

U.S. Environmental Protection Agency Region IX  
Toxic Waste Management Division  
Field Operations Branch

**Field Sampling Plan**  
**SOIL-GAS AND FLUX-CHAMBER SAMPLING**

Frontier Fertilizer  
4309 Second Street  
Davis, California 95617

Site EPA ID Number CAD 071530380

Anticipated Sampling Date: October 1 to November 30, 1997

Prepared by:  
Bechtel Environmental, Inc.  
P.O. Box 193965  
50 Beale Street  
San Francisco, CA 94119

Revision 0  
August 27, 1997

EPA Remedial Project Manager: Janet Rosati

Phone: (415) 744-2403

EPA Contract Number : 68-W9-0060

EPA Work Assignment Number: 60-28-9L4R

---

**For EPA use:**

---

Received by Superfund Project Manager:

Reviewed by: Janet Rosati

Status:

Approved

Date: \_\_\_\_\_

Date: 10/2/97

Not Approved

---

Expedited Review?

Yes

No

Received by QA Management Section:

Reviewed by: Mark C. Ratto

Status:

Approved

Date: \_\_\_\_\_

Date: 10/2/97

Not Approved

Concurrence: Rose Song for Vance King

Date: 10/2/97

Chief, Quality Assurance  
Management Section  
Environmental Services Branch, OPM

# Contents

---

| Section   | Page       |
|---|------------|
| <b>1 Introduction and Objective of Sampling Effort.....</b>                       | <b>1-1</b> |
| <b>2 Background .....</b>   | <b>2-1</b> |
| 2.1 Site Location .....   | 2-1        |
| 2.2 Site Description and Operational History .....                                | 2-1        |
| 2.3 Previous Investigations .....   | 2-4        |
| 2.3.1 Preliminary Assessment Conducted by Ecology and<br>Environment for EPA..... | 2-4        |
| 2.3.2 Remedial Investigation Conducted by Bechtel for EPA .....                   | 2-5        |
| 2.4 Geologic and Hydrogeologic Setting.....                                       | 2-7        |
| 2.5 Nature and Extent of Groundwater Contamination .....                          | 2-9        |
| 2.6 Nature and Extent of Soil Contamination.....                                  | 2-11       |
| <b>3 Sampling and Analysis Program and Rationale.....</b>                         | <b>3-1</b> |
| 3.1 Sampling Recommendations .....  | 3-1        |
| 3.1.1 Soil Gas Sampling Recommendations .....                                     | 3-1        |
| 3.1.2 Flux Chamber Sampling Recommendations.....                                  | 3-1        |
| 3.2 Analysis Recommendations.....   | 3-3        |
| <b>4 Request for Analyses .....</b>   | <b>4-1</b> |
| 4.1 Soil-Gas and Flux-Chamber Sample Analyses Subcontract Laboratory .....        | 4-1        |
| 4.2 Blank Sample Analyses .....   | 4-1        |

Contents (Cont'd)

---

| Section   | Page       |
|---|------------|
| <b>5 Field Methods and Procedures .....</b>   | <b>5-1</b> |
| 5.1 Soil-Gas Sampling .....   | 5-1        |
| 5.2 Flux-Chamber Sampling.....  | 5-1        |
| 5.3 Blank Sampling .....  | 5-2        |
| 5.4 Decontamination Procedures .....  | 5-2        |
| <b>6 Disposal of Investigation-Derived Wastes .....</b>   | <b>6-1</b> |
| 6.1 Used Personal Protective Equipment and Disposable<br>Sampling Equipment .....                                   | 6-1        |
| 6.2 Decontamination Fluids.....   | 6-1        |
| 6.3 Soil Cuttings .....   | 6-1        |
| <b>7 Sample Documentation and Shipment.....</b>   | <b>7-1</b> |
| 7.1 Field Logbooks .....  | 7-1        |
| 7.2 Sample Containers and Preservatives .....   | 7-2        |
| 7.3 Sample Traffic Report and Chain-of-Custody Records and Quality<br>Assurance/Quality Control Summary Forms ..... | 7-2        |
| 7.4 Sample Labeling, Packaging, and Shipment.....   | 7-3        |
| <b>8 Quality Control .....</b>  | <b>8-1</b> |
| 8.1 Blank Samples .....   | 8-1        |
| 8.2 Duplicate Samples .....   | 8-1        |

| Section                   | Page |
|---------------------------|------|
| 8.3 Field Variances ..... | 8-1  |

### Illustrations

| Figure  | Page |
|---|------|
| 2-1 Site Location .....                                     | 2-2  |
| 2-2 Site Features and Well Locations .....                  | 2-3  |
| 2-3 Geologic Cross Section a- a' .....                      | 2-8  |
| 2-4 EDB and Carbon Tetrachloride in S-1 Zone.....           | 2-10 |
| 2-5 EDB in Soil, Disposal Basin Cross-Section .....         | 2-12 |
| 2-6 Extent of EDB in Soils and in S-1 Zone Groundwater..... | 2-13 |
| 3-1 Soil-Gas and Flux-Chamber Sample Locations.....         | 3-2  |

### Appendices

#### Appendix

- A Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber
- B Standard Laboratory Operating Procedure, Method TO-14

## **Introduction and Objective of Sampling Effort**

---

This field sampling plan describes soil-gas and flux-chamber sampling to be conducted by Bechtel Environmental, Inc. (Bechtel) at the Frontier Fertilizer site (CAD 071530380) in Davis, Yolo County, California. This work is part of a Remedial Investigation (RI) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). This field sampling plan has been prepared under contract with the Environmental Protection Agency (EPA), Contract Number 68-W9-0060, as specifically authorized by EPA Region IX, Work Assignment Number 60-28-9LAR.

From 1972 to 1983, the Frontier Fertilizer site was used as a fertilizer and pesticide distribution facility. Pesticides and fertilizers were stored and mixed on site and sold to farmers. When the empty pesticide containers were returned, residual material was rinsed out and deposited in an unlined basin near the northwest corner of the site. Analytical results of soil and groundwater samples collected on or adjacent to the site indicated the presence of several pesticides and other compounds in onsite soils and in the shallow groundwater beneath and downgradient of the site. (The site history, features, and nature and extent of contamination are described in more detail in Section 2.)

The objective of the sampling described in this plan is to obtain sufficient data to support evaluation of the human health risk associated with inhalation of chemicals potentially emanating from the ground at Frontier Fertilizer. To meet this objective, EPA has requested that both soil-gas samples and soil-gas flux-chamber samples be collected and analyzed. Since the contaminants of concern at Frontier Fertilizer are volatile organic compounds, the release of volatiles from contaminated soil and groundwater to the air may be of concern to prospective home buyers north of the site. While standard EPA risk assessment procedures consider the risk associated with the release of volatiles from soil into the air, the risk is estimated based on measurements of the total concentration of contaminants in soil. The flux chamber sampling described in this field sampling plan will directly measure the flux of contaminants from the soil surface and thus provide better quality data for use in a human health risk assessment.

Field sampling will be conducted under protocol accepted by the EPA and the Quality Assurance Project Plan submitted by Bechtel on July 14, 1997. A Bechtel subcontract laboratory will conduct the required Method TO-14 analyses.

## **Background**

---

This section describes the site location; description and operational history; previous investigations; geologic setting; and nature and extent of contamination.

### **2.1 SITE LOCATION**

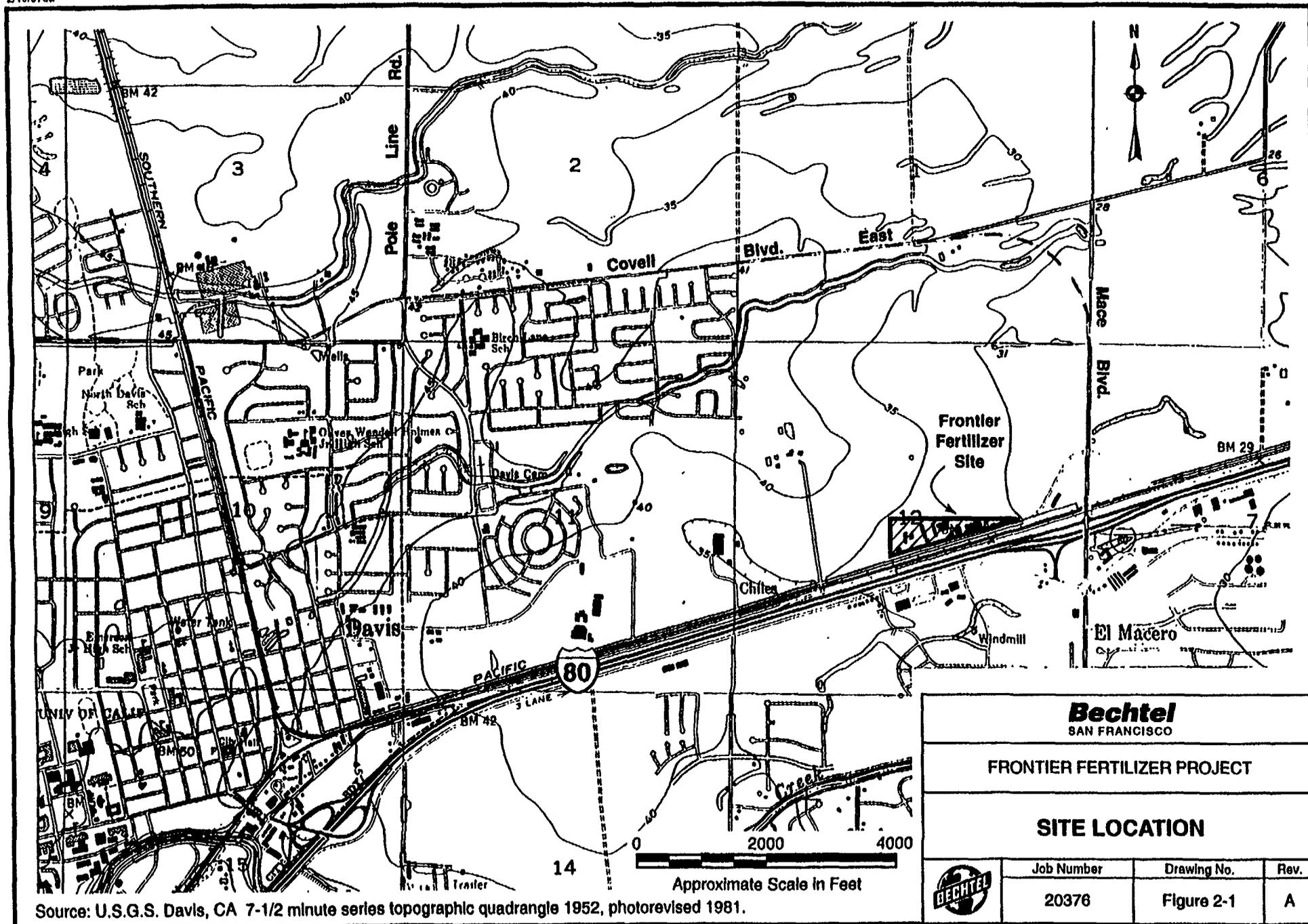
The Frontier Fertilizer site is located at 4309 Second St. in Davis, Yolo County, California (see Figure 2-1). The geographic coordinates of the site are 38° 33' 9.5" N latitude and 121° 42' 7.0" W longitude (Township 8 North, Range 2 East, Section 12, Mt. Diablo Baseline and Meridian, Davis, California, 7.5-minute quadrangle).

### **2.2 SITE DESCRIPTION AND OPERATIONAL HISTORY**

The Frontier Fertilizer site is near the eastern edge of the city of Davis, California. The 18-acre site consists of several warehouses, shops, a pole barn, a labor camp complex, a tomato grading station, several sumps and culverts, and a disposal basin area. The site is bounded on the south by Second Street and Interstate I-80, and on the north, west, and east by agricultural fields. Construction of the Mace Ranch Park industrial and residential development is under way for most of the agricultural land surrounding the site. The nearest residence is approximately 0.2 mile north of the site. The site features are shown in Figure 2-2.

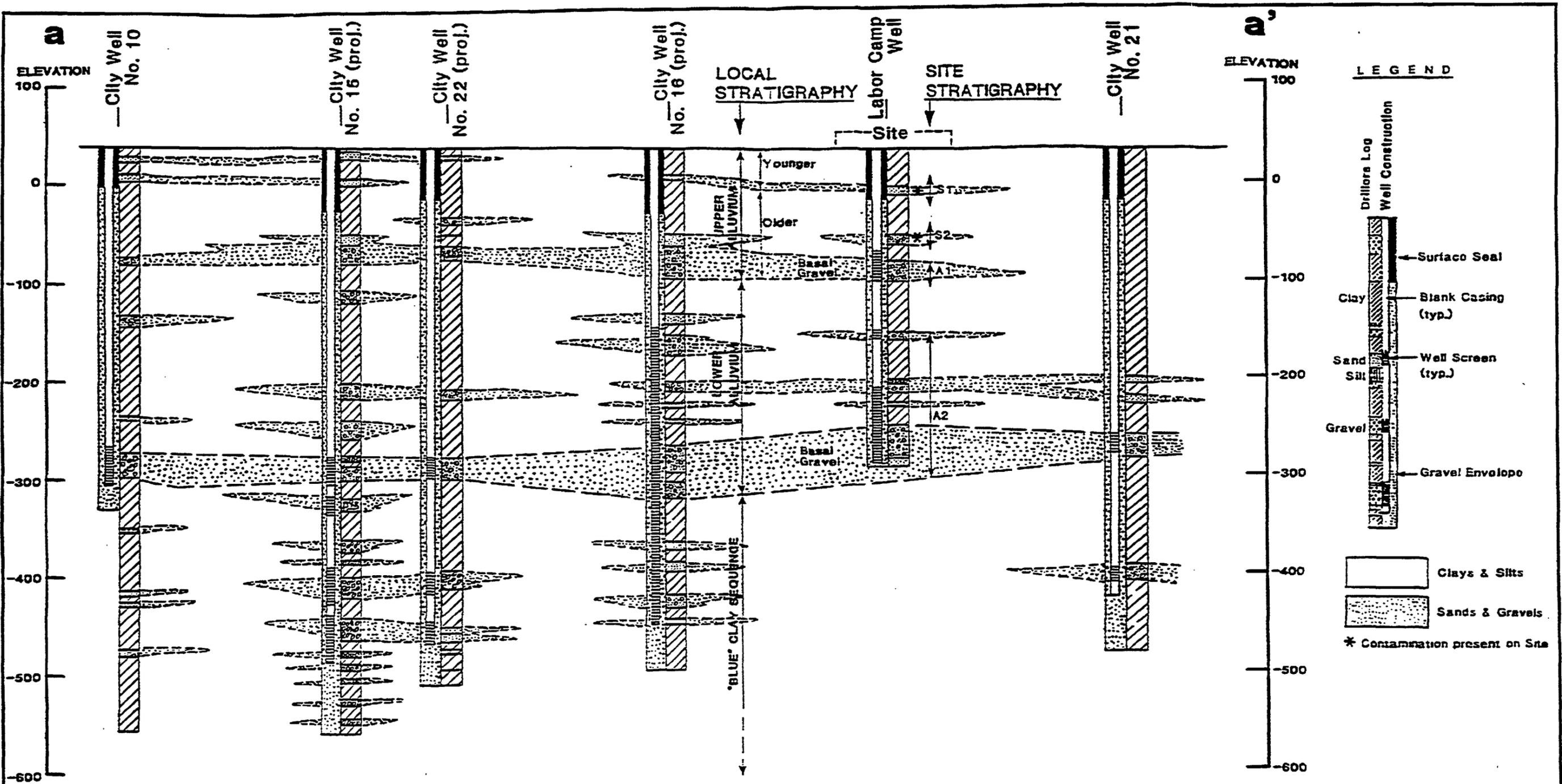
The site was first operated as farm headquarters of the C. Bruce Ranch Company in 1950. Grain warehouses and barns for machinery storage were the first buildings erected. A labor camp for Mexican nationals was constructed between 1952 and 1954. Site development continued from east to west, with the site finally occupying 14 acres in 1970. In 1970, the 14-acre site was sold to Anderson Farms, Inc. The next major improvement of the site and its operations occurred in 1972, when a tomato grading station and a wash rack to rinse off tomato trucks were installed in the south-central area. In addition, Barber-Rowland Company (Barber-Rowland) moved onto the 4 acres to the west of the original 14 acres, completing the expansion of the site to 18 acres.

The arrival of Barber-Rowland in 1972 marked the beginning of fertilizer and pesticide operations on the site. In 1982, Frontier Fertilizer took over the fertilizer and pesticide operations from Barber-Rowland. Frontier's operations were terminated in 1987. During site operations by Barber-Rowland and Frontier Fertilizer, fertilizers and pesticides were stored in containers, sold in bulk, or mixed and placed in 500- to 1,000-gallon trailers that were attached to a purchaser's truck for transport to the farm. If a pesticide container or trailer was returned with residual material inside, the excess pesticide and container rinsate were poured onto the ground or into at least one unlined disposal basin located near the northwest corner of the site (Figure 2-2). In addition, used pesticide, insecticide, and herbicide containers were stored, crushed, and disposed of on site and at other locations off site. Frontier Fertilizer operations were confined to the western end of the property. Currently, the site is fenced and secure, and there are no activities other than those associated with the remediation.



Source: U.S.G.S. Davis, CA 7-1/2 minute series topographic quadrangle 1952, photorevised 1981.

|                                 |             |      |
|---------------------------------|-------------|------|
| <b>Bechtel</b><br>SAN FRANCISCO |             |      |
| FRONTIER FERTILIZER PROJECT     |             |      |
| <b>SITE LOCATION</b>            |             |      |
| Job Number                      | Drawing No. | Rev. |
| 20376                           | Figure 2-1  | A    |



Source: Luhdorff and Scaimanini, November 1987.

|                                 |             |      |
|---------------------------------|-------------|------|
| <b>Bechtel</b><br>SAN FRANCISCO |             |      |
| FRONTIER FERTILIZER PROJECT     |             |      |
| GEOLOGIC CROSS-SECTION<br>a-a'  |             |      |
| Job Number                      | Drawing No. | Rev. |
| 20376                           | Figure 2-3  | A    |

According to California Department of Health Services (DHS) records, on July 27, 1983, an employee's dog came in contact with liquid in the disposal basin. The dog died of pesticide poisoning while being examined by a veterinarian. Yolo County Department of Public Health (YCDPH) personnel visited the site on August 2, 1983, and observed the 20-foot by 15-foot by 4-foot deep basin, with approximately 1,500 gallons of fluid ("dark, oily liquids") in it. YCDPH personnel returned 2 days later to collect fluid samples, but the pit had been pumped out. Soil samples collected from the base of the pit had very high concentrations of disyston and EDB. In September 1983, YCDPH, under the guidance of DHS, stipulated that corrective action be taken at the site. Soil samples taken by YCDPH on March 2, 1984 indicated that soil contamination by EDB, DCP, DBCP, and other pesticide- and herbicide-related compounds existed at the site.

EDB was employed as a soil fumigant to kill nematodes and was normally purchased from manufacturers as a powder, or in a 5 percent solution in water. Its use in California was discontinued in 1982. DBCP was employed as a nematicide and was normally purchased from manufacturers in powder form or in 7.5 percent solutions in water. Its use was discontinued in California in 1977. DCP is still used in California as a nematicide and for weed control.

## 2.3 PREVIOUS INVESTIGATIONS

Three groundwater investigations were carried out prior to EPA's direct oversight of the Frontier Fertilizer Site. These were conducted by Luhdorff and Scalmanini Consulting Engineers (LSCE) for Frontier Fertilizer, Groundwater Technology, Inc. (GTI) for RAMCO Enterprises, and Metcalf and Eddy, Inc. (M&E) for California EPA. LSCE's groundwater investigation focused on characterizing the nature and extent of contaminants in groundwater and site hydrogeologic characterization. GTI's investigation added several wells to the monitoring network and provided additional data to characterize the nature and extent of pesticide contamination. M&E's investigation was directed toward initial containment of the pesticide plume. M&E installed one additional monitoring well cluster, sampled the monitoring wells, and conducted aquifer pumping tests to support the design of a groundwater pump and treat system. The two investigations conducted for EPA are discussed below.

### 2.3.1 Preliminary Assessment Conducted by Ecology and Environment for EPA

In 1993, the EPA Emergency Response Section contracted with E&E to investigate pesticide soil and groundwater contamination at Frontier Fertilizer. The purpose of this investigation was to collect soil samples to determine levels of pesticide contamination remaining in the soil and to attempt to locate a source for the carbon tetrachloride contamination. Analytical data were used to determine if a removal action was warranted for any source area on site. Removal options considered included soil vapor extraction and soil excavation. EPA determined that soil containing concentrations of 1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP),

and 1,2-dichloropropane (DCP) above 1,000 parts per billion (ppb) would be considered for removal action (Ecology and Environment, 1994).

Groundwater sampling and analysis were also conducted as part of the EPA preliminary assessment. Between August 24 and September 1, 1993, 25 of the 39 wells associated with the site were sampled. Wells were selected from all areas of the contaminated groundwater and all three water-bearing zones. The objective of the sampling event was to determine whether contaminant concentrations had changed since the previous sampling. Of particular concern was whether contamination was entering the A-1 aquifer. (Figure 2-2 shows well locations.)

### **2.3.2 Remedial Investigation Conducted by Bechtel for EPA**

Upon review of the previous investigation results, it was determined that additional soil and groundwater sampling were required. Soil sampling was conducted as a hot spot search to determine if all sources of contamination had been identified. The entire Frontier Fertilizer property was sampled on a grid, and samples were analyzed for volatile organic compounds (VOCs), organophosphorus pesticides, carbonate/urea pesticides, and organochlorine pesticides.

Additional soil samples were collected to determine if site soil had been dispersed off site by wind and/or rain and to calibrate a VLEACH model of contaminant transport in the disposal basin area. These samples were also collected to characterize the disposal basin soil for removal and disposal and to determine background soil concentrations of chemicals of concern (COCs).

The results from analysis of these samples are presented in the February 1997 Draft Interim Final Remedial Investigation (RI) Report. Conclusions regarding soil are as follows:

- Contaminated soil has not been transported off site by wind or surface water runoff.
- Soils in the immediate vicinity of the former disposal basin contain levels of contaminants that may not be above RCRA hazardous levels.
- Soils beneath and adjacent to the former disposal basin are contaminated with pesticides to depths corresponding, at a minimum, to the water table at a depth of 32 feet below ground surface (bgs).
- The lateral extent of these contaminated soils has been delineated.
- Other possible sources of contaminants were investigated but none were found.
- Background soils contain detectable concentrations of several pesticides.
- Contaminant levels in soils are indicative of a DNAPL release. The highest levels of EDB and DCP were detected in soils near the former disposal basin.

- DNAPL migration probably extends beyond the water table, and into the S-2 water-bearing zone.
- Site surface soils are not generally contaminated with pesticides at concentrations above PRGs.

Groundwater sampling was conducted as a HydroPunch™ survey to determine the leading edge of the pesticide plume in the S-1 and S-2 water-bearing zones and in the A-1 aquifer. This survey included preparation of geologic logs and water level measurements. In addition, groundwater samples were collected and water level measurements were made at site monitoring wells during the RI. The results from analysis of these data are also presented in the RI Report. Conclusions regarding groundwater are as follows:

- Groundwater occurs in three water-bearing zones. From shallowest to deepest, they are the S-1 zone, the S-2 zone, and the A-1 aquifer. The S-1 and S-2 zones are silty sand lenses surrounded by a clay and silt material. The A-1 aquifer is a more regionally extensive gravel and sand aquifer with one to two orders of magnitude greater transmissivity than that of the shallower sand zones. The site hydrogeology is a three-dimensional flow system. The flow system exhibits a horizontal or lateral anisotropy; therefore, S-1 and S-2 sands and the A-1 aquifer are valid representations of site conditions. However, there are significant vertical flow components that are recognized and integrated into the conceptual model.
- There is an areally extensive clay aquitard between the S-1 and S-2 zones. Although this clay appears to be extensive, there may be localized regions of interconnection between the S-1 and S-2 zones. The aquitard separating the S-2 zone and the A-1 aquifer pinches out to the north. There is evidence from the seasonal water level changes and the geologic data that the S-2 zone and A-1 aquifer are hydraulically interconnected in this area.
- Groundwater contamination was detected at high levels locally in the S-1 and S-2 zones and at much lower levels in the A-1 aquifer.
- The highest concentrations of EDB, DBCP, and DCP were detected in the S-1 and S-2 zone wells located immediately downgradient from the former disposal basin.
- Contaminant levels in the S-1 and S-2 zones indicate a localized presence of DNAPL. Although the DNAPL may no longer be mobile, it does appear to have migrated into the S-2 zone around wells MW-7C and MW-13B.
- Dissolved phase contaminants enter the A-1 aquifer where the intervening aquitard pinches out, and the downward gradients between the A-1 aquifer and S-2 zone induce migration of groundwater from the S-2 into the A-1 aquifer. Because of the low concentrations of DCP, EDB, and DBCP and the limited areal extent of these

compounds in the A-1 aquifer, there was no indication of a DNAPL in the A-1 aquifer.

- Carbon tetrachloride was detected at concentrations above the maximum contaminant level (MCL) in the S-1, S-2, and A-1 zones. The plume configuration is markedly different from the pesticide plume configuration, indicating the carbon tetrachloride source is not the former disposal basin. Soil and groundwater data do not indicate the source for the carbon tetrachloride.
- Background wells, located across I-80 and hydraulically upgradient from the site, contained tetrachloroethene (PCE) and other organic compounds at detectable concentrations. During one sampling event, PCE concentrations were above the MCL (5.0 µg/L) in two upgradient wells.

## 2.4 GEOLOGIC AND HYDROGEOLOGIC SETTING

A generalized geologic cross-section of the site vicinity is provided in Figure 2-3. Frontier Fertilizer is underlain by Quaternary alluvium to depths exceeding 300 feet. This alluvium is made up of lenses of sand and gravel within a clay and silt matrix. Groundwater is transmitted through the sand and gravel, and the rate of groundwater movement is dependent on the thickness, composition (percentage of silt and clay), length, width, and degree of interconnection between the lenses. Four distinct water-bearing zones have been identified in the subsurface. These are, from shallowest to deepest, the S-1 zone, the S-2 zone, the A-1 aquifer, and the A-2 aquifer. Groundwater flow in these zones is three-dimensional, with vertical and horizontal flow components, but is dominated by horizontal flow.

The primary water supply aquifer is the A-2 aquifer, which is below the A-1 aquifer and separated from the A-1 aquifer by a 25- to 30-foot thick clay aquitard. The Remedial Investigation and previous investigations at this site have not explored the A-2 aquifer because there is no indication that site-related contaminants have migrated beyond the A-1 aquifer.

The S-1 zone, the shallowest and most relevant to the work described in this plan was encountered in numerous borings at depths ranging from 35 to 40 feet bgs. The S-1 zone consists of several discontinuous silty sand lenses that are typically 1 to 4 feet thick, and of variable width and length. According to the boring log descriptions, there is some variability in silt and clay content of the sand. In some parts of the site, the S-1 zone was not encountered during drilling. Hydraulic conductivity and transmissivity were measured in seven wells screened in the S-1 zone using slug testing and pumping tests. Hydraulic conductivity values range from 5.3 to 54 ft/day.

A clay aquitard underlies the S-1 zone. This aquitard appears to underlie the S-1 zone throughout the study area, including the offsite areas investigated. This unit is approximately 20 to 25 feet thick. Although the clay aquitard between the S-1 and S-2 zones appears continuous, water level data indicates some interconnection between these zones does exist at least locally.

## 2.5 NATURE AND EXTENT OF GROUNDWATER CONTAMINATION

The extent of EDB, DBCP, and DCP has been delineated in the S-1 and S-2 zones and the A-1 aquifer across the site with some areas of uncertainty. The distribution of these chemicals is similar, each exhibiting high concentrations immediately north of the former disposal basin in the S-1 and S-2 zones, with concentrations rapidly declining in all directions. While the concentrations of EDB and DCP are indicative of a DNAPL release, the DBCP concentrations are low enough to indicate a dissolved phase release or a cosolved compound, meaning DBCP was present as a minor constituent dissolved in the DNAPL.

The data indicate a dissolved phase of EDB, DBCP, and DCP in the A-1 aquifer because the concentrations of these compounds are very low compared with concentrations detected in the overlying S-2 zone. The lateral extent of compounds in the A-1 aquifer indicates that the source of contamination is probably where the aquitard between the S-2 zone and A-1 aquifer is missing and the two permeable units merge, thereby forming a pathway for dissolved contaminants to enter the A-1 aquifer.

The extent of EDB encompasses all other organic compounds that may have originated from releases at the former disposal pit. Therefore, EDB is used to illustrate the extent of contaminants in the different zones. The contaminant plumes in the S-1 and S-2 zones are approximately 600 to 700 feet long, extending from the former disposal basin to some point beyond wells OW-2A and OW-2B (Figure 2-4). The pesticide plume in the A-1 aquifer appears to be limited in extent and to be centered near the region where there is greater potential interconnection between the S-2 zone and the A-1 aquifer. The northernmost edge of the dissolved contaminant plume is not delineated by the existing monitoring well network.

Carbon tetrachloride was detected in the S-1, S-2, and A-1 zones, and soil data do not indicate a carbon tetrachloride source. Concentrations were highest in the S-2 zone (up to 370 µg/L). The highest concentrations of carbon tetrachloride are almost two orders of magnitude lower than the highest EDB and DCP concentrations. Carbon tetrachloride is also distributed differently, with the plume located east of the DCP, EDB, and DBCP plume. Very low concentrations have been detected in wells MW-7A, MW-7B, MW-7C, MW-7D, X-1A, and X-1B, effectively ruling out the disposal basin as the source of this contaminant.



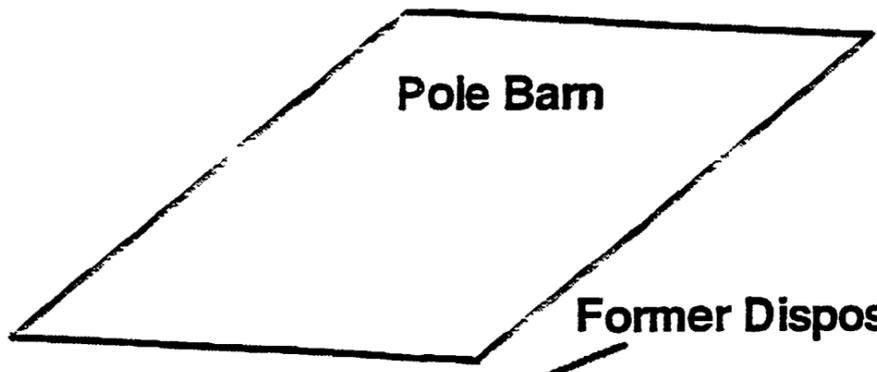
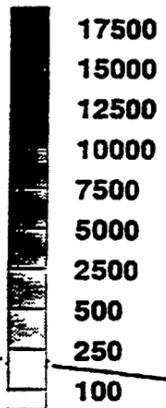
## 2.6 NATURE AND EXTENT OF SOIL CONTAMINATION

The results of the site investigations indicate that approximately 30,000 yd<sup>3</sup> of soil are contaminated with VOCs at concentrations above EPA Region IX Preliminary Remediation Goals (PRGs). As mentioned previously, the most significant area of soil contamination at Frontier Fertilizer is the disposal basin area north of the pole barn. This area was extensively sampled during the preliminary assessment, and adjacent areas were sampled during the remedial investigation. The results of both studies indicate that the contaminated soil is characterized by levels of EDB, DCP, and DBCP that exceed PRGs. This is especially true for EDB, which has a PRG of 21 µg/kg.

To illustrate the vertical extent of vadose zone contamination, Figure 2-5 presents a cross-sectional view of EDB contamination. This figure shows that the greatest concentrations of EDB are found in the depth interval from approximately 15 to 30 feet bgs. This observation is consistent with the previously described removal action excavation depth of approximately 20 feet bgs.

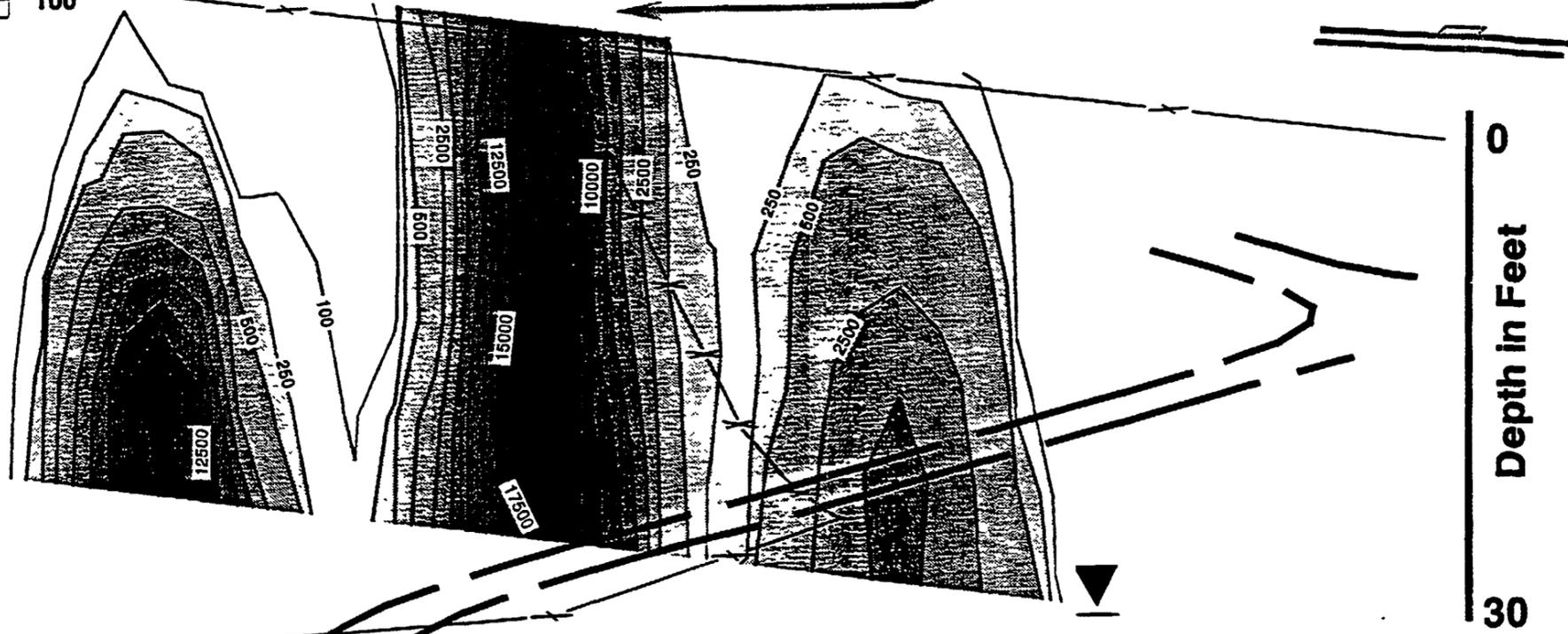
Figure 2-5 also shows that there appear to have been three disposal basins north of the pole barn, which can be inferred from the distribution of relatively high concentrations of contaminants in three discrete areas along the east-west-trending cross section. This finding corroborates historical reports that suggest that more than one disposal basin may have been present. Figure 2-6 illustrates the extent of soil and groundwater contamination.

EDB in ug/kg



Pole Barn

Former Disposal Basin



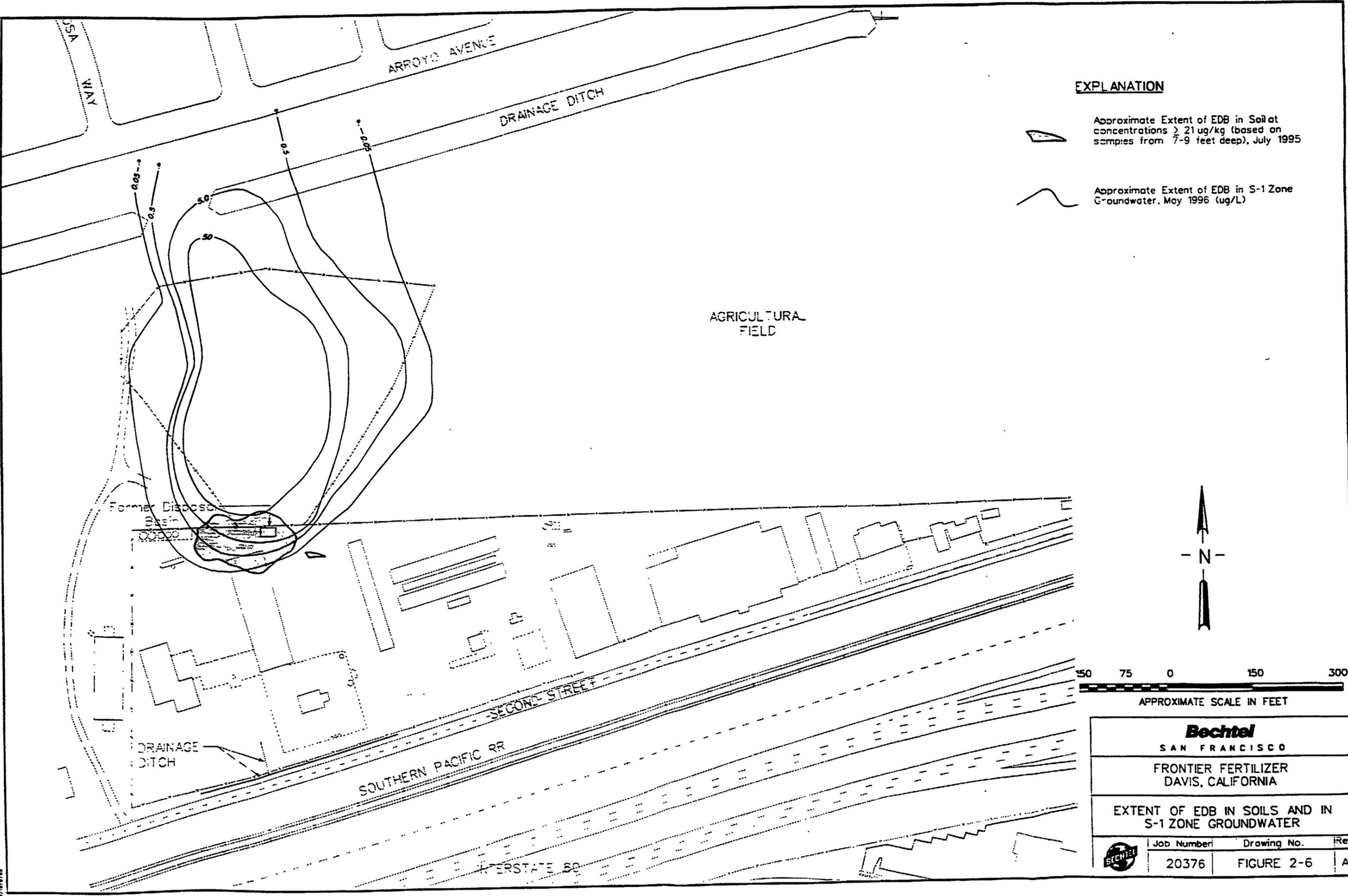
Approx. Groundwater Level

V.E. = 2.5X

|  |            |      |
|--|------------|------|
| <b>BECHTEL</b><br>SAN FRANCISCO              |            |      |
| FRONTIER FERTILIZER PROJECT                  |            |      |
| EDB in Soil, Disposal Basin<br>Cross Section |            |      |
| Job Number                                   | Drawing No | Rev. |
| 20376  | Figure 2-5 | A    |

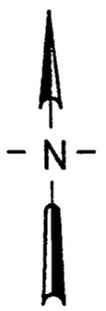
This drawing and the design it covers are the property of BECHTEL. They are loaned and on the borrower's express agreement that they will not be reproduced, copied, loaned, detailed, nor used except in the limited way and for the use permitted by the lender to the borrower.

