

# *Impacts of petroleum production on ground and surface waters: Results from the Osage–Skiatook Petroleum Environmental Research A site, Osage County, Oklahoma*

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## **ABSTRACT**

As part of a multidisciplinary group of about 20 scientists, we are investigating the transport, fate, natural attenuation, and ecosystem impacts of inorganic salts and organic compounds present in releases of produced water and associated hydrocarbons at the Osage–Skiatook Petroleum Environmental Research (OSPER) sites, located in Osage County, Oklahoma. Geochemical data collected from nearby oil wells show that the produced water source is a Na–Ca–Cl brine (~150,000 mg/L total dissolved solids [TDS]), with relatively high concentrations of Mg, Sr, and NH<sub>4</sub>, but low SO<sub>4</sub> and H<sub>2</sub>S. Results from the depleted OSPER A site show that the salts continue to be removed from the soil and surficial rocks, but degraded oil persists on the contaminated surface. Eventually, the bulk of inorganic salts and dissolved organics in the brine will reach the adjacent Skiatook Lake, a 4250-ha (10,501-ac) potable water reservoir.

Repeated sampling of 44 wells show a plume of high-salinity water (2000–30,000 mg/L TDS) at intermediate depths that intersects Skiatook Lake and extends beyond the visibly impacted areas. No liquid petroleum was observed in this plume, but organic acid anions, benzene, toluene, ethylbenzene, and xylene (BTEX), and other volatile organic carbon (VOC) are present. The chemical composition of released brine is modified by sorption, mineral precipitation and dissolution, evapotranspiration, volatilization, and bacterially mediated oxidation-reduction reactions, in addition to mixing with percolating precipitation water, lake water, and pristine groundwater. Results show that only minor amounts of salt

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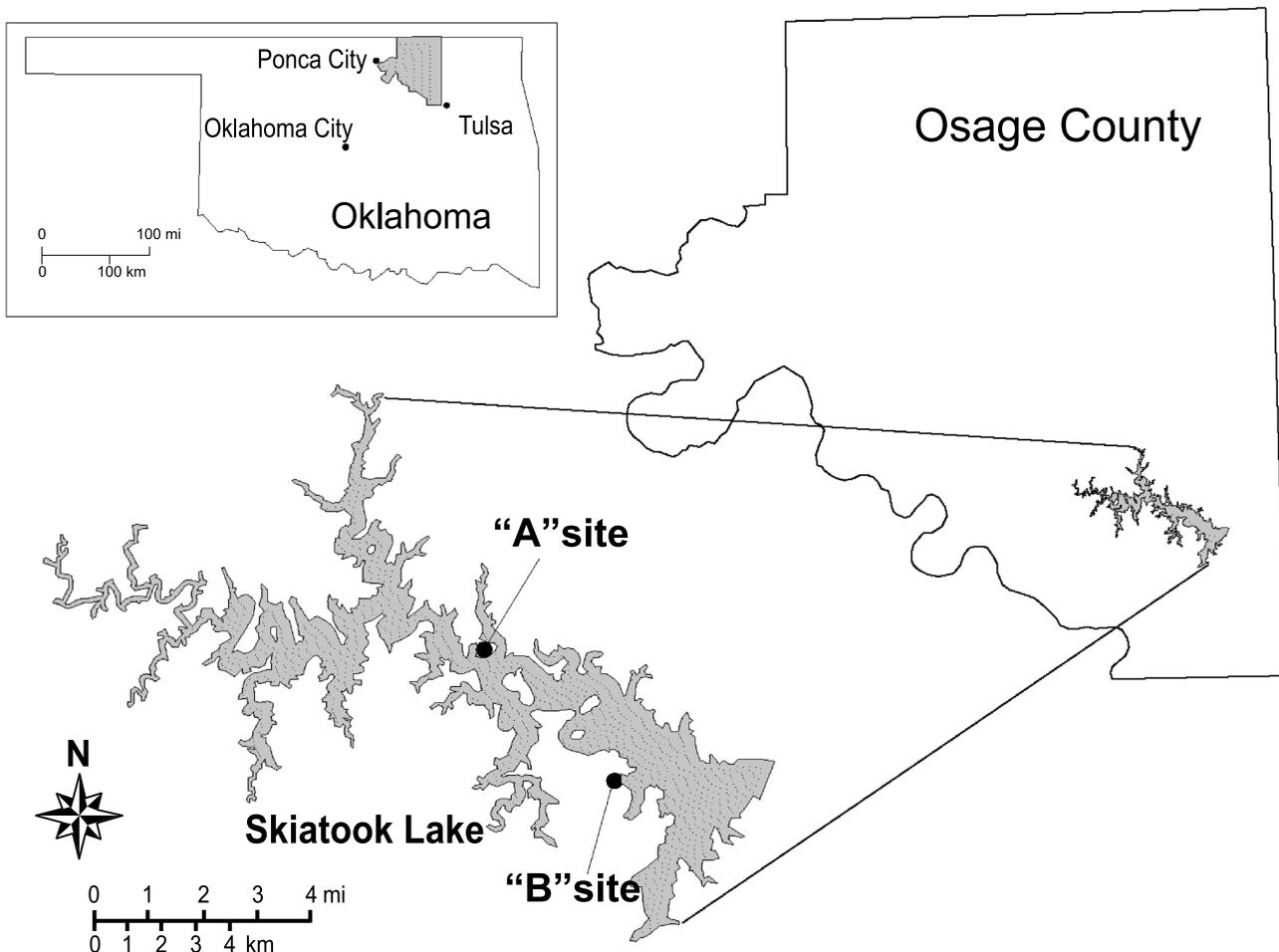
are removed by runoff, supporting the conclusion that significant amounts of salts from produced water and petroleum releases still remain in the soils and rocks of the impacted area after more than 65 yr of natural attenuation.

