

## CARBON TETRACHLORIDE IN VEGETATION AND ITS APPLICATION TO EXPEDITED SITE CHARACTERIZATION

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### ABSTRACT

The use of vegetation analyses to outline areas of near-surface enrichment with metals and organic compounds was pioneered by the mining and petroleum industries. Research and development (R&D) on environmental applications is focusing on the ability of vegetation to remediate soils. Certain contaminants are taken up by plants and either stored in the plant tissue for easy harvesting and removal or changed into products that are not a health concern. In the development of its Expedited Site Characterization (ESC) methodology, our group at Argonne has focused its R&D on the application of vegetation analyses to detect subsurface contamination in vadose zone soils. We have developed the technology to locate past spills or leaks of carbon tetrachloride that penetrated the vadose zone and contaminated underlying drinking water supplies. Vegetation analysis is attractive as a first-step exploratory technique because it is noninvasive, rapid, and inexpensive. The technique requires collection of a uniform, constant sample type and an analytical method with a low detection limit and high-quality results.

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### INTRODUCTION

This paper discusses Argonne's R&D at grain storage facilities that were operated from the early 1950s to the early 1970s by the Commodity Credit Corporation (CCC) of the U.S. Department of Agriculture (USDA), on land temporarily leased from local farmers. Many such facilities were located in the Midwest. To control pests, the CCC/USDA fumigated the grain with a mixture of 80% carbon tetrachloride and 20% carbon disulfide. The problem, as shown in Figure 1, is that the carbon tetrachloride penetrated vertically into the soil beneath the CCC/USDA's storage sheds, small circular storage bins, and Quonset huts and contaminated the drinking water aquifers under the sites.

In the early 1970s the CCC/USDA sold all of its circular bins and Quonset huts to local farmers and returned the leased areas to the owners. Many of the bins and Quonset huts are gone from these sites, and the owners now use the land for many different activities. Even if the surface structures are no longer present at a site, the subsurface soil can still contain remnant carbon tetrachloride, which acts as a continuing source of contamination and requires investigation as part of an ESC.

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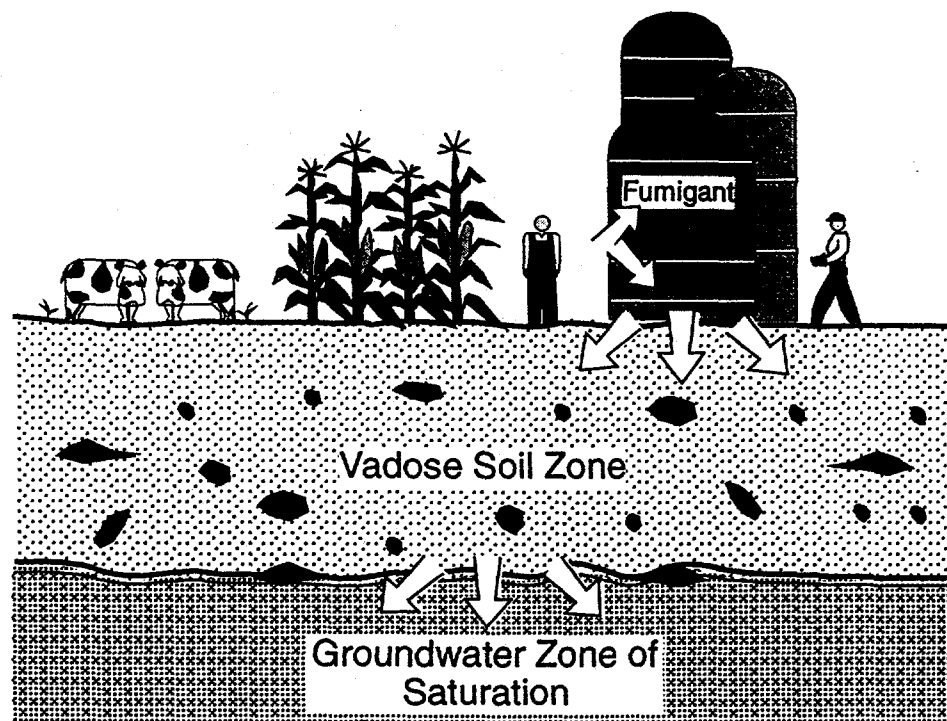
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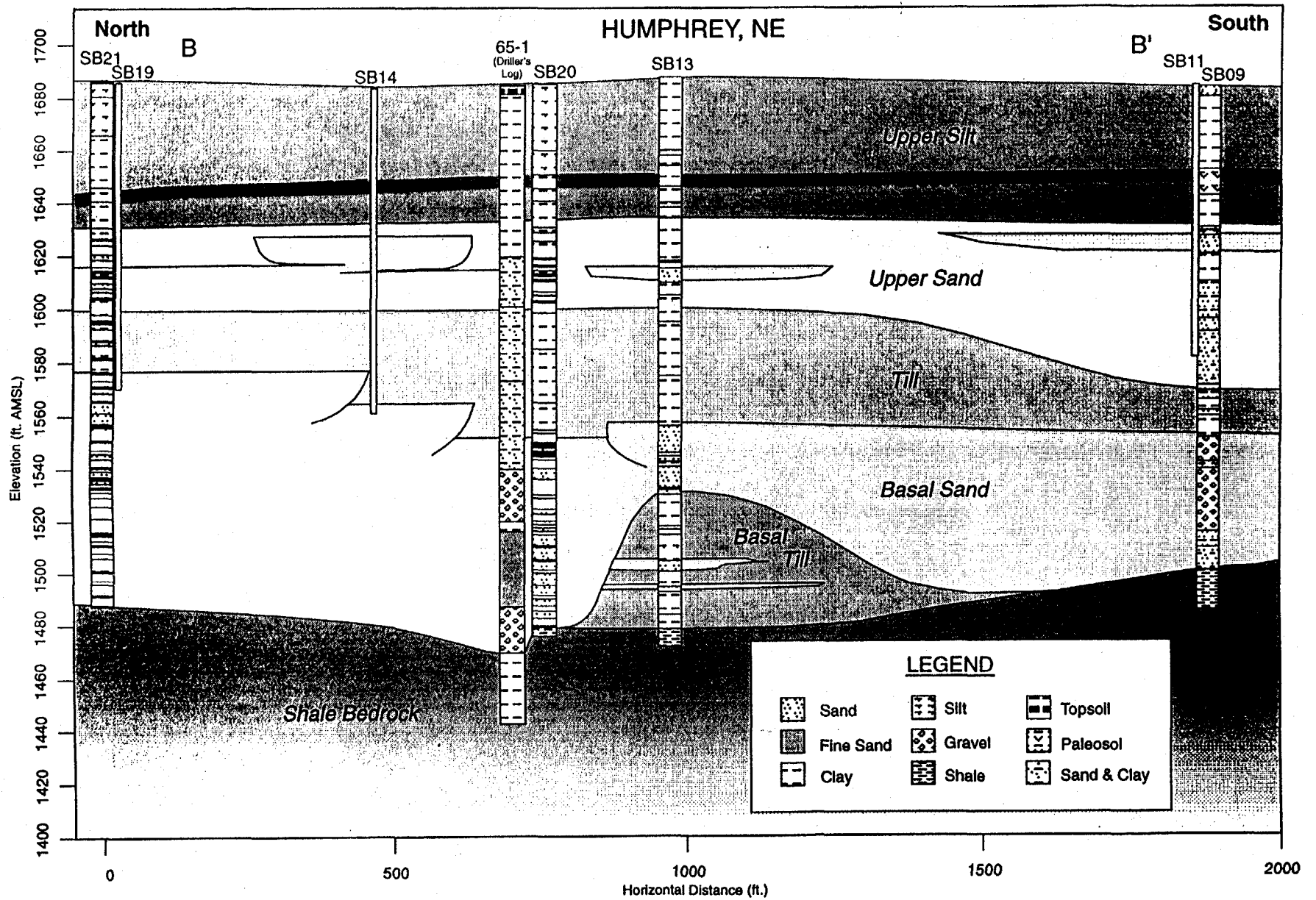


