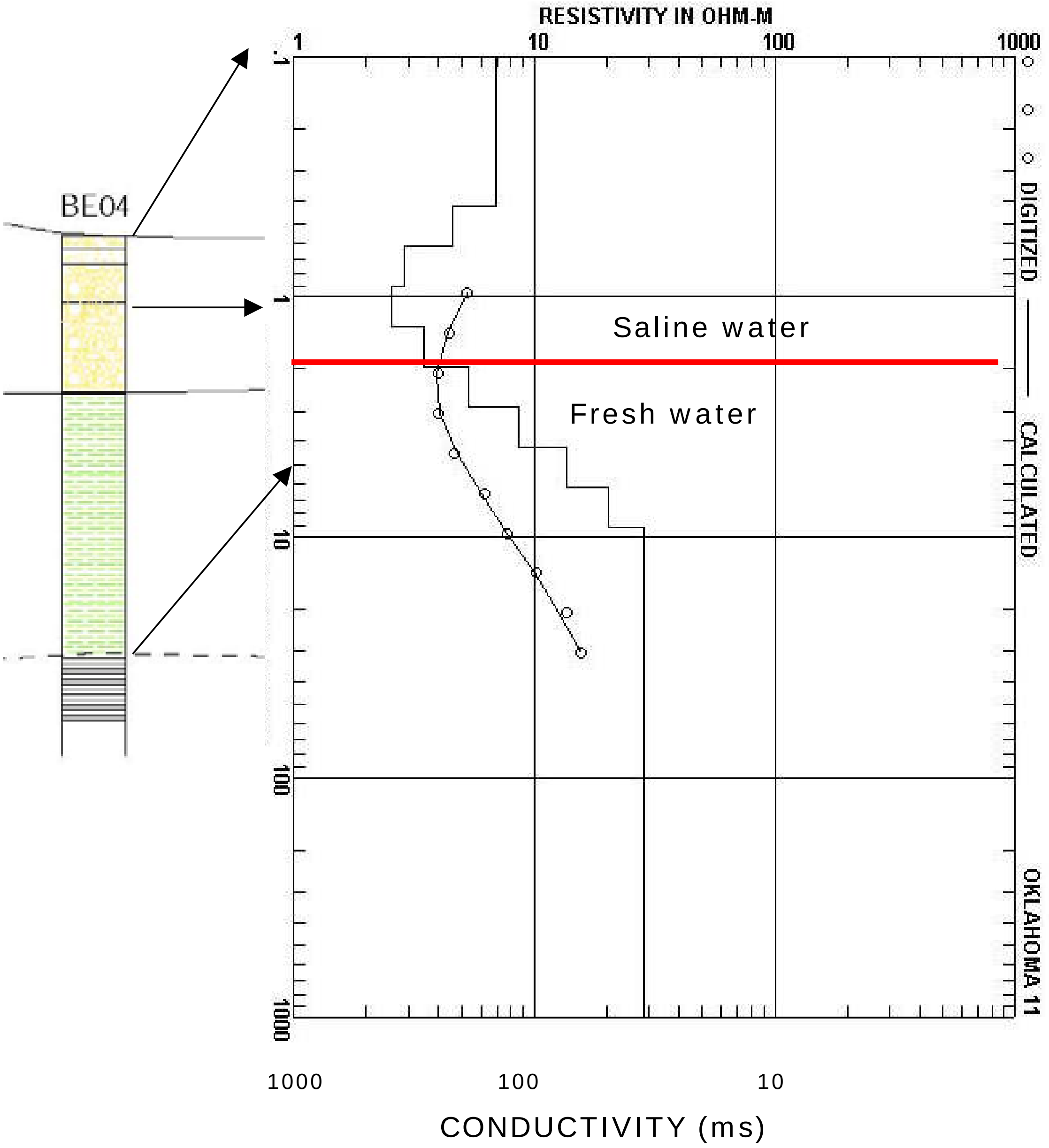

Figure 8. DC resistivity sounding number 11 and geoprobe borehole lithologic log. See Otton and Zielinski (this volume) for a description of lithologies. Yellow is colluvium, green is weathered bedrock, and gray is fresh shale bedrock.

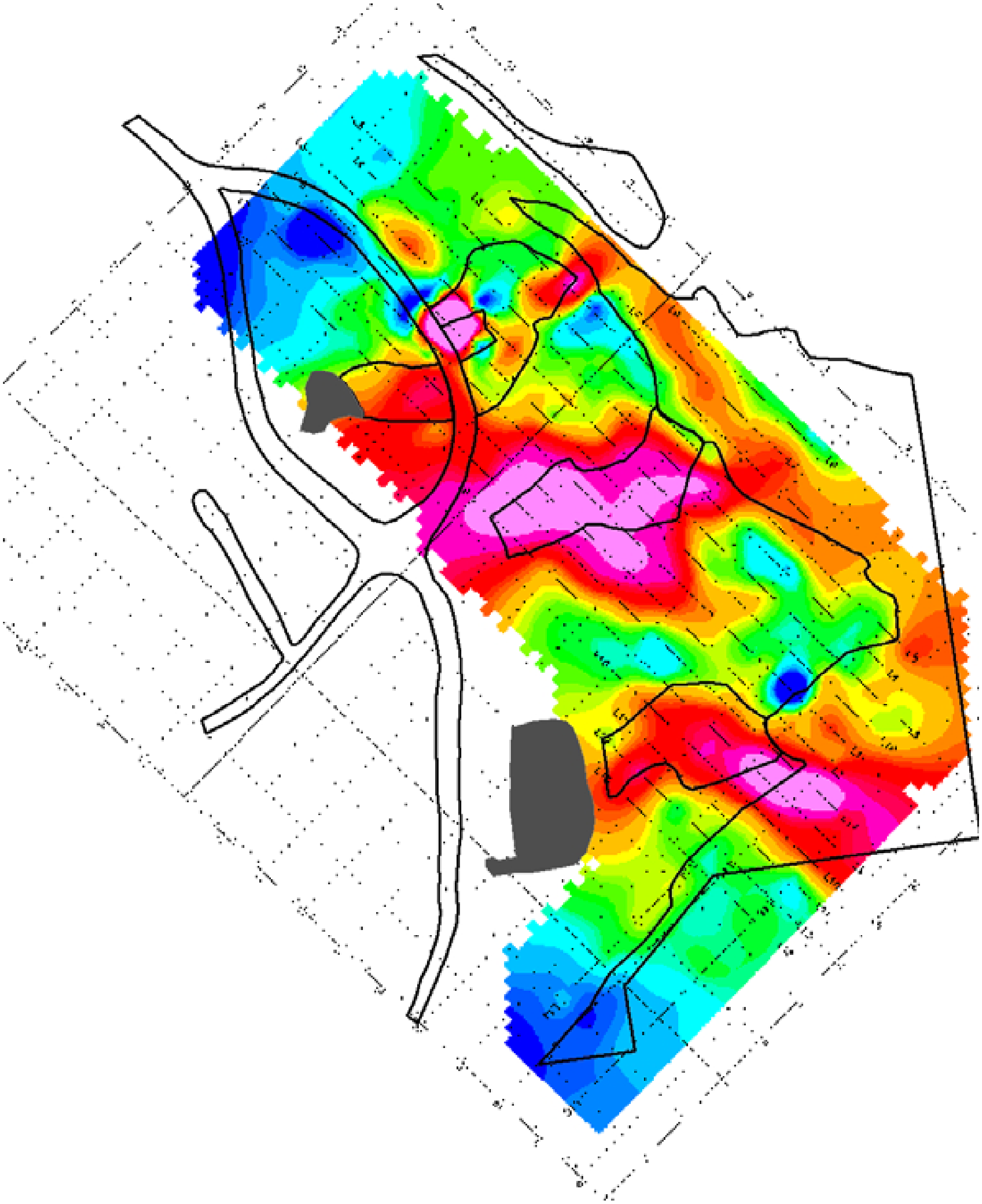

Figure 9. EM31 conductivity map for the horizontal magnetic dipole (2.25 m depth of penetration) of site B at the OSPER study area. The dotted lines show the 10m survey grid. Linework superposed on the map shows selected features from the site geologic map (Otton and Zielinski, this volume). High conductivities are shown in the warmer colors (red and pink) and low conductivities are shown in cooler colors (green and blue).

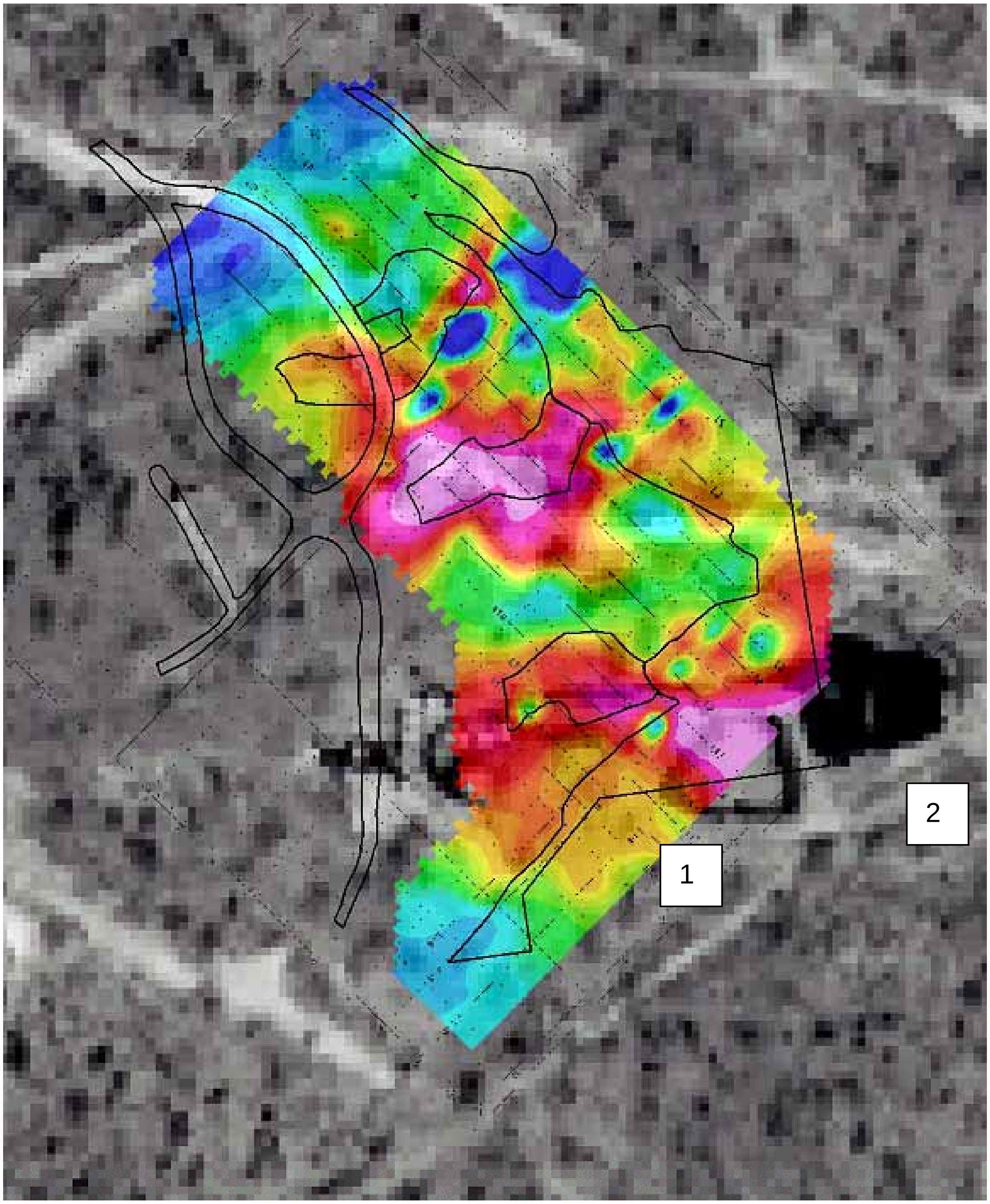

Figure 10. EM31 conductivity map for the vertical magnetic dipole (5.5 m depth of penetration) of site B at the OSPER study area superimposed on 1960 aerial photograph . The dotted lines show the 10m-survey grid. Features on the map are from the site geologic map (Otton and Zielinski, this volume). High conductivities are shown in the warmer colors (red and pink) and low conductivities are shown in cooler colors (green and blue). Areas marked 1 and 2 are likely man-made features associated with past oil production. The darker area (above the 2) is likely a hydrocarbon storage pond and the lighter area (above the 1) is likely a brine storage pond.

Conclusions

Schlumberger dc resistivity soundings show that shales and sandstones at the two study sites have moderately high electrical conductivity ranging from 20-100 mS/m (10-50 ohm meters). Generally shales have a lower electrical conductivity than sandstones due to higher clay content (McNiel, 1980). Shale in this geologic setting has low primary permeability, suggesting that ground-water flow in this unit probably is fracture controlled. Borehole resistivity and natural gamma logs support this interpretation. DC soundings on the hill above site B suggest that local sandstone aquifers carry brackish water but do not indicate highly saline waters. The lack of highly conductive clays in the geologic section reduces the likely hood that they are the source of high measured conductivity. Areas of very high conductivity, more than 100 mS/m are likely to be caused by saline waters.

DC soundings completed near the lakeshore indicate very shallow (less than a meter) highly conductive (perhaps as high as 150 mS/m) layers near site B and several km away from the contamination. Since the shallow high conductivity is at lake level, there is a strong possibility that the lake water, ground water, and sediments are interacting to cause the high conductivity zone. Additional studies are needed to map shallow ground water near the lakeshore.

EM31 ground conductivity surveys at both sites suggest that saline waters associated with salt scars have a more complex subsurface distribution than the scar exposures. At the “B” site, the saline waters are confined to the upper few meters of colluvium and do not appear to significantly penetrate the shale bedrock. At site A, saline waters are also confined to within a few meters of the surface, however the shallow bedrock is porous sandstone. At site B, saline ground water is present at shallow depth including areas that are normally submerged by the lake. All of these observations suggest that saline solutions have a high residency time in the near-surface lithology even under high recharge conditions.

Subsurface contamination from oil production practices is not always obvious. At site A, surficial hydrocarbons occur as tars from past spills and storage. Yet the geophysical data do not show that large volumes of saline water immediately below these areas. Release of saline waters down the hydraulic gradient from the surface tar has caused the local salt scar. There are several salt scars at site B, but only the middle scar appears to have a large enough volume of saline water to cause high ground conductivity.

Geophysical ground conductivity measurements have defined specific locations of subsurface saline water at both sites. These conductivity maps could be used in designing remediation methods and prioritizing areas for additional work.

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The Fate of Inorganic and Organic Chemicals in Produced Water from the Osage-Skiatook Petroleum Environmental Research Sites, Osage County, Oklahoma

By Yousif K. Kharaka, James J. Thordsen, Evangelos Kakouros, and Marvin M. Abbott

Abstract

We are involved in a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, radionuclides and organic compounds present in produced water, and their impacts on soil, surface and ground waters and the local ecosystem at the Osage-Skiatook Petroleum Environmental Research (OSPER) “A” and “B” sites. The two sites, located in Osage County, OK, are within the depleted Lester and active Branstetter leases, respectively. These leases are typical of many depleted and aging petroleum fields in southern mid-continent of USA. About 1.5 and 1.0 hectare of land at the “A” and “B” sites, respectively are affected by salt scarring, soil salinization and brine and petroleum contamination due to the leakage of produced water and associated hydrocarbons from brine pits and accidental releases from active and inactive tank batteries. Results to date show that the produced water source is a Na-Ca-Cl brine (~150,000 mg/L dissolved solids), with high concentrations of Mg, Sr, and NH_4, but low SO_4 and H_2S. With the exception of Fe and Mn, the concentrations of trace metals are low. Eventually, the bulk of inorganic salts and some dissolved organic species in the released brine reach the adjacent Skiatook Lake, a 4,250-hectare reservoir that provides drinking water to the local communities and is a recreational fishery.

For the OSPER “A” site, 35 water samples were obtained from an asphaltic pit and an adjacent weathered-oil pit, from a local stream channel and from 12 of 24 boreholes (1-35 m deep), recently drilled and completed with slotted PVC tubing. Results show that the salinity of water from the asphaltic pit is comparable to that of the produced water source. Also, we have mapped a plume of high salinity water (3,500-25,600 mg/L TDS) that intersects Skiatook Lake. Chemical and isotope analyses of the collected samples, water level monitoring and additional sampling are continuing. Results to date clearly show that significant amounts of salts from produced-water releases still remain in the soils and rocks of the impacted area after more than 60 years of natural attenuation.

About 60 water samples were obtained from the “B” site: from two brine pits, several brine pools and seeps in the impacted area, local streams, Skiatook Lake, and from 24 boreholes (1-71 m deep). Results show diluted brine and minor amounts of oil flow from the brine pits through the shallow eolian sand, colluvial and alluvial deposits to the Skiatook Lake. Its chemical composition is modified further by sorption, mineral precipitation/dissolution, transpiration, volatilization and bacterially mediated oxidation/reduction reactions.

Introduction

Oil and natural gas currently are the main sources of primary energy supplying about 63% of the energy consumption in USA, and forecasts indicate that by 2020 natural gas and oil consumption will increase by 40% and 29%, respectively (EIA, 2000). Exploration for and production of petroleum typically involves activities such as road building, site clearing and leveling, seismic surveys, and drilling. Road building and site clearing impacts the soil and biota, and in arid environments can impact air quality by added dust to the atmosphere, and vehicle traffic can introduce invasive species to undeveloped areas. Drilling can introduce mud of various compositions into the subsurface and onto the surface, and may cause oil spills or drainage of produced waters. The volume of wastes generated from about 26,000 wells drilled in USA for oil and gas in 1993, including drilling mud, circulated cement, rock cuttings, completion fluids and produced water, is estimated at 0.13-1.0 billion bbl (Kharaka and Wanty, 1995). The total number of wells drilled in the United States for the purpose of oil and gas production since 1859 is estimated to be 3.5 million in 36 states; only about 880,000 are currently in production (Breit and others, 2001). Improperly sealed, abandoned wells may act as conduits allowing the flow of high salinity water to the surface and shallow aquifers.

Environmental impacts of petroleum production arise primarily from the improper disposal of large volumes of saline water produced with oil and gas, and from hydrocarbon and produced water releases caused by equipment failures, vandalism, flooding, and accidents. In 1993, about 25 billion and 0.3 billion bbl of produced water were obtained with 2.5 billion bbl of domestic crude oil and 18 trillion ft^3 of natural gas, respectively (Kharaka and Wanty, 1995). The volume of produced water in 1970 was about one-third as great, even though petroleum production was higher (Kharaka and Wanty, 1995, Collins, 1975). This increase resulted because the volume of produced water relative to petroleum increases with time, typically reaching 98% of total fluids during the later stages of field production.

The chemical composition of produced water is variable, but commonly it is highly saline with total dissolved solids (TDS) of about 5,000-350,000 mg/L (Kharaka and Thordsen, 1992). This water generally contains toxic metals, other inorganic chemicals, and BTEX (benzene, toluene, ethylbenzene and xylene) and other organic compounds, and may contain radium-226/228 and other NORMs (naturally occurring radioactive materials) (Collins, 1975; Otton and others, 1997; Kharaka and others, 2000).

Currently about 65% of the produced water from onshore fields is reinjected into producing zones for pressure maintenance and enhanced oil recovery (Kharaka and Wanty, 1995). Deep well injection into formations with water salinities greater than 10,000 mg/l (>3,000 mg/l, with exemption from regulations) accounts for about 30% of total produced water. The remaining water is discharged into surface waters, including coastal waterways, bayous, estuaries, streams, lakes and even evaporation and percolation sumps. Prior to the Federal regulations instituted in the 1970s, disposal of produced water was by the most economic method available. Historical methods included discharge into surface streams, storage in unlined impoundments, disposal in poorly maintained injection wells, and simply running the water over the ground. Impacts of these past practices are apparent in salt scars, dead trees and other vegetation, contamination of soil and surface water, and plumes of saline water that affect groundwater supplies.

Accidental releases of produced water and petroleum and the improper disposal of produced water are national issues that concern managers of Federal, and State lands, as well as oil and gas producers and lessees, mineral rights and lease owners, State and Federal regulators, and surface landowners (USEPA, 1987; ASTM, 1999; Wilson and Frederick, 1999). In 1986, the U.S. Environmental Protection Agency (USEPA, 1987) conducted a survey of states to determine the sources of groundwater pollution. Oil and gas brine pits were identified by 22 states as a significant source of groundwater pollution; two of the states identified these pits as the primary cause of pollution.

About 20 scientists from government agencies and academia are involved in a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, organic compounds and radionuclides present in produced water, and their impacts on soil, surface and ground water and the local ecosystem at the Osage-Skiatook Petroleum Environmental Research (OSPER) “A” and “B” sites, located in Osage County, OK. In this report we present data on the chemical and isotopic compositions of surface and ground waters at the two sites and of oil-field brine and ground water in the region. Results from all the studies will be used to evaluate the long-term and short-term effects of produced water and hydrocarbon releases from these sites. Results are expected to guide estimates of human and ecosystem risk at such sites and the development of risk-based corrective actions (Billingsley, 1999). Corrective actions are particularly needed in aging and depleted fields, where land use is changing from petroleum production to residential, recreational, agricultural or other uses (Carty, and others, 1997).

OSPER Sites

The two research sites, OSPER “A” and “B” are located, respectively, within the Lester and Branstetter leases, and both are adjacent to Skiatook Lake, a 4,250-hectare reservoir completed in 1987 that provides drinking water to the local communities and is a major recreational fishery (figs. 1 and 2). The sites are located in the Central Oklahoma platform in the southeastern part of the Osage Reservation in northeastern Oklahoma. Both sites are in a dissected area of modest relief, with oak forests covering the slopes and tall grass present on most ridge crests. Geological mapping by Otton and Zielinski (Otton and Zielinski, this volume) show the area to be underlain by interbedded shale, siltstone, and sandstone. Thicker resistant sandstone units typically form the hill crests. Hill slopes are underlain by shale, siltstone, and thin sandstone beds.

The geologic and climatic settings of the Lester and Branstetter leases resemble that of much of the major southern mid-continent oil- and gas-producing area of the U.S. The leases are also typical of many depleted and aging petroleum fields in Osage County, which ranks among the top oil and gas producing counties in Oklahoma with close to 40,000 wells (Abbott, 1999). Oil and gas production has occurred in Osage county for over 100 years, but current production is mainly from stripper (<10 bbl/d) wells (averaging ~2.8 bbl/d oil and >30 bbl/d brine) that are shallow, mostly 300-700 m in depth, and produce from several sandstones of Pennsylvanian age. The six oil wells sampled for this study and located in the Branstetter lease and from fields adjacent to the Lester lease, produced 1.5-4 bbl/d oil from Mississippi lime and Bartelsville, Cleveland and Tucker sands at depths of 333-538 m; brine production from these wells

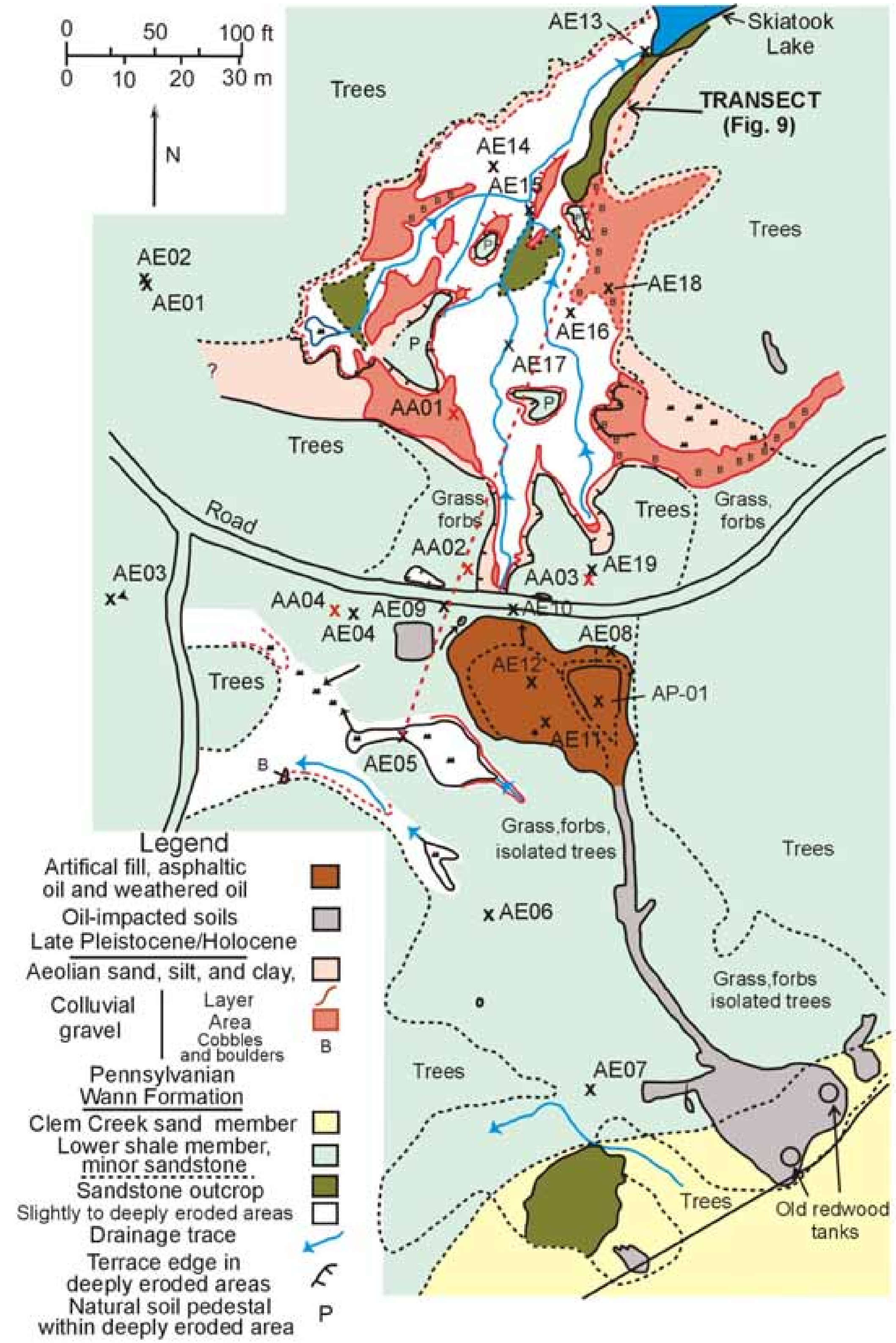


Figure 1. Geologic map of the OSPER “A” site showing the locations of the oil pits, other production features, drilled water wells and outline of the impacted area.

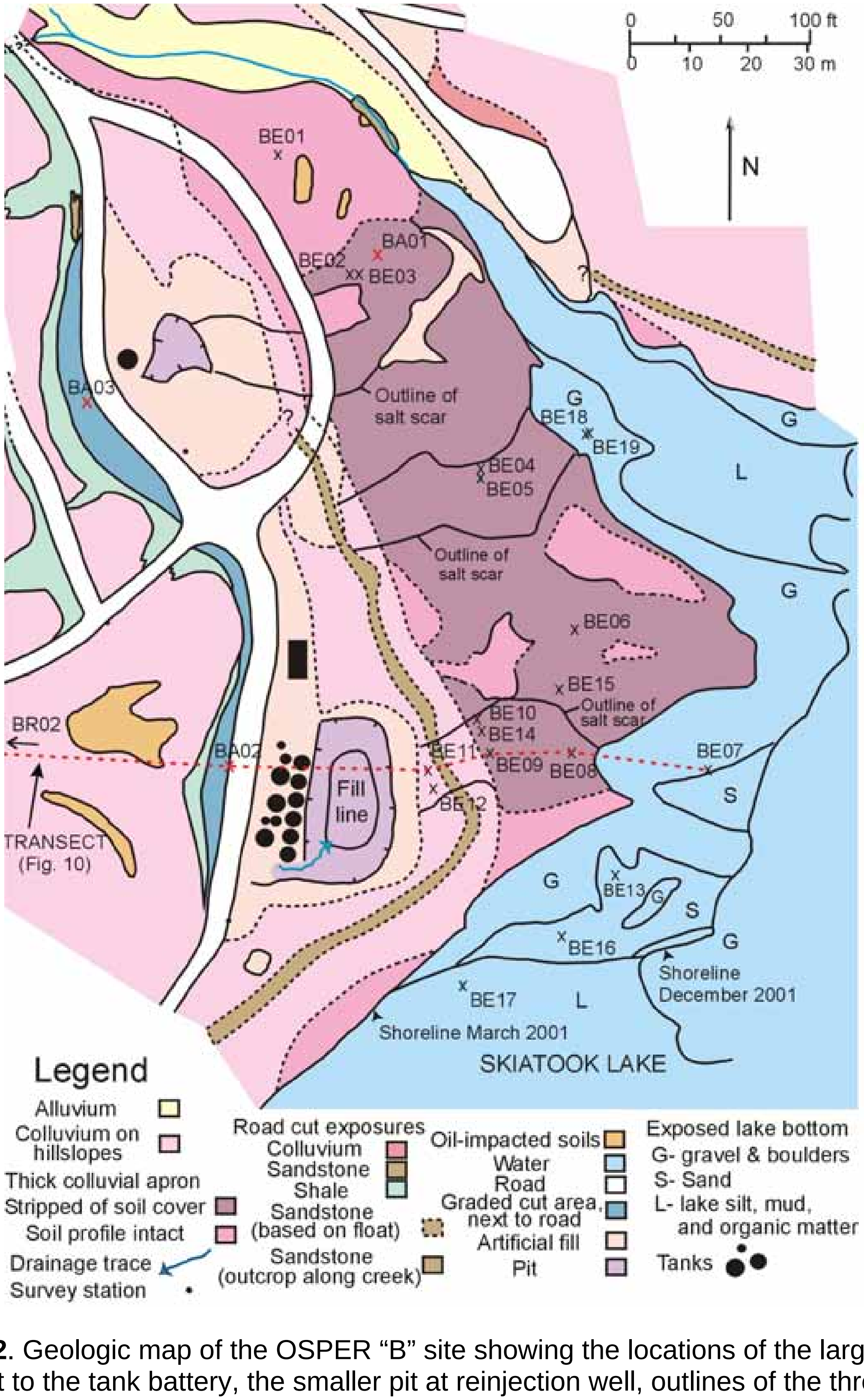


Figure 2. Geologic map of the OSPER "B" site showing the locations of the large oil pit adjacent to the tank battery, the smaller pit at reinjection well, outlines of the three scarred and remediated areas, other production features, drilled water wells and several shorelines for the Skiatook Lake.

comprised 94-99% of produced fluid. The Osage Nation holds the mineral rights, the BIA has trust responsibility, and the Army Corps of Engineers owns the surface at “A” and “B” sites.

Site “A”, located within the Lester lease in section 13, T22N, R10E, has an area of about 1.5 hectare that is impacted by produced water and hydrocarbon releases that occurred primarily 60-85 years ago (fig. 1). The site is underlain by 1) a surface layer of eolian sand of varying thickness (up to about 80 cm); 2) colluvium that ranges from large boulders of sandstone to thin, granule-pebble conglomerate; 3) weathered shale, siltstone, and sandstone; and 4) underlying unweathered bedrock. Much of the site appears to have been impacted by early salt-water releases that killed the oak forest, however a few oak trees grow as single trees or clumps of trees within the original kill area. The gently sloping upper part of the site is slightly eroded in places and has been mostly revegetated with grasses, forbs, sumac, and a few trees. The lower, steeper, more heavily salt-impacted portion has been eroded to depths of as much as 2 m. Seepage of salt water from a shallow sandstone aquifer continues and active salt scarring persists. This area drains into the Cedar Creek arm of Skiatook Lake.

Drilling at the Lester Lease started in 1912, and most of the over 100,000 bbl of oil produced by 1981, was obtained prior to about 1937. Production, which was entirely from Bartlesville sand at depths of 450-524 m, ended about 10 years ago (BIA, unpublished lease records, 2000). Oil and produced water collected in two redwood tanks at the top of the site was transported via ditch to two roadside pits at mid-site. Produced water and hydrocarbon (now highly degraded and weathered oil) releases from pipeline breaks and tank batteries, that are no longer present, are scattered around the site. However, one pit at this site contains relatively fresh asphaltic oil and high salinity brine.

Site “B”, located within the Branstetter lease in sections 29 and 32, T22N, R10E, is actively producing and has ongoing hydrocarbon releases and salt scars that have impacted an area of about one hectare (fig. 2). The site includes an active production tank battery and adjacent large pit, two injection well sites, one with an adjacent small pit, and an old tank battery. The large pit is about 15 m from the shoreline of the Skiatook Lake; all the other sites are within 45 m of the lake. Three salt scars that were partly remediated in 2000 by soil removal, tilling, and soil amendments, extend downslope from the active tank battery, the injection well/pit, and the old tank battery to the lake edge. Two small creeks cross the northern and southern parts of the site. The upper part of the site is characterized by a thin surface layer of eolian sand mixed with sandstone-clast colluvium underlain by weathered and unweathered shale whereas the lower part is underlain by 1) a surface layer of eolian sand (20-70 cm thick); 2) colluvial apron and alluvial deposits of varying thickness comprised of sandstone pebbles, cobbles, and boulders with a fine sand matrix; 3) weathered shale; and 4) unweathered bedrock.

The Branstetter lease was initially drilled in 1938 and increased activity occurred in 1947-51, when A.H. Ungerman purchased the lease. About 110,000 bbl oil was produced from the lease before water flooding started in 1953. Currently there are about 10 wells that produce 1-3 bbl/d oil, and 50-100 bbl/d brine; all the produced fluids are collected and separated in the tank battery adjacent to the large brine pit (S. Hall, oral communication, 2002). The two brine pits at this site are not lined and receive brine and hydrocarbons releases from broken pipes and tank leaks; they also receive large volumes of surface-water flow from precipitation. The brine in these pits is generally pumped into collection tanks by submersible pumps, but these occasionally fail causing filling and overflow of brine pits, as happened in November and December, 2001 for the large brine pit.

Methods and Procedures

We have carried out three major sampling trips (March, 2001; February and June, 2002) and several short trips, where only a few samples were collected, or only few field parameters (e.g. water level, conductance, temperature and dissolved oxygen (DO)) were measured. During March 2001, 15 water, four oil and three gas samples were obtained from wells adjoining the two sites to characterize the source fluids from oil wells, groundwater, and Skiatook Lake (table 1). Water samples were also collected from several seeps, pools and shallow (~20 cm) holes mainly at the "B" site. During February, 2002, about 60 direct-push, auger and rotary wells were drilled at and near the two sites, cored, completed with slotted PVC tubing and, where water was present, sampled. The water level, conductance, temperature and DO were measured in these wells in April-May, 2002, and water sampling was carried out in June, 2002.

A total of about 100 water samples have been collected from the two sites and adjoining areas. For the "A" site, 35 water samples were obtained from the asphaltic pit and adjacent weathered-oil pit, from a local stream channel and the Skiatook Lake, and from 12 of 24 boreholes (1-35 m deep) discussed above. About 60 water samples were obtained from the "B" site, from the two brine pits, several brine pools and seeps in the impacted area, local streams, Skiatook Lake, and from about 20 boreholes (1-71 m deep) recently drilled and completed.

Laboratory Measurements

All of the water samples were analyzed at the USGS Water Resources laboratories in Menlo Park, CA. Concentration of chloride (Cl), bromide (Br), nitrate (NO_3), organic acid anions, and sulfate (SO_4) were determined by ion chromatography (IC) (Kharaka and others, 2000, 2002). Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentrations of calcium (Ca) and other cations, trace metals, boron (B), and silica (SiO_2). The reported concentrations for major cations and anions carry an uncertainty of ±3%. Precision values for minor and trace chemicals are generally ±5%, but could reach ±10% for values close to detection limits (Kharaka and others, 2002).

Water isotopes were determined in the USGS Stable Isotope Laboratory in Menlo Park. Water isotopes are reported in δ – values that are expressed in parts per thousand (per mil, ‰) relative to the Standard Mean Ocean Water (SMOW). The Standard Deviation of reported values are ±0.2 ‰ for $\delta^{18}O$ and ±2 ‰ for δD (Kharaka and others, 2002).

Results and Discussion

Stable water isotopes and concentrations of selected inorganic and organic chemicals from surface and ground water samples from OSPER "A" and "B" sites and adjoining areas in Osage County, OK are listed in tables 2 and 3, respectively. The data listed for water from rotary (AR and BR) wells, drilled with fresh water that likely effected the composition of formation water, and from relatively deep auger (AA and BA) wells, that may have been subject to cross formational flow prior to well completions, are only for the last samples collected in June, 2002. Additional sampling from these and other wells will be carried out in order to distinguish chemical changes related to drilling operations and to investigate spatial and temporal changes related to physical, chemical and biological processes.

Table 1. Chemical (inorganic and organic) and isotopic composition of ground water and produced water samples from Osage County, OK.

	Ground water wells		Produced water from oil wells							
Site Name	Hurn well	Bolin well	Reynolds #4	ECC #10	ECC #3	Lebow #8	Millard #3	ECC #5	Ungermann #1	TEC T1-19
Sample #	01OS-101	01OS-102	01OS-103	01OS-104	01OS-105	01OS-106	01OS-107	01OS-108	01OS-109	01OS-110
Date	03/05/01	03/06/01	03/06/01	03/07/01	03/07/01	03/08/01	03/08/01	03/09/01	03/09/01	03/10/01
pH	6.0	7.2	6.2	6.7	6.1	6.3	6.4	6.4	6.3	6.8
T (°C)	18	18	15	22	23	34	21	22	25	24
Li	0.016	0.008	36	8.0	38	11.5	6.0	27	7.1	6.9
Na	69	36	51700	42400	55000	48600	38100	47000	39200	34100
K	0.96	0.97	690	100	650	270	110	480	150	190
NH_4^+	<0.1	0.5	38	79	45	78	56	48	59	59
Mg	25	19	1980	2350	2070	1830	1530	1910	1510	1830
Ca	57	36	11200	5400	11900	9960	6250	9980	6940	5870
Sr	0.24	0.33	500	905	514	504	521	505	502	565
Ba	0.14	0.21	451	339	461	879	311	309	396	12
Mn	0.002	0.35	6.0	2.8	10.0	0.93	1.28	7.5	0.95	5.4
Fe	0.01	0.12	50	27	31	67	28	24	38	126
Cl	216	24	110000	82100	113000	99500	75400	101000	78500	70100
Br	0.86	0.13	346	285	364	346	335	320	338	257
SO_4	45.1	18.3	0.32	0.23	0.37	0.69	0.16	0.37	0.23	81
HCO_3	72	269	109	244	105	185	146	118	182	280
NO_3	5.2	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H_2S	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	2.5
SiO_2	26	14	<16	<16	<16	<16	<16	<21	<21	<16
B	0.018	0.070	8.8	2.9	8.7	3.6	1.8	6.9	1.8	2.4
TDS	518	420	177000	134000	185000	162000	123000	162000	128000	114000
DOC		0.4	5	3	3	3	2	6	7	4
Phenols (total)			0.10		0.11	0.12		0.18	0.07	0.12
Benzene			0.77		0.70	0.49		0.90	0.23	0.34
Acetate	<0.02	<0.02	0.9	2.2	0.5	2.4	0.6	5.2	1.5	1.4
Formate	0.03	0.05	0.3	0.1	0.4	0.4	0.4	0.3	0.4	0.3
$\delta^{18}O$ (‰)	-5.72	-5.73	-2.03	-2.95	-1.77	-2.57	-3.51	-2.18	-3.38	-2.92
δD (‰)	-35.16	-34.89	-9.91	-13.00	-9.32	-10.60	-19.06	-10.05	-17.09	-14.36

T, temperature; TDS, total dissolved solids; DOC, dissolved organic carbon; solute concentrations in mg/l; <, less than.

Table 2. Chemical (inorganic and organic) and isotopic composition of water samples from OSPER "A" site.

