

Determining the distribution of subsurface salt contamination using the composition of oak leaves: a case study at an oil production site, northeast Oklahoma

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ABSTRACT

Leaves of blackjack oak (*Quercus marilandica*) were collected in November 2002 from 34 trees surrounding a former oil-production site in northeastern Oklahoma (Site A, Osage-Skiatook Project). The objective was to investigate the response of native oak trees to known NaCl contamination in the shallow (1-8 m depth) subsurface. Trees were sampled from a 225 X 300-m area that included locations at various distances (10-200 m) from a salt-scarred area at the site. Locations within about 30 m of the salt scar are subject to subsurface contamination by NaCl as indicated by ground-based geophysical surveys and by anomalous chloride contents of aqueous extracts of core samples. The Cl content of dried oak leaves was determined by ion chromatography and ranged from 184 to 918 ppm. Of the 14 samples with >400 ppm Cl, 6 plotted within 30 m of the salt scar and 10 within 45 m of the scar. The location of these trees confirmed, and also implied an expansion of, the area affected by subsurface salt. Two Cl-enriched trees more removed from the salt scar are spatially associated with a former tank battery site and a trench for transporting produced water. Analyses of 32 additional elements in leaf ash indicated no significant positive correlation with Cl in leaf ash. Biogeochemical sampling and analysis for Cl may provide a less costly alternative to geophysical measurements or drilling when assessing possible contamination by NaCl in the shallow subsurface.

INTRODUCTION

Biogeochemical prospecting for buried mineral deposits (1,2) and phytoextraction of contaminated soils (3) both capitalize on the ability of plants to respond to increased concentrations of bioavailable contaminants in the shallow subsurface. Element enrichments in leaves, twigs, or tree rings are primarily the result of translocation of contaminants following uptake by the roots. Delivery of contaminants to roots is generally assumed to be by ground water or soil moisture within the capillary fringe (3). Plants that are not necessarily strong accumulators of contaminants may still record differences in ground water quality, and thus indicate the presence of contaminant plumes (4,5). Sampling of plants for chemical enrichments can have advantages of cost, speed, and area of coverage compared to sampling of ground water, deep contaminated soils, or geophysical measurements. Disadvantages to biogeochemical surveys are the likely uneven distribution of the sampled plant species and the limited depth of investigation defined by root penetration. The majority of tree roots reside in the upper 1 m of soil (6), but the total depths of root penetration for oak trees are reported to be about 2 m in a temperate climate (7) and as much as 8 m in a desert climate (1). Despite the limitations, a properly designed biogeochemical sampling plan (1) is a potentially useful component of detailed site investigations and may indicate responses of the local plant community to contamination.

The purpose of this biogeochemical study at an oil production site was to investigate the chemical response of oak-tree leaves to saline sediments present only at depths of 1 to 8 meters. Apparently healthy trees adjoining a large salt scar were the primary targets for sampling. The presence of buried salts beneath the trees was documented by a previous surface-geophysical survey of electrical conductivity (8). The buried salts were probably delivered by produced water that infiltrated beneath storage pits located at the head of the salt scar. Similar infiltration plus surface releases of produced water resulted in the highly eroded barren ground now present within the salt scar. Trees sampled at increasing distances from the scar, and at other locations within the site were investigated to determine background concentrations and to indicate possible expansion of the area of contamination beyond that covered by surface geophysical surveys. Multielement analysis of leaves was performed to determine the potential chemical indicators of deep root-zone interaction with NaCl.

SITE DESCRIPTION

The study is located at U.S. Geological Survey research site "A" adjacent to Skiatook Lake, in northeastern Oklahoma, which was established in 2001 to conduct multidisciplinary studies of the environmental impact of historic oil production. The majority of oil production at the site was from 1913 to 1937, but intermittent production continued until 1981. Historical aerial photographs (9) indicate that the majority of surface damage from releases of produced water and hydrocarbons occurred prior to

1937. Damage included a deeply eroded area devoid of vegetation and containing saline soil (the salt scar), areas of former oil spills from pipes and tanks, and a trench and impounding storage pits used to manage oily sludge and produced water (Figure 1). Both storage pits are located at the head of the present salt scar.

Historical aerial photos also indicate that the majority of oak trees in the wooded areas bordering the site were established after 1937 and thus postdate the major period of contamination by produced-water releases. Additional sampling of tree-ring cores at the site support the establishment of most oak trees within the last 65 years (10). The site contains predominantly blackjack oak (*Quercus marilandica*) and post oak (*Quercus stellata*) in approximately equal numbers. These oak species are common to the Cross Timbers ecosystem in the prairie-transition region of Texas and Oklahoma (11). Both species are drought resistant and tolerate thin, nutrient-poor soils (12,13). They favor well-drained sandy or rocky soils and can sprout many times after being burned or cut back. The latter property makes them particularly adapted to savanna and prairie ecosystems where there is the potential for frequent fire. Fire-suppression practices promote the invasion of prairie lands by these oak species.