## INTRODUCTION

Oil and natural gas currently are the main sources of primary energy in the United States, supplying about 63% of the energy consumption, and forecasts indicate that by 2025, their consumption will increase by 48 and 50%, respectively (Energy Information Administration, 2003). Petroleum production started in the United States in 1859, when Drake's well was drilled near Titusville in Venango County, Pennsylvania (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 (Breit et al., 2001). Petroleum production, drilling operations, and improperly plugged abandoned wells have caused major contamination of surface and groundwaters and soils in energy-producing states (Richter et al., 1993; Kharaka et al., 1995; Kharaka and Hanor, 2003). Present-day contamination results mainly from the improper disposal of some of the large volume of saline water produced with oil and gas (total water production presently estimated at 20–30 billion bbl/yr) and from hydrocarbon and produced-water releases caused by equipment failures, vandalism, flooding, and accidents (U.S. Environmental Protection Agency [USEPA], 1987; Kharaka et al., 1995; Veil et al., 2004).

Prior to the institution of federal regulations in the 1970s, produced waters, which are highly saline (3000 to more than 350,000 mg/L dissolved solids) and may contain toxic metals, organic and inorganic components, and radium-226/228 and other naturally occurring radioactive materials, were commonly discharged into streams, creeks, and unlined evaporation ponds, causing salt scars and surface and groundwater pollution (Collins, 1975; Kharaka et al., 1995, 2003; Otton et al., 1997; Zielinski et al., 1998). Federal and state regulations governing the onshore and offshore disposal of produced water, as well as the cost of its management, are summarized in a recent paper (Veil et al., 2004). These historical (legacy) releases and the improper disposal of some produced water have become important national issues that concern petroleum producers, landowners, and state and federal regulators (USEPA, 1987; Carty et al., 1997; Billingsley, 1999; Wilson and Frederick, 1999).

Starting in 2001, about 20 scientists from the U.S. Geological Survey and other governmental agencies and academia have been conducting a multidisciplinary investigation to study the transport, fate, natural attenuation, and impacts of inorganic salts, trace metals, organic compounds, and radionuclides present in produced-water releases at the Osage–Skiatook Petroleum Environmental Research (OSPER) A (depleted oil field) and B (active oil field)



**Figure 1.** Map showing the locations of OSPER A and B sites on the Skiatook Lake in Osage County, Oklahoma.

sites. The sites are located about 30 km (18 mi) northwest of Tulsa in the southeastern part of Osage County (Figure 1), which has many depleted and aging petroleum fields, and ranks among the top oil- and gas-producing counties in Oklahoma, with about 39,000 drilled wells. Petroleum production has occurred in Osage County for more than 100 yr, but current production is mainly from stripper wells (averaging ~2.8 bbl/day oil and >30 bbl/day brine) that are shallow, mostly 300–700 m (1000–2300 ft) in depth, and produce from several sandstones of Pennsylvanian age (Kharaka et al., 2003). Approximately 1.2 and 1.0 ha (2.9 and 2.47 ac) of land at the OSPER A (depleted Lester lease) and B (active Branstetter lease) sites, respectively, are visibly affected by salt scarring, tree kills, soil salinization, and brine and petroleum contamination of surface and groundwaters because of the leakage of produced water and associated hydrocarbons from brine pits and accidental releases from active and inactive pipes and tank batteries.

Initial results of investigations at the OSPER sites, through 2002, are discussed in Kharaka and Otton (2003). Thirteen additional wells that are generally deeper, have two or three perforated zones, and are located outside the central and visibly impacted area were completed at the A site. In this report, we discuss the main results obtained to date from these and the earlier wells from the A site, emphasizing the impacts of petroleum operations on the ground and surface waters. Groundwater impacts are investigated by repeated sampling of all the 44 wells (1–36 m [3.3–118 ft] deep) completed with slotted polyvinyl chloride (PVC) tubing. The rate of salt removal from the site by surface runoff is being determined by measuring the volume and chemical composition of water flowing over a weir installed close to the adjacent Skiatook Lake, a 4250-ha (10,501-ac) reservoir completed in 1987 that provides drinking water to the local communities and is a major recreational fishery. The weir captures most of the surface and base flow from a

1.7-ha (4.2-ac) area at this site following precipitation, which is monitored using a local automated precipitation gauge.

Detailed multidisciplinary studies are continuing at these two sites to evaluate the long- and short-term impacts 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 risks at these and similar sites and the development of risk-based corrective actions by private and governmental groups (American Society for Testing and Materials, 1999; Billingsley, 1999). Corrective actions are particularly needed in aging and depleted petroleum fields, where land use is changing from petroleum production to residential, recreational, agricultural, or other uses (Carty et al., 1997; Kharaka et al., 2003).

## OSPER A SITE

The A site, located within the larger Lester lease in section 13, T22N, R10E, has an area of approximately 1.2 ha (2.9 ac) that is visibly impacted by produced water and hydrocarbon releases that occurred primarily 60–90 yr ago (Figure 2). The gently sloping upper (southern) part of the site is slightly eroded in places and has been mostly revegetated with grasses, forbs, sumac, and a few young oak trees. The lower, steeper, more heavily salt-impacted portion has been eroded to depths of as much as 2 m (6.6 ft). Seepage of saline water from a shallow sandstone aquifer continues, and active salt scarring persists in this area of the site (Figure 2). This site, geologically located in the Central Oklahoma platform, is underlain (Figure 3) by (1) a surface layer of eolian sand (0–120 cm; 0–47 in.); (2) colluvium that ranges from large boulders of sandstone to thin, granule-pebble conglomerate; (3) weathered shale, siltstone, and sandstone; and (4) underlying unweathered shale, siltstone, and sandstone of variable thickness (Otton and Zielinski, 2003).