Site Name	AA-01d	AA-02d	AA-02s	AA-03d	AA-03s	AA-04d	AA-04s	AE-04	AE-05	AE-06
	well	well	well	well	well	well	well	well	well	well
Sample #	02OS-430	02OS-427	02OS-426	02OS-429	02OS-428	02OS-425	02OS-424	02OS-434	02OS-332	02OS-435
Date	06/13/02	06/12/02	06/12/02	06/12/02	06/12/02	06/12/02	06/12/02	06/13/02	03/03/02	06/13/02
pH	6.5	6.9	6.2	6.7	6.6	7.0	5.7			
T (°C)	16	18	19	16	19			22		23
Li	0.16	0.05	0.07	0.13	0.04	0.08	0.04	0.001	0.001	0.002
Na	2180	525	3400	3250	1110	1150	1670	60	11.8	4
K	27	6.8	16	25	3.2	28	5.3	1.0	0.03	0.8
Mg	2520	102	272	166	41	234	63	0.4	0.03	1.1
Ca	3460	176	564	419	98	567	202	2.1	0.18	5.9
Sr	8.6	2.9	8.4	5.2	3.4	4.9	7.7	0.07	0.004	0.26
Ba	0.3	0.1	0.6	1.2	1.9	1.3	6.3	0.026	0.003	0.25
Mn	5.1	0.49	1.7	14.5	2.2	4.3	12.5	0.013	0.001	0.23
Fe	<10	3	<5	6	6.5	<2.5	<2.5	0.1	0.07	0.2
Cl	16100	436	7020	5630	1860	3410	3240	76.7	3.3	2.2
Br	56	1.5	23	19.3	6.4	11.6	11.7	0.27	0.08	0.12
SO_4	696	668	137	23.4	5.7	56.8	5.9	10.2	14.2	6.0
HCO_3	445	824	255	894	301	279	54	ND	ND	ND
NO_3	<1	<0.2	<1	<0.2	<0.2	<0.5	1.8	1.2	1.1	0.32
SiO_2	<43	24	<21	<21	19	18	29	11	10	16
B		0.4			0.1			0.04	0.023	0.033
TDS	25500	2760	11700	10500	3450	5760	5310	180	50	62
DOC	99	113	2	203	53	2	4			
Acetate	171	200	0.08	517	101	<0.04	<0.04			
Formate	<0.08	<0.08	0.09	<0.08	<0.08	<0.08	<0.04			
Propionate	<0.2	<0.2	<0.2	0.7	3.3	<0.1	<0.05			
Butyrate	<0.2	<0.2	<0.2	0.5	<0.2	<0.1	<0.05			
$\delta^{18}O$ (‰)										
δD (‰)										

T, temperature; TDS, total dissolved solids; DOC, dissolved organic carbon; solute concentrations in mg/l; <, less than.

Table 2. Chemical (inorganic and organic) and isotopic composition of water samples from OSPER "A" site -- continued.

Site Name	AE-07 well	AE-08 well	AE-10 well	AE-12 well	AE-13 well	AE-13 well	AE-15 well	AE-19 well	AR-01 well	AP-01* well
Sample #	02OS-334	02OS-326	02OS-331	02OS-328	02OS-329	02OS-431	02OS-437	02OS-433	02OS-438	02OS-324
Date	03/03/02	03/01/02	03/03/02	03/03/02	03/03/02	06/13/02	06/13/02	06/13/02	06/13/02	02/28/02
pH	5.3	6.4	5.7	7.3	5.6	5.6			6.5	5.8
T (°C)		8	20	17	16	22	25	22	17	
Li	0.002	0.048	0.025	0.032	0.024	<0.025	0.09	0.01	0.011	3.2
Na	23	341	24	179	1980	2250	4030	50	23	32900
K	0.13	1.6	0.74	1.7	2.8	3	4	0.5	1.6	89
Mg	0.21	4.8	0.57	1.8	629	808	484	1.4	23	1600
Ca	0.81	19	2.9	8.3	738	1020	1000	5.7	58	5880
Sr	0.037	1.2	0.19	0.59	23.3	25.4	16.9	0.25	0.36	454
Ba	0.066	0.19	0.081	0.023	0.41	0.41	1.2	0.040	0.56	15.5
Mn	0.007	0.39	0.086	0.029	105	87.8	2.8	0.14	2.1	6.3
Fe	0.15	<0.05	0.02	0.05	2.0	6	<10	0.1	0.2	595
Cl	20.0	580	17.4	37.6	6300	7770	9120	58.8	76.8	68100
Br	0.17	1.3	0.07	0.39	22.0	26.6	30.9	0.41	0.57	244
SO_4	20.6	14.3	28.5	4.9	92.3	248	115	16.8	5.6	43.1
HCO_3	3	ND	13	457	14	57		ND	221	239
NO_3	1.2	0.08	0.25	3.1	10	<1	11	0.38	<0.02	<4
SiO_2	11	11	10	2.9	9.6	25	<43	12	23	<32
B	0.012	0.14	0.021	0.34	<0.025			0.08	0.02	1.9
TDS	81	1000	97	700	9930	12300	14800	181	436	110000
DOC			11	69	5	5			4	
Acetate		0.3	0.2	0.5	0.3	0.04	0.07		0.07	210
Formate		0.3	0.1	1.2	0.2	<0.04	<0.08		0.07	3
Propionate		<0.25	<0.05	<0.2	<0.05	<0.05	<0.2		<0.1	44
Succinate		<0.1	0.04	0.3	0.1	<0.12	<0.12		<0.02	1.4
$\delta^{18}O$ (‰)		-5.18	-5.92	-3.06	-5.31					-2.77
δD (‰)		-27.79	-38.29	-18.65	-29.04					-13.58

(*) AP-01 well - butyrate = 4.2 mg/l, malonate = 0.17 mg/l.

Table 3. Chemical (inorganic and organic) and isotopic composition of water samples from OSPER "B" site.

Site Name	BA-01d	BA-01s	BA-02d	BA-02s	BA-03d	BA-03s	BE-03	BE-04	BE-06	BE-07	BE-08
	well	well	well	well	well	well	well	well	well	well	well
Sample #	02OS-405	02OS-403	02OS-401	02OS-318	02OS-402	02OS-320	02OS-411	02OS-408	02OS-409	02OS-305	02OS-422
Date	06/10/02	06/10/02	06/10/02	02/26/02	06/10/02	02/26/02	06/11/02	06/11/02	06/11/02	02/21/02	06/12/02
pH	7.1	5.4	6.8	7.5	6.7	7.3	5.0			6.2	6.7
T (°C)	19	22	18	17	19	16	27	28	24	12	25
Li	0.11	0.010	0.19	0.22	0.13	0.19	<0.013	0.04	0.012	0.21	0.13
Na	1550	2080	831	1220	863	1410	2430	5640	1280	6800	2450
K	16	4.5	19	35	12	30	6	15	1.5	13	11
NH_4^+										10	
Mg	315	174	793	723	538	463	172	388	296	525	1430
Ca	410	509	433	416	477	399	564	1100	195	1410	794
Sr	16.2	17.7	7.0	7.4	12.2	9.9	22.3	51.2	4.0	78.3	15.2
Ba	0.023	0.60	0.010	0.055	0.010	0.042	1.3	1.8	0.46	14.2	0.046
Mn	1.8	21	0.057	0.38	0.20	0.79	25.2	36.0	25.7	89.3	3.5
Fe	<0.13	0.8	<0.13	<0.25	0.9	<0.25	<2.5	<0.25	<0.13	138	<5
Cl	2050	4660	1140	1540	999	1800	5090	12000	3150	14600	5690
Br	8.1	20.3	4.4	6.3	3	7.1	23	49	11	69	24
SO_4	2420	99.0	3700	3910	3080	2840	61	76	96	15.7	4780
HCO_3	424	33	1030	990	808	829	17			178	820
NO_3	<0.4	<0.5	<0.2	0.3	<0.2	<0.1	<0.5	6	<0.5	3	<1
H_2S										0.9	
SiO_2	16	16	15	16	16	19	11	12	13	8.6	<21
B	4.6	0.11	1.9	1.7	5.1	3.9		0.27	0.06	0.11	0.4
TDS	7245	7635	7990	8880	6840	7830	8430	19300	5080	24000	16000
DOC	1	8	12		1		8			28	8
Acetate	<0.04	0.9	0.03		<0.08		<0.04		<0.04	0.3	<0.04
Formate	<0.04	<0.04	<0.04		<0.2		0.05		0.06	0.4	<0.04
Succinate	<0.15	<0.08	<0.02		<0.1		<0.04		<0.15	0.08	<0.12
$\delta^{18}O$ (‰)				-5.54		-5.52				-5.45	
δD (‰)				-32.38		-32.08				-35.50	

T, temperature; TDS, total dissolved solids; DOC, dissolved organic carbon; solute concentrations in mg/l; <, less than.

Table 3. Chemical (inorganic and organic) and isotopic composition of water samples from OSPER "B" site -- continued.

Site Name	BE-09	BE-10	BE-11	BE-12	BE-13	BE-15	BE-16	BE-17	BE-18	BR-01d	BR-02d
	well	well	well	well	well	well	well	well	well	well	well
Sample #	02OS-412	02OS-413	02OS-420	02OS-421	02OS-307	02OS-410	02OS-417	02OS-418	02OS-407	02OS-406	02OS-404
Date	06/11/02	06/11/02	06/12/02	06/12/02	02/21/02	06/11/02	06/11/02	06/11/02	06/11/02	06/10/02	06/10/02
pH	6.0	4.4	6.4	6.7	6.3	6.4	6.1	7.1	6.2	6.4	6.9
T (°C)	24	23	22	22	12	24	23	35	23	18	20
Li	<0.025	<0.025	<0.050	<0.050	0.01	<0.013	0.04	0.08	0.018	0.12	0.13
Na	3300	3060	4860	4000	3520	1180	2140	2030	2780	2360	1270
K	4	5	5	6	5.9	2	5.9	12	7.6	7.1	10
NH_4+					3						
Mg	145	624	1140	1360	974	313	1360	1700	253	347	171
Ca	309	840	1140	1190	874	360	500	502	552	681	271
Sr	16.0	29.8	36.7	25.4	29.8	4.8	8.7	8.5	22.1	11.3	10.9
Ba	0.90	0.51	0.49	0.076	0.23	0.17	0.035	0.037	0.58	1.7	0.42
Mn	51.1	65.2	22.6	3.4	284	9.2	108	15.6	45.4	3.9	0.32
Fe	5	<5	<10	<10	116	<2.5	11	<2.5	32	<0.13	0.3
Cl	6300	8180	12500	10500	9900	3090	3130	2020	5800	5570	2460
Br	29	38	56	49	48	12	15	8	24	26	10
SO_4	125	470	277	2520	583	385	6910	8860	290	96.6	353
HCO_3	185	0	232	447	181	142	325	1260	275	252	493
NO_3	<0.5	<0.5	<1	1.2	<0.5	4	<0.5	<1	<0.5	<0.5	<0.5
H_2S					1.8						
SiO_2	<21	19	<43	<43	4.9	11	<21	15	11	31	15
B					0.04				0.16	0.13	5.2
TDS	10500	13300	20300	20100	17400	5500	14400	16400	10100	9380	5100
DOC	21		9	12	12	19	14	9	18	7	5
Acetate	<0.02	<0.04	<0.04	<0.04	0.6	<0.02	0.04	<0.1	<0.04	0.04	0.1
Formate	0.03	<0.04	<0.04	<0.04	0.7	0.04	0.05	<0.1	0.09	0.06	0.07
Succinate	<0.03	<0.04	<0.04	<0.06	0.04	<0.15	<0.2	<0.2	<0.04	<0.5	<0.02
δ^{18}O (‰)					-5.12						
δD (‰)					-33.16						

Table 3. Chemical (inorganic and organic) and isotopic composition of water samples from OSPER "B" site -- continued.

Site Name	EPA-1 well	injection pit	main pit	small pool at BA-01	large pool at BA-01	stream, at BA-01	Skiatook Lake near ACE	Skiatook Lake at BE-07	reinjection tank
Sample #	01OS-201	02OS-316	02OS-317	01OS-113	01OS-114	02OS-311	01OS-111	02OS-309	02OS-314
Date	12/11/01	02/25/02	02/25/02	03/13/01	03/13/01	02/22/02	03/10/01	02/22/02	02/24/02
pH	4.3	8.5	6.6	7.1	7.3	6.7	6.7	8.1	6.5
T (°C)	12.1	11	7	13	11	11	7	12	24
Li	2.9	1.1	1.4	0.015	0.002	0.029	0.002	0.002	8.5
Na	22700	12500	10600	1930	641	1190	14	21	40400
K	56	37	36	5.4	2.4	4.3	2.2	2.5	230
NH_4+			20	<0.1	0.1				70
Mg	1250	444	442	56	57	129	5.0	6	1590
Ca	5270	2450	1980	288	173	333	20	23	7700
Sr	343	172	141	13.2	4.66	10.0	0.19	0.27	473
Ba	113	88.4	100	4.4	0.56	0.27	0.050	0.072	460
Mn	16.1	0.43	2.9	2.9	3.1	13.8	0.003	0.085	0.79
Fe	130	<1	40	<0.13	<0.05	17	<0.006	<0.01	35
Cl	52000	26200	21600	3560	1470	2550	25	39.7	82100
Br	227	124	100	13.0	6.3	12	0.11	0.20	328
SO_4	12.3	5.1	11.2	9.2	22.5	271	10.0	11.6	2.5
HCO_3	0	57	146	143	134	273	74	80	139
NO_3	<2	<1.5	<1	<0.4	0.7	<0.15	0.8	0.7	<0.5
H_2S			0.4						<0.2
SiO_2	<16.0	<6	4.6	2.0	4.0	8.8	2.8	1.5	<32
B	0.57	0.5	0.6	0.109	0.024	0.05	0.023	0.03	2.9
TDS	82100	42100	35300	6020	2520	4810	153	186	134000
DOC			43	14	9	4	4	4	5
Acetate	0.05		0.6	1.1	0.06				0.7
Formate	<0.08		0.3	0.1	0.2				0.3
Succinate	<0.1		0.06	<1	<0.4				<0.1
$\delta^{18}O$ (‰)	-3.54	-2.44	-4.30	-5.23	-5.83	-5.79	-2.46	-1.75	-3.07
δD (‰)	-21.25	-26.45	-26.66	-31.50	-32.41	-37.70	-15.27	-13.66	-17.23

Results show that the produced water obtained (table 1) from the seven oil wells, one coal-bed methane well (01OS-110) and the composite reinjection tank has a relatively similar chemical composition; it is a hypersaline (115,000-185,000 mg/L total dissolved solids) Na-Ca-Cl brine, that is dominated by Na and Cl, and has relatively high concentrations of Ca, Mg (fig. 3), Sr, Ba and NH_4, but very low amounts of SO_4, HCO_3 (fig. 4) and H_2S. With the exception of Fe, the concentrations of trace metals are low, and the values of organic acid anions and other dissolved organic species are relatively low. The chemical composition of Skiatook Lake water and ground water in the area not impacted by petroleum operations (samples 01OS-111, -101, -102, 02OS-438, table 1) shows major contrast from that of produced water. The water is fresh (153-518 mg/L total dissolved solids) and has comparable values for the equivalent concentrations of Na, Mg and Ca as well as those of Cl, SO_4 and HCO_3; this water, then, has much higher Mg and Ca concentrations relative to Na and much higher HCO_3 and SO_4 relative to Cl, when compared to produced water (figs. 3 and 4). Uncontaminated ground and surface waters are generally oxic, resulting in low concentrations of metals, including Fe (reaction 3, table 4) and Mn, as well as low DOC and organic acid anions (fig. 5). In anoxic water environment, present in produced water and petroleum contaminated water, Fe (reactions 1, 2, table 4) and Mn are mobilized from sediments, and organic acid anions, and thus DOC are generated by bacterial action on petroleum (Kharaka and others, 2000). These and other chemical properties and water isotopes that are different for produced and ground waters (fig. 6) are used to investigate the impact of produced water on the surface and ground waters of the contaminated areas (Abbott, 1999; Richter and Kreitler, 1993; Kharaka and others, 1995).

Table 4. Important water-mineral interactions at OSPER sites that modify the chemical composition of water from various sources.

$2FeS_2 + 7O_2 + 2H_2O \Leftrightarrow 2Fe^{++} + 4SO_4^{--} + 4H^+$	(1)
$FeS_2 + 2NO_3^- + 2H_2O \Leftrightarrow Fe^{++} + 2SO_4^{--} + 4H^+ + N_2$	(2)
$4Fe^{++} + O_2 + 10H_2O \Leftrightarrow 4Fe(OH)_3 + 8H^+$	(3)
$8Fe^{+++} + CH_3COOH + 2H_2O \Leftrightarrow 8Fe^{++} + CO_2 + 8H^+$	(4)
$Fe^{++} + HS^- \Leftrightarrow FeS + H^+$	(5)
$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$	(6)
$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$	(7)
$CH_3COOH \Leftrightarrow CO_2 + CH_4$	(8)
$4.8H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 3.2H_2O \Leftrightarrow .2Ca^{++} + .8Na^+ + 1.2Al^{+++} + 2.8H_4SiO_4$	(9)
$Ca^{++} + SO_4^{--} + 2H_2O \Leftrightarrow CaSO_4.2H_2O$	(10)
$CH_3COO^- + SO_4^{--} \Leftrightarrow 2HCO_3^- + HS^-$	(11)

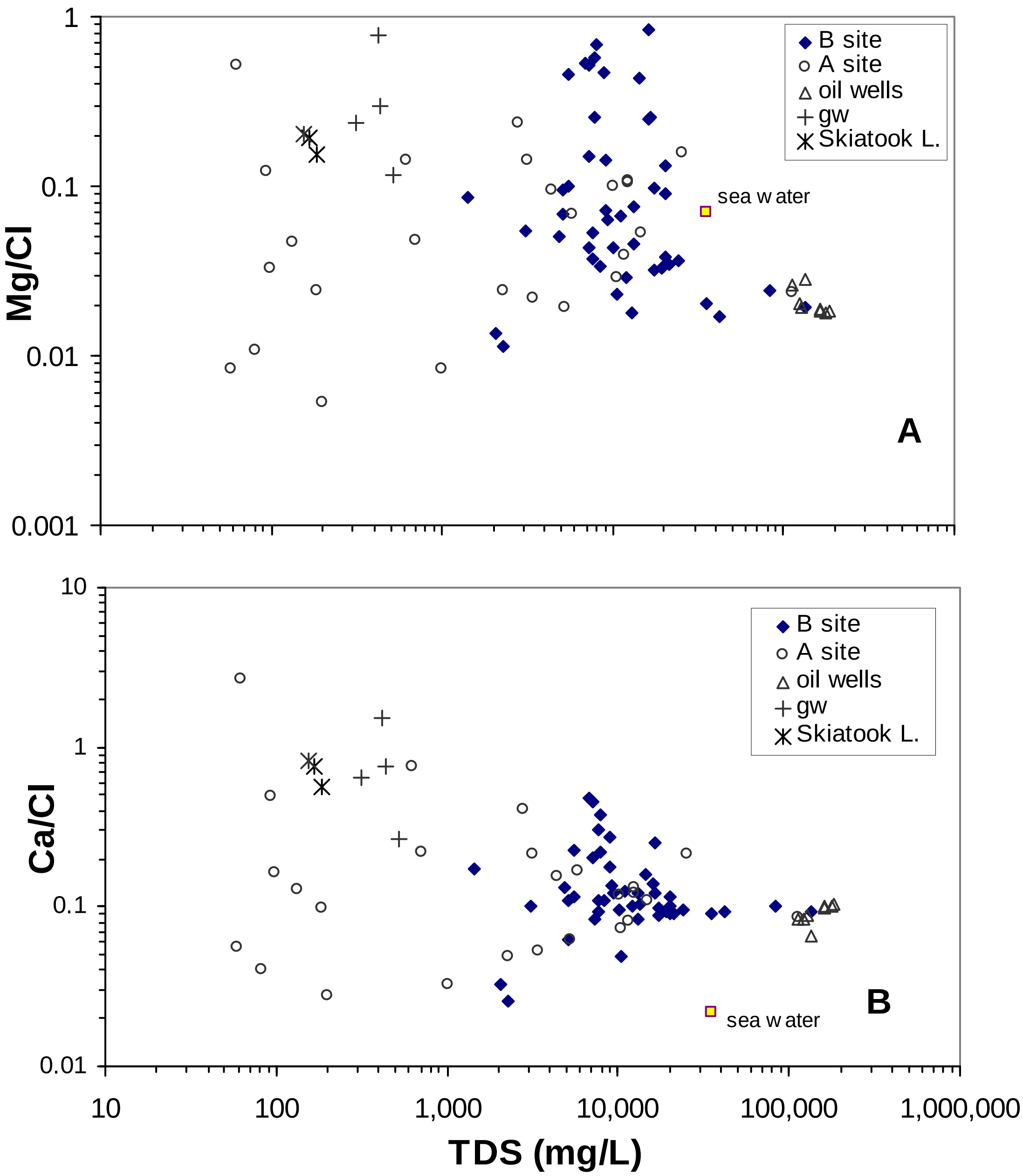


Figure 3. The Ca/Cl and Mg/Cl ratios as a function of water salinity for the oil-field brines, regional ground water (gw), Skiatook Lake and surface and ground waters from the impacted areas in the OSPER “A” and “B” sites. Note the generally lower ratios for the oil-field brines and diluted produced water.

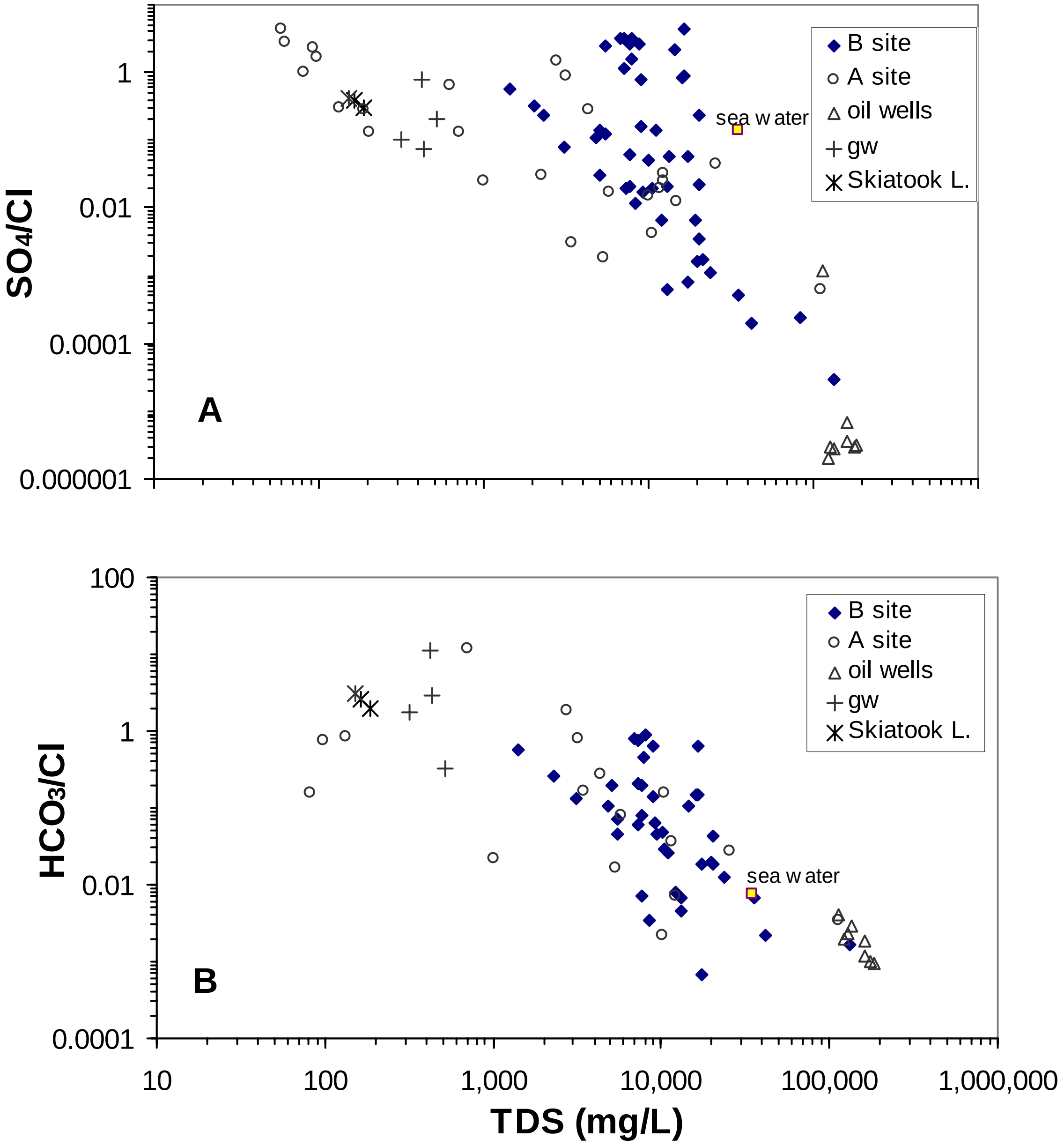


Figure 4. The SO_4/Cl and HCO_3/Cl ratios as a function of water salinity for the oil-field brines, regional ground water (gw), Skiatook Lake and surface and ground waters from the impacted areas in the OSPER “A” and “B” sites. Note the much lower ratios for the oil-field brines and diluted produced water.

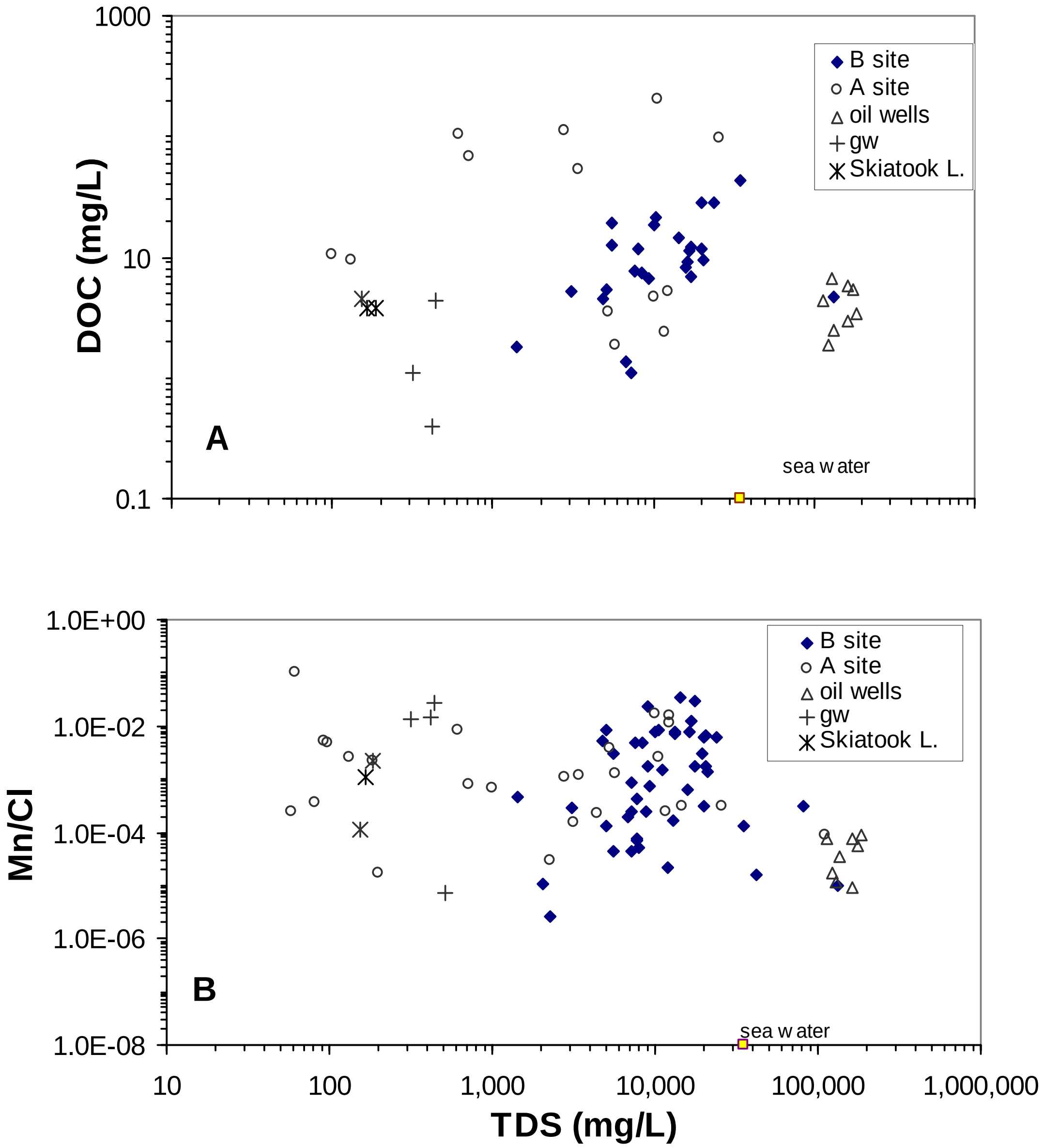


Figure 5. The concentrations of DOC and the Mn/Cl ratios as a function of water salinity for the oil-field brines, regional ground water (gw), Skiatook Lake and surface and ground waters from the impacted areas in the OSPER “A” and “B” sites. Note the much higher DOC and Mn/Cl values for ground water from the impacted wells, especially at the “A” site.

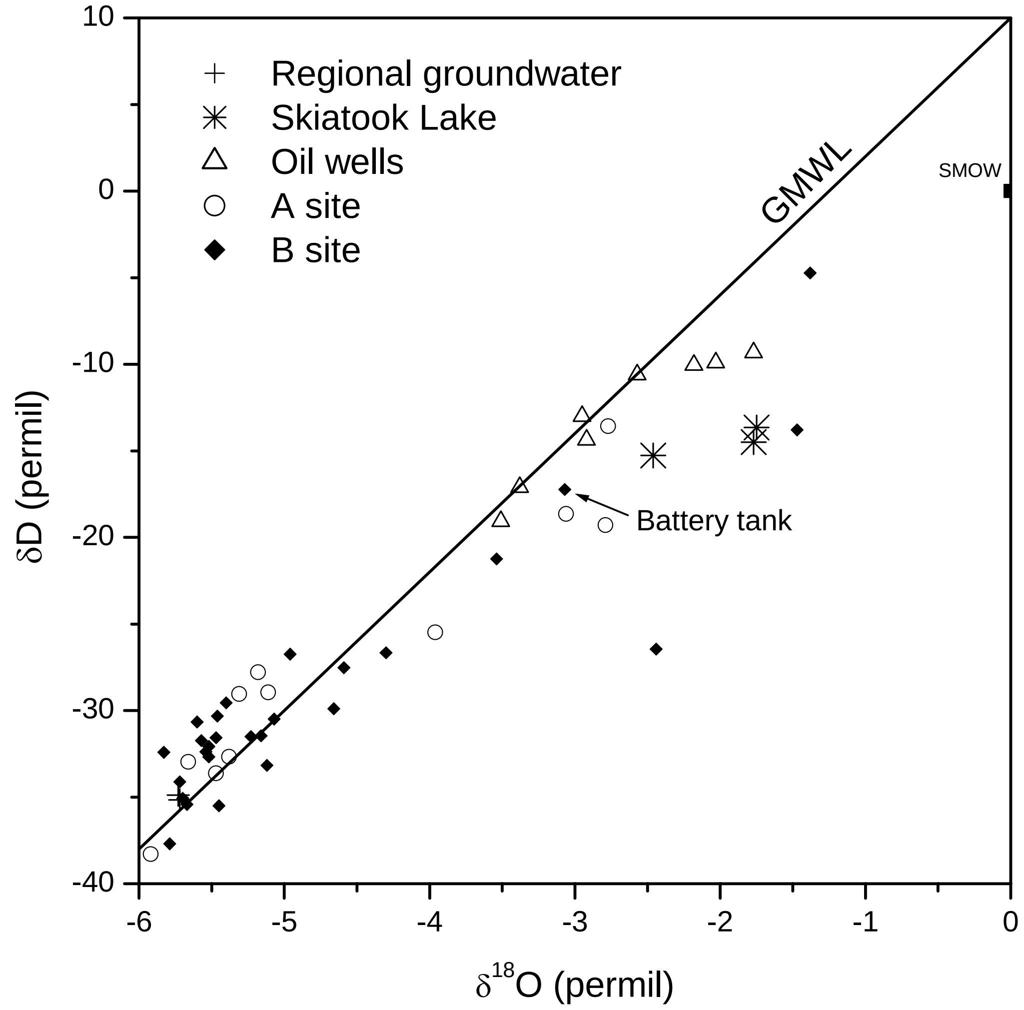


Figure 6. Isotopic composition of water for the oil-field brines, regional ground water (gw), Skiatook Lake and surface and ground waters from the impacted areas in the OSPER "A" and "B" sites. Note the major differences in the isotope values of the produced water relative to ground water.

OSPER "A" Site

At OSPER "A" site, the water obtained from the asphaltic pit (02OS-324) has a salinity (110,000 mg/L TDS) and chemical composition that are comparable to that of the produced water source (fig. 7). The salinity of water obtained from the boreholes in the adjacent pit, which has more weathered and degraded oil (Godsy and others, this volume), and from those boreholes located close to the two pits, all have fresh water (≤ 1,000 mg/L TDS), indicating that the brine in the asphaltic pit is of limited volume and extent. Also, all the direct-push Geoprobe wells (AE designation in table 2) located to the south and west of the two oil pits (fig. 1) have fresh water, with compositions that indicate no mixing with produced water. If produced water was ever present in these shallow wells, then it was flushed and replaced with meteoric water from precipitation. (See also results from soil analysis (Zielinski and others, this volume) and geophysical surveys (Smith and others, this volume)).

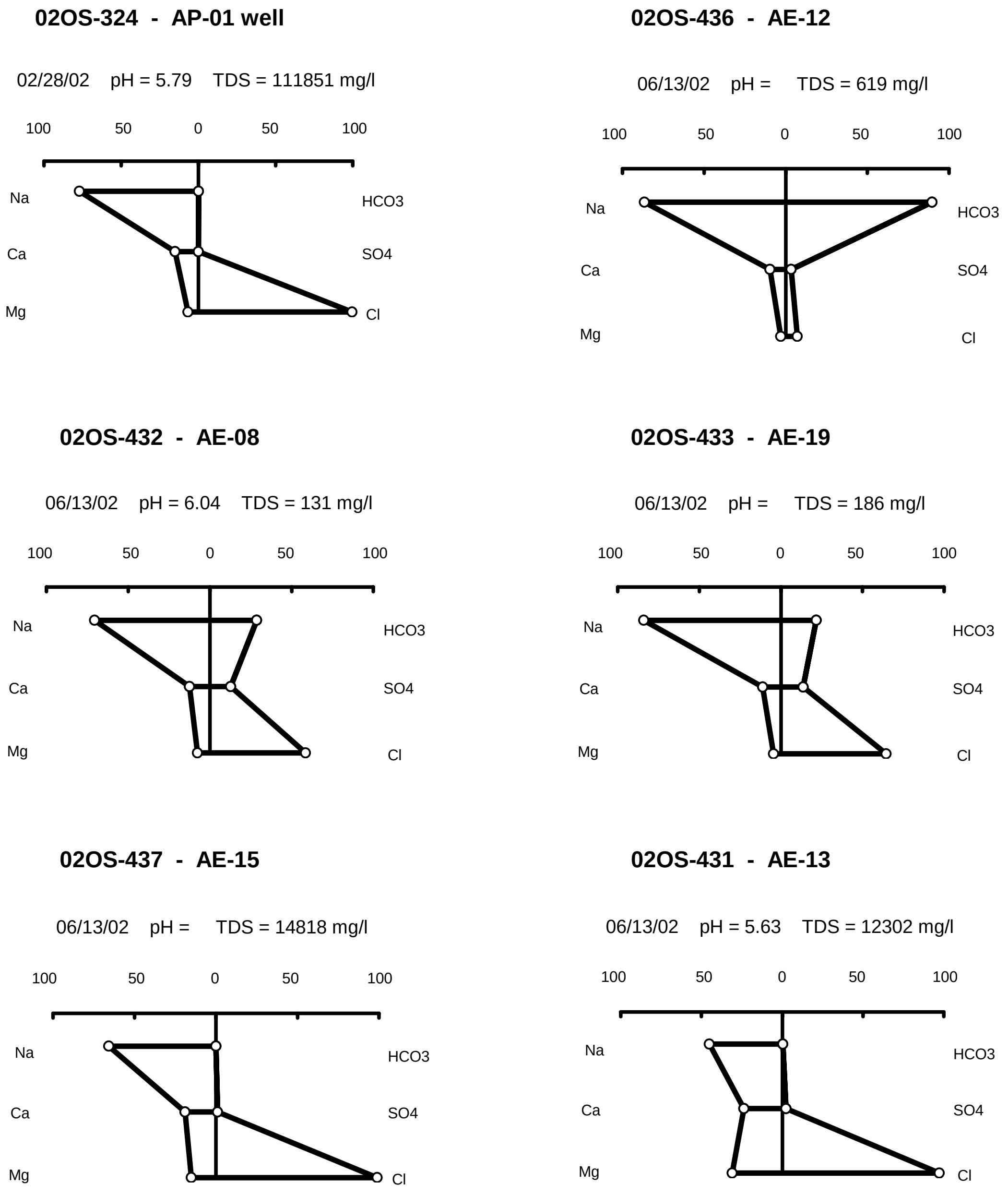
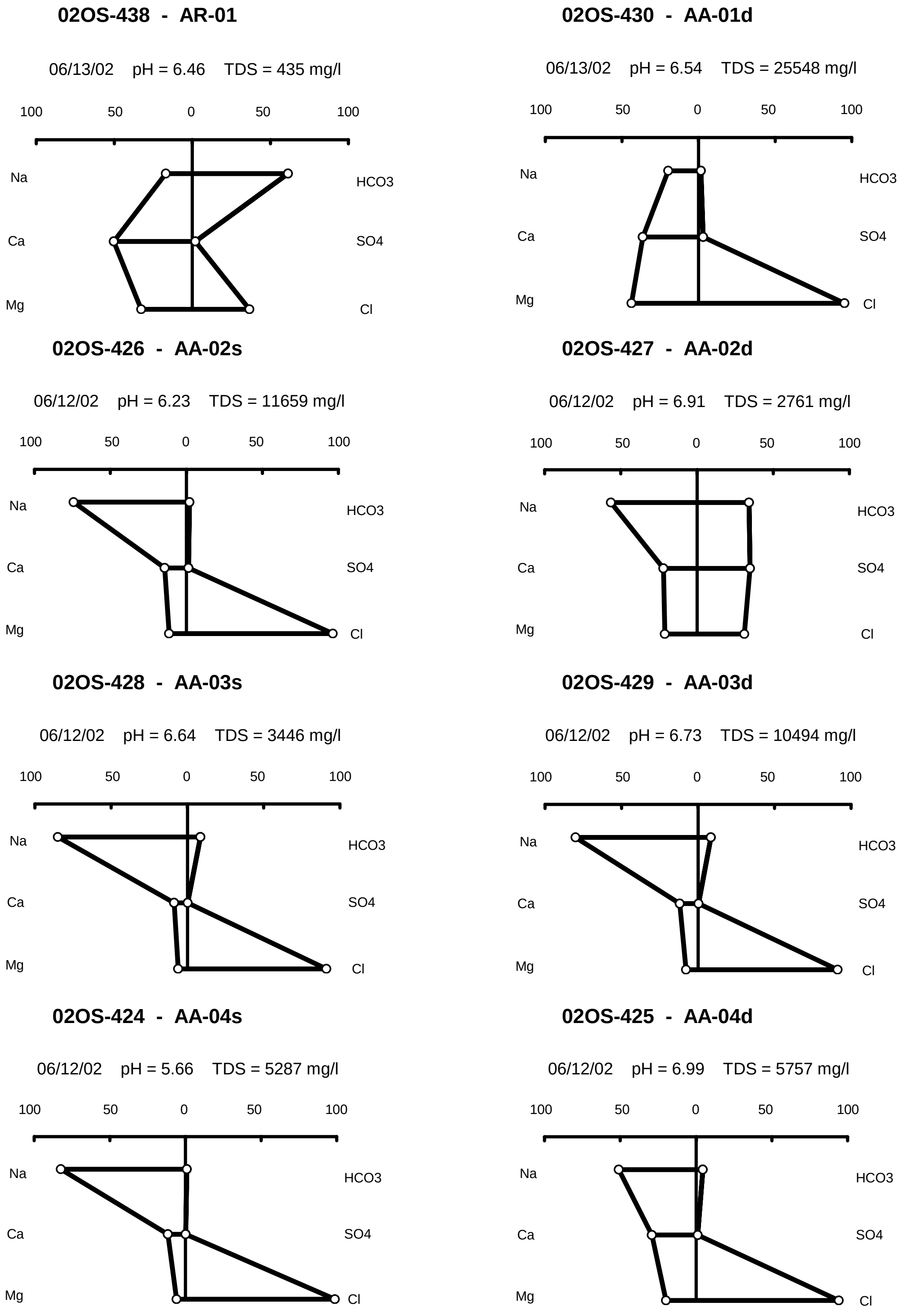


Figure 7. Modified Stiff diagrams showing the salinity of water and the relative concentrations (in equivalent units) of major cations and anions in a transect from the asphaltic pit to Skiatook Lake at the OSPER "A" site.

The salinity and chemical composition of water obtained from all the auger wells (AA designation, table 2) as well as from those direct-push wells (AE, table 2) located to the north of the two oil pits in the salt scarred area at the "A" site, show major impact from produced water operations (figs. 8 and 9). A plume of high salinity water (3,500-25,600 mg/L TDS) dominated by Na and Cl, intersects Skiatook Lake near well AE-13 (fig. 1) that has water salinity of 10,100-12,300 mg/L TDS (see also Smith and others, this volume). The upper and lower boundaries of this plume are tentatively marked on the cross section (fig. 9) that shows the plume apex to be



02OS-438 - AR-01

06/13/02 pH = 6.46 TDS = 435 mg/l

02OS-430 - AA-01d

06/13/02 pH = 6.54 TDS = 25548 mg/l

02OS-426 - AA-02s

06/12/02 pH = 6.23 TDS = 11659 mg/l

02OS-427 - AA-02d

06/12/02 pH = 6.91 TDS = 2761 mg/l

02OS-428 - AA-03s

06/12/02 pH = 6.64 TDS = 3446 mg/l

02OS-429 - AA-03d

06/12/02 pH = 6.73 TDS = 10494 mg/l

02OS-424 - AA-04s

06/12/02 pH = 5.66 TDS = 5287 mg/l

02OS-425 - AA-04d

06/12/02 pH = 6.99 TDS = 5757 mg/l

Figure 8. Modified Stiff diagrams showing the salinity of water and the relative concentrations (in equivalent units) of major cations and anions from the relatively deep rotary (AR) and auger (AA) wells in and near the OSPER “A” site. s- shallow screened interval, d- deep screened interval, see figure 9.