5/10/96 11:00 AM C:\GIS\WORK\FRONTIER\020814\020814.dwg



**EXPLANATION**

-  Approximate Extent of EDB in Soil at concentrations > 21 ug/kg (based on samples from 7-9 feet deep), July 1995
-  Approximate Extent of EDB in S-1 Zone Groundwater, May 1996 (ug/L)



|   |            |                    |
|---|------------|--------------------|
| <b>Bechtel</b>  |            |                    |
| SAN FRANCISCO   |            |                    |
| FRONTIER FERTILIZER<br>DAVIS, CALIFORNIA  |            |                    |
| EXTENT OF EDB IN SOILS AND IN<br>S-1 ZONE GROUNDWATER                                 |            |                    |
|  | Job Number | Drawing No.    Rev |
|   | 20376      | FIGURE 2-6    A    |

## **Sampling and Analysis Program and Rationale**

---

In order to address the objective of determining the maximum flux of volatile contaminants from the soil, the sampling approach will include the following elements:

1. Evaluating the average soil-gas concentrations in the disposal basin area;
2. Measuring the soil-gas concentration gradient in the area north of the disposal basin area; and
3. Collecting soil-gas flux-chamber samples at locations with high soil-gas sample concentrations.

### **3.1 SAMPLING RECOMMENDATIONS**

To evaluate the average soil-gas concentration and the average contaminant soil-gas flux in the former disposal basin area, ten soil-gas samples and ten flux chamber samples will be collected in the approximately half acre contaminated area (Figure 3-1). These samples will be collected on a regular square grid designed, with a randomly selected origin coordinates, to cover the full half acre.

#### **3.1.1 Soil Gas Sampling Recommendations**

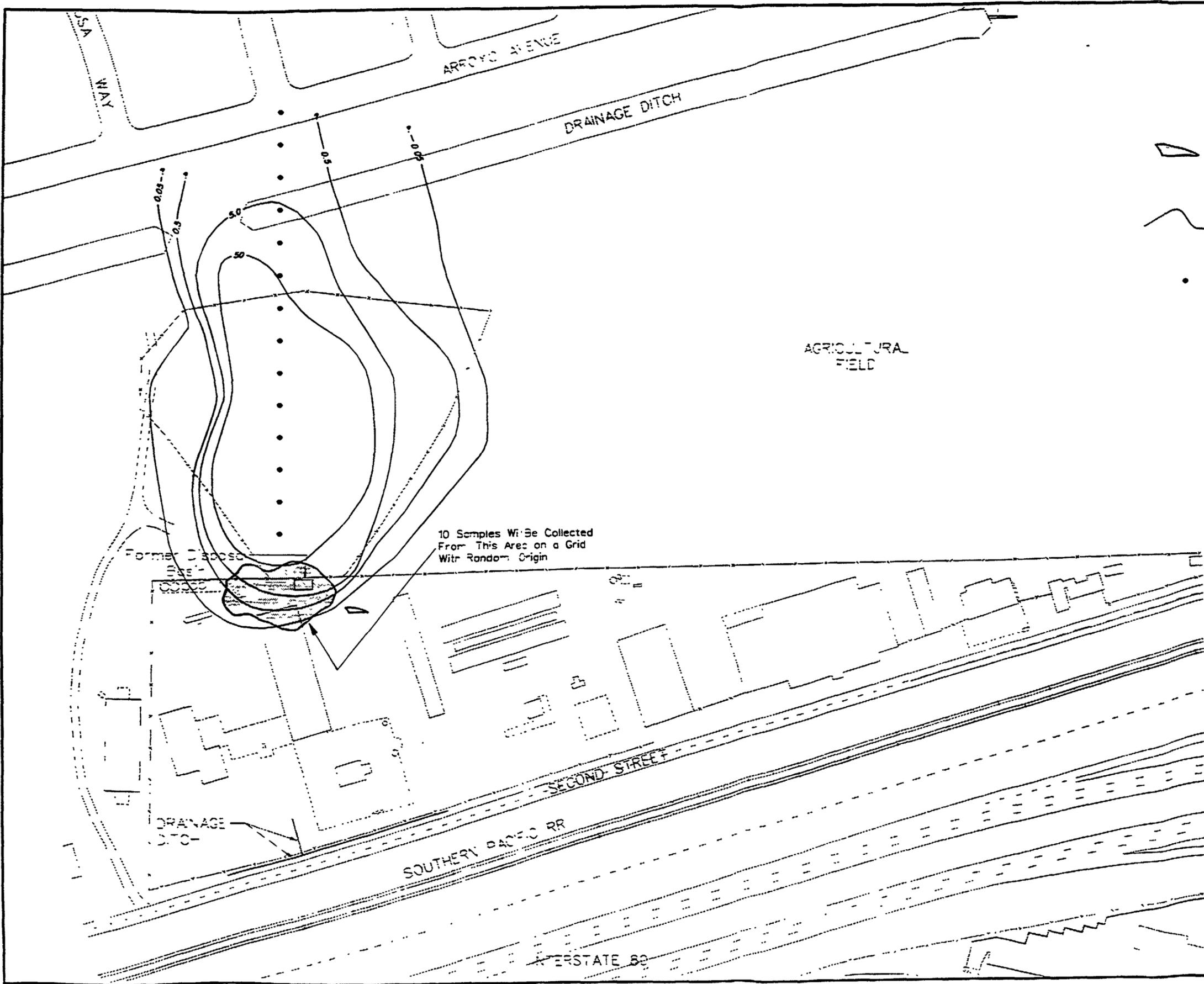
Ten soil gas samples will be collected into SUMMA canisters from five feet below ground surface in the area of soil contamination associated with the disposal basin. In addition to the samples in the disposal basin area, samples will be collected along a north-south transect originating in the disposal basin area and extending approximately 750 north into the planned residential development. Soil-gas samples will be collected along this transect at 50-foot intervals for a total of approximately 15 samples.

#### **3.1.2 Flux Chamber Sampling Recommendations**

Volatilization of organic compounds from contaminated soil and groundwater into the air represents a potential source of exposure and thus a risk to human health which must be evaluated. At Frontier Fertilizer, the potential risk associated with volatilization of organic compounds from contaminated soil has been implicitly evaluated by using EPA Region IX PRGs as soil contamination evaluation criteria. The soil PRGs consider inhalation of vapors as an exposure pathway, but model the ambient air concentration above the contaminated soil based on the total measure concentration in soil. The proposed flux chamber sampling and analysis will directly measure the flux of organic compounds from the soil surface and thus provide a more reliable estimate of the ambient air concentration of chemicals above the contaminated soil. In areas of Frontier Fertilizer where only groundwater contamination occurs, flux chamber sampling and analysis will be used to evaluate the potential risk associated with exposure to organic compound volatilizing from groundwater.

This drawing and the design it covers are the property of BECHTEL. They are hereby loaned to the borrower's express agreement that they will not be reproduced, copied, loaned, distributed, or used except in the limited way and for the purposes permitted by the lender to the borrower.

SF4803155E CAD CHEV/FRONTIER/SF/SP/AN/04/04 6/23/97/04



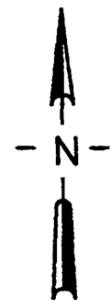
**EXPLANATION**

- Approximate Extent of EDB in Soil at concentrations  $\geq 21 \mu\text{g}/\text{kg}$  (based on samples from 7-9 feet deep), July 1995
- Approximate Extent of EDB in S-1 Zone Groundwater, May 1996 ( $\mu\text{g}/\text{L}$ )
- Planned Soil-Gas Sample Location

**NOTES:**

- 1) Locations of samples in the disposal basin area will be selected in the field.
- 2) Flux-chamber samples will be collected at all disposal basin area sampling locations and at north-south transect locations as determined by the soil-gas concentrations.

10 Samples Will Be Collected From This Area on a Grid With Random Origin



|   |                     |                           |
|---|---------------------|---------------------------|
| <b>Bechtel</b>                                  |                     |                           |
| SAN FRANCISCO                                   |                     |                           |
| FRONTIER FERTILIZER<br>DAVIS, CALIFORNIA        |                     |                           |
| SOIL-GAS AND FLUX-CHAMBER<br>SAMPLING LOCATIONS |                     |                           |
|   | Job Number<br>20376 | Drawing No.<br>FIGURE 3-1 |
|   |                     | Rev<br>A                  |

Ten flux chamber samples will be collected into SUMMA canisters in the area of soil contamination associated with the disposal basin. In addition to the samples in the disposal basin area, samples will be collected along a north-south transect originating in the disposal basin area and extending approximately 750 feet to the residential area at 50-foot intervals. A maximum of 15 flux chamber samples will be collected along this transect. The flux chamber samples along the transect will only be collected if a soil-gas sample collected at the same location contains contaminants of concern at concentrations above 100 times the associated ambient air PRG. If soil-gas samples do not contain contaminants of concern at concentrations above 100 times the associated ambient air PRG, then no flux samples will be collected at that location. Samples will be collected in accordance with the procedures described in the attached flux chamber user's guide, Appendix A. In addition to the investigative samples described above, two duplicate soil flux samples will be collected and one blank sample will be collected per day of sampling for a total of approximately five blank samples.

### **3.2 ANALYSIS RECOMMENDATIONS**

Soil-gas and flux-chamber sampling will be analyzed for contaminants of concern via Method TO-14. The samples will be analyzed by a subcontract laboratory. Method TO-14 relies on a high resolution gas chromatograph to separate the VOCs present in the sample and, for Frontier Fertilizer, a mass spectrometer to detect and identify the VOCs. An aliquot of the sample is introduced into the gas chromatograph via a cyrogenic trap. Bechtel plans to procure commercial laboratory services.

## Request for Analyses

---

The Frontier Fertilizer site was identified as a potential hazardous waste site and entered into the CERCLIS database on August 1, 1985 (CAD 071530380). Bechtel will conduct this field sampling effort as part of a remedial investigation under CERCLA. The anticipated sampling dates for this sampling effort are September 15 through October 31, 1997.

### 4.1 SOIL-GAS AND FLUX-CHAMBER SAMPLE ANALYSES SUBCONTRACT LABORATORY

To assure the comparability of data all soil-gas and flux-chamber samples will be analyzed by the same subcontract laboratory using the same methods. The samples will be analyzed for the chemicals of concern identified in the QAPjP by Method TO-14. The following soil-gas samples will be analyzed:

- A maximum of 25 soil gas
- A maximum of 25 flux chamber samples
- Approximately 4 duplicate samples
- Approximately 5 blank samples

All samples will be collected in SUMMA passivated canisters. Samples will be stored and shipped at ambient temperature. Samples will be held in the field no longer than three days and held prior to analysis no longer than 14 days.

### 4.2 BLANK SAMPLE ANALYSES

Blank samples will be collected each day of sampling by passing zero air through all equipment that comes in contact with contaminated soil, water, and soil gas. These samples will be analyzed for the same contaminants of concern as proposed for the investigative samples.

## Section 5

# **Field Methods and Procedures**

---

This section describes the procedures to be used to collect soil-gas, flux-chamber, and flux-chamber samples. All samples will be handled in accordance with approved Quality Assurance/Quality Control Plan procedures.

Exact sample locations will be recorded in the field logbook after sampling. A sketch of the sample location will be entered into the logbook, and any photographs will be labeled. If appropriate, distances to the reference points will be given.

### **5.1 SOIL-GAS SAMPLING**

A specially equipped sampling rig will be used to collect the soil-gas samples. A bore hole will be drilled, bored, or driven, to a depth of 5 feet. The bottom of the hole will be exposed, then a vacuum will be applied to the bottom 3 to 6 inches of the hole, accomplished by driving a rod equipped with a drive point to the desired depth. The borehole will be developed by retracting the rod slightly, and applying suction through the hole. The borehole will be developed by withdrawing a minimum of five volumes of air. The sample will then be collected into a SUMMA canister.

After successful sample collection, each borehole will be backfilled with soil. Downhole equipment will be decontaminated before use in each hole and the SUMMA canister will be used to collect each sample.

### **5.2 FLUX-CHAMBER SAMPLING**

Flux-chamber samples will be collected in accordance with the detailed procedures in Section 3.5 of the flux chamber user's guide attached as Appendix A and Appendix B.

All exposed flux chamber surfaces will be cleaned with water and wiped dry. The flux chamber will be placed over the area to be sampled and worked in to a depth of 2-3 cm. The flux chamber will be operated in the discrete sample collection mode. Samples will be collected in 2 L SUMMA passivate gas canisters. Once filled, the pressure in the canister will be recorded and it will be packaged for transport to the laboratory for analysis via Method TO-14.

Prior to sample collection the sweep air flow rate will be set to 5 L/min and the flow rate will be recorded at time zero (when the chamber is placed on the soil surface) and at six minute intervals (one residence time in the 30 L chamber); air temperature in the chamber and outside the chamber. After four minutes) collect a sample at no more than 2 L/min. If the sample is collected, air and/or ambient air can be drawn directly into the sample canister effectively measuring the emission rate.

### 5.3 BLANK SAMPLING

Blank soil gas and flux chamber samples will be collected through the same equipment used to collect investigative samples. For blank soil gas samples zero air will be collected through decontaminated tubing. For soil flux chamber samples, the flux chamber will be placed on a clean surface and zero air collected through the sampler.

### 5.4 DECONTAMINATION PROCEDURES

All equipment that comes into contact with potentially contaminated soil or water will be decontaminated prior to and after each use. Disposable equipment intended for one time use will not be decontaminated but will be packaged for appropriate disposal. The decontamination procedures that will be followed are in accordance with approved Quality Assurance Project Plan procedures. All sampling devices will be decontaminated within a predesignated, bermed, and lined decontamination area. All subsurface equipment (i.e., augers, drill or drive rods) will be pressure-washed or scrubbed with a non-phosphate detergent solution with a dedicated brush and rinsed twice with tap water.

The exterior surfaces of drill rigs and any large equipment will be thoroughly pressure-washed with potable water. The equipment will be cleaned of all debris and contaminated fluids (such as obvious leaks from hydraulic lines, couplings, and fittings) to avoid contamination of onsite soils and soil borings. At the end of each work day and/or after the completion of the work, the subcontractor will completely decontaminate its rig and sampling equipment to the satisfaction of Bechtel before leaving the site. Accessible interior portions of augers, pipes, the drill or drive rods, cables, and bits, will be cleaned at the start of the job and between borings. Clean equipment will be stored on plastic sheeting in uncontaminated areas. Materials to be stored more than a few hours will also be covered.

## **Disposal of Investigation-Derived Wastes**

---

In the process of collecting environmental samples at the Frontier Fertilizer site, the following investigation-derived wastes (IDWs), some potentially contaminated, will be generated:

- Used personal protective equipment (PPE) and disposable sampling equipment
- Decontamination fluids
- Soil cuttings

The EPA's National Contingency Plan requires that management of IDW generated during Remedial Investigation/Feasibility Study field investigations comply with all applicable or relevant and appropriate requirements to the extent practicable. The sampling plan will follow the Office of Emergency and Remedial Response Directive 9345.3-02 (May 1991) which provides the guidance for the management of IDW during RI/FS field investigations. In addition, other legal and practical considerations that may affect the handling of IDW were considered in developing these procedures.

### **6.1 USED PERSONAL PROTECTIVE EQUIPMENT AND DISPOSABLE SAMPLING EQUIPMENT**

Used PPE and disposable equipment will be double-bagged and placed in a municipal refuse bin. These wastes are not hazardous and can be sent to a municipal landfill. Any PPE and disposable equipment to be disposed of that can still be reused will be rendered inoperable before disposal.

### **6.2 DECONTAMINATION FLUIDS**

Decontamination fluids that will be generated during this field sampling event will consist of deionized or tap water containing residual contaminants and non-phosphate detergent. The volume and concentration of the decontamination fluids will be sufficiently low to allow disposal at the site. The fluids will be poured onto the ground or into a storm drain.

### **6.3 SOIL CUTTINGS**

Soil cuttings generated will be placed back into the soil borings from which the samples were obtained. Any remaining soil cuttings will be spread on the ground around the borehole location.

## Sample Documentation and Shipment

---

This section describes sample documentation, preparation, handling, and shipment procedures.

### 7.1 FIELD LOGBOOKS

Field logbooks will document where, when, how, and from whom any vital project information was obtained. Logbook entries will be complete and accurate enough to permit reconstruction of field activities. At a minimum, the following sampling information will be recorded:

- Site sketch
- Sample location, depth, and description
- Sampler's name(s)
- Date and time of sample collection
- Type of sample (i.e., matrix)
- Type of sampling equipment used
- Field observations and details important to analysis or integrity of samples (e.g., heavy rains, odors, colors, etc.)
- Type of preservation used
- Instrument reading (e.g., OVM, HNU)
- Sample numbers, chain-of-custody form numbers, and chain-of-custody seal numbers
- Shipping arrangements (air bill number)
- Recipient laboratory(ies)

Logbooks will be bound with consecutively numbered pages. Each page will be dated and the time of entry noted in military time. All entries will be legible, written in black ink, and signed by the individual making the entries. Language will be factual, objective, and free of personal opinions or inappropriate terminology. In addition to the sampling information, the following specifics will also be recorded in the field logbook:

- Team members and their responsibilities
- Times of site arrival/departure
- Other personnel on site
- A summary of any meetings or discussions with the public, any potentially responsible parties (PRPs), representatives of PRPs, or federal, state, or other regulatory agencies

- Any deviations from field sampling plans, site safety plans, and Quality Assurance Project Plan procedures
- Any changes in personnel and responsibilities as well as reasons for the changes
- Levels of safety protection
- Equipment calibration and equipment model and serial number

## **7.2 SAMPLE CONTAINERS AND PRESERVATIVES**

Sampling containers will be pre-cleaned and will not be rinsed prior to sample collection. Preservatives, if required, will be added to the containers prior to shipment of the sample containers to the laboratory. All soil gas, flux chamber and blank samples will be collected in SUMMA passivated canisters and held at ambient temperature prior to and during shipment to the laboratory.

## **7.3 SAMPLE TRAFFIC REPORT AND CHAIN-OF-CUSTODY RECORDS AND QUALITY ASSURANCE/QUALITY CONTROL SUMMARY FORMS**

Chain-of-custody forms will be used to document sample collection and shipment to a laboratory for analysis. The form(s) will be completed and sent with the samples for each laboratory and each shipment (i.e., each day). If multiple coolers are sent to a single laboratory on a single day, the form(s) will be completed and sent with the samples for each cooler.

The chain-of-custody form will identify the contents of each shipment and maintain the custodial integrity of the samples. Generally, a sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, locked up, or kept in a secured area that is restricted to authorized personnel. Until the samples are shipped, the custody of the samples will be the responsibility of Bechtel. The sampler or designee will sign the chain-of-custody form. The sampler or designee will sign the "relinquished by" box and note date, time, and air bill number.

The original chain-of-custody form will accompany the samples to the laboratory and the second form will be sent to the EPA Region IX QA Program. A copy of the original will be made for the Bechtel files.

A quality assurance/quality control summary form will be completed for each laboratory and each matrix of the sampling event. The sample numbers for all rinsate samples, background samples, laboratory quality control samples, and duplicates will be documented on this form (see Section 8). The original form will be sent to the QA Program; a photocopy will be made for the Bechtel master files. This form is not sent to the laboratory.

A self-adhesive custody seal will be placed across the lid of each sample. For water samples for VOC analysis, the seal will be wrapped around the cap. The shipping containers in which samples are stored (usually sturdy picnic cooler or ice chest) will be sealed with self-adhesive custody seals any time they are not in someone's possession or view before shipping. All custody seals will be signed and dated.

The CLP Paperwork Instructions, *Instructions for Sample Shipping and Documentation, October 1994*, will be taken to the field as a reference. Corrections on sample paperwork will be made by placing a single line through the mistake and initialing and dating the change. The correct information will be entered above, below, or after the mistake.

#### 7.4 SAMPLE LABELING, PACKAGING, AND SHIPMENT

All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. All samples will have preassigned, identifiable, and unique numbers. At a minimum, the sample labels will contain the following information: sample number, station location, date of collection, analytical parameter(s), sampler's initials, and method of preservation. All sample containers will be placed in a strong shipping container (such as a steel-belted cooler).

Sample numbers will be consecutive with "SG" as a prefix for soil and "FLX" as a prefix for flux chamber samples. For example SG-1 will be the sample number for the first sample collected and FLX-2 will be the sample number for the second sample collected.

The packaging procedures that will be followed for samples sent to the subcontract laboratory are identified below.

- Secure the drain plug of the cooler with fiberglass tape to prevent any liquids (e.g., melted ice) from leaking out of the cooler.
- Place a 1-inch-thick layer of vermiculite in the cooler.
- Line the bottom of the cooler with bubble wrap to prevent breakage during shipment.
- Check screw caps for tightness and, if not full, mark the sample volume level of liquid samples on the sample containers with indelible ink.
- Secure bottle/container tops with clear tape and custody seal all container tops and caps.
- Affix sample labels onto the containers with clear tape.
- Wrap all glass sample containers in bubble wrap to prevent breakage.

- Seal all sample containers in heavy duty plastic bags. Write the sample numbers on the outside of the plastic bags with indelible ink.
- All samples will be placed in coolers with the appropriate chain-of-custody records.
- All forms will be enclosed in a large plastic bag and affixed to the underside of the cooler lid.
- Fill empty space in the cooler with bubble wrap or styrofoam peanuts to prevent movement and breakage during shipment.
- Double-seal ice in two ziplock plastic bags and place on top and around the samples to chill them to 4°C.
- Securely tape each cooler with nylon strapping tape, and affix custody seals to the front, right, and back of each cooler.

The Region IX Regional Sample Control Center will be notified daily (phone: 415-744-1498) of the sample shipment schedule (Friday shipments must be reported no later than noon) and will be provided with the following information:

- Sampling contractor's name
- The name and location of the site
- Case number
- Sample identification number
- Total number(s) by concentration and matrix of samples shipped to each laboratory
- Carrier, air bill number(s), method of shipment (e.g., priority, next day)
- Shipment date and when it should be received by laboratory
- Irregularities or anticipated problems associated with the samples
- Whether additional samples will be shipped or if this is the last shipment

## Quality Control

---

This section describes the various quality assurance/quality control samples that will be prepared and analyzed.

### 8.1 BLANK SAMPLES

The blank rinsate samples will be prepared as described in Section 5.3. The blank samples will be analyzed chemicals of concern by Method TO-14. A minimum of one blank sample will be collected each day that sampling equipment is decontaminated in the field. A separate sample number and station number will be assigned to each blank, and it will be submitted blind to the laboratory.

### 8.2 DUPLICATE SAMPLES

Duplicate samples will be collected from areas of known or suspected contamination. A minimum of 10 percent of samples will be duplicates. Every analytical group for which a sample is analyzed will also be tested for in one or more duplicate samples. Duplicate samples will be preserved, packaged, and sealed in the same manner as other samples. A separate sample number will be assigned to each duplicate, and it will be submitted blind to the laboratory.

### 8.3 FIELD VARIANCES

As conditions in the field may vary, it may become necessary to implement minor modifications to sampling as presented in this plan. When appropriate, the EPA, QAMS, and Bechtel project managers will be notified of the modifications, and a verbal approval will be obtained before implementing the modifications. Modifications to the approved plan will be documented in the field logbook.

## **Appendix A**

# **Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber**

February 1986

MEASUREMENT OF GASEOUS EMISSION  
RATES FROM LAND SURFACES  
USING AN EMISSION  
ISOLATION FLUX CHAMBER

USER'S GUIDE

by  
M. R. Klenbusch  
Radian Corporation  
P.O. Box 9948  
Austin, Texas 78766

EPA Contract No. 68-02-3889  
Work Assignment 18

Project Officer: Shelly J. Williamson  
Exposure Assessment Division  
Environmental Monitoring Systems Laboratory  
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
LAS VEGAS, NV 89114

REPRODUCED BY  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U.S. DEPARTMENT OF COMMERCE  
SPRINGFIELD, VA. 22161

## TABLE OF CONTENTS

| <u>Section</u> |  | <u>Page</u> |
|----------------|--|-------------|
| 1              | INTRODUCTION . . . . .   | 1-1         |
| 2              | BACKGROUND . . . . .   | 2-i         |
|                | 2.1 Emission Processes. . . . .  | 2-1         |
|                | 2.2 Measurement Techniques. . . . .  | 2-2         |
|                | 2.3 Flux Chamber Operation. . . . .  | 2-3         |
| 3              | MEASUREMENT OF GASEOUS EMISSION RATES FROM LAND SURFACES<br>USING AN EMISSION ISOLATION FLUX CHAMBER - PROPOSED METHOD . . . . . | 3-1         |
|                | 3.1 Applicability and Principle . . . . .  | 3-1         |
|                | 3.1.1 Applicability. . . . .   | 3-1         |
|                | 3.1.2 Principle. . . . .   | 3-1         |
|                | 3.2 Precision, Accuracy, Sensitivity, and Range . . . . .  | 3-1         |
|                | 3.2.1 Precision. . . . .   | 3-1         |
|                | 3.2.2 Accuracy . . . . .   | 3-2         |
|                | 3.2.3 Sensitivity. . . . .   | 3-2         |
|                | 3.2.4 Range. . . . .   | 3-2         |
|                | 3.3 Interferences . . . . .  | 3-2         |
|                | 3.3.1 Flux Chamber Method. . . . .   | 3-2         |
|                | 3.3.2 Emission Process . . . . .   | 3-4         |
|                | 3.4 Apparatus and Materials . . . . .  | 3-4         |
|                | 3.4.1 Flux Chamber and Supporting Equipment. . . . .   | 3-4         |
|                | 3.4.2 Discrete Sample Collection . . . . .   | 3-6         |
|                | 3.4.3 Analysis . . . . .   | 3-6         |
|                | 3.5 Procedure . . . . .  | 3-11        |
|                | 3.5.1 Flux Chamber Operation . . . . .   | 3-11        |
|                | 3.5.2 Sample Collection. . . . .   | 3-11        |
|                | 3.5.3 Sample Analysis. . . . .   | 3-13        |
|                | 3.5.4 Sampling Strategy. . . . .   | 3-15        |
|                | 3.6 Calibration . . . . .  | 3-18        |
|                | 3.6.1 Equipment. . . . .   | 3-18        |
|                | 3.6.2 Analyzers. . . . .   | 3-19        |
|                | 3.7 Quality Control . . . . .  | 3-20        |
|                | 3.7.1 Sampling Equipment . . . . .   | 3-20        |
|                | 3.7.2 Sampling . . . . .   | 3-22        |
|                | 3.7.3 Analytical . . . . .   | 3-22        |
|                | 3.8 Calculations. . . . .  | 3-23        |
|                | 3.8.1 Definitions. . . . .   | 3-23        |
|                | 3.8.2 Percent Recovery . . . . .   | 3-25        |
|                | 3.8.3 Calculation of the Dilution Factor Involved<br>In Gas Canister Analysis . . . . .  | 3-27        |
|                | 3.8.4 Area Source Emission Rate Equations. . . . .   | 3-27        |
| 4              | CASE STUDY . . . . .   | 4-1         |
| 5              | ADDITIONAL INFORMATION . . . . .   | 5-1         |
|                | REFERENCES . . . . .   | R-1         |
|                | APPENDIX A - SELECTION OF A RANDOM SAMPLE. . . . .   | A-1         |

## SECTION 1

### INTRODUCTION

Volatilization of organic compounds from contaminated soil or groundwater into the air represents a major potential source of exposure which has not been assessed. In order to assess this exposure potential, a method is needed to directly measure gas emission rates from contaminated soils and/or groundwater. Additionally, it is recognized that an understanding of the volatilization, transport, and emission processes could lead to a predictive tool for exposure assessment. The information provided by direct measurement and/or predictive modeling will allow state and local regulatory agencies to develop programs to assess and define the need to control gas emissions from area sources contaminated by organic compounds.

The purpose of this User's Guide is to present an approach and protocol, namely the emission isolation flux chamber (or flux chamber) technique, for measuring emission rates of volatile organic compounds from contaminated soils and/or groundwater. Presented is the theory of operation, specifications, sensitivities, method of operation, and data reduction procedures for this technique. It is assumed that the individuals who will use the protocol are, in general, familiar with sample collection and analysis of volatile organic compounds. Also included in this document is a case study that demonstrates the measurement and data reduction processes around a spill site.

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities (hazardous waste land treatment, and landfill facilities), and from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) area sources contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

This protocol does not present the vast amount of work that was required to develop this document. Rather, the protocol is a result of literature reviews selecting a measurement technique and field applications demonstrating the technique and developing a data base and validation studies identifying the method of flux chamber operation. References to the other area sources where this technique was applied, the work performed to validate the technique, and the investigations of variables which control the emission process are also given for those individuals desiring further information.

## SECTION 2

### BACKGROUND

The following subsections discuss the process by which volatile organic compounds are emitted from contaminated land surfaces, the basis upon which the flux chamber technique was selected as an approach for measuring such emission rates, and the principle of the technique.

#### 2.1 Emission Processes

The rate of volatile organic compound (VOC) emissions from contaminated soils is generally believed to be controlled by the diffusion rate of the chemical compound through the air-filled pore spaces of the soil.(1,2,3) The exception occurs when the contaminated material lies on or very near the soil surface. Such is the case when spills occur or immediately after waste is surface-applied to a landtreatment site. In these cases, the emission process will be controlled by the rate of evaporation.

Evaporation is a surface phenomenon, and the parameters that affect the evaporation process are the properties of the waste itself as well as those that have an effect on the air-surface interface (i.e. wind, surface roughness). The important parameters include the volatility or vapor pressure of the waste, ambient meteorological conditions (solar insolation, air and waste temperature, surface wind speed, relative humidity), surface coarseness, and the bulk concentration of the volatile components in the air (although this is usually very low and generally assumed to be negligible).

There are two major types of soil emission processes. Each are treatment dependent. One type occurs in landtreatment facilities and the other at underground facilities such as landfills. In landtreatment applications, the emission rate is generally highly time-dependent. When a fixed amount of waste is applied to the soil surface, it penetrates the soil to a certain depth. The vaporization rate is maximum immediately after waste application, as the material nearest the surface is vaporized and diffuses through a very thin layer of soil. As the waste near the surface is depleted of its VOC content, the volatile material deeper in the soil must diffuse through an increasingly thick soil layer. The soil presents a resistance to VOC diffusion in direct proportion to the VOC depth. Thus, the rate of emissions from the surface decreases with time.

It is common practice in landtreatment to periodically till the soil to provide oxygen for bacterial activity. The tilling effectively mixes the remaining waste in a homogeneous layer near the soil surface. The emission rate is at a maximum immediately following each tilling episode since

volatile waste is again present very near the surface, and resistance to diffusion is at a minimum.

Although also diffusion controlled, the emission process from underground sources such as landfilled waste or material present as a "lens" on the water table has significantly different characteristics than that from surface or near-surface sources. The depth of the emission source is usually quite substantial. Therefore, the emission rate is initially lower due to the resistance to diffusion produced by the column of soil. The initial emission rate is zero, since it takes some time for the volatile material to diffuse through the soil layer. The adsorptive sites on the soil particles must also be initially saturated. Once the emission rate has equilibrated, the rate is relatively constant with time until the underground source is exhausted.

The diffusion process itself through the soil is the same for both types of sources, land treatment (surface) and landfill (underground). Consequently, many of the parameters important to the emission processes are the same, including diffusivity of the VOC in air, soil properties (particle size distribution, soil type, moisture content, particle density, porosity), soil/waste temperature, and volatility of the VOC in the waste. Additional parameters important to the near surface emission processes are the amount of material present in the contaminated soil layer, the initial depth of the contamination, the elapsed time from application (or tilling) and, possibly, ambient conditions such as surface wind speed and relative humidity. The depth of the soil layer above the waste is a very important parameter in the emission process from subsurface sources. Additionally, the adsorptive properties of the soil may also have a significant effect on the emission rate from this latter source type.

An understanding of the emission processes and the important parameters is necessary in the measurement of emission rates from soil surfaces and in the proper interpretation of the test results. As an example, the emission rate from a source is affected by rain since the porosity and, hence, the diffusion rate are reduced with increasing moisture content of the soil. Thus, emission rates immediately after a rainfall will be lower than those from drier soils and may take substantial periods of time to return to the emission rate prior to the rain. (4) Emission rates may vary with the time of day and season, as a result of changes in ambient and soil/waste temperatures. (4) Emission rates from soil areas containing fissures can be higher and much less homogeneous than those from unfractured areas. Thus, considerable care must be taken in planning and implementing a measurement program to determine representative emission rates from such soil surfaces.

## 2.2 Measurement Techniques

Based on a literature review (5), the techniques for determining gas emissions rates from land surfaces contaminated with organic compounds can be divided into three approaches: indirect measurements, direct measurements, and laboratory simulations. Indirect techniques typically require measurements of ambient air concentrations at or near the site. These

measurements are related to the surface area of the area source and local meteorological conditions using a dispersion model to determine an emission rate. The second approach is to directly measure emission rates using for example the flux chamber. The third approach is to create an emission source in the laboratory and model the emissions by various techniques for application to field sites. These three approaches were compared for precision, accuracy, and sensitivity. Other considerations included applicability, complexity, manpower requirements, and costs.

The most promising technique for measuring gas emission rates from land surfaces was determined to be the emission isolation flux chamber technique. The advantages are:

- o lowest (most sensitive) detection limit of the methods examined;
- o easily obtained accuracy and precision data;
- o simple and economical equipment relative to other techniques;
- o minimal manpower and time requirements;
- o rapid and simple data reduction; and
- o applicable to a wide variety of surfaces.

### 2.3 Flux Chamber Operation

The flux chamber technique has been used by researchers to measure emission fluxes of sulfur, nitrogen, and volatile organic species (6,7,8,9,10). The approach uses a flux chamber (enclosure device) to sample gaseous emissions from a defined surface area. Clean dry sweep air is added to the chamber at a fixed, controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is calculated as:

$$E_i = Y_i Q/A \quad (2-1)$$

where:  $E_i$  = emission rate of component i (mass/area-time),  
 $Y_i$  = concentration of component i in the air flowing from the chamber (mass/volume),  
 $Q$  = flow rate of air into the chamber (volume/time),  
 $A$  = surface area enclosed by the chamber (area).

All parameters in Equation 2-1 are measured directly.

Most of the emission rate assessments are of area sources much larger than the enclosed surface area of the flux chamber (0.130 m<sup>2</sup>). In these

cases, an overall emission rate for the area source is calculated from multiple measurements based on random sampling and statistical analysis.

## SECTION 3

### MEASUREMENT OF GASEOUS EMISSION RATES FROM LAND SURFACES USING AN EMISSION ISOLATION FLUX CHAMBER - PROPOSED METHOD

#### 3.1 Applicability and Principle

##### 3.1.1 Applicability

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities such as hazardous waste landtreatment and landfill facilities. This technique is also applicable for emission rate measurements from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) waste sites such as areas contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

##### 3.1.2 Principle

Gaseous emissions are collected from an isolated surface area with an enclosure device called an emission isolation flux chamber (or flux chamber). The gaseous emissions are swept through an exit port where the concentration is monitored and/or sampled. The concentration is monitored and/or sampled either continuously (i.e., "real-time") or discretely. Real-time measurements are typically made with portable total hydrocarbon analyzers and are useful for relative measurements (i.e., the determination of flux chamber steady-state operation, zoning). Discrete samples are taken when absolute measurements are necessary (i.e., steady-state concentrations, emission rate levels). The emission rate is calculated based upon the surface area isolated, the sweep air flow rate, and the gaseous concentration measured. An estimated average emission rate for the area source is calculated based upon statistical sampling of a defined total area.

#### 3.2 Precision, Accuracy, Sensitivity, and Range

##### 3.2.1 Precision

Single chamber precision (i.e., repeatability) of the method is approximately 5 percent at measured emission rates of 3,200 ug/min·m<sup>2</sup>. Variability between different flux chambers (i.e., reproducibility) is approximately 9.5 percent within a measured emission rate range of 39,000 to 65,000 ug/min·m<sup>2</sup>. (4)

The reproducibility results were determined from a bench-scale study. The tests were designed to eliminate temporal variations from the flux chamber reproducibility. However, using the same bench-scale facility, a test design was not possible for measuring flux chamber repeatability without bias from temporal variations. As a result, the repeatability tests were performed in the laboratory. The differences therefore between the stated emission rates for repeatability and reproducibility reflect the differences in laboratory simulated emission rates and those measured from the bench-scale facility.

### 3.2.2 Accuracy

Flux chamber recovery (Section 3.6.1.4.2) results show a recovery range of 77 percent to 124 percent. Table 3-1 lists measured recoveries for a number of compounds tested. The average recovery for the 40 compounds tested is 103 percent.

Flux chamber emission rate measurements made on the soil cells range from 50 percent to 100 percent of the predicted emission rates. That is, the measured emission rates can be expected to be within a factor of one-half of the "true" emission rates.(4) The flux chamber accuracy based upon both the recovery tests and predictive modeling ranges from 50 percent to 124 percent.

### 3.2.3 Sensitivity

The sensitivity of this method depends on the detection limit of the analytical technique used. When discrete samples are collected using gas canisters and analyzed by gas chromatographic methods, the estimated emission rate sensitivity is  $1.2 \text{ ug/min}\cdot\text{m}^2$  for an analytical detection limit of 10 ppbv benzene. When emission rates are measured in a continuous (real-time) method, the estimated sensitivity is  $124 \text{ ug/min}\cdot\text{m}^2$  for an analytical detection limit of 1 ppmv benzene.

### 3.2.4 Range

The range of this method depends upon the analytical technique used. High level emission rates are analyzed by introducing proportional amounts of gas sample to the analyzer. Using this technique, high level emission rates of  $120,000 \text{ ug/min}\cdot\text{m}^2$  have been measured.(4) Low levels are limited by the sensitivity of the analytical technique. Gas chromatographic techniques have been used to measure low level emission rates of  $1.2 \text{ ug/min}\cdot\text{m}^2$  for measured concentrations of 10 ppbv benzene.

## 3.3 Interferences

### 3.3.1 Flux Chamber Method

Impurities in the sweep air and/or organic compounds outgassing from the transfer lines and acrylic chamber top may cause background contamination. The emission isolation flux chamber must be demonstrated to be free

TABLE 3-1  
 COMPOUNDS TESTED IN THE EMISSION ISOLATION FLUX CHAMBER  
 AND THE MEASURED PERCENT RECOVERY

| Compound             | Percent Recovery* | Compound               | Percent Recovery* |
|----------------------|-------------------|------------------------|-------------------|
| Total C <sub>2</sub> | 100               | 3-methylhexane         | 106               |
| Total C <sub>3</sub> | 108               | 2,2,4-trimethylpentane | 106               |
| Isobutane            | 109               | n-heptane              | 103               |
| 1-butene             | 108               | Methylcyclohexane      | 103               |
| n-butane             | 106               | Toluene                | 103               |
| t-2-butene           | 107               | Ethyl benzene          | 94.7              |
| c-2-butene           | 109               | mtp-xylene             | 88.5              |
| Isopentane           | 112               | o-xylene               | 97.3              |
| 1-pentene            | 105               | n-nonane               | 99.4              |
| 2-methyl-1-butene    | 124               | n-propylbenzene        | 95.5              |
| n-pentane            | 107               | p-ethyltoluene         | 92.5              |
| n-pentene            | 103               | 1,3,5-trimethylbenzene | 93.5              |
| c-2-pentene          | 105               | 1,2,4-trimethylbenzene | 88.7              |
| Cyclopentene         | 105               | 2-methyl-2-butene      | 103               |
| n-hexane             | 95.1              | Methyl mercaptan       | 107               |
| Isohexane            | 107               | Ethyl mercaptan        | 107               |
| 3-methylpentane      | 106               | Butyl mercaptan        | 101               |
| Methylcyclopentane   | 105               | Tetrahydrothiophene    | 115               |
| Benzene              | 106               | Trichloroethylene      | 77.1              |
| 1,2-Dimethylpentane  | 105               | Ethylene dichloride    | 103               |

\*Section 3.8.2

from significant (<10 percent of expected measured concentrations) levels of such contamination under the measurement operating conditions by running method blanks. Background levels above this limit will significantly bias the flux chamber measurements. Typical values measured with a real-time analyzer (OVA) range from 0 to 2 ppmv exit gas concentration.

