



# **Geochemical Data from Produced Water Contamination Investigations: Osage-Skiatook Petroleum Environmental Research (OSPER) Sites, Osage County, Oklahoma**

Open-File Report 2007-1055





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

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**A.** Location and construction characteristics of monitoring wells at the Osage-Skiatook Petroleum Environmental Research (OSPER) sites A and B, Osage County, Oklahoma.

**B.** Analytic data for water samples collected for the Osage-Skiatook Petroleum Environmental Research project.

## Conversion Factors

### SI to Inch/Pound

Multiply	By	To obtain
<b>Length</b>		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
<b>Area</b>		
square meter (m <sup>2</sup> )	0.0002471	acre
hectare (ha)	2.471	acre
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
<b>Volume</b>		
cubic meter (m <sup>3</sup> )	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	0.2642	gallon (gal)
<b>Mass</b>		
gram (g)	0.03527	ounce (oz)
kilogram (kg)	2.205	pound (lb)

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Vertical coordinate information is referenced to the insert datum name (and abbreviation) here, for instance, "North American Vertical Datum of 1988 (NAVD 88)"

Horizontal coordinate information is referenced to the insert datum name (and abbreviation) here, for instance, "North American Datum of 1983 (NAD 83)"

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ).

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## **Abstract**

We report chemical and isotopic analyses of 345 water samples collected from the Osage-Skiatook Petroleum Environmental Research (OSPER) project. Water samples were collected as part of an ongoing multi-year USGS investigation to study the transport, fate, natural attenuation, and ecosystem impacts of inorganic salts and organic compounds present in produced water releases at two oil and gas production sites from an aging petroleum field located in Osage County, in northeast Oklahoma. The water samples were collected primarily from monitoring wells and surface waters at the two research sites, OSPER A (legacy site) and OSPER B (active site), during the period March, 2001 to February, 2005. The data include produced water samples taken from seven active oil wells, one coal-bed methane well and two domestic groundwater wells in the vicinity of the OSPER sites.

## **Introduction**

The U.S. Geological Survey is investigating the impacts of produced water and hydrocarbon releases at two research sites under the Osage-Skiatook Petroleum Environmental Research (OSPER) project. The two OSPER research sites “A” and “B” are located within the Lester and Branstetter leases, respectively, in the southeastern part of the Osage Reservation, Osage County, in northeastern Oklahoma (fig. 1). Both of these sites are located on Federal lands (Osage Nation holds the mineral rights and the Army Corps of Engineers holds the surface rights) adjacent to Skiatook Lake, a 4,250-hectare reservoir that provides drinking water to the local communities and is a major recreational fishery. Site A is the legacy or “depleted” site, which is impacted by produced water and hydrocarbon releases that occurred primarily 65-80 years ago. Site B is the “active” site, which is similar to site A in terms of oil production and size of impacted area, but is actively producing from stripper wells and continues to be impacted by ongoing produced water and hydrocarbon releases to this day.

Investigations aimed at mapping and characterizing the geology, hydrology, contaminant sources and impacted areas at the OSPER sites began in February, 2001 and continue to present. Initial results of investigations at the OSPER sites are discussed in Kharaka and Otton, 2003, and reports therein, including location, geologic setting, and oil production history (Otton and Zielinski, 2003), geophysical characterization of subsurface geology and hydrology by ground electromagnetic (EM) and DC resistivity surveys (Smith and others, 2003), aqueous

geochemistry (Kharaka and others, 2003), organic microbial biochemistry of hydrocarbons, (Godsy and others, 2003), hydrology (Herkeleath and Kharaka, 2003), and soil geochemistry (Zielinski and others, 2003; Rice and others, 2003, and Kampbell and others, 2003). The OSPER sites have been extensively surveyed to a high degree of accuracy using real-time kinematic (RTK) global positioning system (GPS) surveys (Abbott, 2003).

In March 2001, a reconnaissance survey was conducted by the USGS in which water, oil, and gas samples were taken from eight active oil wells located in the Branstetter lease (site B) and in areas adjoining the Lester lease (site A) to characterize the crude oil and produced water contaminant sources (fig. 2). Water samples were also obtained from Skiatook Lake and two domestic water wells, to characterize the chemical and isotopic compositions of the pristine local ground and surface waters. Water samples were also collected during this time from several seeps, pools and shallow hand-dug holes at site B.

