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Travis Air Force Base

Natural Attenuation Assessment Plan

DRAFT

60th Air Mobility Wing
Travis Air Force Base, California

Prepared by

CH2MHILL
2485 Natomas Park Drive, Suite 600
Sacramento, California 95833

September 1997

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Travis Air Force Base

Natural Attenuation Assessment Plan

Draft

60th Air Mobility Wing
Travis Air Force Base, California

Prepared By:

CH2MHILL

2485 Natomas Park Drive, Suite 600
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23 September 1997

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Travis AFB CA 94535-2176

SUBJECT: LF006 RD/RA Workplan and NEWIOU NAAP Drafts

1. The subject drafts are attached for your information and review.

2. Natural attenuation has been selected as the interim remedy for Site LF006. The RD/RA Workplan was prepared to describe the additional assessment at that site. At the remaining seven sites, where selection of natural attenuation has been deferred for all or a portion of the groundwater plume, Travis AFB is embarking on a Natural Attenuation Assessment Plan (NAAP) to gather data for final remedy selection.

3. Please provide your comments on the subject documents by October 24, 1997.

4. If you have any questions regarding this submittal, please contact Mr. Bil Alimam at (707) 424-4322.

Dale [illegible] FOR

ALLEN L. BRICKEEN, P.E.
Remedial Program Manager

Attachment:
LF006 Remedial Design/Remedial Action Workplan Draft
Natural Attenuation Assessment Plan Draft

cc: See Attached List

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REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE September 23, 1997	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE North, East, West Industrial Operable Unit Site Remediation Workplans Delivery Order 0023 Draft Natural Attenuation Assessment Plan Data Item No. A012 Paragraph 4.3.2.1	5. FUNDING NUMBERS F41624-94-D-8053
6. AUTHOR(S) CH2M HILL	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CH2M HILL 2485 Natomas Park Drive, Suite 600 Sacramento, California 95833	8. PERFORMING ORGANIZATION REPORT NUMBER Data Acquisition Document No. DI-MISC-80508
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFCEE/ERD 3207 North Road Brooks AFB, Texas 78235-5356	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Statement A: “Approved for Public release: distribution is unlimited.”	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This document presents a plan for assessing natural attenuation at sites at Travis AFB selected for this evaluation in the Groundwater Interim Record of Decision. It also describes natural attenuation principles, and presents the contents for a Natural Attenuation Assessment Workplan and a Natural Attenuation Assessment Report.

14. SUBJECT TERMS Draft Natural Attenuation Assessment Plan for Travis AFB.	15. NUMBER OF PAGES 1 Volume
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

NSN 7540-01-280-5500

Standard Form 298 (rev. 2-89)
Prescribed by ANSI Std 239-18

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Acronyms

AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ARARs	applicable or relevant and appropriate requirements
Base	Air Force Base
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
COC	chemical of concern
CPT	cone penetrometer
COEC	chemical of ecological concern
DCA	dichloroethane
DCE	dichloroethene
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DTSC	California Department of Toxic Substance Control
EPA	U.S. Environmental Protection Agency
FFA	Federal Facility Agreement
FS	Feasibility Study
GSAP	groundwater sampling and analysis program
HHRA	human health risk assessment
IRG	Interim Remediation Goal
IROD	Interim Record of Decision
IRP	Installation Restoration Program
LNAPL	light non-aqueous phase liquid
MCL	maximum contaminant level
mg/L	milligrams per liter
µg/L	micrograms per liter
NAAP	Natural Attenuation Assessment Plan
NAAR	Natural Attenuation Assessment Report
NAAW	Natural Attenuation Assessment Workplan
NAPL	non-aqueous phase liquid

NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NEWIOU	North, East, West Industrial Operable Unit
NPL	National Priority List
OU	Operable Unit
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	tetrachloroethene
POCOS	Petroleum-Only Contaminated Sites
ppmv	parts per million by volume
QAPP	Quality Assurance Project Plan
RAB	Restoration Advisory Board
RD/RA	remedial design/remedial action
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RWQCB	California Regional Water Quality Control Board, San Francisco Bay Region
SARA	Superfund Amendments Reauthorization Act
SOP	Standard Operating Procedure
SVOC	semivolatile organic chemical
TCE	trichloroethene
TOC	total organic carbon
TPH	Total Petroleum Hydrocarbons
TPH-e	Total Petroleum Hydrocarbons-extractable (diesel range)
TPH-v	Total Petroleum Hydrocarbons-volatile (gasoline range)
VOC	volatile organic chemical
VC	vinyl chloride
WABOU	West/Annexes/Basewide Operable Unit
WIMS-ES	Work Information Management System-Environmental Subsystem

1.0 Introduction

1.1 Background

Previous investigations at Travis AFB concluded that groundwater in portions of the Base is contaminated with chlorinated hydrocarbons and petroleum hydrocarbons. The nature and extent of the contamination are described in Remedial Investigation (RI) reports prepared for four operable units (OUs) at Travis AFB. Each OU covers a portion of the Base and encompasses multiple sites. The four OUs are the North OU (Radian, 1995), East Industrial OU (Weston, 1995), West Industrial OU (Radian, 1996), and the West/Annexes/ Basewide OU (WABOU) (CH2M HILL, 1997). The locations of Travis AFB and the OUs are shown in Figure 1-1.

Three of the OUs were combined during remedy selection to form the North, East, and West Industrial OU (NEWIOU), and a feasibility study (FS) (Radian, 1996), Proposed Plan (Radian, 1996), and Groundwater Interim Record of Decision (IROD) (Travis AFB, 1997) were prepared. Natural attenuation of contaminated groundwater is a potential remedy considered for the NEWIOU. In the remedy selection process, the Natural Attenuation alternative (Alternative 2) was compared with the No Action alternative (Alternative 1) and the Extraction, Treatment, and Discharge alternative (Alternative 3). In general, sites considered favorable for natural attenuation are those for which "active" remediation (i.e., extraction, treatment, and discharge) may not be cost-effective because of the relatively low concentrations of contaminants, strong sorption of pollutants on soils, and the potential for natural processes to remediate the contaminant plume in a reasonable amount of time while being fully protective of human health and the environment.

The NEWIOU Groundwater IROD selected natural attenuation as the interim remedy for one site (LF006) and identified two sites and a portion of five other sites where the selection of the interim remedy has been deferred, but where natural attenuation will be assessed further. Table 1-1 summarizes the status of selected NEWIOU sites with respect to natural attenuation. Figure 1-2 shows the locations of sites where natural attenuation will be assessed at all or a portion of the site. More details regarding the relationship of these sites to the Natural Attenuation alternative are provided in the FS, Proposed Plan, and Groundwater IROD.

While the nature and extent of contamination at these sites are characterized in the RI reports, data are lacking with respect to natural attenuation. The understanding of natural attenuation has only recently developed to the point where a systematic assessment of the complex processes involved is possible. Consequently, RI data obtained even a few years ago may lack parameters necessary to perform a complete assessment.

Natural attenuation was selected as the interim remedy for Site LF006 because the results from the RI/FS indicate a high probability that natural attenuation is the appropriate long-term remedy at this site. However, additional field data collection and characterization will be completed to confirm that the plume is not migrating and that natural attenuation is effective. The Interim Remedial Design/Remedial Action (RD/RA) Workplan CH2M HILL, 1997) describes the additional assessment at LF006. If natural attenuation is not effective, the Extraction, Treatment, and Discharge alternative will be implemented.

138673.21.12.01 Fig.1-1/Operable 9/19/97ldh

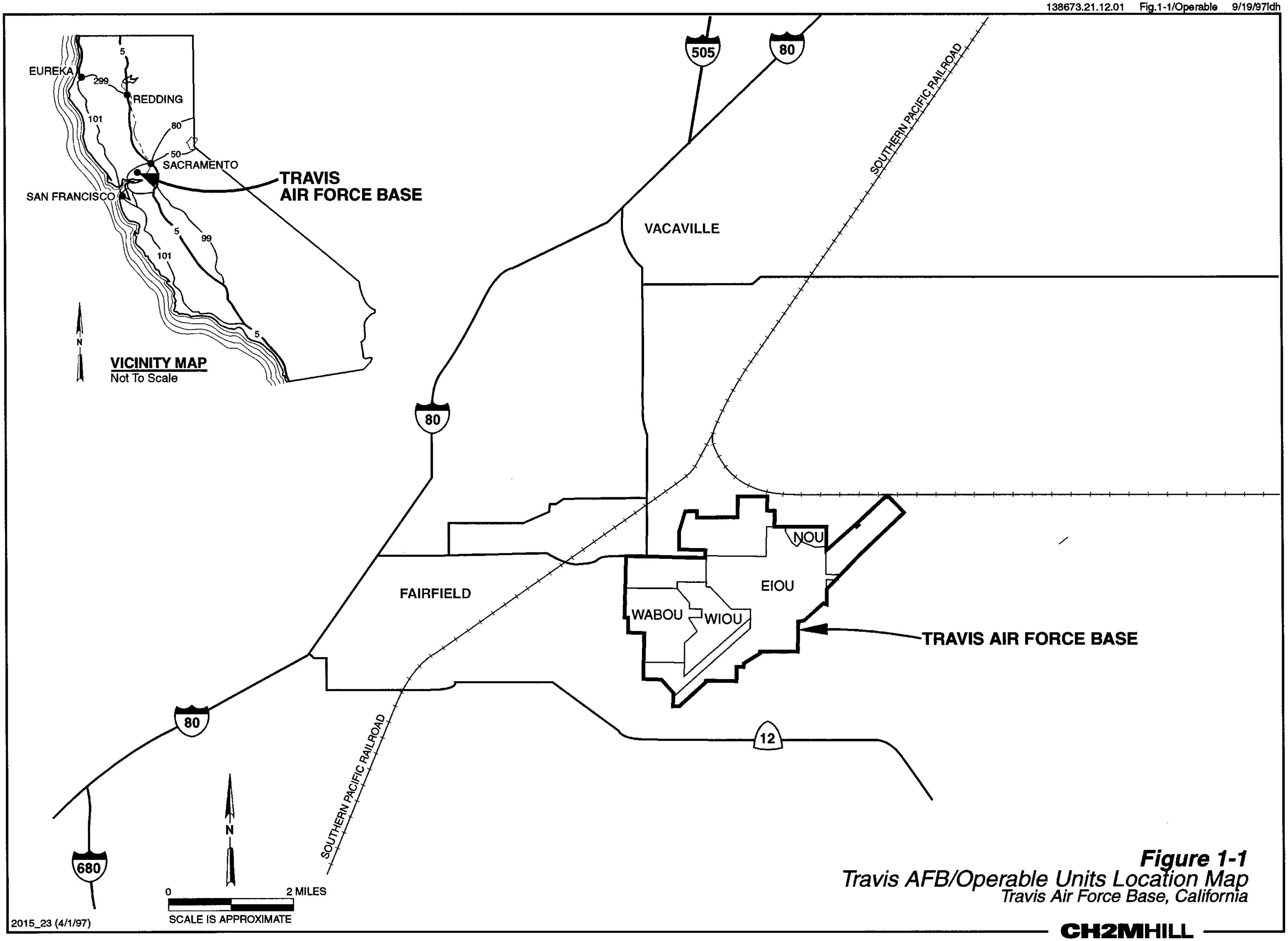

Figure 1-1
Travis AFB/Operable Units Location Map
Travis Air Force Base, California

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138673.21.12.01 Fig.1-2/Sites Selected 9/23/97ldh

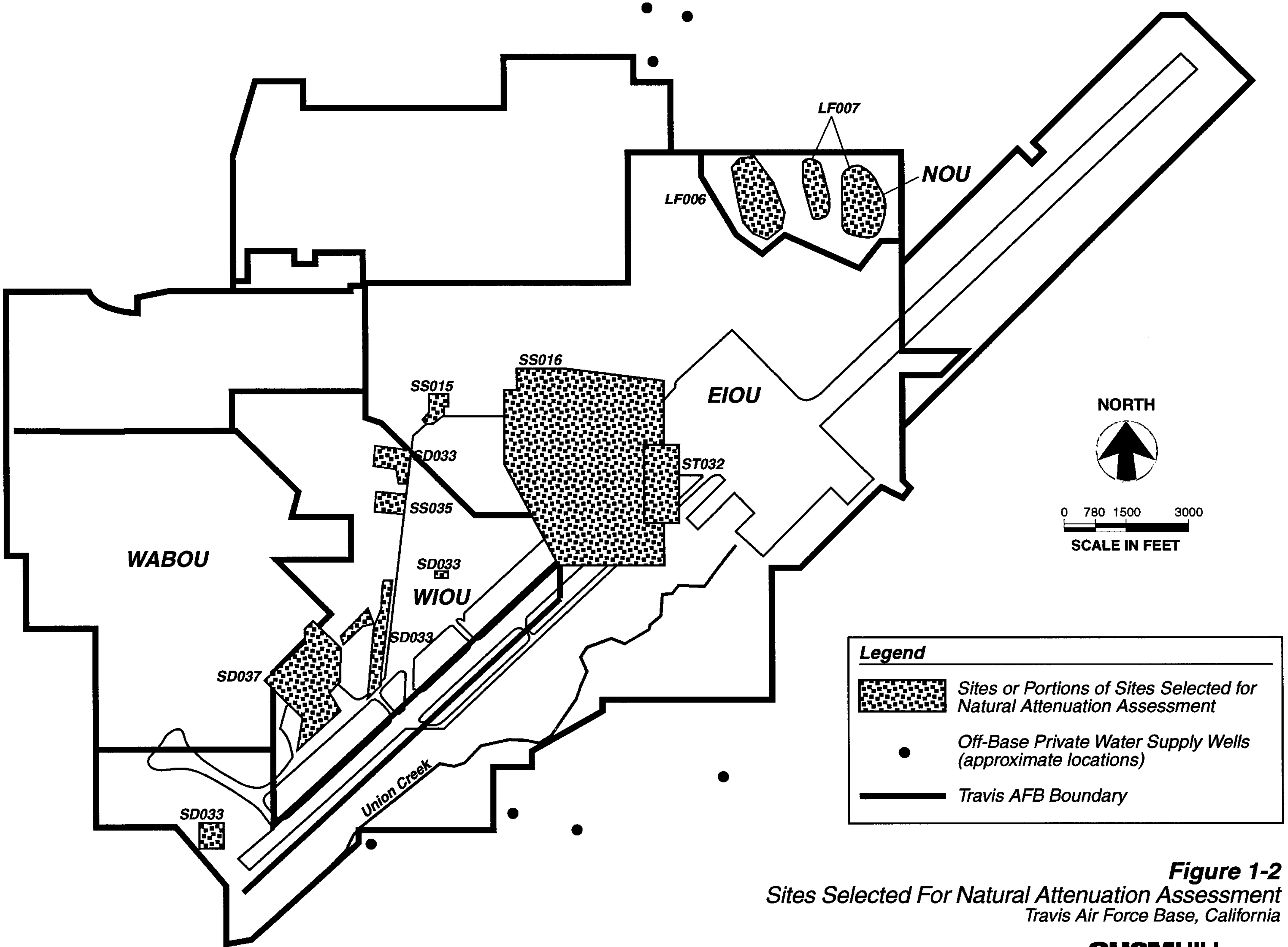

Figure 1-2
Sites Selected For Natural Attenuation Assessment
Travis Air Force Base, California

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TABLE 1-1
Status of Sites Selected for Natural Attenuation Assessment

Site Designator	RI Site Name	Status
LF006	Landfill 1	Selected for Natural Attenuation
LF007	Landfill 2	Interim Remedy Selection Deferred on a Portion of the Plume
SS015	Solvent Spill Area and Facilities 550 and 552	Interim Remedy Selection Deferred
SS016	Oil Spill Area; Facilities 11, 13/14, 20, 42/1941, and 139/144; and Storm Sewer	Interim Remedy Selection Deferred on a Portion of the Plume
ST032	Monitoring Wells 107/246 Areas	Interim Remedy Selection Deferred on a Portion of the Plume
SD033	Facilities 810 and 1917 and the South Gate Area	Interim Remedy Selection Deferred on a Portion of the Plume
SS035	Facility 818/819	Interim Remedy Selection Deferred
SD037	Sanitary Sewer System; Facilities 837/838, 919, 977, and 981; Ragsdale V Area; and the Area G Ramp	Interim Remedy Selection Deferred on a Portion of the Plume

At the remaining seven sites where selection of an interim remedy has been deferred for all or a portion of the groundwater plume, Travis AFB has initiated a natural attenuation assessment program to gather data for final remedy selection. Additional monitoring wells will be installed, data collected, and characterization completed on these sites so that selection of the final remedy can be completed after the first 5-year review (5 years after Groundwater IROD signing). However, if during the next 5 years, natural attenuation is determined to not be effective, or that the plume is migrating, the Extraction, Treatment, and Discharge alternative will be implemented.

The Natural Attenuation Assessment Plan (NAAP) is the guiding document for the evaluation of natural attenuation at Travis AFB. As such, it describes the overall approach that will be followed at each site being considered for natural attenuation, including LF006.

A site-specific Natural Attenuation Assessment Workplan (NAAW) will be prepared for each site that describes how the processes contained in the NAAP will be applied at that site. The first such workplan, for the LF006 site, is available as a companion document to the NAAP. The LF006 workplan will be referred to as an Interim Groundwater RD/RA Workplan, because natural attenuation has been selected as the interim remedial action at this site.

In the site-specific workplans, points of compliance will be established for natural attenuation. These points will consist of monitoring wells at downgradient locations agreed upon by regulatory agencies as establishing containment for the plume of contamination. The point-of-compliance wells will be monitored regularly. Contamination detected in these wells above agreed-upon standards will initiate a verification monitoring program to determine the appropriate alternative.

The schedule for implementation of the NAAP will be included in the RD/RA Schedule for groundwater in the NEWIOU, which will be issued 21 days after the signing of the Groundwater IROD. Implementation schedules are subject to yearly funding levels and project priorities, and both matters are routinely discussed among the Air Force, regulatory agencies, and the Restoration Advisory Board. Because the LF006 site has already been funded, it will proceed first to implementation (pending approval of the LF006 Interim Groundwater RD/RA Workplan by the regulatory agencies).