**FIGURE 1** Source of Carbon Tetrachloride and Chloroform in Soils and Groundwater at Former CCC/USDA Grain Storage Sites

To attain closure these sites, the vadose soil zone needs to be characterized in a way that supports a health risk calculation for the uppermost 0-6 ft of soil. Investigations of the deeper vadose zone contamination are also necessary, because this deeper zone could be a continuing source of contamination to the aquifer. This deeper zone is investigated in detail in the feasibility phase of the ESC.

Sites in the eastern part of Nebraska have glacial/fluvial deposits ranging in thickness from 75 ft to 300 ft (Figure 2). The drinking water aquifers at many of these sites lie within the unconsolidated deposits at depths of approximately 30-180 ft below the ground surface (BGS). To characterize the vadose zone by using continuously cored borings or continuous split-spoon sampling with the cone penetrometer is very costly. For a site measuring 300 ft square, the cost of detailed investigation of the vadose zone can be as high as \$750,000.

Testing has shown that the ground beneath the former locations of the CCC/USDA's circular bins has little to no contamination, whereas the ground beneath and around the former storage sheds and certain Quonset huts contains the bulk of the vadose zone contamination. In our attempts to find a high-quality method for reducing the amount of vadose zone profile sampling of the aquifer, we tested a number of techniques, particularly sampling of near-surface soils. One major disadvantage of soil sampling is the variability of the soil profile, which makes a uniform soil type hard to find over an entire site. Organic-rich soil samples, where present, have provided the most uniform near-surface soil sampling medium that indicates where contaminant concentrations exist in the deeper vadose formations. Unfortunately, coverage of a site with sampling of a uniform soil type has proved feasible in only a few cases. Generally, however, grass coverage is excellent, and at some sites tree coverage, although sparse, is also uniform.



**FIGURE 2** Geologic Cross Section B-B' at Humphrey, Nebraska

Our initial experimentation with vegetation sampling was carried out at the Illinois State Hazardous Waste Research Laboratory, Champaign, Illinois. Young alder trees were fed a nutrient spiked with carbon tetrachloride. Various types of samples from the alder trees were analyzed by using purge-and-trap extraction followed by gas chromatography (GC) and electron capture detection (ECD) or mass spectrometric (MS) determination of carbon tetrachloride. The experiments showed that carbon tetrachloride could be detected in the living tissue and sap of the tree, but no accumulation was apparent in any specific part of the tree. With this positive result and because of the numerous field areas available for testing the approach, field research was initiated to collect field data and focus the laboratory research on the field problem. A number of former CCC/USDA grain storage facilities have been tested to date. Results for two of these — York and Humphrey — are used here to illustrate the integration of vegetation sampling and analysis into the ESC process.