In February, 2002, intensive studies of the OSPER sites began, which included the drilling, coring, and completion of numerous monitoring wells in and around the impacted areas at both sites. Holes were drilled using rotary core, auger core, or direct push (Geoprobe®) rigs. Most of these holes were completed as monitoring wells, with 2.5 or 5.1 cm diameter PVC tubing and screened intervals at favorable water-bearing zones. Most of the rotary- and auger-drilled holes were completed with multiple wells (2 or 3). As of May, 2004, a total of 82 holes were drilled (42 at site A; 40 at site B) and 103 screened monitoring wells (58 at site A, 45 at site B) were completed and conditioned for hydrologic monitoring and water sampling.

We have carried out eight major sampling trips and several minor trips to the OSPER sites to collect water samples and important field parameters, including water levels and in-situ temperature and electrical conductivity measurements, from monitoring wells and other surface waters. Presented in this report are the major and trace inorganic solutes, organic components, and water isotope results from 345 water samples collected through February, 2005. These data are being released at this time with minimal interpretation. Some results, with interpretations, from these data have been presented in Kharaka and others (2003, 2005, 2007). Studies are continuing at the OSPER 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 impacting those effects.

## **Methods**

### **Drilling and well completions**

The locations of monitoring wells for OSPER sites A and B are shown in figures 3 and 4, respectively, and the location and well completion parameters are summarized in Appendix A. Well locations were selected on the basis of: (1)- the presence of salt scars, degraded oil, brine pools, 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) and selected soil profiles (Zielinski and others, 2003); and (3)- results of electromagnetic (EM) and DC resistivity surveys used to map the subsurface distribution of salt in groundwater, soil and bedrock (Smith and others, 2003). Additional wells were sited based on results of chemical analysis of water samples obtained from prior drilled wells.

At each site, relatively deep wells were located and drilled at some distance from the impacted areas in order to characterize the local stratigraphy (Otton and Zielinski, 2003) and local groundwater (Kharaka and others, 2003). These wells, designated as “R” for “rotary” (AR-01 at site A; BR-01 and BR-02 at site B; fig. 2), are distinct from the other monitoring wells in

that they were drilled with a rotary bit, which required water for cooling; also, prior to completion, additional water was introduced to the open holes to facilitate geophysical logging. These wells required additional cleaning and water sampling, compared to the auger-drilled wells (designated as “A”) and direct-push wells (designated as “E”), which were drilled without the aid of water.

After drilling, the holes were prepared for completions. Wet holes were repeatedly cleaned of water and slough using submersible pumps and/or hand bailers. Screen intervals were determined based on shows of water-bearing zones in drill cuttings, recovered core, or the hole itself. The rotary (“R”) wells and auger-core (“A”) wells holes were of sufficient bore diameter (> 20 cm) and usually sufficient depth (~5 to 20 m for “A”) wells; 21-30 m for “R”) wells) that multiple water bearing zones were identified and later screened. Most “A”) and “R”) wells were completed with two screened intervals, typically screened intervals of 5-10 ft using 5.1 cm diameter PVC. The site A wells AA-10 and AA-11 were completed with 3 screened wells. The direct-push “E”) holes were typically shallower (~1-6 m depth) and had a smaller borehole diameter (~4 cm); all of the “E”) holes were completed with a single screened well, generally with screened intervals set at 1 to 2.5 ft, using 2.5 cm diameter PVC. Clean and graded sand was used around the screened intervals and bentonite pellets and chips were used to isolate screened intervals in wells with multiple completions. The bottom of the wells were capped. A single shallow open-hole well was created at site A (AP-01), by hand-pushing a length of core liner into the asphaltic pit (fig. 3).

Monitoring wells, after completion, were cleaned numerous times using hand bailers or submersible pumps until the electrical conductivity was determined to be stable. During sampling trips, which typically were 3 to 12 months apart, the usual procedure was to: (1) measure static water levels in the wells; (2) obtain in-situ measurement of conductivity and temperature using submersible probes; (3) pump the wells (usually 1 to 3 well-bore volumes, depending on recharge rates and conductance stability); and (4) allow the well to refill (usually several hours to overnight). Periodically, in-situ measurements of dissolved oxygen (DO) and Eh were also performed prior to pumping and sampling. Water samples for analysis were collected with either Teflon® bailers or submersible or peristaltic pumps, with Teflon or tygon tubing.