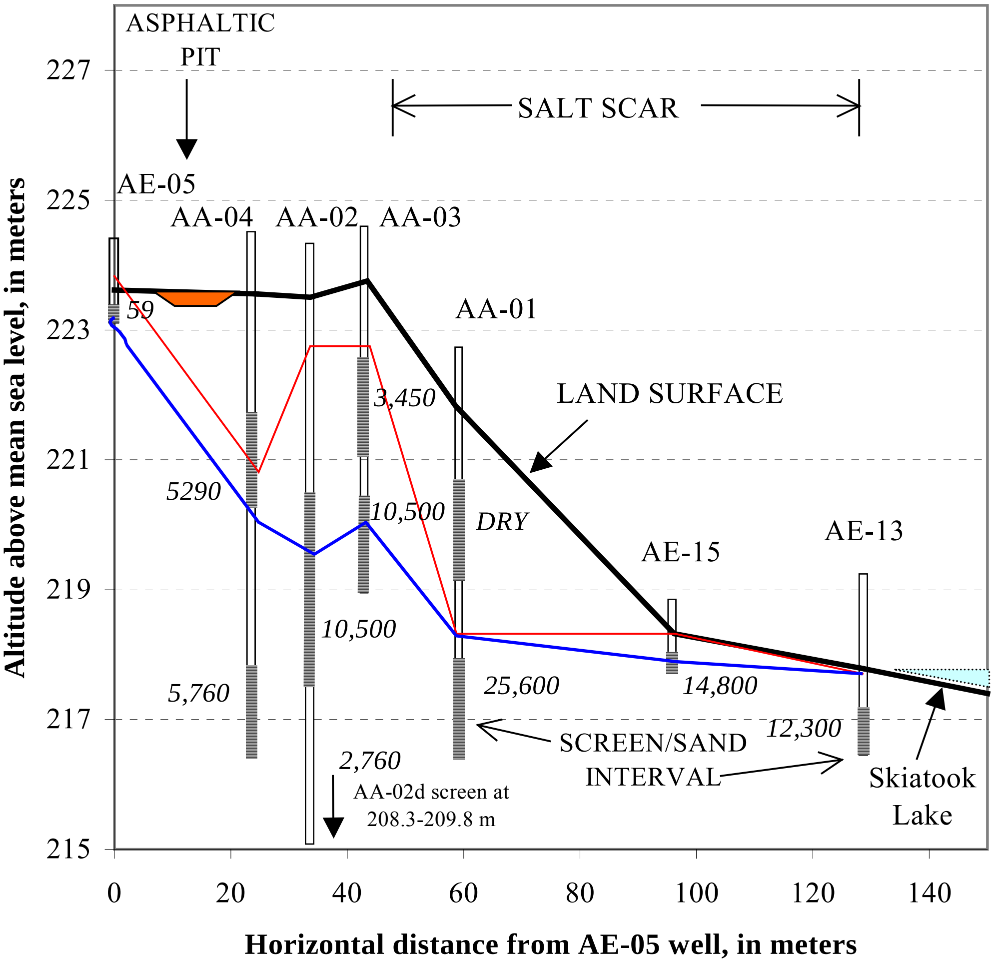


Figure 9. Water levels and salinity of water in wells along a transect from well AE-5 to AE-13, located in the littoral zone of Skiatook Lake at the OSPER "A" site. A plume of relatively high salinity water is present at intermediate depths in wells located below the asphaltic pit. Red and blue lines represent highest and lowest water levels, respectively, observed during the period March, 2001 to June, 2002.

within 1 m from ground surface in well AA-03, which is the closest to the oil pits that likely were also the brine pits. Chemical data for water from the deeper perforated section (13.8-15.2 m below ground level) of well (AA-02), we believe, will ultimately delineate the bottom of the plume. The salinity and chemical composition of water for the last sample from this section (02OS-427, table 2 and fig. 8) indicate a non produced water source; the concentration of acetate, DOC and possibly other components (table 2) could indicate contamination from an oil source or cross formational mixing from the shallow and contaminated section when the well was drilled.

Additional sampling from this and new deeper wells will be used to better delineate the plume boundaries from this site. Results to date, however clearly show that significant amounts of dissolved inorganic and organic chemicals and hydrocarbons from produced-water and oil releases still remain in the soils and rocks of the impacted area after more than 60 years of natural attenuation.

OSPER "B" Site

Even though the number of boreholes drilled at the two sites is comparable, a larger number of water samples (60 vs. 35) have been obtained from the "B" site compared to the "A" site. This results primarily because the "B" site is currently active and brine and associated hydrocarbons are added intermittently via the brine pits and accidental releases from broken pipes. Many of the water wells at the "A" site, in contrast to those at the "B" site, were found dry at the time of sampling because the oil wells in the Lester lease have been depleted for some time and no brine additions occur at this site.

The salinity (133,000 mg/L TDS) and chemical composition of water in the composite water tank (table 3) are similar to those described earlier for the produced water from the sampled oil wells (figs. 3 and 4). The salinity and chemical composition of water in the two brine pits (fig. 2) vary greatly with time, reflecting primarily the mixing of produced water brine with dilute water from precipitation and runoff into the pits. The salinity of water in the small pit adjacent to the injection well, for example, was 13,000 mg/L TDS on 12/11/01 and 42,000 mg/L TDS on 2/25/02. The proportions of major anions and cations in both samples were similar and comparable to those of produced water, but the actual concentration were reduced by a factor close to 10 for the December sample and about three for the February sample. The concentration of a number of minor and trace chemicals that are sensitive to the redox state of the water (e.g. Fe, Mn, NH_4, organic acid anions) are likely to be lowered in oxic conditions (e.g. reactions 1-3 for Fe, table 4) by factors that are greater than those listed above. The concentration of some chemicals (e.g. NH_4, BTEX, organic acid anions) may be reduced also by volatilization. On the other hand, evaporation generally increases the concentrations of dissolved species, and the relatively higher concentrations of HCO_3 in both samples likely result from bacterial degradation of oil.

All the water samples obtained from pools, seeps and boreholes at this site (fig. 2) show variable impacts from produced water. The most saline sample, outside the brine pits, was obtained in December 2001 from a well located about 15 m down gradient and to the east from the large brine pit, which generally has from about 0.2 to 2 m (maximum depth at overflow) of produced water with a thin layer of oil. The well brine (01OS-201, table 3) had a salinity (82,000 mg/L TDS) and chemical composition approaching that of produced water. Water obtained from the same well in February 2002, had a salinity of only 17,400, but the proportions of major cations and anions are similar to those of produced water. Water samples obtained in February and June 2002 from Geoprobe well BE-07 (figs. 2 and 10) located in the littoral zone of Skiatook Lake, about 65 m down gradient and to the east from the large brine pit, show a more uniform salinity (24,000 and 20,000 mg/L TDS, respectively). The chemical composition of water from this well has characteristics that are similar to that of produced water (fig. 11), that together with the presence of oil globules in the water, strong oil odor and high values measured for hydrocarbon gases and other VOCs (see also Godsy and others, this volume), clearly show that brine and minor amounts of hydrocarbons from the large brine pit reach the lake. Minor contamination of Skiatook lake with brine is indicated (02OS-309 vs 01OS-111, fig. 11), but this topic will be covered in detail in future reports.

Additional direct-push wells (BE designation, fig. 2 and table 3) and one dual completion auger well (BA-02) were drilled to investigate the flow paths of brine and associated hydrocarbons from the large brine pit. In addition to well BE-07 discussed, oil globules in the water, strong oil odor and high values measured for hydrocarbon gases and other VOCs were

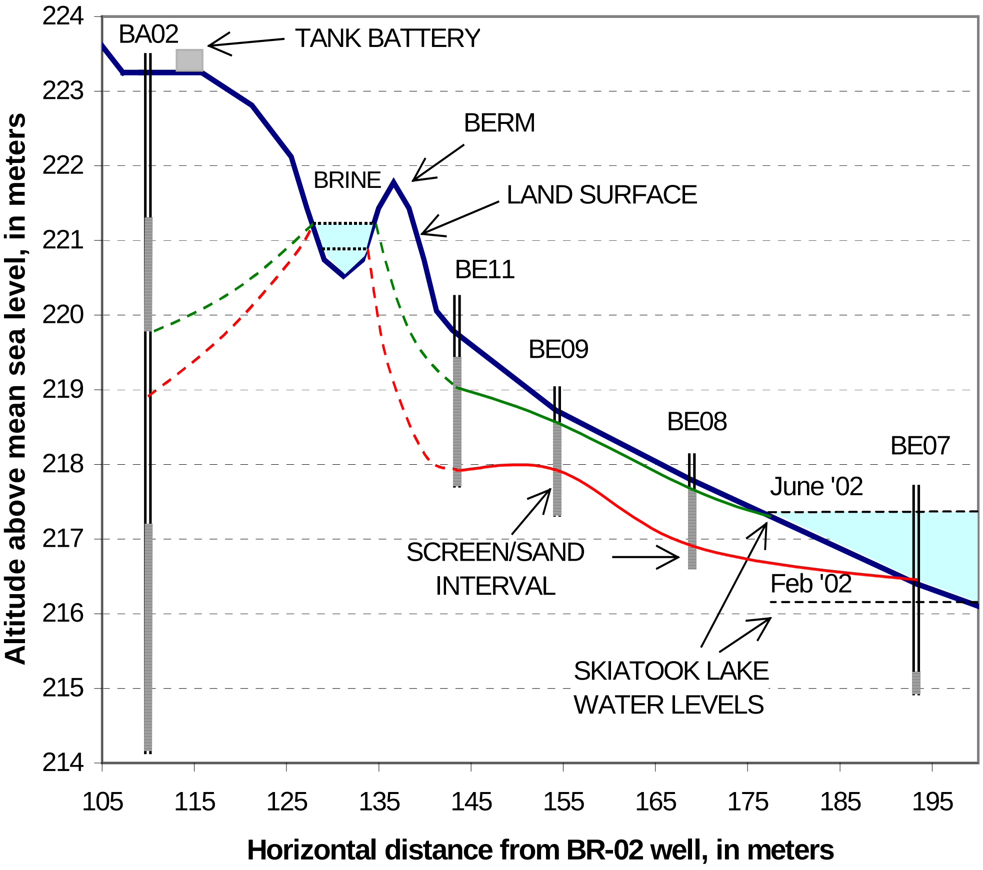


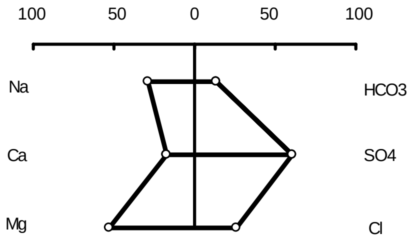
Figure 10. The high (green line) and low (red line) water levels measured wells in the transect A-A`, from well BA-02 to well BE-07, located in the littoral zone of Skiatook Lake at the OSPER “B” site.

observed in well BE-09 and a 30 cm hand-dug well located close and down gradient from BE-11. No visible oil was observed in water from other wells, but oil odor and measured hydrocarbon gases were obtained from most of the other wells located on the salt scarred, but “remediated” area below the brine pit. All the wells located in the salt-scarred area below the brine pit, especially those shown in figure 10, also had saline water with chemical characteristics of produced water (table 3, fig. 11).

Water samples obtained from the two perforated zones of well BA-02 as well as those from wells BE-16 and BE-17 have high salinity (8,000-16,500 mg/L TDS) and chemical characteristics that could indicate a mixture of diluted produced water, high in Na and Cl and ground water, high in Mg, SO_4 and HCO_3 (fig. 12). Geochemical modeling using the latest version of SOLMINEQ (Kharaka and others, 1988) indicates another possible, but less likely explanation for the chemical composition of water from these samples. It includes dilution of produced water source, followed by dissolution of gypsum and dolomite and precipitation of calcite (reactions 10, 7 and 6, table 4). Regardless of the correct explanation, these results indicate a slower flow path from the large brine pit towards wells BA-02, BE-16 and BE-17 than towards the wells depicted in the transect A-A’ (fig. 10). Additional sampling, tracer tests and hydrologic parameter determinations and modeling (see also Herkelrath and Kharaka, this volume) are planned to investigate the flow in this system.

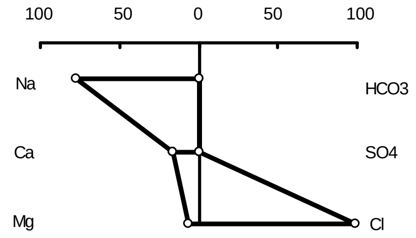
02OS-401 - BA-02d

06/10/02 pH = 6.75 TDS = 7963 mg/l



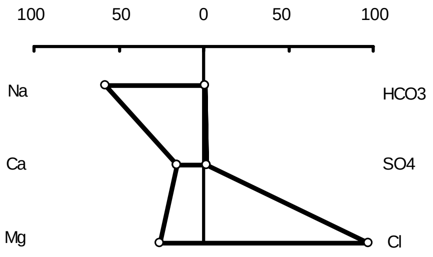
02OS-317 - main pit

02/25/02 pH = 6.62 TDS = 35241 mg/l



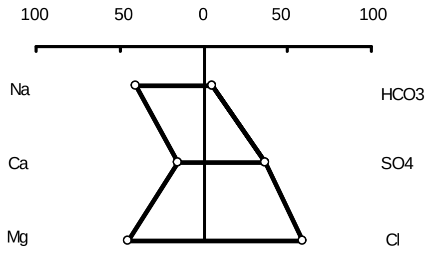
02OS-420 - BE-11

06/12/02 pH = 6.36 TDS = 20259 mg/l



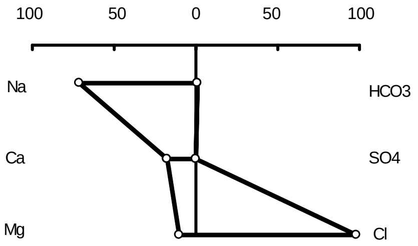
02OS-422 - BE-08

06/12/02 pH = 6.68 TDS = 16029 mg/l



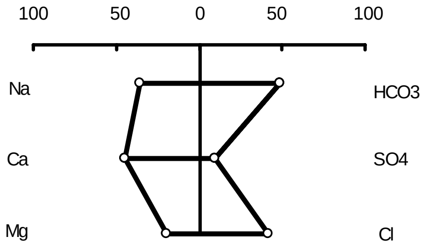
02OS-415 - BE-07

06/11/02 pH = 6.2 TDS = 19726 mg/l



02OS-309 - Skiatook Lake nr.BE-07

02/22/02 pH = 8.08 TDS = 186 mg/l



01OS-111 - Skiatook Lake nr. ACE

03/10/01 pH = 6.71 TDS = 153 mg/l

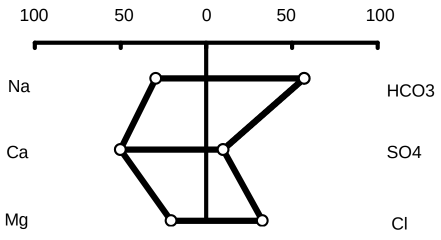


Figure 11. Modified Stiff diagrams showing the salinity of water and the relative concentrations of major cations and anions in a transect from the BA-02 deep well to well BE-07, located in the littoral zone of Skiatook Lake at the OSPER “B” site. Sample 010S-111 taken near Army Corps of Engineers (ACE) field office.

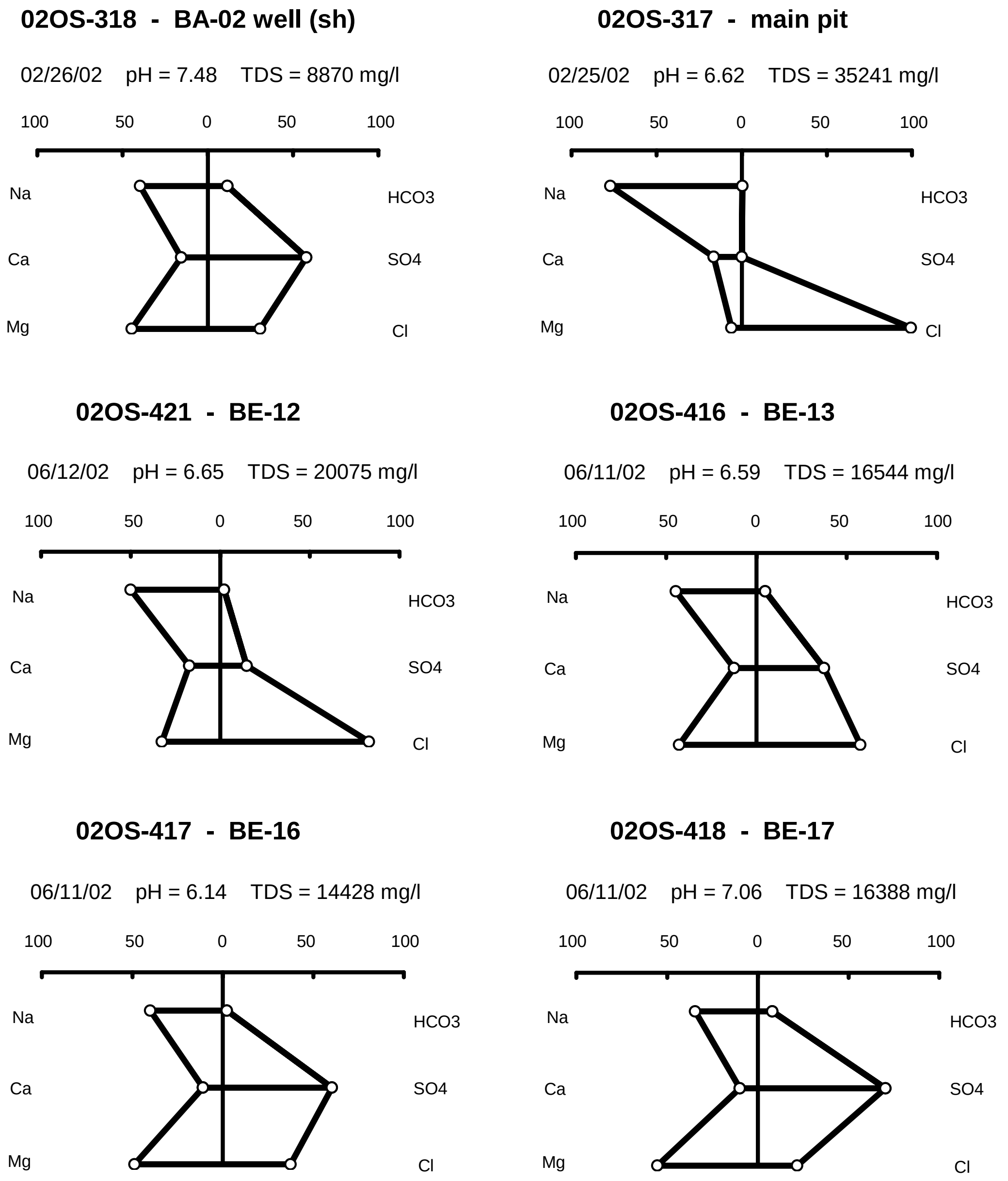


Figure 12. Modified Stiff diagrams showing the salinity of water and the relative concentrations (in equivalent units) of major cations and anions from the main brine pit and Geoprobe wells located to the southeast of this pit; the latter wells appear to have a mixture of produced water and local ground water.

Significant amounts of produced water, but no oil, reach the wells, water pool and even the creek adjacent to the scarred, but "remediated" area down gradient from the reinjection pit (fig. 2). The salinity of water from BE-03 and other wells, small pools and a large pool close to the creek has varied widely, ranging from 2,500 to 13,100 mg/L TDS, but the chemical composition is that of a diluted produced water. Sample 02OS-311, which was collected from the creek to the east of BA-01 well has a salinity of 2,500 mg/L TDS and chemical properties of diluted produced water. A specific water conductance of about 20,000 µsiemens/cm (µS/cm) was obtained with a probe from a location where this sample was obtained.

A high specific water conductance (8,000 µS/cm) was also measured in the creek near well BE-19. This part of the creek, as well as wells BE-04, BE-05, BE-18 and BE-19 are located in the middle salt scarred and "remediated" area of the "B" site. This salt scar had a tank battery, located at its western end that was removed and the site "remediated" in year 2000. The four direct-push wells on this site have generally been dry. However, some water was obtained from BE-04 and BE-19, that gave salinities of 19,200 and 10,100 mg/L TDS, respectively; the water is dominantly Na-Cl and has the other chemical characteristics of produced water.

Summary and Conclusions

About 100 water samples and several oil and natural gas samples were obtained from oil wells, domestic ground water wells, active and inactive brine and oil pits, seeps, pools, local streams, Skiatook Lake and from 50 boreholes (1-71 m deep), recently drilled and completed with slotted PVC tubing. Most of the samples are from OSPER "A" and "B" sites, located, respectively, within the depleted Lester and active Branstetter leases, in Osage County, OK. Results show that large amounts of produced water and associated petroleum from active and inactive brine pits and from accidental releases from broken pipes have impacted about 1.5 and 1.0 hectare of land at the OSPER "A" and "B" sites, respectively. The impacts include salt scarring, soil salinization and oil contamination, and brine and petroleum contamination of ground water and surface water, including Skiatook Lake, a 4,250-hectare reservoir that provides drinking water to the local communities and is a major recreational fishery.

At the "A" site, results show that the salts have essentially been removed by flushing from the soil and surficial rocks; but degraded and weathered oil persists on the surface of old oil and brine pits, close to sites of old tanks, on old channels that carried oil from tanks to the oil pits and other impacted areas. Results show that a plume of high salinity water (3,500-25,600 mg/L TDS) is present at intermediate depths that extend from below the old oil and brine pits to Skiatook Lake. No liquid petroleum was found in the contaminated groundwater, but soluble petroleum byproducts, including organic acid anions and other VOCs are present. Results to date clearly show that significant amounts of salts from produced-water releases and petroleum hydrocarbons still remain in the soils and rocks of the impacted area after more than 60 years of natural attenuation.

At the "B" site, significant amounts of produced water from the two active brine pits percolate into the surficial rocks and flow towards the Skiatook Reservoir; but only minor amounts of liquid petroleum leave the brine pits and reach the Skiatook Reservoir.

The above results and conclusions are tentative and may be modified after additional sampling from existing and new wells, tracer tests, hydrologic parameter determinations and hydrologic and geochemical modeling are completed. These results, however, show that diluted produced water and minor amounts of oil flow from the brine pits through the surficial beds to the Skiatook Lake.

Acknowledgements

We are grateful to the Osage Indian Nation, to the Army Corps of Engineers and Bureau of Indian Affairs, as well as the field operators for permission to conduct research at these sites. We are grateful also for the financial support for this research provided by DOE National

Petroleum Technology Office, E&P Environmental. Gil Ambats and James Palandri participated in field sampling, and Gil Ambats and Kathy Akstin carried out the chemical analysis reported here.

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The Fate of Petroleum and Other Organics Associated with Produced Water from the Osage-Skiatook Petroleum Environmental Research Sites, Osage County, Oklahoma

By E. Michael Godsy, Frances D. Hostettler, Ean Warren, V. Vincenzo Paganelli, and
Yousif K. Kharaka

Abstract

During a multidisciplinary study at two oil production sites of differing ages near Lake Skiatook, Osage County, Oklahoma, a series of oil, water, brine, and soil samples were characterized and analyzed for geochemical parameters that are indicative of microbial activity. Characterization of the resident microbial populations was completed for a number of these samples. The area source oils are paraffinic-naphthenic light oil, containing *n*-alkanes as the dominant components unimpacted by biodegradation. The oils at the inactive OSPER "A" site are similar although vary in stages of biodegradation. Some nearby oils at the active OSPER "B" site do not correlate, suggesting that there is not significant subsurface transport of the spilled oils. Microbial populations at both sites are degrading the water-soluble crude oil compounds. The geochemical evidence and make-up of the microbial populations at both sites indicate that the systems are slightly different but based on free energy yields, are poised at the level of iron reduction.

Introduction

The U.S. Geological Survey is involved in a multidisciplinary investigation to study the transport, fate, and natural attenuation of inorganic salts, trace metals, radionuclides and organic compounds present in produced water and their impacts on surface and ground water and soils on the local ecosystem at the Osage-Skiatook Petroleum Environmental Research (OSPER) site A (fig. 1) and site B (fig. 2). About one hectare of land at each of the sites is affected by salt scarring, soil salinization, and petroleum contamination. The main environmental concern results from the fact that the sites are adjacent to Skiatook Lake, a 4,250-hectare reservoir, that provides drinking water and recreational fishing to the local communities. Petroleum wells and production tank batteries at site A have been inactive for some time and the bulk of the hydrocarbon (now degraded and weathered oil) and produced water releases occurred more than 60 years ago. One pit at this site however, contains relatively fresh asphaltic oil and high salinity brine. In contrast to site A, site B (approximately 6 km SSE.) includes an active production tank battery and adjacent brine and oil pit, an inactive tank battery and an injection well with a small brine pit.

For this portion of the study, samples of sediments, water, oil, and brine were obtained from several oil wells at the site B and areas adjoining the sites A and B, from the main pit at the Site B, from the asphaltic pit and adjacent weathered oil pit at the site A and from several of the 40 boreholes (1-71 m deep), recently drilled and completed. Samples of sediments and/or water

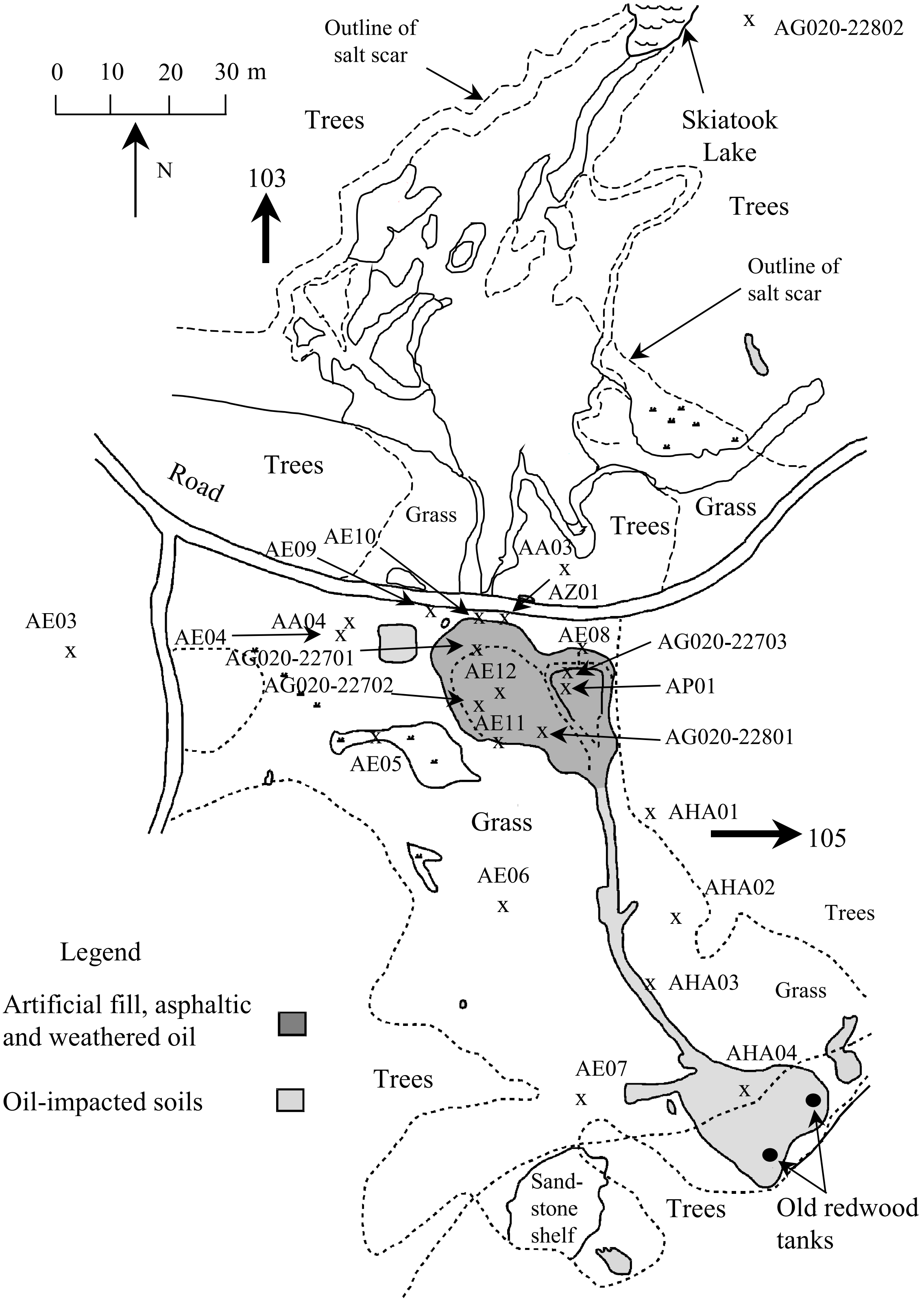

Figure 1. Sample locations for this portion of the study and important features at the site A location. Large arrows point to sample locations that are off the map area.

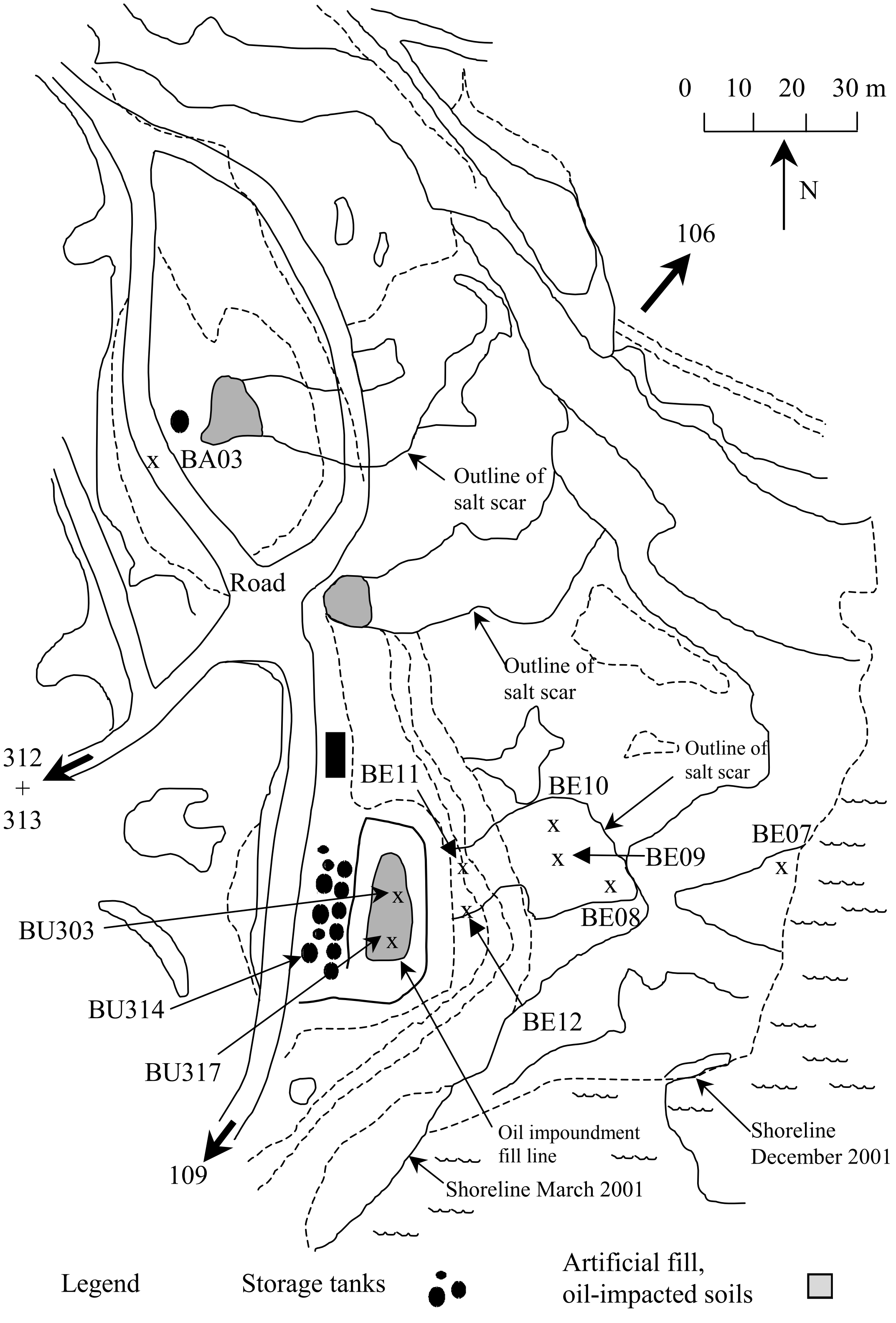

Figure 2. Sample locations for this portion of the study and important features at the site B location. Large arrows point to sample locations that are off the map area.

from these selected boreholes and from the brine and oil pits were obtained for characterization of the microbial population. Water samples for dissolved organics were obtained from selected boreholes with high salinity water and measurable hydrocarbon gases in the unsaturated zone. Soil and rock core samples were obtained from these selected boreholes to determine the amount and composition of oil sorbed onto the sediments.

Results completed to date show the crude oil source throughout the area is a typical paraffinic-naphthenic light oil (API gravity of ~35), containing *n*-alkanes as the dominant components. Even though petroleum production is from shallow sandstones (450-524 m site A and 260-305 m site B, elevation above sea level), the oils show no sign of biodegradation, indicating that microbes are not particularly active in the associated high salinity (~150,000 mg/L total dissolved solids) brine and possible inhibition by the hydrocarbon oil phase (currently under investigation). Microbial action, volatilization and water washing are likely responsible for the transformation of source oil to the asphaltic and weathered oil observed on the surface at site A. The leakage of oil with brine from the main active pit at site B is indicated by the detection of a thin, but discrete oil phase in at least one borehole, the presence of hydrocarbon gases in several boreholes and the smell of oil in many sediment cores from the impacted area located downslope from this pit. The measured concentrations of dissolved organic carbon (DOC), acetate and other organic acid anions, benzene, toluene, ethylbenzene, xylenes (BTEX), phenols and other organics in the source brine are relatively low, but their values in water samples from the impacted areas are higher and indicative of microbial activity.

Materials and Methods

Microbial Number Determinations

Microbial numbers in both water and sediment samples were determined using a five-tube most probable number (MPN) analysis. Samples were serially diluted by an order of magnitude into pre-reduced anaerobically sterilized mineral salts solution. Aliquots of the dilutions were inoculated into six different media, designed to promote growth and the enumeration of aerobic heterotrophic, facultative and strict anaerobic heterotrophic, denitrifying, facultative and strict iron-reducing, sulfate-reducing, and methanogenic microorganisms (Bekins and others, 1999).

Core Sample Collection

Sediment samples were collected in clear polycarbonate liners using a Geoprobe® or with a hand auger using similar polycarbonate liners. The liners were cut and, with O_2-free N_2 flowing over the sediment, about 10 g of sediment was scooped out with a sterile spatula and placed in 25 x 142 mm anaerobic isolation roll streak tubes (Bellco Glass Inc., Vineland, N.J.) filled with 20 mL of prereduced, anaerobically sterilized, mineral salts solution (Holdeman and others, 1977) and 10 mg/L Tween 80® (a nonionic surfactant added to help remove microorganisms from the sediment) (Bekins and others, 1999). The tubes were then sealed, and allowed to stand for 2 hr to permit penetration of the Tween 80 into the sample. The tubes were opened with oxygen (O_2)-free nitrogen (N_2) flowing over the surface and sonicated (10W for 30 s) to dislodge microorganisms into the mineral salts using a Branson Sonifer, Model 200, equipped with a microtip (Branson Corp., Danbury, Conn.). The samples were stored no more than 4 hr on ice (4°C) before microbial enumeration.

Water Sample Collection and Analysis

Water samples were removed using a peristaltic pump equipped with Teflon-lined tubing that had been previously cleaned with a detergent solution, rinsed with tap water and then with deionized water. Water samples were generally collected after pumping long enough to achieve stable pH and temperature values.

Water samples were collected and analyzed for low molecular weight organic acid and inorganic anions by ion chromatography (Kharaka and others, 2000). Inorganic cations were analyzed by inductively coupled plasma/mass spectrometry (Kharaka and others, this volume). Both cation and anion samples were chilled at 4°C until analyzed.

Water samples for dissolved methane (CH_4) analyses of were collected in 60-mL syringes and injected into evacuated 30 mL serum bottles until atmospheric pressure was reached. The serum bottles contained an O_2-free N_2 atmosphere before evacuation. Samples were preserved with 50 mg/L mercury using mercuric chloride. Dissolved CH_4 in the headspace was analyzed by a gas chromatograph equipped with a thermal conductivity detector after equilibration at ambient temperature (Godsy and others, 1992). The dissolved CH_4 present in the water sample was calculated using Henry's Law (Godsy and others, 1992). Water samples (20 mL) for microbial enumeration were collected with a disposable 60-mL sterile syringe and injected into an evacuated sterile 30-mL glass serum bottle. The serum bottles contained an O_2-free N_2 atmosphere before evacuation and were sealed with a butyl rubber stopper and secured with an aluminum crimp seal. All water samples were stored on ice for no more than 4 hr before inoculating the various microbial growth media onsite.

Production Oil Sample Collection

Four oils in current production from local oil wells near the study area are included in the sample set. Samples from site A and B included mud, rocks, sandy soil or sediment collected from surface accumulations or in cores, asphaltic surface oils, oil floating on water, and congealed oil from brine tanks. Table 1 describes the samples. Site samples were collected in pre-cleaned glass jars, refrigerated after collection, and then frozen until analysis. When the samples were unfrozen for analysis, any water was decanted off. One wet sediment sample (BE07) was air-dried and ground to about 30 mesh. Thirty grams was extracted with dichloromethane (DCM), filtered through glass wool, and the filtrate used for analysis (below). All other site samples were extracted with DCM after thawing. If traces of water were present, the water was removed by addition of anhydrous sodium sulfate, followed by filtration. Copper powder, pre-activated with concentrated hydrochloric acid, was also added to the DCM solutions before filtration in order to remove possible traces of sulfur. The four production oils (25 mg each) were dissolved in DCM and treated with copper. Aliquots of each of the site samples were measured so that approximately 25 mg of extractable material was analyzed. For each sample, its DCM solution was concentrated to near-dryness under a gentle stream of dry N_2, and the residue dissolved in 5 mL of hexane.

The hexane solution was then loaded onto a liquid chromatography column layered with alumina and silica gel for compound class separation. The column was eluted with hexane and then 30% DCM in hexane, rinsing the 5 mL container with the 30% solution when the eluting solvent was changed. Two separate fractions were collected-aliphatic (hexane) and aromatic (30% DCM). These fractions were analyzed for aliphatic and aromatic hydrocarbons by gas

Table 1. Sample and site descriptions.

Field designation	Description	Site location	Deg'n*
Locally produced oils			
103	Oil in current production	N of site A	A
105	Oil in current production	E of site A	A
106	Oil in current production	NE of site B	A
109	Oil in current production	SW of site B	A
Site A (02OS-)			
AG020-22701	Oil in mud, surface B/A	Oil/fill, down slope, edge pit	
AG020--22702	Oil in mud, surface	Oil/fill, down slope, old area	C+
AG020-22703	Oil in mud/sed., surface	Oil/fill down slope, new area	A/B
AG020-22801	Mature asphalt, solids	Oil/fill, down slope, old area	D+
AE12-436	Traces oil floating on water	Oil/fill, down slope, well	C+
AP01, Sludge Pit	Oil, sticky mud, 60 cm BLS**	Oil/fill, down slope, new area	A
AP01, Sludge Pit	Oil, sticky mud, 30 cm BLS	Oil/fill, down slope, new area	A
AZ01	Sandy sed./oil, 50 cm BLS	Oil/fill, down slope, edge pits	D&C+
AHA04-20 cm	Oil in mud, water, 20 cm" BLS	Oil-impacted soil, core, upslope	C++
AHA04-46 cm	Oil in sandy mud, 46 cm BLS	Oil-impacted soil, core, upslope	C+
AHA04-66 cm	Oil/ sed., water, 66 cm BLS	Oil-impacted soil, core, upslope	C/D+
AG020a-22802	Sand/sediment, 10 cm	Pit far down slope, near lake	D&A
AG020b-22802	Gray mud/clay, 40 cm	Pit far down slope, near lake	A
AE03	Old surface asphaltic tar	by well, W edge of site A	D
Site B (02OS-)			
BE07	Wet soil, 1.2-2.1 m /66.5 cm	E of tanks and pit	C
BU-314	Residual oil	Brine tank battery (by pit)	A
BU-314	Congealed oil with water	Brine tank battery (by pit)	A
BA03	Rocks/ oil, 5.7-5.8 m BLS	NW of brine tanks and pit	C
BU-303	Viscous surface tar	NW corner of site B	A
BU-317	Congealed oil on water	Large main pit	A
312	Flocculent - water, 34.5 m	West of site B, deep well 2	C
313	Flocculent - water, 35.9 m	West of site B, deep well 2	C

*Deg'n = Degradation State, defined in text
**BLS = below land surface

chromatography/mass spectrometry (GC/MS) as Total Ion Chromatograms (TIC) and in the Selected Ion Monitoring mode (SIM). Compound identifications were made either by comparison with known standards or with published spectra. Chromatograms of a typical local production oil, including a TIC, an Extracted Ion Chromatogram (EIC) of m/z 83 (alkylcyclohexanes), and a SIM chromatogram of terpanes (m/z 191) and steranes (m/z 217), with peaks of interest noted, are shown in figure 3. The TICs were used to evaluate the level of weathering or degradation of the samples. The state of weathering (table 1) ranged from A to D, where A = no/low degradation, *n*-alkanes dominant; B = *n*-alkanes minor, isoprenoids becoming prominent; C = no *n*-alkanes, isoprenoids dominant; and D = highly degraded, almost no residual components except high-molecular-weight biomarkers. Some samples from the site A included some anomalous high-end alkanes, indicated in table 1 with a “+”.