## RESULTS

### York, Nebraska

The town of York, Nebraska, has a population of 9,000 and is located on Interstate Highway 80 some 50 miles west of Lincoln (Figure 3). The former CCC/USDA grain storage

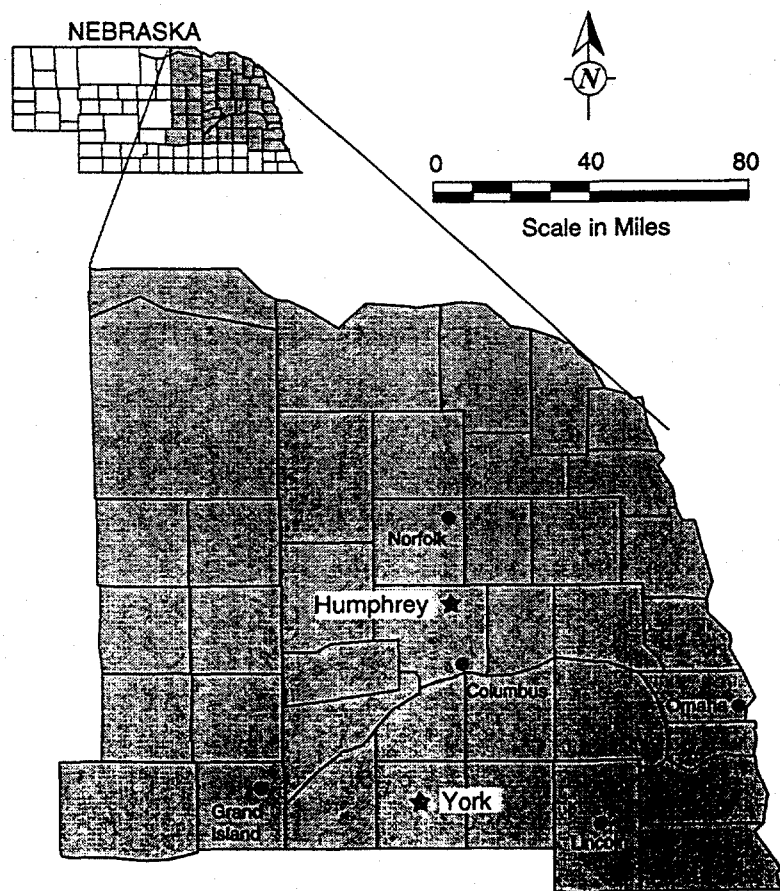


FIGURE 3 Locations of York and Humphrey, Nebraska

facility, at the northwest corner of the town, measures 200 ft by 850 ft (Figure 4). The present site (Figure 5) still has all of the original Quonset huts but no circular bins and no storage sheds. The site is well covered with grass, and the soil profile is very uniform. No trees occur on the actual site, but a number of tree species are found near the site.

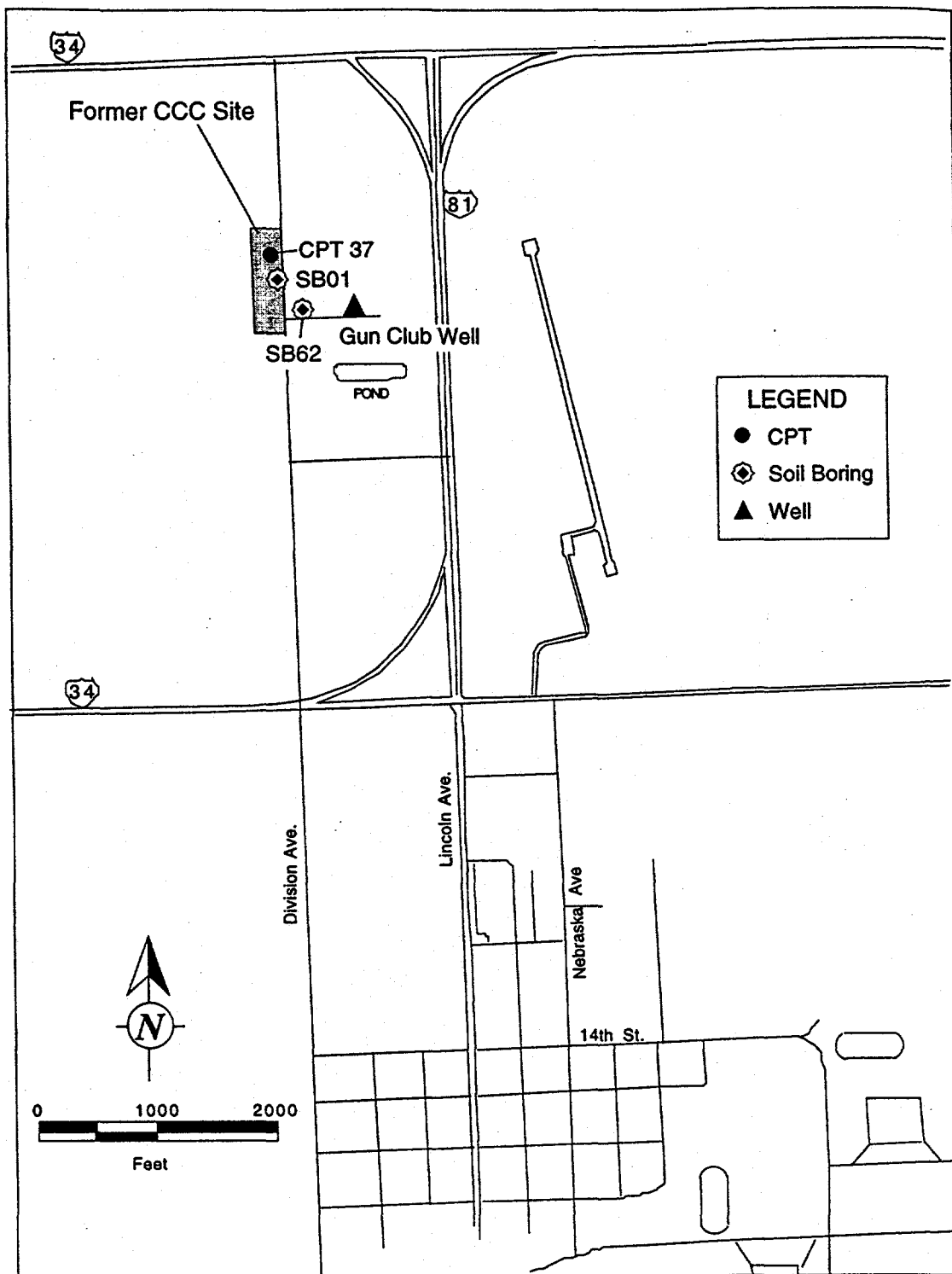
Initially, 19 vegetation samples were collected on or near the site, representing 11 plant species (4 trees and 7 herbs) and 6 different plant tissues. The purpose was to investigate the potential use of vegetation to identify subsurface soil contamination. Analyses of three grass species at four locations on the site gave carbon tetrachloride concentrations well above the detection limit (Figure 5). Samples collected outside the site (at the local Gun Club) from knotwood and Chinese elm trees had the highest contaminant concentrations. This discovery created a dilemma, because the Gun Club site should contain no carbon tetrachloride. However, further investigation revealed that the Gun Club used contaminated groundwater for irrigation. Although knotwood and Chinese elm appear to be particularly good indicators of soil contamination and are common in Nebraska, they are not present on most of the former CCC/USDA sites. The presence of carbon tetrachloride in the grasses, particularly foxtail, at these sites was most important, because most of the sites, including the York site, have a uniform distribution of grasses.

