D-Area Oil Seepage Basin Bio-Venting Optimisim Test Plan

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DISCLAIMER

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1.0 Summary

The D Area Oil Seepage Basin (DOSB) was used from 1952 to 1975 for disposal of petroleum-based products (waste oils), general office and cafeteria waste, and apparently some solvents [trichloroethylene (TCE)/tetrachloroethylene (PCE)]. Numerous analytical results have indicated the presence of TCE and its degradation product vinyl chloride in groundwater in and around the unit, and of petroleum hydrocarbons in soils within the unit. The DOSB is slated for additional assessment and perhaps for environmental remediation. In situ bioremediation represents a technology of demonstrated effectiveness in the reclamation of sites contaminated with petroleum hydrocarbons and chlorinated solvents, and has been retained as an alternative for the cleanup of the DOSB. The Savannah River Site is therefore proposing to conduct a field treatability study designed to demonstrate and optimize the effectiveness of in situ microbiological biodegradative processes at the DOSB. The introduction of air and gaseous nutrients via two horizontal injection wells (bioventing) is expected to enhance biodegradation rates of petroleum components and stimulate microbial degradation of chlorinated solvents. The data gathered in this test will allow a determination of the biodegradation rates of contaminants of concern in the soil and groundwater, allow an evaluation of the feasibility of in situ bioremediation of soil and groundwater at the DOSB, and provide data necessary for the functional design criteria for the final remediation system.

2.0 History and Description of Site

The D-area Oil Seepage Basin (DOSB) is defined as the waste unit located between unimproved dirt Roads A-4.4 and A-4.5, approximately 1.6 km (1 mile) north of the coal-fired D-Area Powerhouse and approximately 3 km (1.9 mile) from the nearest SRS boundary (Fig. 1, 2). It was originally constructed in 1952 as a series of unlined trenches to dispose of waste oils and other fluids not suitable for burning in powerhouse boilers. Based on employee interviews, the DOSB waste unit was constructed as at least three separate unlined trenches, each divided by berms.

The basin received waste oil products from D Area and other areas onsite that were unacceptable for incineration in the powerhouse boilers. These waste oils included seal oil from the Heavy Water Facility, machine cutting oil, and transformer and other shop fluids. The waste oils and fluids were collected in 208-liter (55-gallon) drums, transported to the basin, opened and dumped into the trenches. No historical evidence of overflow of the basin exists. These waste oils were periodically burned along with general office and cafeteria waste. This practice continued until 1973 when open burning ceased at SRS. The DOSB continued to receive waste oils until 1975 when the basin was removed from service and

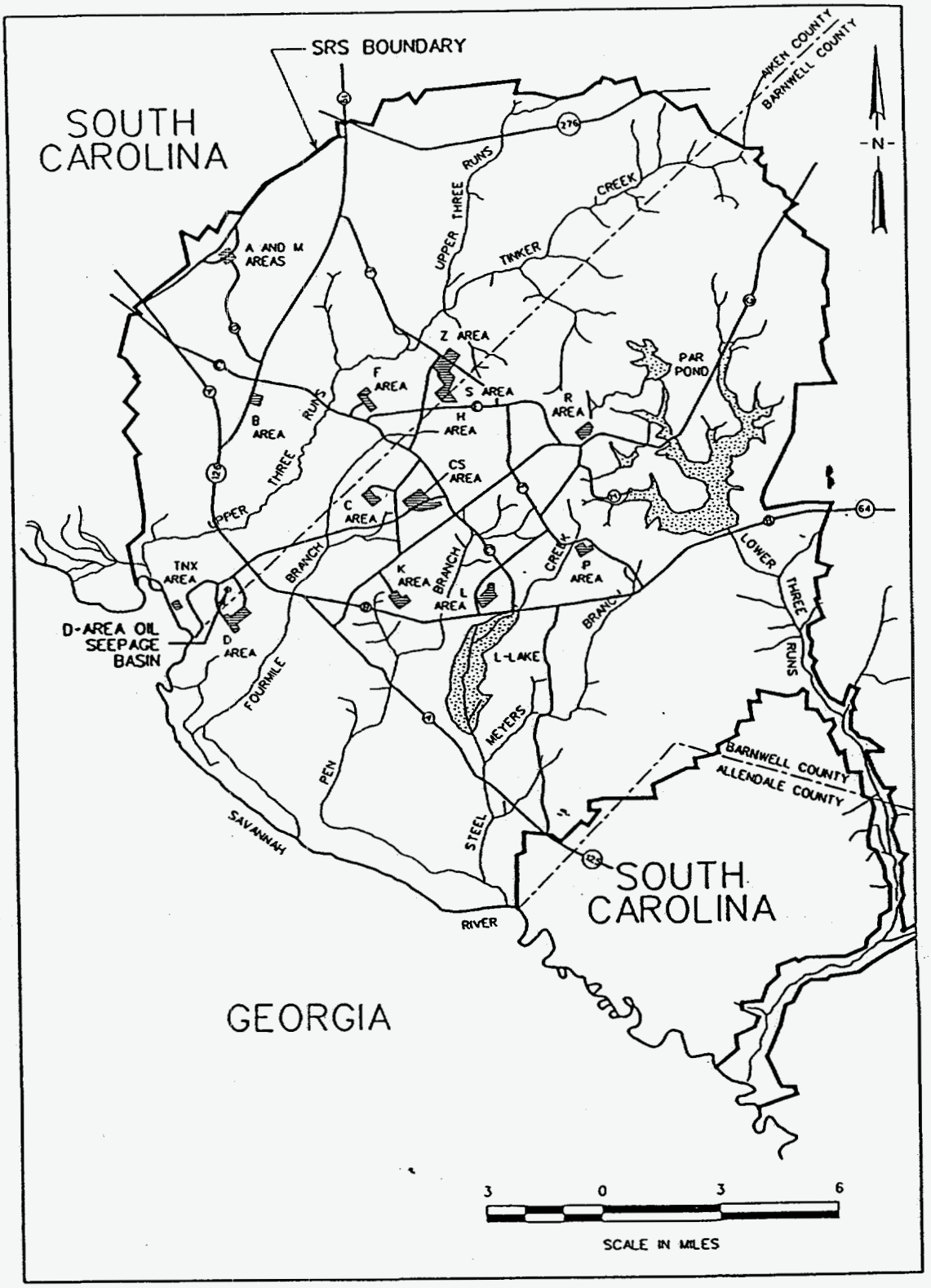

Figure 1. Location of D Area in Relation to Savannah River Site

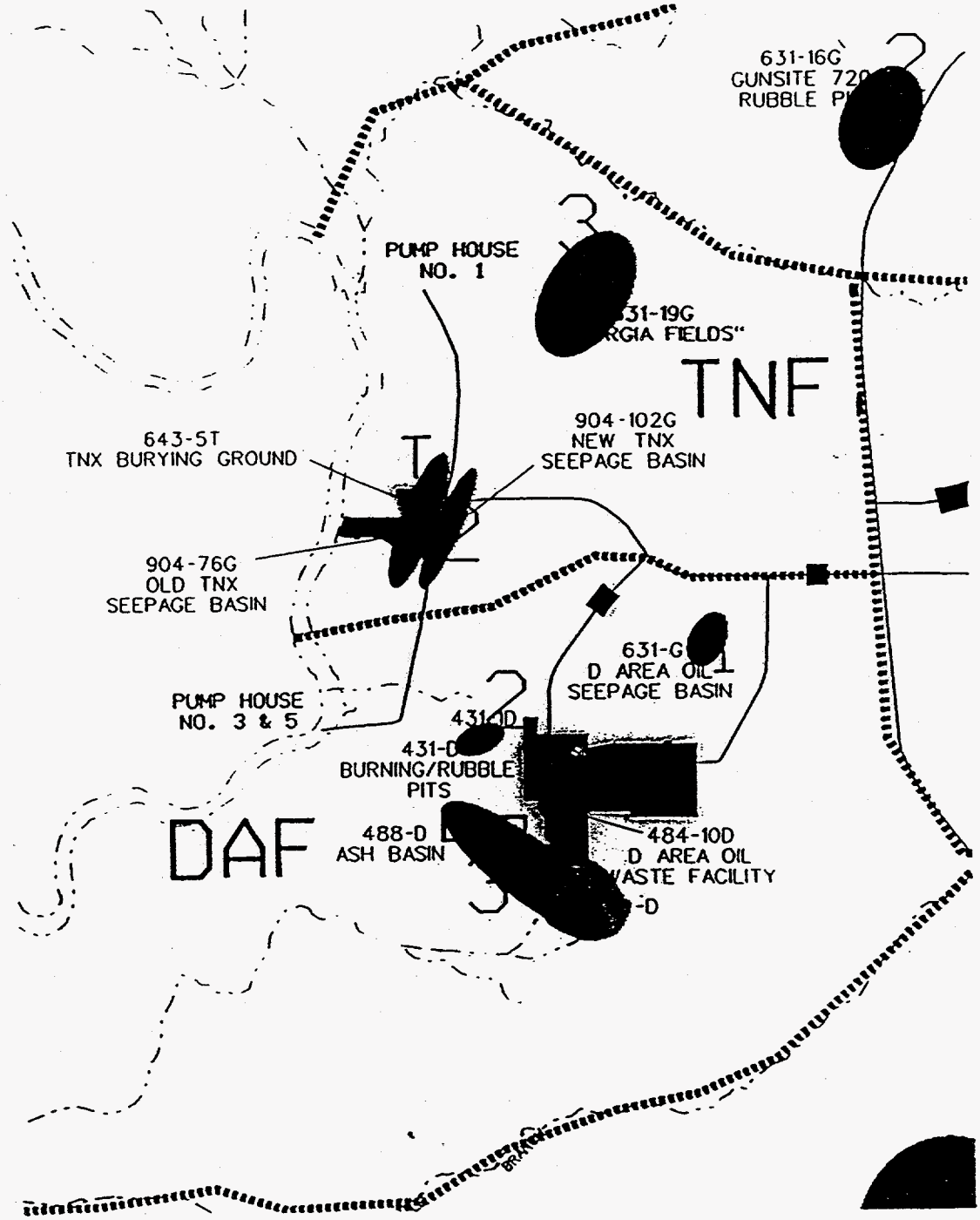

Figure 2. Location of DOSB in Relation to D Area

backfilled with soil. Approximately 0.3 m (1 ft) of standing liquid and debris, plus a number of 208-liter (55-gallon) drums, some containing waste oil, remained in the basin. Suspect drums and other material were detected in the basin through Ground Penetrating Radar (GPR) and magnetometer studies.

Results of groundwater quality monitoring in the areas of the DOSB indicated the presence of trichloroethylene, tetrachloroethylene, and vinyl chloride. However, the data from the four unit-specific monitoring wells installed in 1983 and 1984 was inconclusive and contradictory. As part of unit screening activities in 1988, boreholes were drilled through the basin fill to the water table. Debris was encountered during this drilling activity and a drum was punctured. Liquid from the drum was removed and analyzed. High concentrations of acetone, methylene chloride, 4-methyl-2-pentatone, alkyl benzenes, trichloroethylene, and tetrachloroethylene were found in the drum sample. The primary contaminants detected in soils collected from beneath the DOSB waste unit in 1988 were metals, volatile organic compounds, and semi-volatile organic compounds. Polynuclear aromatic hydrocarbons (PAHs), alkyl benzenes, phthalate, lead, chromium, and antimony were found in moderate concentrations in the soils.

In 1993, a limited scope sampling event was conducted in the basin to confirm the presence or absence of dioxins and furans. The data generated was also used to further delineate the horizontal and vertical extent of contamination detected during the 1988 unit screening. Samples collected in this program were analyzed for radionuclides, metals, and organic compounds. A wide variety of organic and inorganic compounds were detected in the basin soils. Organic compounds detected included pesticides, polychlorinated biphenyls (PCBs), and the congeners di-benzo-p-dioxin and di-benzo-p-furan. Also identified were fractions of oil and oil compounds including benzene, toluene, ethylbenzene, xylene, and naphthalene. In one borehole, a bailed groundwater sample produced a film of free product floating on the surface.