Cross-contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of cross-contamination, the chamber should be purged between samples with ultra high purity air and followed with running a method blank until typical values are achieved.

The use of a transparent chamber may result in gas and surface warming due to greenhouse effects. The degree of gas and surface warming are dependent upon the outside air temperature. For outside air temperatures of 28°C, a temperature gradient between the inside flux chamber air and outside air increases from 9°C at 5τ (30 minutes) to 30°C 2.5 hours later. Such heating is minimized by the use of short sampling times.

As a result of the greenhouse effect, condensation may occur when monitoring moist surfaces. Condensation should be recorded when observed and dried from chamber surfaces and lines between sample runs. Condensation could reduce exit gas concentrations of water soluble compounds.

The emission rate process from soils enclosed by the flux chamber could be suppressed as the internal VOC vapor phase concentration increases. Emission rate suppression is avoided by increasing the sweep air flow rate. Suppression is not a significant factor until flux chamber entrapped vapor concentrations are greater than 10 percent of the equilibrium vapor phase concentration. The equilibrium vapor phase concentration is determined from the headspace concentration measurements of a soil sample. This concern applies only when sampling highly concentrated and volatile waste.

### 3.3.2 Emission Process

Ground moisture resulting from either rain, heavy dew, etc. has a definite effect upon the emission rate from land surfaces. Ground moisture accumulation from trace amounts of rain ( $\leq 0.01$  inches) have little or no effect, whereas ground moisture resulting from a rainfall of 0.30 inches of water has been observed to decrease emission rates by 90 percent.(4) At this level of precipitation, seven days of hot, sunny weather were required before the gas emission rates returned to values equal to that before the rain. As such, emission rate measurements made on soils recently experiencing an elevated ground moisture content would be biased. Emission rate measurements will be below those made at normal soil moisture levels.

## 3.4 Apparatus and Materials

### 3.4.1 Flux Chamber and Supporting Equipment

A diagram of the flux chamber and supporting equipment is shown in Figure 3-1. The flux chamber materials and specifications are listed in

FIGURE 3-1  
A CUTAWY DIAGRAM OF THE EMISSION ISOLATION FLUX CHAMBER AND  
SUPPORT EQUIPMENT

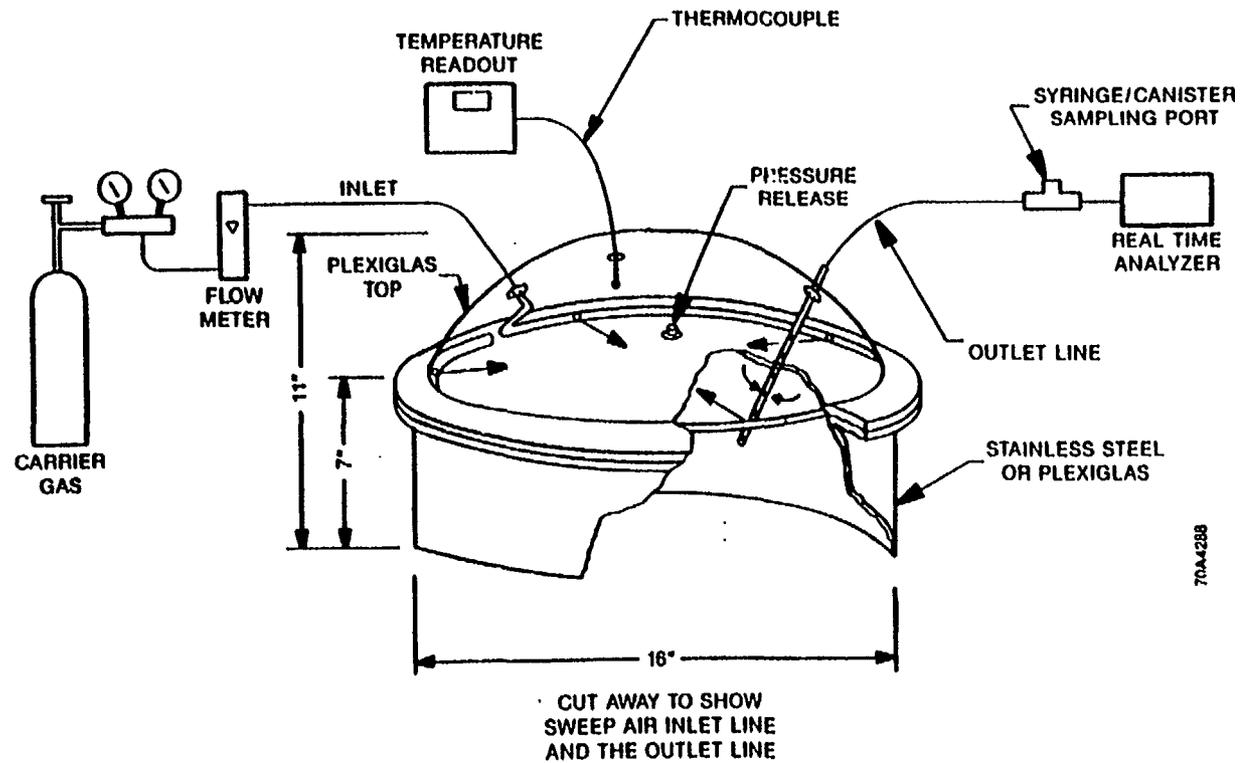


Table 3-2. A construction diagram of the flux chamber is shown in Figure 3-2.

The sweep air carrier gas should be dry, organic free air equal to or better than commercial ultra high purity grade (<0.1 ppmv THC). A gas flow meter with no internal rubber parts and adjustable within the range of 1-10 L/min should be used to control gas flow. Temperature measurements should be made with an accuracy of  $\pm 1.0^\circ\text{C}$ . A fine-wire thermocouple with electronic readout is recommended. Caution should be taken to avoid any contact of a thermocouple with metal. This would give inaccurate air temperature readings. A pressure release port is required to avoid pressure build-up inside the flux chamber during operation. This port should never be blocked. For system blanks, a clean Teflon<sup>™</sup> sheet should be used to provide a clean surface for the flux chamber.

#### 3.4.2 Discrete Sample Collection

Discrete grab samples should be collected with air-tight, inert containers. For on-site analysis, 100 ml precision lock, glass syringes are recommended. Glass plungers are recommended over Teflon<sup>™</sup> tip plungers. If Teflon<sup>™</sup> tip plungers are used, then special controls must be followed to avoid cross-contamination (Section 3.7.1.1). For samples to be transported or to be stored for periods longer than 1 hour, 2L stainless steel gas canisters are recommended.

#### 3.4.3 Analysis

##### 3.4.3.1 Real Time

###### Analyzer

For real-time, continuous monitoring of the exit gas concentration, analyzers with precision of  $\pm 10$  percent of the measured value and a detection limit of 1 ppmv are recommended.

###### Calibration Gases

The portable, real-time analyzers will require the following levels of calibration gases:

- o High-Level Gas: Concentration within 50 percent to 90 percent of the span value (maximum expected concentration or upper limit of instrument linear range).
- o Low-Level Gas: Concentration less than or equal to 0.01 percent of the span value.
- o Zero Grade Gas: Ultra high purity (UHP) air (<0.1 ppmv THC).

The calibration gas for these analyzers can be the same as that used for the on-site discrete analyzer (Section 3.4.3.2.2).

TABLE 3-2  
FLUX CHAMBER MATERIALS SPECIFICATIONS

| Item                                    | Description  | Specification  |
|---|--|--|
| Carrier Gas Lines:<br>Inlet/Outlet      | Teflon <sup>®</sup> (clear)  | 1/4" OD, 5' to 8' long, thin walled, 1/4" stainless steel fittings   |
| Sweep Air Wrap Perforation <sup>a</sup> | Stainless Steel<br>four equidistant holes<br>jetting direction                               | 1/4" OD, 54" long, perforated hole No. 1 (nearest input), 5/64" ID, holes No. 2-4, 3/32" ID, axially, horizontally   |
| Fittings <sup>b</sup>                   | Stainless steel<br><br>Stainless steel   | 1/4" bulkheads with teflon washers for chamber penetration<br>1/4" cap to seal wrap line end   |
| Thermocouples<br>Air (1)                | Fine wire<br>K type  | 36" long, bead tip, teflon coated (extensions optional), penetrate flux chamber 3", support with 1/4" bulkhead with septa  |
| Flux Chamber:<br>Base                   | Stainless steel<br>column  | 16" ID x 7" tall, welded to a support ring flange  |
| Support ring<br>flange                  | Stainless steel  | 16" ID x 20" OD x 1/4" thick   |
| Dome                                    | Acrylic<br><br>four holes<br><br>Inlet/outlet<br><br>Air temperature<br><br>Pressure release | Spherical, 4" displacement at center, 16" ID at seal, 2" lip for seal, 1/4" thick, molded Equidistant, 4" from aluminum gasket<br>1/2" ID with 1/4" stainless steel bulkhead<br>1/2" ID with 1/4" stainless steel bulkhead<br>13/16" ID with 3/4" stainless steel bulkhead |
| Seal<br>Dome to Base                    | Top gasket<br><br>Dome lip   | Aluminum 16" ID, 20" OD, 1/4" thick<br>Below aluminum gasket is the acrylic lip of dome  |

(Continued)

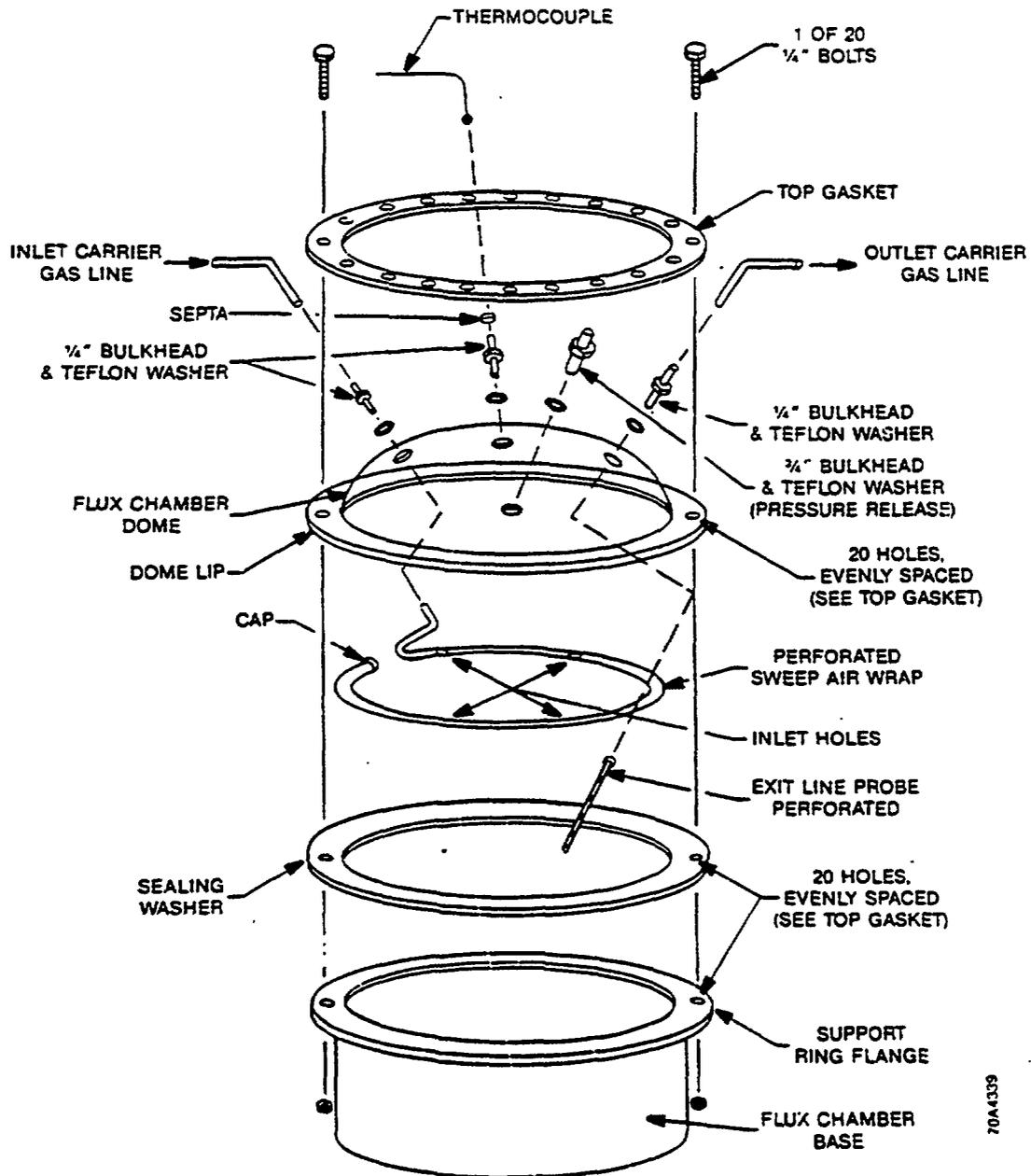
TABLE 3-2  
(Continued)

| Item            | Description              | Specification  |
|-----------------|--------------------------|--|
|                 | Sealing washer           | Teflon, 16" ID, 20" OD, 1/32" thick  |
|                 | Bottom gasket            | Stainless steel support ring   |
|                 | Fasteners                | 20, 1/4" bolts equidistant around lip                                      |
| Volume          | With 1" soil penetration | 0.03 m <sup>3</sup> (30L)  |
| Surface Area    | Enclosed by chamber      | 0.130 m <sup>2</sup>   |
| Exit Line Probe | Teflon <sup>a</sup>      | 1/4" OD, 6" long, stainless steel fitting, perforated                      |
| Perforation     | 2 rows of holes          | 3/32" ID, 5 holes per row, 1" separation, rows are positioned orthogonally |

<sup>a</sup>Avoid placement of exit line probe in jetting path of sweep air inlet holes

<sup>b</sup>All fittings are manufactured by Swagelok® or equivalent manufacturer (bulkheads use Teflon<sup>™</sup> washers for sealing)

FIGURE 3-2  
EXPLODED VIEW OF THE FLUX CHAMBER



70A4339

### Quality Control (QC) Gas

The portable, real-time analyzer will require a quality control (QC) gas concentrated to fall within the span range. The QC gas for this analyzer can be the same as that used for the on-site discrete analyzer.

#### 3.4.3.2 Discrete

##### Analyzer

The analyzer should be sensitive with low detection limits. For on-site analysis of grab samples, instrumentation having precision of  $\pm 5$  percent of the measured value with a detection limit of 1 ppm is recommended. Analyzers with injection loops are recommended to reproduce the sample volumes injected. For off-site analysis, instrumentation with precision of  $\pm 30$  percent at detection limits of 1 ppbv are recommended.

##### Calibration Gases

The concentrations and composition of the calibration gases to be used will vary depending on the species of interest. Preferably, the following gas concentrations should be used for each species of interest:

- o High-Level Gas: 90 percent of the span value.
- o Mid-Level Gas: Average expected concentration.
- o Low-Level Gas: 0.01 percent of the span value.
- o Zero Grade Gas: Ultra high purity (UHP) air, ( $<0.1$  ppmv THC).

Alternatively, a high-level gas may be used with a dilution system to generate the lower level gas concentrations. A dilution system is recommended that meets or exceeds that described in Section 6.2.1.1 of Method 18 of 40 CFR Part 60. If multicomponent species are analyzed, then on-site calibration gases should be benzene or hexane. To identify and quantitate multicomponent responses when a single component (benzene or hexane) is used for calibration, a library of normalized responses relative to the single component calibration gas must be employed. This does not guarantee all species of the multicomponent will be identified. If specific identification and quantitation are not required, then quantitation and identification should be made relative to the calibration gas.

##### QC Gas

The discrete analyzer will require a QC gas that has a concentration within the span range.

## 3.5 Procedure

### 3.5.1 Flux Chamber Operation

The flux chamber is operated identically for real-time and discrete sampling.

#### 3.5.1.1 Preparation

All exposed chamber surfaces should be cleaned with water and wiped dry prior to use. Assemble the sampling apparatus and check for malfunctions and leaks.

#### 3.5.1.2 Operation

Place the flux chamber over the surface area to be sampled and work it into the surface to a depth of 2-3 cm. Initiate the sweep air and set the flow rate at 5 L/min. Record data at time intervals defined by residence times or  $\tau$  (tau), where  $\tau$  = flux chamber volume (30L)/sweep air flow rate (5L/min). One  $\tau$  then has the value of 6 minutes under normal operating conditions. At  $\tau = 0$  (flux chamber placement), record the following: time, sweep air rate, chamber inside air temperature, ambient air temperature, and exit gas concentration (real-time analyzer). The data should be recorded on the data sheet shown in Figure 3-3. At each residence time ( $\tau$ , 6 minutes), the sweep air rate shall be checked (and corrected to 5 L/min if necessary), and the gas concentration shall be recorded (real-time analyzer). After 4 residence times (24 minutes), initiate sample collection. At this time, record the following data: time, sweep air rate, air temperatures inside and outside, exit gas concentration, and sample number(s). If sulfonated organic compounds are of specific interest, then measurements should be taken after 10 residence times (1 hour).

### 3.5.2 Sample Collection

#### 3.5.2.1 Real Time

When real-time monitoring is required, the sample is collected by the real-time analyzer directly from the exit gas line.

#### 3.5.2.2 Discrete Sample Collection

Sample collection should not exceed a flow rate of 2 L/min.

#### Gas Syringes

Sample collection with syringes should be performed after purging the syringe three times with the sample gas. This should be performed without removing the syringe from the sampling line manifold. To ensure fresh sample at each purge, a sampling manifold should be positioned prior to a real-time analyzer (Figure 3-1). The analyzer will then draw the sample past the manifold for sampling.

**FIGURE 3-3  
FLUX CHAMBER GAS EMISSION MEASUREMENTS FIELD DATA SHEET**

**FLUX CHAMBER EMISSIONS MEASUREMENT DATA**

Date \_\_\_\_\_ Sampler(s) \_\_\_\_\_  
 Location \_\_\_\_\_ Zone/Grid Point \_\_\_\_\_  
 Surface Description \_\_\_\_\_  
 Concurrent Activity \_\_\_\_\_

| Time | Sweep Air Rate, Q (L/Min) | Residence No. (Q/V) | Gas Conc. (ppmv) | Air Temperature |             | Sample Type/No. | Comments: |
|------|---------------------------|---------------------|------------------|-----------------|-------------|-----------------|-----------|
|      |                           |                     |                  | Chamber (C)     | Ambient (C) |                 |           |
|      |                           | 0                   |                  |                 |             |                 |           |
|      |                           | 1                   |                  |                 |             |                 |           |
|      |                           | 2                   |                  |                 |             |                 |           |
|      |                           | 3                   |                  |                 |             |                 |           |
|      |                           | 4                   |                  |                 |             |                 |           |
|      |                           | 5                   |                  |                 |             |                 |           |

Comments: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

7-86-24843

## Gas Canister

Sample collection with evacuated gas canisters should be performed with the real-time analyzer replaced by the gas canister (Figure 3-4).

To collect canister samples, remove the real-time analyzer from the exit line sampling manifold. Securely fasten the canister sampling manifold to the exit line manifold. Open the flow control valve ( $V_1$ , Figure 3-4) slightly. If this valve is opened too much, the large pressure drop at the exit line inside the flux chamber could draw direct air jetting from the sweep air inlet manifold. This would reduce the measured emission rate. A large pressure drop inside the flux chamber could also draw ambient air in through the pressure release port. These concerns are important only when the exit line sampling rate approaches that of the entrance sweep air rate (5 L/min). If a 2L gas canister is used, then control the flow to fill the canister in 1 to 2 minutes. The use of a capillary flow controller between the exit line and canister could be used to control gas flow.

After sample collection, seal the sample valve ( $V_1$ ) prior to removal from the sampling line. This prevents contamination. At this time, the sample is labeled and recorded. Record the final pressure of the canister.

### 3.5.3 Sample Analysis

#### 3.5.3.1 Real Time

Real-time analysis is a continuous process with the real-time analyzer connected to the exit line. These data are an initial indication of the exit line concentration.

#### 3.5.3.2 Discrete

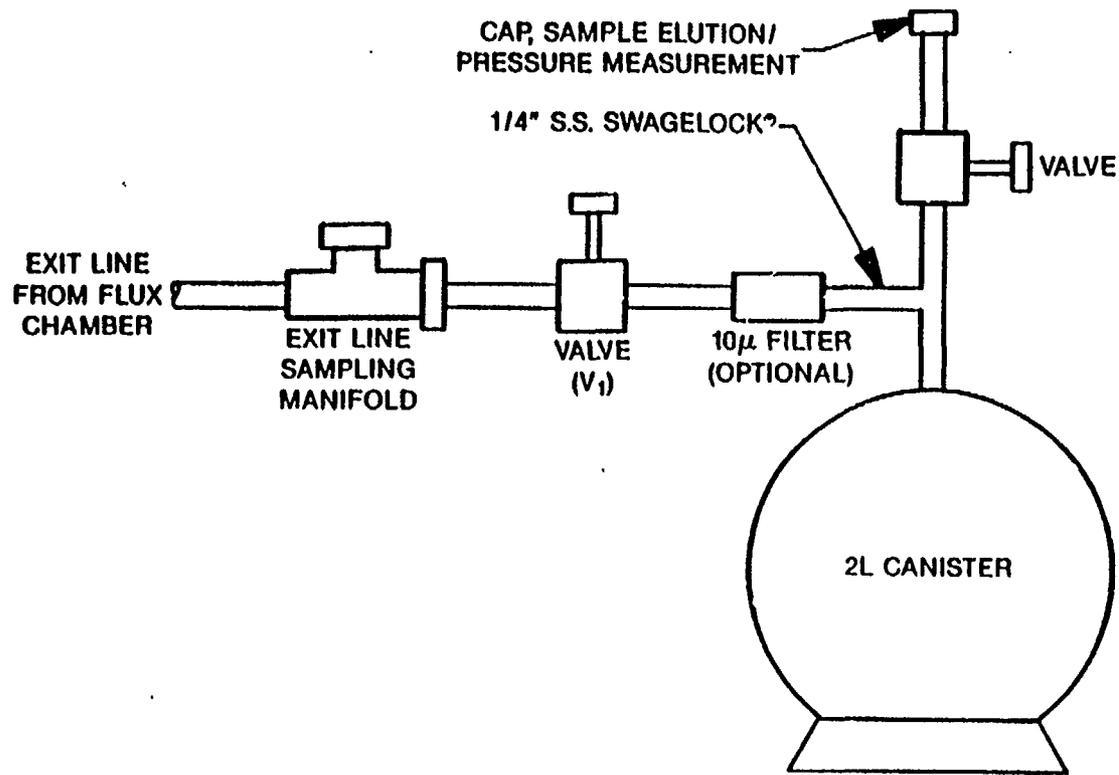
##### Gas Syringes

Gas syringe samples collected should be treated promptly and consistently. Temperature differentials between the flux chamber air and the analytical laboratory air can cause changes in sample volume. It is recommended that the analytical air temperature be constant, recorded twice daily and within 10°F of the ambient outside air temperature. The samples should be analyzed either immediately upon arrival into the analytical area or allowed to thermally equilibrate (1-5 min depending on syringe size). Since immediate analysis is not always possible, the later technique is recommended.

##### Gas Canisters

Prior to sample preparation for analysis, the canister pressure should be measured. The canisters are then pressurized to 18 psi with ultra high purity nitrogen. Measure the final pressure. A known volume of diluted gas canister sample is taken from the canister by releasing sample into an evacuated volumetric stainless steel canister (3.55L). From this volumetric

FIGURE 3-4  
STAINLESS STEEL GAS CANISTER AND SAMPLING MANIFOLD  
(NOT TO SCALE)



3-14

70A4404

gas canister, the sample is then introduced into the gas chromatograph through cryogenic traps. The dilution factor is calculated by Equation 3-2 (Section 3.8.3).

#### 3.5.4 Sampling Strategy

The following sampling strategy provides an accurate and precise estimate of the emission rate for a total area source through random sampling in which any location within the area source has a theoretically equal chance of being sampled. The sampling strategy described below provides an estimated average emission rate within 20 percent of the true mean with 95 percent confidence.

##### 3.5.4.1 Zones

Based on area source records and/or preliminary survey data, subdivide the total area source into zones if nonrandom chemical distribution is exhibited or anticipated. The zones should be arranged to maximize the between-zone variability and minimize the within-zone variability.

##### 3.5.4.2 Grids

Divide each zone by an imaginary grid with unit areas that depend on zone area size ( $Z$ ) as follows:

If  $Z \leq 500 \text{ m}^2$ , then divide the zone area into units with areas equal to 5 percent of the total zone area (i.e., 20 units total).

If  $500 \text{ m}^2 < Z \leq 4,000 \text{ m}^2$ , then divide the zone area into units of area  $25 \text{ m}^2$ .

If  $4000 \text{ m}^2 < Z \leq 32000 \text{ m}^2$ , then divide the zone area into 160 units.

If  $Z > 32000 \text{ m}^2$ , then divide the zone area into units with area equal to  $200 \text{ m}^2$ .

Assign a series of consecutive numbers to the units in each zone.

##### 3.5.4.3 Sample Number

Using Equation 3-3 (Section 3.8.4), calculate the number of units (grid points) to be sampled for the  $K$ th zone ( $n_K$ ).

##### 3.5.4.4 Sample Locations

Using the random numbers table (Appendix A), identify  $n_K$  grid points (units) that will be sampled in zone  $K$ . A grid point shall be selected for measurement only once. (This is not to be confused with duplicate sampling, Section 3.7.2.2.)

#### 3.5.4.5 Emission Rate Calculations

After sample collection, use Equations 3-4, 3-5, 3-6, 3-7, and 3-8 to calculate the measured emission rate ( $E_{CKi}$ ) for each grid point ( $i$ ) in each zone ( $K$ ). Research has shown an emission rate dependency upon the air temperature inside the flux chamber. (4) Through a statistical analysis of both laboratory and field data, a correction factor for temperature variations has been developed. The correction factor compensates a measured emission rate for chamber air temperature variations from the nominal chamber air temperature.

The nominal chamber air temperature can be defined in two ways depending on the purpose of emission rate measurements. If emission rate measurements are for an estimate of an area source, then the nominal chamber air temperature should be the mean chamber air temperature of all the measurements made at that area source. If emission rate measurements are compared between area sources, then the nominal chamber air temperature should be 25°C (298K).

#### 3.5.4.6 Preliminary Estimates

With Equations 3-9, 3-10, and 3-11, calculate the zone mean emission rate ( $\bar{E}_K$ ), variance ( $S_K^2$ ), and coefficient of variation ( $CV_K$ ), respectively. For these calculations, use the first emission rate measurement of a duplicate set.

#### 3.5.4.7 Further Sampling

Use Table 3-3 and  $CV_K$  to determine the total number of samples ( $N_K$ ) required from a given zone to estimate with 95 percent confidence an emission rate within 20 percent of the mean. If  $N_K > n_K$ , then  $N_K - n_K$  additional samples must be collected from zone  $K$ . Locate these additional samples using a random numbers table. Do not duplicate previously sampled locations.

If  $N_K \gg n_K$ , it may be most effective to rezone using the preliminary measured emission rates as a guide. If new zones are established, then these new zones will need to be gridded accordingly (Section 3.5.4.2).

#### 3.5.4.8 Final Estimates

Collect any additional samples and recalculate the emission estimates for the sample mean ( $\bar{E}_K$ ) and variance ( $S_K^2$ ) for each zone (Section 3.5.4.6). Then compute the overall area source mean ( $\bar{E}$ ) and variance ( $S^2$ ) for the total site area using Equations 3-13 and 3-14, respectively. Determine the 95 percent confidence interval for each zone ( $CI_K$ ) and for the site area ( $CI$ ) using Equations 3-15 and 3-16.

TABLE 3-3  
 TOTAL SAMPLE SIZE REQUIRED BASED ON THE PRELIMINARY  
 SAMPLE COEFFICIENT OF VARIATION ESTIMATE\*

| Coefficient of<br>Variation - CV (%)** | Number of Samples<br>Required ( $N_K$ ) per Zone K |
|--|--|
| 0 - 19.1                               | 6  |
| 19.2 - 21.6                            | 7  |
| 21.7 - 24.0                            | 8  |
| 24.1 - 26.0                            | 9  |
| 26.1 - 28.0                            | 10   |
| 28.1 - 29.7                            | 11   |
| 29.8 - 31.5                            | 12   |
| 31.6 - 33.1                            | 13   |
| 33.2 - 34.6                            | 14   |
| 34.7 - 36.2                            | 15   |
| 36.3 - 37.6                            | 16   |
| 37.7 - 38.9                            | 17   |
| 39.0 - 40.2                            | 18   |
| 40.3 - 41.5                            | 19   |
| 41.6 - 42.8                            | 20   |
| 42.9 - 43.9                            | 21   |
| 44.0 - 45.1                            | 22   |
| 45.2 - 46.2                            | 23   |
| 46.3 - 47.3                            | 24   |
| 47.4 - 48.4                            | 25   |
| 48.5 - 49.5                            | 26   |
| 49.6 - 50.7                            | 27   |
| 50.8 - 51.6                            | 28   |
| 51.7 - 52.3                            | 29   |
| 52.4 - 53.4                            | 30   |

\*Value given is the sample size required to estimate the average emission rate with 95 percent confidence that the estimate will be within 20 percent of the true mean.

\*\*For CVs greater than 53.4, the sample size required is greater or equal to  $CV^2/100$ .

## 3.6 Calibration

### 3.6.1 Equipment

#### 3.6.1.1 Flow Meters

The flow meter should be calibrated against an NBS-traceable bubble meter before sampling. The flow meter should have a working range of 2-10 L/min.

#### 3.6.1.2 Thermocouple

Fine wire K-type insulated thermocouples are recommended for temperature measurements. Prior to field use, the thermocouple and readout should be calibrated against a mercury-in-glass thermometer meeting ASTM E-1 No. 63C or 63F specifications. The thermocouple should have an accuracy within  $\pm 1^\circ\text{C}$ .

#### 3.6.1.3 Calibration Gases

For checking the concentrations of the calibration gases, use calibration gases that are documented traceable to National Bureau of Standard Reference Materials. Use Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors (Protocol Number 1) that is available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Mail Drop 77, Environmental Protection Agency, Research Triangle Park, North Carolina 27711. Obtain a certification from the gas manufacturer that the protocol was followed.

#### 3.6.1.4 Flux Chamber System

Several tests should be performed to characterize a new flux chamber prior to use. These tests should be repeated if a chamber is exposed to severe conditions such as corrosive gases, extremely high levels of organic vapors, or organic liquids.

##### Blanks

Check the flux chamber for background by placing the chamber over a clean Teflon<sup>™</sup> surface and running a test using ultra high purity sweep air and routine operating conditions. Sample collection and analysis should be as previously described (Sections 3.5.2 and 3.5.3).

##### Recovery Efficiency

Check the flux chamber sample recovery efficiency by placing the chamber over a flat Teflon<sup>™</sup> surface containing an inlet port at the center for introduction of a calibration gas(es). The calibration gas should be that used for the on-site analyzer at a concentration of at least 1,000 ppmv (high-level gas). The calibration gas should be introduced into the chamber

at a flow rate of no greater than 0.5 L/min. Add ultra high purity sweep air concurrently through the enclosure sweep air inlet (5 L/min) and determine the concentration exiting the enclosure under routine operating conditions. Compare the measured concentration to the true concentration (corrected for dilution), and calculate a percent recovery using Equation 3-1. Results for a variety of volatile organic compounds are presented in Table 3-1. Results should be within 10 percent of the true concentration. The limited data characterizing the recovery efficiency for halogenated compounds indicate an acceptance level that may be larger than 10 percent.

### Corrective Action

If the background levels of the flux chamber are greater than 10 percent of the measured concentrations or 10 ppmv, whichever is smaller, then rerun the blank sample. If high levels persist, then disassemble the flux chamber, clean all internal parts with water and replace those suspected to be contaminated, and reassemble for another blank run. Repeat above until satisfactory levels are reached.

If the recovery efficiency is below 90 percent for non-halogenated compounds, then rerun the recovery test. If low recoveries persist, check for poor sealing and/or inlet gas shortcutting directly from the input line to the exit line and/or misadjusted flow rate settings.

### 3.6.2 Analyzers

The following procedures should be performed at the recommended frequency during the analysis of flux chamber samples.

#### 3.6.2.1 Real Time

Real-time analyzers are used more for relative, continuous measurements than for absolute measurements. If these analyzers are intended for absolute measurements, then they should be calibrated according to Section 3.6.2.2. Real-time analyzers may be used when data quality requirements are less stringent (Section 3.1.2). As such, these analyzers require less stringent quality control practices.

Each day prior to sampling, a three-point calibration should be performed on each analyzer (Section 3.4.3.1.2). Consider the calibration acceptable if responses are within  $\pm 20$  percent of the expected response. If the responses are not acceptable, then recalibrate the instrument.

#### 3.6.2.2 Discrete Analyzer

Discrete analyzers are those that are the most relied upon for absolute, quantitative data of the analyzers used on site. As such, these analyzers require more stringent quality control practices (Section 3.1.2). The calibration procedure suggested here is for linear detectors (i.e., FID, PID). Compensations for non-linear detectors used for analysis of sulfonated compounds (flame photometric detectors) must be made.

Prior to each field investigation, a multipoint calibration including zero and at least three upscale concentrations (Subsection 3.4.3.2.2) should be performed to establish the linearity of the analyzer. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of GC response to amount injected (response factor) is a constant over the multipoint range (<10 percent coefficient of variation, standard deviation/mean), linearity through the origin can be assumed, and the average response factor can be used in place of a calibration curve.

Each day prior to sampling and after every fifth sample, the working calibration curve (or response factor) must be verified by the measurement of one or more calibration standards. If the response for any standard varies from the predicted response by 20 percent, the test must be repeated using a fresh calibration standard. If the analyzer response is still unacceptable, a new calibration curve (or response factor) must be prepared for that compound. A new calibration curve (or response factor) should be calculated after each verification of calibration using the acceptable results of the one or more calibration standards injected.

### 3.7 Quality Control

#### 3.7.1 Sampling Equipment

##### 3.7.1.1 Syringes

Prior to use for sample collection, all syringes should be challenged with one or more of the calibration standards. An acceptable response is within  $\pm 10$  percent of the predicted response. If the response is unacceptable, then repeat the test. Alternatively, check for leakage around the plunger or lock valve by pressurizing the syringe and submerging it under water. Syringes should be checked after every 25 to 30 uses or whenever leakage is suspected. If Teflon<sup>™</sup> tip plungers are used, then suspect memory effects after exposure to high levels of organics. In instances when memory effects are apparent, the Teflon<sup>™</sup> tips should be replaced.

##### 3.7.1.2 Gas Canisters

Gas canisters should be cleaned and evacuated before each use. The pressure should be recorded after each evacuation. Prior to sample collection, check the pressure and compare it to that recorded after cleaning. Acceptable differences are <10 percent of the post evacuation pressure. Canisters having unacceptable pressure differences should not be used for sample collection.

To identify gas canisters and record pressure values, each gas canister should have a chain-of-custody form (Figure 3-5). Copies of this form should be retained for the sampler, laboratory, and sample control.

FIGURE 3-5  
CHAIN-OF-CUSTODY FORM FOR GAS CANISTER SAMPLES

STAINLESS STEEL CANISTER  
CHAIN OF CUSTODY

----- TO BE COMPLETED BY FIELD SAMPLER -----

SAMPLE CONTROL NUMBER: \_\_\_\_\_  
 CANISTER NUMBER: \_\_\_\_\_  
 DATE SAMPLED: \_\_\_\_\_ TIME: \_\_\_\_\_  
 WELL/STATION NUMBER: \_\_\_\_\_  
 OVA READING (PEAK): \_\_\_\_\_  
 ADDRESS/REFINERY LOCATION: \_\_\_\_\_  
 HEIGHT/DEPTH/ROOM: \_\_\_\_\_  
 SAMPLER'S INITIALS: \_\_\_\_\_  
 TASK: \_\_\_\_\_  
 TYPE (CIRCLE ONE):      AMBIENT or POINT SOURCE (specify): \_\_\_\_\_  
 COMMENTS: \_\_\_\_\_

----- TO BE COMPLETED BY LAB (PART ONE) -----

| OPERATION             | DATE  | INITIALS | COMMENTS        |
|-----------------------|-------|----------|-----------------|
| 1. Canister cleaned   | _____ | _____    | _____           |
| 2. Filter cleaned     | _____ | _____    | _____           |
| 3. Canister evacuated | _____ | _____    | Pressure: _____ |
| 4. Canister shipped   | _____ | _____    | _____           |
| 5. Canister received  | _____ | _____    | _____           |
| 6. Analysis completed | _____ | _____    | _____           |
| 7. Sample discarded   | _____ | _____    | _____           |

----- TO BE COMPLETED BY LAB (PART TWO) -----

| PARAMETER             | DILUTION 1 | DILUTION 2 | DILUTION 3 | DILUTION 4 |
|-----------------------|------------|------------|------------|------------|
| Initial Pressure      | _____      | _____      | _____      | _____      |
| Final Pressure        | _____      | _____      | _____      | _____      |
| Add UHP Air           | _____      | _____      | _____      | _____      |
| Dilution Factor       | _____      | _____      | _____      | _____      |
| FINAL Dilution Factor | _____      | _____      | _____      | _____      |

### 3.7.2 Sampling

These tests should be performed at the specified frequency during use of the flux chamber.

#### 3.7.2.1 Sample Blanks

Sample blanks should be performed once daily or after extremely high-level samples. The flux chamber should be cleaned and blanks rerun until exit concentrations are <10 ppmv or <10 percent of expected concentrations, whichever is smaller.

#### 3.7.2.2 Duplicate Samples

A minimum of 10 percent of the sampling points should be sampled in duplicate. Take the two samples over as brief a time span as feasible to minimize any temporal variations in the emitting source.

#### 3.7.2.3 Control Point Samples

One sampling location (grid point or unit) in each zone should be resampled after every ten individual measurements (or a minimum of once per day) when an area source is being investigated. Preferably, this control point should be measured at different times during the diurnal cycle (maximum difference in ambient temperatures). These values provide a measure of temporal variability of the emission rate from the area source.

### 3.7.3 Analytical

#### 3.7.3.1 Real-Time Analyzers

Real-time measurements are typically made with portable total hydrocarbon analyzers. Real-time analyses are useful for relative measurements (i.e., to determine if steady-state operation of the flux chamber has been attained or to determine the zoning boundaries). Each day following calibration, the analyzer should be challenged with the QC gas (Section 3.4.3.1.3). Analyzer performance should be considered acceptable if the measured concentration is within 20 percent of the certified concentration. If this criterion is not met, the QC analysis should be repeated. If the criterion is still not met, then daily calibration should be repeated.

At the conclusion of each day, the QC gas should be reintroduced to the analyzer. The difference between pretesting and posttesting responses provides a measure of upscale drift. Drifts >30 percent should be flagged and not relied upon. If these data are necessary, then resample the grid points sampled on that day.

#### 3.7.3.2 Discrete Analyzers

Each day after calibration, the analyzer should be challenged with the QC gas (Section 3.4.3.2.3). Analyzer performance should be considered

acceptable if the measured concentration is within 10 percent of the certified concentration. If this criterion is not met, repeat the QC gas analysis. If the criterion still cannot be met, then repeat the daily calibration (Section 3.6.2.2).