Surficial geology and shallow-bedrock geology at the site are conducive to the establishment and growth of blackjack and post oak. Surficial sediments are permeable eolian sand (20-120 cm thick) overlying predominantly sandy-to-gravelly colluvium (14). The underlying weathered bedrock is predominantly sandstone but also includes interbedded shale and mudstone that present relatively impermeable barriers to the movement of ground water (15).

Previous auger and rotary drilling of four wells in the open area west and north (down gradient) of the storage pits provided information on deeper bedrock lithology, ground water chemistry, and penetration of introduced salt. The anion composition of aqueous extracts (1:1 by weight) of recovered core samples indicated chloride-rich salt at depths of 1 to 8 meters but not in the upper 1 m (R. Zielinski, unpublished data), which agrees well with results from the geophysical survey. Shallow ground water (1-8 m) from these wells contains sodium and chloride as the major ionic species but also contains appreciable dissolved calcium and magnesium (Figure 2; and (16).

The previous geophysical survey also indicated relatively high electrical conductivity at depth beneath trees bordering the western edge of the salt scar. Only one shallow (1.7 m) direct-push well is located in this wooded area. The well is dry but contains anomalous extractable chloride (700 mg/L) at a depth of 1.6 to 1.7 m. One other direct-push well <3 m deep is located near the western edge of the salt scar and approximately 3 m from the bordering trees. This well contains saline water (E. Kakouros, oral communication, 2003) and also has anomalous extractable chloride (>1000 mg/L) in core samples collected below 1.6 m (R. Zielinski, unpublished data).

SAMPLING AND ANALYTICAL METHODS

Leaves from a total of 34 blackjack oak trees were sampled during a site visit in early November, 2002. The selection of blackjack oak was based on the distribution and availability of trees with remaining green or partly green leaves for sampling. Most of the mature trees sampled in this study were 6 to 9 m high with trunk diameters of 13 to 30 cm measured at chest height. An effort was made to sample leaves from all sides of the tree. Approximately 100 g of leaves from each tree was collected by hand or with the aid of a pole pruner, then placed in cloth sample bags.

In the laboratory, the leaves were transferred to plastic tubs, rinsed extensively under a stream of distilled water, drained in colanders, and allowed to air dry. Dried leaves were finely minced to <2 mm size by passing through rapidly spinning stainless steel blades of a Wiley Mill. A split of 25 g was taken for high temperature ashing at 525°C (17).

Chlorine content of the dried leaves was determined by ion chromatography (18) following decomposition of a 0.1 g aliquot by high temperature (675°C) fusion with Eshka's mixture (two parts MgO and one part Na₂CO₃) (17). The fusion cake was dissolved in water and the solution analyzed for chloride ion using a Dionex 500 chromatography system equipped with an AS-14 anion exchange column. The eluent was a mixture of 1 millimolar sodium bicarbonate and 3.5 millimolar sodium carbonate (pH= 9.0). Background-corrected counts under the chloride peak were converted to concentration values based on a calibration of peak area to chloride concentration in a series of prepared standards. A reagent blank was subtracted, which ranged from 10 to 50 percent of the total recorded counts in the analytical peak. Estimates of accuracy for Cl content were based on simultaneous analyses of three coal standards and are better than ±5 percent relative standard deviation (RSD). The average percent difference from the mean in four blind duplicates of dried leaf samples was 14.9± 9.8 percent.

Ash content of leaves was determined as the amount remaining after heating at 525°C. The major, minor, and trace-element composition of leaf ash was determined by a combination of inductively-coupled plasma-atomic emission spectrometry (ICP-AES) and -mass spectrometry (ICP-MS) (17). A multi-acid decomposition and a sodium peroxide sinter decomposition were used for different suites of elements. Estimated accuracy and precision for 32 elements determined in leaf ash are based on replicate analysis of ashed coal standards and is generally better than 15 percent (RSD). The average percent difference from the mean in four pairs of blind duplicates was 11.0±12.0 percent when results for all 32 elements were combined.

RESULTS AND DISCUSSION

Chlorine in oak leaves

Chlorine is an essential element for plants (1) and should be readily assimilated if available as chloride ion in soil pore water. The tolerance of plants for excessive dissolved chloride is poorly documented and dependant on plant type. For more sensitive plants, a dissolved chloride concentration of about 500 ppm can induce stress (19). A general threshold concentration for Cl in plants is reported as 2700 ppm on a dry weight basis (19). Chloride ion is a major component of produced water and is largely conserved in solution, meaning that dissolved chloride is minimally affected by soil/water or rock/water interactions (precipitation, sorption, ion-exchange). Biogeochemical studies that document increased concentration of Cl in response to contamination are few because chloride ions are not highly concentrated in many types of contaminant plumes and Cl is generally not determined as part of multi-element analytical packages. Two studies (20,21) report Cl enrichment in tree rings as a result of ground water contamination. Another study (5) omitted analysis for Cl but reported enrichment of chemically-similar Br in leaves of cottonwood trees situated near a chloride-bearing ground water plume.