Under the requirements of CERCLA and the FFA, the DOSB is slated for additional assessment and perhaps, environmental remediation. SRS therefore proposed a phased approach, using SAFER (Streamlined Approach for Environmental Restoration) methodology, for investigative activities and unit actions. The SAFER methodology was developed by DOE in response to an identified need for streamlining the remediation process (EPA, 1989b). A Phase I investigation was conducted in June 1995 and involved the characterization of surface soils, the establishment of site-specific background levels for soil and groundwater media, an assessment of whether wetland sediments and surface water were impacted, and an evaluation of groundwater contamination within and immediately downgradient of the unit. Results identified a number of site-specific contaminants (SSCs), which were used as target compounds to guide Phase II

characterization. These were: TCE, PCE, vinyl chloride, α-BHC, arsenic, antimony, beryllium, and manganese (the metals are considered to be probably of natural origin). Phase II was conducted during the summer of 1995. Objectives of this phase were the collection (by geoprobe) and analysis (by mobile lab) of groundwater samples from the basin, the collection of hydrogeological information in the basin vicinity, the analysis of downgradient groundwater samples for COCs (contaminants of concern), analysis of subsurface (vadose and saturated zone) soils for COCs, and limited wetland sampling. Results have not yet been received. Phase III sampling, performed in December 1995, involved the installation of eight monitoring wells and analysis of samples by a conventional lab to confirm Phase II findings.

An interim action was conducted to facilitate final remedy selection. As part of the interim remedial action, all remaining drums, large debris, and principal threat source material were removed during April, May, and June of 1996. During these activities, soils down to eight (sometimes twelve) feet below grade were excavated and sieved to remove debris. Excavated soils were exposed to the atmosphere for a period of time, then raked or pushed back into the previously excavated quadrants. Obviously contaminated soils were mainly placed in the northwestern corner of the excavation. Analytical results from soil samples collected during this operation are not yet available. During the interim action, two horizontal wells for a bioventing remediation system were also installed eight feet below average basin grade. Nine piezometers were also installed. The area is currently being graded and seeded.

Two major remaining data gaps have been identified. The first is that the extent of the leading edges of the TCE and vinyl chloride plumes have not yet been fully characterized, while the second is that activities during the interim action (excavation, sieving, and movement of basin soils) have probably altered the previously quantified contaminant baseline. To address these data needs, a Phase IV sampling plan for soil and groundwater has been proposed. It will involve 1) sampling of groundwater, using cone penetrometer technology (CPT) in a transect across the plume path, and 2) hand auger sampling in a grid pattern within the basin itself. The latter samples will be taken at three depths in each of 14 locations and analyzed for TAL/TCL (Target Analyte List/Target Compound List) components as well as petroleum hydrocarbons.

3.0 Risk Assessment Concerns and Response Actions

An initial step of the SAFER process consists of identifying probable conditions through the development of a preliminary conceptual site model. A preliminary conceptual site model was developed as part of Phase II in order to identify probable conditions that

existed at the DOSB at that time. Based on previous investigations, known unit conditions, and waste disposal records, four primary sources of contamination were identified at the unit. These sources, listed in order of apparent decreasing significance, consisted of waste oil in the former trenches/pits, waste in drums, solid burnable waste, and solid non-burnable waste. Each primary source, through one or more release mechanisms, has impacted environmental media at the unit. The media of concern are primarily the soils inside of the trench boundaries, and groundwater inside and impacted by the DOSB. Since the 1994 evaluation, the removal of drums and larger solid objects during the interim action has halted the release of contaminants from these sources. The potential hazard associated with waste oil in the trenches may have been reduced by excavation, exposure to air, and replacement of part of the contaminated soil, but must still be considered.

The most recent baseline risk assessment results indicate that minimal risks to human health are associated with constituents detected in unit soils at the DOSB. Since a certain volume of contaminated soil remained in the basin after the interim action, a potential still exists for groundwater impact. In the D Area Oil Seepage Basin Technology Scoping Package (June, 1996), the following general response actions were developed for soils at the DOSB, based on the possibility of groundwater impact.

No Further Action: A no action alternative is required by the NCP.
Institutional Controls: To be considered in conjunction with other alternatives.
In situ treatment: Retained alternatives are 1) bioremediation, 2) air sparging, 3) soil vapor extraction.
Ex situ treatment: Retained alternatives are 1) composting/landfarming, 2) thermal desorption, and 3) physical separation.
Disposal (landfill)

Based on previous site characterizations, the identification of remedial technologies for groundwater has focused on those technologies applicable to VOC's. The following general response actions were developed for groundwater at the DOSB (D Area Oil Seepage Basin Technology Scoping Package, June 1996):

No Further Action: A no action alternative is required by the NCP.
Institutional Controls: To be considered in conjunction with other alternatives.
Containment: Retained alternatives are 1) vertical barriers (slurry cut-off walls), 2) extraction wells, and 3) interceptor trenches.
In situ treatment: Retained alternatives are 1) bioremediation, 2) air sparging, 3) dual phase vapor extraction, and 3) UVB (recirculation well).

Ex situ treatment: Retained alternatives are 1) carbon adsorption, 2) air stripping, 3) chemical/UV oxidation, 4) resin adsorption, and 5) reverse osmosis.

Groundwater discharge: Retained alternatives are 1) NPDES outfall, 2) infiltration galleries, and 3) injection wells.

This test plan describes a treatability study designed to test and optimize the in situ treatment alternative for the remediation of soil and groundwater. The selected technology is that of bioremediation by means of bioventing.

4.0 Hydrogeology, Contaminants, and Plume Extent

The DOSB is in a low lying wetlands area of SRS. Water table depth varies from 4 to 14 feet. The nearest surface water feature is a Carolina bay, a natural wetland located approximately 61 m (200 ft) west of the unit. Other wetlands exist approximately 137 m (450 ft) to the south of the unit. Groundwater flows in a southerly direction towards a stream and the Savannah River at an average linear velocity of 0.07 ft/day. A potentiometric map of the water table is shown in Fig. 3, while Appendix A shows calculations used to derive average linear flow velocity. The lithology of the DOSB is variable with numerous interbedded sands and clays. A dominant clay lens seems to occur at a depth of 8 - 12 foot over most of the site. In 1991, soil at four locations (CF-01-DO through CF-04-DO, see Fig. 4) within the basin boundaries was characterized using cone penetrometer technology (CPT) and a laser-induced fluorescence (LIF) system. The cone penetrometer test is used to rapidly evaluate lithography based on tip resistance and sleeve friction. A cone is continuously advanced into the subsurface at a rate of 2 centimeters per second with a twenty ton driving force. Tip resistance and sleeve friction data are used to determine the underground lithography. The LIF probe can be combined with the CPT to obtain a real-time qualitative assessment of aromatic hydrocarbon contamination. Figs 5 - 8 show CPT-based soil classification data and fluorescence intensity data obtained at the sampling sites shown in Fig. 4. Petroleum hydrocarbons were detected at all four locations, mainly between 3.1 and 6.1 m depth (10 - 20 ft). The maximum equivalent diesel concentration seen was approximately 1000 ppm.

During the 1993 limited scope sampling, many volatile and several semivolatile organics were detected in soil samples from the basin. However, many of these compounds were detected at extremely low concentrations and at frequencies lower than expected. PCE, toluene, xylene, TCE, and 2-methylnaphthalene were the most frequently detected volatile and semivolatile constituents at that time. More recent soil sampling data are not yet available.

