

Use of soil extracts to define the extent of brine-impacted soils and bedrock at oil production site “B”, Osage-Skiatook Project, northeastern Oklahoma

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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 have 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 (Otton and Zielinski, 2002, 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 (Figure 1). Whereas the surface expression of highly saline soil is often apparent through loss of vegetation and increased erosion, the 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 (1, 2, 3, 4, 5). 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 (6, 7, 8, 9).

SITE DESCRIPTION

Study site “B”, located northwest of Tulsa in northeastern Oklahoma, is one selected by the U.S. Geological Survey 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 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 Lake Skiatook, which was first filled in 1984. Local soils include windblown sand and silt, slope-wash, colluvium, and alluvium. Local bedrock is predominantly shale with lesser thin interbedded sandstone of Pennsylvanian age. A more detailed description of the geologic setting of the site and the production history (1937 to present) is presented in (10), this volume.

METHODS

Initial surface soil sampling (0-15 centimeter (cm)) was conducted at the site in March, 2001. Thirty samples were collected with a 5-cm-diameter stainless steel soil auger from all 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 cores of 4-cm diameter to depths ranging from approximately 2.13 to 5.48 meter (m) (7 to 18 feet (ft)). The cores were collected in plastic liners, capped, taped, and transported to the USGS core library in Denver. Cores were stored under refrigeration until sampling. One 5.48 m core (site 01) from "offsite" was sampled in detail to characterize the local background soils and shallow bedrock. Other cores were typically sampled at the following depths; 1.22 m (4 ft), 2.13 m (7 ft), and 3.05 m (10 ft), or final depth if less than 3.05 m.

Samples of 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 8000 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 M sodium bicarbonate and 0.0035 M 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 commercial 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% 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 occurs 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 (Figures 2a, 2b). Extracts of uncontaminated sandy soils and sandstone have very 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 windblown sand and silt, sandy colluvium, and reworked sandy to clayey fill material. Most extracts of surface soil from site “B” contain greater than 530 ppm dissolved chloride, which exceeds the highest concentration observed in eight extracts from a 0.9 m soil profile collected offsite (Figure 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 (Figure 2b). All extracts with less than 600 ppm Cl are from a 5.48 m shale-dominated core from offsite, 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 (Figure 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.

The spatial distribution of soluble chloride in surface soils is completely 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 (Y.K. Kharaka, USGS, written communication, 2001). 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 (11).

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 (4 ft) (Figure 4). Deepest salt penetration of 2.13 m (7 ft) to > 3.05 m (>10 ft) 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; Figure 4) showed salt to depths of 1.2 m, suggesting older salt deposits or 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 communication, 2002) indicated that in some places salt has penetrated the entire thickness of sandy colluvium and up to 1 m of underlying weathered shale bedrock.

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 (12) on a small volume of slurry water passed through a syringe-mounted filter. Quickly 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. Rapid 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 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 (4 to 7 ft) but at some locations immediately downslope from an active pit, the salt has penetrated to depths in excess of 3.05 m (10 ft).