The frequency distribution of Cl in 34 samples of oak tree leaves (Figure 3) indicates a range of Cl concentration from 184 to 918 parts-per-million (ppm). The distribution has a positive skewness, a mean value of 399 ppm, and a median value of 350 ppm (Table 1). According to the method of Brooks (1), a plot of cumulative percent frequency on probability paper indicates that a Cl-enriched sub-population is defined by those samples containing greater than 400 ppm Cl.

Six trees with greater than 400 ppm Cl in their leaves are located within 30 m of the salt scar (Figure 4). Three other trees in the same general vicinity are not enriched in Cl despite the probable presence of buried salt. This discrepancy illustrates the potential for biogeochemical surveys to include false negatives that arise from tree-specific variations in the distribution of root systems relative to contaminants. Some false positives are also possible and are caused by compositional outliers within the natural background population. One such outlier could be a tree with marginally elevated Cl (417 ppm) that is located away from obvious production-site activities.

Three trees with elevated Cl in leaves (430, 574, 430 ppm) are located in a wooded area to the east of the salt scar (Figure 4). This area was not originally surveyed for electrical conductance but is considered susceptible to subsurface contamination based on probable ground-water flow paths between the storage pits and the lake. In this case, biogeochemical sampling supports arguments to expand geophysical surveying. Three other trees with elevated Cl in leaves (431, 463, 509 ppm) are located south of the access road. These trees are associated with an old tank battery location, a trench that

transported produced water, and a swale that collects surface drainage from the upper half of the site and directs surface flow to the west. Three trees adjoining a former production well that was converted to an injection well in the 1970s show no evidence of elevated Cl in leaves (Figure 4). One tree farther from the injection well has 751 ppm Cl in leaves, an anomaly that remains unexplained.

Other elements in oak leaves

Correlation calculations were performed to investigate possible relations between the concentration of Cl in leaves or leaf ash (calculated) and concentrations of 32 other elements determined in leaf ash. Most elements showed no significant positive correlation or were negatively correlated with Cl. Most positive correlations were less than 0.2 and no positive correlation rose to the 90-percent level of confidence. Cross-plots of Cl versus each element, or versus ash content (3.86 ± 0.6 wt.%), generally produced a random scattering of points with no strongly sloping best-fit regression line and no systematic grouping of the samples with highest Cl content. A few possible exceptions to this rule are plotted in Figure 5. Six trees with the highest Cl content in leaves, in excess of 570 ppm, tend to have lower Na, Li, and Rb than the average of the remaining 28 samples. In contrast, plots of Cl versus Ca or K illustrate the more common result in which the six high-Cl samples are more equally distributed about the mean of the other 28 samples. The behavior of Na and Ca is of particular interest because they account for the majority of dissolved cations in shallow contaminated ground water at the site (Figure 2). Of these two elements, only Ca is essential for plants.

Oak trees and plants in general may exercise an exclusion mechanism that allows roots to preferentially select essential elements such as Ca over nonessential elements such as Na (1). Any defensive exclusion of Na may also include other nonessential alkali elements (Rb, Li). For most of the measured trace elements in leaf ash the lack of positive correlation with Cl is probably influenced by their concentrations in local contaminated ground water. Such concentrations may be too low or too similar to background concentration to produce a marked increase in root uptake. Such increases are particularly problematic for measured trace elements that are nonessential to plants (Co, Cr, Ni, Sr, Al, V, Y, Ba, As, Bi, Cd, Cs, Ge, Ga, Nb, Pb, Sb, U). Measured trace elements that are essential to plants but that also showed no obvious or systematic enrichment in Cl-rich samples included B, Cu, Fe, Mn, Mo, S, and Zn. For all the above elements the response of oak trees to buried salt may be muted by the fact that contamination is only present at depths >1 m, whereas the majority of elements, nutrients, and moisture are supplied to the tree from depths < 1 m (6). Chlorine may be unique among the other measured essential elements (Ca, Mg, K, P, + essential trace elements) because in zones of subsurface NaCl contamination essential chlorine is much more available at depth than in the shallow root zone.

