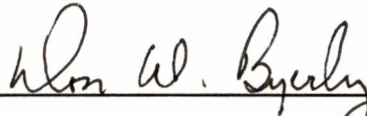


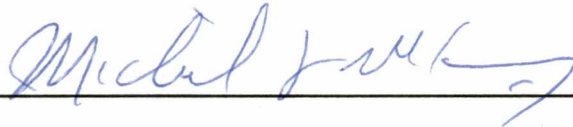
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An In Situ Evaluation of Acid Producing Material Encapsulation

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Michael J. Gunderson

August, 1991

ACKNOWLEDGEMENTS

I would like to express my thanks to my advisor, Dr. Don W. Byerly for his support and encouragement. I would also like to acknowledge my committee members, Dr. Michael L. McKinney, Dr. Claudia I. Mora, and Dr. R. Bruce Robinson for their advice and constructive criticism.

A number of other faculty and staff have also provided me with assistance throughout this project. In particular, Mike Doty and Lee Cooper provided advise and guidance in the Stable Isotope Lab.

I would like to acknowledge The Geological Society of America, Sigma Xi Honor Society, The University of Tennessee Department of Geology Discretionary Fund, The University of Tennessee Department of Geology, and the Federal Highway Administration for funding this project.

I would like to thank my fellow graduate students for the friendship and support through my graduate career. In particular, I am indebted to Anthony R. Tingle for his assistance in field work.

Last, I would to extend a very special thanks to my wife Janet. She provided encouragement and support in addition to editing the final version of the thesis.

ABSTRACT

Road construction on the Tellico Plains - Robbinsville Scenic Highway encountered sulfidic lithologies in rocks of the Precambrian Ocoee Supergroup which upon exposure and weathering can produce acid drainage. Encapsulating fills designed to restrict oxygen and water from contacting the sulfidic material are being utilized to mitigate acid drainage. The encapsulated design utilizes a compacted surface soil layer to restrict reactants for sulfide oxidation, a basal limestone aggregate layer to neutralize any acidic leachate, and a drainage network to divert water around and under sulfidic materials.

The present study proposed to monitor gas and temperature variations within the encapsulated fills and water quality from fill underdrains. The information was used to assess the design integrity in mitigating acid drainage, determine factors which influence fill atmosphere composition, determine gas and water transport pathways, and assess the activity of iron-oxidizing bacteria.

Oxygen, carbon dioxide, and temperature were measured in acid-producing highway fills over a 17 month period to provide *in situ* evaluation of mitigation designs. All parameters measured showed distinct seasonal trends at all depths with carbon dioxide concentration and temperature highest and oxygen concentration lowest in the summer months. Oxygen concentrations generally increased with depth due to a compacted surface soil layer restricting diffusion from the surface and a well oxygenated basal limestone aggregate layer used

for drainage diversion and neutralization of any acidic leachate from the fill. Changes in oxygen and carbon dioxide were correlated throughout the study area. The changes in concentrations could not be related to any single controlling mechanism, rather, as indicated by carbon isotope analyses, a combination of organic and inorganic sources. Oxygen is apparently consumed from both biotic respiration and oxidation reactions and lesser amounts of carbon dioxide result from a combination of neutralization reactions and biotic respiration. Correlations of gas composition with temperature were weak due to the influence of additional variables such as barometric pressure, precipitation, and fill porosity. Temperatures remained conducive to the growth of iron oxidizing bacteria throughout most of the year.

Isotopic data from aqueous carbonate species from saturated upslope soils and fill drainage indicate 2 dominant water transport pathways. In fills constructed on gentle slopes, water is transported as throughflow in sub-fill soils and eventually is discharged into the limestone aggregate layer. Aqueous carbonate species from these fills had $\delta^{13}\text{C}$ values ranging from -15‰ to -25‰ (PDB) indicating that the water chemistry is strongly influenced by organic sources of carbon dioxide ($\delta^{13}\text{C} = -21‰$ to $-26‰$) with only a slight contribution from limestone dissolution ($\delta^{13}\text{C} = -2‰$). In contrast, water transport pathways in fills constructed on steep, rocky slopes occur through fractured bedrock, eventually discharging into the limestone aggregate layer. Isotopic data ($\delta^{13}\text{C} = -5‰$ to $-20‰$) and high concentrations of sulfate in discharge waters indicate a greater interaction of water with

sulfidic fill material and subsequent development and neutralization of acid drainage.

Isotopic data from dissolved sulfate showed that water derived oxygen contributes approximately 75 percent of the oxygen in sulfate. The results indicate that bacteria-catalyzed reactions are the primary mechanism for sulfide oxidation within the encapsulated fills. This conclusion was also supported by confirmatory tests on fill leachate for the presence of the iron- and sulfur-oxidizing bacterium *Thiobacillus ferrooxidans*.

The encapsulating design functions to restrict the transport of water into the encapsulated sulfidic material, limits transport of oxidation products from the fill, and neutralizes acidic drainage prior to release to the environment. Water quality data, however, indicate greater interaction of water with sulfidic material in fills constructed on steep, rocky slopes. Recommendations from this study include increasing the thickness of the basal limestone aggregate, especially on steep, rocky slopes, to provide more efficient drainage and prevent the development of acid drainage. In addition, a short-term feasibility study of the effectiveness of oxygen traps installed within the drainage network is recommended.

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CHAPTER I.

INTRODUCTION

Statement of the Problem

Construction of the Tellico Plains-Robbinsville Scenic Highway has locally encountered sulfidic lithologies in rocks of the Precambrian Ocoee Supergroup. Upon exposure and weathering during and after construction, these rocks can produce acid drainage (AD) which can adversely impact local watersheds. For cost effective construction of this highway, all excavated rock material is utilized as fill. A highway fill design which uses limestone to neutralize AD, a compacted surface soil layer to restrict oxygen availability for sulfide oxidation, and a drainage network that diverts runoff around and under the construction materials is currently used to abate AD. The effectiveness of this design has been evaluated by monitoring leachate from fills, field tanks, and from bench scale models (Jago, 1989; Byerly, 1990). These studies have provided important information regarding the effectiveness of this type of design to abate AD, however the degree to which the design limits the rate of sulfide oxidation by restricting oxygen diffusion and, hence, the development of AD, has not been addressed. This study evaluates the effectiveness of the highway design in restricting oxygen from diffusing into the fill material, discerns gas and water transport pathways, and determines probable zones and reaction pathways of sulfide oxidation by monitoring *in situ* gas and temperature variations and water chemistry.

Location

The study area is located in southeastern Tennessee (Monroe County) and southwestern North Carolina (Graham County) in Nantahala and Cherokee National Forests in the Blue Ridge physiographic province (Figure I-1). Elevation in this area varies from approximately 3600 ft above mean sea level (AMSL) to over 5500 ft AMSL. The study area encompasses approximately 3.5 miles of the Tellico Plains-Robbinsville Scenic Highway presently under construction (Project FLH1-1(22))(Figure I-2). All sampling locations are based on linear distance (ft) along the highway survey line starting from the Tennessee-North Carolina state line (Figure I-3). Two sections of the highway were chosen for long term study of fill atmosphere. These sections were chosen based on total thickness of fill material and the need for encapsulation due to the high concentration of sulfide minerals and low neutralization capacity of the rock material, but differing pre-construction slope morphology. The encapsulated fills are located between stations 382+00 and 387+00 and between stations 395+00 and 403+00, which hereinafter will be referred to as fills EF-1 and EF-2, respectively.

Geologic Setting

The geology of southeastern Tennessee and southwestern North Carolina is dominated by the Late Precambrian Ocoee Supergroup (Rast and Kohles, 1986). The Ocoee Supergroup conformably overlies earlier Precambrian Grenville Basement and is conformably overlain by the Early Cambrian

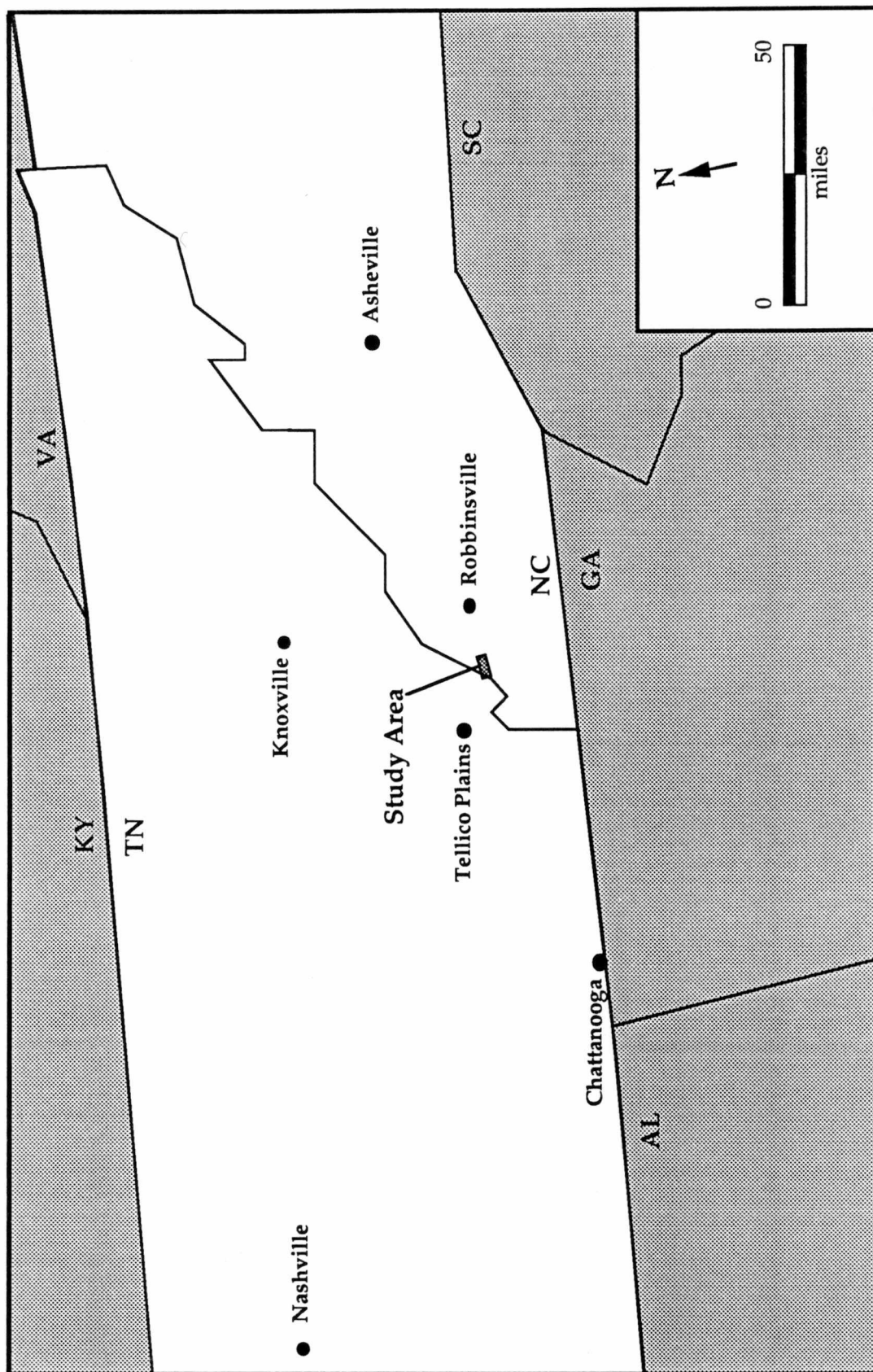


Figure I-1. Location Map of the Study Area

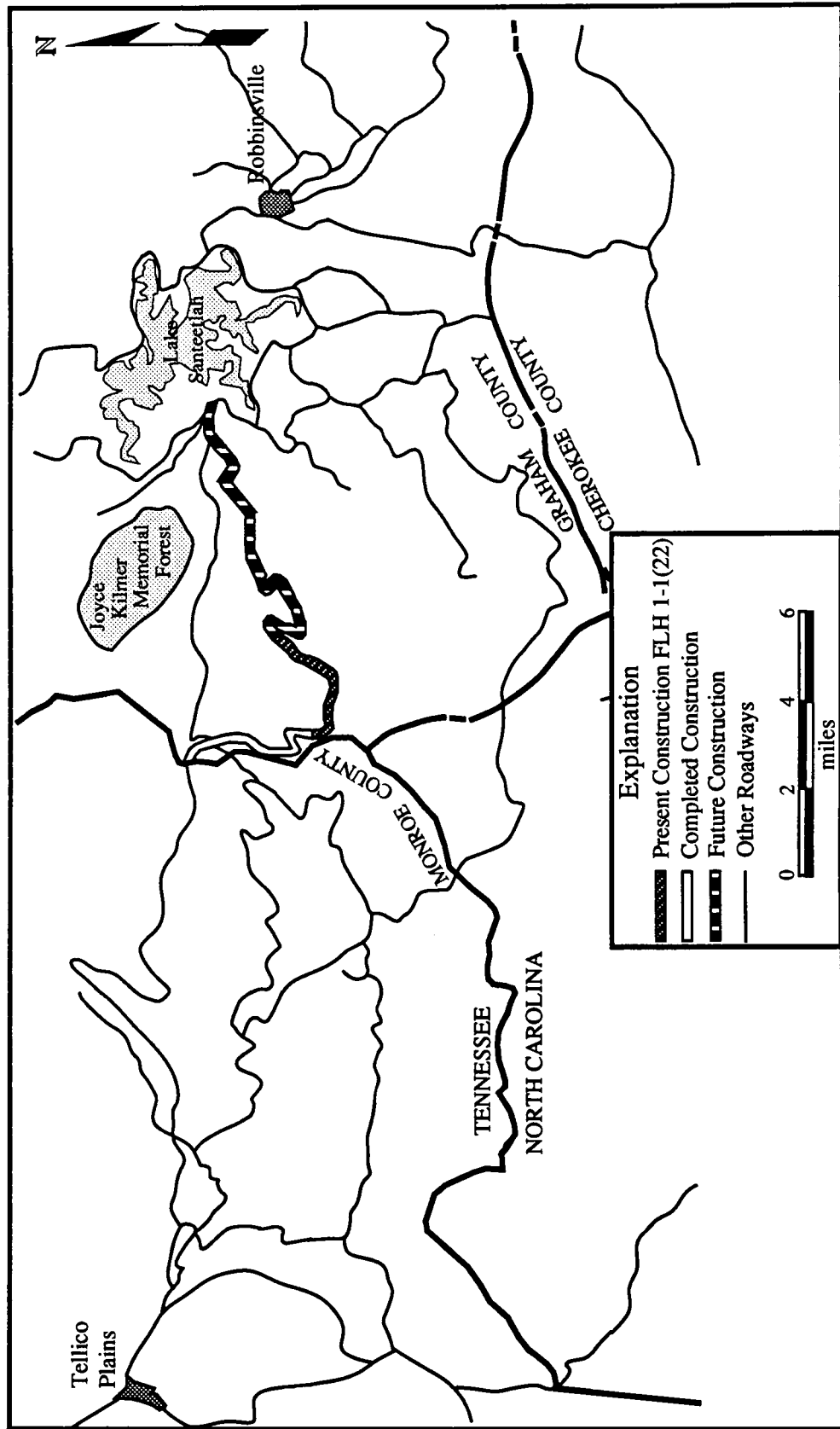


Figure I-2. Location Map of FLH1-1(22)

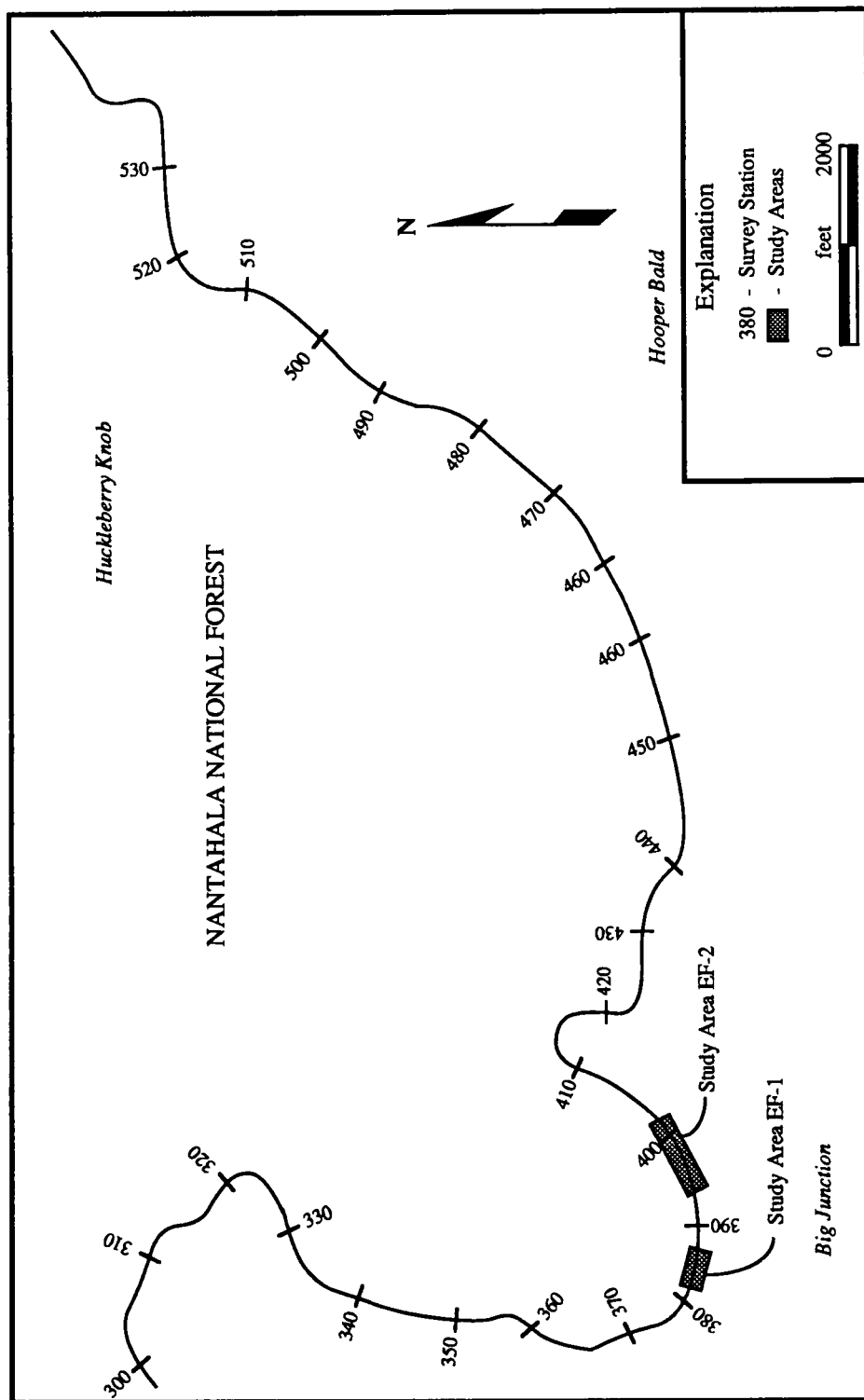


Figure I-3. Detailed Map of FLH 1-1(22)

Chilhowee Group. The region has undergone at least three major episodes of compressional deformation: the Taconian (Ordovician), the Acadian (Devonian), and the Alleghanian (Permo-Carboniferous) events. In the study area, the Ocoee Supergroup is represented by the Precambrian Great Smoky Group. The Great Smoky Group consists of conglomerates, coarse- to fine-grained sandstone, and silty or argillaceous units. Studies by Jago (1989) and Byerly (1980) observed the following units west of the study area:

1. A massively-bedded, medium- to coarse-grained, medium to light-gray, well-cemented, metamorphosed sandstone unit.
2. A medium- to thinly-bedded, dark-gray to brown to black, meta-sandstone/metasiltsone and interbedded argillite unit.
3. A thinly-bedded to fissile, dark-gray to brown to black, meta-shale or argillite unit.

The dominant lithology observed during construction of the fills was the meta-shale assemblage and to a much lesser extent, the light gray meta-sandstone. Sulfide mineralogy occurs in all three lithologies, however it is most prevalent in the argillites. Analytical results from this study and from previous reports identified sulfide phases that include pyrrhotite, pyrite, marcasite, chalcopyrite, sphalerite, and possibly smythite (Merschatt and Larson, 1972; Carpenter, 1974; Jago, 1989).

Purpose of Study

The purpose of this study is to evaluate the effectiveness of the highway design in limiting the formation of, and mitigating, AD. Specific objectives were:

- to determine oxygen transport pathways into the fill;
- to determine carbon dioxide sources within the fill;
- to utilize gas and temperature variations to discern probable zones of sulfide oxidation;
- to determine water transport pathways within the fill; and
- to determine the activity of iron-oxidizing bacteria.

CHAPTER II

THE ACID DRAINAGE PROBLEM

Iron Sulfide Oxidation

The extent of AD is largely determined by 3 interrelated factors: the oxidation rate of sulfide minerals, the presence of bacterial catalysts, and the neutralizing capacity of the geologic material (Sullivan et al., 1986). The oxidation of iron sulfides such as pyrite is controlled by two major reaction pathways: 1) abiotic chemical equilibrium reactions and 2) a bacterially catalyzed reaction (Table II-1; Kleinmann et al., 1981). Acidity in stage 1 is produced from sulfide oxidation by atmospheric and/or dissolved oxygen in groundwater, by the hydrolysis of ferric iron by the aerobic, acidophilic, chemoautotrophic bacteria *Metallogenium* and *Thiobacillus ferrooxidans*. The role of bacteria in this stage is dominantly a direct action mechanism in which the bacteria attach themselves to the surface of sulfides and enzymatically oxidize iron and sulfur at the interface (Silverman, 1967). Both abiotic and bacterial-catalyzed oxidation reactions continue down to a pH of approximately 2.5, however, below a pH of approximately 4.5 abiotic oxidation slows and a succession of acid-tolerant bacteria catalyze the reaction (stage 2)(Lundgren et al., 1978). The iron-oxidizing bacterium *Metallogenium* is active at relatively low free iron concentrations (40 mg/l) and at a pH of 3.5 to 4.5. Below pH 3.5, *T. ferrooxidans* activity increases. Optimal conditions for the growth of *T. ferrooxidans* include high free iron concentrations (75 mg/l) and low pH (2.0 to 3.5). Silverman (1967) refers to bacterial activity at this

Table II-1. Sulfide Oxidation Pathways

$$\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)$$

$$\text{Fe}^{2+} + 1/4\text{O}_2 + \text{H}^+ \rightleftharpoons \text{Fe}^{3+} + 1/2 \text{H}_2\text{O} \quad (2)$$

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_{3(\text{solid})} + 3\text{H}^+ \quad (3)$$

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightleftharpoons 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (4)$$

(1)

(2)

(3)

(4)

Stage 1

Mechanism

Reaction 1: proceeds both abiotically and by direct bacterial oxidation

Reaction 2: proceeds abiotically, rate slows as pH falls

Chemistry

pH above approximately 4.5; high sulfate; low iron; little or no acidity

Stage 2

Mechanism

Reaction 1: proceeds both abiotically and by direct bacterial oxidation

Reaction 2: proceeds at a rate determined primarily by activity of *Metallogenium* and *T. ferrooxidans*

Chemistry

approximate pH range of 2.5 to 4.5; high sulfate; acidity, and total iron increasing; low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio

Stage 3

Mechanism

Reaction 3: proceeds at rate totally determined by activity of *T. ferrooxidans*

Reaction 4: proceeds at rate primarily determined by rate of Reaction 2

Chemistry

pH below approximately 2.5; high sulfate, acidity, total iron, and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio

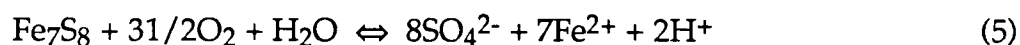
Kleinmann et al., 1981

stage as the indirect action mechanism because pyrite is being oxidized by ferric iron generated from bacterial oxidation. Two interdependent pathways are responsible for sulfide oxidation below pH 2.5 (stage 3). The oxidation of ferrous to ferric iron in reaction (2) consumes hydrogen ions, but the availability of the soluble ferric iron results in a large increase in hydrogen ion production from reaction (4). Under abiotic conditions the resupply of ferric iron to reaction (4) is inhibited by the slow oxidation kinetics of ferrous to ferric iron (reaction (2)) (Singer and Stumm, 1970). Strict chemical oxidation of ferrous iron is extremely slow, with half times on the order of 1,000 days, and is incapable of producing observed AD (Nordstrom et al., 1979). *T. ferrooxidans* catalyzes the reaction reducing the half time for ferrous iron oxidation to approximately 20 to 1,000 minutes. In addition, the hydrolysis of ferric iron in reaction (3) contributes additional acidity. The presence of iron sulfides, oxygen, water, and bacteria perpetuate the oxidation process by continually recycling ferrous and ferric iron (Nordstrom et al., 1979). After the initial abiotic oxidation of pyrite (stage 1), only sufficient oxygen for biotic respiration need be present for sulfide oxidation. Water is also important in the development of AD, acting as a reactant in sulfide oxidation, as medium for bacterial growth, and as a pathway for oxidation products from spoils.

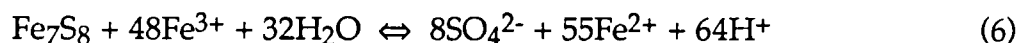
The oxidation of pyrite is not only pH dependent but also governed by chemical equilibrium and/or bacterial mediation. The overall stoichiometry of reaction (1) (the sum of reactions (2) and (4)) leads to the consumption of 3.5 moles of oxygen and 1 mole of water for each mole of pyrite. The products of the reaction are 1 mole of ferrous iron, 2 moles of sulfate, and 2 moles of

hydrogen ion. In addition, 1440 kJ of heat energy are released for each mole of pyrite during the overall oxidation reaction (Lowson, 1982).

Similar oxidation reactions are known to occur with other sulfides such as pyrrhotite, chalcopyrite, and sphalerite (Nordstrom, 1982; Sato, 1960). Pyrrhotite (Fe_{1-x}S), which was identified as the dominant sulfide mineral present in the study area, is oxidized by both oxygen and ferric iron. Balanced reactions for the oxidation of monoclinic pyrrhotite based on work by Toran and Harris (1989) are as follows:



and



The overall reaction (reaction (5)) also produces 6853 kJ of heat energy for each mole of pyrrhotite oxidized (Lowson, 1982).

Stable Isotope Fractionation During Sulfide Oxidation

Oxygen utilized in the oxidation of pyrite may originate from a variety of sources and in various proportions (Taylor and Wheeler, 1982; Taylor et al., 1984a, 1984b). Based on stoichiometry, the oxygen in sulfate may be derived totally from meteoric water (reaction 4) or a combination of meteoric water (12.5%) and dissolved/atmospheric oxygen (87.5%) (reaction 1). Large variations in $\delta^{18}\text{O}$ exist between atmospheric oxygen and oxygen derived from meteoric water (approximately +24‰ and -7‰ (SMOW), respectively)

(Kroopnick and Craig, 1967; Horibe et al., 1973). The oxidation of pyrite in reaction (1) would thus result in isotopically-heavier oxygen in sulfate with respect to oxygen than produced when ferric iron is the oxidant (reaction 4). The relative contribution of oxidation products by reactions (1) and (4) would be reflected in the oxygen isotopic composition of sulfate. Studies by Lloyd (1968) demonstrated that the rate of oxygen isotope exchange between sulfate and water is slow, requiring 1,000 to 100,000 years to reach equilibrium. Therefore, it is expected that sulfate will preserve evidence of the oxygen sources and thus, basic reaction pathways of a system may be elucidated.

Theoretical studies by Taylor and Wheeler (1982), Taylor et al. (1984a, 1984b) and Wheeler and Taylor (1982) and later refinement by van Everdingen and Krouse (1984, 1988) have demonstrated the role of *T. ferrooxidans* in determining the $\delta^{18}\text{O}$ composition of sulfate in acidic systems (approx. pH 2.0) and have calculated the relative contribution to sulfide oxidation by reactions (1) and (4) based on isotopic data. As previously discussed, these bacteria catalyze the oxidation of ferrous iron, which in turn acts as an oxidant for sulfide oxidation. In addition, Toran and Harris (1989) have shown isotopic fractionation in experiments at higher pH values (i.e., pH 3), but stressed that other mechanisms (both abiotic and biotic) could result in similar isotopic fractionation depending on pH and the presence of other species of iron oxidizing bacteria. Their review indicated six possible pathways of sulfide oxidation, with similar isotopic fractionation occurring in both abiotic and biotic reactions. In addition, they stressed that although the sum of known pyrite oxidation pathways are equivalent to the stoichiometric relationship shown in reaction (1), this reaction and others do not adequately

account for the individual pathways of pyrite oxidation. At low pH (i.e., 2-3) and with *T. ferrooxidans* present, however, oxygen isotopic composition of sulfate should be consistent with theoretical studies (Toran, 1990).

Encapsulation Design

Field and laboratory studies of acid producing material encapsulation methods by Jago and Byerly (1989) and Byerly (1990) resulted in the present highway design aimed at mitigating AD. This encapsulation design provides nearly *in situ* disposal of excavated material, thereby reducing haul distances and maintaining engineering requirements. The encapsulated fill is designed to limit the availability of reactants (i.e., water and oxygen) for sulfide oxidation, to limit the release of AD products to the environment, and neutralize any AD that may form.

Prior to construction, representative rock samples taken from outcrops and drill cores are analyzed for an acid-base accounting to determine the net neutralizing potential (NNP) (Sobek et al., 1978). NNP, defined as the natural acid neutralization potential (NP) of the rock minus the net amount of acid a rock potentially could produce upon weathering (acid potential; AP), indicates whether rock can produce AD upon exposure and weathering. The analyses generally over-estimate AP because analytical techniques utilize total sulfur (i.e., from inorganic, organic, and sulfate sources) instead of solely inorganic sulfur which is responsible for the generation of AD. In addition, analyses are conducted on pulverized rock which provides greater surface area for sulfides to react than that of actual fill material. Analytical results

determine whether excavated rock from a particular section requires encapsulation, thereby eliminating unnecessary high-cost encapsulation.

Pre-construction slopes are prepared by removing soil and vegetation and contouring slopes to the surveyed designs (Figure II-1). BIDEM U-14 geotechnical filter fabric is laid on the contoured slope and a six inch layer of limestone aggregate (approximately 1 to 2 inch diameter) is placed on the filter fabric. A drainage network consisting of perforated flexible polyvinyl chloride (PVC) pipe (6 inch inside diameter) is placed within the limestone aggregate. The drainage network functions to remove excess water from the fill, thereby restricting interaction of water with the sulfidic fill material. The drainage network ultimately leads to a single exit drain at the lowest point of the fill base. The aggregate layer is then covered with an additional layer of filter fabric prior to placement of sulfidic fill material. This fabric allows water to percolate through to the limestone aggregate while retaining the overlying soil.