A 50-ft-square grid was laid out, and two sets of samples were collected at each grid corner if possible. One of the samples was foxtail grass, and the other sample was organic-rich soil of the A-1 soil horizon. This particular soil type, found throughout the York site, has been used traditionally as a soil sample for detection of contamination with chlorinated hydrocarbons. Analytical data for the A-1 samples were used as a control on the distribution of carbon tetrachloride in the near-subsurface soils at the site. Figure 6 compares the results for two sets of A-1 soil samples preserved on dry ice and in methanol, respectively, and for foxtail grass samples. Concentrations above 2 ppb and 20 ppb, respectively, for soil and 0.5 ppb for the grass identified the same areas of contamination in the near subsurface.

Two borings, SB01 and SB37, were drilled and sampled continuously from the ground surface to the aquifer. These two sampling locations, shown in Figure 5, coincide with the high concentrations of carbon tetrachloride in the grass. Figure 7 shows the profile of carbon tetrachloride and chloroform concentrations at each location. The concentration levels of greatest concern occurred in SB01, starting at approximately 18 ft BGS and continuing to approximately 63 ft BGS. At SB37, contaminant values were much lower, but the higher concentrations started at approximately the same depth. Integration with the geology showed that the depth zone at 18-29 ft BGS is part of a paleosurface with increased clay, organic material, and iron/manganese oxide contents, developed during exposure to oxidation and weathering. In eastern Nebraska, this finding has become a major clue in identifying one of the most favorable geologic units in the vadose zone for concentration of contaminants.