Bromine, an element with chemical characteristics similar to Cl, was not measured in this study. Though nonessential for plants, Br may be carried along with Cl

during assimilation by roots and thus has the potential for positive correlation with Cl. The Cl/Br ratio in local contaminated ground water is approximately 300 (16) and preferential uptake of Cl may produce an even higher ratio in plants. Ion chromatography has problems measuring low concentrations of bromide ion in the presence of high concentrations of dissolved chloride. If Br concentration in plant matter is to be determined, then the preferred analytical method is by neutron activation analysis of plant ash.

Other relations within the data

Trees with Cl-rich leaves had trunk diameters that were lower than the average value of 22.5 cm (at chest height). Trunk diameter in these slow-growing oaks is not a reliable indicator of age, but trees of smallish diameter that are located at the edge of an encroaching forest could be interpreted as among the more recently established. Many of the Cl-rich trees were located at such sites. The alternative interpretation that Cl-rich trees are more stunted in their growth seems less likely because all the sampled trees appeared equally healthy, chloride enrichments were not excessive (<4X), and the majority of the root systems of all the trees are likely hosted within uncontaminated soil of the upper 1 m.

As a control sample, one blackjack oak was sampled at another nearby oil-production site where there were recent surface releases of produced water and contamination of the entire soil profile, underlying colluvium, and shallow bedrock with NaCl salt. This tree was located at the edge of an active storage pit for produced water and was obviously under stress from recent releases of produced water. Leaves from this tree had higher Cl (1100 ppm) than any of the 34 trees of our study and the Ca and Sr contents in leaf ash were higher than in all but one of our samples. Of the remaining measured elements, only Pb and Bi were anomalously elevated in leaves of this control sample.

One tree located near the access road at the eastern edge of the study site and close to a former central power unit (bandwheel) and associated rods, pipes, and building foundation had slightly elevated Cl in leaves (430 ppm, Figure 4). More importantly, this tree, as well as a nearby tree sampled during an earlier reconnaissance, had the highest (or nearly highest) concentrations of Fe, Cu, and Zn in leaf ash compared to the other sampled trees. These limited data indicate that the trees may respond to additional available iron and trace metals that contaminate soils near the rusted remnants of the power unit. Burial of small pieces of scrap iron, nails, and rusted steel food cans is one low-tech technique for treating iron deficiency in plants (22).

Positive correlation between iron and aluminum ($r=0.70$) and between iron and copper ($r=0.43$) in the 34 leaf-ash samples are the strongest positive correlations observed with iron. A correlation coefficient of 0.44 is significant at the 99th percentile confidence

level for a population of 34 samples. These correlations may be influenced by the formation of strong complexes of Fe, Al, and Cu with tannin molecules (polyphenols) that are particularly abundant in oak leaves (23). Oak trees produce tannins as a defense against browsing by insects, pathogens, and rot (24). Tannins are concentrated in oak leaves during the growing season so the sampling of leaves in late fall may have provided increased concentrations of tannin-bound elements.

CONCLUSIONS

A biogeochemical survey conducted at a site of historic oil production indicated that contamination of the shallow (1-8 m depth) subsurface with NaCl-rich salt from produced water is recorded by blackjack oak trees as elevated chlorine concentrations within leaves. The distribution of Cl-enriched trees surrounding an oil production site and a large associated salt scar provides a qualitative indication of the extent of buried saline soil and shallow saline ground water and thus complements the more detailed and quantitative results of geophysical surveys. Reconnaissance sampling of above-ground plant growth is rapid, low cost, high coverage, and can be used to guide subsequent subsurface characterization of contaminated sites by coring and well drilling. This new application of biogeochemical surveying could have utility at other oil-production sites contaminated by subsurface introduction of produced water salts.

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Marvin M. Abbott of the U.S. Geological Survey (USGS) graciously provided high-resolution location information for the sampled trees using a global positioning system. He also performed accurate registration of tree locations on a base aerial photograph using geographic information system software. James K. Otton of the USGS helped with design of the sampling plan, sample collection, and also provided a base vegetation map of the site. Sample processing was aided by James G. Crock, and Hope Yu, both of the USGS.

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Table 1. Statistical summary of the composition of oak leaves from 34 blackjack oak trees, Research site “A”, northeastern Oklahoma.