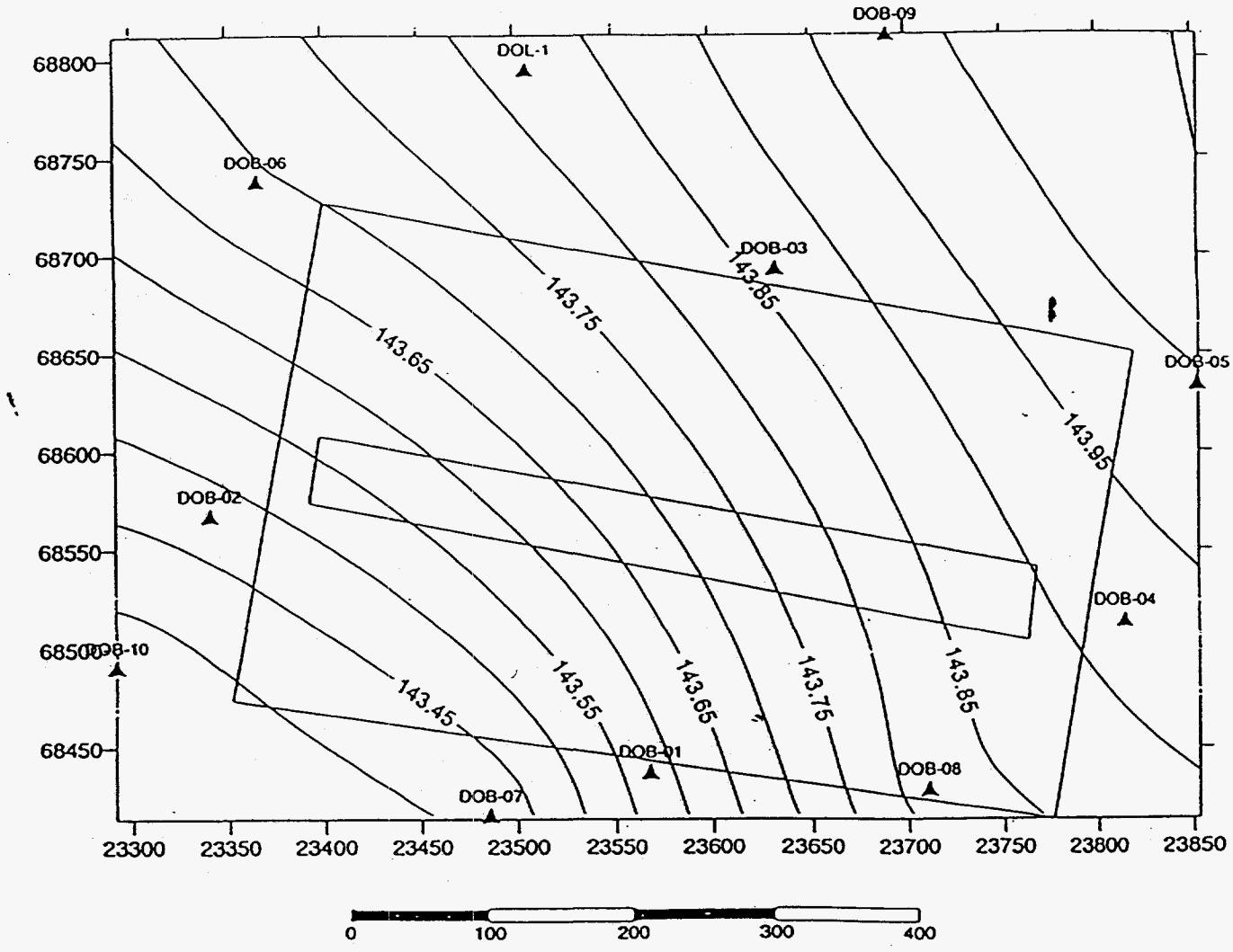

Figure 3. Potentiometric Map of the Water Table, D Area Oil Seepage Basin

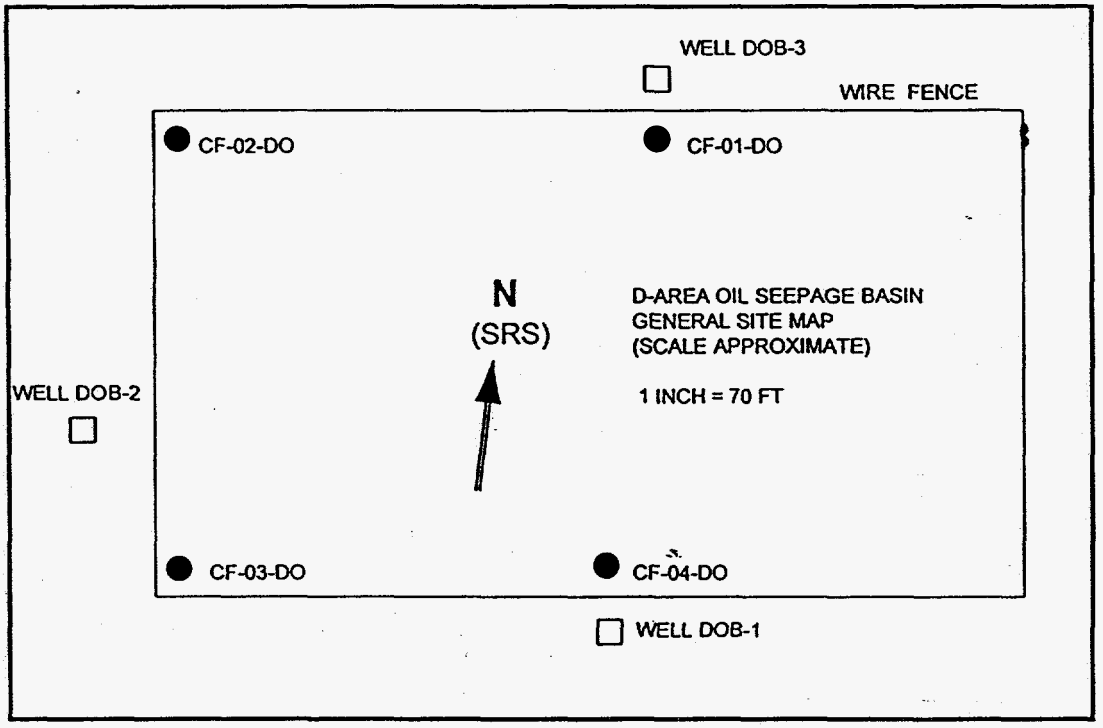

Figure 4. Locations of CPT/LIF Measurements Performed in 1991

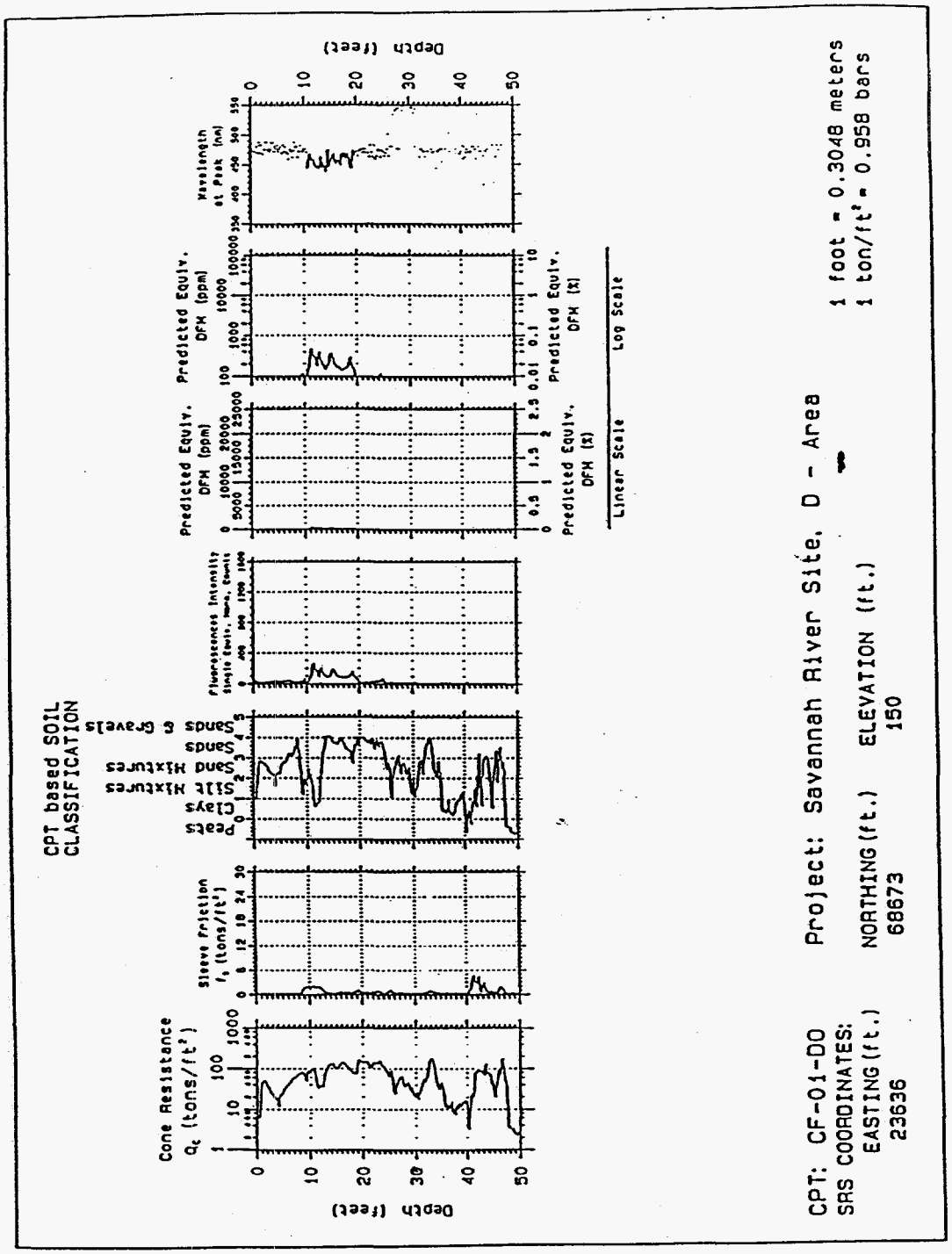

Figure 5. CPT-based soil classification data and fluorescence intensity data obtained at location CF-01-DO (Fig. 4)

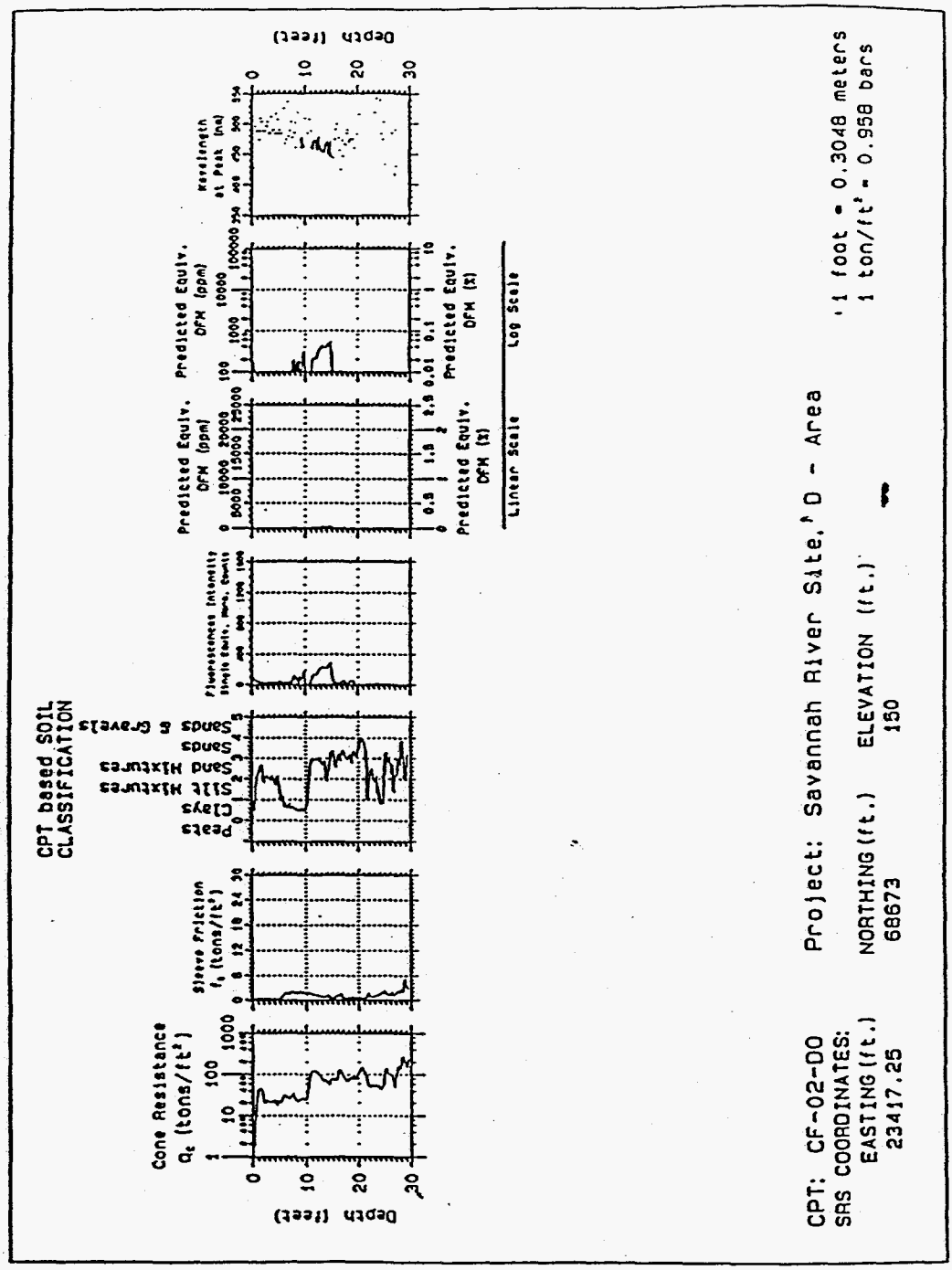

Figure 6. CPT-based soil classification data and fluorescence intensity data obtained at location CF-02-DO (Fig. 4)