Natural attenuation parameters at the SD036 site are being studied through an Air Force Center for Environmental Excellence (AFCEE) Technology Transfer Division contract. A workplan for that assessment was submitted to regulatory agencies (Parsons Engineering Science, 1997), and field work was completed during the summer of 1997. Although funding for the SD036 study was provided separately from the Travis Installation Restoration Program (IRP), the NAAP will follow a similar approach. The SD036 study has, in fact, laid the foundation for the NAAP, and ultimately the NAAP will assimilate the findings at that site as well. The lessons learned at SD036 will be applied at the other sites.

Travis AFB's basewide Groundwater Sampling and Analysis Program (GSAP) now includes natural attenuation monitoring. Data will be gathered by the GSAP at an early stage for use in the NAAP, and this information will be available for review by regulatory agencies. The GSAP also serves as a mechanism for consolidating the natural attenuation data gathering process at Travis AFB.

The NAAP specifically applies to the NEWIOU sites listed in Table 1-1, but it also accounts for conditions and sites existing within the WABOU. Once the WABOU sites proceed through the remedy selection phase, the approach described in this NAAP will also apply to those WABOU sites or portions of sites considered for natural attenuation. The NAAP may also be expanded to Petroleum-Only Contaminated Sites (POCOS) in the future. In essence, this document will become basewide guidance for Travis AFB's natural attenuation assessment program.

1.2 NAAP Approach

Natural attenuation has been defined as follows (Wiedemeier et al., 1996):

> *The term "Natural Attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants.*

Natural attenuation typically occurs at all sites, but with varying degrees of effectiveness, depending on the types of contaminants present and the physical, chemical and biological characteristics of the soil and groundwater.

Monitored natural attenuation can be a viable method of remediation at some sites. However, it will be selected at Travis AFB only where it meets remedy selection criteria (Radian, 1997). Criteria include protecting human health and the environment, meeting remedial action objectives within a reasonable time frame, and satisfying California anti-degradation policies.

Monitored natural attenuation is not a "no action" or "walk away" alternative because adequate site characterization, monitoring, and analysis must be conducted to determine its viability as a remedy. Once in place, monitoring will be ongoing to verify that contaminant levels decrease as anticipated and the remedy protects human health and the environment.

Monitored natural attenuation does not have to be the only remedy at a site, and it is often combined with other remedies (such as source control or soil vapor extraction). It may be used to complete remediation after other remedies have efficiently reduced contaminant levels. Conversely, if natural attenuation proves to be ineffective, an extraction and treatment remedy can (and will) be initiated.

Natural attenuation assessments at Travis AFB will follow guidelines set forth in two documents prepared by the Air Force Center for Environmental Excellence (AFCEE): *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (Wiedemeier et al., 1996); and *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Wiedemeier et al., 1995). These documents were developed jointly with the EPA and have been accepted by other regulatory agencies. The current study at the SD036 site is actually part of a national pilot study for implementation of the 1996 protocol.

The 1996 protocol specifically states that the primary objectives of a natural attenuation assessment are to determine whether natural processes of contaminant degradation will reduce contaminant concentrations in groundwater to below regulatory standards before potential receptor pathways are completed, and to determine if natural attenuation can meet all appropriate federal and state remediation objectives for a given site.

The foregoing considerations form the basis of the NAAP at Travis AFB. In summary, the benchmark features of the NAAP are:

- Fully compatible with the NEWIOU Groundwater IROD, and subsequent Groundwater IRODs or RODs dealing with contaminated groundwater at Travis AFB
- Cost-effective risk-based approach to groundwater remediation
- Protective of human health and the environment
- Cognizant of all regulatory requirements, including anti-degradation policy for clean aquifers

Features of the NAAP approach include:

- Site-by-site technical assessment will determine viability; agreed Air Force/EPA protocols will be followed; site-specific work plans will be prepared and submitted.
- Ongoing monitoring and routine reporting of results will be provided to the regulatory agencies and the Remedial Advisory Board (RAB); monitoring efforts will be integrated with the GSAP.

- If natural attenuation is ineffective, active groundwater remediation through extraction, treatment, and discharge will be implemented.
- Data and lessons learned from the SD036 study will be integrated into the NAAP approach.
- If process improvements are identified during the LF006 interim remedial action or subsequent site assessments, they will also be incorporated into the NAAP.

At each site, an initial screening will be performed based on data from the RI at that site. If data are sufficient to conclude that natural attenuation is not viable, no further natural attenuation assessment will be performed; contingencies will then be implemented. If data are not sufficient, or if data are sufficient to conclude that natural attenuation is viable at the site, additional site characterization will be performed. In either case, one additional field investigation should be sufficient to gather the data necessary to complete the natural attenuation assessment.

Completing the natural attenuation assessment includes the following elements:

- Refining the conceptual site model
- Performing solute fate and transport modeling
- Identifying points of compliance
- Designing a long-term monitoring program
- Considering other treatment alternatives in combination with natural attenuation, such as source control
- Gaining consensus from regulatory agencies and the public for the site-specific approach

1.3 Overview of the NAAP

The NAAP provides the framework for natural attenuation assessments at Travis AFB and contains the following sections:

- **Section 2.0** describes the mechanisms of natural attenuation and provides background on the fate and transport of volatile organic chemicals (VOCs) in groundwater. It also discusses how the Air Force will demonstrate that natural attenuation occurs.
- **Section 3.0** describes the approach to the natural attenuation assessment that will be followed at each site. This section also provides details on long-term monitoring.
- **Section 4.0** describes the contents of the site-specific NAAW for natural attenuation assessment and discusses the additional characterization that will be performed.
- **Section 5.0** provides reporting requirements to complete the individual assessments. The main deliverable for each site will be a Natural Attenuation Assessment Report (NAAR), which will summarize the results of the natural attenuation assessment, draw conclusions regarding the viability of natural attenuation, and recommend points of

compliance and a long-term monitoring program. If necessary, the report will recommend an alternative remediation strategy (including groundwater extraction, treatment, and discharge) and further work that must be completed.

- **Section 6.0** lists references cited in the NAAP.
- **Appendix A** is an addendum to the Travis Remedial Design/Remedial Action Quality Assurance Project Plan (QAPP). This appendix includes analytical methodology for laboratory methods not provided in the Travis RD/RA QAPP that are needed to evaluate natural attenuation.
- **Appendix B** is a Standard Operating Procedure (SOP) for low-flow groundwater sampling that will be used in the natural attenuation assessment.

2.0 Overview of Natural Attenuation

This section provides an overview of natural attenuation mechanisms. An understanding of natural attenuation is necessary to develop a conceptual site model of fate and transport processes potentially at work at a site, and to identify data gaps that must be filled in order to evaluate whether natural attenuation is an appropriate remedial option at the site. The natural attenuation screening process developed by AFCEE, which forms the basis of this workplan, will then be discussed.

2.1 Natural Attenuation Mechanisms

In-situ natural attenuation processes may be divided into two categories: nondestructive and destructive. Nondestructive processes reduce the concentration, toxicity, or mobility of contaminants in a given medium, without reducing the overall mass or volume of the contaminant. Nondestructive processes include diffusion, dispersion, dilution, adsorption, and volatilization. Destructive processes actually reduce the mass and volume of the contaminant by degrading it or transforming it to some other substance. The most important destructive process is biodegradation, or destruction by microbial organisms, although abiotic destruction may also occur under certain circumstances.

2.1.1 Nondestructive Processes

Dissolved VOCs in groundwater migrate through advection, molecular diffusion, and hydrodynamic dispersion. Migration may be retarded by adsorption to organic materials.

Advection is simply the mass transfer of contaminants by the movement of groundwater. Advection results from the mean flow of groundwater and is equal to the average linear velocity of groundwater.

Molecular diffusion attempts to equalize the solute concentration by moving solute from high concentration zones to low concentration zones. The driving force for diffusion is differential concentrations, and the effect of diffusion is to increase the volume of contaminated groundwater, while decreasing the concentration. Diffusion is generally a slow process, but may be significant in systems where the groundwater velocity is low.

Hydrodynamic dispersion is another process that spreads the contamination into a larger volume. Dispersion results from variations from the average groundwater velocity. These variations occur in both the magnitude and direction of actual small-scale velocity. At the microscopic scale, velocity variations result from heterogeneities in the distribution of pore sizes. At the macroscopic scale, velocity variations result from changes in permeability and stratigraphy. Dispersion occurs both in the direction of flow and perpendicular to flow, although a dissolved chemical mass disperses more along the flow path than perpendicular to the flow path.

Diffusion and dispersion result in the dilution of the contaminant, which reduces the concentration without reducing the overall mass. Dilution also occurs through groundwater recharge. For example, at Travis AFB, water from winter storms infiltrates through the soil column to the groundwater, and dilutes the concentration and thus the toxicity of the contamination.

As dissolved VOCs migrate with the groundwater, a portion of the contaminants may adsorb to organic materials in the soil matrix, and thus become fixed to the soil particle surface. The portion of the contaminant that is sorbed to soil and not migrating is said to be "retarded." The extent of retardation is a function of the properties of both the chemical contaminant and the soil. Retardation is a dynamic process where contaminants sorb and desorb as groundwater moves through the aquifer matrix.

The organic carbon partition coefficient (K_{oc}) indicates the tendency of a compound to adsorb to the soil matrix. The higher the value of the partition coefficient, the more likely the chemical will be adsorbed to a given amount of organic carbon exchange sites in the soil matrix. A mobility classification scheme based on K_{oc} indicates that a compound with a value less than 150 is very mobile in groundwater (i.e., less likely to adsorb); a compound with a value from 150 to 500 has intermediate mobility; and a compound with a value higher than 500 has low mobility (Barbee, 1994). Most halogenated VOCs have values less than 150, and thus have little tendency to adsorb. For example, the partition coefficient of trichloroethylene (TCE) is 126.

Retardation is also influenced by the amount of organic materials in the soil matrix. Total organic carbon (TOC) analyses were not performed on soil samples collected at LF006 during the RI. However, TOC analyses performed on samples collected in the western portion of Travis AFB found that the maximum organic content in that area represented only about 0.02 percent of the total mass of the soil. Research indicates that in aquifers with an organic content that varies from 0.01 to 0.1 percent, the retardation factor for TCE varies from 1.1 to 1.8 (Cherry and Feenstra, 1990). This means that the velocity of transport for TCE is retarded to about 0.6 to 0.9 times the linear groundwater flow velocity.

Another nondestructive process, volatilization, also reduces the concentration of VOC contaminants in groundwater. Volatility is a measure of the mass transfer of a compound from the aqueous phase to the gaseous phase. The volatility of a given chemical is affected by its solubility, vapor pressure, and molecular weight. Soil properties also affect volatilization. A permeable soil promotes the movement of soil air, which enhances volatilization. High organic carbon or clay content increases adsorption and reduces volatilization (Cohen and Mercer, 1993).

Henry's Constant, or the vapor pressure divided by the aqueous solubility, describes the tendency of a chemical to volatilize from a dilute aqueous solution in water. The higher the Henry's Constant of a chemical, the more likely that it will volatilize from water. Values of Henry's Constant greater that about 10^{-5} atm-m^3/mol indicate that, at equilibrium, a greater proportion of a particular chemical will be concentrated in the gaseous or vapor phase; less than this value indicates a tendency to accumulate in the aqueous phase (Barbee, 1994). Most VOCs have values of Henry's Constant greater than 10^{-5} atm-m^3/mol, indicating their tendency to volatilize. For example, the Henry's Constant value for TCE is 1.03×10^{-2} atm-m^3/mol.

2.1.2 Destructive Processes

As previously mentioned, biodegradation is the most important destructive natural attenuation mechanism. The following discussion summarizes biodegradation processes, and is taken from the AFCEE *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (Wiedemeier et al., 1996).

The driving force behind most reactions resulting in the destruction of VOCs is electron transfer. Fuel hydrocarbons and chlorinated hydrocarbons typically degrade by different electron transfer mechanisms.

Fuel hydrocarbons tend to be electron donors, and the biodegradation of fuel hydrocarbons is mainly limited by the availability of electron acceptors. In general, there is a sufficient supply of electron acceptors available to the indigenous microbes in the typical groundwater environment to prevent extensive migration of dissolved-phase fuel hydrocarbon plumes. The fuel hydrocarbons are therefore degraded as a primary substrate.

On the other hand, chlorinated hydrocarbons tend to be electron acceptors and typically degrade by a process known as reductive dehalogenation. Chlorinated hydrocarbons may also degrade by other mechanisms and may act as electron donors in certain conditions, but reductive dehalogenation appears to be most important mechanism under natural conditions.

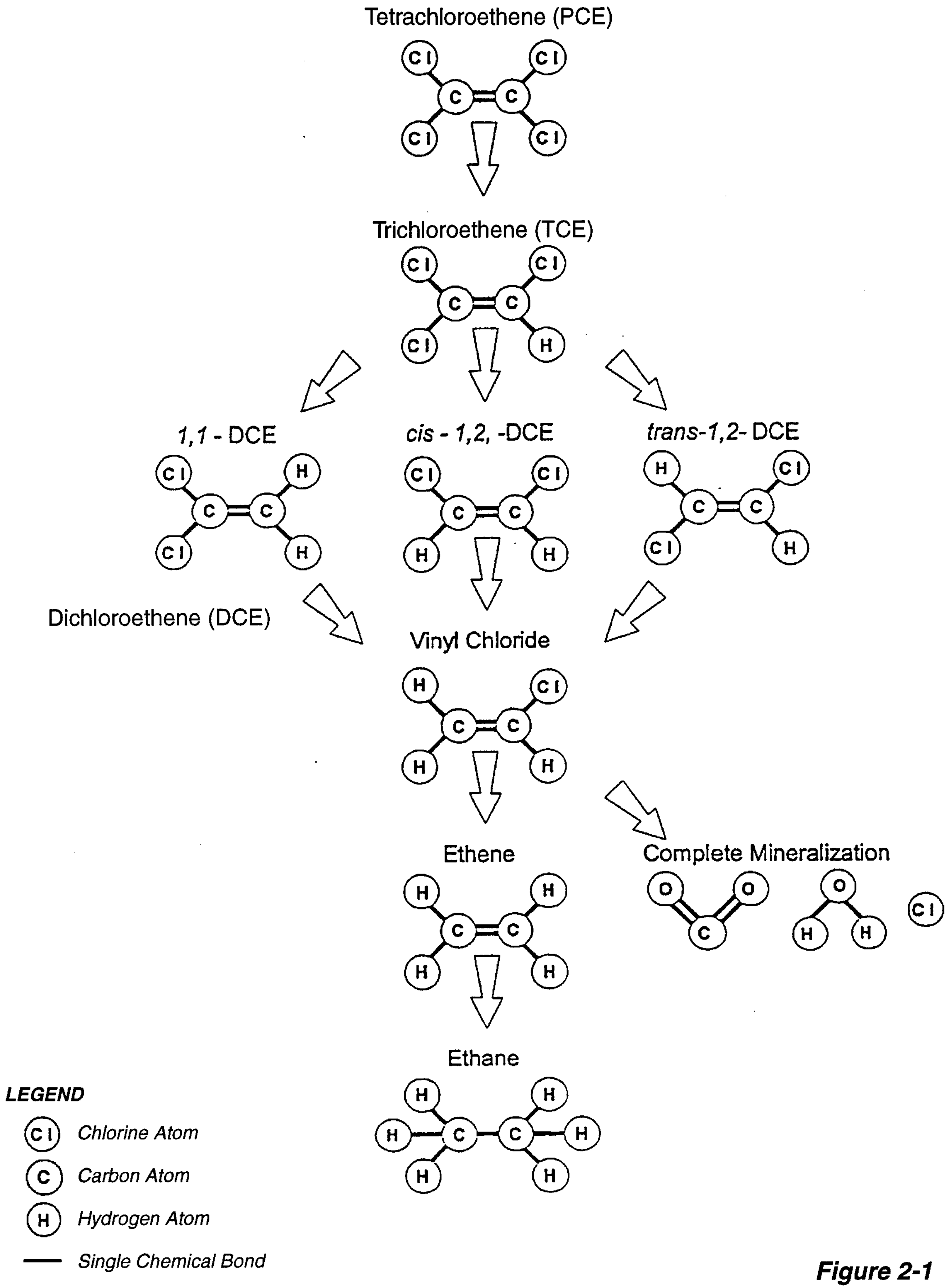
Reductive dehalogenation requires an adequate supply of electron donors. Sources of electron donors include fuel hydrocarbons or other carbon sources such as landfill leachate or natural organic carbon. Electron donors are limited in the typical groundwater environment, and if the supply of electron donors is depleted, natural attenuation of chlorinated hydrocarbons will cease. This means that having both fuel hydrocarbons and chlorinated hydrocarbons in groundwater at LF006 and other sites is fortuitous for natural attenuation.

In addition, chlorinated hydrocarbons must compete with other electron acceptors in the environment for donated electrons. Because of thermodynamic considerations, electrons are transferred to acceptors in an order of preference. Dissolved oxygen (DO) is the primary electron acceptor and will continue to accept electrons until it is consumed. After the DO is consumed, other electron acceptors are used in the following order of preference: nitrate, ferric iron, sulfate, and finally, carbon dioxide (methanogenic reduction). Most of these reactions do not proceed abiotically, but are mediated by microorganisms that use the energy yielded by the reaction.

Biodegradation of chlorinated hydrocarbons typically proceeds through reductive dehalogenation, but may also proceed through two other pathways: use of the chlorinated hydrocarbon as an electron donor, and cometabolism. The following paragraphs briefly summarize the three main pathways for the biodegradation of chlorinated hydrocarbons.