Sulfidic fill material is spread in layers and compacted to approximately 20% porosity. Actual thickness of individual layers varied from approximately 2 ft to 5 ft due to large boulders that were occasionally placed in the fill. After completion of each layer, pulverized limestone is spread over the fill at a rate of 500 lbs/1000 ft², with the grain size of the pulverized limestone ranging from 0.147 mm to 1.98 mm. Following the limestone application, a 3 ft thick soil bank is placed along the outside slope and compacted to less than 5% porosity. The fill is constructed to grade and a base course of low sulfide metasandstone placed on the surface. Paved ditches and concrete culverts are utilized to intercept and divert surface runoff. The

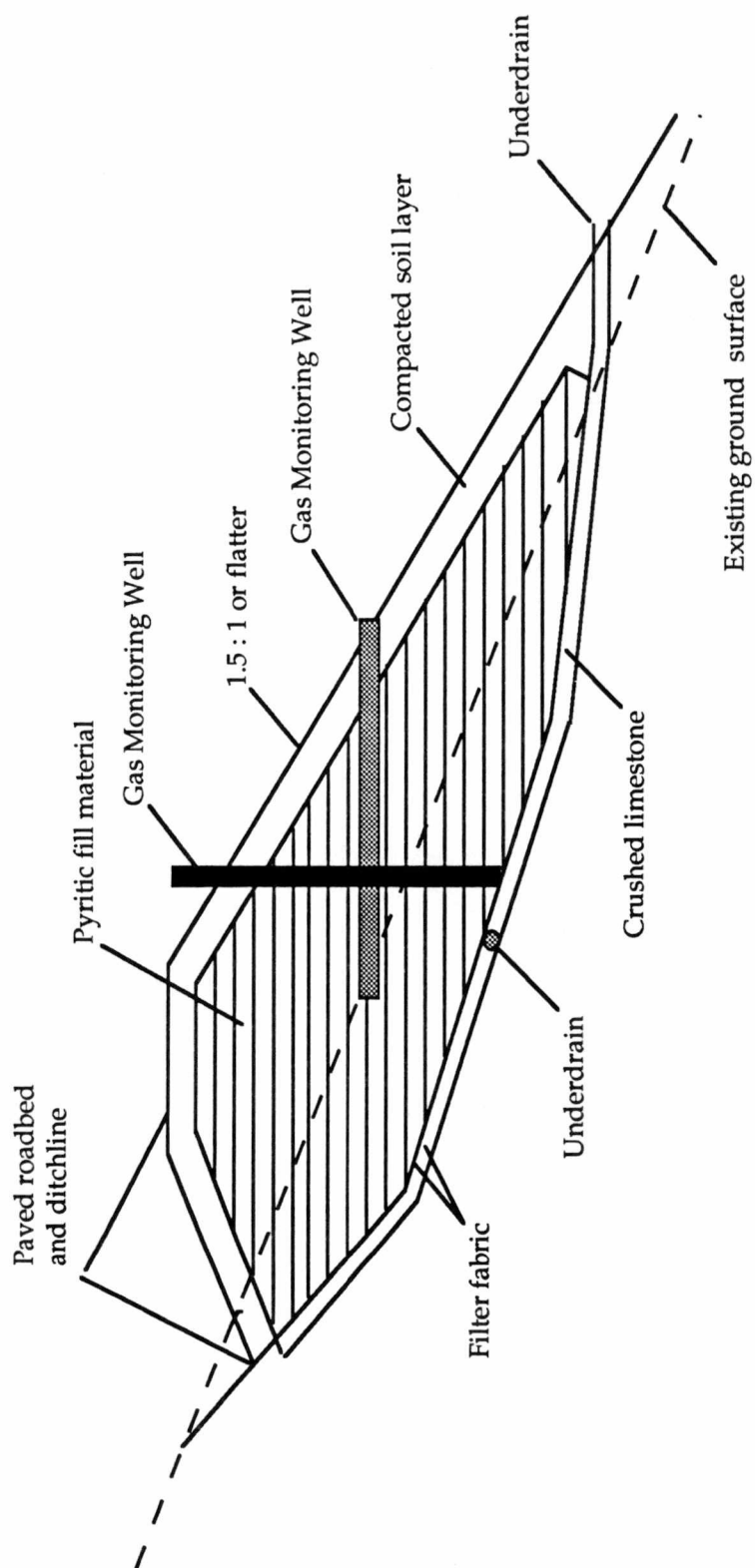


Figure II-1. Encapsulation design. Gas monitoring wells are shown for reference in this study.

slopes are treated with a fertilizer/grass seed mixture and covered with straw mulch to prevent erosion until the vegetation is established. Silt retention fences are utilized downslope of construction to provide additional erosion control. Vegetation was more quickly established on EF-2 relative to EF-1. The highway is completed with an asphalt surface, however this was not in place during the course of this study.

The encapsulation design in terms of highway width and soil slope remains constant between fills; however, the ditchline and pre-construction morphology are site dependent. These variables will influence infiltration and runoff which controls AD. Fill EF-1 was constructed below a steep (i.e., approximately 2:1), rocky slope with thin soils and a narrow ditchline position between the highway and upslope. Fill EF-2 was constructed near the ridgeline on a relatively gentle (i.e., approximately 4:1), well vegetated slope with thicker soils and a ditchline positioned down a gentle slope from the highway.

Sulfidic fill material is generally encapsulated immediately after excavation. Material utilized in the construction of the fills in this study had been exposed for approximately 1 year due to excess fill material excavated during construction of the previous section of highway and also due to the seasonal nature of construction activities. Hoving and Hood (1984), Sullivan et al. (1986), and Cravotta (1991) have shown that the potential of sulfidic rock to generate AD greatly increases with atmospheric exposure prior to disposal. In addition, these studies also indicated that the effectiveness of remediation methods can be greatly diminished due to stored weathering products which

create conditions conducive to the growth of iron- and sulfur-oxidizing bacteria.

Previous Studies of Acid-Soil Atmospheres

Despite the importance of oxygen supply for sulfide oxidation, few studies of soil atmosphere have examined acid producing material. Jaynes et al. (1983) measured soil temperature and oxygen and carbon dioxide concentrations over a 2 year period. Their study revealed large seasonal variations in oxygen concentrations. Isotopic studies by Wallick et al. (1983) in reclaimed mineral lands reported that high carbon dioxide levels in the unsaturated zone were indicative of non-equilibrium geochemical conditions. The sources of carbon dioxide were determined to be both biotic respiration and limestone dissolution and were strongly correlated to calculated carbon dioxide concentrations based on water chemistry. Erickson et al. (1985) also measured oxygen and carbon dioxide concentrations and determined oxygen may be available at depths to 8 meters, regardless of vegetation cover. Carbon dioxide concentrations were determined to be the result of both biotic respiration and carbonate neutralization reactions. In addition, gas composition showed a seasonal dependence with oxygen availability limiting to pyrite oxidation only during portions of the summer months. Studies by Harries and Ritchie (1981, 1985) and Bennett et al. (1988) monitored pre- and post-reclamation gas and temperature variations in an abandoned copper mine. Their results indicated that during pre-reclamation, sulfide oxidation, as evident by elevated overburden temperatures, was

occurring in some portions of the spoils. Post-reclamation results indicated a decline in the oxygen supply and spoil temperatures, reflecting the success of reclamation measures.

Factors Influencing Soil Atmosphere

Soil atmosphere composition is governed by numerous factors including biotic respiration, oxidation/neutralization reactions, atmospheric variables, soil moisture content, soil porosity, mineralogy, and depth. The degree to which any force dominates and the cumulative effect on gas transport mechanisms in porous media is dependent on the physical and chemical properties of the media.

Carbon dioxide and oxygen concentrations may be significantly affected by plant respiration in the root zone or microbial activity. Respiration would result in a 1:1 exchange ratio of oxygen for carbon dioxide. While most organisms consume oxygen and release carbon dioxide during metabolism, certain bacteria, such as the chemoautotrophs which includes *T. ferrooxidans*, also utilize carbon dioxide as a carbon source for metabolism.

Oxidation/neutralization reactions may play a more significant role in the evolution of the soil atmosphere in disturbed overburden. These reactions include the oxidation of organic matter as well as the oxidation of inorganic minerals. Oxidation reactions consume oxygen and may release by-products such as carbon dioxide, hydrogen sulfide, and methane, with the latter two common to anaerobic environments. Neutralization reactions in unsaturated environments may provide a significant source of carbon

dioxide. A simplified example of the neutralization of AD by calcite would be:



The products of this reaction are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - both as a precipitate and as a dissolved phase), carbon dioxide (CO_2 - gaseous and dissolved phases), and increased leachate alkalinity due to the formation of bicarbonate ion (HCO_3^-). The sources of acidic water include acidic atmospheric precipitation or reaction products from the oxidation of sulfide minerals. In addition, chemical reactions may be exothermic or endothermic, and therefore may significantly affect soil temperature.

Precipitation and barometric pressure variations may also affect soil atmosphere composition. During precipitation events, oxygen may be carried into the soil along the wetting front. Changes in barometric pressure can directly alter oxygen concentrations within the soil atmosphere (Erickson et al., 1985; Harries and Ritchie, 1985). The effects of atmospheric changes on soil gas composition are dependent on the physical properties of the soil. In addition, there is a damping effect with depth, whereby diurnal and annual meteorologic cycles such as temperature and barometric pressure changes do not significantly affect soil atmosphere.

The physical properties of soil also affects the composition of the soil atmosphere. Effective porosity controls the exchange rate of atmospheric and soil gas, with higher porosity soils having a greater exchange rate. An increase in moisture content has been shown to decrease the exchange of

atmospheric and soil gas not only from a reduction of pore space but also by decreasing the effective porosity (i.e., the interconnectivity of pores). Furthermore, porosity is dependent on packing and sorting, with well sorted, loose deposits having the greatest void space.

The above-mentioned factors all affect the gas transport mechanisms within soils. Dominant gas transport mechanisms in porous media include diffusion, advection, and convection with the dominance of one mechanism over another dependent on the physical and chemical properties of the soils. Simple diffusion of gas from a source would be common where concentration gradients exist. Convection can also play an important role in the bulk movement of gas in a soil. Convective forces includes thermal effects (advection), barometric pressure changes, wind, and the absorption of oxygen in oxidation reactions.

CHAPTER III

EXPERIMENTAL METHODS

Gas and Temperature Monitoring Wells

Purpose

The purpose of this study was to determine gas transport mechanisms in highway fills designed to limit the formation of and mitigate AD, to determine the primary source(s) of carbon dioxide in the fills, and to determine zones of sulfide oxidation. Gas monitoring wells (GMWs) have been used in other studies to determine zones of sulfide oxidation in mine tailings (Daniel et al., 1980, 1988; Harries and Ritchie, 1981, 1985; Jaynes et al., 1983; Erickson, 1985; Bennett et al., 1988). These studies, which were focused on long-term monitoring of oxygen and carbon dioxide variations and temperature fluctuations, indicated gas transport mechanisms within mine spoils. Gas transport pathways determined from these studies were used to evaluate remedial alternatives and remedial actions of mine reclamation.

Gas Monitoring Well Design

The GMW design used in this study is a modification of the design used in studies by Jaynes et al. (1983). The GMWs were constructed of 5 ft sections of 4 inch inside diameter (i.d.) schedule 40 polyvinyl chloride (PVC) casing (Figure III-1). Gas ports were installed in the lower portion of each section by

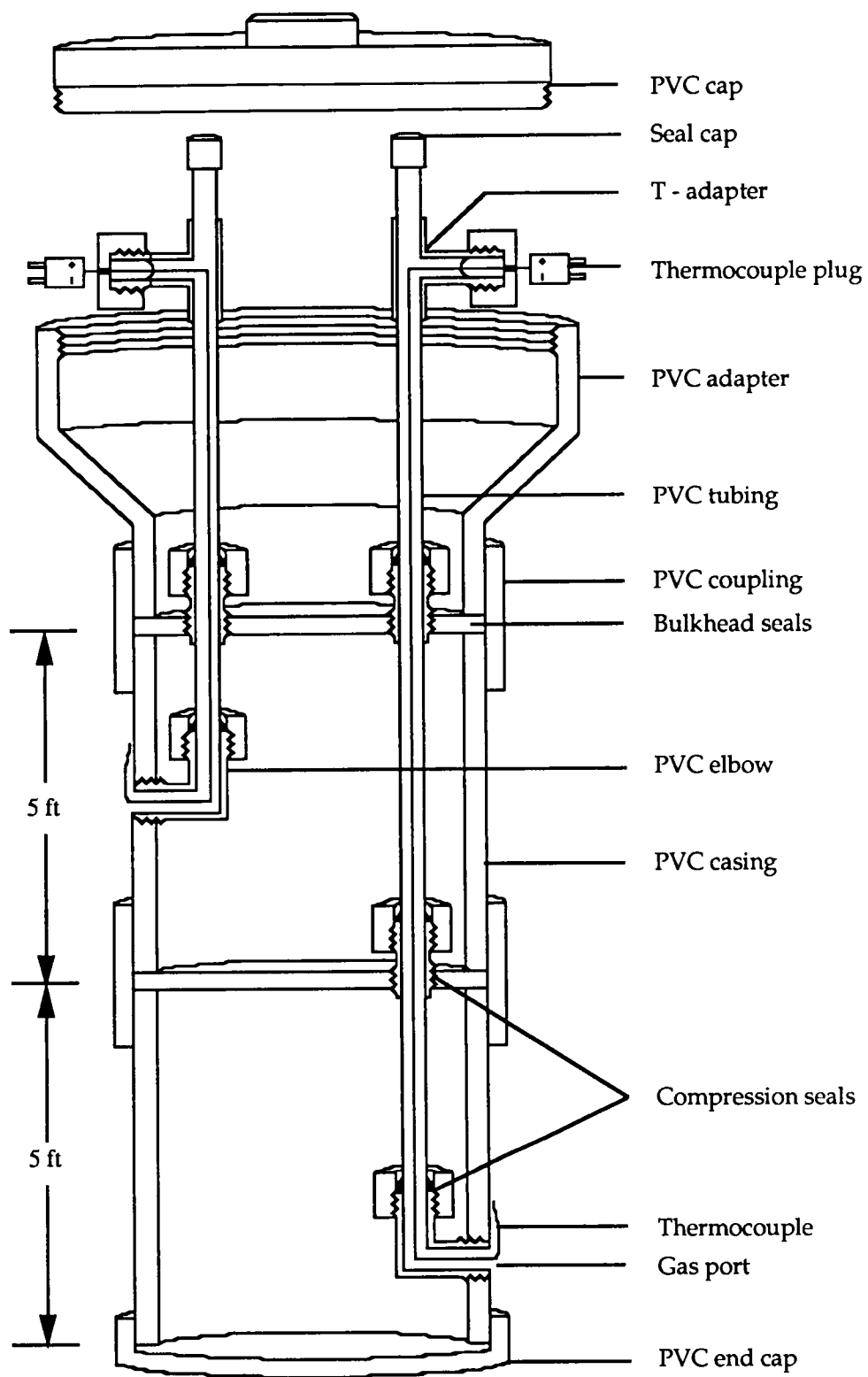


Figure III-1. Gas Monitoring Well Construction. Note: not to scale.

cementing threaded PVC elbows into drilled and tapped 0.5 inch holes. PVC tubing (0.25 inch i.d.) was connected to the elbows and passed through bulkheads to the surface. Air-tight seals around the PVC tubing were obtained with compression seals at the PVC elbows and bulkheads. The bulkheads, consisting of 4 inch diameter PVC plates drilled and tapped for the PVC tubing, were used to isolate individual sections and insure no atmospheric gas could be transported to the gas ports through ruptures in the GMW wall if damage occurred during installation. Omega type K (24 gauge) thermocouples were installed at each gas port by threading the thermocouple wire through the PVC tubing. The soldered thermocouple tip extended beyond the gas sampling port and was cemented with PVC epoxy to the exterior of the GMW. In addition, the thermocouple tip was covered with a small piece of PVC to protect it from chemical and physical damage. Each gas port was surrounded by approximately 30-40 pieces of coarse (1 to 2 inch diameter) low-sulfur rock material and filter fabric to provide additional protection and to prevent fine material from clogging the sampling ports. All GMWs were completed by installing screw caps and T-adapters which allowed individual access to thermocouples and gas sampling ports, vacuum hose end caps, and thermocouple plug adapters.

A total of 7 GMWs were installed in fills EF-1 and EF-2. Three methods of installation were utilized depending on the method of fill construction and GMW orientation (i.e., vertical or horizontal). All locations in the fills were surveyed prior to installation to insure the GMWs were placed in the thickest portions of the fill (i.e., at the slope break). At stations 383+00 and 383+50, a single 5 ft section of the GMW was placed on top of the limestone aggregate

and a two foot layer of fill placed around the base of the section. Following this, successive layers of fill and corresponding pulverized limestone were placed around the GMW and compacted to approximately 20% porosity with a backhoe. Approximately 6 inches of powdered bentonite was utilized to provide a seal around each GMW at the midpoint between adjacent gas ports. Additional GMW sections were added as required until the fill was complete. Vertical GMWs at stations 396+00, 397+00 and 401+00 were installed by allowing the construction to proceed until the GMW locations were covered by approximately 5 ft to 10 ft of fill material. A backhoe was then utilized to excavate a hole down to the limestone aggregate. The GMW was placed in the hole and then backfilled with the excavated soil. This installation in effect, admixed the pulverized limestone and fill material. In addition, compaction of the fill material was completed with a portable soil compactor. The backfilled material was compacted in two layers, each approximately 5 ft thick. Horizontal GMWs (Stations 383+25 and 401+12) were installed in the mid portion of the fill. Trenches, approximately 2 ft deep and 30 ft in length, were excavated perpendicular to the fill outslope. Large rocks were removed and the trench smoothed to prevent damage to the walls of the GMWs. Fully constructed GMWs (total length of 25 ft) were placed in the trenches and the end allowed to protrude approximately 1 foot from the fill edge. The maximum GMW design length (25 ft) did not allow for the horizontal GMWs to reach the limestone aggregate. Bentonite seals were positioned at the midpoints between the gas sampling ports and the GMW buried with additional fill material. Prior to and after the installation of the horizontal GMW at station 383+25, soil was temporarily stored on the fill before

placement and compaction on the outslope. This resulted in a thin, compacted soil layer extending over the entire fill between stations 383+00 and 383+50. Tables III-1 and III-2 summarize sampling depth and geologic material at the respective gas port depths.

Sampling methods/locations

Oxygen and Carbon Dioxide Analyses of Gas Samples

Gas samples were collected for major components (i.e., carbon dioxide and oxygen) and temperature variations were monitored over a 18 month period. Temperature was measured in the field with an Omega Model HH81 digital thermometer (Types K and T thermocouples) to 0.1°C with an operational range of 32°F to 120°F. The digital display was allowed to stabilize (approximately 30 to 60 seconds) prior to recording temperature. Gas sampling consisted of purging at least three times the gas volume of the PVC tubing and estimated annular space surrounding the gas port with a vacuum/pressure pump rated at 20 mm Hg prior to sample collection. The gas samples were collected in evacuated 1.6 liter Tedlar® gas sampling bags. Field duplicates and field blanks were also taken periodically to ensure the integrity of the sampling procedure. Gas samples were transported to the laboratory at ambient temperatures. Samples were analyzed with a Fisher Orsat Gas Analyzer designed to determine carbon dioxide and oxygen concentrations. When possible, a field blank (i.e., atmospheric) sample was collected in the field with the sampling procedure following that of the

Table III-1. EF-1 Gas Monitoring Well Installation Summary

Station	GMW Orientation	Max. Fill Thickness (ft)	Sampling Depths (ft)	Lithologic Description
383+00	Vertical	18.5	3.5	Soil
			8.5	Fill
			13.5	Fill
			18.5	Fill/Limestone
383+25	Horizontal	NA	5.0	Soil
			10.0	Fill
			15.0	Fill
			20.0	Fill
			25.0	Fill/Limestone
383+50	Vertical	19.0	4.0	Soil
			9.0	Fill
			14.0	Fill
			19.0	Fill/Limestone

Table III-2. EF-2 Gas Monitoring Well Installation Summary

396+00	Vertical	17.7	2.7	Soil
			7.7	Fill
			12.7	Fill
			17.7	Fill/Limestone
397+00	Vertical	14.0	4.0	Soil
			9.0	Fill
			14.0	Fill/Limestone
401+00	Vertical	10.0	5.0	Fill
			10.0	Fill
401+12	Horizontal	NA	4.0	Soil
			9.0	Fill
			14.0	Fill
			19.0	Fill
			24.0	Fill/Limestone

subsurface gas sampling. In addition, duplicate samples were also taken periodically to insure the integrity of the sampling protocol.

Isotopic Analysis of Fill Carbon Dioxide

Gas samples for isotopic analysis of carbon dioxide were collected monthly over a five month time period at stations 383+00 (EF-1) and 396+00 (EF-2). These stations were chosen because they have similar fill thickness but significantly different carbon dioxide/oxygen concentrations. In addition, the samples were collected over a period from near maximum observed carbon dioxide levels (early fall) to minimum observed carbon dioxide levels (winter). Samples for isotopic analysis were collected simultaneously with the samples for oxygen and carbon dioxide analyses by connecting an in-line flow-through gas sampling bulb between the vacuum pump and the GMW. Gas samples for isotopic analysis were collected in the sample bulbs by sequentially closing the outlet and inlet stopcock valves after sufficient gas volumes had been purged and a sample collected in the Tedlar sample bags. Gas samples were stored at ambient temperature during transport to the laboratory.

The carbon dioxide for isotopic analysis was purified in the laboratory by connecting the sampling bulbs to a vacuum system and the contents slowly passed through 4 traps. The first trap was cooled by a dry ice/ethanol mixture to remove water vapor and the following 3 traps were cooled by liquid nitrogen to freeze all carbon dioxide. Sample extraction rate was regulated by means of a capacitance manometer. A pressure of approximately 2 mm Hg

was maintained within the vacuum system which allowed for samples to be extracted and purified in approximately 30 minutes. The yield (i.e., the pressure) of the carbon dioxide was determined by a capacitance manometer. The yield was plotted against the concentration of carbon dioxide determined with the Fischer Orsat Gas Analyzer to verify the purification method recovered all of the carbon dioxide. Based on a strong correlation from this plot ($r = 0.99$), it was concluded that the purification method was adequate. This correlation also served as a quality assurance procedure for carbon dioxide quantification and isotopic analysis. Carbonate standards were analyzed at a rate of 10% to insure the mass spectrometer was functioning properly. The carbon dioxide was collected in glass vessels and analyzed utilizing a VG Micromass 903 Mass Spectrometer. All $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are reported in permil as defined by:

$$\delta^{13}\text{C} = ([^{13}\text{C}/^{12}\text{C}]_{\text{sample}}/[^{13}\text{C}/^{12}\text{C}]_{\text{standard}} - 1) \times 1000 \quad (8)$$

$$\delta^{18}\text{O} = ([^{18}\text{O}/^{16}\text{O}]_{\text{sample}}/[^{18}\text{O}/^{16}\text{O}]_{\text{standard}} - 1) \times 1000 \quad (9)$$

The standard for carbon and for oxygen in soil carbon dioxide is the PDB belemnite. For all other types of analyses, the standard for oxygen is standard mean ocean water (SMOW).

Analytical precision based on statistical analysis of multiple standards analyzed with field samples, was determined to be 0.05‰ (SMOW) for $\delta^{18}\text{O}$ and 0.09‰ (PDB) for $\delta^{13}\text{C}$.

Water Quality

Purpose

Parameters most commonly studied in assessing water quality associated with AD are pH, specific conductance, acidity/alkalinity, sulfate content, and elemental analysis. In addition, stable isotopes have been utilized to assess the activity of the iron-oxidizing bacterium *T. ferrooxidans* (Taylor and Wheeler, 1982; Wheeler and Taylor, 1982; Taylor et al., 1984a, 1984b; van Everdingen, 1984, 1988; Toran and Harris, 1989). The purpose of leachate sampling in this study was to assess the water quality of fill drainage, determine the theoretical partial pressure of carbon dioxide above the limestone aggregate based on alkalinity, interpret water/soil/rock interactions from the alkalinity and isotopic results, and determine the activity of iron-oxidizing bacteria.

Sampling Methods and Locations

Water Quality Analysis

Samples were collected for water quality analysis from underdrains at stations 383+00 and 401+00. These locations were selected based on proximity to GMWs. Because of intermittent precipitation, sufficient leachate was not always available for collection. In addition, water samples were collected

from the basal gas port (19 ft depth) of the station 383+50 GMW, but these were only available following heavy precipitation.

Samples were collected and stored in polyethylene bottles that had been washed with detergent, rinsed with distilled deionized water, rinsed with 10% hydrochloric acid (HCl) and rinsed three times with distilled deionized water. The bottles were rinsed an additional three times in the field with sample water. Following collection, samples were stored on ice during transport to the laboratory. Separate samples were collected for laboratory analysis of aqueous sulfate and alkalinity/acidity. In addition to lab analysis, pH, specific conductance, and temperature of the effluent were measured at the time of collection. Field instruments (pH and conductivity meters) were calibrated with standards prior to analysis.

Isotopic Analysis of Aqueous Carbonate Species

Samples for isotopic analysis of carbonate species (predominantly bicarbonate) were collected from underdrains and saturated upslope soils adjacent to the highway at stations 996+50, 190+00, 383+00, 401+00, 432+00, 480+00, 495+00, and 517+00. A summary of sampling location descriptions is contained in Table III-3. Due to intermittent flow at these locations not all samples were collected during each sampling round. Samples were collected in 1 liter polyethylene bottles washed as previously described. The samples were immediately treated with 60 ml of BaCl₂ saturated 38% ammonium hydroxide (NH₃OH) previously filtered to remove any precipitate as described by Friedman (1970). This solution raised the pH above 10.3 to insure that all

Table III-3. Description of Water Sampling Locations

Sampling Location	Water Source	Sulfate (mg/L)	pH	Conductance (umhos)
996+50	Fill	100 to 500	6.0 to 7.2	100 to 1100
190+00	Fill	NA	6.0 to 7.0	0 to 100
383+50	Fill	100 to 200	4.5 to 7.8	500 to 1100
401+00	Fill	0 to 5	6.5 to 7.2	10 to 75
432+65	Fill	100 to 400	2.8 to 4.0	400 to 500
462+00	Spring	0 to 10	6.0 to 7.0	0 to 25
490+00	Fill	NA	6.0 to 7.0	200 to 400
500+12 - 1	Fill	0 to 10	7.0 to 8.0	100 to 200
500+12 - 2	Spring	0 to 10	5.5 to 7.0	0 to 25

carbonate species (predominantly HCO_3^-) were converted to carbonate ion (CO_3^{2-}). Additional BaCl_2 was added in excess of estimated total aqueous carbonate and dissolved sulfate species precipitated all carbonate as BaCO_3 . The bottles were transported to the lab and the precipitate allowed to settle. The supernatant was decanted and the precipitate rapidly filtered through a 0.4 micron membrane filter. The filter and precipitate were immediately placed in an oven and dried at 60°C for one hour. Rapid filtration and oven drying limited the absorption of atmospheric carbon dioxide by the solution. Samples were stored in sealed vials until they could be analyzed. The carbon and oxygen isotope composition was determined on carbon dioxide by reacting the BaCO_3 with 100% phosphoric acid (H_3PO_4) at 25°C for 12 hrs (McCrea, 1950). Prior to analysis, sulfur was removed from the carbon dioxide by reaction with silver phosphate (AgPO_4). The carbon dioxide was cryogenically cleaned and analyzed on the VG Micromass 903 mass spectrometer. Quality assurance samples consisted of carbonate standards extracted with the same procedures as the BaCO_3 . All $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are reported as previously defined.

Isotopic Analysis of Fill Leachate Water and Aqueous Sulfate

Samples for oxygen isotope analysis of dissolved sulfate and water were collected from the GMW 19 foot (basal) gas port at station 383+50. This water sample was preferred over underdrain leachate because there is a fractionation in oxygen which occurs during the precipitation of gypsum and other sulfate minerals (Toran, 1990). The water was collected by connecting

an inline aspirator bottle between the GMW and vacuum pump. The water sample was transferred and stored in sealed polyethylene bottles and refrigerated until they could be analyzed.

Sulfate was quantitatively removed from the solution by slowly passing the solution through a column of Bio-Rad AG-1-X8 anion exchange resin (Taylor et al., 1984a, 1984b). The column was washed with 100 mls of deionized water and the sulfate eluted with 100 mls of 0.5M sodium chloride into a beaker at the same rate as collection. Additional 20 ml aliquots of 0.5M sodium chloride were passed through the column until all sulfate had been eluted. Excess $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was added to precipitate the sulfate, the solution was stirred for 15 minutes, and allowed to settle overnight. The sample was acidified to a pH 4 with 10% HCl for approximately 1 hour to remove dissolved carbon dioxide and bicarbonate ion. The supernatant was aspirated and the precipitate (BaSO_4) washed 3 times with deionized water. The sample was dried and stored until it could be analyzed. The oxygen isotope composition was determined on carbon dioxide prepared by combustion of the BaSO_4 sample with graphite under vacuum at 1000°C .

The oxygen isotope composition of the fill leachate water was determined following the method described by Epstein and Mayeda (1953). Carbon dioxide of a known isotopic content was equilibrated with a known volume of water at 25°C for 48 hours. After equilibration, the carbon dioxide was cryogenically purified. To determine if the sampling procedure used to obtain leachate from basal sampling interval in station 383+50 resulted in isotopic fractionation of the water, a simulation of the sampling procedure was performed in the laboratory. Two simulations were performed in which

water of known isotopic composition was drawn under vacuum through approximately 20 ft of PVC tubing into an aspirator bottle. Both simulations indicated that fractionation had not occurred during the sampling procedure.

Confirmatory Tests for *Thiobacillus ferrooxidans*

Purpose

Confirmatory tests were performed to confirm the presence of the iron-oxidizing bacterium *T. ferrooxidans* which catalyzes the oxidation of ferrous to ferric iron (Nordstrom, 1982). Ferric iron is a superior oxidizer relative to oxygen and hence, the higher its concentration the greater the rate of sulfide oxidation. The tests were done to link results from oxygen isotope analysis of dissolved sulfate to biotic catalysts as previously reported (Taylor et al. 1982, 1984a, 1984b; Wheeler and Taylor 1982; van Everdingen and Krouse, 1984, 1988).

Design

Sterile 9K media consisting of ammonium sulfate, potassium chloride, magnesium sulfate, calcium nitrate, ferrous sulfate and distilled water was prepared and acidified to a pH of 3.0 (Silverman and Lundgren, 1959). Serial dilutions consisting of 10, 1, and 0.1 ml portions of leachate from fills EF-1 and EF-2 were added to sterile tubes containing 4 ml of the 9K media. The test tubes were plugged with tissue and kept at room temperature for three weeks.

A total of 10 replicates was assayed for each dilution in order to estimate bacteria populations.

The presence of *T. ferrooxidans* is confirmed by the formation of an orange precipitate. Inorganic oxidation is indicated by the formation of a yellow precipitate that occurs several days later than biologically mediated oxidation. Bacterial populations were estimated from the dilutions by the most-probable number method (Halvorson and Ziegler, 1932).

Quality assurance procedures for confirmatory tests consisted of the analysis of blank samples. A total of 10 blanks were used which consisted of 4 ml of 9K media pipetted into sterile test tubes. This procedure also ensured that the technique was aseptic and that there was no cross contamination with the transfer procedures.

Rock Analyses

Purpose

Petrographic descriptions, x-ray diffraction analysis, and sulfur and neutralization potential analyses were conducted to determine the dominant mineral phases, total sulfur content, and net neutralizing potential of the fill material. Analytical results were used to determine the relationship between sulfur content, mineral assemblages, and oxygen and carbon dioxide concentrations in the fills.