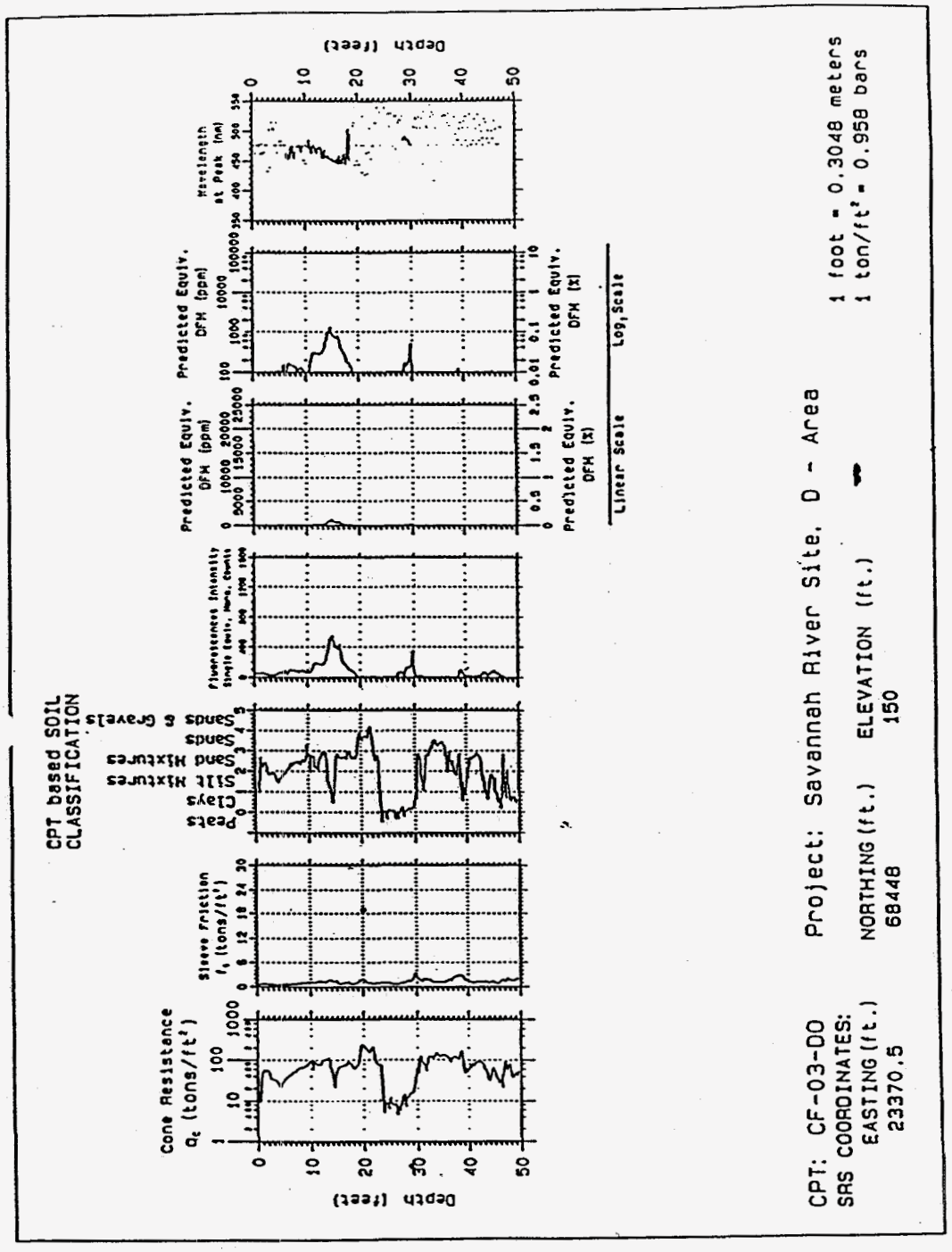

Figure 7. CPT-based soil classification data and fluorescence intensity data obtained at location CF-03-DO (Fig. 4)

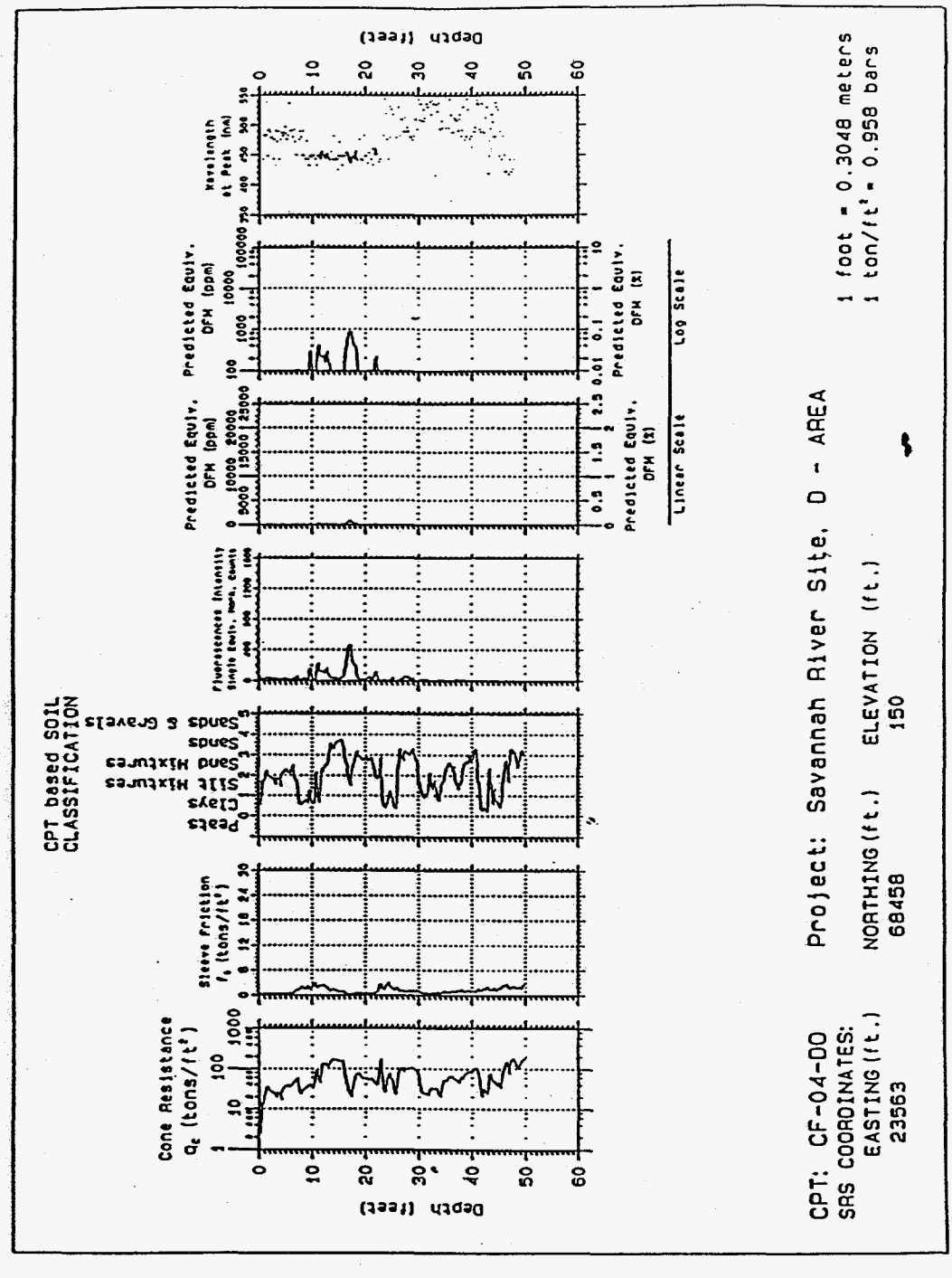

Figure 8. CPT-based soil classification data and fluorescence intensity data obtained at location CF-04-DO (Fig. 4)

The TCE and vinyl chloride groundwater plumes were partially characterized during 1995, using CPT and groundwater monitoring wells. Plume maps are shown in Figs. 9 - 10. Both the TCE and the vinyl chloride plumes extend in a southerly direction from the unit and their leading edges are not yet completely characterized.

5.0 Bioremediation: General Background

Biodegradation of petroleum hydrocarbons by indigenous soil microorganisms is a proven remediation technology. Petroleum land farming has been used in the oil industry for decades to destroy large quantities of oil sludges (Bartha and Bossert, 1984). If adequate amounts of moisture, oxygen, and nutrients are available, complete degradation of petroleum hydrocarbons can occur. The process exploits the ability of many microorganisms (including bacteria, fungi, yeasts, and algae) to metabolize petroleum hydrocarbons to complete destruction and use the carbon substrate to generate new biomass. For example, bacteria under aerobic conditions oxygenate PAHs to form dihydrodiol, which is used in cell production. Figure 11 is an example of the bacterial oxidation pathway of naphthalene to catechol; catechol is further metabolized to CO_2 and biomass in the presence of oxygen. Naphthalene and other arenes are among the most water soluble and potentially toxic compounds of petroleum and associated products. Straight and branched chain hydrocarbons are metabolized in a similar manner; the hydrocarbons are oxygenated to an alcohol which is then converted into fatty acids for the production of energy and cellular intermediates for bacterial growth and CO_2. Indigenous microorganisms in the soil can degrade large quantities of petroleum hydrocarbons if they have water, oxygen, and an adequate supply of nutrients (usually phosphorus and/or nitrogen). Use of this technology has shown that TPH soil concentrations higher than 5000 ppm can be reduced to less than 10 ppm in 6 - 8 weeks or less, depending on ambient temperature. Clearly, biodegradation by indigenous microorganisms is an effective means of remediating petroleum contaminated soils. Furthermore, the presence of hydrocarbon degrading microbes at the Savannah River Site has been demonstrated by Fliermans et al. (1993) during operation of the Petroleum Contaminated Soil Bioremediation Facility in D-Area.

Biodegradation of volatile chlorinated hydrocarbons by anaerobic or aerobic microorganisms is also a well-known phenomenon. Anaerobic PCE/TCE degradative processes are relatively slow and frequently result in the production of other hazardous compounds, including vinyl chloride. Aerobic processes are more rapid and result in complete destruction of the contaminants by mineralization to carbon dioxide and chloride, but involve cometabolic processes and hence require the presence of a primary carbon