## **Sampling methods**

The methods used in sample collection, preservation and field and laboratory determinations of chemical components and isotopes are detailed in Kharaka and Hanor (2004), and Kharaka and others (2000, 2003). 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<sub>2</sub>S and NH<sub>4</sub>. Raw water samples were usually filtered through a 0.1 μm filter using either a syringe, peristaltic pump or compressed nitrogen. Filtered samples were stored in high-density polyethylene bottles prerinsed with deionized water for anions, and prerinsed with 5% nitric acid (HNO<sub>3</sub>) then deionized water for metals and silica. The aliquots for metal and silica were acidified to pH ~1 with ultrex-grade nitric acid (HNO<sub>3</sub>). Sample aliquots for dissolved organic carbon (DOC), carboxylic acid anions, and BTEX organics, were collected without headspace in cleaned and burned 40 ml amber glass vials and were stored below 4°C. Samples for DOC were filtered through 0.1 μm. Samples for carboxylics were filtered through 0.1 μm and preserved with 40 mg/L mercuric chloride (HgCl<sub>2</sub>); Samples for BTEX were stored unfiltered, acidified to pH~1 with ultrex-grade hydrochloric acid (HCl). For water isotopes, two 20-ml glass bottles with polyseal caps were filled with raw water.

Water samples for tritium analyses were collected in 1-liter glass bottles with Teflon<sup>®</sup> polyseal caps.

All of the water samples were analyzed for inorganic and organic solutes at USGS Water Resources laboratories in Menlo Park, CA. Concentrations of major, minor and trace 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 carboxylic acid anions (acetate, butyrate, formate, malonate, oxalate, propionate, and succinate) were determined by ion chromatography (IC). Dissolved organic carbon (DOC) was determined with a MQ-1001 (MQ Scientific) high-temperature, non-catalytic, organic carbon analyzer. Concentrations of BTEX compounds (benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene) were determined with a SRI-8610C gas chromatograph (GC), using flame ionization detector (FID) and 30m MXT-Volatile column. 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, 2004).

Stable water isotopes were determined in the USGS Stable Isotope Laboratories in Menlo Park, CA or Reston, VA. Results for stable isotope measurements are reported in δ-values that are expressed in parts per thousand (per mil, ‰) relative to Standard Mean Ocean Water (SMOW). In the case of oxygen, the equation used is:

$$\delta^{18}\text{O} = \left( \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right) \times 10^3,$$

and in the case of hydrogen, the equation used is:

$$\delta^2\text{H} = \left( \frac{(^2\text{H}/^1\text{H})_{\text{sample}}}{(^2\text{H}/^1\text{H})_{\text{SMOW}}} - 1 \right) \times 10^3.$$

The Standard Deviation of reported values for samples are ±0.2‰ for δ<sup>18</sup>O and ±2‰ for δD. Tritium concentration is reported in Tritium Units (1 TU = 1 tritium atom/10<sup>18</sup> hydrogen atoms) ± 1 sigma uncertainty (Thatcher and others, 1977).

## Data Summary

Appendix A contains a summary of the locations and well completion parameters for the site A and site B monitoring wells. Well names are identified by a letter “A” or “B” which indicates OSPER site A or B, followed by a letter “A”, “E”, “R” or “P” for well type (auger, direct-push Geoprobe, rotary, and hand-pushed), followed by the well number, and for wells having multiple completions, a letter “S”, “M” or “D”, indicating the shallow, middle, and deep completions, respectively.

Appendix B contains analytical results for 345 water samples. The water samples are presented in the following order:

- Local domestic groundwater wells: 2 samples from 2 wells near site A, (fig. 2).
- Local oil/gas wells: 8 samples, 7 from oil wells; and 1 coal-bed methane well (fig. 2).
- Skiatook Lake water: 7 samples, collected during the period October, 2001 to May, 2004. Lake water samples were collected near site A or B, except 01OS-111 which was collected near the Skiatook Lake dam (fig. 2).

- Site A, monitoring well samples: 171 water samples from 58 monitoring wells (fig. 3).
- Site B, monitoring well samples: 146 water samples from 45 monitoring wells (fig. 4).
- Site B, surface samples: 10 water samples from 6 different surface sites and including a sample (02OS-314) of produced water from the brine tank (fig. 4).