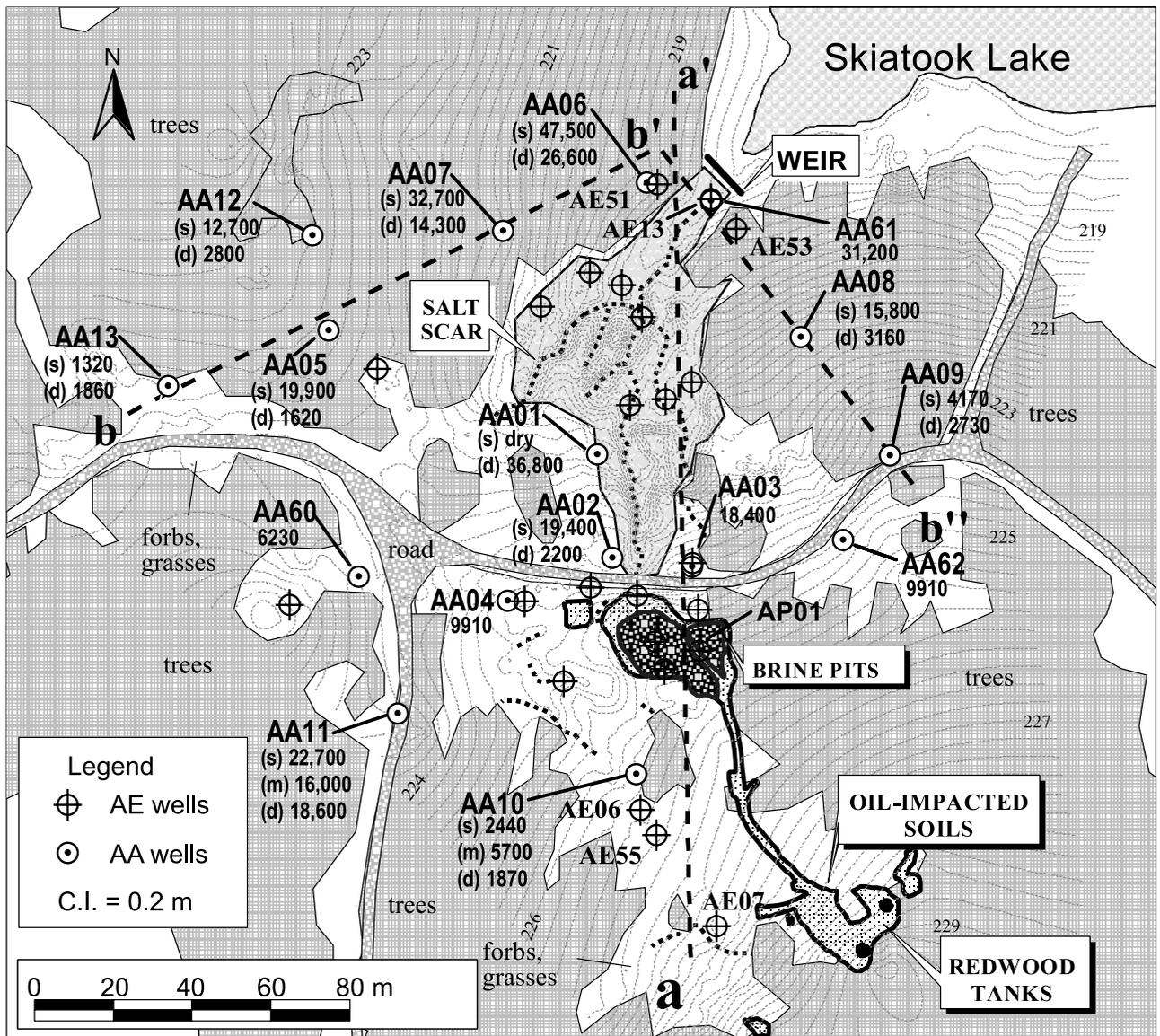
Drilling on the Lester lease started in 1912 and oil production, which was from the Bartlesville sandstone (Pennsylvanian age) at depths of 450–524 m (1476–1719 ft), ended about 10 yr ago. Most of the more than 100,000 bbl of oil produced by 1981 was obtained prior to 1937. Oil and produced water collected in two redwood tanks at the top of the site was transported via ditch to two roadside pits at mid-site (Figure 2). 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 (Godsy et al., 2003; Kharaka et al., 2003).

## Field and Laboratory Methodology

Intensive investigations aimed at mapping and characterizing the geology, hydrology, contaminant sources, and impacted areas at the OSPER A site and the immediate surrounding areas have continued since February 2001 (Kharaka and Otton, 2003). Initially, seven nearby active oil wells and three potable groundwater wells used by the local farmers were sampled to characterize the compositions of the source crude oil and produced water as well as the local groundwater. Groundwater impacts at this site are being investigated by repeated sampling of 44 wells (1–36 m [3.3–118 ft] deep), drilled in stages, and completed with slotted PVC tubing. The well locations were selected on the basis of (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<sub>4</sub> measurements on aqueous leachates from samples of shallow soil (0–15 cm; 0–6 in.), selected soil profiles (0.5–1.7 m; 1.6–5.5 ft), and core samples from prior drilled monitor wells; (3) results of electromagnetic and direct current (DC) resistivity surveys used to map the subsurface distribution of salt in groundwater, soil, and bedrock (Smith et al., 2003); and (4) results of chemical analysis of water samples obtained from prior drilled wells.