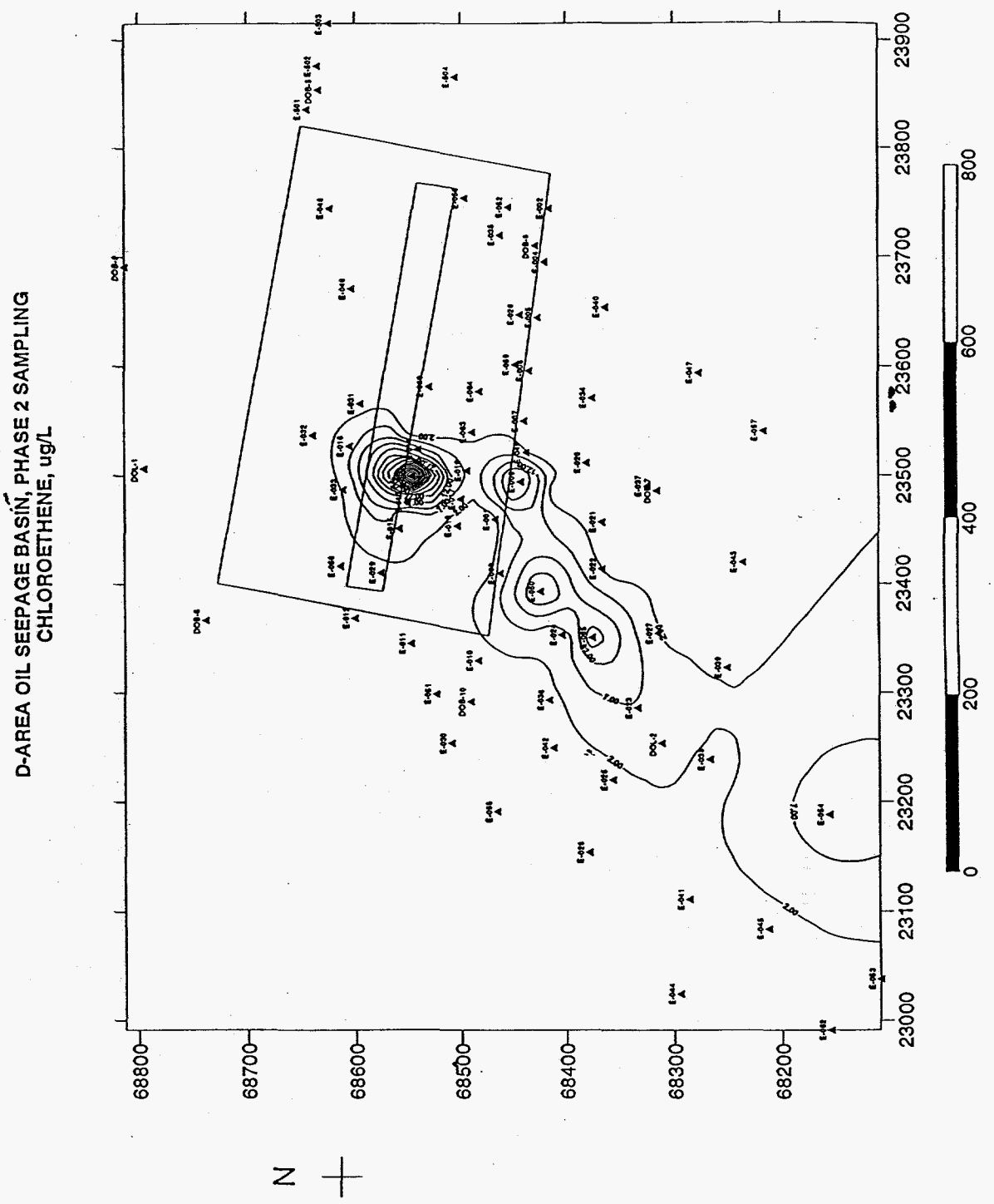

Figure 9. Vinyl Chloride (Chloroethene) Plume

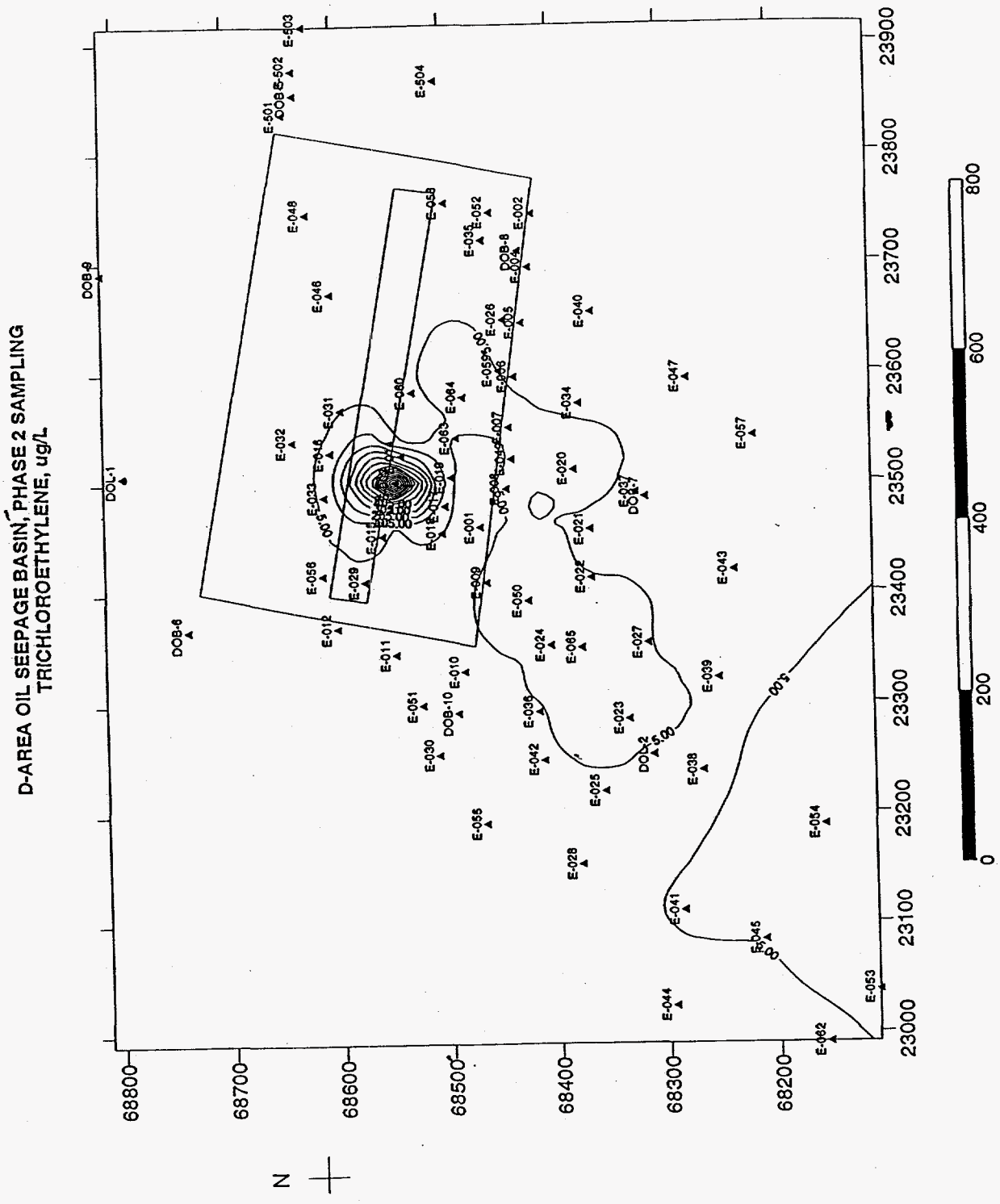

Figure 10. Trichloroethylene Plume

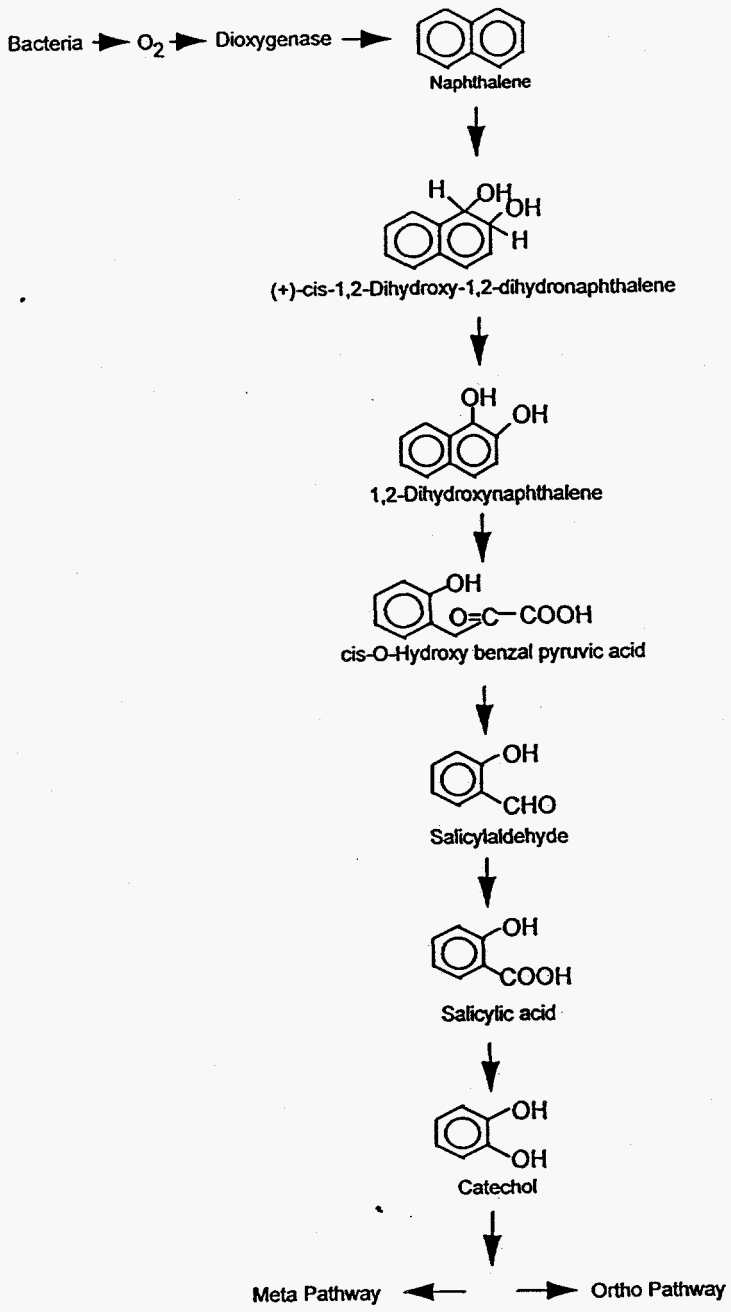

Figure 11. Pathway for microbial oxidation of naphthalene. The eventual end products are CO_2, ATP, and cell biomass when oxygen is in excess.

source as well as oxygen. Both pathways have been exploited in the bioremediation of chlorinated solvents.

The principle of bioventing is generally similar to that of land farming, except that the microbial needs are met without soil removal or land disturbance. Bioventing is a form of air exchange which increases the presence of oxygen, thereby increasing biodegradation rates. This in-situ bioremediation method has been tested at Tinker Air Force Base and Carswell Air Force Base (as well as many other sites) to remediate diesel fuel spills. Greater than 85% total hydrocarbon removal can be attributed to biological removal in properly designed and executed bioventing remediation programs (Miller, 1991).

In many cases biodegradation can be limited by nutrient availability and hence nutrient feed systems are combined with the bioventing process. The nutrients are drawn through the petroleum contaminated zone by pressure changes induced by an installed mechanical vacuum/blower. The amount of nitrogen and phosphorus required for complete degradation depends on the initial concentration of the contaminants or the amount of carbon. Nutrient loading is site and process specific and will depend on the nitrogen and phosphorous concentration in the soil and groundwater. A wide range of carbon/nitrogen/phosphorous ratios have been used in bioremediation processes. It is generally accepted that soil bacteria need a C:N:P ratio of 30:5:1 for unrestricted growth (Paul and Clark, 1989). Stimulation of soil bacteria can generally be achieved when this nutrient ratio is achieved following amendment addition. The actual injection ratio used is usually slightly higher (100:10:2), since nutrients must be bioavailable, which is much more difficult to measure and control in the terrestrial subsurface (Litchfield, 1993).

The key to any nutrient bioremediation process is to add the nutrients at the correct C/N/P ratio to promote growth of the microorganisms. The form of the nutrients (inorganic vs. organic; NH_4 vs. amino acids) is not as important as the ratio of C/N/P. A wide range of nutrients have been successfully used to enhance bioremediation. Nitrogen has been successfully introduced into the terrestrial subsurface for biostimulation using ammonia, nitrate, urea, and nitrous oxide (EPA, 1989a). Several inorganic and organic forms of phosphate have been successfully used to biostimulate contaminated environments (EPA, 1989a). It has been demonstrated at the Savannah River Technology Center and elsewhere that triethylphosphate (TEP) can be added in gas form to stimulate bioremediation (Hazen et al., 1994; Lawrence et al., 1995). Thus, nutrients can be added as a gas in the air injection wells (ie., nitrous oxide, ammonia and TEP) or in liquid form via infiltration galleries or sprinkler systems. For example, commercial fertilizers (NH_4NO_3) have been added to contaminated soil via surface irrigation in biosparging processes (Lord et al., 1995). In the case of liquid addition, nutrients are transported to the contaminated zone by percolation. Gas phase nutrient addition provides a more uniform

and direct transport of nutrients to the contaminated zone. Gaseous injection of TEP overcomes precipitation problems caused by inorganic phosphate.

The use of air and nutrient injection to stimulate the in situ degradation of chlorinated solvents (PCE , TCE and their daughter products) has been demonstrated at SRS during the course of the Integrated Demonstration Project (WSRC, 1993). Results showed that bacterial communities capable of degrading chlorinated solvents were present in the soils and could be stimulated by the injection of air and nutrients in gaseous form to degrade the solvents without producing toxic daughter products. Injection of methane as a carbon source was particularly effective in stimulating biodegradation at this site, while injection of nitrous oxide and TEP allowed rapid biodegradation to continue unhampered by nitrogen or phosphorus limitation (Fig. 12).

In-situ applications such as bioventing are rapidly becoming the accepted practice by virtue of their affordability and practicality. Removal of contaminated soils is no longer necessary unless groundwater is under immediate threat. With the development of the cone penetrometer technology, in-situ bioremediation becomes even more attractive. Benefits include tremendous savings in drilling time, characterization, well installation, decontamination, and waste reduction. The bioventing/nutrient feed alternative is a positive, cost-effective, yet environmentally sound remediation technique. It represents a low risk, and displays proper stewardship of government funding.