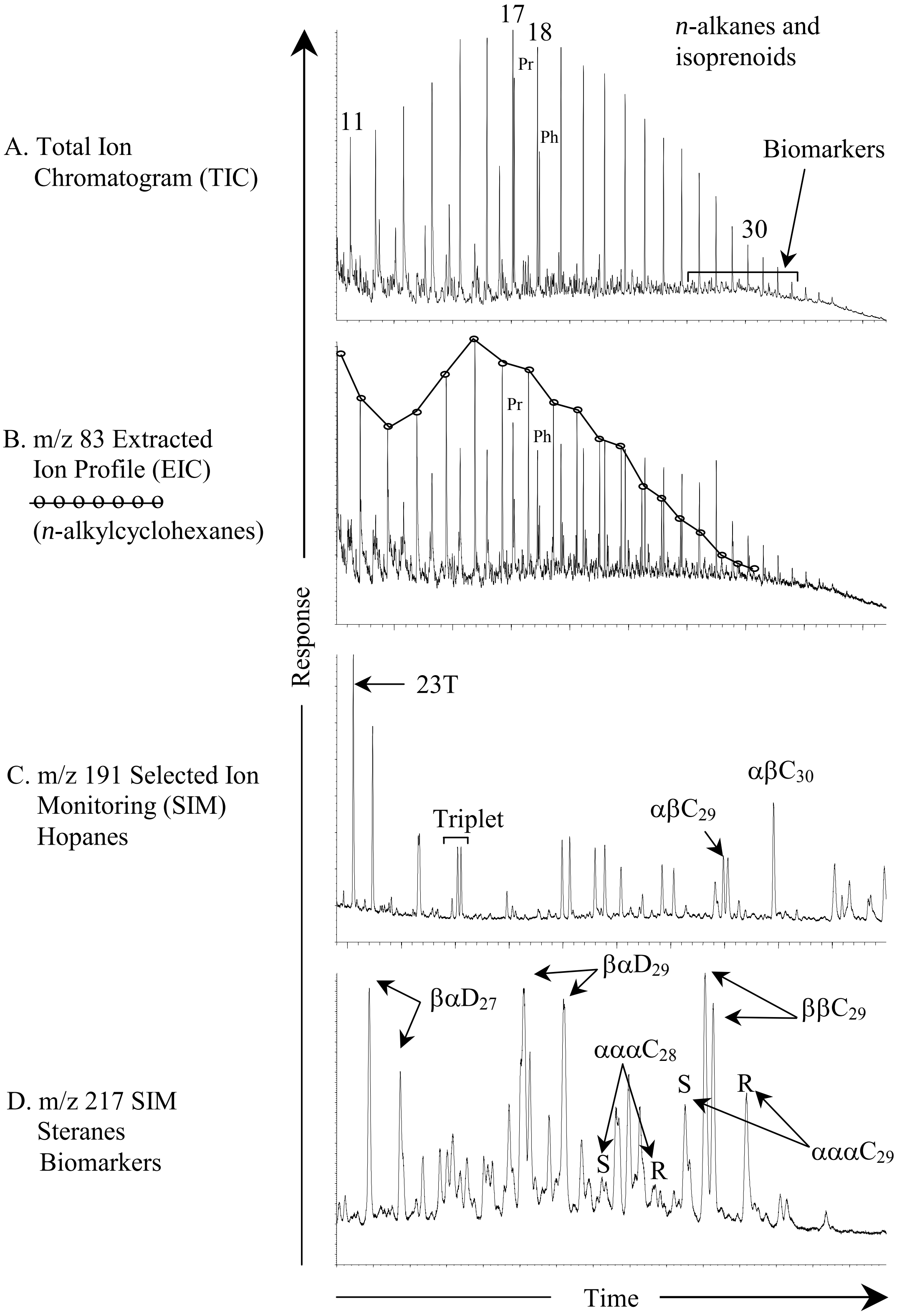

Figure 3. Chromatograms of Production Oil 103. Most compounds of interest are identified in the text. Others: $\beta\alpha D_{27}$ = 13β,17α(H)-diacholestane (S+R); $\beta\alpha D_{29}$ = 24-ethyl-13β,17α(H)-diacholestane (S+R); $\beta\beta C_{29}$ = 24-ethyl-14β,17β(H)-cholestane (S+R).

Selected biomarker ratios, listed below, were calculated from the TIC and SIM chromatograms using peak heights. These biomarker parameters were used to correlate the samples, and included the following ratios (table 2):

1. Pr/Ph, pristane/phytane. This ratio of two ubiquitous isoprenoid hydrocarbons is widely used as a source parameter (Peters and Modlwan, 1993).
2. 23T/C_{30}, C_{23}tricyclic terpane/17α,21β(H)-hopane. This ratio is a source parameter adapted from Peters and Moldowan (Peters and Moldowan, 1993).
3. Tm/Ts, 17α-22,29,30-trisnorhopane/18α-22,29,30-trisnorneohopane. This ratio is used as both a source and maturity parameter (Seifert and Moldowan, 1978).
4. Triplet, [C_{26}-tricyclic terpane (S?) + C_{26}-tricyclic terpane (R?)/C_{24}-tetracyclic terpane. This source parameter was used to distinguish coastal tar residues in Prince William Sound (Kvenvolden and others,1995).
5. C_{30}/C_{29}, 17α,21β(H)-hopane/17α,21β(H)-30-norhopane. This ratio was used by Palacas and others (1984) as a source parameter.
6. C_{29}S/(S+R), 24-ethyl-5α,14α,17α(H)-cholestane (20S)/ 24-ethyl-5α,14α,17α(H)-cholestane (20S+20R). This sterane epimer ratio is commonly used in petroleum geochemistry as a maturity parameter; the equilibrium value at full maturity is ~0.5 (Mackenzie and others, 1980).
7. C_{28}R/C_{29}R, 24-methyl-5α,14α,17α(H)-cholestane (20R)/ 24-ethyl-5α,14α,17α(H)-cholestane (20R). This source parameter has been modified from discussions in Grantham and Wakefield (1988) and Waples and Machihara (1991).
8. RI, Refractory Index. This PAH ratio is a source parameter, the ratio of the major peak in the highly refractory C_{26} to C_{28} triaromatic sterane suite and in the monomethyl chrysenes (Hostettler and others, 1999).

Results and Discussion

Microbial Populations

The general process of biodegradation of the water-soluble fraction (WSF) of crude oil occurs under specialized conditions. In the saturated subsurface, WSF compounds are used by the microorganisms as an electron donor for energy, and dissolved O_2 is utilized preferentially as the primary electron acceptor. Once O_2 is depleted, anaerobic microorganisms typically use available electron acceptors in the following order: nitrate (NO_3^-), producing N_2, or ferric iron (Fe^{3+}), producing ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), producing sulfide (S^{2-}), and carbon dioxide (CO_2), producing CH_4. By looking at both the spatial distribution of the different microbial populations present on/or within the sediment and in the pore water; and the spatial distribution and concentration of oxidation/reduction reactants and products, the mechanism(s) and rates of biodegradation can be assessed. A reconnaissance for the different physiological groups of microorganisms, along with the ground-water geochemistry, can provide information on the major microbial processes that may be occurring in the subsurface environment. The microbial population can be categorized under the following physiological groups:

Table 2. Summary of results of geochemical correlation parameters from tars and oils. Ratios are defined in the text.

		m/z 191				m/z 217		
Site	Pr/Ph	$\frac{23T}{C_{30}}$	$\frac{Tm}{Ts}$	Triplet	$\frac{C_{30}}{C_{29}}$	$C_{29}\frac{S}{S+R}$	$\frac{C_{28}}{C_{29}}$	RI
Locally produced oils								
103	1.5	2.1	0.50	7.1	1.9	0.48	0.20	0.30
105	1.5	1.9	0.56	6.4	1.9	0.48	0.20	0.27
106	1.5	2.6	0.41	7.7	1.9	0.48	0.20	0.25
109	1.5	1.8	0.55	6.4	1.9	0.48	0.20	0.27
Site A (02OS-)								
AG020-22701	1.2	1.4	0.63	5.4	2.0	0.47	0.21	0.33
AG020-22702	1.2	1.3	0.63	5.6	1.9	0.46	0.20	0.40
AG020-22703	1.3	1.3	0.55	5.9	1.9	0.47	0.21	0.39
AG020-22801	nc	1.2	0.57	5.8	1.9	0.47	0.20	0.46
AE12-436	1.3	1.4	0.62	5.7	1.9	0.47	0.20	0.62
AP01-61 cm, Sludge Pit	1.5	1.3	0.64	6.1	1.8	0.46	0.18	0.43
AP01-30.5 cm, Sludge Pit	1.5	1.3	0.60	6.0	1.9	0.45	0.20	0.40
AZ01	1.1	1.2	0.59	4.9	1.9	0.49	0.19	0.52
AHA04-20 cm	1.1	1.5	0.58	5.6	1.9	0.47	0.19	0.33
AHA04-46 cm	1.3	1.5	0.56	5.8	1.9	0.47	0.20	0.46
AHA04-66 cm	1.1	1.4	0.59	5.5	2.0	0.47	0.19	0.40
AGO20a-22802	1.4	0.70	0.63	3.6	1.7	0.58	0.20(*)	0.24
AGO20b-22802	1.6	0.23	1.2	3.1	1.8	0.43	0.33	0.74
AE03	nc	0.56	0.52	1.2	1.8	0.61	0(no C_{28})	0.24
Site B (02OS-)								
BE07	1.4	1.1	0.66	5.0	1.8	0.47	0.20	0.47
BU-314	1.6	1.5	0.59	5.9	1.9	0.48	0.21	0.36
BU-314	1.5	1.4	0.56	5.5	1.9	0.47	0.21	0.39
BA03	1.4	1.2	0.62	4.8	2.0	0.48	0.22	0.78
BU-303	1.5	2.0	0.46	6.5	2.0	0.48	0.20	0.26
BU-317	1.4	2.2	0.48	6.8	1.9	0.47	0.20	0.62
312	1.3	1.0	0.76	3.1	1.8	0.46	0.28	0.78
313	1.4	1.1	0.75	4.8	2.0	0.47	0.20	0.68

nc = not calculatable due to lack of constituents

* = uncertain identification of relevant peak(s)

Aerobes

Microorganisms that utilize O_2 as the terminal electron acceptor are termed aerobes and those that can only use O_2 as the electron acceptor are termed obligate aerobes. The use of O_2 as the electron acceptor always provides the most energy from a given compound and microorganisms capable of using other electron acceptors will always use O_2 first.

Facultative Aerobes

Because diffusion of molecular oxygen in water is about 100,000 times slower than it is in the gas phase, an oxic system can quickly become anoxic in saturated environments. The next most thermodynamically efficient electron acceptor commonly found in the environment is NO_3^-. Nitrate, nitrite (NO_2^-), and nitrous oxide (N_2O) are used as electron acceptors by many common facultative aerobic soil bacteria. These microorganisms simply switch to using the next best electron acceptor (NO_3^-) when O_2 is not available. When NO_3^- has been utilized or is not present, most, but not all, of these microorganisms can switch to Fe^{3+}, the next best electron acceptor based on free energy yields.

Obligate Anaerobes (Respiratory)

These microorganisms are the obligate iron reducers, sulfate reducers, and CO_2 reducing methanogens, each of which may be thought of as having a very truncated respiratory system. These organisms obtain very little energy from these processes, but still prevail under these meager conditions. The obligate iron and sulfate reducers can use acetate and/or molecular hydrogen (H_2) as their energy source. The methanogenic microorganisms in this group use molecular H_2 or formate as their energy source. The H_2 is generated by the other group of anaerobes described immediately below.

Obligate Anaerobes (Fermentative)

Fermentation, by definition, is the use of organic electron donor to give a stoichiometric balance of protons and electrons in lieu of an electron acceptor (*i.e.* oxidation and reduction of the same organic compound). Many of these microorganisms produce H_2 during the production of protons and electrons from more complex native or WSF compounds. Acetate fermenting methanogens are also included in this group.

Site A Microbially Important Geochemistry

Concentrations of low molecular weight fatty acids (*e.g.*, butyrate, propionate, acetate and formate), known intermediates in the anaerobic microbial degradation of crude oil and other complex organic compounds (Godsy and others, 1992), are very high (210 mg/L acetate, site AP01) in the sludge pond near the road. These concentrations generally decrease moving downslope (Kharaka and others, this volume) suggesting anaerobic microbial processes predominate (AE08, AE09, and AE10, generally 0.8-1.2 m below land surface [BLS]). The exception to this trend occurs in the deeper wells AA03s (1.2-2.7 m BLS), and AA03d (3.3-4.9 m BLS) where acetate concentrations reach 101 and 517 mg/L, respectively). Wells AA04s (1.8-3.4 m) and AA04d (5.8-7.3 m), located outside of the area affected by the sludge pits have non-detectable levels of fatty acids; however, they have high total dissolved solids (TDS) and been affected by produced water. The DOC concentrations generally correlate positively with the concentrations of fatty acids. In addition to the volatile fatty acids, low concentrations of benzene (0.29 mg/L) and toluene (0.34 mg/L) were found in a water sample from AP-01.

Sediment Fe^{2+}/Fe^{3+} ratios (Rice and others, this volume) outside the oil-impacted soils (from the old southern tank farm to north of the sludge pits, AE04 to 07) at the site are low (< 0.5) in shallow sediment (0-1.2 m, BLS) samples. The low Fe^{2+}/Fe^{3+} ratios result from low Fe^{2+}

concentrations on the sediments suggesting a lack of crude oil components for microbial biodegradation and thus iron reduction; however, the Fe^{3+} concentrations at these sites range from 0.5 to 1.0 mg/g. The total iron concentration in the water sample from the sludge pit (AP01) is 595 mg/L, strongly suggesting that microbial iron-reduction is occurring at the expense of the water-soluble components of the oil present in the pits.

In addition, very low levels of NO_3^- were found throughout the site (Kharaka and others., this volume), and no measurable amounts of S^{2-} were found even with the probable anoxic conditions as evidenced by the sulfate reducing microorganisms near the oil impacted soils and high concentrations of SO_4^{2-}. Perhaps, the S^{2-} is precipitated as an iron sulfide (FeS) because of the high concentrations of Fe^{3+} throughout the area. Only trace amounts of CH_4 were detected in the water samples throughout the area and downslope near the sludge pits, again strongly suggesting that microbial iron reduction is the predominant microbial process in and around the sludge pit.

Site A Microbial Populations

Microbial populations capable of aerobic growth are equal to or slightly larger than populations capable of fermentation suggesting that the population is mixed aerobic and facultative anaerobes (microorganisms capable of aerobic growth in the presence of O_2, and fermentation or either denitrification and/or iron-reduction in the absence of O_2 (table 3). This observation for the shallow samples AHA01 to 04 is consistent with a flow system that is driven by rainfall events. The rainfall contains dissolved O_2 and when the event has passed, pore spaces with higher dissolved O_2 will remain. Of the samples throughout this site, only a small proportion of the microorganisms are capable of denitrification (AE10 and 12 did not have a denitrifying population); this would be due to very low levels of NO_3^- found at this site.

Presumably, in samples downslope from the sludge pit (AE08, 10, and 12), anaerobic microorganisms should predominate. The iron reducing population at this site appears to be a mixture of facultative aerobes and strict anaerobic microorganisms with the strict anaerobic microorganisms predominating. This can be seen from the differences in the populations of iron reducing microorganisms minus the populations of denitrifying microorganisms. Relatively large numbers of microorganisms capable of sulfate reduction are present in samples throughout the site; however, they may not be particularly active since concentrations of S^{2-} are very low even with the abundance of SO_4^{2-} or the S^{2-} at the site is removed as FeS. In addition, only very low numbers (< 100 MPN/g) of methanogenic microorganisms were found at three sites (AHA01, AHA03 and AE12) indicating they may not be particularly active except near the sludge pits.

Study Area Production Oils

The four oils from currently producing oil wells serve as representative baseline samples for oils produced throughout this local area. These four oils share similar characteristics. They are typical paraffinic-naphthenic light oils, with an API gravity of approximately 35, containing *n*-alkanes as their dominant components. They are fully mature oils with very similar chemical fingerprints, as shown by the correlation parameters given in table 2. Small numerical differences in these parameters allow some differentiation between the four oils, but their overall natures are quite similar. Even though petroleum production is from shallow sandstones, these

Table 3. Sample locations and Most Probable Numbers (MPN) of microbial populations on sediment and in water samples.

[BLS = below land surface; ND = < 20-40/mL or g; >> = > E+6/mL or g; ~~ = approximate value E+2-4/g]

Site #	Notes	Aerobes MPN/mL	Aerobes MPN/g	Fermentors MPN/mL	Fermentors MPN/g	Denitrifyers MPN/mL	Denitrifyers MPN/g
AEO8A	0-1.2 m, bottom		3.5E+06		2.8E+05		8.8E+03
AE08B	0-1.2 m, 25 cm from top		>>		2.0E+05		8.7E+02
AE10	0-1.2 m, 25 cm from bottom		2.2E+05		1.1E+06		ND
AE12	0-1.2 m, 41 cm from top		1.4E+03		1.6E+05		ND
AHA01	~20-30 cm BLS		5.2E+05		1.7E+05		9.7E+01
AHA02	~20-30 cm BLS		1.8E+05		7.4E+04		ND
AHA03	~20-30 cm BLS		8.3E+05		2.5E+06		1.4E+02
AHA04	20 cm BLS		1.8E+05		2.8E+04		1.4E+02
AHA04	46 cm BLS		>>		8.7E+03		8.0E+01
AHA04	66 cm BLS		2.1E+06		1.5E+04		2.7E+01
BEW07	1.2 m BLS	2.4E+03		7.9E+02		ND	
BE07A	0-1.2 m, 66.5 cm top		9.9E+04		9.3E+02		ND
BE07B	1.2- 2.1 m, 35.5 cm top		4.6E+04		1.3E+04		3.8E+01
BE08	1.2-2.1 m, top		6.0E+03		4.4E+03		ND
BE09S	1.2-2.1 m, bottom Shale		2.6E+03		8.8E+02		ND
BE09	1.2-2.1, 26 cm top		2.4E+03		6.0E+03		ND
BE10	0-1.2 m, 70 cm top		8.4E+04		1.0E+03		ND
BE11	1.2-2.1 m, 40.5 cm top		5.7E+03		5.7E+03		ND
BE12	1.2-2.1 m, 15 cm top		7.2E+05		7.9E+05		ND

Site #	Iron Reducers MPN/mL	Iron Reducers MPN/g	Sulfate Reducers MPN/mL	Sulfate Reducers MPN/g	Total Methanogens MPN/mL	Total Methanogens MPN/g
AEO8A		2.0E+06		9.4E+05		1.0E+00
AE08B		>>		5.0E+03		ND
AE10		3.3E+06		2.6E+05		ND
AE12		2.6E+05		2.6E+03		4.0E+00
AHA01		5.2E+05		1.8E+04		4.3E+00
AHA02		1.4E+05		7.4E+03		ND
AHA03		2.5E+06		1.4E+04		7.7E+01
AHA04		9.2E+04		2.0E+03		ND
AHA04		>>		1.5E+04		ND
AHA04		>>		3.2E+05		ND
BEW07	2.4E+05		3.1E+02		7.0E+00	
BE07A		1.3E+02		9.9E+02		ND
BE07B		4.6E+04		6.3E+03		2.5E+01
BE08		ND		1.5E+02		ND
BE09S		ND		ND		ND
BE09		ND		1.4E+03		ND
BE10		4.9E+04		~~		ND
BE11		1.4E+03		3.9E+02		ND
BE12		3.1E+06		1.8E+04		1.1E+02

fresh oils show no sign of biodegradation, indicating that their reservoirs and the associated high salinity brines are not conducive to microbial action on the hydrocarbon phase. However, as the oil has been mined, brought to the surface, and spilled throughout the study areas, the resultant oils exhibit widely varying levels of degradation. Volatilization, water washing, and microbial action are likely responsible for the transformation of the source oil to the surficial weathered, biodegraded, and sometimes asphaltic oils observed at the study sites.

Characterization of Site A Oils

The majority of oil samples from OSPER "A" site correlate closely with each other, despite being at highly variable stages of degradation (tables 1 and 2). Three samples in a core at the top of the production area (AHA04, samples from 20 cm, 46 cm, and 66 cm BLS), most likely represent older oil spilled from earlier production. They are degraded to the point of complete loss of the *n*-alkanes ("C"-stage), with the sample lowest in the core showing the most degradation, containing a highly weathered component ("D") and only low levels of the isoprenoids characteristic of the C-stage. Degradation to the C-stage in a fuel oil spill is estimated to take at least 20 years (Christensen and Larsen, 1993).

Down slope, approximately 60-90 m from these samples, are eight samples from different areas of a sludge disposal pit. One area is obviously old and weathered, and its oils (AG020-22702, AG020-22801) and oil floating on water from a well in its midsection (AE12) are at the C- or D-stages. Another section, where the oil is fresher and probably more recently dumped, three oils (AP01 30 cm and AP01 60 cm, along with AG020-22703) are at A-stage or slightly beyond, at an A/B-stage. Two samples from the downslope edge of the same pit area, where there is some overlap, are fairly fresh (AG020-22701, B/A-stage) and quite old (AZ01, D- with some C-stage), respectively. It is not known whether the eight pit-area oils migrated downslope from the production area over time or were dumped during and after production, but these eleven oils are clearly related (table 2).

However, the other three oils from this site are not so closely related. Samples a- AG020-22802 and b- AG020-22802, from two different horizons in a pit about 110 m further downslope, adjacent to the lake, are not the same as the upslope samples, and in fact, are somewhat dissimilar to each other. The first, from 10 cm depth, is a mix of highly degraded oil and fresh oil (D- and A-stages), and the second, from 40 cm depth, is quite fresh (A-stage). The old surface oil at the west edge of the site (AE03) is the most different, and probably is a remnant of a very old disposal pocket, possibly older than 100 years. Despite individual differences in the four different disposal pockets at site A, all the oils reflect the characteristics of the local oil province in their biomarker distributions. In addition, however, there is perhaps some extraneous oil product at some sites. Samples from the core at the production site and from downslope in the old part of the sludge pit contain additional components, low levels of an anomalous group of high molecular weight *n*-alkanes. The two new sludge pit samples, AP01-30 cm and AP01-60 cm, also contain some high molecular weight *n*-alkanes, giving their GC/MS TIC two distribution maxima, the typical primary maximum at n-C_{18} and another at n-C_{28}. These sample sites, therefore, may also be contaminated with some extraneous oil product such as lubricating oil or the like.

There is no generally applied method to determine from the chemical profile whether the oil has been degraded aerobically or anaerobically. However, some recent work on crude oil spillage in Bemidji, Minnesota, suggests that in the latter stages of degradation, the profile of the homologous *n*-alkylcyclohexanes (m/z 83 chromatograms) can shed some light on this differentiation (Hostettler and Kvenvolden, 2002). These compounds are more refractory than *n*-alkanes, and thus retain their contribution to the chemical signature of the source oil for a longer period after exposure to the environment. Their original distribution in a fresh oil is usually bell-shaped (figs. 3B and 4). Weathering (aerobic degradation) attacks and removes the low molecular weight end of the series (Wang and others, 1998), whereas anaerobic biodegradation, particularly in the subsurface, slowly degrades homologs from the high molecular weight end (Hostettler and Kvenvolden, 2002). At site A the samples show variable amounts of low-end loss, even in the relatively undegraded samples, indicating that all the samples have undergone some physical weathering or aerobic loss. However, the more degraded samples (at about the C-stage, but beyond this stage samples are too degraded to interpret) show some loss from the high molecular weight end as well, indicating some anaerobic losses also. This pattern occurs to some extent in the old fill-area (samples AG020-22702 and AE12) and possibly in the upslope oil-impacted soil samples at AHA04.

Site B Microbially Important Geochemistry

In contrast to the "A" site, the tank battery above the main pit at the "B" site is actively pumping oil and reinjecting the produced brine. A sample from the oil separation tank at this site (BU314) contains indicators of microbial activity, in spite of the extremely high TDS (133,000 mg/L). In addition to acetate and formate (0.5 and 0.3 mg/L, respectively), benzene (4.0 mg/L), toluene (0.87 mg/L), ethylbenzene (0.73 mg/L), *m*- and *p*-xylene (0.71 mg/L), and *o*-xylene (0.43 mg/L) were detected in the water sample. The water sample also contained 70 mg/L ammonia, 35 mg/L total iron, and a lower pH (6.5) than other water samples in the area. These observations suggest the WSF of the oil is, even in the presence of extremely high TDS brines, undergoing biodegradation. The higher molecular weight fractions of the oil apparently do not biodegrade in the formation or in the oil separation system or tanks. These observations require further investigation before they can be confirmed.

Water samples from the main pit just in front of the tank battery (BU317) also showed signs of microbial degradation of the WSF of the oil. In addition to high total dissolved iron (40 mg/L), higher total organic carbon (43 mg/L), and a lower pH (6.6), the sample contained acetate (0.6 mg/L) and formate (0.3 mg/L). Benzene (0.23 mg/L) was also detected. Down slope from the main pit to the lake, only low concentrations of acetate and formate (≤ 0.6 mg/L) were found.

Sediment Fe^{2+}/Fe^{3+} ratios (Hostettler and others, 1999) at this site are high (~45 to ~11) in shallow (0-1.2 m) samples near the lake water line and below the main pit (BE07, BE09, BE11, and BE16) strongly suggesting microbial iron reduction. The Fe^{2+}/Fe^{3+} ratios in deeper samples (1.2-2.1 m) in the same holes and all samples further from the shore and the main pit have ratios generally < 1, with the exception of BE09 (12.6). This well is just downslope from the main pit and appears to be in the flow path from the main pit to the lake. The low values for wells closer to the lake and out of the flow path suggests that these sites are influenced by the O_2-rich lake water and aerobic microbial processes may predominate.

As at site A, very low levels of NO_3^- were found throughout site B (Kharaka and others, this volume), and no measurable amounts of S^{2-} were found, even with the probable anoxic conditions as evidenced by the sulfate-reducing microorganisms near the oil impacted soils and high concentrations of SO_4^{2-}. Only trace amounts of CH_4 were detected in the water samples throughout the area and downslope near main pit, again strongly suggesting that microbial iron reduction is the predominant microbial process in and around the main pit to the lake.

Site B Microbial Populations

Microbial populations capable of aerobic growth are equal to or less than populations capable of fermentation suggesting that the population is predominantly facultative aerobes (table 3). Only one sample, BE07 at 1.2 to 2.1 m, at this site contained microorganisms (38 MPN/g) capable of denitrification, again due to the very low levels of NO_3^- found at this site. The iron reducing population would be strictly anaerobic since there are not a significant numbers of denitrifyers at this site.

Relatively large numbers of microorganisms capable of sulfate reduction are present throughout; however, as at Site A, they may not be particularly active or the S^{2-} may have been precipitated out of solution. Only very small numbers (< 100 MPN/g) of methanogenic microorganisms were found at two sites (BE07 and BE12) indicating they may not be particularly active, as is the case with the sulfate reducing microorganisms. The water sample from BE07 has a population that is essentially the same as the two sediment samples from this site. The fact that the total population is evenly distributed between both the water and the sediment strongly suggests that the population is quite active. In situations where little or no microbial activity is taking place, up to 90% of the population is attached to the sediment (Bekins and others, 1999). In contrast to this finding, the sample taken in the shale (BE09S) has a population composed of only aerobic and fermenting microorganisms. Denitrifying, iron reducing, sulfate reducing, and methanogenic microorganisms were not detected in this sample. This is may be due to the overall impermeability of the shale and will be investigated in detail.

Characterization of Site B Oils

Samples from site B show more variation in their correlation parameters, indicating that the oils are probably from several slightly different collection sources. Two samples of fresh oil (BU314, congealed oils from the brine tank battery, at degradation state A) correlate with each other, and perhaps are similar to those in the main body of oils from site A (table 2). Two other fresh oil samples from the main pit just in front of the tank battery (sample BU317 and 303), which might be expected to be the same as the oils from the brine tanks, actually have slightly different parameters although they are at the same A-state of degradation. A C-degraded oil, BE07, from a subsurface core of wet soil, about 50 m in front of the main pit (sometimes submerged under the lake water), is again similar but not identical to that from the brine tanks or the main pit. Another sample from the subsurface, BA03, present in low amounts on rocks at almost 5.8 m below land surface, is also at the C-stage and is similar to the oil in BE07 except for one parameter. The two oils associated with flocculent material from the deep well just off-site west (312 and 313) are C-degraded and correlate fairly well with one another, and, again, are slightly different from the other oils.

With respect to the type of degradation that has impacted the samples, all four A-state oils (from the brine tanks and the main pit) show only low-end, aerobic or weathering loss on the *n*-alkylcyclohexane chromatograms. The other four samples, all at C-degradation, show both low-end and high-end losses, indicating both weathering and anaerobic biodegradation. Examples are shown in figure 4.

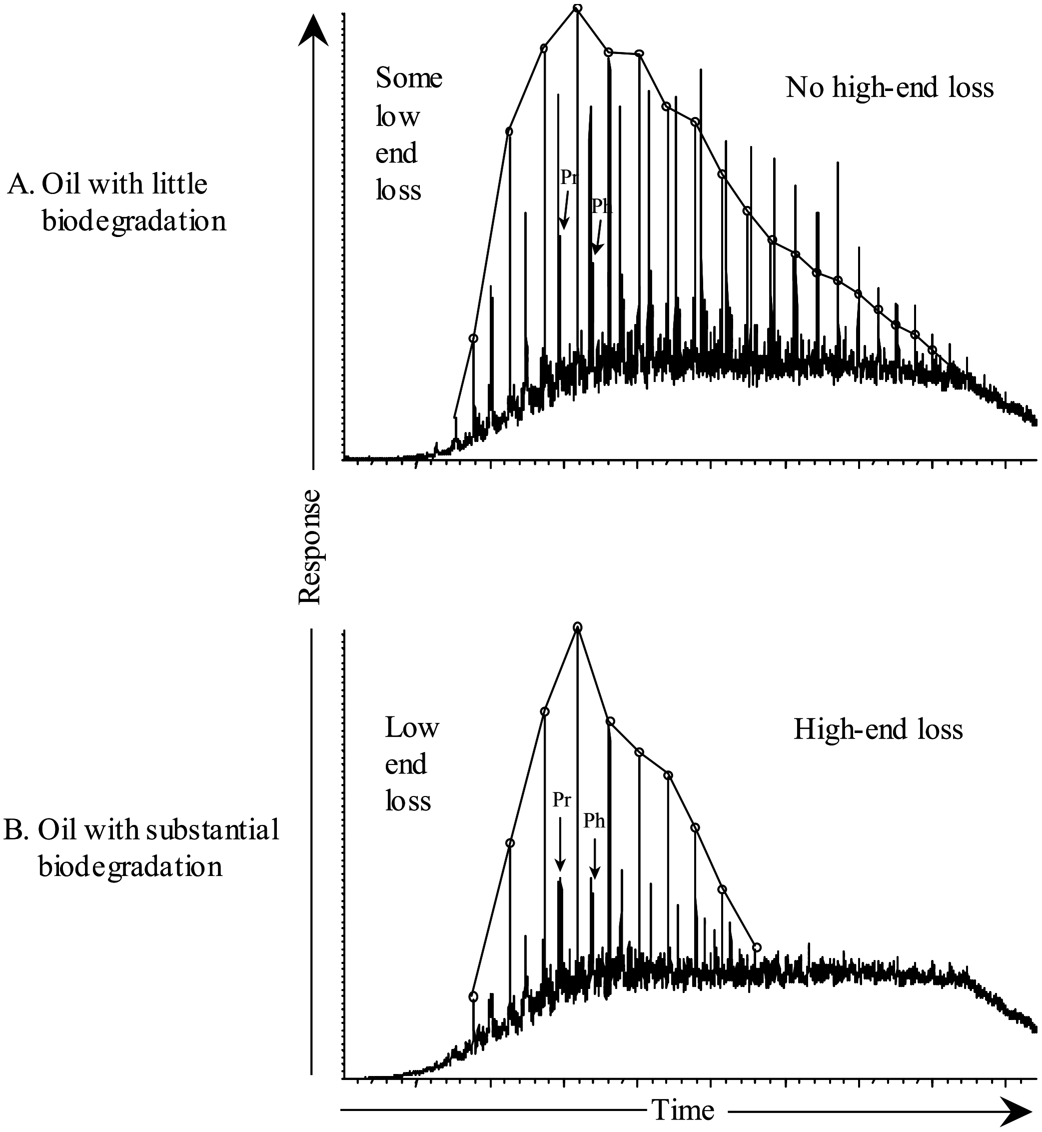

Figure 4. m/z 83 (*n*-cyclohexane profile showing an A-degradation sample (BU-317) and a C-degradation sample (BE-07). Also, compare figure 3A with figure 3B at a similar degradation level.

Conclusions

At both sites, the native microbial populations are degrading the low molecular weight WSF crude oil compounds. This fraction includes low molecular weight alkanes, one and two ring aromatic compounds, phenolic compounds, BTEX compounds, and *n*-alkylcyclohexanes. These fractions along with some anthropogenic carbon are being used by the resident microbial populations as electron donors, extracting the energy available, and reducing the appropriate inorganic electron acceptors for that population (with the exception of the fermenting populations). Both the geochemical evidence and make-up of the microbial populations in the oil-impacted soils at sites A and B suggests that the systems are thermodynamically poised at the level of iron reduction (fig. 5).

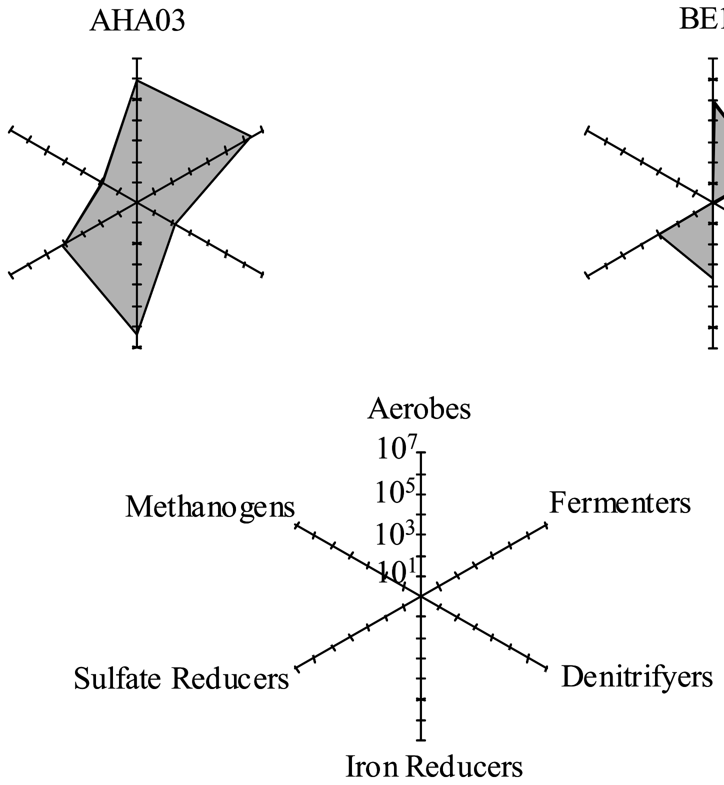

Figure 5. Star radial diagrams showing MPNs of six physiological microbial types present on the sediment at representative samples from OSPER “A” and “B” sites (See table 3 for actual numbers). Refer to the lower diagram for key to the arms’ labels and MPN values. All values are in numbers per g dry weight sediment. Values less than the minimum detectable numbers are plotted at the lowest tick mark.

Because the shallow system upslope from the sludge pit at site A is apparently rainfall driven (intermittent rainfall dissolved O_2 input), the microbial populations, in general, are comprised of aerobes, facultative aerobes, and strict anaerobes. However, the high concentrations of volatile fatty acids and high dissolved iron and other geochemical parameters of the system near and just downslope of the sludge pit suggests that the microbial population should be predominantly facultative aerobes and strict anaerobes, with iron reducing microorganisms predominating. This was confirmed by microbial population analyses. In addition, the population of sulfate reducers is only an order of magnitude less the iron reducers and the potential for a more active sulfate reducing population cannot be ruled out.

In contrast to site A, it appears that the microbial populations are exclusively comprised of facultative aerobes and strict anaerobes at site B, due to the water-saturated soils throughout the site. The hydraulic pressure from the main pond and the lake would tend to keep these soils saturated. It is unclear at this time the effect of the fluctuating water levels and input of anthropogenic carbon from the lake has on the nature of the microbial populations and the overall degradation pathways at this site.

Oil residues throughout the study areas are all similar in their general characteristics, indicating that they are all from the same regional oil province. There are, however, enough small differences in correlation parameters within the oil samples that several slightly different sub-groups of oils can be observed. Thus, it appears that at Site A all the oils in the roughly 100 m area from the oil-impacted soil where original production occurred, downslope to where the oil either flowed or was dumped, is the same oil, although at significantly variable stages of biodegradation. Oil samples from the three other, more distant sites are somewhat different and thus probably represent different oil spillages. Oils that give possible evidence of anaerobic degradation are the four oils at the C-degradation level. These occur generally beneath land surface (the core at the upslope production site and the well sample in the fill area), except for AG020-22702, which is from a surface mud in the older part of the fill area. In samples in a D-degradation, the oils are too degraded for the method outlined in this work to determine the nature of the degradation.

At site B the samples sort out in small groupings. These groupings are the two samples from the brine tanks, the two samples from the main pit, and two from a deep well, then BE07 downslope from the pit and BA03 NW of the pit, the last two from the subsurface. There does not seem to be a correlation between the oils at closely adjacent sites, that is, oil in the brine tanks, the main pit, or the downslope sample, indicating that there probably is not significant subsurface transport of the non-water soluble, or high molecular weight components of the spilled oils. As at site A, the samples which show tentative evidence of anaerobic degradation are the subsurface oils in the C-degradation stage, that is, the two from the deep well, BE07, and BA03 listed above.

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Impact of Oil Production Releases on Some Soil Chemical Properties at the OSPER Sites

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Abstract

As part of a site characterization to develop guidelines for stabilizing or restoring degraded areas, surface and soil core samples were collected from two sites, a depleted and a producing field in old oil production areas near Skiatook Lake in Osage County, Oklahoma. The soil samples were analyzed for nitrate, organic matter, total petroleum hydrocarbons (TPH), conductivity, chloride, and dehydrogenase activity (DHA - a measure of viable biomass). Low levels of nitrate were observed for most of the samples, except those where animal activity had occurred recently. There was a direct relationship between high conductivity and high chloride values. The higher TPH values were associated with the presence of asphaltic oil waste in the soil. Viable biomass was detected in 80% of the 20 soil and core samples collected.

Introduction

Hydrocarbon and produced-water releases occur in oilfield operations as a result of equipment failures and other accidents. These releases, the disposal by injection of water co-produced with oil and gas, and the restoration of affected areas are national issues that concern watershed managers as well as regulators, surface landowners, and local residents. Most of the releases were related to past acceptable oilfield practices. Studies are now needed to evaluate and restore the ecosystems using cost-effective techniques.

The two field sites studied have a long history of petroleum production (Otton and Zielinski, this volume). Crude oil and brine water have impacted the landscape surface, subsurface, and plant ecosystem. Measurements of soil salt content, nutrients, organic matter, petroleum hydrocarbons, and bacterial activity provide indicators of the level of contamination, the health of the soil, and possible success of restoration efforts. The information obtained will be helpful for developing an effective restoration program at these two sites.

Experimental Methods

Surface soil samples to a depth of six inches and core samples to a depth of four feet were collected from the depleted OSPER "A" (fig. 1) and producing OSPER "B" (fig. 2) sites, with locations described in table 1. Sample locations were selected on and away from the salt-scarred and/or asphaltic oil contaminated soils. Sampling was completed during April 2002 when temperatures were moderately warm. Soil samples were moist and had a friable texture. Dehydrogenase activity (DHA) was determined on freshly collected soil material. The procedure is described in Stevenson (1959) and the values are reported herein as micrograms of triphenylformazan per gram (μg/g) of moist soil. The remaining soil was air-dried and passed through a 10-mesh sieve (0.079 in.). Soil nitrates were measured on a dilute acid extract of 95% distilled water, 2% sulfuric acid, and 3% hydrochloric acid of the soil using a cadmium reduction method (EPA Standard Method 353.3). Percent organic matter of the air-dried soil samples was determined using a Model ST-OR 5020 LaMotte Company kit. Total petroleum hydrocarbons (TPH) were determined by an EPA-approved protocol by PetroFLAG identified as EPA-SW 846 Method 9074.