Sampling Methods

Approximately 10 hand samples were randomly collected within 1 to 2 meters of gas ports on vertical probes and approximately 30 samples were collected along the length of the horizontal probes. This collection methodology was based on the assumption that fill material used in the construction had a relatively uniform chemical composition within small areas of source location and that bulk chemical composition would vary significantly only as fill source areas changed.

Mineralogy and Bulk Chemistry

Bulk mineralogy was determined by petrographic examination of thin sections and x-ray diffraction (XRD). Total sulfur was determined on rock samples collected during the construction of EF-1 and EF-2 fills. Rocks were crushed and sieved to a uniform size (60 μm) and analyzed for total sulfur using a Leco Sulfur Analyzer (Model SC-132). Sulfur speciation (i.e., inorganic sulfur, organic sulfur, and sulfate) was determined using methods described by Sobek et al., (1978). To determine the amount of sulfate-bound sulfur, a subsample (0.5 gms) was placed in a paper filter and rinsed with 50 ml of hydrochloric acid (HCl) and rinsed twice with 50 ml aliquots of deionized water. The second rinseate was collected and tested for the presence of chloride which causes analytical interferences. If chloride was detected, the sample was rinsed with additional deionized water. The sample was then dried and analyzed for total sulfur. The difference between the total

sulfur content of the untreated sample and the HCl-treated sample represents sulfate-bound sulfur. To determine the amount of inorganic-bound sulfur, a second subsample (0.5 gms) was placed in a flask with dilute nitric acid (HNO_3^-) for approximately 12 hrs then filtered and rinsed twice with 50 ml aliquots of deionized water. The second rinseate was collected and tested for the presence of nitrates which causes analytical interferences. If nitrate was detected, the sample was rinsed with additional deionized water. The sample was then dried and analyzed for total sulfur. The total sulfur after the HNO_3^- treatment represents organic-bound sulfur and the difference between the sulfur content of HCl-treated sample and the HNO_3^- -treated sample represents inorganic-bound sulfur.

The neutralizing potential (NP) was determined using the methods described by Sobek et al. (1978). This procedure involves reaction of all titratable bases with a set volume and normality of HCl. The solution is then back titrated to pH 7.0 with an equivalent normality of sodium hydroxide. The difference between amounts of acid and base added represents the NP and is given in tons of CaCO_3 per ton of rock material.

The quality assurance protocol for sulfur analyses consisted of standards analyzed at 10%.

CHAPTER IV

RESULTS

Temperature and Gas Data

General

Temperature and gas data represent samples collected from August 1989 to January 1991. These data are summarized in Tables IV-1 and IV-2. Graphical representations of raw data (Appendix A) are shown in Figures IV-1 to IV-8. These data are described in the following sections.

Temperature Trends

Temperature data showed annual cyclic variations at all depths (Tables IV-1 and IV-2 and Figures IV-1 to IV-8). Minimum and maximum temperatures were observed in the winter and summer and ranged from 1.2°C to 28.9°C. Temperature damping of seasonal effects was observed with depth in all GMWs. Differences between minimum and maximum temperatures were generally greatest in the surface soil layer and decreased with depth. In addition, there was a phase lag with depth, with temperature minima and maxima reached most rapidly in the near surface zones.

Temperatures also varied between the two fills. EF-1 temperatures ranged from 2.3°C to 28.9°C with mean temperatures of individual sampling intervals ranging from 12.2°C to 16.1°C. EF-2 temperatures ranged from 1.2°C

Table IV-1. Summary of EF-1 Gas and Temperature Data

Station	Depth (ft)	Carbon Dioxide (percent)			Oxygen (percent)			Temperature (C)		
		mean	max.	min.	mean	max.	min.	mean	max.	min.
383+00	3.5	3.7	9.6	0.3	14.3	18.0	0.7	13.6	25.1	4.3
	8.5	2.9	7.1	0.8	11.2	18.3	0.9	15.5	28.9	7.7
	13.5	3.1	7.5	0.8	11.8	18.5	0.3	14.4	23.1	8.1
	18.5	3.7	8.4	0.9	13.4	19.6	1.1	12.8	19.2	8.0
383+25	5.0	3.5	6.9	1.2	8.9	14.6	2.3	12.2	19.6	2.3
	10.0	4.3	7.8	1.6	2.9	11.2	0.3	13.6	21.1	7.2
	15.0	4.2	7.2	1.5	3.4	9.8	0.3	14.7	21.0	8.8
	20.0	4.3	7.6	1.6	3.7	11.7	0.1	15.0	20.7	9.1
	25.0	4.1	8.0	1.1	2.7	10.2	0.1	14.6	20.5	8.4
383+50	4.0	3.7	7.4	1.3	5.3	16.0	1.1	13.2	20.7	4.4
	9.0	3.8	7.0	1.2	7.8	17.7	0.0	16.1	24.1	9.5
	14.0	3.4	7.1	1.0	10.3	18.4	0.8	15.8	21.5	9.3
	19.0	4.4	7.4	2.2	11.0	17.2	1.0	13.7	18.9	9.0

Table IV-2. Summary of EF-2 Gas and Temperature Data

Station	Depth (ft)	Carbon Dioxide (percent)			Oxygen (percent)			Temperature (C)		
		mean	max.	min.	mean	max.	min.	mean	max.	min.
396+00	2.7	5.6	12.3	2.6	10.6	18.6	0.8	10.9	20.2	1.2
	7.7	8.8	14.9	3.0	6.5	15.1	0.5	12.8	21.8	5.5
	12.7	8.0	16.6	1.5	9.2	19.4	0.6	13.2	20.8	7.5
	17.7	8.4	17.0	1.0	9.1	19.8	0.4	12.9	18.9	8.1
397+00	4.0	5.7	11.0	1.6	10.1	17.8	2.0	12.0	21.9	2.7
	9.0	8.7	13.8	4.2	5.4	14.0	0.2	13.4	22.1	6.5
	14.0	4.8	11.3	0.6	12.4	19.6	0.8	13.2	20.7	8.2
401+00	5.0	9.3	19.0	4.3	7.8	15.3	0.5	12.2	21.8	3.9
	10.0	9.1	18.2	3.8	7.7	15.7	0.8	12.7	22.3	6.1
401+12	4.0	5.2	10.4	2.5	13.5	17.4	5.1	11.5	20.9	1.5
	9.0	10.7	19.6	5.9	7.2	17.6	1.2	12.4	22.0	4.7
	14.0	12.9	19.6	6.8	5.5	12.2	0.9	12.8	21.9	6.6
	19.0	11.7	17.2	6.5	6.4	12.9	0.5	12.9	21.3	7.7
	24.0	9.1	14.0	3.9	8.4	15.6	1.0	12.9	21.3	7.2

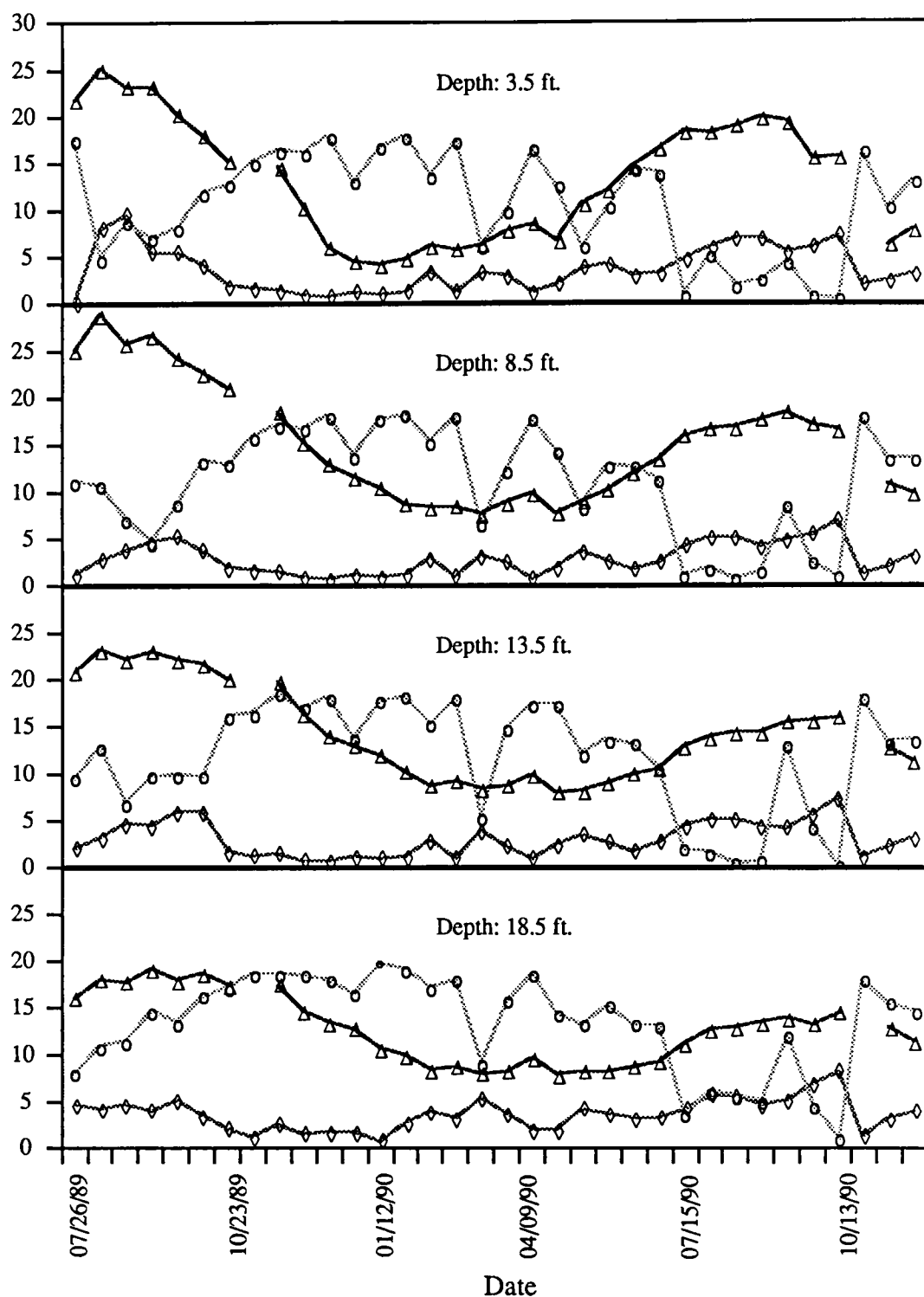


Figure IV-1. Station 383+00 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

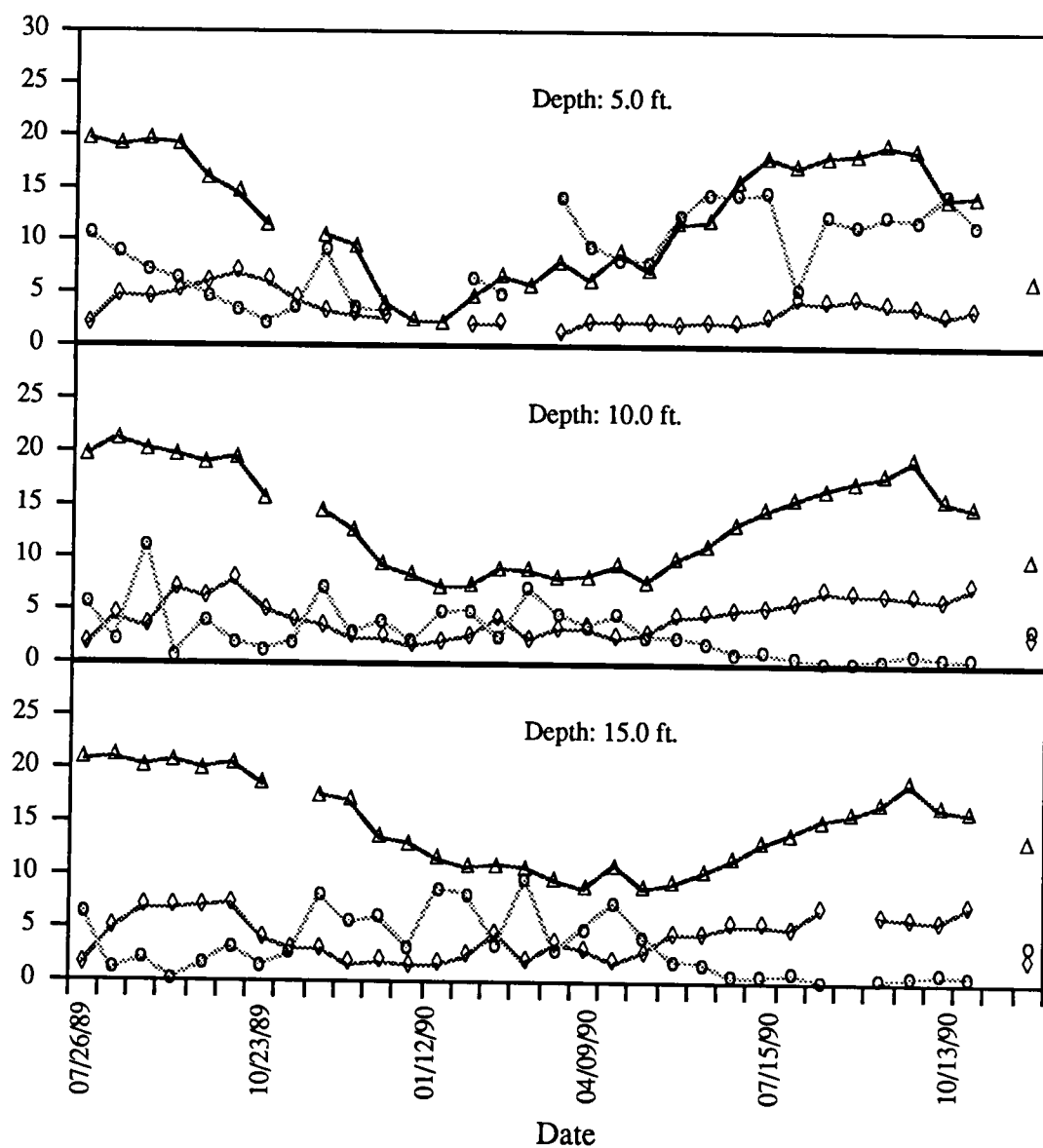


Figure IV-2. Station 383+25 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

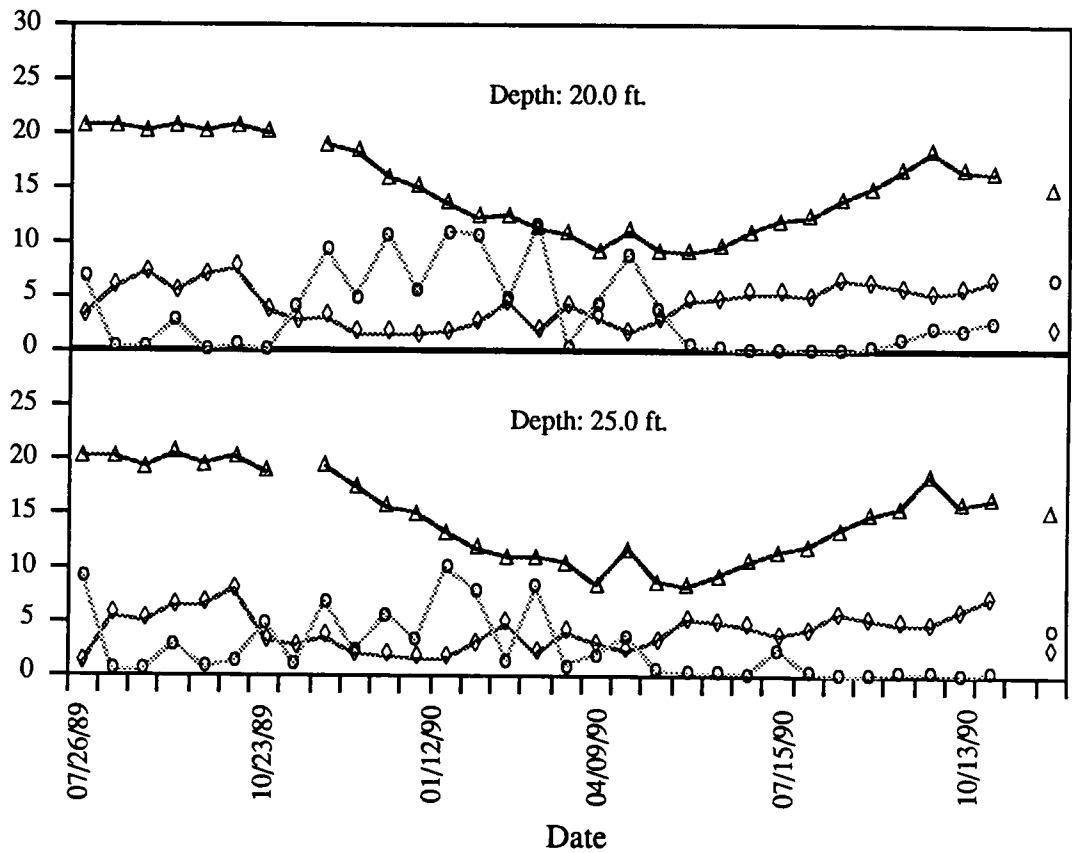


Figure IV-2 (continued). Temperature (°C) (Δ) and carbon dioxide (◇) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

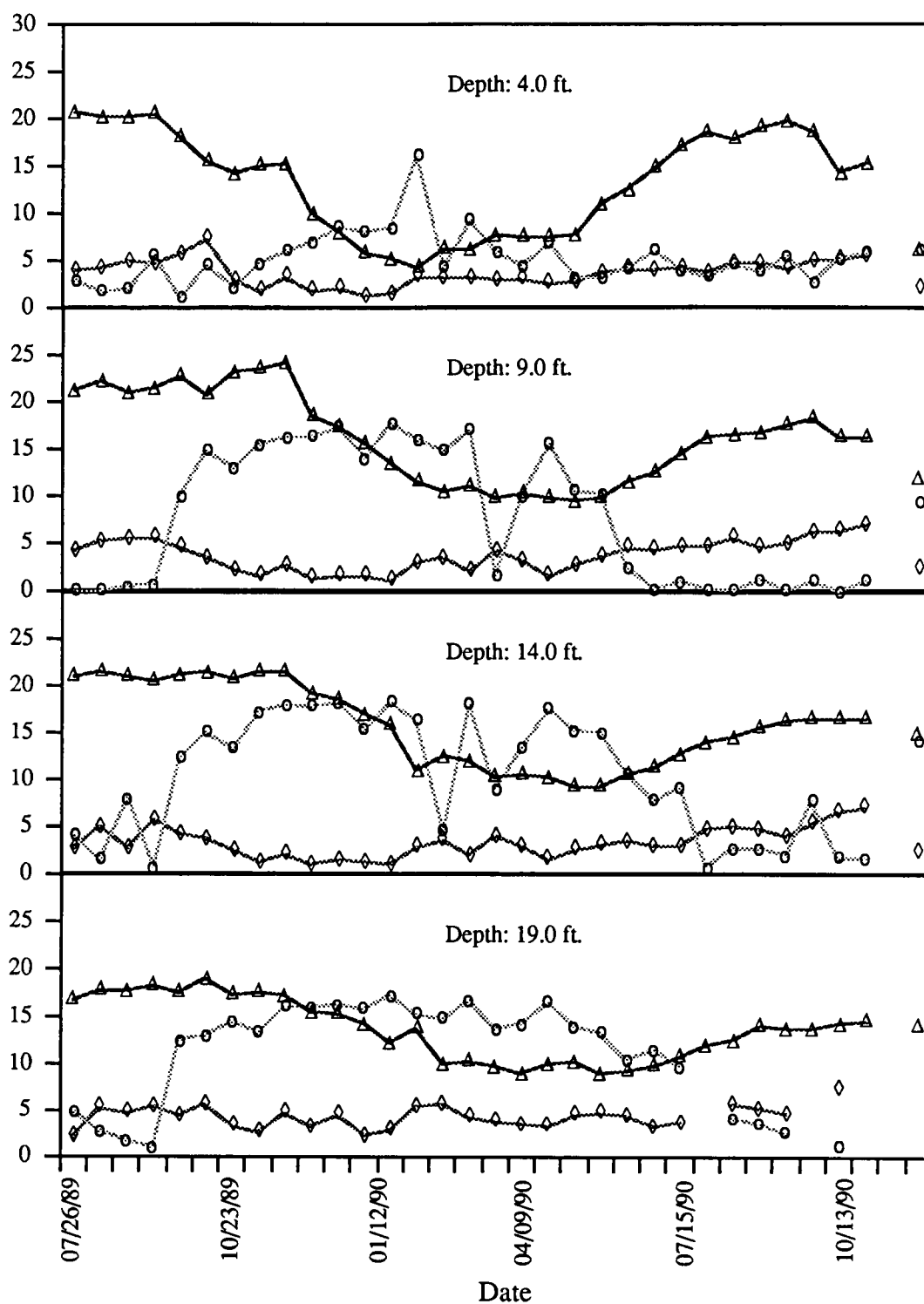


Figure IV-3. Station 383+50 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (o) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

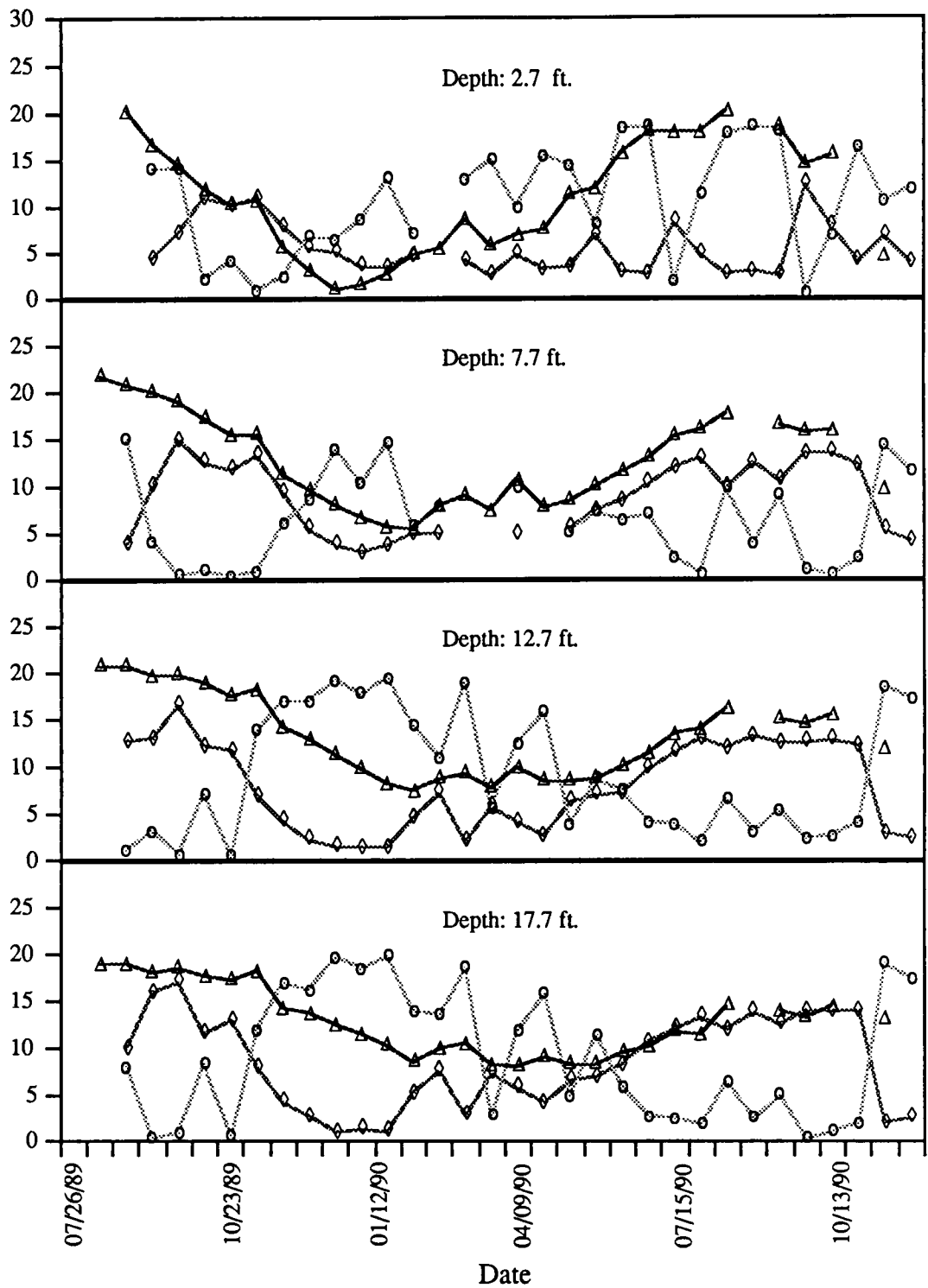


Figure IV-4. Station 396+00 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

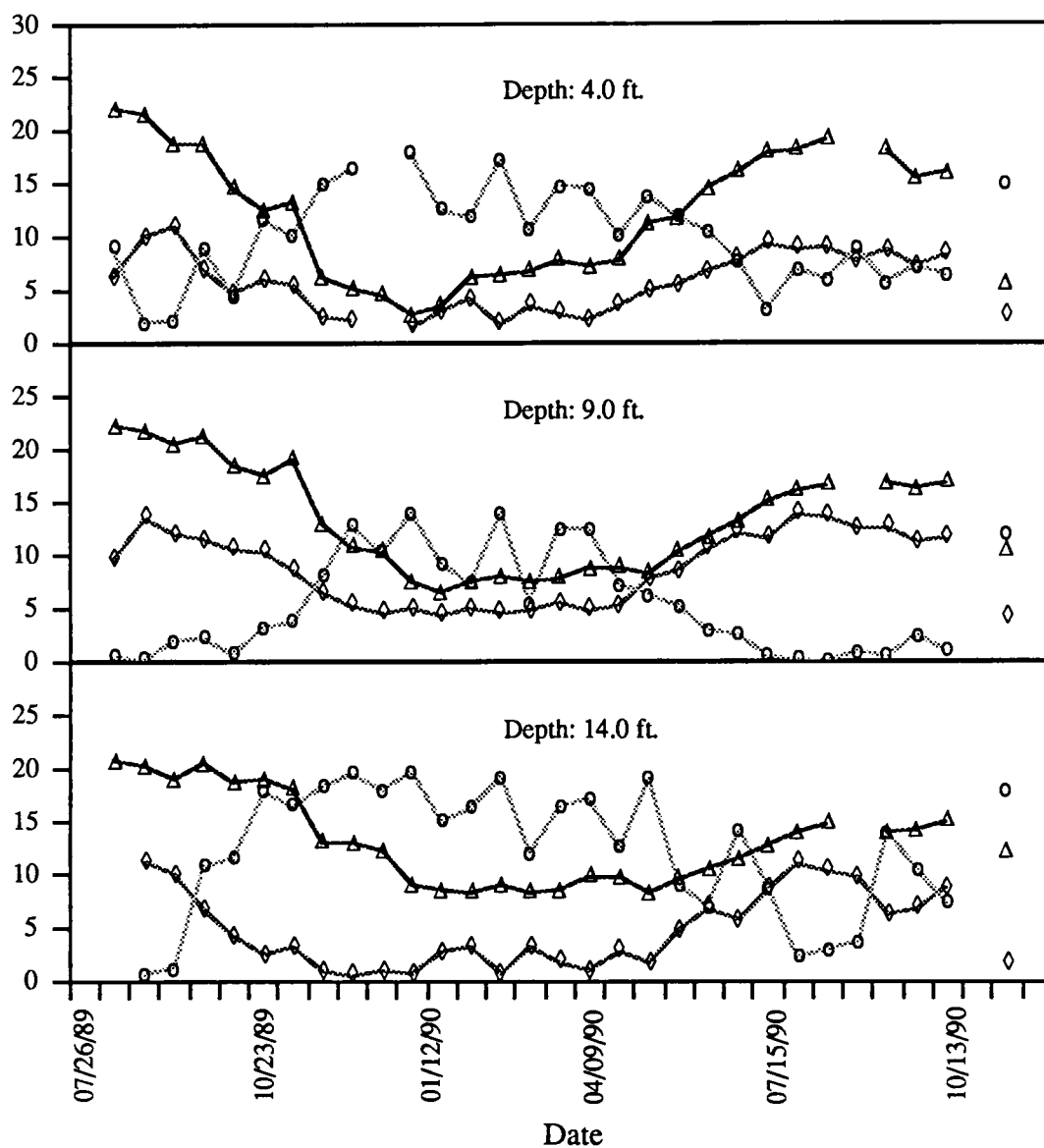


Figure IV-5. Station 397+00 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◇) and oxygen (o) concentrations (%) versus time for specified depths in Station 397+00 GMW. Note: gaps indicate missing data.