The shallow wells (0.5–4 m; 1.6–13 ft) were drilled without using water, employing an Environmental Protection Agency Geoprobe (direct-push) rig that was unable to penetrate the unweathered sandstones. The deepest (36-m; 118-ft) well, AR01, and well AA02 were drilled using a rotary rig that required water (possible contaminant) for cooling; the other deeper wells were drilled with an auger rig without water. The Geoprobe wells were completed using a 2.5-cm (1-in.) PVC tubing that generally had a 0.61-m (2-ft) screened interval with a bottom cap starting at total depth. The deeper rotary and auger wells had two or three completions using a 5.1-cm (2-in.) PVC tubing, with generally 1.5-m (4.9-ft) screened intervals selected based on indications of water-bearing zones while drilling the wells. Clean and graded sand was used around the screened intervals, and bentonite pellets and chips

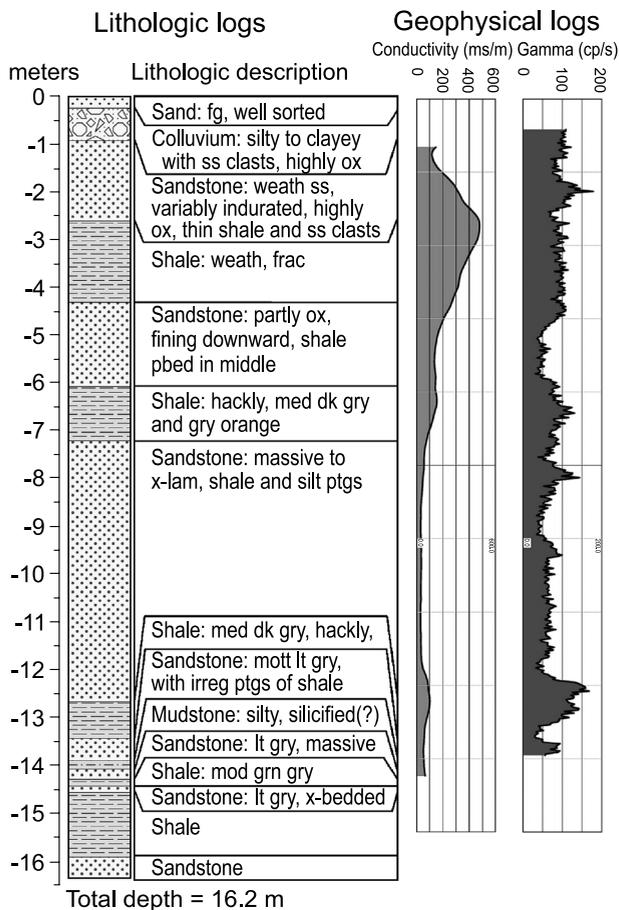


**Figure 2.** Surface map (contours in meters) of the OSPA A site showing the locations of the brine pits, other production features, drilled water wells with conductance measured in January 2004, outline of the treed and impacted areas, and transect lines. s = shallow; d = deep.

were used to isolate the screened intervals in wells with multiple completions.

The methods used in sample collection, preservation, and field and laboratory determinations of chemical components and isotopes are detailed in Kharaka and Hanor (2003) and Kharaka et al. (2003). Down-hole probes were used to obtain profiles of conductivity, dissolved oxygen, pH,  $E_h$ , and temperature. Most field chemistry was performed in a mobile laboratory equipped with pH meters, a spectrophotometer, and filtration, titration, and other field equipment. Field determinations included conductance, pH, alkalinity,

$H_2S$ , and  $NH_4$ . Raw water samples were commonly filtered through a 0.1- $\mu m$  filter using either a syringe pump or compressed nitrogen. Filtered samples were stored in high-density polyethylene bottles prerinse with deionized water for anions and prerinse with 5% nitric acid ( $HNO_3$ ) then deionized water for metals and silica. For water isotopes, two 20-mL glass bottles with polyseal caps were filled with raw water. Samples for solute isotopes, organic compounds, silica, and other chemical components were collected and diluted and/or preserved by procedures detailed in Kharaka et al. (2003).



**Figure 3.** Lithologic and geophysical logs of AA02 well at OSPER A site.

All of the water samples were analyzed at the U.S. Geological Survey Water Resources Laboratories in Menlo Park, California. Concentrations of Ca and other cations, B, and SiO<sub>2</sub> were determined by inductively coupled plasma–mass spectrometry (ICP-MS). Concentrations of Cl, Br, NO<sub>3</sub>, PO<sub>4</sub>, SO<sub>4</sub>, and organic acid anions were determined by ion chromatography. 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 be ±10% for values close to detection limits (Kharaka and Hanor, 2003).

## RESULTS AND DISCUSSION

The concentrations of selected inorganic and organic chemicals from an oil well and surface and groundwater samples from OSPER A site and adjoining areas in Osage County, Oklahoma, are listed in Table 1. Results

show that the produced water obtained from the Lebow 8 well (Table 1) and seven other oil wells reported in Kharaka et al. (2003) have a relatively similar chemical composition; the water is a hypersaline (115,000–185,000 mg/L TDS) Na-Ca-Cl brine that is dominated by Na and Cl and has relatively high concentrations of Ca, Mg, Sr, Ba, and NH<sub>4</sub> but very low values for SO<sub>4</sub>, HCO<sub>3</sub>, and H<sub>2</sub>S. With the exception of Fe and Mn, the concentrations of trace metals are low, and the values of organic acid anions and other dissolved organic species are relatively low.