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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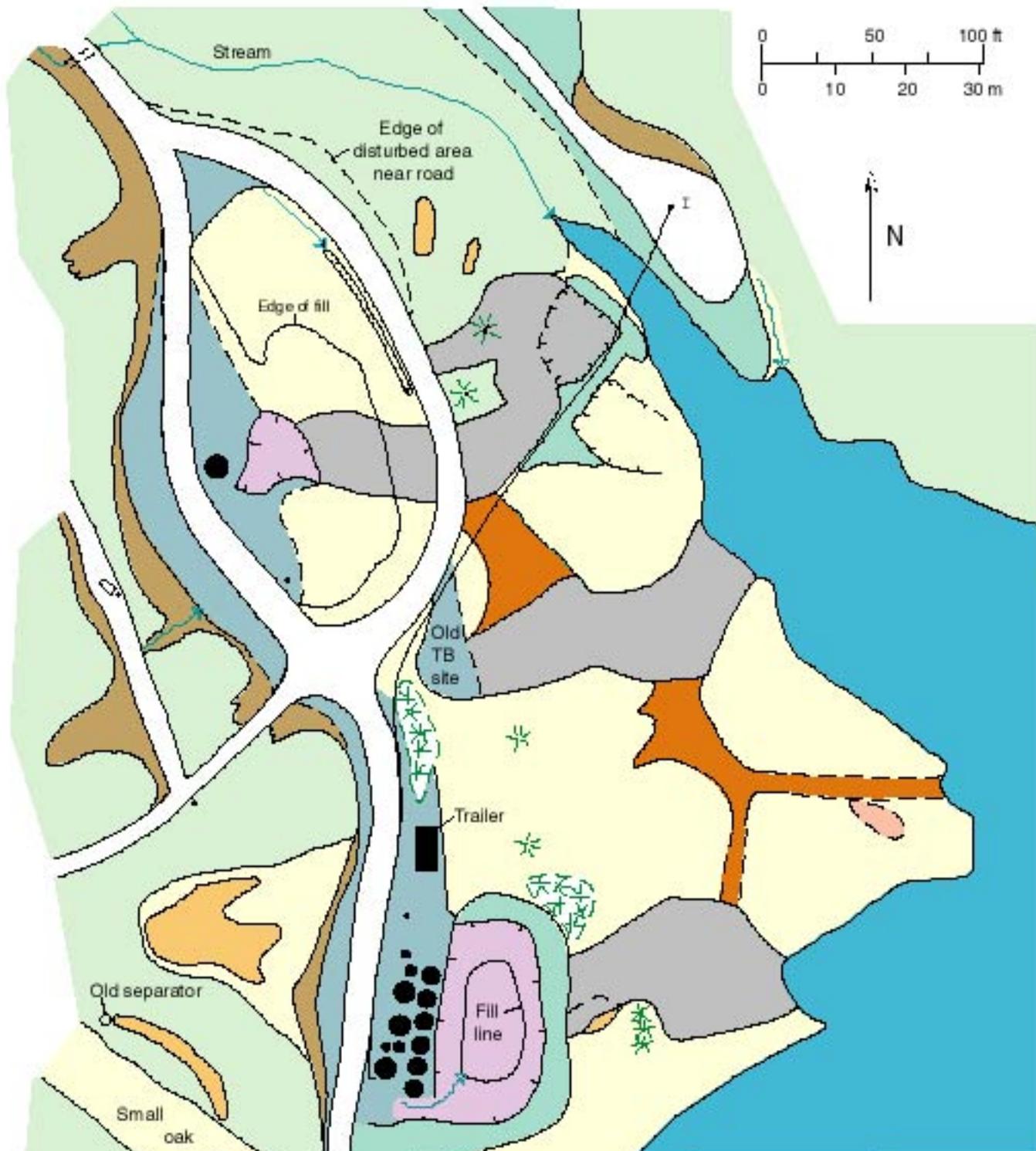
Figure Captions

Figure 1. Base map of oil production site "B", Osage-Skiatook Project. Three areas of salt scarring are shown in gray color and identified as "remediated areas".

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).

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.