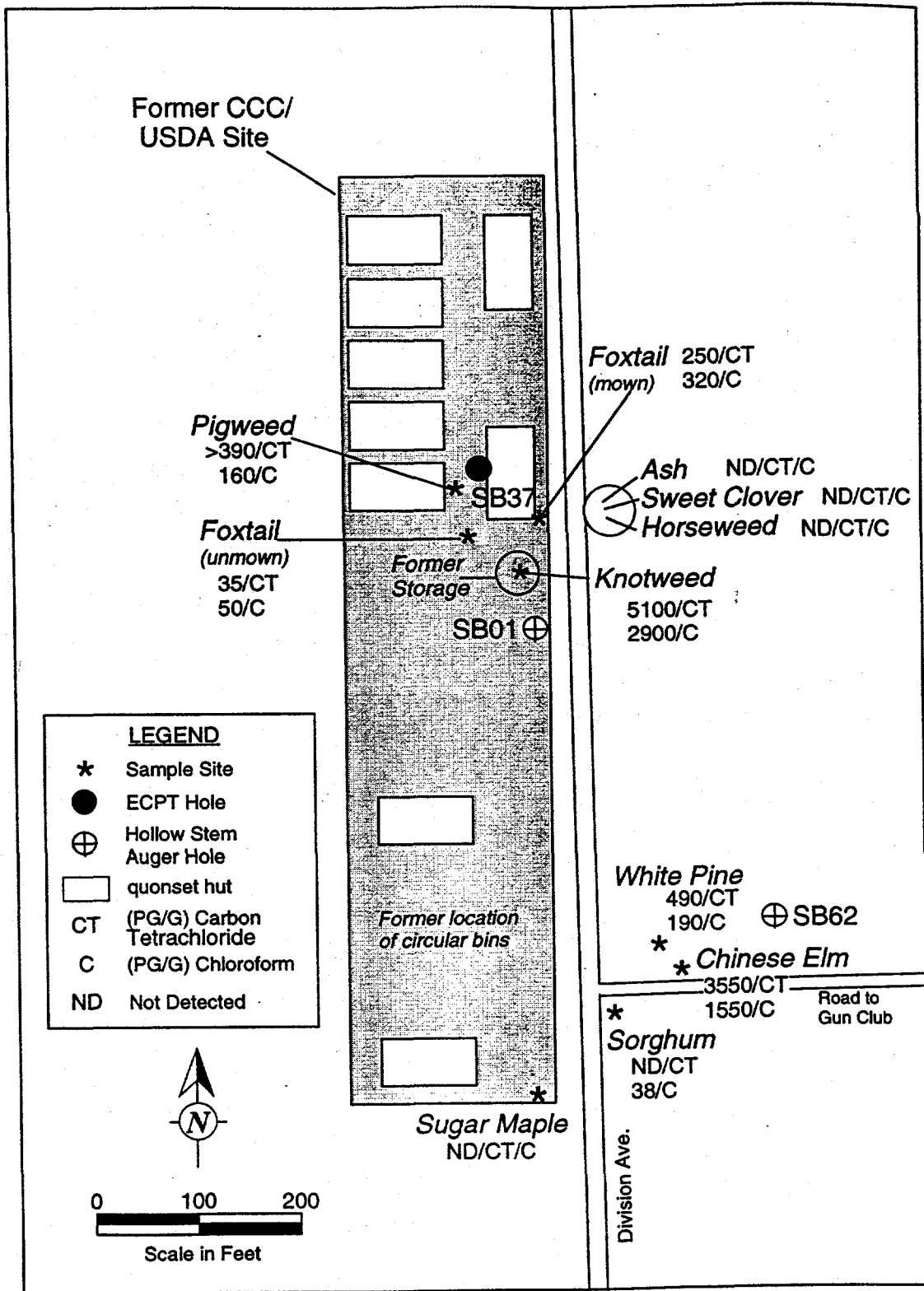
### **Humphrey, Nebraska**

The town of Humphrey, Nebraska, has a population of 750 and is located 100 miles northwest of Lincoln on State Highway 81 (Figure 1). The former CCC/USDA grain storage facility lies on the southern boundary of the residential community; it was leased from 1957 to 1972 from a local farmer who still owns the property. Figure 8 is a 1964 air photo showing all of



**FIGURE 4** Locations of Soil Borings Used for Vadose Zone Soil Sampling at York

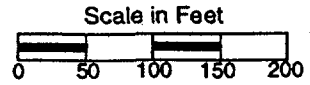




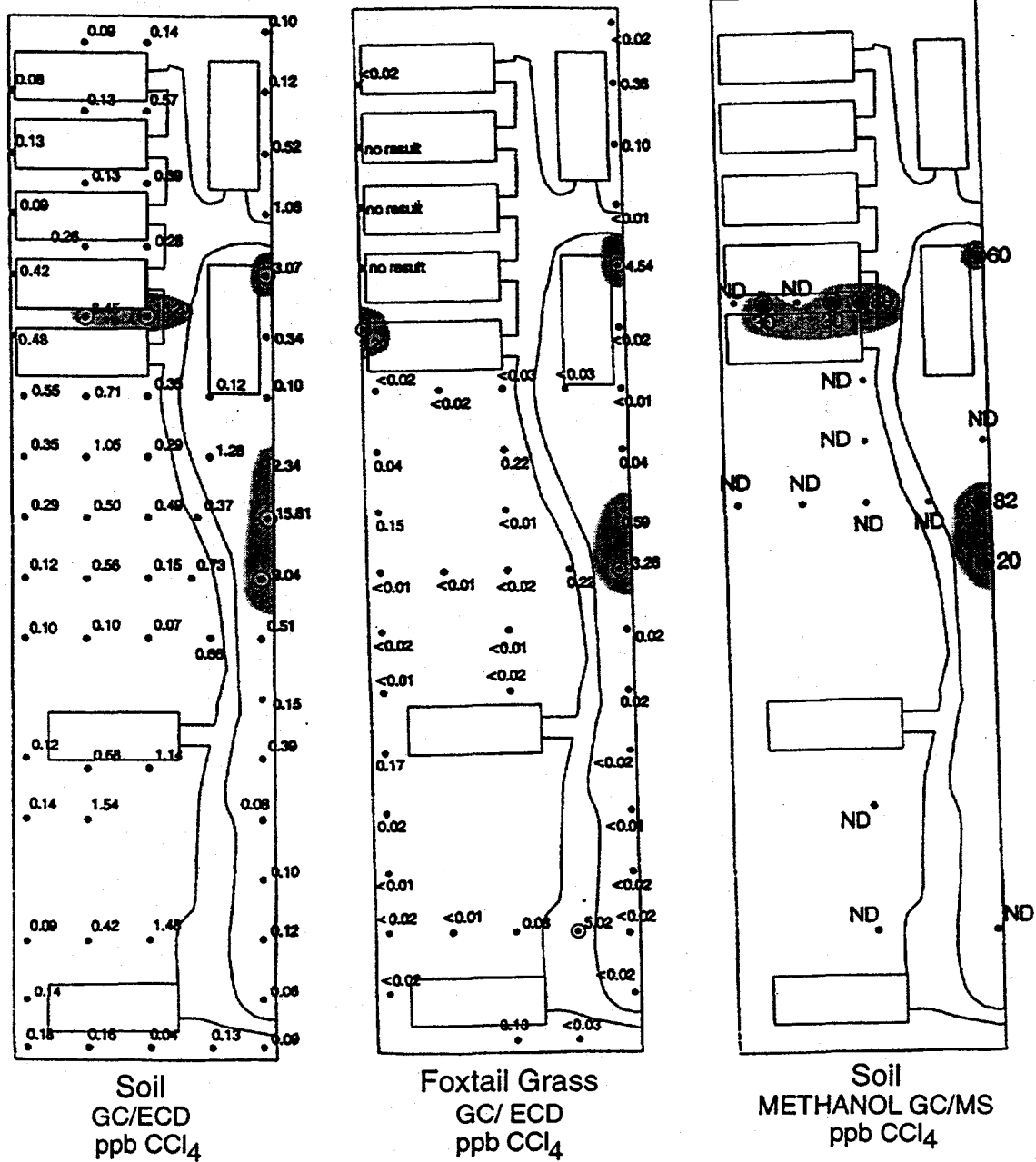
**FIGURE 5** Distribution of Carbon Tetrachloride and Chloroform in Various Plant Species at York