Parameter	Minimum	Maximum	Mean	Std. deviation	Median
Dry leaf basis					
Cl (ppm)	184	918	399	182	350
Ash (%)	2.8	5.5	3.9	0.6	3.7
Ashed leaf basis					
Cl (ppm) in ash (calc.)	4842	23691	10462	4796	9048
Na ₂ O (%)	0.11	0.51	0.24	0.10	0.22
CaO (%)	27.0	41.1	36.3	3.6	37.1
MgO (%)	2.6	18.3	9.6	3.1	9.4
K ₂ O (%)	6.3	18.3	10.6	2.9	9.9
Fe ₂ O ₃ (%)	0.13	0.32	0.21	0.04	0.21
Al ₂ O ₃ (%)	0.21	0.55	0.37	0.08	0.36
SiO ₂ (%)	1.5	28.5	6.4	4.6	5.9
P ₂ O ₅ (%)	2.2	6.2	4.3	1.0	4.4
Co (ppm)	3.8	24.7	11.3	5.2	10.7
Cr (ppm)	3.8	14.1	8.3	2.8	7.9
Cu (ppm)	80	174	130	20.8	130
Li (ppm)	58.7	175	100.5	27.6	91.4
Mn (ppm)	5600	93600	40900	23200	37500
Ni (ppm)	24.8	208	98.5	48.9	95.0
V (ppm)	13.5	268	115.0	67.8	105.5
Y (ppm)	7.7	24.4	13.4	3.6	13.6
Zn (ppm)	200	2550	640.4	363.6	567.0
Ba (ppm)	2500	13100	5640	2100	5290
As (ppm)	0.67	8.5	2.6	1.5	2.4
Bi (ppm)	0.10	3.0	0.32	0.50	0.19
Cs (ppm)	0.24	1.9	0.64	0.40	0.48
Ga (ppm)	0.60	2.1	1.2	0.39	1.2
Ge (ppm)	0.10	2.5	0.26	0.42	0.16
Mo (ppm)	0.35	8.8	2.9	1.7	2.7
Nb (ppm)	0.10	11.4	0.73	2.1	0.19
Pb (ppm)	0.64	15.5	8.3	3.3	8.2
Sr (ppm)	820	8930	3020	2180	2130
B(ppm)	550	2430	1220	360	1200
Cd (ppm)	1.9	8.8	5.8	1.6	5.9
Sb (ppm)	0.10	6.5	0.57	1.2	0.20
U (ppm)	0.24	0.85	0.42	0.15	0.36