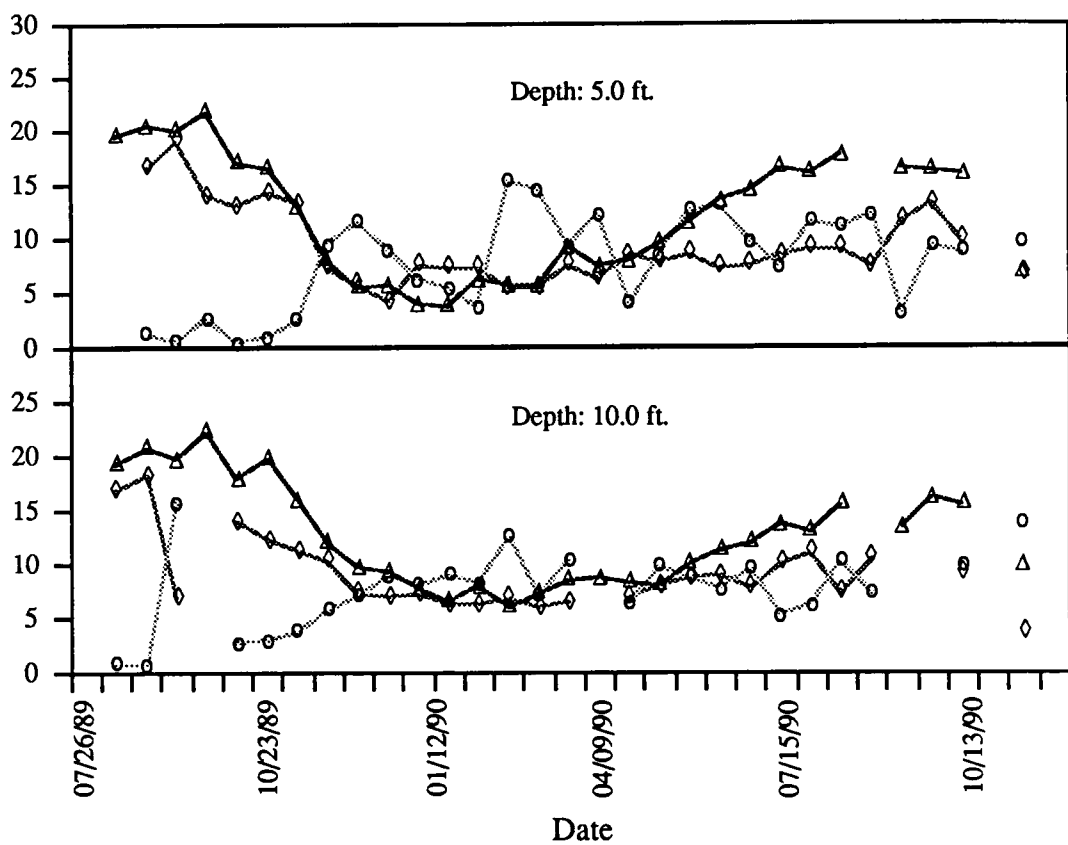


Figure IV-6. Station 401+00 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

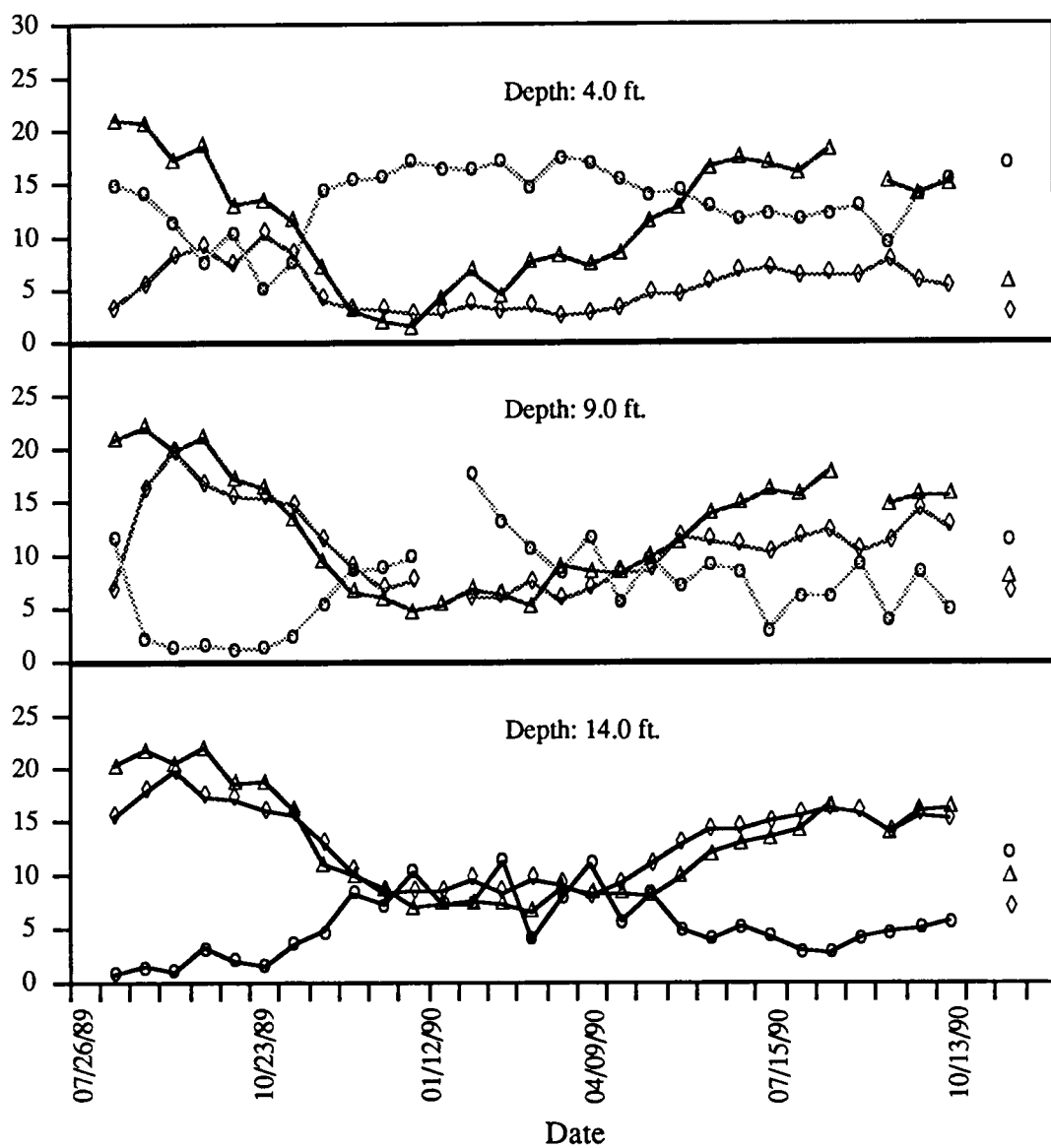


Figure IV-7. Station 401+12 Temperature and Gas Trends. Temperature (°C) (Δ) and carbon dioxide (◇) and oxygen (○) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

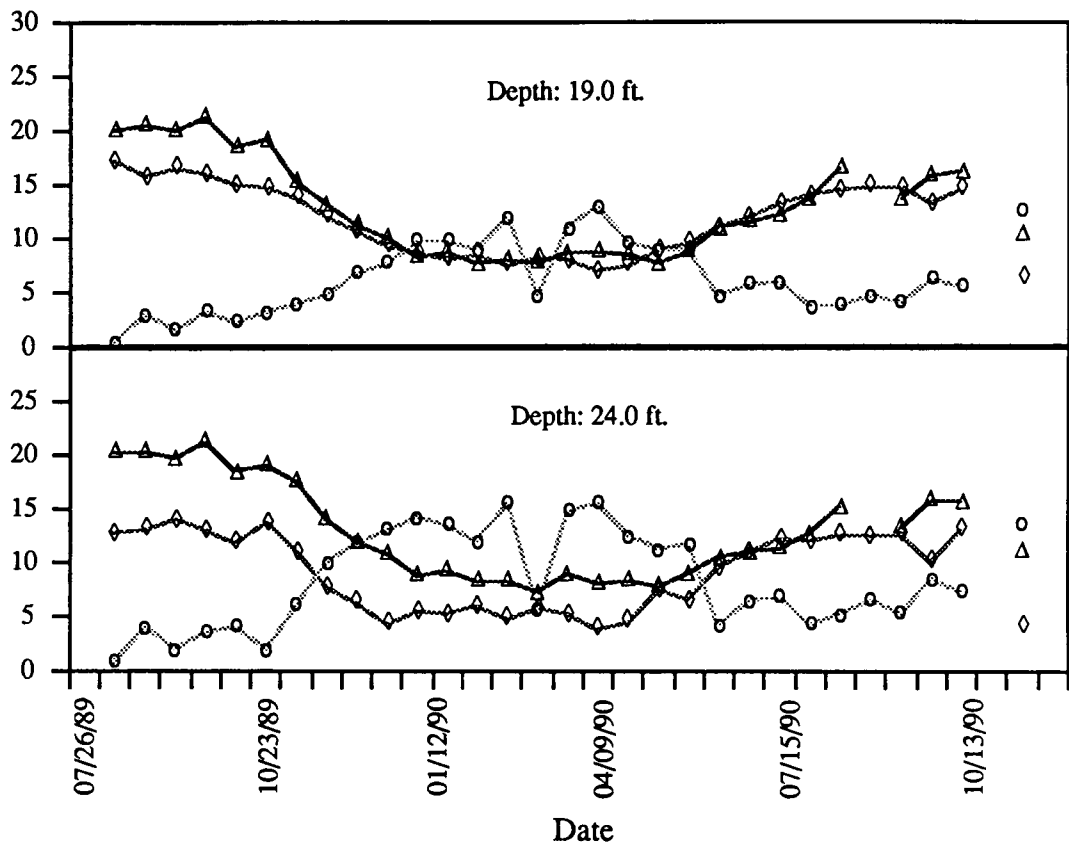


Figure IV-7 (continued). Temperature (°C) (Δ) and carbon dioxide (◊) and oxygen (o) concentrations (%) versus time for specified depths. Note: gaps indicate missing data.

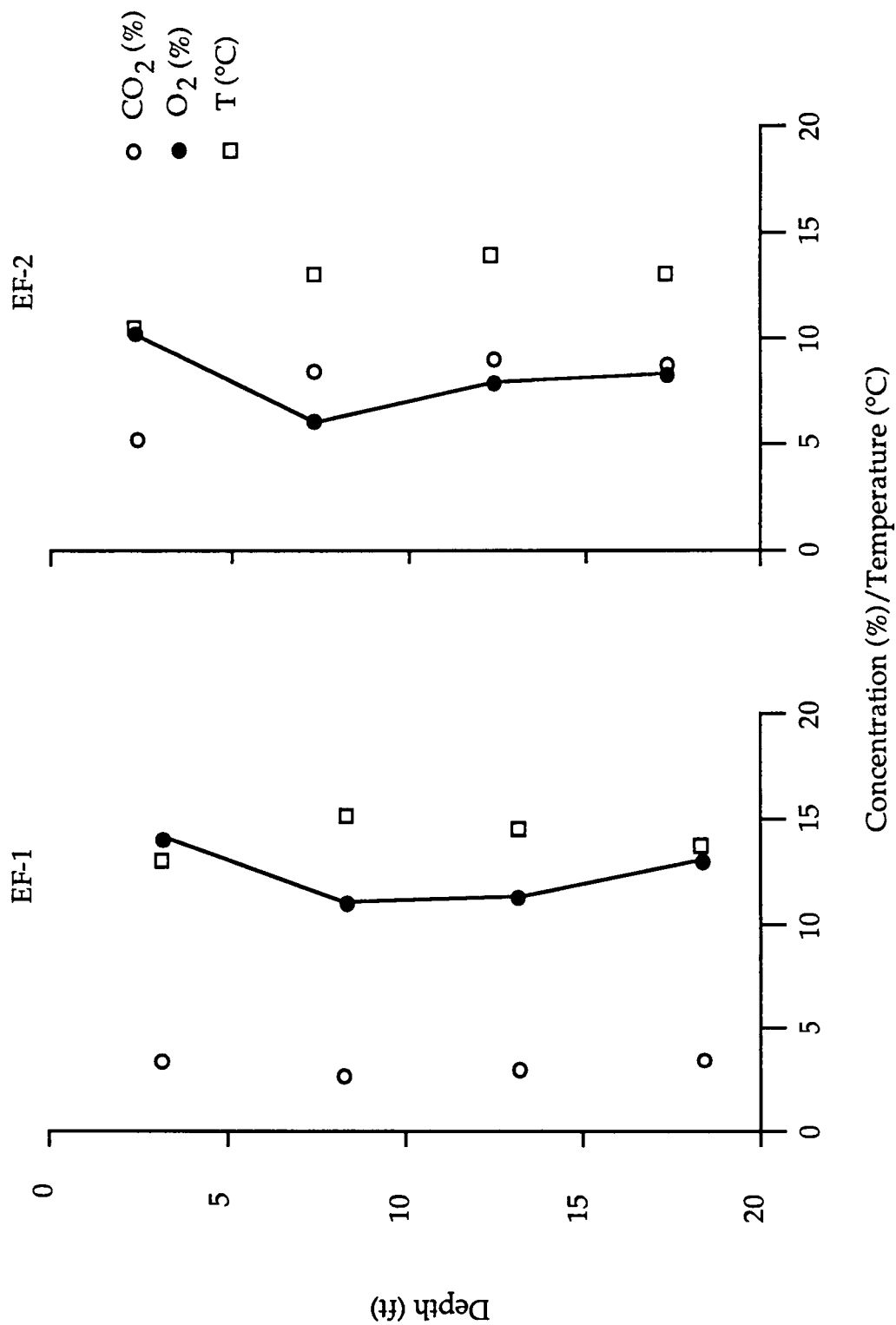


Figure IV-8. Representative Gas and Temperature Trends with Depth in Fills EF-1 and EF-2.

to 22.3°C with mean temperatures of individual sampling intervals ranging from 10.9°C to 13.4°C.

All vertical GMWs showed similar temperature trends with depth. In general, mean temperatures were lowest in the soil layer. Immediately below the soil/fill interface, mean temperatures increased and then gradually decreased with depth in all GMWs. Horizontal GMWs (stations 383+25 and 401+12) also had the lowest observed temperatures in the soil layer. Temperature increased with horizontal distance to a maximum near the deepest gas ports.

Oxygen Trends

Oxygen concentrations showed cyclic seasonal variations at all depths with minimum and maximum concentrations observed in the summer and winter (Tables IV-1 and IV-2 and Figures IV-1 to IV-8). Oxygen concentrations ranged from non-detectable levels (<0.1%) to 19.8%. Differences between maximum and minimum oxygen concentrations at individual sampling intervals varied from approximately 9.5% to 19.4%.

Oxygen concentrations, in general, did not vary significantly between the fills. Mean values for individual sampling intervals ranged from 5.4% to 13.5% in EF-2 and from 5.3% to 14.3% in EF-1 with the exception of station 383+25. At station 383+25, all sampling intervals below the soil layer had anomalously low levels of oxygen, with mean values ranging from 2.9% to 3.7%.

Unlike temperature, phase lags were not apparent due to the erratic behavior of oxygen concentration, which obscures overall trends. Changes in oxygen concentrations as great as 16% were observed between sampling events. These anomalous changes occurred at all depths in some GMWs, but not in others. For example, station 383+00 showed a significant decline in oxygen concentration at all depths on 3/12/90 (Figure IV-1). Throughout the sampling period for this station, similar trends in oxygen concentration were observed at all depths. In station 383+50, anomalous changes in oxygen concentration are independent of depth (Figure IV-3). For instance, between 1/12/90 and 4/9/90, changes in oxygen concentration greater than 9% between sampling events occurred on four occasions. These changes, however, occurred only at discrete sampling intervals and at different dates.

Oxygen distribution with depth was similar to observed temperature trends (Tables IV-1 and IV-2 and Figure IV-8). Mean oxygen concentrations in vertical GMWs decreased immediately below the soil layer and then increased with depth in fill material in 3 of the 5 GMWs. The 2 vertical GMWs that did not show this trend (stations 396+00 and 401+00) had variations in mean concentrations of approximately 0.1% between basal sampling interval and the sampling interval immediately above the basal zone. Lack of significant variation between these intervals may reflect the different methods of GMW installation at these stations. In addition, station 401+00 did not have a sampling interval in the soil layer and therefore, no direct conclusion can be drawn. Between the horizontal GMWs (i.e., stations 383+25 and 401+12), oxygen concentrations vary with depth. In both stations, maximum oxygen concentrations were observed in the shallow sampling

intervals. With depth, minimum or near minimum oxygen levels occur near the mid portion of the GMWs. Oxygen concentration in general then increases with depth.

Oxygen concentrations were in general, greatest in the shallow sampling intervals. Because station 401+00 did not have a sampling port situated in the soil layer, no conclusion can be made concerning oxygen concentration at that location. Of the remaining 6 GMWs, 4 had maximum oxygen concentrations in the shallow sampling interval.

Carbon Dioxide Trends

Like oxygen and temperature, carbon dioxide concentrations also showed seasonal variations (Tables IV-1 and IV-2 and Figures IV-1 to IV-8). Highest concentrations were observed during the summer months, when soil temperature was highest and oxygen concentration lowest. Significantly higher concentrations of carbon dioxide were observed in fill EF-2, with maximum mean concentrations approximately three times greater than those of EF-1. Carbon dioxide concentrations in EF-1 ranged from 0.3% to 9.6%, and from 0.6% to 19.6% in EF-2. Mean values of individual sampling intervals ranged from 2.9% to 4.4% for EF-1 and from 4.8% to 12.9% for EF-2. Phase lags were not observed in the trends for carbon dioxide.

Unlike temperature and oxygen, changes in carbon dioxide concentrations with depth were not consistent (Tables IV-1 and IV-2 and Figure IV-8). Mean carbon dioxide concentrations in the near surface sampling ports were lowest in only 3 of 7 GMWs. Carbon dioxide concentrations were greatest in the

basal fill at stations 383+00 and 383+50. Horizontal variation at station 383+25 in EF-1 was minimal and observed levels corresponded to basal concentrations observed at the other EF-1 GMWs. Carbon dioxide concentrations in EF-2 had highest mean concentrations in the mid portions of the fill.

Anomalous changes in carbon dioxide concentration was observed only in one GMW (station 397+00) in EF-2 (Figure IV-4). Large changes in carbon dioxide concentration at this location corresponded to anomalous oxygen changes. For example, between 2/11/90 and 2/26/90, carbon dioxide concentrations declined by approximately 5% in EF-2 (station 397+00) while oxygen increased by 5% to 8%.

Gas and Temperature Correlations

Data trends indicate there are relationships between oxygen, carbon dioxide, and temperature. To determine the strength of the relationships, regression lines and correlation coefficients were calculated between these variables for all sampling intervals. The regression line takes the form:

$$Y = mX + b \quad (10)$$

where:

Y = oxygen concentration (%);

X = carbon dioxide concentration (%);

m = slope of the regression line; and

b = constant (Y intercept).

The results of regression analyses performed on raw data are summarized in Tables IV-3 and IV-4. In all following discussions, a significant correlation is defined by a correlation coefficient (r) greater than 0.6.

Significant correlations between oxygen and carbon dioxide were observed at 24 of 27 sampling depths with correlation coefficients ranging from 0.40 to 0.96. Three sampling depths showed weak correlations, all located in fill EF-1. The ratio of change (i.e., the slope (m) of the regression line) of carbon dioxide versus oxygen concentration varied from -0.7 to -8.3 with intercepts ranging from 6.5 to 22.9.

Correlations between carbon dioxide and temperature, and oxygen and temperature are weaker. The correlation between carbon dioxide and temperature was significant at only 13 of 27 sampling depths. In addition, 10 of the 13 sampling depths were located in fill EF-2. Correlation between oxygen and temperature was significant at only 7 of 27 sampling depths. Again, 6 of 7 sampling depths were located in fill EF-2.

Stable Isotopes of Fill Gas

Gas samples for isotopic analysis of soil atmosphere carbon dioxide were collected from September 1990 to January 1991 from 2 GMWs located at stations 383+00 and 396+00 in fills EF-1 and EF-2. Graphical representations of the isotopic data and carbon dioxide concentrations are shown in Figure IV-9. Raw data are found in Appendix B.

During this time period, similar oxygen isotope trends were observed in both fills. $\delta^{18}\text{O}$ shows a monotonic increase from approximately -6‰ to -3‰

Table IV-3. Summary of EF-1 Regression Analysis

Station	Depth (ft)	CO2-O2 r	CO2-O2 m	CO2-O2 b	CO2-T r	O2-T r
383+00	3.5	-0.83	-1.9	17.8	0.7	-0.51
	8.5	-0.88	-3.0	20.1	0.39	-0.37
	13.5	-0.84	-2.6	20.3	0.35	-0.20
	18.5	-0.86	-2.6	22.9	0.17	-0.10
383+25	5.0	-0.49	-1.3	13.5	0.51	-0.30
	10.0	-0.62	-8.2	6.5	0.64	-0.17
	15.0	-0.78	-1.1	8.1	0.46	-0.32
	20.0	-0.79	-1.6	10.7	0.33	-0.10
	25.0	-0.67	-1.1	7.3	0.24	-0.10
383+50	4.0	-0.40	-0.9	8.5	0.66	-0.63
	9.0	-0.88	-3.8	22.3	0.17	-0.10
	14.0	-0.82	-3.3	21.3	0.04	-0.10
	19.0	-0.44	-2.0	19.7	0.09	-0.33

Table IV-4. Summary of EF-2 Regression Analysis

Station	Depth (ft)	CO2-O2 r	CO2-O2 m	CO2-O2 b	CO2-T r	O2-T r
396+00	2.7	-0.87	-1.7	20.4	0.26	-0.10
	7.7	-0.85	-1.1	15.9	0.68	-0.45
	12.7	-0.92	-1.3	19.7	0.59	-0.40
	17.7	-0.93	-1.3	20.3	0.39	-0.20
397+00	4.0	-0.90	-1.4	18.3	0.91	-0.84
	9.0	-0.90	-1.6	16.4	0.81	-0.78
	14.0	-0.95	-1.6	20.2	0.52	-0.45
401+00	5.0	-0.74	-0.9	16.4	0.81	-0.44
	10.0	-0.83	-0.9	15.8	0.75	-0.45
401+12	4.0	-0.96	-1.3	20.4	0.66	-0.57
	9.0	-0.83	-0.9	17.0	0.75	-0.64
	14.0	-0.87	-0.7	15.1	0.91	-0.78
	19.0	-0.91	-0.9	17.4	0.93	-0.81
	24.0	-0.90	-1.1	18.7	0.82	-0.77

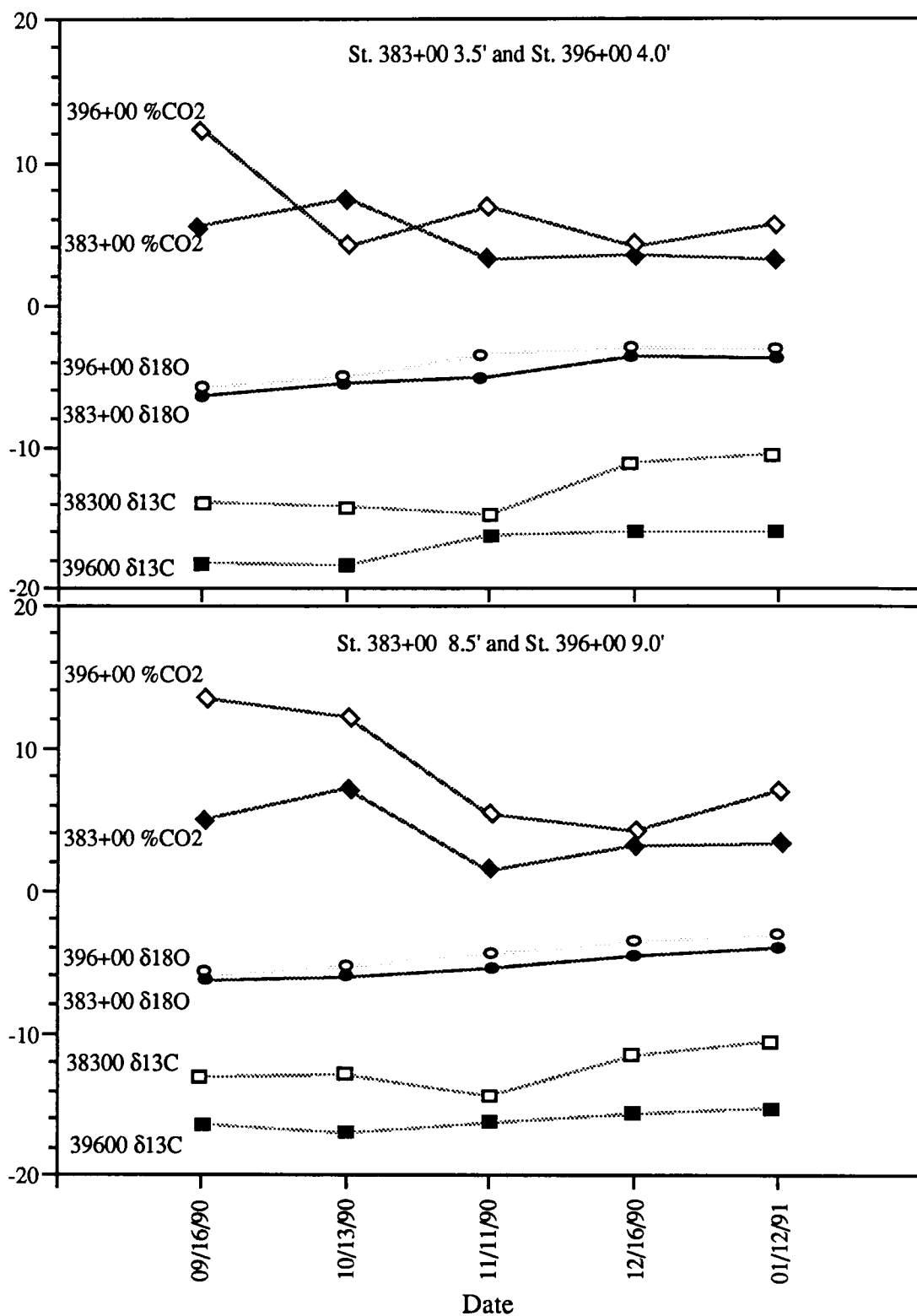


Figure IV-9. Isotopic Data Trends of Fill Carbon Dioxide. Carbon dioxide concentrations (%), and isotopic composition of carbon and oxygen (‰ PDB) versus time for specified depths.

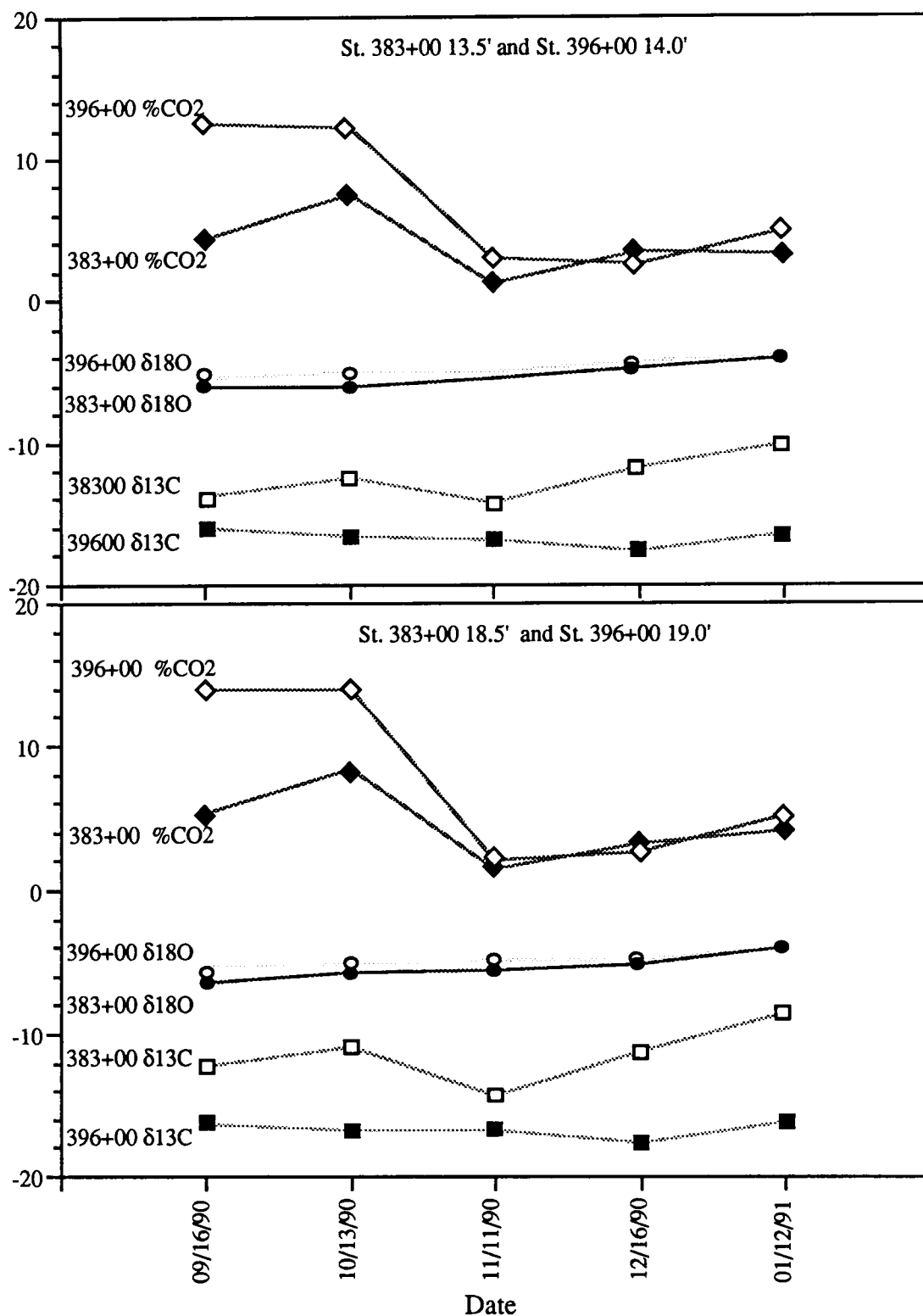


Figure IV-9 (continued). Carbon dioxide concentrations (%), and isotopic composition of carbon and oxygen (‰ PDB) versus time for specified depths .

(PDB) over the period. Trends in $\delta^{13}\text{C}$, however, were significantly different between the two fills. At station 396+00, $\delta^{13}\text{C}$ did not vary significantly over time, with values ranging from approximately -15‰ to -18‰. Greater variation in station 383+00 was observed, with $\delta^{13}\text{C}$ values ranging from approximately -8‰ to -15‰. Using a mass balance approach, relative contributions of carbon dioxide from inorganic and organic sources were determined from following relationship:

$$\delta^{13}\text{C} = xA + (1-x)B \quad (11)$$

where:

x = mole fraction of inorganic carbon dioxide;

$(1-x)$ = mole fraction of organic carbon dioxide;

A = $\delta^{13}\text{C}$ of inorganic carbon dioxide; and

B = $\delta^{13}\text{C}$ of organic carbon dioxide.

The inorganic value for $\delta^{13}\text{C}$ is based on the isotopic composition of the limestone used in the fill construction and was determined to be approximately -2‰. The isotopic data for the inorganic source is highly constrained, with $\delta^{13}\text{C}$ of limestone aggregate and pulverized limestone used in fill construction ranging from approximately -1.3‰ to - 2.4‰. Values of $\delta^{13}\text{C}$ from organic sources are not as well constrained. Published $\delta^{13}\text{C}$ values for biotic respiration range from approximately -10‰ to -20‰ for C4 vegetation to -20‰ to -30‰ for C3 vegetation (Deines, 1980). Maxima occur at -16‰ and -23‰ for C4 and C3 vegetation. Examples of C4 vegetation include corn and tropical grasses while mixed hardwood forests such as those

present in the study area are classified as C3 vegetation. Thus, $\delta^{13}\text{C}$ of -23‰ was used in the mass balance calculations based on vegetation type. Fractions derived from equation (11) were multiplied by total carbon dioxide concentrations to determine theoretical organic and inorganic concentrations. Results are shown in Figures IV-10 to IV-11 with the raw data contained in Appendix B. In addition to the carbon dioxide concentrations, precipitation for the 14 day period prior to the sampling date are also shown. Precipitation is illustrated because it is necessary to transport acidity to fill limestone which would liberate carbon dioxide during AD neutralization.

In general, carbon dioxide trends closely followed precipitation trends at all depths in station 383+00 (Figure IV-10). $\delta^{13}\text{C}$ results indicate that total carbon dioxide concentrations are predominantly from limestone dissolution in fill EF-1. The periods of highest inorganic carbon dioxide correlate to either high precipitation preceding sampling (i.e., 10/13/90 sampling event) or after the decline in soil temperature. Between the October and December sampling events in EF-1, fill temperatures decreased by 9.3°C at the near surface and by 1.7°C at the basal sampling interval. Although temperature data for the November sampling is lacking, it appears that temperature began to decline between October and November based on the carbon dioxide concentration decline.