At the conclusion of each day's testing, the QC gas and zero grade gas should be reintroduced to the analyzer. The differences between pretesting and posttesting values provide a measure of upscale and zero drifts. Daily drift results that show >20 percent should be flagged and tests repeated if determined necessary.

### 3.7.3.3 Analysis of Integrated Samples

Quality control for the analysis of integrated samples should include a minimum of 10 percent analytical blanks and 10 percent duplicate analysis. It is recommended that duplicate samples each be analyzed in duplicate to provide information on analytical as well as sampling variation. A convenient technique is the use of a nested sampling scheme as shown in Figure 3-6.

## 3.8 CALCULATIONS

### 3.8.1 Definitions

A = surface area enclosed by the flux chamber ( $0.130 \text{ m}^2$ )

a = number of carbon atoms per compound molecule

CI = confidence interval for the area source emission rate mean ( $\pm \text{ug}/\text{min}\cdot\text{m}^2$ )

CI<sub>K</sub> = confidence interval for the zone K emission rate mean ( $\pm \text{ug}/\text{min}\cdot\text{m}^2$ )

C<sub>IM</sub> = measured concentration of species I (ppmv) corrected for dilution

C<sub>IT</sub> = theoretical concentration of species I (ppmv)

C<sub>KI</sub> = measured concentration for point I in zone K, total NMHC (ppmv-C)

CV<sub>K</sub> = coefficient of variance for zone K (%)

$\bar{E}$  = mean emission rate for the area source ( $\text{ug}/\text{min}\cdot\text{m}^2$ )

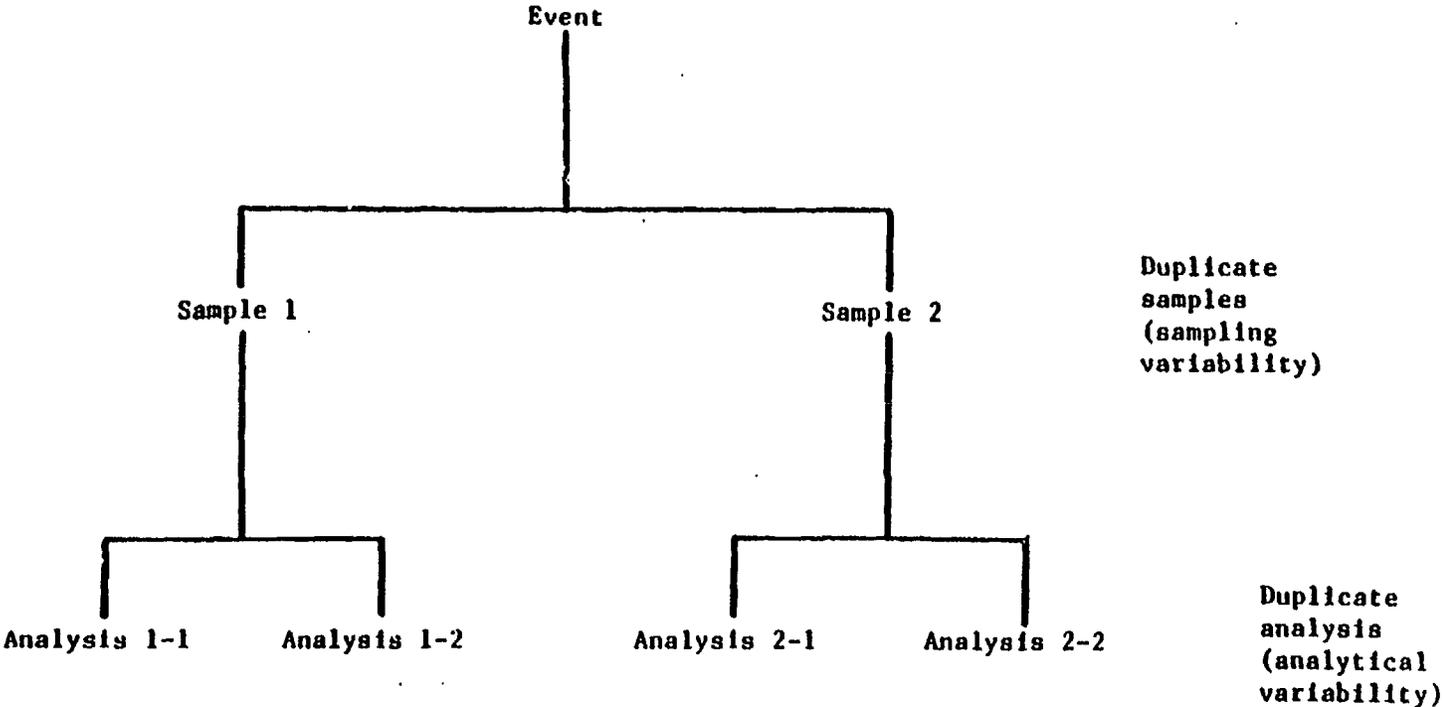
$\bar{E}_K$  = zone K emission rate mean ( $\text{ug}/\text{min}\cdot\text{m}^2$ )

E<sub>KI</sub> = measured emission rate for point I in zone K ( $\text{ug}/\text{min}\cdot\text{m}^2$ )

E<sub>CKI</sub> = measured emission rate for point I in zone K ( $\text{ug}/\text{min}\cdot\text{m}^2$ ) corrected for temperature variations

M<sub>M</sub> = molecular weight of compound (g/mole)

FIGURE 3-6  
NESTED SAMPLING SCHEME



3-24

- $N$  = total number of grid points sampled in the area source (all zones)  
 $N_K$  = final number of grid points (units) sampled in zone K  
 $n_K$  = initial number of grid points (units) sampled in zone K  
 $P$  = atmospheric pressure (atm)  
 $Q$  = sweep air flow rate (L/min)  
 $R$  = gas constant (0.08205 L·atm/mol·K)  
 $S$  = standard error of the overall area source emission rate mean (ug/min·m<sup>2</sup>)  
 $S_K^2$  = zone K emission rate variance  
 $T$  = temperature of laboratory where analyzer is located (K)  
 $TEMP$  = temperature of the flux chamber air (°C)  
 $t_{0.025}$  = the 97.5th percentage point of a student's t-distribution (Table 3-4)  
 $V$  = volume enclosed by the flux chamber (30L)  
 $W_K$  = the fraction of the site represented by the zone K (zone area (m<sup>2</sup>)/site area (m<sup>2</sup>))  
 $Y_{KI}$  = measured concentration for point i in zone K, total NMHC (ug/L)  
 $\alpha$  = parameter defining the level of confidence 100(1-2 $\alpha$ ) percent  
 $\gamma$  = total number of zones in the total area source  
 $\rho$  = confidence interval (%)  
 $\tau$  = measure of residence time V/Q (min)

### 3.8.2 Percent Recovery

The percent recovery measurements used to characterize the flux chamber performance are calculated accordingly:

$$\text{Percent Recovery} = (C_{IM}/C_{IT}) \times 100 \quad (3-1)$$

where:  $C_{IM}$  = the measured concentration of species i (ppmv) corrected for dilution as follows:

$$C_{IM} = (1/DF) \times C \quad (3-1a)$$

TABLE 3-4  
TABULATED VALUES OF STUDENT'S "t"

| Degrees of Freedom* | Tabulated "t" Value** | Degrees of Freedom* | Tabulated "t" Value** |
|---------------------|-----------------------|---------------------|-----------------------|
| 1                   | 12.706                | 21                  | 2.080                 |
| 2                   | 4.303                 | 22                  | 2.074                 |
| 3                   | 3.182                 | 23                  | 2.069                 |
| 4                   | 2.776                 | 24                  | 2.064                 |
| 5                   | 2.571                 | 25                  | 2.060                 |
| 6                   | 2.477                 | 26                  | 2.056                 |
| 7                   | 2.365                 | 27                  | 2.052                 |
| 8                   | 2.306                 | 28                  | 2.048                 |
| 9                   | 2.262                 | 29                  | 2.045                 |
| 10                  | 2.228                 | 30                  | 2.042                 |
| 11                  | 2.201                 | 40                  | 2.021                 |
| 12                  | 2.179                 | 60                  | 2.000                 |
| 13                  | 2.160                 | 120                 | 1.980                 |
| 14                  | 2.145                 | ∞                   | 1.960                 |
| 15                  | 2.131                 |                     |                       |
| 16                  | 2.120                 |                     |                       |
| 17                  | 2.110                 |                     |                       |
| 18                  | 2.101                 |                     |                       |
| 19                  | 2.093                 |                     |                       |
| 20                  | 2.086                 |                     |                       |

\*Degrees of freedom (df) are equal to the number of samples collected less one.

\*\*Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.05 (the same values are applicable to a one-tailed confidence interval and a probability of 0.025).

where C is the sample concentration (ppmv) and  
DF is the dilution factor calculated as follows:

$$S_1 / (S_2 + S_1) \quad (3-1b)$$

where  $S_1$  is the flow rate of the trace gas and  
 $S_2$  is the sweep air flow rate

$C_{IT}$  = the true concentration of species I, gas cylinder value (ppmv)

### 3.8.3 Calculation of the Dilution Factor Involved In Gas Canister Analysis

Analyzing the gas canisters requires pressurizing the canister with nitrogen. This introduces a dilution which must be accounted for as follows:

$$DF = (P_2 - P_1) / (14.7 + P_3) \quad (3-2)$$

where:  $P_1$  = the measured pressure after cleaning and canister evacuation prior to sampling (psig)  
 $P_2$  = the measured pressure after sample collection (psig)  
 $P_3$  = the measured pressure after pressurizing with nitrogen (psig)

The temperature is not required if all pressure measurements used in this equation are performed in the same laboratory (i.e., same temperature) after the canisters have thermally equilibrated.

### 3.8.4 Area Source Emission Rate Equations

The number of units or grids ( $n_K$ ) to be sampled per zone (K) is dependent upon the zone area as follows:

$$n_K = 6 + 0.15 \sqrt{\text{area of zone K (m}^2\text{)}} \quad (3-3)$$

Flux chamber measurements taken at each of the  $n_K$  sampling units are measured in terms of ppmv-C. To calculate an emission rate representing the sampled unit, the measured concentration ( $C_{KI}$ ) must first be converted from ppmv-C to ug/L as follows:

$$Y_{KI} = (P / (R \cdot T)) (MW/a) C_{KI} \quad (3-4)$$

where P is pressure (atm), R is Rydberg's gas constant (L·atm/mole·K), T is the flux chamber air temperature (K) (Section 3.5.4.5), MW is the species' molecular weight (g/mole), a is the number of moles of carbon per mole,  $C_{KI}$  is the measured concentration of sampled unit i in zone K (ppmv-C), and  $Y_{KI}$  is the measured concentration of sampled unit i in zone K (ug/L).

The emission rate for point i in zone K ( $E_{KI}$ ) is then calculated using the converted gas concentration (ug/L) as follows:

$$E_{KI} = (Q \cdot Y_{KI}) / A \quad (3-5)$$

where Q is the flux chamber sweep air flow rate (L/min), A is the enclosed surface area measured (m<sup>2</sup>), and E<sub>KI</sub> is the emission rate measured for point I in zone K (ug/m<sup>2</sup>·min).

Prior to calculating a mean emission rate for the zone measured, the emission rates measured for the individual sampling points need to be corrected for fluctuations in chamber air the temperature (i.e., atmosphere temperature).

The approach used to develop the correction procedure involved developing an empirical equation to predict emission rates as a function of chamber air temperature. (4) The resulting emission rate equation was then used to define the correction factor (C), as follows:

$$C = EF_s / EF_a \quad (3-6)$$

where: EF<sub>s</sub> = emission factor calculated at the nominal chamber air temperature (Section 3.5.4.5)  
 EF<sub>a</sub> = emission factor calculated at the measured chamber air temperature

Both EF<sub>s</sub> and EF<sub>a</sub> are predicted using the proper chamber air temperatures and the following equation:

$$EF_{(s \text{ or } a)} = \exp [0.013(\text{TEMP}_{(s \text{ or } a)})] \quad (3-7)$$

where TEMP is measured in °C.

The measured emission rate (E<sub>KI</sub>) is then corrected to the nominal emission rate (E<sub>cKI</sub>) accordingly:

$$E_{cKI} = C \cdot E_{KI} \quad (3-8)$$

The above procedure has a significance level (i.e., probability that the correlation between chamber air temperature and emission rate measured is due to chance) of 0.4 percent. The standard error of the coefficient in Equation 3-7 is ±0.003.

The mean emission rate for each zone is then calculated accordingly:

$$\bar{E}_K = \frac{1}{n_K} \sum_{i=1}^{n_K} E_{cKI} \quad (3-9)$$

where E<sub>cKI</sub> is the temperature corrected emission rates (Equation 3-8) and n<sub>K</sub> is the number of points sampled in zone K (Section 3.5.4.7).

For each zone (K) sampled, the zone variance (S<sub>K</sub><sup>2</sup>) and coefficient of variance (CV<sub>K</sub>) must be determined as follows:

$$S_K^2 = \frac{1}{n_K - 1} \left[ \sum_{i=1}^{n_K} (E_{CKI})^2 - n_K \bar{E}_K^2 \right] \quad (3-10)$$

$$CV_K = 100 \cdot S_K / \bar{E}_K \quad (3-11)$$

where  $n_K$ ,  $E_{CKI}$ , and  $\bar{E}_K$  are defined in Equations 3-3, 3-8, and 3-9, respectively. The standard deviation ( $S_K$ ) should be calculated for  $n_K - 1$  degrees of freedom for populations ( $n_K$ ) less than or equal to 30. Larger sample sizes require  $n_K$  degrees of freedom.

Prior to calculating the overall emission rate that represents all the zones measured, the data must be tested for level of confidence. That is, for the given coefficient of variance ( $CV_K$ ) of zone K, the zone sample size ( $n_K$ ) must be equal to or greater than the sample size required ( $N_K$ ), listed in Table 3-3, to estimate the overall emission rate with 95 percent confidence that the estimate will be within 20 percent of the true mean.

Table 3-3 lists sample sizes required for 95 percent confidence and a 20 percent confidence interval. The total number of samples ( $N_K$ ) to be collected for different levels of confidences are calculated accordingly:

$$N_K \geq \frac{t_\alpha^2 CV_K^2}{\rho^2} \quad (3-12)$$

where a study requires  $100(1-2\alpha)$  percent confidence that the emission rate estimates will be within  $\rho$  percent of the true mean. The parameter  $t_\alpha$  is the  $(1-\alpha)$  percentage point of a student's t-distribution with  $N_K$  degrees of freedom. A table of t-values can be found in any book on standard statistical techniques. Recommended values for  $t_\alpha$  are listed in Table 3-4.

Use Table 3-3 and  $CV_K$  to determine the total number of samples ( $N_K$ ) required from a given zone. If  $N_K > n_K$ , then  $N_K - n_K$  additional samples must be collected from zone K.

Collect any additional samples and recalculate the emission estimates for the zone mean ( $E_K$ ) and variance ( $S_K^2$ ) using Equations 3-9 and 3-10, respectively. If  $N_K - n_K$  additional samples were collected, then use  $N_K$  samples instead of  $n_K$  in the recalculations. The overall area source mean emission rate ( $\bar{E}$ ) is then calculated as follows:

$$\bar{E} = \frac{\gamma}{\sum_{K=1}^{\gamma} W_K} \bar{E}_K \quad (3-13)$$

where  $\bar{E}_K$  is defined by Equation 3-9,  $W_K$  is the fraction of site covered by zone K (zone area/site area) and  $\gamma$  is the total number of zones sampled.

Finally, calculate the variance of the overall area source mean ( $S^2$ ) and the confidence intervals for each zone K ( $CI_K$ ) and area source (CI) emission rate mean as follows:

$$S^2 = \sqrt{\sum_{K=1}^Y W_K^2 \cdot S_K^2 / N_K} \quad (3-14)$$

$$CI_K = \bar{E}_K \pm t_{0.025} \sqrt{S_K^2 / N_K} \quad (3-15)$$

$$CI = \bar{E} \pm t_{0.025} \cdot S \quad (3-16)$$

## SECTION 4

### CASE STUDY

To supplement the protocol presented in Section 3, a case study will be reviewed. This study will illustrate an actual application of the protocol. Calculations and pertinent decisions will be presented.

The site, referred to as the Bonifay Spill Site, was the scene of an accidental spill of 5500 gallons of JP-4 aviation fuel. The spill site occurred near the intersection of two roads. The majority of the contaminated soil was excavated. The residual product extended over two areas, 30 feet of unvegetated right-of-way along the highway and into a pine forest containing dense underbrush.

The free surface of the water table was three feet below the land surface. The thickness of the unconsolidated sediments that comprised the water table aquifer at the site ranged from 20 to 50 feet. The state aquifer underlaid this sediment layer. Contamination of the free water table surface was expected since it was only 3 feet below landsurface. However, the state aquifer was not considered threatened due to the contaminants net upward hydraulic gradient.

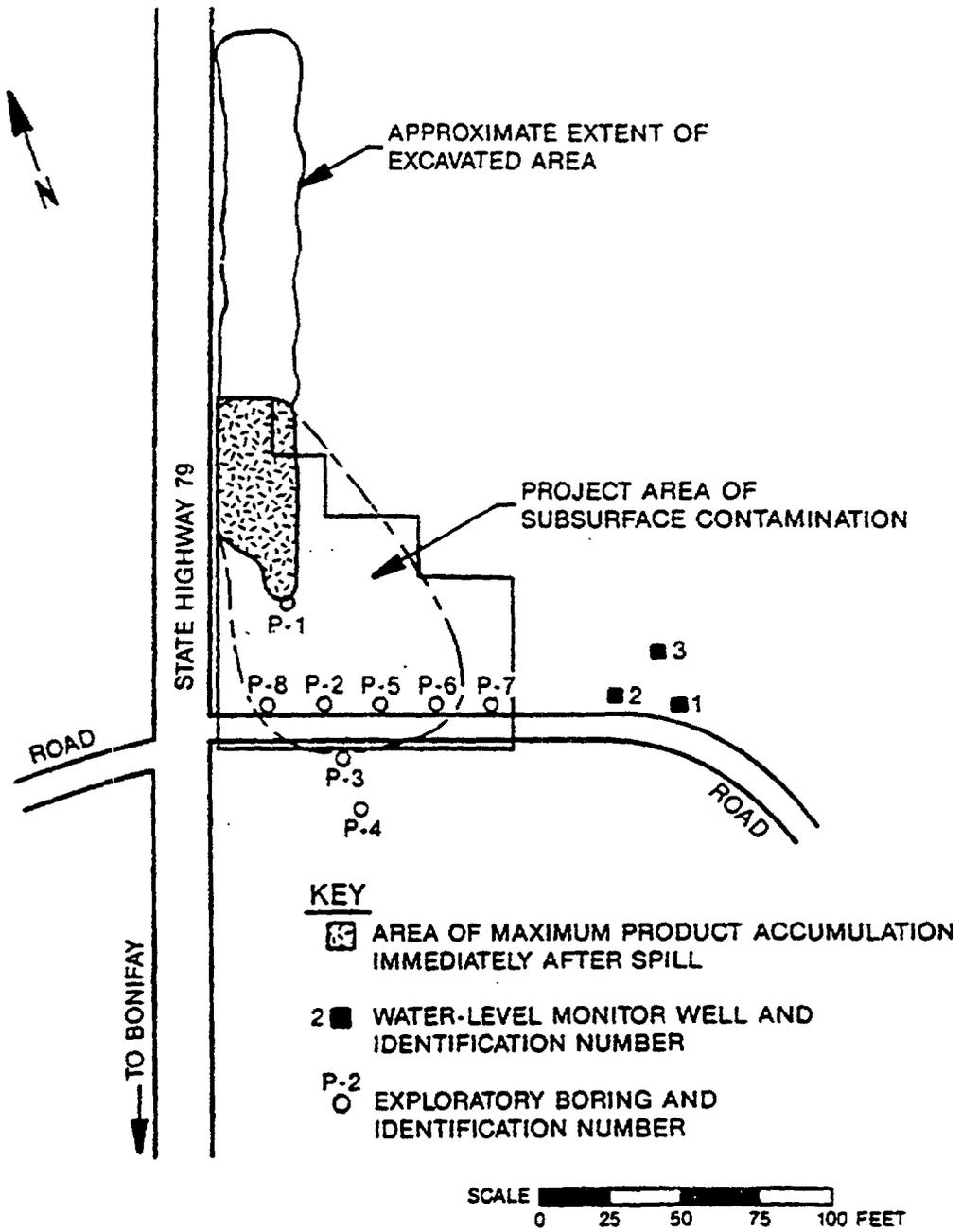
A preliminary survey was performed to define the contaminated area. A series of ten borings indicated that the contaminants had percolated downward to the capillary fringe and moved laterally down gradient. A lens of product several inches thick was detected at a depth of seven feet below land surface. The estimated extent of contamination at the time of the survey study was 7,000 square feet (Figure 4-1).

Results from a preliminary emissions survey performed with a portable real-time analyzer (organic vapor analyzer) held a few inches above ground were used to divide the area source into emission zones for gridding purposes. The survey indicated only one zone was present, and the site was gridded accordingly. The field data for the survey is shown in Table 4-1. The grid system used is shown in Figure 4-2.

Surface emission measurements were made initially at eight sampling grid points. The protocol, at that time, called for the minimum number of sampling points per zone,  $n_k$ , to be selected according to the following equation (note, this equation has since been changed to Equation 3-3).

$$n_k \geq 6 + 0.1 \sqrt{\text{zone area (m}^2\text{)}}$$

FIGURE 4-1  
 SCHEMATIC DIAGRAM OF BONIFAY SPILL SITE, MONITOR WELLS, AND  
 EXPLORATORY BORINGS (BROWN AND KIRKNER, INC., 1983)



70A4344

TABLE 4-1  
FIELD DATA SHEET FOR UNDISTURBED SURFACE SURVEY

Operator: BME Date: 1-12-84

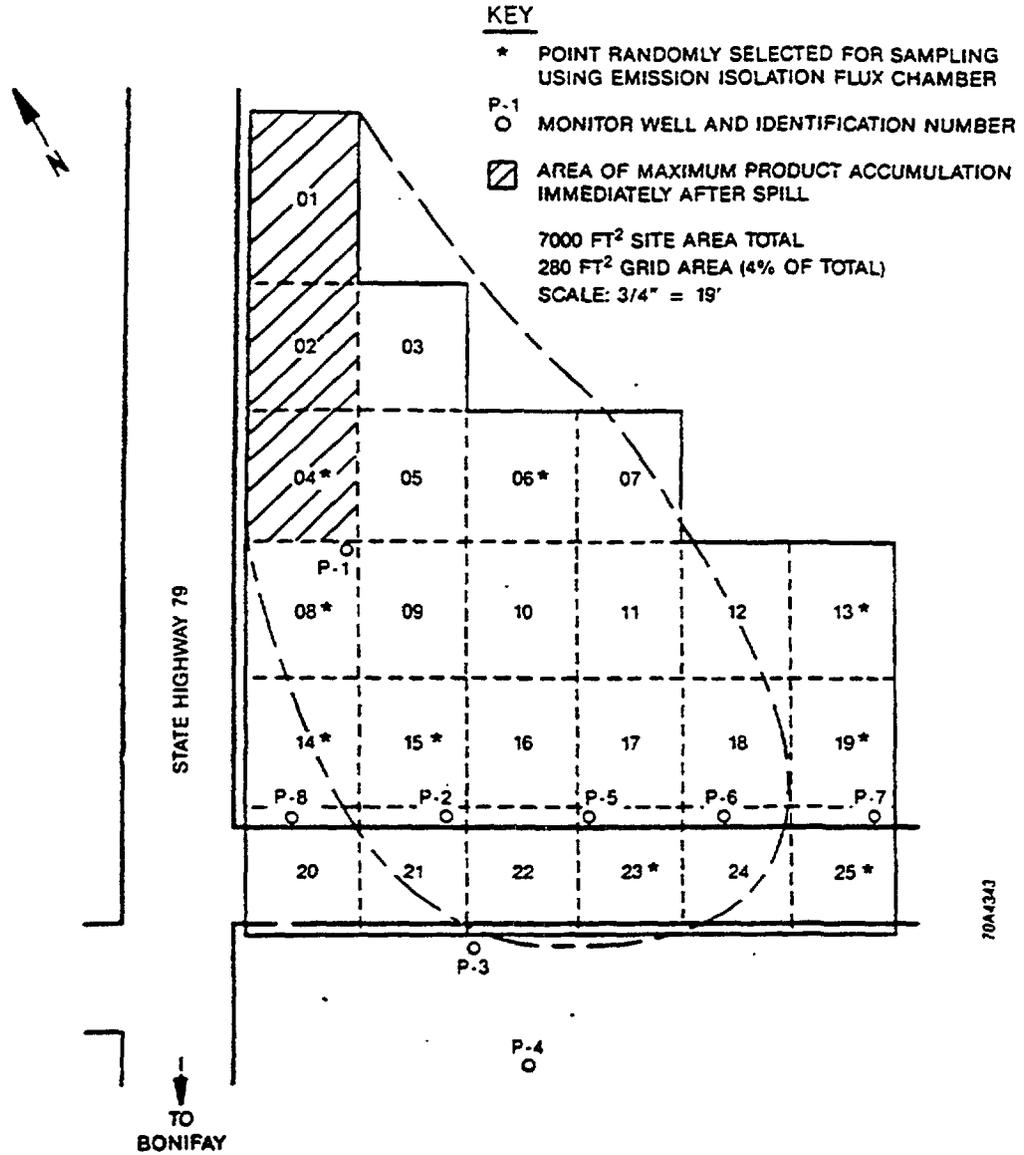
Weather: Temperature = 45°F. Light breeze, partly cloudy

| Grid Point | Surface Temperature | Air Temperature | GC-PID      |                | Comment                              |
|------------|---------------------|-----------------|-------------|----------------|--------------------------------------|
|            |                     |                 | Peak (ppmv) | Average (ppmv) |                                      |
| 01         | 40-42               | 45°F            |             | 0.10           | Sampler was 2"-6" above soil surface |
| 02         |                     |                 | 0.10        |                |                                      |
| 04         | 0.10                |                 |             |                |                                      |
| 08         | 0.10                |                 |             |                |                                      |
| 14         | 0.10                |                 |             |                |                                      |
| 20         | 0.10-0.12           |                 |             |                |                                      |
| 21         | 0.10-0.12           |                 |             |                |                                      |
| 22         | 0.10-0.12           |                 |             |                |                                      |
| 23         | 0.10-0.12           |                 |             |                |                                      |
| 24         | 0.10-0.12           |                 |             |                |                                      |
| 25         | 0.10-0.12           |                 |             |                |                                      |
| 16         | 0.10                |                 |             |                |                                      |
| 18         | 0.10                |                 |             |                |                                      |
| 19         | 0.10                |                 |             |                |                                      |
| Well P-3   |                     |                 |             | 5-6            |                                      |
| Well P-4   |                     |                 | 25          | 7              |                                      |
| Well P-7   |                     |                 |             | 40-70          |                                      |
| Well P-7   |                     |                 |             | 65             | Measurement on 1/14/84 (with GC-FID) |

Comments: Survey done at Midday. Results indicate only one zone

4-3

FIGURE 4-2  
SCHEMATIC DIAGRAM OF SAMPLING GRID AT BONIFAY SPILL SITE



For the single zone at Bonifay, this reduced to:

$$n_k \geq 6 + 0.1 \sqrt{650 \text{ m}^2} = 8.5$$

The 8 locations were selected through the use of a random number table, Appendix A. Grid point 08 was selected to be the control point (i.e., a sampling point to be repeated each day) since it was believed that emissions would be of the largest magnitude at that location. At each sampling location a gas syringe sample was taken for on-site analysis. At several sampling locations, a gas canister was collected in addition to the syringe samples for off-site detailed analysis. A sample field data sheet is shown in Figure 4-3. The results of the emission rate measurement are given in Table 4-2, and a sample calculation is given in Table 4-3.

Total non-methane emission rates were calculated for each grid point based on the on-site analytical data. These emission rates are also presented in Table 4-2. The variation (spatially and temporally) in measured emission rates over the extent of the contaminated area was large (93.8 percent coefficient of variation). Replicate sampling at the control point allowed an estimate of the emission rate temporal variability. The temporal variability was also large (96.0 percent). The major contributor to the variation in measured emission rates from point-to-point can, therefore, be attributed to day-to-day (temporal) variability. The spatial variability was then estimated to be negligible. Using Table 3-3 to determine the total number ( $N_k$ ) of samples to be collected based upon the spatial variability shows that at least 17 samples should have been collected. Although additional samples were required to be collected, sampling was terminated due to rain. It was realized that the lack of a complete data set would then result in a larger emission rate confidence interval.

Using the following equation, the 95 percent confidence interval (CI) for the zone emission rate was estimated.

$$CI = ER \pm t_{0.025} \sqrt{s^2/N_k}$$

where ER is the mean emission rate of the zone,  $s^2$  is the zone variance,  $N_k$  is the total number of sites sampled, and  $t_{0.025}$  is obtained from Table 3-4. The 95 percent confidence interval for the zone emission rate is from 11.3 ug/min·m<sup>2</sup> to 55.2 ug/min·m<sup>2</sup>.

FIGURE 4-3  
FIELD DATA SHEET FOR ISOLATION FLUX CHAMBER SAMPLING AT GRID POINT 08

Date 1-13-84 Samplers BNE

Location Bonifay Spill Site, Grid Point 08

Concurrent Activity None

Surface Description Sand

| Time | Purge Air or Flowrate | Residence Time Number ( $\tau$ ) | Temp. °F |     | Gas Data |          | Air Sample Number |
|------|-----------------------|----------------------------------|----------|-----|----------|----------|-------------------|
|      |                       |                                  | Surface  | Air | OVA ppmv | HNU ppmv |                   |
| 0658 | 4.86 L/min            | 0                                | 46       | 48  | -        | 0.15     |                   |
| 0902 | 4.86 L/min            | 1                                |          |     | -        | 0.16     |                   |
| 0906 | 4.86 L/min            | 2                                |          |     | -        | 0.16     |                   |
| 0910 | 4.86 L/min            | 3                                |          |     | 4.0      | 0.16     |                   |
| 0914 | 4.86 L/min            | 4                                |          |     | 4.0      | -        |                   |
| 0918 | 4.86 L/min            | 5                                |          |     | -        | -        | Canister B003     |
| 0933 | 4.86 L/min            | 9                                |          |     | 4.0      | 0.16     | Gas Syringe B002  |

Comments OVA background = 4 ppm. Some trouble with syringe needle plugging

TABLE 4-2  
RESULTS OF GC ANALYSIS OF GAS SYRINGE TAKEN DURING FLUX CHAMBER SAMPLING

| Grid Point | Sample No. | Date    | Total NMHC Syringe |        | Sweep Air Rate (L/min) | Atmospheric Temperature |      | Average Emission Rate (ug/m <sup>2</sup> ·min) |
|------------|------------|---------|--------------------|--------|------------------------|-------------------------|------|--|
|            |            |         | (ppmv-C)           | (ug/L) |                        | °F                      | °C   |  |
| 4          | B004       | 1/13/84 | 1.0                | 0.62   | 2.60                   | 47                      | 8.3  | 14.4   |
| 6          | B017-A     | 1/14/84 | 6.8                | 4.2    | 2.60                   | 51*                     | 10.6 | 72.6   |
| 8          | B001       | 1/12/84 | 2.0                | 1.2    | 5.00                   | 42                      | 5.5  | 79.6   |
| 8          | B002       | 1/13/84 | 1.0                | 0.62   | 4.86                   | 48                      | 8.9  | 24.9   |
| 8          | B016       | 1/14/84 | 1.0                | 0.62   | 2.60                   | 52                      | 11.1 | 10.0   |
| 14         | B006       | 1/13/84 | 1.0                | 0.62   | 2.60                   | 45                      | 7.2  | 16.6   |
| 15         | B013       | 1/13/84 | 1.0                | 0.62   | 2.60                   | 51                      | 10.6 | 10.7   |
| 19         | B009       | 1/13/84 | 1.0                | 0.62   | 2.60                   | 51                      | 10.6 | 10.7   |
| 23         | B011       | 1/13/84 | 1.0                | 0.62   | 2.60                   | 50                      | 10.0 | 11.5   |
| 25         | B008       | 1/13/84 | 8.8                | 5.4    | 2.60                   | 53                      | 11.7 | 81.4   |

4-7

Variability

Spatial and Temporal:

Mean 33.24  
Standard Deviation 31.17  
CV(%) 93.8

Temporal: (Control Point 8)

Mean 38.2  
Standard Deviation 36.6  
CV(%) 96.0

\*Surface temperature used rather than the chamber air temperature due to a large temperature differential not present in the other measurements. This is suggestive of an error in chamber air temperature measurement.

TABLE 4-3  
 SAMPLE CALCULATIONS OF THE EMISSION RATE FOR GRID POINT 08 ON 1/13/84

Concentration Conversion:

$$Y_i = (P/(R \cdot T))(MW/a)(C_i) \quad \text{(Equation 3-4)}$$

where:  $P = 1 \text{ atm}$   
 $R = 0.08205 \text{ L} \cdot \text{atm}/\text{mole} \cdot \text{K}$   
 $T = 282.6\text{K}$  (average area site air temperature)  
 $MW = 86.18 \text{ g}/\text{mole}$  (referenced to hexane)  
 $a = 6 \text{ moles of carbon}/\text{mole of hexane}$   
 $C_i = 1.0 \text{ ppmv-C}$

$$Y_i = \frac{1 \text{ atm}}{(0.08205 \text{ L} \cdot \text{atm}/\text{mole} \cdot \text{K})(282.6\text{K})} \times \frac{86.18 \text{ g}/\text{mole}}{6 \text{ mole C}/\text{mole}} \times 1.0 \text{ ppmv-C}$$

$$Y_i = 0.6194 \text{ ug}/\text{L}$$

Emission Rate (uncorrected)

$$E_i = (Q \cdot Y_i)/A \quad \text{(Equation 3-5)}$$

where:  $Q = 4.86 \text{ L}/\text{min}$   
 $Y_i = 0.6194 \text{ ug}/\text{L}$   
 $A = 0.130 \text{ m}^2$

$$E_i = \frac{4.86 \text{ l}/\text{min} \cdot 0.6194 \text{ ug}/\text{L}}{0.130 \text{ m}^2}$$

$$E_i = 23.15 \text{ ug}/\text{min} \cdot \text{m}^2$$

Emission Rate Correction Factor

$$EF_S = \exp[0.13(\text{TEMP}_S)] \quad \text{(Equation 3-7)}$$

where:  $\text{TEMP}_S = 9.45^\circ\text{C}$  (nominal chamber air temperature  $^\circ\text{C}$ )  
 $EF_S = \text{emission factor at nominal chamber air temperature}$

$$EF_S = \exp(0.13 \cdot 9.4)$$

$$EF_S = 3.416$$

(Continued)

TABLE 4-5  
(Continued)

---

---

$$EF_a = \exp[0.13(\text{TEMP}_a)]$$

where:  $\text{TEMP}_a = 8.9^\circ\text{C}$  (measured chamber air temperature  $^\circ\text{C}$ )  
 $EF_a$  = emission factor at the measured chamber air temperature.

$$EF_a = \exp(0.13 \cdot 8.9)$$
$$EF_a = 3.180$$

$$C = EF_s / EF_a \quad \text{(Equation 3-6)}$$
$$C = 3.416 / 3.180$$
$$C = 1.074$$

Emission Rate (corrected for temperature variation)

$$E_{c1} = C \cdot E_1 \quad \text{(Equation 3-8)}$$
$$E_{c1} = 1.074 \cdot 23.15 \text{ ug/min} \cdot \text{m}^2$$
$$= 24.86$$
$$= 24.9 \text{ ug/min} \cdot \text{m}^2$$

---

---

SECTION 5  
ADDITIONAL INFORMATION

For further information on vapor/liquid equilibria (VLE) for organic systems, the following reference is suggested. The intent of this bibliography was to provide a ready listing of the references for data on VLE.

Nelson, T.P., N.P. Meserole, Annotated Bibliography of Published Material on Vapor/Liquid Equilibria. EPA, July 1983.

For further information on the selection of the flux chamber enclosure method for direct measurement of gas emission rates from contaminated soils and/or groundwater, the following reference is suggested.

Radian Corporation. Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Interim Report. EPA Contract No. 68-02-3513, Work Assignment 32, August 1983.

For further information on the actual field applications of this technique, the following references are suggested:

Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment: Tustin Spill Site Data Volume. EPA Contract No. 68-02-3513, Work Assignment 32. July 27, 1984.

Radian Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Bonifay Spill Site Data Volume. EPA Contract No. 68-02-3513, Work Assignment 32, 1984.

For further information on the validation of the flux chamber technique for emission rate measurements on soil surfaces, the following reference is suggested:

Klienbusch, M.R., D. Ranum, Validation of Flux Chamber Emission Measurements on Soil Surfaces. EPA Contract No. 68-02-3889, Work Assignment 18, December 1985.

For information concerning the emission process including diffusion and adsorption, the following reference is suggested:

Manos, C.G., Jr., Effects of Clay Mineral Organic Matter Complexes on VOC Adsorption, Draft Report. EPA Contract No. 68-02-3889, Work Assignment 18, October 3, 1985.

Radian Corporation. Soil Gas Sampling Techniques of Chemicals for Exposure Assessment; Laboratory Study of Emission Rates from Soil Columns, Draft Final Report. EPA Contract No. 68-02-3513, Work Assignment 32, October 1984.

## REFERENCES

1. Farmer, W.J., M.S. Yang, and J. Letey. Land Disposal of Hexachlorobenzene Wastes--Controlling Vapor Movement in Soil. EPA-600/2-80-119, Municipal Environmental Research Laboratory, Cincinnati, Ohio, August 1981.
2. Shen, T.T. Estimating Hazardous Air Emissions from Disposal Sites, Pollution Engineering, August 1981.
3. U.S. EPA, Office of Solid Waste. Guidance Document for Subpart F, Air Emission Monitoring, Land Disposal Toxic Air Emissions Evaluation Guideline. December 1980.
4. Kienbusch, M.R, D. Ranum. Validation of Flux Chamber Emission Measurements on Soil Surfaces. EPA, EMSL, Contract No. 68-02-3889, Work Assignment 18, December 1985.
5. Radlan Corporation, Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Interim Report, EPA Contract No. 68-02-3513, Work Assignment 32, U.S. EPA EMSL, EAD, August 1983.
6. Adams, D.F., M.R. Pack, W.L. Barnesberger, and A.E. Sherrard, "Measurement of Biogenic Sulfur-Containing Gas Emissions from Soils and Vegetation." In: Proceedings of 71st Annual APCA Meeting, Houston, TX, 1978, p. 78-76.
7. Adams, D.F., Sulfur Gas Emissions from Flue Gas Desulfurization Sludge Ponds. J. Air Pol. Contr. Assoc. Vol. 29, No. 9, p. 963-968, 1979.
8. Denmead, O.T. Chamber Systems for Measuring Nitrous Oxide Emission from Soils in the Field. Soil Sciences Soc. of Am. J., 43, p. 89-95, 1979.
9. Balfour, W.D. and C.E. Schmidt, Sampling Approaches for Measuring Emission Rates from Hazardous Waste Disposal Facilities. In: Proceedings of 77th Annual Meeting of the Air Pollution Control Association, San Francisco, California, June 1984.
10. Zimmerman, P. Procedures for Conducting Hydrocarbon Emission Inventories of Biogenic Sources and Some Results of Recent Investigations. In: Proceedings of 1977 Environmental Protection Agency Emission Inventory/Factor Workshop, Raleigh, NC, 1977.