6.0 Test Plan Rationale and Objectives

The D-area Oil Seepage Basin was used for disposal of petroleum-based products and apparently at least some solvents (TCE/PCE). The characterization has thus far shown that much of the TCE/PCE has already been converted to vinyl chloride by anaerobic bacteria present in the soil. These findings suggest an environment that is oxygen limited and is already actively degrading the petroleum contaminants present. The introduction of air from the drum removal (source) should greatly increase the biodegradation rate of the remaining petroleum components and stimulate the co-metabolic biodegradation of the remaining chlorinated solvents. Studies at the SRS Sanitary Landfill have shown that biostimulation of the soil microbiota in high carbon environments via air injection alone can stimulate the bacteria to biodegrade all BTEX and chlorinated solvents in the groundwater and soil to below detection limits (< 2 ppb). At the SRS Integrated Demonstration Site, gaseous nutrient injection (methane, nitrous oxide, and TEP) in conjunction with air injection has been demonstrated to enhance TCE biodegradation. Thus, the focus of this test will be to determine the intrinsic rate of bioremediation at the site and the ability of the air injection to enhance the in situ biodegradation rate of the

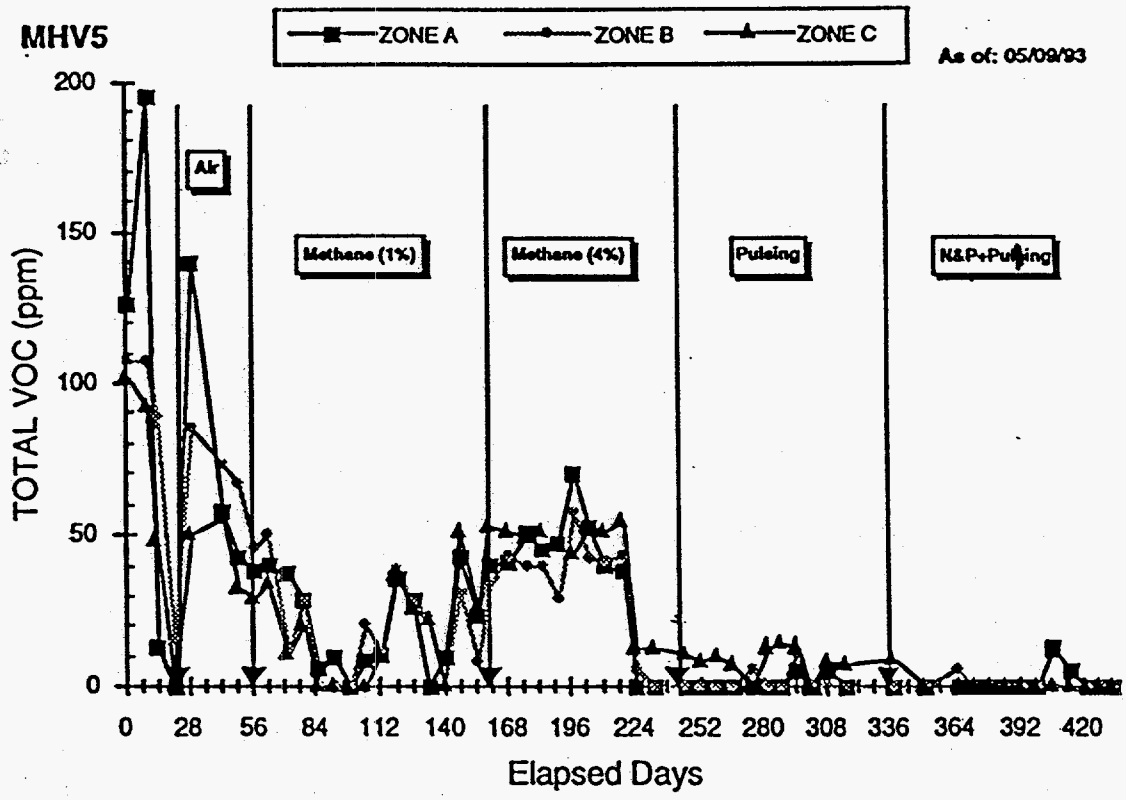

Figure 12. VOC (Volatile Organic Carbon) Degradation at the SRS Integrated Demonstration Site as a Result of Air and Nutrient Injection

contaminants of concern. Nutrients will be injected in gaseous form as needed to enhance biodegradation rates. The data gathered from this test will be used to determine the final disposition/remediation strategy for the site.

The objectives of the D-area Oil Seepage Basin test are as follows:

1. **Determine the intrinsic rate of biodegradation of organics in the soil and groundwater.**

2. **Determine the biodegradation rates of contaminants of concern in the soil and groundwater during biostimulation from air and gaseous nutrient injection.**

3. **Establish the feasibility of in situ bioremediation of groundwater and soil at the site.**

4. **Provide data necessary for the functional design criteria for the final remediation system.**

The use of in situ respirometry will play a major role in achieving these objectives. In-situ respirometry has been used to estimate hydrocarbon degradation rates in bioventing and biopile processes (Ong et al., 1991; Lawrence et al., 1994; Alleman et al., 1995; Hinchee and Ong, 1992). In an in-situ respiration test, air is injected at a known flow rate (pressure) into a vadose zone piezometer, usually over a determined test period. The injection period is determined by injecting an inert gas such as argon or nitrogen to displace all of the oxygen in the zone of influence. Then a vacuum is pulled on the piezometer and the oxygen concentration in the soil gas is measured. The time in which the oxygen concentration is close to zero represents the time in-situ respirometry tests can be conducted without oxygen diffusion and interference from outside the zone of influence. A typical in-situ respiration test performed in soil contaminated with diesel fuel is shown in Figure 13 (taken from Ong et al., 1991). Notice that the rate of oxygen consumption in the control soil (clean soil) was much lower than the contaminated soil.

A large number and variety of microorganisms are found in soil; estimates by direct microscopy range from 10^8 to 10^9 bacteria per gram of soil. Of the types of bacteria isolated from soil, many have been shown to degrade a wide range of hydrocarbons (i.e. the genus *Pseudomonas*). Many of the microorganisms found in soil and groundwater are aerobic and require oxygen to degrade hydrocarbons at a high rate (including PAHs). This is because oxygen is incorporated into the hydrocarbon by the bacteria (Figure 11). Once

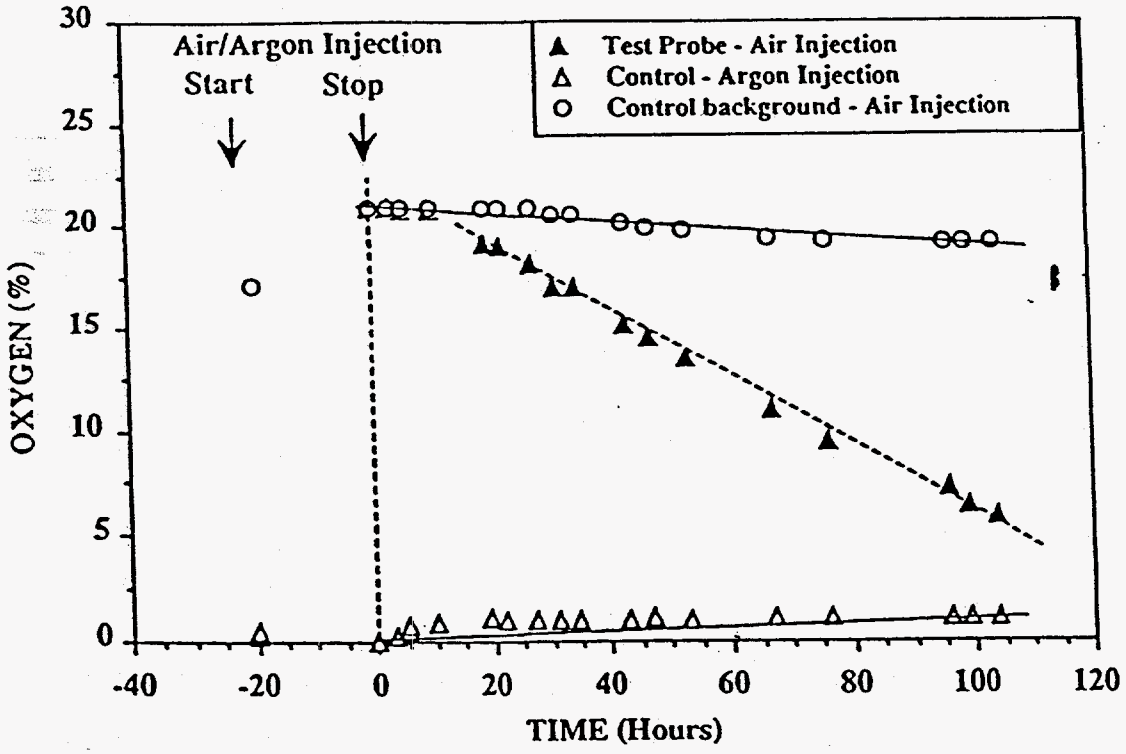

Figure 13. Example of an In-situ Respiration Test Used By Ong et al. (1991) to Estimate the Rate of Hydrocarbon Degradation in Diesel Contaminated Soil

oxygen is incorporated into the hydrocarbon, bacteria use an array of enzymatic reactions to convert the hydrocarbon into protein for cell growth. Carbon dioxide is a by-product of the oxidation process and is indicative of bacterial metabolism. The amount of oxygen needed by microorganisms to degrade hydrocarbons can be estimated by writing the oxidation equation for the hydrocarbon of interest. For example the oxidation of phenanthrene can be written as:

$$C_{14}H_{10} + 16.5O_2 \rightarrow 14\ CO_2 + 5H_2O$$

Using the equation above one can estimate the amount of hydrocarbon degraded (and potentially the rate) by measuring oxygen utilization. Although there are potential sources of abiotic loss of oxygen, such as oxidation of iron in soil, these reactions have typically been shown to be very slow due to low iron concentrations in most soils. Moreover, there are no abiotic reactions that can produce CO_2 (in soil with air and water only at ambient temperatures). Hence, measurement of oxygen consumption and carbon dioxide production is an good indicator of microbial activity and biodegradation in heterogeneous environments such as soil.

7.0 Bioventing System

Two 390-foot horizontal wells (2" diameter) at a depth of 8 feet below average grade will be used for the injections. These are designated DOB-1HW (northernmost well) and DOB-2HW (southernmost well). An as-built drawing of the site, indicating the locations of the injection wells and piezometers, is shown in Fig. 14. Fig. 15 shows a schematic of the injection system, while Fig. 16 shows details of piezometer construction and their relationship to the injection wells.

A compressor will be used to inject air and gaseous nutrients into the two horizontal wells. The maximum injection rate will be 50 standard cubic feet per minute (scfm) per well. Maximum injection pressure is estimated at 6 psig. Operation of the system will be carried out in accordance with EPA-recommended practices (EPA, 1995). Projected air emissions of volatile, semivolatile, and Standard 8 contaminants are estimated to be insignificant (Appendix B).