Carbon dioxide temporal trends at station 396+00 GMW varied with depth (Figure IV-11). At the shallowest depth, the trend is inversely related to precipitation rate. All trends at greater depths are similar, with a rapid decline in total concentration between October and November resulting from declines in both inorganic and organic carbon dioxide sources. The decline in

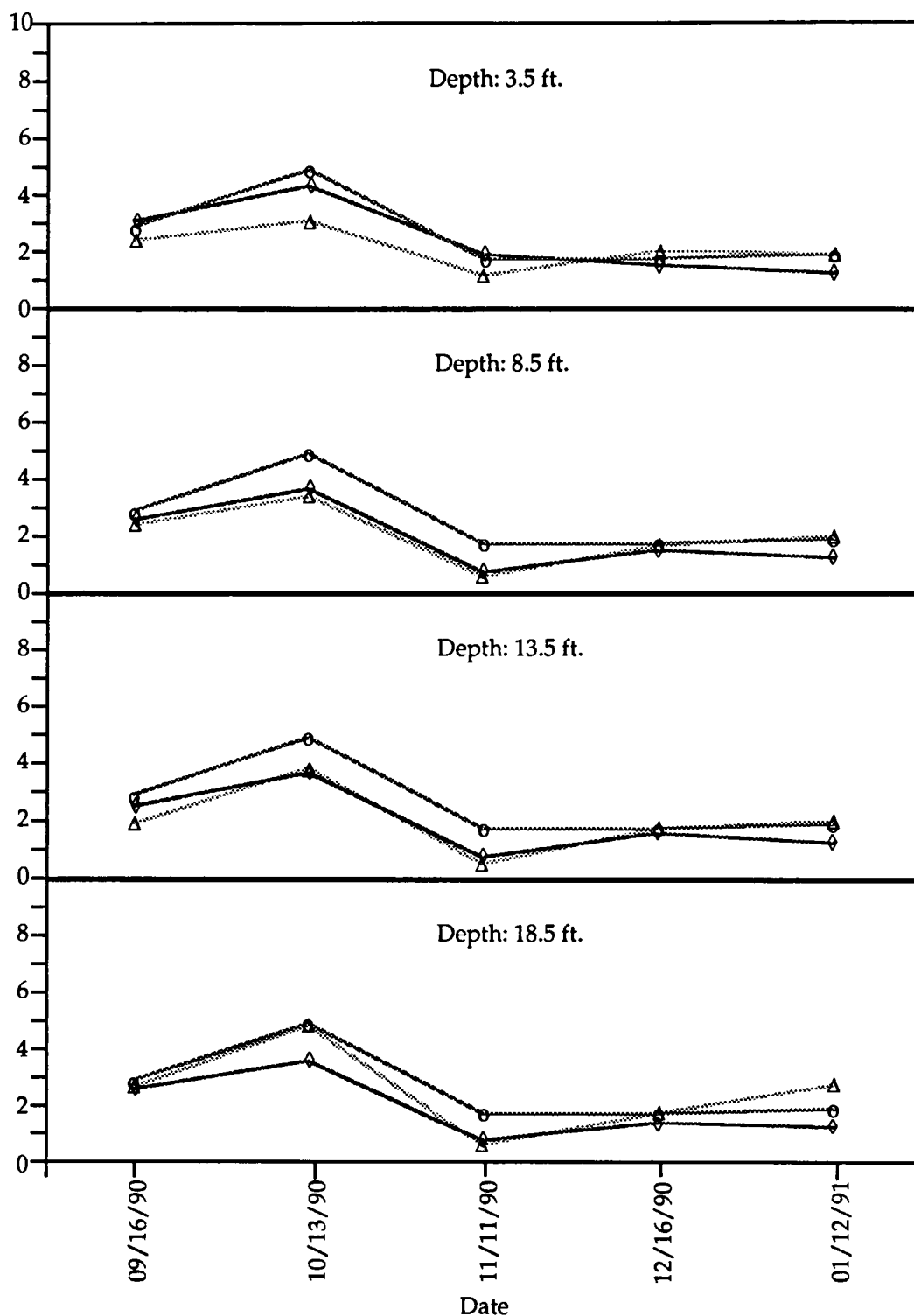


FIGURE IV-10. Theoretical Concentrations of Organic- and Inorganic-Derived Carbon Dioxide in EF-1. Cumulative precipitation (14 days - inches)(o) and calculated carbon dioxide concentrations (%) from inorganic (Δ) and organic (◇) sources for specified depths.

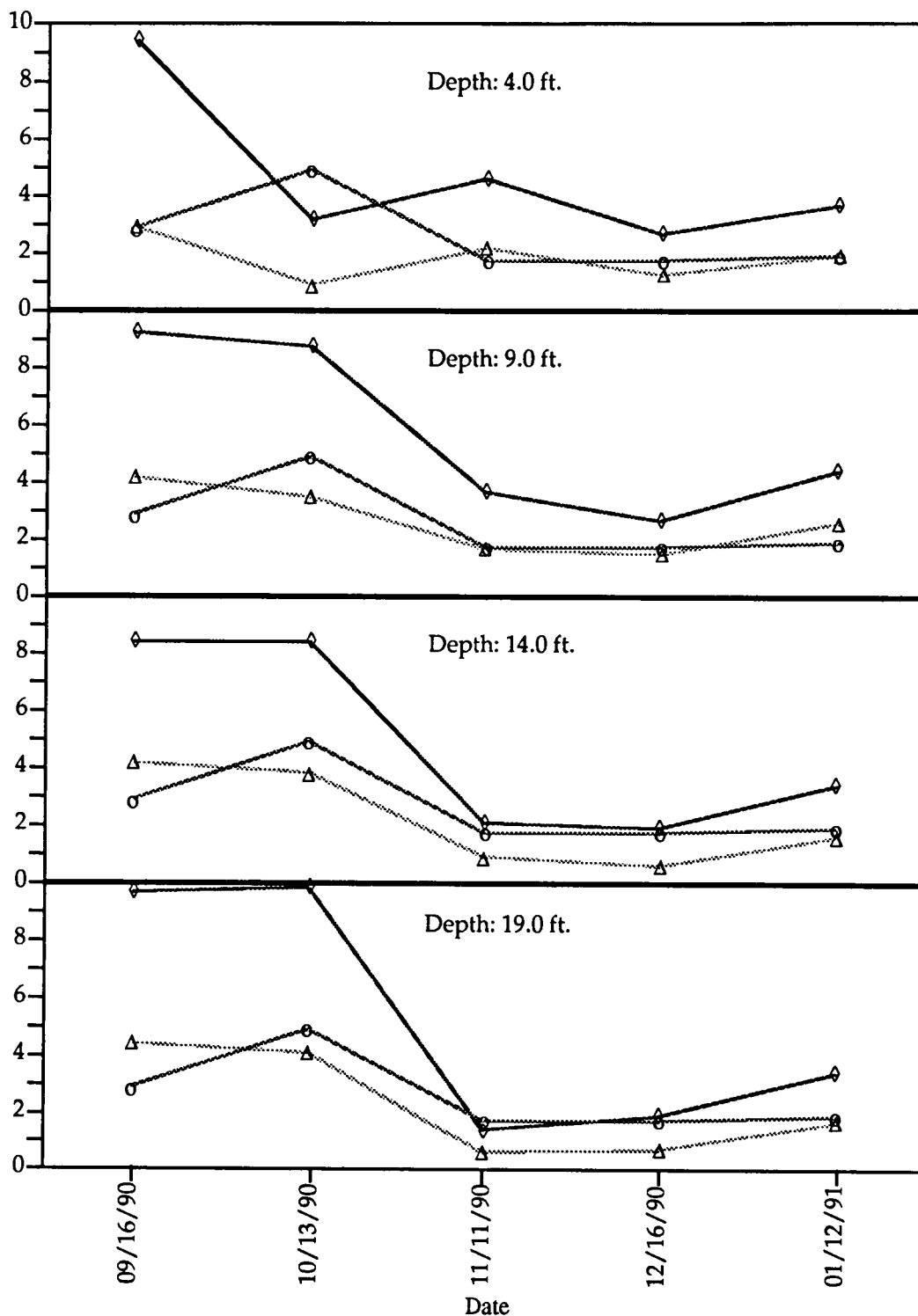


FIGURE IV-11. Theoretical Concentrations of Organic- and Inorganic-Derived Carbon Dioxide in EF-2. Cumulative precipitation (14 days - inches) (o) and calculated carbon dioxide concentrations (%) from inorganic (Δ) and organic ($\diamond$) sources for specified depths.

total carbon dioxide concentration also corresponds to a decline in soil temperature. Between the October and December sampling event in EF-2, fill temperatures decreased by 11.0°C at the near surface and by 1.3°C at the basal sampling interval. Again, temperature data for November is lacking but it is assumed the temperature must have begun to decline in November. Unlike station 383+00, organic carbon dioxide accounts for the greatest portion of total carbon dioxide based on the $\delta^{13}\text{C}$ isotopic data.

During a given sampling event, the $\delta^{13}\text{C}$ trends varied with depth between the fills (Figures IV-12 and IV-13). In station 383+00, $\delta^{13}\text{C}$ increased with depth with maximum values recorded at the basal sampling interval from 4 of the 5 sampling events (Figure IV-12). $\delta^{18}\text{O}$ trends were relatively stable with increasing depth. Depth trends in station 396+00 were, in general, opposite those observed in station 383+00 with the lightest $\delta^{13}\text{C}$ values observed in the basal sampling intervals (Figure IV-13). Again, $\delta^{18}\text{O}$ trends were relatively stable with depth.

The uniform temporal trends imply a single controlling mechanism for $\delta^{18}\text{O}$ of soil carbon dioxide. To determine if the controlling mechanism was an isotope exchange reaction between soil water and carbon dioxide, theoretical $\delta^{18}\text{O}$ values were calculated based on oxygen isotope data of soil water and carbon dioxide sampled during September and November, 1990. The enrichment factor between soil carbon dioxide and soil water of known isotopic ratios ($m\epsilon_{\text{CO}_2\text{-H}_2\text{O}}$) taken from Fritz and Fontes (1980) is expressed by:

$$m\epsilon_{\text{CO}_2\text{-H}_2\text{O}} = (\delta^{18}\text{O}_{\text{CO}_2} - \delta^{18}\text{O}_{\text{H}_2\text{O}}) / (1 + \delta^{18}\text{O}_{\text{H}_2\text{O}} / 1000) \quad (12)$$

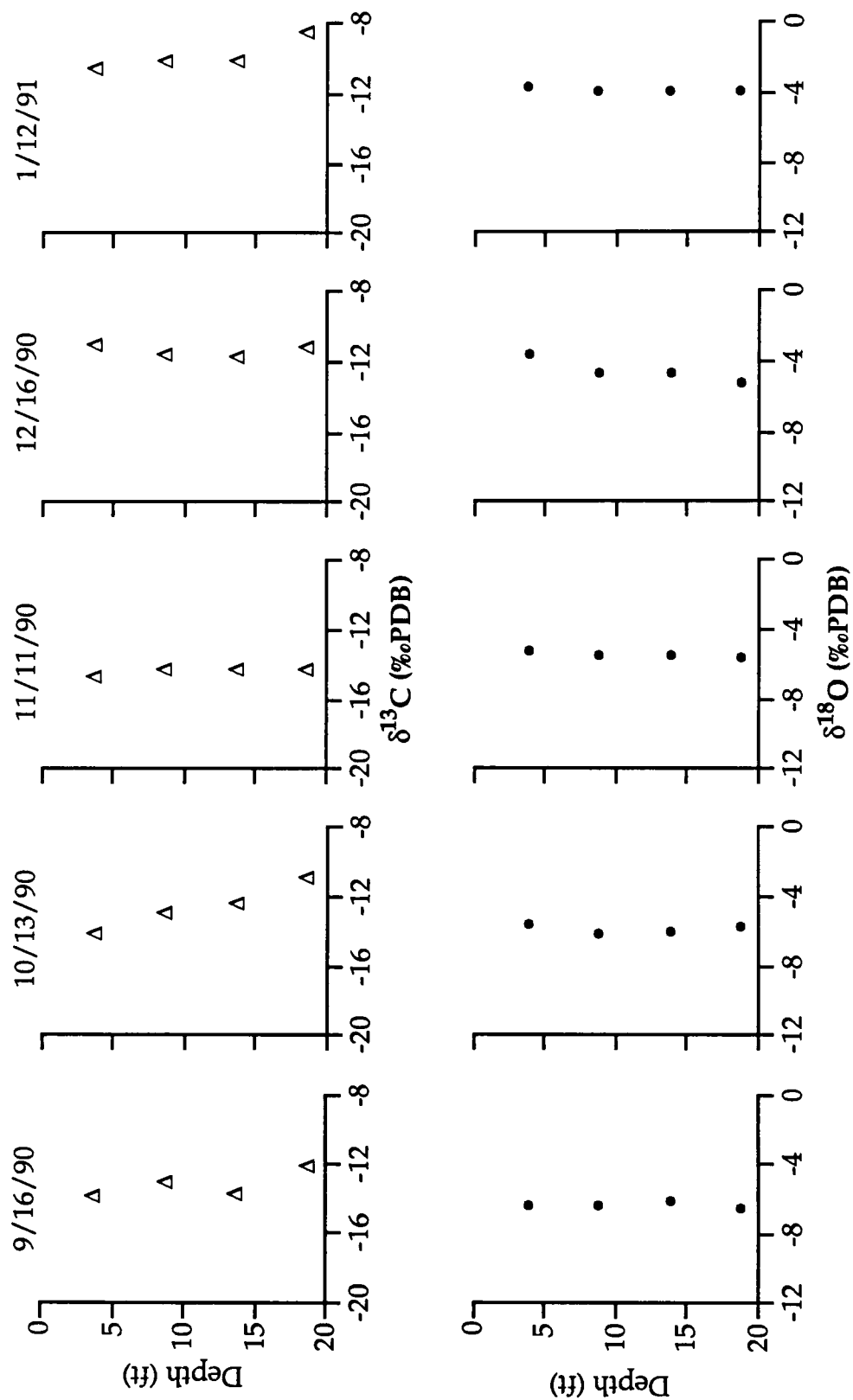


Figure IV-12. Carbon Dioxide Isotopic Trends with Depth in Fill EF-1

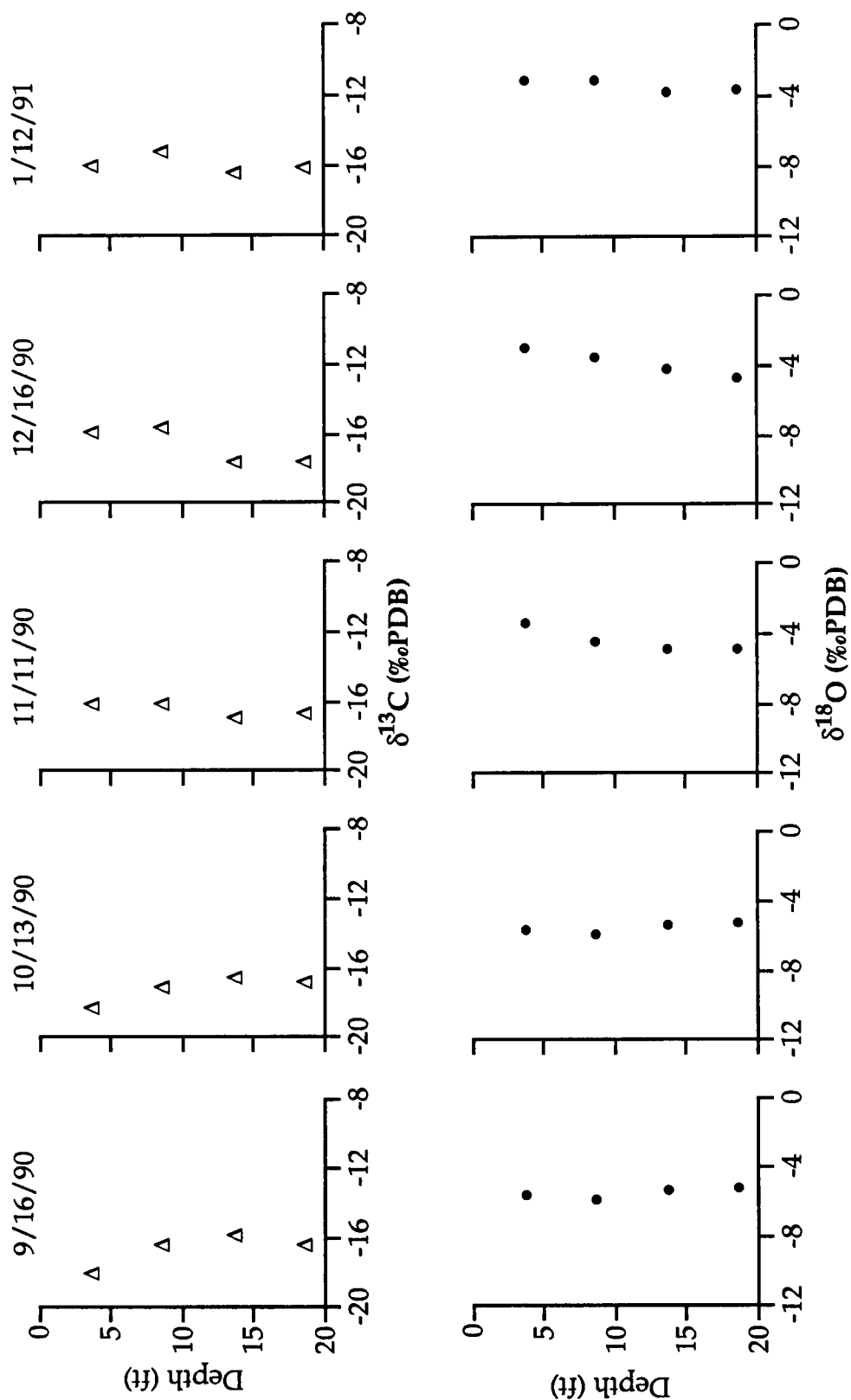


Figure IV-13. Carbon Dioxide Isotopic Trends with Depth in Fill EF-2

Equation (12) may also be used to express a theoretical equilibrium enrichment between carbon dioxide and water ($\epsilon_{\text{CO}_2\text{-H}_2\text{O}}$) based on temperature dependent fractionation factors provided by Friedman and O'Neil (1977). Comparison of theoretical with measured enrichment factors would provide information concerning $\delta^{18}\text{O}$ equilibrium conditions between carbon dioxide and water. Results of these calculations are summarized in Table IV-5. The theoretical enrichment factor at the soil temperatures measured during sampling events show a poor correlation with measured enrichment factors. The difference in these two values is approximately 10‰, indicating the system is in disequilibrium. Although disequilibrium conditions exist, it is apparent that the exchange reactions still must influence the isotopic composition of carbon dioxide. This conclusion is based on similar temporal trends in both fills (Figure IV-9).

Water Quality

General

Although a rigorous examination of water quality was not conducted, the basic parameters measured provide some indication of the effectiveness of fill encapsulation. Water quality results are reported in Appendix E.

The water quality from EF-1 was degraded relative to EF-2. EF-1 underdrain leachate was typically near neutral, but contained high levels (approximately 200 mg/l) of dissolved sulfate. In addition, leachate samples were collected from the basal sampling port in station 383+50. These samples

Table IV-5. Isotopic Enrichment Between Fill Carbon Dioxide and Fill Water

Station	Date Sampled	Temperature (°C)	$\delta^{18}\text{O}$ Water (‰SMOW)	$\delta^{18}\text{O}$ CO_2 (‰SMOW)	Theoretical ϵ (‰SMOW)	Measured ϵ (‰SMOW)
383+00	9/16/90	14.4	-7.7	24.3	41.9	32.2
396+00	9/16/90	14.0	-7.7	24.3	41.9	32.2
383+00	11/11/90	10.7	-7.4	24.6	42.6	32.2
396+00	11/11/90	10.7	-7.4	24.2	42.6	32.1

were light to deep red in color, and had high sulfate (approximately 2000 mg/L), high specific conductivity (approximately 2500 umhos), and a pH ranging from 2 to 3. EF-2 underdrain leachate was excellent, with a near neutral pH, low conductivity (< 50 umhos), and low levels (< 5 mg/l) of sulfate.

Theoretical partial pressure of carbon dioxide may be determined from alkalinity results from water quality analysis. The calculations were done based on the following relationship as defined by Stumm and Morgan (1981):

$$[\text{Alkalinity}] = \{(K_H P_{\text{CO}_2} / \alpha_0) \times (\alpha_1 - 2\alpha_2) + [\text{OH}^-] - [\text{H}^+]\} \quad (13)$$

where:

$[\text{Alkalinity}] = \text{mg CaCO}_3/\text{L}$

K_H = Henry's constant

P_{CO_2} = partial pressure of carbon dioxide (atm)

α_0 = ionization fractionation factor ($\text{CO}_2\text{-HCO}_3^-$)

α_1 = ionization fractionation factor (HCO_3^-)

α_2 = ionization fractionation factor ($\text{CO}_2\text{-HCO}_3^-$)

The results of these calculations are reported in Appendix E. Regression analysis indicates a poor correlation ($r = 0.30$) between carbon dioxide concentrations measured in the fills and the theoretical results based on alkalinity measurements. The regression analysis, however, is strongly influenced by 3 data points which indicate anomalous carbon dioxide partial pressures, on the order of 1 to 6 atmospheres. The anomalous theoretical

results indicate supersaturation with respect to bicarbonate. Bicarbonate concentration of natural water is held within a moderate range by carbonate equilibria but processes releasing carbon dioxide (such as AD neutralization reactions) can result in anomalously high concentrations (Hem, 1972). The plot of theoretical versus measured carbon dioxide concentrations excluding the anomalous points is shown in Figure IV-14. Correlation is strong, with a correlation coefficient of 0.70 and a regression line slope of 5. This also indicates that not all alkalinity is the result of equilibration of fill carbon dioxide with the water. If alkalinity were the result of equilibration of fill carbon dioxide with fill leachate, the theoretical values should correlate with analytical results.

Stable Isotopes of Aqueous Carbonate Species

Water samples for isotopic analysis of aqueous carbonate species were collected in April, October, and November 1990 from various underdrains and natural springs throughout the study area. Graphic representations of the isotopic data of aqueous carbonate species and limestone are shown in Figure IV-15. Raw data are located in Appendix C. Data shown have been corrected for differing fractionation factors of carbon dioxide liberated from calcite and witherite (Sharma and Clayton, 1965).

Aqueous carbonate species from different locations show a wide range in isotopic composition. Natural springs emanating from saturated upslope soils and/or bedrock have the lightest $\delta^{13}\text{C}$ values while those collected from fill underdrains having a history of AD are isotopically heaviest with respect

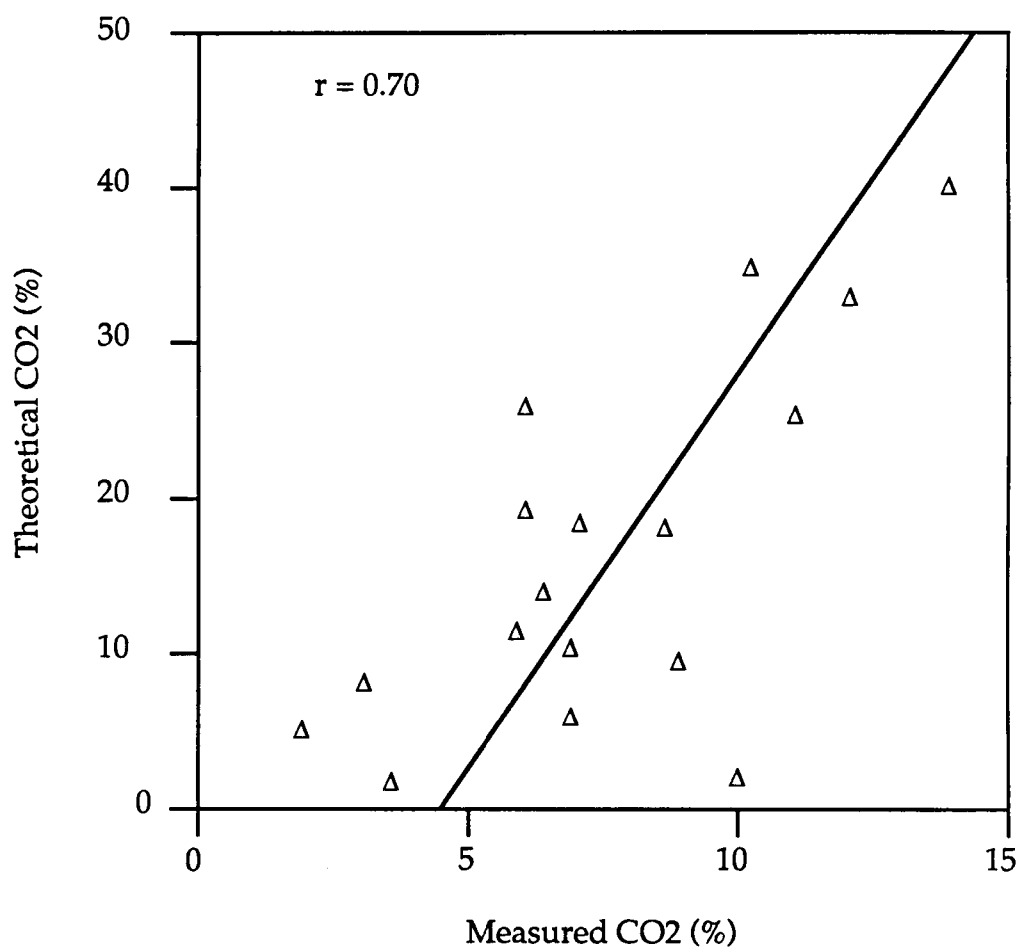


Figure IV-14. Theoretical Versus Measured Carbon Dioxide Concentrations in Fills EF-1 and EF-2. Note: anomalous data described in text not included in regression analysis..

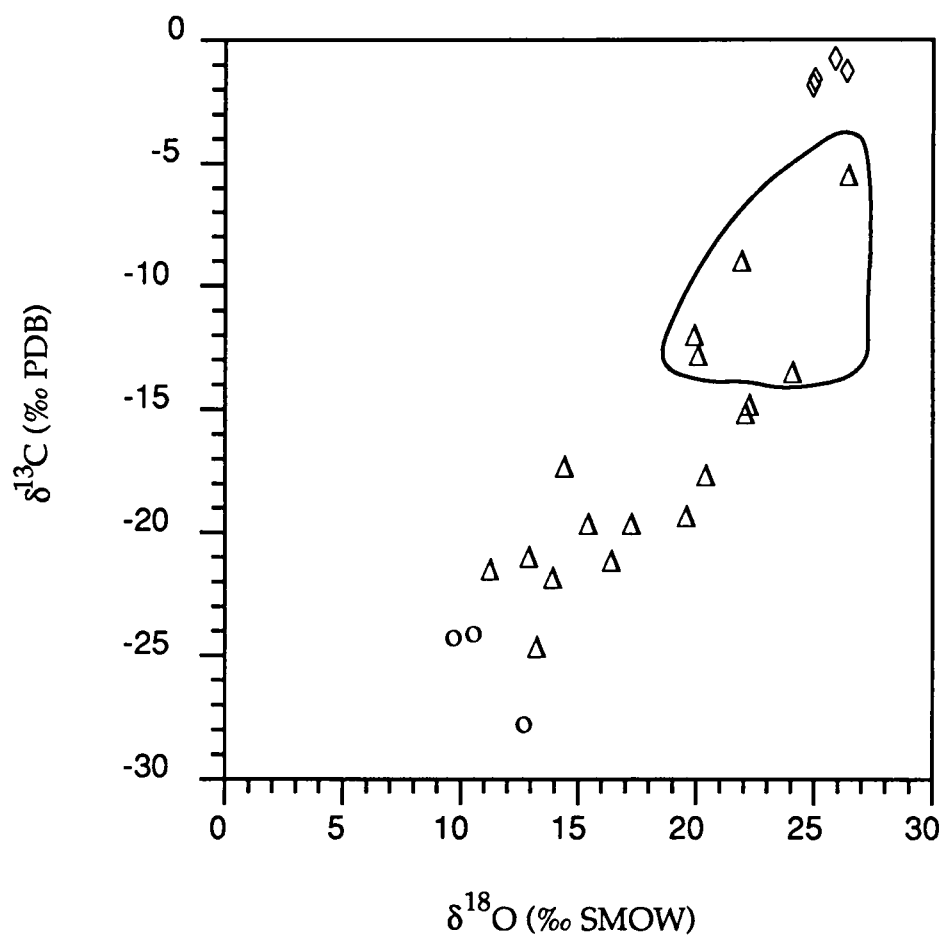


Figure IV-15. $\delta^{13}\text{C}$ Versus $\delta^{18}\text{O}$ of Aqueous Carbonate Species. Data represent samples from springs (o) and fill leachate (Δ) and from limestone ($\diamond$) from FLH1-1(22). Circled data indicates leachate samples obtained from fills with water quality suggesting AD development.

to carbon. The overall trend is curvilinear with a strong correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. These data indicate that 2 sources of carbon dioxide most significantly affect the alkalinity, an organic source from biotic respiration and an inorganic source from limestone dissolution.

The theoretical equilibrium isotopic composition of aqueous carbonate was calculated based on analytical results of the isotopic composition of soil carbon dioxide, carbon dioxide concentration, and water temperature and pH. Because of the ephemeral nature of fill leachate, data were available for only 2 samples collected on October 13, 1990 and November 11, 1990. The distribution of carbonate species as provided by Stumm and Morgan (1981) is pH dependent:

$$\alpha_0 = (1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2)^{-1} \quad (14)$$

$$\alpha_1 = (1 + [\text{H}^+]/K_1 + K_2/[\text{H}^+])^{-1} \quad (15)$$

$$\alpha_2 = (1 + [\text{H}^+]^2/K_1K_2 + [\text{H}^+]/K_2)^{-1} \quad (16)$$

$$[\text{H}_2\text{CO}_3] = K_H P\text{CO}_2 \quad (17)$$

$$[\text{HCO}_3^-] = (\alpha_1/\alpha_0)K_H P\text{CO}_2 \quad (18)$$

$$[\text{CO}_3^{2-}] = (\alpha_2/\alpha_0)K_H P\text{CO}_2 \quad (19)$$

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

where :

$\alpha_0, \alpha_1, \alpha_2$ = ionization fractions for
 $\text{H}_2\text{CO}_3, \text{HCO}_3^-,$ and CO_3^{2-}

K_1, K_2 = equilibrium constants for the carbonate system

K_H = Henry's constant

[] = concentrations of individual species (mg/L)

C_T = total concentration of aqueous species (mg/L)

The isotope equilibrium constants interrelating the various carbon species are provided below using the methodology of Deines et al. (1974):

$$K_3 = (^{13}\text{C}/^{12}\text{C})_{\text{H}_2\text{CO}_3} / (^{13}\text{C}/^{12}\text{C})_{\text{CO}_{2\text{gas}}} \quad (20)$$

$$K_4 = (^{13}\text{C}/^{12}\text{C})_{\text{HCO}_3^-} / (^{13}\text{C}/^{12}\text{C})_{\text{CO}_{2\text{gas}}} \quad (21)$$

$$K_5 = (^{13}\text{C}/^{12}\text{C})_{\text{CO}_3^{2-}} / (^{13}\text{C}/^{12}\text{C})_{\text{CO}_{2\text{gas}}} \quad (22)$$

The formulas to calculate isotopic composition of each carbonate species and estimated isotopic composition of carbon in solution are provided below using the methodology of Deines et al. (1974):

$$\delta^{13}\text{C}_{\text{H}_2\text{CO}_3} = K_3 \delta^{13}\text{C}_{\text{CO}_{2\text{gas}}} + (K_3 - 1) \times 1000 \quad (23)$$

$$\delta^{13}\text{C}_{\text{HCO}_3^-} = K_4 \delta^{13}\text{C}_{\text{CO}_{2\text{gas}}} + (K_4 - 1) \times 1000 \quad (24)$$

$$\delta^{13}\text{C}_{\text{CO}_3^{2-}} = K_5 \delta^{13}\text{C}_{\text{CO}_{2\text{gas}}} + (K_5 - 1) \times 1000 \quad (25)$$

$$\delta^{13}\text{C}_{\text{total}} = ([\text{H}_2\text{CO}_3] \delta^{13}\text{C}_{\text{H}_2\text{CO}_3} + [\text{HCO}_3^-] \delta^{13}\text{C}_{\text{HCO}_3^-} + [\text{CO}_3^{2-}] \delta^{13}\text{C}_{\text{CO}_3^{2-}}) / C_T \quad (26)$$

The results of these calculations are summarized in Table IV-6 along with isotopic analytical results taken from Appendix C. Lack of correlation

Table IV-6. Carbon Isotope Results for Aqueous Carbonate Species

Station	Date Sampled	Analytical Results (‰PDB)	Theoretical Results (‰PDB)
383+00	10/13/90	-10.9	-5.7
401+00	10/13/90	-16.8	-12.0
383+00	11/11/90	-14.3	-2.8
401+00	11/11/90	-16.7	-14.6

between theoretical values and the analytical results suggests the system fails to reach equilibrium, most probably the result of variable mixing of 2 sources of carbon dioxide of significantly different isotopic ratios, varying temperature and pH, and residence time of water as it flowed through soils and fill material, and short residence time of water in the fills.