The groupings of groundwater wells, oil/gas wells, and Skiatook Lake samples are ordered by date. The site A and site B well sample groups are ordered by well number, then by date. The site B surface waters are order by sample location, then by date.

The analytic data for water samples are organized in Appendix B (from left to right) by site identification, date and time, field parameters (specific conductance, pH, temperature, alkalinity), total dissolved solids, major inorganic solutes (in alphabetical order), minor solutes (including infrequently analyzed solutes, such as H<sub>2</sub>S and ammonia), organic compounds, and finally stable water isotopes and tritium. Solutes and organic compounds that have qualify information, such as “below” (indicated by “<” symbol) or “near” (indicated by “n”) lower detection limit, are preceded by a qualifier column. The water temperatures reported are the temperature from the conductivity/temperature at the time the water sample was processed; and they are not necessarily the in-situ water temperature.

## **Acknowledgements**

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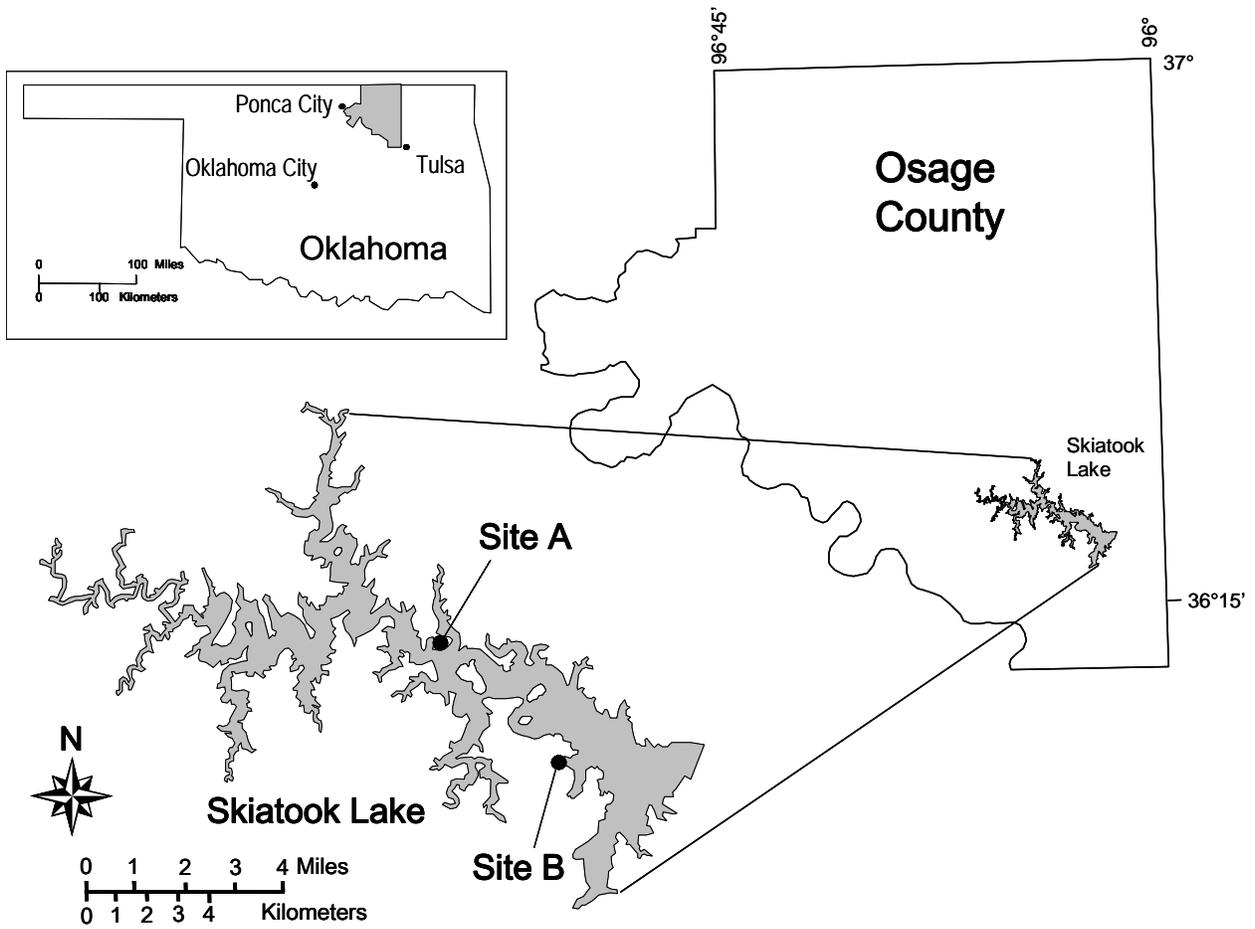
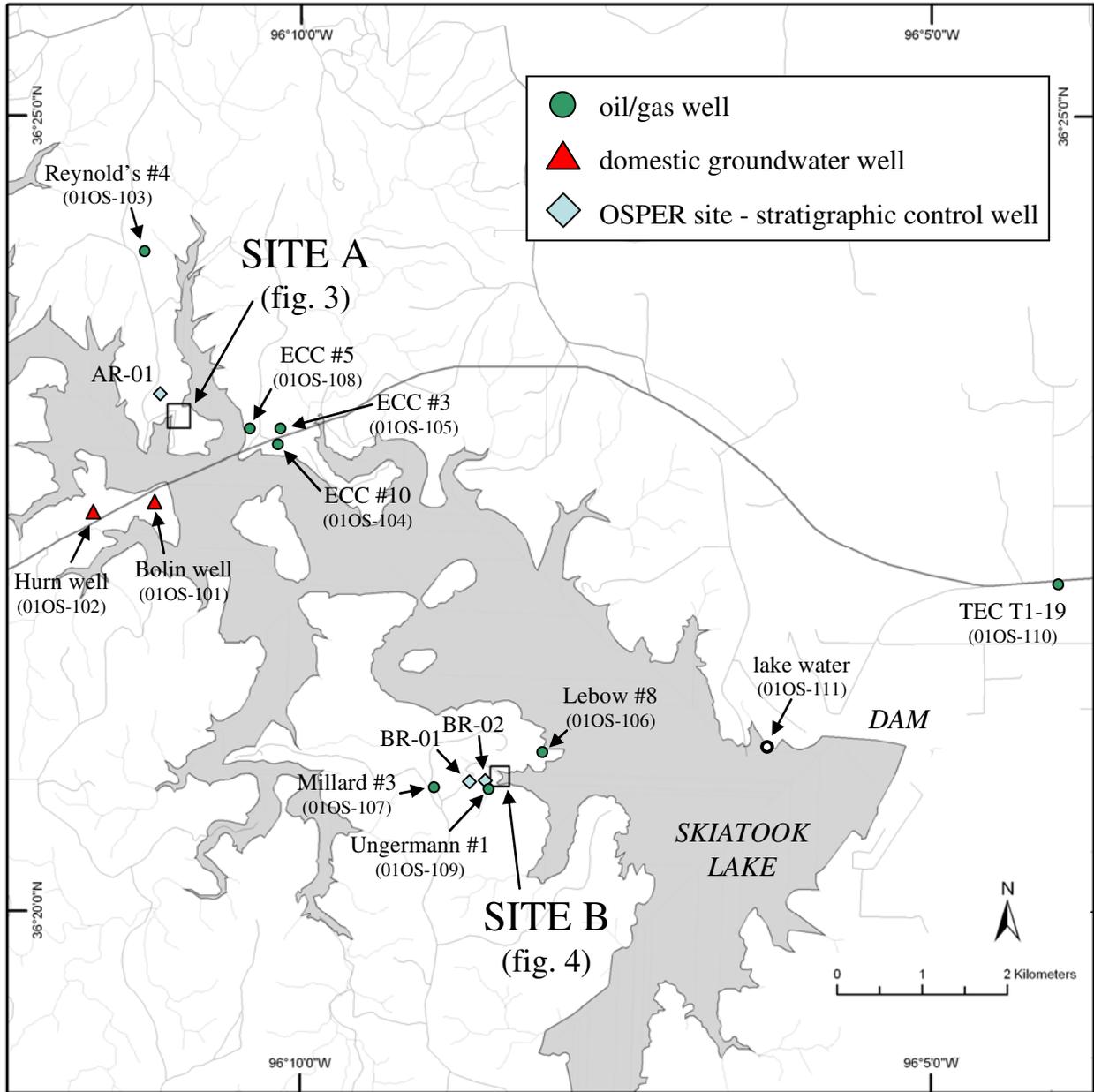


Figure 1. Map showing the locations of OSPER sites A and B, adjacent to Skiatook Lake in Osage County, Oklahoma.