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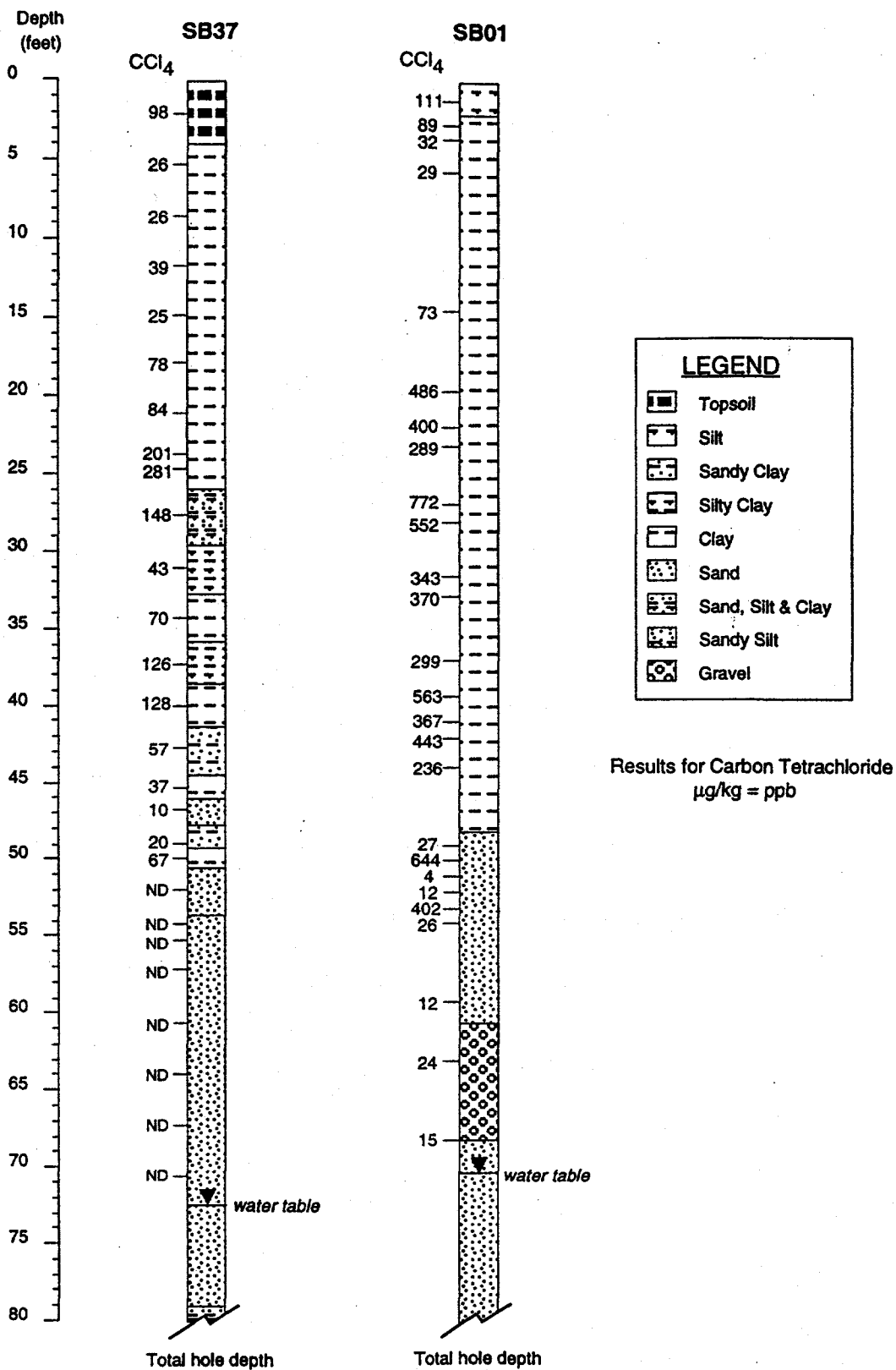
- <0.01 = not detected above quantitative limit
- ND = non detect
- = high concentration of carbon tetrachloride