2.1.2.1 Reductive Dehalogenation

During reductive dehalogenation, the chlorinated hydrocarbon is used as an electron acceptor, and a chlorine atom is removed and replaced with a hydrogen atom (see Figure 2-1). In general, this occurs sequentially, with more highly halogenated chemicals transforming to less highly halogenated chemicals as chlorine atoms are successively replaced with hydrogen atoms. In addition, the rate of reductive dechlorination decreases



SOURCE: Wiedemeier et al, 1996/

Figure 2-1
Reductive Dehalaogenation of Chlorinated Ethenes
Travis Air Force Base, California

as the degree of chlorination decreases. Thus, more highly oxidized chemicals like TCE will undergo reductive dehalogenation more quickly than less oxidized chemicals like vinyl chloride (VC), and VC may accumulate during reductive dehalogenation.

As shown in Figure 2-1, TCE will theoretically degrade to cis-1,2-dichloroethylene (cis-1,2-DCE), trans-1,2-DCE, or 1,1-DCE. However, research has shown that degradation to cis-1,2-DCE is most common, while degradation to 1,1-DCE is least common. Reductive dehalogenation occurs most rapidly and affects more compounds under sulfate-reducing and methanogenic conditions. It occurs less rapidly under nitrate- and iron-reducing conditions. Finally, as mentioned previously, there must be an electron donor source for reductive dehalogenation to occur. Sources of carbon for microbial growth include natural organic matter, fuel hydrocarbons, or landfill leachate.

2.1.2.2 Electron Donor Reactions

Some chlorinated hydrocarbons may be degraded by acting as electron donors, rather than electron acceptors. More highly oxidized chemicals, such as tetrachloroethylene (PCE) and TCE, are not likely to degrade this way. However, less oxidized chlorinated hydrocarbons such as VC can be used as primary substrate in biologically mediated reactions under aerobic (and some anaerobic) conditions. The chlorinated hydrocarbon in this instance supplies organic carbon and energy to the microorganism. In addition to VC, other chemicals such as 1,2-DCA and methylene chloride have been observed to degrade under aerobic conditions. Methylene chloride may also degrade as an electron donor under anaerobic conditions, and VC may degrade under iron-reducing conditions as long as there is sufficient ferric iron (III).

2.1.2.3 Cometabolism

When a chlorinated hydrocarbon is biodegraded through cometabolism, it serves as neither an electron acceptor nor a primary substrate. Instead, the degradation is catalyzed by an enzyme that is produced by the microorganism for other purposes. The microorganism receives no known benefit from the degradation, and in fact may be harmed by it. The chlorinated hydrocarbon does not enhance the degradation of the fuel hydrocarbon or other carbon source, nor will it interfere with the use of electron acceptors involved in the oxidation of those carbon sources. Depletion of suitable carbon substrates may limit the cometabolism of the chlorinated hydrocarbons.

Cometabolism has been documented in aerobic environments, although it could potentially occur under anaerobic conditions. Under aerobic conditions, all of the chlorinated ethenes with the exception of PCE are potentially susceptible to cometabolic degradation. Further, the rate of cometabolism increases as the degree of dehalogenation decreases.

2.2 Behavior of Chlorinated Hydrocarbon Plumes

Chlorinated hydrocarbon plumes may exhibit complex behavior when undergoing natural attenuation. However, three main trends characterize most plumes. The behavior exhibited depends on variables such as the concentration and distribution of chlorinated hydrocarbons present, the amount of biologically available carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors used. Further, a single chlorinated hydrocarbon plume may exhibit different behaviors in different portions of the plume. The main behaviors are described below.

2.2.1 Type 1 Behavior

Type 1 behavior occurs where the primary biodegradation mechanism is reductive dehalogenation and the primary substrate is anthropogenic carbon (such as petroleum hydrocarbons or landfill leachate). Type 1 behavior results in the degradation of the more highly chlorinated hydrocarbons such as TCE and DCE. The following questions must be resolved when evaluating natural attenuation of a plume exhibiting Type 1 behavior:

- Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms run out of chlorinated hydrocarbons used as electron acceptors before they run out of anthropogenic carbon used as the primary substrate?
- What is the role of competing electron acceptors (e.g., dissolved oxygen, nitrate, ferric iron [III], and sulfate)?
- Has VC accumulated? Is it oxidized or reduced?

2.2.2 Type 2 Behavior

Type 2 behavior is similar to Type 1 behavior, except that native carbon rather than anthropogenic carbon serves as the primary substrate for microorganism growth and drives the reductive dehalogenation. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents, but, in areas with sufficient natural organic carbon, may result in the complete degradation of the contaminants. The same questions posed for Type 1 behavior should be addressed when evaluating plumes with Type 2 behavior.

2.2.3 Type 3 Behavior

Type 3 behavior occurs where there is an inadequate supply of native or anthropogenic carbon, and aerobic conditions prevail in the aquifer (i.e., the DO concentration is greater than 1.0 mg/L). Reductive dehalogenation will not occur under these conditions. For the more highly chlorinated hydrocarbons, such as TCE and DCE, natural attenuation will occur mainly through nondestructive processes (e.g., dispersion, dilution, sorption). However, less highly chlorinated hydrocarbons, such as VC, may be oxidized under these conditions.

2.2.4 Mixed Behavior

Chlorinated hydrocarbon plumes may exhibit more than one type of behavior in different portions of the plume. For example, Type 1 behavior near the source area may result in the reductive dehalogenation of TCE and DCE, with accumulation of VC. The VC may then be oxidized further downgradient (Type 3 behavior), either aerobically or by iron reduction. The end product of this series of reactions is carbon dioxide, with no ethene being produced:

$$\mathrm{TCE} \rightarrow \mathrm{DCE} \rightarrow \mathrm{VC} \rightarrow \mathrm{CO_2}$$

In this scenario, the TCE, DCE, and VC attenuate at about the same rate. Vinyl chloride is removed at a faster rate under oxidizing conditions than under reducing conditions.

Another example of mixed behavior is a combination of Type 1 and Type 2 behavior. All of the chlorinated ethenes could be reductively dehalogenated in this situation, although the rate of attenuation would be unequal, resulting in the accumulation of VC. The VC would be reduced to ethene in this situation, as follows:

TCE → DCE → VC → Ethene → Ethane

2.3 Demonstrating Natural Attenuation

To support remediation by natural attenuation, Travis AFB must demonstrate that attenuation of site contaminants occurs at a rate sufficient to stabilize the plume, and prevent contaminant concentrations at point-of-compliance monitoring wells from exceeding cleanup goals. According to AFCEE protocol, three lines of evidence may be used to support natural attenuation:

1. Observed reductions in contaminant concentrations along the flow path downgradient from the source of contamination
2. Documented loss of contaminant mass at the field scale, using:
    - Chemical and geochemical data, including:
        —decreasing parent compound concentrations
        —increasing daughter compound concentrations
        —depletion of electron acceptors and donors
        —increasing metabolic by-product concentrations
    - A rigorous estimate of residence time along the flow path to document contaminant mass reduction and calculate biological decay rates at the field scale
3. Microbiological laboratory or field data that support biodegradation and give rates of biodegradation

The investigator should provide either the first two lines of evidence or the first and third line of evidence. The first line of evidence, reduction in concentrations along the flow path, may indicate natural attenuation. However, this line of evidence does not demonstrate whether reduction is due to nondestructive or destructive natural attenuation mechanisms.

To support remediation by natural attenuation, destructive mechanisms must be demonstrated. In other words, the destruction of contaminant mass through biodegradation normally needs to be demonstrated (for certain chemicals, abiotic reactions may also be important). This is done using either or both of the second or third lines of evidence.

The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed. This line of evidence has two components:

- Showing that decreases in contaminant and electron acceptor/donor concentrations can be directly correlated to increases in metabolic end products/daughter compounds. The objective is to prove that electron acceptor and donor concentrations in groundwater are adequate to facilitate degradation of dissolved contaminants. Solute fate and transport modeling can be used to facilitate this demonstration.

- Using measured contaminant concentrations in conjunction with aquifer hydrogeological parameters to show a reduction in contaminant mass, and to calculate biodegradation rate constants.

The third line of evidence involves collecting microbiological data to show that indigenous biota degrade the contaminants at a particular rate. AFCEE protocol recommends that the first and second line of evidence should be used in the natural attenuation demonstration, if possible, and that microbiological evidence should be used only when biodegradation rate constants cannot be obtained using the second line of evidence. This approach will be followed at Travis AFB natural attenuation sites.

3.0 Natural Attenuation Approach at Travis AFB

The natural attenuation assessment at Travis AFB will follow a similar progression at each site: the collection of existing data; an initial screening of the site for natural attenuation potential; the preparation of a NAAW (a secondary document); a field investigation to fill data gaps and evaluate natural attenuation; data analysis and groundwater modeling; and the preparation of a NAAR (a secondary document) that presents the results of the evaluation, concludes whether natural attenuation is appropriate at the site, and proposes a long-term monitoring program. The LF006 Interim Groundwater RD/RA Workplan and LF006 NAAR are primary documents. Groundwater monitoring will be ongoing as part of the GSAP, both before and after the natural attenuation assessment.

3.1 Overview

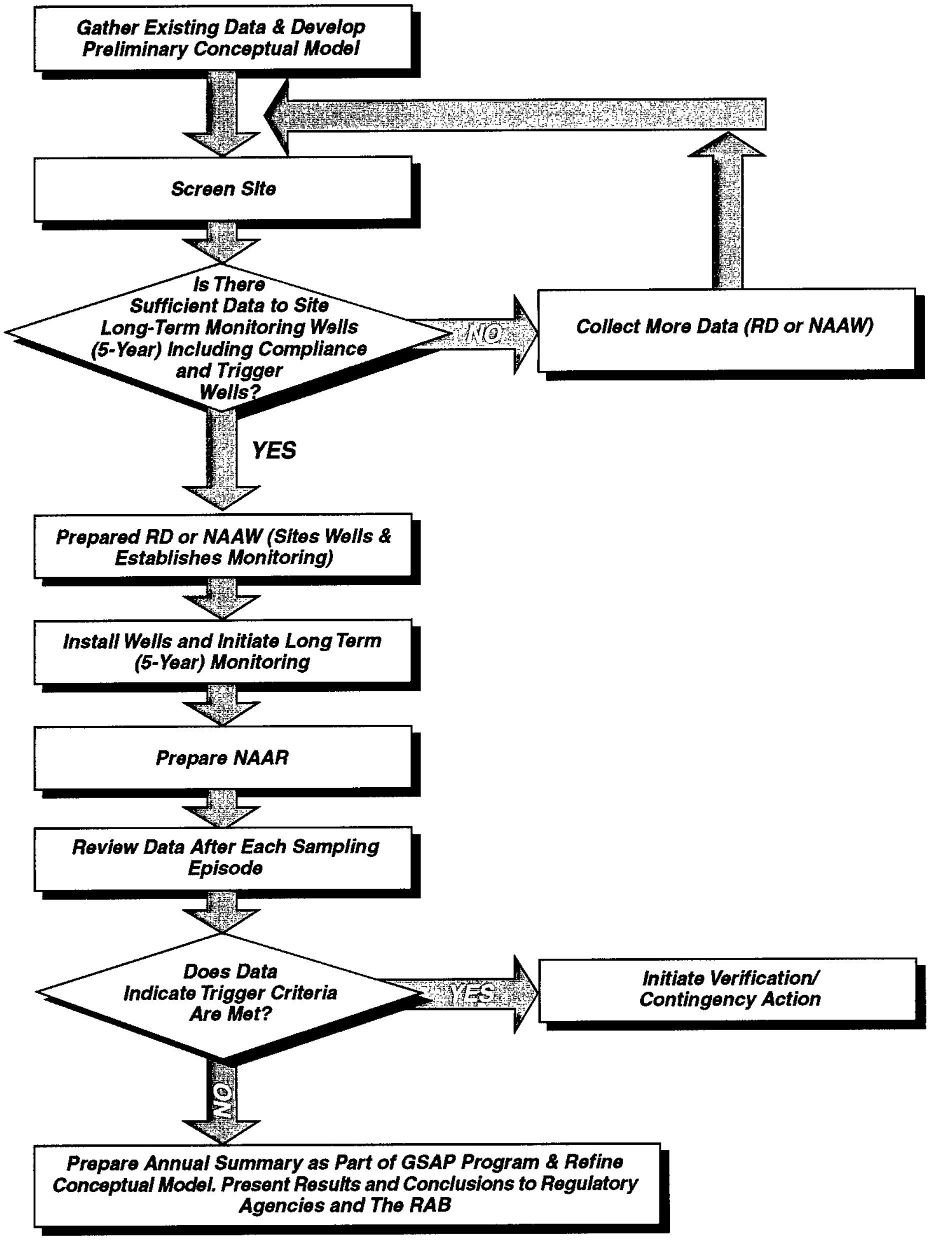
Figure 3-1 outlines the evaluation process at Travis AFB. This figure has been modified slightly from the AFCEE guidance, in that it specifies only one phase of field investigation followed by monitoring, where the AFCEE guidance specifies two phases of field investigation. This modification is reasonable at Travis AFB for three reasons: (1) data from the Ris are fairly extensive; (2) the NAAP adds strict requirements for trigger wells and point-of-compliance monitoring directly downgradient from the plume of contamination; and (3) a final decision regarding a natural attenuation remedy for a site will not be made until the ROD is signed. Where data are not sufficient to determine the extent of contamination or the source of contamination, more than one phase of field investigation may be necessary.

As shown in Figure 3-1, the first step of the natural attenuation assessment is to review existing data. This review includes revising the conceptual site model developed during the RI, if necessary, to account for new information gathered by the GSAP or to reflect potential impacts of nearby pump and treat activities. Nearby pumping may be particularly significant at sites proposed for both natural attenuation and pumping, or at sites near other sites being actively remediated.

Following the data review, investigators will screen the site. At this point, data may be sufficient to conclude that natural attenuation is not viable at the site (or portion of the site). If so, then remediation by Alternative 3 (engineered remediation) will be implemented.

Alternatively, investigators may conclude that natural attenuation is potentially viable at the site, or that data are not sufficient to make a decision. This conclusion is likely at most of the sites being evaluated for natural attenuation at Travis AFB. Investigators will then design a field investigation to determine if natural attenuation should be selected as the preferred alternative for the site, and to fill data gaps identified during the data review and initial screening.

The NAAW (referred to as the Interim Groundwater RD/RA Workplan at Site LF006) will document these initial steps of the evaluation. The NAAW will summarize site data, present a preliminary conceptual site model, screen the site for natural attenuation potential, and conclude whether natural attenuation is potentially viable. If so, the workplan will identify the data gaps and present a design for additional site characterization, based on AFCEE guidance. Finally, the NAAW will include a schedule and identify project staff to complete the investigation.