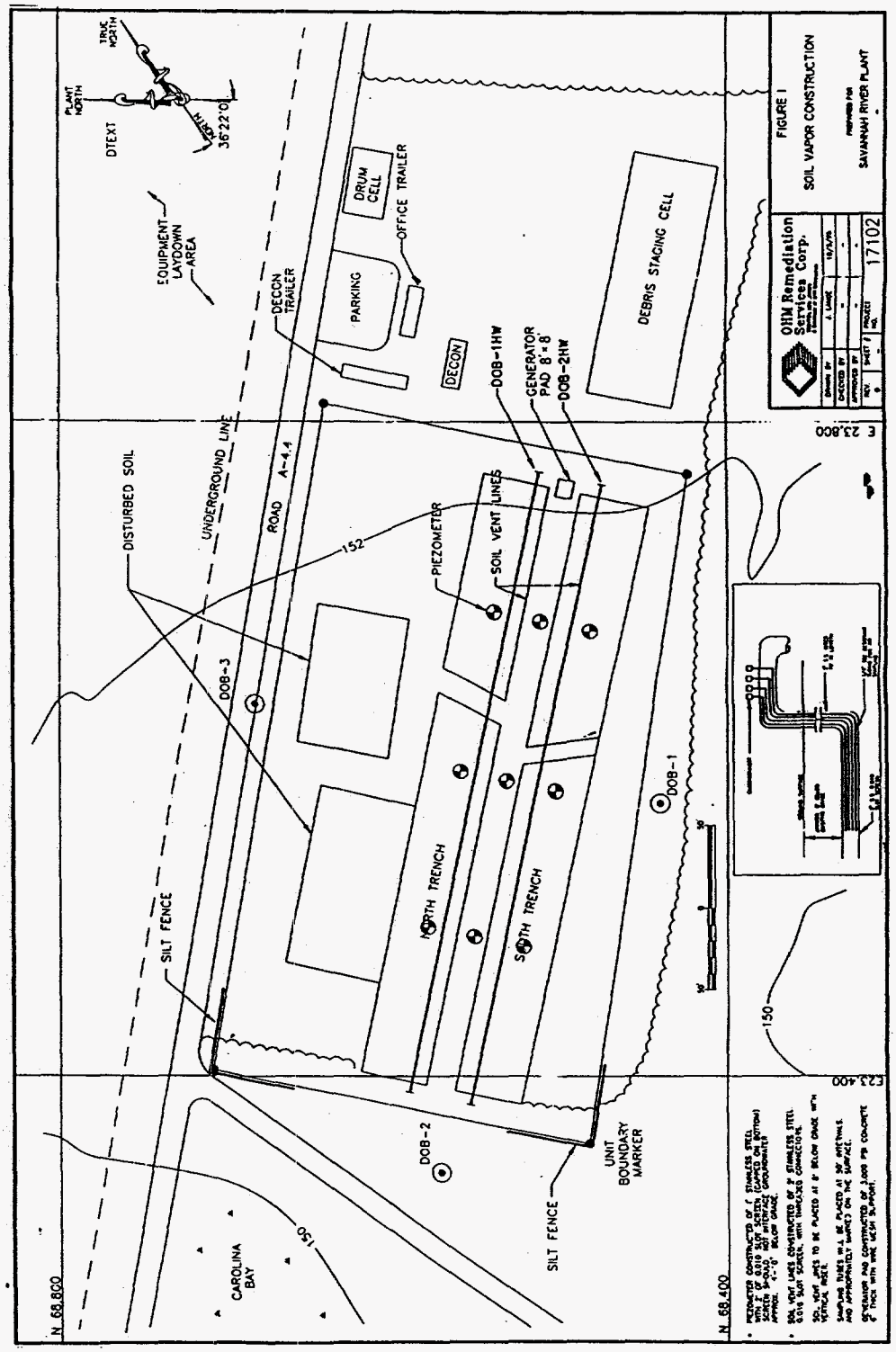

Figure 14. As-Built Drawing

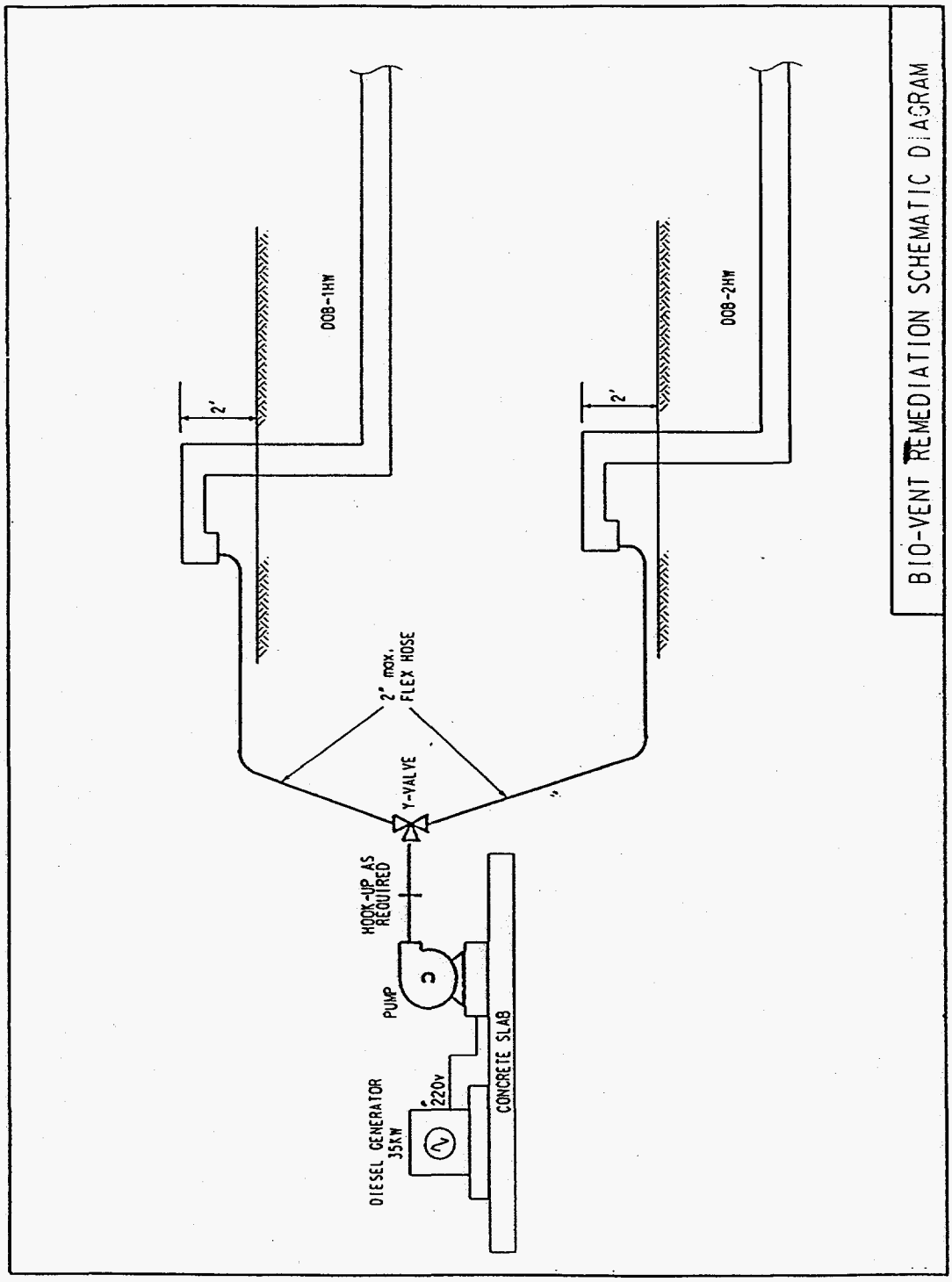

Figure 15. Schematic of Injection System

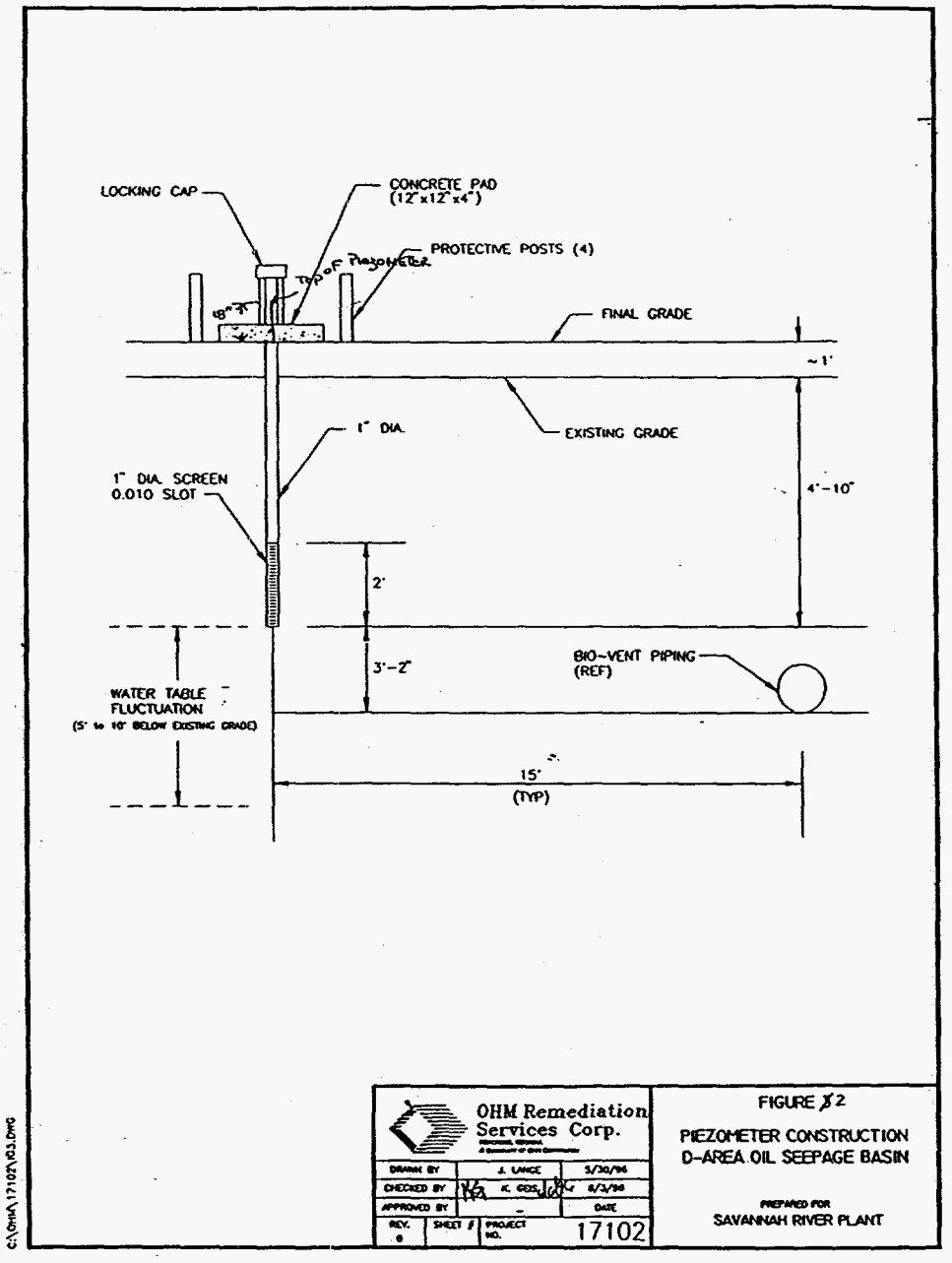

Figure 16. Piezometer Construction

8.0 Injection, Sampling and Analysis Plan

8.1 Experimental Plan

The study will be carried out in three phases. First, baseline data will be collected prior to the commencement of air injection. Next, air will be injected so that in situ respiration studies can be carried out. Lastly, the effects of air and gaseous nutrient injection (together with air injection) will be measured. The three phases and the data to be collected are described in detail below:

Phase I. Intrinsic Rate Determinations. Immediately after vadose zone well completion, soil gas will be monitored to determine the natural rates of biodegradation. These measurements will be done weekly for all 9 piezometers for 6 weeks or until regulatory approval is received for air/nutrient injection.

Phase II. In Situ Respiration and Conservative Tracer Determinations. Air and helium (maximum level 0.1% in air) will be injected until steady state is reached and then turned off and monitored until pre-injection conditions resume. This will be repeated until an accurate determination of biodegradation rates is achieved (2-4 weeks). Soil gas and groundwater (see 8.2, Sampling Locations) will be monitored for all parameters (see 8.3, Analytical Methods) before and after the injection, and will be monitored continuously for oxygen, redox potential, conductivity, pH, temperature, carbon dioxide, methane, and pressure.