## APPENDIX A

### SELECTION OF A RANDOM SAMPLE

An illustration of the method of use of tables of random numbers follows. Suppose the population consists of 87 items, and we wish to select a random sample of 10. Assign to each individual a separate two-digit number between 00 and 86. In a table of random numbers, pick an arbitrary starting place and decide upon the direction of reading the numbers. Any direction may be used, provided the rule is fixed in advance and is independent of the numbers occurring. Read two-digit numbers from the table, and select for the sample those individuals whose numbers occur until 10 individuals have been selected. For example, in Table A-1, start with the second page of the table, column 20, line 6, and read down. The 10 items picked for the sample would thus be numbers 38, 44, 13, 73, 39, 41, 35, 07, 14, and 47.

The method described is applicable for obtaining simple random samples from any sampled population consisting of a finite set of individuals. In the case of an infinite sampled population for the target population of weighings as comprising all weighings which might conceptually have been made during the time while weighing was done. We cannot, by mechanical randomization, draw a random sample from this population, and so must recognize that we have a random sample only by assumption. This assumption will be warranted if previous data indicate that the weighing procedure is in a state of statistical control; unwarranted if the contrary is indicated; and a leap in the dark if no previous data are available.

TABLE A-1  
SHORT TABLE OF RANDOM NUMBERS

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 46 | 96 | 85 | 77 | 27 | 92 | 36 | 26 | 45 | 21 | 89 | 91 | 71 | 42 | 64 | 64 | 58 | 22 | 75 | 81 | 74 | 91 | 48 | 46 | 18 |
| 44 | 19 | 15 | 32 | 63 | 55 | 87 | 77 | 33 | 29 | 45 | 00 | 31 | 34 | 84 | 05 | 72 | 90 | 44 | 27 | 78 | 22 | 07 | 62 | 17 |
| 34 | 39 | 80 | 62 | 24 | 33 | 81 | 67 | 28 | 11 | 34 | 79 | 26 | 35 | 34 | 23 | 09 | 94 | 00 | 80 | 55 | 31 | 63 | 27 | 91 |
| 74 | 97 | 80 | 30 | 65 | 07 | 71 | 30 | 01 | 84 | 47 | 45 | 89 | 70 | 74 | 13 | 04 | 90 | 51 | 27 | 61 | 34 | 63 | 87 | 44 |
| 22 | 14 | 61 | 60 | 86 | 38 | 33 | 71 | 13 | 07 | 72 | 08 | 16 | 13 | 50 | 56 | 48 | 51 | 29 | 48 | 30 | 93 | 45 | 66 | 29 |
| 40 | 03 | 96 | 40 | 03 | 47 | 24 | 60 | 09 | 21 | 21 | 18 | 00 | 05 | 86 | 52 | 85 | 40 | 73 | 73 | 57 | 68 | 36 | 33 | 91 |
| 52 | 33 | 76 | 44 | 56 | 15 | 47 | 75 | 78 | 73 | 78 | 19 | 87 | 07 | 98 | 47 | 48 | 02 | 62 | 03 | 42 | 05 | 32 | 55 | 02 |
| 37 | 59 | 20 | 40 | 93 | 17 | 82 | 24 | 19 | 90 | 80 | 87 | 32 | 74 | 59 | 84 | 24 | 49 | 79 | 17 | 23 | 75 | 83 | 42 | 00 |
| 11 | 02 | 55 | 57 | 48 | 84 | 74 | 36 | 22 | 67 | 19 | 20 | 15 | 92 | 53 | 37 | 13 | 75 | 54 | 89 | 56 | 73 | 23 | 39 | 07 |
| 10 | 33 | 79 | 26 | 34 | 54 | 71 | 33 | 89 | 74 | 68 | 48 | 23 | 17 | 49 | 18 | 81 | 05 | 52 | 85 | 70 | 05 | 73 | 11 | 17 |
| 67 | 59 | 28 | 25 | 47 | 89 | 11 | 65 | 65 | 20 | 42 | 23 | 96 | 41 | 64 | 20 | 30 | 89 | 87 | 64 | 37 | 93 | 36 | 96 | 35 |
| 93 | 50 | 75 | 20 | 09 | 18 | 54 | 34 | 68 | 02 | 54 | 87 | 23 | 05 | 43 | 36 | 98 | 29 | 97 | 93 | 87 | 08 | 30 | 92 | 98 |
| 24 | 43 | 23 | 72 | 80 | 64 | 34 | 27 | 23 | 46 | 15 | 36 | 10 | 63 | 21 | 59 | 69 | 76 | 02 | 62 | 31 | 62 | 47 | 60 | 34 |
| 39 | 91 | 63 | 18 | 38 | 27 | 10 | 78 | 88 | 84 | 42 | 32 | 00 | 97 | 92 | 00 | 04 | 94 | 50 | 05 | 75 | 82 | 70 | 80 | 35 |
| 74 | 62 | 19 | 67 | 54 | 18 | 28 | 92 | 33 | 69 | 98 | 96 | 74 | 35 | 72 | 11 | 68 | 25 | 08 | 95 | 31 | 79 | 11 | 79 | 54 |
| 91 | 03 | 35 | 60 | 81 | 16 | 61 | 97 | 25 | 14 | 78 | 21 | 22 | 05 | 25 | 47 | 26 | 37 | 80 | 39 | 19 | 06 | 41 | 02 | 00 |
| 42 | 57 | 66 | 76 | 72 | 91 | 03 | 63 | 48 | 46 | 44 | 01 | 33 | 53 | 62 | 28 | 80 | 59 | 55 | 05 | 02 | 16 | 13 | 17 | 54 |
| 06 | 36 | 63 | 06 | 15 | 03 | 72 | 38 | 01 | 58 | 25 | 37 | 66 | 48 | 56 | 19 | 56 | 41 | 29 | 28 | 76 | 49 | 74 | 39 | 50 |
| 92 | 70 | 96 | 70 | 89 | 80 | 87 | 14 | 25 | 49 | 25 | 94 | 62 | 78 | 26 | 15 | 41 | 39 | 48 | 75 | 64 | 69 | 61 | 06 | 38 |
| 91 | 08 | 88 | 53 | 52 | 13 | 04 | 82 | 23 | 00 | 26 | 36 | 47 | 44 | 04 | 08 | 84 | 80 | 07 | 44 | 76 | 51 | 52 | 41 | 59 |
| 68 | 85 | 97 | 74 | 47 | 53 | 90 | 05 | 90 | 84 | 87 | 48 | 25 | 01 | 11 | 05 | 45 | 11 | 43 | 15 | 60 | 40 | 31 | 84 | 59 |
| 59 | 54 | 13 | 09 | 13 | 80 | 42 | 29 | 63 | 03 | 24 | 64 | 12 | 43 | 28 | 10 | 01 | 65 | 62 | 07 | 79 | 83 | 05 | 59 | 61 |
| 39 | 18 | 32 | 69 | 33 | 46 | 58 | 19 | 34 | 03 | 59 | 28 | 97 | 31 | 02 | 65 | 47 | 47 | 70 | 39 | 74 | 17 | 30 | 22 | 65 |
| 67 | 43 | 31 | 09 | 12 | 60 | 19 | 57 | 63 | 78 | 11 | 80 | 10 | 97 | 15 | 70 | 04 | 89 | 81 | 78 | 54 | 84 | 87 | 83 | 42 |
| 61 | 75 | 37 | 19 | 56 | 90 | 75 | 39 | 03 | 56 | 49 | 92 | 72 | 95 | 27 | 52 | 87 | 47 | 12 | 52 | 54 | 62 | 43 | 23 | 13 |
| 78 | 10 | 91 | 11 | 00 | 63 | 19 | 63 | 74 | 58 | 69 | 03 | 51 | 38 | 60 | 36 | 53 | 56 | 77 | 06 | 69 | 03 | 89 | 91 | 24 |
| 93 | 23 | 71 | 58 | 09 | 78 | 08 | 03 | 07 | 71 | 79 | 32 | 25 | 19 | 61 | 04 | 40 | 33 | 12 | 06 | 78 | 91 | 97 | 88 | 95 |
| 37 | 55 | 48 | 82 | 63 | 89 | 92 | 59 | 14 | 72 | 19 | 17 | 22 | 51 | 90 | 20 | 03 | 64 | 96 | 60 | 48 | 01 | 95 | 44 | 84 |
| 62 | 13 | 11 | 71 | 17 | 23 | 29 | 25 | 13 | 85 | 33 | 35 | 07 | 69 | 25 | 68 | 57 | 92 | 57 | 11 | 84 | 44 | 01 | 33 | 66 |
| 29 | 89 | 97 | 47 | 03 | 13 | 20 | 86 | 22 | 45 | 59 | 98 | 64 | 53 | 89 | 64 | 94 | 81 | 55 | 87 | 73 | 81 | 58 | 46 | 42 |
| 16 | 94 | 85 | 82 | 89 | 07 | 17 | 20 | 29 | 89 | 89 | 80 | 98 | 36 | 25 | 36 | 53 | 02 | 49 | 14 | 34 | 03 | 52 | 09 | 20 |
| 04 | 93 | 10 | 59 | 75 | 12 | 98 | 84 | 60 | 93 | 68 | 16 | 87 | 60 | 11 | 50 | 46 | 56 | 58 | 45 | 88 | 72 | 50 | 46 | 11 |
| 95 | 71 | 43 | 68 | 97 | 18 | 85 | 17 | 13 | 08 | 00 | 50 | 77 | 50 | 46 | 92 | 45 | 26 | 97 | 21 | 48 | 22 | 23 | 08 | 32 |
| 86 | 05 | 39 | 14 | 35 | 48 | 68 | 18 | 36 | 57 | 09 | 62 | 40 | 28 | 87 | 08 | 74 | 79 | 91 | 08 | 27 | 12 | 43 | 32 | 03 |
| 50 | 30 | 60 | 10 | 41 | 31 | 00 | 69 | 63 | 77 | 01 | 89 | 94 | 60 | 19 | 02 | 70 | 88 | 72 | 33 | 38 | 88 | 20 | 60 | 86 |
| 05 | 45 | 35 | 40 | 54 | 03 | 98 | 96 | 76 | 27 | 77 | 84 | 80 | 08 | 64 | 60 | 44 | 34 | 54 | 24 | 85 | 20 | 85 | 77 | 32 |
| 71 | 85 | 17 | 74 | 66 | 27 | 85 | 19 | 35 | 56 | 51 | 36 | 48 | 92 | 32 | 44 | 40 | 47 | 10 | 38 | 22 | 52 | 42 | 29 | 96 |
| 80 | 20 | 32 | 80 | 98 | 00 | 10 | 92 | 57 | 51 | 52 | 83 | 14 | 55 | 31 | 99 | 73 | 23 | 40 | 07 | 64 | 54 | 44 | 99 | 21 |
| 13 | 50 | 78 | 02 | 73 | 39 | 66 | 82 | 01 | 28 | 67 | 51 | 75 | 66 | 33 | 97 | 47 | 58 | 42 | 44 | 88 | 09 | 28 | 58 | 06 |
| 67 | 92 | 65 | 41 | 45 | 36 | 77 | 96 | 46 | 21 | 14 | 39 | 56 | 36 | 70 | 15 | 74 | 43 | 62 | 69 | 82 | 30 | 77 | 28 | 77 |
| 72 | 56 | 73 | 44 | 26 | 04 | 62 | 81 | 15 | 35 | 79 | 26 | 99 | 57 | 28 | 22 | 25 | 94 | 80 | 62 | 95 | 48 | 98 | 23 | 86 |
| 28 | 86 | 85 | 64 | 94 | 11 | 58 | 78 | 45 | 36 | 34 | 45 | 91 | 38 | 51 | 10 | 68 | 36 | 87 | 81 | 16 | 77 | 30 | 19 | 36 |
| 69 | 57 | 40 | 60 | 44 | 94 | 60 | 82 | 94 | 93 | 98 | 01 | 48 | 50 | 57 | 69 | 60 | 77 | 69 | 60 | 74 | 22 | 05 | 77 | 17 |
| 71 | 20 | 03 | 30 | 79 | 25 | 74 | 17 | 78 | 34 | 54 | 45 | 04 | 77 | 42 | 59 | 75 | 78 | 64 | 99 | 37 | 03 | 18 | 03 | 36 |
| 89 | 98 | 55 | 98 | 22 | 45 | 12 | 49 | 82 | 71 | 57 | 33 | 28 | 69 | 50 | 59 | 15 | 09 | 25 | 79 | 39 | 42 | 84 | 18 | 70 |
| 58 | 74 | 82 | 81 | 14 | 02 | 01 | 05 | 77 | 94 | 65 | 57 | 70 | 39 | 42 | 48 | 56 | 84 | 31 | 59 | 18 | 70 | 41 | 74 | 60 |
| 50 | 54 | 73 | 81 | 91 | 07 | 81 | 26 | 25 | 45 | 49 | 61 | 22 | 88 | 41 | 20 | 00 | 15 | 59 | 93 | 51 | 60 | 65 | 65 | 63 |
| 49 | 33 | 72 | 90 | 10 | 20 | 65 | 28 | 44 | 63 | 95 | 86 | 75 | 78 | 69 | 24 | 41 | 65 | 86 | 10 | 34 | 10 | 32 | 00 | 93 |
| 11 | 85 | 01 | 43 | 65 | 02 | 85 | 69 | 56 | 88 | 34 | 29 | 64 | 35 | 48 | 15 | 70 | 11 | 77 | 83 | 01 | 34 | 32 | 91 | 04 |
| 34 | 22 | 46 | 41 | 84 | 74 | 27 | 02 | 57 | 77 | 47 | 93 | 72 | 02 | 95 | 63 | 75 | 74 | 69 | 69 | 61 | 34 | 31 | 92 | 13 |

TABLE A-1  
(CONTINUED)

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 05 | 57 | 23 | 06 | 26 | 23 | 08 | 66 | 16 | 11 | 75 | 28 | 81 | 56 | 14 | 62 | 82 | 45 | 65 | 80 | 36 | 02 | 76 | 55 | 63 |
| 37 | 73 | 16 | 06 | 57 | 12 | 46 | 22 | 90 | 97 | 78 | 67 | 39 | 06 | 63 | 60 | 51 | 02 | 07 | 16 | 75 | 12 | 90 | 41 | 16 |
| 23 | 71 | 15 | 08 | 82 | 64 | 87 | 29 | 01 | 20 | 46 | 72 | 05 | 80 | 19 | 27 | 47 | 15 | 76 | 51 | 58 | 67 | 06 | 80 | 74 |
| 42 | 67 | 98 | 41 | 67 | 44 | 28 | 71 | 45 | 08 | 19 | 47 | 76 | 30 | 26 | 72 | 33 | 69 | 92 | 51 | 95 | 23 | 26 | 57 | 76 |
| 05 | 83 | 03 | 84 | 32 | 62 | 83 | 27 | 48 | 83 | 09 | 19 | 84 | 90 | 20 | 20 | 50 | 87 | 74 | 93 | 51 | 62 | 10 | 23 | 30 |
| 60 | 46 | 18 | 41 | 23 | 74 | 73 | 51 | 72 | 90 | 40 | 52 | 95 | 41 | 20 | 89 | 48 | 98 | 27 | 38 | 81 | 33 | 83 | 82 | 94 |
| 32 | 80 | 64 | 75 | 91 | 98 | 09 | 40 | 64 | 89 | 29 | 99 | 46 | 35 | 69 | 91 | 50 | 73 | 75 | 92 | 90 | 56 | 82 | 93 | 24 |
| 79 | 86 | 53 | 77 | 78 | 06 | 62 | 37 | 48 | 82 | 71 | 00 | 78 | 21 | 65 | 65 | 88 | 45 | 82 | 44 | 78 | 93 | 22 | 78 | 09 |
| 45 | 13 | 23 | 32 | 01 | 09 | 46 | 36 | 43 | 66 | 37 | 15 | 35 | 04 | 88 | 79 | 83 | 53 | 19 | 13 | 91 | 59 | 81 | 81 | 87 |
| 20 | 60 | 97 | 48 | 21 | 41 | 84 | 22 | 72 | 77 | 99 | 81 | 83 | 30 | 46 | 15 | 90 | 26 | 51 | 73 | 66 | 34 | 99 | 40 | 60 |
| 67 | 91 | 44 | 83 | 43 | 25 | 56 | 33 | 28 | 80 | 99 | 53 | 27 | 56 | 19 | 80 | 76 | 32 | 53 | 95 | 07 | 53 | 09 | 61 | 98 |
| 86 | 50 | 76 | 93 | 86 | 35 | 68 | 45 | 37 | 83 | 47 | 44 | 92 | 57 | 66 | 59 | 64 | 16 | 48 | 39 | 26 | 94 | 54 | 66 | 40 |
| 66 | 73 | 38 | 38 | 23 | 36 | 10 | 95 | 16 | 01 | 10 | 01 | 59 | 71 | 55 | 99 | 24 | 88 | 31 | 41 | 00 | 73 | 13 | 80 | 62 |
| 55 | 11 | 50 | 29 | 17 | 73 | 97 | 04 | 20 | 39 | 20 | 22 | 71 | 11 | 43 | 00 | 15 | 10 | 12 | 35 | 09 | 11 | 00 | 89 | 05 |
| 23 | 54 | 33 | 87 | 92 | 92 | 04 | 49 | 73 | 96 | 57 | 53 | 57 | 08 | 93 | 09 | 69 | 87 | 83 | 07 | 46 | 39 | 50 | 37 | 85 |
| 41 | 48 | 67 | 79 | 44 | 57 | 40 | 29 | 10 | 34 | 58 | 63 | 51 | 18 | 07 | 41 | 02 | 39 | 79 | 14 | 40 | 68 | 10 | 01 | 61 |
| 03 | 97 | 71 | 72 | 43 | 27 | 36 | 24 | 59 | 88 | 82 | 87 | 26 | 31 | 11 | 44 | 28 | 58 | 99 | 47 | 83 | 21 | 35 | 22 | 88 |
| 90 | 24 | 83 | 48 | 07 | 41 | 56 | 68 | 11 | 14 | 77 | 75 | 48 | 68 | 08 | 90 | 89 | 63 | 87 | 00 | 06 | 18 | 63 | 21 | 91 |
| 98 | 98 | 97 | 42 | 27 | 11 | 80 | 51 | 13 | 13 | 03 | 42 | 91 | 14 | 51 | 22 | 15 | 48 | 67 | 52 | 09 | 40 | 34 | 60 | 85 |
| 74 | 20 | 94 | 21 | 49 | 96 | 51 | 69 | 99 | 85 | 43 | 76 | 55 | 81 | 36 | 11 | 88 | 68 | 32 | 43 | 08 | 14 | 78 | 05 | 34 |
| 94 | 67 | 48 | 87 | 11 | 84 | 00 | 85 | 93 | 56 | 43 | 99 | 21 | 74 | 84 | 13 | 56 | 41 | 90 | 96 | 30 | 04 | 19 | 68 | 73 |
| 58 | 18 | 84 | 82 | 71 | 23 | 66 | 33 | 19 | 25 | 65 | 17 | 90 | 84 | 24 | 91 | 75 | 36 | 14 | 83 | 86 | 22 | 70 | 86 | 89 |
| 31 | 47 | 28 | 24 | 88 | 49 | 28 | 69 | 78 | 62 | 23 | 45 | 53 | 38 | 78 | 65 | 87 | 44 | 91 | 93 | 91 | 62 | 76 | 09 | 20 |
| 45 | 62 | 31 | 06 | 70 | 92 | 73 | 27 | 83 | 57 | 15 | 64 | 40 | 57 | 56 | 54 | 42 | 35 | 40 | 93 | 55 | 82 | 08 | 78 | 87 |
| 31 | 49 | 87 | 12 | 27 | 41 | 07 | 91 | 72 | 64 | 63 | 42 | 06 | 66 | 82 | 71 | 28 | 36 | 45 | 31 | 99 | 01 | 03 | 35 | 76 |
| 69 | 37 | 22 | 23 | 46 | 10 | 75 | 83 | 62 | 94 | 44 | 65 | 46 | 23 | 65 | 71 | 69 | 20 | 89 | 12 | 16 | 56 | 61 | 70 | 41 |
| 93 | 67 | 21 | 56 | 98 | 42 | 52 | 53 | 14 | 86 | 24 | 70 | 25 | 18 | 23 | 23 | 56 | 24 | 03 | 86 | 11 | 06 | 46 | 10 | 23 |
| 77 | 56 | 18 | 37 | 01 | 32 | 20 | 18 | 70 | 79 | 20 | 85 | 77 | 89 | 28 | 17 | 77 | 15 | 52 | 47 | 15 | 30 | 35 | 12 | 75 |
| 37 | 07 | 47 | 79 | 60 | 75 | 24 | 15 | 31 | 63 | 25 | 93 | 27 | 66 | 19 | 53 | 52 | 49 | 98 | 45 | 12 | 12 | 06 | 00 | 32 |
| 72 | 08 | 71 | 01 | 73 | 46 | 39 | 60 | 37 | 58 | 22 | 25 | 20 | 84 | 30 | 02 | 03 | 62 | 65 | 58 | 38 | 04 | 06 | 89 | 94 |
| 55 | 22 | 48 | 46 | 72 | 50 | 14 | 24 | 47 | 67 | 84 | 37 | 32 | 84 | 82 | 64 | 97 | 13 | 69 | 86 | 20 | 09 | 80 | 46 | 75 |
| 69 | 24 | 98 | 90 | 70 | 29 | 34 | 25 | 33 | 23 | 12 | 69 | 90 | 50 | 38 | 93 | 84 | 32 | 28 | 96 | 03 | 65 | 70 | 90 | 12 |
| 01 | 86 | 77 | 18 | 21 | 91 | 66 | 11 | 84 | 65 | 48 | 75 | 26 | 94 | 51 | 40 | 51 | 53 | 36 | 39 | 77 | 69 | 06 | 25 | 07 |
| 51 | 40 | 94 | 06 | 80 | 61 | 34 | 28 | 46 | 28 | 11 | 48 | 48 | 94 | 60 | 65 | 06 | 63 | 71 | 06 | 19 | 35 | 05 | 32 | 56 |
| 58 | 78 | 02 | 85 | 80 | 29 | 67 | 27 | 43 | 07 | 67 | 23 | 20 | 28 | 22 | 62 | 97 | 59 | 62 | 13 | 41 | 72 | 70 | 71 | 07 |
| 33 | 75 | 88 | 51 | 00 | 33 | 56 | 15 | 84 | 34 | 28 | 50 | 16 | 65 | 12 | 81 | 56 | 43 | 54 | 14 | 63 | 37 | 74 | 97 | 59 |
| 58 | 60 | 37 | 45 | 62 | 09 | 95 | 93 | 16 | 59 | 35 | 22 | 91 | 78 | 04 | 97 | 98 | 80 | 20 | 04 | 38 | 93 | 13 | 92 | 30 |
| 72 | 13 | 12 | 95 | 32 | 87 | 99 | 32 | 83 | 65 | 40 | 17 | 92 | 57 | 22 | 68 | 98 | 79 | 16 | 23 | 53 | 56 | 56 | 07 | 47 |
| 22 | 21 | 13 | 16 | 10 | 52 | 57 | 71 | 40 | 49 | 95 | 25 | 55 | 36 | 95 | 57 | 25 | 25 | 77 | 05 | 38 | 05 | 62 | 57 | 77 |
| 97 | 94 | 83 | 67 | 90 | 68 | 74 | 88 | 17 | 22 | 38 | 01 | 04 | 33 | 49 | 38 | 47 | 57 | 61 | 87 | 15 | 39 | 48 | 87 | 00 |
| 09 | 03 | 68 | 53 | 63 | 29 | 27 | 31 | 66 | 57 | 39 | 34 | 88 | 87 | 04 | 35 | 80 | 69 | 52 | 74 | 99 | 16 | 52 | 01 | 65 |
| 29 | 95 | 61 | 42 | 65 | 05 | 72 | 27 | 28 | 18 | 09 | 85 | 24 | 59 | 46 | 03 | 91 | 55 | 38 | 62 | 51 | 71 | 47 | 37 | 38 |
| 81 | 96 | 78 | 90 | 47 | 41 | 38 | 36 | 33 | 95 | 05 | 90 | 26 | 72 | 85 | 23 | 23 | 30 | 70 | 51 | 56 | 93 | 23 | 84 | 80 |
| 44 | 62 | 20 | 81 | 21 | 57 | 57 | 85 | 00 | 47 | 26 | 10 | 87 | 22 | 45 | 72 | 03 | 51 | 75 | 23 | 38 | 38 | 56 | 77 | 97 |
| 68 | 91 | 12 | 15 | 08 | 02 | 18 | 74 | 56 | 79 | 21 | 53 | 63 | 41 | 77 | 15 | 07 | 39 | 87 | 11 | 19 | 25 | 62 | 19 | 30 |
| 29 | 33 | 77 | 60 | 29 | 09 | 25 | 09 | 42 | 28 | 07 | 15 | 40 | 67 | 56 | 29 | 58 | 75 | 84 | 06 | 19 | 54 | 31 | 16 | 53 |
| 54 | 13 | 39 | 19 | 29 | 64 | 97 | 73 | 71 | 61 | 78 | 03 | 24 | 02 | 93 | 86 | 69 | 76 | 74 | 28 | 08 | 98 | 84 | 08 | 23 |
| 75 | 16 | 85 | 64 | 64 | 93 | 85 | 68 | 08 | 84 | 15 | 41 | 57 | 84 | 45 | 11 | 70 | 13 | 17 | 60 | 47 | 80 | 10 | 13 | 00 |
| 36 | 47 | 17 | 08 | 79 | 03 | 92 | 85 | 18 | 42 | 95 | 48 | 27 | 37 | 99 | 98 | 81 | 94 | 44 | 72 | 06 | 95 | 42 | 31 | 17 |
| 29 | 61 | 08 | 21 | 91 | 23 | 76 | 72 | 84 | 98 | 26 | 23 | 66 | 54 | 86 | 88 | 96 | 14 | 82 | 57 | 17 | 99 | 16 | 28 | 99 |

TABLE A-1  
(CONTINUED)

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 03 | 46 | 38 | 56 | 84 | 81 | 20 | 89 | 68 | 52 | 45 | 41 | 01 | 71 | 55 | 14 | 18 | 05 | 18 | 01 | 74 | 94 | 50 | 66 | 07 |
| 74 | 12 | 14 | 57 | 25 | 12 | 48 | 83 | 67 | 04 | 88 | 69 | 05 | 27 | 23 | 68 | 84 | 23 | 52 | 07 | 21 | 67 | 13 | 52 | 01 |
| 08 | 23 | 73 | 51 | 23 | 92 | 93 | 05 | 54 | 32 | 84 | 46 | 61 | 33 | 92 | 13 | 30 | 91 | 73 | 11 | 30 | 44 | 21 | 71 | 20 |
| 99 | 21 | 30 | 24 | 79 | 30 | 18 | 06 | 96 | 20 | 62 | 06 | 47 | 96 | 07 | 04 | 82 | 93 | 01 | 56 | 62 | 70 | 43 | 22 | 85 |
| 96 | 82 | 59 | 39 | 23 | 22 | 20 | 95 | 72 | 00 | 24 | 85 | 63 | 57 | 75 | 88 | 05 | 79 | 13 | 75 | 78 | 64 | 25 | 89 | 85 |
| 62 | 16 | 18 | 23 | 64 | 50 | 90 | 57 | 50 | 54 | 04 | 96 | 09 | 08 | 17 | 14 | 63 | 17 | 80 | 80 | 56 | 10 | 17 | 11 | 57 |
| 21 | 40 | 82 | 41 | 45 | 41 | 41 | 89 | 46 | 18 | 55 | 86 | 94 | 32 | 57 | 44 | 12 | 64 | 75 | 12 | 78 | 01 | 13 | 69 | 81 |
| 13 | 83 | 48 | 82 | 60 | 78 | 96 | 30 | 57 | 13 | 40 | 28 | 10 | 24 | 48 | 73 | 50 | 92 | 70 | 18 | 72 | 86 | 54 | 09 | 76 |
| 29 | 65 | 33 | 93 | 92 | 99 | 26 | 01 | 86 | 11 | 85 | 42 | 48 | 86 | 59 | 24 | 96 | 35 | 07 | 87 | 67 | 31 | 25 | 89 | 62 |
| 17 | 49 | 05 | 12 | 13 | 58 | 01 | 98 | 80 | 17 | 83 | 35 | 38 | 14 | 79 | 82 | 83 | 56 | 44 | 51 | 35 | 40 | 70 | 68 | 22 |
| 14 | 36 | 47 | 29 | 15 | 14 | 22 | 27 | 62 | 93 | 15 | 60 | 43 | 13 | 05 | 25 | 75 | 40 | 08 | 85 | 44 | 70 | 89 | 64 | 13 |
| 78 | 09 | 76 | 61 | 07 | 48 | 31 | 27 | 48 | 28 | 96 | 11 | 26 | 95 | 03 | 06 | 86 | 81 | 52 | 72 | 66 | 74 | 71 | 60 | 25 |
| 83 | 17 | 94 | 28 | 39 | 01 | 48 | 68 | 56 | 97 | 05 | 76 | 82 | 89 | 15 | 66 | 81 | 63 | 81 | 96 | 12 | 44 | 71 | 57 | 43 |
| 87 | 12 | 89 | 46 | 85 | 58 | 09 | 94 | 39 | 92 | 09 | 08 | 76 | 54 | 88 | 82 | 73 | 24 | 94 | 39 | 02 | 79 | 07 | 58 | 27 |
| 44 | 30 | 30 | 40 | 85 | 96 | 34 | 99 | 87 | 03 | 93 | 03 | 00 | 74 | 18 | 67 | 13 | 97 | 11 | 12 | 59 | 30 | 54 | 51 | 66 |
| 54 | 56 | 85 | 50 | 81 | 32 | 42 | 53 | 60 | 36 | 98 | 03 | 65 | 10 | 60 | 26 | 52 | 64 | 74 | 35 | 28 | 13 | 24 | 65 | 23 |
| 65 | 99 | 30 | 88 | 88 | 44 | 91 | 22 | 50 | 72 | 61 | 95 | 90 | 98 | 80 | 65 | 03 | 45 | 04 | 27 | 88 | 70 | 88 | 40 | 49 |
| 55 | 56 | 01 | 94 | 09 | 94 | 02 | 71 | 85 | 10 | 27 | 20 | 51 | 27 | 86 | 09 | 15 | 11 | 62 | 41 | 03 | 22 | 82 | 10 | 60 |
| 55 | 78 | 63 | 40 | 57 | 16 | 20 | 17 | 73 | 02 | 76 | 09 | 62 | 95 | 85 | 67 | 75 | 45 | 99 | 63 | 59 | 55 | 88 | 27 | 99 |
| 83 | 78 | 98 | 57 | 23 | 38 | 95 | 61 | 06 | 58 | 69 | 07 | 35 | 82 | 10 | 35 | 61 | 61 | 66 | 06 | 75 | 45 | 83 | 33 | 70 |
| 20 | 14 | 56 | 25 | 85 | 78 | 33 | 37 | 34 | 15 | 50 | 63 | 78 | 74 | 56 | 49 | 84 | 72 | 58 | 00 | 93 | 68 | 11 | 47 | 46 |
| 48 | 04 | 07 | 78 | 13 | 43 | 03 | 62 | 46 | 20 | 06 | 94 | 09 | 27 | 69 | 00 | 71 | 51 | 43 | 84 | 21 | 12 | 86 | 03 | 51 |
| 61 | 10 | 14 | 39 | 57 | 87 | 76 | 60 | 77 | 02 | 06 | 50 | 15 | 60 | 46 | 22 | 27 | 52 | 87 | 43 | 89 | 58 | 65 | 79 | 02 |
| 64 | 91 | 36 | 96 | 42 | 22 | 57 | 18 | 13 | 44 | 46 | 81 | 95 | 15 | 37 | 91 | 81 | 63 | 33 | 38 | 39 | 50 | 47 | 46 | 94 |
| 89 | 53 | 11 | 10 | 33 | 10 | 46 | 41 | 63 | 84 | 20 | 46 | 86 | 41 | 05 | 82 | 95 | 56 | 76 | 23 | 03 | 13 | 94 | 28 | 49 |
| 96 | 45 | 86 | 42 | 40 | 85 | 95 | 17 | 28 | 74 | 65 | 20 | 70 | 90 | 34 | 33 | 61 | 11 | 01 | 31 | 37 | 28 | 81 | 00 | 31 |
| 84 | 11 | 25 | 39 | 49 | 31 | 80 | 86 | 53 | 51 | 35 | 48 | 22 | 28 | 25 | 27 | 06 | 38 | 71 | 90 | 50 | 77 | 40 | 41 | 58 |
| 29 | 75 | 56 | 28 | 29 | 23 | 26 | 12 | 23 | 48 | 89 | 28 | 34 | 08 | 52 | 21 | 05 | 73 | 08 | 04 | 83 | 42 | 91 | 01 | 91 |
| 68 | 92 | 40 | 32 | 19 | 49 | 20 | 85 | 32 | 69 | 34 | 17 | 99 | 11 | 56 | 39 | 15 | 67 | 55 | 53 | 65 | 29 | 15 | 51 | 32 |
| 94 | 19 | 67 | 99 | 27 | 70 | 71 | 04 | 43 | 18 | 44 | 18 | 75 | 11 | 70 | 53 | 21 | 60 | 78 | 30 | 92 | 54 | 21 | 02 | 42 |
| 86 | 84 | 68 | 46 | 85 | 58 | 91 | 23 | 65 | 24 | 71 | 19 | 67 | 18 | 79 | 90 | 83 | 47 | 86 | 32 | 48 | 69 | 97 | 10 | 87 |
| 63 | 22 | 84 | 35 | 10 | 02 | 05 | 03 | 47 | 93 | 45 | 70 | 25 | 27 | 90 | 32 | 98 | 41 | 45 | 96 | 39 | 86 | 91 | 78 | 79 |
| 42 | 53 | 20 | 46 | 19 | 11 | 16 | 93 | 21 | 93 | 14 | 91 | 74 | 92 | 31 | 97 | 68 | 24 | 20 | 35 | 19 | 54 | 75 | 37 | 84 |
| 37 | 90 | 78 | 51 | 58 | 49 | 25 | 58 | 28 | 69 | 55 | 55 | 73 | 10 | 22 | 66 | 79 | 23 | 80 | 03 | 51 | 11 | 00 | 81 | 37 |
| 20 | 12 | 97 | 40 | 25 | 45 | 94 | 35 | 18 | 65 | 10 | 99 | 31 | 24 | 42 | 14 | 53 | 78 | 41 | 79 | 36 | 57 | 79 | 19 | 76 |
| 24 | 11 | 65 | 19 | 92 | 46 | 11 | 76 | 64 | 37 | 33 | 23 | 96 | 23 | 73 | 93 | 99 | 53 | 14 | 49 | 40 | 01 | 63 | 17 | 74 |
| 98 | 21 | 62 | 16 | 29 | 73 | 52 | 06 | 26 | 35 | 30 | 52 | 74 | 61 | 20 | 57 | 45 | 86 | 36 | 54 | 75 | 29 | 64 | 49 | 43 |
| 02 | 82 | 14 | 07 | 19 | 72 | 77 | 97 | 39 | 77 | 25 | 32 | 60 | 39 | 04 | 04 | 88 | 65 | 47 | 20 | 81 | 72 | 40 | 65 | 48 |
| 97 | 20 | 87 | 54 | 01 | 93 | 38 | 53 | 07 | 38 | 61 | 00 | 22 | 95 | 65 | 79 | 69 | 26 | 90 | 49 | 24 | 61 | 78 | 19 | 40 |
| 17 | 86 | 31 | 34 | 32 | 29 | 40 | 23 | 66 | 71 | 14 | 91 | 93 | 75 | 02 | 10 | 13 | 86 | 27 | 32 | 59 | 36 | 40 | 06 | 61 |
| 75 | 50 | 70 | 16 | 34 | 21 | 99 | 87 | 09 | 37 | 27 | 40 | 66 | 07 | 73 | 13 | 44 | 06 | 10 | 43 | 91 | 11 | 73 | 13 | 97 |
| 47 | 53 | 77 | 58 | 88 | 52 | 47 | 37 | 21 | 60 | 83 | 58 | 21 | 59 | 82 | 88 | 05 | 35 | 17 | 66 | 33 | 62 | 15 | 09 | 88 |
| 20 | 93 | 99 | 78 | 58 | 93 | 00 | 39 | 77 | 75 | 59 | 39 | 49 | 61 | 13 | 68 | 11 | 80 | 07 | 72 | 81 | 65 | 95 | 94 | 53 |
| 91 | 02 | 65 | 18 | 16 | 57 | 93 | 64 | 76 | 45 | 21 | 49 | 51 | 58 | 96 | 12 | 62 | 42 | 10 | 79 | 57 | 44 | 97 | 35 | 66 |
| 58 | 49 | 25 | 97 | 76 | 12 | 90 | 94 | 85 | 25 | 36 | 40 | 97 | 46 | 71 | 83 | 36 | 55 | 41 | 38 | 49 | 98 | 82 | 70 | 96 |
| 98 | 51 | 20 | 13 | 77 | 75 | 86 | 22 | 62 | 68 | 36 | 87 | 02 | 47 | 99 | 68 | 80 | 27 | 34 | 10 | 09 | 22 | 84 | 59 | 33 |
| 06 | 32 | 54 | 17 | 31 | 87 | 20 | 77 | 78 | 80 | 98 | 42 | 48 | 42 | 47 | 41 | 76 | 11 | 41 | 79 | 41 | 48 | 26 | 94 | 59 |
| 40 | 96 | 49 | 91 | 79 | 57 | 18 | 61 | 50 | 48 | 06 | 07 | 68 | 43 | 07 | 01 | 04 | 06 | 22 | 03 | 11 | 11 | 75 | 95 | 02 |
| 58 | 43 | 93 | 93 | 53 | 01 | 61 | 75 | 76 | 90 | 25 | 97 | 08 | 76 | 69 | 35 | 65 | 24 | 83 | 85 | 00 | 49 | 37 | 05 | 46 |
| 76 | 98 | 86 | 43 | 60 | 47 | 85 | 65 | 73 | 62 | 66 | 15 | 98 | 17 | 20 | 43 | 96 | 27 | 87 | 53 | 57 | 37 | 92 | 86 | 46 |

TABLE A-1  
(CONTINUED)