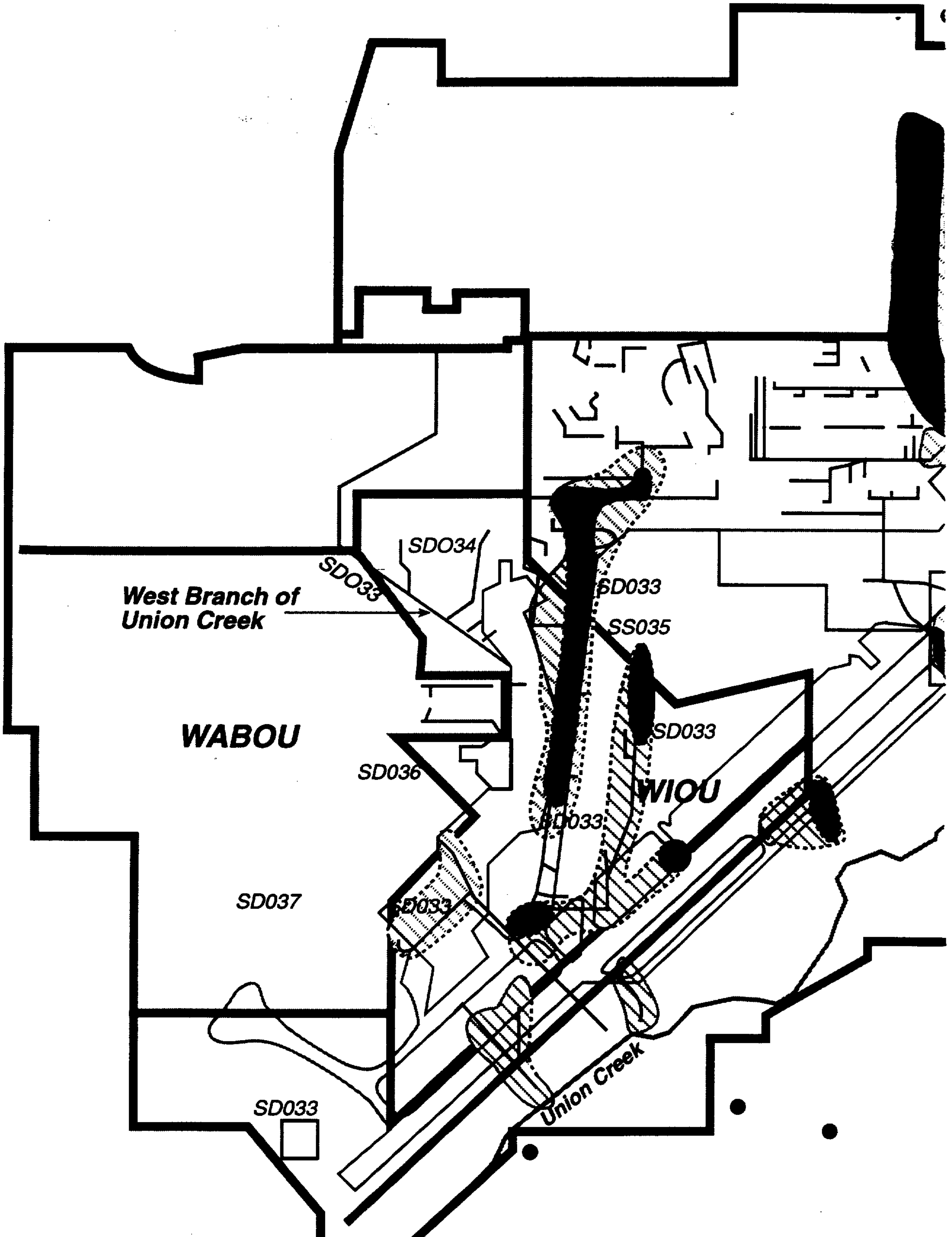


SOURCE: Wiedemeier et al, 1996

Figure 3-1

Natural Attenuation Decision Process

Travis Air Force Base, California



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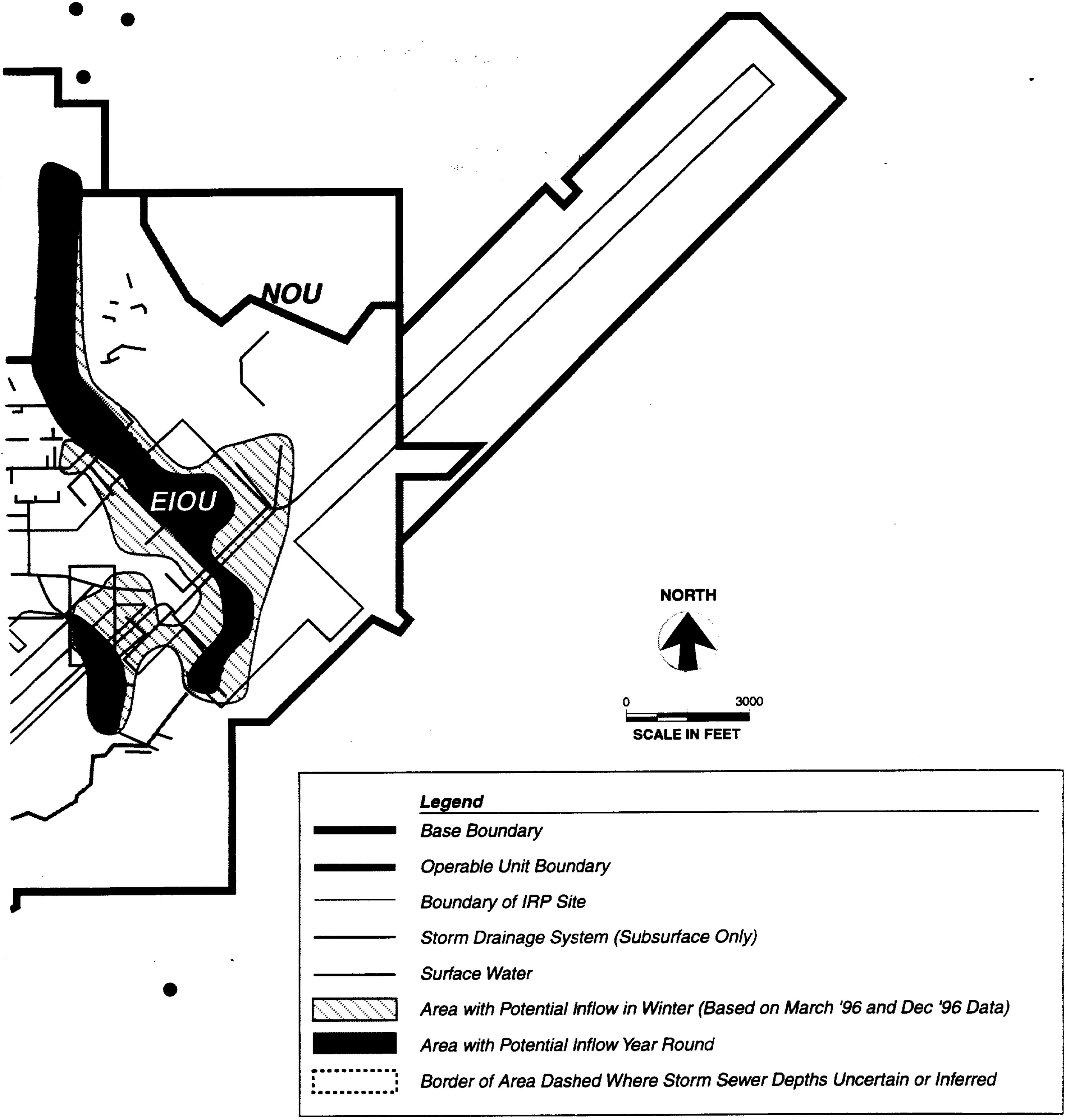


Figure 3-2
Areas of Potential Groundwater Inflow into Stormwater Sewer System
Travis Air Force Base, California

Following the field investigation, investigators will review the data and refine the conceptual site model. Travis AFB will demonstrate that natural attenuation occurs at the site at a rate sufficient to prevent contaminant migration above Interim Remedial Goals (IRGs) at points of compliance. Refining the conceptual site model, key to this demonstration, includes such elements as the preparation of geologic logs, hydrogeologic sections, groundwater contour maps, contaminant and daughter product isopleth maps, and electron acceptor and metabolic byproduct isopleth maps.

The refined conceptual site model will support contaminant fate and transport modeling. Input calculations for the model may include sorption and retardation calculations, groundwater flow velocity calculations, and biodegradation rate-constant calculations. Performing Non Aqueous-Phase Liquids (NAPL)/water partitioning calculations may not be necessary because the sites selected for natural attenuation assessment do not appear to contain NAPLs. However, these calculations will be performed if necessary.

Solute fate and transport modeling will then be performed to predict the migration and attenuation of the contaminant plume through time. Several well-documented and accepted models are available for simulating the fate and transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation. The groundwater flow system will be modeled using Micro-Fem (Hemkert and Nijsten, 1996), an integrated finite element groundwater modeling package capable of three-dimensional particle tracking in multilayered aquifer systems. Micro-Fem also tracks water table declines in unconfined aquifers while updating transmissivities. Other comparable models may also be used if specified in the NAAW.

A comparison of the rate of solute transport to the rate of attenuation will also be accomplished through modeling. Several solute fate-and-transport models are available—the selected model will be specified in the NAAW. This model will be capable of simulating solute transport under the influence of advection, dispersion, sorption, and biodegradation. It will be comparable to BIOSCREEN, a non-proprietary model developed by the Technology Transfer Division of AFCEE. This model allows use of either a first-order biodegredation rate or an instantaneous reaction between contaminants and electron acceptors to simulate the effects of biodegradation. Sensitivity analyses will be performed to evaluate the confidence in the model. The outcome of the modeling will predict the future extent and concentrations of the contaminant plume, which will be used to evaluate whether the Chemicals of Concern (COC) concentrations will exceed IRGs at points of compliance.

Data collected in the field investigation, together with the updated conceptual site model and the modeling results, will be presented in the NAAR. This report, also a primary document, will conclude whether natural attenuation occurs at the site at a rate sufficient to prevent contamination from reaching point-of-compliance wells at concentrations above IRGs. In other words, it will conclude whether natural attenuation has the potential to be effective as the remedial alternative for the site. The NAAR may also conclude that natural attenuation is appropriate for some portion of the site, but that additional remedial action must be taken at the source area or some other portion of the site.

The NAAR will also present a long-term monitoring plan to verify over time that natural attenuation is successfully remediating the plume. This plan will include monitoring at "trigger" wells and at point-of-compliance wells. Long-term monitoring will be conducted as part of the GSAP.

3.2 Monitoring

Sites selected for natural attenuation assessment will be monitored from the 3rd Quarter 1997 until the end of the interim (5-year) period. Before the natural attenuation assessment, each site will be monitored as part of the GSAP. During the natural attenuation assessment, additional monitoring wells may be installed. These include wells to monitor natural attenuation processes inside and outside the plume of contamination, as well as trigger wells and point-of-compliance wells.

As described above, the NAAR will prescribe long-term monitoring to verify the effectiveness of natural attenuation over time. Data will be reviewed during the preparation of the ROD in the year 2002. At that time, a final decision will be made regarding whether natural attenuation is the most technologically and economically reasonable final remedy for the site.

3.2.1 Groundwater Sampling and Analysis Program

Currently, the sites selected for natural attenuation assessment are monitored on a semi-annual basis as part of the 1997 GSAP. This monitoring includes 38 monitoring wells at 17 sites, as shown in Table 3-1. Several of these sites are downgradient from designated natural attenuation sites, are in the WABOU, or are being evaluated as part of the POCOS program. Laboratory analyses include VOCs, methane, ethane, ethene, sulfate, sulfide, TOC, and nitrate. Field analyses include DO, ferrous iron, carbon dioxide, oxidation-reduction potential, temperature, pH, and specific conductance (Radian, 1997). The relevance of these analyses to natural attenuation is discussed in Section 4. In addition, semi-annual groundwater elevation surveys from a network of 223 monitoring wells at Travis AFB will help monitor the direction and gradient of groundwater flow.

TABLE 3-1
Sites and Monitoring Wells Evaluated for Natural Attenuation as Part of the 1997 Groundwater Sampling and Analysis Program

Site	Monitoring Wells
FT004	MW-266, MW-1000
FT005	MW-119, MW-121, MW-308
LF006	MW-130, MW-209, MW-304, MW-1743
LF007B	MW-128, MW-303
LF007C	MW-125
LF007D	MW-261, MW-264
SS015	MW-216, MW-238
SS016	MW-328, MW-1022
ST018	MW-135, MW-138, MW-139, MW-141, MW-210, MW-211
SS029	MW-280, MW-329
SD031	MW-206, MW-1727
ST032	MW-1024, MW-1025, MW-1026
SD033	MW-1202
SS035	W0818M01
SD037	MW-1208, MW-1209
DP039	B755M02, B755M04
SD043	B916M03

Analytical results and groundwater elevation data will provide inputs to the initial screening at natural attenuation sites, begin to build a database of long-term trends, and help track the movement of contamination. Data collected during the 1997 GSAP will be evaluated in the 1997 Annual Report for the GSAP. Laboratory or field analyses may be reduced over time as the site becomes more fully understood.

3.2.2 Trigger and Point-of-Compliance Wells

Trigger wells are new or existing wells located at or near the maximum contaminant level (MCL) isopleth of the COC furthest downgradient in the plume of groundwater contamination, based on data obtained during the natural attenuation assessment. Trigger wells will be used as an early indicator of significant horizontal contaminant migration. Significant migration is defined as an increasing trend that indicates that point-of-compliance wells could become contaminated above IRGs within a year. Vertical migration will also be monitored as necessary on a site-by-site basis.

Point-of-compliance wells are new or existing wells located downgradient from the nondetect isopleth of the COC furthest downgradient in the plume of contamination. The location of the point-of-compliance wells at a particular site will be proposed in that site's NAAR as part of the long-term monitoring plan. Locations will be based on the position of the plume, the hydrogeology of the site, proximity of other sites and other remedial actions, velocity of contaminant migration, and the geochemistry of the plume. Point-of-compliance wells detect movements of the plume outside the perimeter of containment and identify the need to manage potential expansion.

The complexity of natural attenuation processes impedes using statistical methods to evaluate whether increases in chemical concentrations in trigger wells indicate significant contamination migration. For example, a gradual increase in vinyl chloride concentrations, accompanied by a gradual decline in TCE concentrations, could indicate natural attenuation, rather than contaminant migration. Seasonal fluctuations in contaminant concentrations may be misinterpreted as increases or decreases because of insufficient baseline data. In addition, baseline data may not be available at appropriately located trigger wells. Finally, the complexity of the hydrogeology and of the plumes themselves, together with the complexity of the natural attenuation process, requires that data be analyzed on a well-by-well basis.

To establish a data baseline at trigger wells, monitoring will take place quarterly for 2 years following the natural attenuation assessment as part of the GSAP. Time-series plots will be prepared each year for each contaminant at the site and included in the GSAP Annual Report. These plots will show whether contaminant concentrations increased or decreased, and should also document seasonal fluctuations. Decisionmakers may interpret the data in the context of natural attenuation processes and site conditions. Because trigger wells will be used to help assess whether contaminants are migrating toward point-of-compliance wells, data from the trigger wells will determine the frequency with which both the trigger wells and point-of-compliance wells are monitored.

After the data baseline has been established, data trends may be used to establish the frequency of ongoing monitoring. The GSAP Annual Report will provide an opportunity to review the data and establish the monitoring frequency for the coming year. The monitoring frequency will be established as follows:

1. *Trend of increasing concentration of a COC or other toxic contaminant (e.g., vinyl chloride)*: continue sampling trigger wells and point-of-compliance wells on a quarterly basis.
2. *No trend or stable concentrations*: Sample trigger wells and point-of-compliance wells on a semi-annual basis.
3. *Trend of decreasing concentrations or non-detections*: Sample trigger wells and point-of-compliance wells on an annual basis.

Analytical results in point-of-compliance wells will be used to trigger a contingency corrective action. As previously mentioned, corrective action will be necessary if concentrations of COCs (or other toxic transformation products of COCs) exceed IRGs in point-of-compliance wells. Any exceedance of IRGs in a point-of-compliance monitoring well will initiate a verification monitoring program, in which the well is sampled monthly for 3 consecutive months. The verification monitoring will establish whether the exceedance represents actual contaminant migration, or represents a false positive result.

At the end of the 3 months, the 95 percent Upper Confidence Level of the average of the concentrations of the contaminant exceeding the IRG will be calculated. If this value exceeds the IRG, a contingency corrective action will be initiated. This action will likely consist of implementing Alternative 3 (Extraction, Treatment, and Discharge). The actual scope of the action will depend on site conditions and consultations with regulatory agencies. The Air Force will request funding and implement the contingency action as soon as funding becomes available. Monitoring will continue quarterly until the action is implemented.

3.3 Preferential Pathways

Preferential pathways are subsurface locations of relatively greater permeability, in which contaminants may potentially migrate more quickly than in surrounding materials. Examples include utility corridors and highly permeable geologic formations such as sands or gravels. Because the permeability in these materials is greater than in surrounding materials, the groundwater hydraulic conductivity will be greater, resulting in higher groundwater velocity. In addition, the groundwater in adjacent materials will flow toward the preferential pathways. If undetected, preferential pathways could result in significant contaminant migration beyond point-of-compliance wells and short-circuit the natural attenuation process.

Preferential pathways may affect groundwater migration at sites undergoing natural attenuation assessment at Travis AFB (e.g., Sites SD033 [Storm Sewer II] and SD037 [Sanitary Sewer System]). Other sites may be adjacent to preferential pathways that could affect groundwater migration. Figure 3-2 shows areas of potential groundwater inflow into the Travis AFB storm sewer system.

Investigators will summarize known information regarding potential preferential pathways at each site in the NAAW. This workplan will also establish investigative procedures to assess the impact the preferential pathway may have on groundwater flow and contaminant migration at the site. The NAAR will present the results of the preferential pathway assessment and determine its impact on natural attenuation at the site.

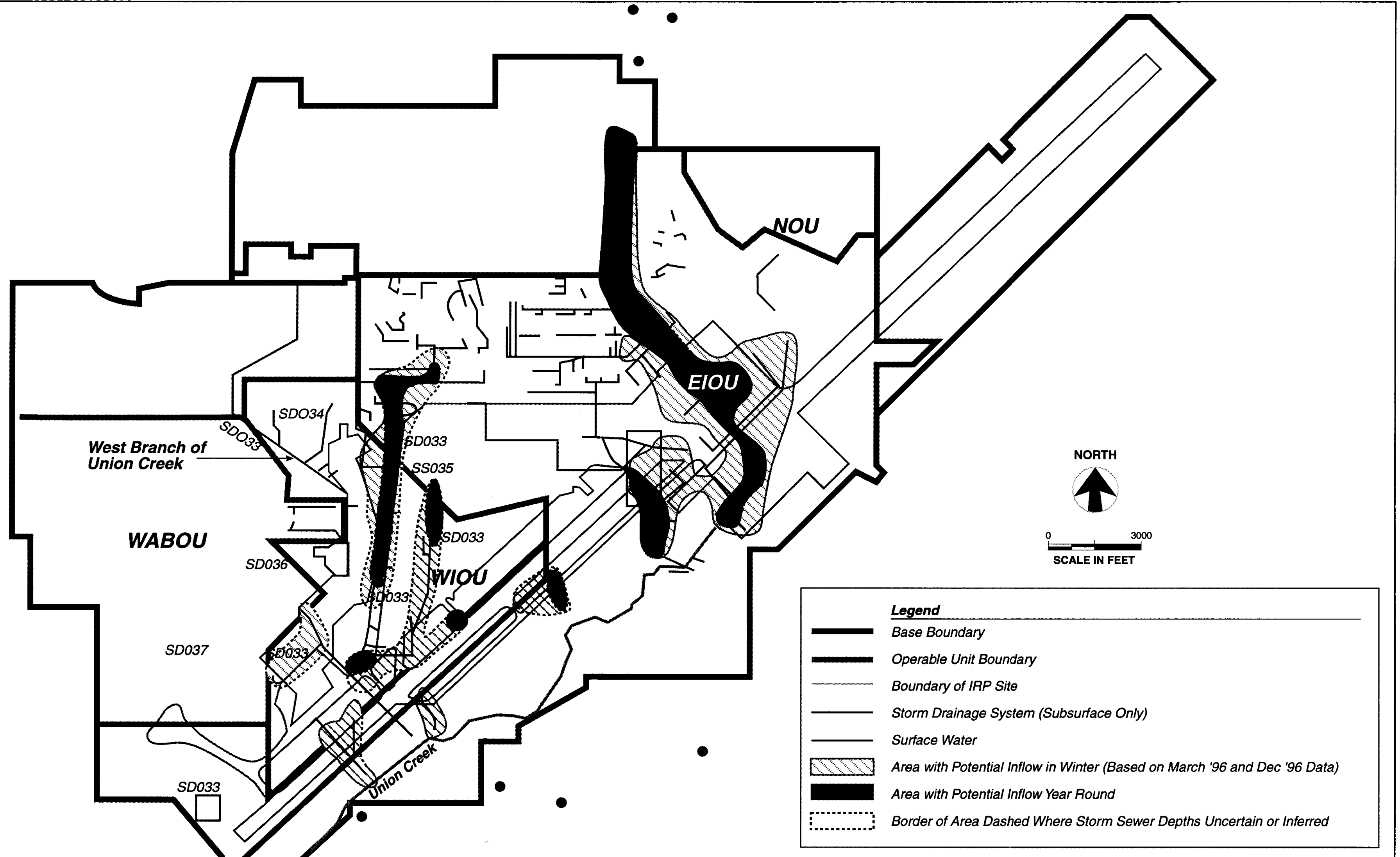


Figure 3-2
Areas of Potential Groundwater Inflow into Stormwater Sewer System
Travis Air Force Base, California

CH2MHILL

Source: Travis AFB, 1997

3.4 Adjacent Groundwater Pumping

Certain sites evaluated for natural attenuation may be affected by nearby groundwater pumping. These sites may be proposed for both natural attenuation and extraction and treatment in different portions of the site, or may be near other sites scheduled for extraction and treatment. Nearby groundwater extraction may alter the existing flow paths at the site, potentially causing contamination to bypass monitoring wells. Alternatively, nearby extraction may capture all or a portion of the contamination at the site.