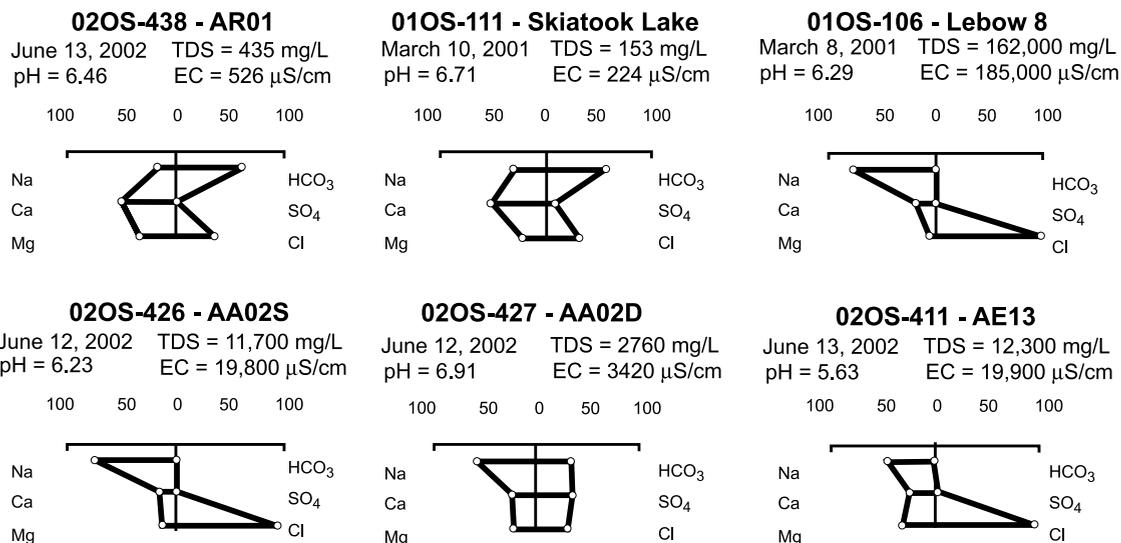
The chemical composition of Skiatook Lake water and groundwater in the area not impacted by petroleum operations (e.g., Bolin's groundwater well, Table 1) shows major contrast from that of produced water. The water is fresh (150–500 mg/L TDS) and has comparable values for the equivalent concentrations of Na, Mg, and Ca, as well as those of Cl, SO<sub>4</sub>, and HCO<sub>3</sub>; this water, then, has much higher Mg and Ca concentrations relative to Na and much higher HCO<sub>3</sub> and SO<sub>4</sub> relative to Cl, when compared to produced water (Lebow 8, Figure 4). Uncontaminated ground and surface waters are generally oxidic, with relatively high concentrations of dissolved oxygen but low values of metals, including Fe and Mn, as well as low dissolved organic carbon (DOC) and organic acid anions. In anoxic water environments, present in produced water and petroleum-contaminated water, Fe and Mn are mobilized from sediments, and organic acid anions and other organic species, and thus, DOC are generated by bacterial degradation of petroleum (Kharaka et al., 2000; Sirivedhin and Dallbauman, 2004). These and other chemical properties (Figure 4) and water isotopes are used to investigate the impact of produced water on the surface and groundwaters of the contaminated areas (Richter et al., 1993; Whittemore, 1995; Abbott, 2000).

The water sample obtained from the asphaltic pit (AP01, Table 1) has a salinity (110,000 mg/L TDS) and chemical composition that is comparable to that of the produced water from nearby oil wells (e.g., Lebow 8, Table 1). The salinity of water obtained from the boreholes in the adjacent pit, which has more weathered and degraded oil (Godsy et al., 2003), and from those boreholes located close to the two pits, all have fresh water (≤1000 mg/L TDS), indicating that the brine in the asphaltic pit is of limited volume and extent. In addition, all the shallow (<2 m; <6.6 ft) direct-push wells located to the south and west of the two oil pits have fresh water, with compositions that indicate no mixing with produced water (Kharaka

**Table 1.** Chemical (Inorganic and Organic) Composition of Selected Surface Water, Groundwater, and Produced-Water Samples from and near OSPER A Site, Osage County, Oklahoma

Sample Name	Skiatook Lake, near ACE									
	Bolin's GW	AR01	reservoir	AP01	Lebow 8	AA02S	AA02D	AA03D	AE13	
Type	drinking water well	monitor well	reservoir	pit monitor well	oil well	monitor well	monitor well	monitor well	monitor well	
Date	March 6, 2001	June 13, 2002	March 10, 2001	February 28, 2002	March 8, 2001	June 12, 2002	June 12, 2002	March 25, 2003	June 13, 2002	
EC ( $\mu\text{S}/\text{cm}$ )	490	526	224	133,000	184,800	19,800	3420	20,300	19,900	
pH	7.18	6.46	6.71	5.79	6.29	6.23	6.91	6.67	5.63	
T ( $^{\circ}\text{C}$ )	17.8	16.6	7.2	18.0	34.0	18.5	17.8	15.0	21.5	
Na	36	23	14.0	32,900	48,600	3400	525	3540	2250	
K	1.0	1.5	2.2	89.2	266	13.2	5.7	19.8	3.0	
Mg	19	23	5.0	1610	1830	273	103	259	815	
Ca	36	56	20	6050	9960	547	171	573	975	
Cl	24	77	25	68,100	99,500	7030	436	6,830	7770	
SO <sub>4</sub>	18	6	10	43	1.0	137	668	375	248	
HCO <sub>3</sub>	269	221	74	239	185	255	824	516	57	
Li	0.01	0.01	<0.01	3.22	11.5	0.08	0.05	0.10	0.03	
Sr	0.3	<0.1	<0.1	454	504	8.3	2.8	7	23.2	
Ba	0.2	1	<0.1	15	879	0.7	0.1	1	0.4	
Mn	0.3	2	<0.1	6	1	1.7	0.5	14	84.2	
Fe	0.1	<0.1	<0.1	595	67	0.1	2.8	7	4.7	
Br	0.1	0.6	0.1	233	346	23.2	1.4	21.5	25.7	
NO <sub>3</sub>	<0.1	<0.1	1.0	4.0	<0.1	1.0	0.2	1.0	1.0	
SiO <sub>2</sub>	14.4	22.9	2.8	32.1	16.0	13.9	24.5	24.0	15.3	
B	0.1	<0.1	<0.1	1.9	3.6	<0.1	0.3	0.1	0.0	
DOC	0.4	4.4	4.5	ND	3.0	2.4	113.0	18.9	5.1	
Formate	0.1	0.1	ND	3.1	0.4	0.1	0.1	0.1	<0.1	
Acetate	<0.1	0.1	ND	209	2.4	0.1	200	0.1	<0.1	
TDS	420	434	153	110,000	162,000	11,700	2,770	12,400	12,300	