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 24 | 81 | 06 | 14 | 98 | 24 | 93 | 58 | 63 | 66 | 58 | 26 | 24 | 45 | 65 | 91 | 42 | 68 | 67 | 42 | 51 | 74 | 77 | 93 | 46 |
| 75 | 55 | 54 | 29 | 67 | 02 | 81 | 01 | 67 | 54 | 08 | 81 | 34 | 00 | 79 | 62 | 38 | 52 | 14 | 88 | 38 | 66 | 59 | 41 | 97 |
| 49 | 71 | 80 | 54 | 37 | 73 | 34 | 11 | 74 | 14 | 91 | 86 | 82 | 41 | 02 | 76 | 12 | 36 | 71 | 38 | 43 | 72 | 84 | 36 | 27 |
| 04 | 19 | 48 | 35 | 54 | 98 | 00 | 41 | 47 | 44 | 63 | 13 | 27 | 50 | 18 | 75 | 16 | 72 | 40 | 90 | 02 | 45 | 87 | 82 | 15 |
| 66 | 15 | 52 | 42 | 22 | 91 | 22 | 96 | 38 | 41 | 03 | 27 | 15 | 67 | 26 | 36 | 81 | 75 | 11 | 82 | 94 | 33 | 62 | 08 | 94 |
| 10 | 80 | 17 | 67 | 83 | 05 | 31 | 23 | 08 | 07 | 40 | 09 | 60 | 44 | 65 | 70 | 16 | 31 | 73 | 05 | 46 | 41 | 47 | 64 | 68 |
| 40 | 42 | 27 | 55 | 76 | 82 | 88 | 42 | 76 | 51 | 58 | 43 | 58 | 75 | 38 | 23 | 57 | 66 | 64 | 69 | 46 | 90 | 09 | 55 | 68 |
| 05 | 57 | 21 | 21 | 25 | 12 | 05 | 41 | 70 | 28 | 03 | 39 | 97 | 37 | 64 | 42 | 63 | 48 | 59 | 60 | 89 | 76 | 35 | 83 | 05 |
| 07 | 07 | 64 | 54 | 98 | 88 | 33 | 70 | 86 | 59 | 46 | 84 | 08 | 32 | 31 | 75 | 61 | 19 | 49 | 11 | 28 | 46 | 75 | 79 | 28 |
| 09 | 06 | 09 | 49 | 63 | 83 | 78 | 78 | 76 | 36 | 89 | 31 | 16 | 47 | 35 | 86 | 69 | 96 | 69 | 28 | 91 | 22 | 47 | 24 | 84 |
| 41 | 37 | 75 | 51 | 02 | 17 | 47 | 53 | 31 | 09 | 60 | 31 | 34 | 61 | 93 | 65 | 01 | 64 | 37 | 13 | 24 | 09 | 75 | 29 | 21 |
| 55 | 42 | 48 | 76 | 30 | 13 | 89 | 63 | 00 | 05 | 99 | 43 | 82 | 01 | 53 | 85 | 62 | 51 | 36 | 50 | 75 | 23 | 17 | 94 | 47 |
| 80 | 30 | 67 | 85 | 01 | 97 | 76 | 21 | 64 | 34 | 62 | 43 | 02 | 84 | 38 | 13 | 69 | 26 | 32 | 36 | 81 | 42 | 17 | 56 | 41 |
| 03 | 61 | 65 | 44 | 62 | 75 | 41 | 33 | 91 | 28 | 82 | 97 | 57 | 38 | 49 | 27 | 26 | 97 | 34 | 44 | 25 | 12 | 00 | 68 | 24 |
| 14 | 53 | 75 | 37 | 91 | 43 | 95 | 15 | 12 | 26 | 33 | 27 | 45 | 48 | 33 | 80 | 80 | 26 | 69 | 76 | 04 | 87 | 53 | 58 | 32 |
| 01 | 64 | 40 | 36 | 30 | 71 | 24 | 75 | 92 | 73 | 07 | 81 | 13 | 35 | 46 | 88 | 62 | 80 | 64 | 69 | 86 | 25 | 73 | 92 | 98 |
| 09 | 38 | 79 | 42 | 17 | 77 | 99 | 55 | 32 | 85 | 13 | 35 | 48 | 49 | 80 | 83 | 59 | 06 | 34 | 94 | 06 | 03 | 61 | 85 | 02 |
| 74 | 96 | 24 | 94 | 89 | 54 | 66 | 29 | 35 | 88 | 50 | 46 | 65 | 50 | 26 | 62 | 45 | 80 | 61 | 95 | 07 | 99 | 57 | 10 | 54 |
| 21 | 16 | 54 | 55 | 77 | 46 | 38 | 33 | 88 | 55 | 21 | 56 | 18 | 93 | 32 | 94 | 24 | 80 | 97 | 03 | 78 | 39 | 73 | 87 | 70 |
| 58 | 51 | 99 | 53 | 96 | 73 | 60 | 77 | 21 | 06 | 76 | 59 | 78 | 55 | 96 | 99 | 07 | 53 | 91 | 95 | 99 | 60 | 56 | 61 | 79 |
| 46 | 98 | 27 | 95 | 19 | 22 | 29 | 41 | 56 | 76 | 83 | 48 | 49 | 82 | 79 | 79 | 20 | 00 | 26 | 40 | 22 | 50 | 14 | 30 | 73 |
| 58 | 46 | 36 | 76 | 19 | 18 | 00 | 60 | 50 | 28 | 32 | 44 | 18 | 35 | 99 | 28 | 91 | 50 | 53 | 62 | 21 | 61 | 26 | 46 | 81 |
| 43 | 05 | 50 | 00 | 20 | 39 | 25 | 46 | 84 | 39 | 27 | 39 | 92 | 42 | 59 | 04 | 64 | 15 | 09 | 35 | 07 | 11 | 25 | 51 | 17 |
| 84 | 07 | 33 | 83 | 87 | 14 | 33 | 79 | 07 | 66 | 60 | 43 | 66 | 57 | 57 | 57 | 59 | 01 | 78 | 80 | 13 | 77 | 63 | 58 | 10 |
| 93 | 31 | 25 | 72 | 77 | 09 | 35 | 16 | 24 | 04 | 74 | 05 | 65 | 29 | 64 | 67 | 37 | 28 | 13 | 98 | 01 | 43 | 29 | 75 | 89 |
| 11 | 12 | 02 | 01 | 02 | 81 | 00 | 52 | 96 | 14 | 01 | 27 | 32 | 41 | 71 | 04 | 85 | 90 | 01 | 07 | 50 | 87 | 03 | 41 |    |
| 01 | 01 | 03 | 16 | 01 | 46 | 00 | 47 | 22 | 87 | 16 | 23 | 65 | 82 | 01 | 45 | 01 | 49 | 80 | 17 | 03 | 70 | 74 | 03 |    |
| 76 | 01 | 00 | 00 | 00 | 00 | 00 | 84 | 04 | 82 | 28 | 46 | 64 | 05 | 89 | 81 | 01 | 09 | 09 | 56 | 13 | 21 | 81 | 44 |    |
| 14 | 01 | 07 | 63 | 02 | 15 | 00 | 04 | 01 | 20 | 82 | 92 | 25 | 34 | 88 | 81 | 00 | 76 | 62 | 25 | 13 | 04 | 36 | 02 |    |
| 00 | 20 | 05 | 12 | 56 | 75 | 97 | 49 | 14 | 85 | 01 | 58 | 31 | 16 | 20 | 53 | 74 | 03 | 27 | 05 | 80 | 39 | 15 | 67 | 19 |
| 09 | 68 | 02 | 96 | 36 | 34 | 10 | 77 | 95 | 88 | 90 | 84 | 52 | 16 | 52 | 58 | 87 | 51 | 31 | 71 | 68 | 53 | 11 | 35 | 50 |
| 01 | 66 | 22 | 15 | 54 | 63 | 83 | 64 | 15 | 30 | 21 | 86 | 48 | 17 | 11 | 68 | 92 | 16 | 17 | 49 | 36 | 05 | 17 | 80 | 24 |
| 67 | 85 | 26 | 91 | 23 | 14 | 28 | 01 | 76 | 47 | 65 | 12 | 58 | 24 | 27 | 61 | 59 | 43 | 20 | 15 | 93 | 47 | 30 | 56 | 27 |
| 13 | 91 | 16 | 76 | 91 | 97 | 85 | 48 | 99 | 50 | 40 | 96 | 30 | 66 | 97 | 82 | 66 | 06 | 90 | 97 | 65 | 28 | 44 | 98 | 08 |
| 95 | 82 | 20 | 95 | 52 | 65 | 95 | 03 | 48 | 75 | 64 | 25 | 04 | 13 | 85 | 80 | 13 | 37 | 08 | 18 | 09 | 28 | 63 | 07 | 69 |
| 44 | 06 | 82 | 49 | 28 | 27 | 34 | 53 | 42 | 35 | 44 | 12 | 40 | 64 | 35 | 06 | 28 | 14 | 37 | 23 | 97 | 38 | 07 | 60 | 80 |
| 99 | 22 | 26 | 64 | 15 | 71 | 06 | 96 | 22 | 93 | 77 | 46 | 73 | 57 | 51 | 22 | 54 | 82 | 37 | 99 | 96 | 27 | 25 | 87 | 77 |
| 08 | 44 | 26 | 12 | 87 | 72 | 42 | 13 | 57 | 77 | 61 | 07 | 94 | 24 | 62 | 17 | 76 | 19 | 45 | 18 | 98 | 11 | 47 | 40 | 31 |
| 14 | 96 | 76 | 06 | 37 | 32 | 09 | 72 | 81 | 22 | 87 | 70 | 81 | 92 | 78 | 93 | 37 | 22 | 32 | 25 | 38 | 45 | 38 | 03 | 31 |
| 27 | 86 | 41 | 53 | 58 | 16 | 49 | 99 | 19 | 03 | 62 | 98 | 79 | 81 | 98 | 18 | 03 | 62 | 32 | 93 | 68 | 24 | 14 | 44 | 50 |
| 99 | 67 | 81 | 61 | 25 | 52 | 97 | 87 | 98 | 15 | 85 | 99 | 01 | 86 | 59 | 00 | 11 | 39 | 32 | 53 | 49 | 18 | 62 | 51 | 65 |
| 89 | 14 | 37 | 94 | 03 | 22 | 32 | 45 | 42 | 61 | 97 | 83 | 04 | 28 | 30 | 48 | 49 | 40 | 99 | 99 | 69 | 96 | 13 | 94 | 21 |
| 34 | 13 | 53 | 15 | 32 | 42 | 02 | 58 | 32 | 14 | 83 | 73 | 02 | 82 | 49 | 25 | 62 | 91 | 14 | 94 | 70 | 72 | 64 | 50 | 51 |
| 72 | 11 | 79 | 75 | 79 | 36 | 07 | 12 | 92 | 61 | 89 | 93 | 77 | 82 | 08 | 23 | 74 | 75 | 67 | 56 | 37 | 45 | 35 | 13 | 44 |
| 19 | 72 | 57 | 61 | 99 | 08 | 62 | 02 | 26 | 82 | 52 | 90 | 72 | 51 | 94 | 84 | 59 | 79 | 34 | 19 | 95 | 76 | 21 | 49 | 91 |
| 96 | 99 | 76 | 63 | 90 | 27 | 60 | 94 | 15 | 70 | 17 | 74 | 92 | 31 | 85 | 24 | 47 | 55 | 64 | 51 | 91 | 47 | 13 | 39 | 69 |
| 44 | 15 | 86 | 76 | 18 | 15 | 57 | 29 | 31 | 62 | 95 | 84 | 20 | 83 | 01 | 11 | 90 | 86 | 80 | 81 | 40 | 43 | 65 | 87 | 35 |
| 33 | 83 | 94 | 07 | 50 | 18 | 89 | 86 | 16 | 50 | 09 | 97 | 04 | 76 | 51 | 41 | 20 | 56 | 50 | 20 | 33 | 53 | 70 | 10 | 22 |
| 53 | 07 | 06 | 16 | 30 | 84 | 43 | 40 | 57 | 32 | 18 | 09 | 47 | 16 | 69 | 41 | 03 | 38 | 24 | 02 | 16 | 41 | 58 | 39 | 58 |

**Appendix B**

**Standard Laboratory Operating Procedure  
Method TO-14**

**To be provided upon award of laboratory Subcontract**

U.S. Environmental Protection Agency Region IX  
Toxic Waste Management Division  
Field Operations Branch

Field Sampling Plan  
DNAPL CONFIRMATION AND PLUME CHARACTERIZATION

Frontier Fertilizer  
4309 Second Street  
Davis, California 95617

Site EPA ID Number CAD 071530380

Anticipated Sampling Dates: October 1 to November 31, 1997

Prepared by:  
Bechtel Environmental, Inc.  
P.O. Box 193965  
50 Beale Street  
San Francisco, CA 94119

Revision 0  
August 27, 1997

EPA Remedial Project Manager: Janet Rosati

Phone: (415) 744-2403

EPA Contract Number : 68-W9-0060

EPA Work Assignment Number: 60-28-9L4R

---

For EPA use:

---

Received by Superfund Project Manager:

Reviewed by: Janet Rosati

Status:

Approved

Date: \_\_\_\_\_

Date: 10/2/97

Not Approved

---

Expedited Review?

Yes

No

Received by QA Management Section:

Reviewed by: Mario C. Plata

Status:

Approved

Date: \_\_\_\_\_

Date: 10/2/97

Not Approved

Concurrence: Rose King for Vance King

Date: 10/2/97

Chief, Quality Assurance  
Management Section  
Environmental Services Branch, OPM

# Contents

---

| Section |   | Page |
|---------|---|------|
| 1       | <b>Introduction and Objectives of Sampling Effort</b> .....                 | 1-1  |
| 2       | <b>Background</b> .....   | 2-1  |
| 2.1     | Site Location .....   | 2-1  |
| 2.2     | Site Description and Operational History .....                              | 2-1  |
| 2.3     | Previous Investigations.....  | 2-3  |
| 2.3.1   | Preliminary Assessment Conducted by Ecology<br>and Environment for EPA..... | 2-4  |
| 2.3.2   | Remedial Investigation Conducted by Bechtel for EPA.....                    | 2-5  |
| 2.4     | Geologic and Hydrogeologic Setting .....                                    | 2-7  |
| 2.4.1   | S-1 Zone .....  | 2-7  |
| 2.4.2   | S-2 Zone .....  | 2-9  |
| 2.4.3   | A-1 Aquifer/A-2 Aquifer.....  | 2-9  |
| 2.5     | Nature and Extent of Groundwater Contamination.....                         | 2-9  |
| 3       | <b>Sampling and Analysis Program and Rationale</b> .....                    | 3-1  |
| 3.1     | Sampling Recommendations.....   | 3-1  |
| 3.1.1   | Well Sump Sediment Sampling Recommendations .....                           | 3-1  |
| 3.1.2   | Dialysis Multiple-Level Groundwater Sampling<br>Recommendations .....       | 3-3  |
| 3.1.3   | Monitoring Well Installation Recommendations .....                          | 3-4  |
| 3.1.4   | Monitoring Well Decommissioning Recommendations.....                        | 3-6  |
| 3.2     | Analysis Recommendations .....  | 3-6  |
| 3.2.1   | Well Sump Sediment Field Testing .....                                      | 3-7  |

| <b>Section</b>   | <b>Page</b> |
|--|-------------|
| 3.2.2 Well Sump Sediment Analyses .....                | 3-7         |
| 3.2.3 Groundwater Sample Analyses .....                | 3-7         |
| <b>4 Request for Analyses</b> .....                    | <b>4-1</b>  |
| 4.1 Well Sump Sediment Analyses .....                  | 4-1         |
| 4.2 Monitoring Well Groundwater Sample Analyses .....  | 4-1         |
| 4.3 DMSL Groundwater Sample Analyses .....             | 4-1         |
| 4.4 Equipment Rinsate Sample Analyses.....             | 4-1         |
| <b>5 Field Methods and Procedures</b> .....            | <b>5-1</b>  |
| 5.1 Well Sump Sediment Sampling .....                  | 5-1         |
| 5.2 Well Sump Sediment Analysis.....                   | 5-1         |
| 5.3 Dialysis Multiple-Level Groundwater Sampling ..... | 5-2         |
| 5.4 Monitoring Well Installation and Sampling.....     | 5-2         |
| 5.4.1 Drilling and Soil Sampling.....                  | 5-2         |
| 5.4.2 Monitoring Well Installation.....                | 5-3         |
| 5.4.3 Monitoring Well and Site Surveying.....          | 5-3         |
| 5.4.4 Monitoring Well Development .....                | 5-3         |
| 5.4.5 Water Level Measurements.....                    | 5-5         |
| 5.4.6 Monitoring Well Groundwater Sampling .....       | 5-5         |
| 5.5 Decontamination Procedures.....                    | 5-5         |
| 5.6 Well Decommissioning Procedures .....              | 5-5         |
| 5.7 Well Decommissioning Procedures .....              | 5-6         |

| <b>Section</b> | <b>Page</b>   |
|----------------|---|
| <b>6</b>       | <b>Disposal of Investigation-Derived Wastes ..... 6-1</b>   |
| 6.1            | Used Personal Protective Equipment<br>and Disposable Sampling Equipment ..... 6-1                                   |
| 6.2            | Decontamination Fluids ..... 6-1  |
| 6.3            | Soil Cuttings ..... 6-1   |
| 6.4            | Purged Groundwater ..... 6-1  |
| 6.5            | Decommissioned Monitoring Well Materials ..... 6-2  |
| <b>7</b>       | <b>Sample Documentation and Shipment ..... 7-1</b>  |
| 7.1            | Field Logbooks ..... 7-1  |
| 7.2            | Sample Containers and Preservatives ..... 7-2   |
| 7.2.1          | Well Sump Sediment Samples ..... 7-2  |
| 7.2.2          | Groundwater Samples ..... 7-2   |
| 7.2.3          | Equipment Rinsate Samples ..... 7-2   |
| 7.3            | Sample Traffic Report and Chain-of-Custody Records and Quality<br>Assurance/Quality Control Summary Forms ..... 7-2 |
| 7.4            | Sample Labeling, Packaging, and Shipment ..... 7-3  |
| <b>8</b>       | <b>Quality Control ..... 8-1</b>  |
| 8.1            | Equipment Rinsate Samples ..... 8-1   |
| 8.2            | Duplicate Samples ..... 8-1   |
| 8.3            | Laboratory Quality Control Samples ..... 8-1  |
| 8.4            | Field Variances ..... 8-2   |

## Illustrations

| Figure |  | Page |
|--------|--|------|
| 2-1    | Site Location .....                            | 2-2  |
| 2-2    | Site Features and Well Locations .....         | 2-3  |
| 2-3    | Geologic Cross Section a- a' .....             | 2-8  |
| 2-4    | Hydrogeologic Cross Section A-A' .....         | 2-10 |
| 2-5    | Hydrogeologic Cross Section C-C' .....         | 2-11 |
| 2-6    | EDB and Carbon Tetrachloride in S-1 Zone ..... | 2-13 |
| 2-7    | EDB and Carbon Tetrachloride in S-2 Zone ..... | 2-14 |
| 2-8    | EDB and Carbon Tetrachloride in A-1 Zone ..... | 2-15 |
| 3-1    | Proposed Monitoring Well Locations .....       | 3-2  |
| 3-2    | Proposed Monitoring Well Designs .....         | 3-5  |

## Tables

| Table |                            | Page |
|-------|----------------------------|------|
| 4-1   | Request for Analyses ..... | 4-3  |

## Appendices

### Appendix

- A Client Request Forms
- B DMLS Sampling Depths

## Section 1

# **Introduction and Objectives of Sampling Effort**

---

This field sampling plan describes well sump sediment sampling and analysis, monitoring well installation, discrete groundwater sampling and analysis, and monitoring well decommissioning to be conducted by Bechtel Environmental, Inc. (Bechtel) at the Frontier Fertilizer site (CAD 071530380) in Davis, Yolo County, California. This work is part of a Remedial Investigation under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). This field sampling plan has been prepared under contract with the Environmental Protection Agency (EPA), Contract Number 68-W9-0060 and specific authorization of EPA Region IX, Work Assignment Number 60-28-9L4R.

From 1972 to 1983, the Frontier Fertilizer site was used as a fertilizer and pesticide distribution facility. Pesticides and fertilizers were stored and mixed on site and sold to farmers. When the empty pesticide containers were returned, residual material was rinsed out and deposited into an unlined basin near the northwest corner of the site. Analytical results of soil and groundwater samples collected on or adjacent to the site indicated the presence of several pesticides and other compounds in onsite soils and in the shallow groundwater beneath and downgradient of the site. The site history, features, and nature and extent of contamination are described in more detail in Section 2.

The objectives of the sampling described in this plan are:

1. To provide more conclusive evidence of the presence and nature of a dense non-aqueous phase liquid (DNAPL) in the subsurface. This evidence is needed for assessing the technical practicability of site cleanup and to delineate a DNAPL zone for a possible technical impracticability evaluation
2. To delineate the extent of the pesticide plume to the north and northwest of the OW-2 well cluster in the S-1 and S-2 zones, and the A-1 aquifer and the carbon tetrachloride plume to the east and north of the OW-4 well cluster
3. To reduce the potential for cross-contamination of aquifer zones through existing wells

Field sampling will be conducted under a protocol accepted by the EPA and the Quality Assurance Project Plan submitted by Bechtel on April 28, 1995 and revised July 14, 1997. A laboratory designated by the EPA Region IX will conduct the analyses. Laboratory services will be obtained and coordinated through the EPA QA Program.

## **Background**

---

This section describes the site location; description and operational history; previous investigations; hydrogeologic setting; and nature and extent of contamination.

### **2.1 LOCATION**

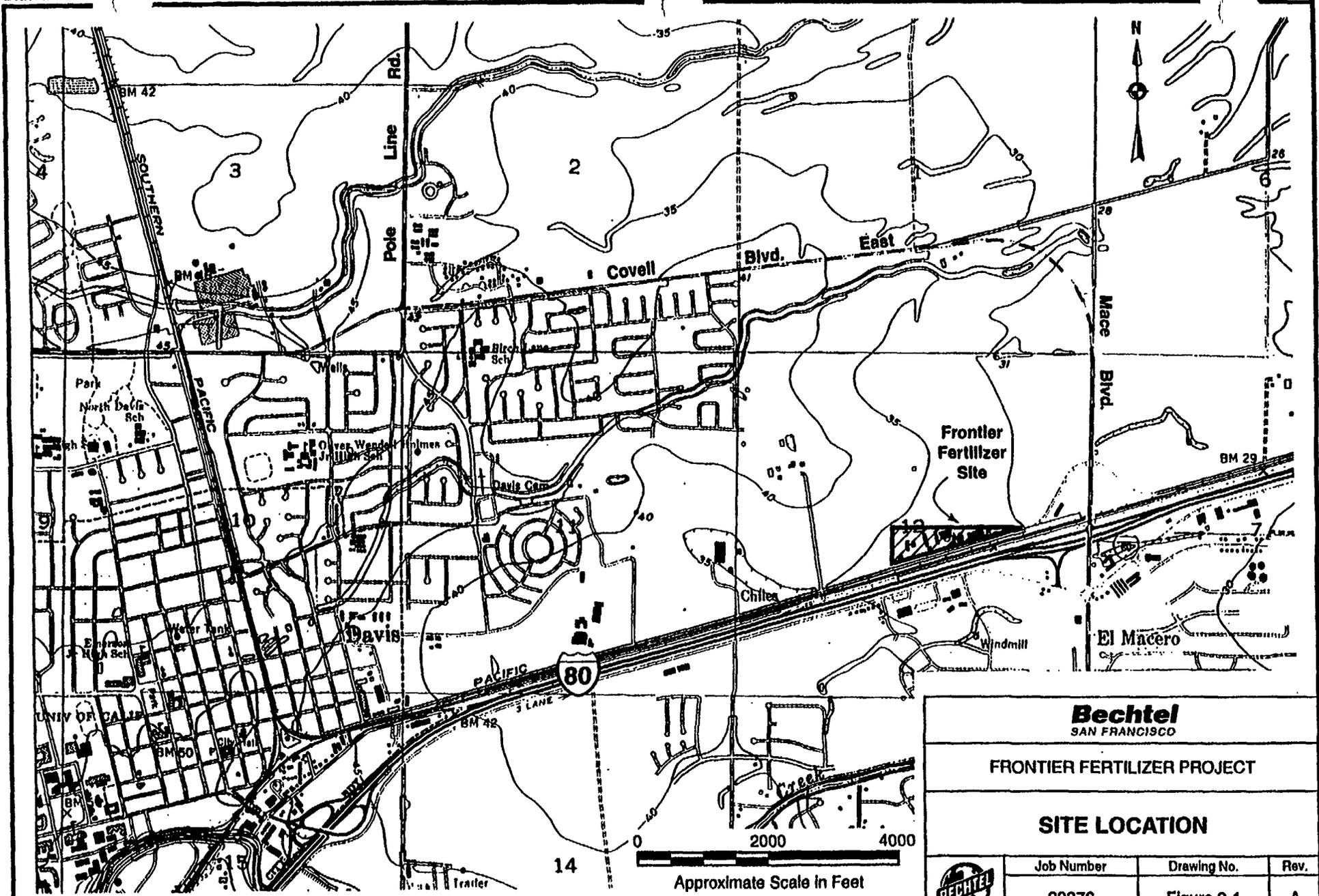
The Frontier Fertilizer site is located at 4309 Second St. in Davis, Yolo County, California (see Figure 2-1). The geographic coordinates of the site are 38° 33' 9.5" N latitude and 121° 42' 7.0" W longitude (Township 8 North, Range 2 East, Section 12, Mt. Diablo Baseline and Meridian, Davis, California, 7.5-minute quadrangle).

### **2.2 SITE DESCRIPTION AND OPERATIONAL HISTORY**

The Frontier Fertilizer site is near the eastern edge of the city of Davis, California. The 18-acre site consists of several warehouses, shops, a pole barn, a labor camp complex, a tomato grading station, several sumps and culverts, and a disposal basin area. The site is bounded on the south by Second Street and Interstate I-80, and on the north, west, and east by agricultural fields. Construction of the Mace Ranch Park industrial and residential development is under way for most of the agricultural land surrounding the site. The nearest residence is approximately 0.2 mile north of the site. The site features are shown in Figure 2-2.

The site was first operated as farm headquarters of the C. Bruce Ranch Company in 1950. Grain warehouses and barns for machinery storage were the first buildings erected. A labor camp for Mexican nationals was constructed between 1952 and 1954. Site development continued from east to west, with the site finally occupying 14 acres in 1970. In 1970, the 14-acre site was sold to Anderson Farms, Inc. The next major improvement of the site and its operations occurred in 1972, when a tomato grading station and a wash rack to rinse off tomato trucks were installed in the south-central area. In addition, Barber-Rowland Company (Barber-Rowland) moved onto the 4 acres to the west of the original 14 acres, completing the expansion of the site to 18 acres.

The arrival of Barber-Rowland in 1972 marked the beginning of fertilizer and pesticide operations on the site. In 1982, Frontier Fertilizer took over the fertilizer and pesticide operations from Barber-Rowland. Frontier's operations were terminated in 1987. During site operations by Barber-Rowland and Frontier Fertilizer, fertilizers and pesticides were stored in containers, sold in bulk, or mixed and placed in 500- to 1,000-gallon trailers that were attached to a purchaser's truck for transport to the farm. If a pesticide container or trailer was returned with residual material inside, the excess pesticide and container rinsate were poured onto the ground or into at least one unlined disposal basin located near the northwest corner of the site (Figure 2-2). In addition, used pesticide, insecticide, and herbicide containers were stored, crushed, and disposed of on site and at other locations off site. Frontier Fertilizer operations were confined to the western end of the property. Currently, the site is fenced and secure, and there are no activities other than those associated with the remediation.

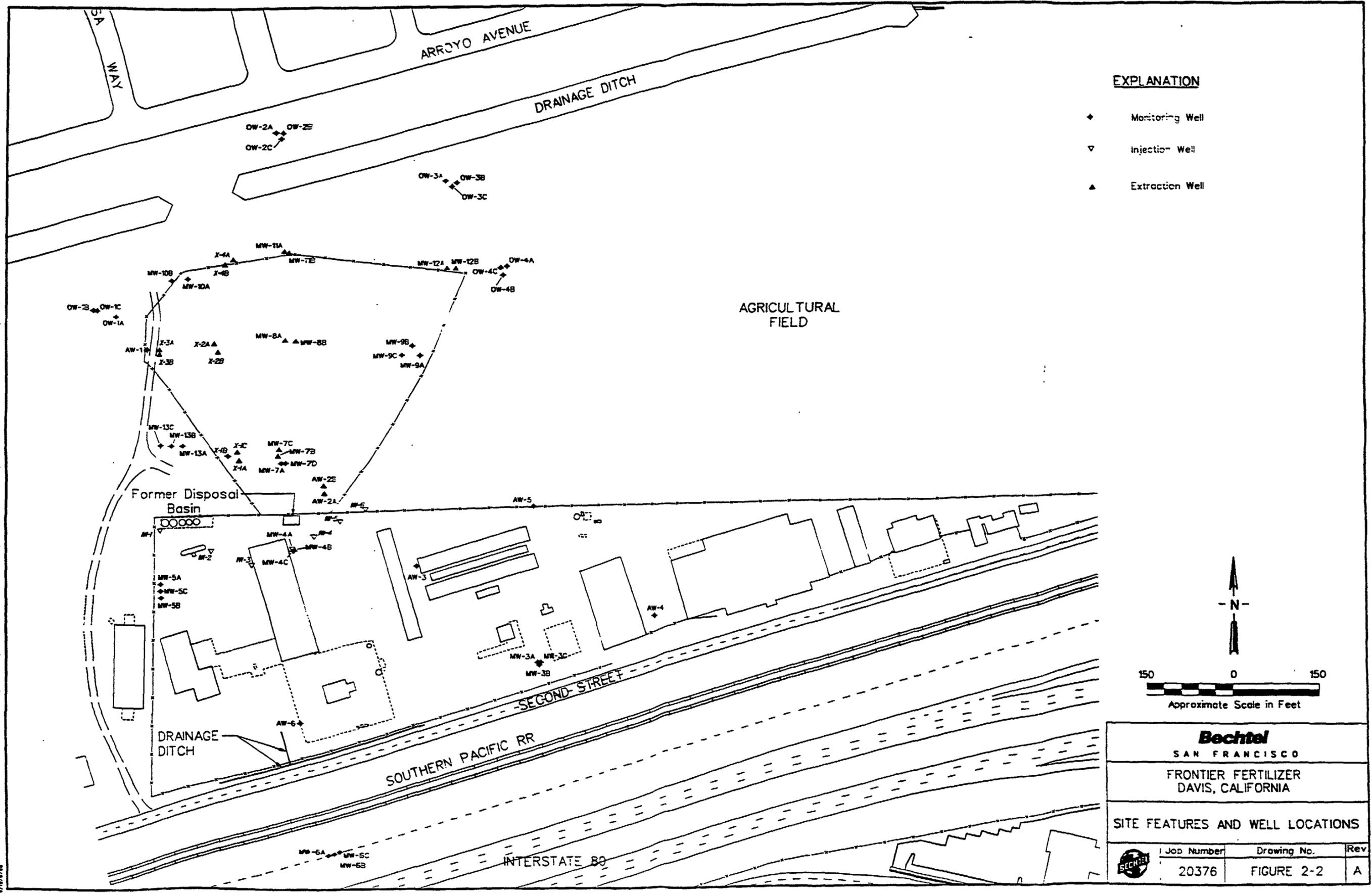


Source: U.S.G.S. Davis, CA 7-1/2 minute series topographic quadrangle 1952, photorevised 1981.

|                                 |             |      |
|---------------------------------|-------------|------|
| <b>Bechtel</b><br>SAN FRANCISCO |             |      |
| FRONTIER FERTILIZER PROJECT     |             |      |
| <b>SITE LOCATION</b>            |             |      |
| Job Number                      | Drawing No. | Rev. |
| 20376                           | Figure 2-1  | A    |

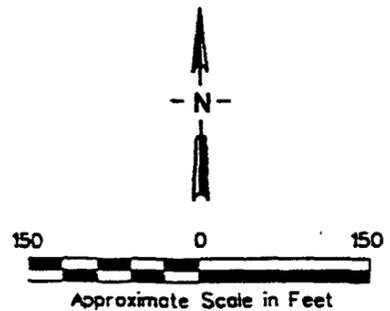
This drawing and the design it covers are the property of BECHTEL. They are hereby loaned and on the borrower's express agreement that they will not be reproduced, copied, loaned, certified, or used except in the limited way and under the conditions permitted by any written consent given by the lender to the borrower.

S:\000001\01-00-000\01\000001\000001.dwg 2/11/82



**EXPLANATION**

- ◆ Monitoring Well
- ▽ Injection Well
- ▲ Extraction Well



|  |             |     |
|--|-------------|-----|
| <b>Bechtel</b>                           |             |     |
| SAN FRANCISCO                            |             |     |
| FRONTIER FERTILIZER<br>DAVIS, CALIFORNIA |             |     |
| <b>SITE FEATURES AND WELL LOCATIONS</b>  |             |     |
| Job Number                               | Drawing No. | Rev |
| 20376                                    | FIGURE 2-2  | A   |

According to California Department of Health Services (DHS) records, on July 27, 1983, an employee's dog came in contact with liquid in the disposal basin. The dog died of pesticide poisoning while being examined by a veterinarian. Yolo County Department of Public Health (YCDPH) personnel visited the site on August 2, 1983, and observed the 20-foot by 15-foot by 4-foot deep basin, with approximately 1,500 gallons of fluid ("dark, oily liquids") in it. YCDPH personnel returned 2 days later to collect fluid samples, but the pit had been pumped out. Soil samples collected from the base of the pit had very high concentrations of disyston and EDB. In September 1983, YCDPH, under the guidance of DHS, stipulated that corrective action be taken at the site. Soil samples taken by YCDPH on March 2, 1984 indicated that soil contamination by EDB, DCP, DBCP, and other pesticide- and herbicide-related compounds existed at the site.

EDB was employed as a soil fumigant to kill nematodes and was normally purchased from manufacturers as a powder, or in a 5 percent solution in water. Its use in California was discontinued in 1982. DBCP was employed as a nematicide and was normally purchased from manufacturers in powder form or in 7.5 percent solutions in water. Its use was discontinued in California in 1977. DCP is still used in California as a nematicide and for weed control.

## 2.3 PREVIOUS INVESTIGATIONS

Three groundwater investigations were carried out prior to EPA's direct oversight of the Frontier Fertilizer Site. These were conducted by Luhdorff and Scalmanini Consulting Engineers (LSCE) for Frontier Fertilizer, Groundwater Technology, Inc. (GTI) for RAMCO Enterprises, and Metcalf and Eddy, Inc. (M&E) for California EPA. LSCE's groundwater investigation focused on characterizing the nature and extent of contaminants in groundwater and site hydrogeologic characterization. GTI's investigation added several wells to the monitoring network and provided additional data to characterize the nature and extent of pesticide contamination. M&E's investigation was directed toward initial containment of the pesticide plume. M&E installed one additional monitoring well cluster, sampled the monitoring wells, and conducted aquifer pumping tests to support the design of a groundwater pump and treat system. The two investigations conducted for EPA are discussed below.

### 2.3.1 Preliminary Assessment Conducted by Ecology and Environment for EPA

In 1993, the EPA Emergency Response Section contracted with E&E to investigate pesticide soil and groundwater contamination at Frontier Fertilizer. The purpose of this investigation was to collect soil samples to determine levels of pesticide contamination remaining in the soil and to attempt to locate a source for the carbon tetrachloride contamination. Analytical data were used to determine if a removal action was warranted for any source area on site. Removal options considered included soil vapor extraction and soil excavation. EPA determined that soil containing concentrations of 1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP),

and 1,2-dichloropropane (DCP) above 1,000 parts per billion (ppb) would be considered for removal action (Ecology and Environment, 1994).

Groundwater sampling and analysis were also conducted as part of the EPA preliminary assessment. Between August 24 and September 1, 1993, 25 of the 39 wells associated with the site were sampled. Wells were selected from all areas of the contaminated groundwater and all three water-bearing zones. The objective of the sampling event was to determine whether contaminant concentrations had changed since the previous sampling. Of particular concern was whether contamination was entering the A-1 aquifer. (Figure 2-2 shows well locations.)

### **2.3.2 Remedial Investigation Conducted by Bechtel for EPA**

Upon review of the previous investigation results, it was determined that additional soil and groundwater sampling were required. Soil sampling was conducted as a hot spot search to determine if all sources of contamination had been identified. The entire Frontier Fertilizer property was sampled on a grid, and samples were analyzed for volatile organic compounds (VOCs), organophosphorus pesticides, carbonate/urea pesticides, and organochlorine pesticides.

Additional soil samples were collected to determine if site soil had been dispersed off site by wind and/or rain and to calibrate a VLEACH model of contaminant transport in the disposal basin area. These samples were also collected to characterize the disposal basin soil for removal and disposal and to determine background soil concentrations of chemicals of concern (COCs).

The results from analysis of these samples are presented in the February 1997 Draft Interim Final Remedial Investigation (RI) Report. Conclusions regarding soil are as follows:

- Contaminated soil has not been transported off site by wind or surface water runoff.
- Soils in the immediate vicinity of the former disposal basin contain levels of contaminants that may not be above RCRA hazardous levels.
- Soils beneath and adjacent to the former disposal basin are contaminated with pesticides to depths corresponding, at a minimum, to the water table at a depth of 32 feet below ground surface (bgs).
- The lateral extent of these contaminated soils has been delineated.
- Other possible sources of contaminants were investigated but none were found.
- Background soils contain detectable concentrations of several pesticides.
- Contaminant levels in soils are indicative of a DNAPL release. The highest levels of EDB and DCP were detected in soils near the former disposal basin.

- DNAPL migration probably extends beyond the water table, and into the S-2 water-bearing zone.
- Site surface soils are not generally contaminated with pesticides at concentrations above PRGs.

Groundwater sampling was conducted as a HydroPunch™ survey to determine the leading edge of the pesticide plume in the S-1 and S-2 water-bearing zones and in the A-1 aquifer. This survey included preparation of geologic logs and water level measurements. In addition, groundwater samples were collected and water level measurements were made at site monitoring wells during the RI. The results from analysis of these data are also presented in the RI Report. Conclusions regarding groundwater are as follows:

- Groundwater occurs in three water-bearing zones. From shallowest to deepest, they are the S-1 zone, the S-2 zone, and the A-1 aquifer. The S-1 and S-2 zones are silty sand lenses surrounded by a clay and silt material. The A-1 aquifer is a more regionally extensive gravel and sand aquifer with one to two orders of magnitude greater transmissivity than that of the shallower sand zones. The site hydrogeology is a three-dimensional flow system. The flow system exhibits a horizontal or lateral anisotropy; therefore, S-1 and S-2 sands and the A-1 aquifer are valid representations of site conditions. However, there are significant vertical flow components that are recognized and integrated into the conceptual model.
- There is an areally extensive clay aquitard between the S-1 and S-2 zones. Although this clay appears to be extensive, there may be localized regions of interconnection between the S-1 and S-2 zones. The aquitard separating the S-2 zone and the A-1 aquifer pinches out to the north. There is evidence from the seasonal water level changes and the geologic data that the S-2 zone and A-1 aquifer are hydraulically interconnected in this area.
- Groundwater contamination was detected at high levels locally in the S-1 and S-2 zones and at much lower levels in the A-1 aquifer.
- The highest concentrations of EDB, DBCP, and DCP were detected in the S-1 and S-2 zone wells located immediately downgradient from the former disposal basin.
- Contaminant levels in the S-1 and S-2 zones indicate a localized presence of DNAPL. Although the DNAPL may no longer be mobile, it does appear to have migrated into the S-2 zone around wells MW-7C and MW-13B.
- Dissolved phase contaminants enter the A-1 aquifer where the intervening aquitard pinches out, and the downward gradients between the A-1 aquifer and S-2 zone induce migration of groundwater from the S-2 into the A-1 aquifer. Because of the low concentrations of DCP, EDB, and DBCP and the limited areal extent of these

compounds in the A-1 aquifer, there was no indication of a DNAPL in the A-1 aquifer.

- Carbon tetrachloride was detected at concentrations above the maximum contaminant level (MCL) in the S-1, S-2, and A-1 zones. The plume configuration is markedly different from the pesticide plume configuration, indicating the carbon tetrachloride source is not the former disposal basin. Soil and groundwater data do not indicate the source for the carbon tetrachloride.
- Background wells, located across I-80 and hydraulically upgradient from the site, contained tetrachloroethene (PCE) and other organic compounds at detectable concentrations. During one sampling event, PCE concentrations were above the MCL (5.0 µg/L) in two upgradient wells.