Nearby groundwater extraction will be noted in the NAAW for the site. The investigation will evaluate the potential influence of pumping on natural attenuation at the site. Groundwater modeling will also evaluate the effect of nearby pumping. The location of trigger wells and point-of-compliance wells may be altered based on the modeling.

4.0 Natural Attenuation Assessment Workplan

The NAAW forms the basis for the natural attenuation assessment at Travis AFB. This document summarizes the existing information about the site, refines the conceptual site model if necessary, screens the site for natural attenuation potential, identifies data gaps, and specifies the field investigation at the site. It also provides a schedule to accomplish the evaluation and identifies key staff. The NAAW is a secondary document as defined in the FFA; regulatory agencies will have an opportunity to review and comment on the plan. At Site LF006, the document is referred to as the Interim Groundwater RD/RA Workplan (a primary document), because natural attenuation was selected as the interim remedy in the Groundwater IROD. However, the LF006 Interim Groundwater RD/RA Workplan will contain the same components as the NAAW. The following section describes this document and its contents in more detail.

4.1 Review of Existing Information

The first step in the natural attenuation assessment is to review site-specific data from previous IRP investigations, the RI, and the GSAP. These data will be used to refine the conceptual site model developed during the RI and perform a preliminary natural attenuation screening. The conceptual site model and screening will then help to identify data gaps and to place additional data collection points in the most advantageous and cost-effective manner possible.

If available, the following information will be obtained during the review of existing data and summarized in the NAAW:

Site History

- Site description and current status
- Site operational history
- Nature and history of contaminant releases
    —catastrophic release or gradual release?
    —single or multiple source areas?
    —chemicals released?
    —dates of release?
- Previous investigations
- Nearby extraction and treatment remedies
- Man-made features potentially creating preferential pathways for groundwater movement

Geology and Hydrogeology

- Lithology and stratigraphic relationships

- Bedrock boundaries
- Aquifer hydraulic conductivity
- Groundwater flow gradients and groundwater elevation contours
- Groundwater flow velocity
- Geologic features potentially creating preferential pathways for groundwater movement
- Potential groundwater and surface water interactions

Nature and Extent of Contamination

- One or multiple plumes
- Presence of NAPLs
- Soil data
- Vertical and horizontal distribution of contamination
- Historical water quality data showing variations in contaminant concentrations
- COCs identified in the RI
- Chemical and physical characteristics of the contaminants
- Presence of transformation products
- Presence of mixtures of fuel hydrocarbons and chlorinated hydrocarbons
- Anthropogenic or naturally occurring carbon sources

4.2 Refinement of the Conceptual Site Model

Existing data will be used to refine the conceptual site model developed for the site during the RI. The revised conceptual site model will then be presented in the NAAW. The conceptual site model, a three-dimensional representation of the contaminant source area, migration pathways, and potential receptors, takes into account the known information regarding contaminant distribution and the groundwater flow regime. It also identifies unusual factors that may influence contaminant migration, such as induced migration resulting from nearby groundwater extraction or possible highly permeable pathways. The conceptual site model helps define the problem, provides a framework for presenting and integrating data, and helps determine the optimal placement of additional data collection points.

4.3 Initial Site Screening

An initial screening of natural attenuation potential will be performed to identify data gaps and help in the design of the field investigation. In some cases, the initial screening may be sufficient to determine that the site does not have potential for natural attenuation. In that case, no further effort is required and the site is evaluated for possible additional remediation. The NAAW will present the results of the initial screening, as described in this section.

To evaluate natural attenuation at a site, a logical procedure must be followed based on the processes of natural attenuation. Six primary steps compose the initial screening process.

The first step is to analyze available site data to evaluate whether natural attenuation occurs. AFCEE protocol recommends that groundwater analyses from at least six locations be reviewed in the initial screening. Figure 4-1 shows these locations and indicates the use of the data from each location. The evaluation itself involves scoring the site for natural attenuation potential using the parameters listed in Table 4-1. After assigning points to the data, the points are summed and the following interpretation made:

- 0 to 5 points: Inadequate evidence or insufficient data to conclude that biodegradation occurs
- 6 to 14 points: Limited evidence for biodegradation of chlorinated hydrocarbons
- 15 to 20 points: Adequate evidence for biodegradation of chlorinated hydrocarbons
- > 20 points: Strong evidence for biodegradation of chlorinated hydrocarbons

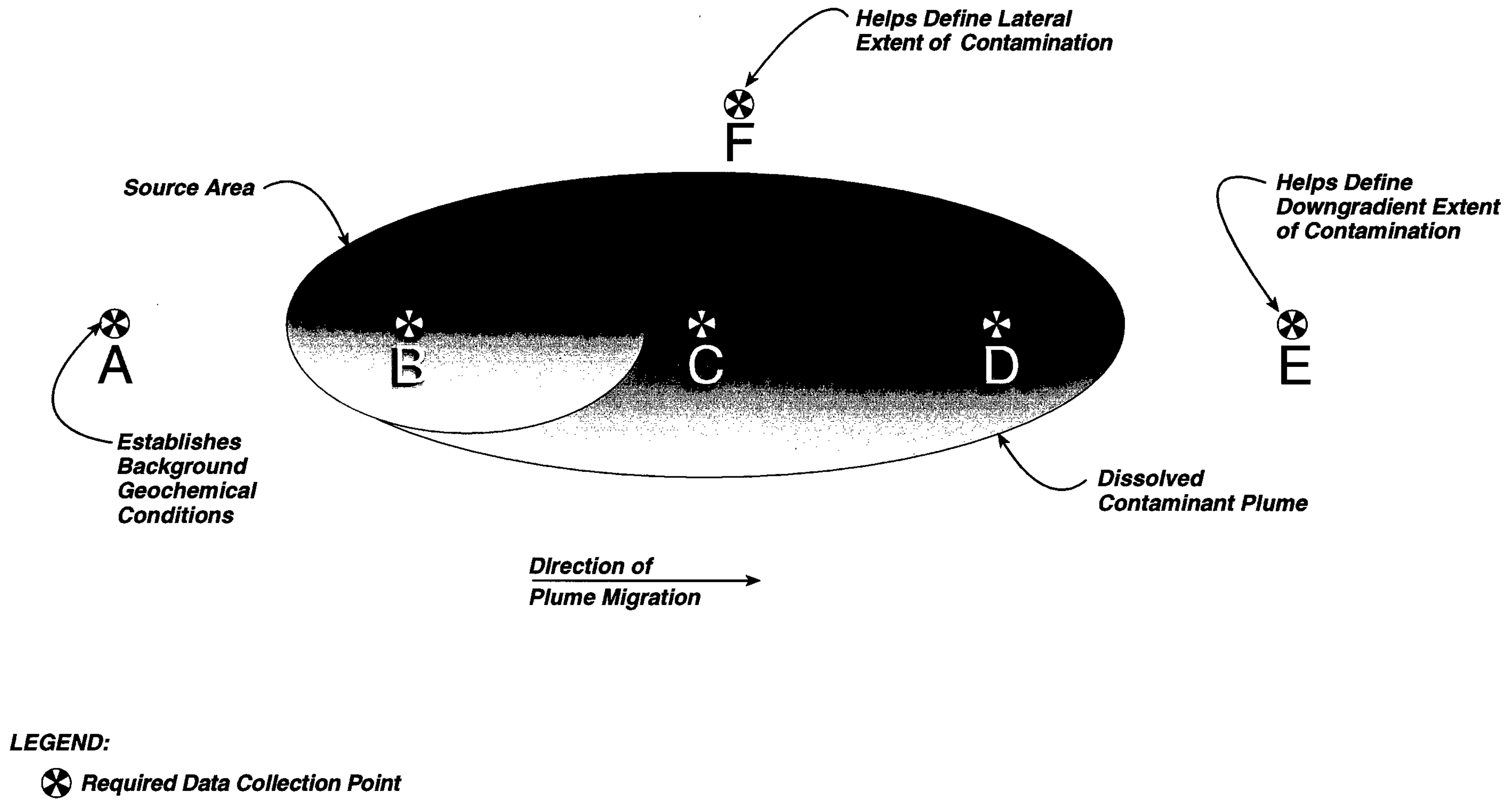
If five or fewer points are awarded at the site, then the issue is whether the low score resulted from insufficient data, or whether data are adequate to determine that natural attenuation does not occur at the site. As shown in Table 4-1, if data are not sufficient, more screening data are needed.

The second step in the initial screening process is to determine groundwater flow and solute transport parameters. These data will be used as inputs to a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. The main inputs are the *hydraulic conductivity*, estimated from aquifer tests; the *hydraulic gradient*, estimated from survey of groundwater elevations; *porosity*, usually estimated from literature values for the types of sediments at the site; and *dispersivity*, normally estimated from literature values. If soil TOC values are available, estimates of *retardation* may also be made.

The third step is to locate the contaminant source area, the extent of contamination, and the receptor exposure points. The objective is to estimate the distance between the source area and the distance that contamination has migrated to date, and the distance to any downgradient or cross-gradient exposure points or points of compliance.

The fourth step is to estimate the rate of biodegradation. Of course, biodegradation rates may be estimated only after it has been determined that biodegradation actually occurs at the site. The biodegradation rate is used as an input to the solute transport model and can be estimated from site-specific data, if available. Methods for estimating the biodegradation rate are provided in the AFCEE protocol (Wiedemeier et al., 1996).

The fifth step is to compare the rate of transport to the rate of attenuation. The objective is to estimate whether the contamination is stable. Normally, the comparison is made through groundwater modeling.



Not to Scale

Figure 4-1
Data Collection Points
Required for Screening
Travis Air Force Base, California

138673.21.12.01 Fig 4-1/Data Collection 9-11-97afo

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TABLE 4-1
Analytical Parameters and Weighting for Preliminary Screening[a/]

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen*	>1 mg/L	VC may be oxidized aerobically	-3
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	2
Iron II*	>1 mg/L	Reductive pathway possible	3
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	>1 mg/L	Reductive pathway possible	3
Methane*	<0.5 mg/L	VC oxidizes	0
	>0.5 mg/L	Ultimate reductive daughter product, VC accumulates	3
Oxidation Reduction Potential* (ORP)	<50 millivolts (mV)	Reductive pathway possible	1
	<-100 mV	Reductive pathway likely	2
pH*	5 < pH < 9	Optimal range for reductive pathway	0
	5 > pH > 9	Outside optimal range for reductive pathway	-2
TOC	>20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	>20°C	At T>20°C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter produce	1
Alkalinity	>2x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	>0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX*	>0.1 mg/L	Carbon and energy source; drive dechlorination	2
PCE*		Material Released	0
TCE*		Material Released	0
		Daughter product of PCE	2[a/]
DCE*		Material Released	0
		Daughter product of TCE	2[a/]
		If cis is greater than 80 percent of total DCE it is likely a daughter product of TCE	
VC*		Material Released	0
		Daughter product of DCE	2[a/]
Ethene/Ethane	>0.01 mg/L	Daughter product of VC/ethene	2
	>0.1 mg/L		3
Chloroethane*		Daughter product of VC under reducing conditions	2
1,1,1-Trichloroethane*		Material released	0
1,2-dichlorobenzene*		Material released	0
1,3-dichlorobenzene*		Material released	0
1,4-dichlorobenzene*		Material released	0
chlorobenzene*		Material released or daughter product of dichlorobenzene	2[a/]
1,1-DCE*		Daughter product of TCE or chemical reaction of 1,1,1-TCA	2[a/]

*Required analysis

[a/] Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

The sixth and final step is to evaluate whether the screening criteria are met. AFCEE protocol simplifies this evaluation with the following questions:

- Has the plume moved a shorter distance than expected based on the time since the contaminant was released and the velocity of contaminant migration in groundwater?
- Is natural attenuation likely occurring at a rate sufficient to stabilize the plume?

If the answers to these questions are "yes," a full-scale demonstration of natural attenuation is appropriate.

4.4 Additional Site Characterization

Data gaps identified during the data review, the revision of the conceptual site model, and the initial screening must be filled by additional site characterization. This characterization has two main objectives: (1) collect sufficient site-specific data to determine whether natural attenuation occurs at a rate sufficient to prevent contaminant migration; and (2) collect data to support solute fate and transport modeling in order to estimate future extent and concentrations of the contaminant plume.

The NAAW will specify the field investigation that will be conducted to support the natural attenuation assessment. This investigation will fill data gaps, as necessary, so that the data described above are available for the evaluation. All site characterization must be accomplished in accordance with Standard Operating Procedures previously approved for the RIs. Sample Quality Assurance/Quality Control and laboratory analysis procedures must comply with the IRP Analytical Quality Assurance Project Plan for RD/RA, Long-Term Monitoring, and Long Term Operation Programs (Radian, 1996a). Appendix A presents an amendment to the QAPP that applies to certain natural attenuation analyses. The following section is based on the AFCEE Guidance (Wiedemeier et al., 1996).

4.4.1 Soil Characterization

Soil characterization is necessary to define the subsurface geologic system and may be necessary to delineate the distribution of NAPL that could act as a continuing source of groundwater contamination. Extensive soil characterization has already been completed at most sites at Travis AFB as part of previous IRP investigations and the RI. In addition, VOC concentrations at sites designated for natural attenuation are sufficiently low to argue against the likelihood of extensive NAPL in source areas, although residual NAPL may be present. However, investigators may uncover important data gaps that must be filled during the natural attenuation assessment.

Soil characterization may be accomplished through the use of conventional soil borings or direct-push methods such as Geoprobe or cone penetrometer testing (CPT). Usually, soil characterization may be accomplished simultaneously with other activities. For example, geologic data gaps may often be filled during the construction of additional monitoring wells, if these are necessary. Geologic data and bedrock delineation may be collected during a CPT investigation to confirm the extent of contamination. Soil gas sampling is a good method to help define source areas.

The analytical protocol for soil and soil gas sampling includes the parameters necessary to document natural attenuation. Analytical methods, sample containers, preservation, and holding times are provided in the QAPP (Radian, 1996a). Samples should be analyzed for the following parameters:

- **Volatile Organic Compounds.** For soil samples, VOC sampling provides knowledge of the location, distribution, concentration, and total mass of chlorinated and fuel (aromatic) hydrocarbons sorbed to soils or present as mobile or immobile NAPL. This information is necessary to calculate contaminant partitioning from the NAPL to groundwater, and to support remedial decisionmaking. For soil gas samples, VOC sampling helps estimate the extent of soil contamination.
- **Total Organic Carbon.** Knowledge of the TOC content of the aquifer matrix supports sorption and retardation calculations. Soil samples should be collected on a one-time basis from the stratigraphic horizon where contaminant transport is expected, such as in the screened interval of monitoring wells.
- **Oxygen and Carbon Dioxide.** These parameters should be collected and analyzed in the field during soil gas sampling to identify areas in the vadose zone where biodegradation occurs and to help identify source areas.

4.4.2 Groundwater Geochemical Characterization

Groundwater sampling should be conducted to determine the concentrations and distributions of contaminants, daughter products, and groundwater geochemical parameters. As discussed in Section 2, biodegradation of organic compounds brings about measurable changes in the chemistry of the groundwater in the affected area. Measuring these changes allows documentation of the significance of natural attenuation at a site.

In-situ groundwater samples collected with point-source sampling equipment such as Geoprobe, hydropunch, or CPT, are useful for characterizing the extent of contamination. Once the extent of contamination is known, monitoring wells should be constructed (if necessary) and sampled.

Monitoring wells should be located to track the changes in groundwater chemistry. A minimum of six locations is necessary, as shown in Figure 4-1. These include a background well, a well within the source area, two wells downgradient from the source area but within the plume of contamination, and at least two wells to define the downgradient extent of contamination. Additional wells may be necessary in larger plumes. Finally, if the extent of contamination is known, trigger and point-of-compliance wells should be selected and constructed if necessary.

The analytical protocol for groundwater sampling includes the parameters necessary to delineate dissolved contamination, support groundwater modeling, and document natural attenuation, including the effects of sorption and biodegradation. Analytical methods, sample containers, sample preservation, and sample holding times are provided in the QAPP or in Appendix A. A well purging and groundwater sampling approach that is best-suited for the collection of samples for natural attenuation analyses is presented in Appendix B. This sampling methodology should be regarded as an amendment to existing groundwater sampling SOPs at Travis AFB.