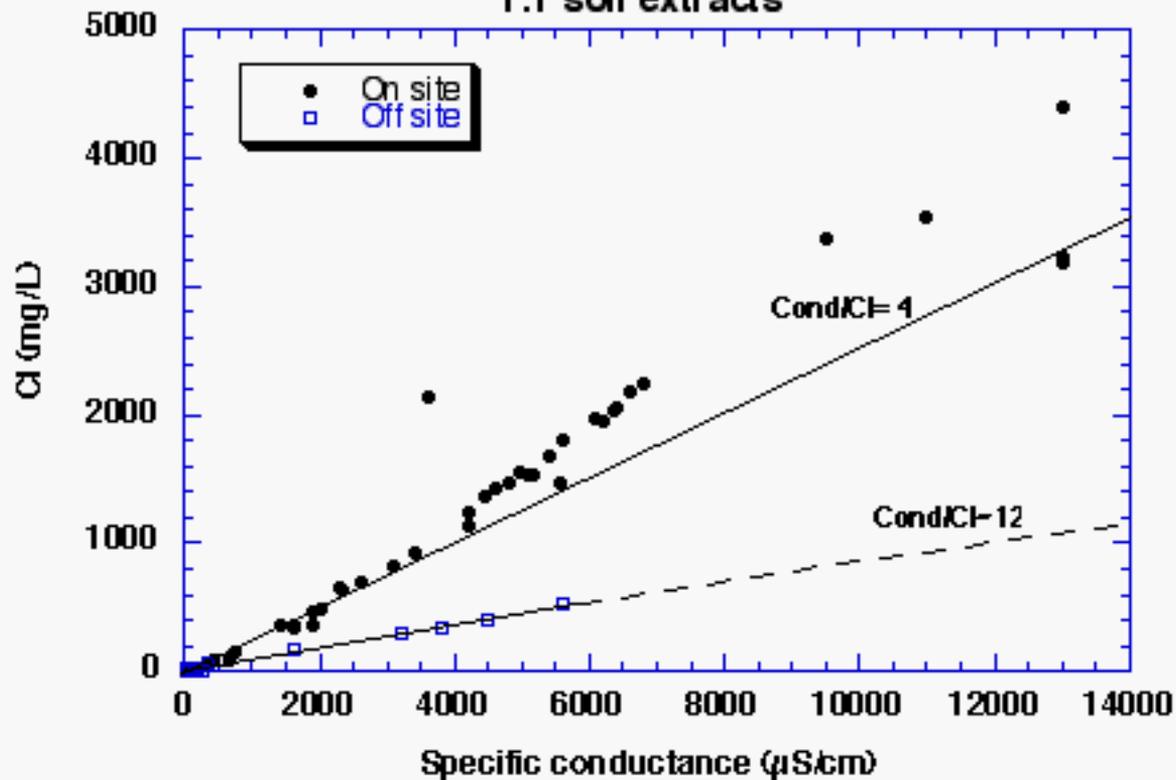


Legend

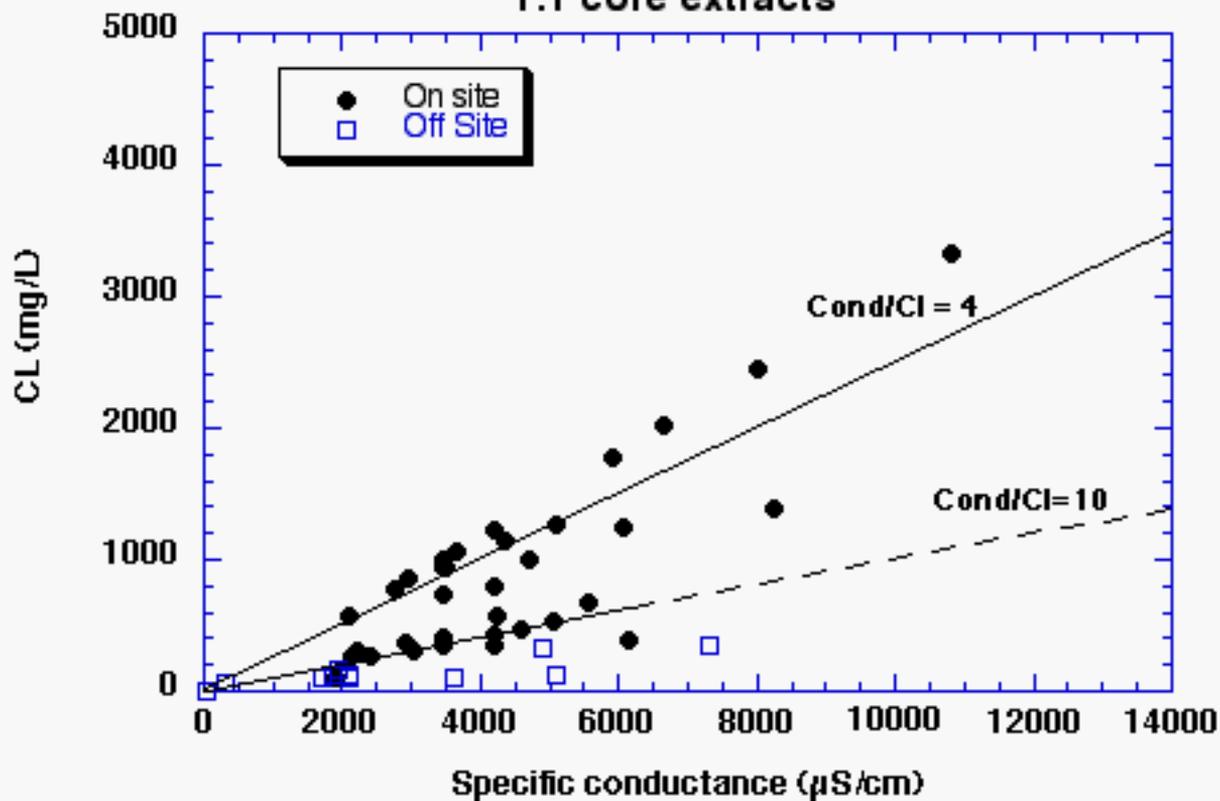
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|--|--|----------------------|--|
| Oak trees | | Oil-impacted soils | |
| Grasses and forbs some on old fill | | Water | |
| Graded cut and fill area, next to road | | Survey station | |
| Road | | Pipeline | |
| Artificial fill little or no vegetation | | Drainage trace | |
| Remediated area | | Individual oak trees | |
| Old road bed, partly gravelled, sparsely vegetated | | Small oak grove | |
| Pit, no vegetation | | Pumping unit | |
| Road cut | | Injection well | |
| Barren, salty soil | | Tanks | |