Stable Isotope Trends of Dissolved Sulfate

Water samples for isotopic analysis of aqueous sulfate species were collected in February, May, July, September, and November 1990 from the basal sampling interval at station 383+50. The isotopic data ($\delta^{18}\text{O}$) for both water and sulfate are listed in Table IV-7. The quality assurance samples for the sampling procedure are also listed.

Data trends indicate water to be isotopically heavier with respect to oxygen during the summer, which is consistent with other studies (Hoefs, 1985). Variation of sulfate $\delta^{18}\text{O}$ was not significant, with $\delta^{18}\text{O}$ values ranging from -0.36‰ and -1.16‰.

Studies by Taylor and Wheeler (1982), Taylor et al., (1984a, 1984b) and Wheeler and Taylor (1982) and further refinement van Everdingen et al. (1984, 1988) have resulted in the determination of relative proportions in which oxygen or ferric iron act as the electron acceptor in sulfide oxidation based on AD sulfate and water $\delta^{18}\text{O}$ plots. Although those studies were done on pyrite, similar oxidation reactions occur with other sulfides (Toran and Harris, 1989). Hexagonal pyrrhotite ($\text{Fe}_{11}\text{S}_{12}$) was the dominant sulfide mineral identified in the study area. Using the methodology of Toran and

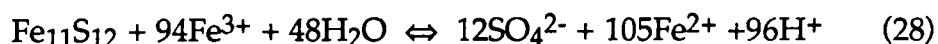
Table IV-7. Leachate Water and Sulfate Oxygen Isotope Data

Station	Date Sampled	$\delta^{18}\text{O}$ Sulfate (‰ SMOW)	$\delta^{18}\text{O}$ Water (‰ SMOW)	Δ ‰
383+50 GMW	2/11/90	-0.6	-8.9	8.3
383+50 GMW	2/11/90	-0.4	-8.9	8.5
383+50 GMW	5/6/90	-0.8	-8.5	7.7
383+50 GMW	7/15/90	-0.7	-7.4	6.7
383+50 GMW	7/15/90	-0.9	-7.4	6.5
383+50 GMW	9/16/90	-1.2	-7.7	6.5
383+50 GMW	11/11/90	-0.5	-7.4	6.9
383+50 GMW	11/11/90	-0.5	-7.4	6.9
Test Sample #1	NA	NA	-6.8	NA
Test Control #1	NA	NA	-6.8	NA
Test Sample #2	NA	NA	-6.9	NA
Test Control #2	NA	NA	-7.0	NA

Harris (1989), a balanced reaction for the oxidation of hexagonal pyrrhotite would be:



and



The isotopic composition of the oxygen incorporated in sulfate during sulfide oxidation may be expressed by the isotopic balance equation as defined by van Everdingen and Krouse (1988):

$$\begin{aligned} \delta^{18}\text{O}_{\text{SO}_4^{2-}} = & Y \times (\delta^{18}\text{O}_w + \epsilon_w) + (1-Y) \times [(0.979 \times (\delta^{18}\text{O}_m + \epsilon_m) \\ & + 0.021 \times (\delta^{18}\text{O}_w + \epsilon_w))] \end{aligned} \quad (29)$$

where:

Y = fraction of sulfate ions produced by reaction (28)

O_m = molecular oxygen

O_w = water oxygen

ϵ_w, ϵ_m = shifts in $\delta^{18}\text{O}_w$ and $\delta^{18}\text{O}_m$ during incorporation of O_w and O_m into sulfate.

Lloyd (1967) determined the isotope fractionation of water oxygen (ϵ_w) and of molecular oxygen (ϵ_m) into sulfate to be 0‰ and -8.7‰. Assuming $\delta^{18}\text{O}_m = +23.8‰$, equation (24) can be written as:

$$\delta^{18}\text{O}_{\text{SO}_4^{2-}} = \delta^{18}\text{O}_w \times (0.979 \times Y + 0.021) + (-15.7825 \times Y + 15.7825) \quad (30)$$

The relative contributions (i.e., 100, 75, 50, 25, and 0%) of reaction (26) calculated from equation (28) are shown as solid lines in Figure IV-16. In addition, oxygen isotope data for field samples collected during the course of this study are also shown. Based on the Toran and Harris (1989) review, it must be stressed that these relationships may only be valid for systems at low pH (i.e., 2-3). The leachate collected from the basal port at station 383+50 had pH values from 2 to 3 and the presence of *T. ferrooxidans* was confirmed by standard microbiological techniques. The results indicate that approximately 75% of sulfide oxidation is occurring with ferric iron being the oxidizer. The lack of temporal trends in $\delta^{18}\text{O}$ indicate a continuous supply of ferric iron and therefore, iron-oxidizing bacteria must remain active throughout the year.

Confirmatory Tests for *Thiobacillus ferrooxidans*

Confirmatory tests for the presence of *T. ferrooxidans* were performed on underdrain leachate. In addition, serial dilutions were done to provide an estimate of viable populations. Results of these tests indicated higher populations of *T. ferrooxidans* in EF-1 (>100 microbes/ml) than EF-2 (< 1 microbe/ml) (Table IV-8). These correspond to observed water quality, with leachate from EF-1 containing much higher concentrations of dissolved sulfate than EF-2.

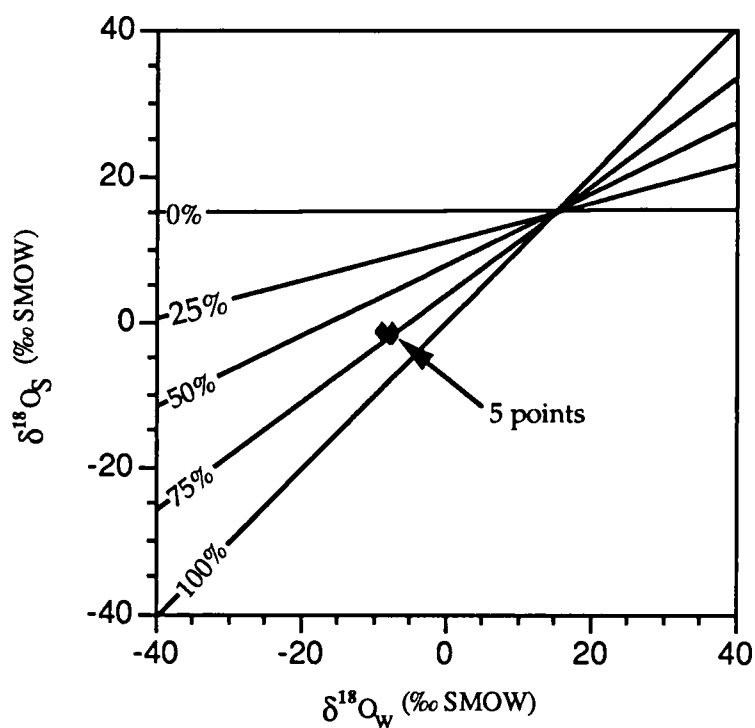


Figure IV-16. $\delta^{18}\text{O}$ Data for Sulfate Versus Water from EF-1 Leachate. Solid lines represent relative contribution of reaction (28) to the overall oxidation of pyrrhotite.

Table IV-8. Confirmatory Tests for *T. ferrooxidans*

Station	Positive Results for Specified Dilutions			Viable Populations (bacteria/ml)
	10 ml (10 total)	1 ml (10 total)	0.1 ml (10 total)	
383+00	10	10	10	>100
383+50	10	10	10	>100
401+00	9	1	1	<2
Control	0	0	0	0

Rock Analyses

Mineralogy

Thin sections and XRD powder mounts of argillites were analyzed to determine the mineralogy of the argillites used for fill construction. The dominant non-opaque minerals identified include quartz, muscovite, euhedral garnet, feldspar, and chlorite. Opaque minerals identified from polished thin sections and from diffraction patterns were hexagonal pyrrhotite, pyrite, chalcopyrite, sphalerite, and ilmenite. Pyrrhotite, which accounted for approximately 95% of the total sulfide minerals, was distributed as disseminated grains or in elongate masses along cleavage planes typically associated with quartz. Pyrite was distributed in fractures within larger masses of pyrrhotite. Chalcopyrite was associated with pyrrhotite and as disseminated grains with sphalerite inclusions. Ilmenite occurred predominantly as lamellae oriented along cleavage planes.

Sulfur Speciation

During construction of the highway, approximately 270 rock samples were collected to determine sulfur phase distribution (i.e., inorganic-, organic-, and sulfate-bound phases) and the effects on fill geochemistry. Sulfur speciation along with AP and NNP results based on total and inorganic sulfur are represented in Figure 17, with raw data located in Appendix D.

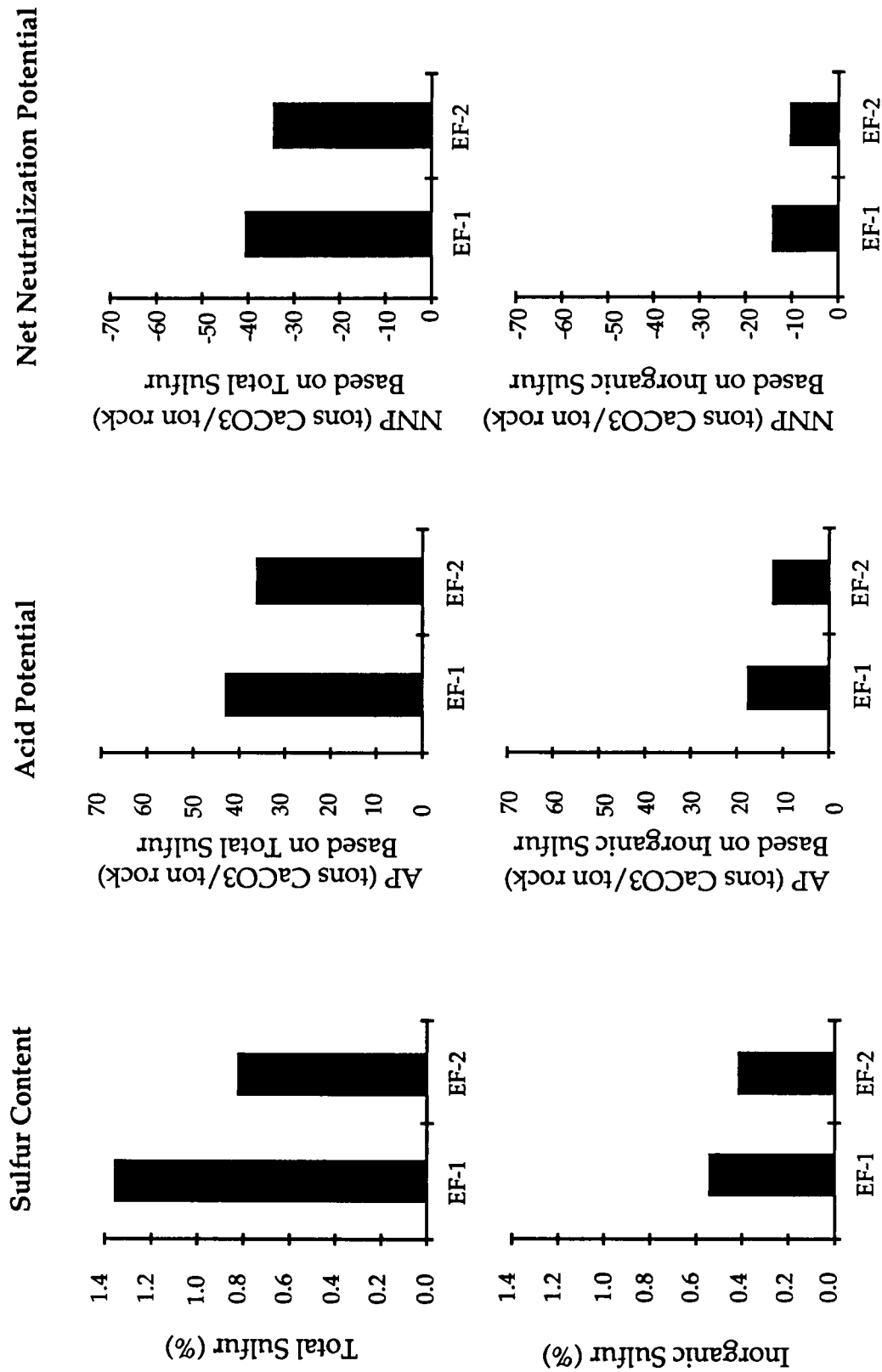


Figure IV-17. Acid-Base Accounting for Fills EF-1 and EF-2.

Sulfate accounted for approximately 16% of the total sulfur. This may be due to the fact that fill material was exposed for approximately 1 year after excavation and may not be typical of encapsulated material. Organic-bound sulfur comprised approximately 42% of the total sulfur, undoubtedly related to the high initial organic content of the argillites. Inorganic sulfur accounted for approximately 42% of the total sulfur. Total sulfur from composite samples in the encapsulated fills ranged from 0.54% to 2.44% with the mean total sulfur concentration greater in EF-1 (1.35%) than EF-2 (0.82%). Inorganic sulfur for EF-1 and EF-2 averaged 0.55% and 0.42%, respectively.

Based on total sulfur, the AP of fills EF-1 and EF-2 are 44 and 38 tons CaCO_3 /ton of rock material. Using only inorganic sulfur, the AP was determined to be 17 and 13 tons CaCO_3 /ton rock material. NP for EF-1 and EF-2 averaged 4 and 3 tons CaCO_3 /ton of rock material. Results of NNP using total sulfur ranged from -40 tons CaCO_3 /ton rock material for EF-1 to -35 tons CaCO_3 /ton rock material for EF-2. Based on inorganic sulfur, NNPs for EF-1 and EF-2 are approximately -13 and -10 tons CaCO_3 /ton rock material. Differences in AP and NNP are relatively insignificant because they indicate that upon weathering, both fills are capable of producing AD. In addition, the NP is also relatively insignificant because it is low and because the added limestone in fills overwhelms natural NP.

CHAPTER V

DISCUSSION

Temperature and Gas Trends

Temperature Trends

Temperature trends were strongly dependent on seasonal meteorological variations. As seen in all temporal data trends, temperature reached minimum and maximum values during ambient temperature extremes (Figures IV-1 to IV-7). Although sulfide oxidation is exothermic, no significant temperature differences that could be attributed to an *in situ* heat source were observed in either fill. Station 383+25 (Figure IV-2) exhibited anomalously low levels of oxygen, possibly indicative of increased oxidation rates, but did not have a corresponding elevated temperature trend. The lack of observable temperature effects from exothermic oxidation reactions may be explained by a number of factors. First, fill thickness may be insufficient to dampen annual climatic trends and therefore, background temperature variation obscured *in situ* heat sources. Second, based on the relatively high oxygen concentrations in the fills throughout much of the year, sulfide oxidation is probably occurring throughout the fill and not restricted to a specific zone. Third, the fill material is relatively homogeneous in terms of sulfur distribution and specific oxidation zones would not be expected unless there was a restriction of other reactants (i.e., oxygen and water) to portions of

the fill. The latter explanation probably is not significant in the fills based on fill oxygen distributions and high precipitation amounts in the study area.

Although temperatures varied between fills EF-1 and EF-2, this variation is probably the result of more lush vegetative cover on fill EF-2. Vegetation affects surface temperatures by reducing soil insolation and by retaining greater soil moisture from reduced surface runoff. The relatively barren, dark soils of fill EF-1 also tends to absorb incident radiation and are more susceptible to desiccation.

Mean temperature variations with depth in vertical GMWs in EF-1 and EF-2 indicate that seasonal variations affect the fill temperature by influencing both the near-surface soil temperatures and the basal fill/limestone aggregate temperatures (Tables IV-1 and IV-2 and Figure IV-8). This is evident by the fact that at all stations, mean temperatures from individual sampling intervals were highest in the central portions of the fill and oxygen concentrations in the fill material were highest at the base. These data indicate the fill drainage network and limestone aggregate are providing connectivity with ambient atmospheric conditions. Atmospheric connectivity is significant because lower temperatures reduce rates of oxidation during the winter months and may also inhibit the activity of iron oxidizing bacteria, particularly in the basal zones of the fills that may be more susceptible to leaching. The temperatures within the fill material however, remained conducive to the growth of *T. ferrooxidans* throughout the year (Buchanon and Gibbons, 1974).

Oxygen Trends

Gas trends indicate that the fills remain well oxygenated throughout much of the year (Figures IV-1 to IV-8). Studies by Erickson et al. (1985) and Myerson (1981) indicate that oxygen concentration below 2% may be limiting to abiotic sulfide oxidation and oxygen below 0.9% may be limiting to iron-oxidizing bacteria. Based on these assumptions, oxygen supply is limiting to sulfide oxidation only during portions of the summer months. Low oxygen concentrations during the summer months have two possible explanations. First, the oxidation rate of inorganic and organic matter is greater at higher temperatures. Second, oxygen is replaced by carbon dioxide from biotic respiration and displaced by carbon dioxide from AD neutralization reactions which may also occur at higher rates during the summer months. Even at levels below 0.9%, sulfide oxidation may occur if ferric iron is present to act as an electron acceptor.

Oxygen trends with depth also indicate that soil layers remain highly oxygenated throughout the year. This is surprising since the soil layer was initially compacted to less than 5% porosity. One-dimensional gas flow models predict that at this porosity, oxygen concentrations should decrease rapidly to non-detectable levels with depth (Campbell, 1985). It is evident from these models that the porosity of the soil layer has increased over time as the result of vegetation establishing a root zone, natural settling, and erosion of the fill. It is also possible that the observed oxygen concentrations in the soil layer may be the result of "short-circuiting" by atmospheric gas from overpumping during purging sampling. However, assuming a porosity

of 5% to 10% and extraction of a total of 3 liters of soil gas, sampling of the soil atmosphere would result in a sphere of influence with a radius of approximately 1.2 to 1.8 ft. The resulting volume should be insufficient to cause atmospheric contamination because the shallowest gas sampling port was located approximately 3 ft below ground surface. In addition, the increased porosity in the sulfidic fill 1 to 2 ft below the soil gas ports would result in preferential transport of soil gas to the sampling port rather than transport of atmospheric gas through the lower porosity soil. Atmospheric contamination should not have been transported along the GMW because of the bentonite seals.

The initial decrease in oxygen concentrations between the soil layer and fill material followed by an increase with depth in most vertical GMWs indicates that soil layers do impede oxygen from diffusing downward into the fills (Figure IV-8). The fact that the upper (i.e., 1 to 3 ft bgs) soil layers remain oxygenated indicates porosity must decrease with depth due to lesser effects of plant roots, erosion, and freeze/thaw actions below 1 to 2 ft. The effects of soil compaction are compromised by the highly oxygenated basal aggregate layers which act as the main oxygen source for the fills. The underdrain network, designed to keep the fill well drained, also functions to supply the basal fill zones with oxygen. The uniform oxygen increase with depth indicates that throughout the fill, diffusion is the dominant gas transport mechanism. The higher oxygen concentrations which result from the limestone aggregate offset any effects from lower temperatures previously discussed. Interpretive geologic logs of similar fills by Jago (1989) indicate slightly more oxidized

zones in the basal portions of encapsulated fills which is consistent with the observed oxygen concentrations at depth.

Erratic changes in oxygen concentrations are probably the result of oxygen consumption by biotic respiration and oxidation reactions with relatively slow rates of oxygen diffusion into the fill. Following large declines in oxygen (i.e., approximately 10%), diffusion may require weeks to re-establish equilibrium conditions. This is evident from Figure IV-1 which shows a rapid decline during March followed by a slow (i.e., 1 month) recovery to pre-decline levels. Anomalously low levels of oxygen at station 383+25 (Figure IV-2) may be the result of the placement of soil layers in the fill. These soil layers, although thin (i.e., 3 to 6 inches), may effectively reduce the diffusion of oxygen through this portion of the fill.

Although other gas transport mechanisms (i.e., advection) may affect the soil atmosphere, these could not be discerned through the available data. To determine the influence of advection, continuous monitoring of meteorologic variables such as barometric pressure changes are required. Although barometric pressure data were available, they were inadequate because the barometric pressure data were collected on gas sampling events. The consequences of barometric pressure changes would depend on the long term trends (i.e., days), not point data obtained during sampling events.

Carbon Dioxide Trends

The highest observed carbon dioxide concentrations were in the summer, correlated with periods of higher ambient temperatures and vegetation

growth. Oxidation would also be greatest during this period and hence, the possibility of AD neutralization reactions in the fills would also be greater.

Mean trends with depth indicate different dominant sources of fill carbon dioxide (Tables IV-1 and IV-2 and Figure IV-8). In fill EF-1, mean concentrations were highest in the basal zones while EF-2 had highest concentrations in the mid portions of the fill. Since highest concentrations should be observed near the source, these carbon dioxide distributions indicate separate sources. In EF-1, basal limestone dissolution is the dominant carbon dioxide source while elevated concentrations in the mid portions of the EF-2 fill suggest a second source of carbon dioxide, possibly microbial respiration.

Differing carbon dioxide concentrations in EF-1 and EF-2 indicate that fills have different dominant carbon dioxide sources which is supported by the isotopic data from soil carbon dioxide. Lower $\delta^{13}\text{C}$ values from EF-2 indicate that biotic respiration is more important in this fill. This is probably the result of biotic respiration, thicker subfill soils, and greater fill surface area on EF-2. Studies of soil carbon dioxide (e.g., Reardon et al., 1979; Haas et al., 1983; Thorstenson et al., 1983) have shown diffusion of plant-respired carbon dioxide to depths up to 8 meters, this probably does not account for the elevated levels in EF-2. The soil layer is assumed to prevent diffusion of gases downward from the surface based on oxygen trends across the soil-fill interface. The soil layer must not only restrict oxygen transport into the fill from the surface but carbon dioxide transport as well. The source of organic-derived carbon dioxide is probably due to microbial activity within the fill along with the oxidation of organic matter. The fill is also larger with fewer

underdrain exits per fill volume, reducing atmospheric connectivity. These conclusions are also supported by the theoretical concentrations of inorganic and organic-derived carbon dioxide determined from isotopic data.

Temperature must be considered when analyzing the isotopic trends in carbon dioxide. Fill temperatures decreased in both fills from 10/13/90 to 12/16/90 which corresponds to a decline in total carbon dioxide concentration. Following this, temperatures decreased by approximately 1.0°C to 2.6°C. The correlation between temperature and carbon dioxide concentration indicates biotic activity is responsible for some of the carbon dioxide generation in both fills. Based on this evidence and lack of correlation between the calculated inorganic carbon dioxide and precipitation, it is concluded that biotic respiration is the primary source of carbon dioxide in EF-2. It was evident, particularly in the basal portion of EF-1, that the dominant carbon dioxide source for fill EF-1 following periods of heavy precipitation is limestone dissolution by AD. This most probably is the result of leaching in basal saturated zones such as that observed at station 383+50 (EF-1). The pH of incident precipitation ranges from approximately 3.6 to 4.5, which could conceivably liberate carbon dioxide from limestone without having to interact with sulfidic material.

The observed levels of carbon dioxide concentrations were also sufficient to sustain *T. ferrooxidans* activity. This bacterium requires carbon dioxide as its carbon source for metabolism.

Correlations Between Carbon Dioxide, Oxygen, and Temperature

Carbon dioxide and oxygen concentration changes are strongly correlated throughout the study area (Tables IV-3 and IV-4). The slope of the regression lines, which vary from -0.7 to -8.3, indicate that single and dual mechanisms control the evolution of the soil atmosphere. Where slopes are greater than -2, intercepts are also high (i.e., > 13.5). This trend is ubiquitous in fill EF-2 and was also observed in soil layers of EF-1, implying a single controlling mechanism providing a nearly 1:1 exchange between oxygen and carbon dioxide. Based on isotopic data, EF-2 contains significantly higher organic carbon dioxide concentration than does EF-1, suggesting biotic respiration is the dominant controlling process in EF-2.

For fill material in EF-1, regression line slopes range from -1.1 to -8.2 with intercepts ranging from 6.5 to 22.9. The slopes indicate an exchange of oxygen for carbon dioxide greater than 1:1. This suggests a greater influence of abiotic mechanisms (i.e., limestone dissolution) controlling the EF-1 fill atmosphere. Again, this conclusion is supported by $\delta^{13}\text{C}$ data of soil carbon dioxide.

Temperature and carbon dioxide concentrations were correlated in 13 of the 27 sampling intervals. Again, 10 of the observed correlations were from sampling intervals in EF-2 and the remainder were from shallow sampling intervals in EF-1. The strong correlation in 10 of the 14 sampling intervals in EF-2 is the result of increased biotic activity at higher temperatures. This conclusion is supported by the nearly 1:1 exchange between carbon dioxide and oxygen and also by isotopic data suggesting a dominant organic-derived carbon source. In EF-1, carbon dioxide and temperature were correlated in

only 3 of 13 sampling intervals, 2 of which were in the soil layers. This suggests that the dominant process controlling carbon dioxide is independent of temperature. Although sulfide oxidation rates increase with temperature, oxidation products must be transported to limestone, a process which is independent of temperature.

Temperature and oxygen concentration were correlated in only 7 of the 27 sampling intervals. Again, only 1 of these correlations was observed in EF-1. Although oxygen consumption and carbon dioxide generation are linked by biotic respiration and possibly by oxidation/neutralization reactions, the lack of similar correlation observed between carbon dioxide and temperature is due to the different sources of carbon dioxide and oxygen. The consumption of oxygen in oxidation reactions creates a vacuum that, unless replaced by a source within the fill (either carbon dioxide or water vapor), must be filled from atmospheric gases diffusing into the fill. Diffusion of oxygen into the fill is dependent on temperature, but other factors such as moisture content are also important. With increased moisture content, capillary forces tend to bridge gaps between particles which reduce effective porosity and diffusion rates. Conversely, the greater temperature dependence of carbon dioxide is because it is generated *in situ* by temperature dependent mechanisms (i.e., biotic respiration) and is not dependent on transport mechanisms into the fill.

Stable Isotopes of Fill Carbon Dioxide

Trends in $\delta^{18}\text{O}$ of EF-1 and EF-2 soil carbon dioxide did not vary significantly with time or depth (Figures IV-9, IV-12, and IV-13). Over the

sampling period, $\delta^{18}\text{O}$ in both fills showed a uniform increase from approximately -6‰ to -3‰ (PDB) at all depths. The similar behavior in both fills implies that one mechanism strongly influences the $\delta^{18}\text{O}$ of soil carbon dioxide. Differences between theoretical enrichment factors based on soil temperature and the $\delta^{18}\text{O}$ of soil water and analytical enrichment factors were approximately 10‰. These differences indicate soil carbon dioxide and fill water do not reach equilibrium because of rapid flow rates of percolating water. Diffusion rates do not appear to be a factor in the disequilibrium because of similar $\delta^{18}\text{O}$ values with depth (Figure IV-12 and IV-13). Although meteoric water and soil carbon dioxide may not achieve equilibrium, meteoric water still appears to be the common factor controlling the $\delta^{18}\text{O}$ of soil carbon dioxide.

EF-1 $\delta^{13}\text{C}$ temporal trends at all depths indicate a dual source of carbon dioxide (Figure IV-10). During warmer periods, higher carbon dioxide concentrations were the result of both limestone dissolution and biotic respiration. Following the decline in soil temperature, limestone dissolution became the dominant source of carbon dioxide.

Temporal trends in EF-2 $\delta^{13}\text{C}$ indicate that biotic activity is very significant (Figure IV-11). The $\delta^{13}\text{C}$ and theoretical estimate of inorganic carbon dioxide in EF-2 may be elevated due to the method of GMW installation at station 396+00. As previously described, a hole was excavated for the GMW and then backfilled with the excavated soil and pulverized limestone. This, in effect, mixed the pulverized limestone with the fill material resulting in greater AD neutralization due to shorter transport distances of oxidation products to limestone.

The $\delta^{13}\text{C}$ trends with depth varied between EF-1 and EF-2 (Figures IV-12 and IV-13). $\delta^{13}\text{C}$ increased with depth in EF-1 and decreased with depth in EF-2. This implies 2 possible factors which influence the composition of soil carbon dioxide: 1) a kinetic fractionation of soil carbon dioxide due to more rapid diffusion rates of isotopically lighter carbon dioxide through the basal aggregate and 2) a isotopically heavy carbon source (i.e., the limestone aggregate) in the fill base. The former reasoning is plausible; however, the fact that the fills show opposite trends does not support this explanation. Neutral, high sulfate leachate from fill EF-1 supports the conclusion that the trends with depth in this fill are significantly influenced by limestone dissolution. Similarly, the trends in EF-2 support the conclusion that both kinetic fractionation and limestone dissolution are relatively insignificant and that biotic respiration controls the fill of EF-2.

Water Quality

General

The correlation between measured and theoretical carbon dioxide concentrations in the fills indicate that the alkalinity is affected by equilibration with the fill atmosphere. The total alkalinity cannot be attributed entirely to equilibrium conditions because the slope of the regression line indicates a greater theoretical partial pressure of carbon dioxide in fill material than those measured. Theoretical carbon dioxide

concentrations are greater than measured concentrations because of the increased alkalinity due to AD neutralization by calcite.

Aqueous Carbonate Geochemistry

The curvilinear dependence of $\delta^{18}\text{O}$ on $\delta^{13}\text{C}$ (Figure IV-15) indicates that in general, the isotopic composition of aqueous carbonate can be used as an indicator of water transport pathways in soil and fill systems. Water from underdrains with near neutral pH, low sulfate, and low conductivity showed similar isotopic composition as natural springs with $\delta^{13}\text{C}$ ranging from -15‰ to -30‰ and $\delta^{18}\text{O}$ ranging from +10‰ to +20‰. Underdrain leachate having characteristics of AD (e.g., low pH, high conductivity, or high sulfate) have isotopic compositions approaching that of limestone. Observed isotopic values from leachate with AD characteristics had $\delta^{13}\text{C}$ values of 0‰ to -20‰ and $\delta^{18}\text{O}$ values ranging from +20‰ to +30‰ which may suggest interaction of water with fill material.