To standardize the analyses of different soils the extraction was done as soon as possible on freshly collected samples. It is important to note that the results of TPH methods can widely vary, but the method selected for TPH analyses is an EPA-approved reference method. All soil/core analyses were done by standardized published protocols. It should be noted that salt scars adjacent to the lake at the OSPER "B" site were subjected to some remediation using a straw/hay mulch application and grass seeding. Localized spots were partially successful. The organic measurement (OM) is for total organic matter while TPH is for petroleum hydrocarbons, but soluble plant organic matter can result in higher TPH amounts. Conductivity was determined in a 1:1 soil-water slurry using a conductivity meter (Orion Model 105 with conductance cell 011510) as specified in USDA Handbook 60, 1954. Soluble chlorides were determined on a filtrate derived from a mixture of 30 mL water and 10 grams dry soil using a Waters Capillary Ion Analyzer. This report does not endorse the instruments or products used. They are mentioned merely as what was available in our analytical laboratory.

Agronomists made measurements of soluble salts in a soil-water extract as far back as 1897 (Whitney and Means, 1897). The choice of our methodology, however was not to correlate soluble salt levels with plant growth, but to measure relative differences between soil and core samples in contaminated and uncontaminated sites. A dehydrogenation process usually occurs during the biological oxidation of organic compounds in soil. The process usually involves a soil organic compound as a hydrogen donor and another component that acts as a hydrogen acceptor. These dehydrogenase systems are an integral part of viable microbial populations. In this study, DHA was used as an index of viable biomass. Changes in soil biomass have been used as a sensitive indicator of toxicity of pollutants (Horwath and Paul, 1994).

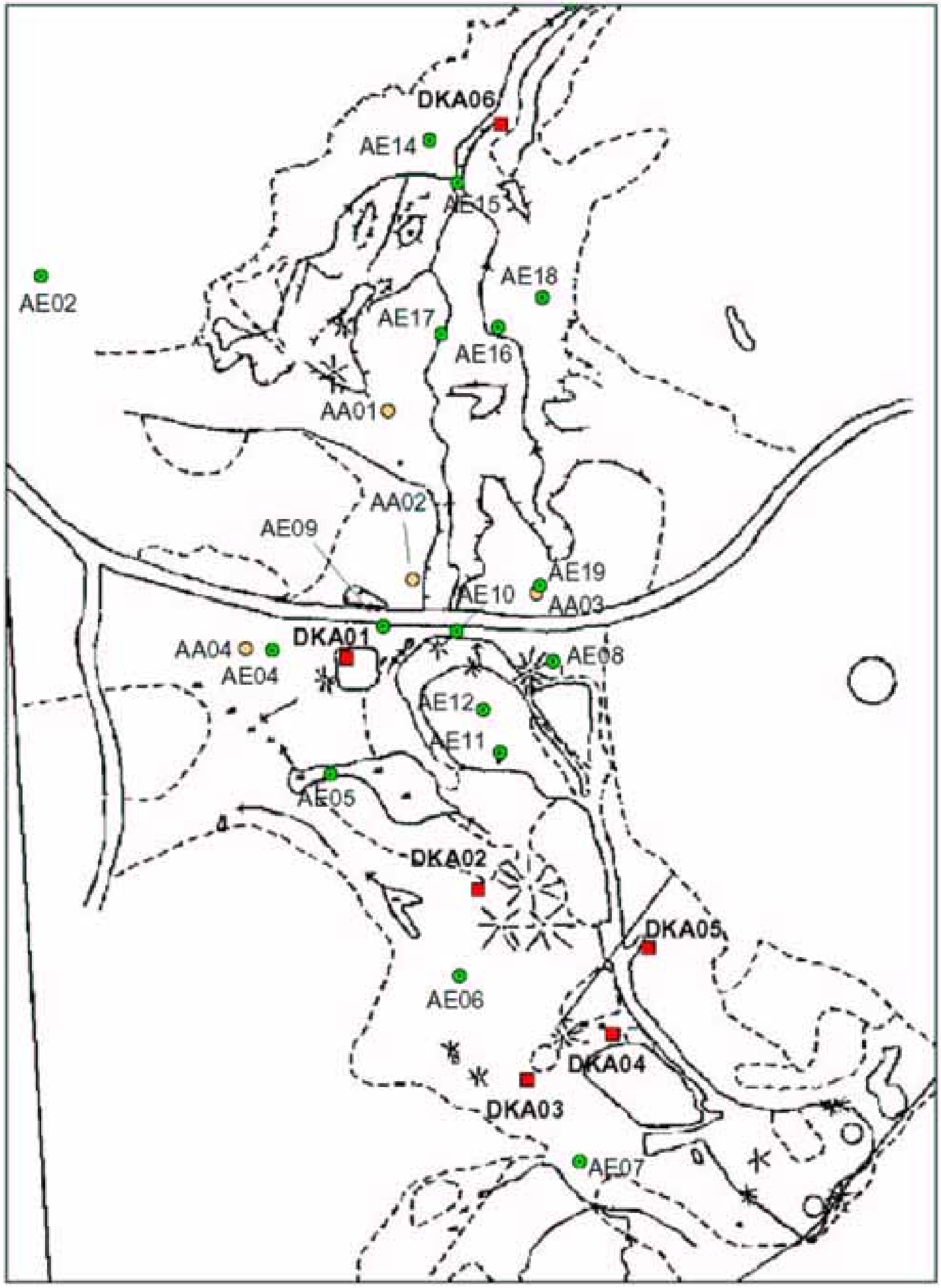

Figure 1. Sample locations at the "A" site. DKA01-DKA06 are soil and auger sites for this study. For an explanation of the features portrayed, see Otton and Zielinski (this volume). The green and light orange dotted locations are other site wells.

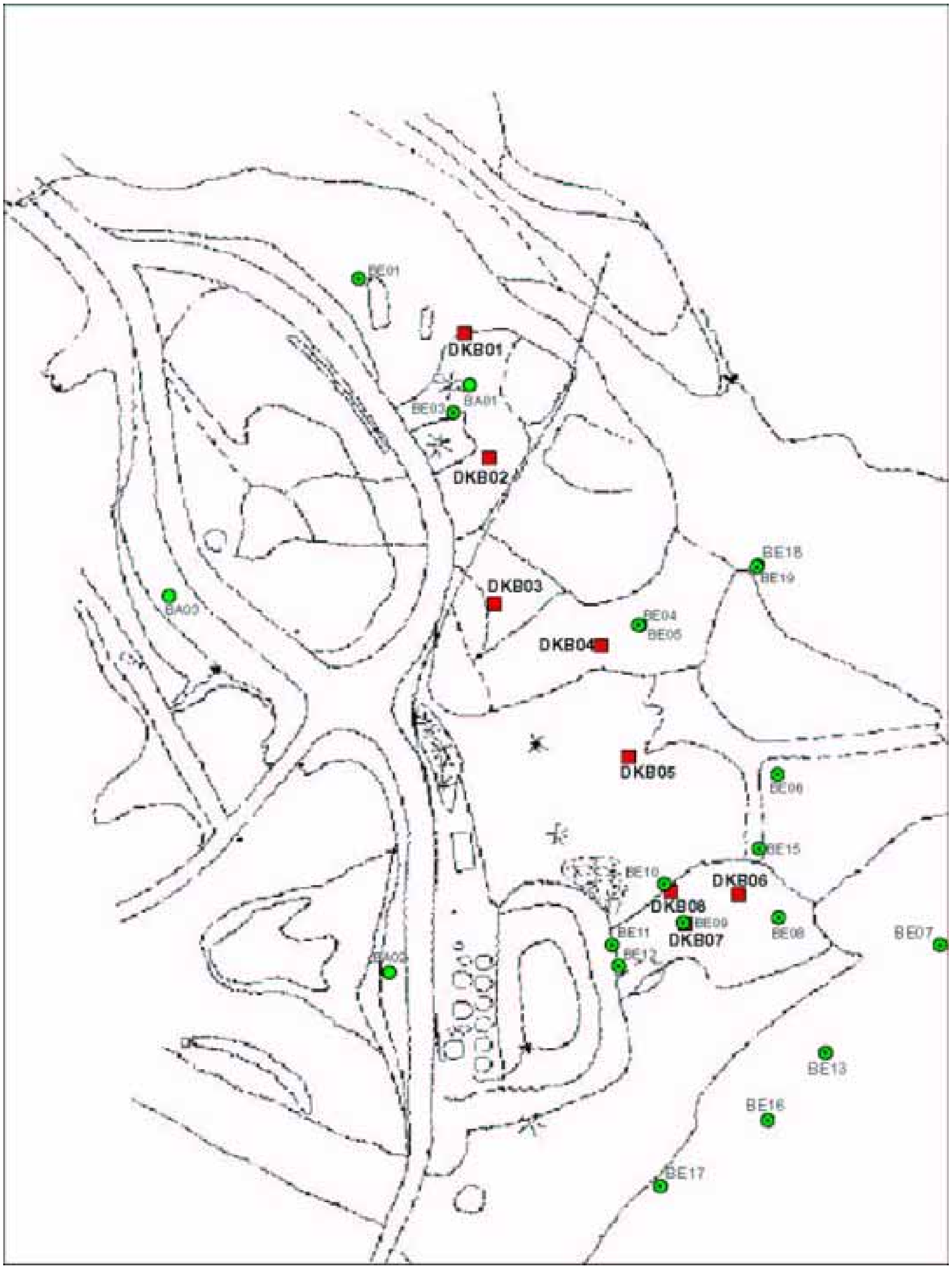

Figure 2. Sampling locations at the "B" site. DKB01-DKB08 are soil and auger sites for this study. For an explanation of the features portrayed, see Otton and Zielinski (this volume). The green dotted locations are other site wells.

Table 1. Location notes for surface and core samples, OSPER “A” and “B” sites.

Location	Notes
“A” site	
DKA01	Within patch of highly weathered asphaltic oil at site of old tank
DKA02	Open area of grasses and forbs adjacent to three large oak trees
DKA03	Open area of grasses and forbs near wet spot
DKA04	Open area at edge of asphaltic oil-saturated soil along trench
DKA05	Open area at edge of asphaltic oil-saturated soil along trench
DKA06	Low end of substantial salt-scarred, deeply eroded area
“B” site	
DKB01	Zone between salt-scarred and treed area
DKB02	Open salt-scarred area downslope from pit and injection well, remediated in November of 1999
DKB03	Depression in open area below old tank battery, highly saline water present after rain events
DKB04	Midpoint of salt scar below old tank battery, remediated in November of 1999
DKB05	Open grassy disturbed area between salt scars.
DKB06	Salt scar below active pit and tank battery, remediated in November of 1999
DKB07	Salt scar below active pit and tank battery, remediated in November of 1999
DKB08	Edge of salt scar below active pit and tank battery, remediated in November of 1999

Results and Discussion

The concentrations of selected key chemicals in soil samples from OSPER “A” and “B” sites are reported in table 2. Results show low nitrate concentrations with most below the ppm; such low values are typical for non-fertilized soils in Oklahoma. Two soil-sample locations show several fold higher nitrate values, which most likely resulted from animal activity in the area. Although the nitrate levels were low they are sufficient to support the growth of native grasses. The nitrates were nearly uniformly distributed down to the deepest sampling depth of four feet. Organic matter ranged from 1.2 to 5.6%, which is typical for forest soils in this area of Oklahoma, but values > 2.5% may reflect a contribution from asphaltic oil contamination.

Total petroleum hydrocarbons in soil were as high as 6320 ppm. The solvent for TPH may not have dissolved all of the dry weathered crude oil. TPH values above 1000 ppm were indicative of the presence of asphaltic oil in the soil. Although the TPH method used may have inherent problems with accuracy such as solvent extractable plant organic matter, it is an EPA approved procedure for petroleum hydrocarbons in soils. At the three profile locations, the highest TPH was detected at the two-foot depth. The “A” site had a more sandy textured soil, which would enhance downward movement of liquid crude oil. The relationship between TPH and organic matter is presented in figure 3. Correlation Coefficient was $r = 0.595$. The data shown in figure 3 suggests that up to two percent organic matter was primarily from natural sources such as plant material. Organic matter in the 2.5 to 5.5 percent range reflected a contribution from asphaltic oil contamination.

Conductivity and chloride concentrations were used to detect the presence of produced water salts. Conductivity and chloride concentrations ranged from 64 to over 25000 µS/cm and 3.9 to 5170 ppm, respectively. The relationship between conductivity and chloride concentrations is shown in figure 4. Correlation coefficient was $r = 0.981$.

Table 2. Soil and core analyses from OSPER “A” and “B” sites.

Sample	Depth (ft)	Nitrate (ppm)	OM (%)	TPH (ppm)	Conductivity (µS/cm)	Chloride (mg/L)	DHA (µg/g soil)
“A” site							
DKA01	0.0 - 1.3	0.15	3.3	1580	90	3.9	2.7
DKA01	1.3 - 2.6	0.12	3.3	6320	418	31	2.3
DKA01	2.6 - 4.0	0.15	3.8	6080	571	52	<0.1
DKA02	0 - 0.5	0.06	1.8	262	86	4.2	3.6
DKA03	0 - 0.5	0.18	2.7	122	125	4.1	33.2
DKA04	0 - 0.5	0.21	5.0	1695	122	4.8	2.3
DKA05	0 - 0.5	0.12	4.2	2336	64	4.2	5.4
DKA06	0 - 0.5	0.12	1.2	89	572	147	4.4
“B” site							
DKB01	0 - 0.5	0.12	1.8	365	184	11	3.3
DKB02	0 - 0.5	0.12	1.5	31	4500	1310	9.9
DKB03	0 - 0.5	14.4	2.4	166	25200	5170	5.8
DKB04	0 - 1.3	0.18	1.5	257	3600	643	<0.1
DKB04	1.3 - 2.6	0.18	1.2	42	1766	619	<0.1
DKB04	2.6 - 4.0	0.12	1.5	<10	743	771	23.4
DKB05	0 - 0.5	0.15	1.8	374	1470	133	37.9
DKB06	0 - 1.3	0.15	2.7	2054	3800	745	15.1
DKB06	1.3 - 2.6	0.15	2.7	2900	1156	518	<0.1
DKB06	.18 - 1.5	0.18	1.5	90	391	327	17.8
DKB07	0 - 0.5	0.15	2.4	1985	6700	1270	11.5
DKB08	0 - 0.5	1.2	5.6	2584	4300	1460	43.8

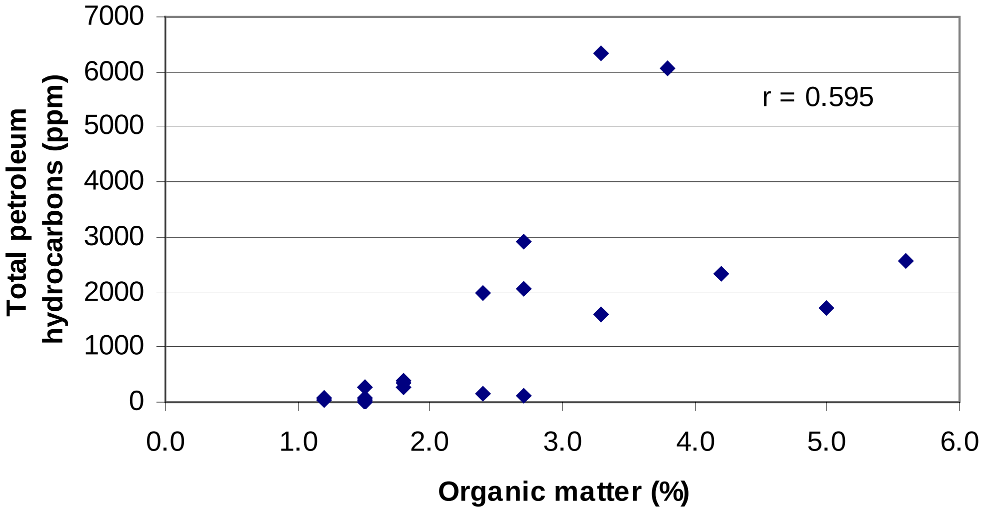

Figure 3. Relationship between total petroleum hydrocarbon (TPH) and organic matter (OM).

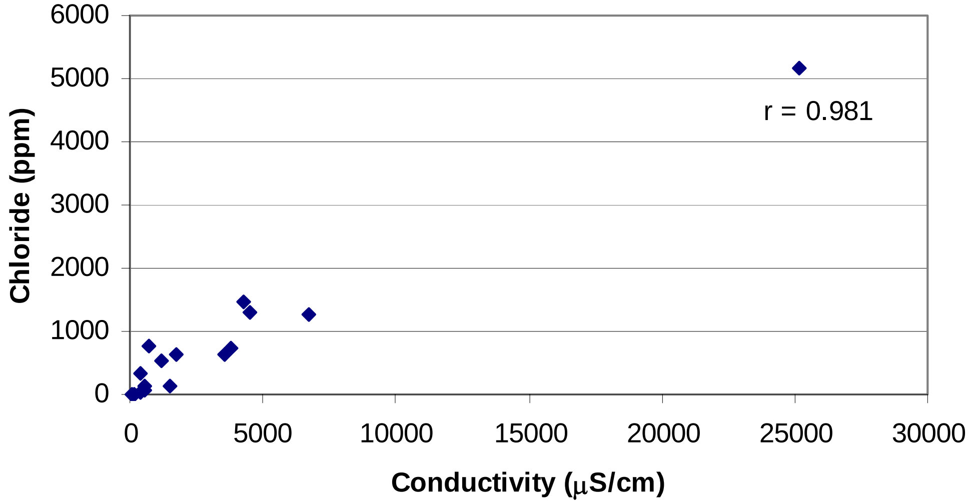

Figure 4. Relationship between chloride and conductivity. Note the high correlation between these parameters.

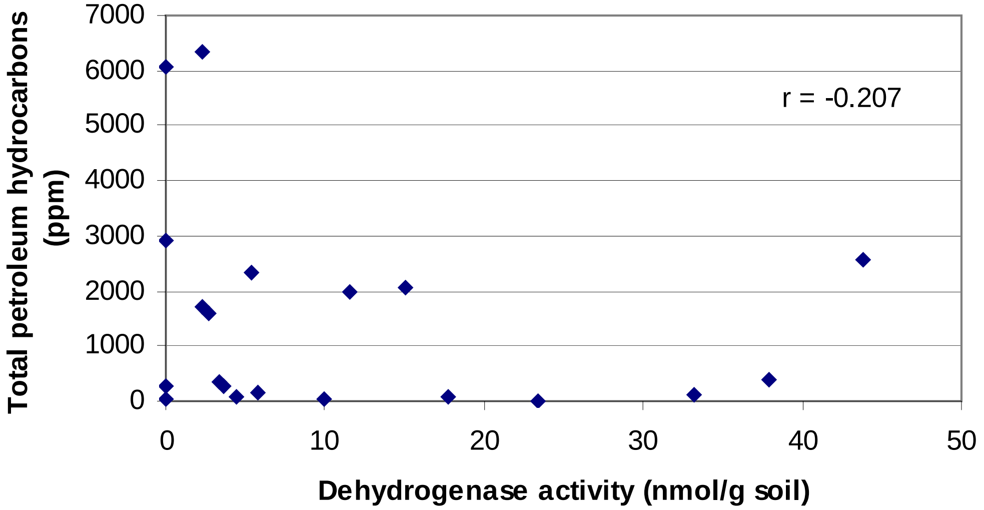

Figure 5. Relationship between total petroleum hydrocarbon (TPH) and dehydrogenase activity (DHA) showing no correlation.

The relationship between TPH and DHA is shown in figure 5. A calculated correlation coefficient of r = -0.207 indicates that the relationship is not direct. DHA values listed in table 2 indicate that most of the soil/core samples exhibited a variable biomass. High salt concentrations in the soil generally did not have an adverse effect on DHA values as indicated by figure 6. Low DHA in the vertical profiles appeared related to high TPH and conductivity for most samples. Interactions between TPH and conductivity did not generally influence DHA. High TPH and water-extractable chlorides did not cause low DHA in many samples because the oily residue may have combined with the brine salts to reduce solubility of chlorides while the vigorous water extraction for chlorides permitted an increase in this component. Chloride levels up to

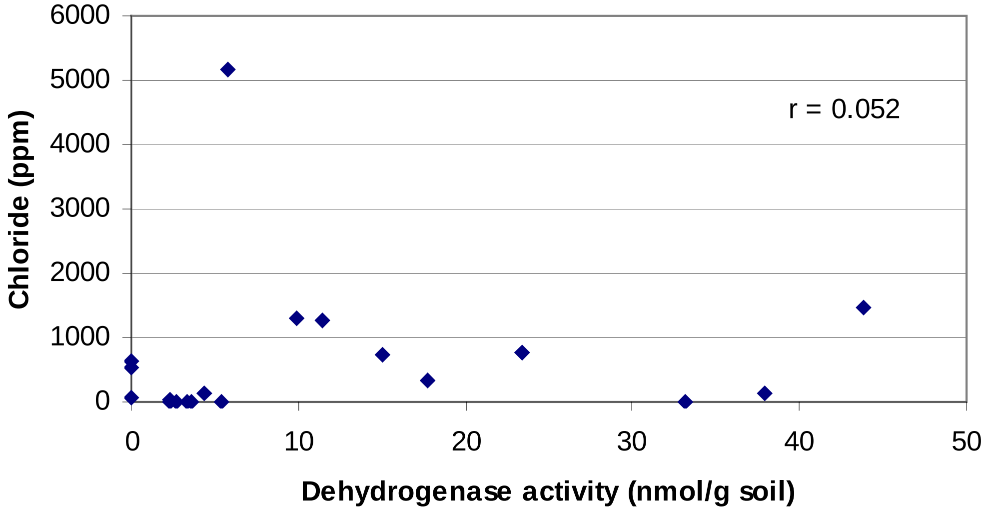

Figure 6. The chloride and dehydrogenase activity (DHA) plot shows lack of any correlation.

1500 ppm did not seem to suppress bacteria activities measured by DHA. Best fit by linear regression calculations between any two parameters was for conductivity versus chlorides.

Notice: The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here through in-house efforts. This document has not been subjected to agency review and therefore does not necessarily reflect the views for the agency and an official endorsement should not be inferred.

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Hydrologic Controls on the Subsurface Transport of Oil-field Brine at the Osage-Skiatook Petroleum Environmental Research "B" Site, Oklahoma

By William N. Herkelrath and Yousif K. Kharaka

Abstract

As a part of a multidisciplinary study of the impact of oil wells and oil production on the environment, we are investigating the hydrology and the fate and transport of contaminants at the Osage-Skiatook Petroleum Environmental Research (OSPER) "B" site, which is located at Skiatook Lake in Osage County, Oklahoma. Salt and crude oil from oil-well waste pits and accidental releases from oil tank batteries have contaminated soil, ground water, and surface water at this site. Based on soil cores, water table measurements, chemical analyses of water samples, and field observations, we developed conceptual models of the hydrology and solute transport mechanisms near a waste pit at the south end of the site. We propose two main mechanisms for solute transport from the waste pit to the lake. One mechanism is the relatively slow and steady flow of saline ground water from the waste pit to the lake in a near-surface aquifer. The other mechanism is relatively fast overland flow of salt-laden runoff during rainfall. Using the USGS model SUTRA, we simulated steady-state ground-water flow and solute transport from the pit to the lake. Preliminary modeling results indicated that the solute travel time from the pit to the lake in saline ground water is 2-4 years.

Introduction

A large quantity of water containing high concentrations of dissolved salts is produced as a byproduct of oil production. In the early days of the oil business in the United States, brine was commonly "disposed of" by dumping into streams or infiltration into the soil (Yergin, 1991). Present law requires that most brine be injected into deep formations. However, even today oil-field brine and oil are often spilled on the soil surface and into shallow emergency or reserve holding pits. The brine often flows out the bottom of unlined holding pits and into the ground-water system. Movement of the brine and the oil into the subsurface poses a threat to ground water quality. Nearby streams and lakes may also be threatened. It is important to understand the processes that influence subsurface transport of oil-field brine and associated oil and to document the effects on the environment in order to help regulators and other responsible parties make informed decisions regarding oil well siting and site remediation.

In 2001 the U.S. Geological Survey, in cooperation with the U.S. EPA, began a multidisciplinary study of the impact of oil production on the near-field environment. Two oil-field sites, designated "Osage-Skiatook Petroleum Environmental Research" (OSPER) sites "A" and "B", located near Skiatook Lake in Northeastern Oklahoma, were selected for intensive study. Oil and brine from producing oil wells has entered the subsurface at these sites, resulting in extensive killing of vegetation and degradation of local ground water and surface water quality. A research team of geologists, geophysicists, geochemists, hydrologists, microbiologists, and biologists is evaluating data obtained in the first field season at the OSPER sites.

In this paper only results from the OSPER "B" site are presented. The purpose of the paper is to describe conceptual models of the hydrology and solute transport processes at the "B" site, and to present preliminary computer modeling simulations of ground-water flow and associated transport of dissolved salt from a waste pit at the southern end of the site B to Skiatook Lake. The general concepts developed in this paper are applicable to nearby areas where oil-field brines have been spilled.

Field Site Description

As shown in the site map (fig. 1), at site B there is an oil tank battery and a waste pit located about 20 meters from Skiatook Lake. There also is a brine injection well and an associated smaller pit at the north end of the site. The land surface slopes upward west of the lake at approximately a 5% grade. Three areas where salt has killed the vegetation are denoted "salt scars" in figure 1. There are salt scars east of the oil tank battery, east of the injection well, and east of a location in the center of the site where a tank battery and pit have been removed. As a part of a remediation effort, in 2000 about 6 inches of saline topsoil was replaced, grasses planted, and hay mulch applied in the salt-scarred areas. However, as of 2002, there were only limited patches of grasses growing on the salt-scarred areas.

Soil and rock cores (Otton and Zielinski, this volume) obtained at the site show that beneath 0.5-2 meters of surficial deposits (eolian sand, colluvium, fill, and alluvium), a layer of shale at least 6 meters thick underlies the site. The near-surface material near the waste pit is mapped as "fill" or "colluvium." The colluvium consists of variable amounts of weathered shale and sandstone clasts in a sandy to clayey matrix. The fill is similar to the colluvium but often contains wood or construction debris. There is generally weathered shale beneath the colluvium. The soil which has formed in the eolian layer has been removed from much of the area near the salt scars. Pits and roads were made by cutting and filling local materials with a bulldozer. Much of the near-surface material near the waste pit is "fill."

A Geoprobe (direct-push) rig was used to obtain shallow (<6 meters deep), 2-inch diameter cores at 19 locations at the site. Sampling wells were installed at each of these locations. The wells were made by placing 1-inch diameter PVC pipe with a 1 to 6 foot well screen at bottom into the Geoprobe boreholes. Clean sand was packed into the annulus between the PVC pipe and the borehole. These wells are labeled "BE#" in figure 1.

Six-inch diameter boreholes that were up to 16 meters deep were also cored at three locations using an auger rig. Two 2-inch diameter PVC wells with 5 to 10 foot long well screens at the bottom were installed in each borehole. There was a "deep" and a "shallow" well in each borehole. Sand was packed around the PVC pipe in the screened intervals. Bentonite was used to isolate the screened intervals from one another. These wells are labeled "BA#" in figure 1.

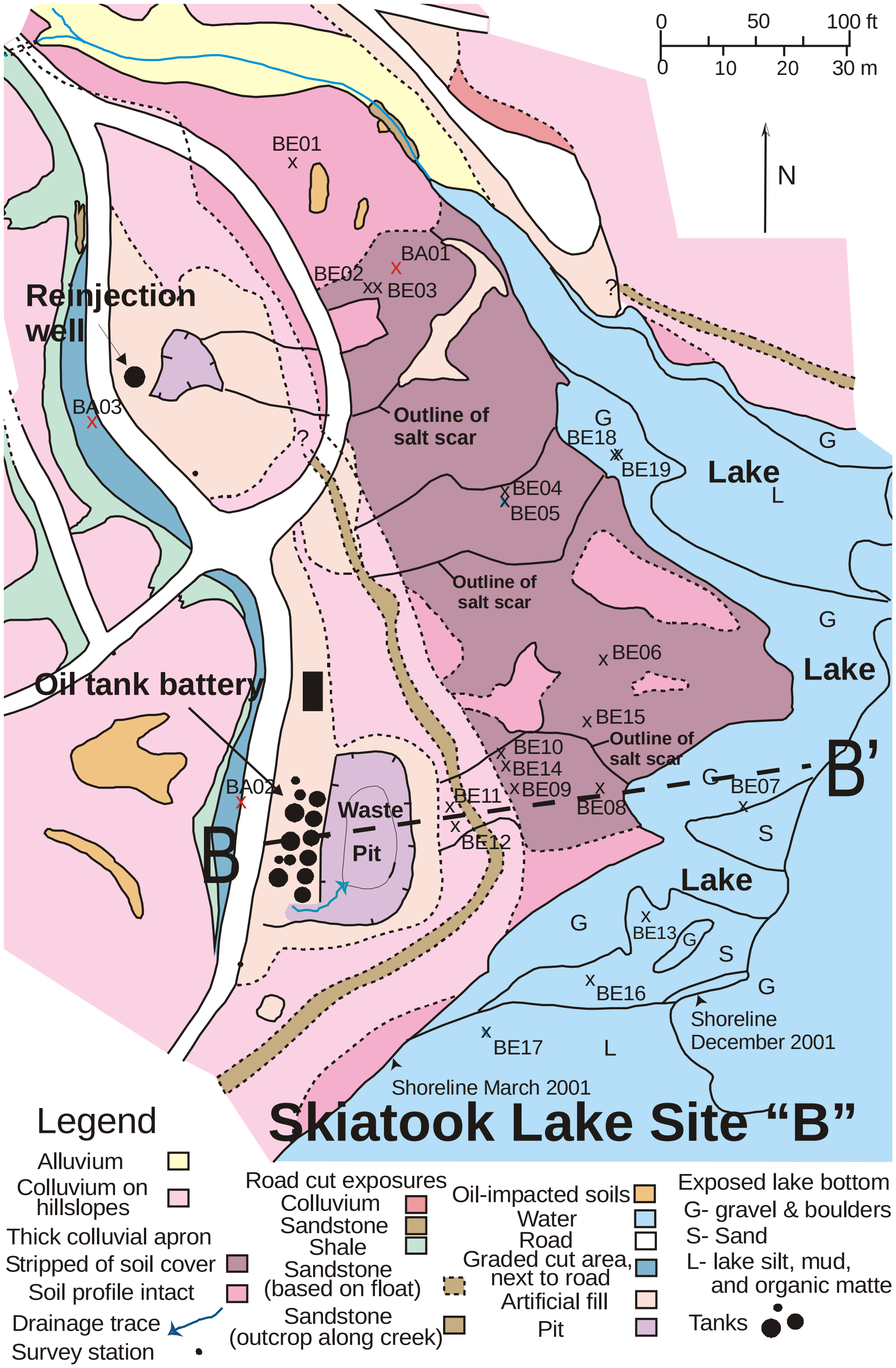

Figure 1. Map of OSPER "B" research site.

Hydrology and Solute Transport in the Waste Pit Area

Based on analysis of the soil cores, water table measurements in the wells, chemical analysis of water samples obtained from the wells and the waste pit, and other field observations, we developed preliminary conceptual models of the hydrology and solute transport mechanisms in the waste pit area.

The Brine Source in the Waste Pit

Equipment failures at the active oil production facility at the site lead to a periodic spillage of brine and associated oil into the waste pit at the south end of the site (fig. 1). Brine from the oil wells has a concentration of about 150,000 mg/L total dissolved solids (Kharaka and others, this volume). The brine fills the waste pit to a variable extent depending on the volume of the spill. Once in the pit, the brine is diluted by precipitation. The pit collects some of the runoff from an area of about 600 m^2.

Water and brine leave the pit by several mechanisms. The oil-field operator periodically pumps water out of the pit via an automated sump-pump system into water tanks that are pumped into the injection well. Also, we observed that when the pit contains water, brine often flows out through seeps on the east side of the pit berm at the top of the salt scar. The water flows out of the seep, on top of the soil for a few feet, and then infiltrates into the soil down slope from the pit. At times in the past, the pit has overflowed the east side of the berm. We hypothesize that brine also flows out through the bottom of the unlined pit. When the weather is hot, water may evaporate from the pit, which increases the brine concentration. However, there is generally a thin layer of oil on top of the water in the pit, which may inhibit evaporation of water.

It is likely that quantitative understanding of the fate and transport of contaminants from the waste pit will be limited by how accurately the source is characterized. The measured salinity of the brine that enters the ground near the pit varies greatly as a function of time (Kharaka and others, this volume). The flow rate out of the pit also varies as a function of liquid depth in the pit. Accurate characterization of the source will require frequent monitoring of the solute concentration and the water level in the pit.

Ground-Water Flow from the Waste Pit to the Lake

Figure 2 shows a simplified cross section of the subsurface beneath the B-B' transect (fig. 1). We hypothesize that the primary subsurface pathway for water flow from the pit to the lake is in the surface "fill" or "colluvium" layer (F/C). We hypothesize that the underlying undisturbed "weathered shale" layer is much less permeable than the F/C layer.

The water table elevations measured in wells in June 2002 line up well with the measured water levels in the pit and the lake (fig. 2). The water-level measurements suggest that whenever there is water in the pit, there is ground-water flow from the pit to the lake in response to a hydraulic head gradient of about 0.05 m/m.

We carried out slug tests in the wells in order to estimate the hydraulic conductivity of the F/C layer. A slug test was initiated by inserting a solid volume of stainless steel into a well in order to displace water and rapidly raise the water level in the well. The subsequent transient decline in water level in the well was monitored with a pressure transducer. The slug tests were analyzed using the Bouwer and Rice (1976) method, as described by Butler (1997). Hydraulic conductivity values estimated from the slug test data ranged from about 1 cm/day to about 10 cm/day.

One can use the Darcy flow equation to estimate the flow rate from the waste pit to the lake. For example, assuming the F/C layer in figure 2 is a uniform, homogeneous, one-dimensional aquifer, the flow rate per unit cross section is $q = k\ (dp/dx)$, where k is the hydraulic conductivity, and dp/dx is the hydraulic gradient. Assuming the hydraulic conductivity is 10 cm/day, and the gradient is 0.05, $q \sim 1.8$ m/year.

Water Flow in the Unsaturated Zone

Inspection of soil cores and observation of rainfall events at the site suggest that there is relatively little infiltration and recharge of fresh rainwater into the saturated zone. In the bare, salt-scarred areas of the site, because the soil is clay-rich, the drainable porosity of the soil is low. Drying of bare soil by evaporation is limited to a thin layer at the soil surface. Even after a long dry period, the subsoil remains nearly saturated. When it rains, the available porosity is quickly filled, the water table rises rapidly to the surface, and runoff begins. Soil surface sealing by mobile clays and air entrapment in the soil also enhance runoff. Most of the water that falls on bare soil flows toward the lake as runoff. Infiltration and recharge of fresh rainwater into the saturated zone is limited. After the rain, the water table falls rapidly back to the level that is supported by outflow from the waste pit.

In vegetated areas, soil drying is more extensive because of plant root uptake. As a result, there is more infiltration and less runoff from vegetated areas. However, evapotranspiration is generally so high at the site that the plants rapidly remove water that has infiltrated into the root zone, and there is little ground-water recharge.

Solute Transport

We propose two main mechanisms for transport of solutes from the waste pit to the lake. One mechanism is the flow of saline ground water in the F/C aquifer. Brine from the pit flows down through the bottom of the pit and travels laterally in the aquifer to the lake. The weathered shale beneath the F/C layer is relatively impermeable, and not much brine penetrates into this layer. The saline ground-water flow is relatively slow and steady, and not much influenced by the weather, except that the level of water in the pit changes in response to rainfall and evaporation. We hypothesize that there is relatively little dilution of the saline ground water by rainwater once the brine has entered the aquifer.

The second mechanism for solute transport is the overland flow of salt-laden surface runoff. Rainfall at the site generally comes in short bursts followed by dry periods lasting many days. During dry periods, as the bare soil surface dries by evaporation, ground water containing dissolved salts is pulled upward from the aquifer toward the surface by capillary action. The salt concentration in the water near the surface is increased by evaporation of water. Salt crystals may precipitate near the soil surface. We hypothesize that during rainfall rainwater rapidly mixes with the highly saline water in the surface soil, dissolves salt crystals, and carries dissolved salt down slope in runoff. It is likely that solute transport via the runoff mechanism is much faster than via the saline ground water flow mechanism.

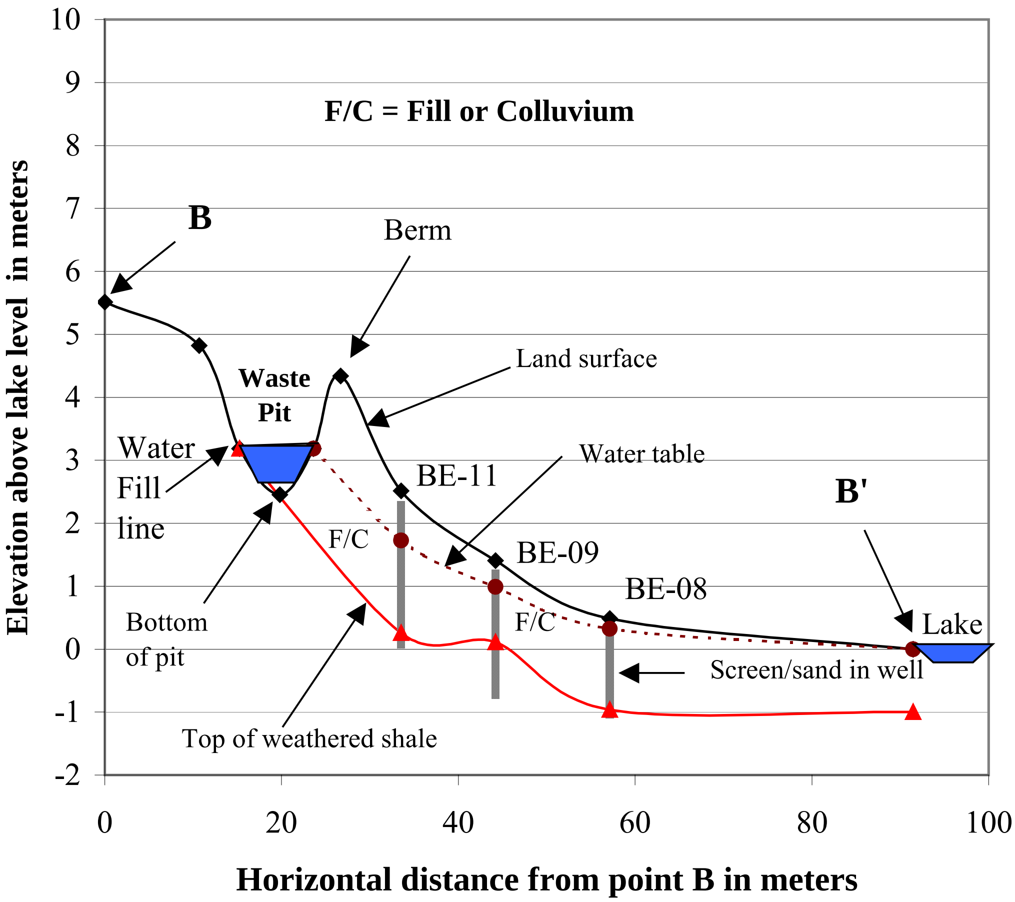

Figure 2. Simplified cross section beneath the B-B' transect at OSPER "B" site.

The fact that the brine is denser than water may influence mixing and solute transport. Fingers of brine tend to move downward into a porous material that is initially saturated with fresh water. This effect tends to increase mixing when salt water lies above fresh water. However, fresh rainwater infiltrating on top of a brine-filled aquifer tends to remain stratified and not mix with the brine.

Preliminary Modeling Results

We used the U.S. Geological Survey model SUTRA (Voss, 1984) to simulate steady-state flow of ground water and subsurface transport of solutes from the waste pit to the lake. SUTRA is a two-dimensional, finite element model that solves the Darcy flow equation and the convection dispersion equation. The model is convenient to use because a graphical-user interface (Voss and others, 1997) is available to set up a problem and display results. Another advantage of SUTRA is that the program enables simulation of subsurface transport when the density of the flowing water solution varies as a function of solute concentration. Although this feature will be important in future work, in the simulations reported in this paper water density was assumed to be that of pure water.

As a first approximation, we assumed that the area near the waste pit is underlain by a homogeneous aquifer that is one meter thick. The idealized aquifer roughly corresponds to the F/C layer in figure 2. We assumed the following values for aquifer parameters: hydraulic conductivity = 10.0 cm/day; porosity = 0.3; longitudinal dispersivity = 10.0 m, transverse dispersivity = 1.0 m. Hydraulic conductivity was assumed to be isotropic.