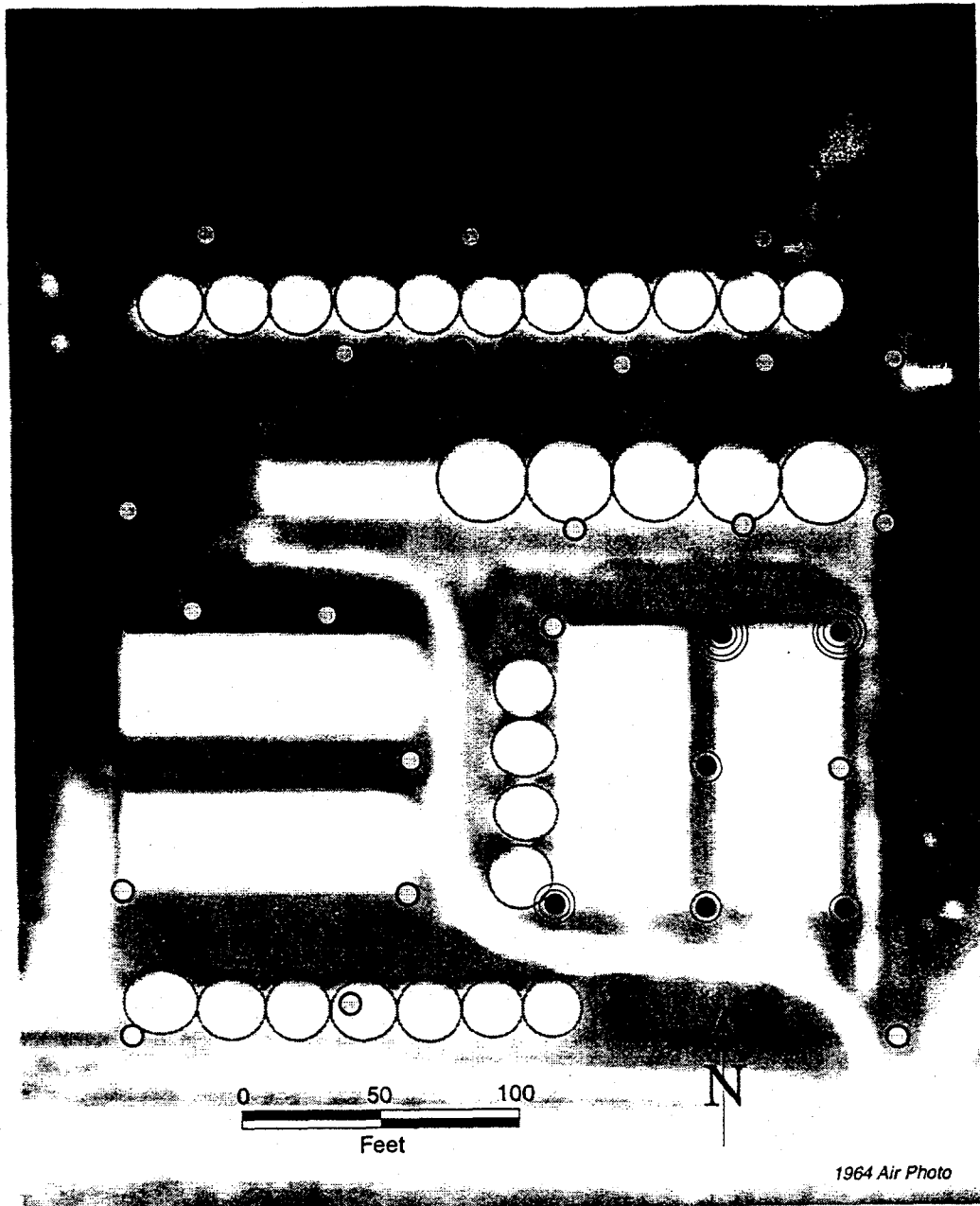
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**FIGURE 6** Carbon Tetrachloride Concentration Patterns in Soil and Vegetation at York



**FIGURE 7** Vertical Distribution of Carbon Tetrachloride Concentrations in SB01 and SB37 at York



1964 Air Photo

LEGEND			
●	< 0.1 ppb	⊙	≥ 1.0 ppb
○	Not detected	⊖	≥ 0.1 ppb

**FIGURE 8** Locations of Vegetation Samples at the Former CCC/USDA Site at Humphrey and Distribution of Carbon Tetrachloride in Those Samples

the circular bins and Quonset huts in the former CCC/USDA facility. The site measures 300 ft by 300 ft square. Grass covers the entire site, apart from the gravel tracks around the Quonset huts. The soil profile across this site was highly variable, and collecting a uniform coverage of organic-rich (A-1) soil samples was impossible. A total of 51 grass samples were collected on a 50-ft square grid and analyzed for carbon tetrachloride. The sample locations and the distribution of carbon tetrachloride are shown in Figure 8. The highest carbon tetrachloride concentrations were found near the Quonset huts in the southeast portion of the site. Only one sample from the northern portion of the site contained a detectable concentration of the contaminant. Groundwater sampling at this site also indicated that the highest contaminant concentrations were in the southeastern part of the site. Low concentrations were found in groundwater samples collected in the northern part of the site. The groundwater data alone, however, did not rule out a soil source that had not yet reached the aquifer.