ND = not determined; GW = groundwater; ACE = Army Corps of Engineers; EC = electrical conductance; DOC = dissolved organic carbon; TDS = total dissolved solids. Concentrations are in milligrams per liter; AA = auger well; AE = direct-push well; AP = hand-dug well; AR = rotary well.



**Figure 4.** Modified Stiff diagrams showing the salinity of water and the relative concentrations (in equivalent units) of major cations and anions in selected water and oil wells from and near the OSPA A site.

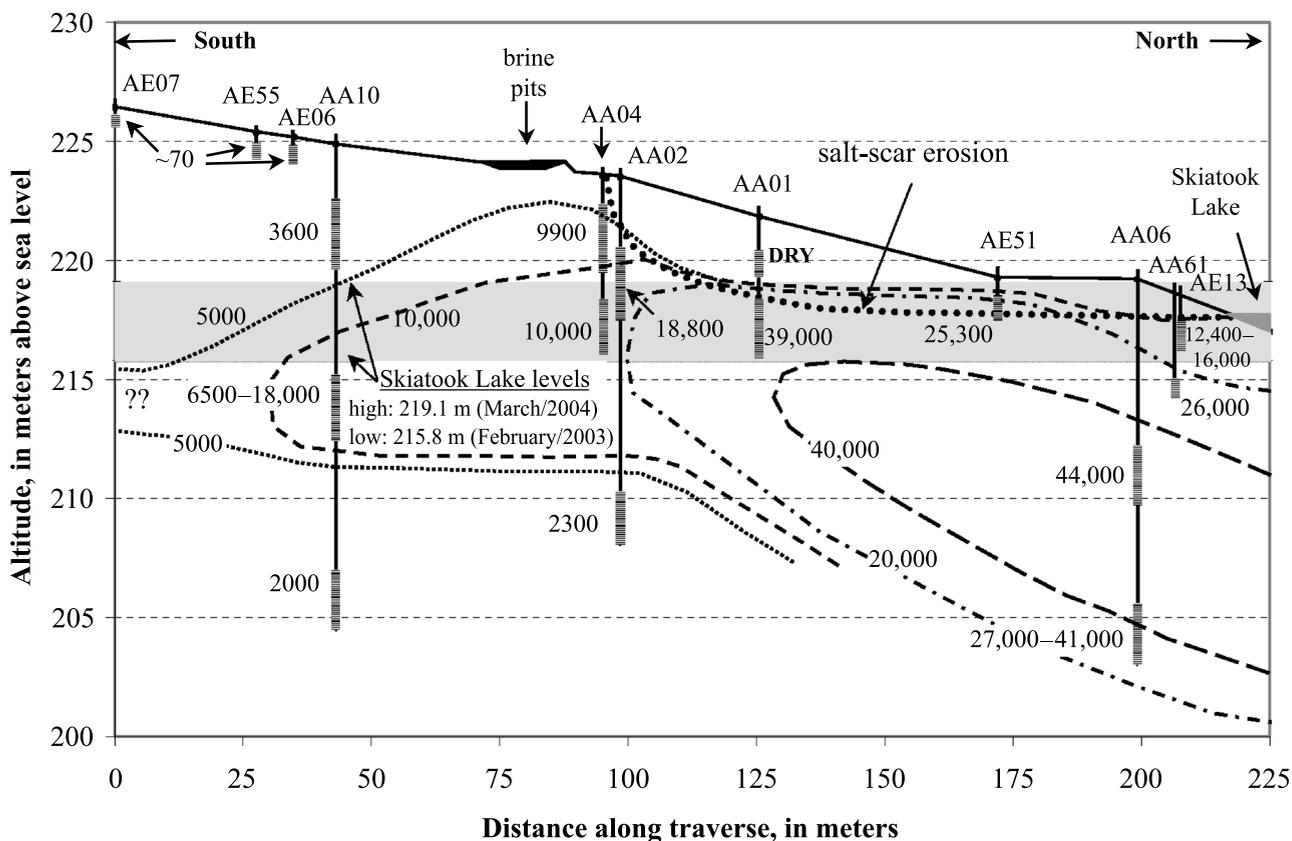
et al., 2003). It is possible that produced water was present in these shallow wells because they are located downgradient from the brine source in the redwood tanks; if so, then the brine was subsequently flushed and replaced with meteoric water from precipitation. Results from soil analysis (Zielinski et al., 2003) and geophysical surveys (Smith et al., 2003) are in general agreement with this interpretation.

Except for well AA13, the salinity and chemical composition of water obtained from the auger wells (A designation, Figures 2, 5, 6), as well as from those direct-push wells (E designation, Figures 2, 5, 6) located to the north and west of the two oil pits in the salt-scarred area at the A site, show major impact from produced-water operations (Figures 5, 6). A three-dimensional (3-D) plume of high-salinity water (2000–30,000 mg/L TDS) dominated by Na and Cl intersects Skiatook Lake near well AE13 that has water salinity of about 10,000 mg/L TDS. This plume is not limited to the salt-scarred area (~0.5 ha; ~1.2 ac) and the visibly impacted area of this site (~1.2 ha; ~2.9 ac) but extends beneath a total area of about 3 ha (7.4 ac); the trees, shrubs, and grass in the outlying areas show no visible impacts from oil operations (Figure 2).