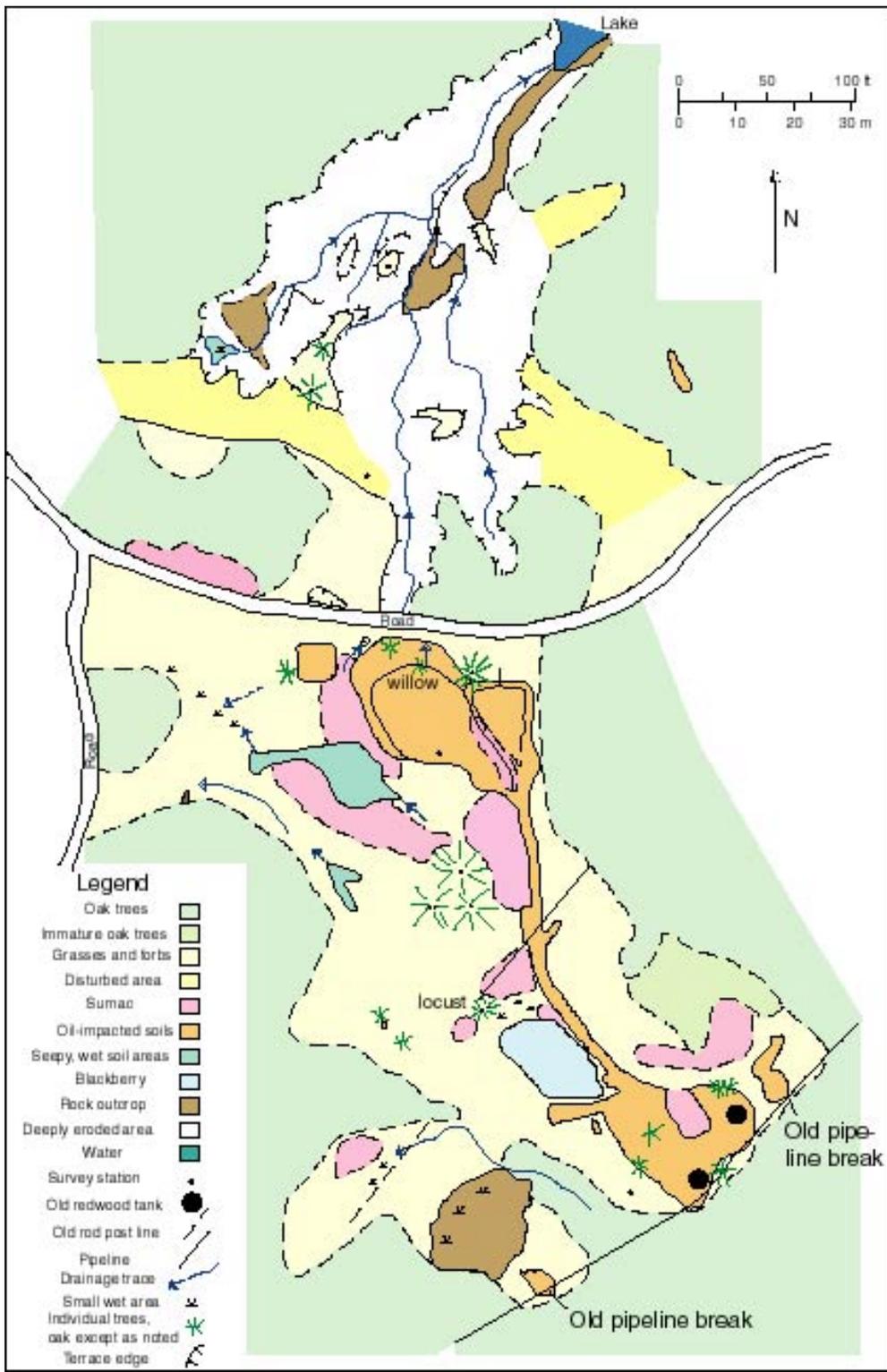


Figure 1. Vegetation map of USGS study site “A”, northeastern Oklahoma, reproduced from Otton and Zielinski, 2002. The deeply eroded salt scar is shown in white. Other areas impacted by site operations (orange color) include a trench that connects a tank battery site with an area located at the head of the salt scar that contains a pair of storage pits.

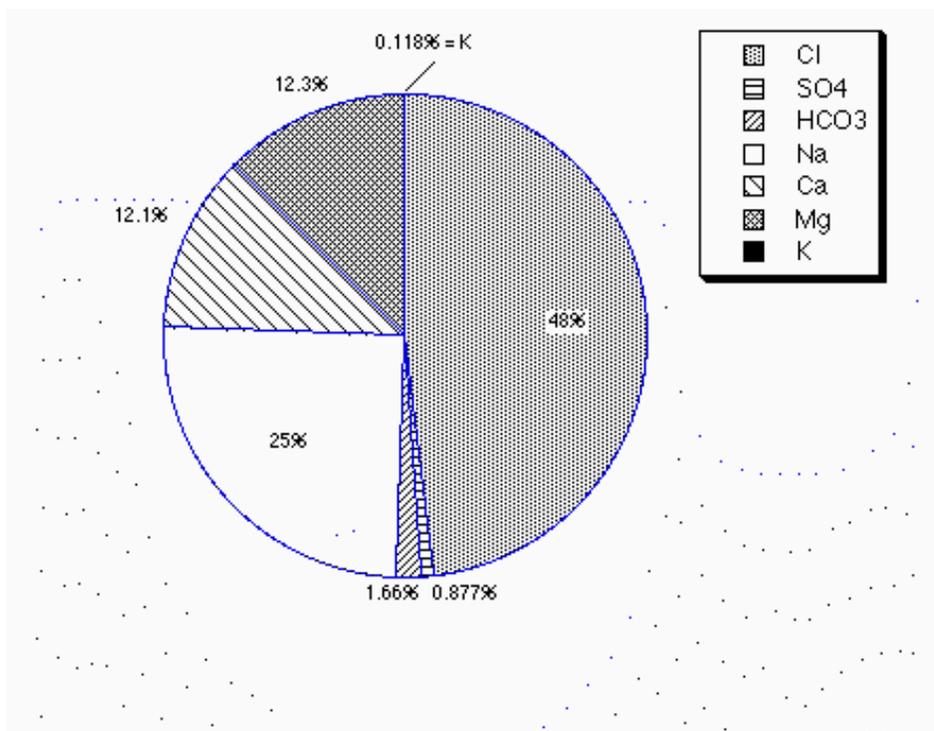


Figure 2. Average composition of shallow (<8 m) contaminated ground water at the study site. Compiled from data supplied by Y. Kharaka (USGS, written communication, 2002) for six samples collected in June, 2002. Percentages are based on concentrations in milliequivalents per liter.