**Figure 2.** Map of the Skiatook Lake region of Osage County, Oklahoma, showing locations of sampled oil wells, domestic groundwater wells, and stratigraphic control wells at OSPER sites A and B. Also shown is the lake water sample 01OS-111, near dam.

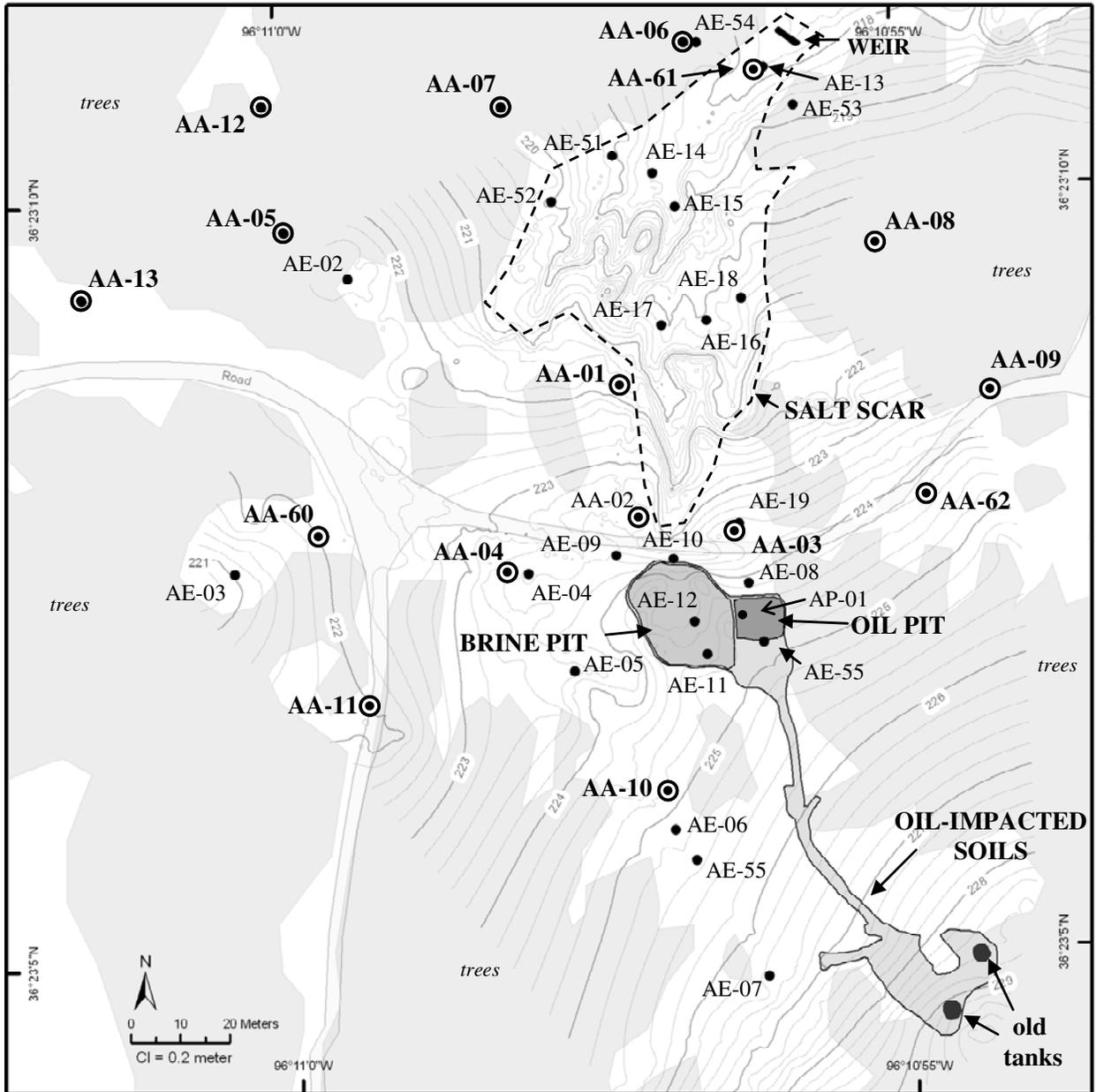


Figure 3. Map of OSPer site A, showing location of monitoring wells.