The layout of the homogeneous aquifer problem and the boundary conditions are illustrated in figure 3. We used SUTRA to solve the areal flow problem. For the purposes of this simulation the waste pit was assumed to be a rectangle 7.6 meters wide and 15.2 meters long. The hydraulic head at the pit boundary was assumed to be constant, three meters above the constant head boundary at the lake. The domain boundaries to the west and north were assumed to be no-flow boundaries.

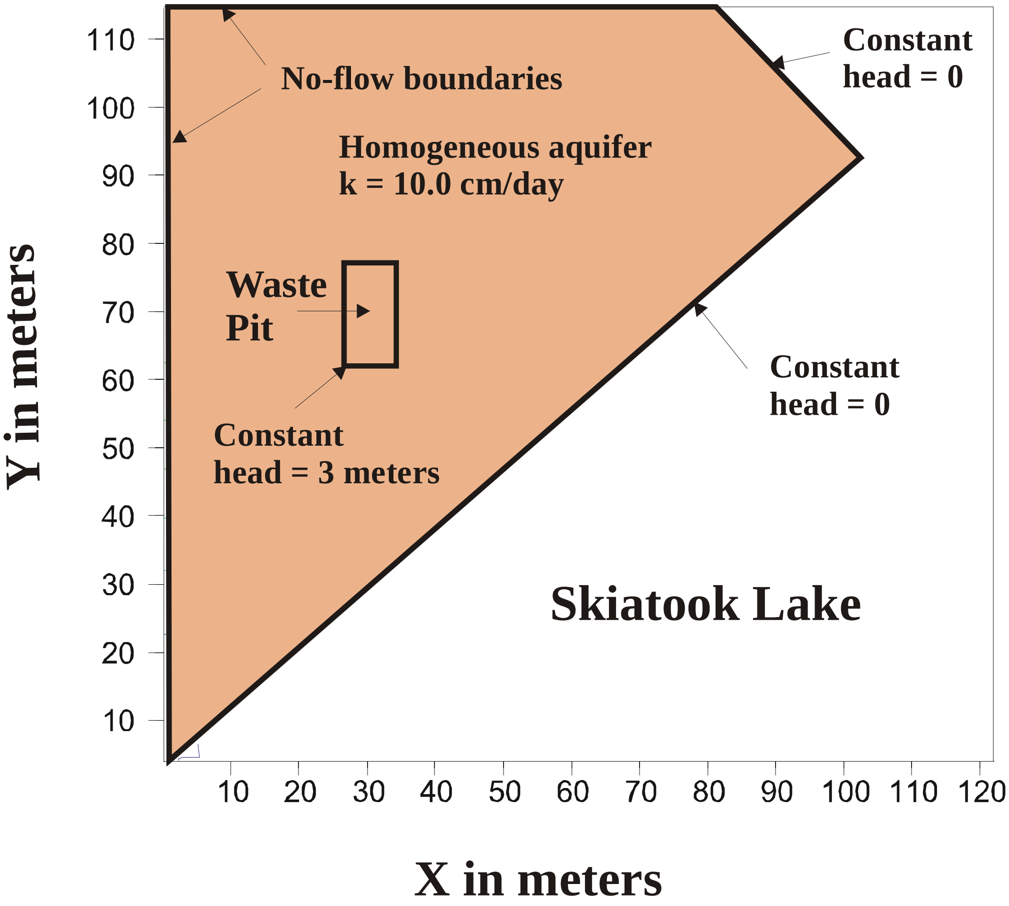

Figure 3. Problem layout and boundary conditions for the homogeneous, steady-state areal ground-water flow and transport problem at OSPER “B” site.

Flow and transport were simulated for two years. Water flow was assumed to be steady state. We assumed the initial salt concentration in the aquifer was zero. At t=0, brine with a solute concentration of 100,000 mg/L was assumed to enter the aquifer at the pit boundary. Solute concentration in the lake was assumed to be zero.

Results of the homogeneous simulation are illustrated in figures 4 and 5. Figure 4 shows the simulated distributions of hydraulic head and flow velocity. In figure 4, the flow velocity at a point is proportional to the length of the flow vector. As shown in figure 4, in the homogeneous simulation there was flow outward from the pit in all directions. The maximum flow velocity was toward the southeast, where the distance from the pit to the lake is minimum. Simulated concentration profiles after 600 days are shown in figure 5. Concentrations are expressed as a percentage of the initial source concentration, which was 100,000 mg/L. As shown in figure 5, in this simulation the brine plume spread out in all directions from the pit, but the concentration profiles were slightly advanced toward the southeast. Travel time of the solute from the pit to the lake, indicated by the arrival time of the 50% concentration profile at the lake, was about two years.

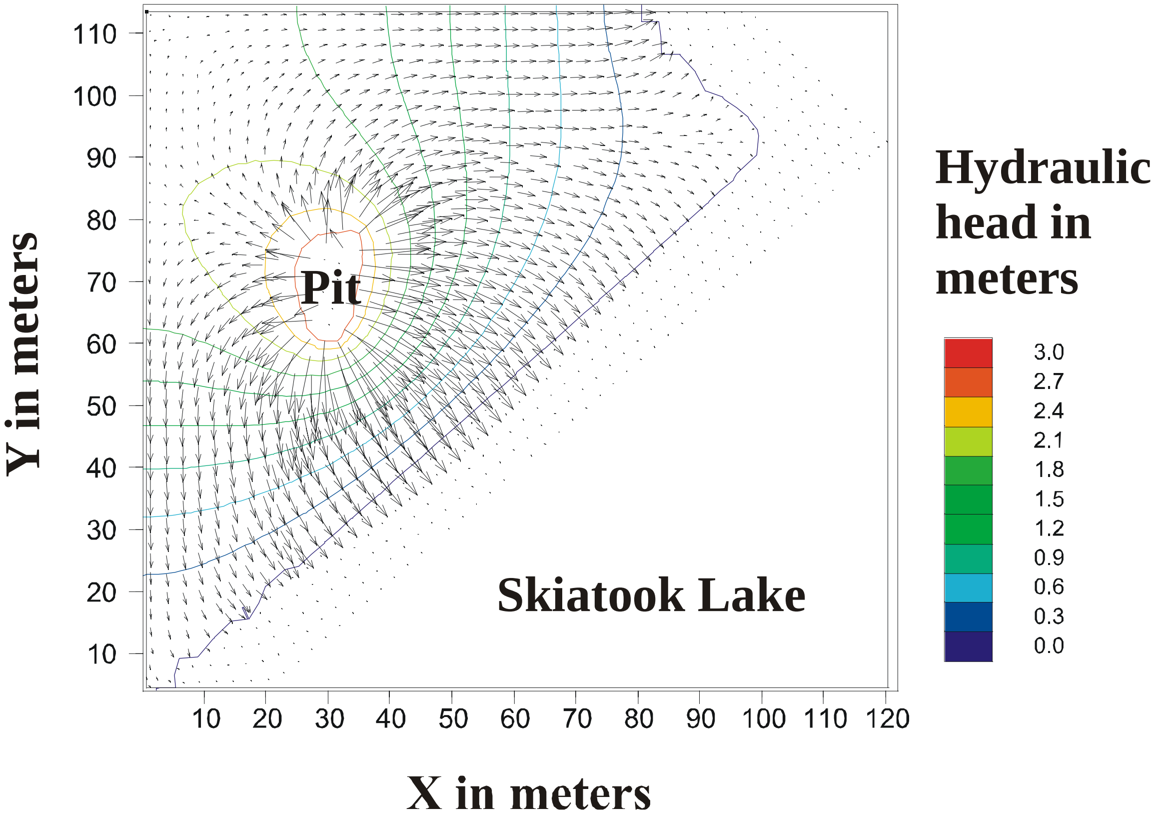

Figure 4. Simulated hydraulic head distribution and ground-water flow velocities at OSPER “B” site. Flow velocity at a point is proportional to the length of the flow vector. In this simulation hydraulic properties were assumed to be uniform.

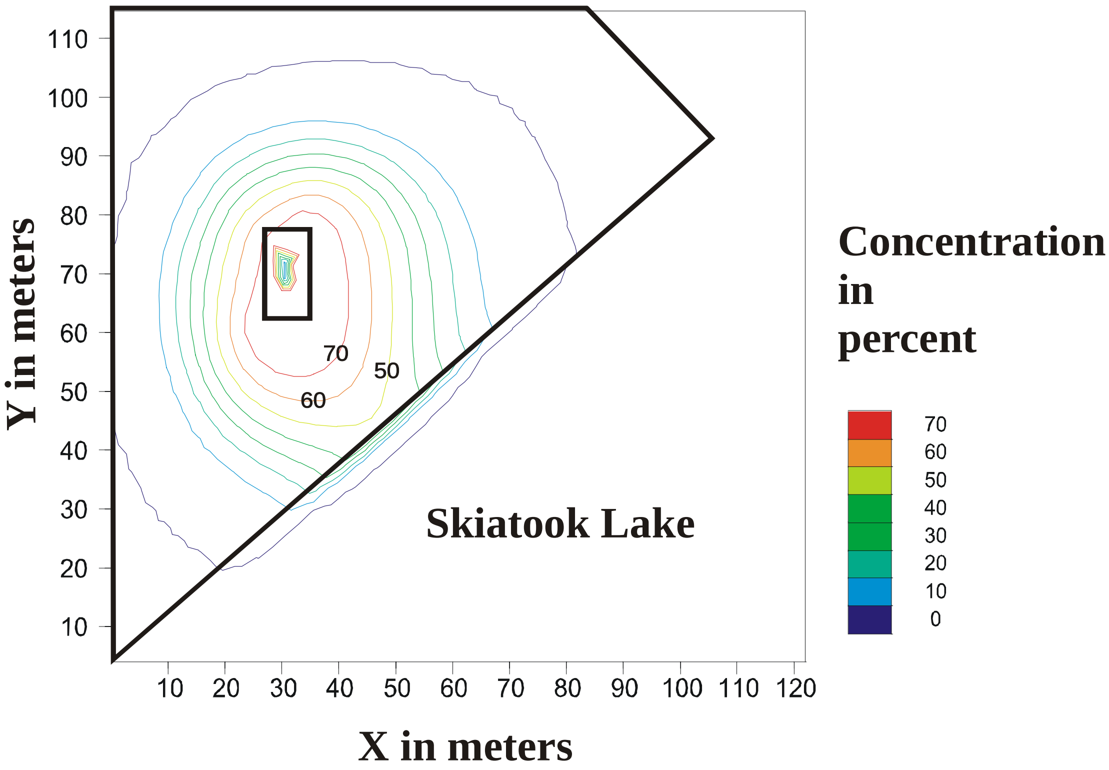

Figure 5. Simulated solute concentration profiles at OSPER "B" site 600 days after oil-field brine was placed in the waste pit. Concentration values are in percent of the source concentration. In this simulation the aquifer beneath the pit was assumed to be homogeneous.

In contrast to the results of the homogeneous simulation, field evidence suggests that most of the flow is to the east, and there is reduced flow of brine south and west of the pit (Kharaka and others, this volume). One explanation of the discrepancy between the homogeneous simulation and the field results is that the hydraulic conductivity of the near-surface materials south and west of the pit is reduced. We simulated the effect of a permeability barrier using SUTRA. As shown in figure 6, for this simulation the hydraulic conductivity west and south of the pit was assumed to be 1.0 cm/day, or 1/10 the assumed hydraulic conductivity of the rest of the aquifer. Flow and transport were simulated for five years. All other model parameters were unchanged.

Results of the simulation with the permeability barrier are illustrated in figures 7 and 8. As shown by the velocity vectors in figure 7, in this simulation most of the flow was directed to the northwest. The concentration profiles shown in figure 8 are also lengthened toward the northwest. In this simulation, travel time of the solute front from the pit to the lake, indicated by the arrival time of the 50% concentration profile at the lake, was about four years.

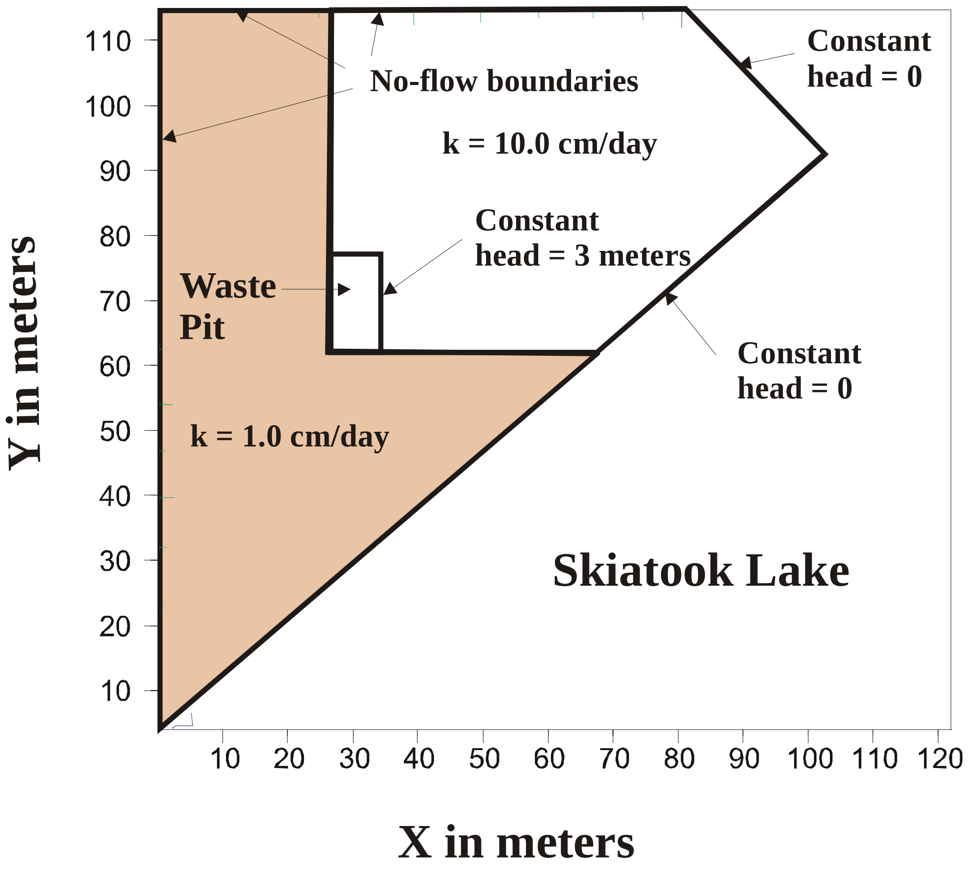

Figure 6. Problem layout and boundary conditions for the steady-state areal ground-water flow and transport problem with reduced hydraulic conductivity west and south of the waste pit at OSPER "B" site.

Discussion

The ground-water flow and transport problems we solved were highly simplified, designed only to provide first-order hypotheses as an aid in organizing future experiments and data collection at the site. The model has many shortcomings. For example, a major problem is lack of knowledge of the effective aquifer porosity. According to the convection-dispersion solute transport model, the velocity of a solute front, v_s, is approximately q / ϕ, where q is the Darcy flow velocity and ϕ is porosity. Assuming $q = 1.8$ m/year, and $\phi = 0.3$, $v_s \sim 6$ m/year. However, the velocity of a solute front traveling through a porous medium containing clay may be greatly increased compared to this estimate. Because the clay-rich fill/colluvium material at this site is highly heterogeneous, preferential pathways for flow probably exist in the F/C layer. Most of the pore space in the clay may be bypassed. As a result, subsurface transport of solute from the pit to the lake may occur much more rapidly. In order to gain an improved understanding of large-scale solute transport at the site, we plan to carry out tracer tests in order to measure solute travel times from the pit to the wells.

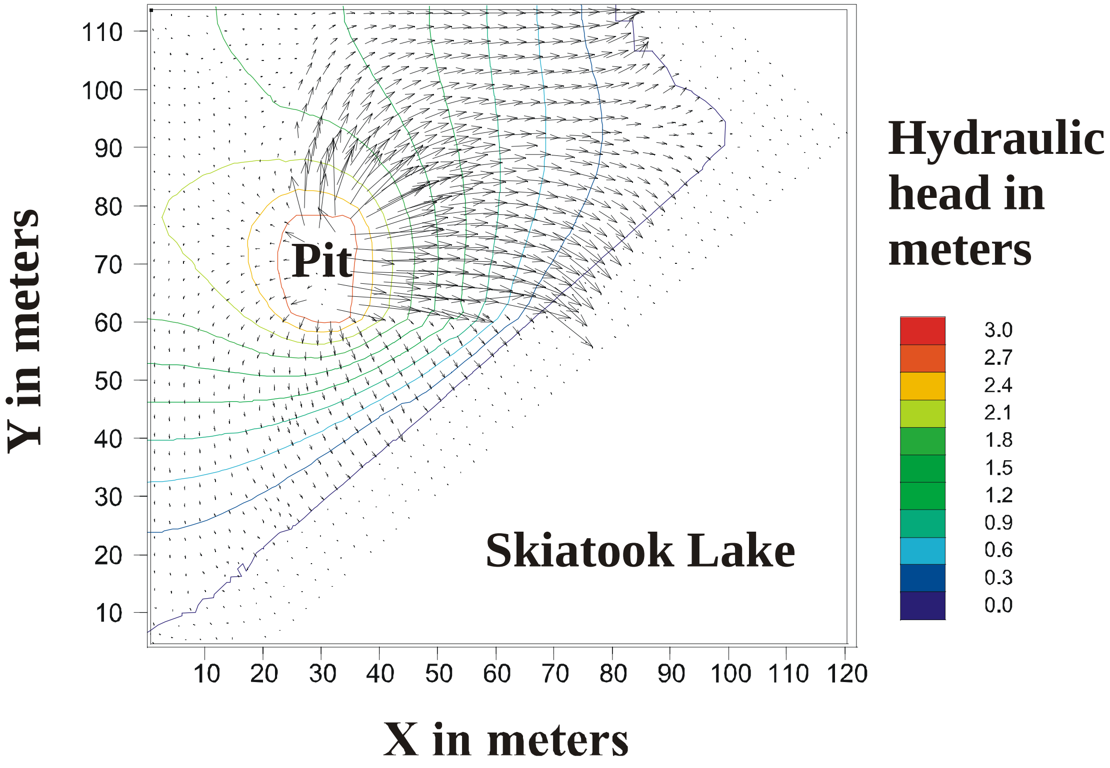

Figure 7. Simulated hydraulic head distribution and ground-water flow velocities at OSPER “B” site. Flow velocity at a point is proportional to the length of the flow vector. In this simulation, hydraulic conductivity west and south of the waste pit was reduced by a factor of 10.

Summary and Conclusions

As part of a multidisciplinary investigation of the impact of oil production on the environment, we are investigating the hydrology and the fate and transport of contaminants at the OSPER “B” field site, which is located at Skiatook Lake, Oklahoma. Salt and crude oil from oil-field operations have contaminated soil, ground water, and surface water at this site.

Based on analysis of soil cores, well data, and field observations, we developed conceptual models of the hydrology and solute transport mechanisms at the southern end of the site, where oil-field brine from a waste pit has killed vegetation near the lake. We propose two main mechanisms for solute transport from the waste pit to the lake. One mechanism is the relatively slow and steady flow of saline ground water in an aquifer formed by a near-surface layer formed of fill and colluvium (F/C). We hypothesize that brine from the pit flows down through the bottom of the pit and laterally in the F/C aquifer to the lake. The second mechanism for solute transport is overland flow of saline surface runoff. Evaporation from bare soil leads to high salt concentration near the soil surface. We hypothesize that during rainfall rainwater rapidly mixes with highly saline water at the soil surface and carries dissolved salt down slope in runoff. It is likely that solute transport via salt-laden runoff is much faster than via saline ground-water flow.

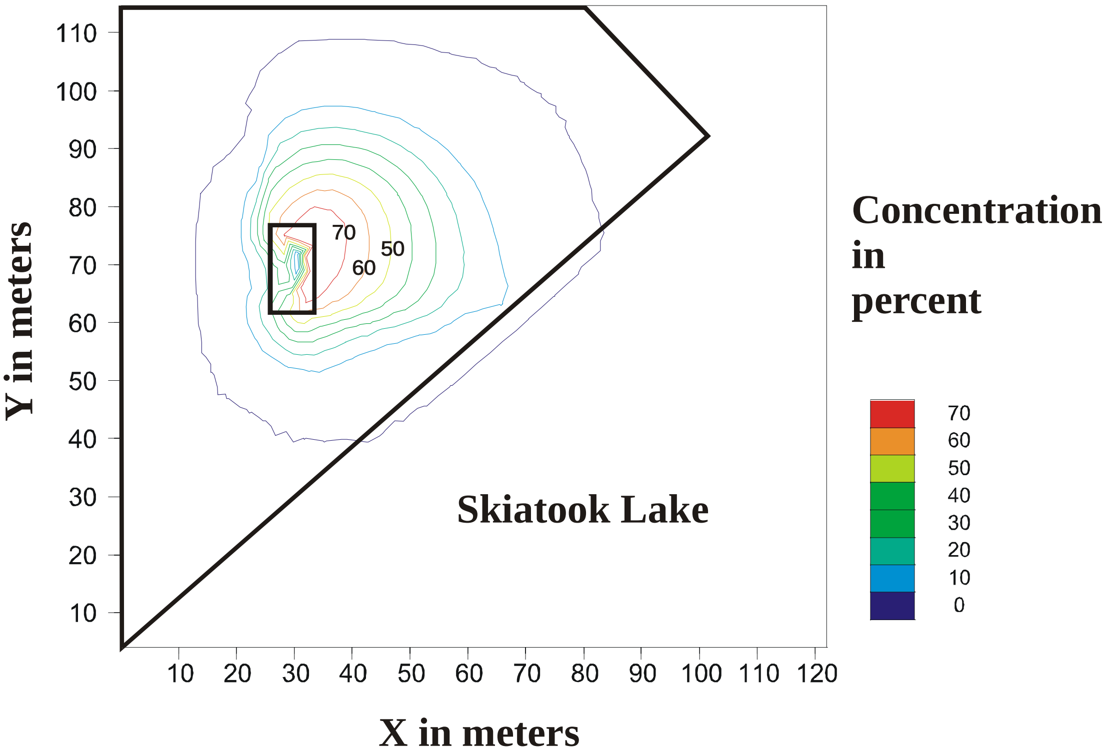

Figure 8. Simulated solute concentration profiles at Skiatook Lake site "B" 600 days after oil-field brine was placed in the waste pit. Concentration values are in percent of the source concentration. In this simulation the assumed aquifer permeability west and south of the waste pit was reduced by a factor of 10.

Using the USGS model SUTRA, we carried out preliminary computer simulations of steady-state ground-water flow and solute transport from the waste pit to the lake. Results obtained assuming homogeneous aquifer characteristics implied that there is ground-water flow and solute transport outward from the pit in all directions. The most rapid transport was toward the southeast, where the distance from the pit to the lake is minimum. In the homogeneous simulation, travel time of solute from the pit to the lake was about two years. However, field evidence suggests that there is reduced flow of brine south and west of the pit. In order to explain this discrepancy, we hypothesize that the near-surface materials have a reduced hydraulic conductivity west and south of the pit. We ran a second SUTRA simulation with assumed reduced permeability west and south of the pit. With the permeability barrier in place, most of the flow was directed to the northwest. Inserting a permeability barrier increased the simulated solute travel time from the pit to the lake to about four years.

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Use of Soil Extracts to Define the Extent of Brine-impacted Soils and Bedrock at the Osage-Skiatook Petroleum Environmental Research “B” Site, Northeastern Oklahoma

By Robert A. Zielinski, Cynthia A. Rice, and James K. Otton

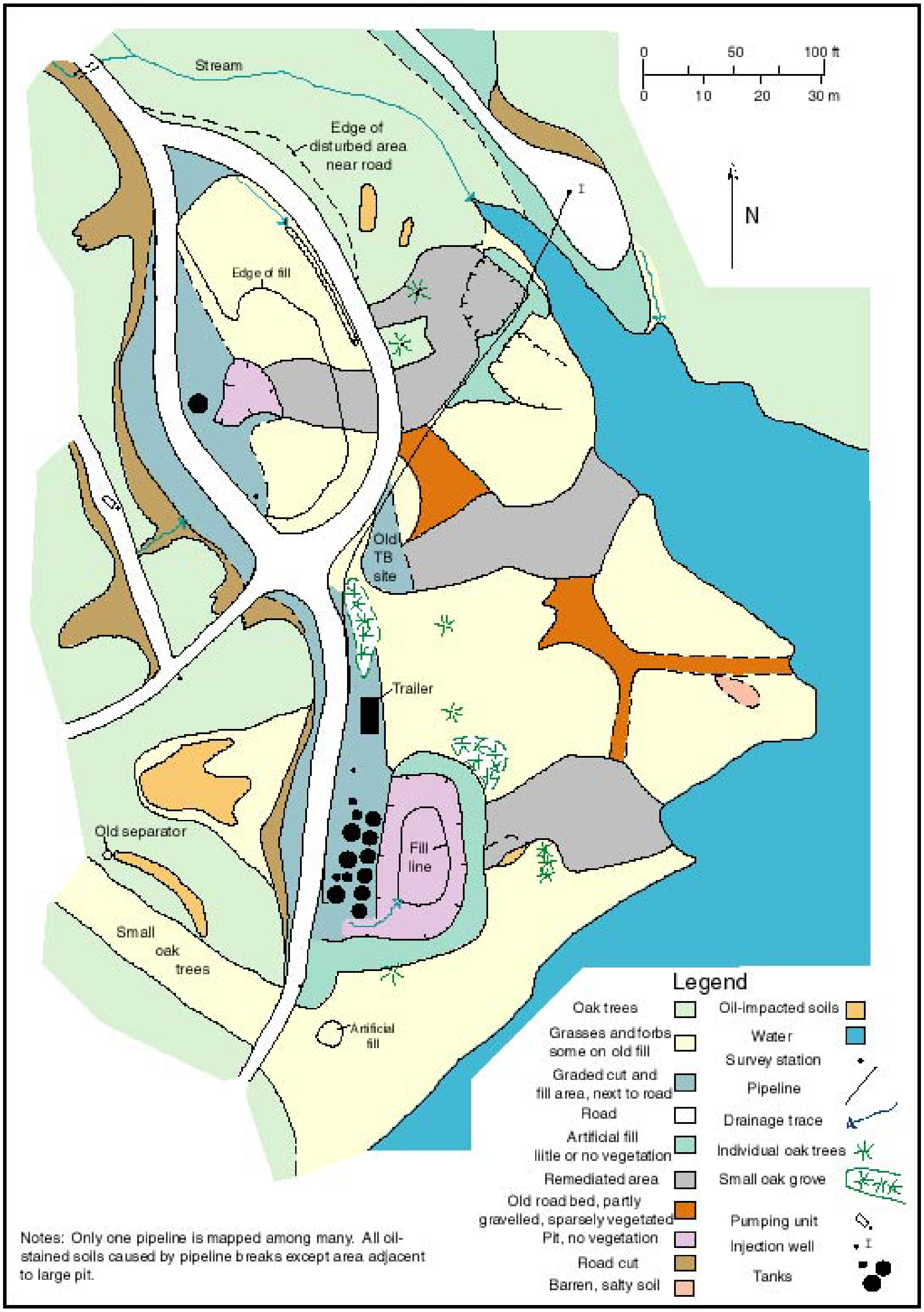
Abstract

Soil and underlying weathered bedrock at an active oil production site were investigated to determine the chemical signature of added salts and the spatial distribution of soil salinity in relation to areas of visible salt scarring. Aqueous extracts (1:1 by weight) of brine-impacted soil/bedrock have elevated (anomalous) Cl concentrations or relatively low ratios of conductance/Cl compared to extracts from samples collected offsite. The latter have low dissolved chloride and conductance (sandstone-derived) or sulfate as the dominant dissolved anion (shale-derived). Sampling of the upper 0-15 centimeters of the soil profile indicated that areas of high soil salinity are largely confined to locations of obvious salt scarring. Ratios of Cl/Br in extracts of chloride-rich surface soil are 250±30 and fall within the range of 220 to 320 reported in local produced waters. Within the area of salt scars, elevated salinity persists to depths of from 1.2 to >3.0 meters based on samples obtained by direct-push techniques.

Introduction

Three distinct areas of salt scarring are present at an active oil production site (site “B”) that is under study by the U.S. Geological Survey (USGS) (Otton and Zielinski, this volume). The spatial distribution of these three areas of barren ground is directly related to three distinct point sources that provided recent and/or historical releases of highly saline produced water as surface spills or subsurface seepage from brine storage pits (fig. 1). Whereas the surface expression of highly saline soil is commonly apparent through loss of vegetation and increased erosion, the areal extent of less saline soils and the depth of salt penetration are not obvious. Such information is critical for assessing the full extent of environmental damage, the cost of any planned remediation, and the ongoing dispersion of introduced salt.

Study site “B” provides an opportunity to test geochemical and geophysical methods that estimate the extent and severity of salt contamination. This report describes a geochemical method based on aqueous extracts of readily soluble salts. Dissolved salts derived from produced water are identified by their distinctive chloride-rich composition and Cl/Br ratio compared to the sulfate-dominant salts of local soils and bedrock. Similar chemical indicators are used to identify sources of salinity in ground water near oil and gas production sites (Whittemore, 1983, 1988; Richter and Kreitler, 1987; Knuth, and others, 1990; Abbott, 1998). This method expands the scope of salinity-source investigations to include aqueous extracts of soil and bedrock and builds on the success of previous studies using soil extracts (Otton and Zielinski,1998, 2000; Zielinski, and others, 2000, 2001).



Notes: Only one pipeline is mapped among many. All oil-stained soils caused by pipeline breaks except area adjacent to large pit.

Figure 1. Map of oil production site “B” showing oil production facilities, three areas of salt scarring (shown in gray), and vegetation.

Site Description

Study site "B," located northwest of Tulsa in northeastern Oklahoma, was selected by the USGS for detailed studies of environmental impacts related to oil and gas production, associated natural attenuation, and remediation strategies. Multidisciplinary studies were initiated in 2001 and are being conducted in cooperation with the landowner, lease holder, the Osage Nation, Federal, State, and local government agencies, and local universities. The site is situated along the present shore of Skiatook Lake, which was first filled in 1984. Local surficial deposits include eolian sand and silt, slope-wash, colluvium, and alluvium. Local bedrock of Pennsylvanian age is predominantly shale with lesser amounts of thin interbedded sandstone. A more detailed description of the geologic setting of the site and its production history (1937 to present) is presented in Otton and Zielinski, this volume.

Methods

Initial surface soil sampling (0-15 centimeter (cm)) was conducted at site "B" in March, 2001. Thirty samples were collected with a 5-cm-diameter stainless steel soil auger from the three salt scars, intervening areas, and other locations. All soil auger samples were stored in sealable plastic bags. In February of 2002, the site was sampled with hydraulically driven direct-push equipment that provided continuous 4-cm diameter cores to depths ranging from 2.13 to 5.48 meter (m). The cores were collected in plastic liners, capped, taped, and then transported to the USGS core library in Denver. Cores were stored under refrigeration until sampling. One 5.48 m long core from a locality at the margin of the site was sampled in detail to characterize the local background soils and shallow bedrock. Other direct-push cores were typically sampled at the following depths; 1.22 m, 2.13 m, and 3.05 m, or final depth if less than 3.05 m.

Samples weighing approximately 200 grams were air-dried at 40°C and passed through a ceramic-plate jaw crusher with 3-millimeter opening. For soil samples the primary purpose of the crusher was to disaggregate clay-cemented clumps formed during drying, but small (<1 cm diameter) rock fragments were also coarsely crushed during the process. For bedrock samples the crusher produced a similar average size of rock fragments for extraction. Exactly 100 g of crushed sample was weighed into a plastic beaker and 100 milliliters (ml) of deionized water added. Each 1:1 (by weight) mixture was stirred vigorously, allowed to stand overnight at room temperature, and again stirred vigorously prior to pouring into a 250-ml polycarbonate centrifuge bottle. The slurries were centrifuged at 8,000 revolutions per minute for 40 minutes to remove suspended particles larger than approximately 0.1-micrometer diameter. Clear solution (~60 ml) was decanted and passed through a filter membrane of 0.45 micrometer pore size under pressure from nitrogen gas.

Specific conductance and pH of each clear extract were measured immediately. Extracts were analyzed for dissolved chloride, sulfate, and bromide by ion chromatography using a Dionex 500 chromatography system equipped with an AS-14 anion exchange column. The eluent was a mixture of 0.0010 molar sodium bicarbonate and 0.0035 molar sodium carbonate (pH=9.0). Background-corrected counts under the peaks of interest were converted to concentration values based on a calibration of peak area (or peak height for Br) to concentration, as determined by contemporaneous analysis of a series of prepared standards. Sample dilutions were optimized to fall well within the concentration ranges of the standards. Analytical precision and accuracy were estimated based on replicate analysis of prepared and commercially certified standards and are better than 5 percent relative standard deviation (RSD) for chloride and sulfate, and better than 12 percent RSD for bromide values in excess of 1 part per million (ppm). Similar analytical precision of 1-14 percent RSD was obtained from three samples processed in duplicate.

The detection limit for bromide by this technique is approximately 0.1 ppm. In cases where the bromide peak lies on a sloping shoulder of a much larger chloride peak, best results are obtained by inspecting the chromatogram and performing software optimization that permits operator subtraction of a visually determined background contribution. For bromide the reported concentrations are based on a calibration using only the most closely bracketing standards. Use of the "method of additions" is also recommended to best determine Br in solutions of high and variable Cl content.

Results and Discussion

Graphs of specific conductance versus dissolved chloride help distinguish extracts of chloride-contaminated samples from extracts containing natural salts (figs. 2a, 2b). Extracts of uncontaminated sandy soils and sandstone have low dissolved solids and chloride contents and plot near the origin. Extracts of uncontaminated shale-derived soils and shale can have elevated dissolved solids, but are dominated by dissolved sulfate rather than chloride. These latter extracts plot along trend lines that are closer to the conductance axis. Extracts that plot well outside the areas on the graph defined by local soils and bedrock are those with unusually high chloride concentration for their conductance and are interpreted to be variably contaminated with chloride-rich salts.

At site "B" the upper 0-15 cm of soil is typically composed of eolian sand and silt, sandy to clayey colluvium, and reworked sandy to clayey fill material. Most extracts of surface soil from site "B" contain more than 530 ppm dissolved chloride, which exceeds the highest concentration observed in eight extracts from a 0.9-m soil profile collected offsite (fig. 2a). In addition, the conductance/Cl ratio for chloride-rich sandy surface soils is 4 or less, compared to a value of about 12 for the extracts of offsite sandy/silty soils. Extracts of deeper, direct-push core samples also fall into two distinct populations (fig. 2b). All extracts with less than 600 ppm Cl are from the 5.48 m-long shale-dominated core from the site margin, or from deeper portions of some onsite cores. These Cl-poor extracts show conductance/Cl ratios of ten or more. In contrast, most extracts of >600 ppm Cl are highly enriched in chloride and have conductance/Cl ratios of 6 or less.

Spatial-chemical data (fig. 3) indicate that the chloride content of surface soil extracts is consistently elevated within, and adjacent to, the salt scars. The highest chloride concentrations are immediately downslope from the active brine storage pit (sample L3A), or adjacent to a pool of saline water located near the toe of one salt scar (sample T1P). Surface soils located between salt scars have lesser, but still anomalous chloride contents in their aqueous extracts. Earth-moving operations at the site probably contributed to this broader distribution of near-surface salts. One surface soil (T2B) located uphill from the large tank battery, adjacent to an old oil spill and just below an old separator tank, also showed locally anomalous chloride content (460 ppm) in its extract.

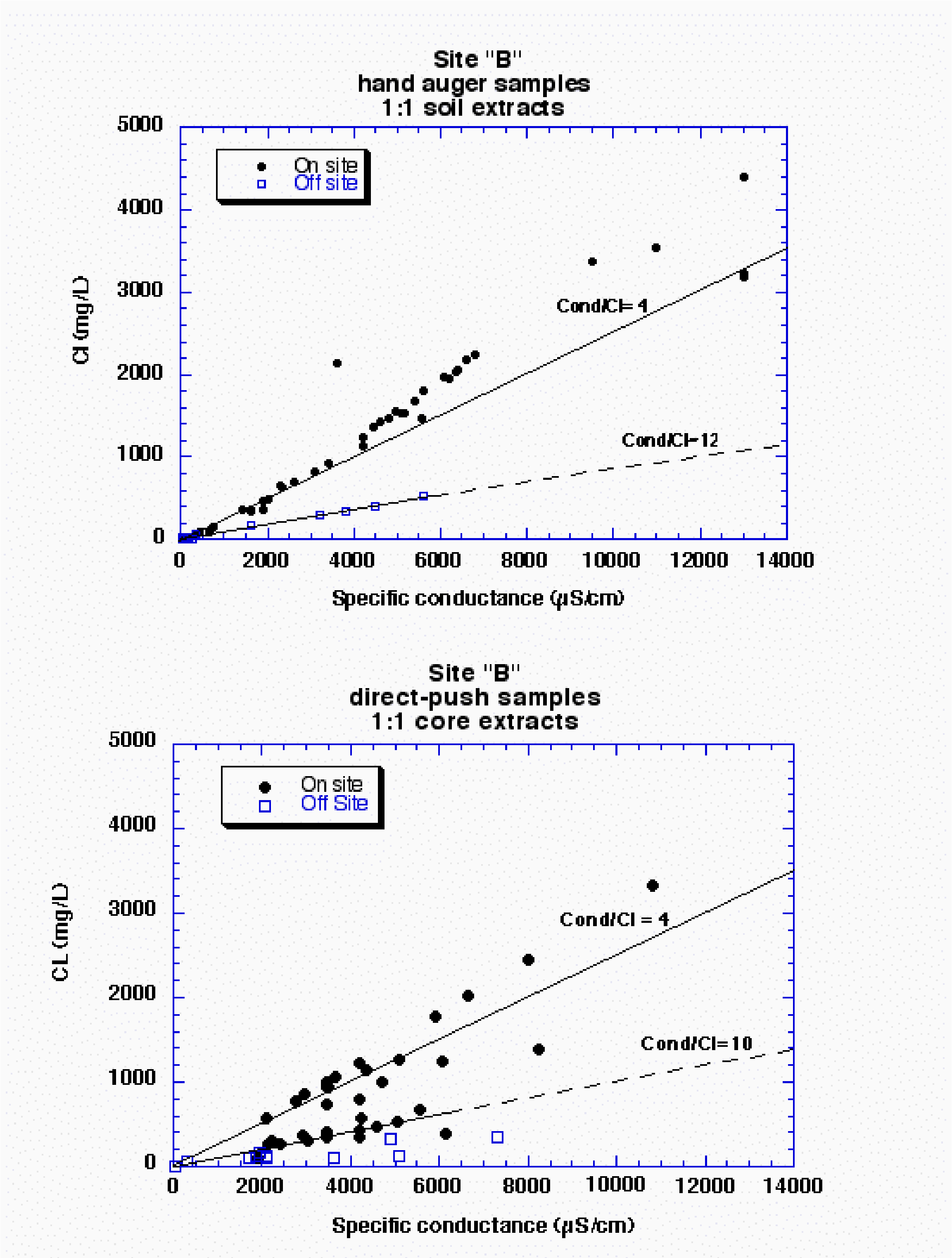


Figure 2. Chloride versus specific conductance in 1:1 aqueous extracts of (a) surface soils and (b) direct-push core samples from site "B." Lines corresponding to selected conductance/chloride ratios are included for reference.