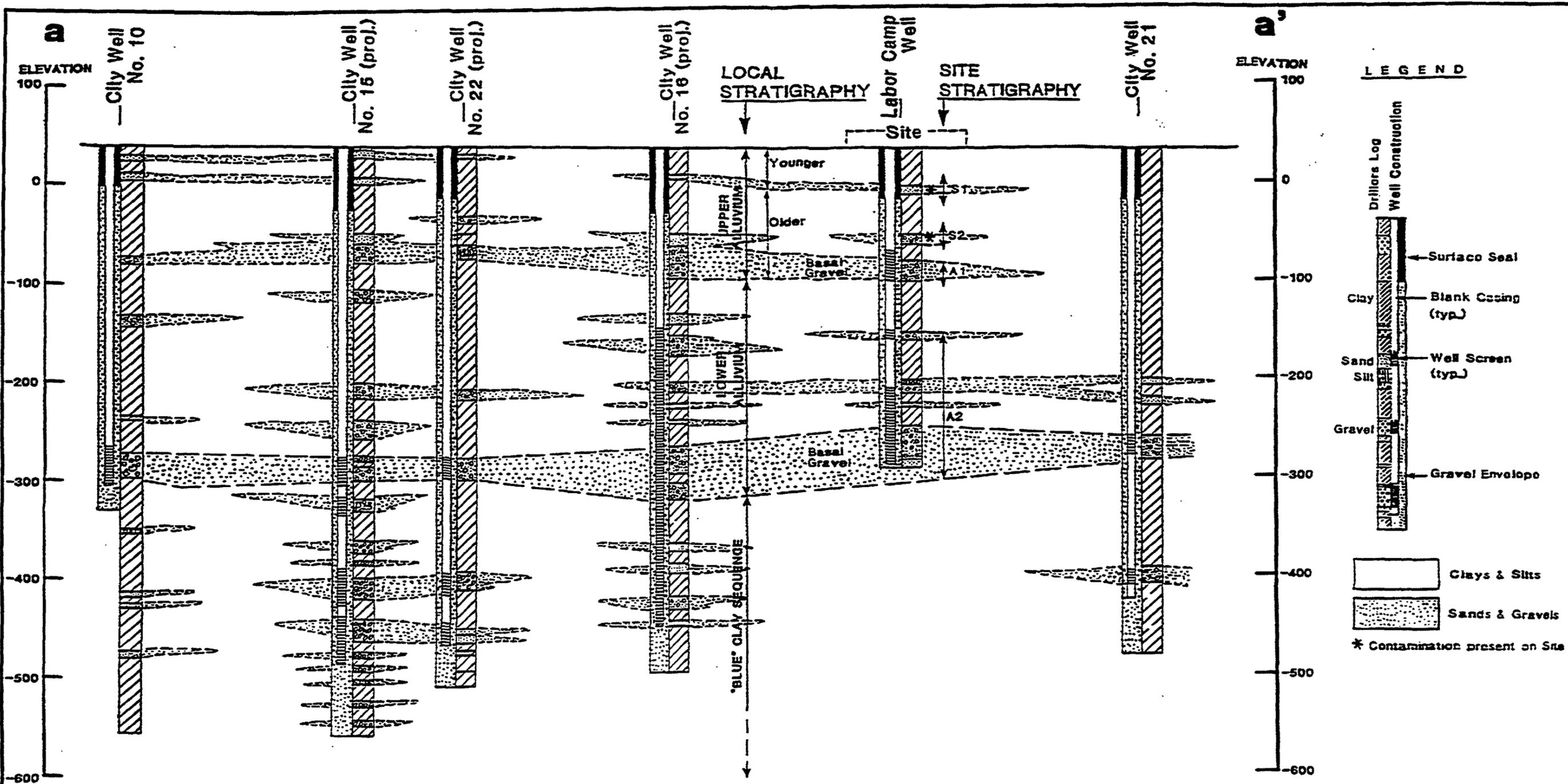
## 2.4 GEOLOGIC AND HYDROGEOLOGIC SETTING

A generalized geologic cross-section of the site vicinity is provided in Figure 2-3. Frontier Fertilizer is underlain by Quaternary alluvium to depths exceeding 300 feet. This alluvium is made up of lenses of sand and gravel within a clay and silt matrix. Groundwater is transmitted through the sand and gravel, and the rate of groundwater movement is dependent on the thickness, composition (percentage of silt and clay), length, width, and degree of interconnection between the lenses. Four distinct water-bearing zones have been identified in the subsurface. These are, from shallowest to deepest, the S-1 zone, the S-2 zone, the A-1 aquifer, and the A-2 aquifer. Groundwater flow in these zones is three-dimensional, with vertical and horizontal flow components, but is dominated by horizontal flow.

The primary water supply aquifer is the A-2 aquifer, which is below the A-1 aquifer and separated from the A-1 aquifer by a 25- to 30-foot thick clay aquitard. The Remedial Investigation and previous investigations at this site have not explored the A-2 aquifer because there is no indication that site-related contaminants have migrated beyond the A-1 aquifer.

### 2.4.1 S-1 Zone

The S-1 zone was encountered in numerous borings at depths ranging from 35 to 40 feet bgs. The S-1 zone consists of several discontinuous silty sand lenses that are typically 1 to 4 feet thick, and of variable width and length. According to the boring log descriptions, there is some variability in silt and clay content of the sand. In some parts of the site, the S-1 zone was not encountered during drilling (see Figures 2-4 and 2-5). Hydraulic conductivity and transmissivity were measured in seven wells screened in the S-1 zone using slug testing and pumping tests. Hydraulic conductivity values range from 5.3 to 54 ft/day.



Source: Luhdorff and Scatmanini, November 1987.

|                                 |             |      |
|---------------------------------|-------------|------|
| <b>Bechtel</b><br>SAN FRANCISCO |             |      |
| FRONTIER FERTILIZER PROJECT     |             |      |
| GEOLOGIC CROSS-SECTION<br>a-a'  |             |      |
| Job Number                      | Drawing No. | Rev. |
| 20376                           | Figure 2-3  | A    |

A clay aquitard underlies the S-1 zone. This aquitard appears to underlie the S-1 zone throughout the study area, including the offsite areas investigated. This unit is approximately 20 to 25 feet thick. Although the clay aquitard between the S-1 and S-2 zones appears continuous, water level data indicates some interconnection between these zones does exist at least locally.

#### **2.4.2 S-2 Zone**

The S-2 zone is less extensive than the S-1 zone, and underlies the area beneath the disposal basin at depths of 60 to 70 feet bgs. The S-2 zone is a silty sand of variable thickness and permeability. In the central portion of the contaminated area, this S-2 zone is about 30 feet thick and pinches out to the northeast and north. Slug test and pumping test results indicate the S-2 zone has a lower hydraulic conductivity compared to the S-1 zone, with values ranging from 2.4 to 24 ft/day.

A clay and silt aquitard underlies the S-2 zone, but this aquitard is not present in the northern fenced area, approximately 700 feet north of the former disposal basin. In this area, the S-2 zone appears to be vertically continuous with the underlying A-1 aquifer.

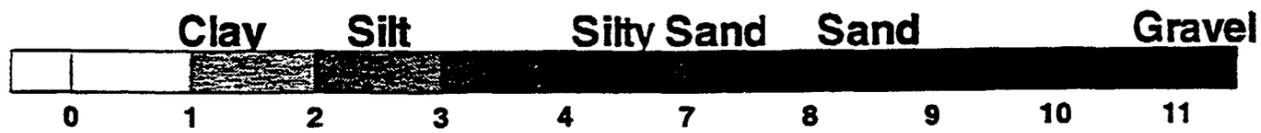
#### **2.4.3 A-1 Aquifer/A-2 Aquifer**

The A-1 aquifer is encountered at depths of 105 to 130 feet bgs. It was encountered throughout the investigation area and is laterally continuous throughout the region. This aquifer is a thick, coarse-grained unit with high transmissivity. The hydraulic conductivity measured in A-1 zone well MW-9C was 490 to 630 ft/day. These values are approximately one to two orders of magnitude greater than the hydraulic conductivities measured in the S-1 and S-2 zones. The A-1 aquifer is pumped for agricultural irrigation, but is not used as a municipal drinking water supply.

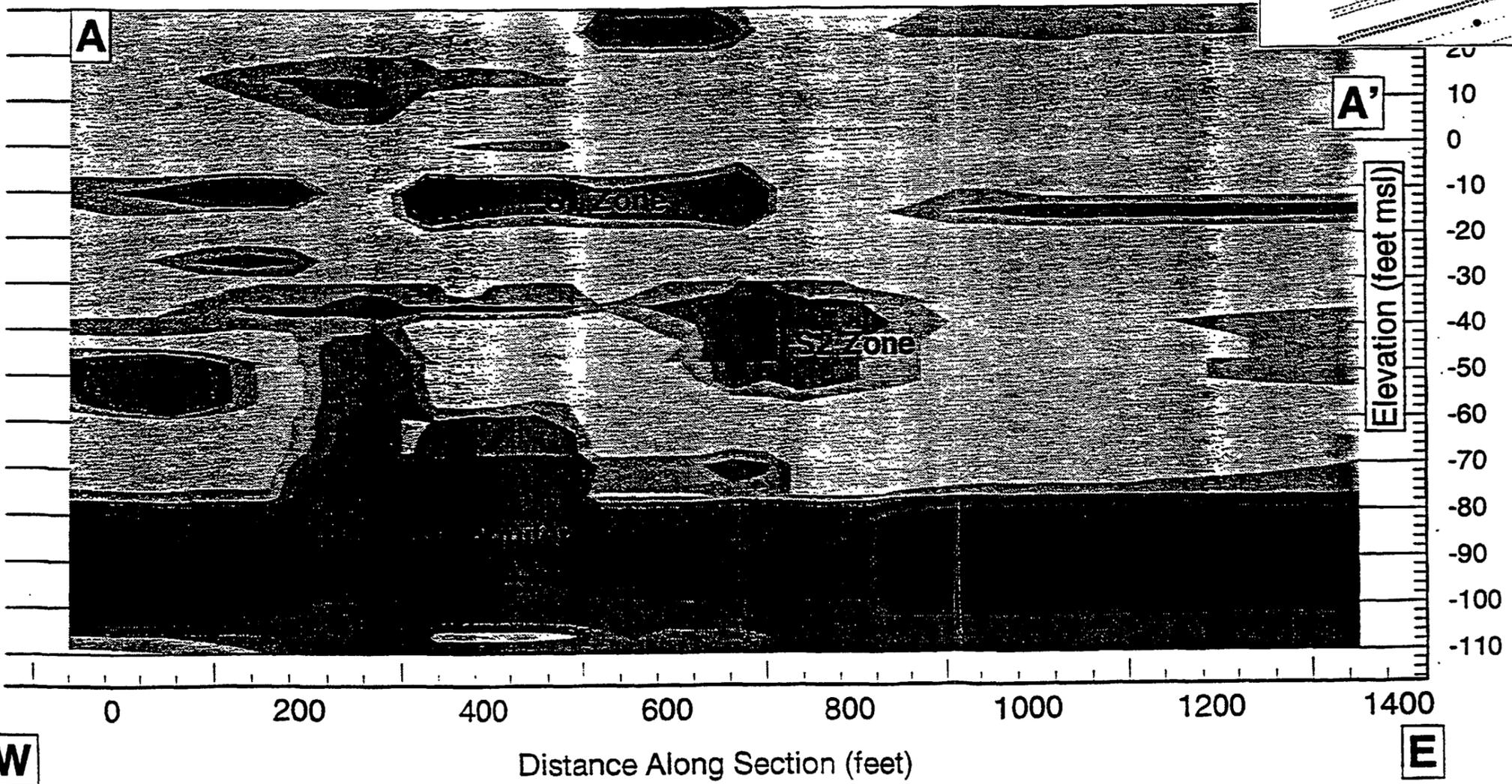
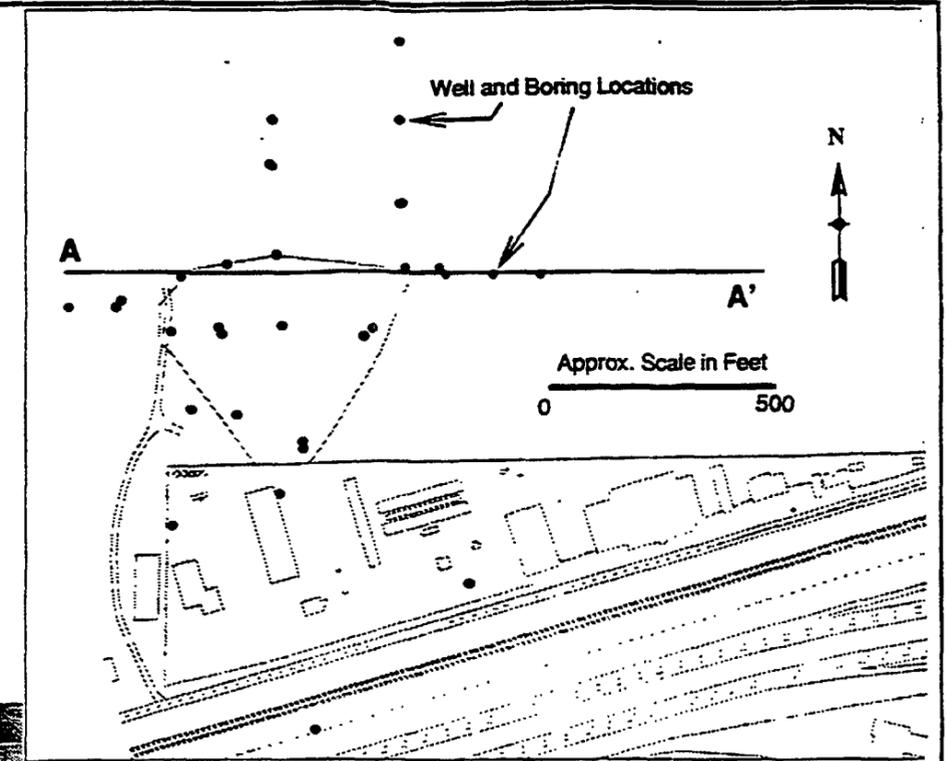
The A-2 aquifer is the primary water supply aquifer in the Davis area. It is a gravel aquifer extending from 180 to 350 ft bgs and is separated from the A-1 aquifer by 25 to 30 feet of clay aquitard. The A-2 aquifer is not a continuous single bed, but is a series of large gravel lenses that are grouped within the depth range between 180 and 350 ft bgs.

### **2.5 NATURE AND EXTENT OF GROUNDWATER CONTAMINATION**

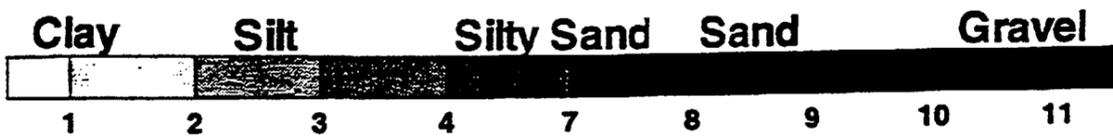
The extent of EDB, DBCP, and DCP has been delineated in the S-1 and S-2 zones and the A-1 aquifer across the site with some areas of uncertainty. The distribution of these chemicals is similar, each exhibiting high concentrations immediately north of the former disposal basin in the S-1 and S-2 zones, with concentrations rapidly declining in all directions. While the concentrations of EDB and DCP are indicative of a DNAPL release, the DBCP concentrations are low enough to indicate a dissolved phase release or a cosolved compound, meaning DBCP was present as a minor constituent dissolved in the DNAPL.



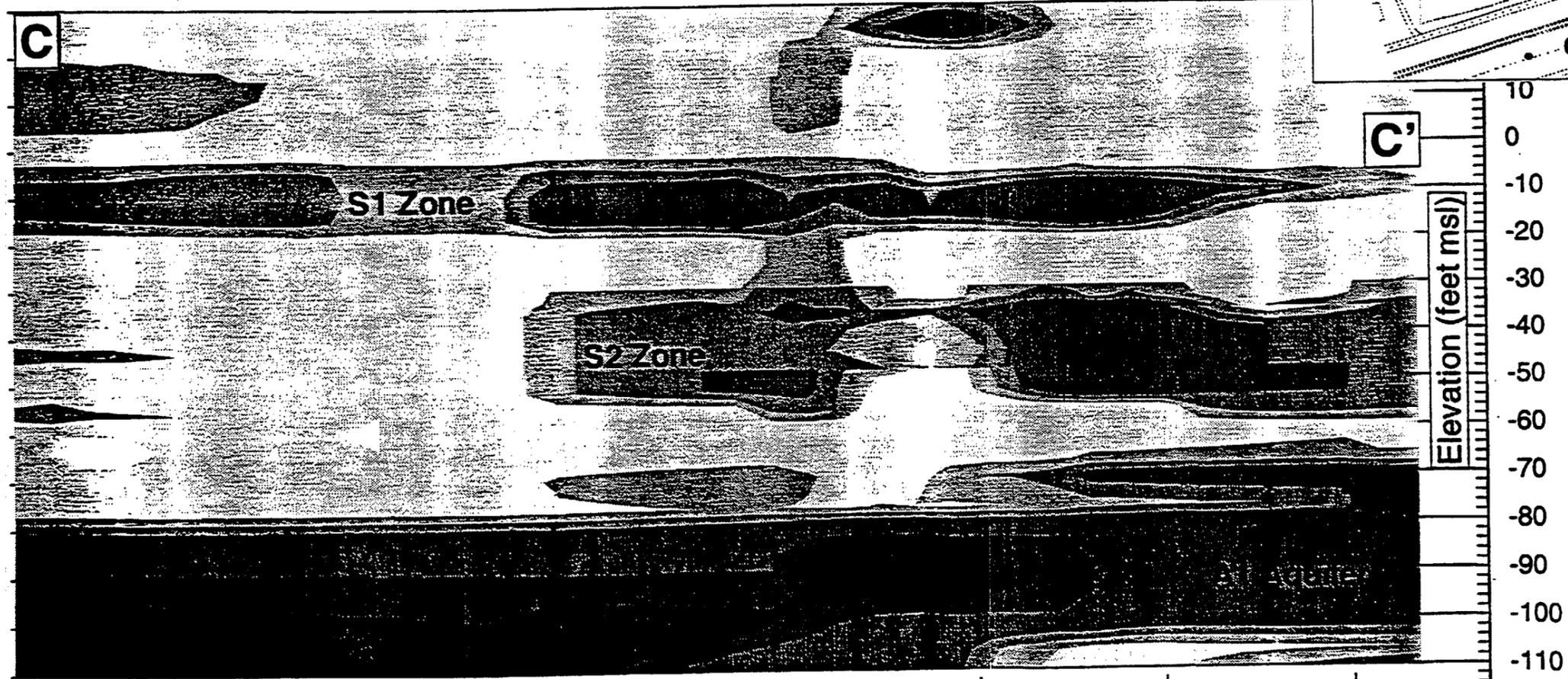
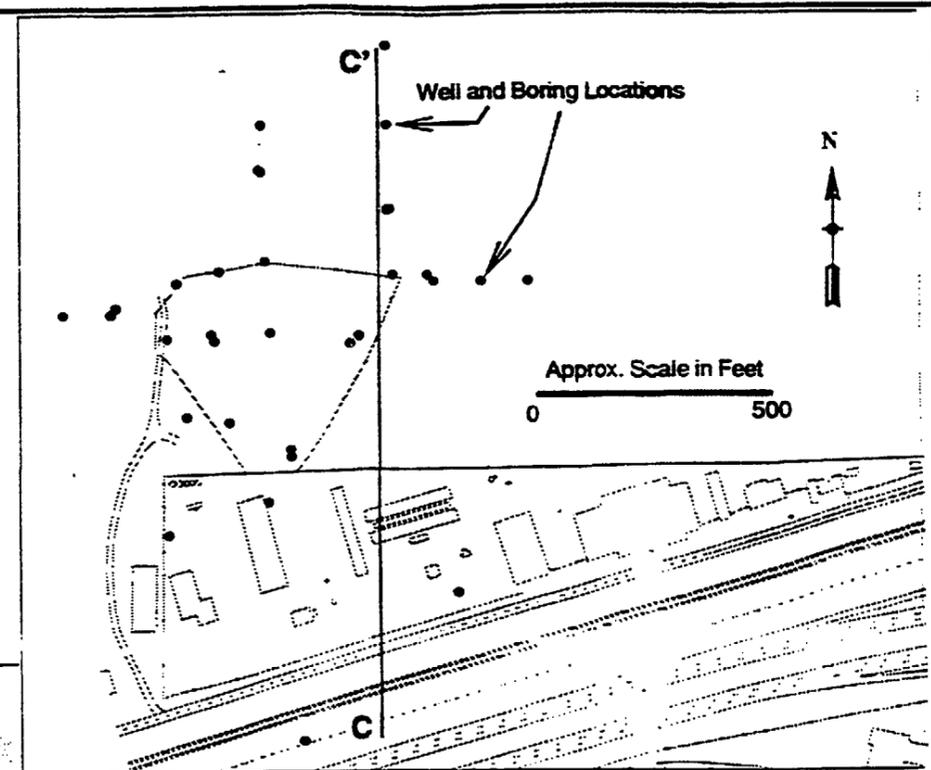
V.E. = 5x



|                                  |            |      |
|----------------------------------|------------|------|
| <b>Bechtel</b><br>SAN FRANCISCO  |            |      |
| FRONTIER FERTILIZER PROJECT      |            |      |
| Hydrogeologic Cross Section A-A' |            |      |
| Job Number                       | Drawing No | Rev. |
| 20376                            | Figure 2-4 | A    |



V.E. = 5x



Cross Section Location Map

|                                  |                     |                           |
|----------------------------------|---------------------|---------------------------|
| <b>Bechtel</b><br>SAN FRANCISCO  |                     |                           |
| FRONTIER FERTILIZER PROJECT      |                     |                           |
| Hydrogeologic Cross Section C-C' |                     |                           |
|                                  | Job Number<br>20376 | Drawing No.<br>Figure 2-5 |
|                                  |                     | Rev.<br>A                 |

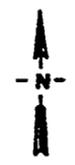
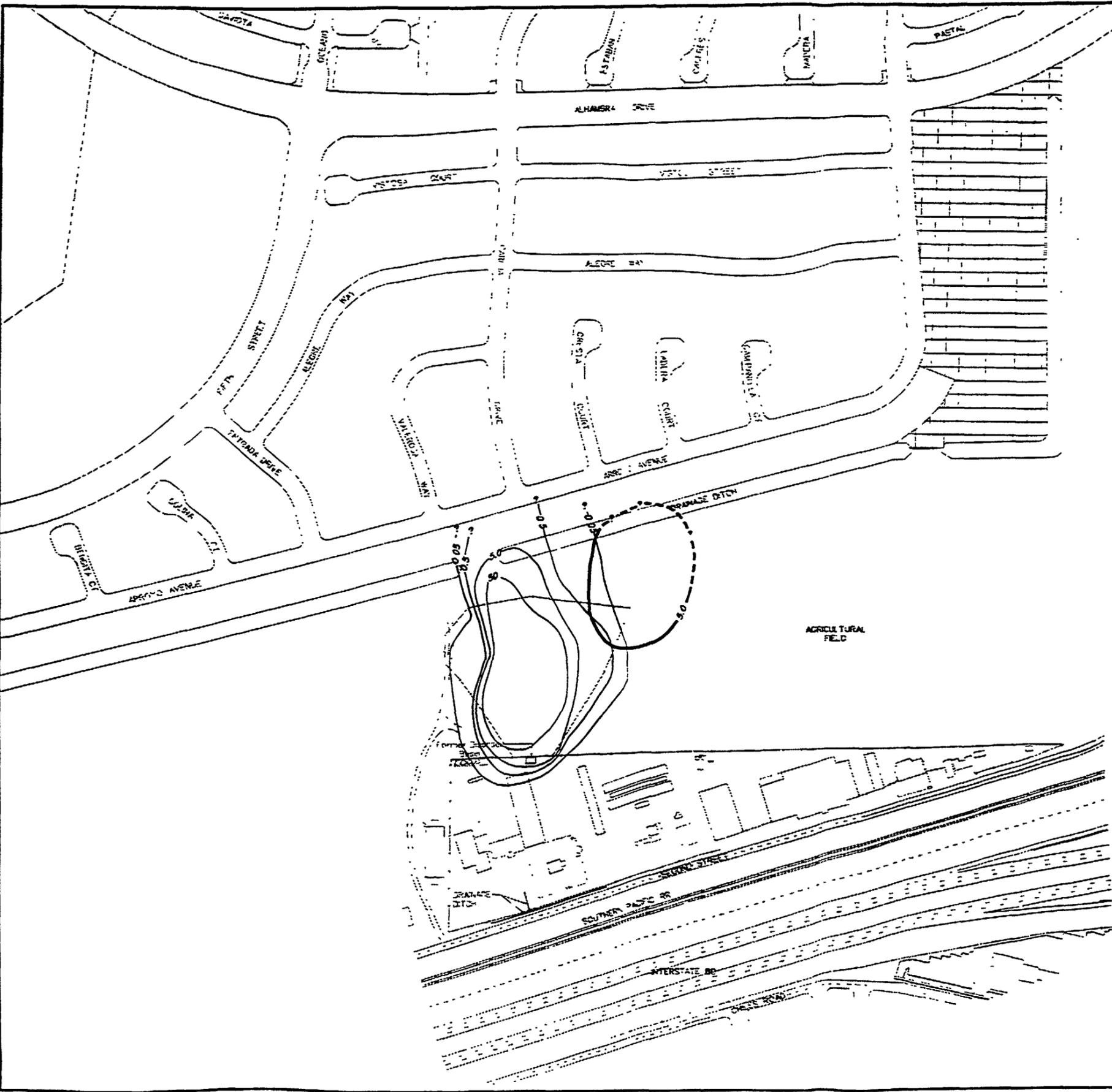
The data indicate a dissolved phase of EDB, DBCP, and DCP in the A-1 aquifer because the concentrations of these compounds are very low compared with concentrations detected in the overlying S-2 zone. The lateral extent of compounds in the A-1 aquifer indicates that the source of contamination is probably where the aquitard between the S-2 zone and A-1 aquifer is missing and the two permeable units merge, thereby forming a pathway for dissolved contaminants to enter the A-1 aquifer.

The extent of EDB encompasses all other organic compounds that may have originated from releases at the former disposal pit. Therefore, EDB is used to illustrate the extent of contaminants in the different zones. The contaminant plumes in the S-1 and S-2 zones are approximately 600 to 700 feet long, extending from the former disposal basin to some point beyond wells OW-2A and OW-2B (Figures 2-6 and 2-7). The pesticide plume in the A-1 aquifer appears to be limited in extent and to be centered near the region where there is greater potential interconnection between the S-2 zone and the A-1 aquifer (Figure 2-8). The northernmost edge of the dissolved contaminant plume is not delineated by the existing monitoring well network.

Carbon tetrachloride was detected in the S-1, S-2, and A-1 zones, and soil data do not indicate a carbon tetrachloride source. Concentrations were highest in the S-2 zone (up to 370 µg/L). The highest concentrations of carbon tetrachloride are almost two orders of magnitude lower than the highest EDB and DCP concentrations. Carbon tetrachloride is also distributed differently, with the plume located east of the DCP, EDB, and DBCP plume (Figures 2-6 through 2-7). Very low concentrations have been detected in wells MW-7A, MW-7B, MW-7C, MW-7D, X-1A, and X-1B, effectively ruling out the disposal basin as the source of this contaminant.

This drawing and the design it covers are the property of BECHTEL. They are to be used only in the limited way and for the limited purpose intended and no part of this drawing shall be reproduced, copied, loaned, exhibited, or used in any way without the written consent given by the lender to the borrower.

S:\ENR\1996\04\04\FRONTIER\FRONTIER.DWG 4/23/96 11:54 AM



**EXPLANATION**

- Interpreted 1,2-Dibromoethane (EDB) Concentration: Contour, May 1996 (ug/L)
- Interpreted Carbon Tetrachloride Concentration: Contour, May 1996 (ug/L)

150 0 150 300  
Approximate Scale in Feet

|   |                           |          |
|---|---------------------------|----------|
| <b>Bechtel</b><br>SAN FRANCISCO             |                           |          |
| FRONTIER FERTILIZER<br>DAVIS, CALIFORNIA    |                           |          |
| EDB AND CARBON TETRACHLORIDE<br>IN S-1 ZONE |                           |          |
| Job Number:<br>20376                        | Drawing No.<br>FIGURE 2-6 | Rev<br>A |





## **Sampling and Analysis Program and Rationale**

---

In order to address the objective of confirming the presence of DNAPLs in the subsurface, well sump sediment samples will be collected from several wells and qualitative DNAPL testing will be performed in the field. If no DNAPL is detected, then groundwater sampling with the dialysis multiple-level sampler (DMLS) will be conducted in several wells. The rationale for these activities is discussed in Sections 3.1.1 and 3.1.2.

In order to address the objective of defining the northern and western boundaries of the pesticide plume and the northern and eastern boundaries of the carbon tetrachloride plume, a well installation and sampling program will be conducted. The proposed well installation program will include up to 21 new monitoring wells. The wells will be installed in up to seven clusters of three wells each, one each screened in the S-1, S-2, and A-1 zones, respectively. In the three deeper borings (to the A-1 aquifer), soil samples will be collected every 5 feet to determine the depth of the water-bearing zones at each well cluster location.

Groundwater sampling and quick turnaround analysis will be used to determine the presence and concentration of the pesticides and carbon tetrachloride in groundwater at the OW-5 and OW-6 cluster locations, Figure 3-1. The rationale for the well installation program is discussed in Section 3.1.3.

In order to address the objective of reducing the potential for cross-contamination of aquifer zones through existing wells, a program of well decommissioning is recommended in Section 3.1.4.

### **3.1 SAMPLING RECOMMENDATIONS**

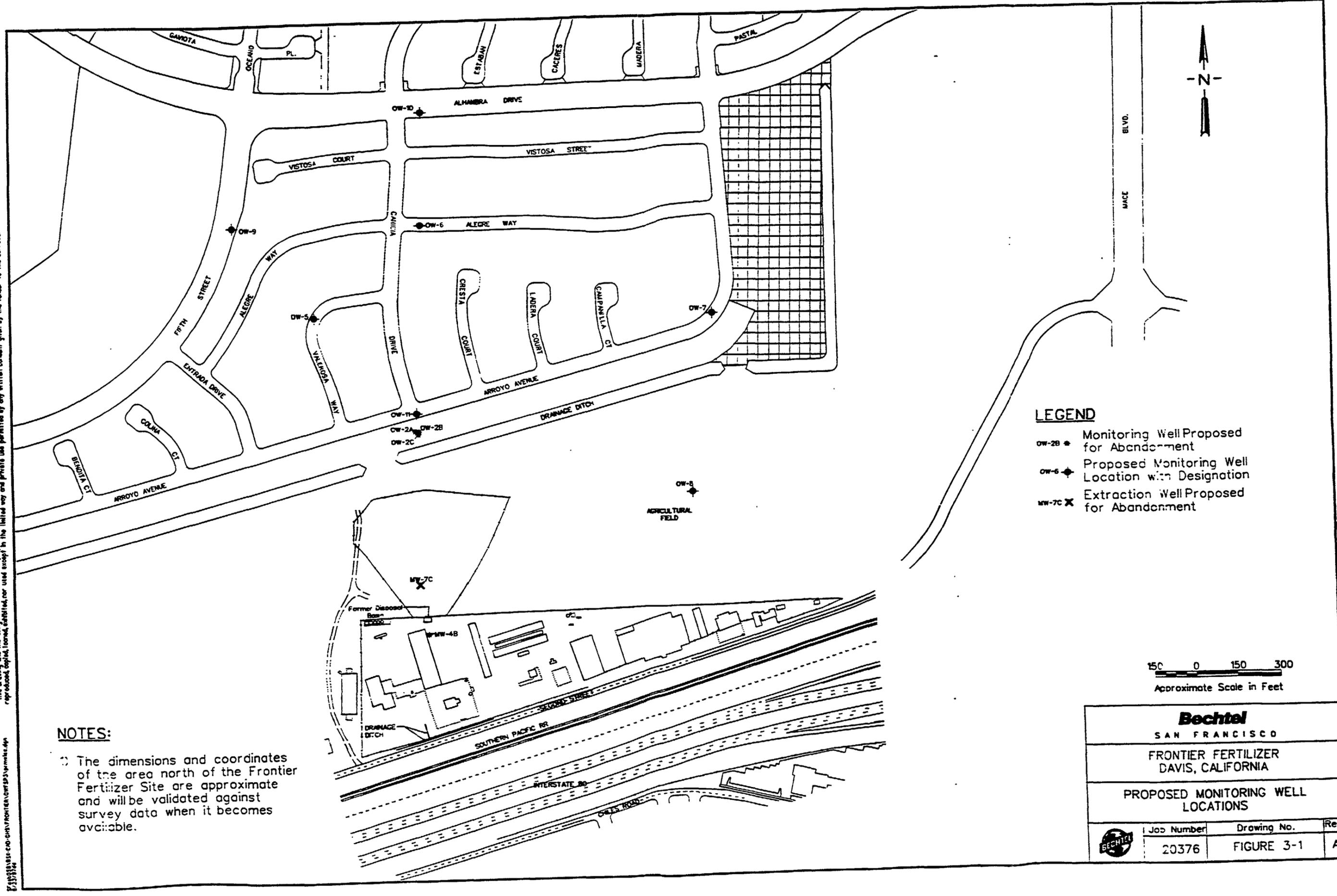
This section presents recommendations for monitoring well sump sediment sampling and analysis, multiple level groundwater sampling and analysis, and monitoring well installation, sampling, and decommissioning.

#### **3.1.1 Well Sump Sediment Sampling Recommendations**

It is recommended that well sump sediment sampling be conducted first in wells X-1A and X-1B. Wells X-1A and X-1B have well sumps that are 2 to 3 feet of blank casing with an end cap. These wells were installed in 1995 and therefore, accumulated sediments should not be very thick. A stainless steel bailer will be lowered to the bottom of these wells to collect sump sediments and liquids for testing. Testing will consist of UV fluorescence and Sudan IV dye-shaker tests. If no DNAPL is positively identified in either of these wells, similar sump sampling will be conducted in wells MW-7B and MW-7C.

This drawing and the design it covers are the property of BECHTEL. They are hereby loaned and on the borrower's express agreement that they will not be reproduced, copied, loaned, exhibited, or used except in the limited way and private use permitted by any written consent given by the lender to the borrower.

P:\33311\11-11-00-014\1\FRONTIER\DWG\33311\msh.dwg  
6/23/94



**LEGEND**

- OW-2B \* Monitoring Well Proposed for Abandonment
- OW-6 ◆ Proposed Monitoring Well Location with Designation
- MW-7C X Extraction Well Proposed for Abandonment

150 0 150 300  
Approximate Scale in Feet

**NOTES:**

- 1) The dimensions and coordinates of the area north of the Frontier Fertilizer Site are approximate and will be validated against survey data when it becomes available.

|  |            |             |     |
|--|------------|-------------|-----|
| <b>Bechtel</b>                           |            |             |     |
| SAN FRANCISCO                            |            |             |     |
| FRONTIER FERTILIZER<br>DAVIS, CALIFORNIA |            |             |     |
| PROPOSED MONITORING WELL<br>LOCATIONS    |            |             |     |
|  | Job Number | Drawing No. | Rev |
|  | 20376      | FIGURE 3-1  | A   |

Wells MW-7C and MW-7B were installed about 4 years after the disposal basin was closed in late 1983. At the time these wells were installed, a DNAPL released from the basin may have been mobile. If either MW-7B or MW-7C intercepted a DNAPL pool, the DNAPL may have entered the well and flowed to the well sump. If this occurred, then the DNAPL will be present in the well sump, probably mixed with sediment. This situation makes these wells more likely to contain a DNAPL, but these wells were constructed with sumps that are 10 feet deep and well screens with 0.040-inch openings. The large screen openings likely permitted a fairly large amount of silt and clay to enter the well, and the deep sumps allow a deep column of these sediments to accumulate. Therefore, if initial soundings for total well depth indicate less than four feet of sediment are present, a stainless steel bailer will be used to collect sump sediments. If more than four feet of accumulated sediments are present, the sump materials will be sampled with piston coring equipment.

In the event any of the sampled well sumps contain a DNAPL that can be positively identified by UV fluorescence or Sudan IV, the investigation will be concluded and a sample of the DNAPL containing sediments will be submitted for VOC analysis. If DNAPL is not identified in the four well sump sediment samples, then multiple level groundwater sampling and analysis will be conducted.

### 3.1.2 Dialysis Multiple-Level Groundwater Sampling Recommendations

DNAPL residuals can be highly stratified within alluvial material, and extremely high concentrations can be found in very thin intervals within the saturated zone. For example, in well X-1B, where there has been up to 21,000  $\mu\text{g/l}$  DCP, there is up to 20 feet of well screen. If DNAPL is present near this well, it is likely that there is a thin zone (1 to 5 feet) that is supplying very high DCP concentrations to the well as it is pumped, and the remainder of the saturated zone supplies much lower DCP concentrations. The 21,000  $\mu\text{g/l}$  represents an average concentration across the entire screen zone.

If DNAPL is not identified as discussed above, groundwater sampling using DMLS will be conducted in order to determine if such high-concentration zones are present. The DMLS is a sampler designed to passively collect samples of groundwater as it flows horizontally across a well screen. DMLS permits sampling at discrete, thin depth intervals to assess the distribution of potential DNAPLs, and to measure the true maximum groundwater concentrations.

Wells X-1A, MW-7C, and OW-4B are proposed for sampling with the DMLS. Well X-1A is an S-1 zone well located within the EDB plume. Well MW-7C is an S-2 zone well in the plume, and has historically contained some of the highest concentrations of dissolved pesticides. Well OW-4B, located in the carbon tetrachloride plume, contains the highest concentrations of dissolved carbon tetrachloride (300  $\mu\text{g/l}$ ). Each well will be sampled at 1-foot intervals along 10

feet of the well screen. A total of 30 investigative samples will be collected. Appendix B illustrates the depths at which the DMLS sampler will be placed in each well.

Information obtained with the DMLS sampling will not unequivocally answer if DNAPL is present, but it will provide much stronger inferential data for the presence, nature, and extent of a DNAPL.