The following parameters will be addressed in the groundwater sampling program:

- **Volatile Organic Compounds.** These analytes are used to evaluate the type, concentration, and distribution of contaminants and daughter products in the aquifer. The analysis (SW8260) provides data on both chlorinated and aromatic hydrocarbons. Samples should be analyzed for VOCs at the laboratory in each sample round.
- **Dissolved Oxygen.** DO is the most thermodynamically favored electron acceptor used by microbes for the biodegradation of organic carbon. During aerobic respiration, DO concentrations will gradually decrease. Anaerobic microbes begin to function at DO concentrations of about 0.5 mg/L and less, and reductive dehalogenation begins at that point. After the DO is depleted, anaerobic microbes will use nitrate as an electron acceptor, followed by ferric iron, sulfate, and finally carbon dioxide. Measurements of DO therefore indicate how favorable conditions are to biodegradation, whether aerobic or anaerobic. Measurements should be collected in the field during and after purging using a direct-reading meter. Well purging can cause aeration of samples, thereby affecting the DO measurements. Appendix B provides a groundwater sampling protocol that minimizes the aeration of water samples
- **Nitrate.** Nitrate may be used as an electron acceptor for the anaerobic biodegradation of organic carbon through denitrification. For reductive dehalogenation to occur, nitrate concentrations in the zone of contamination must be less than about 1 mg/L. Nitrate samples should be collected each sampling round and analyzed at the laboratory (Method E300).
- **Ferrous Iron (Iron II).** Following the depletion of nitrate, ferric iron (iron III) may be used as an electron acceptor. During this process, the iron III is reduced to iron II. Concentrations of iron II in the water may indicate the anaerobic degradation of fuel hydrocarbons or vinyl chloride. Iron II samples should be collected each sampling round. Samples may be analyzed in the field using a Colorimetric Hach test kit and a spectrophotometer.
- **Sulfate.** After DO and nitrate have been depleted, sulfate may be used as an electron acceptor for anaerobic biodegradation. Sulfate reduction produces sulfide. Concentrations of sulfate in groundwater greater than 20 mg/L may cause the competitive exclusion of dechlorination. Sulfate samples should be collected each sampling round and may be analyzed either in the laboratory or in the field using a colorimetric Hach test kit.
- **Methane, Ethane, Ethene.** During methanogenesis, acetate is broken down to form carbon dioxide and methane, or carbon dioxide is used as an electron acceptor and is reduced to methane. Methanogenesis generally occurs after oxygen, nitrate, and sulfate have been depleted and indicates strongly reducing conditions. If methane is present above background with fuel contaminants, the fuel is likely undergoing microbial degradation. Ethane and ethene are ultimate breakdown products of reductive dehalogenation. Groundwater samples should be analyzed for methane, ethane, and ethene during each sampling round at the laboratory (Method SW3810).
- **Alkalinity.** Alkalinity is measure of groundwater's buffering capacity, or capacity to neutralize acid. Alkalinity is important in the maintenance of groundwater pH and

buffers the system against acids generated during aerobic and anaerobic biodegradation. Alkalinity is defined as the net concentration of strong base in excess of strong acid and results from the presence of hydroxides, carbonates, and bicarbonates. These species result from natural mechanisms, including the respiration of microorganisms. Alkalinity measurements should be taken in the field using a Hach test kit during each sampling round. After the groundwater geochemical profile is established, alkalinity measurements may be discontinued.

- **Oxidation-Reduction Potential.** The ORP indicates the relative tendency of a solution to accept or transfer electrons. The ORP of groundwater generally ranges from about -400 millivolts to +800 millivolts, and depends and influences the rate of biodegradation of organic compounds. Some biological processes only occur within a prescribed range of ORP. These measurements provide useful information on the location of the contaminant plume, particularly portions undergoing anaerobic biodegradation. ORP measurements should be taken each sampling round, in upgradient and downgradient wells, and during and following purging. Measurements should be taken in the field using a direct-reading meter. Appendix B describes purging and measurement techniques that should be used when measuring ORP.

- **pH, Temperature, and Conductivity.** The pH of the groundwater affects the presence and activity of the microorganisms, with most aerobic and anaerobic biodegradation taking place in a range of 6 to 8 standard units. Temperature affects the solubility of oxygen, with oxygen being more soluble in cold water than in warm water. Temperature also affects the rates of hydrocarbon biodegradation, with rates doubling for each 10° C increase between 5° C and 25° C. Conductivity, the measure of the ability of the solution to conduct electricity, is directly related to the concentration of ions in the solution. These parameters are also used during purging to indicate when formation water has been obtained for sampling. Direct-reading measurements should be taken in the field during each sampling round.

- **Chloride.** Chloride is released into the groundwater during biodegradation of chlorinated hydrocarbons, resulting in elevated chloride concentrations in the contaminant plume relative to background conditions. Chloride samples should be collected in each well during every sample round and analyzed at the laboratory (Method E300). If background chloride concentrations are high, this method may be discontinued.

- **Total Organic Carbon.** TOC analyses indicate the supply of carbon electron donors within the hydrogeologic system in the absence of anthropogenic carbon such as fuels. Samples should be collected for TOC analyses during each sampling round and analyzed in the laboratory. However, if anthropogenic carbon sources compose most of the TOC, and are quantified separately, then TOC analyses may be discontined.

4.4.3 Aquifer Characterization

Geologic data collected during drilling at the site will provide useful information on the heterogeneity, anisotropy, and effective porosity of the system, and help to identify preferential pathways for groundwater flow. These data should be collected through continuous coring with a hollow-stem auger rig, or from CPT tests.

Aquifer parameters are used to estimate the direction and velocity of groundwater flow, and are necessary as inputs to fate and transport modeling. The two main aquifer parameters that should be measured are the hydraulic conductivity and the hydraulic gradient. Aquifer pumping tests are the best way to measure hydraulic conductivity. Tests should be performed in wells that are screened in the most transmissive zone of the aquifer, and measurements made during both the drawdown and recovery phases of the test. Water levels should also be monitored during the test in nearby wells, if possible. Subject to budget limitations and the limitations of storing the discharged groundwater for disposal at the SS016 treatment facility, longer tests provide better data than shorter tests. Slug tests provide much less reliable data and should not be used to measure hydraulic conductivity unless there is no alternative.

The hydraulic gradient is derived by measuring groundwater elevations in each of the monitoring wells screened in the same interval at the site. Wellheads should be surveyed by professional surveyors, with vertical wellhead elevations within 0.001 foot. Depth-to-groundwater measurements should be collected for all wells at the site during the same day, if at all possible. To determine the potential effect of seasonal variations in groundwater flow direction on contaminant transport, quarterly groundwater level measurements should be collected for a full year. These data should be available at most sites at Travis AFB.

4.5 Schedule and Staffing

The NAAW will include a schedule for completing the natural attenuation assessment, taking into account that the workplan and the NAAR are both primary documents. In addition, it will identify key project staff, their roles on the project, and their interrelationships.

5.0 Natural Attenuation Assessment Report

To support remediation by natural attenuation, Travis AFB must demonstrate that attenuation of site contaminants occurs at a rate sufficient to stabilize the plume and to prevent contaminant concentrations at point-of-compliance wells from exceeding cleanup goals. The NAAR will present the evidence for natural attenuation and recommend whether it should be selected as a final remedy for the site. The report, a primary document as defined in the FFA, will undergo review by regulatory agencies and the public. This section summarizes the contents of the NAAR and discusses the evaluation that will lead to a conclusion for the site. Details of the evaluation are taken from AFCEE guidance (Wiedemeier et al., 1996).

5.1 Summary of the Field Investigation

Work performed during the field investigation will be summarized in the NAAR. If there were any deviations from the sample design presented in the NAAW, these will be noted with an explanation for the variance.

Data will also be provided, but in the form of data summaries. Raw data will be included in appendices. For example, appendices may contain laboratory data, field data (including soil gas results, field analyses performed on groundwater samples, and instrument direct-reading measurements), lithologic logs, well construction diagrams, aquifer testing data, geodetic survey data, and groundwater level survey data.

5.2 Update of the Conceptual Site Model

Site investigation data will be used to refine the conceptual site model and quantify groundwater flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to help simulate natural attenuation over time. Conceptual site model updating involves integrating newly gathered site characterization data to refine the model that was developed on the basis of previously collected site data. Available site-specific data will be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This refined conceptual site model will then be used for contaminant fate and transport modeling. The NAAR will contain the elements described in the following sections.

5.2.1 Geologic Logs

Geologic logs of all subsurface materials encountered during the soil boring phase of the field work will be constructed. Descriptions of the subsurface geology will follow the procedures outlined in ASTM D 2487 (Standard Practice for Description and Identification of Soils), and in existing SOPs. Wherever possible, descriptions of geologic materials will include major textural elements, color, porosity, relative moisture content, plasticity of fines, grain size, structure or stratification, visible contamination, and odor. Soil samples will also be collected in the field for VOC headspace analysis, and results reported on the log.

5.2.2 Hydrogeologic Cross Sections

Hydrogeologic cross sections will be prepared from boring logs or CPT data. At least two cross sections will be prepared: one parallel to the direction of groundwater flow, and one perpendicular to the direction of flow. Potentiometric surface or water table elevation data will also be plotted on the cross section. Cross sections will help locate potential preferential contaminant migration pathways and support the simulation of contaminant transport using solute fate and transport models.

5.2.3 Groundwater Contour Maps

Groundwater contour maps will be prepared from water level measurements and surveyors' data. The maps will be used to estimate the probable direction of plume migration and to calculate hydraulic gradients. Water level data used in the construction of the maps will be taken from wells screened in the same position, and within the same geologic unit if possible. Separate maps will be prepared for different horizons in the aquifer to document vertical variations in groundwater flow.

At Travis AFB, the saturated zone above the bedrock is relatively thin, so these maps will usually be prepared from "shallow" wells screened at or near the water table, and from "deep" wells screened just above the bedrock, if there are three or more of these deep wells at the site. In addition, vertical gradients should be calculated from groundwater elevation data taken from shallow and deep monitoring well pairs. This calculation will indicate whether there is a consistent vertical gradient either upward or downward at the site. Groundwater contour maps prepared as part of the GSAP will be reviewed to identify discrepancies between the contours prepared for the natural attenuation assessment and contours prepared for the GSAP.

5.2.4 Contaminant and Geochemical Contour Maps

Contaminant and daughter product contour maps will be prepared for the contaminants present at the site. These maps allow interpretation of the data distribution and the relative transport and degradation rates of contaminants. Contaminant contour maps may also be used for input into a numerical transport model. Daughter products such as cis-1,2-DCE and vinyl chloride provide evidence for reductive dechlorination.

Contour maps will also be prepared for electron acceptors, if possible, including DO, nitrate, and sulfate. Because DO concentrations will decrease downgradient during aerobic biodegradation, and nitrate and sulfate concentrations will decrease during anaerobic biodegradation, the contour maps will provide visible evidence of biodegradation. They also facilitate the interpretation of data based on the distribution of the electron acceptors and the degradation rates of contaminants in the subsurface, and show the relationship between the contaminant plume and the metabolic byproducts.

5.3 Results of Groundwater Modeling

Groundwater modeling will be performed to predict the movement of the plume, and to provide evidence that the plume is stable and that natural attenuation will remediate the contamination. The NAAR will present the results of calculations made prior to modeling, as well as the results of the modeling.

5.3.1 Pre-Modeling Calculations

Three main calculations will be made prior to modeling. These include sorption and retardation calculations, groundwater flow velocity calculations, and biodegradation rate-constant calculations. If NAPL remains at the site, NAPL/water partitioning calculations will be made to account for the partitioning from this phase into groundwater. However, Dense NAPL is not expected to be present at Travis AFB sites undergoing natural attenuation assessment. If Light NAPL (LNAPL) is found, then remediation will likely include the removal of the LNAPL. A brief description of the calculations follows:

- **Sorption and Retardation Calculations.** Sorption and retardation calculations will be made based on the TOC content of the aquifer matrix and the organic carbon partitioning coefficient for each contaminant. The average TOC concentration from the most transmissive zone of the aquifer will be used for the calculations. However, a sensitivity analysis will be performed during modeling using a range of TOC concentrations, including the lowest TOC concentration measured at the site.
- **Groundwater Flow Velocity Calculations.** The average linear groundwater flow velocity will be calculated to check the accuracy of the fate and transport model and to allow calculation of first-order biodegradation rate constants. The flow velocity is calculated using Darcy's Law.
- **Biodegradation Rate Constant Calculations.** Biodegradation rate constants are needed to simulate the transport of contaminants in groundwater. These calculations include separating the effects of dilution, sorption, and volatilization from biodegradation. AFCEE guidance provides two methods for calculating biodegradation rate constants.

5.3.2 Fate and Transport Modeling

Fate and transport modeling allows prediction of the migration and attenuation of the contaminant plume through time, under physical and chemical conditions documented at the site. As such, it is a useful tool to draw conclusions regarding the ability of natural attenuation processes to remediate the contamination at a site. Modeling can also be used to evaluate the influence of groundwater extraction at adjacent sites, and to evaluate natural attenuation in conjunction with other remedial actions such as source removal. As noted in Section 3, the groundwater flow system will be modeled using Micro-Fem, while solute transport will be modeled using BIOSCREEN or another comparable model. Use of models other than Micro-Fem or BIOSCREEN will be documented in the NAAW.

5.4 Conclusions and Recommendations

Based on the data collected during the field investigation, the updated conceptual site model, and the groundwater modeling, the NAAR will determine whether natural attenuation occurs at the site at a rate sufficient to prevent contamination from migrating to point-of-compliance wells at concentrations above IRGs. If so, natural attenuation will be selected as the preferred remedy for the site. If natural attenuation is not sufficient to remediate the site, the report will evaluate whether natural attenuation is appropriate for some portion of the site, e.g., in combination with source control or groundwater extraction and treatment.

As described in Section 2.2, the following elements will demonstrate that natural attenuation should be selected:

- Observed reductions in contaminant mass along the flow path downgradient from the source area
- A convincing presentation of geochemical data, including such components as decreasing parent compound concentrations, increasing daughter compound concentrations, depletion of electron acceptors and donors, and increasing metabolic by-product concentrations
- A rigorous estimate of residence time along the flow path documenting contaminant mass reduction and calculating biological decay rates

5.5 Monitoring Plan

The NAAR will include a long-term monitoring plan to verify the effectiveness of natural attenuation over time. The monitoring, part of the GSAP, will include trigger wells and point-of-compliance wells. If these wells are not in place at the end of the natural attenuation assessment, the monitoring plan will specify locations and construction details for the wells.

6.0 References

(in progress)

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Appendix A—RD/RA QAPP Addendum

Appendix A—RD/RA QAPP Addendum

The following methods will be used to characterize samples collected during the natural attenuation investigations at Travis Air Force Base. These alternate methods are not included in the IRP Analytical Quality Assurance Project Plan (QAPP) for Remedial Design/Remedial Action and Long Term Operation Programs (Radian, 1996). Tables A-1 through A-6 provide the project-specific measurement quality objectives (MQOs) for each method.

A.1 Determinative Methods

Method E376 Total Sulfides (acid soluble + acid insoluble). This method is suitable for the determination of total sulfides. Under acidic conditions, the sample is heated and hydrogen sulfide is distilled and carried to scrubbing bottles containing zinc. The subsequent zinc sulfide precipitate is oxidized to sulfur with a known volume of excess iodine. The excess iodine is determined by titration with sodium thiosulfate. Quantitation is based on sodium thiosulfate. The QC criteria are defined in Tables A-1 through A-3.

Method SW3810M Methane, Ethene, and Ethane (modified). This method is applicable to the preparation of water samples for analysis of generated headspace. The quantification of methane at part-per-billion levels is determined by gas chromatography/flame ionization detector and is based upon equilibration techniques employing the Henry's Law relationship. A copy of the standard operating procedure is included as an attachment to this appendix. The QC criteria are defined in Tables A-1 through A-3.

A.2 Field Screening Methods

Hach Method 8146 Ferrous Iron. This method has been developed by Hach and is defined in the Water Analysis Handbook 3RD Edition (July 1997). The DR2000 spectrophotometer, method reagents, sample containers and necessary equipment are provided by Hach in a ready to use field kit. This method is suitable for the analysis of ferrous iron in water samples by colorimetry within an analytical range of 0-10 mg/L. A phenanthroline indicator in a ferrous iron reagent reacts with the ferrous iron in the sample to form an orange color proportional to the concentration of ferrous iron in the sample. The ferrous iron concentration in the sample is measured by the change in absorbance measured at 510 nm wavelength.

Hach Method Carbon Dioxide. This field method has been developed by Hach for a quick colorimetric determination of carbon dioxide concentration in a water sample. The method reagents and necessary equipment are provided by Hach in a ready-to-use field kit. This method is suitable for the analysis of carbon dioxide in water samples by colorimetry within an low, medium, and high analytical range (by difference in sample volume). A phenolphthalein indicator in the water sample changes to a pink color proportional to the concentration of carbon dioxide as sodium hydroxide is added to the water sample. The carbon dioxide concentration in the sample is quantified by the number of added sodium hydroxide drops.

Table A-1
Precision and Accuracy
Criteria for General Chemistry and Miscellaneous Methods

		Spikes			
		Water		Soil	
Method	Analyte	Accuracy (% Recovery)	Precision (RPD)	Accuracy (% Recovery)	Precision (RPD)
E376	Sulfide	80-120[a]	≤20[b]	NA	NA
SW3810M	Methane	80-120[c]	≤20[c]	NA	NA

Legend:
E = EPA Methods for Chemical Analysis of Water and Wastes.
SW = Methods from SW-846, 3rd edition, 1986, or subsequent updates may be used provided MQOs are met.
RPD = Relative percent difference.
NA = Not applicable.

Notes:

[a] Accuracy for sulfide is determined by evaluation of the matrix spike, matrix spike duplicate, and blank spike recoveries.

[b] Precision for sulfide is determined by evaluation of matrix spikes and matrix spike duplicates.

[c] Precision and accuracy for methane is determined by evaluation of laboratory control samples, laboratory control sample duplicates, and laboratory duplicates.

Table A-2
Practical Quantitation Limits

		PQL
Analytes	Method	Water (mg/L)
Sulfide	E376	2
Methane	SW3810M (Modified)	1

Legend:
E = EPA Methods for Chemical Analysis of Water and Wastes.
PQL = Practical quantitation limit.
SW = Methods from SW-846, Third Edition, 1986, or subsequent updates may be used provided MQOs are met.
mg/L = Milligram per liter.