The data also suggest that results are dependent on precipitation amounts and intensity. The relationship between AD generation/neutralization and isotopic data is not consistent following periods of low precipitation. Water samples from April 1990 were collected following a period of low precipitation totals (i.e., approximately 0.52 inches). The $\delta^{13}\text{C}$ values of aqueous carbonate ranged from -15‰ at station 401+00 to -20‰ at station 383+00. This suggests greater interaction of water with limestone at station 401+00, which is inconsistent with observed water quality. Station 401+00 had excellent water quality while station 383+00 was degraded, containing

high concentrations of dissolved sulfate. Other water samples were collected following periods of higher precipitation totals (greater than 1 inch). $\delta^{13}\text{C}$ values ranged from near background levels for station 401+00 to -6‰ for station 383+00. These data imply that a critical amount of precipitation may be required to leach fill material.

Two basic modes of water transport are implicated by these data. First, water may percolate into the fills from the surface. This process should be consistent in all fills and therefore should result in AD throughout the study area. This mode of water transport is not supported by the water quality data of this study or in the study by Jago (1989) who found relatively unoxidized sulfides present in the upper portions of similar encapsulated fills. The second and more plausible explanation is that the underdrain network is inefficient in removing water following high precipitation events, at least in fills with pre-construction slope morphologies similar to that of EF-1.

Conceptual models of water transport in these 2 fills are shown in Figures V-1 and V-2 with supporting data in Tables V-1 and V-2. The hypothetical flow paths shown are based on isotopic and water quality data and assumptions of recharge rates, storage capacities, and points of discharge. Fills constructed on gentle slopes (i.e., EF-2) may allow for greater infiltration due to better developed soils than those found on steep, rocky slopes. Depending on precipitation amounts, water transport may occur by overland flow to paved ditchlines circumventing fills or it may infiltrate into soils. Soil water may then be transported as throughflow if field capacity is exceeded. The water will remain as throughflow and be transported under the fills, discharging as surface water at some point downslope. The soil may however

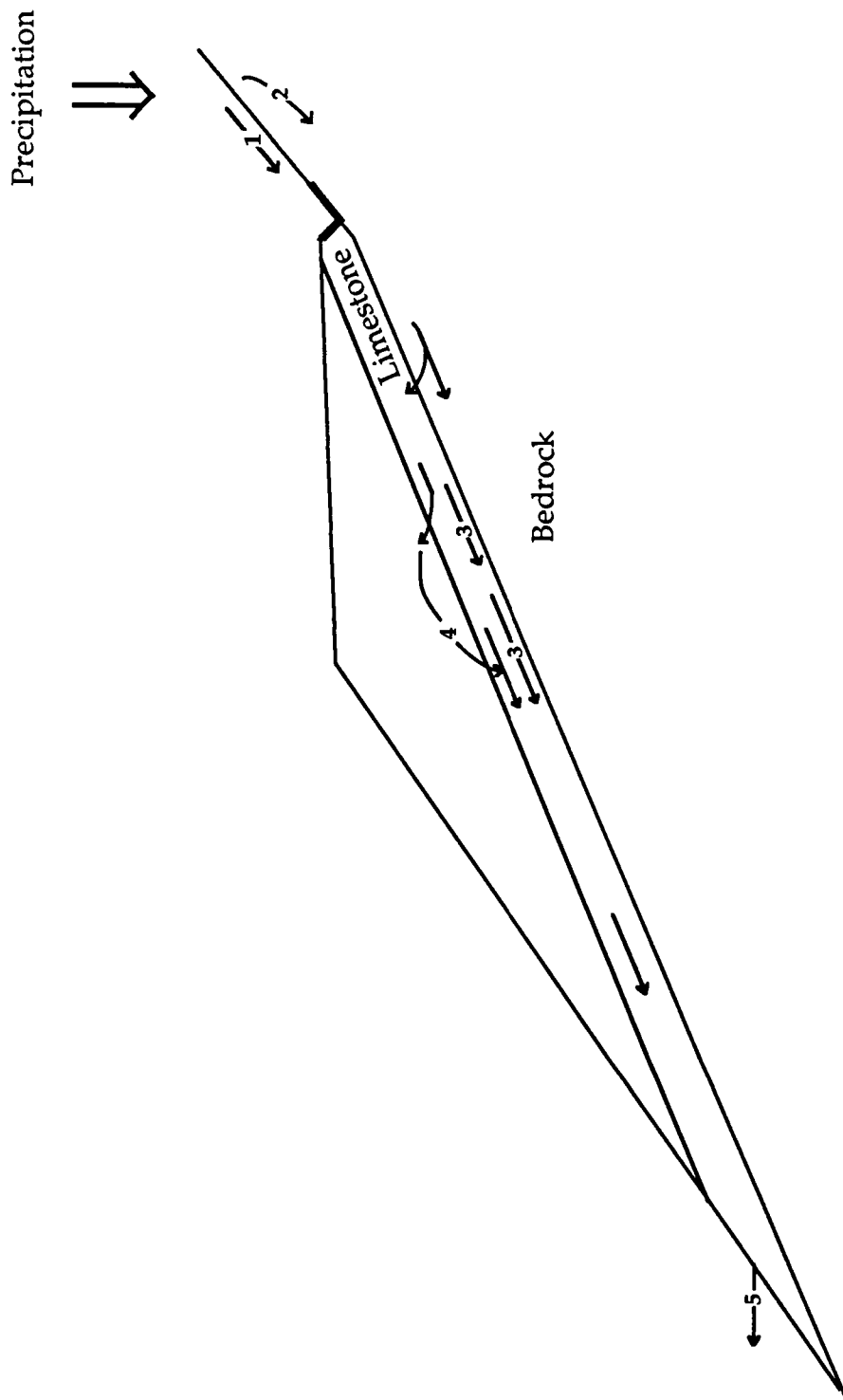


Figure V-1. Water Transport Pathways in Fill EF-1.

Table V-1. Description of Water Transport Pathways in EF-1.

Pathway	Flow Path	Carbon dioxide sources	Estimated d13C (source)	Measured d13C (aqueous carbonate)
1	Surface flow	Atmosphere	-7‰	NA
2	Fractured rock	Biotic respiration	-21‰ to -26‰	-20‰ to -30‰
3	Limestone	Biotic respiration, minor limestone dissolution	-21‰ to -26‰ 0‰ to -4‰	-15‰ to -25‰
4	Fill and limestone	Limestone dissolution from AD	0‰ to -4‰	-2‰ to -15‰
5	Underdrain exit	Combination of pathways 2, 3, and/or 4 dependent on precipitation amounts.	0‰ to -26‰	-2‰ to -25‰
		High precipitation - pathways 2, 3, and 4.	0‰ to -26‰	-2‰ to -15‰
		Low precipitation - pathways 2 and 3.	0‰ to -26‰	-15‰ to -25‰

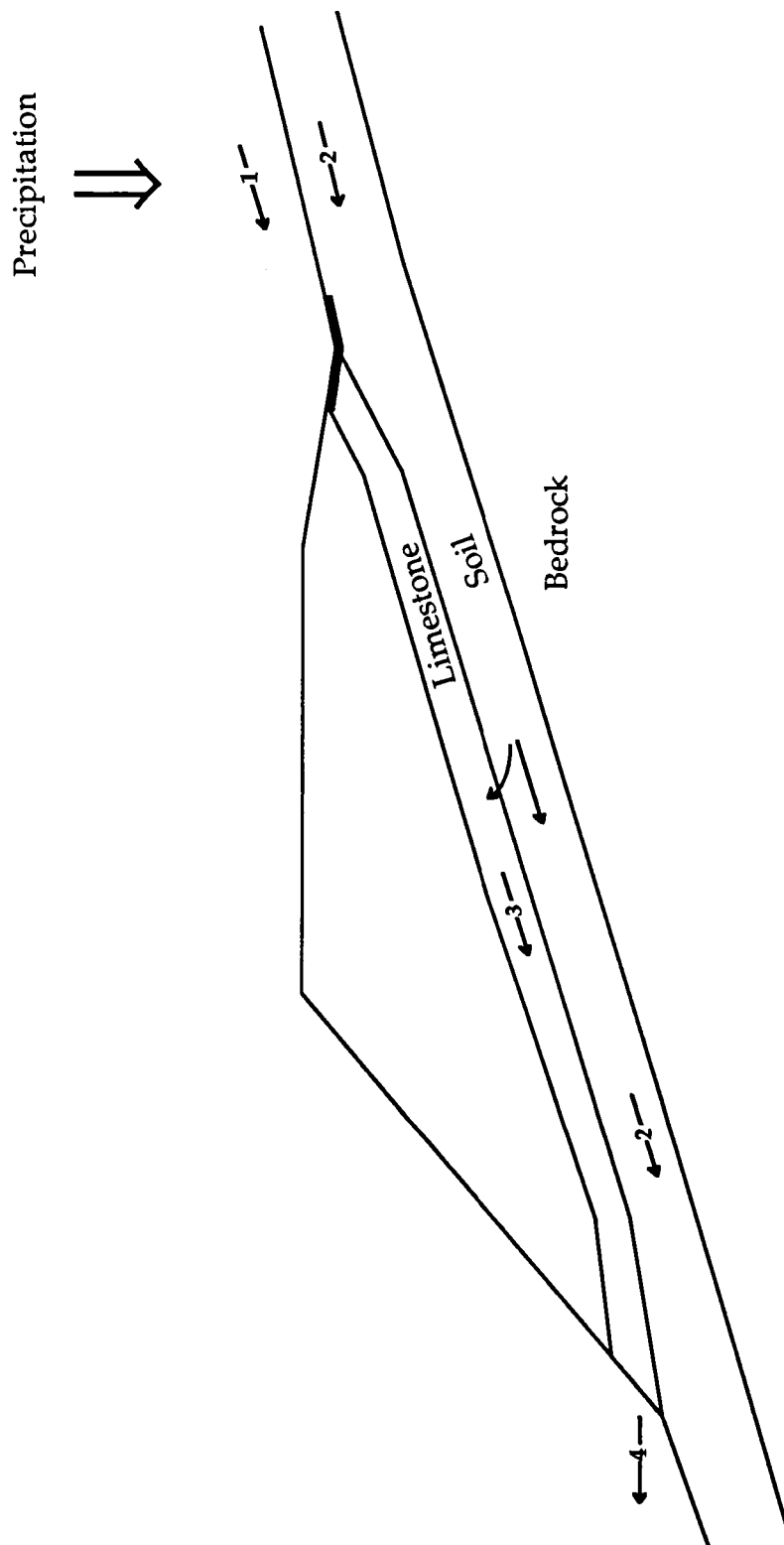


Figure V-2. Water Transport Pathways in Fill EF-2 .

Table V-2. Description of Water Transport Pathways in EF-2.

Pathway	Flow Path	Carbon dioxide sources	Estimated d13C (source)	Measured d13C (aqueous carbonate)
1	Surface flow	Atmosphere	-7‰	NA
2	Soil	Biotic respiration	-21‰ to -26‰	-20‰ to -30‰
3	Limestone	Biotic respiration, minor limestone dissolution	-21‰ to -26‰ 0‰ to -4‰	-15‰ to -25‰
4	Underdrain exit	Biotic respiration, minor limestone dissolution	-21‰ to -26‰ 0‰ to -4‰	-15‰ to -25‰

reach saturation under the fills and discharge into the limestone aggregate. If this occurs and the hydraulic conductivity of the limestone aggregate is exceeded, basal saturated zones in the fill material will develop, leading to AD. The observed water quality and isotopic data from EF-2 does not support AD development, rather the limestone and drainage network is relatively efficient at transporting water out of the fill. In addition, the constant discharge from the EF-2 underdrain indicates longer retention times in soils.

Fills constructed on steep, rocky slopes such as EF-1 have lower storage capacities due to thin to nonexistent soils. On steep rocky slopes, incident precipitation would be transported primarily as overland flow. Immediately above the ditchline, two transport pathways exist. First, water continues as overland flow and eventually is intercepted by the paved ditchlines. The second pathway follows fractures in the upslope rock formed from blasting during construction activities. This water would flow beneath the ditchlines and eventually discharge into subfill soils. The soils, being thin relative to those on gentle slopes, would not be able to store significant quantities of water and eventually would discharge water into the limestone aggregate. Again, the interaction of water with fill material would be dependent on the drainage capacity of the limestone aggregate. If the total quantity of water entering the aggregate exceeds the capacity of the drainage network, temporary saturated zones in the fill would develop. This flow regime is supported by the flashy discharge and the poor water quality from the EF-1 underdrain and the saturated basal sampling interval of station 383+50.

Aqueous Sulfate Geochemistry

Isotopic data from dissolved sulfate indicates that approximately 50% to 75% of sulfide oxidation is produced by biotic (i.e., *T. ferrooxidans* catalyzed) pathways and the remainder is the result of chemical oxidation (Figure IV-16). These results are consistent with other studies of high sulfate acidic waters (e.g. Taylor and Wheeler, 1982; Taylor et al. 1984a, 1984b; van Everdingen and Krouse, 1984, 1988). Levels of abiotic oxidation and bacterial-catalyzed oxidation remained relatively stable throughout the year. The $\delta^{18}\text{O}$ behavior of the sulfate/water system may be explained by the fact that fill temperatures remained conducive to the growth of *T. ferrooxidans* throughout the year. Research by Sullivan et al. (1986) and Cravotta (1991) also indicates the source of sulfate does not need to be the direct result of *T. ferrooxidans* catalyzed reactions but may be the result of the formation of soluble ferric sulfate "salts" during extended periods without precipitation. Upon leaching, the ferric iron and sulfate in these minerals is released. The ferric iron then may oxidize more sulfides and the sulfate transported with the leachate. Potential ferric sulfate salts include roemerite, coquimbite, and copiapite. Copiapite was identified by Jago (1989) as a potential sulfate mineral present in similar encapsulated fills. Attempting to eliminate sulfide oxidation by excluding oxygen after the formation of these compounds may be futile because of the release of ferric iron, sulfate, and stored acidity. This hypothesis is also supported by Hoving and Hood (1984) who concluded that sulfide oxidation, once initiated, is difficult to impede. Approximately 15% of sulfur was in the form of sulfate, indicating this source may affect the rate of

sulfide oxidation and formation of AD, even during periods of low oxygen concentration.

Rock Analyses

Mineralogy

The mineralogy of the argillite unit is typical of garnet grade rocks with the most common minerals being quartz, garnet, muscovite, feldspar, and chlorite. Hexagonal pyrrhotite is the dominant opaque mineral, but other phases identified include pyrite, chalcopyrite, sphalerite, and ilmenite. The presence of hexagonal pyrrhotite follows observations of Carpenter (1974) of this phase occurring only in high temperature environments such as high-grade metamorphic rocks.

Fill Geochemistry

There appears to be no relationship between sulfur content and soil atmosphere in either fill. Homogeneity in terms of sulfur distribution provides similar geochemical conditions in both fills. In addition, any relationship with the natural NNP of the fill material is insignificant because of the large amounts of limestone placed within the fill. As previously stated, the transportation of oxidation products to soil carbonates may be the critical factor controlling levels of inorganic carbon dioxide.

Encapsulation Technology

Recommendations

The results of this study have provided insight into gas transport mechanisms in highway fills. Oxygen utilized in the oxidation of sulfide minerals within the fills is supplied to the basal limestone aggregate layer through the underdrain network. In order to limit sulfide oxidation, restriction of oxygen may be necessary. This could be achieved through the installation of oxygen traps at underdrain exits. Because EF-1 is relatively small and has only one underdrain exit, this fill could be retrofitted with an oxygen trap to test design feasibility with the GMWs utilized to evaluate the traps effectiveness. Retrofitting fills would not, however, reduce sulfide oxidation in fills generating AD because of the presence of ferric iron. Oxygen traps would be effective only if installed during fill construction. This would prevent the development of acidic environments conducive to the growth of *T. ferrooxidans*. A paucity of published data exists on the effects of low oxygen concentration on sulfide oxidation rates and on the activity of *T. ferrooxidans*. In addition, it is not known if *T. ferrooxidans*, a facultative anaerobe, catalyzes the oxidation process under anaerobic conditions. Still, the conditions and instrumentation in place in EF-1 could provide important information for highway design improvement as well as insight into oxidation rates and activities of iron-oxidizing bacteria under low oxygen conditions.

It may be that observed AD problems (i.e., low pH and/or high sulfate) at some fills (i.e., 996+00, 190+00, 383+00, 432+00) cannot be solved by trying to prevent sulfide oxidation. Improving the efficiency underdrains may be the most cost-effective means for preventing deleterious impacts from AD. Modifications to the highway design based on studies by Jago (1989) and Byerly (1990) reduced the basal limestone from 1 ft to 0.5 ft. The neutralization potential of this layer as a whole has not been seriously affected, however more serious concern is the effect of the decrease in thickness on water flow. The construction process is imperfect, and undulations in topography and compaction of fill have resulted in zones where water may not drain properly, creating saturated zones in the basal fill. The AD in the study area is presently being neutralized but it is impossible to predict future water quality based on observed geochemistry. Thicker basal aggregate layers would provide better drainage with less chance of restrictions from topography. A thicker basal layer does not need to be constructed totally of limestone aggregate. Admixing locally quarried low-sulfur rock would increase the thickness while still maintaining the neutralization potential. In addition, this would not be required for all fills. Conclusions from this study indicate that the greatest potential for deleterious leachate occurs in fills constructed on steep rocky slopes.

CHAPTER VI

CONCLUSIONS

Conclusions drawn from the research include:

- Measured soil temperatures could not be used to discern specific zones of sulfide oxidation because the fills were of insufficient thickness to eliminate the ambient seasonal cyclic effects. In addition, fill homogeneity in terms of oxygen distribution and geochemical properties (i.e., sulfur content) may have resulted in relatively uniform oxidation occurring throughout the fill.
- Fill temperatures remain conducive to the growth to *T. ferrooxidans* in sulfide material throughout most of the year.
- Based on the isotopic composition of sulfate, sulfide oxidation pathways are dominated by biologically catalyzed reactions. $\delta^{18}\text{O}$ of sulfate did not vary significantly throughout the year, supporting the previous conclusion that temperature variations do not affect the activity of *T. ferrooxidans*. However, the sulfate may have been result of soluble ferric iron sulfate salts formed during drier periods under different temperature regimes.
- Based on temperature and oxygen distribution in and immediately below the soil layer, it was determined that the soil layer effectively restricts transport of oxygen into the fill material from the surface.
- Oxygen concentration uniformly increases with depth to maximum levels near the basal limestone aggregate indicating that the underdrain network

is the major source of fill oxygen. In addition, the fills remain well oxygenated throughout most of the year.

- The uniform oxygen increase with depth indicates that gas transport occurs predominantly by diffusion.
- Sources of carbon dioxide present within fill EF-1 include biotic respiration and limestone dissolution with contributions from biotic respiration directly dependent on temperature. Carbon dioxide contribution from limestone dissolution was determined to be dependent on precipitation.
- Carbon dioxide sources in fill EF-2 are dominated by biotic respiration. Highest concentrations in the mid portion of the fill indicate that bacterial respiration is the dominant source.
- Carbon dioxide concentrations were strongly correlated with temperature due to increased biotic activity at higher temperatures.
- The composition of the fill atmosphere showed seasonal cyclic variations all depths. The dependence of soil atmosphere composition on sulfur concentration was insignificant due to fill homogeneity with respect to sulfur.
- AD development is significantly greater in fills with steep upslopes based on carbon isotopes of aqueous carbonate species, observed water chemistry, and relative populations of *T. ferrooxidans* in fill leachate. AD probably develops as the result of a malfunctioning underdrain system causing localized saturated zones in the fill material.

Assessment of the Fill Design

- The fill design is efficient in limiting oxygen diffusion from the surface, diverting water around most fills, and neutralizing AD.
- Oxygen is supplied to the fill through the basal limestone aggregate layer. The installation of oxygen traps in the underdrains may provide a reduction in the oxygen supply.
- Fills constructed on steep slopes are susceptible to poor internal drainage, resulting in basal saturated zones and AD development. In these instances, increasing the thickness of the limestone aggregate layer may improve hydrologic properties.

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APPENDICES

Appendix A
Temperature and Gas Data

Table A-1. Analytical Data File For Station 383+00 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)					Oxygen Conc. (%)					Temperature (C)				
	Depth (feet)					Depth (feet)					Depth (feet)				
	3.5	8.5	13.5	18.5		3.5	8.5	13.5	18.5		3.5	8.5	13.5	18.5	
7/26/89	0.3	1.3	2.2	4.8		17.6	11.2	9.6	8.2		21.8	25.0	20.8	16.1	
8/11/89	8.1	2.9	3.2	4.3		5.0	10.9	13.0	11.0		25.1	28.9	23.1	18.1	
8/25/89	9.6	3.9	4.8	4.7		8.8	7.2	7.0	11.4		23.3	25.7	22.2	17.8	
9/8/89	5.7	4.8	4.5	4.1		7.1	4.8	9.9	14.8		23.3	26.6	23.0	19.2	
9/25/89	5.6	5.4	6.0	5.2		8.2	8.8	10.0	13.5		20.3	24.3	22.1	17.9	
10/9/89	4.3	3.9	6.0	3.5		11.9	13.4	9.9	16.3		18.1	22.7	21.6	18.7	
10/23/89	2.0	2.0	1.8	2.2		12.9	13.1	16.2	17.2		15.3	21.0	20.0	17.4	
11/3/89	1.8	1.8	1.4	1.3		15.2	16.0	16.4	18.7		NA	NA	NA	NA	
11/17/89	1.5	1.6	1.7	2.6		16.5	17.2	18.5	18.7		14.7	18.6	19.8	17.6	
12/1/89	1.0	1.0	0.9	1.6		16.2	16.8	17.0	18.5		10.5	15.4	16.4	14.7	
12/14/89	0.9	0.8	0.8	1.8		17.9	18.2	18.2	18.0		6.1	13.1	14.1	13.4	
12/29/89	1.4	1.2	1.3	1.7		13.1	14.0	13.9	16.5		4.6	11.7	13.1	12.8	
1/12/90	1.1	1.0	1.2	0.9		16.9	17.8	17.8	19.6		4.3	10.6	12.1	10.7	
1/28/90	1.4	1.3	1.3	2.7		18.0	18.3	18.4	19.2		4.9	8.9	10.4	10.0	
2/11/90	3.5	3.0	3.0	4.0		13.7	15.5	15.4	17.2		6.3	8.5	8.9	8.5	
2/26/90	1.4	1.2	1.2	3.2		17.5	18.1	18.0	18.0		5.9	8.6	9.3	8.8	
3/12/90	3.4	3.2	4.0	5.5		6.2	6.8	5.5	9.2		6.4	7.7	8.5	8.1	
3/23/90	3.0	2.6	2.5	3.7		10.0	12.4	14.9	15.8		7.9	9.0	8.8	8.4	
4/9/90	1.2	1.0	1.2	2.0		16.6	17.9	17.4	18.6		8.6	10.0	10.0	9.7	
4/20/90	2.2	2.1	2.6	2.0		12.6	14.5	17.5	14.5		6.7	7.9	8.1	8.0	
5/6/90	3.9	3.7	3.7	4.4		6.1	8.5	12.3	13.3		10.7	9.1	8.2	8.3	
6/2/90	4.2	2.8	2.9	3.7		10.4	13.0	13.8	15.3		12.1	10.4	9.1	8.3	
6/16/90	3.0	2.0	1.9	3.3		14.4	12.9	13.3	13.4		14.7	12.1	10.1	8.9	
7/1/90	3.2	2.6	2.9	3.4		13.9	11.4	10.7	13.3		16.5	13.6	10.6	9.4	
7/15/90	4.8	4.4	4.5	4.4		1.0	1.3	2.2	3.7		18.4	16.1	13.0	11.2	
7/28/90	6.0	5.3	5.2	5.9		5.2	2.0	1.8	6.2		18.3	16.8	14.0	12.7	
8/12/90	7.0	5.2	5.3	5.8		2.0	0.9	0.7	5.8		19.0	16.9	14.4	13.0	

Table A-1. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)		
	Depth (feet)			Depth (feet)			Depth (feet)		
	3.5	8.5	13.5	18.5	3.5	8.5	13.5	18.5	
8/25/90	7.0	4.2	4.5	4.8	2.6	1.6	0.9	5.2	17.8
9/16/90	5.5	5.0	4.4	5.3	4.5	8.6	13.2	12.1	19.4
9/30/90	6.1	5.6	5.8	7.0	0.9	2.6	4.5	4.7	15.6
10/13/90	7.4	7.1	7.5	8.4	0.7	1.1	0.3	1.1	15.7
11/11/90	2.1	1.4	1.3	1.4	16.3	18.1	18.2	18.0	16.1
12/16/90	2.5	2.2	2.4	3.2	10.3	13.7	13.5	15.6	NA
1/12/91	3.2	3.3	3.3	4.1	13.2	13.7	13.7	14.7	NA
									11.5

Table A-2. Analytical Data File For Station 383+25 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)					Oxygen Conc. (%)					Temperature (C)				
	Depth (feet)					Depth (feet)					Depth (feet)				
	5.0	10.0	15.0	20.0	25.0	5.0	10.0	15.0	20.0	25.0	5.0	10.0	15.0	20.0	25.0
7/26/89	2.0	1.7	1.5	3.3	1.1	10.6	5.7	6.5	6.9	9.3	19.6	19.6	20.8	20.6	20.1
8/11/89	4.8	4.4	4.9	5.9	5.6	8.8	2.2	1.2	0.5	0.7	19.0	21.1	21.0	20.7	20.1
8/25/89	4.6	3.4	6.8	7.3	5.1	7.3	11.2	2.2	0.5	0.6	19.5	20.2	20.1	20.2	19.2
9/8/89	5.2	7.0	6.9	5.5	6.6	6.4	0.8	0.3	2.9	3.0	19.1	19.7	20.6	20.7	20.5
9/25/89	6.0	6.2	7.0	7.0	6.6	4.7	4.0	1.7	0.2	0.9	15.9	18.9	19.9	20.1	19.4
10/9/89	6.9	7.8	7.2	7.6	8.0	3.5	2.0	3.2	0.6	1.4	14.6	19.4	20.4	20.7	20.2
10/23/89	6.1	5.0	4.0	3.8	3.2	2.3	1.3	1.5	0.2	4.9	11.4	15.7	18.5	20.0	18.8
11/3/89	4.3	4.0	3.0	2.7	2.8	3.7	2.1	2.6	4.1	1.2	NA	NA	NA	NA	NA
11/17/89	3.3	3.5	3.0	3.2	3.6	9.1	7.2	8.1	9.4	7.0	10.5	14.4	17.4	18.9	19.3
12/1/89	2.9	2.4	1.6	1.7	2.0	3.6	2.9	5.7	5.0	2.5	9.5	12.7	17.0	18.3	17.4
12/14/89	2.6	2.4	1.9	1.7	1.9	3.4	4.0	6.1	10.7	5.8	4.0	9.3	13.6	15.9	15.6
12/29/89	NA	1.6	1.5	1.6	1.6	NA	2.1	3.2	5.6	3.4	2.4	8.3	12.9	15.1	14.9
1/12/90	NA	2.0	1.7	1.8	1.7	NA	4.9	8.7	11.0	10.2	2.3	7.2	11.6	13.6	13.2
1/28/90	2.0	2.6	2.4	2.6	3.0	6.5	5.0	8.2	10.7	8.0	4.6	7.3	10.8	12.3	11.8
2/11/90	2.2	4.2	4.5	4.5	4.8	5.0	2.4	3.5	4.9	1.6	6.6	9.0	11.0	12.4	11.0
2/26/90	NA	2.3	2.0	1.9	2.1	NA	7.1	9.8	11.7	8.4	5.8	8.9	10.7	11.3	11.0
3/12/90	1.2	3.2	3.7	4.3	4.2	14.3	4.8	2.9	0.5	1.1	8.0	8.1	9.6	10.8	10.5
3/23/90	2.2	3.4	3.0	3.1	3.0	9.5	3.5	5.0	4.5	2.0	6.2	8.2	8.9	9.2	8.5
4/9/90	2.3	2.4	1.9	1.8	2.4	8.3	4.7	7.5	9.0	3.8	8.9	9.4	10.9	11.1	11.7
4/20/90	2.3	2.8	2.8	2.9	3.3	8.0	2.6	4.2	4.0	0.7	7.1	7.7	8.8	9.2	8.7
5/6/90	2.0	4.4	4.6	4.6	5.2	12.4	2.6	2.1	0.6	0.4	11.6	9.8	9.4	9.1	8.4
6/2/90	2.3	4.6	4.6	4.8	5.0	14.4	2.0	1.8	0.5	0.4	11.8	11.1	10.3	9.6	9.2
6/16/90	2.2	5.0	5.4	5.4	4.6	14.3	1.0	0.7	0.2	0.3	15.7	13.2	11.6	10.9	10.6
7/1/90	2.6	5.2	5.4	5.4	3.8	14.6	1.2	0.6	0.3	2.6	17.9	14.6	13.1	12.0	11.4
7/15/90	4.4	5.7	5.0	5.0	4.3	5.4	0.6	0.9	0.2	0.4	17.0	15.5	13.9	12.3	12.0
7/28/90	4.1	6.9	6.8	6.5	5.7	12.3	0.3	0.3	0.1	0.1	17.9	16.4	15.2	13.8	13.4
8/12/90	4.5	6.6		6.2	5.2	11.3	0.3		0.4	0.2	18.2	17.2	15.8	14.9	14.8

Table A-2. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)					Oxygen Conc. (%)					Temperature (C)				
	5.0	10.0	15.0	20.0	25.0	5.0	10.0	15.0	20.0	25.0	5.0	10.0	15.0	20.0	25.0
9/30/90	2.9	6.0	5.8	5.6	6.0	14.3	0.6	0.9	2.0	0.2	13.9	15.5	16.5	16.6	15.8
10/13/90	3.5	7.3	7.2	6.5	7.2	11.5	0.6	0.8	2.7	0.4	14.2	14.8	16.0	16.3	16.3
11/11/90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/16/90	NA	2.4	2.2	2.0	2.4	NA	3.4	3.7	6.6	4.4	6.2	9.9	13.5	14.9	15.0