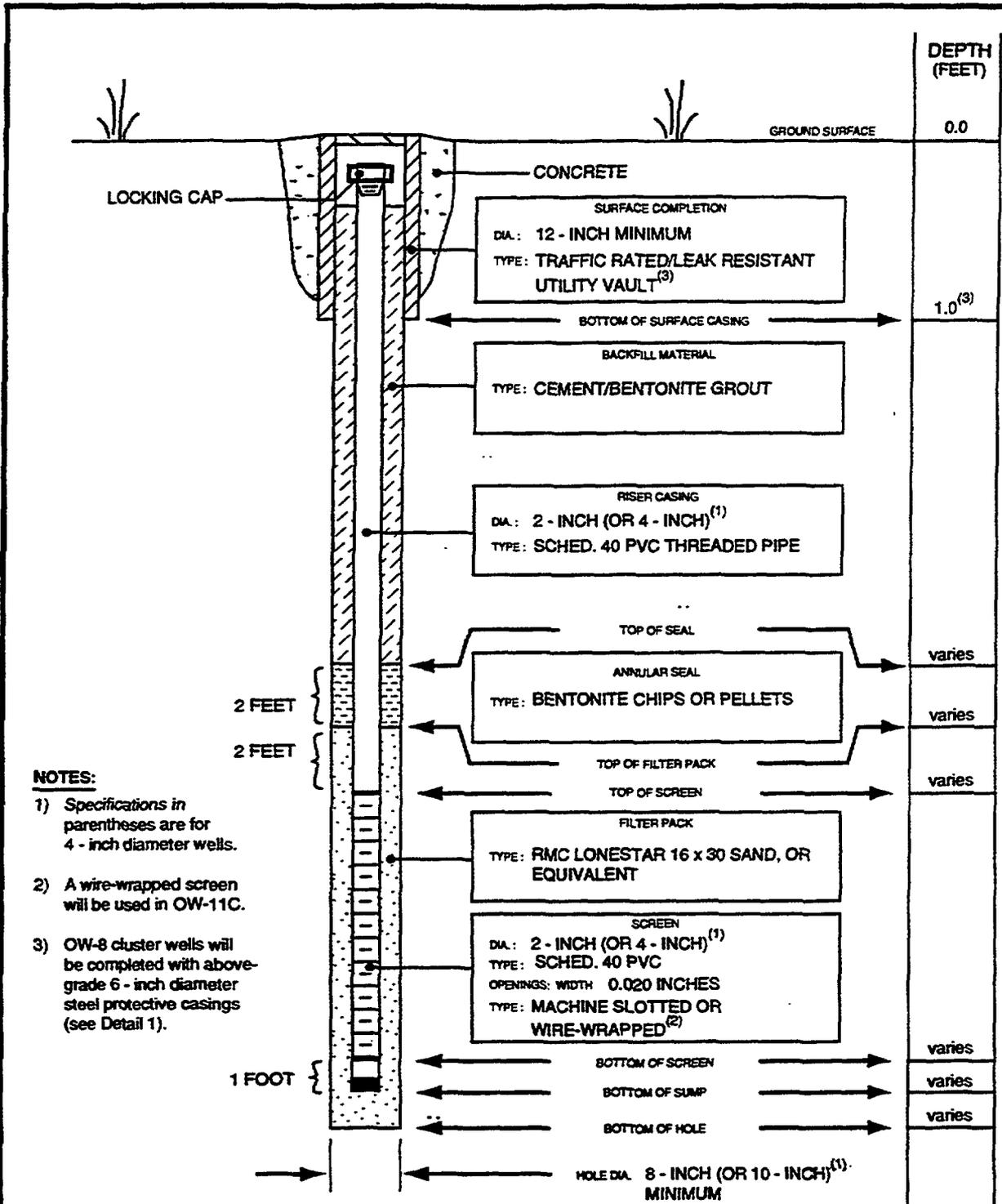
### 3.1.3 Monitoring Well Installation Recommendations

The groundwater flow direction in the S-1 and S-2 zones is to the north, based on numerous rounds of groundwater elevation data collected from 1985 through 1997, as well as the plume configuration in these zones. The groundwater chemistry data from HydroPunch™ sampling done during the remedial investigation indicate that the leading edge of the pesticide plume extends farther north than the OW-2 and OW-3 well clusters. Similarly, although the previous HydroPunch™ sampling delineated the eastern extent of carbon tetrachloride, there is no monitoring well cluster located to delineate the eastern edge of the plume. In order to address these data gaps, six groundwater sampling locations are proposed (see Figure 3-1). The six locations are designated OW-5, OW-6, OW-7, OW-8, OW-9, and OW-10. At each location, three wells will be installed, one well in each of the S-1 and S-2 zones and the A-1 aquifer. The proposed well design is shown in Figure 3-2.

The rationale for the well siting is that monitoring wells at these locations will satisfy the need to delineate the pesticide plume and the carbon tetrachloride plume in the S-1, S-2, and A-1 zones to concentrations at or below MCLs. These wells will also serve as sentinel wells or guard wells to monitor groundwater conditions between the site and the nearest municipal water supply wells. The placement of the sentinel wells is such that there will be sufficient time to respond before any Frontier Fertilizer contaminants can reach the water supply wells. There are two water supply wells that are of concern. One is located approximately 5,000 feet northwest of the Frontier Fertilizer site and one well is located approximately 3,000 feet north of the site.

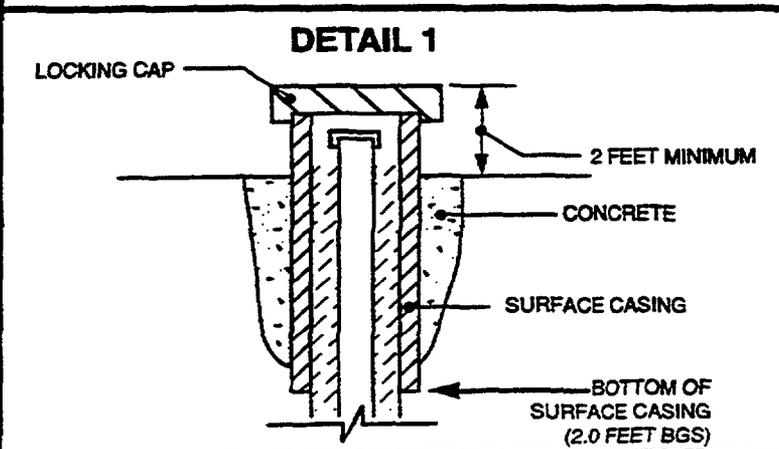
The first four well clusters, drilled in the sequence indicated by the assigned numbers, will be used to define the "leading edge" of the pesticide-contaminated groundwater and carbon tetrachloride/pesticide-contaminated groundwater in the S-1 and S-2 groundwater zones. The leading edge is defined by EDB and carbon tetrachloride MCLs of 0.05 µg/l and 0.5 µg/l.

Well cluster OW-5 will be located approximately 550 feet northwest of the OW-2 well cluster. The OW-5 site was selected to accommodate some uncertainty in groundwater flow directions in the three water-bearing zones in the region beyond OW-2. In other words, groundwater flow directions may change from north to northwest in the area beyond OW-2. The OW-5 wells will also provide plume delineation in that direction.



**NOTES:**

- 1) Specifications in parentheses are for 4 - inch diameter wells.
- 2) A wire-wrapped screen will be used in OW-11C.
- 3) OW-8 cluster wells will be completed with above-grade 6 - inch diameter steel protective casings (see Detail 1).



NOT TO SCALE

**Bechtel**  
SAN FRANCISCO

FRONTIER FERTILIZER PROJECT

**PROPOSED MONITORING WELL DESIGNS**



Job Number

20376

Drawing No.

FIGURE 3-2

Rev.

A

The OW-6 well cluster will be located approximately 725 feet north of the OW-2 well cluster. The site was selected because the plume's northern extent in 1995 was likely near previous boring B5, based on the very low pesticide concentrations detected in the S-1 and S-2 zones and the A-1 aquifer. It is anticipated that the groundwater at proposed location OW-6 will not be affected by the site-related pesticides in any of the upper water-bearing zones.

The OW-7 well cluster will be located approximately 900 feet northeast of the OW-3 well cluster. This well cluster is intended to delineate the northern extent of the carbon tetrachloride plume in the S-1, S-2, and A-1 zones.

The OW-8 well cluster will be located approximately 550 feet east of OW-4. The OW-8 wells will be used to delineate and monitor the eastern extent of the carbon tetrachloride plume.

The OW-5 and OW-6 wells will be installed, developed, and sampled so that analytical results will be available during the field program. The OW-9 wells, to be located 400 to 500 feet northwest from the OW-5 cluster, will be installed only if the OW-5 wells contain concentrations of EDB or carbon tetrachloride above the MCL. Similarly, the OW-10 wells will be installed if the OW-6 wells contain concentrations above MCLs. The OW-10 wells will be located on Alhambra Avenue approximately 400 to 500 feet north of the OW-6 wells.

Following installation of the wells, each well will be developed and sampled and the samples will be analyzed as described in Section 3.2. Each monitoring well in the clusters will have a unique well identification number. The location name will be appended with either the letter A, B, or C for the S-1, S-2, and A-1 zones, respectively.

### **3.1.4 Monitoring Well Decommissioning Recommendations**

Three wells, MW-4B, MW-7C, and OW-2B, will be decommissioned because they appear to be located near interconnected zones of the S-2 zone and A-1 aquifer. Wells OW-2A and OW-2C will also be decommissioned. All three OW-2 wells will be replaced with a well cluster (OW-11) located on the roadway immediately north of the original OW-2 wells. Replacement of these wells is needed because the wells are currently located on a future residential lot slated for development in the next 6 to 12 months. They are also in an area of the pesticide plume that is very important for monitoring the effectiveness of the groundwater remediation system.

## **3.2 ANALYSIS RECOMMENDATIONS**

Initial field testing of well sump sediments will be conducted. Each sample in which a DNAPL is positively identified will be analyzed for VOCs by the EPA designated laboratory. All groundwater samples will also be analyzed for VOCs by the EPA designated laboratory.

### **3.2.1 Well Sump Sediment Field Testing**

Field DNAPL testing of the well sump sediment samples will be conducted using ultraviolet fluorescence and Sudan IV dye-shaker tests.

### **3.2.2 Well Sump Sediment Analyses**

As mentioned above, if DNAPL is identified in the sump samples, they will be analyzed for VOCs using EPA CLPAS VOCs plus EDB and DBCP.

### **3.2.3 Groundwater Sample Analyses**

Each groundwater sample collected will be analyzed for EDB and DBCP using EPA Method 504 to achieve a detection limit of 0.05 µg/l. Samples will also be analyzed for CLPAS VOCs using a 25 ml purge volume. The analyses will be used to characterize the concentration of pesticides and carbon tetrachloride in groundwater at each monitoring well location. Specific conductance, pH, and temperature will also be measured in the field for every groundwater sample collected.

## **Request for Analyses**

---

The Frontier Fertilizer site was identified as a potential hazardous waste site and entered into the CERCLIS database on August 1, 1985 (CAD 071530380). Bechtel will conduct this field sampling effort as part of a remedial investigation under CERCLA. The anticipated sampling dates for this sampling effort are September 15 through October 31, 1997.

Table 4-1 shows the preservative requirements, analytical and contract-required holding times, and sample container requirements for each analyses. Client Request Forms are included as Appendix A.

### **4.1 WELL SUMP SEDIMENT ANALYSES**

If a DNAPL is positively identified in any of the sump sediment samples through field testing, they will be analyzed for VOCs using EPA RAS VOCs plus EDB and DBCP. The EPA Region IX designated laboratory will be used for these analyses. A maximum of four analyses are anticipated. These analyses will not have QC samples associated with them since the objectiveness will be to identify the compound present in the DNAPL and their relative concentrations are not their absolute concentration.

### **4.2 MONITORING WELL GROUNDWATER SAMPLE ANALYSES**

The monitoring well groundwater samples will be collected and analyzed for RAS VOCs plus EDB and DBCP via the 25 ml purge method and by EPA Method 504. These samples will consist of:

- Six samples from the new monitoring wells;
- A minimum of one duplicate sample; and
- Approximately one sample will be designated as laboratory quality control (QC) samples.

### **4.3 DMSL GROUNDWATER SAMPLE ANALYSES**

The DMSL groundwater samples will be collected and analyzed for RAS VOCs plus EDB and DBCP via the standard 5 ml purge method. Since the objective of this sampling is to screen for groundwater concentrations in the percent saturation range, no QC samples will be associated with these analyses.

### **4.4 EQUIPMENT RINSATE SAMPLE ANALYSES**

Approximately two equipment rinsate samples will be collected and analyzed. Equipment rinsate samples will be collected each day that monitoring well sampling equipment is decontaminated

in the field as described in Section 5. Equipment rinsate samples will be analyzed for RAS VOCs plus EDB and DBCP via the 25 ml purge method and EPA Method 504. The EPA designated laboratory will be utilized for all equipment rinsate analyses.

**Table 4-1  
Request for Analyses**

| CLP Analytical Services Requested |                 |             |                     | Special Analytical Services     |  |                                 |
|-----------------------------------|-----------------|-------------|---------------------|---------------------------------|--|---------------------------------|
| Chemistry Type                    |                 |             |                     | Organics                        |  |                                 |
| Specific Analyses Requested       |                 |             |                     | RAS VOCs plus EDB and DBCP      | RAS VOCs plus EDB and DBCP by using the 25 ml purge method | EPA Method 504 for EDB and DBCP |
| Preservatives                     |                 |             |                     | Add 1:1 HCl to pH<2 Chill to 4C | Add 1:1 HCl to pH<2 Chill to 4C                            | Chill to 4C                     |
| Analytical Holding Times          |                 |             |                     | Hold <14 days                   | Hold <14 days  | Hold <14 days                   |
| Contract Holding Times            |                 |             |                     | Hold <10 days                   | Hold <10 days  | Hold <10 days                   |
| Sample Number                     | Sample Location | Sample Date | Special Designation | Number and type of container    | Number of 40 ml glass vials                                | Number of 40 ml glass vials     |
| X-1A                              | X-1A            |             | Sump Sediment       | 1-8 oz jar                      | 0  | 0                               |
| X-1B                              | X-1B            |             | Sump Sediment       | 1-8 oz jar                      | 0  | 0                               |
| MW-7B                             | MW-7B           |             | Sump Sediment       | 1-8 oz jar                      | 0  | 0                               |
| MW-7C                             | MW-7C           |             | Sump Sediment       | 1-8 oz jar                      | 0  | 0                               |
| X-1A1                             | X-1A1           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A2                             | X-1A2           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A3                             | X-1A3           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A4                             | X-1A4           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A5                             | X-1A5           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A6                             | X-1A6           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A7                             | X-1A7           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A8                             | X-1A8           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A9                             | X-1A9           |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| X-1A10                            | X-1A10          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |

**Table 4-1  
Request for Analyses (Cont'd)**

| CLP Analytical Services Requested |                 |             |                     | Special Analytical Services     |  |                                 |
|-----------------------------------|-----------------|-------------|---------------------|---------------------------------|--|---------------------------------|
| Chemistry Type                    |                 |             |                     | Organics                        |  |                                 |
| Specific Analyses Requested       |                 |             |                     | RAS VOCs plus EDB and DBCP      | RAS VOCs plus EDB and DBCP by using the 25 ml purge method | EPA Method 504 for EDB and DBCP |
| Preservatives                     |                 |             |                     | Add 1:1 HCl to pH<2 Chill to 4C | Add 1:1 HCl to pH<2 Chill to 4C                            | Chill to 4C                     |
| Analytical Holding Times          |                 |             |                     | Hold <14 days                   | Hold <14 days  | Hold <14 days                   |
| Contract Holding Times            |                 |             |                     | Hold <10 days                   | Hold <10 days  | Hold <10 days                   |
| Sample Number                     | Sample Location | Sample Date | Special Designation | Number and type of container    | Number of 40 ml glass vials                                | Number of 40 ml glass vials     |
| MW-7C1                            | MW-7C1          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C2                            | MW-7C2          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C3                            | MW-7C3          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C4                            | MW-7C4          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C5                            | MW-7C5          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C6                            | MW-7C6          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C7                            | MW-7C7          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C8                            | MW-7C8          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C9                            | MW-7C9          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| MW-7C10                           | MW-7C10         |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B1                            | OW-4B1          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B2                            | OW-4B2          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B3                            | OW-4B3          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B4                            | OW-4B4          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B5                            | OW-4B5          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B6                            | OW-4B6          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B7                            | OW-4B7          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |

**Table 4-1  
Request for Analyses (Cont'd)**

| CLP Analytical Services Requested |                 |             |                     | Special Analytical Services     |  |                                 |
|-----------------------------------|-----------------|-------------|---------------------|---------------------------------|--|---------------------------------|
| Chemistry Type                    |                 |             |                     | Organics                        |  |                                 |
| Specific Analyses Requested       |                 |             |                     | RAS VOCs plus EDB and DBCP      | RAS VOCs plus EDB and DBCP by using the 25 ml purge method | EPA Method 504 for EDB and DBCP |
| Preservatives                     |                 |             |                     | Add 1:1 HCl to pH<2 Chill to 4C | Add 1:1 HCl to pH<2 Chill to 4C                            | Chill to 4C                     |
| Analytical Holding Times          |                 |             |                     | Hold <14 days                   | Hold <14 days  | Hold <14 days                   |
| Contract Holding Times            |                 |             |                     | Hold <10 days                   | Hold <10 days  | Hold <10 days                   |
| Sample Number                     | Sample Location | Sample Date | Special Designation | Number and type of container    | Number of 40 ml glass vials                                | Number of 40 ml glass vials     |
| OW-4B8                            | OW-4B8          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B9                            | OW-4B9          |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-4B10                           | OW-4B10         |             | DMSL                | 1 40 ml vial                    | 0  | 0                               |
| OW-5A                             | OW-5A           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-5B                             | OW-5B           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-5C                             | OW-5C           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-6A                             | OW-6A           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-6B                             | OW-6B           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-6C                             | OW-6C           |             | Groundwater         | 0                               | 3  | 3                               |
| OW-20A                            | OW-5A           |             | Duplicate           | 0                               | 3  | 3                               |
| OW-20B                            | OW-5A           |             | Rinsate             | 0                               | 3  | 3                               |
| OW-20C                            | OW-5A           |             | Lab QA/QC           | 0                               | 3  | 3                               |
|                                   |                 |             |                     |                                 |  |                                 |
|                                   |                 |             |                     |                                 |  |                                 |
|                                   |                 |             |                     |                                 |  |                                 |
|                                   |                 |             |                     |                                 |  |                                 |

## **Field Methods and Procedures**

---

This section describes the procedures to be used to collect well sump sediment, dialysis multiple-level and conventional groundwater samples, and equipment rinsate samples.

### **5.1 WELL SUMP SEDIMENT SAMPLING**

Wells X-1A and X-1B have well sumps consisting of 2 to 3 feet of blank casing with an end cap. These wells were installed in 1995 and, therefore, accumulated sediments should not be very thick. A stainless steel bailer will be lowered to the bottom of these wells to collect sump sediments and liquids for testing as described in Section 3.2.1.

Because wells MW-7C and MW-7B were constructed with sumps that are 10 feet deep and well screens with 0.040-inch openings, a large amount of sediment may be present in the sumps of these wells. The large screen openings likely permitted a fairly large amount of silt and clay to enter the well, and the deep sumps allow a deep column of these sediments to accumulate. Therefore, if initial soundings for total well depth indicate less than 4 feet of sediment are present, a stainless steel bailer will be used to collect sump sediments. If more than 4 feet of accumulated sediments are present, the sump materials will be sampled with piston coring equipment.

### **5.2 WELL SUMP SEDIMENT FIELD ANALYSIS**

An approximately 200 g aliquot of well sump sediment will be transferred with a spoon from the bailer to the inner of two sealable polyethylene bags. The bags will be sealed and the contents examined for evidence of two liquid phases. The presence of two phase may be indicated by two different color immisible liquids or refractive index differences that highlight the boundary between the two immisible liquids. The results of this examination will be recorded in the field log book.

*The sample aliquot will then be examined under uv light for indications of fluorescence. In a dark room, the bags containing the sample will be exposed to uv light. The light source will be an inexpensive, portable, battery-powered uv light capable of emitting both 254 nm and 300 to 400 nm light. The bag will be scanned with the uv light while it is manipulated to squeeze fluid against the bag beneath the lamp. The presence of a DNAPL may be indicated by observing the emission of light from the sample as it is illuminated by the uv light. The results of this examination will be recorded in the field log book.*

A milky white fluorescence has been observed when soil samples containing kerosene, tetrachloroethene, or chlorobenzene are exposed to uv light. It is unlikely that EDB, DCP, and DBCP will fluoresce, but other sight related contaminants of concern, that may be dissolved in the DNAPL, such as benzene, chlorobenzene, dichlorobenzene, and dichloroethene may be present at high enough concentrations to detect by this method.

Following the fluorescence examination, approximately 20 cm<sup>3</sup> will be transferred using a spoon into a 50 ml polypropylene centrifuge tube and 20 ml of water will be added and the tube shaken by hand for 10 seconds to create a soil-water suspension. This suspension will be visually examined for the presence of immisible liquid phase and the results recorded in the field log book.

The suspension will then be centrifuged at about 1250 rpm for one minute and again examined for the presence of immisible liquid phases. The results of this examination will be recorded in the field log book. After the centrifuge test, approximately 2 mg (an amount that would rest on the edge of a toothpick) of Sudan IV, a non-volatile hydrophobic dye, will be placed in the centrifuge tube. The contents of the tube will then be mixed by shaking manually for approximately 10 to 30 seconds and then visually examined.

Sudan IV is a reddish brown powder that dyes organic liquids red upon contact, but is practically insoluble in water at ambient temperatures. The presence of a non-aqueous phase liquid will be indicated by the presence in the tube of a red liquid. Since it is insoluble in water the Sudan IV will remain suspended and undissolved in the aqueous phase of the sample.

As a final check, the sample will again be centrifuged and visually examined. The presence of a non-aqueous phase liquid will indicated by a red liquid phase in the tube. The results of these observations will also be recorded in the field log book.

### 5.3 DIALYSIS MULTIPLE-LEVEL GROUNDWATER SAMPLING

The dialysis multiple-level groundwater samples will be collected using the DMLS sampler. The DMLS sampler assembly will be pressure-washed, then fitted with the sample collection cells. It will then be lowered into the designated interval of the well screen on cleaned pump hoist rods. The sampler will be anchored in place for 100 hours, at which time it will be removed and the sample cells retrieved.

### 5.4 MONITORING WELL INSTALLATION AND SAMPLING

This section describes procedures for monitoring well drilling (and soil sampling), installation, developing, sampling, surveying, and decommissioning.

#### 5.4.1 Drilling and Soil Sampling

A 10-inch-diameter hollow-stem auger drill rig will be used to bore to the desired depths for well installation. In the deeper borings (to the A-1 aquifer), which will be drilled first at each cluster location, soil samples will be collected every 5 feet to determine the depth of the water-bearing zones and select the screen interval for each well in the cluster. The soil samples will be

collected using a split-spoon sampler. The soil samples will be examined by the field geologist, classified according to the Unified Soil Classification System, then discarded with the other soil cuttings.

#### 5.4.2 Monitoring Well Installation

The proposed monitoring well designs are shown in Figure 3-2. As described above, a hollow-stem auger drill rig will be used to bore to the desired depths for well installation. At the completion of each boring, a 2-inch (4-inch-diameter for well cluster OW-11) Schedule 40 PVC monitoring well with a 0.020-inch slot screen will be installed. This slot screen size was utilized in existing monitoring wells on site and is expected to be suitable for the proposed monitoring wells. A mill-slotted screen will be used in all of the wells except in well OW-11C, where a PVC wire-wrapped screen will be used to increase the open area. Screen length will be between 5 and 10 feet, except in well OW-11C, which will be 10 to 20 feet. Under no conditions will the open intervals of the wells (screens and filter pack) cross into two water-bearing zones. No glues or solvents will be used during well installation.

The annulus of each well will be packed with a clean, well-sorted silica filter sand. The filter sand will be placed with a tremie pipe from the total depth of the boring to approximately 5 feet above the top of the screen. Bentonite chips will be placed on top of the filter pack interval and hydrated. Type II Portland cement and bentonite grout will be tremied into the annular space above the seal to the ground surface. The wellheads will consist of a traffic-rated, leak-resistant utility vault or a 5-foot length of 6-inch-diameter steel casing, depending on the well location (see Figures 3-1 and 3-2). The steel casing (where used) will be grouted into place approximately 3 feet bgs. As-built drawings will be completed for each well installed.

#### 5.4.3 Monitoring Well and Site Surveying

Surveying will be performed by a registered surveyor to determine the horizontal coordinates of each newly installed well and the reference point elevation at the top of the well casing. Elevation will be measured at a point marked and notched on the PVC riser casing of each well. This point will be used for water-level measurements for that well. The surveyor will provide an updated site map showing the new well locations.

#### 5.4.4 Monitoring Well Development

Newly installed wells will be developed using the surge-block method as follows:

1. A weighted stainless steel surge-block or "swab" attached to a rigid pipe or a line will be lowered into the upper 2 feet of the well screen. A surge-block is cylindrical, with a diameter approximately 0.2 inch less than the inside diameter of the well

casing and screen. Water can flow between the block plate and well screen, relieving excess pressure to prevent collapse of the well screen. The water is gently agitated by moving the swab in a continuous up-and-down motion. After several up-and-down cycles, a more vigorous motion can be used to agitate the water.

2. After 5 to 10 minutes of swabbing, the surge-block will be removed from the well and groundwater will be purged from the well. Purging will be accomplished by pumping or bailing, depending on the well yield. Additional agitation caused by purging will further develop the well. Water quality parameters (pH, temperature, and conductivity) will be measured during purging as described in Section 5.3.5.
3. Each 2-foot section of the well screen will be swabbed and purged as described above. Ideally, at least 10 casing volumes of water will be produced from each well during development. All groundwater produced during development will be transferred to the onsite holding tank prior to treatment and disposal by the onsite treatment system.
4. All well sounding and developing equipment will be decontaminated immediately after use in each well to avoid cross-contamination. Decontamination procedures are outlined in Section 5.6.

During development, at least five samples (one after one to two purging casing volumes) will be collected from the well for field testing of the following water quality parameters:

- pH (pH standard units)
- Specific conductance ( $\mu\text{mhos/cm}$ )
- Temperature ( $^{\circ}\text{F}$ )
- Turbidity (nephelometric turbidity units).

Well development should proceed until the wells yield water which is low enough in suspended solids content for sampling purposes and water quality parameters have stabilized (each parameter is within 10 percent of the prior sample's value).

Total well depths will be measured during well development to ascertain progress in removing any silt buildup which may be present. During development, silt and sand production will also be observed.

### 5.4.5 Water Level Measurements

All newly installed wells will be sounded for depth to water from top of casing and total well depth prior to purging. An electronic sounder, accurate to the nearest  $\pm 0.01$  feet, will be used to measure depth to water in each well. Total well depth will be sounded from the surveyed top of casing by lowering the weighted probe to the bottom of the well. Because the weighted probe will sink into silt at the bottom of well screens, total well depths will be measured and recorded to the nearest 0.1 feet.

### 5.4.6 Monitoring Well Groundwater Sampling

Groundwater samples will be collected from the newly installed monitoring wells between 24 hours and 48 hours after completion of well development.

Prior to sampling, the water level in the well will be measured as described in Section 5.3.6. Clean nitrile gloves will be worn while collecting samples. Groundwater samples will be collected using a Teflon bailer. Groundwater will be transferred from the Teflon bailer to the appropriate sample container using a bottom emptying device to reduce agitation of the water samples during transfer. When transferring samples, care will be taken not to touch the discharge device to the sample container. The flow will be adjusted so that a gentle stream is obtained. A flow rate of less than 100 milliliters per minute is recommended for samples to be analyzed for VOCs to minimize volatilization. The samples will then be preserved as described in Section 7.2. The sample container will be inverted and checked for air bubbles to ensure there is no entrained air. If bubbles are present, the vial will be discarded and a new sample will be collected.

When collecting duplicate groundwater samples, the containers with the two different sample designations will be alternately filled.

## 5.5 EQUIPMENT RINSATE SAMPLES

Equipment rinsate samples will be collected to evaluate field sampling and decontamination procedures by pouring laboratory-grade, certified organic-free water over the decontaminated sampling equipment. One equipment rinsate sample will be collected each day that samples are collected.

## 5.6 DECONTAMINATION PROCEDURES

All equipment that comes into contact with potentially contaminated water or soil will be decontaminated prior to and after each use. Disposable equipment intended for one-time use will not be decontaminated but will be packaged for appropriate disposal. Decontamination will

occur prior to and after each use of a piece of equipment. The decontamination procedures that will be followed are in accordance with approved Quality Assurance Project Plan procedures. All sampling devices will be decontaminated within a pre-designated, bermed, and lined decontamination area.

All purging equipment (i.e., submersible pumps) will be decontaminated according to the following procedure:

1. Non-phosphate detergent wash, including scrubbing the outside of the hose and running soapy water through the lines for a minimum of 5 minutes.
2. Tapwater rinse, minimum 3 minutes recirculating. Rinse outside of hose.
3. Tapwater rinse, minimum 3 minutes non-recirculating. Fresh tapwater should be pumped through the hose for 3 minutes.

All boring and soil sampling equipment will be pressure-washed or cleaned by scrubbing with a non-phosphate detergent solution and a dedicated brush, then rinsing twice with tapwater.

The exterior surfaces of drill rigs and any large equipment will be thoroughly pressure-washed with potable water. The equipment will be cleaned of all debris and contaminated fluids (such as obvious leaks from hydraulic lines, couplings, and fittings) to avoid contamination of onsite soils and soil borings.

At the end of each work day and/or after the completion of the work, the subcontractor will completely decontaminate its drill rig and soil sampling equipment to the satisfaction of Bechtel before leaving the site. Accessible interior portions of augers, pipes, hoist rods, cables, and bits will be cleaned at the start of the job and between borings. Clean equipment will be stored on plastic sheeting in uncontaminated areas. Materials to be stored more than a few hours will also be covered.

## **5.7 WELL DECOMMISSIONING PROCEDURES**

Wells will be decommissioned according to the following procedure:

1. The well casing and screen will be sealed by grouting with neat cement grout. The grout will be pumped through a tremie pipe placed within 2 feet of the bottom of the casing. Grout will be pumped into the well until the casing remains full of grout at a depth of 3 feet below ground surface. A minimum of one casing volume of grout will be placed.
2. The grout will be allowed to cure for 24 hours. The depth to the top of the grout will be checked and additional grout will be added if necessary to bring it to 3 feet below grade.

3. All of the well materials above 3 feet bgs, including the surface casing, riser casing, and concrete pad, will be demolished and removed. The resulting excavation will be backfilled with native soil or clean imported backfill, tamped in place.

## **Disposal of Investigation-Derived Wastes**

---

In the process of collecting environmental samples at the Frontier Fertilizer site the following types of investigation-derived wastes (IDW), some potentially contaminated, will be generated:

- Used personal protective equipment (PPE) and disposable sampling equipment
- Decontamination fluids
- Soil cuttings
- Purged groundwater
- Decommissioned well materials

The EPA's National Contingency Plan requires that management of IDWs generated during RI/FS field investigations comply with all applicable or relevant and appropriate requirements to the extent practicable. The sampling plan will follow the Office of Emergency and Remedial Response Directive 9345.3-02 (May 1991) which provides the guidance for the management of IDW during RI/FS field investigations. In addition, other legal and practical considerations that may affect the handling of IDW are considered in developing these procedures.

### **6.1 USED PERSONAL PROTECTIVE EQUIPMENT AND DISPOSABLE SAMPLING EQUIPMENT**

Used PPE and disposable sampling equipment will be double-bagged and placed in a municipal refuse dumpster. These wastes are not hazardous and can be sent to a municipal landfill. Any PPE and disposable equipment that is to be disposed of that can still be reused will be rendered inoperable before disposal in the refuse dumpster.

### **6.2 DECONTAMINATION FLUIDS**

Decontamination fluids that will be generated during this field sampling event will consist of deionized water and tapwater, containing residual contaminants and non-phosphate detergent. The volume and concentration of the decontamination fluids will be sufficiently low to allow disposal at the site. The fluids will be poured onto the ground or into a storm drain.

### **6.3 SOIL CUTTINGS**

Soil cuttings that are generated when the wells are drilled will be contained in 20-yard bins. Once full, the bins will be hauled off site to a municipal landfill for disposal.

### **6.4 PURGED GROUNDWATER**

Groundwater will be purged from newly installed monitoring wells during development. Purged groundwater water will be treated on site using the groundwater remediation system.

**6.5 DECOMMISSIONED MONITORING WELL MATERIALS**

The riser and surface casings, demolished concrete, and other well materials removed during decommissioning will be disposed of at a municipal landfill.

## **Sample Documentation and Shipment**

---

*This section describes sample documentation, preparation, handling, and shipment procedures.*

### **7.1 FIELD LOGBOOKS**

Field logbooks will document where, when, how, and from whom any vital project information was obtained. Logbook entries will be complete and accurate enough to permit reconstruction of field activities. At a minimum, the following sampling information will be recorded:

- Site sketch
- Sample location number, depth, and description
- Sampler's name(s)
- Date and time of sample collection
- Type of sample (i.e., matrix)
- Type of sampling equipment used
- Field observations and details important to analysis or integrity of samples (e.g., heavy rains, odors, colors, etc.)
- Type of preservation used
- Instrument reading (e.g., OVM, HNU, temperature, pH, etc.)
- Sample numbers, chain-of-custody form and seal numbers
- Shipping arrangements (air bill number)
- Recipient laboratory(ies)

Logbooks will be bound with consecutively numbered pages. Each page will be dated and the time of entry noted in military time. All entries will be legible, written in black ink, and signed by the individual making the entries. Language will be factual, objective, and free of personal opinions or inappropriate terminology. In addition to the sampling information, the following specifics will also be recorded in the field logbook:

- Team members and their responsibilities
- Times of site arrival and departure
- Other personnel on site
- A summary of any meetings or discussions with the public, any potentially responsible parties (PRPs), or federal, state, or other regulatory agencies
- Any deviations from field sampling plans, site safety plans, and Quality Assurance Project Plan procedures

- Any changes in personnel and responsibilities as well as reasons for the changes
- Levels of safety protection
- Equipment calibration and equipment model and serial number

## 7.2 SAMPLE CONTAINERS AND PRESERVATIVES

The types of sample containers are listed in the Table 4-1. The containers will be precleaned and will not be rinsed prior to sample collection. Preservatives, if required, will be added to the containers prior to shipment of the sample containers to the laboratory.

### 7.2.1 Well Sump Sediment Samples

Well sump sediment samples for laboratory analysis will be collected in precleaned 8-ounce glass jars. The jars will be completely filled to minimize headspace.

### 7.2.2 Groundwater Samples

Groundwater samples for analysis via either the 5 ml or 25 ml purge method for VOCs will be collected in 40 ml amber glass vials or in 38 ml DMLS vials. Approximately two drops of 1:1 hydrochloric acid (HCl) will be added to the conventional (40-ml vial) sample containers prior to sample collection (no preservatives will be used in the DMLS vials). During purging, the pH will be measured using a pH meter on at least one vial at each sample location to ensure the pH is less than 2. The tested vial will be discarded. If the pH is greater than 2, additional HCl will be added to the sample vials. Another vial will be pH-tested to ensure the pH is less than 2. The tested vial will be discarded. The vials will be filled so that no headspace occurs. The samples will be chilled to  $4 \pm 2^{\circ}\text{C}$  immediately upon collection. Groundwater samples collected for analysis via Method 504 will only be preserved by chilling.

### 7.2.3 Equipment Rinsate Samples

Equipment rinsate samples will be collected in 40 ml glass vials and preserved as described in Section 7.2.2.

## 7.3 SAMPLE TRAFFIC REPORT AND CHAIN-OF-CUSTODY RECORDS AND QUALITY ASSURANCE/QUALITY CONTROL SUMMARY FORMS

Chain-of-custody forms will be used to document sample collection and shipment to laboratory for analysis. The form(s) will be completed and sent with the samples for each laboratory and each shipment (i.e., each day). If multiple coolers are sent to a single laboratory on a single day, the form(s) will be completed and sent with the samples for each cooler.

The chain-of-custody form will identify the contents of each shipment and maintain the custodial integrity of the samples. Generally, a sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, locked up, or kept in a secured area that is restricted to authorized personnel. Until the samples are shipped, the custody of the samples will be the responsibility of Bechtel. The sampler or designee will sign the chain-of-custody form. The sampler or designee will sign the "relinquished by" box and note date, time, and air bill number.

The original chain-of-custody form will accompany the samples to the laboratory and the second copy will be sent to the EPA Region IX QA Program. A copy of the original will be made for the Bechtel files.

A quality assurance/quality control summary form will be completed for each laboratory and each matrix of the sampling event. The sample numbers for all rinsate samples, laboratory quality control samples, and duplicates will be documented on this form (see Section 8). The original form will be sent to QA Program; a photocopy will be made for the Bechtel files. This form is not sent to the laboratory.

A self-adhesive custody seal will be placed across the lid of each sample. For water samples for VOC analysis, the seal will be wrapped around the cap. The shipping containers in which samples are stored (usually sturdy picnic cooler or ice chest) will be sealed with self-adhesive custody seals any time they are not in someone's possession or view before shipping. All custody seals will be signed and dated.

The CLP Paperwork Instructions, *Instructions for Sample Shipping and Documentation, October 1994*, will be taken to the field as a reference. Corrections on sample paperwork will be made by placing a single line through the mistake and initialing and dating the change. The correct information will be entered above, below, or after the mistake.

#### **7.4 SAMPLE LABELING, PACKAGING, AND SHIPMENT**

All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. All samples will have preassigned, identifiable, and unique numbers. At a minimum, the sample labels will contain the following information: sample number, station location, date of collection, analytical parameter(s), sampler's initials, and method of preservation. All sample containers will be placed in a strong shipping container (such as a steel-belted cooler).

The following outlines the packaging procedures that will be followed for samples sent to an (offsite) EPA designated laboratory:

1. Secure the drain plug of the cooler with fiberglass tape to prevent any liquids (e.g., melted ice) from leaking out of the cooler.
2. Place a 1-inch-thick layer of vermiculite in the cooler.
3. Line the bottom of the cooler with bubble wrap to prevent breakage during shipment.
4. Check screw caps for tightness and, if not full, mark the sample volume level of liquid samples on the sample containers with indelible ink.
5. Secure container caps with clear tape and custody seal all container caps.
6. Affix sample labels onto the containers with clear tape.
7. Wrap all glass sample containers in bubble wrap to prevent breakage.
8. Seal all sample containers in heavy duty plastic bags. Write the sample numbers on the outside of the plastic bags with indelible ink.
9. Enclose all appropriate chain-of-custody forms in a large plastic bag and affix the bag to the underside of the cooler lid.
10. Fill the empty space in the cooler with bubble wrap or styrofoam peanuts to prevent movement and breakage during shipment.
11. Double-seal ice in two zip-lock plastic bags and place them on top and around the samples to chill them to 4°C.
12. Securely tape shut each cooler with nylon strapping tape, and affix custody seals to the front, right and back of each cooler.

The Region IX Regional Sample Control Center will be notified daily (phone 415-744-1498) of the sample shipment schedule (Friday shipments must be reported no later than noon) and will be provided with the following information:

- Sampling contractor's name
- The name and location of the site
- Case number
- Sample identification number
- Total number(s) by concentration and matrix of samples shipped to each laboratory
- Carrier, air bill number(s), method of shipment (e.g., priority next day)
- Shipment date and when it should be received by laboratory

- Irregularities or anticipated problems associated with the samples
- Whether additional samples will be shipped or if this is the last shipment

## Quality Control

---

This section describes the various quality assurance/quality control samples that will be prepared and analyzed for this sampling event.

### 8.1 EQUIPMENT RINSATE SAMPLES

The equipment rinsate samples will be prepared as described in Section 5.3. The equipment rinsate samples will be analyzed for VOCs plus EDB and DBCP via the 25 ml purge method and by EPA Method 504 by the EPA designated laboratory. A minimum of one equipment rinsate sample will be collected each day that sampling equipment is decontaminated in the field. Equipment rinsate samples will not be used for duplicate or laboratory QC samples.

The equipment rinsate samples will be preserved, packaged, and sealed as appropriate for water samples. A separate sample number and station number will be assigned to each rinsate sample, and it will be submitted blind to the laboratory.

### 8.2 DUPLICATE SAMPLES

Duplicate samples will be collected from areas of known or suspected contamination. A minimum of 10 percent or one per week, whichever is greater, of samples will be duplicates. At least one duplicate will be collected for each sample matrix. Every analytical group for which a standard sample is analyzed will also be tested for in one or more duplicate samples.

Duplicate samples will be preserved, packaged, and sealed in the same manner as other samples of the same matrix. A separate sample number and station number will be assigned to each duplicate, and it will be submitted blind to the laboratories.

### 8.3 LABORATORY QUALITY CONTROL SAMPLES

At a minimum, one laboratory quality control sample is required per week or one per 20 samples (including blanks and duplicates), whichever is greater.

A routinely collected sample may not contain sufficient volume for both routine sample analysis and additional laboratory quality control analyses. Therefore, a double sample volume is submitted. (For the sampling described in this plan, the sump sediment volume is adequate for QC analysis, but the water sample volume must be doubled.) The laboratory is alerted as to which sample is to be used for QC analysis by notation on the sample container label and the chain-of-custody form. Laboratory QC samples should be collected from areas of known or suspected contamination.

#### 8.4 FIELD VARIANCES

Since conditions in the field may vary, it may become necessary to implement minor modifications to the sampling as presented in this plan. When appropriate, the EPA, QA Program, and Bechtel project managers will be notified of the modifications and a verbal approval will be obtained before implementing the modifications. Modifications to the approved plan will be documented in the field logbook.