Table A-3
Sample Storage and Preservation Requirements

Reference Parameter	Method	Holding Time	Container/Minimum Sample Volume	Preservation	Storage Requirements
Sulfide	E376	7 days	500 ml polyethylene	Zn(Ac)$_2$ + NaOH [a]	4°C
Methane	SW3810M (Mod)	7 days	2 x 40 ml VOA Vials	None	4°C

ml = milliliter
VOA = Volatile organic analyte
[a] Zinc acetate and sodium hydroxide

Table A-4
Summary of Calibration and Internal Quality Control Procedures for SW3810M (Methane)

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action*
SW3810M (Modified)	Methane	Initial Calibration	Prior to sample analysis when continuing calibration verification fails to meet criteria	$R^2 \geq 0.995$ Calibration must meet calibration criteria prior to sample analysis.	1)Repeat calibration. 2)If still out, stop, identify and correct problem before proceeding.
		Continuing Calibration Verification (CCV)	Daily prior to sample analysis. Once per analytical batch or every 20 samples or every 12 hours whichever is more frequent.	% recovery must be within 80-120% of the true value	1)Repeat analysis of CCV. 2)If still out, identify and correct problem prior to sample analysis.
		Method Blank	Once per analytical batch or every 20 samples or every 12 hours whichever is more frequent.	No target analytes detected above the reporting limit	1)If sample analyte concentration is <PQL or if the sample analyte concentration is > 10 times the concentration in the method blank, then report results and write QCER 2)If preparative method blank does not meet item 1), re-extract/re-analyze if still within HT and enough sample volume; if not within HT or enough sample, contact project QA officer for decision.
		Laboratory control sample (LCS) Laboratory control sample Duplicate (LCSD)	Once per analytical batch or every 20 samples or every 12 hours whichever is more frequent.	80 - 120% recovery RPD ≤ 20%	1)If the preparative LCS recovers high outside the acceptance criteria and the analyte is ND, flag the LCS results and write a QCER. 2)If the preparative LCS fails the acceptance criteria (other than shown in item

Table A-4
Summary of Calibration and Internal Quality Control Procedures for SW3810M (Methane)

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action[a]
					1), re-extraction and reanalysis will be necessary if samples are still within holding time and enough sample volume; if not, contact the project QA officer for a decision for possible resampling. 3) If RPD criteria is exceeded, flag all data in the analytical batch.
		Duplicate	Once per analytical batch or every 20 samples or every 12 hours whichever is more frequent.	RPD £ 20	If RPD criteria is exceeded, flag all data in the analytical batch as estimated values.
		Equipment blank	See Field Sampling Plan	< PQL (Practical Quantitation Limits)	Immediately notify project QA officer or field chemist so they can correct sampling or sample transfer procedures to eliminate contamination.[b]
		Temperature blank	Every cooler	4°C ± 2°C	Immediately notify project QA officer or field chemist so they can modify sample packing and/or preservation procedures; recollect samples if necessary.
		Field duplicate	See Field Sampling Plan	RPD £ 50	Project chemist will evaluate results for possible source of variability; notify data users.

[a] All corrective actions associated with Travis project work shall be documented and the records maintained by the laboratory, as specified in the IRP Handbook, September 1993.

[b] If equipment blank is submitted to the laboratory blind, the corrective action is not applicable.

Table A-5
Summary of Calibration and Internal Quality Control Procedures for E376 (Sulfide)

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action[a]
E376	Sulfide	Titrant standardization	Daily (prior to sample analysis)	Percent difference ≤ 5	Repeat standardization.
		Method blank	1 per analytical batch and 1 per each 20 samples.	< PQL (Practical Quantitation Limits)	1) If sample analyte concentration is <PQL or if the sample analyte concentration is > 10 times the concentration in the method blank, then report results and write QCER 2) If preparative method blank does not meet item 1), re-extract/re-analyze if still within HT and enough sample volume; if not within HT or enough sample, contact project QA officer for decision.
		Matrix Spike/Matrix Spike Duplicate	1 per analytical batch and 1 per each 20 samples.	80-120% recovery RPD £ 20	1) If the preparative matrix spikes recover high outside of the acceptance criteria and the analyte is ND, flag the spike results and write a QCER. 2) If the preparative matrix spikes fail the acceptance criteria (other than shown in item 1), re-analysis will be necessary if samples are still within holding time and enough sample volume remains; If not, contact the QA Officer for a decision regarding possible resampling. 3) If the RPD criteria is exceeded, Flag all data from sample site.
		Equipment blank	See Field Sampling Plan	< PQL	Immediately notify project QA officer or field chemist so they can correct sampling or sample transfer procedures to eliminate contamination.[b]

Table A-5
Summary of Calibration and Internal Quality Control Procedures for E376 (Sulfide)

Analytical Method	Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action[a]
E376 (cont.)		Temperature blank	Every cooler	4°C ± 2°C	Immediately notify project QA officer or field chemist so they can modify sample packing and/or preservation procedures; recollect samples if necessary.
		Field duplicate	See Field Sampling Plan	RPD £ 50	Project chemist will evaluate results for possible source of variability; notify data users.

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[a] All corrective actions associated with Travis project work shall be documented and the records maintained by the laboratory, as specified in the IRP Handbook, September 1993.

[b] If equipment blank is submitted to the laboratory blind, the corrective action is not applicable.

Table A-6
Summary of Calibration and Internal Quality Control Procedures for Field Measurements

Analytical Method	Applicable Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action[a]
HACH 8146 (0-10 mg/L)	Ferrous Iron	Initial calibration	Once per day and once per new lot of reagent.	$R^2 \geq 0.990$	If calibration is not achieved, check photometer and standard solutions. Replace if necessary.
		Accuracy check std	Once per analytical batch	±20%	Recalibrate.
		Field duplicate	10% of field samples	±50%	Evaluate results for possible source of variability; repeat measurement.

[a] All corrective actions associated with Travis project work shall be documented and the records maintained by the laboratory, as specified in the IRP Handbook, September 1993.

Attachment

Standard Operating Procedure for

METHANE, ETHANE, AND ETHENE IN WATER BY GC-FID WITH HEADSPACE GENERATION

SW3810M

Prepared by:

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Approved by:

Organics Supervisor Date

Laboratory QA/QC Coordinator Date

April 1997
Revision 1.0

METHANE, ETHANE, AND ETHENE IN WATER BY GC-FID WITH HEADSPACE GENERATION

1.0 Scope and Application

This method is applicable to the preparation of water samples for analysis of the headspace to quantify part-per-billion levels of dissolved methane, ethane, and ethene in water samples, by an equilibration technique utilizing the Henry's Law relationship.

Henry's law states that the equilibrium value of the mole fraction of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface, or $x = p/H$, where p = equilibrium partial pressure of gas, x = mole fraction of dissolved gas, H = Henry's law constant. Henry's law is applicable at low concentrations and low partial pressures of a gas at or below one atmosphere pressure. Solubility data can be obtained from technical handbooks relating H values to temperature.

Procedures are based on *Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique* by D.H. Kampbell and J.T. Wilson, found in *International Journal of Environmental Analytical Chemistry, Vol. 36, pgs. 249-257.* Specific techniques have been developed and customized to the CH2M HILL Applied Sciences Laboratory in Corvallis, Oregon.

2.0 Target Analytes and Detection Limits

2.1

Analyte	CAS Number	Analytical MRL (ppm in headspace)	Typical Sample MRL† (ppb in sample)
Methane	74-82-8	1	0.28
Ethane	74-84-0	1	0.76
Ethene	74-85-1	1	0.84

† Sample MRL depends on the volume of headspace generated.

3.0 Summary of Method

A water sample is collected, in the field or in the laboratory, in a borosilicate glass headspace vial with aluminum seals and Teflon faced butyl rubber septa. A headspace is prepared using high purity helium. The bottle is shaken for several minutes and a sample is taken from the headspace and injected onto a gas chromatographic column. Once on the column, the gaseous components are separated and detected by a flame ionization detector (GC/FID). By using Henry's law, the concentration of the gas in the headspace, the bottle volume, and temperature of the sample, the concentration of dissolved gas in the original water sample can be determined.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in glassware and gases. A method blank must be analyzed with every batch to demonstrate there is no interference due to the syringe and helium, see (10.3.1).

4.2 During the headspace generation procedure, see (11.1), helium gas should be allowed to flow through the Teflon tubing and purge needle prior to preparation of samples.

4.3 The sample syringe should be flushed with helium between chromatographic injections.

4.4 Compounds that closely match the chromatographic retention times of the target analytes may result in false identification and/or cause a positive bias in the results.

5.0 Safety

All normal laboratory safety procedures should be followed at all times. This includes proper safety clothing, handling of combustible gases, handling of needles, etc.

6.0 Sample Collection, Preservation, and Storage

6.1 Grab samples must be collected in accordance with conventional sampling practices, using borosilicate glass headspace vials with aluminum seals and Teflon faced butyl rubber septa. Clear, 40-mL capacity vials are recommended. Use sample containers that are pre-cleaned by vendor and identified as being specific for organic parameters.

6.1.1 Sampling containers and samples should not be preserved

6.1.2 In the field, open the sample vial, set the cap in a clean place and collect the sample. Each sample should be collected in duplicate.

6.1.3 Fill the vials to just overflowing. Do not rinse the vials, There should be a convex meniscus on the top of the vials.

6.1.4 Place the cap directly over the top of the vial and screw down firmly. Do not over-tighten because the cap or the sample vial could break.

6.1.5 Invert the vial gently. Look for air bubbles. If air bubbles appear, discard the sample and refill.

6.1.6 Each field sample must be labeled with sample date, monitoring well information, sample number, and initials of the person collecting the sample.

6.1.7 Put the headspace vial in the vial container and place in a sample cooler. Ice the cooler and transport to laboratory for analysis.

6.2 Samples must be refrigerated at 4°C and in a light-free environment until extraction. Technical holding time requirements are not available for this analysis.

7.0 Apparatus and Materials

7.1 Analytical balance, capable of measuring ±0.0001 g.

7.2 Gas chromatograph --
Hewlett Packard GC-5890, Series II. Equipped with flame ionization detector, splitless injection capability, temperature programming, and Microsoft-Windows compatible HP-ChemStation programming.

7.2.1 Column --
SPB-1 (Supelco), fused silica, 30 m × 0.53 mm ID, 5.0 μm film thickness.

7.2.2 Liquid Nitrogen for Cryogenic Program

7.3 Needles

7.4 pH paper

7.5 Syringes, gas-tight

7.6 Teflon tubing

7.5 Borosilicate glass headspace vials with aluminum seals and Teflon faced butyl rubber septa (40 mL recommended)

8.0 Gases and Consumable Materials

8.1 Helium gas -- Grade 5

8.2 Methane gas standards

8.2.1 100 ppm Methane in Helium (Instrument Services)

8.2.2 998 ppm Methane in Nitrogen (Scott Specialty Gases)

8.2.3 4.00% Methane in Helium (Scott Specialty Gases)

8.2.4 1.00% Methane in Helium (Pacific Airgas)

8.3 Ethane gas standards

8.3.1 998 ppm Ethane in Nitrogen (Scott Specialty Gases)

8.3.2 1.01% Ethane in Nitrogen (Scott Specialty Gases)

8.4 Ethene gas standards

8.4.1 15.5 ppm Ethene in Nitrogen (Scott Specialty Gases)

8.4.2 1.01% Ethene in Nitrogen (Scott Specialty Gases)

9.0 Standards

Commercially available prepared methane, ethane, and ethene gas standards are used. Standards are certified by the manufacturer as to content and concentration of analyte. Standards with different lot numbers are used if standards are from the same manufacturer.

10.0 Quality Assurance

10.1 Before using this method, laboratory capability must be demonstrated by analyzing replicate samples. Seven replicates at 1.0 ppmv must be analyzed to establish the method detection limit (MDL). A calculated MDL is determined annually in order to demonstrate laboratory capability meets or exceeds reporting limit for method, see attached (Table 1).

10.1.1 Calculate the variance and standard deviation of the seven replicate samples, [Equations 1 & 2]:

$$S^2 = (1/6) \times [\Sigma x_i^2 - (\Sigma x_i)^2 / 7] \qquad \text{Equation 1}$$

$$S = (S^2)^{1/2} \qquad \text{Equation 2}$$

where:

S^2 = variance
x_i = analyte concentration is sample
S = standard deviation

10.1.2 Calculate the MDL, [Equation 3]:

$$MDL = 3.143 \times S \qquad \text{Equation 3}$$

where:

MDL = method detection limit
S = standard deviation

10.2 Initial calibration

10.2.1 The initial calibration curve is based on the linear fit of the calibration standard responses. By utilizing the least squares method of linear regression on all the standard points, a "best-fit" line is generated and serves as the calibration curve. The origin is included as a standard point for calculation purposes, [Equations 4-6]:

$$m = \frac{2\Sigma(X_iY_i) - \Sigma X_i \Sigma Y_i}{2\Sigma(X_i)^2 - (\Sigma X_i)^2} \qquad \text{Equation 4}$$

$$b = \frac{\Sigma(X_i)^2 \Sigma Y_i - \Sigma X_i \Sigma(X_iY_i)}{2\Sigma(X_i)^2 - (\Sigma X_i)^2} \qquad \text{Equation 5}$$

$$y = mx_a + b \qquad \text{Equation 6}$$

where:

m = slope
X_i = calibration standard concentration
Y_i = calibration standard peak area
b = y-intercept
y = area
x_a = concentration of analyte

10.2.2 A common measure of the "best-fit" line is called R^2. This value represents how well the data points "fit" the regression line. If R^2-values are <0.995, then the initial calibration must be redone. However, if there is one point that seems to be the problem, then this point is deleted from the calibration table and R^2 is recalculated.

10.3 Quality control measures

10.3.1 Method blank or purge blank --
A method blank is defined as a reagent water sample in which a helium headspace is generated, and the headspace is analyzed with each batch of samples. A method blank must be analyzed for every batch of samples, to a maximum of 20 samples, or analyzed once every 12 hours, whichever comes first. For each additional 20 or fewer samples, another method blank must be analyzed. Target analyte concentration in the method blank must be below the reporting limit.

10.3.2 Calibration check or continuing calibration --
A calibration check is defined as a standard used to verify quantitation. A calibration check must be analyzed for every batch of samples, to a maximum of 20 samples, or analyzed once every 12 hours, whichever comes first. For each additional 20 or fewer samples, another calibration check must be analyzed. Analyte recovery for a calibration check must not be <80% or >120% of the standard.

10.3.3 Laboratory control sample --
A laboratory control sample (LCS) is defined as a standard from a secondary source used to verify quantitation. A LCS must be analyzed for every batch of samples, to a maximum of 20 samples, or analyzed once every 12 hours, whichever comes first. Typically, a laboratory control sample duplicate (LCSD) is also analyzed for every batch of samples, to a maximum of 20 samples, or analyzed once every 12 hours, whichever comes first. For each additional 20 or fewer samples, another LCS/LCSD must be analyzed. Analyte recovery for a LCS/LCSD must not be <80% or >120% of the standard, and relative percent deviation (RPD) between the LCSD and LCS must not be >20%, [Equation 7]:

$$\text{RPD} = \frac{|X_{LCSD} - X_{LCS}|}{X_{LCSD} + X_{LCS}} \times 200 \qquad \text{Equation 7}$$

where:

X_{LCSD} = analyte concentration in laboratory control sample duplicate
X_{LCS} = analyzed concentration in laboratory control sample.

10.3.4 Duplicate --
A duplicate is defined as a replicate sample that is prepared and analyzed with each batch of samples. A duplicate must be prepared and analyzed for every batch of samples, to a maximum of 20 samples. For each additional 20 or fewer samples, another duplicate must be prepared and analyzed. Relative percent deviation (RPD) between the duplicate and sample must not be >20%, [Equation 8]:

$$\text{RPD} = \frac{|X_d - X_s|}{X_d + X_s} \times 200 \qquad \text{Equation 8}$$

where:

X_d = analyte concentration in duplicate
X_s = analyte concentration in sample

10.3.5 QA/QC Summary

QC Measure	Frequency‡	Criterion
Method blank	1/batch	<MRL
Calibration check	1/batch	80-120% recovery
LCS/LCSD	1/batch	80-120% recovery <20% RPD
Duplicate	1/batch	<20% RPD

‡ A batch of samples is defined as a group of samples, to a maximum of 20, that are to be prepared and analyzed. Method blanks, calibration checks, and etc., do not count towards the maximum of 20 samples.

10.4 If the criterion for a QC measure is not met, the following possibilities should be considered:

10.4.1 Check calculations for possible errors

10.4.2 Check chromatograms for possible peak identification and/or peak integration errors.

10.4.3 Check sample identification numbers for possible mislabeling.

10.4.4 Check other QC measures to determine if the problem is isolated to one sample or characteristic of whole analysis batch.

10.4.5 If QC measures for the batch fail (e.g. blank, calibration check) take corrective actions and reanalyze before analyzing any samples.

10.4.6 Check instrument parameters and overall instrument performance.

10.4.7 If QC measures continually fail in spite of reanalysis (e.g. calibration check, LCS), then the instrument needs to be recalibrated.

11.0 Procedure

11.1 Headspace Generation

Proprietary Information - Not included

12.0

12.1 Instrument Conditions

Proprietary Information - Not included

12.2 Qualitative analysis

12.2.1 Peak identification is based upon relative retention time comparison to the calibration standards. Retention times are established every batch of samples. A target analyte should be identified in a sample only if the chromatographic peak matches the predicted retention time within 0.1 minutes, [Equation 9]:

$$RT_{diff} = \left| RT_{std} - RT_{samp} \right| \qquad \text{Equation 9}$$

where:

RT_{diff} = difference between actual and predicted retention times
RT_{std} = analyte retention time in calibration standard
RT_{samp} = analyte retention time in sample

12.2.2 Due to the variable nature of manual air-matrix injections, the predicted retention time difference should only serve as a recommended method of peak determination. Other chromatographic features such as peak shape, peak width, resolution, interference, and distance from the landmark peaks need to be considered.

12.3 Quantitative analysis

12.3.1 The HP ChemStation software automates the quantitation process by employing the calculations found in the following paragraphs. In order to manually duplicate the software calculations, the steps and equations have been provided.