Table A-3. Analytical Data File For Station 383+50 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)						Oxygen Conc. (%)						Temperature (C)					
	Depth (feet)						Depth (feet)						Depth (feet)					
	4.0	9.0	14.0	19.0	24.0	29.0	4.0	9.0	14.0	19.0	24.0	29.0	4.0	9.0	14.0	19.0	24.0	29.0
7/26/89	4.1	4.3	2.7	2.2	2.2	2.2	3.0	0.2	4.1	5.0	5.0	5.0	20.7	21.1	21.0	16.8		
8/11/89	4.3	5.2	5.0	5.4	5.4	5.4	1.9	0.2	1.6	2.7	2.7	2.7	20.2	22.2	21.5	17.8		
8/25/89	5.0	5.5	2.8	4.9	4.9	4.9	2.2	0.5	8.0	1.8	1.8	1.8	20.2	20.9	21.0	17.7		
9/8/89	4.7	5.6	5.8	5.5	5.5	5.5	5.6	0.8	0.8	1.0	1.0	1.0	20.5	21.4	20.5	18.3		
9/25/89	5.7	4.6	4.3	4.5	4.5	4.5	1.1	10.0	12.3	12.5	12.5	12.5	18.0	22.8	21.1	17.5		
10/9/89	7.4	3.5	3.8	5.7	5.7	5.7	4.6	14.8	15.0	13.0	13.0	13.0	15.6	20.8	21.4	18.9		
10/23/89	3.0	2.3	2.6	3.4	3.4	3.4	2.2	13.0	13.4	14.5	14.5	14.5	14.2	23.1	20.8	17.3		
11/3/89	2.0	1.7	1.3	2.6	2.6	2.6	4.8	15.5	17.2	13.4	13.4	13.4	15.0	23.5	21.5	17.5		
11/17/89	3.4	2.8	2.2	4.9	4.9	4.9	6.1	16.1	18.0	16.0	16.0	16.0	15.2	24.1	21.5	17.2		
12/1/89	1.9	1.4	1.0	3.3	3.3	3.3	7.0	16.3	17.8	16.0	16.0	16.0	10.0	18.5	19.1	15.4		
12/14/89	2.2	1.6	1.5	4.6	4.6	4.6	8.6	17.4	18.1	16.2	16.2	16.2	8.0	17.3	18.5	15.3		
12/29/89	1.3	1.6	1.3	2.2	2.2	2.2	8.1	14.0	15.3	15.8	15.8	15.8	5.9	15.6	16.9	14.2		
1/12/90	1.5	1.2	1.0	2.9	2.9	2.9	8.5	17.7	18.4	17.2	17.2	17.2	5.2	13.5	15.8	12.2		
1/28/90	3.4	3.0	2.9	5.6	5.6	5.6	16.0	16.0	16.4	15.4	15.4	15.4	4.4	11.6	10.9	13.8		
2/11/90	3.3	3.5	3.6	5.7	5.7	5.7	4.4	14.8	4.7	14.8	14.8	14.8	6.4	10.5	12.4	10.0		
2/26/90	3.2	2.1	2.0	4.4	4.4	4.4	9.3	17.1	18.0	16.6	16.6	16.6	6.3	11.1	11.9	10.3		
3/12/90	3.0	4.2	4.0	3.9	3.9	3.9	6.0	1.8	9.0	13.8	13.8	13.8	7.7	9.9	10.4	9.7		
3/23/90	3.1	3.3	3.0	3.6	3.6	3.6	4.6	10.0	13.3	14.3	14.3	14.3	7.6	10.4	10.6	9.0		
4/9/90	2.6	1.7	1.6	3.4	3.4	3.4	6.9	15.5	17.6	16.6	16.6	16.6	7.6	9.9	10.2	10.0		
4/20/90	2.8	2.8	2.7	4.6	4.6	4.6	3.3	10.7	15.2	14.0	14.0	14.0	7.7	9.5	9.4	10.2		
5/6/90	3.8	3.6	3.2	4.9	4.9	4.9	3.3	10.2	15.0	13.4	13.4	13.4	11.0	9.9	9.3	9.0		
6/2/90	4.1	4.7	3.5	4.5	4.5	4.5	4.3	2.5	10.7	10.5	10.5	10.5	12.4	11.5	10.6	9.3		
6/16/90	4.0	4.4	3.0	3.2	3.2	3.2	6.1	0.3	7.8	11.4	11.4	11.4	14.8	12.6	11.3	9.9		
7/1/90	4.2	4.8	3.0	3.7	3.7	3.7	4.1	1.0	9.2	9.7	9.7	9.7	17.1	14.4	12.7	10.8		
7/15/90	3.7	4.8	4.8	NA	NA	NA	3.4	0.3	0.8	NA	NA	NA	18.6	16.2	14.0	12.0		
7/28/90	4.7	5.6	5.0	5.7	5.7	5.7	4.6	0.1	2.8	4.3	4.3	4.3	17.8	16.4	14.4	12.4		
8/12/90	4.7	4.6	4.8	5.2	5.2	5.2	3.9	1.3	2.8	3.6	3.6	3.6	19.0	16.7	15.5	14.1		

Table A-3. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)					
	Depth (feet)			Depth (feet)			Depth (feet)					
	4.0	9.0	14.0	19.0	4.0	9.0	14.0	19.0	4.0	9.0	14.0	19.0
9/30/90	5.1	6.4	6.6	7.4	5.3	0.0	1.9	1.2	14.2	16.3	16.6	14.2
10/13/90	5.5	7.0	7.1	NA	5.9	1.2	1.8	NA	15.2	16.3	16.5	14.6
11/11/90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/16/90	2.2	2.4	2.4	NA	6.1	9.4	14.2	NA	6.2	11.8	14.8	14.1

Table A-4. Analytical Data File For Station 396+00 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)		
	Depth (feet)			Depth (feet)			Depth (feet)		
	2.7	7.7	12.7	2.7	7.7	12.7	2.7	7.7	12.7
7/26/89	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/11/89	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/25/89	NA	3.9	12.7	NA	15.1	1.3	NA	21.8	18.9
9/8/89	4.5	10.1	12.9	14.1	4.2	3.2	0.5	20.2	20.8
9/25/89	7.2	14.9	16.6	17.0	0.7	0.8	1.0	16.7	18.0
10/9/89	11.0	12.6	12.2	11.6	2.3	1.2	8.4	14.6	19.8
10/23/89	10.2	11.8	11.7	12.9	4.3	0.5	0.7	12.0	18.9
11/3/89	10.9	13.3	7.0	8.0	1.1	1.0	13.8	12.0	17.3
11/17/89	7.9	9.4	4.4	4.4	2.5	6.1	17.0	16.9	18.2
12/1/89	5.7	5.6	2.4	2.8	6.8	8.6	17.0	16.2	14.2
12/14/89	5.2	3.9	1.6	1.0	6.5	13.9	19.2	19.6	13.7
12/29/89	3.6	3.0	1.5	1.4	8.7	10.3	17.8	18.4	12.4
1/12/90	3.5	3.8	1.5	1.2	13.1	14.7	19.4	19.8	11.4
1/28/90	4.8	5.0	4.6	5.2	7.2	5.9	14.5	14.0	10.4
2/11/90	NA	5.0	7.4	7.6	NA	7.9	10.9	13.6	8.6
2/26/90	4.2	NA	2.1	2.9	13.0	NA	18.9	18.6	10.0
3/12/90	2.6	NA	5.9	7.4	15.0	NA	5.8	2.9	10.5
3/23/90	4.9	5.0	4.2	5.9	10.0	10.0	12.5	11.9	8.2
4/9/90	3.2	NA	2.8	4.2	15.4	NA	15.8	15.8	8.1
4/20/90	3.5	5.6	6.4	6.6	14.5	5.2	4.0	5.0	9.1
5/6/90	7.0	7.5	7.1	7.0	8.1	7.4	8.9	11.4	8.3
6/2/90	3.0	8.5	7.2	8.2	18.4	6.6	7.6	6.0	8.4
6/16/90	2.7	10.4	9.8	10.7	18.5	7.1	4.2	2.7	9.6
7/1/90	8.4	12.0	11.6	12.1	2.0	2.5	4.0	2.5	10.2
7/15/90	4.9	12.9	13.0	13.3	11.4	0.8	2.1	1.9	11.8
7/28/90	2.8	9.8	11.9	11.9	17.8	9.9	6.7	6.5	11.5
8/12/90	3.0	12.4	13.2	13.8	18.6	4.0	3.2	2.6	14.6

Table A-4. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)					
	Depth (feet)			Depth (feet)			Depth (feet)					
	2.7	7.7	12.7	17.7	2.7	7.7	12.7	17.7	2.7	7.7	12.7	17.7
9/30/90	8.0	13.6	12.8	14.0	7.0	0.6	2.8	1.1	14.6	15.8	14.6	13.3
10/13/90	4.1	12.2	12.2	13.9	16.4	2.4	4.2	2.0	15.6	15.9	15.4	14.5
11/11/90	6.8	5.4	3.0	2.0	10.6	14.5	18.4	19.0	NA	NA	NA	NA
12/16/90	4.0	4.2	2.5	2.6	11.9	11.7	17.2	17.4	4.6	9.6	11.8	13.2
1/12/91	5.6	7.0	5.0	5.1	7.2	6.2	15.6	15.9	5.9	7.7	9.2	10.4

Table A-5. Analytical Data File For Station 397+00 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)		
	Depth (feet)			Depth (feet)			Depth (feet)		
	4.0	9.0	14.0	4.0	9.0	14.0	4.0	9.0	14.0
7/26/89	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/11/89	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/25/89	6.2	9.6	NA	9.1	0.6	NA	21.9	22.1	20.7
9/8/89	10.0	13.6	11.3	2.0	0.4	0.8	21.4	21.6	20.1
9/25/89	11.0	12.0	10.0	2.3	2.0	1.3	18.7	20.4	18.9
10/9/89	7.0	11.4	6.7	9.0	2.4	10.8	18.7	21.2	20.4
10/23/89	4.8	10.6	4.2	4.5	0.9	11.6	14.6	18.4	18.7
11/3/89	6.0	10.3	2.5	11.6	3.2	17.8	12.4	17.4	18.9
11/17/89	5.5	8.6	3.3	10.1	3.9	16.6	13.2	19.0	18.1
12/1/89	2.5	6.5	1.0	14.8	8.2	18.4	6.3	12.9	13.1
12/14/89	2.3	5.4	0.6	16.3	12.9	19.6	5.2	10.8	12.9
12/29/89	NA	4.6	1.0	NA	10.4	18.0	4.6	10.4	12.2
1/12/90	1.6	5.0	0.8	17.8	14.0	19.6	2.7	7.5	9.0
1/28/90	3.0	4.3	2.8	12.6	9.3	15.1	3.6	6.5	8.5
2/11/90	4.2	5.0	3.3	11.8	7.4	16.3	6.3	7.5	8.4
2/26/90	1.8	4.7	0.7	17.2	14.0	19.1	6.5	8.0	9.0
3/12/90	3.6	4.7	3.3	10.6	5.5	12.0	6.8	7.5	8.4
3/23/90	2.9	5.6	2.0	14.8	12.5	16.3	7.9	7.8	8.5
4/9/90	2.3	4.9	1.0	14.4	12.5	17.2	7.2	8.7	9.9
4/20/90	3.6	5.3	2.9	10.1	7.3	12.6	7.8	8.9	9.7
5/6/90	5.0	7.8	1.8	13.7	6.3	19.0	11.2	8.4	8.2
6/2/90	5.5	8.5	4.8	11.8	5.3	9.0	11.7	10.3	9.6
6/16/90	6.7	10.6	6.8	10.5	3.1	7.0	14.4	11.7	10.5
7/1/90	7.8	12.1	5.8	7.7	2.6	14.2	16.1	13.2	11.4
7/15/90	9.4	11.6	8.6	3.3	0.6	8.8	17.8	15.0	12.7
7/28/90	8.8	13.8	11.1	7.0	0.4	2.4	18.1	16.1	13.9
8/12/90	9.0	13.6	10.4	6.0	0.2	3.0	19.0	16.6	14.8

Table A-5. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)			Oxygen Conc. (%)			Temperature (C)		
	Depth (feet)			Depth (feet)			Depth (feet)		
	4.0	9.0	14.0	4.0	9.0	14.0	4.0	9.0	14.0
9/30/90	7.2	11.2	6.9	7.2	2.5	10.5	15.4	16.2	14.2
10/13/90	8.4	11.6	8.7	6.5	1.2	7.4	15.9	16.8	15.1
11/11/90	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/16/90	2.8	4.2	1.6	14.8	11.8	17.8	5.6	10.3	12.1

Table A-6. Analytical Data File For Staion 401+00 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)		Oxygen Conc. (%)		Temperature (C)	
	Depth (feet)		Depth (feet)		Depth (feet)	
	5.0	10.0	5.0	10.0	5.0	10.0
7/26/89	NA	NA	NA	NA	NA	NA
8/11/89	NA	NA	NA	NA	NA	NA
8/25/89	NA	16.8	NA	0.9	19.5	19.3
9/8/89	16.6	18.2	1.4	0.8	20.4	20.8
9/25/89	19.0	6.8	0.7	15.7	20.0	19.6
10/9/89	14.0	NA	2.8	NA	21.8	22.3
10/23/89	13.0	14.0	0.5	2.8	17.1	17.9
11/3/89	14.2	12.2	1.0	3.1	16.5	19.8
11/17/89	13.2	11.2	2.7	3.9	13.0	15.9
12/1/89	7.4	10.4	9.5	5.9	8.1	12.1
12/14/89	5.9	7.4	11.5	7.1	5.6	9.7
12/29/89	4.3	7.0	9.0	9.0	5.8	9.4
1/12/90	7.7	7.2	6.3	8.1	4.0	7.7
1/28/90	7.4	6.2	5.5	9.1	3.9	6.6
2/11/90	7.4	6.2	3.8	8.2	6.3	8.0
2/26/90	5.5	6.9	15.3	12.6	5.8	6.1
3/12/90	5.5	6.0	14.5	7.1	5.8	7.4
3/23/90	7.6	6.5	9.2	10.5	9.2	8.6
4/9/90	6.4	NA	12.2	NA	7.5	8.7
4/20/90	8.5	7.0	4.1	6.5	8.0	8.3
5/6/90	7.8	8.0	8.5	9.8	9.6	8.1
6/2/90	8.6	8.8	12.6	8.9	11.5	10.1
6/16/90	7.4	9.0	13.1	7.7	13.5	11.3
7/1/90	7.6	7.8	9.7	9.6	14.4	12.1
7/15/90	8.5	10.1	7.5	5.3	16.6	13.7
7/28/90	9.1	11.1	11.6	6.3	16.0	13.1
8/12/90	9.1	7.4	11.1	10.4	17.7	15.5

Table A-6. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)		Oxygen Conc. (%)		Temperature (C)	
	Depth (feet)		Depth (feet)		Depth (feet)	
	5.0	10.0	5.0	10.0	5.0	10.0
9/30/90	13.2	NA	9.4	NA	16.3	16.2
10/13/90	9.8	9.2	8.8	10.0	15.9	15.5
11/11/90	NA	NA	NA	NA	NA	NA
12/16/90	6.6	3.8	9.6	14.0	7.0	10.0

Table A-7. Analytical Data File For Station 401+12 Gas Monitoring Well

Date Sampled	Carbon Dioxide Conc. (%)					Oxygen Conc. (%)					Temperature (C)				
	Depth (feet)					Depth (feet)					Depth (feet)				
	4.0	9.0	14.0	19.0	24.0	4.0	9.0	14.0	19.0	24.0	4.0	9.0	14.0	19.0	24.0
7/26/89	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/11/89	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8/25/89	3.3	6.7	15.3	17.2	12.8	14.9	11.7	0.9	0.5	1.0	20.9	20.8	20.2	20.0	20.3
9/8/89	5.5	16.2	17.8	15.7	13.1	14.1	2.3	1.5	3.0	4.0	20.6	22.0	21.7	20.5	20.3
9/25/89	8.2	19.6	19.6	16.6	14.0	11.4	1.4	1.2	1.6	2.0	17.2	19.8	20.4	20.0	19.6
10/9/89	9.1	16.7	17.3	15.9	12.9	7.7	1.7	3.2	3.4	3.6	18.5	21.0	21.9	21.3	21.3
10/23/89	7.3	15.4	17.0	15.0	11.8	10.4	1.2	2.2	2.4	4.2	13.0	17.2	18.6	18.6	18.4
11/3/89	10.4	15.3	15.9	14.8	13.7	5.1	1.4	1.7	3.2	2.0	13.5	16.3	18.7	19.1	19.0
11/17/89	8.5	14.7	15.6	13.9	11.0	7.7	2.5	3.7	4.0	6.2	11.6	13.4	16.1	15.3	17.5
12/1/89	4.1	11.4	12.9	12.1	7.8	14.4	5.5	4.8	4.9	10.0	7.2	9.5	11.0	13.2	14.1
12/14/89	3.3	9.0	10.3	10.8	6.4	15.3	8.7	8.4	6.9	11.8	3.1	6.6	10.0	11.3	11.9
12/29/89	3.1	6.8	8.4	9.3	4.4	15.5	8.9	7.2	7.9	13.1	2.0	6.0	8.7	10.1	10.8
1/12/90	2.7	7.6	8.5	8.7	5.6	17.1	9.8	10.4	9.9	14.2	1.5	4.7	7.0	8.3	8.9
1/28/90	2.9	NA	8.5	8.1	5.2	16.5	NA	7.4	9.9	13.6	4.2	5.4	7.4	8.8	9.4
2/11/90	3.6	6.0	9.6	8.6	6.0	16.3	17.6	7.4	9.0	11.9	6.9	6.9	7.5	7.7	8.4
2/26/90	3.0	6.1	8.4	7.7	4.9	17.0	13.2	11.3	12.0	15.5	4.5	6.4	7.3	8.1	8.3
3/12/90	3.4	7.5	9.6	8.3	5.7	14.7	10.8	4.2	4.8	5.8	7.6	5.3	6.6	7.8	7.2
3/23/90	2.5	5.9	9.1	8.0	5.2	17.4	8.4	7.9	11.0	14.8	8.2	9.0	8.8	8.7	9.0
4/9/90	2.7	6.8	8.0	7.0	3.9	17.0	11.7	11.1	12.9	15.6	7.4	8.5	8.4	8.9	8.1
4/20/90	3.2	8.4	9.3	7.6	4.6	15.3	5.6	5.7	9.6	12.4	8.5	8.3	8.4	8.6	8.3
5/6/90	4.6	8.6	10.9	9.0	7.5	14.0	9.8	8.3	9.0	11.2	11.5	9.8	8.1	7.7	7.9
6/2/90	4.5	11.7	12.8	9.6	6.5	14.3	7.1	5.0	9.1	11.7	12.7	11.2	9.9	8.9	9.0
6/16/90	5.6	11.3	14.2	10.9	9.5	12.8	9.1	4.1	4.7	4.3	16.4	13.8	12.0	11.0	10.5
7/1/90	6.6	10.8	14.4	12.0	11.0	11.6	8.5	5.3	5.9	6.5	17.3	14.8	12.9	11.6	10.9
7/15/90	7.0	10.2	14.9	13.2	12.2	12.2	3.0	4.4	6.0	6.8	16.8	16.0	13.5	12.2	11.3
7/28/90	6.3	11.6	15.6	13.9	11.9	11.6	6.3	3.0	3.7	4.4	15.9	15.5	14.2	13.7	12.7
8/12/90	6.4	12.2	16.2	14.4	12.6	12.2	6.1	2.9	3.9	5.3	18.0	17.7	16.4	16.5	15.2

Table A-7. (cont.)

Date Sampled	Carbon Dioxide Conc. (%)					Oxygen Conc. (%)					Temperature (C)				
	Depth (feet)					Depth (feet)					Depth (feet)				
	4.0	9.0	14.0	19.0	24.0	4.0	9.0	14.0	19.0	24.0	4.0	9.0	14.0	19.0	24.0
9/30/90	5.8	14.2	15.6	13.2	10.1	13.8	8.5	5.1	6.4	8.5	13.9	15.5	16.1	15.8	15.8
10/13/90	5.3	12.6	15.2	14.6	13.1	15.3	5.1	5.8	5.6	7.3	14.9	15.6	16.3	16.2	15.7
11/11/90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/16/90	2.7	6.4	6.8	6.5	4.2	16.8	11.4	12.2	12.7	13.6	5.8	7.9	9.9	10.3	11.1

Appendix B
Stable Isotope Data of Soil Carbon Dioxide

Table B-1. Analytical Data File For Fill Gas Isotopes. Carbon dioxide concentration determined by Fisher Gas Analyzer. Inorganic and organic carbon dioxide determined by multiplying fractions from equation (11) by carbon dioxide concentration.

Station	Depth (feet)	Date Sampled	CO2 Conc. (%)	Yield (umoles)	delta 13C (‰ PDB)	delta 18O (‰ PDB)	Inorg. CO2 Conc. (%)	Org. CO2 Conc. (%)
383+00	3.5	9/16/90	5.5	270.6	-14.0	-6.4	2.4	3.1
383+00	8.5	9/16/90	5.0	257.2	-13.1	-6.4	2.4	2.6
383+00	13.5	9/16/90	4.4	215.8	-13.8	-6.1	1.9	2.5
383+00	18.5	9/16/90	5.3	267.5	-12.2	-6.5	2.7	2.6
383+00	3.5	10/13/90	7.4	378.2	-14.2	-5.6	3.1	4.3
383+00	8.5	10/13/90	7.1	369.4	-12.9	-6.1	3.4	3.7
383+00	13.5	10/13/90	7.5	380.0	-12.4	-6.0	3.8	3.7
383+00	18.5	10/13/90	8.4	438.3	-10.9	-5.7	4.8	3.6
383+00	3.5	11/11/90	3.1	113.4	-14.7	-5.1	1.2	1.9
383+00	8.5	11/11/90	1.4	76.9	-14.3	-5.5	0.6	0.8
383+00	13.5	11/11/90	1.3	77.8	-14.3	-5.5	0.5	0.8
383+00	18.5	11/11/90	1.4	81.5	-14.3	-5.6	0.6	0.8
383+00	3.5	12/16/90	3.5	102.4	-11.1	-3.6	2.0	1.5
383+00	8.5	12/16/90	3.2	98.4	-11.6	-4.7	1.7	1.5
383+00	13.5	12/16/90	3.4	100.6	-11.7	-4.7	1.8	1.6
383+00	18.5	12/16/90	3.2	128.0	-11.2	-5.2	1.8	1.4
383+00	3.5	1/12/91	3.2	175.7	-10.5	-3.7	1.9	1.3
383+00	8.5	1/12/91	3.3	166.1	-10.2	-4.0	2.0	1.3
383+00	13.5	1/12/91	3.3	167.6	-10.1	-3.9	2.0	1.3
383+00	18.5	1/12/91	4.1	217.6	-8.5	-4.0	2.8	1.3

Table B-1. (cont.)

Depth (feet)	Date Sampled	CO ₂ Conc. (%)	Yield (umoles)	delta 13C (‰ PDB)	delta 18O (‰ PDB)	Inorg CO ₂ Conc. (%)	Org. CO ₂ Conc. (%)
2.7	9/16/90	12.3	655.4	-18.1	-5.7	2.9	9.4
7.7	9/16/90	13.4	668.0	-16.4	-6.0	4.2	9.2
12.7	9/16/90	12.6	709.5	-15.9	-5.4	4.2	8.4
17.7	9/16/90	14.0	730.3	-16.4	-5.4	4.4	9.6
2.7	10/13/90	4.1	213.7	-18.3	-5.1	0.9	3.2
7.7	10/13/90	12.2	616.5	-17.1	-5.3	3.5	8.7
12.7	10/13/90	12.2	691.3	-16.5	-5.0	3.8	8.4
17.7	10/13/90	13.9	692.9	-16.8	-5.1	4.1	9.8
2.7	11/11/90	6.8	363.5	-16.2	-3.4	2.2	4.6
7.7	11/11/90	5.4	282.4	-16.2	-4.5	1.7	3.7
12.7	11/11/90	3.0	163.0	-16.9	-5.0	0.9	2.1
17.7	11/11/90	2.0	162.1	-16.7	-4.9	0.6	1.4
2.7	12/16/90	4.0	183.4	-15.9	-3.0	1.3	2.7
7.7	12/16/90	4.2	186.7	-15.7	-3.7	1.5	2.7
12.7	12/16/90	2.5	118.9	-17.6	-4.2	0.6	1.9
17.7	12/16/90	2.6	110.9	-17.7	-4.8	0.7	1.9
2.7	1/12/91	5.6	264.9	-16.0	-3.1	1.9	3.7
7.7	1/12/91	7.0	339.5	-15.2	-3.2	2.6	4.4
12.7	1/12/91	5.0	262.4	-16.4	-3.8	1.6	3.4
17.7	1/12/91	5.1	253.0	-16.1	-3.8	1.7	3.4

Appendix C
Stable Isotope Data of Aqueous Carbonate Species

Table C-1. Analytical Data File For Underdrain Carbonate Isotopes

Sample ID	Date Sampled	Carbonate Source	delta 13C (‰ PDB)	delta 18O (‰ SMOW)	pH	Spec. Cond. (umhos)	Temperature (°C)
996+50	11/11/90	Fill Leachate	-13.9	24.4	6.75	308	12.4
190+00	4/9/90	Fill Leachate	-25	-13.5	NA	NA	NA
190+00	10/13/90	Fill Leachate	-22.3	14.1	6.45	28	12.7
190+00	11/11/90	Fill Leachate	-20.1	15.7	6.05	42	11.9
383+00	4/9/90	Fill Leachate	-20.0	17.5	NA	NA	NA
383+00	10/13/90	Fill Leachate	-5.9	26.7	6.59	950	14.4
383+00	11/11/90	Fill Leachate	-13.2	20.3	7.80	440	10.7
401+00	4/9/90	Fill Leachate	-15.6	22.4	NA	NA	NA
401+00 DUP	4/9/90	Fill Leachate	-15.2	22.5	NA	NA	NA
401+00	10/13/90	Fill Leachate	-19.7	19.9	6.56	42	14.0
401+00	11/11/90	Fill Leachate	-18.0	20.6	6.20	40	10.7
432+00	10/13/90	Fill Leachate	-21.4	13.1	3.05	430	14.4
432+00	11/11/90	Fill Leachate	-17.7	14.7	2.88	330	10.2
490+00	10/13/90	Fill Leachate	-21.5	16.6	6.40	400	14.4
490+00	11/11/90	Fill Leachate	-21.9	11.5	7.05	250	12.2
500+12 - 1	10/13/90	Fill Leachate	-9.4	22.2	7.51	141	12.4
500+12 - 1	11/11/90	Fill Leachate	-12.4	20.1	7.85	112	10.2
500+12 - 2	10/13/90	Spring	-24.5	10.0	6.83	25	11.3
500+12 - 2	11/11/90	Spring	-24.4	10.7	5.55	NA	10.5
460+00	11/11/90	Spring	-28.1	12.9	5.90	12	8.3
LA - 1	NA	Limestone	-2.0	24.6	NA	NA	NA
LA - 2	NA	Limestone	-1.3	25.4	NA	NA	NA
LA - 3	NA	Limestone	-1.7	25.9	NA	NA	NA
PL - 2	NA	Limestone	-2.4	24.5	NA	NA	NA

Appendix D
Acid Potential, Neutralization Potential,
and Net Neutralization Potential Data

Table D-1. Analytical Data File for Net Neutralization Potential Based on Inorganic Sulfur

Station	Depth (feet)	Inorganic Sulfur (%)	Acid Potential*	Neutral Potential*	Net Neutral. Potential*
383+00	3.5	0.99	30.94	4.55	-26.39
383+00	8.5	1.25	39.06	4.47	-34.59
383+00	13.5	0.11	3.56	4.52	0.96
383+00	18.5	0.08	2.41	5.41	3.00
383+25	Upper Lift	0.20	6.25	3.59	-2.66
383+25	Lower Lift	1.08	33.66	2.76	-30.90
383+50	4.0	0.58	18.09	2.80	-15.29
383+50	9.0	0.71	22.19	4.84	-17.35
383+50	14.0	0.06	1.88	2.90	1.02
383+50	19.0	0.43	13.28	4.10	-9.18
396+00	7.7	0.54	17.00	4.29	-12.71
396+00	12.7-17.7	0.45	14.03	3.78	-10.25
397+00	9.0-14.0	0.31	9.63	4.78	-4.85
401+00V	5.0	0.22	6.72	0.13	-6.59
401+00V	10.0	0.36	11.38	1.96	-9.42
401+00H	4.0 to 14.0	0.55	17.28	3.69	-13.59
401+00H	14.0 to 24.0	0.44	13.66	2.53	-11.13

Table D-2. Analytical Data File for Net Neutralization Potential Based on Total Sulfur

Station	Depth (feet)	Total Sulfur (%)	Acid Potential*	Neutral. Potential*	Net Neutral. Potential*
383+00	3.5	1.59	49.81	4.55	-45.26
383+00	8.5	2.30	71.87	4.47	-67.40
383+00	13.5	0.64	20.07	4.52	-15.55
383+00	18.5	0.57	17.66	5.41	-12.25
383+25	Upper Lift	0.67	20.85	3.59	-17.26
383+25	Lower Lift	1.98	61.73	2.76	-58.97
383+50	4.0	1.25	39.17	2.80	-36.37
383+50	9.0	2.26	70.58	4.84	-65.74
383+50	14.0	0.95	29.73	2.90	-26.83
383+50	19.0	1.96	61.31	4.10	-57.21
396+00	7.7	1.22	40.59	4.29	-36.31
396+00	12.7-17.7	0.99	30.86	3.78	-27.08
397+00	9.0-14.0	1.29	40.29	4.78	-35.51
401+00V	5.0	0.57	29.56	0.13	-29.43
401+00V	10.0	0.65	31.45	1.96	-29.49
401+00H	4.0 to 14.0	0.71	22.26	3.69	-18.57
401+00H	14.0 to 24.0	0.72	22.59	2.53	-20.06

Water Quality Data
Appendix E

Table E-1. Analytical Data File for Underdrain Water Quality

Station	Date	pH	Conductivity (μ mhos)	Temperature °C	Alkalinity eq. CaCO ₃	Sulfate (mg/L)	pCO ₂ (atm)
401+00	8/28/89	7.2	NA	NA	37.5	1.5	NA
401+00	9/8/89	7.0	NA	NA	45.0	0.0	NA
401+00	9/25/89	6.2	75	NA	41.0	1.0	NA
401+00	10/10/89	6.7	49	14.0	27.5	0.0	0.28
401+00	10/23/89	6.6	58	13.2	31.3	5.0	0.39
401+00	11/8/89	6.8	59	11.0	42.5	0.0	0.32
401+00	11/17/89	6.6	38	8.0	21.4	1.0	0.25
401+00	12/1/89	6.6	42	13.5	26.0	0.0	0.34
401+00	12/14/89	5.8	31	5.6	23.8	2.0	1.53
401+00	12/28/89	7.2	35	4.0	22.1	1.0	0.05
401+00	1/12/90	6.8	31	5.5	25.0	1.0	0.18
401+00	1/28/90	5.5	40	NA	21.3	2.5	NA
401+00	2/11/90	6.6	16	11.0	13.8	0.0	0.19
401+00	2/26/90	6.5	30	6.0	19.6	2.0	0.25
401+00	3/12/90	6.9	41	11.7	17.3	7.0	0.11
401+00	3/22/90	6.8	35	8.2	20.3	2.0	0.13
401+00	4/9/90	6.7	35	10.1	19.9	NA	0.19
401+00	4/23/90	7.1	32	9.9	24.6	NA	0.10
401+00	5/6/90	6.3	32	NA	3.8	NA	NA
401+00	6/2/90	6.8	33	9.6	21.5	0.0	0.17
401+00	6/16/90	7.2	28	13.1	31.3	8.0	0.09
401+00	7/15/90	6.5	31	NA	17.1	2.0	0.02
383+00	2/11/90	4.8	1000	7.0	8.3	160	6.10
383+00	2/26/90	7.6	1000	7.0	70.8	180	0.07
383+00	1/26/90	6.4	1100	16.0	90.0	94	1.97
383+00	3/22/90	7.3	980	NA	97.5	200	0.01
383+00	4/9/90	8.0	500	8.6	89.6	NA	0.04

VITA

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