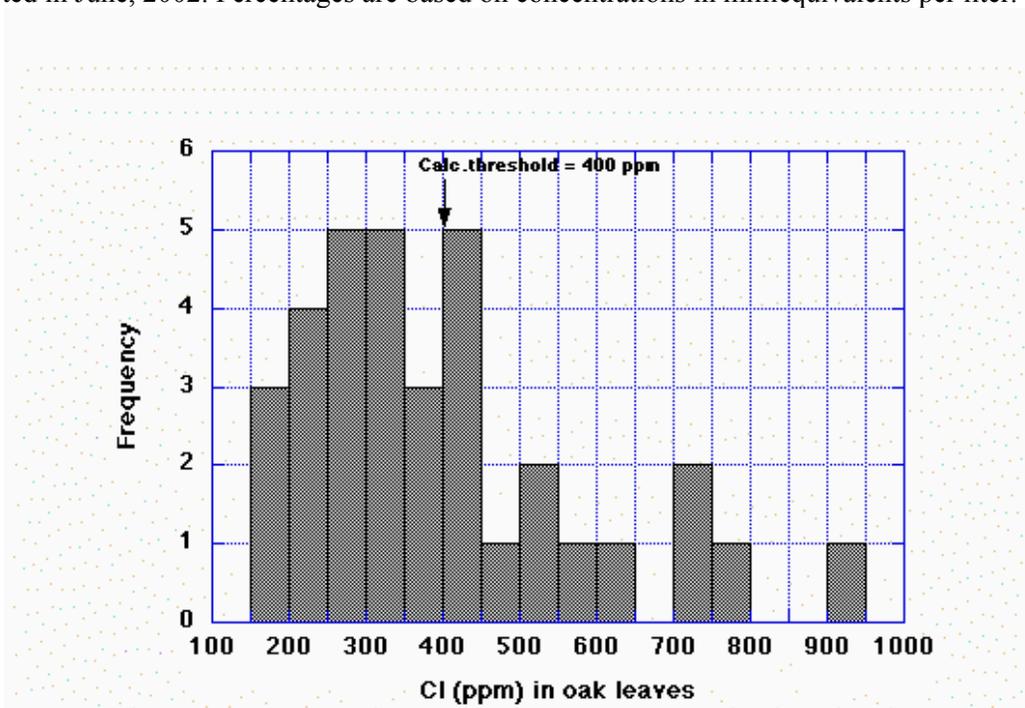


Figure 3. Frequency distribution of Cl concentration in 34 samples of dried oak leaves collected in November, 2002. A calculated threshold value of 400 ppm defines a sub-population of high Cl content.