12.3.2 The HP ChemStation software automates the analytical quantitation process. Dilution factors are shown by the use of multipliers in the ChemStation program. The multiplier used here is based on a normalized injection volume of 1-mL, and calculates the value based on a 1-mL injection even if a different volume was used, [Equation 10]:

$$M = 1\text{-mL} / I \qquad \text{Equation 10}$$

where:

M = multiplier
I = sample injection volume in mL

12.4 Technical acceptance criteria

12.4.1 All specified QA/QC criteria for initial calibration, method blanks, LCS/LCSD, etc., must meet acceptance criteria, [see 10.3.5].. If there is an exception, [see 10.4], then this must be documented on the case narrative of the affected samples.

12.4.2 The target analyte concentrations must not exceed 50% of the highest calibration level. If there is an exception, then the sample is diluted to the point where the target analyte concentration will safely fall within the calibration range. This is done by injecting a smaller injection volume. Adjust the mulitplier accordingly.

12.4.3 At the GC analyst's discretion, any sample may be reanalyzed or new headspace generated. This may be done if the analyst feels that the sample results are "incorrect" or do not achieve expected values, despite positive QA/QC results.

13.0 Post-Analysis Procedures

13.1 Print chromatogram and report hard-copies for all samples.

13.2 Print sequence parameter and sample table hard-copies.

13.3 Report analytical results according to format requested on chain-of-custody or by prior agreement. Data deliverables without special considerations will follow normal CH2M Hill ASL level 1, 2, or 3 formats.

13.4 File chromatogram and report hard-copies by date. Label folder with date of analysis and test method.

13.5 File a copy of sample table with chromatograms, and file another copy in the run-log notebook.

13.6 Archive electronic data and sequence information by instrument ID and quarter/year. Also archive the methods used to generate the data.

Appendix B—FSP Addendum

STANDARD OPERATION PROCEDURE

MINIMAL AERATION
GROUNDWATER SAMPLING METHOD
FOR
GEOCHEMICAL INDICATORS
OF
NATURAL ATTENUATION

INTRODUCTION

This document presents a protocol for measurements and groundwater sampling in support of intrinsic bioremediation characterizations. This protocol was developed because of the potential adverse effects of commonly employed groundwater sampling methodology on the quality of intrinsic bioremediation data.

Naturally occurring contaminant biodegradation can result in groundwater that is in dramatic non-equilibrium with the atmosphere. Commonly employed sampling collection techniques include use of bailers and excessive rates of groundwater purging. These practices may result in exposure of the groundwater to the atmosphere and will often produce groundwater samples with a geochemistry that is different than formation groundwater. Parameters for characterization of natural attenuation are listed in Table 1. The specific mechanisms in which the geochemistry of groundwater samples can be altered through sample collection techniques include the following:

- Excessively lowering the water level in the well by purging at high flow rates. During recharge, water trickling into the well may be exposed to the atmosphere, resulting in artificial aeration of the groundwater sample, which can cause loss of volatiles, introduction of oxygen, and elevation of the sample Eh.
- Sample aeration caused by sample collection with a bailer and/or excessive exposure of the groundwater to the atmosphere during field measurements or filling of sample containers.
- Increased turbidity caused by bailing the well, or purging the well at high flow rates creating high entrance velocities through the well screen and mobilizing sediment in the well, sand pack, and formation.
- De-pressurization of samples of deep groundwater can result in super-saturation of the groundwater with certain constituents and de-gassing of the constituents from the sample. (However, this should not be a significant problem at LNAPL sites, where the groundwater zone of interest is typically the uppermost saturated interval.)

The "minimal aeration method" described in this protocol will enable collection of representative groundwater samples for characterization of intrinsic bioremediation, except at sites of very low permeability. Considerations for very low permeability settings are discussed.

Table 1. Intrinsic Bioremediation Groundwater Characterization[a]

Parameter	Objective	Method
Dissolved oxygen	Preferred electron acceptor	**SM4500-O.G (Membrane electrode)** and/or HACH Winkler Field test kit (Azide modified Winkler)
Nitrate	Electron acceptor	**SM4110/EPA 300** or SM 4500-NO_3-C
Sulfate	Electron acceptor	**SM4110/EPA300** or SM 4500-SO4-E
Ferrous iron (Fe^{2+})	Produced when ferric iron is the electron acceptor	**SM 3120B/EPA 200.7** or SM 3500-Fe-D
Methane/Carbon Dioxide	Produced when carbon dioxide or acetate is the electron acceptor	**R.S. Kerr 175** (Kampbell *et al.*, 1989)
Alkalinity (Carbonate and bicarbonate)	Indicators of contaminant mineralization	**SM 2320.B**
Oxidation/reduction potential (ORP)	Confirmation of general redox state as determined from electron acceptor chemistry	Field measurement **SM 2580-B**
pH, electrical conductance	Standard water quality parameters. Determination of pH especially important	Field Instruments **SM 4500-H-B**
Temperature	Standard water quality parameter	Field measurement **SM 2550.B**

Preferred method is in bold type face.

[a] This list is the "typical minimum" for characterizing site groundwater geochemistry to support evaluations of intrinsic bioremediation. Refer to other protocols and guidance documents to determine the complete suite of parameters that best meets the project needs.

SM - Standard Methods for the Examination of Water and Wastewater, 18th Edition, Greenberg, *et al.*, 1992.

STANDARD OPERATING PROCEDURE

The minimal aeration method described herein has been adapted from the protocols specified by EPA in their most recent groundwater monitoring guidance (EPA, 1992), demonstrated by Barcelona for providing consistent monitoring results for volatile constituents (Barcelona *et al.,* 1994), and discussed in a recent EPA technical support document (Puls and Barcelona, 1996). The method is described below.

EQUIPMENT REQUIREMENTS

Equipment needed for sample collection are provided in the attached checklist (Attachment A).

GENERAL PRE-SAMPLING PROCEDURE

Prior to purging and groundwater sampling, the routine procedures listed in the attached check list (Attachment B) should be conducted.

MONITORING WELL PURGING

The objective of purging the monitoring well is to collect groundwater samples representative of the formation groundwater. At most petroleum hydrocarbon sites, the groundwater near the water table surface will have the highest constituent concentrations, and monitoring wells are therefore screened across the water table. In these wells, the pump intake should be placed approximately 1 foot below the water level. If the well has a discrete screen length that is entirely submerged, the pump intake should be placed within the screened interval.

To collect intrinsic bioremediation parameter samples, monitoring wells should be purged at a rate that does not lower the water level significantly (i.e., less than 10 percent of the screen length). The specific pumping rate that will not cause excessive drawdown is dependent on the size of the well, permeability of the formation, etc. Check previous purge records for insight into the proper rate. When this information is not available, start with a flow rate of approximately 0.5 L/min and check the water level response in the well, increasing or decreasing the rate accordingly. The purging rate should be controlled as needed using the pump's variable speed flow controller and/or the gate valve in the discharge line. Collect water level measurements frequently during purging to ensure that the water level has not dropped lower than desired (see the attached sampling form). Monitoring wells should be purged until the field parameters have stabilized to within the ranges presented in Table 2. If an electric submersible pump is used, temperature may slightly increase rather than stabilize during low flow rate purging.

Table 2. Criteria for Stabilization of Indicator Parameters During Purging

Field Parameter	**Stabilization Criterion**
Dissolved Oxygen	0.10 mg/L or 10% of value (whichever is greater)

Electrical Conductivity	3% Full Scale Range
pH	0.10 pH unit
Temperature	0.2° C

The method described above is recommended as an alternative to the conventional "three well volume" purging protocol. Purging until the parameters in Table 3 have stabilized is a technically sound method for obtaining groundwater samples that are representative of formation groundwater. Most regulatory agencies accept this newer method based on its technical merits. However, some regulatory agencies may still require the older "three well volume" method. For wells completed in very transmissive zones, it may not be practical to purge at a slow rate with minimal water table depression while still achieving the required purge volume. In these cases, a higher purge rate may be acceptable initially, but purging rates should be decreased as the required purge volume is approached, with the objective of producing groundwater samples that are not turbid and have not been artificially aerated.

As a cost control measure, it may be appropriate to terminate purging and collect the sample at predetermined, arbitrary endpoints (e.g., after 3 well volumes, after one hour of purging, etc.), regardless of whether or not the criteria in Table 2 have been achieved.

FIELD INDICATOR PARAMETER MEASUREMENT

During purging, continuously measure DO, electrical conductance, pH, Eh, and temperature with the flow cell or equivalent arrangement (e.g., discharge line from pump to small beaker in which the probes are immersed). Flow cells are commercially available from a number of vendors including QED, Hydrolab, and YSI.If using the beaker arrangement for measuring the field indicator parameters, direct the discharge into the bottom of the beaker and allow the beaker to continuously overflow during measurements to minimize aeration. Allowing the discharge to pour into the container will artificially aerate the water, thus altering the properties of the water with respect to key parameters such as dissolved oxygen and oxidation reduction potential.

Record indicator parameter and water level measurements in a field notebook or onto well development logs every three to five minutes or at a minimum frequency of approximately 1/4 well volume increments (see the attached sampling form). Purging is complete once the parameters have stabilized to within the ranges presented in Table 2 regardless of the number of well volumes purged.

If using the electric submersible pump (i.e., Redi-Flo 2) care must be taken to prevent flow interruption. If the flow is interrupted for any reason (e.g., loss of power), entry of air into the tubing usually occurs, with the potential result of artificially aerating the groundwater sample. In addition, restarting the pump may cause a surge in flow that will suspend particulate matter in the well.

GROUNDWATER SAMPLE COLLECTION

When purging is complete, collect aliquots for the analytical parameters listed in Table 1. To ensure the most consistent, comparable results, individual samples/measurements from all wells should be collected in the same order. The order used in this protocol is based on the approximate order of susceptibility to artificial aeration: volatile organics, total organic carbon (TOC), methane, iron, alkalinity, and sulfate.

Reduce the pumping rate and/or use the 3-way valve to collect the methane, volatile organics and TOC samples. Direct the discharge toward the bottom, inside wall of the jar to minimize volatilization, and fill to overflowing. Filter the discharge prior to filling the ferrous iron sample jar using an in-line 0.45 micron filter. Filtration is recommended to eliminate bias introduced with particulates. In-line filtration is recommended to prevent artificial aeration of the sample.

If additional samples are collected for dissolved oxygen analysis using field kits (i.e. Hach or Winkler), submerge the sample jar into the bottom of the large container, continue to fill the container to overflowing, and allow the sample jar to fill without aeration.

Preserve and analyze the samples as described in the sampling and analysis plan.

QUALITY CONTROL CHECK FOR FIELD MEASUREMENTS

Field checks should be performed to ensure that representative measurements are being made. At a minimum, Eh and DO readings should be in agreement. DO readings should be less than one when the Eh is negative. If this is not the case, one or the other measurement is in error. When additional geochemical parameters are measured in the field, additional checks can be made. For example, ferrous iron should be present in elevated concentrations only when DO is less than one and the Eh is negative. When all measurements are not in agreement, measurements should be repeated until agreement is reached. In this process of achieving consistent results, there may be merit in trying alternative measurement techniques; for example, use of a Hach field kit for DO rather than a DO measurement probe.

Another check for representative results can be made by comparing the DO and Eh of well water before and after purging. In almost all cases, the DO/Eh measurements taken from the well water prior to purging should be equal to or higher than the DO/Eh of the formation groundwater. Increase in the D.O. and Eh as a result of purging is an indication of artificial aeration of the water.

In many cases, generation of valid field measurements for these parameters is not a trivial matter. Consideration should be given to including an analytical chemist on the field sampling crew. If this is not practical, the field crew should have familiarity with the problems that may arise in obtaining valid measurements and/or have access to an analytical chemist during the sampling effort to assist in resolution of measurement difficulties and apparent anomalies.

TIPS AND RECOMMENDATIONS

Following are tips that will facilitate implementation of the minimal aeration method and improve the representativeness of data collected.

- Dedicated pumps are recommended by many investigators (Kearl, *et al.,* 1994), (Barcelona, *et al.,* 1994), and (Kearl, *et al.* 1992) to reduce data quality variations due to inconsistent sampling technique, avoid cross contamination from sampling equipment, save time during sampling events, and reduce the overall cost of sampling.
- Wells should be thoroughly developed when installed at pumping rates greater than anticipated purging and sampling rates to eliminate or minimize production of sediment and colloidal particulates.

- Determine the depth of the well from well construction logs. Measuring the depth to the bottom of the well will cause suspension of settled solids and mixing of water within the well, thus requiring longer purge times. If well depth measurements are desired, perform the measurements after sampling is completed.
- Lower the pump slowly into the well to minimize surging the water column. Have the pump tubing measured and marked off before placing it down the well so you know where exactly to place the pump intake (i.e., one foot below water level or a minimum of one foot below the top of screen, whichever is lower).
- If using a submersible electric pump, use a generator that will allow the pump to run smoothly. Usually, a generator with 10 amps or greater of power and an automatic throttle (i.e., Honda 3500) works well.
- Do not start the pump too quickly. This may create a surge of water flow and cause unwanted turbidity in the sample. On the same note, make sure that you have a check valve on the pump tubing. If the pump shuts off accidentally, the check valve will prevent water in the tubing from rushing back into the well causing the groundwater to be aerated.
- Select a pump setting low enough that it will not break suction and stop pumping. Check any previous records on the purge rates vs. drawdown in the well. It is helpful to have some prior knowledge about the well's recharge rate and drawdown, so that stopping the pump, and/or lowering the pump are avoided. Periodically measure the water level in the well to prevent pump shutdown or drawdown that is too far down the well screen.
- Record data regarding the well's purge rate and drawdown for the next sampling event.
- Use tubing with as small a diameter as possible. If the submersible pump requires larger tubing, use a reducer to minimize the diameter of the tubing. Small diameter tubing will reduce the chance of aeration within the tubing and improve the responsiveness of flow cell measurements (see the following bullet).
- Minimize the volume of water within the tubing and flow cell or beaker in which probe measurements are made. A large volume of water up-stream of the monitoring point (i.e. probe location) increases the amount of time required for steady-state conditions in the well to manifest themselves at the monitoring point. Flow cells or measurement beakers with a large volume and residence time are particularly probelematic, due to the dilution effects and the longer time required to achieve a steady-state reading at the measurement point. Small diameter flow cells that most closely acheive plug flow are preferred. If using a beaker set-up, try to ensure flow from the discharge tubing directly across the probes.
- Be careful of air bubbles trapped in the pump tubing. To minimize bubbles, hold the end of the groundwater discharge tubing vertical and higher than any other point in the tubing. It is also helpful to tap the tubing lightly to force bubbles to rise to the end of the tubing. It is important to minimize air bubbles because they could potentially aerate the groundwater sample.
- A three-way valve or tee with valves on two legs is recommended so that the pump rate is not altered and a constant flow rate can be maintained while sampling. The valve is configured so that one leg is connected to the discharge tubing, one leg flows into the flow-cell, the third is turned on only when filling sample bottles.

CONSIDERATIONS FOR VERY LOW PERMEABILITY SETTINGS

Monitoring wells screened across very low permeability materials (silts, clays, etc.) typically purge dry and are then allowed to recharge prior to sampling. However, recharge into a dewatered well results in increased exposure of the water entering the well to the air present at the water table interface and in the well, potentially altering the groundwater geochemistry. To attempt to minimize these effects, the pump intake should be placed 2-3 feet below the water level and operated at as low a rate as is achievable, ideally equal to the recovery rate. In this manner, water drawn into the pump would be primarily from the formation and sand pack pore spaces. Close monitoring of the indicator parameter measurements is necessary since stabilization should occur prior to one bore-hole volume.

In some cases, a well may recharge so slowly that it may be impractical or even impossible to collect a groundwater sample that is truly representative of formation groundwater with respect to key geochemical parameters. If there is a need to collect samples/measurements for intrinsic bioremediation parameters in such cases, slowly purge the well dry and collect the groundwater samples as soon as the necessary volume has recharged into the well. As previously described in Section 2.6, the DO and Eh should be measured prior to, during, and after purging. An increase in DO or Eh is an indication of artificial aeration of the water, and results should be qualified accordingly.

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Attachment A: Equipment Checklist

___	Monitoring well construction details (geologic log, screened interval, well depth, bore-hole diameter, etc.).
___	Water level indicator
___	Submersible positive displacement pump and controller, bladder pump, or peristaltic pump (e.g. Grundfos Redi-Flo, QED Well Wizard, etc.)
___	Fluoroethylene polymer (FEP) tubing in sufficient quantity to use new tubing for each well. Note: Teflon is quite permeable to certain gases.
___	Throttling valves and 3-way flow-tee sampling valve (See Figure 1)
___	Field meters for pH, Eh, dissolved oxygen, temperature, electrical conductance (including instrument manuals and calibration materials)
___	Calibrated bucket or beaker to measure flow rate
___	Flow cell with ports for each of the field meter probes (optional).
___	Field note book and/or well purging log forms
___	Sample containers, preservatives, ice and cooler(s)
___	Decontamination supplies
___	Personal protective equipment

Attachment B: Pre-Purging Checklist

___	Decontaminate submersible pump (if not a dedicated pump).
___	Decontaminate or replace discharge tubing (if not a dedicated pump).
___	Calibrate field meters (pH, Eh, specific conductance, dissolved oxygen, HNu, etc.) If possible, perform two point calibration on DO meter.
___	Decontaminate water level indicator probe and tape.
___	Unlock the monitoring well and measure vapor concentrations in accordance with the site specific Health and Safety Plan.
___	Measure depth to water.
___	Evaluate whether water table surface is above or within the screened interval.
___	Calculate the volume of water in the well and borehole filter sand pack pore space (borehole volume).
___	Insert dissolved oxygen probe into the monitoring well and measure the dissolved oxygen in the water column. If practical, also measure Eh of water in well.
___	Install submersible pump into the well slowly to minimize aeration, placing the pump intake within the screened interval or approximately 1 foot below the water level.
___	If gasoline or diesel powered generators or compressors are used to operate the pump, take precautions to prevent the exhaust from contaminating the samples.
___	Configure the discharge tubing with a gate valve and 3-way valve, with discharge directed through the 3-way valve and flow cell (optional), and into a calibrated decontaminated bucket (See Figure 1).