Phase III. In Situ Biostimulation Using Air and Gaseous Nutrients. Air will be injected for 2 - 4 weeks or until contaminants are below detection limits. If needed, subsequent injection campaigns will involve additions of air plus nitrous oxide and triethyl phosphate (TEP), followed by air plus methane (CH_4), nitrous oxide, and TEP. Up to 0.1% nitrous oxide (in air), 0.1% methane (in air), and 4% methane (in air) will be used. Each injection campaign (maximum of 3) will be done for 2-4 weeks, depending on rapidity of environmental responses. Soil gas and groundwater groundwater (see 8.2, Sampling Locations) will be monitored for all parameters (see 8.3, Analytical Methods) before and after each injection campaign and weekly for oxygen, redox potential, conductivity, pH, temperature, carbon dioxide, methane, and pressure.

It is expected that the data gathered in these tests will allow a determination of the biodegradation rates of contaminants of concern in the soil and groundwater, allow an evaluation of the feasibility of in situ bioremediation of soil and groundwater at the site, and provide data necessary for the functional design criteria for the final remediation system.

8.2 Sampling Locations

Groundwater will be sampled via a series of groundwater monitoring wells (DOB-01 through DOB-16) located around the periphery of the site. Approximate locations of nearby monitoring wells are shown in Fig. 17. In addition, bundle tubes located within the horizontal wells for the purpose of gas sampling will also be used for groundwater sampling in the event that groundwater should enter the horizontal wells.

Soil gas sampling and pressure measurements will be carried out via nine vadose zone piezometers, designated DOB-BV1 through DOB-BV9. These are shown in Figs. 14, 16, and 17.

8.3 Analytical Methods

Groundwater Measurements. Water will be analyzed on site via flow-through cells for dissolved oxygen, redox potential, conductivity, pH, and temperature. Water samples will be analyzed using EPA approved procedures for BTEX, vinyl chloride, dichloroethylene, trichloroethylene, tetrachloroethylene, total petroleum hydrocarbons, PAH, chloride, nitrate, nitrite, phosphate, and ammonia. Microbial analyses will consist of total bacterial counts using direct enumeration and contaminant degrader viable counts using enrichments with the contaminants of concern. All the constituents being measured are either contaminants, their biodegradation products, or nutrients required by the soil microbes.

Soil Gas Measurements. Soil gas will be analyzed for volatile organic compounds (VOCs), methane (indicative of anaerobic metabolism and degradation), CO_2 and O_2 (low oxygen levels and high carbon dioxide levels would be indicative of microbial activity in the soil). A LANDTEC GEM-500 will be used to measure CH_4, CO_2, and O_2 in the gas from the vadose zone piezometers. A Teledyne Brown portable oxygen analyzer may also be used to measure % O_2 in the soil. The Teledyne can be set to measure % O_2 at three different ranges (0-5%, 0-10%, and 0-25%). The flux or emission (grams/area/time) of volatile organics from the soil will be measured using a flux chamber and an infra-red analyzer (Bruel & Kjaer type 1302 infra-red photoacoustic multi-gas monitor). Pressure within the vadose zone piezometers will be measured using Dwyer Magnehelic pressure gages (0-5 inches of water and 0-15 inches of water).

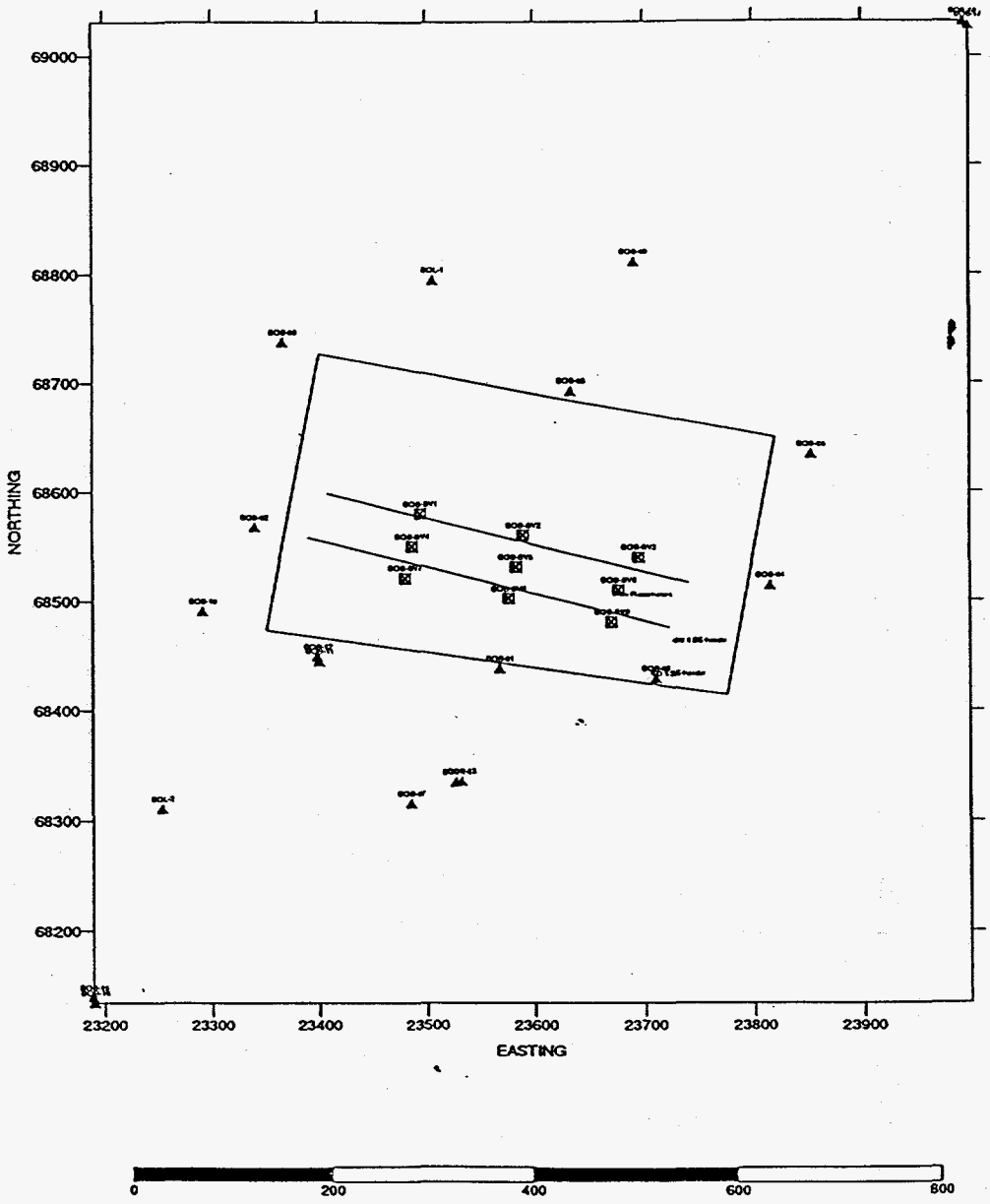

Figure 17. Locations of Nearby Monitoring Wells

9.0 Final Report and Recommendation Schedule

Phase I. Intrinsic Rate Determinations. 6 weeks, June 17- July 31

Phase II. In Situ Respiration and Conservative Tracer Determinations. 2-4 weeks, August 1-September 1.

Phase III. In Situ Biostimulation Using Air and Gaseous Nutrients. 6-12 weeks, September 1-November 15.

Final Report and Recommendations. November 15-December 15.

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Appendix A. Calculations Used to Derive Linear Flow Velocity

Statement of Problem

This calculation determines the average linear flow velocity of the groundwater in the upper most aquifer at the D-Area Oil Seepage Basin.

Calculation Approach

The following equation (Reference 1) was used to calculate the average linear flow velocity:

$$V = \frac{K \cdot \left(\frac{\Delta h}{\Delta l}\right)}{n_e}$$

where:

V = average linear velocity
K = hydraulic conductivity (18.8 ft/day from Reference 2)
Δh = change in head (0.6 ft from potentiometric surface map, Figure F-2)
Δl = change in length or distance (690 ft from potentiometric surface map, Figure F-2)
n_e = effective porosity (0.24 literature value for fine sand from Reference 3)

Basis for variables

The hydraulic conductivity was determined from slug testing of piezometers at the D-Area Oil Seepage Basins (see Reference 2). Figure F-2 presents the potentiometric surface map that was generated using water level measurement taken 8/17/95. The gradient ($\Delta h/\Delta l$) was determined using Figure F-2. Reference 3 contains effective porosity (n_e) values based on grain size. The effective porosity (n_e) of 0.24 is representative of fine sand. This is a conservative value which will tend to increase the velocity calculated for this unit. Soils at the site are generally silty sands.

Assumptions

1. The hydraulic conductivity (K) of the site is 6.62E-05 m/sec or 18.8 ft/day.
2. The effective porosity (n_e) of 0.24 obtained from the literature is representative of the site.

Results

$$V = \frac{18.8 \text{ ft/day} \cdot \left(\frac{0.6 \text{ ft}}{690 \text{ ft}}\right)}{0.24} = 0.07 \text{ ft/day}$$

The average linear velocity is 0.07 ft/day.

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1. R. Wallace, Applied Hydrogeology, 2nd Edition, Macmillan Publishing Company, 1988, p. 126.
2. Letter from David Wonder of AMES LABORATORY to Lucy Smith, *Subject: Slug test results*, dated September 21, 1995.
3. Ghislain de Marsily, Quantitative Hydrogeology: Groundwater Hydrology for Engineers, Academic Press, Inc., 1986, p. 36.

Appendix B. Air Emissions Calculations

Estimation of Particulate Emissions

No particulate emissions are anticipated.

Estimation of Soil Gas Emissions

The following assumptions and design parameters were used in calculating soil gas emissions:

Length of horizontal wells = 2 wells, each 380 feet long
Average radius of influence = 15 feet
Soil bulk density = 90 lb/ft^3
Affected soil volume= $2 \cdot 380 \text{ ft} \cdot \pi \cdot (15 \text{ ft})^2 = 5.4 \cdot 10^5 \text{ ft}^3$
Affected soil weight = $5.4 \cdot 10^5 \text{ ft}^3 \cdot 90 \text{ lb/ft}^3 = 4.9 \cdot 10^7$ lb
Minimum hours pumping time = 24 h · 2 in situ respirometry tests + 4 weeks · 168 h/wk for biostimulation = 720 h

A maximum (worst case) soil gas emission rate was then calculated by assuming total volatilization of each pollutant over the minimum projected pumping time. Pollutant concentrations were derived from data obtained during the 1993 limited scope sampling (WSRC, 1994b)

Compound	Est. avg. mg/kg	Est. total wt (lbs)	Est. max. emission (lbs/h)
Benzene	$8 \cdot 10^{-3}$	0.368	$5 \cdot 10^{-4}$
Chlordane	$1 \cdot 10^{-4}$	0.005	$7 \cdot 10^{-6}$
Vinyl chloride	6.5×10^{-5}	0.003	$4 \cdot 10^{-6}$
Ethylbenzene	$2.2 \cdot 10^{-3}$	0.108	$1.5 \cdot 10^{-4}$
Lindane	$3.8 \cdot 10^{-4}$	0.018	$2.3 \cdot 10^{-5}$
Naphthalene	.0509	2.49	0.0035
PCB's	0.105	5.145	0.007
PCE	0.025	1.225	0.0017
Toluene	0.0056	0.274	$3.8 \cdot 10^{-4}$
TCE	0.008	0.368	$5 \cdot 10^{-4}$
Xylene	0.0078	0.382	$5 \cdot 10^{-4}$
2-methylnaphthyl	0.048	2.352	0.0033
benzo(g,h,i)perylene	0.0048	0.235	$3.3 \cdot 10^{-4}$
bis(2-ethylhexyl)phthalate	0.0039	0.191	$2.65 \cdot 10^{-4}$
n-butylbenzyl-phthalate	0.00175	0.086	$1.19 \cdot 10^{-4}$

These rates appear insignificant. Furthermore, actual emission rates will be lower due to the facts that volatilization will not be complete, intrinsic biodegradation may have occurred since the site was last sampled, much of the remaining material will be

biodegraded rather than volatilized, and that pumping time will likely be longer than the estimate used in the calculations.