The highest water salinity in the plume (electrical conductance [EC] of 44,000  $\mu\text{S}/\text{cm}$ , equivalent to ~30,000 mg/L TDS) is obtained from the intermediate depth of well AA06 (Figures 5, 6), also located close to Skiatook Lake. The plume extension underneath Skiatook Lake to the north of well AA06 (Figure 2) is presently unknown, because we have no

wells drilled there, but data from existing wells show water salinities decreasing in all directions from this well (Figures 5, 6). No liquid petroleum was found in the contaminated groundwater, but soluble petroleum by-products, including organic acid anions, BTEX, and other VOCs, are present.

The salinity decrease is more rapid to the east of well AA06 (Figure 6), which is consistent with our conceptual model of water moving at higher rates westward along the dip (1–2° west) of the sandstone aquifers. The shape of the plume indicates recharge from the brine pit located at mid-site (Figures 2, 5), which is also consistent with local topography and production practices at this site, where large volumes of saline water and oil, collected in redwood tanks at the south end of the site (near AE07, Figure 2), were allowed to flow in a ditch to two oil and brine pits located at mid-site. During peak oil production (1913–1937), most of the produced water likely flowed downgradient in a creek channel into the northern eroded part of the site and then flowed outside of the site because the Skiatook reservoir was not completed until 1987. Because of its higher density, a large portion of this produced water infiltrated through the bottom of pits and channels into the underlying sandstone beds. Dissolution, precipitation reactions, and especially mixing with precipitation water, groundwater, and/or recently with Skiatook Lake water, resulted in modifying brine composition (Figure 2), including lowering brine salinity from about 150,000 mg/L TDS to that of water residing in the sandstone beds (up to 30,000 mg/L).



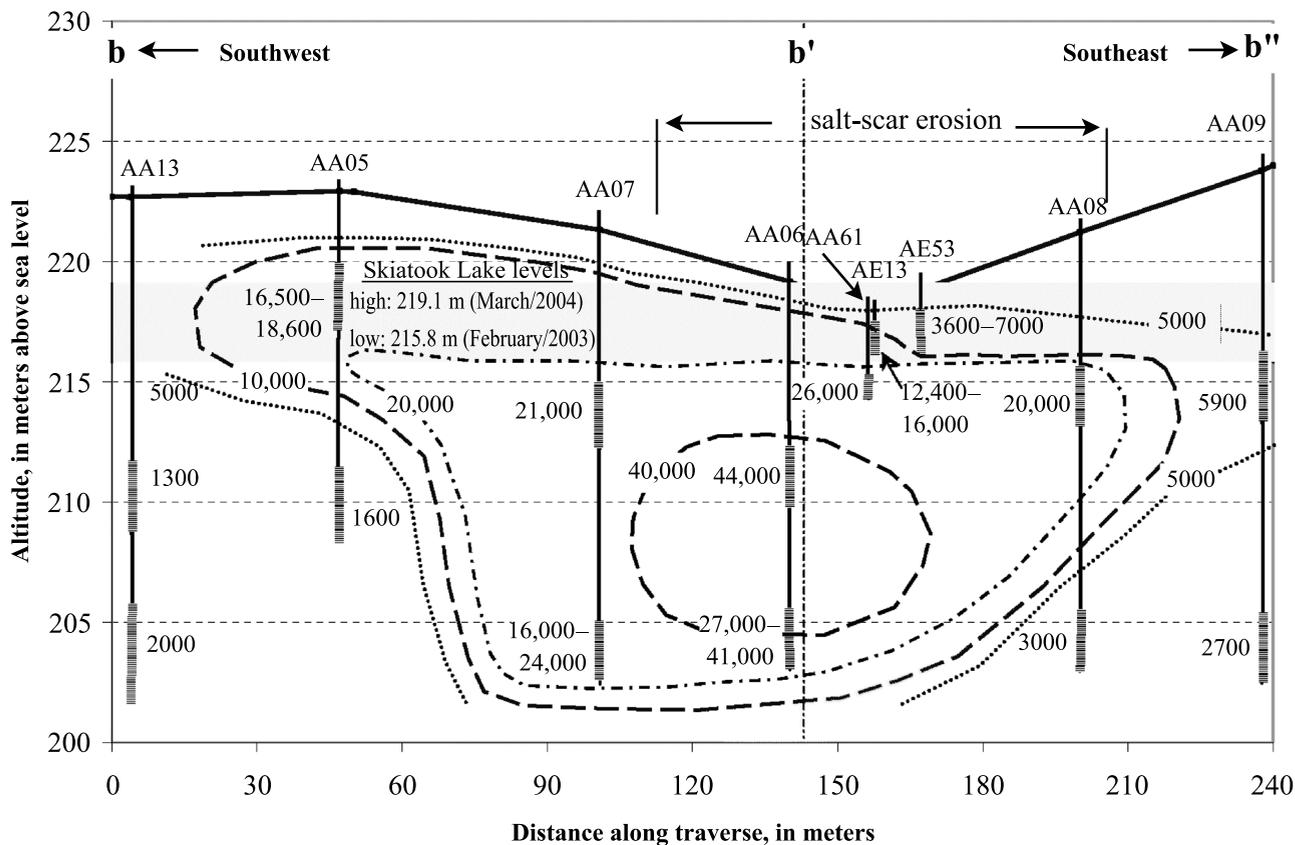
**Figure 5.** Water levels and salinity of water (from January 2004) in wells along a south-north transect aa' (Figure 2), from well AE07 north to AE13, located in the littoral zone of Skiatook Lake at the OSPER A site. A plume of high-salinity water is present at intermediate depths, especially in wells located below the brine pits. The highest and lowest water levels of Skiatook Lake are indicated by shading.