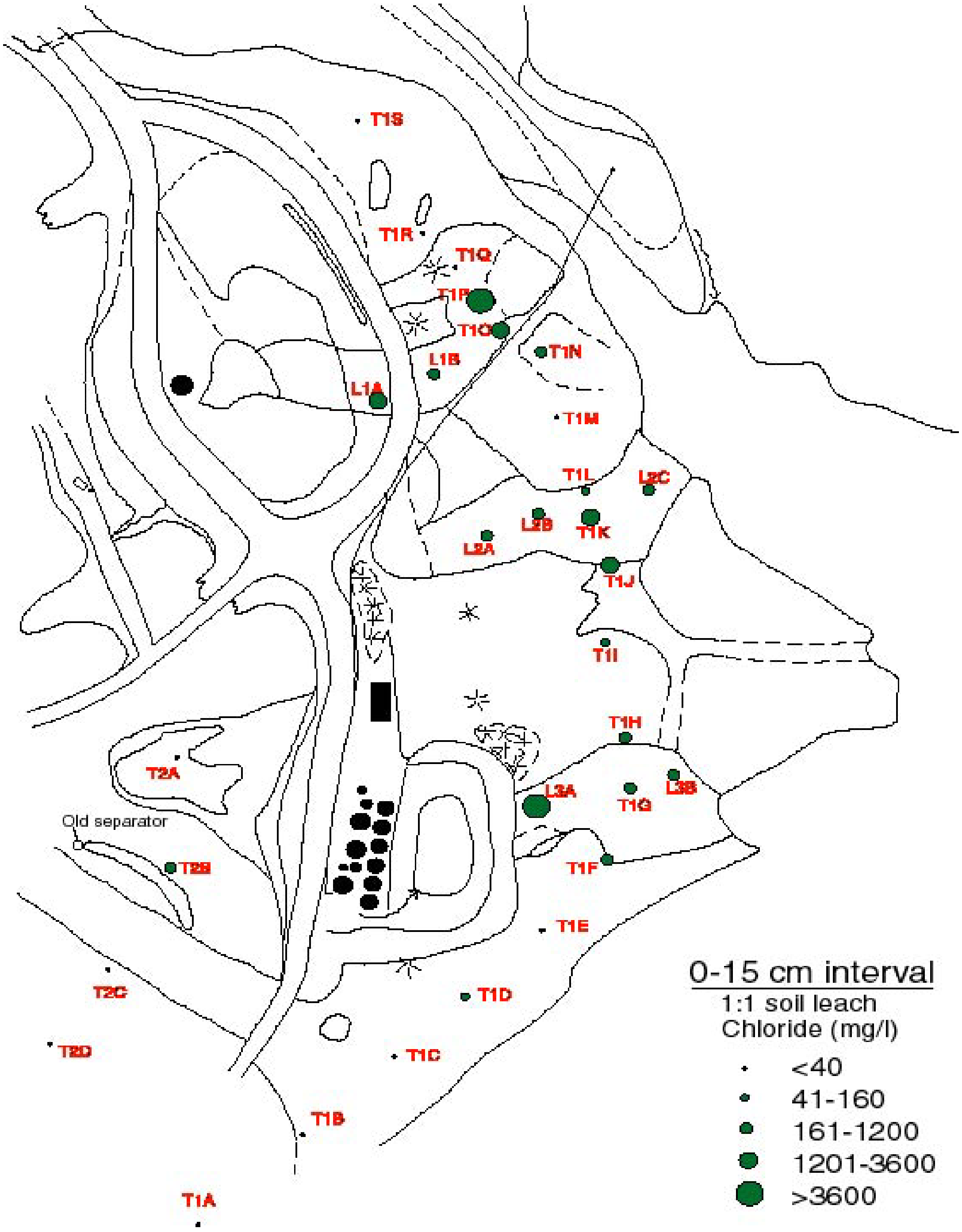


Figure 3. Geochemical map showing the distribution of chloride–rich surface soils at site "B." The size of plotted circles is indexed to ranges of chloride concentration in soil extracts, as indicated in the inset. The outlines of mapped areas are the same as in figure 1. Soil sample locations are indicated as site traverse (T prefix) or along the long axis of salt scars (L prefix).

The spatial distribution of soluble chloride in surface soils is consistent with the introduction of chloride-rich salt from oil production operations. Additional support for a produced-water source is provided by Cl/Br ratios. Cl/Br ratios in extracts of 20 contaminated surface soils (255±30) fall within the range of 220-320 found for eight local produced waters collected in March, 2001 (Kharaka and others, this volume). In contrast, the Cl/Br ratio in extracts of seven uncontaminated surface soils was <100. For reference, the Cl/Br mass ratio in seawater is between 288 and 292 (Davis and others, 1998).

Preliminary hand-auger sampling within the salt scars in May, 2001 indicated salt contamination to depths of refusal of 0.6 m and 0.8 m in older scars and 1.7 m in the scar from the active pit. Deeper sampling with direct-push equipment in February 2002 indicated that anomalous chloride contents (>600 ppm) and low conductance/Cl ratios (<6.0) persisted in extracts of sandy to clayey colluvium and fill, and underlying weathered shale to depths of at least 1.22 m (fig. 4). Deepest salt penetration of 2.13 m to > 3.05 m was found in the salt scar from the active pit. Periodic spills of produced water or continuous seepage from the pit or from an older pit located at the same site may account for the greater penetration of salt within this scar. Some direct-push sites located outside the present salt scars (sites 06, 13; fig. 4) showed salt to depths of 1.2 m, indicating the presence of older salt deposits or the lateral dispersion of salt by shallow ground water. Low lake levels at the time of direct-push sampling permitted more extensive sampling along the projected axes of salt scars (sites 07, 18) and confirmed that periodic submersion of sites does not remove the record of salt contamination in deeper horizons. Comparisons of salt penetration depths with lithologic descriptions of core samples (J.K. Otton, USGS, written commun., 2002) indicated that in some places salt has penetrated the entire thickness of sandy colluvium and as much as 1 m of underlying weathered shale.

Additional Considerations

The laboratory method described herein can be modified and adapted to provide real-time data for field application. In this case, specific conductance is measured on a freshly prepared 1:1 slurry of sample and distilled water. Dissolved chloride concentration is measured with a commercially available chloride test strip (Hach Company, 1999) on a small volume of slurry water passed through a syringe-mounted filter. Rapidly measured field values of chloride concentration and conductance/Cl ratio will differ from laboratory values, but still provide useful relative comparisons between similarly measured background samples and contaminated samples. Such field measurements can provide preliminary reconnaissance of sites contaminated by produced water or can guide removal of saline soils from such sites.

Conclusions

Anomalous concentrations of chloride are present in aqueous extracts of soils and underlying weathered bedrock at study site “B.” The spatial distribution of chloride-rich soils indicates at least three point sources of introduced salt, and the Cl/Br ratio of salt in contaminated surface soils falls within the range of values for local produced water. Salt contamination is not entirely confined to areas of obvious salt scars but persists to a lesser extent over a broader area at the site. Depth of salt penetration is generally between 1.22 to 2.13 m but at some locations immediately downslope from an active pit, the salt has penetrated to depths in excess of 3.05 m.

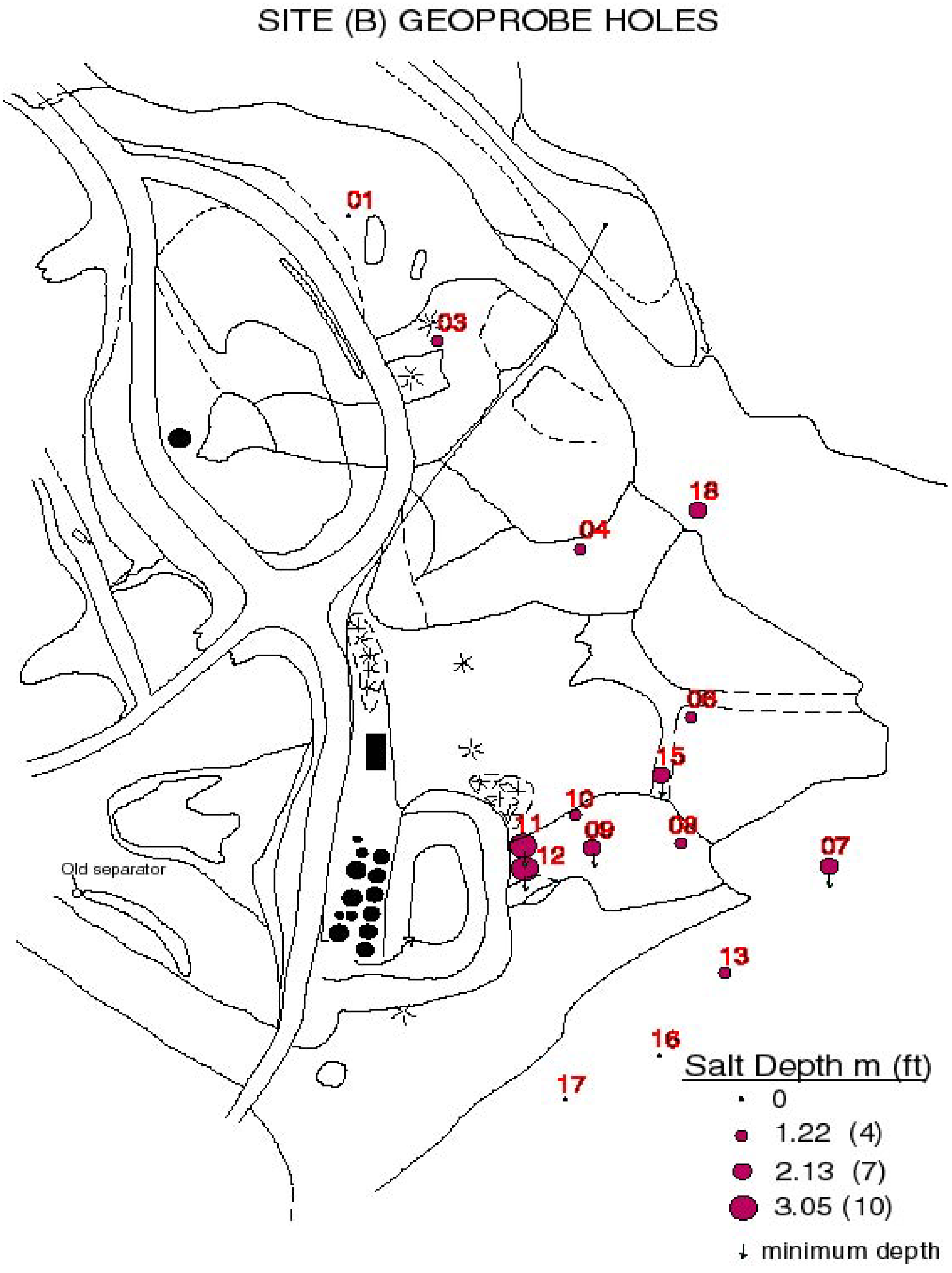


Figure 4. Depths of penetration of chloride-rich salt in direct-push cores from site "B." The size of plotted circles increases with apparent depth of chloride-rich salt, based on aqueous extracts of core samples. Circles with downward arrows indicate that anomalous chloride persisted to the bottom of the core. The outlines of mapped areas are the same as in figure 1. Numbers assigned to circles identify direct-push sites. Sites 07, 13, 16, 17 and 18 were cored during a low stand of the lake.

The use of aqueous extracts to define the nature and extent of salt contamination in soils has broad applicability at sites where chloride-rich salts from oil and gas operations contrast with the composition of natural salts. The technique can be modified to provide rapid, real-time assessments during field-based operations.

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Characterization of Soils at an Active Oil Production Site: Effects of Brine and Hydrocarbon Contamination

By Cynthia A. Rice, James D. Cathcart, Robert A. Zielinski, and James K. Otton

Abstract

An active oil field, the Osage-Skiatook Petroleum Environmental Research (OSPER) site “B” in Osage County, Oklahoma is under study to determine the impacts of produced brine and hydrocarbon spills on soils. Characterization of soils in areas known to be contaminated as well as those believed to be uncontaminated were studied using visual and microscopic description, X-ray powder diffraction of the bulk soil and clay-sized fraction, particle size analysis, cation exchange capacity, and selective extraction of iron species. Results indicate that most brine and hydrocarbon contamination at site “B” occurs at shallow depths (< 240 cm) where the soil color and type varies from a dark brown topsoil to a red-orange sand, to a greenish-gray clay. Quartz is the dominant soil mineral with substantial clay minerals composed of kaolinite, illite, smectite or mixed-layer illite/smectite, and minor amounts of feldspar. The cation exchange capacity of bulk soil samples in uncontaminated and contaminated areas is similar, but the percentage of sodium on exchange sites is substantially higher in soils from contaminated areas. Some soil samples from areas contaminated by produced water have high soluble salts, but low percentages of sodium on exchange sites. High amounts of reduced iron (up to 98 % of the total iron) in soils from contaminated areas may record the passage of hydrocarbon-rich ground water.

Introduction

Release of produced saline water and hydrocarbons at oil- and gas-production sites can have a range of impacts on the environment. The scale and level of impacts depend on the size and frequency of the release(s) and the types and times of remediation (API, 1997). Impacts range from unsightly effects, such as oil-stained soils or salt scars to changes in the physical and chemical properties of soils and water. Characterization of soils at sites where produced saline water or hydrocarbons are released is thus important.

Characterization of pre-spill and post-spill soil pH, mineralogy, exchangeable ion ratios, and other specific soil characteristics is necessary following a produced water or hydrocarbon release. The soil characterization assists in determining: 1) whether remediation is necessary; 2) the most effective type of remediation; and 3) any long-term monitoring requirements. At oil and gas production sites where saline and hydrocarbon releases may have occurred in the past, with or without remediation, soils may provide evidence of the release, the extent of contamination, the effectiveness of remediation, and an understanding of long-term consequences of releases.

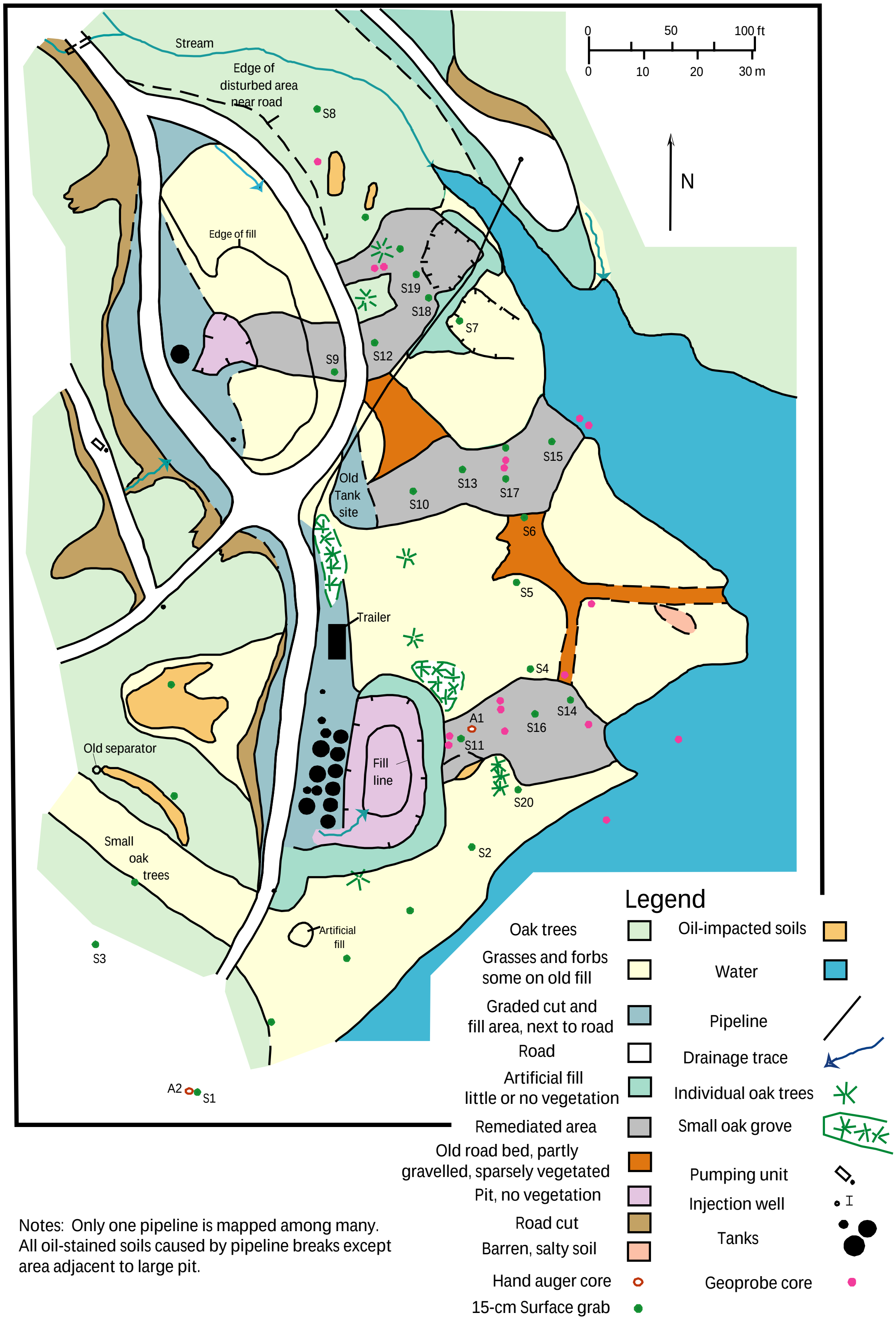
Soils were studied at an oil production site in Osage County, Oklahoma that had been subjected to both produced saline water and hydrocarbon releases and the preliminary results are presented in this report. The goals of the soil characterization are to: 1) document the extent of brine and hydrocarbon contamination; 2) understand controls on the movement and retention of brine and hydrocarbons; and 3) determine the role of solid phases, such as clay and iron-bearing minerals, in natural mitigation. The types and amounts of clay minerals and oxidizers (particularly iron) are important because of the capacity of clay minerals to exchange cations that are dissolved in brines and the capacity of reactive ferric iron species to oxidize hydrocarbons. Releases of production fluids at the site (OSPER site "B", fig. 1) have occurred as recently as 1999 and sporadically prior to that time (Otton and Zielinski, this volume). The site is still active and has a tank battery containing produced water brine and oil, an unlined overflow pond below the tank battery, and a water disposal injection well (fig. 1). Three areas at the site (labeled as remediated area in fig. 1) were remediated after saline water releases in 1999 by removing the top 6 inches of soil, placing uncontaminated topsoil on the areas, and planting the areas with grass. The three remediated areas are considered contaminated areas in this study and are referred to herein as "affected areas", while areas surrounding and away from the remediated areas, tank battery, and pond are considered "background areas", even though future study may find that it is difficult to find truly pristine areas in a contaminated site such as this. A complete description of the site including the topography, geology, hydrology, vegetation, and history is given in Otton and Zielinski, this volume.

Methods

Samples were taken at site "B" (fig. 1) to characterize soils geographically as well as vertically. Surface soils were collected in May, 2001 as 15-cm-deep "grab" samples (fig. 1). Hand-auger cores were also collected in May 2001 at locations contaminated by saline produced water and hydrocarbons; samples were also taken in areas not exposed to contaminants (fig. 1). Hand-auger core penetration was maximized at each location with total depths varying from 58 to 166 cm. In February 2002, 2-inch-diameter cores were also taken using the Geoprobe system (fig. 1); depths of the cores varied from 1 to about 5.5 meters.

Several methods were utilized for soil and solid-phase characterizations, including grain size analysis (percent sand or larger-size, silt, and clay), X-ray powder diffraction (XRD) analysis of bulk soils and clay-size (<2 μm) fractions, whole soil cation exchange capacity (CEC) analysis, and selective chemical extractions for iron.

Percent of sand and larger-sized fraction (> 63 μm) was measured by wet sieving through a 230 mesh sieve. Silt-size (2-63 μm) and clay-size (<2 μm) fractions were separated by centrifugation. XRD was performed on bulk soils ground with a mortar and pestle and packed in a randomly-oriented powder specimen. Clay minerals were identified after XRD of a preferred oriented specimen of the < 2 μm fraction after the following treatments: 1) air-drying; 2) ethylene glycol saturation; 3) heating to 400ºC; and 4) heating to 550ºC. XRD patterns were analyzed by matching them with standard patterns using digital software (Jade, 1998) and a standard pattern reference library (International Centre for Diffraction Data powder diffraction file (McClune, 1998)). Semi-quantitative (± 20 percent) mineralogies of bulk samples were determined using reference intensity ratios (Snyder, 1992).



Notes: Only one pipeline is mapped among many. All oil-stained soils caused by pipeline breaks except area adjacent to large pit.

Figure 1. Site and sample location map of OSPER "B" site, Osage County, OK. Modified from Otton and Zielinski, this volume. Geoprobe core sites in "offshore" positions were sampled during a lake lowstand.

Cation exchange capacity was determined on 10 g of bulk soil using a modification of the method by Breit (1990). About 10 g of soil was placed in 250 mL polyethylene bottles with about 150 mL of a 1 M solution of $SrCl_2 \cdot 6H_2O$; with weight of the bottle, sample, and solution recorded. Samples were periodically shaken over a period of about 16 hours to disaggregate the sample and replace Na, Ca, Mg, and K with Sr^{2+}. At the end of the saturation period, the samples were placed on a wrist shaker for one hour. Most of the Sr solution was then separated from the solid by centrifuging and decanting and saved for analysis. Weight of the remaining solution, solid, and bottle was again recorded to determine the amount of residual fluid. An additional 150 mL of Sr solution was added to the bottle containing the solid and residual Sr solution and the saturation exchange procedure was repeated.

Amounts of Na, Ca, Mg, and K in solutions were determined by atomic absorption spectrophotometry (AAS). Amounts of Na, Ca, Mg, and K in the saturation solutions represented both exchangeable cations as well as cations from soluble salts. The amounts of Na, Ca, Mg, and K from soluble salts were measured by dissolving the soluble salts in a separate 1 g of bulk soil in 15 mL of deionized water for 16 hours, followed by analyzing the solution separated by centrifugation. The amounts of Na, Ca, Mg, and K from soluble salts were then subtracted from amounts measured in the saturation solutions.

Percentage of reduced iron (Fe^{2+}) versus oxidized iron (Fe^{3+}) in readily soluble iron phases was determined on 2 to 5 g of Geoprobe core samples immediately after collection. Samples were taken from the core interior and sealed in amber septum vials previously prepared with 40 mL of 0.5 N hydrochloric acid (HCl) flushed with nitrogen gas. Vials were periodically shaken for 24 hours to leach available iron (ion-exchangeable and dissolved) as well as iron in readily dissolved phases (iron monosulfides, siderite, and poorly crystalline iron phases, such as iron oxyhydroxides). This method is a modification of Heron and others (1994) who also reported recoveries of various species of iron. Concentrations of Fe^{2+} and total Fe leached from the samples after 24 hours were determined using the ferrozine spectrophotometric method.

Results and Discussion

Size fractions and XRD analyses were performed on two hand-auger cores (A1 and A2) at site "B" (fig. 1). The two cores represent an "affected" area (core A1) and a "background" area (core A2) and field descriptions of these cores are given table 1.

Particle size analysis indicates that the silt plus sand-size or larger fraction dominates both cored soils with the background soil core (A2) containing more silt in the upper section of the core (fig. 2). Clay-sized material in the background core (A2) is high (25 weight percent) near the surface, but decreases with depth to about 6 weight percent. In the affected core A1, the amount of clay-sized material is fairly constant in the upper meter of the core, then increases to over 25 percent at the base of the core. The silt-sized fraction is greater than the clay-sized fraction and also increases in lower portions of the core. Size analysis indicates a distinct lithologic change in affected core A1 just below a meter in depth that represents a contact between shallow soils and the areally extensive weathered shale of the Wann Formation described by Otton and Zielinski, this volume.

The XRD mineralogy of whole-rock (bulk) soils from both cores show primary and secondary soil minerals that include quartz, feldspar, goethite, kaolinite, and other clay minerals that were indistinguishable in whole-rock XRD. Goethite was found in core in two samples

Table 1. Field descriptions of samples from Core A1 (affected) core and Core A2 (background) core.

Core	Depth (cm)	Description
A1	0 - 18	Color: 10YR 5/6 yellowish brown overall. Sandy clayey silt to sandy silty clay. Soft, some faintly mottled. Some roots. Abundant grit and granules. Some yellow red weathered clasts. Faint hydrocarbon odor.
	18 - 30	Color: 2.5Y 4/4 olive brown. Sandy clayey silt to sandy silty clay. Soft. Minor roots. Flecks and mottles of 10YR 5/8 yellowish brown weathered and unweathered sandstone chunks. Very faint hydrocarbon odor.
	30 - 44	Color: 10YR 5/6 yellowish brown. Sandy clayey silt to sandy silty clay. Soft. Clasts of sandstone to 2 cm. Small orange to red-colored weathered sandstone flecks. Moderate hydrocarbon odor.
	44 - 55	Color: 2.5Y 4/4 olive brown. Sandy clayey silt. Relatively dry. A few sandstone clasts to 2.2 cm. Uniform color. Faint to moderate hydrocarbon odor.
	55 - 65	Color: 2.5Y 4/4 olive brown overall. Sandy clayey silt to sandy silty clay. Color is greenish gray on freshly broken clods. Sandstone and siltstone clasts to 2.4 cm (sandstone clasts are red to orange). Moderate hydrocarbon odor.
	65 - 76	Color: 2.5Y 4/4 olive brown. Sandy to silty clay. Sandstone fragments to 1 cm. Thin roots and other pieces of black organic matter. Moderate hydrocarbon odor.
	76 - 86	Color: 2.5Y 4/4 olive brown overall. Sandy silty clay with abundant granules to small fragments of shale, siltstone, and sandstone. Mottled. Green gray on broken clods. Moderate to strong hydrocarbon odor.
	86 - 96	Color: 2.5Y 5/4 light olive brown. Chunks of sandstone clasts 2.5YR 4/6. Red dark reddish brown, also 10YR 5/8 yellowish brown, siltstone clasts yellow gray. Sandy clayey silt to sandy silty clay. Minor roots. Pieces of black plastic rope? Black organic fragments. Moderate hydrocarbon odor.
	96 -105	Color: mottled 10YR 5/6 yellowish brown and about 1/3 5Y 5/2 olive gray. Sandy clayey silt to sandy silty clay with abundant grit and granules. Soft. Sandy clasts, clay, colluvium. Hydrocarbon odor weaker. Clay matrix, clasts of reddish brown-largest pebble, flat, about 2 cm across.
	105-117	Color: mottled 2.5Y 6/2 light brownish gray and 2.5Y 5/6 light olive brown. Reddish brown color toward bottom; 2.5YR 5/4 reddish brown as before. Sandy clayey silt to sandy silty clay with grit and granules. Still soft, but not as soft as above. Mostly clay; fragments of silty to clayey sandstone. Faint hydrocarbon odor persists.
	117-125	Color: 2.5Y 4/4 olive brown and mottled 10YR 5/6 yellowish brown with spots of clayey shale 2.5YR 4/8 red to reddish brown. Silty clay, mottled light olive brown, green gray and “red” (2.5YR 4/8 to 10R 4/8). Clay is stiff. Faint hydrocarbon odor. Upper portion – colluvium; lower portion – clayey shale near bottom, probably getting into shale alone.

Table 1. Field descriptions of samples from Core A1 (affected) core and Core A2 (background) core – continued.

Core	Depth (cm)	Description
A1	125-136	Color: 2.5Y 5/4-5/6 light olive brown overall. Silty clay. Mottled olive brown, green gray, and light brown(7.5YR 6/6). Stiff. Faint overall hydrocarbon odor, clay with root impressions, slightly mottled with roots; hydrocarbon odor strongest in root impressions probably following root casts.
	136-147	Color: 2.5Y 5/4 light olive brown. 5Y 5/2 olive gray. Mottled clay with roots, a few siltstone or shale rock fragments. Clay is stiff. Faint hydrocarbon odor, root casts, abundant mottling around root casts. Small quartz pebbles to 1 cm. Making a small amount of water.
	147-157	Color: mottled 5Y 5/4 olive and 10YR 6/6 brownish yellow mottled with gray. Mottled clay. Still making a small amount of water, stronger hydrocarbon odor. Fragments of rock, siltstone; out of shaley zone siltstone fragments to 3 cm. 2 distinct colors; sparse black organic plant fragments still in colluvial material (fill?).
A2	0 - 17	Color: mottled 10YR 6/6 Brownish yellow with darker surface soil 10YR 4/2 dark grayish brown. Sandy silty clay with minor grit and granules of siltstone. Roots. Abundant organic matter responsible for darker color at surface.
	17 - 30	Color: 10YR 5/8 yellowish brown; slight mottling. Silty clay with minor grit and granules. Siltstone clast to 1.3 cm. Some rootlets and thin roots.
	30 - 44	Color: mottled 10YR 6/8 brownish yellow with speckles of 2.5YR 4/8 red. Mottled silty clay with minor grit and granules to 1.2 cm. Some rootlets. Clay content; harder to get out of auger; some decaying plant fragments.
	44 - 58	Color: 10YR 5/6 yellowish brown with specks of 2.5YR 4/8 red. Mottled sandy silty clay with siltstone clasts to 1.5 cm. Several large root fragments at bottom.
	58 - 69	Color: mottled 10YR 6/6 brownish yellow with 5Y 6/3 pale olive and 5YR 5/8 yellowish red. Mottled sandy silty clay with siltstone and sandstone clasts to 2 cm. Sandstone clasts are oxidized. Root material.
	69 - 79	Color: 10YR 5/8 yellowish brown mottled with 10YR 7/1 light gray. Sandy silty clay with highly weathered sandstone. Clasts (friable, breakable in fingers). Relatively stiff. Weathered colluvium; siltstone clasts with hematite? Stains; some 2.5YR 4/8 red.
	79 - 88	Color: Mottled 10YR 5/8 yellowish brown. 7.5YR 5/8 strong brown; 2.5YR 4/8 red and light gray. Mottled sandy silty clay. Green gray shale clasts to 1 cm. Minor roots. Four different colors in this sample. Some plant fragments, sandy to clayey with some Mn oxide staining.
	89 - 93	Color: 10YR 5/8 yellowish brown mottled with 10YR 7/1 light gray. Mottled sandy silty clay. Sandstone and siltstone clasts to 2 cm. Light gray rock with hematitic rind. Numerous siltstone chips with Mn oxide staining. Hole terminated at 1:17 PM by large rock at bottom.

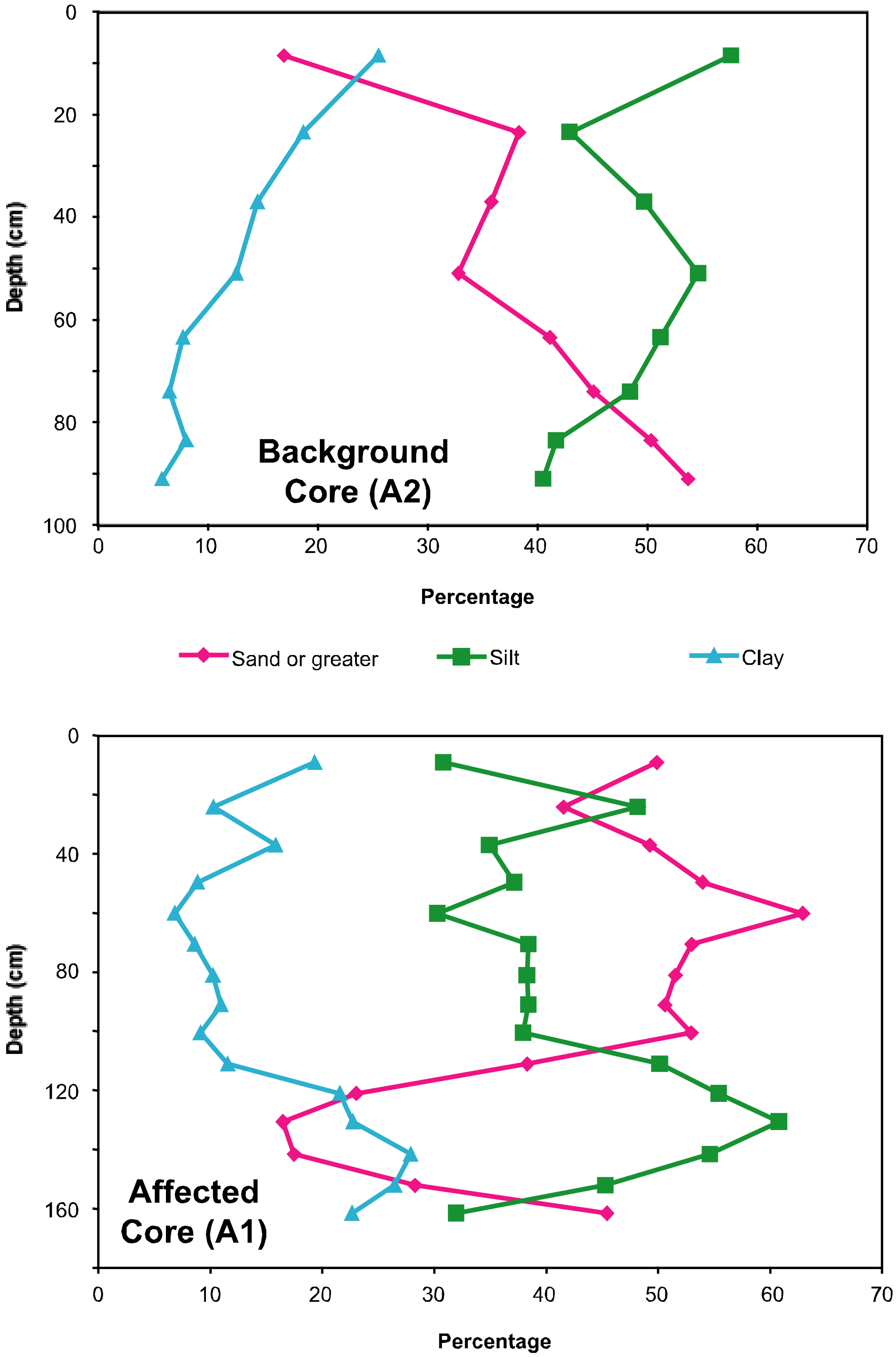


Figure 2. Percentages of three major size fractions in samples from two hand auger cores at OSPER "B" site.

below the contact between shallow soils and the regional weathered shale (between 105-136 cm). Figure 3 shows the relative abundance of major minerals in cores A1 and A2. Quartz is the dominant mineral in both cores and kaolinite is the second most abundant. Also shown on figure 3 is the percent of sand and larger-sized plus silt-sized content of the two cores. Quartz content in both cores is considerably less than the amount of material larger than clay-sized indicating that significant portions of the other minerals, especially mica and feldspar, are larger than clay-size and may represent detrital material. Detailed XRD examination of the clay-sized fraction (< 2 μm) from the two cores showed a mixture of clay minerals including kaolinite, illite, and smectite or mixed-layer illite/smectite.

The CEC and exchangeable cation analyses of whole-rock soil from surface samples and from cores A1 and A2 are given in table 2 and plotted in figures 4 and 5. The range of CEC in the whole-rock samples of this study (1.5-28 meq/100g) fall within the ranges measured in soils (API, 1997). Although the CEC in a soil can be contributed by a variety of phases such as clay minerals, organic matter, and amorphous material, a simple exercise was performed on the whole-rock CEC ranges that assumed the CEC was primarily from clay minerals. The whole-rock CEC values were normalized to the amount of material that was not quartz or feldspar and the resulting range of CEC values varied from 11-69 meq/100g in the affected core A1, and from 24-66 meq/100g in the background core A2. The lower normalized values (11 meq/100g) may represent samples that contain predominantly kaolinite (2-15 meq/100g) while the higher normalized values (66 and 69 meq/100g) may represent a mixture of clays such as illite (10-40 meq/100g) and smectite (80-150 meq/100g). This would be consistent with the XRD analysis of the soils that showed varying amounts of kaolinite and other clay minerals; however, additional analytical work is required to confirm this hypothesis. Results show little difference in total CEC on a whole-rock basis or a normalized basis between the affected and background cores (fig. 4) or between the 15-cm surface grab samples relative to affected areas at the site (fig. 5).

Results however show large differences among most samples in affected areas and elsewhere when the percentage of Na in exchange sites (the exchangeable sodium percentage or ESP) is examined. Because the produced water released at the Skiatook site is predominantly a Na-Cl type brine having total dissolved solids (TDS) as high as 185,000 mg/L and Na concentrations as high as 55,000 mg/L (Kharaka and others, this volume), the amount of Na on exchange sites in soils exposed to these brines is expected be relatively high. The range in ESP of core samples and surface samples is shown in table 2 and figures 4 and 5. The ESP is higher in most samples in the affected core A1 as compared to the background core A2. Figure 5 shows a similar pattern for the surface samples in that most samples in affected areas contain higher ESP than samples in areas not affected by produced water, independent of the total CEC.

Surprisingly, there are a few samples from affected areas that have a low (<1) percentage of exchangeable Na (table 3, fig. 5). Some of these samples, however, have relatively high concentrations of water-soluble Na (fig. 6). All of the surface samples in figure 6 that have high (> 500 μg/g) water-soluble Na and very low (<1) ESP are within or very near areas exposed to produced saline waters. Total CEC for these samples range from 5-10 meq/100g, but the exchange sites within the soil are not affected by the high water-soluble Na in the samples. This may be controlled by the exposure time of soils to solution and/or the presence of competing cations such as Ca and Mg.

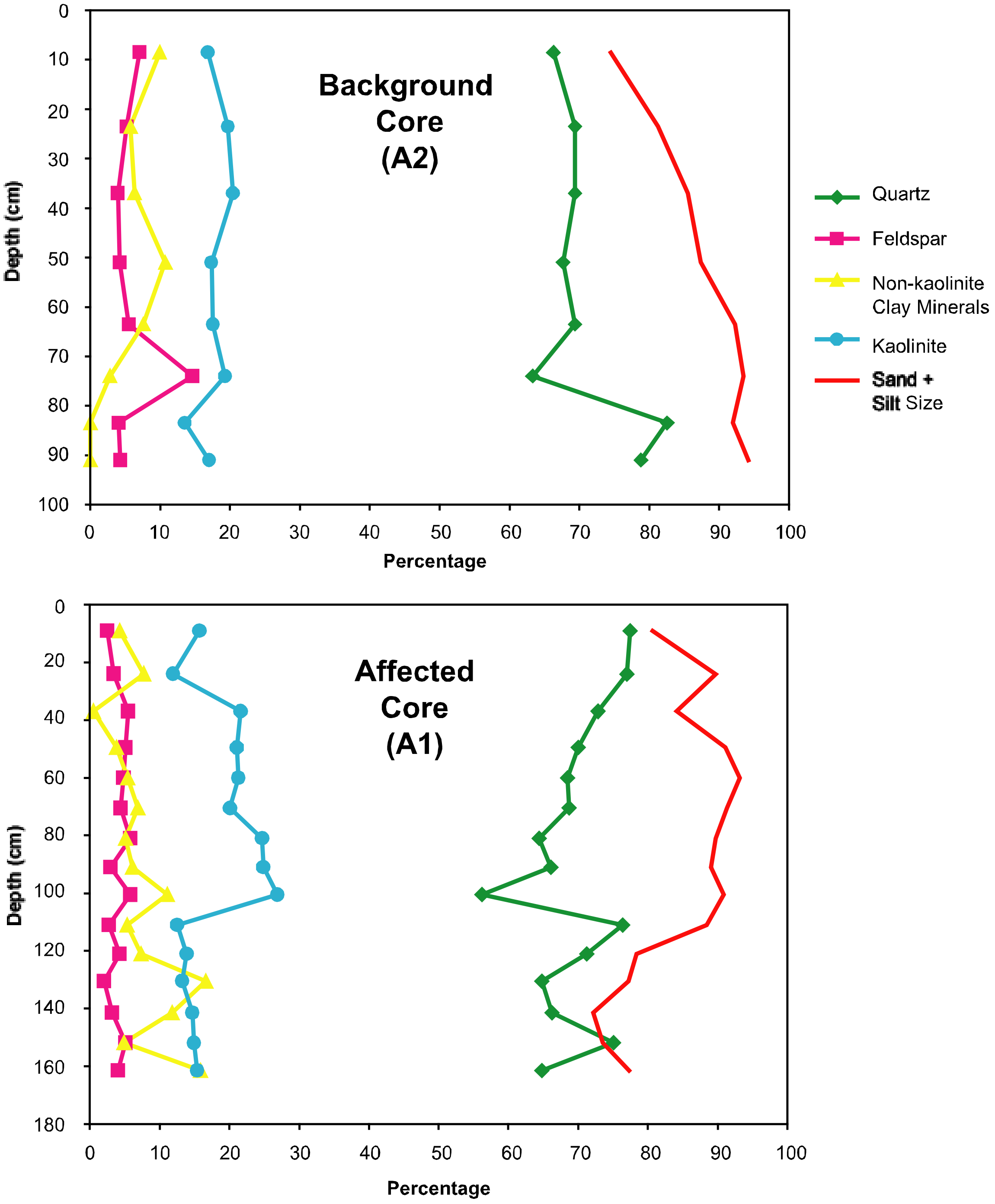


Figure 3. Semi-quantitative percentages of minerals identified by X-ray diffraction of bulk samples from two hand auger cores at the "B" site. Clay minerals is a generic term that includes undifferentiated (in bulk) mica, illite, smectite or mixed layer illite/smectite. The percentage of sand or greater and silt-sized material in each sample is also shown.