Two borings were located to test the vadose zone contaminant profile. Samples were collected from continuous cores drilled at locations SB28 in the northern part of the site and SB32 in the area of high concentrations of carbon tetrachloride in grass (Figure 8). Figure 9 shows the major lithologic units of the stratigraphic sequence at these soil borings and the corresponding concentrations of carbon tetrachloride and chloroform at the sampled depths. The higher concentrations of carbon tetrachloride in SB32 than in SB28 correlate well with the higher concentrations found in the grass samples near SB32. Concentrations of carbon tetrachloride up to 2,600 ppb were found at 44 ft BGS in SB32, again in a iron/manganese-rich clay unit associated with a paleosol similar to that at York. The results from SB32 indicate that a source of carbon tetrachloride remains in the vadose zone at this location. The general decrease in contaminant concentration with greater depth in the lower part of the soil boring suggests that although downward migration is transporting carbon tetrachloride to the aquifer, a high concentration of contaminant is retained in the paleosol. The results from SB28 suggest that no major source of soil contamination is present at this location and confirm the low concentrations found in the grasses and the aquifer in the northern part of the site.

## CONCLUSION

Vegetation is an excellent sampling medium for carbon tetrachloride detection in the Nebraska environment. Vegetation provides uniform sample coverage of a site, and the analytical techniques used have a detection limit of less than 0.5 ppb with a precision of  $\pm 10\%$ . Combining the results of grass analysis with groundwater analytical data provides the initial step in the characterization of the vadose zone and identifies the areas where concentrations of contaminants are most likely to remain in the deeper subsurface (vertically beneath the high concentrations found in the vegetation). Although carbon tetrachloride can be present at all levels in the vadose zone profile, present data indicate that it will be concentrated in the surface grass/organic materials, in units rich in iron/manganese oxides, and in clays or clay-sized silica. This information helps to focus the more detailed feasibility studies on areas of greater subsurface soil contamination.

## ACKNOWLEDGMENT

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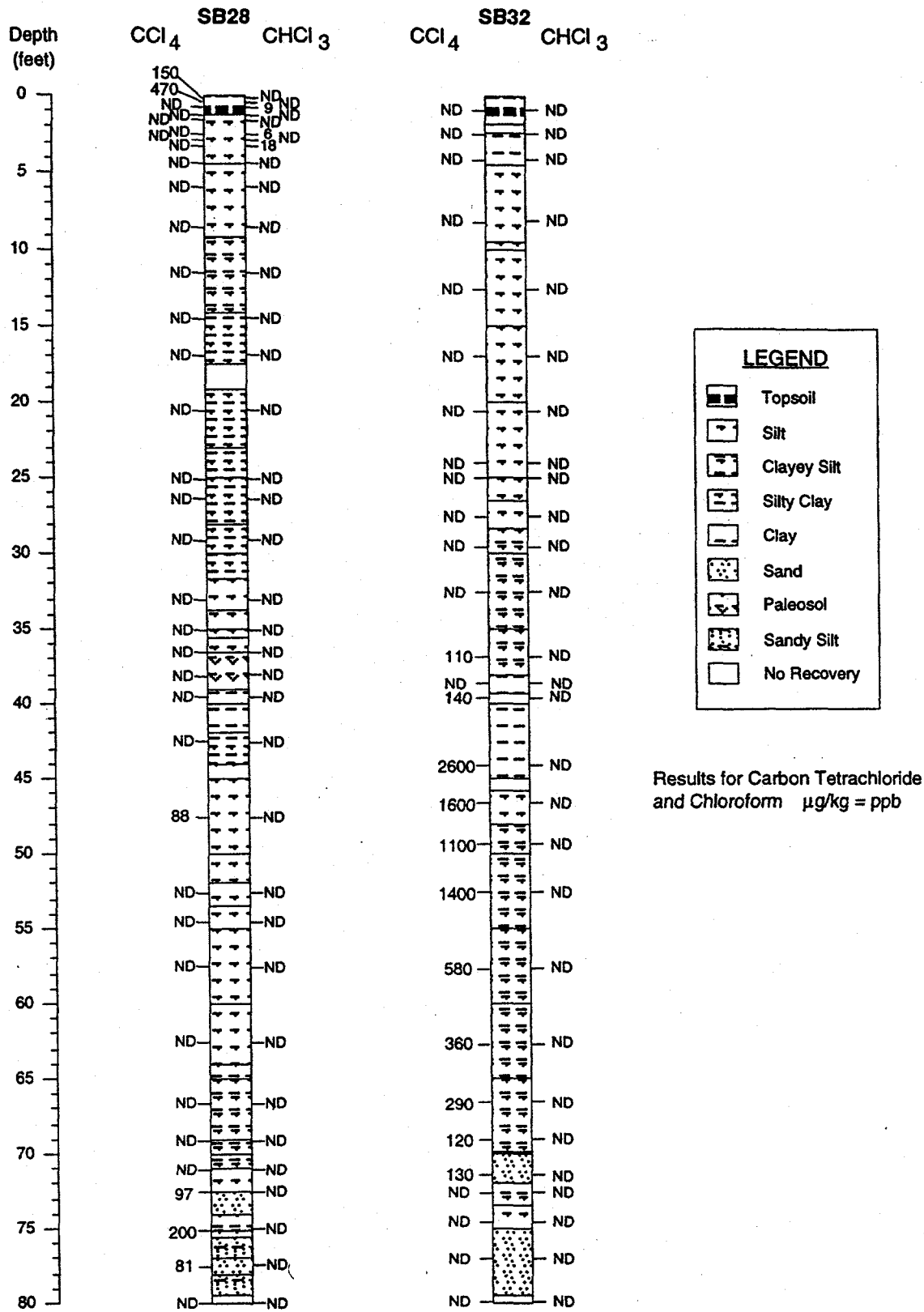


FIGURE 9 Vertical Distribution of Carbon Tetrachloride and Chloroform Concentrations in SB28 and SB32 at Humphrey