The boundaries of the plume were delineated during deep drilling completed in January 2004. The chemical compositions of water samples obtained from the two perforated zones of well number AA13 (Figures 2, 6), as well as a sample collected from a depth of 6.4 m (21 ft) while drilling the well, indicate that the groundwater is not impacted by produced water, thus indicating the western limit of the plume. The bottom of the plume, although problematical, is tentatively defined by the EC contour of about 2000  $\mu\text{S}/\text{cm}$ , equivalent to about 1200 mg/L TDS obtained from several wells (see EC contour of 5000  $\mu\text{S}/\text{cm}$ , equivalent to  $\sim 3000$  mg/L TDS, depicted in the cross sections, Figures 5, 6). The difficulty of defining the lower boundary of the plume can be appreciated by examining the chemical data for water from the deeper perforated section (13.8–15.2 m [45.2–49.8 ft] below ground level) of well AA02. The salinity and concentrations of major cations and anions of water for this section (AA02D, Table 1; Figure 4) indicate a groundwater not contaminated by NaCl-rich produced water

source. However, the concentrations of DOC, acetate, and other VOCs, as well as Fe and Mn (Table 1), indicate reducing conditions and contamination by degradation products from an oil source.

Defining the impacts of produced water and associated hydrocarbons on the shallowest beds, which may be unsaturated or with unconfined, confined, or perched water tables, is also difficult. In wells located to the north of the brine and oil pits, contamination by produced water is shown by the high salinity and high concentrations of Na and Cl relative to the other cations and anions (Figure 4). In shallow (<2-m; <6.6-ft) wells located to the south of the brine pit, the shallowest sandstone is generally dry but has a perched water layer following precipitation; water salinities are very low ( $\sim 70$  mg/L) and dominated by Na and Cl, with Na probably residual from produced water and  $\text{CO}_2$ , a by-product of oil degradation.

Contamination by oil and its degradation products is more obvious in a background well, drilled 0.6 km (0.4 mi) downdip, to the northwest of the OSPER A site.



**Figure 6.** Water levels and salinity of water (from January 2004) in wells along the transect bb'b'' (Figure 2) at the OSPA A site. A plume of high-salinity water centered on well AE06 is present at intermediate depths, especially in wells located below and to the west of the brine pits. The highest and lowest water levels of Skiatook Lake are indicated by shading.

Initially (March 2002), groundwater in this well was fresh (450 mg/L TDS), with low DOC values and other characteristics of the pristine local groundwater (AR01, Table 1). Repeated sampling did not change the inorganic composition of water from this well appreciably, but DOC concentrations continued to increase. A sample collected in June 2003 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 observed. The source of this petroleum contamination was initially not clear because no plugged oil well was mapped close to this site. However, additional search indicated some concrete and other trace remains of an old abandoned oil well located about 10 m (33 ft) south-east of the groundwater well.

Additional sampling from these and new deeper wells will be used to better delineate the plume boundaries at this site. However, results to date 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 65 yr of natural attenuation.

## FUTURE PLANS

We expect that detailed geological, geophysical, hydrological, geochemical, and ecological studies at these two sites will continue for 3–5 yr more, 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 may be necessary to better define the depth and the horizontal boundaries of the 3-D plume of high-salinity water at this site. The existing and future wells will be sampled to investigate the natural processes that modify the chemical composition of the groundwater plume, including mixing with pristine groundwater and percolating water from precipitation, sorption, mineral precipitation

and dissolution, evapotranspiration, 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 the exchange with the Skiatook water column.

The rate of salt removal from this 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 reservoir in a location that captures most of the surface and base flow from this site following precipitation. For example, a weir and an automated precipitation gauge were installed close to the Skiatook Lake to investigate the natural overland transport of salts from this site by measuring the volume and chemical composition of surface runoff from precipitation events draining a 1.7-ha (4.2-ac) area. Results to date show that the initial runoff that leaches the previously precipitated surficial salts can have a relatively high salinity (up to 3000 mg/L TDS), but that only small amounts of total salts (500–1000 kg/yr of salt) are removed by this process.

Slug tests run on selected wells indicate that the hydraulic conductivity of the permeable sandstone units is only about 1 cm/day (0.4 in./day), indicating that brine flow and transport in the confined sandstone beds is low under present conditions (Herkeleth and Kharaka, 2004). These slug-test results and other relevant data were used in a two-dimensional (2-D) flow and brine transport simulation using subsurface transport over multiple phases (STOMP) code (White and Oostrom, 2004). Preliminary results indicate that when oil production was active (1912–1937), a large volume of saline produced water infiltrated downward from the bottom of brine ponds and moved relatively rapidly northward, along the topographic gradient, to its present depth in the sandstone beds (Figures 5, 6). These simulations also show that once the main brine source was removed, about 1937, recharge and flow through the salt plume zone was greatly reduced; the brine flow was further reduced when the Skiatook Lake was completed in 1987, effectively trapping the saline water in the present location for a considerable time. These results support the conclusion that large amounts of salts from produced-water and petroleum releases still remain in the rocks of the impacted area after more than 65 yr of natural attenuation.

Additional future studies would include the fate and transport of hydrocarbon-degradation products, hydrocarbon-related trace elements, produced-water salts, and trace elements, especially the toxic components, including uptake and residence in soils, reservoir

sediments, oak trees, and other macrobiota. Our goal is to establish the sublethal 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). In addition, there is a proposal 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.

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