Table 2. Cation exchange capacity and water-soluble cation determinations for soils from core and 15-cm surface grab samples at Skiatook site "B."
[CEC = cation exchange capacity; ESP = exchangeable sodium percent; Norm. = normalized]

Depth	Exchangeable Bases (meq/100g)				CEC	Norm. CEC	ESP	Water Soluble Cations (μg/g)			
(cm)	Ca	Mg	K	Na	(meq/100g)		%	Ca	Mg	K	Na
Affected Core (A1):											
0-18	8.0	1.9	0.04	1.8	12	59	15	0.42	11	66	730
18-30	6.6	1.8	0.11	2.2	11	54	20	1.1	5.5	22	860
44-55	2.0	0.83	0.04	0	2.8	11	0	52	17	15	940
76-86	3.0	2.3	0.09	2.0	7.5	25	27	75	31	11	880
105-117	2.3	2.9	0.08	1.3	6.6	32	20	34	35	5.2	600
125-136	5.3	8.6	0.29	2.3	16	49	14	1.1	2.9	3.5	470
147-157	2.7	8.3	0.21	2.4	14	69	18	0.33	6.0	23	330
Background Core (A2):											
0-17	11	3.5	0.18	0.19	14	54	1.3	10	14	14	52
17-30	2.4	3.3	0.14	0.09	6.0	24	1.5	0.56	7.1	16	51
30-44	1.5	4.7	0.15	0.37	6.7	25	5.6	1.5	7.3	4.3	58
44-58	1.1	6.0	0.22	0.41	7.7	27	5.3	14	100	8.9	190
58-69	0.68	6.1	0.19	0.75	7.7	31	10	20	180	6.6	330
69-79	0.52	4.6	0.21	0	5.3	24	0	41	300	16	580
79-88	0.77	7.5	0.23	0.30	8.8	66	3.4	31	230	8.2	580
89-93	0.10	4.7	0.24	0	5.0	30	0	150	460	20	730
15-cm Surface Grab Samples:											
S1	1.9	1.6	0.12	0.02	3.7		0.6	11	15	15	6.0
S2	10	3.7	0.28	0.09	14		0.6	3.7	8.3	23	35
S3	7.7	6.6	0.47	0.07	15		0.4	1.5	4.7	10	11
S4	9.4	2.9	0.05	0.99	13		7.4	0.56	7.9	31	310
S5	9.5	2.7	0.14	0.49	13		3.8	11	5.6	2.2	140
S6	3.7	1.4	0.06	0	5.2		0	220	130	8.4	1,50
S7	4.9	1.4	0.05	0	6.3		0	8.1	13	14	400
S8	0.79	0.54	0.09	0.03	1.5		2.3	10	10	28	2.9
S9	8.0	2.2	0.13	0	10		0	50	29	18	2,00
S10	4.6	0.82	0	0.72	6.2		12	0.44	17	120	590
S11	8.0	2.1	0.21	1.3	12		11	430	130	36	3,40
S12	14	2.0	0.19	0.16	16		1.0	110	20	19	190
S13	7.1	1.1	0.10	1.2	9.4		13	120	13	12	450
S14	2.3	1.6	0.07	1.3	5.3		25	0.92	4.5	13	460
S15	6.4	1.1	0.06	0.63	8.2		7.6	3.5	10	26	380
S16	5.6	1.7	0.01	1.4	8.8		16	0.70	14	49	560
S17	5.4	0.86	0.03	0	6.3		0	15	15	21	1,10
S18	11	2.4	0.10	3.5	17		20	0.41	12	78	750
S19	14	2.7	0.15	11	28		40	4.0	15	55	1,60
S20	5.7	2.4	0.06	1.8	9.9		18	0.44	4.4	16	190

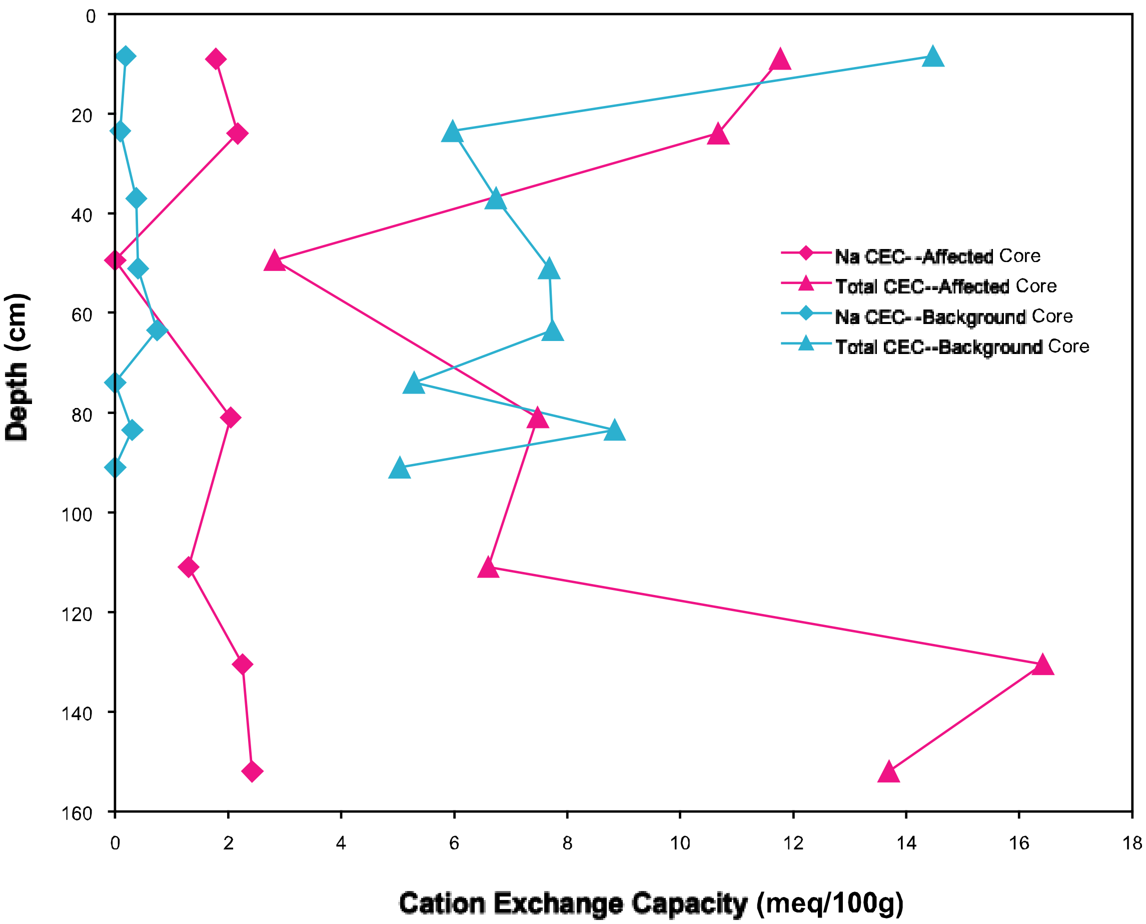
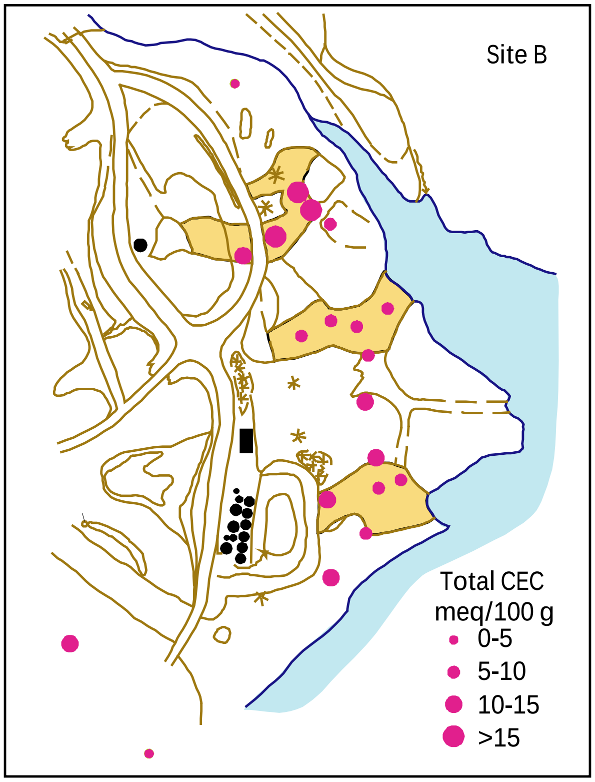


Figure 4. Total cation exchange capacity (CEC) and the amount of CEC occupied by Na for samples from two hand auger cores from OSPER "B" site.

Some samples from the background core A2 and one grab sample have low ESP and high soluble Na; they also contained abundant soluble Ca and/or Mg. Therefore, while the amount of Na in the samples was relatively high, it was not present in sufficient amounts to compete with the more strongly preferred Ca and Mg on exchange sites. Another surface sample with low ESP and high soluble Na was collected on a high gradient slope. Soluble Na in this sample probably represents salt residue from rapid flow of produced water brine through soils that did not allow Na to exchange on all soil sites. Two other samples contained low ESP and high soluble Na, but it is not clear why the exchange sites did not have high Na. Although some samples from Skiatook site "B" do not present a clear relation between water-soluble Na and ESP, the majority of samples indicate a positive correlation (fig. 6).

Results from the measurement of water-soluble Na and ESP in soils from site "B" can provide an understanding of effects of produced water releases and efficiencies of remediation efforts on plant populations at the site. Plant growth is dependent on many factors, but two of the most important are soil salinity and sodicity and vegetation health and distribution at site "B" most likely reflects the relative soil salinity and sodicity at the site. The ESP and water-soluble results also identify two distinct populations of samples (fig. 6) that represent two separate effects from saline water that have to be addressed when considering mitigation measures.



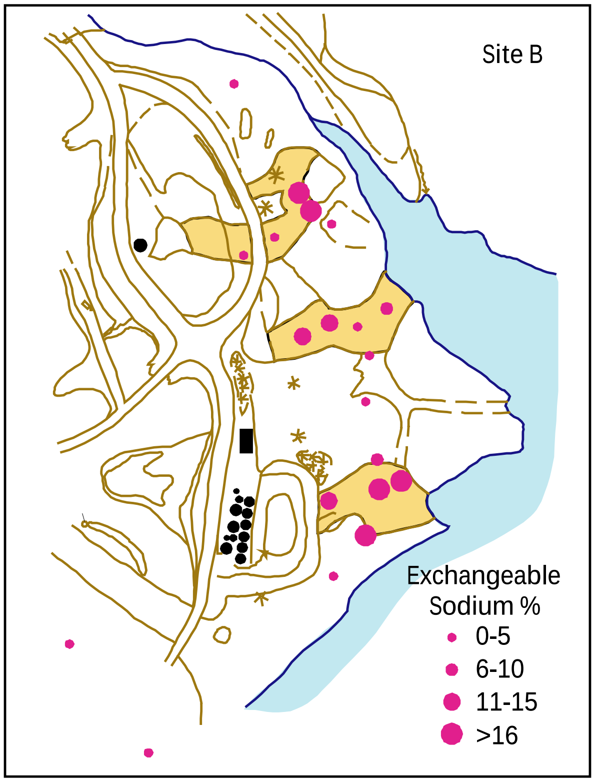


Figure 5. Areal distribution of the total cation exchange capacity (CEC) and the percentage of exchange sites occupied by Na (ESP) for 15 cm surface grab samples at OSPER "B" site. Site outline and structures are described in figure 1.

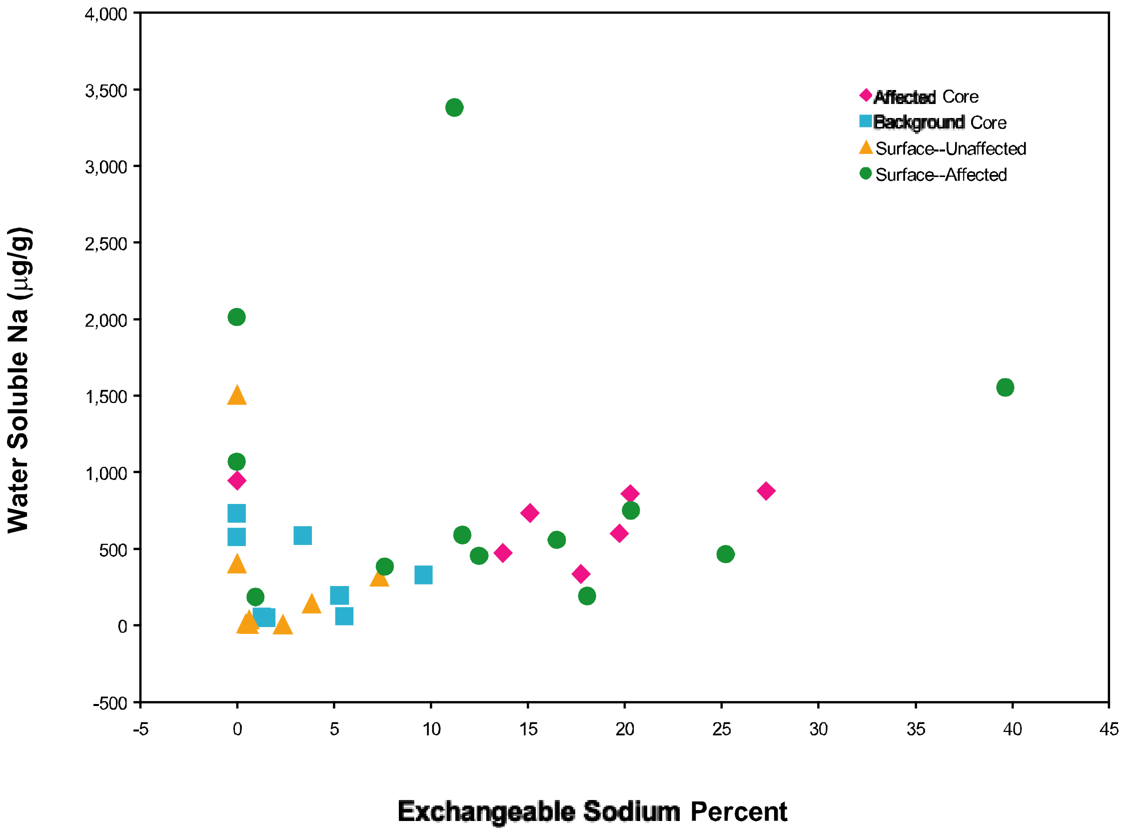


Figure 6. Amounts of water-soluble sodium versus the percent of exchange sites occupied by sodium in samples from two hand auger cores and 15-cm surface grab samples at OSPER “B” site.

Rapid flushing of soluble salts from the soil zone may be sufficient to mitigate areas that have samples with high soluble Na, but low ESP. The solution used to flush the area would need to contain a sufficient amount of soluble Ca or be applied in a manner that prevents the soluble Na from exchanging onto the soils. On the other hand, samples from areas with high soluble Na and high ESP may be more difficult to remediate because Na has exchanged onto clay minerals, soil dispersion may have occurred, and soil permeability may have decreased so infiltration of remediating fluids may be limited. Soil amendments and mechanical mixing of soil amendments and remediating solutions may be necessary to remediate areas where Na exchange onto clay minerals has already occurred.

The release of hydrocarbons at oil production sites can also impact soils at a site through both physical and chemical reactions. In particular, natural remediation of hydrocarbons in soils may occur as bacteria biodegrade the hydrocarbons by oxidation-reduction reactions that oxidize the organic matter using minerals as sources of electron acceptors in the process (Delin and others, 1998). Iron oxyhydroxides and other iron-bearing minerals are commonly sources of easily-reduced iron in many soils. A product of the oxidation-reduction reactions using iron phases is reduced iron (Fe^{2+}) instead of oxidized iron (Fe^{3+}) in soils and pore water. High percentages of Fe^{2+} in the readily available iron species in a soil, therefore, may reflect the passage and bioremediation of hydrocarbons. Preliminary analysis of reduced iron in 0.5 N HCl extractions of 19 samples from fresh core indicated that 11 of 19 samples had greater than 25 percent reduced iron, with as much as 98 percent in some samples. Four samples from a core down gradient of the overflow pit at the active tank battery at Site B had reduced iron ranging from 12 to 98 percent suggesting that hydrocarbons had been biodegraded in soils below the pit, but that the biodegradation was occurring within relatively narrow (<1 m) bands of soil probably as a result of preferred flow of fluids in the soil. In addition, the 0.5 N HCl extractions indicated the presence of abundant available iron (230-3,000 μg/g) in the soils to aid in natural remediation processes.

Summary

Soils from shallow core and surface grab samples at OSPER "B" site, an active oil production site, display characteristics indicating the passage of produced saline water and hydrocarbons. Many samples in areas known to have been exposed to produced fluid release contain significant ESP as well as residual soluble Na. However, some samples in these impacted areas have elevated soluble Na, but low ESP, indicating that the presence of high soluble Na alone may not indicate that produced saline water has affected soil characteristics. Topographical controls on the passage of produced fluids as well as the chemistry of the exchange reactions may explain the lack of relation between many of these samples. Samples from areas considered to represent background conditions have ESP values that are generally readily distinguishable from affected areas even though bulk mineralogy may be similar.

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Real-time Kinematic (RTK) Surveying at the Osage-Skiatook Petroleum Environmental Research Sites, Osage County, Oklahoma

By Marvin M. Abbott

Abstract

RTK methods offer high accuracy in real time. The RTK surveys require a GPS-base station, a GPS-rover unit, and radio link between the units. Some preparation is required before the RTK survey so a differential correction can be applied during the data collection. This preparation may include establishing a base station location by a static GPS survey.

RTK surveys can be interrupted by tree canopy, minimum number of satellites, solar storms, distance from the base station, other radios in the area on the same frequency, and battery failure. Nearly all the factors affecting GPS positioning are eliminated by differential GPS methods. RTK surveys are not limited by line of sight from base station, darkness, lakes, or the minimum number of people needed. A single person can conduct RTK surveys, and multiple rover units can utilize one base station.

Wells at the sites were surveyed with the RTK GPS equipment in June and July, 2002. The Northing difference ranged from –4 to +6 cm and the Easting difference ranged from –9 to +5 cm. The elevation difference ranged from –9 to +6 cm.

Introduction

Osage County is located in northeastern Oklahoma (fig. 1). There are two sites included in the Osage-Skiatook Petroleum Environmental Research program. Both sites are immediately adjacent to Skiatook Lake (figs 1, 2).An initial drilling investigation of both sites was conducted in February and March, 2002. These locations included auger and rotary-drilled wells, geoprobe holes, hand-driven holes, other surface and soil sampling sites, and lake and stream sites (Otton and Zielinski, this volume).Real-time kinematic (RTK) global positioning system (GPS) surveys were used, because it is stable, fast, and accurate. Survey-grade GPS technology was used at the sites to document the locations of field investigations by 15 research scientists and associates, many reporting in this volume.

This report presents a general discussion of the global positioning system (GPS) and discusses the equipment, methods, and limitations of the RTK-GPS. The report presents data from two RTK surveys in June and July, 2002. The data were used to evaluate the accuracy of the RTK-GPS technology.

Thirty-eight permanent wells completed in February and March, 2002 were surveyed. The survey location for a well was marked so it could be measured on different dates. The surveys are in two different areas and utilize two different base station survey markers.

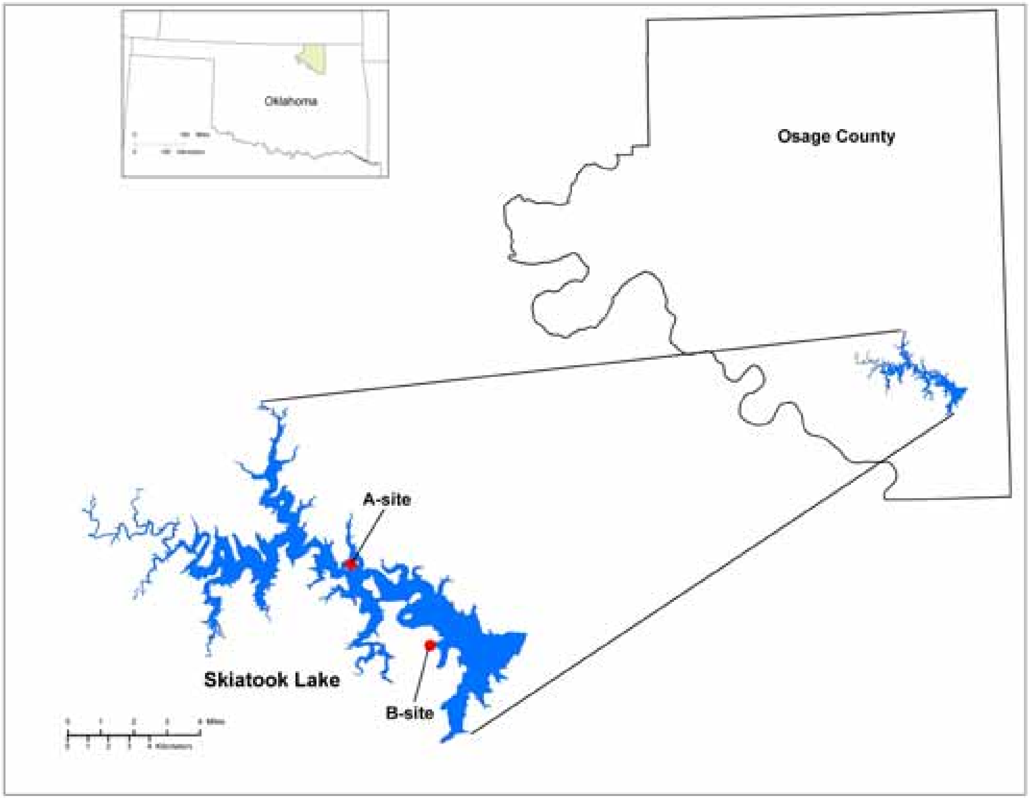


Figure 1. Map showing the location of Osage County, Skiatook Lake, and the location of the two OSPER sites on Skiatook Lake.

Figure 2. Aerial photograph of a part of the "B" site (photo courtesy of Ken Jewell, USEPA).

Global Positioning System

GPS is a worldwide radio-navigation system of 24 satellites and associated ground stations established by the U.S. Department of Defense (Trimble, 2003). The satellite locations are monitored by the Department of Defense. Each satellite transmits location data along with a pseudo random code (PRC) for identification to the GPS receiver. Positioning is determined by measuring travel time of radio signals from at least 4 satellites. The difference of the PRC from the satellite and the PRC at the receiver is the travel time of the signal. Travel time is converted to distance by multiplying by the speed of light.

Factors that affect GPS positioning are discussed in Trimble (2003); they include:

1. Atmospheric disturbances in the ionosphere and troposphere;
2. satellite signal reflected into a longer travel time before reaching the receiver by tall objects;
3. satellite signal is blocked from the receiver;
4. dilution of precision by satellite geometry or position;
5. satellite location or orbit errors referred to as ephemeris errors;
6. satellite clock error; and
7. geoid height model precision of the area.

Differential GPS methods involve two or more receivers, which are used either in static or kinematic surveys. One receiver is stationary and positioned on a known accurately surveyed point. The stationary receiver is referred to as a base station receiver. The base station receiver computes corrections between the surveyed point location and the satellite reported location with errors related to the factors listed above. Nearly all the factors affecting GPS positioning are eliminated by differential GPS methods.

Static surveys use observations from receivers that are stationary during measurements (Sickle, 2001). Kinematic surveys have a base station receiver and a moving receiver, referred to as a rover unit, during measurements. Static surveys require differential correction to be made after the survey is completed. Kinematic surveys can differentially correct the data after the survey is completed or during the survey. During RTK surveying the base station provides the correction information to the rover unit by a radio link. The rover unit then performs the differential correction of the data during the survey.

Equipment Requirements and Methods

The RTK surveys require a GPS base station and a radio link between the base station and the rover unit (fig. 3) and a GPS rover unit (fig. 4).

New survey-monument pins were established at both the “A” and “B” sites (fig. 5). These were used as the base station location during the RTK surveys.

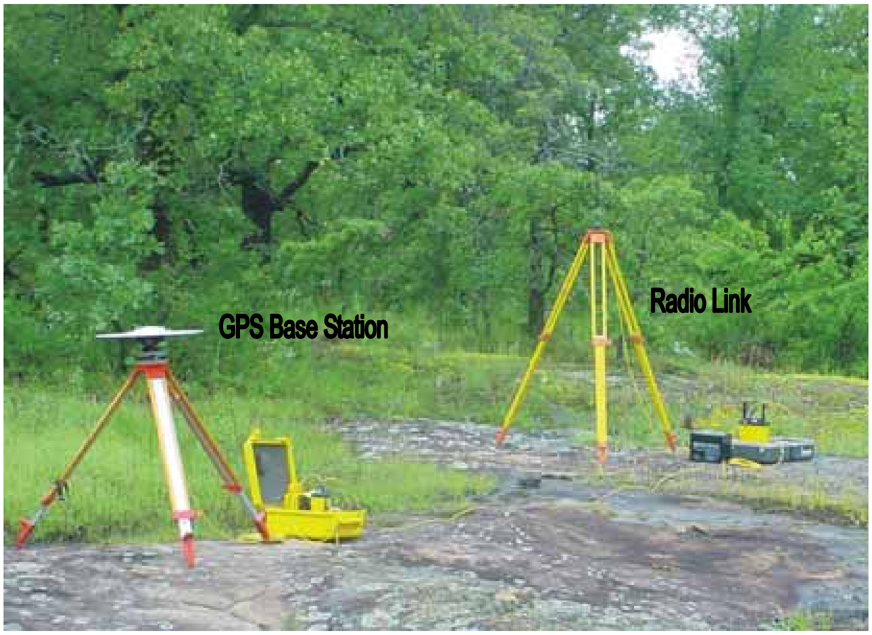


Figure 3. Base station equipment for RTK survey.

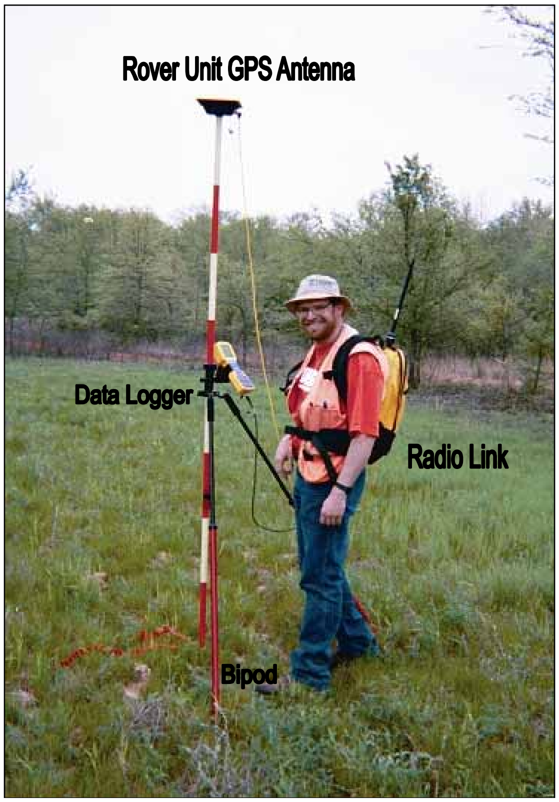


Figure 4. Rover unit GPS for a RTK survey.

Figure 5. Monument pin used for the base station location during a RTK survey.

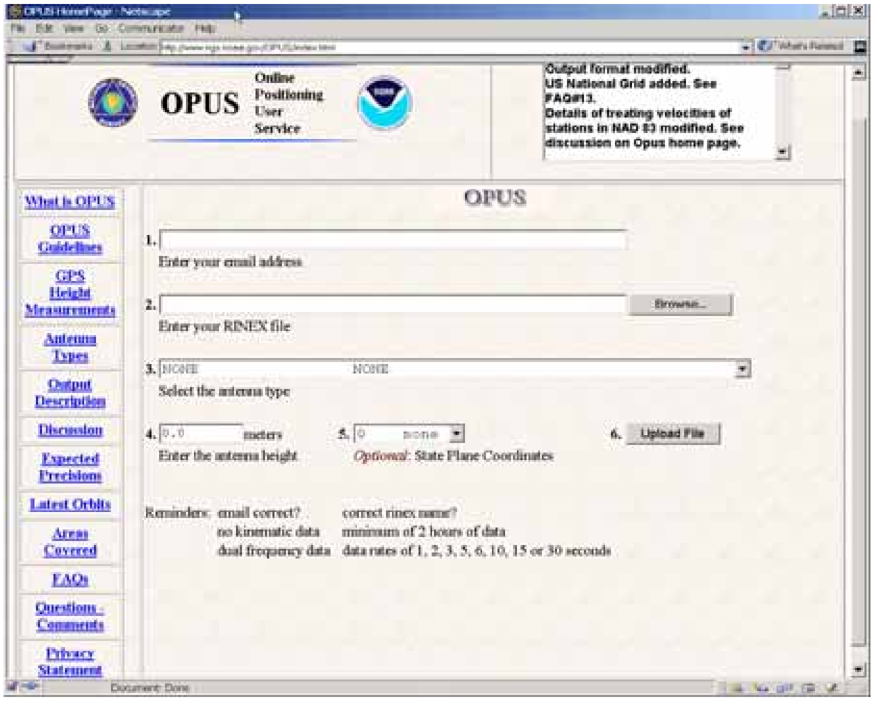
Prior to the RTK surveys, the locations of the monuments were established by differential static GPS surveys. These surveys occupied each of the two monuments for four hours. Post-processing the data was by the Online Positioning User Service (OPUS) maintained by the NOAA-National Geodetic Survey (NGS). The data files were uploaded to the OPUS internet page at http://www.ngs.noaa.gov/OPUS/index.html using the form in figure 6.OPUS processed the data relative to three sites on the NGS Continuously Operating Reference Station network (CORS). CORS provides GPS carrier phase and code range measurements in support of three-dimensional positioning activities throughout the United States.

OPUS establishes both horizontal and vertical positioning accuracies of a few centimeters relative to the National Spatial Reference System. A report is electronically returned to the sender. The first item required on the form is an electronic address (fig. 6). The time between uploading the static survey data and receiving the electronic report from OPUS was 2-3 minutes.

A differential static survey of a NGS monument near Hominy, Oklahoma, west of Skiatook Lake (fig. 1), produced the following results.The differentially corrected static survey differed from the NGS Data Sheet for the monument by a millimeter for both the northing and easting coordinates or about 1/16 of an inch. The vertical data for the NGS monument was not determined by differential survey leveling and therefore was not a measured value.

During a RTK survey the rover unit must maintain lock on at least four of the same satellites that the base station is tracking. Setup time at each rover unit survey location is less than a minute, if the rover unit maintains lock on the satellites and the radio link to the base station. Each rover unit location was occupied for 3 minutes.

It is important the range pole and antenna be vertical and stationary during the 3 minutes of data collection. The legs of the bipod are secured in the ground and the pole is positioned before data collection begins.



Output format modified.
US National Grid added. See FAQ#13.
Details of treating velocities of stations in NAD 83 modified. See discussion on Opus home page.

OPUS

1. Enter your email address

2. Enter your RINEX file

3. NONE NONE
Select the antenna type

4. 0.0 meters
Enter the antenna height

5. 0 none
Optional: State Plane Coordinates

6. Upload File

Reminders: email correct? correct rinex name?
no kinematic data minimum of 2 hours of data
dual frequency data data rates of 1, 2, 3, 5, 6, 10, 15 or 30 seconds

Figure 6. Online Positioning User Service uploading form.

Distance from the base station to the rover unit is limited to 10 kilometers (6 miles). Accuracy of the rover unit location in the horizontal component is 1 centimeter (cm) plus 2 parts per million (ppm) times the distance from the base station and in the vertical component is 2 cm plus 2 ppm times the distance from the base station. Maximum distance from the base stations at the A- and B-sites was 430 meters. The accuracy for the surveys would be 1 cm in the horizontal and 2 cm in the vertical. The red and white antenna pole in the picture (fig. 4) is 2 meters in height and 3 cm in diameter.

Tree cover, solar storms, and moisture affect the rover unit (Trimble, 2003). Surveying under tree cover is difficult because the leaves blocks the satellite signal from the rover receiver and lock on the same satellites as the base station is lost. Solar storms affect the radio link between the rover unit and base station. Precipitation creates multiple paths to the receiver because of particles in the air. Although the equipment is water resistant, it is not recommended to submerge the equipment in water. A single person can conduct RTK surveys and multiple rover units can utilize one base station.

Accuracy of the RTK GPS Technology

All wells were marked with a measure point on the pipes. The wells were surveyed at the measure points in June and again in July, 2002 to test the precision of the RTK survey data. Table 1 presents the data and summary statistics comparing the two surveys, of the 38 wells and geoprobe holes at the two sites. The three columns on the right in table 1 were the calculated difference between the June and July, 2002 surveys. The Northing difference ranged from –4 to +6 cm and the Easting difference ranged from –9 to +4 cm. These differences are plotted in figure 7. The elevation difference ranged from –9 to +6 cm. The expected values of the elevation difference were twice the Northing and Easting mean value (Sickle, 2001).

Table 1. Real-time kinematic survey data for wells at the A-site and B-site of the Osage-Skiatook Petroleum Environmental Research program, June and July, 2002.

	June, 2002			July, 2002			DIFFERENCE		
WELL ID	NORTHING (m)	EASTING (m)	ELEVATION (m)	NORTHING (m)	EASTING (m)	ELEVATION (m)	NORTHING (m)	EASTING (m)	ELEVATION (m)
AR01	4030607.05	752464.69	209.92	4030607.00	752464.75	209.96	0.05	-0.06	-0.06
AA01	4030423.77	752716.02	193.39	4030423.80	752716.03	193.39	-0.03	-0.01	0.00
AA02	4030396.94	752719.98	195.06	4030396.95	752719.96	195.06	-0.01	0.02	0.00
AA03	4030394.66	752739.50	195.32	4030394.67	752739.47	195.31	-0.01	0.03	0.01
AA04	4030386.12	752693.42	195.11	4030386.10	752693.42	195.12	0.02	0.00	-0.01
AE02	4030445.16	752660.91	194.06	4030445.18	752660.95	194.11	-0.02	-0.03	-0.05
AE03	4030385.59	752638.20	192.60	4030385.58	752638.20	192.60	0.01	0.00	0.00
AE04	4030385.85	752697.55	195.16	4030385.83	752697.61	195.15	0.02	-0.05	0.01
AE05	4030365.89	752706.92	195.18	4030365.89	752706.93	195.17	0.00	-0.01	0.01
AE06	4030333.87	752727.31	196.78	4030333.88	752727.33	196.74	-0.01	-0.02	0.04
AE07	4030304.58	752746.41	198.00	4030304.59	752746.37	197.99	-0.01	0.04	0.01
AE08	4030384.01	752742.21	195.79	4030384.04	752742.22	195.79	-0.03	-0.01	0.00
AE09	4030389.43	752715.20	195.04	4030389.46	752715.23	195.03	-0.03	-0.03	0.01
AE10	4030388.78	752726.88	194.85	4030388.77	752726.89	194.83	0.01	-0.01	0.02
AE13	4030488.62	752744.93	189.36	4030488.61	752744.92	189.35	0.01	0.01	0.01
AE14	4030466.66	752722.66	189.96	4030466.66	752722.65	189.97	0.00	0.01	-0.01
AE15	4030459.94	752727.09	189.87	4030459.91	752727.09	189.88	0.03	0.00	-0.01
AE16	4030437.12	752733.51	191.61	4030437.11	752733.49	191.62	0.01	0.02	-0.01
AE17	4030435.93	752724.42	191.71	4030435.92	752724.43	191.70	0.01	-0.01	0.01
AE18	4030441.64	752740.44	192.01	4030441.66	752740.47	192.01	-0.02	-0.03	0.00
AE19	4030396.01	752740.09	195.28	4030396.01	752740.10	195.26	0.00	-0.01	0.02
BR01	4026214.70	756269.58	241.11	4026214.64	756269.54	241.12	0.06	0.04	-0.01
BA01	4026349.57	756584.28	190.46	4026349.57	756584.24	190.46	0.00	0.04	0.00
BA02	4026258.26	756572.21	194.79	4026258.30	756572.20	194.74	-0.04	0.01	0.05
BA03	4026316.87	756539.08	194.87	4026316.91	756539.10	194.87	-0.04	-0.02	0.00
BE01	4026366.07	756567.57	191.32	4026366.09	756567.66	191.41	-0.02	-0.09	-0.09
BE03	4026345.30	756581.89	190.51	4026345.27	756581.91	190.48	0.03	-0.02	0.03
BE04	4026312.29	756609.96	189.62	4026312.28	756609.96	189.61	0.01	0.00	0.01
BE05	4026312.15	756609.76	189.63	4026312.17	756609.75	189.60	-0.02	0.01	0.03
BE06	4026289.01	756630.66	189.67	4026289.03	756630.63	189.65	-0.02	0.03	0.02
BE08	4026266.78	756630.83	189.28	4026266.79	756630.84	189.29	-0.01	-0.01	-0.01
BE09	4026265.91	756616.42	190.20	4026265.94	756616.38	190.21	-0.03	0.04	-0.01
BE10	4026271.90	756613.66	190.21	4026271.91	756613.65	190.23	-0.01	0.01	-0.02
BE11	4026262.41	756605.74	191.31	4026262.45	756605.73	191.28	-0.04	0.01	0.03
BE12	4026259.14	756606.73	191.37	4026259.17	756606.73	191.39	-0.03	0.00	-0.02
BE15	4026277.50	756627.90	189.72	4026277.52	756627.92	189.72	-0.02	-0.02	0.00
BE18	4026321.39	756627.71	189.06	4026321.40	756627.68	189.00	-0.02	0.03	0.06
BE19	4026321.22	756627.49	189.06	4026321.21	756627.49	189.05	0.01	0.00	0.01
						Summary Statistics of Difference (meter			
						Minimum	-0.04	-0.09	-0.09
						1st Quartile	-0.02	-0.02	-0.01
						Median	-0.01	0.00	0.00
						3rd Quartile	0.01	0.01	0.01
						Maximum	0.06	0.04	0.06

Thirty of the 38 locations in figure 7 are within the larger shaded area for the 5 to 95 percentile. The interquartile area on the plot is 3 cm, which is about the diameter of the red and white antenna pole for the rover unit (fig. 4).

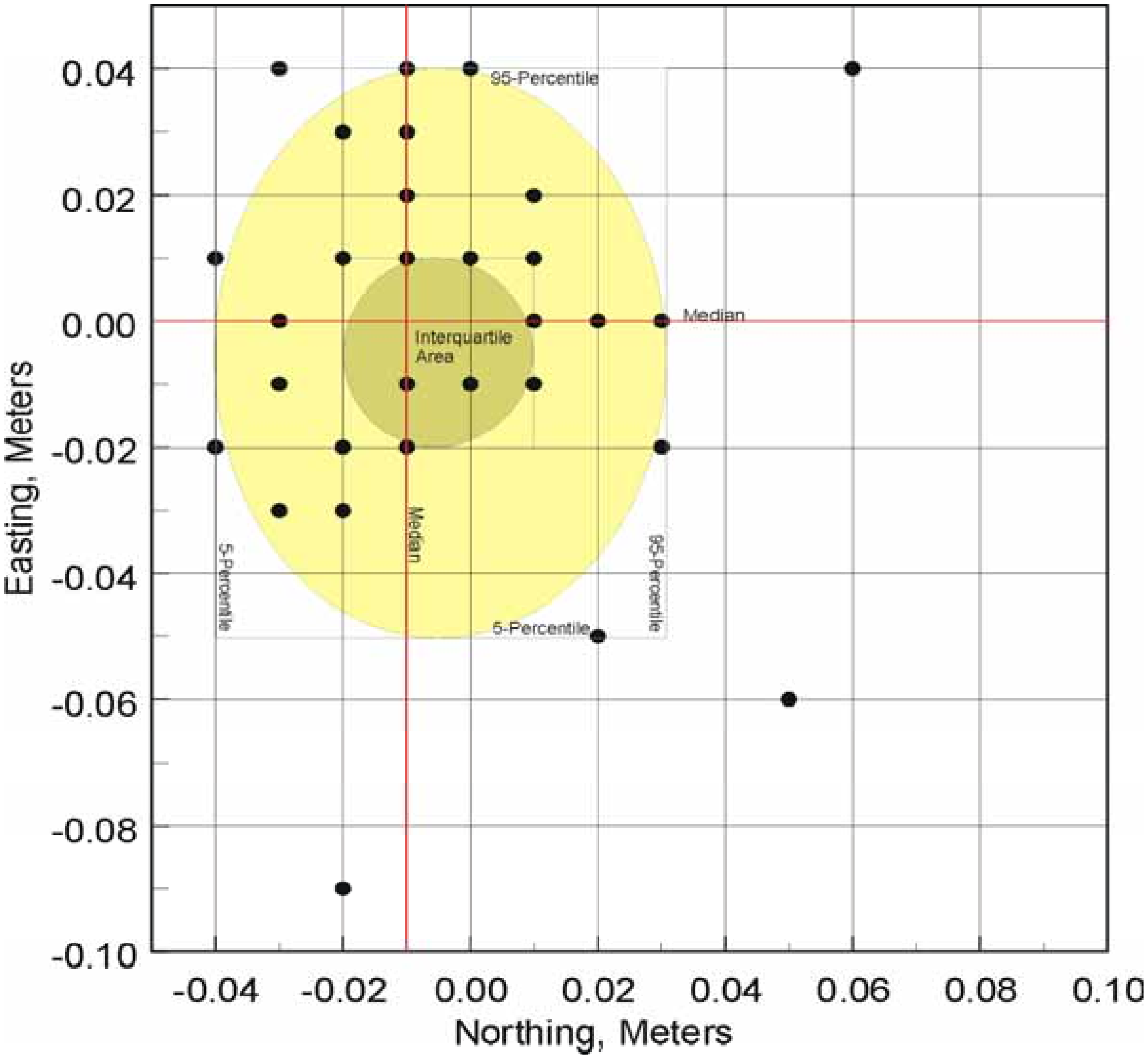


Figure 7. Plot of the difference between the Northing and Easting values for the June and July, 2002 surveys.

Summary

RTK methods offer high accuracy in real time. The RTK surveys require a GPS base station, a GPS rover unit, and radio link between the units. Some preparation is required before the RTK survey so a differential correction can be applied during the data collection. This preparation may include establishing a base station location by a static GPS survey. RTK surveys can be interrupted by tree canopy, minimum number of satellites, solar storms, distance from the base station, other radios in the area on the same frequency, and battery failure. A single person can conduct RTK surveys. Multiple rover units can utilize one base station. Nearly all the factors affecting GPS positioning are eliminated by differential GPS methods. RTK surveys are not limited by line of sight from base station, darkness, lakes, or the minimum number of people needed. Wells at the sites were surveyed with the RTK GPS equipment in June and July, 2002. The Northing difference ranges from –4 to +6 cm and the Easting difference ranges from –9 to +5 cm. The elevation difference ranged from –9 to +6 cm.

References

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