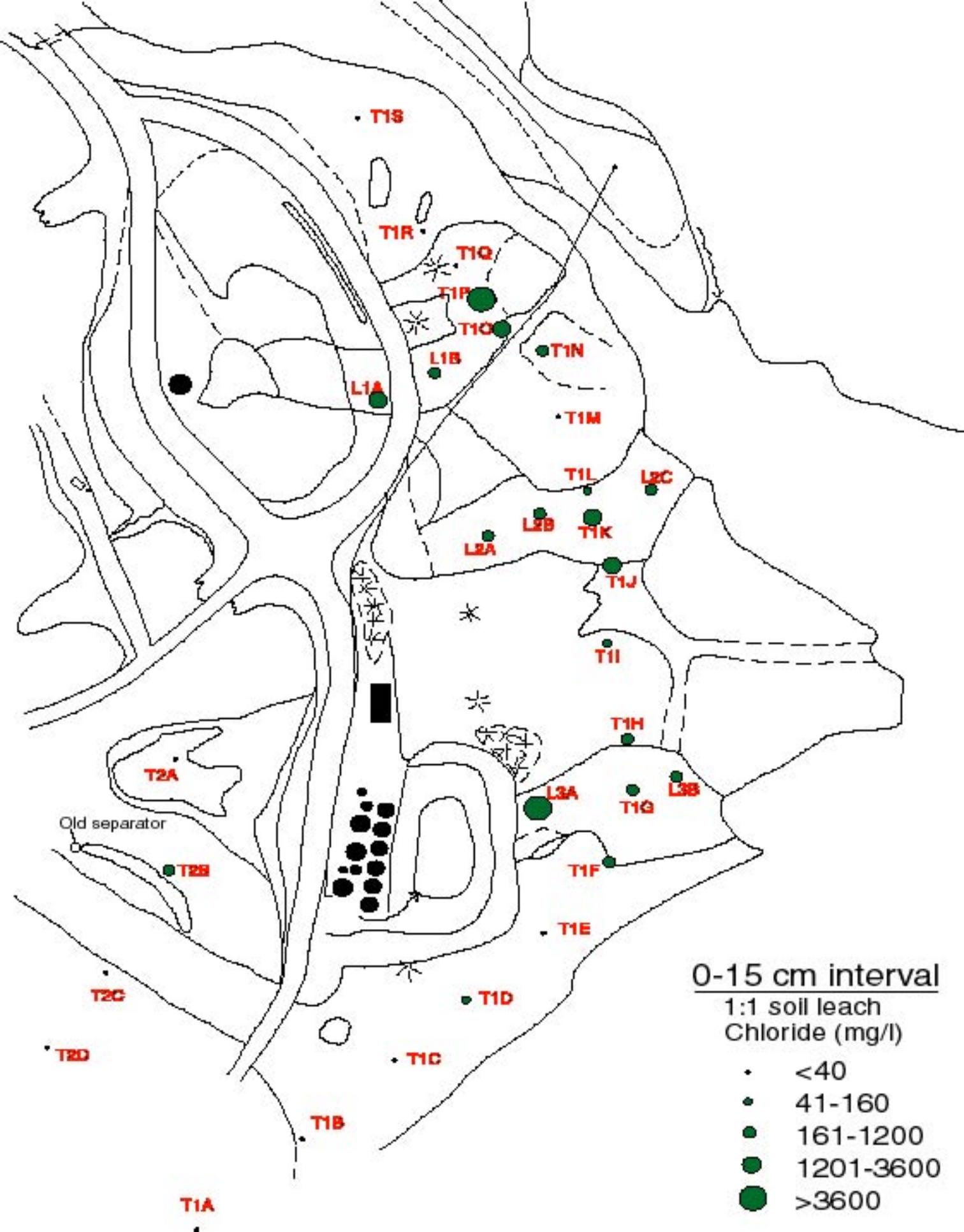
Notes: Only one pipeline is mapped among many. All oil-stained soils caused by pipeline breaks except area adjacent to large pit.

Site "B"
hand auger samples
1:1 soil extracts



Site "B"
direct-push samples
1:1 core extracts





SITE (B) GEOPROBE HOLES