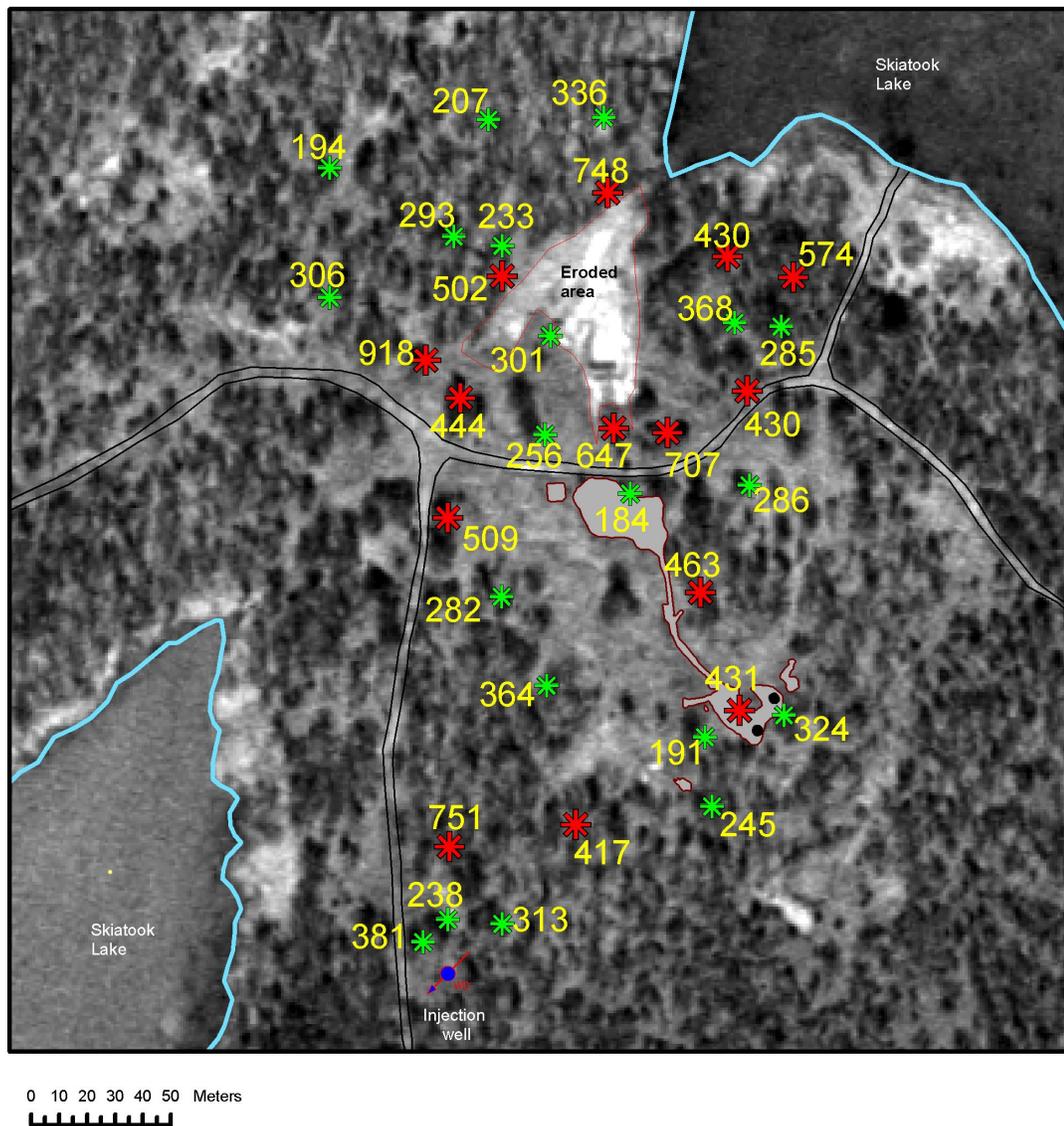


Figure 4. The spatial distribution of sampled oak trees. Numbers by each symbol indicate the Cl concentration (ppm) in sampled oak leaves. Samples with >400 ppm Cl are shown in red.

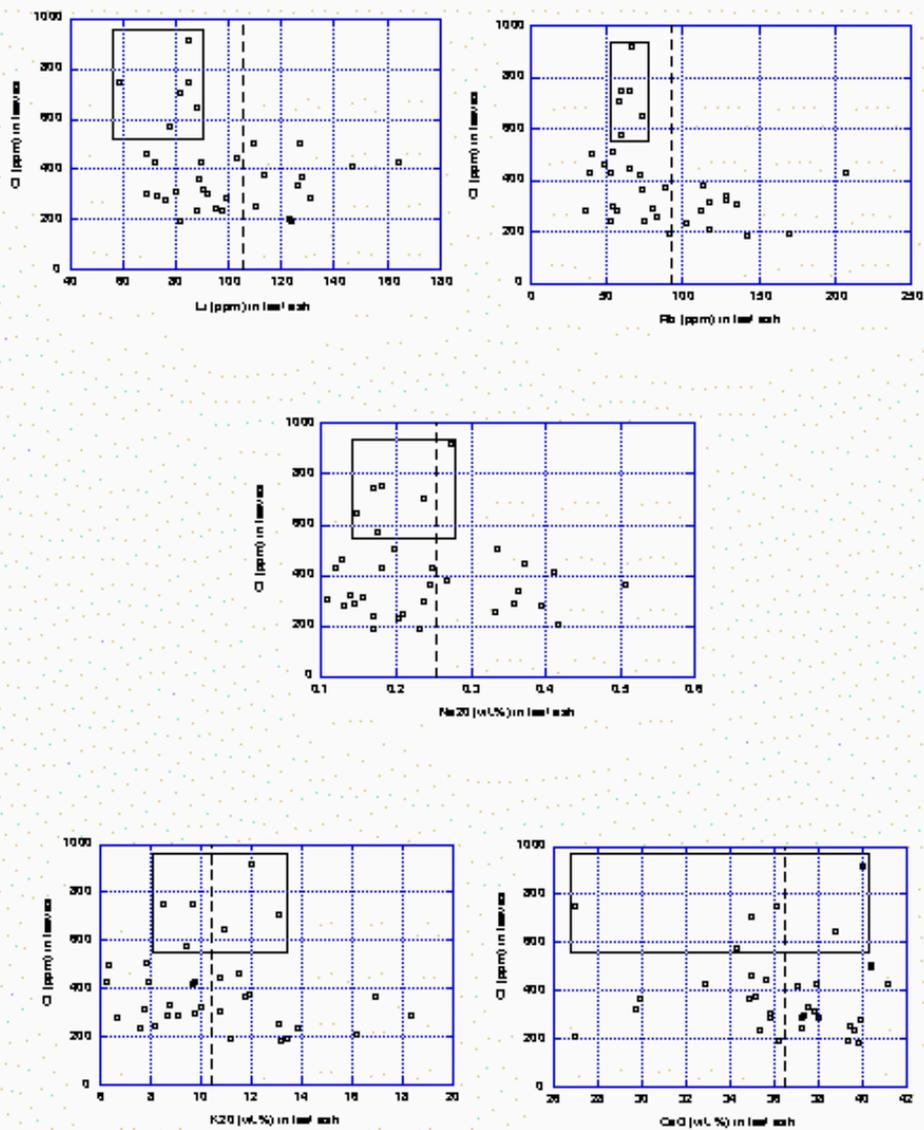


Figure 5. Plots of the concentration of Cl in dried leaves versus the concentration of selected elements in leaf ash. Six samples of highest Cl content (>570 ppm) are enclosed in boxes. A vertical dashed line in each plot indicates the average concentration of the selected element in the remaining 28 samples.