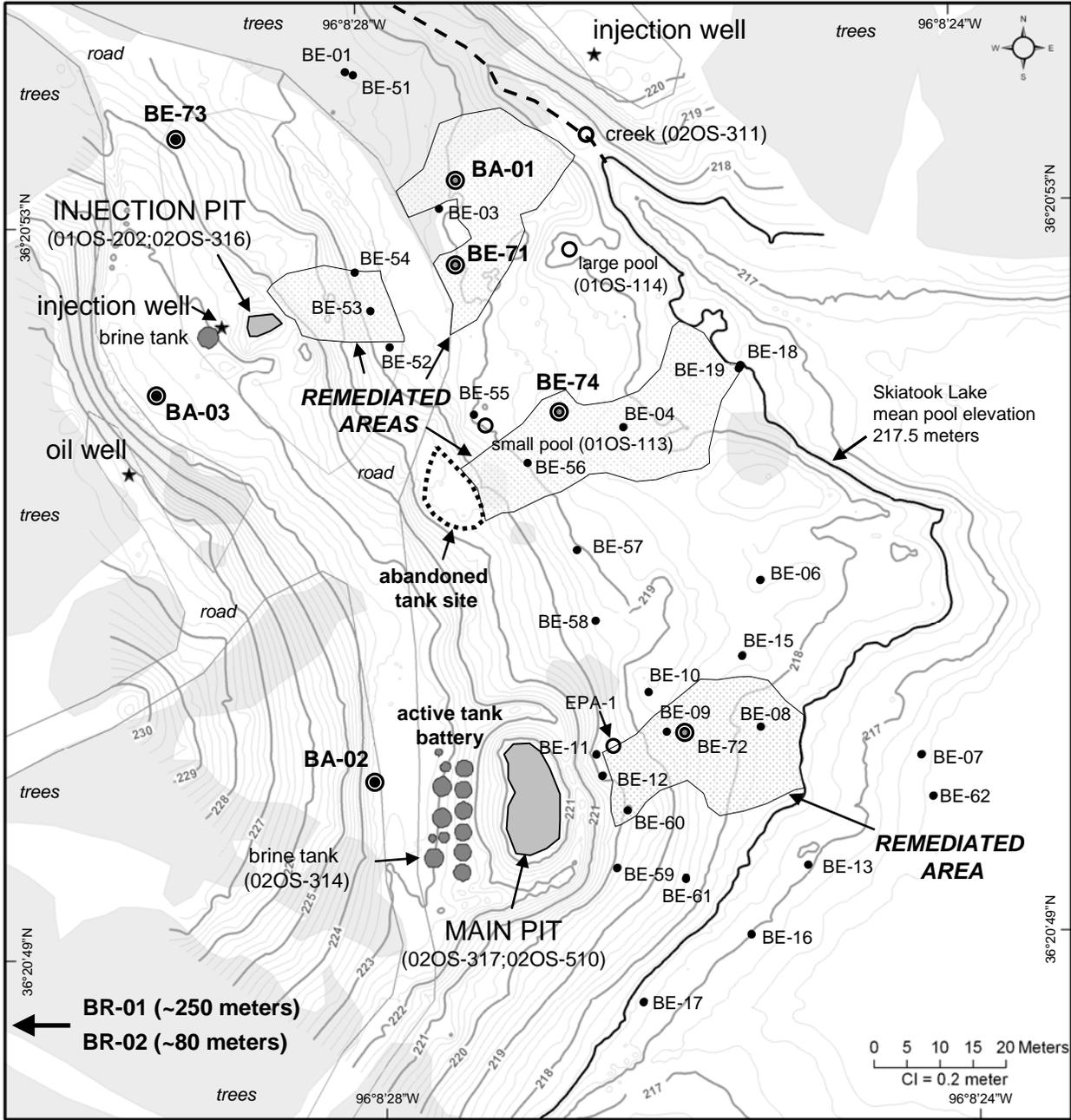


Figure 4. Map of OSPER site B, showing location of monitoring wells and surface water sampling sites.